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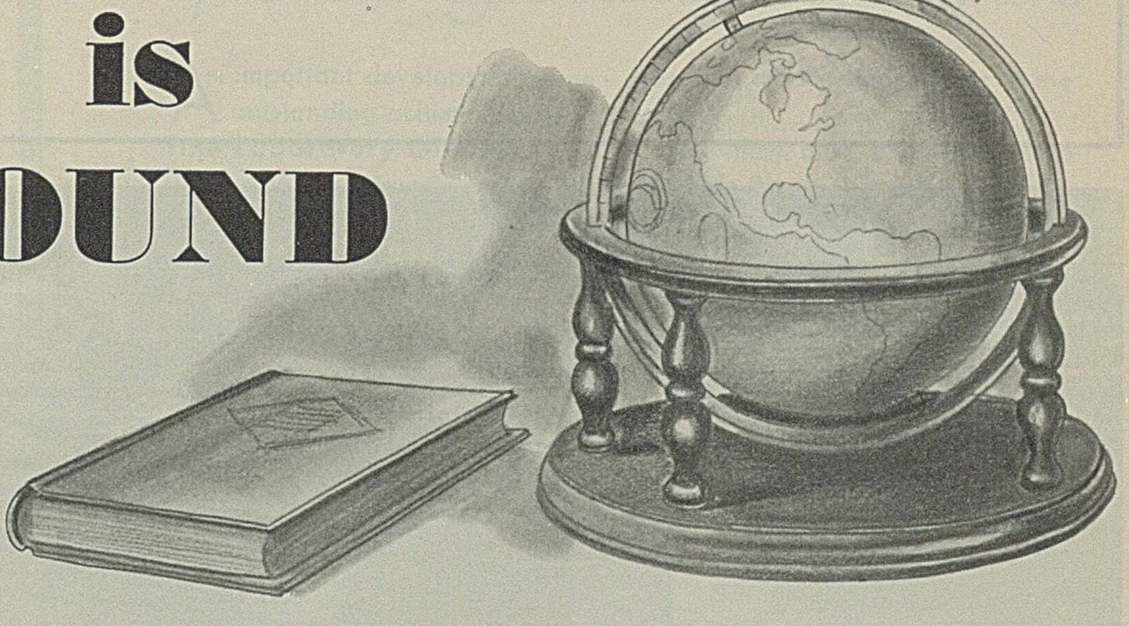

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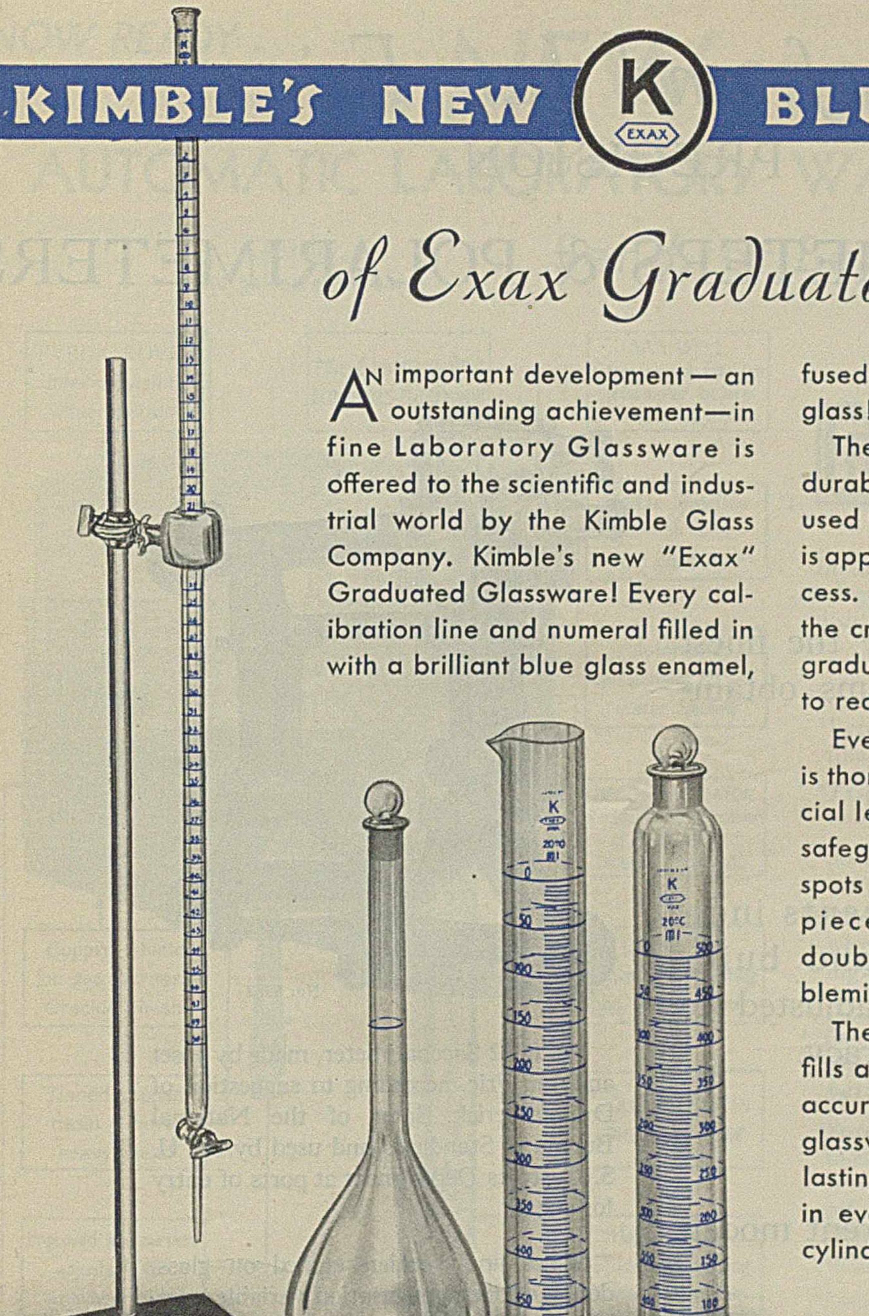

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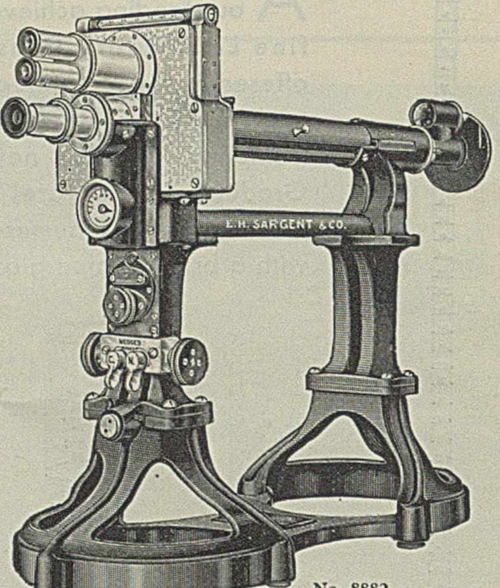
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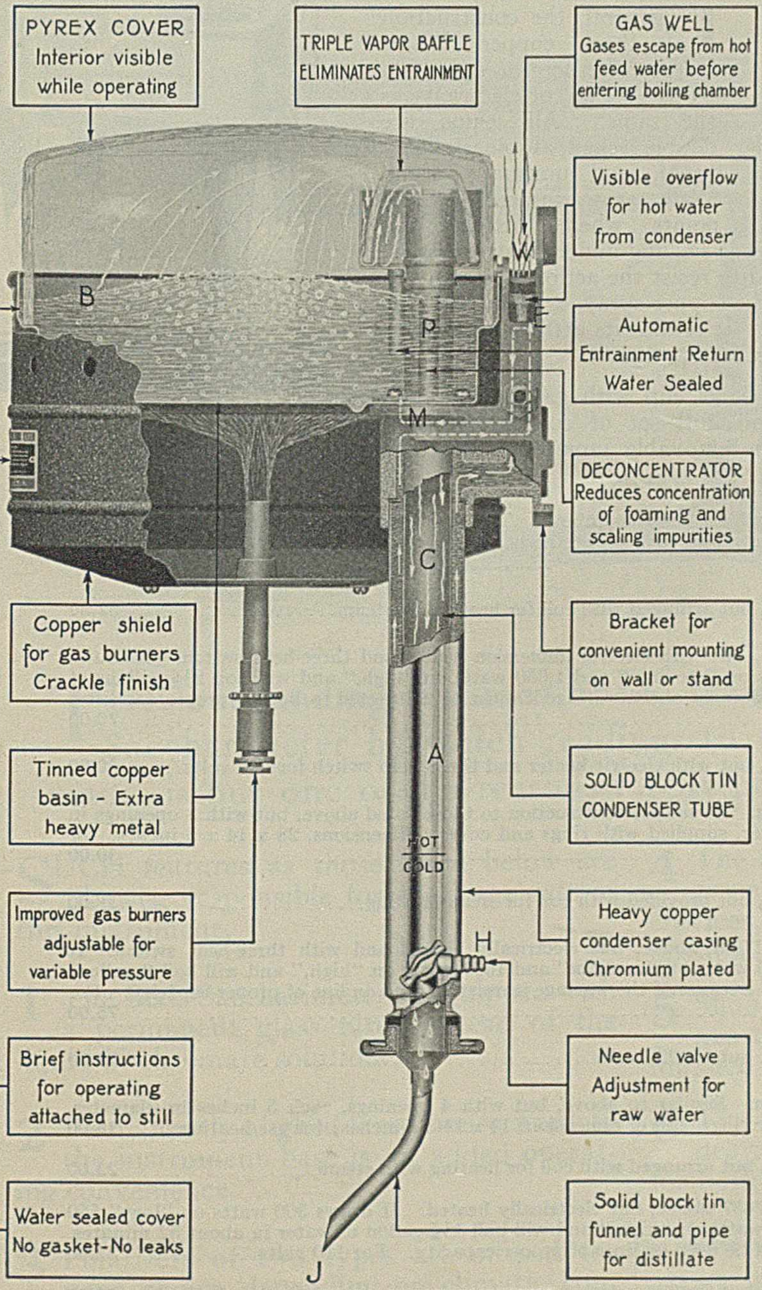

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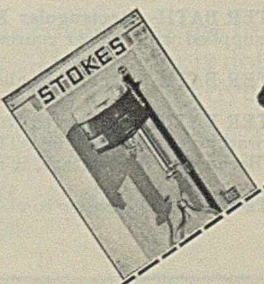

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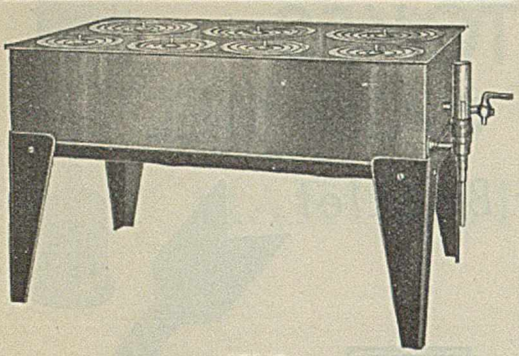

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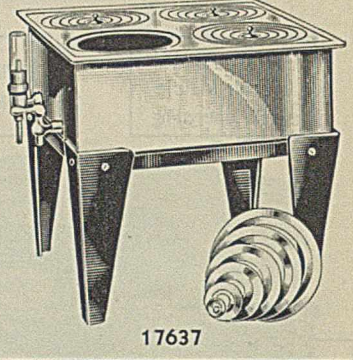

17637

In general, the construction of these copper Water Baths, whether for operation by gas, steam, or electricity, is the same. All seams are double locked, absolutely leakproof, and unusually rigid. Walls are reinforced at all points where fittings are attached, the top is braced lengthwise to prevent sagging under heavy vessels. The inside is thoroughly and uniformly tinned to resist the action of steam and hot water, the exterior is coated with a metallic copper spray, a finish that has been found more satisfactory than any other. It retains its attractive appearance, needs no polishing, and acts as a protective coating.

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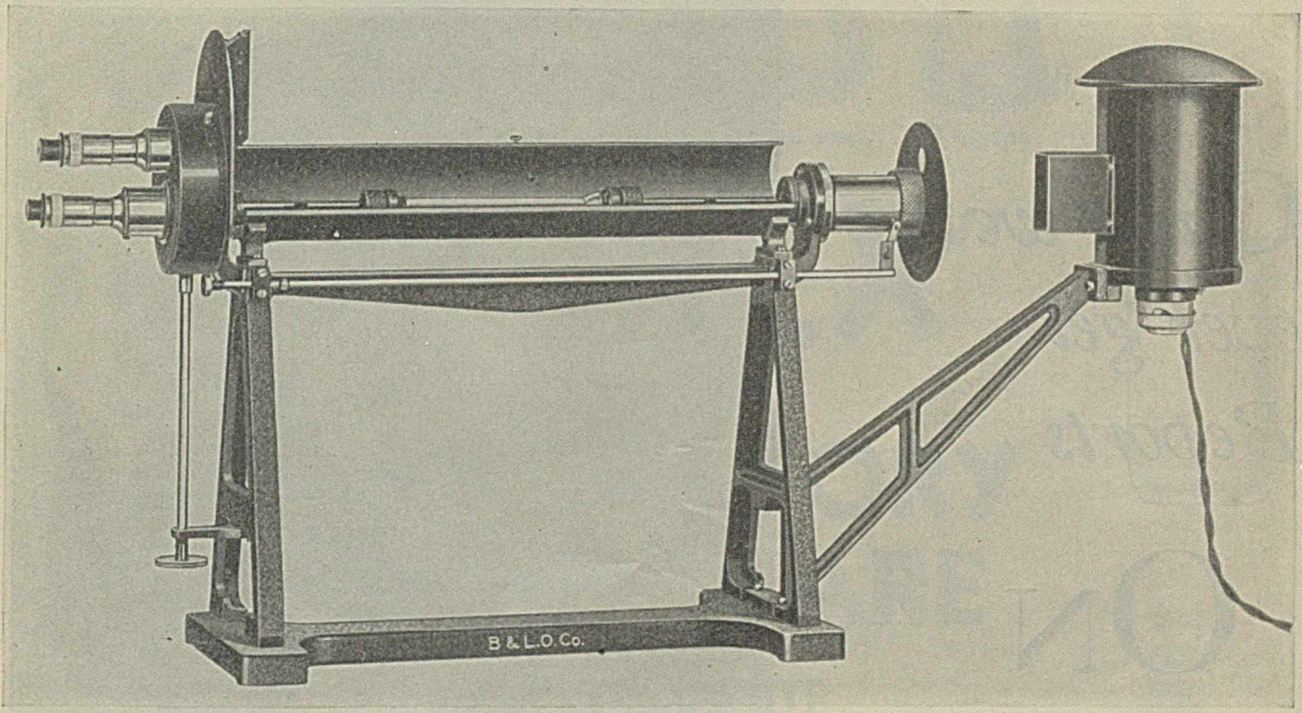

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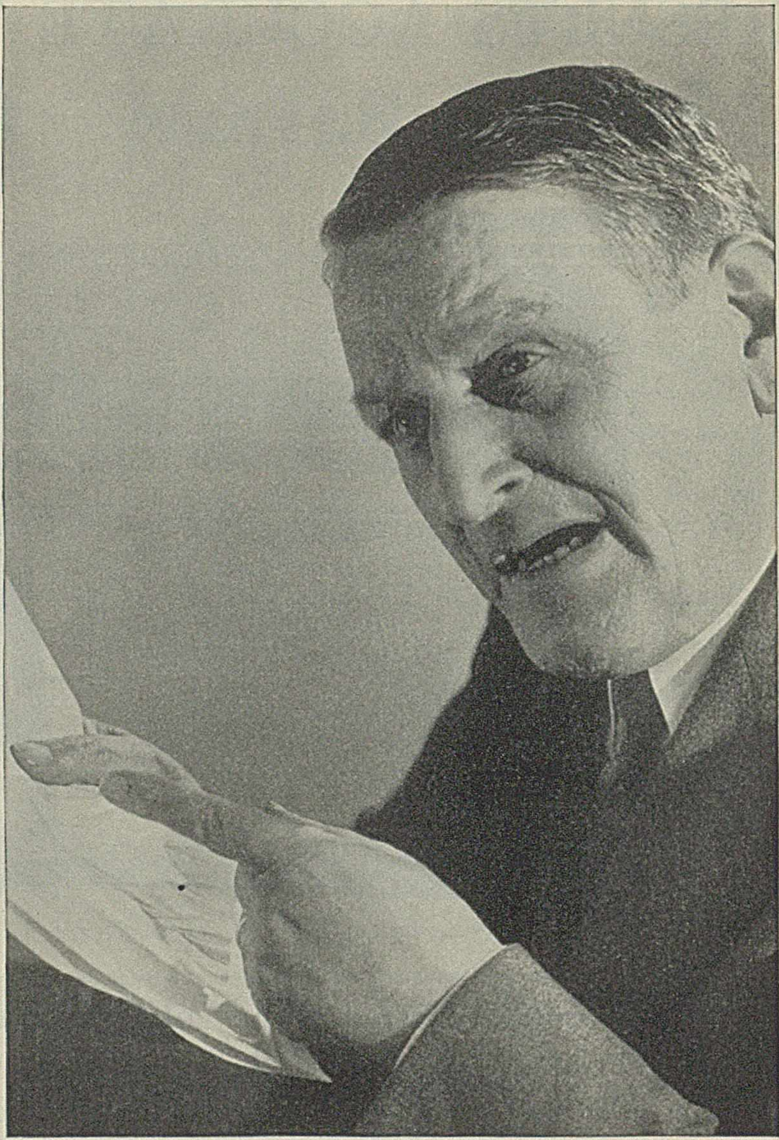

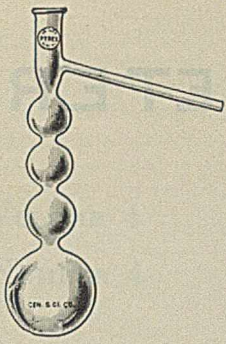
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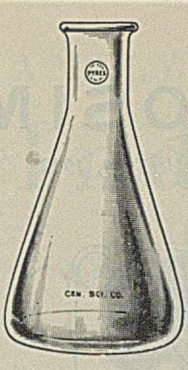
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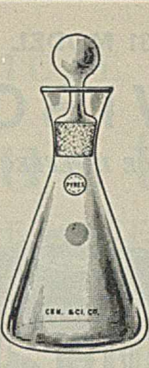
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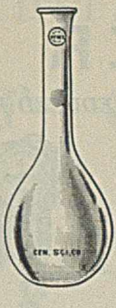
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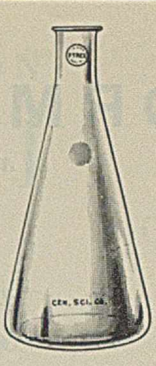
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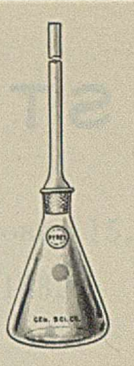
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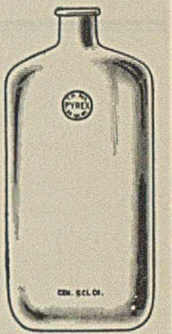
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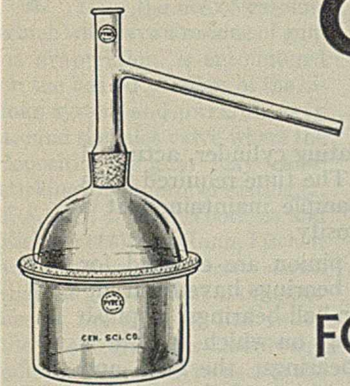
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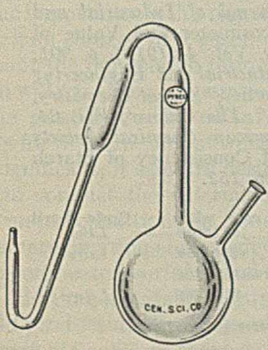
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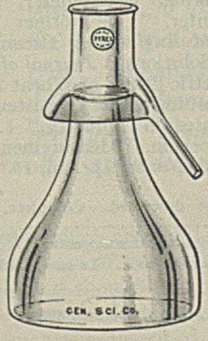
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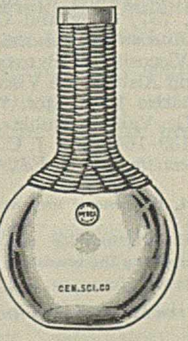
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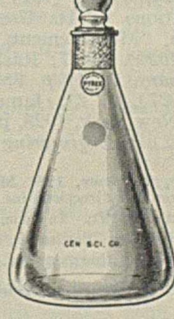
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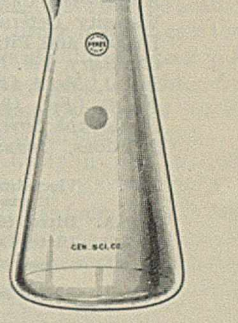
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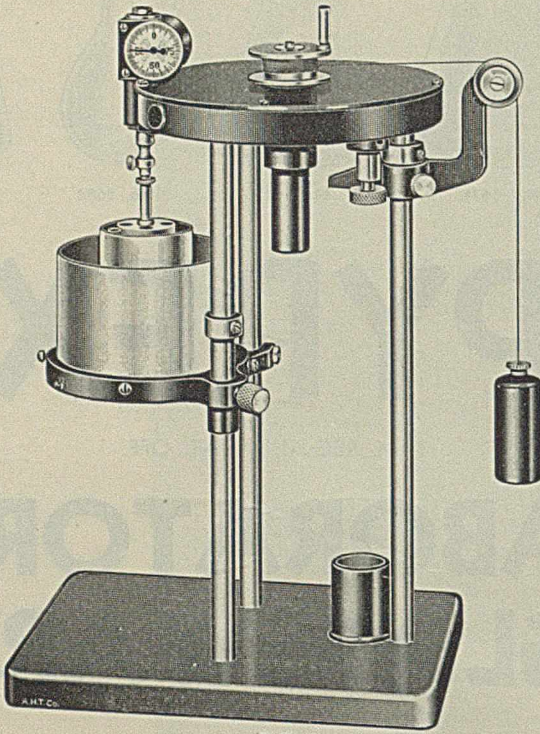

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VISCOSIMETER, STORMER, 1931 MODEL. The speed of a rotating cylinder, actuated by a weight, is measured by a revolution counter attached to the spindle. The time required for a definite number of revolutions of the cylinder when immersed in the sample maintained at a desired temperature and driven by a definite weight is the measure of viscosity.

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See Rodgers and Sabin, "Consistency of Paints by the Stormer Viscosimeter," *Journal of Industrial and Engineering Chemistry, Vol. 3 (1911), p. 737;* Rigg and Carpenter, "The Stormer Viscosimeter and Value of Viscosity Determinations by Its Use," *Journal of Industrial and Engineering Chemistry, Vol. 4 (1912), p. 901;* Higgins and Pitman, "Measurement of Viscosity of Pyroxylin Solutions," *Journal of Industrial and Engineering Chemistry, Vol. 12 (1920), p. 587;* Rask and Alsberg, "A Viscosimetric Study of Wheat Starches," *Cereal Chemistry, Vol. 1, No. 1, (January, 1924), p. 7;* Charles J. Meister, "Recording Corn Consistency," *The Canner, Vol. 64, No. 9, (Feb. 19, 1927), p. 23;* James G. Vail, "Soluble Silicates in Industry," (*American Chemical Society Monograph Series*), New York, 1928, pp. 139–154; and J. C. Ripperton, "Measurement of Consistency of Starch Solutions," *Industrial and Engineering Chemistry, Anal. Ed., Vol. 3, No. 2 (Apr. 15, 1931), p. 152.*

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7649.	**Viscosimeter, Stormer, 1931 Model,** for general use, as above described. Complete, in case with thermometer and directions for use	$110.00	*Letok*
7649-A.	**Ditto, Silicate Outfit.** In case, with directions for use but without thermometer	$107.50	*Letre*
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Number 4

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1932

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Harrison E. Howe, Editor

Determination of Gum in Gasoline

A High-Temperature Modification of Air Jet Method

M. J. Mulligan, Wheeler G. Lovell, and T. A. Boyd
General Motors Research Laboratories, Detroit, Mich.

A simple and rapid method for the determination of the gum content of gasoline has been devised to approximate in some regards the conditions which exist during the deposition of gum in the intake system of an automobile engine. The procedure is essentially a high-temperature modification of the conventional air jet method. A glass beaker containing the gasoline is held in a well in a constant-temperature bath vessel, containing a liquid boiling at about 200° C. Air flowing at the rate of one liter per second and heated in passing through a tube incorporated in the bath vessel is used to evaporate the gasoline and dry the residual gum. The time required to obtain a sample of gum of substantially constant weight from 50 ml. of gasoline is 20 to 25 minutes. Oxidation during the determination is not an important source of error, reproducible results are obtained, and difficulties from creeping have not been experienced. Comparative data by this and by other methods are given.

THE most serious trouble in an automobile engine from the use of gasoline which will leave a residue of gum on evaporation, is encountered on the heated portions of the intake system and particularly around the inlet valve where the deposition of gum may cause sticking and improper seating (*1*, *6*, *8*, *12*, *14*, *16*). Voorhees and Eisinger (*14*), and Hunn, Fischer, and Blackwood (*8*) have shown that the gum content of the gasoline at the time the fuel enters the intake system is the only significant figure with respect to the content of gum formed in the engine, and that potential gum is of no importance in this regard.

By gum content of a gasoline is meant the nonvolatile residue which will remain on evaporation of the gasoline. To obtain values for the gum content which are significant, it appears desirable to conduct the determination under conditions in some way approximating engine conditions, which are rapid evaporation on heated surfaces and in a stream of warm air.

In addition, a suitable routine method should be rapid and should produce duplicable results. A method which seems to approximate some of these requirements is described in this paper. It is a high-temperature air jet method, which is essentially a modification of the Hunn, Fischer, and Blackwood air jet method (*8*), and includes certain desirable features of the Norris and Thole method (*12*) and of that used by Mardles and Moss (*10*).

High-Temperature Air Jet Method

The apparatus required for this method for the determination of the gum content of gasoline, and the procedure found most satisfactory are described below and illustrated in Figure 1.

Apparatus. The dish used is a Berzelius-type beaker of heat-resistant glass, without lip, of 100 ml. nominal capacity.

The design of the bath is shown in Figure 1. The bath, which contains 0.5 to 0.75 liter of ethylene glycol (b. p. 195° to 200° C.), is fitted with a reflux condenser at the top of which a drying tube containing calcium chloride is connected. The bath should preferably be insulated with asbestos paper, and an electric hot plate capable of keeping the bath liquid boiling actively is the preferred heating means. In the absence of a satisfactory hot plate the bath may be heated by a gas burner, in which case the apparatus should be placed in a hood with a good draught. An electric immersion heater would probably be satisfactory also.

Tetrahydronaphthalene (tetralin), b. p. 200° to 205° C., was used initially as bath liquid, but it was found after it had been in use for a considerable time that it had decomposed somewhat with the formation of tar. A more stable liquid is therefore advisable, and ethylene glycol appears to be more satisfactory in this respect than tetralin and is tentatively recommended as the bath liquid to be used. One disadvantage in the use of ethylene glycol is that it readily takes up water with a consequent lowering of the bath temperature. The drying tube connected to the condenser will prevent this to a great extent. Objectionable amounts of water can readily be removed by detaching the condenser and boiling the liquid for a very short time, or by means of suitable drying agents. Certain other liquids which boil near 200° C. might be preferable to those mentioned.

For the air supply, low-pressure air is passed through a cotton or glass wool filter and is delivered to the preheater inlet of the bath. A flowmeter or other metering device is provided. A flowmeter is indicated in the diagram, but is not drawn to scale.

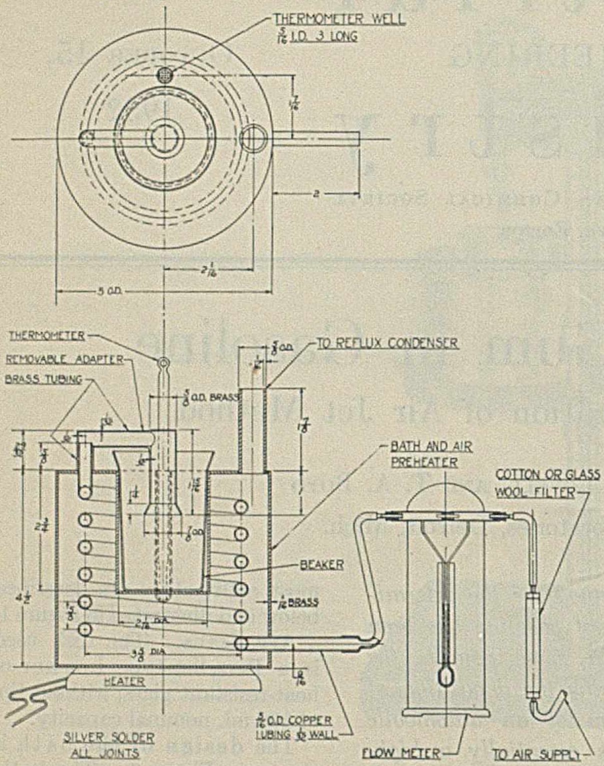

FIGURE 1. APPARATUS FOR DETERMINATION OF GUM CONTENT OF GASOLINE

(High-temperature air jet method)

PROCEDURE. Since the gum content of most commercial gasolines is very small, it is essential that care be taken in making the weighings, and it has been found that these must be made by tare to insure accuracy. A similar beaker which is subjected to exactly the same treatment as the test beaker (omitting the gasoline) is used as tare. In weighing such small amounts of gum as are frequently obtained, adsorbed moisture and temperature variations between the test beaker and the tare may seriously affect the results. To insure equilibrium in these respects, it has been found advisable to place the beakers, after they have cooled to room temperature, directly in the balance case, where they should remain one-half hour before the weighings are made.

The beaker is washed free of gum with a solution of acetone (or alcohol) and benzene, soaked for a few minutes in hot chromic acid solution, rinsed with water, dried with a lint-free cloth, and while held with crucible tongs, dried in the flame of a Bunsen burner. After cooling and weighing as described above, the beaker is placed in the well of the heated bath. The air rate is adjusted to one liter per second ± 10 per cent. The metal adapter[1] is removed and 50 ml. of the test gasoline are poured into the beaker, after which the adapter is replaced on the air outlet so that the air stream is directed into the center of the beaker. After the gasoline has evaporated, which should require from 5 to 10 minutes, the beaker is left in place for an additional 15 minutes, the air supply being maintained. If the sample of gum obtained is very small, it is sometimes of advantage to evaporate a further 50-ml. sample in the same test beaker before drying the residue. The beaker is then allowed to cool and is weighed as described above. As is customary, the results are computed and expressed as milligrams of gum per 100 ml. of gasoline; this procedure is generally followed, but it is apparent from data in the literature, and it has been the authors' experience, that the gum value obtained on evaporating a 100-ml. sample is not twice that from a 50-ml. sample in the case of most gasolines. In this paper all gum values represent the actual weight of gum obtained.

COMPARISON OF GUM CONTENT VALUES BY VARIOUS METHODS

Comparative data on a number of gasolines have been obtained by the high-temperature air jet method and by certain other methods, which are briefly described here.

STEAM OVEN METHOD (*4*, *7*, *11–15*). The technic employed in these experiments resembled that of the Voorhees and Eisinger (*14*) modification of this method. The samples (50 ml.) of gasoline contained in glass evaporating dishes were held in an atmosphere of superheated steam at a temperature of 155° C. for 16 hours, in which time substantially constant weight has been reached. It has been the authors' experience with the steam oven method that, in general, at lower oven temperatures higher gum values are obtained.

AIR JET METHOD (*2*, *8*, *9*, *11*). This method, designated in this paper as the conventional air jet method, was devised by Hunn, Fischer, and Blackwood (*8*). A 50-ml. sample of gasoline contained in an evaporating dish of heat-resistant glass (with lip; diameter of top 9 cm., and of base 4.5 cm.; depth 5 cm.) is held on a steam bath at 100° C., and the gasoline evaporated by means of a jet of unheated air flowing at the rate of about one liter per second; the evaporation requires about 15 minutes. The residue is then dried for one hour in an air oven at 150° C. It has been shown (*8*) and the observation confirmed in this laboratory that, if nitrogen or carbon dioxide be substituted for air during the evaporation of the gasoline, the results are in agreement with those found when using air; a fact which shows that at least during the evaporation of the gasoline atmospheric oxygen has been without effect. However, it has been the experience of Voorhees and Eisinger (*14*) with gum residues obtained by the steam oven test that drying in an air oven may sometimes permit the undried residue to take up oxygen and increase in weight.

100° C. DRIP METHOD. The conditions of the test are the same as for the conventional air jet method except that the gasoline is dripped from a separatory funnel into the evaporating dish at the rate of 3 to 4 ml. per minute. It has been found that the results obtained by this method, which was suggested by Fischer (*5*), do not differ greatly from those obtained by the conventional air jet method, and since supervision of the rate of dripping is necessary, no advantage is had over the latter method.

HOT DRIP METHOD. This method was devised prior to work on the high-temperature air jet method and, in view of certain data which are presented later, is described here, although it is not as convenient as the high-temperature air jet method. It was thought that there would be danger of very considerable oxidation occurring in an air jet method at upwards of 200° C., and so it was considered advisable to make preliminary experiments with a high-temperature drip method, in which each drop of gasoline evaporates in a very short time. The separatory funnel, as used in the 100° C. drip method, was found to be unsatisfactory under the conditions of this test, and the device which was utilized was the all-glass combined dripper and air-lead shown in Figure 2, the gasoline flowing from the reservoir through a capillary tube and being delivered at the rate of about 5 ml. per minute to the beaker, where the gum is deposited. Hot air is introduced simultaneously through the larger tube which surrounds the capillary at the rate of about one liter per second. The bath vessel shown in Figure 1 was also used here. With the device used, splashing of the dripping gasoline and creeping of the gummy deposit up the sides of the beaker were avoided and a fairly regular flow of gasoline was obtained, there being not more than one ml. of unevaporated gasoline in the beaker at any one time. Under these conditions, the evaporation of a 50-ml. sample of gasoline required about 10 minutes.

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[1] In a private communication, Graham Edgar, of the Ethyl Gasoline Research Laboratories, has informed us that with a similar apparatus trouble was experienced in initial experiments from copper oxide, apparently from the copper spiral, being deposited in the test beaker, but that an asbestos filter held in place with brass gauze was inserted in the adapter and the trouble was not experienced thereafter.

As in the high-temperature air jet method, the residue was dried in the hot air stream for 15 minutes. Since it was found that the values obtained with the hot drip method did not differ appreciably from those with the high-temperature air jet method, and since the latter method is simpler, it has been given the preference.

MODIFIED AIR JET METHOD. Data have also been obtained by a modified air jet method in which the bath vessel resembled that shown in Figure 1, but with a well designed to hold an evaporating dish of the type used in the conventional air jet method. The temperature on the bottom center of the dish directly below the adapter outlet was 175° C., when using tetralin as the bath liquid and with an air flow of one liter per second. Because of the shape it was not possible to dry the gum satisfactorily by means of the hot air jet, so the samples were dried for one hour in an air oven at 150° C.

In Table I data are given on six samples of gasoline which have been examined for gum content by the various methods described above. In the high-temperature air jet and the hot drip methods the bath liquid was tetralin, boiling at about 200° C. Samples A and E were found to be increasing rapidly in gum content, and to obtain comparative results, redetermination by certain methods was necessary. In general the values obtained in the high-temperature air jet method are near those of the hot drip and steam oven methods, and are about one-half those obtained by the conventional air jet and the 100° C. drip methods, and those of the modified air jet method are intermediate in value.

TABLE I. COMPARISON OF GUM-CONTENT VALUES BY VARIOUS METHODS

(Results expressed as mg. of gum per 50 ml. of gasoline evaporated)

GASOLINE	HIGH-TEMP. AIR JET, 190° C.	HOT DRIP, 190° C.	STEAM OVEN, 155° C.	CONV. AIR JET 100° C.–EVAPN., 150° C.–DRYING	100° C. DRIP, 100° C.–EVAPN., 150° C.–DRYING	MODIFIED AIR JET, 175° C.–EVAPN., 150° C.–DRYING
	Mg.	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*
A (original)		118 127 137	135 138	313 316	319 323	153 162
A (later)	174 172.5		193	474		
B	2.5 2.4	2.9 3.0	2.9 2.8	4.8 4.6	5.2 5.1	3.5 2.7
C	5.3 5.2	6.3 6.2	5.6 6.0	10.4 10.1	11.9 11.4	6.6 6.5
D	10.0 9.9 10.4 10.3	10.6 10.3	11.4 12.5	18.7 18.2	17.6 19.8	11.0
E	38.1 37.8	39.0	40.4 43.8 45.7	70 78 90 95 111	68 79 85 105	40.4 41.2
F	20.7 21.0 21.0	21.7 19.9	25.7 25.9		44.1	
Time in minutes to obtain dry sample of gum:	20–25	25-30	Several hrs.	70-80	70–80	70

EFFECT OF PROLONGING DRYING OF GUM

Littlejohn, Thomas, and Thompson (*9*) found that the time required for drying residues of gum obtained by air jet tests to substantially constant weight depended greatly on the temperature, and that the final gum value was also dependent, as would be expected with residues of a volatile nature, on the temperature of drying. Bridgeman and Aldrich (*2*) likewise found that there was a change in weight of the residue with time of heating and that at a drying temperature of 102° C. gum residues of the conventional air jet method required from 3 to 16 hours to reach approximately constant weight.

It has been found that the gum residues of the conventional air jet method are not dried to constant weight on heating in a 150° C. air oven for one hour, but the subsequent loss in weight does not materially affect the results. This is also the case with the gum residues of the high-temperature air jet method, where the major part of the drying takes place in the specified 15-minute period, but a further small decrease in weight may result with certain types of gum on prolonged drying. The residue is dried to such an extent after 15 minutes in the hot air stream that no further decrease in weight occurs on subsequent drying in an air oven at 150° C. for a few hours. But if, on completion of the evaporation, the sample is dried to substantially constant weight, first in an air oven at 150° C., and then in the hot air stream at 200° C., it is found that these weights are not the same, but that a considerable decrease in weight has occurred as a result of the drying in the hot air stream. It also appears that as a result of the preliminary drying in the air oven the final weight attained, after a treatment such as that just outlined, is greater than had the drying been done in the hot air stream initially. This may be the result of oxidation occurring during the drying of the residue in the air oven. Data from nine experiments are given in Table II.

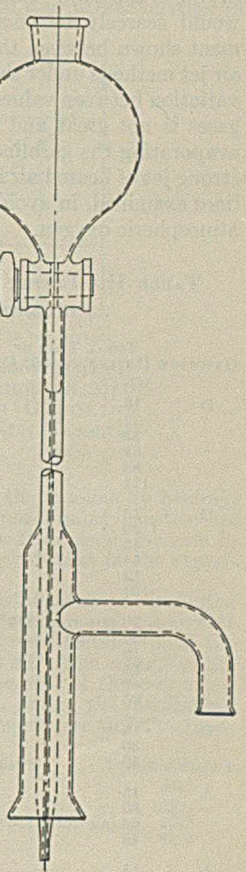

FIGURE 2. COMBINED DRIPPER AND AIR-TUBE ADAPTER, ALL GLASS
(Hot drip method)

Various samples of gum obtained during the preparation of data for Table I by the conventional air jet, the modified air jet, and the 100° C. drip methods were dried further after the initial drying period of one hour in a 150° C. air oven, and were found to have decreased in weight by percentages ranging from zero to 17 after 45 hours at 150° C., and from 6.5 to 30 after 45 hours at 180° C. When a calculation was made on the basis of the total weight of gum of all samples so treated, it was found that the prolonged drying at 150° C. had brought about a decrease in weight of approximately 4 per cent, and at 180° C. of about 10 per cent.

Two such experiments with gum residues of the conventional air jet method in which the drying was done in an air oven at 150° C. are:

	Gram
Gum from gasoline sample A:	
Dried one hour	0.4740
Dried 16 hours further	0.4577
Decrease in weight	3.5%
Gum from gasoline sample E:	
Dried one hour	0.1110
Dried 16 hours further	0.1021
Decrease in weight	8%

EFFECT OF ATMOSPHERE

Yule and Wilson (*17*) point out that with a method of evaporation of the gasoline such as the conventional air jet method the atmospheric oxygen may cause considerable oxidation to take place during the test. Norris and Thole (*12*) find that under their conditions of test this effect may not be very great, the values obtained using nitrogen being only 10 to 15 per cent less than when using air. The process of gum deposition by the hot drip method is not unlike that by the Norris and Thole method, and it is probable that there would be agreement between gum values obtained by these two methods. In Table III are given values on five samples of gasoline, obtained with air, nitrogen, and carbon dioxide as the gases used for the evaporation of the gasoline and the drying of the gum. Samples H, P, and I are very gummy and would scarcely be encountered commercially. The agreement shown between the hot drip and the high-temperature air jet methods under the same conditions is excellent, and the variation between values obtained using air and the other two gases is not great and indicates that the simple method of evaporating the gasoline and drying the residual gum with a strong jet of heated air is satisfactory, in the case of the gasolines examined, in avoiding very considerable oxidation from atmospheric oxygen.

TABLE II. EFFECT OF PROLONGING DRYING OF GUM

(High-temperature air jet method)

GASOLINE	TOTAL TIME OF DRYING AT 190° C.	AIR RATE	GUM PER 50 ML. OF GASOLINE	DECREASE FROM INITIAL
	Min.	*Liters/sec.*	*Mg.*	%
D	16	0.3 to 0.5	10.4	
	32	0.3 to 0.5	10.4	
	52	0.3 to 0.5	10.3	1
	67	0.3 to 0.5	10.1	3
	88	0.3 to 0.5	10.1	3
	111	1.3 to 1.6	10.1	3
D	15	1.4 to 1.7	10.3	
	30	1.4 to 1.7	10.3	
	45	1.4 to 1.7	10.0	3
	64	1.4 to 1.7	9.8	5
	79	1.0 to 1.2	9.8	5
	101	1.3 to 1.6	9.8	5
D	70 (air oven, 150° C.)		13.7	
	130 (total)		13.5	(1.5)
	19	0.5	11.6	(15), 0
	34	0.5	11.2	
	49	1.0 to 1.2	11.3	(17.5), 2.5
	65	1.0 to 1.2	11.3	(17.5), 2.5
D	15	1	9.9	
	30	1	9.4	5
	45	1	9.3	6
A	15	1	174.1	
	30	1	172.9	0.7
	60 (air oven, 150° C.)		172.9	0.7
	45	1	172.8	0.7
A	15	1	172.3	
	60 (air oven, 150° C.)		172.2	
	30	1	171.3	0.6
C	15	1	5.2	
	30	1	5.1	
	45	1	5.2	
C	15	1	5.3	
	60 (air oven, 150° C.)		5.4	
	30	1	5.3	
E	15	1	37.8	
	30	1	36.4	4
	45	1	36.2	4.5

VARIATION IN GUM CONTENT WITH AIR RATE

In determining the gum content of gasoline by the high-temperature air jet method it is essential that the air flow be sufficiently rapid to remove the gasoline and dry the gum effectively in a short time, in order to minimize tendencies towards excessive oxidation and abnormal polymerization of gum-forming constituents of the gasoline. This is apparent from data given on sample I (Table III), and further corroborative data are shown in Figure 3. The values were obtained on the same sample of gasoline, but at two different temperatures; this was sample H, a composite of gummy gasolines of high-gum content, on which data are also given in Table III at an experimental temperature intermediate between the temperatures here. For the values shown on curve 1, the bath liquid was a technical grade of ethylene glycol, and for those on curve 2 tetralin, the temperature of the hot air jet being about 8° C. higher in the latter case. It is seen from Figure 3 that this variation in temperature has but a very small effect on the gum value in comparison with that resulting from variation in air rate. It also appears that as the air rate is raised, the tendency towards decrease in the gum value is approaching a limit which may be near that which would be obtained when using an inert gas jet. It is seen from the curves that the variation in gum values with air rate is not great when the air rate is near one liter per second, and since in using somewhat greater rates of air flow there are difficulties encountered, such as entrainment of droplets of the gasoline in the very strong air stream, the air rate was set as one liter per second in the high-temperature air jet method.

TABLE III. EFFECT OF SUBSTITUTING NITROGEN AND CARBON DIOXIDE FOR AIR DURING EVAPORATION AND DRYING PERIODS IN HIGH-TEMPERATURE METHODS

GASOLINE	GAS	RATE OF FLOW	GUM PER 50 ML. BY HIGH-TEMPERATURE AIR JET METHOD	GUM PER 50 ML. BY HOT DRIP METHOD
		Liters/sec.	*Mg.*	*Mg.*
G	Air	1	9.6	
	Nitrogen	1	9.1	
H	Air	0.9	35	34
	Nitrogen	0.9	30	30.5
	Carbon dioxide	0.9	29.5	30
I	Air	1	198, 201	
	Air	0.4 to 0.5	240	
	Air	1.25	192	
	Nitrogen	1	168, 168.5	
	Nitrogen[a]	1	186.5	
	Carbon dioxide	1	167	
	Carbon dioxide[b]	1	205	
P	Air	1	47.7	
	Nitrogen	1	44.7	
	Carbon dioxide	1	45.4	
P-1	Air	1	16.1	
	Nitrogen	1	14.9	
	Carbon dioxide	1	15.6	

[a] Gasoline evaporated with nitrogen and gum dried with air, same rate of flow in both cases.

[b] Gasoline evaporated with carbon dioxide, dried in carbon dioxide atmosphere at very small gas flow (gum, 223 mg.), then dried with air flowing at 1 liter per second for 15 minutes (gum, 205 mg.).

TEMPERATURES RECORDED DURING AN EXPERIMENT

The temperatures, as recorded by a thermometer touching the bottom center of the beaker below the adapter outlet, both during the evaporation of a sample and the drying of the residual gum by the high-temperature air jet method, are given in Table IV. In this experiment the bath liquid was tetralin (b. p. 202° C.), and the air rate was one liter per second. It is seen that the temperature of the gasoline is quite moderate during most of the short time required for evaporation, a fact which may account for the good correlation found between the hot drip and the high-temperature air jet methods.

TABLE IV. TEMPERATURES RECORDED DURING HIGH-TEMPERATURE AIR JET GUM DETERMINATION

(By thermometer touching bottom center of beaker)

TIME[a]	TEMP.	TIME[a]	TEMP.
Min.	*° C.*	*Min.*	*° C.*
0	43	8	188
1	62	8.5	190
2	78	9	192.5
3	96	10	193.5
4	112	11	193.5
5	129	18	194
6	150	22	194
7	167		
7.3	Evaporation over		

[a] From start of evaporation.

The temperature distribution is very even at points where gum may be deposited in the beaker used in the high-temperature air jet method. The temperature was explored by means of a thermocouple under the variety of conditions recorded in Table V. The thermometer temperature with different rates of flow is also given. The bath liquid was ethylene glycol with a boiling point of 195.5° C.

Table V. Temperatures Measured by Thermocouple Held in Various Positions in Beaker

(High-temperature air jet method; bath liquid, ethylene glycol)

Air flow, liters/sec.	0.4	0.5	0.75	1.0	1.2
	° *C.*	° *C.*	° *C.*	° *C.*	° *C.*
Positions of thermocouple					
1. At levels where gum may be deposited:					
Touching bottom center	182.5	186	184.5	187.5	188
Touching bottom side	185	183	186.5	187.5	188
In air jet below outlet	179	182	181.5	186	186
At adapter outlet level halfway to beaker wall	178.5		184	184.5	186
Touching side 1/3 way up	182.5	186	186	187	187
Same half way up	182.5		182	185.5	185.5
Same 2/3 way up					184.5
Av.	181.7	184.2	184.1	186.3	186.4
2. At levels where gum is not deposited:					
Touching side at well top	152				172
Same opposite side	160			160	160
Touching side 3/4 way up				175	
Thermometer resting on bottom center	179	182	183	185.5	187

Volatility of Gum-Forming Constituents

Brookes (*3*) has pointed out the complex nature of the gum-forming constituents of gasoline, and Yule and Wilson (*17*) have shown that certain of these can be prevented from taking part in the deposition of the gum if the evaporation is carried out with rapidity and at a sufficiently high temperature. Under the conditions of evaporation existing in the intake system of an engine, and also in the high-temperature air jet method, the observations of Yule and Wilson should also be true. Certain data, presented later, obtained with the high-temperature air jet method on the effect of dilution on gum content values made it advisable to obtain further evidence as to the volatility of gum-forming constituents.

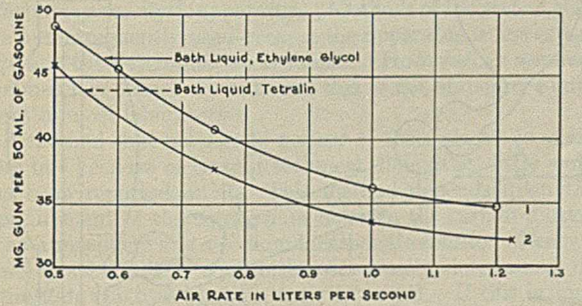

Figure 3. Variation in Values with Air Rate
(High-temperature air jet method)

These experiments show that the gum-forming constituents are not completely removed from a gasoline containing gum by relatively slow distillation, and that in such a distillation the residual gum may increase very considerably.

Steam Distillations. In one experiment where 200 ml. of distilled water and 110 ml. of sample H, which had increased somewhat in gum content from the value previously obtained, were distilled until about 5 ml. of water remained in the flask, it was found that the total gasoline in the distillate had a gum content of 3.6 mg. by the high-temperature air jet method. The residue in the flask was taken up in acetone and the gum determination showed 140 mg. In another similar experiment with sample H, it was found that when only one-half the gasoline was distilled off, the gum content of the total gasoline distilled was 1.2 mg.

It was thought that atmospheric oxygen might have been responsible for part of the gum formation in the above experiments, and so an experiment was made in which the distillation took place in a nitrogen atmosphere and the gum determinations were made with a high-temperature nitrogen jet. Distillation was made of 100 ml. of sample H and 200 ml. of distilled water until about 5 ml. of water remained in the flask. The residue of gum from the total gasoline distilled was 2.7 mg. and that in the flask was 142 mg., indicating that atmospheric oxygen had apparently been without appreciable influence in the former experiments. However, this does not exclude the possibility of oxidation occurring in these cases from compounds containing oxygen, or from atmospheric oxygen dissolved in the gasoline.

The gum content of sample H by the high-temperature air jet method, at the time these experiments were made, was 38.1 mg. per 50 ml. The very considerable increase in total gum in the sample over this value may be due to acceleration of formation of gum from constituents of the gasoline by heating; and to chemical reaction of certain gum-forming constituents with the steam may perhaps be ascribed the small increase in total gum formation here as compared with that in the experiments described below.

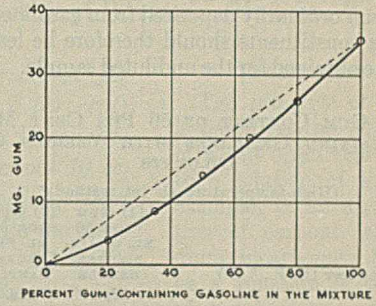

Figure 4. Gum Determinations by High-Temperature Air Jet Method on Mixtures of Gum-Containing Gasoline with Gum-Free Straight-Run Gasoline (Total Volume, 50 ml.)

Other Distillations. In these distillations an undiluted sample of gasoline H and 50 per cent mixtures of gasoline H with xylene and with petroleum ether were distilled until the residue in the flask amounted to about 3 ml. The volume of the sample was 50 ml. in each case. In the case of the petroleum ether mixture, there was a loss of 2 ml. during the distillation. The values were obtained by the high-temperature air jet method.

	Distillate	Flask Residue
	Mg.	*Mg.*
Undiluted sample H	2.3	102
Sample H and xylene	0.2	45.5
Sample H and petroleum ether	0.7	47.5

These experiments confirm the observations of Yule and Wilson that some gum-forming constituents can be distilled with the gasoline. These distillations were made at a slow rate; Yule and Wilson found, under a condition of flash evaporation at a temperature near 200° C., that 90 per cent of the peroxide content of a gasoline could be distilled without taking part in gum formation. Such data indicate that gum which will separate on evaporation of gasoline is greatly dependent on the conditions existing during the process of evaporation. The great increase in gum content of sample H, which results from holding the gasoline at an elevated temperature for a relatively short time, indicates the advantage of having a rapid and efficient method of evaporating the gasoline and drying the residual gum, if it is desired to approximate the conditions of rapid evaporation on heated surfaces and in a stream of warm air, which presumably exist in an engine.

Effect of Dilution on Gum-Content Values

Some workers (*2*, *11*) have intimated that a possible criterion for accuracy in gum determination methods is that the value obtained for a 50 per cent mixture of a gummy gasoline with a gum-free gasoline should be one-half that for the undiluted gummy gasoline sample. If gum were a pure substance dissolved in the gasoline this might be expected to be the case, but the gum ordinarily obtained on the evaporation of gasoline does not meet this requirement. To cite only one exception, gum when once separated by evaporation can only rarely be dissolved in the parent gasoline, whether deposited in laboratory tests or under the conditions existing in an engine. It has been pointed out above that a certain amount of the gum-forming material present in the gasoline can be distilled even in a relatively slow process of distillation. The amount of residual gum obtained on evaporation should be expected to be greater when dilution of the gasoline is made with an equal volume of liquid of low boiling point than when the diluent is of high boiling point. In the former case the amount of gum ordinarily deposited from gasolines containing gum-forming constituents should therefore be less than one-half the value obtained for the undiluted sample.

TABLE VI. GUM CONTENT OF 50 PER CENT MIXTURES OF GUM-CONTAINING GASOLINES WITH VARIOUS GUM-FREE DILUENTS

(High-temperature air jet method)[a]

GASOLINE	DILUENT (B. P., ° C.)	(1) GUM FROM 50 ML. OF UNDILUTED SAMPLE	(2) GUM FROM 50 ML. OF DILUTED SAMPLE	RATIO OF (2) TO (1)
		Mg.	*Mg.*	%
H	Mineral Seal oil (260–320)	38.1	22.6	59
H	Xylene (140)	38.1	23.4	61
H	"Cellosolve acetate" (140–160)	38.1	17.3	45
H	*n*-Heptane (98)	38.1	15.2	40
H	Commercial cracked gasoline (I. B. P. 30, E. P. 200)	38.1	15.1	39.6
H	Petroleum ether	38.1	15.0	39.4
H	Straight-run gasoline (I. B. P. 30, E. P. 175)	38.1	14.7	38.6
L	Straight-run gasoline (I. B. P. 30, E. P. 175)	8.4	3.1	37
J	Straight-run gasoline (I. B. P. 30, E. P. 175)	18.3	7.2	39
K	Straight-run gasoline (I. B. P. 30, E. P. 175)	25.4	9.6	38
N	Straight-run gasoline (I. B. P. 30, E. P. 175)	41.7	16.9	41
Q	Straight-run gasoline (I. B. P. 30, E. P. 175)	5.0	2.5	50
R	Straight-run gasoline (I. B. P. 30, E. P 175)	15.5	7.1	46

[a] All gums were of resinous type, except in case of gasoline Q where gum was of oily type, and in case of gasoline R where residue was partly oily, partly resinous, and partly composed of water-soluble solid.

In Table VI are given the results of a number of experiments on 50 per cent mixtures of gummy gasolines with various diluents, and in Figure 4 are shown the gum-content values obtained for different concentrations of a gummy gasoline with a gum-free straight-run gasoline. Gum determinations were made on all liquids used as diluents in the pure state, and of these only Mineral Seal oil left a residue of gum; in this case the value given in Table VI has been corrected. The results point to the presence of gum-forming constituents in most of the gummy gasolines used. Only in the case of gasoline Q could the deposited gum be completely redissolved in the original gasoline. It is also evident, from the results with gasoline H, that when the diluent is of high boiling point the gum-content value found approaches one-half the value for the undiluted sample more nearly than is the case when the diluent is of low boiling point. In certain cases the value found is greater than one-half the value for the undiluted sample, and in the case of Mineral Seal oil this may be ascribed to a prolongation of the evaporation period, thereby enabling the gum-forming material to play its role more effectively than during the evaporation of the undiluted gasoline.

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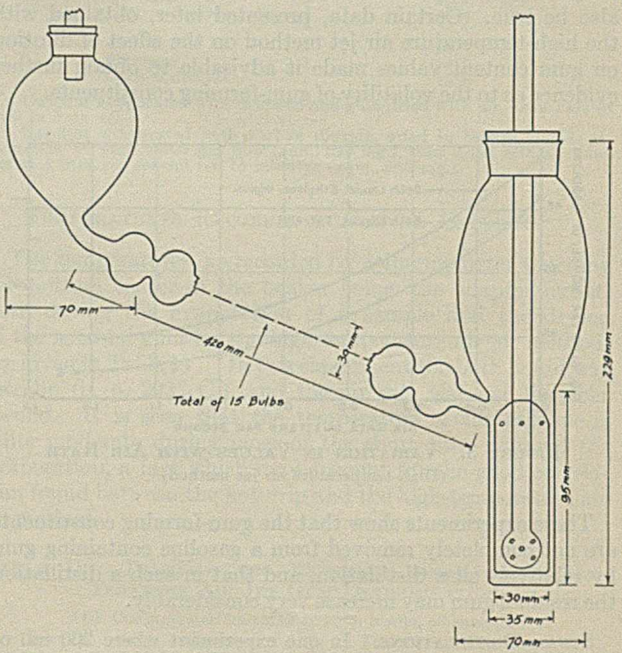
RECEIVED May 25, 1932.

An Efficient Absorption Tube

E. F. DEGERING, Purdue University, Lafayette, Ind.

THE accompanying figure shows a combination of the Folin and Meyer absorption tubes. This type of tube has proved much more efficient as a gas scrubber than either the Folin or the Meyer tubes, and is especially useful as absorption apparatus where a rather rapid flow of a gas is being scrubbed by suitable liquid absorbents.



The dimensions given in the drawing are for a tube holding about 150 cc. of the absorbing liquid or solution. Tubes of proportionate size would satisfy the requirements for smaller or larger amounts of the absorbent.

If made of Pyrex glass and properly handled, tubes of this type are quite durable and very satisfactory in analytical procedures. These tubes were designed and made as a means of affording more accurate determination of carbon dioxide by the wet method where a rapid flow of the gases was required.

RECEIVED May 5, 1932. Tube designed and made in connection with a research problem at the University of Nebraska.

Determination of Carbon Dioxide in Gas Mixtures

A Potentiometric Method

P. W. Wilson, F. S. Orcutt, and W. H. Peterson, University of Wisconsin, Madison, Wis.

A rapid, accurate method is described for measuring low percentages (0.03 to 7 per cent) of carbon dioxide in gas mixtures. It consists of bubbling the gas mixture through about 10 cc. of dilute sodium bicarbonate solution, then determining the pH of the solution with the glass electrode. From a calibration curve the pCO_2 *can be readily ascertained. The theory upon which the method is based is discussed. For routine analyses a set-up is described which combines speed and ease of operation with a maximum error of 4 per cent. For a greater accuracy, certain refinements are indicated. The method can be modified for use with a pH colorimeter, if a suitable potentiometric set-up is not available.*

The need for a rapid, accurate method of estimating carbon dioxide is common to many branches of science. A large number of studies in both theoretical and applied chemistry demand simple methods for determining small percentages of carbon dioxide in air and other gaseous mixtures. It is not surprising that many ingenious devices have been developed in an effort to satisfy this need. The majority of the proposed methods can be classified into the following types: (1) those in which the $PV = K$ property of gases is utilized; (2) those in which the carbon dioxide in a known volume of gas is absorbed in alkali and subsequently measured by chemical or physical means. The first class includes those methods in which special apparatus is required—e. g., the Haldane, Van Slyke, or Warburg gas analysis apparatus. Methods of the second class are more frequently used because the apparatus is less expensive and the determination is simple. However, an accurate gas meter is often required, and this is not standard equipment in most laboratories.

A method that belongs to neither of these classes is available but because of certain technical difficulties, little work has been reported on it. This method depends upon the measurement of the equilibrium between the carbon dioxide in an atmosphere and a sodium bicarbonate solution of known concentration. The equilibrium is usually determined by estimating the hydrogen-ion activity or pH. If this is done by means of the hydrogen electrode, elaborate precautions must be maintained to avoid displacement of the equilibrium, hence the method becomes too tedious for routine analyses. Recourse to colorimetric methods, such as proposed by Haas (*4*), Higgins and Marriot (*7*), and McClendon (*11*), has proved of value, but this expedient has sacrificed accuracy to ease of operation. Since colorimetric standards can be read to less than 0.1 pH only with difficulty, the error involved in a determination may be considerable. The accuracy of this method has been increased by determining the pH potentiometrically with the glass electrode, and thus the qualities necessary for routine analyses—i. e., rapidity, simplicity, and ease of operation—have been preserved. The method as finally developed is accurate to 0.02 pH (one millivolt) which is the limit of accuracy of the potentiometer set-up in this laboratory. The only apparatus required is a vacuum-tube potentiometer, or any other devices suitable for measuring pH with the glass electrode. Since the glass electrode method for the determination of pH is gaining favor in biological and chemical laboratories, this method should be available to many without the expense of additional equipment.

Theoretical Data

The principle of the method is based on the buffering effect of a salt of an acid when added to a solution of the acid; for example, in an aqueous solution of carbonic acid and sodium bicarbonate the pH will be a function of the activities of the bicarbonate ion and carbonic acid present. The latter depends on the partial pressure of the carbon dioxide in the atmosphere which is in equilibrium with the solution. If the activity of the bicarbonate ion is fixed, then the pH is a function solely of the partial pressure of the carbon dioxide that is in equilibrium with the sodium bicarbonate solution. Since carbonic acid is only very slightly ionized in solution, the effective concentration (or activity) of the bicarbonate ion is sensibly that of the sodium bicarbonate present in the solution. It follows that if a dilute solution of sodium bicarbonate of known concentration is brought to equilibrium with an atmosphere containing carbon dioxide, the final pH of the solution measures the pCO_2 in the atmosphere and is independent of the volume of gas passed through or the volume of sodium bicarbonate used.

Because of the importance of this sodium bicarbonate–carbonic acid equilibrium in physiological chemistry, intensive studies of the reaction have been made by a large number of investigators. Hasselbach (*5*) studied this equilibrium and derived the equation

$$\mathrm{pH} = pK + \log \delta + \log \frac{(\mathrm{HCO_3^-})}{(\mathrm{CO_2})} \qquad (1)$$

where pK represents the negative log of the first dissociation constant of carbonic acid, and δ the degree of dissociation of sodium bicarbonate in the solution used.[1] Warburg (*13*) discussed the equation and the data of Hasselbach in light of the new theory of complete dissociation of strong electrolytes, and pointed out that Hasselbach's treatment was merely a first approximation, since concentrations rather than activities were employed. Warburg then developed the corrected mathematical relations for use under various assumptions and conditions. He showed that the bicarbonate ion due to the dissociation of the carbonic acid can be neglected if a concentration of sodium bicarbonate is used such that

$$\frac{cH}{cM} < 0.01$$

where cH is the concentration of hydrogen ions and cM is the concentration of the sodium bicarbonate. Also, he

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[1] If δ is the activity coefficient of sodium bicarbonate, this equation is correct and is independent of any theory (see Equation 2).

demonstrated that if the measured pH was less than 8.0, the error arising through neglect of the second dissociation constant of carbonic acid is negligible. Hastings and Sendroy (*6*) studied the application of the Debye-Hückel theory of electrolytic dissociation to the sodium bicarbonate–carbonic acid system in the presence and absence of other ions—e. g., sodium chloride. The theoretical equation applicable to the system that was derived by these investigators is:

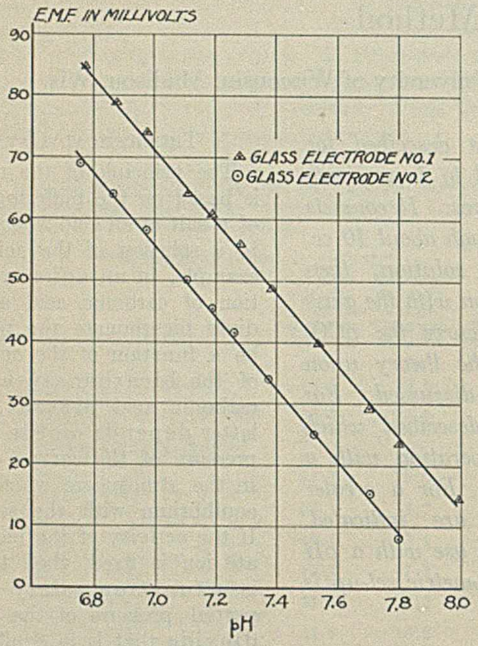

Figure 1. Change of E. M. F. with pH Using Glass Electrodes

$$pK_1 + \log \gamma_1 = \text{pH} - \log (\text{NaHCO}_3) + \log p\text{CO}_2 + \log \frac{\alpha_{\text{CO}_2}}{760 \times 22.4} \qquad (2)$$

where pK_1 = $-\log K_1$
K_1 = apparent first dissociation constant of carbonic acid
γ_1 = activity coefficient of sodium bicarbonate in concentration used
(NaHCO_3) = molal concentration of NaHCO_3
$p\text{CO}_2$ = partial pressure of CO_2
α_{CO_2} = solubility coefficient of carbon dioxide in water at temperature used

If $pK_1 + \log \gamma_1$ is designated by pK_1', this latter will be a constant for a given concentration of sodium bicarbonate, and according to the Debye-Hückel theory should vary with the concentration in dilute solutions according to the following equation:

$$pK_1' = pK_\infty' - 0.5\sqrt{\mu} \qquad (3)$$

where pK_∞' = value of pK_1' at infinite dilution
μ = ionic strength = $^1/_2 \Sigma c_i v_i^2$
v_i = valence of ions
c_i = molal concentration of ions

Using very exact experimental technic, Hastings and Sendroy determined the value of pK_1' over a range of concentrations of sodium bicarbonate extending from 0.01 to 0.03 normal with and without added sodium chloride, so that the ionic strength varied from 0.01 to 0.18. Their results closely followed the equation predicted by the theory and gave a value of pK_∞ of 6.33 at 38° C. Stadie and Hawes (*12*) extended this work and verified the value of pK_∞. These workers also discuss the variation of the value of this constant with temperature. The value of $\Delta pK_\infty / \Delta T$ varied from 0.005, based on e. m. f. measurement, to 0.0069 based on Thomsen's colorimetric determinations; the best agreement was among the e. m. f. measurements.

EXPERIMENTAL PROCEDURE

Determination of pH. The method was developed to measure the carbon dioxide in air supplied to plants grown in atmospheres containing 0.1 to 1 per cent of this gas. It was necessary to use 0.001 *N* solutions of sodium bicarbonate for the lower concentrations of carbon dioxide and 0.01 *N* for the higher. An attempt was made to use the quinhydrone electrode to measure the pH, but this proved unsatisfactory because of the drifting of the e. m. f. Glass electrodes were next tried and proved very satisfactory. The vacuum-tube potentiometer used to measure the e. m. f. was a modification of the type described by Allyn and Baldwin (*1*). This set-up employs a UX-199 vacuum tube, the grid bias of which is adjusted as closely as possible to the value at which there is zero grid current (floating grid potential). The actual grid current obtained, although varying considerably, was never greater than 10^{-12} amperes. This potentiometer is simple in construction, inexpensive, and gives reproducible results with a minimum of care. It is sensitive to one millivolt which was sufficiently accurate for these purposes. Glass electrodes as described by MacInnes and Dole (*8*, *9*) were first tried, but because of the necessity for frequent handling, transportation, etc., these were found to be too fragile. The electrode finally adopted was made by sealing about 3 cm. of 6-mm. Corning 015 glass (*9*) to 20 cm. of ordinary soft glass, then blowing a fairly thin bulb about 10 mm. in diameter on the special glass end. The thickness of this bulb is limited to the sensitivity of the potentiometer employed and can best be determined by trial. The desiderata of these electrodes are that they should be sturdy enough to withstand considerable shock in handling and yet give a constant, reproducible potential when used to measure the pH of a standard buffer solution. As the bulbs increase in thickness, the potentials become less reproducible, because of changes in body capacity, leakage currents in the circuit, variations in grid current, etc. With a little practice the desirable thickness is readily ascertained; an actual test is the final criterion as to whether or not a suitable bulb has been blown. Measurements on a typical bulb indicated that the glass membrane was about 50 microns in thickness; the resistance of these bulbs is of the order of 200 to 250 megohms.

After a suitable bulb has been blown, the electrode is filled with saturated potassium chloride solution and aged in this solution for 3 weeks. It is then tested daily for about a week against a standard buffer solution. In these tests the e. m. f. measurement is made on the cell:

$$+\,\text{Hg} \mid \text{HgCl} \mid \text{sat. KCl} \parallel \begin{matrix}\text{buffer}\\ \text{soln.}\end{matrix} \parallel \text{glass} \parallel \begin{matrix}\text{sat.}\\ \text{KCl}\end{matrix} \mid \text{HgCl} \mid \text{Hg}^-$$

Since the two calomel half-cells cancel each other, the observed e. m. f. is due to difference in pH of the solutions on either side of the glass membrane plus the "asymmetrical potential"—i. e., the potential in the glass (*3*, *9*). An ordinary type of calomel half-cell is used in the above cell, and contact is made with the glass electrode by filling the latter completely with saturated potassium chloride solution. When the electrodes were first prepared, the asymmetric potential was found to vary, but after aging, it remained very constant in the majority of the electrodes.

If, after aging, the electrode is found to have a constant potential against a standard buffer solution (constant asymmetric potential), it is sealed to a calomel half-cell as shown in Figure 2. This half-cell is readily made by sealing a side arm of 6-mm. glass tubing into about 10 cm. of 10-mm. glass tubing, the lower end of which has had a platinum wire sealed in as shown in the figure. Near the upper end of this 10-mm. tube, a constriction is made. The glass electrode is now sealed to the side arm, after which the mercury calomel and saturated potassium chloride are added. In order to fill completely the side arm and electrode, it is necessary to apply suction occasionally to remove trapped air. After filling, the half-cell is sealed off at the constriction. Electrodes made at the same time and aged in the same way give fairly constant values with the same buffer solutions, as shown in Table I. These measurements were made on Sorensen's phosphate buffer mixtures in the range covered by this method. The results indicate that, although the apparent asymmetric potential may differ to some extent among various electrodes, the difference is independent of the pH that is measured.

TABLE I. COMPARISON OF DIFFERENT GLASS ELECTRODES FILLED WITH SATURATED POTASSIUM CHLORIDE

BUFFER	ELECTRODE			
	1	2	3	4
pH	*E. m. f.*	*E. m. f.*	*E. m. f.*	*E. m. f.*
7.78	0.022	0.022	0.030	0.026
7.53	0.033	0.034	0.044	0.039
7.38	0.043	0.044	0.053	0.049
7.18	0.053	0.054	0.063	0.059
6.87	0.072	0.073	0.082	0.078

MacInnes and associates (*9*, *10*) have shown that from pH 1 to 9 the glass electrode described by them gives potentials which vary with the hydrogen-ion activity exactly as the hydrogen electrode. To determine if the electrode described behaved as a hydrogen electrode in the range employed in this method, potentials were taken on Sorensen's phosphate buffer solutions ranging in pH from 6.7 to 8.0. The data for two electrodes which differ in the asymmetric potential by 15 mv. are given in Figure 1. The points fall on a straight line which has the correct slope, 0.059. These data indicate that the behavior of the electrodes is quite consistent in this range of pH.

A calibration curve was prepared for the method by determining the pH of sodium bicarbonate solutions of known concentration which had been brought to equilibrium with an air mixture containing a known percentage of carbon dioxide. The air mixtures were prepared by the addition of pure carbon dioxide from a cylinder to air in a 20-liter Pyrex bottle. Acidulated water was used as a confining liquid, and each mixture was allowed to stand 2 hours with occasional shaking to allow the gas to come to equilibrium with the water. The mixture was displaced with acidulated water, passed through two Truog towers in series containing 0.1 *N* sodium hydroxide, then through a tell-tale containing bromothymol blue as an indicator, and finally measured by a gas meter. In order to reduce the error arising from the solubility of the carbon dioxide in the displacing liquid, the latter was run in quite rapidly so that the time required for a determination was about 10 minutes. The gas mixture was divided as it came from the mixing bottle and part passed through a sodium bicarbonate solution of known concentration. The sodium bicarbonate solution was prepared by diluting a standard solution of sodium hydroxide and adding carbon dioxide until a pH of about 6.0 was reached. Phenol red indicator (75 cc. of a 0.01 per cent solution per liter) was added to the sodium hydroxide solution during dilution to aid in the estimation of the end point. The apparatus used for equilibrating the bicarbonate solution is shown in Figure 2. The gas passes through the inlet *a* which is drawn to a fine point, bubbles through the sodium bicarbonate solution, and out at *b*. The presence of phenol red in the bicarbonate helps to decide when equilibrium is reached. Five minutes' bubbling at a rapid rate suffices to bring about 10 cc. of solution to equilibrium. During the aëration, the Pyrex tube containing the bicarbonate was kept in a water bath maintained at 26° ± 0.1° C.[2] After equilibrium was reached, the stopcocks were closed and the pH of the solution determined. It was found that the pH does not change even though the bicarbonate solution is allowed to stand 1 to 2 hours after equilibrium is reached.

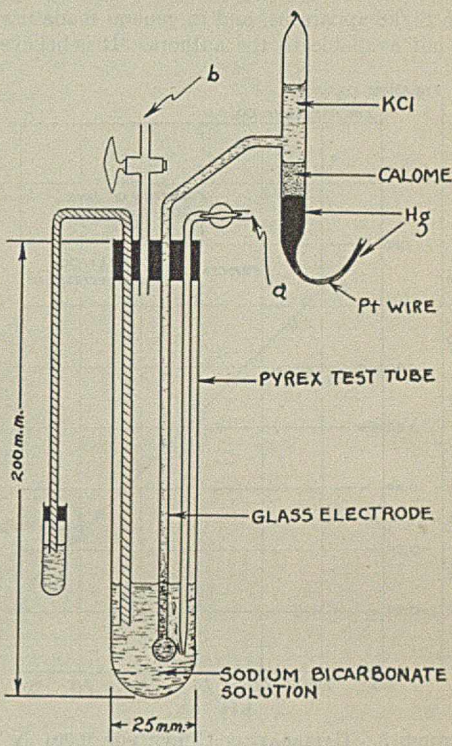

FIGURE 2. DIAGRAM OF APPARATUS

After obtaining the reading on the bicarbonate solution, the electrode was checked by determining the e. m. f. of a known buffer solution. The pH of the bicarbonate solution was calculated from the formula:

$$pH_1 = pH_2 + \frac{e.\ m.\ f._2 - e.\ m.\ f._1}{0.0593} \text{ at } 26^\circ \text{ C.} \qquad (4)$$

where subscript 1 refers to the bicarbonate solution and subscript 2 to the standard buffer solution. All pH determinations were made in duplicate, and checks with 0.02 pH units were constantly obtained. The carbon dioxide in the gas was determined by a double titration modification of the official volumetric method (*2*). With the volume of gas passed through the towers and the temperature and pressure known, the partial pressure of carbon dioxide in the gas mixture can readily be calculated. Assuming that the concentration of the bicarbonate ion is equal to that of the sodium bicarbonate solution used and taking α_{CO_2} equal to 0.738, Equation 2 reduces to:

$$pK_1' = pH + \log pCO_2 - 1.362$$

Fourteen determinations gave a value for pK_1' of 6.31 ± 0.007, indicating that the results were quite consistent.

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[2] This temperature was used because the incubator room in which the potentiometer was set up was kept at this temperature.

From the results obtained by Hastings and Sendroy (*6*) at 38° C. and using $\Delta pK_1'/\Delta T = 0.005$, the value of pK_1' at 26° C. and for 0.001 *N* sodium bicarbonate concentration should be 6.375. The agreement is certainly all that could be expected in view of the differences in technic. Hastings and Sendroy determined the carbon dioxide in the gas mixtures by the Haldane apparatus, estimated the free and bound carbon dioxide in the bicarbonate solution by means of the Van Slyke apparatus, and in general made use of refinements not available to the authors. It is believed that use of this empirical calibration curve constructed from the results obtained under the conditions in use in the laboratory (in regard to saturation, e. m. f. measurement, etc.), is more satisfactory than would be the use of a theoretical curve based on data obtained under more ideal conditions. It is desirable that anyone adopting the method construct his own calibration curve, but if this is not possible and if the analyses are made exactly as described, the graph in Figure 3 can probably be used without introduction of appreciable error. The points located by use of the 0.001 *N* sodium bicarbonate are marked in Figure 3 by circles.

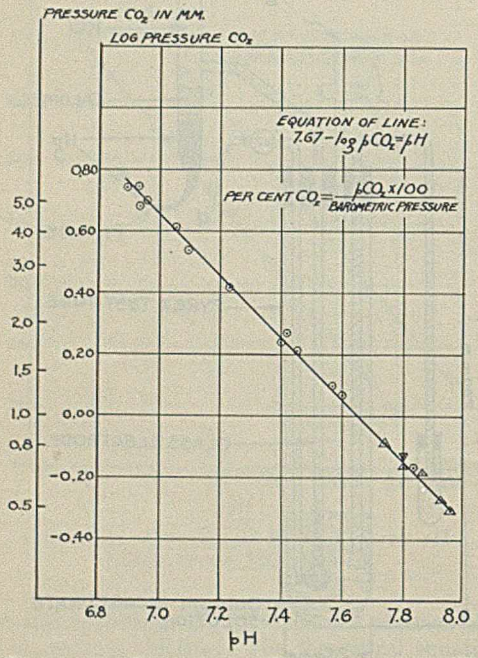

FIGURE 3. CALIBRATION CURVE FOR 0.001 *N* AND 0.0107 *N* SODIUM BICARBONATE

(For 0.0107 *N* sodium bicarbonate solution, multiply ordinate reading by 10)

If the pCO_2 in the gas mixture is plotted against the equilibrium pH for a given concentration of sodium bicarbonate, a logarithmic curve results. For the most accurate results (speed and stability of equilibrium), it is desirable to keep the pH measurements on the part of the curve at which the curvature is greatest. This can be done by increasing the concentration of the sodium bicarbonate solution, whenever the pCO_2 is such that the pH measured lies on the flat part of the curve. Thus for mixtures containing more than 0.7 per cent carbon dioxide, it is advantageous to increase the concentration of the sodium bicarbonate solution to about 0.01 *N*. Since the theoretical pK_1' for this strength of bicarbonate is 6.34, it is necessary that a slightly stronger solution of sodium bicarbonate be used in order that the same line will represent partial pressures of carbon dioxide that are ten times as strong as those indicated by the ordinates. For example, if 0.001 *N* sodium bicarbonate is used, a pH of 7.67 represents a partial pressure of 1 mm. of carbon dioxide. If 0.01 *N* sodium bicarbonate is used, a pH of 7.67 represents a pCO_2 of only 9.33 mm.[3] Use of Equation 3 shows that if 0.0107 *N* sodium bicarbonate is used, a pH of 7.67 will represent 10.0 mm. of pCO_2, and hence one line will serve for a ten-fold increase in concentration. The points designated by triangles were obtained by use of 0.0107 *N* sodium bicarbonate and were placed on the graph after dividing the pCO_2 by 10—i. e., subtracting 1.00 from the log pCO_2.

METHOD

APPARATUS. The apparatus and solutions required for the determination of carbon dioxide in a gas mixture are: a glass electrode fitted in the aëration device shown in Figure 2, a potentiometer capable of measuring the pH of a solution with the glass electrode, and a standard solution of 0.001 or 0.0107 *N* sodium bicarbonate. The construction of the glass electrode has been given in detail in the text. The sodium bicarbonate solution is made by dilution of standard solution of sodium hydroxide and passing in carbon dioxide until a pH of about 6.0 is reached; phenol red indicator can be added to the solution during dilution to aid in the estimation of this end point.

PROCEDURE. For the analysis of a gas mixture containing 0.03 to 0.7 per cent carbon dioxide, about 10 cc. of 0.001 *N* sodium bicarbonate are placed in the aëration device, (Figure 2), and the mixture to be analyzed passed through at the rate of 4 to 5 bubbles per second. After approximately 5 minutes of aëration, the stopcocks are closed and the e. m. f. determined by a suitable potentiometric set-up. The pH of the bicarbonate solution is calculated from Equation 4, and the partial pressure of carbon dioxide determined from the calibration curve, Figure 3. For concentrations of carbon dioxide ranging between 0.7 and 7 per cent, 0.0107 *N* sodium bicarbonate solution is used. If the "asymmetric potential" of the glass electrode remains constant as shown by e. m. f. readings on a standard buffer solution, the calibration curve can be constructed to read pressures of carbon dioxide directly from the e. m. f. determination.

APPLICATION AND MODIFICATIONS

The method was tested by determining the carbon dioxide in gas mixtures that were used in the greenhouse; these mixtures were prepared by adding pure carbon dioxide to air, controlling the proportions of each by flowmeters. The tubes of the aëration apparatus were kept in a cheap and easily built water bath made from a large battery jar placed in a box and insulated with shavings. The temperature was maintained at 26° C. by adding cold water or by heating with a blackened 200-watt electric lamp. Temperature control of 0.1° to 0.2° C. for 10 to 15 minutes is readily obtained, and this suffices for routine analyses. At the same time that the equilibrium measurements were taken, check analyses were made by absorbing from a known volume of gas the carbon dioxide present by the method already described. The results were quite satisfactory, as the average recovery on mixtures whose carbon dioxide content ranged from 0.15 to 0.9 per cent was 103 ± 1.29 per cent. The accuracy of this method is limited by the accuracy of the pH determination, which is about 0.02 of a pH unit, corresponding to a maximum error of about 4 per cent.

Whenever a determination is made of the carbon dioxide content of an air mixture, the electrode is checked after the

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[3] Assuming that the pK_1' corresponding to the authors' technic would be 0.035 less than that found for 0.001 *N* sodium bicarbonate—i. e., 6.275. The mean of seven determinations of 0.0107 *N* sodium bicarbonate was 6.28 ± 0.005, which is consistent with the values for 0.001 *N* sodium bicarbonate.

determination by means of a standard buffer solution. This added reading requires only a few minutes and serves to determine if the asymmetric potential is unchanged. Over a period of weeks, no change in two electrodes used in analysis has been observed, and hence this added determination may appear to be redundant. However, the extra labor is repaid by increased confidence in the results.

The method as described here was developed for the specific purposes of routine analyses of air samples in greenhouse work. Great accuracy was not essential for this purpose, since 5 per cent error could be tolerated. It is apparent that the method as described can be readily applied to other problems similar to this. If higher accuracy is desired, certain modifications can be made—e. g., increased accuracy of the potentiometer readings, analysis of the sodium bicarbonate solution for bound carbon dioxide content, etc. It might also be desirable to use a silver-silver chloride electrode in 0.1 *N* hydrochloric acid instead of the calomel half-cell. If the electrodes are not required to stand much shock in handling, the glass electrode described by MacInnes and Dole (*9*) and MacInnes and Belcher (*10*) might be advantageous. The calibration curve should also be determined by more refined technic, if high accuracy is desired.

Laboratories which do not have the facilities for use of the glass electrode can readily adapt the method for their needs by use of an accurate colorimetric method. With one of the newer types of pH colorimeter, an accuracy of 0.05 pH can be obtained, and this would suffice for most routine work. For example, the $p\mathrm{CO}_2$ in an atmosphere could readily be determined by the insertion of the apparatus (Figure 2) without the glass electrode in the line supplying the gas mixture. Whenever desirable, colorimetric readings could be taken and the $p\mathrm{CO}_2$ read from Figure 3, and in this way it would be possible to maintain a close check on the carbon dioxide content of the atmosphere. The accuracy of the results would not be as high as with the glass electrode, but a high degree of accuracy is usually achieved by the expenditure of considerable time and care. Often for routine work, ease and speed of manipulation are more desirable than the next decimal place.

DISCUSSION

It appeared to be of interest to check the results against those of other investigators who have made use of this principle for the determination of carbon dioxide. Higgins and Marriot (*7*), who determined the pH colorimetrically, state that they arrived at the carbon dioxide values of the pH standards used by empirical methods. An examination of the values obtained indicate that these are in great error. For example, a plot of their data (assuming a constant barometric pressure of 760 mm.) gives points that lie on a fairly straight line except at the higher concentrations of carbon dioxide. The equation of the line for 0.001 *N* sodium bicarbonate is:

$$\mathrm{pH} = 7.42 - 0.89 \log p\mathrm{CO}_2 \qquad (5)$$

Calculations of the value of pK_1' from this line show that this "constant" varies from 5.99 to 6.12. If a barometric pressure of 740 mm. is assumed, these values are lowered slightly. The variation in the value of this constant is due to the slope of the line differing from unity. As already noted, the correct value for the constant at 26° C., according to the careful work of Hastings and Sendroy, is 6.375. Some difference would be expected if less careful technic were used, but the difference noted is larger than one might expect from mere difference in procedure and suggests that the results were subjected to a rather large systematic error. Higgins and Marriot advise use of 0.0085 *N* sodium bicarbonate for concentrations of carbon dioxide ten times as great as those determined with the 0.001 *N* sodium bicarbonate. It has already been shown that this concentration should be 0.0107 *N*. Calculations of pK_1' for 0.0085 *N* sodium bicarbonate from Higgins and Marriot's data give values ranging from 6.05 to 6.19—i. e., values higher than with 0.001 *N* sodium bicarbonate. Reference to Equation 3 shows that this value should decrease with increasing concentration of the bicarbonate.

McClendon (*11*) also gives graphs showing plots of the pH of sodium bicarbonate solution of varying concentration in equilibrium with atmospheres containing carbon dioxide. He suggests a method for determining carbon dioxide in air, similar to that of Higgins and Marriot. The slopes of the lines are around 0.8, hence the values of pK_1' calculated from them vary greatly and in all cases are low. McClendon, however, states that this report is preliminary and great accuracy is not claimed for the data.

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A Composite Reagent for Calcium

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IN AN extensive study involving the determination of calcium in bone ash dissolved in dilute hydrochloric acid, a combination of some of the separate solutions used in the precipitation of calcium oxalate was found convenient.

The reagent employed is prepared by dissolving 200 grams of oxalic acid ($\mathrm{H_2C_2O_4.2H_2O}$) and 500 grams of ammonium chloride in 3500 cc. of water. Then 1000 cc. of glacial acetic acid and 10 cc. of 0.04 per cent methyl red are added, and if any precipitate is formed, the solution is filtered. For the amounts of calcium concerned, 50 cc. of the reagent were measured in a cylinder and added to the properly diluted calcium solution. The mixture was heated to boiling and ammonium hydroxide added to make the reaction slightly alkaline to methyl red.

This composite reagent is satisfactory for the precipitation of calcium oxalate from bone ash solutions. For use in the analysis of other materials, different proportions may be necessary. The combination of the four reagents into one solution is obviously always advantageous because of the consequent saving in time and the uniformity of procedure without loss of precision.

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Phospholipide Content of Fluid Cream

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INTEREST in the phospholipide content of various food substances has been stimulated by recent nutritional studies demonstrating the value of lecithin in the diet and by a recognition of its remarkable emulsifying powers. This has led to a desire for more exact data on the occurrence of phospholipides in fluid milk and cream. The following report covers work conducted in this laboratory on its determination in cream.

The comparatively few results reported in the literature on the phospholipide content of fluid cream show great variations. Although three phospholipides (*1*, *6*, *7*), lecithin, cephalin, and a diaminophospholipide, have been identified in cow's milk, it has been a common practice to express the total phospholipide content as distearyl lecithin. The methods used by investigators for the extraction of the phospholipide and for the subsequent determination of the phosphorus content of the extract have differed greatly. This may account in part for the lack of uniformity in results. Moreover, although the phospholipide content of cream is known to vary with the butter fat content, data reported in the literature are the results obtained with creams containing varying amounts of fat. If the reported data are calculated to milligrams of phosphorus per 100 grams of cream, assuming the lecithin when reported as such to be the distearyl type,[1] the values range from 3.62 to 13.3 mg. of phosphorus per 100 grams of cream.

A determination of the phospholipide content of fluid cream involves two major steps: (1) the quantitative removal of phospholipide from the cream, (2) the determination of the phospholipide in the extract.

The Mojonnier modification of the alkaline Roese-Gottlieb procedure has been recommended for the extraction of phospholipides along with the butterfat from milk products (*3*, *8*, *9*). Whether or not all of the lecithin-like material is recovered by this procedure is still a debatable question. Petersen and Herreid (*8*) quantitatively recovered known amounts of lecithin which had been added to buttermilk. Chapman (*3*), on the other hand, was unable to recover all the added lecithin from buttermilk by this method. He does not specify the form in which the lecithin was added. In the experiment conducted by Petersen and Herreid, the lecithin was weighed into the flask containing buttermilk and was not added as an emulsion. This may account for the higher percentage recovery obtained by the latter workers. It is likely that the form in which the lecithin appears in a mixture, whether or not it is hydrated—i. e., thoroughly emulsified—plays an important part in the ease with which it is extracted.

METHOD OF EXTRACTION

Experiments conducted in this laboratory on the extraction of known quantities of lecithin from aqueous dispersion indicate that inorganic salts and possibly other materials exert definite effects on the extraction of the phospholipide. Fugii (*5*) found that the addition of either egg albumin or salt to an aqueous dispersion of lecithin increased the amount of lecithin extracted with ether. The combined effect of albumin and salt, however, was not additive, owing, according to Fugii, to the formation of compounds of albumin and salt.

The source of lecithin in these experiments was a sample of commercial soy-bean lecithin (lipinol). The product contains some 30 per cent soy-bean oil, but is completely soluble in both ethyl and petroleum ether.

It is apparent from the data reported in Table I that the presence of skim milk solids[2] or inorganic salts increases materially the percentage recovery of lipinol from aqueous dispersion. Although small amounts of sodium and calcium chloride have been found to be carried over in the ether extracts, when these salts are added to an aqueous emulsion of lipinol, the increased recovery obtained is more than the amount of the contaminating salt. Differences of a few per cent in the latter cases, however, are not significant. Neither sodium nor potassium sulfate was found in the ether extracts. When sodium sulfate alone was added to the aqueous dispersion, the recoveries were equal to those in which both skim milk solids and sodium sulfate were added. These recoveries were 93 to 96 per cent, showing an increase of 10 per cent over the recovery without the addition of salt or skim milk solids. Since the lecithin used in these experiments was highly hydrated, the added salts together with the alcohol used in the extraction mixture probably caused a dehydration of the lecithin and thus made possible a more complete extraction with ether.

Table I. Roese-Gottlieb Extraction of Lipinol from Aqueous Dispersion

Sample	Amt.	Reaction	Salt, 1 Gram	Recovery
	Gram			%
Lipinol	0.1	Neutral		83.5
				83.4
				85.4
Lipinol	0.1	Neutral	NaCl	98.8
		Neutral	NaCl	101.8
		Neutral	$CaCl_2$	112.9
		Neutral	$CaCl_2$	98.8
		Neutral	Na_2SO_4	92.6
		Neutral	Na_2SO_4	92.2
		Neutral	K_2SO_4	93.2
		Neutral	K_2SO_4	92.3
Lipinol + skim milk solids[2]	0.1 + 0.9	Neutral		89.4
		Neutral		91.6
		Neutral		89.7
		Neutral		90.8
Lipinol + skim milk solids	0.1 + 0.9	Neutral	NaCl	87.9
		Neutral	$CaCl_2$	92.8
		Neutral	Na_2SO_4	93.9
		Neutral	K_2SO_4	89.5
Lipinol	0.1	Alkaline		83.8
		Alkaline		82.8
		Alkaline	NaCl	99.2
		Alkaline	$CaCl_2$	104.6
		Alkaline	Na_2SO_4	97.2
		Alkaline	K_2SO_4	89.6
Lipinol + skim milk solids	0.1 + 0.9	Alkaline		90.4
		Alkaline		92.4
		Alkaline	NaCl	90.1
		Alkaline	$CaCl_2$	92.0
		Alkaline	Na_2SO_4	96.1
		Alkaline	K_2SO_4	94.6
		Acid	NaCl	93.3
		Acid	$CaCl_2$	94.6
		Acid	Na_2SO_4	93.6
		Acid	K_2SO_4	91.6

Other methods of extraction were attempted in an effort to find a solvent or combination of solvents which would re-

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[1] The phospholipides in the extract do not consist solely of distearyl lecithin.

[2] Blanks on the skim milk solids were subtracted from the total extracts.

move lecithin quantitatively from an aqueous emulsion. From the data reported in Table II, it is evident that only a small amount of lecithin was extracted by petroleum ether alone or after the addition of alcohol. Extraction with alcohol and a mixture of ethyl and petroleum ether gave the best results when the concentration of alcohol was 50 per cent. Acetone was substituted for alcohol in the extraction mixture, but without a noticeable increase in the recovery of the extract. The best method of extraction, therefore, appeared to be the Mojonnier modification of the Roese-Gottlieb procedure, after the addition of skim milk solids or inorganic salts to the dispersion.

TABLE II. EXTRACTION OF LIPINOL FROM AQUEOUS DISPERSION

ALCOHOL CONCENTRATION	SOLVENT	RECOVERY OF LIPINOL
%		%
..	Petroleum ether	2.27
20.0	Petroleum ether	2.70
33.3	Petroleum ether	2.05
42.8	Petroleum ether	23.65
50.0	Petroleum ether	49.24
20.0	Ethyl and petroleum ether	2.52
42.8	Ethyl and petroleum ether	Bad emulsion
45.0	Ethyl and petroleum ether	73.18
50.0	Ethyl and petroleum ether	71.78
55.0	Ethyl and petroleum ether	68.44
60.0	Ethyl and petroleum ether	59.37
75.0	Ethyl and petroleum ether	48.18
77.0	Ethyl and petroleum ether	51.61
80.0	Ethyl and petroleum ether	51.51
45.0	Neutral Roese-Gottlieb	86.08
50.0	Neutral Roese-Gottlieb	85.63
55.0	Neutral Roese-Gottlieb	80.64
50.0	Alkaline Roese-Gottlieb	85.03
ACETONE CONCENTRATION		
50.0	Alkaline Roese-Gottlieb	20.96

The procedure described above does not extract appreciable amounts of inorganic phosphate. Alcoholic and Roese-Gottlieb extracts of aqueous solutions of potassium dihydrogen phosphate and calcium monophosphate were made and the phosphorus content of the extracts determined. The concentrations of inorganic phosphorus were greater than those which exist in milk or cream. It will be noted from Table III that only small amounts of phosphorus were found in the residues resulting from the alkaline Roese-Gottlieb extractions. By use of this procedure, therefore, the amount of contaminating inorganic phosphate in an extract of cream is negligible.

TABLE III. EXTRACTION OF INORGANIC PHOSPHORUS WITH SOLVENTS

SAMPLE	AMT.	METHOD OF EXTRACTION	PHOSPHORUS Present	PHOSPHORUS Extracted
	Gram		*Mg.*	*Mg.*
KH_2PO_4	0.05	Alkaline Roese-Gottlieb	11.4	0.007
KH_2PO_4	0.10	Alkaline Roese-Gottlieb	22.8	0.016
$CaH_4(PO_4)_2$	0.05	Alkaline Roese-Gottlieb	12.3	0.004
$CaH_4(PO_4)_2$	0.10	Alkaline Roese-Gottlieb	24.6	0.016
KH_2PO_4	0.05	95% alcohol	11.4	0.040
KH_2PO_4	0.10	95% alcohol	22.8	0.030
$CaH_4(PO_4)_2$	0.05	95% alcohol	12.3	0.85
$CaH_4(PO_4)_2$	0.10	95% alcohol	24.6	0.90
KH_2PO_4	0.05	100% alcohol	11.4	0.018
KH_2PO_4	0.10	100% alcohol	22.8	0.022
$CaH_4(PO_4)_2$	0.05	100% alcohol	12.3	0.39
$CaH_4(PO_4)_2$	0.10	100% alcohol	24.6	0.81

Although the addition of sodium chloride, calcium chloride, or sodium sulfate with or without skim milk solids to an aqueous dispersion of lipinol resulted in an increase in the recovery of lipinol, the data reported in Table IV show that the addition of these salts to 40 per cent fluid cream does not alter greatly the percentage of total extract.

PHOSPHORUS DETERMINATION

After removal of the phospholipide from cream by extraction, the extract was completely oxidized and the phosphorus content of the ash determined by the method described below. Since inorganic phosphates are not extracted by the Roese-Gottlieb procedure, at least not in sufficient quantity to affect the final result, the phosphorus content of the fatty extract is taken as a measure of the amount of lecithin or phospholipide in the cream. The proportions of lecithin, cephalin, and sphingomyelin in the extract are not known. In fact, very little is known of the composition of milk phospholipides. The most logical expression for the phospholipide content of cream, therefore, appears to be in terms of milligrams of phosphorus per 100 grams of cream of specified fat content, or milligrams of phosphorus per 100 grams fatty extract. This avoids any assumptions for the composition of the extract or the fatty acid content of the lecithin, provided all the phospholipide is attributed to lecithin. Differences in the fat content of the cream are also eliminated when the results are reported in terms of milligrams of phosphorus per 100 grams of fatty extract.

TABLE IV. ALKALINE ROESE-GOTTLIEB EXTRACTION OF HEAVY CREAM (6.5 TO 7.5 GRAMS)

NO SALT	$NaCl$, 1.0 GRAM	$CaCl_2$, 1.0 GRAM	Na_2SO_4, 1.0 GRAM	Na_2SO_4, 0.7 GRAM	Na_2SO_4, 0.5 GRAM
%	%	%	%	%	%
38.93	38.94	38.82	39.10		
40.31		40.00	40.31		
40.33		40.16	40.21		
39.88			39.87		
39.93			39.84		
39.84			39.88		
39.79			39.84		
39.80			39.87		
40.81			40.59	40.69	40.73
40.78			40.69	40.62	40.69
40.80			40.69	40.56	40.65
40.71			40.46	40.49	40.52
40.53			40.45	40.60	40.50
40.68			40.56	40.64	40.59

A dry method of oxidation of the extract—i. e., ashing in the presence of magnesium nitrate—was adopted because of the necessity of oxidizing a comparatively large amount of fat. The addition of magnesium nitrate serves two purposes: (1) it aids the oxidation of the fat, and (2) it provides a base for binding the phosphorus. The excess magnesium nitrate is decomposed on heating, leaving magnesium oxide in the ash.

PROCEDURE

Six to seven grams of 40 per cent cream are weighed into a Mojonnier extraction flask, 1.5 cc. of concentrated ammonium hydroxide added, and the mixture extracted with alcohol, ethyl ether, and petroleum ether according to the Mojonnier modification of the Roese-Gottlieb procedure. In the first two extractions 25 cc. of each ether are used. Three extractions are made. After evaporation of the solvents, the fatty extract is dried until constant weight is attained, and the percentage calculated. The fatty extract is then washed into a 3.5-inch (8.9-cm.) sillimanite evaporating dish (platinum dishes may be used, but sillimanite proves very satisfactory) by means of either ethyl or petroleum ether, 2 cc. of 50 per cent alcoholic magnesium nitrate added, and the mixture evaporated to dryness on an electric hot plate. The use of alcoholic magnesium nitrate and ethyl ether allows the fat and lecithin to mix uniformly with the magnesium nitrate and avoids the spattering which results with an aqueous solution of the salt. One cubic centimeter of nitric acid is then added, drop by drop, and the contents of the dish gently heated over a low flame until the mass is completely charred. It is important that the heating be done very slowly at first. The heat is gradually increased and the ashing completed in a muffle furnace. The ashing process is conducted at a sufficiently low temperature to avoid ignition. If the ash is slightly grayish or brownish in color, the addition of a few cubic centimeters of water to the cooled ash, followed by evaporation to complete dryness and a few seconds' heating, yields a white ash which is readily soluble in dilute hydrochloric acid. Just enough dilute acid is added to dissolve the ash. The solution is diluted to a volume of 20 cc. and phosphorus determined colorimetrically in 3- to 4-cc. aliquots.

Both the Briggs (*2*) modifications of the Bell-Doisy procedure for blood phosphorus and the Fiske-Subbarow (*4*) method have been used. Several determinations were carried out in which known amounts of inorganic phosphorus were added to the oxidizing agents, the samples evaporated, ashed, and phosphorus determined by both procedures. Magnesium chloride resulting from the excess magnesium nitrate did not interfere with the development of the blue color. The ash is free from other inorganic salts which cause the inaccuracies pointed out by Fiske and Subbarow. The inorganic phosphorus was recovered quantitatively. The Fiske-Subbarow reagent was freshly prepared, but the Briggs reagent was two to three weeks old at the time the first determinations were made. A week later, determinations were made on the same phosphorus solutions, using the same reagents. The following results were obtained:

Procedure	P Added	P Recovered	One Week Later
	Mg.	*Mg.*	*Mg.*
Briggs	5.0	5.00	4.98
Briggs	5.0	5.00	5.00
Briggs	5.0	4.99	4.98
Briggs	5.0	4.99	4.99
Fiske-Subbarow	5.0	5.00	4.95
Fiske-Subbarow	5.0	5.00	5.05
Fiske-Subbarow	5.0	5.00	5.00
Fiske-Subbarow	5.0	5.00	5.09

Under the described experimental conditions, neither procedure appeared to possess an advantage in so far as the accuracy of the determination is concerned. However, the Briggs procedure was adopted because it was found more convenient in running a series of determinations to make the readings 30 minutes after the reagents were added rather than after 5 minutes, as recommended in the Fiske-Subbarow method. The former reagents appear to keep better than the latter ones. This is a convenience when phosphorus determinations are made at intervals of several weeks.

In unknown samples, dilutions are such as to give readings near that of the standard. Good comparisons are made with a standard containing 0.1 mg. of phosphorus per 10 cc. If the standard is set at 25 mm., the unknowns read between 20 and 30 mm.

It is believed that the method described for the oxidation of the fatty extract does not result in the loss of phosphorus. Check determinations were made on a petroleum ether solution of soy-bean lecithin with the addition of known amounts of melted, filtered butter fat. The results are given in Table V.

TABLE V. LIPINOL OXIDIZED IN PRESENCE OF BUTTER FAT

Sample	Briggs Method		Fiske-Subbarow Method	
	Butter fat	Lipinol, 0.1 gram	Butter fat	Lipinol, 0.1 gram
	Mg. P	*Mg. P*	*Mg. P*	*Mg. P*
Butter fat + 0.1 gram of lipinol	0.08	2.31	0	2.36
	0.08	2.31	0	2.34
	0.09	2.37	0	2.44
	0.08	2.36	0	2.40
		Av. 2.34 ± 0.03		
0.1 gram lipinol (aqueous)		2.30		
		2.35		
		2.45		
		2.37		
		Av. 2.37 ± 0.04		

From aqueous solution, the average value is 2.37 mg. of phosphorus per 0.1 gram of lipinol, or 2.37 per cent as compared with 2.34 mg. of phosphorus per 0.1 gram of lipinol (2.34 per cent) in the presence of 3 grams of butter fat. This difference is within the experimental error.

Phospholipide Content of Fluid Cream

The phospholipide content of a number of samples of heavy cream is given in summary in Table VI. The uniform values obtained indicate that approximately the same percentage of phospholipide is extracted from all samples having approximately the same butter fat content. Inasmuch as the addition of sodium sulfate to the samples of cream reported in Table IV did not result in an increase in the per cent of extract from the cream, sodium sulfate was not added to the samples reported in Table VI. Actually, the addition of sodium sulfate to cream increases the phosphorus content of the extract slightly, as shown by the following data from two experiments:

Cream Sample	Fatty Extract	Phosphorus	
		Extract, 100 grams	Cream, 100 grams
	%	*Mg.*	*Mg.*
1	39.14	18.3	7.2
1 + Na_2SO_4	39.18	18.9	7.4
2	39.01	17.9	7.0
2 + Na_2SO_4	39.02	18.6	7.2
		Av. 18.2 ± 0.38	Av. 7.2 ± 0.10

The average value for the samples of cream reported in Table VI is slightly higher than the average value for the above samples. The latter experiments were conducted on a winter cream, as contrasted with the cream reported in Table VI which was produced in the late summer and early fall. Although the difference may be indicative of a seasonal variation, the data are too meager to consider the difference significant. In all cases, however, the wide variations reported in the literature have not been observed.

TABLE VI. PHOSPHOLIPIDE CONTENT OF FLUID CREAMS

Fatty Extract	Phosphorus	
	Extract, 100 grams	Cream, 100 grams
%	*Mg.*	*Mg.*
40.35	21.2	8.5
40.06	19.4	7.7
39.87	20.5	8.0
39.67	18.8	7.4
40.70	19.7	8.0
41.94	20.5	8.5
40.27	19.2	7.6
40.53	20.4	8.2
40.57	19.7	7.9
40.79	19.7	8.0
40.11	20.0	8.0
	Av. 19.9 ± 0.55	Av. 8.0 ± 0.24

Each figure represents the average of two to four determinations on the same sample of cream. If the ashing is carefully carried out at a slow rate, duplicate determinations check within 0.1 to 0.5 mg. of phosphorus per 100 grams of cream.

Extraction of Lipinol from Cream

In an attempt to determine the percentage recovery of phospholipide from cream, 0.2 and 0.4 per cent of soy-bean lecithin were added to heavy cream, the modified alkaline Roese-Gottlieb extraction made with and without the addition of sodium sulfate, the fatty extracts ashed, and the phosphorus content of the ash determined. The results are given in Table VII.

The results in Table VII show that at least the major part of the phospholipide occurring normally in cream is recovered by the described procedure. The addition of sodium sulfate to the cream before extraction increases the recovery only slightly. The addition of the salt becomes more important, however, as the phospholipide content of the cream is increased. The per cent of fatty extract may not be materially affected, but the amount of lecithin-like materials in the extract is greater in every case. Therefore, to insure the maximum recovery of phospholipide from cream, sodium sulfate should be added before the extractions are made.

Forty per cent cream was dried at 70° C. under reduced pressure, and a Soxhlet extraction with absolute alcohol made. Since inorganic phosphates are appreciably soluble in alcohol, the alcoholic extracts were concentrated under reduced pressure, the residues taken up with petroleum ether and filtered before the extracts were ashed. The following values compared with the Roese-Gottlieb extraction of the fluid cream resulted:

SAMPLE	PHOSPHORUS/100 GRAMS OF CREAM Roese-Gottlieb extraction	Alcohol extraction
	Mg.	*Mg.*
Control cream	7.9	6.8
Cream + 0.2% lipinol	11.6	10.1
Cream + 0.4% lipinol	15.2	16.1

The phospholipide content of the control sample of cream which was extracted with alcohol is lower than any value obtained heretofore. The values for the samples containing 0.2 and 0.4 per cent lipinol are scarcely better than those obtained by direct extraction of the fluid cream and require a much longer time for completion.

The Mojonnier modification of the Roese-Gottlieb procedure for the extraction of fat has been found the most feasible and effective method for the removal of phospholipide from fluid cream. This procedure extracts the major part of the lecithin-like materials and is far more practical than an alcoholic extraction of the dried cream. It does not extract measurable amounts of inorganic phosphorus.

Phospholipides may be completely oxidized in the presence of comparatively large amounts of fat by direct ashing, if an excess of base is present and the ashing is done at a very low temperature at the beginning.

The phospholipide content has been found to be very uniform and lies between 18 and 20 mg. of phosphorus per 100 grams of fatty extract for cream produced in New York State during the late summer and early fall. There is a slight indication of a small seasonal variation. It is recommended that phospholipide content be expressed in terms of milligrams of phosphorus per 100 grams of extract.

TABLE VII. RECOVERY OF LIPINOL FROM FLUID CREAM

	FATTY EXTRACT	PHOSPHORUS/100 GRAMS OF CREAM Found	Calcd.[a]	RECOVERY
	%	*Mg.*	*Mg.*	%
Control cream	40.17	7.9		
Cream + 0.2% lipinol	40.07	11.6	12.5	92.8
Cream + 0.4% lipinol	40.08	15.2	17.1	88.8
Control cream	39.14	7.2		
Control cream + 0.7 grams Na_2SO_4	39.18	7.4		
Cream + 0.2% lipinol	39.14	10.7	11.8	90.6
Cream + 0.2% lipinol + 0.7 gram of Na_2SO_4	39.16	11.4	12.0	95.0
Cream + 0.4% lipinol	39.10	14.7	16.4	89.9
Cream + 0.4% lipinol + 0.7 gram of Na_2SO_4	39.00	15.7	16.6	94.6
Control cream	39.10	7.0		
Control cream + 0.7 gram of Na_2SO_4	39.02	7.3		
Cream + 0.2% lipinol	38.89	10.6	11.6	91.3
Cream + 0.2% lipinol + 0.7 gram of Na_2SO_4	39.00	11.4	11.9	95.8
Cream + 0.4% lipinol	38.95	15.1	16.2	93.2
Cream + 0.4% lipinol + 0.7 gram of Na_2SO_4	38.98	15.5	16.5	93.9

[a] 0.1 gram of lipinol $\approx$ 2.3 mg. of phosphorus.

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New Molecular Weight Micromethod

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IN VIEW of the simplicity and ease of operation of the Victor Meyer method of determining molecular weights, it was considered desirable to adapt the apparatus to the use of micro samples, and to simplify somewhat its construction. Since the accurate measurement of the volume of a micro sample in the vapor state would present some difficulty, it was decided to employ the change in pressure of an isothermal system before and after vaporization of the substance as an index of the molecular weight, the volume of the system being known. Several pieces of apparatus for molecular weight determination have been described (*1*, *2*, *3*) which operate on a similar principle, but all of them are inefficient or complicated, and none employs truly micro samples.

CONSTRUCTION OF APPARATUS

The final form of the apparatus is as shown in Figure 1, which is self-explanatory. It is essentially an inner jacket, *A*, fitted with a mercury manometer; the inner jacket is surrounded by an outer jacket, *B*, to maintain constant temperature during a determination. The outer jacket is constructed from a 25 by 200 mm. Pyrex test tube, a 200-mm. side arm, *J*, of 5-mm. tubing being fused on as shown to serve as a condenser for the vapors of the heating medium. The inner jacket is made from a 15 by 150 mm. test tube. A 40-mm. length of 4-mm. tubing is fused to the bottom of the test tube, and three short lengths of thin rod, *C*, are sealed equidistant around the circumference of the tube about 10 mm. from the sealed end. These rods should be of such length that the inner jacket will be centered in the outer jacket when the apparatus is assembled. A 50-mm. length of the 4-mm. tubing is fused to the upper end of the test tube.

A Pyrex stopcock, *D*, which has a bore of 1.5 to 2 mm., is sealed to the upper end of the inner jacket. The plug of the cock should be well ground, and the channel of the plug should coincide with the channel of the barrel of the cock, in order that an unobstructed passage of at least 1.5 mm. be made through the stopcock. A short distance below the seal, an 80-mm. length of capillary tubing, *E*, of 0.5-mm. bore is sealed to the inner jacket, and the end bent downward as shown. A 100-mm. length of 5-mm. tubing is fused to the end of the capillary with a neat joint at *F*. A short length of 5-mm. tubing, *G*, is fused to the manometer arm as shown, and sealed off to a 15-mm. length. This trap serves to retain any air bubbles that may rise up the manometer tube. A reference mark for the mercury in the manometer is etched around the side arm about 4 mm. below seal *F*, as shown in Figure 1. Before use, the inner jacket is filled with water to the reference mark to ascertain the volume of the inner jacket.

The apparatus is now assembled as shown in Figure 1. An asbestos board, *N*, with a hole of just the right size to admit outer jacket *B*, is used to prevent superheating of vapor in *B*. The inner jacket is supported in the outer jacket by means of a split cork stopper. A 300-mm. reference scale, *H*, completes the apparatus. A stopcock, *L*, fitted with a short length of pressure tubing, *K*, and a length of thick-walled tubing, *M*, is also provided. Its use will be described later.

Determination of Molecular Weights

In case the substance whose molecular weight is to be determined does not decompose at temperatures 20° to 30° C. above its boiling point under atmospheric pressure, the procedure is relatively simple. Melting point tubes 50 mm. in length and of such diameter to slip rather easily through the bore of stopcock *D*, are used to contain the samples. A tube of the correct dimensions is dried carefully and weighed on the microbalance. A sample of 2 to 10 mg. is pipetted into the tube with a micropipet, large sample weights being used when the molecular weight anticipated is large. The tube is then heated gently at a point about 10 mm. from the open end over a microflame to distil back into the tube that part of the liquid adhering to the central portion. That part of the liquid from the heated portion of the tube to the open end is distilled out, of course. Now the tube is heated more strongly and is drawn out into a capillary about one-third the original diameter of the tube, as shown in *a*, Figure 2. The upper end of the constriction is heated with the pointed flame of a blast lamp until the tube closes and a bead of glass is formed which will not pass through the plug of *D*. When completed, the sealed tube resembles *b*, Figure 2. The open end of the sample tube is now passed through the flame to make certain that all liquid has been removed from that portion of the tube. The sample tube is cooled and weighed on the balance. It has been found that no error due to vaporization of glass occurs in this method of sealing the sample tubes.

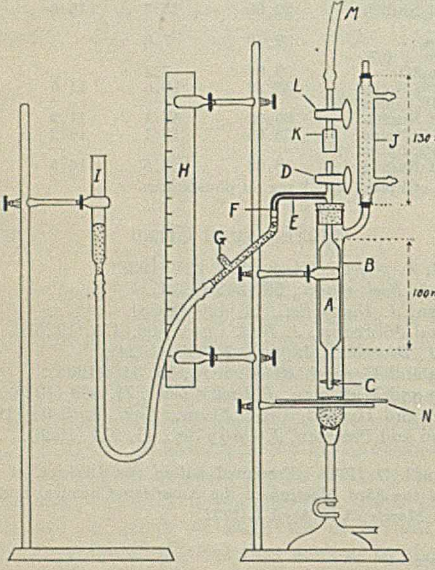

Figure 1. Assembled Apparatus

A liquid with boiling point 15° to 20° C. above that of the sample is chosen as the heating medium. It is poured into *B* to such depth that the liquid level will be at least 10 mm. below the end of the inner jacket. The manometer is filled with mercury, and the inner jacket is tilted to fill trap *G*. The inner jacket is placed in position inside *B*, stopcock *D* is closed, and the burner under *B* is lighted. The liquid in *B* is boiled just vigorously enough to insure *B*'s being filled at all times with vapor. It has been found convenient to wrap *B* with asbestos paper to minimize condensation. The level of the mercury in the right hand manometer arm is brought to the reference mark, and *D* is closed. If the level drops, *D* should be opened until *A* will come to the temperature of *B*. When no change in mercury level is noted when *D* is closed, the determination may be begun. Equilibrium is usually established within two minutes after the heating liquid begins to boil.

D is now opened and the sample tube inserted, the tube projecting downward into *A* with the bead resting on the upper end of the plug channel, thus preventing the tube from dropping into *A*. The mercury level is brought to the reference mark and the level of the mercury in bulb *I* is read off on scale *H*, estimating to 0.2 mm. *D* is closed, thus breaking the capillary of the sample tube and allowing the tube to drop to the bottom of *A*. As the sample vaporizes, the leveling bulb is raised to keep the mercury in the side arm approximately at the reference mark. When there is no further increase of pressure in *A*, the mercury level in the side arm is adjusted to the reference mark and the level of the mercury in the leveling bulb is read off. The difference in the initial reading and final reading of mercury levels gives the change of pressure within *A*. *I* is lowered, the plug of *D* is removed, a long capillary tube is inserted into *A*, and the vapor of the sample is removed by suction. *A* is now removed, and the temperature of the vapor bath determined. The treatment of results will be described below.

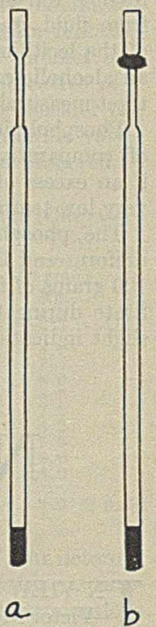

Figure 2. Method of Sealing Sample Tubes

In case the compound tends to decompose at its atmospheric boiling point, the initial pressure within *A* may be lowered sufficiently to allow vaporization of the sample at a temperature below the decomposition point. In such a case, the final pressure within *A* will still be below atmospheric. In fact, it is often desirable to start below atmospheric pressure, even in the case of compounds that do not decompose at their boiling points, allowing the use of a heating vapor not over 10° C. above the boiling point of the substance. In addition, the inner jacket may be filled with an inert gas to hinder decomposition. To start below atmospheric pressure requires the use of the auxiliary stopcock, *L*. When the sample tube has been inserted in *D*, the top of *D* is lightly greased with vaseline and *L* is connected by means of the pressure tubing, *K*. *L* is closed and *M* is connected with the vacuum line. *I* should be lowered sufficiently to place the mercury level in the side arm of *A* to some point just above trap *G*. *L* is opened slowly, and as the mercury level rises in the side arm, *I* is lowered until the mercury level is from 100 to 200 mm. below *F*. *L* is then closed, and the mercury level in the side arm brought to the reference mark. If the mercury level remains constant, the level of the mercury in *I* is recorded on *H*, the sample tube broken by turning *D*, and the determination completed as previously described. Calculations in this case will be identical in procedure with the first case.

Calculation of Constant for Apparatus

The molecular weight of a substance may be calculated from the following equation, adapted from that of Lumsden (*3*):

$$\text{M. W.} = \frac{22410 \times 760 \times T \times W}{1000 \times 273 \times V \times \Delta p}$$

where T = absolute temperature of vapor bath
W = weight of sample taken, mg.
V = volume of inner jacket, ml.
Δp = change of pressure within A, mm.

Collecting constants, the above equation becomes:

$$\text{M. W.} = K \times \frac{T \times W}{\Delta p}$$

It is apparent that the constant, K, of any apparatus may be calculated, once the volume of the inner jacket is known.

DISCUSSION

The average accuracy of the method is within 2.5 per cent; with accurate estimation of pressure change, the error is usually lower. Table I illustrates some typical results obtained with the apparatus; some of the data were first trials of students in a class of advanced organic chemistry. As the sample can be weighed out in less than 15 minutes, and the vaporization requires less than 5 minutes, the entire determination can be made in 20 minutes with accuracy comparable with the large Victory Meyer apparatus.

TABLE I. TYPICAL MOLECULAR WEIGHT DETERMINATIONS

(Constant for apparatus, 3.059)

COMPOUND	B. P.	TEMP. OF BATH	WT. OF SAMPLE	ΔP	M. W. FOUND	M. W. CALCD.	ERROR
	° *C.*	° *C.*	*Mg.*	*Mm.*			%
$C_4H_{10}O_2$	134.7	140.0	6.605	95.0	87.8	90.1	−2.5
		140.0	6.624	94.0	89.0	90.1	−1.2
C_6H_6	80.4	99.6	3.704	53.5	78.9	78.1	+1.0
		99.6	5.977	88.0	77.4	78.1	−0.9
CCl_4	76.0	100.5	5.540	41.0	154.4	153.8	+0.4
		100.5	4.591	33.5	156.6	153.8	+1.8
$CHCl_3$	61.2	100.5	6.074	57.3	121.1	119.4	+1.4
		100.5	6.087	57.5	121.0	119.4	+1.3
CH_3COCH_3	56.5	100.5	1.754	34.0	58.9	58.1	+1.4
		100.5	8.087	160.8	57.4	58.1	−1.2

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RECEIVED July 15, 1932.

Note on Measurement of Activity of Commercial Invertase

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THE enzyme invertase is now on the market in extremely active form in aqueous solution preserved in glycerol. It is used in the food industries for the inversion of cane sugar, especially to prevent crystallization. Its action in cream centers and fondant coatings, in which the slow inversion caused by the invertase offsets the tendency of the sucrose to crystallize, has recently been described by Paine (*5*).

Our knowledge of the laws of its action is due to O'Sullivan and Tompson, Hudson, Nelson, Willstätter, and to many others; information on the solubility relations of sucrose, invert sugar, and water at equilibrium has been published by Jackson (*3*). We still lack, however, a rapid, convenient, and exact method for measuring the activity of commercial invertase. The unimolecular reaction constant has been used extensively as a means of measuring invertase activity. Nelson (*4*) showed conclusively, however, that the reaction does not follow the unimolecular law, except under unusual conditions, but that the unimolecular constant values steadily increase during the course of the inversion.

The method described below is offered as a contribution to the problem. It is based on the method used by Hudson and Paine (*2*), and the activity is expressed in a similar manner. It differs from it essentially in that an arbitrary reaction time has been selected. Ammonia is used in terminating the inversion, as suggested by Bayliss (*1*), avoiding on the one hand the uncertainty incident to the use of dry sodium carbonate, and on the other the possibility of destruction of the sugar by use of excessive amounts of strong alkali.

The sample of invertase is diluted fifty-fold with water—e. g., 2 grams are diluted to 100 cc. Of the diluted sample, 5 cc. are placed in a flask and 50 cc. of sucrose solution added at 20° C., with the time noted using a fast-running 50-cc. pipet. (The sucrose solution contains per liter 100 grams of cane sugar and 40 cc. of Walpole acetate buffer of 4.6 pH; 10.2 cc. of 1 *N* acetic acid and 9.8 cc. of 1 *N* sodium acetate diluted to 100 cc.) The solution is then incubated at 20° C. for a 50-minute interval, when 0.5 cc. of strong ammonia is added. The solution, after standing for a few minutes, is polarized at 20° C. in a 2-decimeter tube.

The initial polarization is determined by polarizing at 20° C. a mixture of 5 cc. of the diluted sample, 0.5 cc. of strong ammonia, and 50 cc. of the sugar solution, mixed in the order named.

The activity K_{50} is evaluated by the formula

$$K_{50} = \log \frac{a}{a - x}$$

where a is the calculated range through which the polarization changes upon complete inversion by invertase, and x is the fall in polarization observed. The value a is calculated from the formula

$$a = \frac{P'}{100} \times \left(141.7 - \frac{t}{2}\right)$$

where P' is the original polarization, P, corrected for the zero reading of the polariscope, and t is the temperature. Example: The initial reading was 34.8° V. The zero reading of the polariscope was 0.5° V. The reading after the 50-minute digestion period was 18.0° V.

$$\text{Then } a = \frac{34.8 - 0.5}{100} \times 131.7 = 45.17° \text{ V.}$$

$$x = 34.8 - 18 = 16.8° \text{ V. and } K_{50} = 0.20$$

Thus, the activity is simply the unimolecular reaction constant calculated at the 50-minute interval and multiplied by the dilution.

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RECEIVED May 13, 1932. Presented before the Division of Sugar Chemistry at the 83rd Meeting of the American Chemical Society, New Orleans, La., March 28 to April 1, 1932.

Determination of Reducing Sugars

Application of Shaffer and Hartmann Iodometric Cuprous Titration

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SHAFFER and Hartmann (*6*) have reported that the iodometric cuprous titration could be adapted to the determination of reducing sugars by the use of Fehling-Soxhlet solution and the amounts and conditions of heating prescribed by Munson and Walker (*3*). Using the Munson and Walker tables for the conversion of copper into terms of sugar, they have obtained substantially correct values for the sugar present when the equivalence factor of 6.36 mg. of copper per cc. of 0.1 *N* sodium thiosulfate was used. However, from previous investigations conducted in this laboratory, by others as well as the writers, this theoretical factor seemed too low to give complete recovery of sugar. Therefore we have undertaken to determine if such is the case, and, if possible, to determine the cause.

Munson and Walker have demonstrated the accuracy of the direct weighing of cuprous oxide so that the chief source of difference between the results obtained by the procedure as carried out by Shaffer and Hartmann and that prescribed by Munson and Walker apparently is due to the difference in conditions of reduction used. Shaffer and Hartmann did not strictly adhere to the conditions of heating prescribed by Munson and Walker. The solutions were heated in a 300- or 400-cc. Erlenmeyer flask covered with a small beaker instead of in a 400-cc. beaker covered with a watch glass. Quisumbing (*5*) and others (*1*, *2*, *7*) have shown that the type of container used for reduction affects the results obtained.

Table I. Comparison of Lateral Area and Total Area of Containers of Various Types

Container	Diam.	Ht. of Liquid in Container	Lateral Area to Liquid Exposed to Glass	Area of Bottom Surface	Surface of Liquid Exposed to Air	Total Area of Liquid Exposed to Glass
	Cm.	*Cm.*	*Sq. cm.*	*Sq. cm.*	*Sq. cm.*	*Sq. cm.*
400-cc. beaker	7.5	2.4	56.6	44.2	44.2	100.8
300-cc. Erlenmeyer	8.7	2.1	50.5	35.3	59.5	85.8
400-cc. Erlenmeyer	9.2	1.9	55.6	39.6	66.5	95.2
500-cc. Erlenmeyer	9.7	1.7	55.2	41.9	73.9	97.1

Quisumbing shows "that when the action of air is excluded, reduction is proportional not to *total* but to *lateral* area of liquid exposed to the glass." He believes that this relationship is due to the fact that as the reduction proceeds the cuprous oxide formed drops from the sides of the container to the bottom, thereby decreasing the accelerating action of the glass along the bottom, leaving the free surface along the sides for catalytic action. A comparison between total area and lateral area of a number of containers is shown in Table I. It is seen there that the lateral area of the liquid exposed to glass is approximately the same in the 400-cc. beaker and the 500-cc. Erlenmeyer flask, so that if this is the controlling factor the substitution of the flask for the beaker should not markedly affect the results. However, owing to the increased surface area exposed to air in the flask, there is more danger from loss of cuprous oxide by oxidation.

Analytical Procedure

The dextrose used in these determinations was obtained from the Bureau of Standards. It was weighed against brass weights in air, and transferred to calibrated volumetric flasks. The solutions were made to volume at room temperature (22.5° C. average), and a record was kept of the temperature. The chemicals used were the purest that could be obtained on the open market. Stock solutions were made up in only 4-liter lots according to the procedure recommended by Munson and Walker, and Shaffer and Hartmann. The thiosulfate solution was adjusted to exactly 0.1 *N* at 22.5° C. against recrystallized potassium dichromate. It was stored in a 10-liter Pyrex stock solution bottle and was preserved with a few cubic centimeters of carbon disulfide. Blank determinations on the stock solutions were frequently run and showed only slight variations. The 500-cc. Pyrex Erlenmeyer flasks and 400-cc. Pyrex beakers used in these tests were carefully selected to have the same distribution of glass by choosing flasks or beakers of the same weight.

It was found that, as reported by Shaffer and Hartmann, it was necessary to dissolve the cuprous oxide precipitate completely in the presence of the iodate-iodide solution after acidification, and subsequently to dissolve the cuprous iodide formed in order to obtain close agreement between duplicate or triplicate determinations. It was found that the cuprous iodide precipitate dissolved more readily in the presence of a large excess of iodine than when but a slight excess was present. When the solutions were cooled to from 35° to 40° C., the solution of both precipitates was rapid, but at about 20° C. the precipitates dissolved with difficulty. The end point in the titration of solutions cooled to temperatures below 35° C. were somewhat obscured by a precipitation which occurs, apparently composed of tartrates.

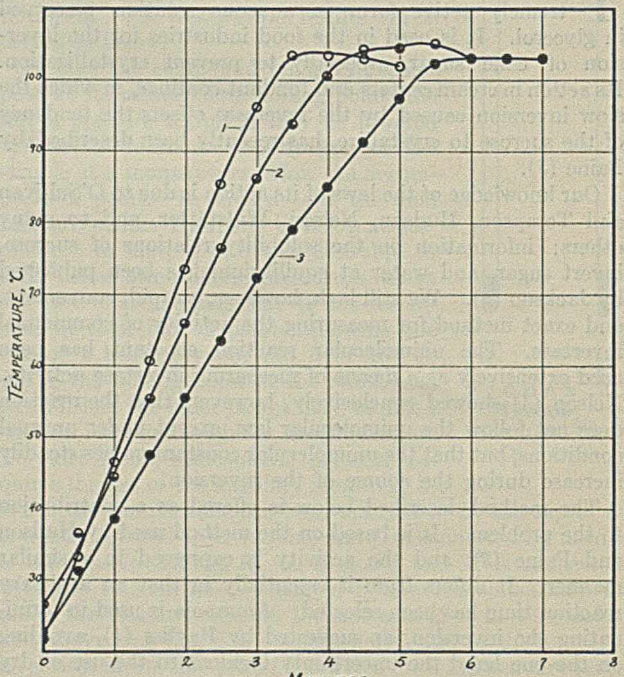

Figure 1. Rate of Temperature Change of 100 cc. of Solution in Erlenmeyer Flask

Flame adjusted to bring solution to boil in (1) 3 min., (2) 4 min., (3) 5 min.

DISCUSSION

EFFECT OF BOILING CONDITIONS. Quisumbing (4) has shown that changes in barometric pressure affect the amount of copper reduced by reducing sugars when the Munson and Walker technic is used. He has also shown that the temperature of boiling under their conditions is not constant, ranging from 101° to 105° C. depending on conditions of heating.

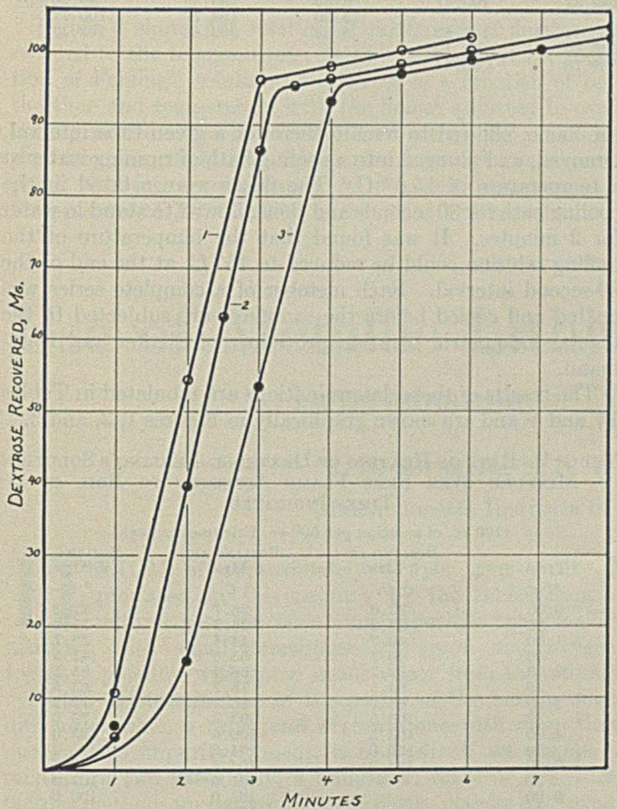

FIGURE 2. EFFECT OF HEATING CONDITIONS ON RECOVERY OF DEXTROSE

Flame adjusted to bring solution to boil in (1) 3 min., (2) 4 min., (3) 5 min.

In carrying out the reduction both in Erlenmeyer flasks and in beakers superheating was found to occur with such regularity that it is almost impossible to decide when to begin to reckon the time of boiling. It was impossible to obtain triplicate determinations agreeing within 0.6 mg. of copper on samples when some had superheated to varying degree and extent during boiling, and when some had not superheated. It was thought that glass beads (4 mm. in diameter) placed in the flask would reduce the danger of superheating. In addition to covering the flask with a 50-cc. inverted beaker, it was thought that covering with a small funnel might allow the release of steam pressure more freely than the heavier water-sealed beaker. Slight improvement resulted from the use of the funnel alone, but superheating still persisted, making it very difficult to obtain checks with triplicate determinations. Leaving the flask uncovered, however, almost completely stopped the superheating. The glass beads prevented superheating when used in either an uncovered or covered flask.

The results shown in Table II indicate that superheating is of considerable importance in the determination. The determinations in which superheating occurred gave values which exceeded the actual amount of dextrose present. The covered flask containing 20 glass beads was very close to the actual, whereas the uncovered flask containing glass beads was below the actual, probably owing to surface oxidation caused by increase in the surface of the liquid exposed by the more vigorous boiling. Where the glass beads are used, there is a vigorous agitation of the cuprous oxide precipitate causing it to rise and drop back to the bottom of the flask. In the uncovered flask without beads in which the liquid boils without superheating, such agitation does not occur. The boiling is less vigorous, the cuprous oxide precipitate does not rise to the surface of the liquid, and surface oxidation is reduced.

TABLE II. EFFECT OF BOILING CONDITIONS ON OXIDATION OF DEXTROSE BY FEHLING'S SOLUTION

(100 mg. of dextrose per determination)

TREATMENT	THIOSULFATE TITRATION[a]	CU REDUCED	DEXTROSE RECOVERED
	Cc.	*Mg.*	*Mg.*
Uncovered 500-cc. Erlenmeyer containing 20 glass beads	6.07	197.86	99.76
500-cc. Erlenmeyer covered with 50-mm. funnel with 20 glass beads	5.92	198.81	100.21
Uncovered 500-cc. Erlenmeyer	5.84	199.32	100.47
500-cc. Erlenmeyer covered with 50-mm. diameter funnel	5.81	199.51	100.58
500-cc. Erlenmeyer covered with 50-cc. beaker	5.67	200.40	101.08

[a] Figures represent average of at least three determinations which varied by not more than 0.1 cc.

Glass beads, although alleviating superheating, are objectionable for other reasons. During the titration they tend to increase the crystallization of tartrates. Although this does not interfere with the reaction, it does interfere slightly in securing a sharp end point. For reasons given, the remaining tests reported for Erlenmeyer flasks were carried out in uncovered containers.

COMPARISON OF BEAKER AND FLASK. A comparison of the relative extent of recovery of dextrose when reduction was carried out in Erlenmeyer flasks and in covered beakers is shown in Table III. The Shaffer and Hartmann procedure was followed, using both the flask and beaker with the same dextrose solution. The determinations were carried out at the same time so that the conditions of heating would be identical for the two. Quadruplicate determinations were run in the tests, while "blanks" were run in duplicate at the conclusion of each test.

The analyses show that consistently higher results were obtained with the beaker, also in all instances except the 50-mg. sample, the milligrams of dextrose found are higher than the actual amount contained in the sample. The lower amount of dextrose recovered in the flasks was probably due either to increased surface oxidation of the cuprous oxide precipitate, since they were uncovered, or to the superheated condition prevailing in the covered beakers, causing an increased yield of reduced copper. It can safely be concluded from the results that the uncovered Erlenmeyer flask can be used in the method to give yields which are very close to the actual amount of dextrose present.

TABLE III. COMPARISON OF BEAKER AND FLASK AS RECEPTACLES

DEXTROSE PER 25-CC. ALIQUOT	BEAKERS[a]			ERLENMEYER FLASKS[b]		
	Thiosulfate titration	Cu reduced	Dextrose recovered	Thiosulfate titration	Cu reduced	Dextrose recovered
Mg.	*Cc.*	*Mg.*	*Mg.*	*Cc.*	*Mg.*	*Mg.*
50.0	20.87	101.83	49.87	21.13	101.63	49.75
100.08	5.40	199.77	100.73	5.81	199.07	100.34
150.12	28.92	291.35	151.17	29.17	290.08	150.47
200.16	15.47	376.89	201.29	15.82	374.99	200.20

[a] 400 cc. capacity, 7.5 cm. in diameter.
[b] 500 cc. capacity.

RATE OF REDUCTION OF FEHLING'S SOLUTION BY DEXTROSE. It was observed that during the heating process there was a definite time at which the reduction of Fehling's solution by dextrose became visible, as noted by a change from the clear dark blue of the unheated liquid to a cloudy bluish red liquid. The time at which this change occurred

TABLE IV. RATE OF REDUCTION OF FEHLING'S SOLUTION BY DEXTROSE OVER FREE FLAME ADJUSTED TO BOIL IN TIME INDICATED

(100 mg. of dextrose per determination)

Time	Boiling in 3 Min.			Boiling in 4 Min.			Boiling in 5 Min.		
	Thiosulfate titration[a]	Cu reduced	Dextrose recovered	Thiosulfate titration[a]	Cu reduced	Dextrose recovered	Thiosulfate titration[a]	Cu reduced	Dextrose recovered
Min.	*Cc.*	*Mg.*	*Mg.*	*Cc.*	*Mg.*	*Mg.*	*Cc.*	*Mg.*	*Mg.*
1	33.57	23.02	10.93	35.56	10.30	4.72	35.16	13.03	6.05
2	19.69	111.30	54.66	24.30	81.92	39.90	32.23	31.67	15.05
3	7.09	191.44	96.30	10.01	172.80	86.48	20.04	109.20	53.55
4	6.35	196.14	98.81	7.09	191.37	96.26	8.00	185.78	93.30
5	5.81	199.58	100.50	6.37	195.95	98.70	6.87	193.27	97.25
6	5.34	202.57	102.24	5.84	199.32	100.47	6.30	196.59	99.06
7							5.80	199.77	100.72
8				4.93	205.11	103.85	5.38	202.44	102.17
2.5				17.07	127.90	63.10			
3.5				7.34	189.78	95.42			

[a] Figures represent averages of triplicate determinations.

varied slightly with the amount of dextrose in the sample; the temperature was about 70° C.

The rate of reduction of Fehling's solution by dextrose was determined at minute intervals on 100-mg. samples with the flame of the gas burner adjusted to cause boiling in 3, 4, and 5 minutes. The rate of heating of the dextrose–Fehling's solution mixture was determined by the use of a mercury-in-glass chemical thermometer with a range of 10° to 110° C., graduated at 2° C. intervals. In most cases ten runs were made at each flame adjustment using the different flasks employed in the determinations.

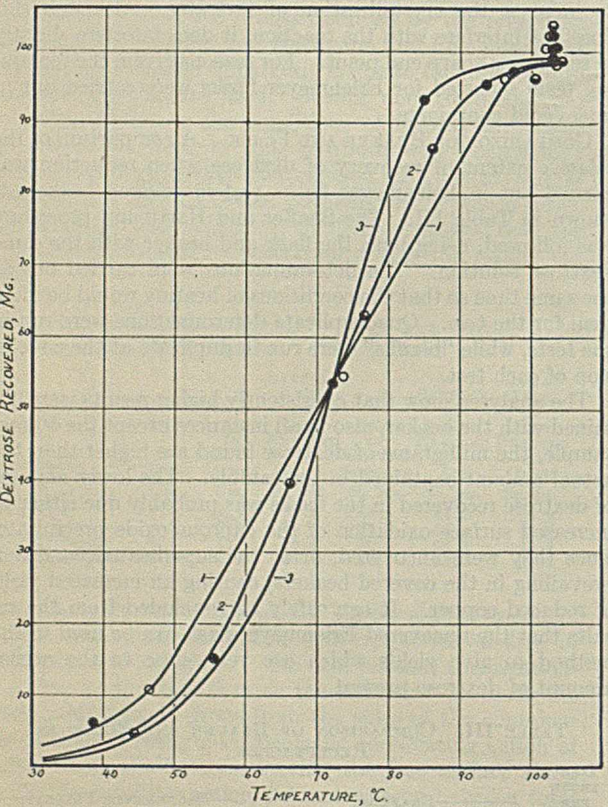

FIGURE 3. EFFECT OF TEMPERATURE ON AMOUNT OF DEXTROSE RECOVERED DURING HEATING

Flame adjusted to bring solution to boil in (1) 3 min., (2) 4 min., (3) 5 min.

The method used in determining the rate of reduction of the Fehling's solution consisted of adjusting the flame so that boiling began at the times indicated. The dextrose solution containing 100 mg. per 25 cc. of aliquot was pipetted, over as short a time interval as possible, into enough Erlenmeyer flasks so that triplicate determinations could be made at minute intervals from the start of heating up to and including 3 minutes of boiling. After adding 25 cc. of distilled water and 25 cc. of Fehling's A and B, the samples were placed on the flame, allowed to remain there for a given time interval, removed, and plunged into a cooling bath of running water at a temperature of 15.6° C. The flasks were rotated in the cooling bath for 30 seconds and then allowed to stand in water for 2 minutes. It was found that the temperature of the boiling solution could be reduced to 45° C. at the end of the 30-second interval. Each member of a complete series was heated and cooled before the samples were subjected to the regular iodometric titration procedure of Shaffer and Hartmann.

The results of these determinations are tabulated in Tables IV and V and are shown graphically in Figures 1, 2, and 3.

TABLE V. RATE OF HEATING OF DEXTROSE–FEHLING'S SOLUTION MIXTURE OVER FREE FLAME ADJUSTED TO BOIL IN TIMES INDICATED

(100 cc. of solution per 500-cc. Erlenmeyer flask)

Time	Boiling in 3 Min.	Boiling in 4 Min.	Boiling in 5 Min.
Min.	*° C.*	*° C.*	*° C.*
0:00	22.0	26.7	22.8
30	33.2	26.7	31.2
1:00	46.7	44.4	38.7
30	60.7	55.6	47.5
2:00	73.7	66.1	55.5
30	85.5	76.7	63.5
3:00	96.2	86.1	72.2
30	103.5	93.9	79.0
4:00	103.5	100.6	85.0
30	103.0	104.2	91.2
5:00	102.0	104.4	97.5
30		105.6	102.2
6:00		103.0	103.0
30		103.0	103.0
7:00		103.0	103.0
30		103.0	
8:00		103.0	

Figure 1 shows the rate of heating of the solutions under the conditions specified. The curves follow the averages of the points obtained. It will be seen that there is a change in slope in each of the curves at approximately 70° C., corresponding to the time at which the reduced cuprous oxide first becomes visible. This is probably owing to a change in the rate of heat transfer caused by the cuprous oxide formed.

Figure 2 shows the milligrams of cuprous oxide formed with the flame adjusted to cause boiling at 3, 4, and 5 minutes, respectively. It is seen that enough cuprous oxide is formed in the preliminary heating to boiling to give 96 to 99 per cent recovery of dextrose regardless of the time of the heating period. At the end of 2 minutes of boiling, complete recovery is obtained regardless of the time required to heat the solution to boiling. The curves also show a steady increase in the amount of copper reduced to cuprous oxide by dextrose with increase in the time of boiling. Apparently the essential factor in the procedure of heating used by Munson and Walker is not the time necessary to bring the solution to boiling, but the time elapsed from the start of boiling until the flask is removed and cooled by immersion in a cold water bath. Munson (*2*) and Walker evidently realized this to be the case, but did not give data to support the selection of their particular procedure. In his preliminary work, Munson showed that the reduction was from 99 to 99.5 per cent complete at the time boiling starts, using the amounts of copper recovered after 2 minutes of boiling as 100 per cent. His data also show that reduction proceeds at a steady rate for at least 4 minutes after boiling starts.

From our data it is safe to conclude that the preliminary heating period is of minor importance and that the time should be reckoned from the start of boiling and continued for exactly 2 minutes in order to secure accurate results by the use of Munson and Walker tables. At sea level the time of boiling should be reckoned from the time the solution first reaches 102.5° C.

Figure 3 shows the relation of milligrams of dextrose recovered to the temperature. It will be seen that the reduction of Fehling's solution by dextrose is a function of both the time and temperature with the flames adjusted to cause boiling in the times indicated. Two interesting points are shown by the graph. All three curves intersect at a common point, showing approximately 50 per cent reduction at a temperature of 70° C. This is the point in the preliminary heating period where the reduction first becomes visible. The curves again come together at a temperature between 102° and 103° C., corresponding to the boiling point of the solution at which the reduction is from 96 to 99 per cent complete.

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Use of Metallic Lithium in Analysis of Gases

Determination of Nitrogen in Inert Gases

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HELIUM of approximately 97 per cent purity is produced in this country by the liquefaction of natural gas, the remaining impurities being mainly nitrogen, with small percentages of argon and oxygen, together possibly with some water vapor from the storage cylinder. Determination of the purity of the helium offers difficulties when a rapid and accurate one with more than one gaseous impurity present, is desired. If we assume a mixture of two gases only, a number of more or less satisfactory methods for determining the purity may be employed. Thus, the Edwards balance (*1*) measures the density of the gas mixture, but requires a trained operator and the use of an expensive precision instrument. The use of the viscometer (*2*) requires a thorough knowledge of the properties of the gases involved, and also an appreciation of the limitations of the apparatus; the device, furthermore, is not very sensitive. The katharometer (*3*) is excellent as a recording purity meter, but in practice it has been found that it cannot be completely trusted without periodical calibration. The charcoal adsorption apparatus as arranged by H. P. Cady is probably the most accurate and sensitive instrument in use. However, considerable time is required for each determination, and the apparatus is elaborate. Furthermore, a supply of liquid air, which may not always be available, is necessary.

If the impure helium under test is known to contain oxygen as well as nitrogen, and the air-nitrogen ratio is not in a definite and known proportion, the problem becomes more difficult. Of the devices mentioned, only the Cady instrument does not require that the composition of the impurities be known. The others measure some property of the helium as modified by the presence of a known impurity, and the purity of the helium is derived thereby.

APPARATUS

A device has been constructed which uses metallic lithium to form nonvolatile compounds with nitrogen, oxygen, and water vapor contained in a given volume of impure helium, and from the change in pressure produced by the removal of these gases the purity is calculated. The device does not distinguish helium from the other rare gases, but if the contamination of the helium has been due to admixed air (resulting from its use in balloons) the determination of the nitrogen content becomes a matter of first importance rather than the detection of very small quantities of argon or neon which may be present.

The apparatus, which has been quite satisfactory in analyzing samples, is shown in Figure 1. A 400-cc. round-bottomed Pyrex flask is supplied with three capillary stopcocks sealed to the bottom; one leads to a capillary manometer, another to a high-vacuum pump, and the third to the source of gas sample. Since lithium must be heated to the melting point before rapidly combining with the nitrogen—owing to protective action at room temperature of the surface film—a heating element is introduced. This consists of a small resistance coil similar to that in an ordinary automobile cigar lighter. The current is conducted through heavy wires supported by a Pyrex tube held firmly in a rubber stopper. The outer end of the tube is sealed gas-tight with de Khotinsky cement. The heating element serves the dual purpose of supplying heat and supporting a small shallow boat of sheet iron containing the lithium.

PROCEDURE

A small piece of lithium is introduced into the boat and the stopper is tightly inserted. The flask is thoroughly evacuated and the tightness of the apparatus is confirmed by comparing the manometer reading with the barometric height. The sample of gas to be analyzed is next admitted slowly into the bulb. When the sample to be taken is part of a stream flowing constantly through a train of apparatus, it is convenient to allow the analyzer to fill slowly so that but a small fraction of the gas current is withdrawn for analysis, the rest being vented through a trap or bubble tube. When the flask has filled to the desired pressure, say 550 mm., the stopcock admitting the gas is closed and the manometer reading again taken. Current is then applied, conveniently derived from a small transformer. As the lithium melts it rapidly absorbs oxygen and nitrogen. Although the removal of the water vapor by molten lithium with the production of relatively nonvolatile products is complete after sufficient time, it will usually be preferable to remove water vapor by passage of the gas through suitable absorbents and to carry out the analysis of the dry gas in the analyzer. The time required in heating usually is not over 2 minutes, but depends on the amount and character of the impurities present. In any case, until experience is gained, it is well to reheat the lithium until it is known that absorption is complete. When the current is cut off, the gas cools completely in about 10 minutes owing to the high thermal conductivity of helium. When equilibrium is reached, as shown by constancy of the manometer readings, the pressure, now being due to helium only (together with argon, if present), is again recorded. The second pressure divided by the first is the fractional purity of the sample. The room temperature during the period of a single determination in general will not vary by a significant amount, so that thermostating of the analyzer is quite unnecessary in order to attain reasonable accuracy.

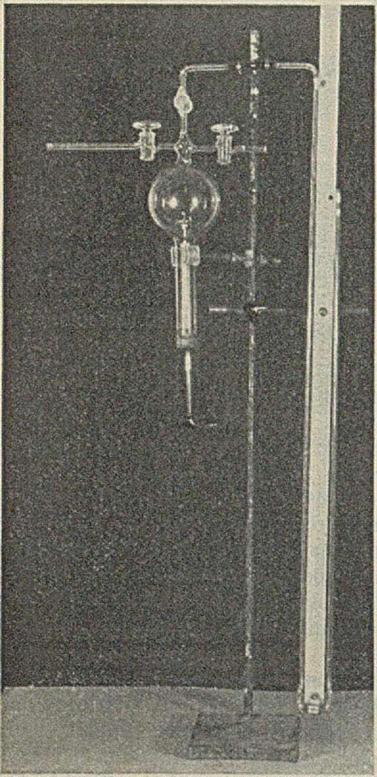

FIGURE 1. APPARATUS FOR DETERMINING PURITY OF HELIUM

Tests show that impurities are quantitatively removed, and that sensitivity and accuracy are limited chiefly by the reading of the manometer. Measured volumes of dry air, dry nitrogen, and water vapor were introduced separately into measured volumes of fairly pure helium, giving a known percentage purity of the mixture. The purity of the helium employed was qualitatively determined by the examination of the spectrum. The presence of argon, nitrogen, oxygen, and water vapor was reported, as well as the absence of hydrogen. The absence of carbon dioxide was determined by independent tests.

A quantitative analysis gave the following results:

	%
Water vapor (absorption by P_2O_5)	0.17
Oxygen (absorption by hot Cu)	0.41
Nitrogen (absorption by hot Li)	3.03
Total impurities	3.61

Argon was present as a trace only and so neglected. The analysis, therefore, shows the helium used to be 96.39 per cent pure. To check this, a density determination was made, the average molecular weight of the impurities being taken as 28.0. By this method the helium was determined 96.42 per cent pure.

Known mixtures were tested in the lithium analyzer; series of representative results are given in Tables I to IV.

TABLE I. TEST OF KNOWN MIXTURES

	%
Helium	96.39
Impurities:	
Nitrogen	3.03
Oxygen	0.41
Water vapor	0.17

RUN	PRESSURE BEFORE REACTION	PRESSURE AFTER REACTION	PRESSURE DUE TO IMPURITIES	IMPURITIES FOUND
	Mm.	*Mm.*	*Mm.*	%
1	552	532	20	3.6_3
2	546	526.5	19.5	3.5_7
3	564	543.5	20.5	3.6_4
4	553	533	20	3.6_2
5	559	539	20	3.5_8

TABLE II. TEST OF HELIUM-NITROGEN MIXTURES

NITROGEN PRESENT	PRESSURE BEFORE REACTION	PRESSURE AFTER REACTION	PRESSURE DUE TO IMPURITIES	NITROGEN FOUND
%	*Mm.*	*Mm.*	*Mm.*	%
0.98	510	505	5	0.9_8
2.35	510	498	12	2.3_5
3.40	530	512	18	3.4_0
5.22	536	508	28	5.2_0
10.21	539	484	55	10.2_0

TABLE III. TEST OF HELIUM–DRY AIR MIXTURES

DRY AIR PRESENT	PRESSURE BEFORE REACTION	PRESSURE AFTER REACTION	PRESSURE DUE TO IMPURITIES	DRY AIR FOUND
%	*Mm.*	*Mm.*	*Mm.*	%
1.17	513	507	6	1.1_7
2.54	531.5	518	13.5	2.5_4
3.15	508	492	16	3.1_5
10.27	526	472	54	10.2_6

TABLE IV. TEST OF HELIUM, NITROGEN, OXYGEN, AND WATER VAPOR MIXTURES

IMPURITIES PRESENT				PRESSURE BEFORE REACTION	PRESSURE AFTER REACTION	IMPURITIES FOUND
Nitrogen	Oxygen	Water	Total			
%	%	%	%	*Mm.*	*Mm.*	%
3.01	0.39	1.81	5.21	585	554.5	5.2_2
2.92	0.38	3.76	7.06	556	517	7.0_1
0.00	0.00	100.00	100.00	17.5	0.0	100.0_0

The reactions of lithium with nitrogen, oxygen, and water vapor are complete for all practical purposes at temperatures attained in the apparatus, and the compounds formed are nonvolatile at ordinary temperatures. Carbon dioxide, which is in part reduced by lithium to carbon and in part to carbon monoxide, must be removed by appropriate absorbents before the gas is admitted to the analyzer.

The possibility of reactions taking place in the cold, especially in the case of water vapor, was considered, as this would affect the result, possibly materially. In no case, even with water vapor alone, was any reaction detected over a period of 5 minutes in the analyzer. Apparently the surface film which covers lithium in the air even after being freshly cut is sufficient to retard any reaction in the cold. In one case the analyzer was evacuated completely, and then water vapor to a pressure of 17.5 mm. was admitted. This was allowed to stand at room temperature to determine whether the vapor reacted with lithium to form hydroxide and liberate hydrogen with a consequent change in volume, and therefore a change of pressure: $2Li + 2H_2O \longrightarrow 2LiOH + H_2$. After standing 5 minutes without heat, no change of pressure was noticeable. When the lithium was heated to melting, the reaction proceeded rapidly, and within one minute the pressure within the flask had fallen to zero. It is evident that molten lithium removes water vapor completely, with formation of hydride and hydroxide.

With the manometer used for the above tests, it was considered that each leg could be read to within 0.25 mm., making a maximum error on each recording of 0.5 mm. Using an initial mixture pressure of above 500 mm., the maximum error of each determination was considered not more than 0.1 per cent.

ACKNOWLEDGMENT

The authors wish to express their gratitude to J. M. Gaines, Jr., of the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology, for photographs of the spectrum.

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Determination of Hydrophyllic Colloid Content of Cane Juice

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THE ability of certain plants to resist droughts and others to resist low or freezing temperatures has long interested scientific observers. Gortner (*1*) and Newton (*4*) and later Newton and his co-workers (*5*) explain the resistance of plants to the desiccating effect of drought or low temperatures as due to their ability to hold water in a "bound" condition by means of hydrophyllic colloids which the resistant plants or varieties have elaborated. They believe the hydrophyllic colloids in Xerophytic plants prevent excessive moisture losses during severe desiccation such as is induced by periods of drought. Likewise, in the case of winter hardy plants, which are not killed by temperatures considerably below 0° C., these colloids prevent streaming of water from the interior of the cells to the intercellular spaces where it may form ice crystals and injure the plant. It has been previously shown that the type of material of which these colloids are composed is probably polysaccharides, such as pentosans in the case of drought-resistant plants, and protoplasmic proteins in the case of frost-resistant plants. However, since both of these classes of substance may act as hydrophyllic colloids, we may use the same mechanism for measuring both these phenomena.

Any method, then, which will measure either the amount of hydrophyllic colloids in the plant or the amount of water bound by these colloids will be of value in increasing our knowledge of the physical conditions of the constituents of the plant sap. This knowledge may be of value also as a means of distinguishing those varieties of canes which are the most resistant to low temperature. Also, any increase in our knowledge of the conditions of the colloids in cane juice may be of value in sugarhouse practice. With these objectives in view, investigations were undertaken in the fall of 1930 in an attempt to determine the cold resistance of the various new varieties of sugar canes which have been introduced into Louisiana within the past few years.

In 1922 Newton and Gortner (*4*) proposed a method for determining the per cent of bound water in plant juice, which is based upon the observation that the depression of the freezing point of a plant juice, upon the addition of sufficient sucrose to make a molal solution of it in the total water present in the juice, is greater than the theoretical amount which should be obtained. This excess depression they explain on the assumption that all the water in the juice is not free to dissolve the sucrose, and therefore the actual concentration is somewhat greater than the apparent molal concentration. The assumption is also made, based upon Scatchard's (*6*) work, that sucrose in molal concentration forms the hexahydrate. If sucrose hexahydrate is formed in solution, then we will have one mole of sucrose hexahydrate dissolved in 1000 − (18 × 6) or 892 grams of water, which gives a depression of 2.085° C. instead of the value 1.86° C. In their original paper, Newton and Gortner use the following formula for calculating the grams of bound water:

$$\text{Bound water} = \frac{dT_0 - (dT_1 + Km)}{dT_0 - dT_1} \times 892 \qquad (1)$$

where dT_1 = freezing point depression of freshly expressed juice
dT_0 = freezing point depression of juice after addition of sucrose
Km = 2.085° C. on basis that sucrose forms hexahydrate

In a later publication Newton and co-workers (*5*) have modified this formula by changing the value of Km from 2.085° C. to the value experimentally obtained by determining the freezing point of a molal solution of the sucrose in distilled water. This change was found necessary because the various lots of sucrose used gave values for molal solutions somewhat higher than this theoretical value of 2.085° C.

In applying the method of Newton and Gortner to cane juices, several correction factors must be introduced. By determining the freezing points of sucrose solutions of varying concentrations, the increments of increase of the freezing point with increasing amounts of sucrose in solution are not constant. This is brought out in Table I.

TABLE I. FREEZING POINTS OF SUCROSE SOLUTIONS

SUCCESSIVE ADDITIONS OF SUCROSE	SUCROSE ADDED	AV. INCREASE IN FREEZING POINT DEPRESSION DUE TO 0.25-MOLE SUCROSE
	Mole	° *C.*
1st	0.25	0.546
2nd	0.25	0.533
3rd	0.25	0.533
4th	0.25	0.543
5th	0.25	0.555
6th	0.25	0.562
7th	0.25	0.572
8th	0.25	0.583

Accordingly the depression of the freezing point of sucrose solutions has been plotted against concentration, as shown in Figure 1. Then by knowing the sucrose content of the cane juice, by use of the graph, the depression of the freezing point due to the sucrose present in the juice can be obtained. Likewise the depression of the freezing point can be determined for the total amount of sucrose after the addition of a mole of sucrose. By this means then, errors due to the fact that the freezing point depressions of sucrose solutions are not directly proportional to concentration can be eliminated. By the use of this method it will be noted that the freezing point of the original juice has been divided into two factors: that due to the sucrose present, and that due to the nonsucrose solutes.

A second correction must be introduced as pointed out by Moran and Smith (*3*) and applied by Grollman (*2*), and one which Newton and Gortner failed to take into consideration. However, the correction of Grollman—i. e., multiplying dT_1 by 1000/892—cannot be applied successfully to juices which are high in sucrose, such as cane juice, or even some samples of winter wheats which may contain as high as 6 per cent sucrose.

As mentioned previously, the abnormally high depressions of the freezing points of sucrose solutions are explained on the basis that the sucrose is hydrated. This means, then, that sucrose is removing water from solution. In a cane juice, which contains solutes other than sucrose, the addition of sucrose to the juice will cause the nonsucrose solutes to be dissolved in an amount of water different from that in which they were dissolved in the original juice. Since the degree of hydration of sucrose varies with the concentration, a graphical method was also used in making this correction for changes in the amount of solvent water. Figure 2 was obtained by plotting depressions of the freezing point of sucrose solution against amount of solvent water, which can be readily calculated by using the formula:

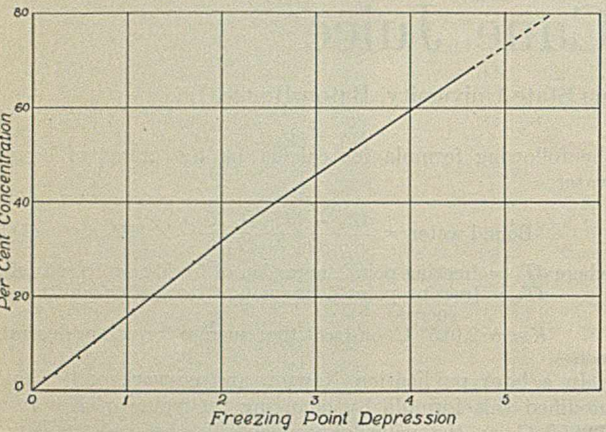

FIGURE 1. DEPRESSION OF FREEZING POINT OF SUCROSE SOLUTIONS *vs.* CONCENTRATION

$$\text{Solvent water} = \frac{1.86 \times 1000 \times M}{dT_M}$$

where M = molal concentration of sucrose
dT_M = depression of freezing point of sucrose solution of M concentration

The depression of the freezing point due to the nonsucrose solutes can now be corrected for changes in the amount of solvent water caused by the addition of sucrose to the cane juice. This can be calculated as follows:

$$dT_2 = (dT_1 - dT_4) \times W_1/W_2$$

where dT_2 = depression of freezing point of non-sucrose solutes corrected for sucrose change in solvent water
dT_1 = depression of freezing point of original juice
dT_4 = depression of freezing point due to sucrose in original juice
W_1 = amount of solvent water in original juice
W_2 = amount of solvent water after addition of one mole of sucrose to juice

The formula for calculating bound water then becomes:

$$\text{Grams bound water} = \frac{dT_0 - (dT_2 + dT_3)}{dT_0 - dT_1} \times W_2 \qquad (2)$$

where dT_0 = freezing point depression after addition of sucrose
dT_1 = freezing point depression of juice
dT_2 = freezing point depression of nonsucrose solutes corrected for change in solvent water
dT_3 = freezing point depression due to total sucrose present after addition of one mole of sucrose
W_2 = grams free water in juice after addition of sucrose

The experimental determinations were carried out on samples of juice obtained from the various new varieties of canes which have been introduced into Louisiana. The juice was expressed from representative samples by means of an experimental mill. The brix, sucrose content, freezing point depression of the original juice and the juice plus a definite amount of sucrose were determined on each sample. The freezing point determinations were made using the Beckman set-up, the usual precautions being observed. The samples were collected beginning October 27 to December 12.

TABLE II. AVERAGE VALUES OF BOUND WATER

Cane	Av. Sucrose	Bound Water			
		Formula 1	Formula 2	Sucrose	Total
	%				
P. O. J. 36	8.79	38.3	12.7	143	155.7
P. O. J. 36M	10.20	48.8	14.0	125	139.0
P. O. J. 213	10.10	42.0	10.0	133	143.0
C. O. 281	17.00	50.2	15.4	121	136.4
P. O. J. 234	11.60	45.5	11.6	125	136.6
C. P. 807	12.00	45.3	12.0	127	139.0

Since the values of bound water for a given variety of cane varied rather widely for samples collected during the season, the average values have been tabulated and are shown in Table II. There is no apparent correlation between bound water content and the ability of the various varieties to withstand frosts or freezing temperature as calculated by this method (Formula 2). Since Newton and Gortner have shown a correlation between winter hardiness and bound water for wheat plants, their formula (Formula 1) was applied to the data without again showing any correlation.

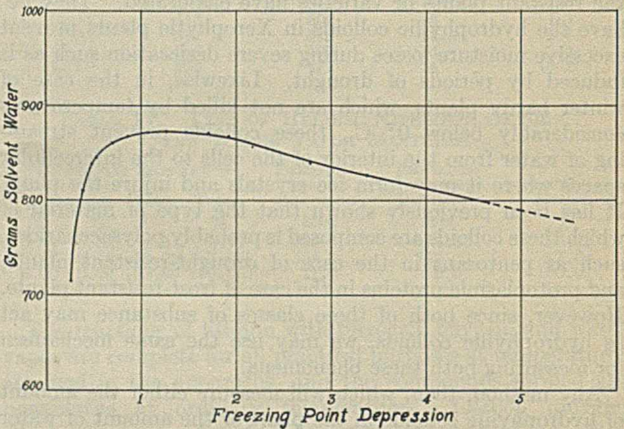

FIGURE 2. DEPRESSION OF FREEZING POINT OF SUCROSE SOLUTIONS *vs.* AMOUNT OF SOLVENT WATER

The amount of water of hydration of the sucrose in the original juice is also included in the table. The amount of water held by the sucrose is tremendously greater than that held by the colloids. In the last column is tabulated the total bound water content. Although these values are in the approximate order of hardiness of the cane varieties toward frost, there is not sufficient difference between them to be significant. It appears as a logical explanation, then, that the production of sucrose by plants as cold weather approaches is an extremely effective means of protection. For the cane plant, at least, we need not postulate the production of colloids, since the production of sucrose is equally as effective if not more so. This is borne out by the rapid increase in sucrose content and purity with the advent of low temperatures in the fall.

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Collecting Train for Recovering Traces of Iodine from Ashed Samples

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In carrying out determinations of iodine in minute amounts in large samples of organic material, in ashing apparatus of the McClendon or Pfeiffer type (*7,9-13*), it is necessary that the iodine in the gaseous combustion products be collected in some kind of train. The type of train usually used has contributed to the difficulty of the analysis in a number of ways. Its interference with the egress of combustion products from the apparatus complicates the burning process. The elimination of the liquid and solid reagents contained in the train, as must be done before the final determination is made, adds to an already cumbersome procedure. The use of large amounts of reagent in a few recommended types of train, some of which is difficult to render iodine-free, offers the possibility of introducing a considerable correction for the blank determination.

The collecting train described herein was devised to collect iodine with a minimal interference with the gas stream and without the use of large amounts of liquid or solid reagent. It may be employed with any type of ashing device in which the stream of evolved gas is sufficiently slow, such as the wet ashing method of Pfeiffer or the ashing bulb previously described by the writer (*3*). Figure 1, showing the assembled apparatus with such a bulb, and Figure 2, illustrating individual parts of the apparatus, make a detailed description unnecessary. The function of each part, however, will be discussed briefly.

Operation of Apparatus

A normal operation of the apparatus is without the development of any back pressure. The manometer, therefore, is inserted into the system to serve as a warning device only. The activating mechanism for the Cottrell precipitators is similar to that described by other authors on iodine analysis (*8*). The coils in the last three collecting tubes are made from No. 20 nichrome wire by wrapping it about a rod of such size that the finished coil will fit tightly between the input tube and the wall of the collecting tube. They are stretched till there are about ten turns to the inch before being wrapped about the inner tube and inserted in their proper place. These coils undergo very little corrosion except when nitrogenous materials are burned. The salts resulting from this corrosion cause no difficulty in the final determination when the alcohol-potassium carbonate extraction method is used in concentrating the sample. The coils are present to facilitate heat exchange between the tube and the gas. For this purpose, other materials than nichrome would undoubtedly serve better, but the particular coils described are satisfactory for reasons hereinafter indicated, and at the same time are low in cost. Rubber connections and rubber stoppers are used throughout the entire train, with the usual precautions to expose as little rubber as possible to the gas stream.

The first tube serves to condense most of the moisture of combustion. With it is caught considerable solid smoke. The packing of glass wool assists in bringing smoke and moisture into contact. In this first tube from 32 to 37 per cent of the iodine is collected from representative samples.

The second freezing tube removes most of the remainder of the moisture. This step is necessary in order that the gas stream will not be saturated with water when it reaches the first Cottrell precipitator. It is also essential to avoid the freezing-shut of the third collecting tube.

The precipitator as illustrated, under the conditions herein described, is adequate for collecting the solid material which has passed through the glass wool in the first condensing tube from most types of sample. In some samples, however, in which the mineral content is quite high, this precipitator is rendered ineffective by the deposited material in the latter part of runs on 60-gram samples. In such cases it is well to have available a second precipitator connected into the system in parallel, by means of a three-way stopcock and T-tube. The amount of iodine caught in the precipitator is governed largely by the form in which it occurs and by the mineral constituents present with it. The amount usually runs from 3 to 8 per cent of the total. Whether or not the precipitators may be eliminated from the system, as has been done by some investigators, depends on the nature of the samples and the familiarity of the operator with them. It is the author's experience that the precipitator illustrated is more easily cleaned than a tower containing beads or glass wool that may be substituted for it.

The third collecting tube immersed in acetone and solid carbon dioxide collects 38 to 50 per cent of the total iodine, and the second similar tube 3 to 8 per cent. When samples containing considerable nitrogen are burned, nitrogen dioxide is frozen out in these last two collecting tubes. Care must be taken to neutralize this condensed material before the tube has warmed completely, lest elemental iodine be swept out with the expanding vapors.

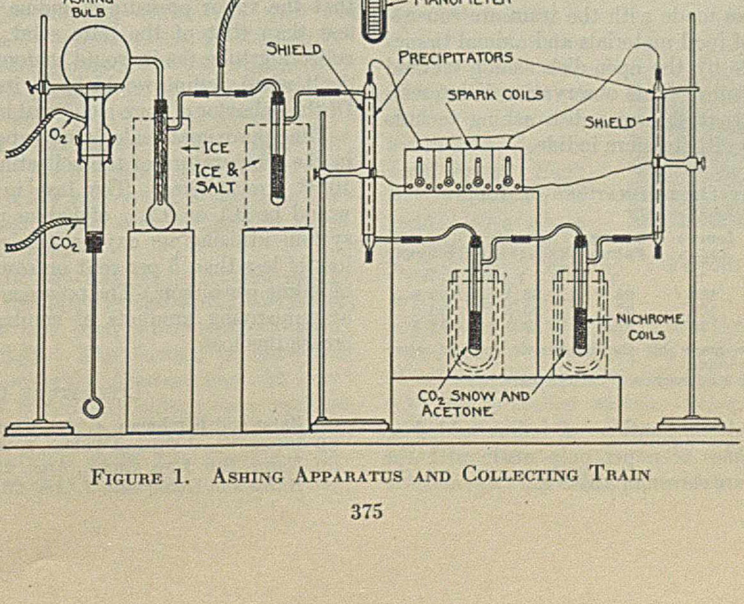

Figure 1. Ashing Apparatus and Collecting Train

The final precipitator is appended as a precautionary measure and in a normal run collects very little material.

The train at the end of the run contains nothing but precipitated solid ash and the condensable products of the combustion. These combustion products are washed from the train with water containing sufficient potassium carbonate to assure distinct alkalinity in order that the iodine will be retained during concentration and subsequent treatment. The entire washings from the train and from the bulb type of ashing apparatus previously described usually amount to about 300 cc.

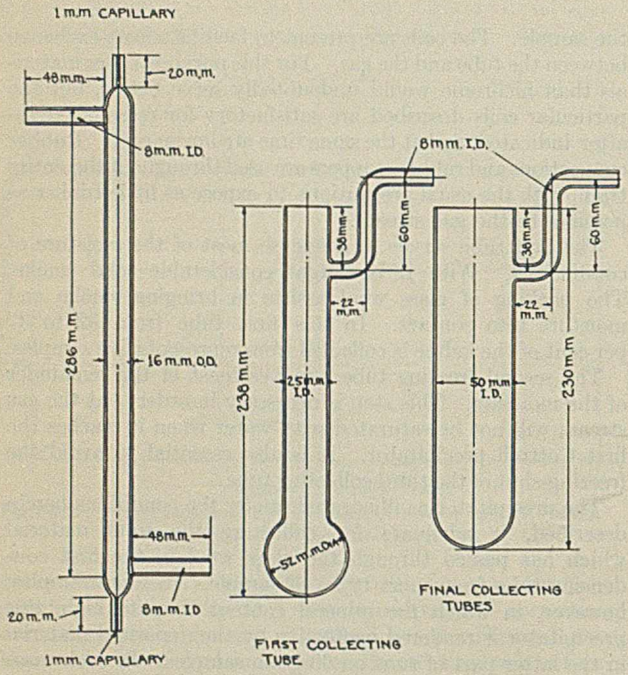

Figure 2. Precipitator

The efficiency of collection in this type of train is dependent to a considerable extent on the speed of the gas stream. The latter, in turn, is dependent on the initial oxygen-input rate, the completeness of oxygen utilization, the amount of condensable combustion products, and the cross section of the gas stream in the selective portions of the apparatus. The recovery of approximately 90 per cent, using an oxygen input of 1.4 liters per minute, although no higher than that reported using other types of train, is considerably more consistent than that obtained with other types in the author's experience. The recoveries made with the train are consistently higher on samples of food materials and animal tissues than determinations made by the open-dish ashing method using controlled temperatures. This observation is interesting in view of the fact that the open-dish ashing technic used gave good recoveries of potassium iodide.

Table I. Recovery Determinations of Iodine

Accompanying Material	Iodine Contained in Pulp		Iodine Added	Iodine Found	Iodine Recovered	Recovery
Grams	γ/*kg.*	γ	γ	γ	γ	%
6.5	280	1.8	106	98.2	96.4	90.9
6.2	280	1.7	106	97.2	95.5	90.0
18.0	750	13.5	20	31.8	18.3	91.5

Note. Determinations were made by the titrimetric method after oxidation with iodine-free (*4*) bromine.

The Greek letter γ is used for 1 microgram (= 0.001 mg.).

Examples of recovery determinations of iodine added as potassium iodide to samples of paper pulp made with the collecting train described are shown in Table I.

Limitations of Apparatus

A collecting train of this type has certain inherent limitations which it is well to point out. Under ideal operating conditions, the limit of recovery in any train is set by the vapor pressure of the pure products in the train, the partial pressure of the products in solution, and the volume and approach to saturation of the emerging gas. In those types of train using reagents, the desired products are converted to compounds which have negligible vapor pressure at room temperature. In the train described, the collected materials are modified only as the products of combustion act as reagents, the effectiveness of collection depending on the fact that the vapor pressure of the products is negligible at the temperatures attained in the collecting tubes. We are dealing with a number of possible iodine compounds as products, whose actual nature is dependent largely on the original state of combination and the nature of the other material in the sample. At the temperature of combustion we would expect that, in the absence of basic metals, most of the iodine would be released as the free element, both hydrogen iodide and oxides of iodine being unstable at elevated temperatures. Most of the metallic iodide salts would probably be decomposed as well. The basic products capable of being volatilized on assuming the form of dust beyond the elevated temperature zone might recombine with iodine to give iodides and oxy-salts of iodine. These products would condense and settle in the system, dissolve in the water of condensation, or be thrown out in the precipitators. The dissolved salts with acid products of combustion would tend to form acids, the most volatile of which, hydriodic acid, in the dilution formed with the water of condensation from most samples, would have a negligible partial pressure (*1*, *5*) even in the first collecting tube. If samples giving no water were being burned, it would be well to add a few cubic centimeters to the first collecting tube.

If we assume that the possible organic combinations of iodine are unstable under the conditions of combustion, it is evident that iodine itself is the next most probable source of loss under ideal operating conditions.

Of that part of the free iodine that is not held by basic materials after recombination, some will remain in solution in the condensed water vapor. Its slight solubility, however, will not allow us to depend on this factor for recovery, especially since the products of combustion of nitrogenous materials will insure the absence of iodides in solution. Aside from solution in water, we may expect iodine to be held as the condensed pure solid or more probably as a solid mixture with ice and other condensable combustion products. Concerning the state of these mixtures we know little except that the vapor pressure of iodine from them will likely be less than that of the pure solid. Occurring alone in the collecting tube (as it would seldom do with samples usually dealt with), iodine would be in its most fugitive condition. Of the behavior of pure elemental iodine we may speculate.

The approximate calculated vapor pressure (*2*, *6*) of iodine in the temperature of the collecting tubes is of the order of 10^{-10} atmospheres. The loss in saturated emerging gas would be 0.1 or 0.2 γ of iodine per hundred liters. In a system utilizing its oxygen efficiently, this would mean a loss of less than 5 per cent on samples containing 100 parts of iodine per billion. The presence of almost any conceivable accompanying products of combustion would tend to decrease this loss.

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Determination of Copper Number of Paper

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An investigation into the service deterioration of the oil-impregnated paper insulation of 24,000-volt underground cable led to the use of the copper number test for following the changes which occurred in the paper. In a series of experiments in which oil and paper were subjected *in vacuo* to electric discharge (which had been shown to be one of the chief causes of service deterioration), it was found that an increase in the time or intensity of bombardment was accompanied by an increase in the copper number of the paper (*12*). The copper number was therefore used as an indication of the amount of deterioration.

Early tests in 1928 soon demonstrated the necessity of experimental work to modify one of the existing test methods for the determination of this factor so as to obtain a reliable test procedure for the requirements. The method finally adopted (*7*) has proved exceedingly satisfactory, and although essentially a standard method, the modifications are thought worthy of description as of general interest.

A copper number test, to be satisfactory for the purpose mentioned, must be rapid, sensitive, and capable of yielding results which are reproducible within reasonable limits on a sample not larger than 1.5 grams. In addition the apparatus required must not be expensive.

Early determinations were made by means of Schwalbe's method (*13*) and some of its modifications, but the results were unsatisfactory. The values obtained were erratic because of the instability of the Fehling solution during the boiling period, and because of the error due to adsorption by the paper of bivalent copper. Differences in paper samples subjected to different deteriorating treatments were not always brought out, probably because of the effect of caustic alkali in modifying the reducing properties of the cellulose (*4*).

In later work the method described by Braidy (*2*) and others (*9*), in which the Fehling solution is replaced by a sodium carbonate-bicarbonate solution, was used with more satisfactory results. As Clibbens and Geake point out (*4*), the method gives a low and constant blank, is sensitive to slight modifications of the cellulose, and is reproducible within reasonable limits.

Finally, the improved Braidy method as worked out by the Bureau of Standards and later published (*3*) was found, after minor modifications had been introduced, to satisfy the requirements completely. The Bureau of Standards specified a method of thoroughly disintegrating the paper without heating the fibers in order to obtain more accurate results. The Gault-Mukerji molybdophosphoric acid method (*5*) of determining the cuprous oxide was adopted. The size of the sample was reduced to 1.5 grams.

Modifications of Old Method

The modifications of the Bureau of Standards method are as follows:

1. The shredder recommended by the Bureau of Standards was too large and costly for the type of work being carried out in these laboratories. A Hamilton-Beach malted milk mixer modified in the manner described by the Okonite Callender Cable Company (*11*) was found to meet the requirements.

The shredder is shown in Figure 1. The stirring motor was mounted on a telescoping shaft, *A*, so that it, together with the stirrer, could be raised or lowered to any desired height. A variable rheostat, *B*, was included to control the rate of stirring. A hotplate, *C*, was installed for heating the liquid during the shredding process. The original stirring shaft was replaced by a brass shaft, *D*, on which were mounted two shredding wheels 1.5 inches in diameter made from $^1/_{32}$-inch sheet brass. Each wheel consisted of eight blades whose cutting edges were sharpened. The two wheels were mounted so that the liquid was thrown upwards by the lower wheel and downwards by the upper wheel. The brass fingers, *E*, are important since they help to throw the fibers constantly into the shredding wheels. When used at high speed with a hot solution, the disintegration of the paper is complete after one minute. The short time involved eliminates the irregularities attendant upon long continued beating (*8*, *10*).

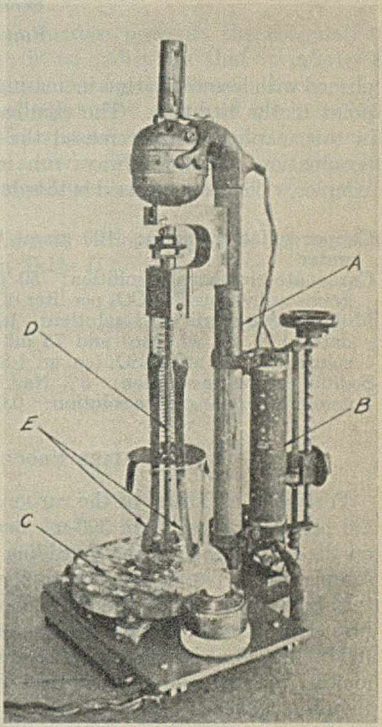

Figure 1. Paper Shredder

2. Anhydrous sodium carbonate was used instead of the hydrated form because it was found that the latter form dehydrates and thus makes the concentration of the carbonate-bicarbonate solution uncertain.

3. The samples were weighed to the third decimal place to insure the accuracy of the second decimal place.

4. Coarse Jena filters suggested by Heyes (*6*) and Barthelemy (*1*) were substituted for filter paper on a Büchner funnel because, by so doing, thorough washing could be accomplished with less water, thus increasing the sharpness of the end point in the titration. The elimination of the filter paper in this manipulation decreased the value of the blank determination which is always run in conjunction with the samples. The reagents used in this determination are (*3*):

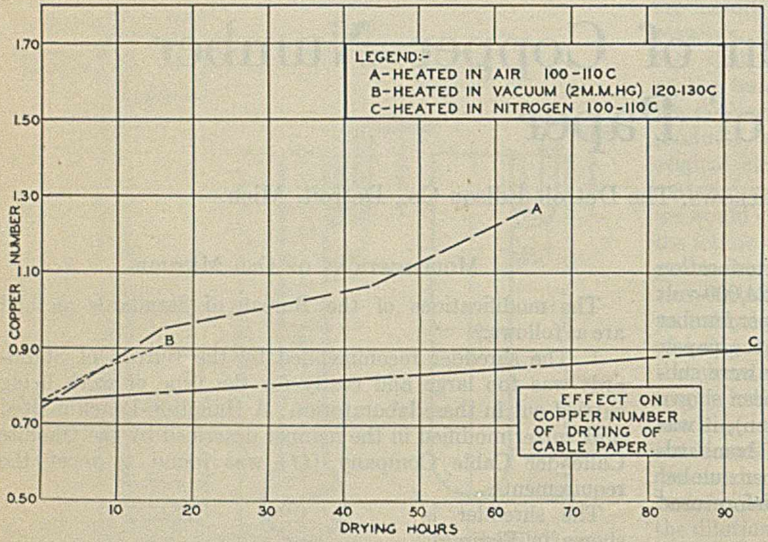

FIGURE 2

Copper sulfate solution: 100 grams $CuSO_4 \cdot 5H_2O$ per liter of water

Carbonate-bicarbonate solution: 50 grams $NaHCO_3$ and 132 grams anhydrous Na_2CO_3 per liter of water

Molybdophosphoric acid solution: 100 grams sodium molybdate (43% by wt. Mo) and 75 ml. 83% H_3PO_4 added to a solution of 275 ml. H_2SO_4 (sp. gr. 1.86) and 1750 ml. water

Sodium carbonate solution: 5% Na_2CO_3

Potassium permanganate solution: 0.02 *N*

DETAILED PROCEDURE

Forty-five milliliters of the carbonate-bicarbonate solution are placed in a tall form 300-ml. beaker and the beaker set on the hotplate, *C*, of the shredding apparatus. A 1.5-gram sample of the paper, weighed to the third decimal place, is torn into pieces about one quarter of a square inch. At the first sign of steam rising from the solution on the hotplate (90° to 95° C.), the heater is turned off and the bits of paper making up the sample are transferred to the beaker. The shredding wheel is then lowered into the mixture and the machine run at full speed for exactly one minute. During the shredding the beaker is pushed off center to facilitate cutting the pieces of paper which might otherwise escape the process. At the end of one minute of shredding the wheel is lifted above the surface of the mixture, but not above the top of the beaker, and the motor stopped. The contents of the beaker are then transferred to a 125-ml. Erlenmeyer flask. (A funnel with the stem cut off facilitates this step.)

Fifty milliliters of the cold carbonate-bicarbonate solution are then added to the beaker and the motor run as before. This treatment removes the fibers clinging to the grinding apparatus to within the limits of accuracy as defined by weighing. The fibers clinging to the beaker are rinsed free and the mixture is added to that in the Erlenmeyer flask. Five milliliters of the copper sulfate solution are added to the contents of the Erlenmeyer flask which is then swirled to mix the contents well, closed with a Bunsen valve, and submerged in a steam bath.

In actual practice, several samples are prepared up to the addition of the copper sulfate solution and a number of samples placed on the bath at one time.

At the end of 3 hours the flasks are removed from the bath and the contents filtered through Jena crucibles. When several samples are being run at once, all but those which can be filtered immediately are quickly cooled. The pulp is then washed with 75 to 100 ml. of 5 per cent sodium carbonate solution, and thoroughly washed with hot water. The washed pulp is transferred to a beaker containing 25 ml. of the molybdophosphoric acid solution and well macerated with a glass rod. Since particles of cuprous oxide clinging to the inside of the Erlenmeyer flasks are not removed when the flasks are rinsed into the crucibles, the flasks are rinsed with a portion of the molybdophosphoric acid solution, washed with water, and the solution added to the filtrate to be titrated. The mixture is allowed to stand for about 10 minutes and is then filtered through the same crucible as before. The filtrate is washed into a clean suction flask, and the solution transferred to a beaker and titrated with the standard potassium permanganate to a faint pink color. A blank is run on the reagents alone in exactly the same manner as if they contained a paper sample. The value for the blank is subtracted from that of each sample.

Since the copper number is defined as the number of grams of metallic copper in the cuprous oxide reduced from the copper sulfate by 100 grams of sample, the following formula may be used:

$$\text{Copper number} = \frac{6.357 \times \text{ml. of } KMnO_4 \times N}{W}$$

where *N* is the normality of the potassium permanganate and *W* is the weight in grams of the sample. In order to correct for the moisture content of paper, it is necessary either to make the moisture determination on a separate sample, or to remove the moisture under conditions which do not alter the paper in such a way as to effect changes in the copper number. Since the specimens used were so small as to preclude the use of the former method, it was desirable to use the latter. By drying the sample (100° to 110° C.) 2 hours in a stream of dry nitrogen, the moisture is removed to the point where any further change in weight does not affect the accuracy of the result. However, even when care is taken to displace the air surrounding the samples before starting the drying, the mild heat treatment raises the copper number slightly more than the probable error of the determinations (Figure 2). This is shown by the following table:

COPPER NO. OF PAPER DRIED 2 HOURS IN N	COPPER NO. OF UNDRIED PAPER COR. FOR MOISTURE
1.02	1.01
1.02	1.01
1.03	1.00
1.03	1.00

Unless care is taken to displace the air before heating is started, the difference is greater. In all cases where possible it seems advisable, therefore, to determine the moisture content of the paper on separate samples.

It frequently has been pointed out that the empirical nature of the copper number determination renders it highly dependent on the details of the experimental procedure. The temperature during the digestion period (*2*, *4*, *14*), the time of digestion (*2*, *9*), and the concentration of the alkaline solution (*1*) must be kept constant if strictly comparable results are to be obtained.

The reproducibility of the results can be illustrated from the following:

Ten copper number determinations made on a given cable paper averaged 0.96. The highest value was 0.98 and the lowest 0.95. However, abnormal values, both high and low, are occasionally obtained from the same sheet of cable paper. Whether these are due to actual differences in the paper or to errors in manipulation is not known. Determinations made on a large number of samples of cable paper indicate that it is advisable to interpret the value of a single determination plus or minus about 2.5 per cent.

ACKNOWLEDGMENT

The authors are greatly indebted to K. S. Wyatt of this organization for his aid in assembling and organizing the data of other investigators and reviewing this work.

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RECEIVED December 17, 1931.

Impurities in White Sugars

VI. Direct Determination of Chlorides

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CHLORIDES in sugarhouse products are often determined in the lixiviated ash, although Browne and Gamble (*1*) have shown that chlorine is lost during the charring preparatory to the lixiviation and recommend the direct gravimetric determination of chlorides in these products. With high concentrations of sucrose and low content of chlorides, however, the sucrose exerts a dispersing action on the precipitated silver chloride, so that collection of the silver chloride upon a filter is very difficult and often impossible. To overcome this difficulty, Budlovsky (*2*) has proposed a method of coagulating the silver chloride formed in sucrose solutions by precipitating ferric phosphate in the solution containing the suspended silver chloride. The precipitate of silver chloride and ferric phosphate is then treated in a special distilling apparatus with sulfuric acid. The hydrogen chloride liberated is distilled into water and determined by a nephelometric titration with mercuric nitrate.

TABLE I. DETERMINATION OF CHLORIDES IN PRESENCE OF SUCROSE

Cl^- ADDED	Cl^- FOUND IN ABSENCE OF SUCROSE	Cl^- FOUND IN PRESENCE OF 100 GRAMS OF SUCROSE
Mg.	*Mg.*	*Mg.*
0.35	0.21	0.21
0.71	0.74	0.82
1.42	1.49	1.42
2.13	2.06	2.20
2.84	2.91	2.84
3.55	3.48	3.62
4.26	4.11	4.33
4.96	5.11	5.25
5.67	5.75	5.75
6.38	6.31	6.45
7.09	7.09	6.81

The proportion of chlorides present in white consumption sugars is so small that gravimetric determination is impractical. The direct volumetric determination of chlorides in white sugars has not been reported, so far as the authors are aware. The experiments reported in Table I show that Mohr's method (*3*) of titration of chlorides with silver nitrate and potassium chromate as indicator may be successfully applied. Although sucrose prevents the coagulation of silver chloride, there is no indication that it interferes with the removal of chloride ions by the silver ions.

One hundred grams of sugar were dissolved in about 150 cc. of distilled water, and about 0.5 cc. of saturated potassium chromate solution was added. The solution was titrated with 0.02 *N* silver nitrate solution as usual for the volumetric titration of chlorides.

The content of chlorides in various grades of commercial white sugars is shown in Table II.

TABLE II. CHLORIDE IN COMMERCIAL WHITE SUGARS

SUGAR	Cl^-	SUGAR	Cl^-
	P. p. m.		*P. p. m.*
a	7.8	k	33.3
b	1.4	l	27.7
c	40.4	m	0.0
d	17.7	n	5.0
e	33.3	o	22.7
f	0.7	p	39.0
g	31.9	q	44.0
h	14.2	r	31.9
i	16.3	s	20.6
j	2.1	t	10.6

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RECEIVED May 9, 1932. Contribution 124, Carbohydrate Division, Bureau of Chemistry and Soils.

CORRECTION. In the article on "Apparatus for Reactions in Liquid Phase at Elevated Temperatures and Pressures" [IND. ENG. CHEM., Anal. Ed., 4, 342 (1932)], the length of the tubing for the steel spiral referred to in the thirteenth line from the bottom of the first column, page 343, should have been given as 4.3 meters, or 14 feet.

HOMER ADKINS

Improved McLeod Gage and Manometer

Harold Simmons Booth, Western Reserve University, Cleveland, Ohio

In spite of the numerous improvements made in the McLeod gage since the original devised by McLeod (*3*), it still suffers from certain defects. In order to overcome some of these, there has been devised in this laboratory the modification shown in Figures 3 and 4.

A better appreciation of this device may be obtained, perhaps, if the original McLeod gage, as shown in Figure 1, be considered first. In this device the apparatus whose pressure is to be measured is connected to the body of the McLeod gage through the capillary between B and F. When equilibrium has been attained between the McLeod gage and the apparatus, the mercury reservoir, R, is slowly raised, imprisoning above the cut-off, C, the gas of volume V_1 and compressing it into the calibrated capillary, OT. Simultaneously, the mercury will rise in the capillary BF. This instrument may then be used in either of two ways: First, the mercury may be allowed to rise in capillary OT exactly to O, and the difference in height, H, between O and the top of the column of mercury in the capillary side tube, BF, noted. Then it is obvious that, assuming the perfect gas laws, the true pressure, P, in the system connected to the gage is

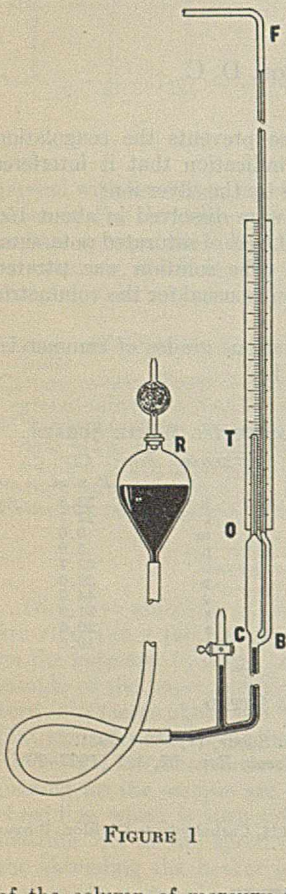

Figure 1

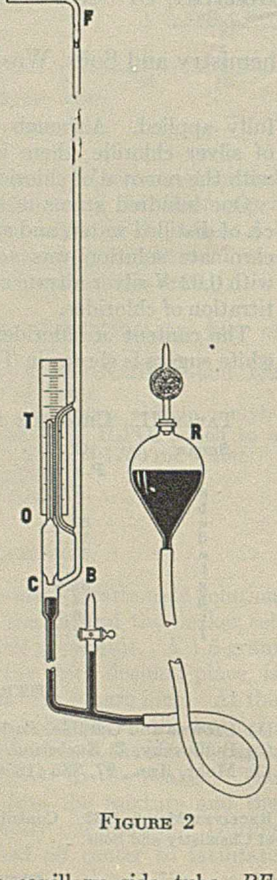

Figure 2

$$P = H \times \frac{V_2}{V_1} \qquad (1)$$

where V_2 is the volume of the gas in the capillary OT.

In the other method of operation, which is particularly useful for low pressures, the mercury is adjusted so that the height of the column in the capillary BF (Figures 1 and 2) or OF (Figures 3 and 4) coincides exactly with the height of T, the mercury in the capillary OT being at some height, L. If we let H represent the difference in height in mm. between L and T, and if v represents the volume of the capillary OT per mm. of height, then the equation becomes

$$P = H \times \frac{Hv}{V_1} \qquad (2)$$

However, in neither of these formulas is the fact recognized that pressure H should be corrected for pressure P being measured. Formula 1 then becomes

$$P = (H + P)\frac{V_2}{V_1}, \quad \text{whence } P = H\frac{V_2}{V_1 - V_2} \qquad (3)$$

and Formula 2 becomes

$$P = (H + P)\frac{Hv}{V_1}, \quad \text{whence } P = \frac{H^2v}{V_1 - Hv} \qquad (4)$$

In measuring low pressures this correction may be omitted. However, in the use of the vacuometer to measure pressures of the order of several millimeters, it should be included. The type of vacuometer shown in Figure 1 is usually used for measuring relatively low vacuums, whereas that in Figure 2 is more commonly used for measuring high vacuums.

In Figure 2 the diffusion of the gas between the vacuometer and the apparatus has been greatly facilitated by using a tube of large bore and making the capillary a by-pass. However, this type of apparatus can only be used according to the second method.

If one desires, therefore, to measure a considerable range of low pressure, it is necessary to have two vacuometers, one such as Figure 1 and the other such as Figure 2. This has been obviated in our design as shown in Figure 3. A tube of large bore, B, connects the vacuometer and the apparatus whose pressure is to be measured. At a distance of about 85 cm. below the constriction, C, the side tube, EOF, is attached. The upper part of the tube is made of capillary tubing of the same piece as was used in the body of the vacuometer. Thus there is no capillary error due to differences in diameter. Above the capillary tube at F there is a short space of 7-mm. tubing surmounted by another capillary tube, which is bent downward and again upward at the overflow well, W. The distance from the top of the capillary tube to W should be about 760 mm. The total length of the capillary from O to F should be about 1 meter.

Calibration and Preparation of Gage

The volume v of the capillary tube in cubic millimeters per mm. of length should be determined before attaching the capillary to the body of the tube. The capillary should be tested first for uniformity by placing in a suitable length of the capillary tubing a drop of mercury and measuring the length of this drop in different positions in the capillary. In a capillary of uniform bore the length of the drop of mercury will be constant. To calibrate it the capillary tube is almost filled with pure mercury. The length of this mercury column is measured, the temperature noted, and the mercury run out and weighed. The capillary tube is then sealed on to the gage body and sealed off at the top, T, with as blunt an end inside as possible. The gage is then clamped in inverted position and filled with pure mercury up to the constriction, *C*, the temperature noted, and the mercury removed and weighed. If the temperature at which both the capillary and whole gage are filled are the same, it is unnecessary to calculate the true volumes, and the relative weights may be used instead to get the constant v/V_1 for the gage.

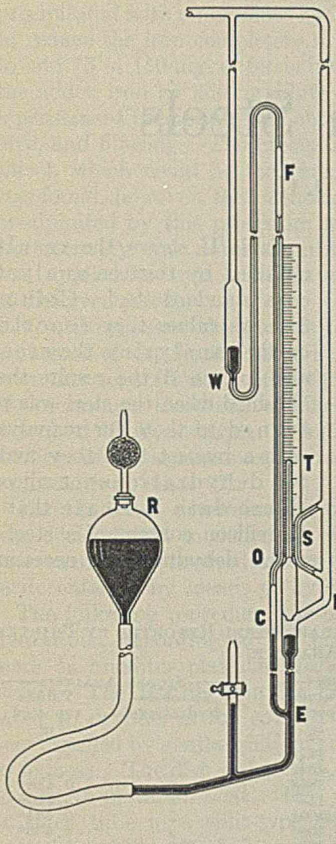

FIGURE 4

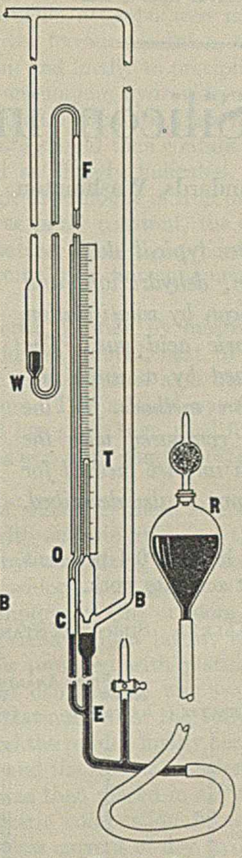

FIGURE 3

In operation the vacuometer is first carefully cleaned and thoroughly dried by passing dry air through it for a number of days, or better, by repeated rinsings with dry air followed by evacuations. Then the reservoir, *R*, is filled with pure mercury and kept at such a low level that when a vacuum is applied to the gage the mercury will slowly rise in the lower tube. When a satisfactory vacuum has been obtained, the reservoir, *R*, is raised until the mercury overflows into *W*. The reservoir is then lowered at once as low as possible, the column of mercury breaks at *F*, and opportunity is given for adsorbed gases to escape from the walls of *OF*. After a few minutes, *R* is again raised, thus driving over any minute amounts of gas which may have escaped from the walls of *OF*. The instrument should then be allowed to stand with reservoir *R* as low as possible, and at daily intervals *R* should be raised to drive over any gas while the space above *W* is evacuated to expand the bubble and prevent its lying down in the capillary. When no evidence is seen of a bubble of gas being carried over into *W*, it may be assumed that the space in *OF* is completely evacuated, and the gage is ready for use.

This instrument may be used over a wide range of pressures. One made in this laboratory is sensitive over the range from 760 to 0.00001 mm., although according to Gaede (*1*) accurate measurements below 0.0001 mm. can be made only on hydrogen or nitrogen, or a similar inert noncondensable gas. Oxygen at these low pressures tends to smut the mercury, probably because of the formation of ozone by the activation of the oxygen by the electrical discharge produced by the moving mercury. This smut deposits as a film in the capillary, obviously introducing errors. From pressures between 17 and 0.1 mm. (gage *A* in Table I), the procedure is as follows: The reservoir is raised slowly until mercury in the body of the tube has risen to the etched mark, *O*, in the capillary, *OT*. The difference in height, *H*, between *O* and the column of mercury in *OF* is noted. Whence

$$P = H \times \frac{V_2}{V_1}$$

where V_2 represents the volume of the gas compressed in the capillary above *O*. Since there is no pressure above the side capillary, *OF*, no correction for this is necessary as was the case in the original design shown in Figure 1 (see Equation 3).

TABLE I. DIMENSIONS AND CONSTANTS OF TWO TYPICAL NEW TYPE GAGES

		A	B
Inner diam. of capillary *OT*, mm.		1.75	1.07
Length of capillary *OT*, mm.		260	320
Inner diam. of body of gage, mm.		16	28
Approx. length of body of gage, mm.		90	150
Volume v of capillary, cu. mm. per mm.		1.030	0.9052
Volume V_1 of whole gage, cu. mm.		15,260	77,720
Gage constant V_2/V_1 (Equation 1)		1/56.98	1/268.3
Gage constant v/V_1 (Equation 2)		1/14,815	1/85,856
OPERATING GAGE ACCORDING TO EQUATION 1			
If $P =$ 1 mm., H	=	56.98 mm.	268.3 mm.
3 mm., H	=	170.94 mm.	804.9 mm.
10 mm., H	=	569.8 mm.	Beyond range
17 mm., H	=	968.7 mm.	Beyond range
OPERATING GAGE ACCORDING TO EQUATION 2			
If $P =$ 1.00 mm., H	=	122.0 mm.	293.0 mm.
0.01 mm., H	=	12.2 mm.	29.3 mm.
0.0001 mm., H	=	1.22 mm.	2.93 mm.
0.00001 mm., H	=	0.39 mm.	0.93 mm.

If low pressures are to be measured, the mercury is allowed to rise in *OF* to the same level, *T*, as the top of the inside of the capillary on the body of the gage. The difference in level, *H*, between *T* and the mercury column of the capillary on the body of the gage is noted. Then the true pressure

$$P = H^2 \times \frac{v}{V_1}$$

where V_1 equals the total volume in cubic millimeters of the gage above the constriction *C*, and v equals the volume in cubic millimeters per mm. of length of the capillary on the body of the gage. Again there is no correction for the pressure in the external system (see Equation 4).

To measure higher pressures—that is, to use the gage as a manometer—the design shown in Figure 4 equipped with capillary side tube *S* is required. The reservoir is adjusted so that the mercury level in *S* is at *O* and the difference in levels between the mercury in *OF* and in *S* is the pressure of the outside system being measured.

In building a gage of this new type it is important to have the proper ratio between the total volume of the gage, V_1, and the total volume of the capillary. To avoid sticking of the mercury in the capillary, its inner diameter should be greater than 0.5 mm. Although for very low pressures the body of the gage may be even as large as 500 cc., for most uses in the laboratory it is best to have this volume around 50 cc. For the convenience of those wishing to build one of these new gages, there is described in Table I the complete dimensions and pressure data of two gages of this type of different range actually in use in this laboratory.

To minimize smutting of the mercury, these gages may be operated by vacuum-pressure control arrangements, such as that devised by Gaede (*1*) or the General Electric Company modification (*2*), provided the reservoir is connected to an air-pressure line to force the mercury over the top when evacuating capillary *OF*.

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Determination of Silicon in Steels

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The silicon content of three typical steels has been determined by solution, dehydration, and recovery of the dissolved silicon by volatilization of the iron with hydrochloric acid gas. The percentage of silicon obtained by a single dehydration with five common methods for the determination of silicon is compared with the values for total silicon. An umpire method for silicon in very low-silicon irons is also described.

ALTHOUGH it is a well-known fact that in the determination of silica in silicates accurate results can be obtained only when several dehydrations are made, it has long been the practice of steel chemists to consider the amount of silica left in iron solutions after a single dehydration as being negligible. However, in the last few years there have been several attempts to show that for accurate work more than one dehydration is necessary, especially if the silicon content is high. For example, Pinsel (*6*) claims that when cast irons are analyzed by the nitro-sulfuric acid method the results are low, and that for umpire work several evaporations cannot be avoided.

Stadeler (*7*), while studying the relative advantages of the various methods for silicon, had three steels of different silicon contents analyzed by twelve laboratories, employing five different methods. All of these laboratories found silicon in the filtrate after a single dehydration. The twelve laboratories varied widely in the percentages of silicon recovered in a second dehydration, averaging 0.01, 0.02, and 0.14 per cent on an 0.08, a 0.3, and a 4 per cent silicon steel, respectively. However, the results for the first evaporation differed so greatly as to throw doubt on any conclusion as to the amount of silicon recoverable in a second dehydration. Wolf and Heilingötter (*10*) analyzed a sample of high-silicon steel by five methods, making four dehydrations by each method. For their standardization procedure they chose a nitro-sulfuric acid method, which yielded an average of 4.004 per cent of silicon in the first dehydration, 0.068 in the second, 0.039 in the third, and 0.019 in the fourth. The total, 4.130 per cent, was considered to be the silicon content of the steel. Four dehydrations by each of the other methods gave values ranging from 4.078 to 4.116 per cent, results which were from 0.014 to 0.062 per cent lower than those obtained by the nitro-sulfuric acid method.

In the analysis of Bureau of Standards standard samples of steel it has been the practice to make two dehydrations by the sulfuric acid method. The results obtained on a number of these standards are given in Table I.

TABLE I. SILICON OBTAINED BY SULFURIC ACID METHOD

TYPE OF STEEL	WT. OF SAMPLE	Si OBTAINED IN 1ST DEHYDRATION	Si OBTAINED IN 2ND DEHYDRATION	TOTAL SILICON
	Grams	%	%	%
0.4 Carbon, B. O. H.	10	0.017	0.001	0.018
0.1 Carbon, Bessemer	10	0.020	0.001	0.021
0.4 Carbon, Bessemer	10	0.062	0.002	0.064
0.6 Carbon, A. O. H.	10	0.105	0.002	0.107
Medium manganese	10	0.192	0.003	0.195
Chrome-nickel	10	0.213	0.007	0.220
0.6 Carbon, A. O. H.	5	0.276	0.004	0.280
1.0 Carbon, A. O. H.	10	0.381	0.007	0.388
Acid electric	10	0.434	0.007	0.441

Table II shows the results obtained by thirteen analysts on a standard steel. Column 3 shows values they reported on first analyzing the steel, and column 5 the results they obtained when the steel was returned to them for reanalysis with a request that they make two dehydrations for silicon. These data indicate that if the silicon content of a steel is as high as 0.4 per cent, a second dehydration is necessary for accurate work.

TABLE II. SILICON IN STANDARD STEEL REPORTED BY THIRTEEN ANALYSTS

ANALYST	FIRST ANALYSIS		SECOND ANALYSIS	
	No. of dehydrations	Values reported	No. of dehydrations	Values reported
		%		%
1	2	0.441[a]	...	...
2	1	0.434[a]	...	...
3	1	0.388[a]	2	0.438[a]
4	1	0.412[a]	2	0.440[a]
5	1	0.409[b]	2	0.441[a]
6	1	0.408[b]	2	0.436[a]
7	1	0.420[b]	2	0.446[a]
8	1	0.407[d]	2	0.441[a]
9	1	0.422	2	0.439[a]
10	1	0.417	...	0.440
11	1	0.427[c]	2	0.451[c]
12	1	0.422[d]	1	0.434[b]
13	1	0.435[e]	...	...
		Av. 0.419		Av. 0.441

[a] Sulfuric acid method.
[b] Nitro-sulfuric acid method.
[c] Nitro-hydrochloric acid method.
[d] Hydrochloric acid method.
[e] Perchloric acid method.

DETERMINATION OF MOST PROBABLE VALUES FOR SILICON

In view of the uncertainty concerning the amount of silicon remaining in solution after dehydration by the usual procedures, it was decided to attempt to determine the true silicon content of three typical steels and then to compare these values with those obtained when the usual procedures were applied. Steels representing the ranges of silicon usually encountered in steel laboratories were selected for this work. The samples were in the form of fine chips as prepared for Bureau of Standards standard samples (*4*). For convenience they will be referred to as steels A, B, and C throughout this paper. Their silicon contents were approximately 4.7, 0.4, and 0.1 per cent.

The other constituents were as follows:

STEEL	TYPE	C	Mn	P	S	Ni	Cr	V
		%	%	%	%	%	%	%
A	Unknown	0.064	0.10	0.010	0.024	...	...	...
B	Acid electric	0.258	0.748	0.036	0.048	0.242	0.178	0.007
C	A. O. H.	0.574	0.630	0.062	0.030	0.161	0.166	0.008

In the analysis of silicate materials, such as rocks, it is usually assumed that the silica which escapes the dehydrating treatment will be found in the ammonia precipitate, and that it can be recovered by igniting this precipitate and volatilizing the silica in the usual manner with hydrofluoric acid. As it would have been inconvenient to filter, ignite, and weigh the oxide which would be obtained if 5 grams of steel were precipitated with ammonium hydroxide, attempts were made to reduce the iron completely to the ferrous condition, then to add 75 to 150 mg. of ferric iron, and finally to precipitate the added iron by adding dilute ammonium hydroxide until a permanent precipitate was obtained, boiling for a few minutes, and filtering. The precipitate should then contain the silicon which could be recovered as already indicated. It was found, however, that although the amount of iron oxide precipitated by this procedure was fairly constant, the silicon recovery was never quantitative when the procedure was applied to iron solutions containing known amounts of dissolved silicon.

Volatilization of the iron as ferric chloride by means of a current of dry hydrochloric acid gas seemed, next to the ammonia separation, to offer the most promise as a means of determining the dissolved silicon. This method was first described by Boussingalt (*1*) and has since been used for a number of the separations, such as iron from alumina (*2*) and tungsten from silica (*3*).

For the exact determination of silicon in these steels, it was decided first to dehydrate with sulfuric acid and then to recover the dissolved silicon by volatilizing the iron as ferric chloride by means of hydrochloric acid gas.

The following procedure was employed: One or more dehydrations, according to the procedure given below, were made in one-liter platinum dishes provided with platinum covers. The filtrate from the last dehydration was evaporated to dryness in the covered platinum dish, the sulfuric acid expelled by gentle ignition, and the residue finally heated to redness. The dish was cooled, and the residue transferred to a small platinum boat. This was then placed in a Pyrex or silica tube in a split-type electric combustion furnace, heated to 400° to 700° C., and a slow current of dry hydrochloric acid gas passed through the tube. The hydrochloric acid gas was generated by dropping sulfuric acid upon heated ammonium chloride and dried by bubbling through sulfuric acid.[1] The residue adhering to the dish was treated with a few milliliters of hydrochloric acid, transferred to a platinum crucible, and the solution evaporated to dryness. When most of the iron in the boat had been volatilized, the residue was carefully brushed into the crucible containing the residue from the dish. The contents of the crucible were treated with a few drops of dilute sulfuric acid, which was then driven off by heating the crucible on a radiator. The residue was next ignited in a muffle at 1050° to 1100° C. to constant weight, treated with 10 ml. of hydrofluoric acid and a few drops of dilute sulfuric acid (1 to 3), and the amount of silica determined by evaporation to dryness on a radiator, igniting, and weighing. The weight of the nonvolatile residues averaged about 0.15 gram.

The first few times the volatilization procedure was used, the initial dehydration was made by the perchloric acid method because it was believed that residues from perchloric acid solutions could be converted to oxides more readily than those from sulfuric acid solutions. Later experiments with sulfuric acid showed that the residue from a sulfate solution was in a better condition to be attacked with hydrogen chloride than residues from perchloric acid solutions. When perchloric acid was used, the procedure given under "Perchloric Acid Method" below was followed. The results obtained for total silicon by both methods are listed in Table III. The values given were corrected by complete blank determinations.

Table III. Silicon Obtained by Sulfuric Acid and Perchloric Acid Methods and Recovery of Dissolved Silicon

Wt. of Sample	Method	Silicon Obtained				
		1st dehydration	2nd dehydration	3rd dehydration	After HCl volatilization	Total
Grams		%	%	%	%	%
			STEEL A			
2.336	H_2SO_4	4.634[a]	0.036	0.006	0.007	4.683
2.336	H_2SO_4	4.666	0.026	0.006	0.008	4.706
2.336	H_2SO_4	4.646	0.036	0.006	0.007	4.695
2.336	H_2SO_4	4.638	0.038	0.006	0.008	4.690
2.336	H_2SO_4	4.678	...	...	0.024	4.702
2.336	$HClO_4$	4.672	...	...	0.022	4.694
2.336	$HClO_4$	4.678	...	...	0.020	4.698
2.336	$HClO_4$	4.678	...	...	0.022	4.700
						Av. 4.696
			STEEL B			
5.00	H_2SO_4	0.435	0.005	0.005	0.006	0.451
5.00	H_2SO_4	0.435	0.005	0.005	0.008	0.453
5.00	H_2SO_4	0.435	...	...	0.016	0.451
5.00	H_2SO_4	0.438	...	...	0.009	0.447
5.00	$HClO_4$	0.437	...	...	0.012	0.449
5.00	$HClO_4$	0.438	...	...	0.010	0.448
						Av. 0.450
			STEEL C			
5.00	$HClO_4$	0.106	...	...	0.008	0.114
5.00	$HClO_4$	0.105	...	...	0.006	0.111
5.00	$HClO_4$	0.107	...	...	0.004	0.111
5.00	H_2SO_4	0.107	0.002	0.001	...	...
5.00	H_2SO_4	0.106	0.001	0.002	...	...
5.00	H_2SO_4	0.104	0.003	0.003	...	...
						Av. 0.112

[a] Results obtained in single determinations are obviously not accurate to third decimal place for high-silicon steels, but are so given because averages are computed.

The average values shown in Table III are believed to be very close to the true silicon contents of the steels. These may be considered to be as follows: steel A, 4.696 per cent ± 0.005; steel B, 0.450 per cent ± 0.002; steel C, 0.112 per cent ± 0.002.

Subsequent work on the determination of silicon by dissolving the steel in nitric acid, evaporating, igniting, and volatilizing the iron as above, indicated small losses of silicon in the case of steels A and C when this procedure was followed. Steel B gave slightly higher results. The results in the case of steels B and C are practically within the limits of error of the volatilization method, whereas the error in the case of steel A, amounting to an average of 1.5 mg. of silica, is probably due to mechanical loss in transferring the silica from the boat to the crucible. Results for the direct determination are listed in Table IV.

Table IV. Silicon Obtained by Direct Method

Wt. of Sample	Silicon	
	Found	Present
Grams	%	%
	STEEL A	
2.336	4.670	
	4.668	
2.336	4.663	
	4.665	
	Av. 4.667	4.696 ± 0.005
	STEEL B	
2.336	0.452	
	0.454	
5.000	0.456	
	0.445	
	Av. 0.452	0.450 ± 0.002
	STEEL C	
5.00	0.107	
	0.108	
	0.109	
	Av. 0.108	0.112 ± 0.002

Silicon Recovered by Single Dehydration

As repeated evaporations are laborious and the hydrochloric acid volatilization method time-consuming, it was

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[1] The hydrogen chloride generator consisted of a 6-liter Florence flask, fitted with a Kjeldahl bulb and a dropping funnel, and heated with a Bunsen burner. Technical sulfuric acid was allowed to drop slowly from the funnel on heated ammonium chloride. The hydrogen chloride generated, together with some water vapor, passed through the spray trap into a wash bottle containing concentrated technical sulfuric acid, and then into the furnace. The sulfuric acid was renewed frequently.

thought desirable to find out what kind of results could be expected if single dehydrations were made by the ordinary methods for the determination of silicon in steels. In an attempt to eliminate errors other than those inherent in the methods, all evaporations except those with hydrochloric acid were made in liter platinum dishes provided with platinum covers, and all ignitions were made in an electric muffle controlled with a pyrometer. Blanks were run on all the reagents and any silicon found deducted.

The following methods were studied (*5*):

SULFURIC ACID METHOD. The sulfuric acid method as used at the Bureau of Standards is as follows: Dissolve the sample, 4.672 grams of steels containing less than 0.5 and 2.336 grams of steels containing over 0.5 per cent silicon, in 100 ml. of sulfuric acid (1 to 4). Evaporate the solution, taking care to avoid spattering, until copious fumes of sulfuric acid are evolved. Continue the fuming for 2 to 4 minutes, but no longer lest insoluble sulfates be formed. Cool somewhat and add 125 ml. of warm water (40° to 50° C.) at one stroke. Stir until salts are in solution, heating lightly if necessary, but never to boiling. Immediately filter through rapid paper such as S & S No. 589 Black Band (tighter paper for low-silicon steels), scrubbing the dish thoroughly with a rubber "policeman." Wash the paper several times with dilute hydrochloric acid (5 to 95) to remove most of the iron salts, and then several times with hot water. Transfer the paper and contents to a platinum crucible, char the paper at a low temperature, preferably in an electric muffle, and finally ignite to constant weight at 1050° to 1150° C. Cool in a desiccator and weigh. Moisten the silica with a few drops of dilute sulfuric acid (1 to 3), add an excess of hydrofluoric acid (3 to 5 ml.), evaporate to dryness in an air bath, ignite, and weigh. This method gave the results listed in column 3 of Table V.

TABLE V. SILICON OBTAINED IN SINGLE EVAPORATIONS

WT. OF SAMPLE	SILICON PRESENT	SILICON BY FOLLOWING METHODS: H_2SO_4	HNO_3-H_2SO_4	$HClO_4$	HCl	HCl-NH_4Cl
Grams	%	%	%	%	%	%
		STEEL A				
2.336	4.696 ± 0.005	4.634	4.612	4.672	4.628	4.638
		4.646	4.594	4.678	4.628	4.642
		4.678	4.598	4.658	4.638	4.642
		4.660	4.570	4.670	4.638	4.640
		4.664	4.612	4.664	4.628	4.642
		4.650	4.610	4.678	4.628	4.634
		4.666		4.656		
		4.666		4.672		
		4.638		4.664		
		4.678				
		4.660				
		4.660				
		4.672				
		4.666				
	Av.	4.660	4.599	4.668	4.631	4.640
		STEEL B				
4.672	0.450 ± 0.002	0.435	0.427	0.437	0.429	0.430
		0.435	0.433	0.435	0.427	0.429
		0.435	0.432	0.432	0.427	0.425
		0.433		0.438		
		0.435		0.436		
		0.438		0.435		
	Av.	0.435	0.431	0.436	0.428	0.428
		STEEL C				
4.672	0.112 ± 0.002	0.107	0.105	0.105	0.102	0.101
		0.104	0.105	0.105	0.100	0.106
		0.104	0.105	0.105	0.103	0.103
		0.107		0.106	0.103	0.102
		0.104		0.106	0.108	0.104
		0.106		0.106		
		0.105		0.107		
		0.105		0.105		
		0.106				
	Av.	0.105	0.105	0.106	0.103	0.103

NITRO-SULFURIC ACID METHOD. Dissolve the sample, 4.672 grams of steels containing less than 0.5 per cent of silicon and 2.336 grams of steels containing over 0.5 per cent of silicon, in 80 ml. of nitro-sulfuric acid mixture (2000 ml. of sulfuric acid, sp. gr. 1.84, 1500 ml. of nitric acid, sp. gr. 1.42, and 5500 ml. of water). Evaporate until copious fumes of sulfuric acid are evolved. Cool somewhat and cautiously add to the warm residue 5 ml. of hydrochloric acid (sp. gr. 1.19) and 125 ml. of warm water (40° to 50° C.). Stir and warm until salts are in solution, but do not heat strongly unless the salts cannot be otherwise dissolved. The heating should not require more than 5 minutes. Immediately filter and proceed as above.

This method gave the results shown in column 4 of Table V.

PERCHLORIC ACID METHOD. The perchloric acid method (*9*) has rapidly come into favor with the increasing use of steels containing considerable amounts of chromium and nickel, which yield difficultly soluble sulfates in the sulfuric acid methods. Perchloric acid forms salts with these metals that are very readily soluble. The following method was used:

Dissolve the sample, 4.672 grams of steels containing less than 0.5 per cent and 2.336 grams of steels containing more than 0.5 per cent silicon, in 60 or 40 ml., respectively, of dilute nitric acid (1 to 1). When solution is complete, add 60 or 40 ml. of perchloric acid (60 to 70 per cent), depending on the weight of sample taken. Evaporate to fumes of perchloric acid, cover the dish, and continue heating at such a rate that the solution boils and perchloric acid refluxes on the sides of the dish for 15 to 20 minutes. Cool somewhat, add 125 ml. of hot water at one stroke, and proceed as above, with the exception that the larger residues from high-silicon steels must be washed well with hydrochloric acid (1 to 1) or they will decrepitate badly when ignited.

This method gave the results shown in column 5 of Table V.

HYDROCHLORIC ACID METHOD. Dissolve the sample, 4.672 grams of steels containing less than 0.5 per cent and 2.336 grams of steels containing over 0.5 per cent of silicon, in 60 ml. of hydrochloric acid (1 to 1) in a 400-ml. beaker, evaporate to dryness, and bake for one hour at 105° to 120° C. Baking at temperatures higher than 120° C. will produce residues which dissolve with difficulty. Drench the hot residue with 15 ml. of hydrochloric acid (sp. gr. 1.19), stir for about one minute, add 125 ml. of hot water, continue the stirring until salts are in solution, and proceed as in the sulfuric acid method.

This method gave the results shown in column 6 of Table V.

HYDROCHLORIC ACID–AMMONIUM CHLORIDE METHOD. Proceed exactly as in the hydrochloric acid method but add 5 grams of ammonium chloride before evaporating the solution to dryness. The addition of ammonium chloride causes the baked residue to be more readily soluble.

This method gave the results shown in column 7 of Table V.

The difference in the results obtained by the sulfuric acid and perchloric acid methods in the case of steel A is of about the same order of magnitude as the limits of error of the two methods. The other three methods gave results which were definitely lower, and hence are not so satisfactory with single dehydrations for high-silicon steels. For low-silicon steels such as steels B and C, all five methods give acceptable results, although those obtained by dehydration with hydrochloric acid and hydrochloric acid and ammonium chloride are lower than the other three.

TABLE VI. SILICON OBTAINED IN BUREAU OF STANDARDS STANDARD SAMPLE OF INGOT IRON NO. 55

METHOD	RUN	WT. OF SAMPLE	SILICA FOUND	SILICON FOUND
		Grams	*Gram*	%
Single dehydration with H_2SO_4	1	20	0.0001	0.0002
	2	20	0.0001	0.0002
	3	10	0.0001	0.0005[a]
	4	10	0.0001	0.0005[a]
Sample dissolved in H_2SO_4, evaporated, residue ignited, iron volatilized with HCl, etc.	5	10	0.0003	0.0014
	6	10	0.0005	0.0023
	7	20	0.0009	0.0021
	8	20	0.0010[b]	0.0023

[a] Analysis made by C. P. Larrabee in 1923.

[b] Hydrochloric acid residue fused with Na_2CO_3, melt dissolved in sulfuric acid, solution fumed, and silica determined. Soluble silica in filtrate, amounting to 0.2 mg., was estimated colorimetrically by ammonium molybdate method of Thayer (*8*).

DETERMINATION OF SILICON IN IRONS AND STEELS CONTAINING VERY LITTLE SILICON

Although volatilizing the iron as ferric chloride is not a suitable method for routine determinations of silicon in steels, it is particularly valuable for the accurate determination of the very small amounts of silicon in materials such as ingot iron. The silicon content of these materials is often so low that the results obtained by the usual dehydration with acid are of about the same order of magnitude as the blank. Determinations 1 to 4 of Table VI were made by dehydrating 10- to 20-gram samples of the Bureau of Standards Ingot Iron No. 55 with sulfuric acid, as described in the sulfuric acid method above. Determinations 5 to 8 were made by dissolving 10- to 20-gram samples of the iron in sulfuric acid, evaporating, igniting, and volatilizing with hydrochloric acid. Blanks were determined on all reagents used, and any silica found was subtracted. In no case was a blank of more than 0.2 mg. of silica obtained, whereas in most cases the amount was 0.1 mg. or less. These results show that the true silicon content of this iron is of the order of 0.002 per cent, as compared with 0.0005 per cent or less indicated by dehydration with sulfuric acid.

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Determination of Boron Spectroscopically

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A new spectroscopic method for the determination of boron is described. The procedure consists in ashing the plant material at a low temperature in the presence of an excess of an alkali, and dissolving the ash in a solution of citric acid. Boron is separated from the solution of salts by converting it into methyl borate and distilling. The methyl borate is burned in oxygen by a special type of apparatus and the spectrum absorbed by the addition of a standard solution of potassium permanganate from a buret into a glass cell containing distilled water and converting the permanganate factor to its equivalent in boron. Extreme sensitivity was obtained by burning the methyl borate in an atmosphere of oxygen. Boron can be determined quantitatively on samples of plant tissues containing 0.05 to 0.3 mg. of boron with an accuracy of ±0.0095 mg.

THE essential nature of boron in plant metabolism has been ascertained physiologically by several investigators. Bertrand and Agulhon (*2*, *3*, *4*) have demonstrated the presence of the element in normal tissues of various species of plants and animals. Jay (*7*), investigating the occurrence of boron in natural foods, found it to be widely distributed. Tests for boron in plant and animal tissues have, for the most part, been measurements of the depth of color imparted to standardized strips of turmeric paper. Details of methods using turmeric, curcumin, and tincture of mimosa blossoms have been described by several investigators (*4*, *5*, *6*, *8*). These methods are very sensitive to small quantities of boron, but are only roughly quantitative. Bertrand and Agulhon (*2*) confirmed their results with turmeric paper by spectroscopic examination of the color imparted to the flame of burning hydrogen.

The green color imparted to the flame of burning alcohol is a very sensitive test for boron. To test for boron in the presence of other compounds producing a green flame, Bordas and Touplain (*6*) vaporized the acid solution of the sample in methyl alcohol and ignited the vapor at the end of a glass tube. Boric acid with methyl alcohol in the presence of a dehydrating acid forms methyl borate, $(CH_3)_3BO_3$. The difference in the boiling points of the boric acid ester and of methyl alcohol is 1° C., and it has been found that with small amounts of the ester present the boiling point is constant.

Spectroscopic examination of the flame of the mixed vapors of the alcohol and ester showed four bands between the sodium line and the first blue caesium line, the most intense being close to that of thallium in the green portion of the spectrum. With less than 0.033 gram of boron per liter of alcohol, it was found that the bands were not visible. Increase in the boron content of the solution resulted in a spectrum of greater intensity. To measure the relative intensity of the spectrum, a number of solutions of colored salts were tried as light filters. A dilute solution of potassium permanganate as well as solutions of several organic dyes were capable of absorbing the green portion of the spectrum. Potassium permanganate was considered the most suitable because it can be standardized readily, and is the least subject to change under laboratory conditions.

Measurement of the intensity of the spectrum was effected by adding 0.01 *N* potassium permanganate solution from a buret to 50 ml. of distilled water in a glass cell placed between the spectroscope and the flame, until the band was just eliminated. Ten milliliters of acid alcohol containing a known amount of boron were placed in a 50-ml. Erlenmeyer flask fitted to a short hard glass tube fixed in a glass chimney (Figure 1). Two glass tubes projecting from the chimney fixed the distance of the spectroscope from the flame at 6 cm. and supported a cell of 2 cm. thickness under a buret. The flask was immersed in a constant-temperature water bath, and the temperature was raised until the flame was 1.5 cm. high. A direct-vision Schmidt and Haensch spectroscope was placed before the cell, and 0.01 *N* potassium permanganate solution was added slowly, with stirring, until the first green band of the spectrum was absorbed. It was found that a definite normality of potassium permanganate solution 2 cm. thick would just eliminate the lines from the spectrum produced by the presence of a definite quantity of boron in the solution, other conditions being identical.

Conditions other than the quantity of boron present that might affect the intensity of the spectrum were investigated.

It was found (Table I) that the distance of the spectro-

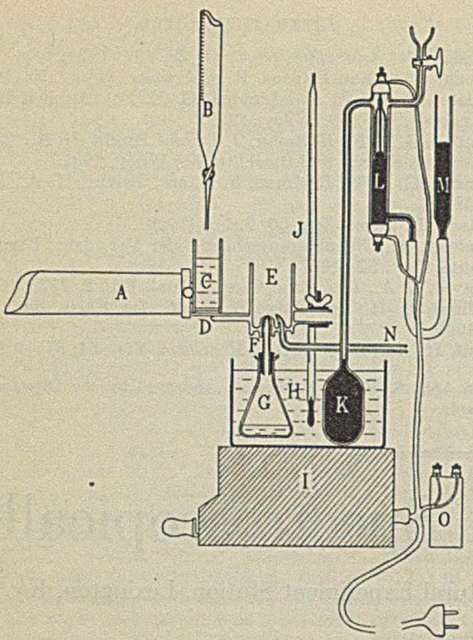

FIGURE 1. APPARATUS FOR SPECTROSCOPIC DETERMINATION OF BORON

A. Spectroscope
B. Buret
C. Cell
D. Support
E. Chimney
F. Burner
G. Sample flask
H. Bath
I. Heater
J. Thermometer
K. Mercury bulb
L. Thermostat
M. Regulation
N. Pilot light
O. Condenser

scope from the flame affected the intensity of the spectrum, especially with the smaller quantities. This distance was fixed at 6 cm. by glass stops for all determinations. The position of the cell did not exert any noticeable influence so long as it was perpendicular to the spectroscope. Differences in the height of the flame resulted in different intensities, the intensity decreasing as the size of the flame increased. The flame must be over 1 cm. in height in order to burn smoothly and quietly. This was accomplished by heating the bath slowly until the top of the flame was just opposite the 1.5-cm. mark on the chimney, and adjusting the thermostat for this temperature. The setting of the slit of the spectroscope also influenced the intensity by varying the amount of light admitted. It was opened until the bands were sharp, and set at the same figure for all determinations. Dissolved salts, platinum wire, and other catalysts exert a minor influence that is overcome by the presence of 5 per cent phosphoric acid in the alcohol. The effect is due to hastening the formation of methyl borate.

The difference in the boiling points of the alcohol and ester did not affect the intensity for quantities of boron within the range of the method. The amounts of potassium permanganate solution required for a given amount of boron were checked 15 minutes after igniting the vapor. The curve (Figure 2) shows the exact quantities of 0.01 *N* potassium permanganate solution necessary to produce sufficient color in 50 ml. of water to absorb the first green band of the spectrum of known amounts of boron. The position of each point measured on the curve is the average of from three to five determinations.

A table showing the boron equivalent of each 0.1 ml. of 0.01 *N* potassium permanganate solution can be prepared by calculations from the data on known quantities of boron for convenience in converting buret readings to grams per liter of boron.

TABLE I. MINOR FACTORS INFLUENCING INTENSITY OF SPECTRUM

(Average of 3 experiments)

Factor	Potassium Permanganate Solution, 0.01 *N* B = 0.05 gram/liter	 B = 0.10 gram/liter	 B = 0.5 gram/liter
	Ml.	*Ml.*	*Ml.*
1. Distance of spectroscope from flame			
3 cm.	4.8	7.1	10.15
6 cm.[a]	4.6	7.0	10.1
8 cm.	4.2	6.8	9.9
2. Position of cell			
Against chimney	4.6	7.1	10.1
Against spectroscope[a]	4.6	7.0	10.1
Intermediate	4.6	7.0	10.05
3. Height of flame			
0.5 cm.	5.0	7.3	10.7
1.0 cm.	4.7	7.0	10.4
1.5 cm.[a]	4.65	7.0	10.1
3.0 cm.	4.5	6.9	9.95
4. Opening of slit			
Slight (Na to 3060)	4.1	6.7	10.0
Moderate (Na to 3053)[a]	4.6	7.0	10.15
Wide (Na to 3045)	4.8	7.2	10.3

[a] Found to be most satisfactory condition.

The practice of adding boric acid or borates to foods as preservatives has been responsible for the development of several methods for the extraction of boron from plant material. These methods are commonly used in conjunction with volumetric or gravimetric determinations, and were found to be unsatisfactory for the analysis of minute quantities, as small losses occur in the preparation of the sample. It was found that losses may occur on ignition above 800° C. and on evaporation of the acid solution.

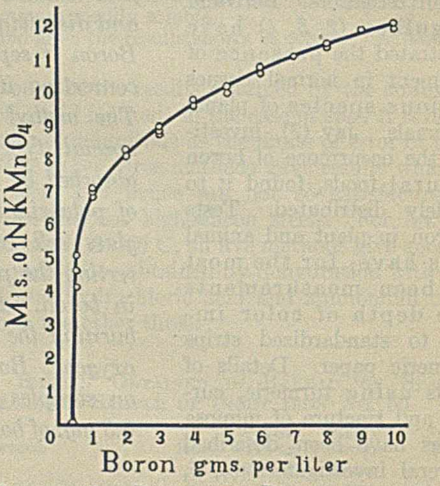

FIGURE 2. POTASSIUM PERMANGANATE SOLUTION REQUIRED TO ELIMINATE FIRST GREEN BAND FROM SPECTRA OF BORON BURNED IN AIR

Table II shows recoveries from salt mixtures comparable to plant ash.

TABLE II. EXTRACTION OF BORON IN PRESENCE OF Ca, Mg, AND K IN HCl SOLUTION

Treatment	B Present	B Recovered
	Gram	*Gram*
Evaporated (acid), extracted with methyl alcohol, and filtered	0.0016 0.0035	0.0002 0.0005
Evaporated with K_2CO_3, extracted with methyl alcohol, and filtered	0.0016 0.0035	0.0008 0.0020
Evaporated with methyl alcohol containing 25% NH_4OH, extracted with methyl alcohol, and filtered	0.0016 0.0035	0.00097 0.00294
Evaporated with methyl alcohol containing 25% NH_4OH, extracted with methyl alcohol for 3 hours in Soxhlet tube	0.0016 0.0035	0.00167 0.00343

Evaporation of acid solutions on the water bath results in a loss of boron amounting to 75 per cent or more, if very small quantities are present. The addition of an alkali to the solution prevents losses on evaporation, but forms precipitates insoluble in water and methyl alcohol that interfere with the quantitative extraction of boron by the alcohol. The precipitation of insoluble compounds by an alkali in the presence of considerable methyl alcohol does not present this difficulty if the alcohol is added slowly to the cold solution. By evaporating with small additions of alcoholic ammonia, approximately 90 per cent of the boron present will be easily soluble in methyl alcohol, and practically 100 per cent can be recovered by extracting for 3 hours in a Soxhlet tube.

Determinations of plant material gave similar results to those obtained with salt mixtures. The recoveries from additions of boron (boric acid) to watercress are given in Table III.

TABLE III. RECOVERY OF ADDED BORON FROM WATERCRESS

(Average of three 25-gram samples)

TREATMENT	B ADDED	B PRESENT	B FOUND
	Gram	*Gram*	*Gram*
Ashed 750° F.	...	...	0.003
Ashed 750° F.	0.001	0.004	0.00393
Ashed 750° F.	0.002	0.005	0.00517
Ashed 750° F.	0.005	0.008	0.00798
Ashed 850° F.	...	0.003	0.003
Ashed 850° F.	0.001	0.004	0.00375
HCl soln. of residue of previous extraction	...	...	None
HCl soln. of fused silicates	...	...	None

To avoid the handling of large quantities of salts insoluble in methyl alcohol and the extraction of soluble salts other than borates, distillation was substituted for extraction by using the apparatus shown in Figure 3. The sample (plant ash) was dissolved in an excess of citric acid and transferred to flask *C*, using approximately 20 ml. of water. Washing was completed with methyl alcohol (30 to 40 ml.) and the flask connected. Flask *F* contains 0.1 ml. of 0.5 *N* potassium hydroxide in 10 ml. of distilled water. Boron is absorbed by the solution in *F* from the vapors produced in *C*. The alcohol vapor is condensed in the reflux *A* and returned to flask *C*. The boiling point is higher in flask *C* and the alcohol is completely condensed, resulting in a major portion of the alcohol being retained in flask *C*. Boron was completely extracted from plant ash by this method in 1.5 hours. Boron could not be found in the small washing tube at the top of the condenser even when relatively large quantities of boron were distilled.

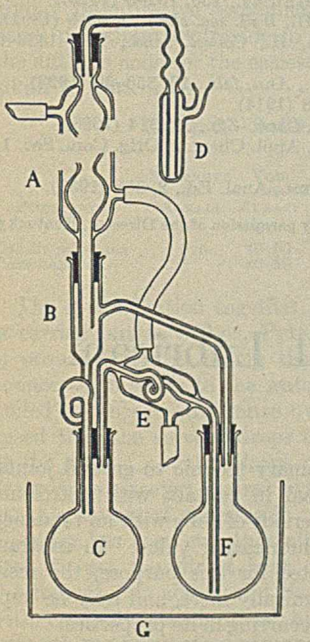

FIGURE 3. APPARATUS FOR SEPARATION OF BORON BY DISTILLATION

A. Condenser
B. Adapter
C. Sample flask
D. Absorption tube
E. Condenser
F. Receiver
G. Water bath

The procedure for plant material found to be the most rapid and accurate is as follows:

Weigh a sufficient quantity of the ground sample of plant material (calculated to the moisture-free condition) to give 0.0005 to 0.005 gram of boron. If the plant material yields an acid ash, add sufficient potassium carbonate to make the ash alkaline, and char in a silica dish over a low flame. Ash the sample in a muffle furnace at or below 400° C. Cool in a desiccator, moisten the ash with distilled water, cover with a watch glass, and add a strong solution of citric acid with a finger pipet until the solution is strongly acid. Wash into the extraction flask with a small quantity of water and 30 to 35 ml. of methyl alcohol. Add 0.1 ml. of 0.5 *N* potassium hydroxide to 10 ml. of distilled water in the second flask, and distil for 1.5 hours. Wash the alkaline solution into a 50-ml. dish, add 5 ml. of ammonium hydroxide, and evaporate to dryness on the water bath. Dissolve the residue in 5 per cent phosphoric acid in methyl alcohol, and make up to a suitable volume with acid alcohol at 20° C. Transfer to an Erlenmeyer flask, connect to the burner, and, after the flame meets the prescribed conditions of 1.5 cm., add 0.01 *N* potassium permanganate solution to 50 ml. of water in the cell until the bright green band of the boron spectrum is eliminated. Refer the required quantity of potassium permanganate solution to a table showing grams of boron per liter for the quantity present, and divide by the weight of the sample to obtain the per cent of boron present (grams of boron per liter × 10/1000 × 100/sample). The table showing grams per liter of boron present for any quantity of potassium permanganate solution used should be prepared by the operator from known quantities of boron, because the sensitivity of different spectroscopes and their adjustments vary widely. Reagents used must be free from boron.

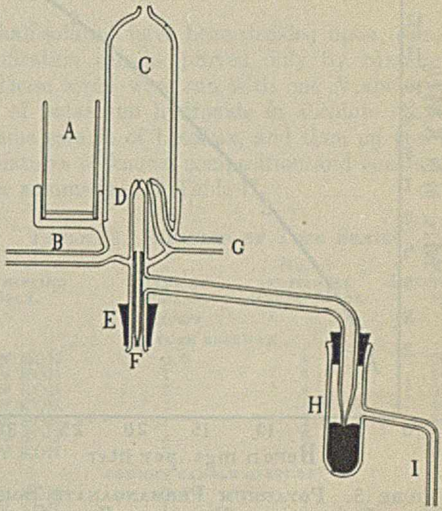

FIGURE 4. APPARATUS FOR BURNING METHYL BORATE IN OXYGEN

A. Cell
B. Oxygen inlet
C. Chimney
D. Microburner
E. Connection for flask
F. Vapor inlet (capillary)
G. Gas inlet for pilot light
H. Pressure regulator
I. Alcohol overflow

The method is also applicable to the determination of boron in animal tissue and waters as well as plant tissues by slight modifications of the procedures for obtaining the boron in suitable form for solution in methyl alcohol.

The method is sensitive to much smaller quantities of boron if the vapors are burned in an atmosphere of oxygen. Figure 4 shows the apparatus used for burning methyl alcohol–methyl borate vapors in oxygen under controlled conditions. The quantity of vapor burned in oxygen is greater than in air and cannot be controlled by the size of the flame, as marked changes in the rate of vaporization make but slight differences in the size of the small, hot flame. To insure the burning of the vapor at the same rate in each determination, constant pressure was kept in the distillation flask by a mercury valve and capillary tube. The tubes *D* and *G* are of thick-walled hard glass tubing (not Pyrex). Attempts at sealing these tubes (and *B*) into a glass support for the cell and chimney were unsatisfactory, so a rubber stopper and a short glass collar of slightly greater diameter than the chimney were substituted. A metallic base supported with a ringstand clamp is recommended for the introduction of the gas tubes and support of the cell and chimney. The chimney is of heat-resistant glass. An unsteady flame due to currents of oxygen can be avoided by placing glass wool in the bottom of the chamber.

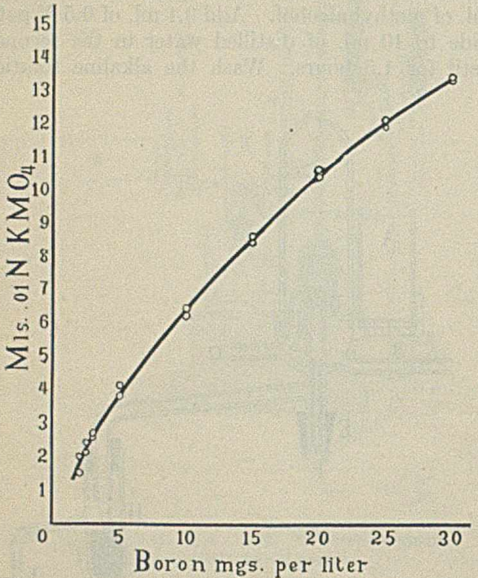

FIGURE 5. POTASSIUM PERMANGANATE SOLUTION REQUIRED TO ELIMINATE FIRST GREEN BAND FROM SPECTRA OF BORON BURNED IN OXYGEN

Figure 5 shows the grams per liter of boron in methyl alcohol represented by any quantity of 0.01 *N* potassium permanganate solution within the limits of the method.

The possibility of replacing the buret and cell with a scale and sliding glass wedge similar in color to potassium permanganate solution was considered but was not investigated. The use of the wedge would probably simplify the absorption of the spectrum and shorten the method, but to approach the accuracy of the buret and cell, the lengths of the scale and wedge would probably be too great for convenience. The spectroscopic method by burning in oxygen will detect the presence of less than 0.5 part per million of boron in methyl alcohol. Quantities of boron between 3 and 30+ parts per million can be determined quantitatively with an accuracy of ±0.35 part per million.

Plant materials could not be checked as accurately as could solutions of boric acid, but could be checked within the limits of ±0.95 part per million, or ±0.000095 per cent on a moisture-free basis.

The method of Wilcox (*10*) and the A. O. A. C. (*1*) volumetric method were not applicable to the determination of such minute quantities of boron as occur in normal plant tissues. The low buret readings on extremely large samples of plant material and the necessity of two additions of standard alkali resulted in a wide range of inaccuracy.

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An Esterification Resin as a Ground-Joint Lubricant

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IN A paper by Bruun and Schicktanz (*1*), mention is made of the use of a mixture of diethylene phthalate and triethylene phthalate resins as a stopcock lubricant for use in contact with petroleum distillates. Although this mixture was found to have the desired consistency and stability for a ground-joint lubricant, it was not adapted for use with distillates rich in the aromatic hydrocarbons, since these resins are readily soluble in benzene and toluene. It was found that a resin made with a polyglycol and a tri-reactive acid, in which the esterification was allowed to proceed only to the fusible stage, provided a lubricant having the proper viscosity which was insoluble in both the aromatic and aliphatic hydrocarbons.

One mole of citric acid and 1.5 moles of tetraethylene glycol were heated together at 180° to 185° C. for 90 minutes. The flask was then removed from the oil bath and allowed to cool to room temperature. Prolonged heating of this mixture results in an infusible product. The resin obtained was clear, amber-colored, of balsam consistency, and possessed marked adhesiveness. It was found to be readily soluble in water, alcohol, and acetone, but insoluble in petroleum ether and toluene. Chemical analysis indicated about 65 per cent esterification.

When applied by the customary technic to ground joints, it provided a satisfactory seal in contact with petroleum distillates over considerable periods of time with no tendency to become thin, and of low lubricating value. In contrast with many lubricants suggested for this purpose, the resin offers greater stability, is chemically inert, and may be kept indefinitely without changes occurring in its properties.

Tetraethylene glycol, $CH_2OH(CH_2OCH_2)_3CH_2OH$, may be synthesized from ethylene oxide and triethylene glycol in a pressure reaction. It boils at 190° C. at 3-mm. pressure. The presence of the long chain separating the two reactive groups imparts fluidity when it is used as a resin base. A similar resin made with citric acid and triethylene glycol was more viscous and, when used at room temperature, presented too much resistance to turning of the stopcock.

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Determination of Beeswax in Candles

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IN ASCERTAINING the constants of beeswax and of candle mixtures, the determination of the saponification number seems to be the one about which the authors disagree most as regards detailed procedures, and the analyst who reads the considerable volume of literature on this general subject (*1, 3, 6, 7, 8, 10, 12, 14*) is inclined to agree with Werder (*16*) when he complains about the many different methods that have been suggested for this particular determination. Winkler (*17*), however, is about the only one who presents detailed experimental proof for his particular procedures. Having been called upon some years ago to conduct a good many "candle analyses," we were struck with this abundance of methods and paucity of experimental evidence, and after considerable preliminary experimentation we fixed upon a certain detailed procedure which we are satisfied gives accurate results.

Determination of Saponification Number

In Table I is summarized the method recommended as giving quantitative saponification in the shortest time, using potassium hydroxide in absolute ethyl alcohol, which the authors consider the easiest, cheapest, and most accurate alkali to work with.

Table I. Summary of Method

Substance	Strength of Alkali	Vol. of Alkali	Wt. of Sample	Time of Boiling	1% Phenolphthalein Used as Indicator
	N	Cc.		Hours	Cc.
Candle mixtures	0.5	40–50	3.5 ± 0.4 gr.	2.5	1
Pure beeswax	1	40–50	3.5 ± 0.4 gr.	2	1

The saponification together with the subsequent titration is carried out in 500-cc. Pyrex Kjeldahl flasks. Refluxing is provided for by fitting them with test-tube condensers connected in series to the water supply (*5*). The flasks are boiled on an asbestos gauze over a Bunsen flame at such a speed that the solvent drops back into the boiling mixture at the rate of about 2 drops per second. The sides of the flasks are protected against overheating by placing over the gauze a square of asbestos in which a hole about 4.5 cm. in diameter has been cut, thus allowing only the bottom of the flask to get the direct heat of the gauze. After boiling, the indicator is added and the mixture titrated boiling hot with carefully standardized hydrochloric acid of the same strength as the alkali used.

The following precautions must be observed: The burets must be accurately calibrated, and the one containing the alcoholic solution should be allowed to drain 10 minutes before reading. The alkali after filtering must be kept in a tightly stoppered brown bottle and its potassium hydroxide equivalent checked frequently by running at least two blanks in exactly the same way as the saponification itself is conducted. The wax sample should be introduced in the form of a little ball, weighed to the nearest milligram, and a few small glass beads added to insure quiet boiling. The determination must be run in duplicate and, in case these do not agree within about a milligram, another pair should be run.

Once a certain sample weight and a certain kind and quantity of alkali solution have been decided upon, completeness of saponification can be proved only by running a time series. These series were run with one N and with 0.5 N solutions of potassium hydroxide in absolute ethyl alcohol on the same sample of beeswax, and then on two common candle mixtures of known composition and constants. The results are summarized in Table II.

Table II. Results of Time Series

Saponifying Soln.	Time of Boiling	No. of Individual Detns. Made	Av. Saponification No.
	Hours		
	PURE BEESWAX		
1 N KOH	0.5	4	96.2
1 N KOH	1	4	96.4
1 N KOH	2	4	98.2
1 N KOH	3	4	98.3
0.5 N KOH	1	2	93.9
0.5 N KOH	2	6	97.9
0.5 N KOH	3	6	98.0
	COMMON CANDLE MIXTURE[a]		
1 N KOH	0.5	4	111.0
1 N KOH	1	4	112.5
	SECOND KNOWN CANDLE MIXTURE[b]		
1 N KOH	0.5	2	44.0
1 N KOH	1	2	44.0
1 N KOH	2	5	45.4
1 N KOH	3	3	46.0
0.5 N KOH	3	3	46.3

[a] Beeswax, 51 per cent; stearic acid, 30 per cent; paraffin, 19 per cent; calcd. saponification no., 112.2.

[b] Beeswax, 15 per cent; stearic acid, 15 per cent; paraffin, 70 per cent; calcd. saponification no., 45.8.

Complete time series were not run on other saponification media, but one N potassium hydroxide in absolute methanol and one N sodium ethylate gave satisfactory results in 2 hours, as might be expected, and the results of Kettle (*11*), who uses one N potassium hydroxide in isopropyl alcohol to saponify beeswax in 10 minutes were also confirmed. However, unless time is the primary consideration, this method is not recommended, as the isopropyl alcohol, besides being more expensive to buy, cannot be recovered profitably from the saponification mixtures as can ethyl alcohol, about 75 per cent of which can be recovered by the use of a 2-foot Vigreaux column.

Determination of Acid Number

The conditions for accuracy for this determination are the use of a fairly large sample, on account of the small numerical value of this constant for most candle mixtures, and the use of an alkali which does not induce appreciable saponification. As these conditions are easily met, most of the methods given in the literature will be found suitable. A good method is titrating a 10-gram sample dissolved in 250 cc. of 95 per cent ethyl alcohol with 0.5 N aqueous potassium hydroxide solution, using 10 drops of one per cent phenolphthalein as indicator, and finishing at a noticeable pink color which persists on half a minute's boiling. A blank is run on the alcohol. This treatment causes no appreciable hydrolysis of the esters present unless the mixture contains about 35 per cent or more Japan wax. Pure Japan wax is so easily hydrolyzed that its acid number had to be determined by dissolving 2.5 grams of it in 250 cc. of carbon tetrachloride and titrating the warm solution with 0.1 N sodium ethylate; the end point lasted about a minute.

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INTERPRETATION OF RESULTS

The practice of using beeswax candles in the liturgy of the Catholic Church can be traced far back into Christian antiquity, but the actual decree of the Sacred Congregation of Rites which gives rise to this particular analytical problem dates from 1904 (*2*). The passage of interest to the chemist may be translated as follows: "........the Paschal candle, the candle used in blessing the baptismal water, and the two candles lit on the altar during Mass are to be of beeswax, at least in largest part (maxima pars); the other candles on the altar should be either in greater part or of a noticeable proportion of the same wax." This "maxima pars" is usually taken to mean 51 per cent. The following compositions are common in American candles sold for church use:

	%	%	%	%	%
Beeswax	100	60	51	13	15
Stearic acid	...	20	30	37	15
Paraffin	...	20	19	50	70

In examining candles made by any reputable American manufacturer, it may be assumed that they contain only these three substances; and as the only esters in a ternary mixture of this kind are present in the beeswax, analysts usually calculate the percentage of this substance by using the principle given by Hehner (*9*), although not in exactly the same form as he published it. Since the stearic acid, if any, affects both the acid number and the saponification number equally, the percentage of beeswax may be calculated from the expression:

$$\%\ \text{beeswax} = \frac{\text{ester number of candle}}{\text{ester number of beeswax}}$$

For example, in the case of the 51 per cent candle used in one of the time series (Table II) and whose acid number was found to be 75.1, we have

$$\%\ \text{beeswax} = \frac{112.5 - 75.1}{73.1} = 51.2\%$$

From this the amount of stearic acid is calculated to be 30.0 per cent, and that of the paraffin (by difference) to be 18.8 per cent. Comparison with the actual composition of this mixture (which was unknown to the analyst) shows very satisfactory agreement, and about of the order to be expected when the procedure is conducted carefully and the constants of the candle ingredients are known. As a rule, however, these are not known, hence no analysis of this kind should be "guaranteed" closer than 5 per cent. As regards the value for the ester number of beeswax, a minimum value evidently works to the favor of the manufacturer, yet to be fair to the purchaser as well, it is customary to use the value of 72 for this constant (when it is not known), this being its lowest value given by the U. S. P.

In case the candle seems to be composed of other substances than the three mentioned, the chemist will find the problem (which may become very complicated) treated quite adequately in the literature cited, to which may be added the general method given by Elser (*4*) based on the melting points of the products obtained by the fractional crystallization of the candle mixture from benzene, and also the method of Watson (*15*) for estimating carnauba wax. A glycerol test (qualitative at least) should always be run on a large sample of all candle mixtures to see if any Japan wax is present, from which "synthetic beeswax" may be made (*13*) which can simulate exactly the ester number of true beeswax. It has been our experience, however, that candles notably below par in beeswax content are made so by the addition to the beeswax of unduly large amounts of stearic acid and paraffin, rather than by the substitution of any other ingredients for the beeswax itself. In fact, so far we have not met with any indications of dishonest practice in cases where the beeswax content was stamped on the candle.

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Atomic Weights
1932

In response to requests of readers, we reprint here from the *Journal of the American Chemical Society* for April, 1932, page 1277, the second report of the Committee on Atomic Weights of the International Union of Chemistry, of which G. P. Baxter is chairman.

	Symbol	Atomic Number	Atomic Weight		Symbol	Atomic Number	Atomic Weight
Aluminum	Al	13	26.97	Molybdenum	Mo	42	96.0
Antimony	Sb	51	121.76	Neodymium	Nd	60	144.27
Argon	A	18	39.944	Neon	Ne	10	20.183
Arsenic	As	33	74.93	Nickel	Ni	28	58.69
Barium	Ba	56	137.36	Nitrogen	N	7	14.008
Beryllium	Be	4	9.02	Osmium	Os	76	190.8
Bismuth	Bi	83	209.00	Oxygen	O	8	16.0000
Boron	B	5	10.82	Palladium	Pd	46	106.7
Bromine	Br	35	79.916	Phosphorus	P	15	31.02
Cadmium	Cd	48	112.41	Platinum	Pt	78	195.23
Calcium	Ca	20	40.08	Potassium	K	19	39.10
Carbon	C	6	12.00	Praseodymium	Pr	59	140.92
Cerium	Ce	58	140.13	Radium	Ra	88	225.97
Cesium	Cs	55	132.81	Radon	Rn	86	222
Chlorine	Cl	17	35.457	Rhenium	Re	75	186.31
Chromium	Cr	24	52.01	Rhodium	Rh	45	102.91
Cobalt	Co	27	58.94	Rubidium	Rb	37	85.44
Columbium	Cb	41	93.3	Ruthenium	Ru	44	101.7
Copper	Cu	29	63.57	Samarium	Sm	62	150.43
Dysprosium	Dy	66	162.46	Scandium	Sc	21	45.10
Erbium	Er	68	167.64	Selenium	Se	34	79.2
Europium	Eu	63	152.0	Silicon	Si	14	28.06
Fluorine	F	9	19.00	Silver	Ag	47	107.880
Gadolinium	Gd	64	157.3	Sodium	Na	11	22.997
Gallium	Ga	31	69.72	Strontium	Sr	38	87.63
Germanium	Ge	32	72.60	Sulfur	S	16	32.06
Gold	Au	79	197.2	Tantalum	Ta	73	181.4
Hafnium	Hf	72	178.6	Tellurium	Te	52	127.5
Helium	He	2	4.002	Terbium	Tb	65	159.2
Holmium	Ho	67	163.5	Thallium	Tl	81	204.39
Hydrogen	H	1	1.0078	Thorium	Th	90	232.12
Indium	In	49	114.8	Thulium	Tm	69	169.4
Iodine	I	53	126.932	Tin	Sn	50	118.70
Iridium	Ir	77	193.1	Titanium	Ti	22	47.90
Iron	Fe	26	55.84	Tungsten	W	74	184.0
Krypton	Kr	36	83.7	Uranium	U	92	238.14
Lanthanum	La	57	138.90	Vanadium	V	23	50.95
Lead	Pb	82	207.22	Xenon	Xe	54	131.3
Lithium	Li	3	6.940	Ytterbium	Yb	70	173.5
Lutecium	Lu	71	175.0	Yttrium	Y	39	88.92
Magnesium	Mg	12	24.32	Zinc	Zn	30	65.38
Manganese	Mn	25	54.93	Zirconium	Zr	40	91.22
Mercury	Hg	80	200.61				

A New Vacuum-Furnace Design

KENNETH K. KELLEY, Pacific Experiment Station, U. S. Bureau of Mines, Berkeley, Calif.

EXPERIMENTATION under conditions of high temperature and high vacuum involves numerous difficulties. Many of the older types of furnaces are a source of continual trouble because of mechanical imperfections and unsuitable operating characteristics, and necessitate a constant battle by the experimenter against vacuum leaks and electrical derangements. Consequently the efficiency of such experimentation suffers.

The Pacific Experiment Station, in connection with its program of specific heat measurements at high temperatures on metals and metallurgically important compounds, recently completed the construction and testing of a new vacuum furnace for calorimetric measurements at high temperatures. The design adopted has several new features which greatly improve the ease and certainty of experimentation.

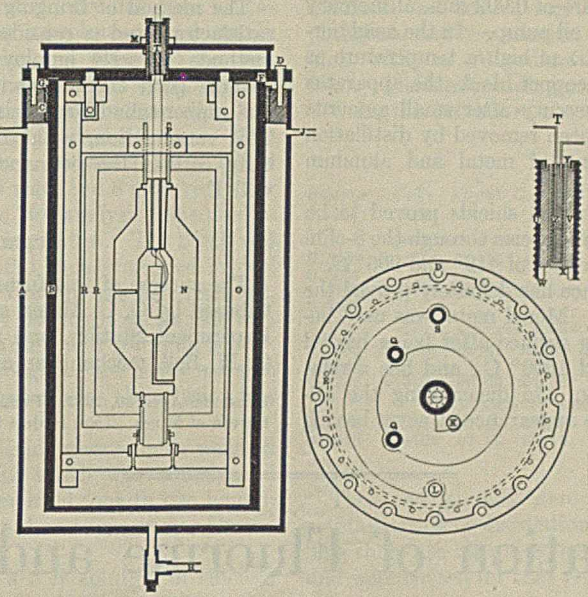

FIGURE 1. DIAGRAM OF FURNACE AND IMPORTANT PARTS

DESCRIPTION OF FURNACE

The furnace is an electrically heated, water-cooled type, 76 cm. long and 40.5 cm. in diameter. It has been built of unit parts in such a manner that it may be repaired or altered easily and economically. Figure 1 shows a cross section, a plan of the jacket-head, and the design of the construction for bringing out electrical lead wires.

VACUUM JACKET. The vacuum jacket consists of two concentric cylindrical shells of heavy steel pipe, the outer shell, *A*, being 0.64 cm. thick, and the inner shell, *B*, 1.59 cm. thick, surmounted by a heavy, removable head. The cylindrical shells have welded boiler-plate bottoms and are held together at the top by a circularly split ring, *C*, which is screwed on the outside of the inner shell and on the inside of the outer shell. The two parts of this ring telescope with a driving fit, which enables the jacket to be taken apart by applying a few pounds of air pressure between the walls and to be assembled by applying a vacuum similarly. The pressure or vacuum required is less than one atmosphere. This arrangement has been found to be of great value in that it permits easy repair of minute leaks which may develop.

The jacket-head consists of a bottom of 1.59-cm. boiler plate and a top of 0.95-cm. boiler plate separated by a ring cut from a section of 30.5-cm. pipe 0.95 cm. thick, the width being 3.18 cm. The head is assembled with 0.64-cm. ($^1/_4$-inch) S. A. E. cap screws, *E*, which pass through the top plate and screw into the bottom plate. A cork gasket and cement are used on each side of the ring. The head is fastened to the jacket by 1.11-cm. ($^7/_{16}$-inch) S. A. E. cap screws, *D*, and is recessed at *F* to fit the projecting upper end of the inner jacket shell. A fiber gasket was found to be satisfactory in this recess. A narrow bearing surface 0.95 cm. wide enables satisfactory compression of the gasket to be secured. A simple arrangement of rubber and metal bands (not shown in the diagram) is incorporated for filling annular space *G* with mercury to assure the gas-tightness of this joint for work at very high vacuums.

The cooling water enters the jacket through tube *H*, passes out tubes *J*, enters the head through tube *K*, and leaves by tube *L*. A metal spiral (shown in the plan of the head) assures the absence of dead spaces, a precaution that experience has proved to be essential for satisfactory cooling of the gaskets and lead-out wire seals.

HEATER. At present the furnace contains a copper block, *N*, of some 22 kg. mass, which is heated by a coil of nichrome ribbon of 8 ohms resistance, wound helically, and insulated by alundum cement of the grade used for platinum-wound furnaces. This block is supported by framework *O* of 2.54-cm. (1-inch) square cold-rolled steel suspended from the head, and is held in place and thermally insulated by porcelain tubes *P*. For other purposes any suitable heating coil may be similarly installed.

The heater lead wires pass through the compression-joint tubes Q, which are of a special type and will be described later.

The heater unit is surrounded by two thin 0.04-cm. (27-gage) monel metal radiation shields, *R*, which also are supported by frame *O*.

JOINTS AND SEALS FOR LEAD WIRES AND VACUUM CONNECTION. The heater lead tubes *Q*, evacuation tube *S*, and fitting *T*, through which thermocouples and other lead wires pass, are threaded and screwed into holes in the bottom plate of the head and are soldered to it on the upper side. This is necessary since all the joints must be vacuum-tight at this point. At the junctions with the upper plate of the head, which need be water-tight only, two nuts screwed to each tube and a gasket below the plate, such as shown at *M*, were found to make satisfactory, removable, and water-tight seals.

The tubes for the heater leads are beveled in at the top to form wells and hold close-fitting Pyrex glass tubes, which extend just below the head. The heater wires are enclosed by the glass and the wells filled with de Khotinsky cement.

Fitting *T* for the thermocouple leads consists of an outer heavy copper tube, *U*, and a close-fitting copper cylinder, *V*, held in place by split-ring nut *W*. The thermocouples are brought out through Pyrex glass tubes held in holes *X*, and well *Y* is filled with de Khotinsky cement. *Z* is a hollow copper cylinder set in *V* and equipped with tubes for water cooling, which gives additional protection to the de Khotinsky seal.

Operation of Furnace

The furnace operates for all except the highest vacuums without using the mercury seal. No difficulty was encountered in pumping out to a pressure of 0.002 mm. of mercury at room temperature with a good oil pump. In the neighborhood of 1000° C., which is about as high a temperature as may be reached safely with the copper block, the apparatus pumped down to 0.1 mm. of mercury after small amounts of impurities in the copper had been removed by distillation and the original rapid degassing of metal and alundum cement had diminished.

The heating unit and monel metal shields proved to be entirely satisfactory, 4.5 and 13.8 amperes through the 8-ohm coil giving, respectively, temperatures of 412° and 906° C.

The experience with this furnace has definitely proved the great value of radiation shields. Monel metal was used because it retains a good reflecting surface after being heated *in vacuo* to temperatures around 1000° C., and has a relatively low thermal conductivity. On dismantling the apparatus, the outer shield had the appearance of never having been hot, which is substantiated by the fact that the temperature of the cooling water was only slightly higher on leaving the furnace than on entering. In reducing the heat losses, the radiation shields also protect the de Khotinsky seals, which were a great source of trouble in a previously used furnace which was not equipped with radiation shields completely surrounding the heater unit.

The method of bringing out lead wires also proved very satisfactory and is considered a marked improvement over methods formerly employed. Fitting *T* was constructed to give good thermal contact between copper cylinder *V* and copper tube *U*, which is surrounded by the cooling water. This construction, with the cooling unit *Z*, makes practically certain the permanence of the de Khotinsky seal in well *Y*.

Acknowledgment

The success of this furnace is largely due to designs contributed by C. C. Maier, supervising engineer of the Pacific Experiment Station, and to the excellent workmanship of C. M. Bell, mechanician at the Pacific Experiment Station.

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Determination of Fluorine and Boron in Organic Compounds

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In some of the researches being carried on in this department on organic boron trifluoride compounds, the problem of finding a dependable method of analysis for both fluorine and boron arose. A number of more or less unsuccessful attempts to do this have been made in the past. Kraus and Brown (*4*) prepared various amino derivatives of boron trifluoride, and analyzed them for fluorine, boron, and nitrogen, in establishing their structures. Their analyses for fluorine and boron indicate the need of a more reliable method. Bowlus and Nieuwland (*1*) were able to analyze for boron with an average error of about 6 per cent, by decomposition of the sample through continued heating with fuming nitric acid in a sealed tube, and titrating the boric acid formed with base and mannitol, according to the standard procedure (*5*). These authors did not report fluorine on the analyses. Vaughn and Nieuwland (*10*) presented a new method of analysis for organic fluorides, using sodium in liquid ammonia, but boron was not present in their compounds.

There are a number of difficulties peculiar to the analysis of compounds containing boron and fluorine. Fusions of the samples with alkali carbonates (*6*) proved to be unsuccessful, as there was difficulty in decomposing the compounds, and there was evidently some loss through volatilization. It was finally decided to destroy the organic matter by combustion in a Parr sulfur bomb with an oxidizing mixture of sodium peroxide, potassium chlorate, and sugar. Most of the organic boron trifluoride compounds are deliquescent fuming substances, liquids or solids, which interact instantly with the fusion mixture. Recourse was had to weighing them in gelatin capsules and placing them in the bomb, thus inclosed. The capsules were completely destroyed by the ignition and did not interfere with quantitative combustion of the compound.

When the products of the fusion were dissolved in water, a solution containing a high concentration of alkali hydroxide and carbonate was obtained, and these interfered with the precipitation of calcium fluoride. When an attempt was made to remove them by treatment with hydrochloric acid, low results for fluorine were invariably obtained. According to Mellor (*7*), it is possible that the stable fluoborate ion was formed and not completely broken up by the weakly alkaline solutions permissible for the precipitation of calcium fluoride. Whatever the explanation, any appreciable concentration of hydrogen ion resulted in low values for fluorine. Although acetic or other weak acids are suitable for destroying hydroxide and carbonate without causing too high hydrogen-ion concentration, they interfere with the subsequent titration for boron.

The method finally chosen was to destroy the carbonate and alkali by boiling the solution with ammonium chloride. Some trouble was had in the proper coagulation of the precipitate of calcium fluoride, but this was overcome by the use of Fisher "filter accelerators." It was found that calcium fluoride was filterable when these were used, even without the addition of ammonium hydroxide, according to the method of Carrière and Rouanet (*2*). Coprecipitation of fluoride and carbonate (*9*) was unnecessary, and has been attacked recently on theoretical grounds by Mougnaud and others (*8*). Clarke and Bradshaw (*3*) have shown that the calcium fluoride method can be made to give accurate results by substituting these paper-pulp filter-aids for the coprecipitation and subsequent washing with acetic acid.

The next difficulty occurred through the presence of the excess ammonium chloride in the filtrate containing boron. Ammonium ion causes the end point to appear too late, through buffer action. It was removed by the addition of strong sodium hydroxide solution and boiling until the vapors ceased to affect litmus paper. The calcium ion in excess from the calcium fluoride precipitation, which partially precipitated as hydroxide, was removed by filtration, the solution transferred to a volumetric flask, and aliquot portions titrated by the standard method, using mannitol (*5*). Good results were also obtained for boron.

The experimental procedure as finally decided upon was as follows: Approximately half-gram samples were accurately weighed in No. 00 gelatin capsules and placed in the cup of a Parr sulfur bomb of the electrical ignition type, together with a fusion mixture of 10 grams of sodium peroxide, one gram of potassium chlorate, and 0.5 gram of sugar. The bomb was tightly closed, well shaken, and shorted with direct or alternating current of about 20 volts and 8 amperes. For the fusion wire, standard iron wire "for analysis" was used in order not to introduce additional impurities. The bomb was permitted to become quite hot, and then immersed in cool water until it could be handled. The cup was then removed, and the contents dissolved out by placing it on its side in a 400-cc. beaker, covering it with water, and warming gently. After boiling for a few minutes to coagulate the heavy metallic hydroxides from the cup and the fusion wire, the solution was filtered.

Fifteen grams of ammonium chloride were roughly weighed and introduced into the solution, which was boiled until the odor of ammonia no longer persisted (one to two hours). If a new precipitate formed during the boiling, it was filtered out before proceeding.

To the hot solution, 10 cc. of a 2 *N* solution of calcium nitrate were added drop by drop, with stirring. This provided a large excess of calcium ion to depress the solubility of the precipitate. A filter accelerator was dropped in and macerated well, and the boiling was continued for a few minutes. Occasionally it was necessary to add one cc. of approximately 3 *N* ammonium hydroxide to assist in coagulating the precipitate. The solution was cooled in running water until cold, and filtered, using strong suction and a platinum filter cone. The filtrate was reserved for the boron analysis. The volume of wash-water should not exceed 50 cc. The paper containing the precipitate was dried at 110° C. and ignited to constant weight in a platinum crucible over a Fisher burner.

To the filtrate was added sufficient 4 *N* sodium hydroxide to produce a precipitate of calcium hydroxide and carbonate. The solution was then boiled until the vapors no longer affected red litmus paper, and filtered into a 250-cc. volumetric flask. After being diluted to the mark and mixed thoroughly by shaking, a 50-cc. portion was withdrawn. This was titrated to neutrality with methyl orange, using 0.1 *N* hydrochloric acid. The remainder of the solution was neutralized with an equivalent amount of hydrochloric acid, but no methyl orange was added. The necessary amount of mannitol was added, together with a few drops of phenolphthalein, and the solution titrated to the first faint tinge of pink with 0.1 *N* sodium hydroxide solution (carbonate-free). The buret reading was calculated to boron.

Using this procedure, the following results were obtained:

Sample	CaF_2	F Found	F Calcd.	Aliquot Part Titrated	NaOH Solution Normality	NaOH Solution Amt. used	B Found	B Calcd.
Gram	*Gram*	*%*	*%*			*Cc.*	*%*	*%*
METHYL ACETATE BORON TRIFLUORIDE ($CH_3COOCH_3:BF_3$)								
0.5398	0.4446	40.12	40.19	...	....	...	...	....
0.5057	....	...	...	4/5	0.1258	22.59	7.60	7.627
0.3716	0.3100	40.64	40.19	...	....	...	...	....
0.5861	....	....	...	4/5	0.1258	26.20	7.61	7.627
ETHYL ACETATE BORON TRIFLUORIDE ($CH_3COOC_2H_5:BF_3$)								
0.4554	0.3404	36.41	36.56	...	....	...	...	....
0.3442	....	...	...	4/5	0.1258	14.40	7.12	6.97
0.4238	0.3189	36.66	36.56	4/5	0.1258	17.60	7.07	6.97
MONOAMMONO BORON TRIFLUORIDE (NH_3BF_3)								
0.2540	0.3510	67.32	67.18	4/5	0.1258	18.90	12.66	12.75
0.2976	0.4106	67.20	67.18	4/5	0.1258	22.30	12.75	12.75

These compounds were freshly made and purified by crystallization or distillation immediately before the analysis. The three are all solids, easy to obtain in a pure condition, and were chosen for that reason.

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A Gas Buret for Catalase Apparatus

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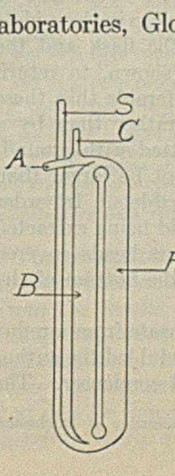
The buret described is believed to be of some general service as well as being an improvement for the catalase apparatus devised by Appleman (*1*). This buret was constructed so as to be placed in the water bath for maintaining a constant temperature for the gas to be measured.

The apparatus consists of a short length of buret, a parallel reservoir tube, a siphon which allows the leveling bottle to be operated from without the bath, and connections for the reaction bottle and the outlet. The lower ends of the buret, *B*, and reservoir tube, *R*, are drawn out into tube, *S*, which serves as the apparatus support and forms one arm of the siphon connecting with the leveling bottle. The upper ends of *B* and *R* are drawn out into tube *A*, which connects with the reaction bottle. Tube *A* is also provided with an outlet tube, *C*. The buret with its reservoir tube is calibrated in centimeters for the readings on the buret. This apparatus permits all the chambers containing gas to be submerged in water. It must be kept in mind that as the buret is shortened and the volume of the reservoir is increased, the errors of reading are increased in proportion.



This arrangement has been in service for one year with good results.

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Received August 2, 1932.

Large-Capacity Soxhlet Extractor and Reflux Condenser

ANGUS E. CAMERON,[1] University of Minnesota, Minneapolis, Minn.

THE need for a device of large capacity which would serve for the extraction of considerable quantities of solid material led the author to design a modification of the Soxhlet extractor. The extractor described here, shown in detail in Figure 1, is rugged in design and construction and is not particularly difficult to make. The most convenient starting point seemed to be a 5-liter Pyrex balloon flask. Larger flasks would involve such quantities of solvent that it seemed more desirable to build a battery of 5-liter extractors rather than to make larger ones.

The stem, *A*, which carries the vapor to the condenser, is made of tubing having an outside diameter of 30 to 35 mm. and contains the siphon tube, *B*, which is made of 8-mm. tubing. To insure certain siphoning, the bend at the top of the siphon tube is allowed to flatten somewhat and the opening where the lower end is sealed through the stem is allowed to constrict until it is about 3 mm. in diameter. Thorough annealing of the extractor is necessary.

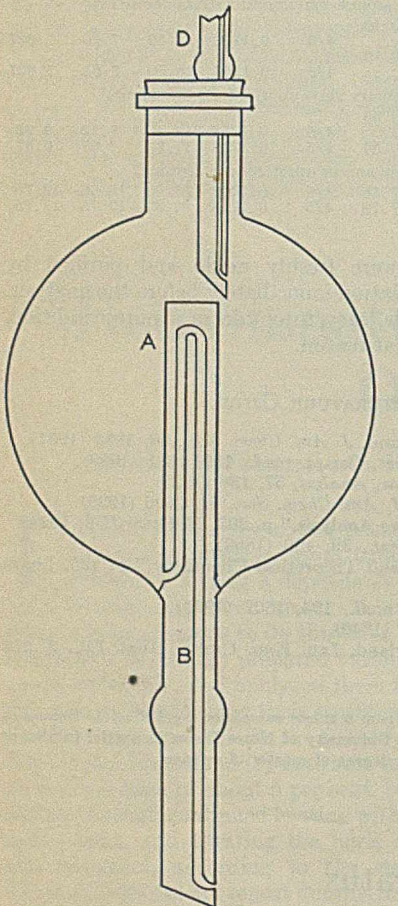

FIGURE 1

The stem can be lined up in the middle of the flask and the reflux condenser, *D*, offset somewhat, as shown, to return the condensate to the extractor. It is preferable that these extractors be supported by a large ring rather than by a clamp around the neck. They may be fitted with ground-glass joints if desired. The joints need not be larger than those used with the customary small Soxhlets. In order to prevent clogging of the siphon, if the solid being extracted has a tendency to crumble, a layer of glass beads covered with cotton may be used as a support in the bottom of the flask.

The problem of securing sufficient condensate from a reflux condenser to make extractors of this size useful led the author to develop what he believes to be a novel condenser. The proper design of a large-capacity reflux should take several factors into account. It is preferable that the condensate not be returned down the tube, which is carrying vapor to the cooling surface, for with high vapor velocities, choking will occur. It would be desirable to avoid passing vapor over portions of the condensing surface which are already working at capacity, and the vapor should have only a short way to go before reaching the condensing surface. To secure these desired features, the use of a straight or bulbed tube of large diameter is not of itself desirable. The condenser must be efficient in operation, simple in design, and rugged in construction if it is to be practical for laboratory use.

The condenser is shown in Figure 2. A large tube, *A*, 25 to 30 mm. inside diameter thin-wall Pyrex, is used for the inner tube. Up the center of this passes another tube, *B*, 10 mm. smaller, which is sealed off at the upper end and is perforated with two vertical, diametrically opposite, rows of holes 8 to 10 mm. in diameter and spaced 18 to 20 mm. apart, measured from center to center. The vapor is directed against the condensing surface from these ports, and their arrangement in vertical rows allows uninterrupted flow of condensate down part of the condenser wall. The condensate is returned to the flask from sump *D* through a 6-mm. tube, *E*, sealed in as shown in the sketch.

Three glass guide-pins, *F*, sealed to the manifold, *B*, are fitted by filing the ends before the manifold is sealed in at *G*. They provide the support necessary to prevent breakage due to rough handling, and yet allow the manifold to expand when hot vapor passes through it.

The inner tube of the condenser is constricted 2 to 3 cm. above the end of the manifold, giving room for a safety bulb, *H*, about 6 to 8 cm. long, which will take care of surges when the condenser is working at capacity. It is advantageous to bend the water inlet and outlet downward as shown and to have an enlargement, *I*, in the nose of the condenser to rest upon the stopper.

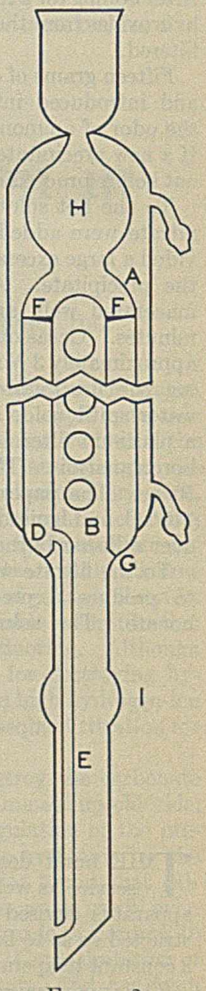

FIGURE 2

The approximate dimensions of the condensers which the author has constructed are as follows: length of jacket and condensing surface, 60 to 70 cm.; over-all length, 90 cm.; length of nose of condenser, 20 cm. Condensers of these dimensions have a capacity of 8 to 10 liters of acetone per hour with cooling water temperature of 7° C. They will not reach capacity with alcohol or acetone in a 5-liter

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flask heated on a steam bath. The capacity for ether is surprising, and only a faint odor can be detected at the top. Since condensation is favored by a film of cold liquid running down the inner tube, the condenser has not reached capacity when the vapor is condensing clear to the top of the manifold.

ACKNOWLEDGMENT

The author wishes to acknowledge the valuable assistance of Milton E. Ryberg, also of the University of Minnesota, in the construction of the extractors.

RECEIVED April 29, 1932.

Specific Test for Orange Honey

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OWING to its pleasant flavor, orange honey is generally considered to be one of the most desirable floral types for table use. In California orange is one of the important sources of honey. The trees bloom in April, and the flow of nectar is extremely abundant, at times being secreted in such quantities that men working in the orchards are saturated with it. The flow lasts about three weeks, and during this time strong colonies of bees usually average 60 or more pounds of orange honey per colony. One case is recorded in which more than 170 pounds of orange honey were stored by a single colony of bees in 10 days.

The honey from orange is white in color, heavy in body, of the finest quality, and is much in demand in the markets. This has created an incentive for some unscrupulous honey dealers to attempt the marketing of honey labeled "orange" in which some less expensive light colored honey is substituted for part of the orange. In some cases honey is sold as orange honey which contains very little orange or none at all. The writer recently secured a sample of honey being sold in California as orange that proved from examination of the pollen[1] to consist chiefly of Hawaiian algaroba honey. Although microscopic examination of the pollen was effective for determining the floral source of the honey in this particular case, this method cannot be relied on for determining the floral source with reasonable certainty in all cases. As pointed out by Nelson (*1*), the distinctive pleasant aroma of orange honey is due to the presence of methyl anthranilate. Methyl anthranilate, or the methyl ester of *o*-amidobenzoic acid, $C_6H_4(NH_2)$ $(COOCH_3)$, is rather widely distributed in nature. It occurs as a constituent of oil of orange flowers, to which it imparts the characteristic aroma. It also occurs in a number of other fragrant oils in small amounts. A test for detecting methyl anthranilate in fruit juices in quantities as small as 0.1 mg. has been devised by Power (*2*).

In order to determine whether or not detectable quantities of methyl anthranilate are present in other floral types of honey besides orange, tests for methyl anthranilate were conducted on a considerable number of representative floral honeys, special attention being given to those which constitute the main source of honey produced in California. The test for methyl anthranilate, essentially that described by Power, was carried out as follows:

One kilogram of the honey to be tested is dissolved in 600 to 800 cc. of distilled water, and the resulting solution distilled in a current of steam until about 700 cc. of distillate are collected. The distillate is extracted with three successive portions of chloroform of 35 cc. each, the united chloroform liquids are passed through a dry filter and carefully evaporated in a small beaker on a water bath, a current of air being passed over the surface until the solvent is just completely removed. The residue is then immediately treated with 2 cc. of 10 per cent sulfuric acid, and the solution is transferred to a test tube, when it is ready for the specific test. (If a residue obtained by the evaporation of the chloroform is kept for any length of time exposed to the air before treatment with the dilute acid, volatilization of the ester will occur.) The acid liquid is cooled, one drop of a 5 per cent solution of sodium nitrite is added, and subsequently a few crystals of urea are added in order to destroy any possible excess of nitrous acid.

The diazotized liquid is now added to a mixture consisting of one cc. of 0.5 per cent pure β-naphthol (prepared by dissolving 0.5 gram of pure β-naphthol in 2 cc. of 10 per cent sodium hydroxide, and diluting to 100 cc.), one cc. of 10 per cent sodium hydroxide, and one cc. of 10 per cent monohydrated sodium carbonate. If not less than 0.0001 gram of methyl anthranilate is present, a yellowish red precipitate will be produced.

TABLE I. RESULTS OF TESTS FOR METHYL ANTHRANILATE IN HONEYS OF VARIOUS FLORAL TYPES

PREDOMINANT FLORAL SOURCE[a]	ORIGIN	QUANTITY DISTILLED	RESULTS OF TEST
		Grams	
Algaroba	Hawaiian Islands	1000	Negative
Sage	California	1000	Negative
Alfalfa	California	1000	Negative
Holly	California	1000	Negative
Manzanita	California	1000	Negative
Tarweed	California	1000	Negative
Eucalyptus	California	1000	Negative
Sumac	Connecticut	1000	Negative
Cotton	Texas	1000	Negative
White clover	Ohio	1000	Negative
Buckwheat	Ohio	1000	Negative
Tulip poplar	Maryland	1000	Negative
Tupelo	Florida	1000	Negative
Palmetto	Florida	1000	Negative
Orange	Florida	500	Strong positive test
Calif. orange 1	California	500	Strong positive test
Calif. orange 2	California	1000	Strong positive test (heavy orange-red ppt.)
Mixture: 50% orange and 50% tulip poplar	....	1000	Strong positive test
Mixture: 25% orange and 75% tulip poplar	....	1000	Strong positive test
Mixture: 10% orange, and 90% tulip poplar	....	1000	Positive
Mixture: 5% orange and 95% tulip poplar	....	1000	Negative

[a] Considerable care was taken to procure samples that truly represented floral types given. Each sample was obtained from a reliable dealer in a region which is known to produce that particular kind of honey, and at a time of year when honey is ordinarily extracted. Floral types were checked by careful notation of physical properties, such as flavor and aroma, color, and granulation properties, and a comprehensive chemical analysis of each was made. In addition, pollen of each sample was examined to obtain confirmatory data relative to floral source.

The results obtained by application of the test described above to honeys of various floral sources are given in Table I. From the results it is seen that, of the honeys tested, only orange responded positively to the test. Apparently methyl anthranilate is a flavoring compound peculiar to orange honey, not occurring in other floral types, at least in amounts that can be detected by this test. Its detection in honey, therefore, serves as a specific test for orange honey. By using

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[1] The examination of the pollen of this sample was carried out by G. L. Keenan, microanalyst of the Food and Drug Administration, U. S. Department of Agriculture.

one-kg. portions of honey for distillation, it is possible to detect as little as 10 per cent orange in a mixed honey. The distillation of quantities greater than one kg. would make it possible to detect less than 10 per cent orange in a mixed honey. A one-kg. portion is used, as it represents the largest amount that can be conveniently distilled with ordinary laboratory equipment.

Since pure orange honey can usually be recognized by its characteristic flavor, it might seem superfluous to resort to chemical tests as a means for detecting it. The test described is easy to carry out, however, and might be particularly useful for detecting the presence of orange in mixed or blended honey. In addition, it eliminates the personal equation involved in an organoleptic test (based on gustatory senses). The method might also be used to obtain a rough estimate of the relative amount of orange present in a blended honey.

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Determination of Arsenic

Iodometric Acidimetric Method

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ARSENIC readily forms volatile compounds. A very common method for determining arsenic is by distilling it as arsenious chloride. Attempts have also been made to determine arsenic by converting it to arsine and absorbing the arsine in some standard solution.

Lochman (*2*) determined arsenic qualitatively by passing the arsine formed through mercuric chloride solution. Ericsson (*1*) conducted arsine through 0.1 *N* silver nitrate and precipitated the silver with hydrochloric acid. The arsenic was then titrated with 0.002 *N* iodine. Many other methods have been devised for measuring arsine by passing it through standard solutions. The well-known Gutzeit method is, of course, a colorimetric means of measuring arsine.

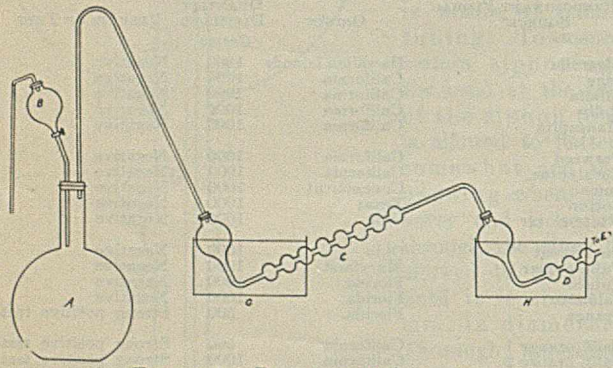

FIGURE 1. DIAGRAM OF APPARATUS

The basis for the method described here is, first, conversion of the arsenic to arsine, and next absorption of the arsine by a standard iodine solution. This is followed by the titration of the residual iodine and the titration of the acids formed in the oxidation.

For this investigation the following solutions were prepared:

0.1 *N* I
0.1 *N* $Na_2S_2O_3$
0.1 *N* NaOH
0.1 *N* As_2O_3
0.01 *N* As_2O_3
0.01 *N* $Na_2S_2O_3$

In addition, arsenic-free sulfuric acid and zinc were used. All solutions were carefully standardized and the zinc and sulfuric acid were found nearly free of arsenic by the Gutzeit test. A blank was run on all reagents.

All rubber tubing and stoppers used were first boiled in a solution of sodium hydroxide, washed, and boiled in dilute hydrochloric acid. They were then soaked overnight in water.

PROCEDURE

The solution of the sample, in which the arsine must be in the arsenious state, is placed in the flask and about 10 grams of 20-mesh zinc are added. The volume of the solution should not be more than 20 to 30 cc. The stopper is now placed in the flask and a measured amount of standard iodine solution distributed through the Meyer bulb tubes, *C* and *D* of Figure 1, with sufficient water to bring the volume in each tube to about 75 cc. The bulb tube, *E*, which is not shown, contains a 1 per cent solution of potassium iodide to dissolve any iodine vapor from *D*. As a further precaution, another bulb tube, *F*, is connected to *E* and is filled with water. On rare occasions *F* is found useful. A piece of mercuric chloride paper is inserted in *F* to indicate any escaping arsine. The tubs, *G* and *H*, should be filled with cold water.

The separatory funnel, *B*, is now filled with 75 per cent sulfuric acid and about 5 cc. are allowed to run into *A*. The acid is added in 10-cc. portions at about 10-minute intervals for about 40 minutes. At the end of this time most of the zinc will be dissolved. The contents of the flask are then heated to gentle boiling for about 5 minutes. The solution in *C*, however, should not become warm. The contents of *C*, *D*, *E*, and *F* are then washed into a beaker and titrated with standard sodium thiosulfate using starch for an indicator.

After the titration with thiosulfate, one of the following procedures was adopted:

1. When a large amount (more than 0.05 to 0.07 gram of arsenious oxide) of arsenic was present, the solution was neutralized with sodium bicarbonate and titrated back with standard iodine.
2. When a small amount (less than 0.05 to 0.07 gram of arsenious oxide) of arsenic was present, the solution was titrated with standard sodium hydroxide, using phenolphthalein as indicator.

DISCUSSION

In method 2, when the arsine is completely oxidized, the following reaction takes place:

$$AsH_3 + 4I_2 + 4H_2O \longrightarrow H_3AsO_4 + 8HI \text{ and}$$
$$H_3AsO_4 + 8HI + 10NaOH \longrightarrow Na_2HAsO_4 + 8NaI + 10H_2O$$

It will thus be seen that 1 cc. of 0.1 *N* iodine is equivalent to 0.001237 gram of arsenious oxide, and 1 cc. of 0.1 *N* sodium hydroxide is equivalent to 0.0009896 gram of arsenious oxide.

The above reaction between arsine and iodine goes to completion when the arsine generated from not more than 0.05 to

0.07 gram of arsenious oxide is passed into 100 cc. of 0.05 *N* solution of iodine. The determination should be arranged so that not more than this amount of arsenic is present if it is desired to titrate both the residual iodine and acid formed.

TABLE I. ARSENIOUS OXIDE FOUND AND PRESENT BY IODOMETRIC AND ACIDIMETRIC METHODS

	As_2O_3 BY IODOMETRIC METHOD			As_2O_3 BY ACIDIMETRIC METHOD		
SAMPLE	Present	Found	Diff.	Present	Found	Diff.
	Gram	*Gram*	*Gram*	*Gram*	*Gram*	*Gram*
I	0.02475	0.02461	−0.00014	0.02475	0.02475	0.00000
II	0.02475	0.02480	+0.00005	0.02475	0.02493	+0.00018
III	0.02475	0.02492	+0.00017	0.02475	0.02458	−0.00017
IV	0.02475	0.02477	+0.00002	0.02475	0.02459	−0.00018
V	0.02475	0.02492	+0.00017	0.02475	0.02464	−0.00011
VI	0.02475	0.02480	+0.00005	0.02475	0.02483	+0.00008
VII	0.02475	0.02475	0.00000	0.02475	0.02464	−0.00011
VIII	0.002475	0.002596	+0.00012	0.002475	0.00282	+0.00033
IX	0.04950	0.04941	−0.00009	0.04950	0.04928	−0.00022
X	0.04950	0.04979	+0.00029	0.04950	0.04948	−0.00002
XI	0.04950	0.04954	+0.00004	0.04950	0.04948	−0.00002
XII	0.04950	0.04964	+0.00014	0.04950	0.04928	−0.00022

TABLE II. RESULTS OBTAINED BY PROCEDURE 1 WITH ARSENATES AND ARSENITES PRESENT IN RECEIVING IODINE SOLUTION

SAMPLE	As_2O_3 PRESENT	As_2O_3 FOUND	DIFFERENCE
	Gram	*Gram*	*Gram*
1	0.09893	0.10019	+0.00116
2	0.09893	0.09809	−0.00084
3	0.09893	0.09840	−0.00053
4	0.09893	0.09842	−0.00051
5	0.09893	0.09809	−0.00084
6	0.08000	0.08032	+0.00032
7	0.12000	0.11976	−0.00024
8	0.10000	0.09987	−0.00013

When larger than the above-mentioned amounts of arsenic are present in the sample, the receiving iodine solution will contain both arsenate and arsenite. In such cases, the volume of iodine originally added and the amount used in back titration are added, and from this is subtracted the volume of thiosulfate used in titration. The arsenic present is found by multiplying the difference by the proper factor. For example, suppose 120 cc. of 0.1 *N* iodine were used as the receiving solution and 30 cc. of 0.1 *N* thiosulfate were used to titrate the residual iodine, and also that 7 cc. of 0.1 *N* iodine were used to titrate back after neutralization.

0.1 *N* I, cc.	120
0.1 *N* $Na_2S_2O_3$, cc.	30
	90
0.1 *N* I used in back titration, cc.	7
	97

97 × 0.001237 = 0.119989 gram As_2O_3 present

Tables I and II show results obtained.

COMMENTS

Since in going from arsine to orthoarsenic acid arsenic changes 8 in valence, it is possible to determine very small quantities of arsenic in a volumetric way. It has been found practical to use 0.01 *N* solution of iodine, one cc. of which equals 0.0001237 gram of arsenious oxide. Since one can check readily to about 0.2 cc., it has been found possible to determine quantities of arsenic as small as 0.00002 gram. The method herein described should be four times as sensitive as the ordinary titration of arsenic with iodine.

The acidimetric titration is a valuable check on the accuracy of the iodometric titration.

The work done shows that it is impossible to liberate all the arsenic from a sample as arsine without boiling. The boiling has gone far enough when the last particle of metal has been dissolved. Although the reaction of the acid on the material in the flask may have ceased before boiling, it will be found that when the contents of the flask are brought to boiling particles of dark-colored material will dissolve. No doubt arsine is also dissolved in the liquid in the flask, and this is liberated upon boiling.

Sufficient standard iodine solution should be present in tubes *C* and *D* so that all of it is not reduced by the arsine, else unreliable results will be obtained.

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RECEIVED June 23, 1932.

A Laboratory Extractor

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THE accompanying photograph shows an extractor of considerable capacity which was constructed almost entirely by the assembly of common laboratory apparatus. Within a tall-form liter beaker was placed a glass tripod which was readily constructed of glass rod. A 35 by 70 mm. crystallizing dish rested in an inclined position on this tripod. A 15-cm. folded filter within this dish contained the material to be extracted. Suspended in the mouth of the beaker was a 250-cc. distilling flask which served as the condenser.

The extractor is particularly well adapted to the purification of organic compounds. It resembles in some respects an extractor described in the literature (*1*), wherein a large funnel is used to support the filter. It has numerous advantages, however, over the "funnel" extractor. Comparative tests showed that it has a much higher speed of extraction; the solvent is condensed more effectively when boiled vigorously; the drip from the condenser flask does not channel through the charge in the filter; "choking" of ascending vapor with condensate in the funnel stem is avoided; and contamination by material from stoppers does not occur.

When used with 200 cc. of carbon tetrachloride as the extraction medium, no appreciable amount of solvent escaped during a 6-hour run. Decolorizing charcoal, intimately mixed with the material to be extracted prior to filling up the filter, frequently assisted purification.

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RECEIVED June 21, 1932. Contribution 102 from the Experimental Station, E. I. du Pont de Nemours & Co.

Practical Vacuum-Tube Potentiometer for pH Measurement with Glass Electrodes

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An easily operated vacuum-tube potentiometer for pH measurements is described. Use is made of a low grid-current, low plate-voltage tube now available for this work. Galvanometer drift has been reduced to a negligible minimum by automatic compensation for filament voltage changes, and "floating" of filament battery on a charging source. Suggestions for a shielded thermostat box and a high-insulation vacuum-tube switch are given. One galvanometer is used for both potentiometer standardization and as a plate-current indicator, working as a null instrument in both functions.

THE instrument to be described is the result of a series of trials and experiments growing out of a demand in this department for a satisfactory means of determining the pH of intestinal contents. The glass electrode has been shown by McInnes and Dole (*5*) to develop potentials directly proportionate to pH even in the presence of substances which interfere seriously with pH measurements by other electrometric means, and therefore to promise greater accuracy than other methods. The high resistance of the glass membrane has, however, by necessitating the use of a very sensitive electrostatic device for measuring the potential, proved a serious obstacle to the development of a satisfactory instrument.

Because of this high resistance, it is obviously not possible to balance the potential against that of a potentiometer directly. The Compton electrometer, as employed by McInnes, has apparently been found unsatisfactory by other workers. Several attempts have been made to construct a potentiometer on the vacuum-tube principle (*2, 9, 10*) but inability to control grid-current fluctuations arising from leakage or electrostatic charges, and those of the various battery voltages, has been a source of great annoyance in the operation of these instruments.

A four-element, low grid-current, low anode-potential vacuum tube recently put on the market[1] (*3, 4, 6*), and the incorporation of a number of new features of construction and assembly, have now eliminated this source of trouble. The present instrument has the additional decided advantage of relative simplicity of operation.

The principles (*7, 8, 11*) upon which this instrument operates will be clear from a study of the vacuum-tube circuit, shown in Figure 1. For any given grid voltage, all other conditions being maintained constant, the anode current, as indicated by a galvanometer, will assume a specific value. Insertion in the grid circuit of an additional voltage, that of the electrode system, causes the anode current to change, but upon opposing an equal voltage from the potentiometer, the anode current resumes its original value. The system used differs from that of Dubois (*2*) in that no attempt is made to work the tube at its floating grid potential, where the grid current is zero. With suitable precautions, the FP-54 tube can be made to have a grid current of 10^{-15} amperes or less, which is low enough to preclude appreciable polarization effects.

Anode current drifts due to filament- and grid-battery fluctuations have been reduced to a negligible minimum in two ways. Part of the voltage drop across the filament is utilized to supply a current which is passed through the galvanometer in opposition to the normal anode current (*1*). This method not only has the advantage of allowing the galvanometer to be operated from its true zero, but also

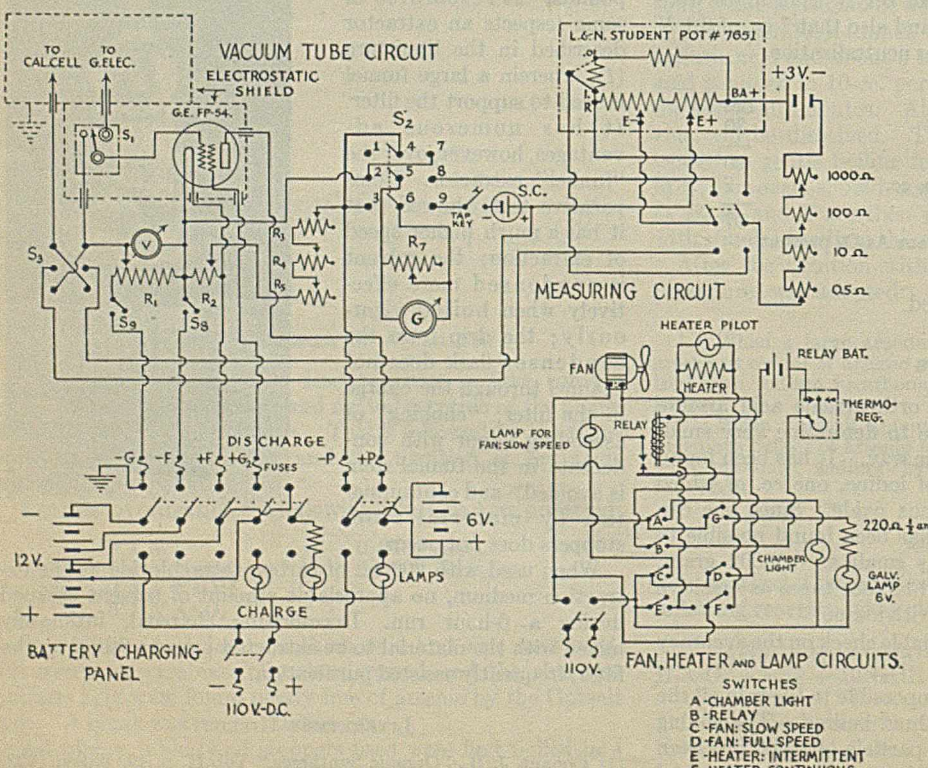

FIGURE 1. WIRING CIRCUITS FOR COMPLETE GLASS ELECTRODE SET-UP

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[1] General Electric FP-54.

automatically compensates for filament-battery fluctuations; a rise in filament voltage causes increased electron flow and hence a rise in anode current, but the counteracting current increases simultaneously, thus preventing a change in galvanometer deflection. In addition, large filament-battery fluctuations have been circumvented by floating this and the grid battery during use on a direct current charging source through a resistance of appropriate size so that the charging current will be slightly less than that of the load.

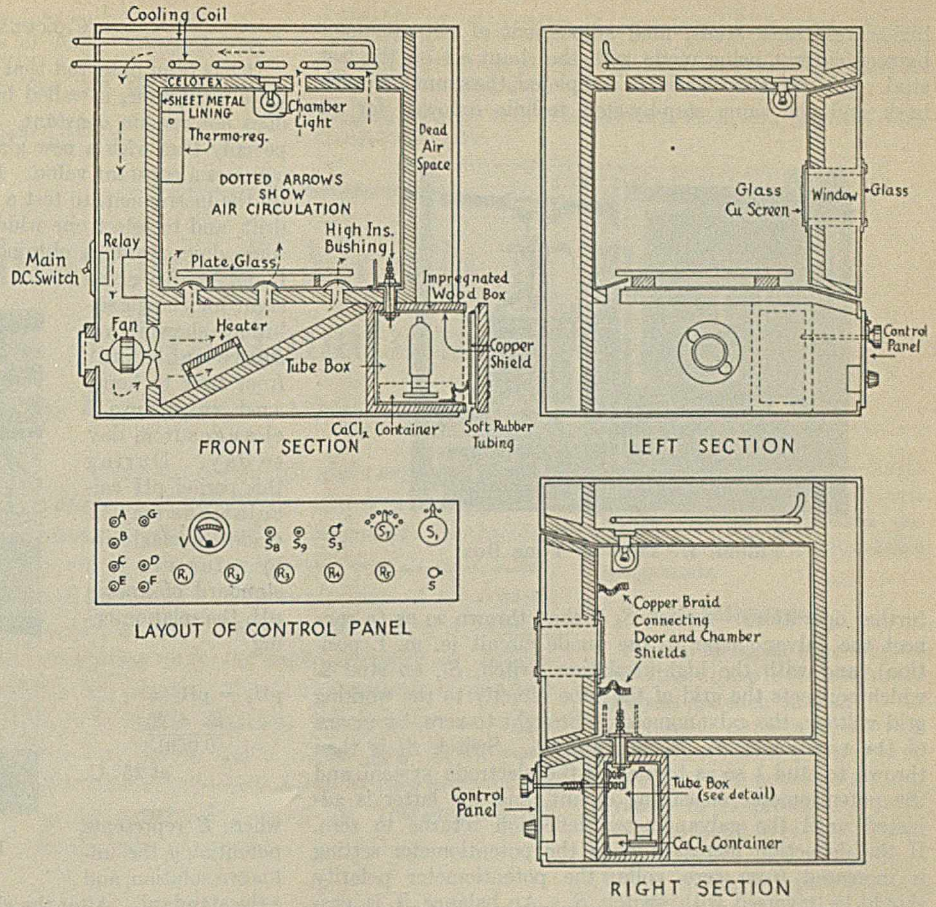

Figure 3. Construction of Thermostat Box

Construction

Electrical. A three-pole double-throw switch, S_2 in Figure 1, allows the galvanometer to be used in standardizing the potentiometer as well as in the tube plate circuit. The contacts 4 and 7 prevent the interruption of plate current when the galvanometer is being used for standardization. Switch S_3 reverses the potentiometer polarity for measuring solutions of low pH. Resistance R_1 provides a means of varying the grid voltage, which is indicated by a small panel voltmeter of proper range. R_7 is the galvanometer protective and damping shunt, which consists of a series of resistors connected to the studs of a rotary switch. The values of these resistors for use with the L. & N. type 2500-e galvanometer are 10, 100, 500, 1000, and 500 ohms, which give convenient steps of galvanometer sensitivity with good damping characteristic. A view of the inside of the chamber showing the electrode system is given in Figure 2.

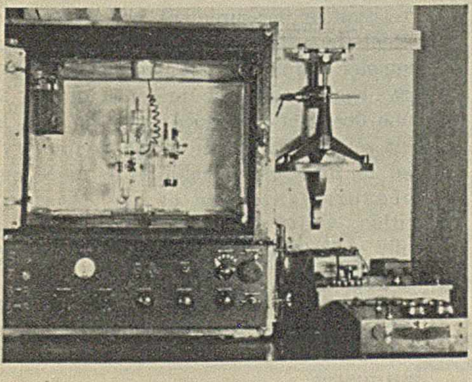

Figure 2. Inside of Chamber Showing Electrode System

Mechanical. It is necessary to enclose the entire assembly, with the exception of the potentiometer, galvanometer, batteries, and associated apparatus, in an electrically shielded box arranged to maintain constant temperature. A thermoregulator within the main chamber operates a heating resistance (Electrad 200 ohms-75 watts) through a small relay whose coil is energized by one or two dry cells. A thermometer placed in the test solution or in some other convenient place may be observed through the gauze-shielded window and illuminated with a small candelabra-base 110-volt lamp operated by a switch on the front panel. The connections for this light and for the air-conditioning system are shown in Figure 1. Diagrams showing the box constructed by the author, which is a modification of one used by Dubois, are given as a suggestion (Figure 3). The vacuum tube and switch S_1 are housed in a separate wooden box, lined inside with sheet copper and impregnated against air and moisture with hot wax or pitch; this box is built into a corner of the thermostat box. Its shield and that of the main chamber are to be thoroughly grounded. An arrangement of the apparatus with a good view of the tube box is shown in Figure 4. Details of the high-insulation switch, S_1, bushings, and connections, are shown in Figure 5. Much depends upon the insulating qualities of this switch so that careful thought should be given to its construction and placement. Three six-volt 100 ampere-hour storage batteries are recommended for use with this instrument. Figure 6 shows a complete set-up.

Operation

The potentiometer is standardized in the usual way, making use of the galvanometer switch, S_2. As balance is approached, the galvanometer shunt is moved toward the higher resistance studs, final adjustment of potentiometer battery current being made with the shunt set on the last stud. After standardization is completed, the shunt is thrown back and the same step-by-step technic followed for all further operations. Switch S_2 is then thrown so as to connect the galvanometer to the anode circuit (e. m. f. position), and with the high-insulation switch, S_1, on stud 2, which connects the grid of the tube directly to the working grid voltage, the galvanometer is brought to zero, by means of the resistances R_2, R_3, R_4, and R_5. Switch S_1 is then thrown to stud 1 so as to include the electrode system and the potentiometer measuring circuit, and the latter is adjusted until the galvanometer deflection returns to zero. If the deflection increases when the potentiometer setting is increased from zero volts, the potentiometer polarity should be reversed with switch S_3. At balance it is possible to throw switch S_1 back and forth without causing a deflection of the galvanometer, and this provides a check on the accuracy of the potentiometer setting, which, at zero galvanometer deflection, is the e. m. f. of the electrode system.

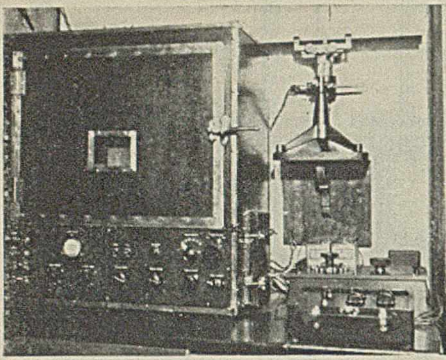

Figure 4. View of Tube Box

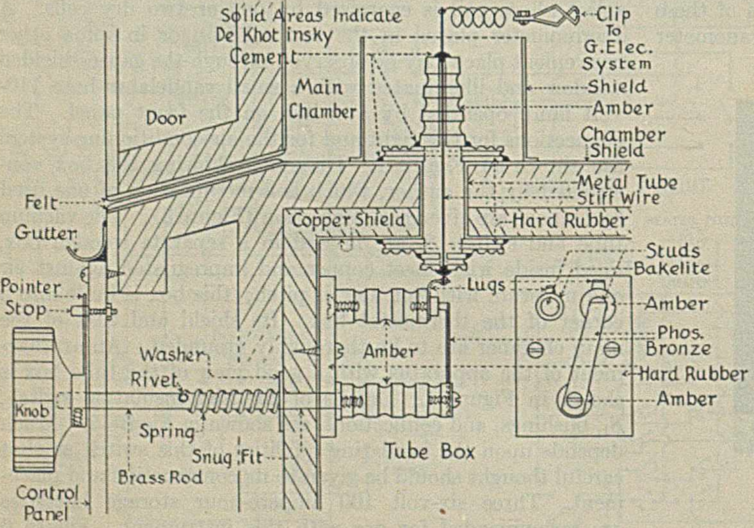

Figure 5. Details of High Insulation Switch and Bushings

In measuring grid current, a high resistance (100 megohms or more) of known value is substituted for the electrode system and the procedure as given above is followed. The voltage as read on the potentiometer and the known resistance are applied in Ohm's law.

Calculation of pH

It has been observed that the asymmetry potential of the glass membrane, so-called by McInnes and Dole (*5*), often does not remain constant. This has been found to be especially true with a new glass cell; after a period of use it assumes a constant value. It is advisable, when first setting up the instrument, to test a batch of glass cells for potential drift, and to select one which shows relatively little. After some days readings obtained with this membrane will be found nearly constant for a single solution, showing no appreciable drift from hour to hour, and only small changes from day to day. During this period pH calculations may be made satisfactorily by reference to a standard of known pH, the relation being

$$\text{pH}_g = \text{pH}_s \pm \frac{E_s \pm E_g}{0.0591} \text{ at } 25° \text{ C.}$$

where E represents potential, g the unknown solution, and s the standard. After the glass membrane attains a constant asymmetry potential, the use of a standard is necessary only to check this fact from day to day; pH may then be calculated by the use of an empirical formula involving the combined constants, x in the following equation, for glass, silver, and calomel electrodes, as determined for a given set-up with solutions of known pH:

$$\text{pH} = \frac{E_g \pm x}{0.0591} \text{ at } 25° \text{ C.}$$

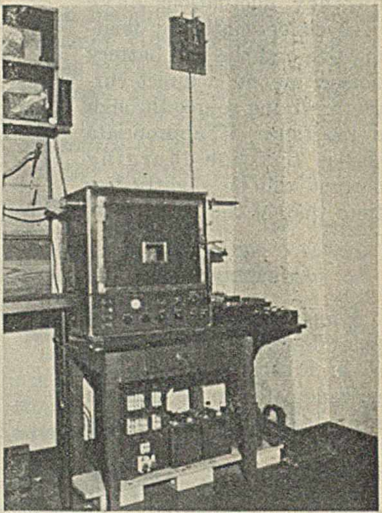

Figure 6. Complete Set-Up

Precision in measurement will depend to some extent upon the galvanometer and potentiometer employed. Numerous repeated tests have shown that the presence of the vacuum tube does not introduce errors of any kind in this set-up. Even before the asymmetry potential of the glass membrane becomes constant, measurements are easily attainable to within ±0.03 pH; with a constant and carefully calibrated instrument the average error is reducible to the third decimal place.

Besides its usefulness in pH measurement, many other applications involving determination of e. m. f. might be suggested for this instrument.

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Determination of Metals in Organic Combination

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A study has been made of the action of fuming sulfuric acid and 30 per cent hydrogen peroxide upon organo-metallic compounds containing mercury, arsenic, antimony, bismuth, gold, silver, and germanium. Decomposition of all organic matter is rapid and complete, leaving a solution containing only the metal, usually as sulfate. To this solution, customary methods of analysis may be readily applied; precipitation as sulfide has been found useful particularly in the cases of mercury, antimony, bismuth, and germanium, as has a modification of the Newberry method in the case of arsenic.

As pointed out in the report of the Sub-Committee on Synthetic Organic Chemicals of the American Drug Manufacturers Association, "organic compounds of mercury are assuming an ever increasing importance in medicine as antiseptics, anti-syphilitics, and diuretics." During the year 1930, ten selected methods for the analysis of organic mercury compounds were studied in five different laboratories under the supervision of this committee. Variations of surprising magnitude were found to occur. Using the same method for a given compound, differences as great as 2 or 3 per cent were noted. The results for a different mercurial by different methods show even greater variation, being as much as 7 per cent in the cases of mercury salicylate and mercurochrome. About this time, during the course of a study of certain synthetic organo-metallic compounds in this laboratory, it became very desirable to secure a more rapid method of metal analysis.

Experience in the foregoing analyses suggested strongly that greatest progress could be made by devising a simpler and more satisfactory mode of decomposing the organic compound than the sulfuric acid–permanganate, sulfuric-nitric acid, hydrochloric acid, perchloric acid, and persulfate mixtures commonly employed in the past. This was found in the use of fuming sulfuric acid and 30 per cent hydrogen peroxide (Superoxol). The fuming acid (15 per cent SO_3) dissolved the organic compounds either in the cold or on gentle warming, facilitating complete oxidation, and the excess hydrogen peroxide on spontaneous decomposition left no residue of inorganic salts. With nearly all of the compounds studied, oxidation was found to be complete within 3 to 5 minutes, giving a water-white solution containing only sulfuric acid and the metal as sulfate.

The use of hydrogen peroxide for hastening decomposition during Kjeldahl digestions was first suggested by Kleeman (*5*) in 1921, and has subsequently found application in biological assays (*6, 7, 12*). Oakdale and Powers (*9*) have employed it as a secondary oxidizing agent in a new method of halogen determination.

Since the completion of most of the following work, the authors have found that Graham (*2*) employed a sulfuric-peroxide mixture of the decomposition of mercurial insecticide samples, and Schulek and Villecz (*10*) have utilized it in the determination of arsenic. These methods do not, however, seem to be well known in this country, and to the best of our knowledge perhydrol–sulfuric acid decomposition has not been applied to the systematic decomposition of organo-metallic compounds.

Mercury

Several methods were studied for the completion of the analysis in each instance. In the absence of halogen, dilution with water and titration of mercury with potassium sulfocyanate in the presence of nitric acid was found to be satisfactory and apparently accurate. Where speed is important, this technic has many advantages, enabling the complete analysis to be carried out in 15 to 30 minutes. Precipitation by Jamieson's reagent and either titration with potassium iodate or weighing as mercury zinc sulfocyanate (*3*) were looked upon with favor until, in the case of mercury salicylate, the titration gave low and inconsistent results; the reason for this has not been found.

Since the chief aim of this study was the elaboration of a method applicable with equal accuracy to all types of organic mercurials, with and without halogens, precipitation as sulfide seemed to offer the greatest possibilities.

It was found that the oxidation mixture, after dilution and cooling, could be precipitated directly by hydrogen sulfide; in the absence of inorganic salts, the authors not only failed to observe the inaccuracies reported by Fenimore and Wagner (*1*), but found that precipitation was complete within 15 minutes. No formation of sulfur was observed. If the precipitate was washed successively with alcohol, carbon disulfide, and ether, drying was complete in 20 minutes at 105° C.

Procedure in Absence of Iodine. The sample containing approximately 0.1 gram of mercury is placed in a Kjeldahl flask with 7 to 10 cc. of 15 per cent fuming sulfuric acid. (With easily decomposable substances, ordinary sulfuric acid is satisfactory.) The substance is dissolved, if possible, by gentle warming. Thirty per cent hydrogen peroxide (Superoxol) is added drop by drop, being allowed to flow down the side of the flask, which is agitated gently by hand. Oxidation takes place at once. Addition of hydrogen peroxide is continued until the liquid is the most straw colored, when warming is increased until fumes of SO_3 are abundant. Sometimes a little more hydrogen peroxide is required for complete decolorization; the total amount required will vary from 1 to 5 cc. It is essential that everything be in solution at this point. In the absence of halogen, no loss of mercury was observed on heating, but in the presence of chlorine or bromine, too much warming is to be avoided. If desired, the reaction may be carried out under a reflux condenser as described subsequently. The reaction is complete when no more oxygen is evolved.

The water-white solution is diluted with water and precipitated directly with hydrogen sulfide, the mercuric sulfide filtered through a Gooch crucible, washed with carbon disulfide, alcohol, and ether, dried at 105° C. for 20 to 30 minutes, and weighed.

Procedure in Presence of Iodine. In the presence of iodine the decomposition must be carried out in a 200-cc. flask connected by a ground-glass joint to a spiral reflux condenser through which the hydrogen peroxide is added. During the oxidation as tested upon a mixture of mercurosal and sodium tetraiodophenolphthalein, some iodine and mercuric iodide sublimes, and the solution is colored by dissolved iodine. The portion in the condenser is washed back several times with small amounts of water, and a little more hydrogen peroxide added to insure complete oxidation. A small final sublimate of iodine does no harm if it does not contain yellow mercuric iodide.

To the diluted liquid in the flask is added about 0.1 to 0.2 gram of aluminum powder (c. p.); on warming, a vigorous reaction takes place and a black sediment of amalgam settles out. Warming is continued (a little more aluminum may be added) gently for 15 to 30 minutes until the precipitation of mercury is complete and a small residue of aluminum metal remains unchanged. After cooling, this is filtered (suction) through a small folded filter which is returned to the flask in which the reduction has taken place. Under the reflux, 2 cc. of concentrated nitric acid and 3 to 5 cc. of bromine water are added. When the main reaction is over, a small drop of liquid bromine may be employed to dissolve the residual globules of mercury, which sometimes resist even prolonged warming without the bromine water.

Table I. Analysis of Mercurials by Various Methods

	Calcd. (Known)	Jamieson Titr.	Jamieson Grav.	H_2S, Av.
	%	%	%	%
Metaphen	57.07	57.2		57.42
Merthiolate	49.55	49.44		49.05
Mercurochrome	24.93	24.84		24.88
Mercury salicylate	58.5[a]	58.81 (KCNS)	59.1	58.25
Mercurosal	43–43.8[a]		43.3	43.95
Mercurophen	(51.5)[a]		51.71	52.14
Mercuric diphenyl	56.57		56.3	56.94
Mercurosal + tetraiodophenolphthalein	43–43.8			43.17

[a] With those substances not completely pure, the average metal content as determined by several laboratories was selected.

The diluted contents of the flask are warmed to remove most of the bromine, filtered, and carefully decolorized with dilute sodium acid sulfate. Hydrogen sulfide is then passed in and the mercuric sulfide determined as described above.

The methods outlined have been tested upon standard samples of the six pharmaceutical mercurials listed below, upon pure mercury diphenyl, and upon more than a dozen synthetic mercury compounds to be described in a separate paper. The results of duplicate or triplicate determinations were in each case close either to theory, or to the known mercury content.

During the past three months, the method described above has been applied by the coöperating laboratories to the standard samples of the mercurials with "distinctly encouraging" results.

In the analysis of mercury ointments, the peroxide–sulfuric acid decomposition has been found more satisfactory than the official U. S. P. method employing nitric acid. In this analytical laboratory, it is now routinely applied to pharmaceutical preparations involving organic mercurials such as "Tincture Metaphen" and "Metaphen 2500." These are merely concentrated rapidly to a small volume and the above procedure applied as usual.

Arsenic

The decomposition of organic arsenicals is carried out in a similar manner. Because of the ease with which arsenic is determined volumetrically, volumetric methods have been employed almost exclusively, and that of Newberry (*8*) has been best adapted to the conditions at hand.

The solution after cooling is diluted with 100 to 150 cc. of water, and 10 cc. of 10 per cent potassium iodide are added. The liberated iodine is expelled by boiling and the liquid concentrated to about 40 to 50 cc. Any iodine is decolorized by one drop of sodium sulfite, the solution is made just alkaline with 20 per cent sodium hydroxide, then slightly acid with dilute sulfuric acid, and finally alkaline with 5 to 10 grams of sodium bicarbonate. It is then titrated with 0.1 *N* iodine, employing starch indicator at the end. The Lehman method (U. S. P.) may also be used. The results are given in Table II.

Table II

	Known Arsenic	Found, Av.
	%	%
Arsphenamine	31.2	31.0
Neoarsphenamine	20.3	20.5
Sulfarsphenamine	21.6	21.4
Stovarsol	27.6	27.5

Bismuth and Antimony

After decomposition as above, employing an excess of hydrogen peroxide, the bismuth and antimony exist as -ic sulfates. With hydrogen sulfide, precipitation was complete within 15 minutes, and no difficulty was encountered in filtration upon a Gooch crucible. The sulfides were precipitated in the presence of carbon disulfide, washed with this solvent, then with alcohol and ether, and dried at 100° C. for 30 minutes, or to the lowest weight observed. Although this procedure was satisfactory in the case of antimony, it was found better to reduce the dilute bismuth solution with sulfur dioxide solution, expel the excess of the latter by boiling, and precipitate as bismuth sulfide.

As alternative methods, precipitation of bismuth as basic carbonate and as metal (formaldehyde in alkaline solution) were tried with only moderate success. The results are given in Table III.

Table III

	Known Metal Content	Found
	%	%
Potassium antimony tartrate + sugar	36.4	36.7
Bismuth subsalicylate	54+	54.5
Bismuth camphor carboxylate	40.5	40.7
Potassium bismuth tartrate + sugar	64.95	64.8

Silver

The Superoxol decomposition was employed on several samples of silver protein in place of the more tedious nitric acid method. The diluted solution was titrated directly with potassium sulfocyanate after the addition of nitric acid and ferric sulfate. The results are given in Table IV.

Table IV

	Known Ag	Found
	%	%
Silver protein A	19.9	19.75
Silver protein B	19.9	19.93

Gold

With gold, the reaction is different, hydrogen peroxide precipitating metallic gold.[1] It is therefore preferable to dis-

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[1] N. A. Hansen of this organization has developed a similar method employing nitric acid.

solve soluble gold salts in dilute sulfuric acid, add 3 to 5 cc. of hydrogen peroxide, and warm. The precipitated mass of gold is washed with water, then with alcohol, dried at 105° C., and finally ignited. The results are as follows:

	Calcd. Au %	Found %
Gold sodium thiosulfate	37.0	37.0

Germanium

The germanium compound is oxidized by sulfuric acid and hydrogen peroxide in a Kjeldahl flask, the sulfide precipitated from strongly acid solution, filtered as soon as coagulation is complete, and dissolved in strong ammonium hydroxide. This ammonia solution is filtered directly into a large crucible, the sulfide decomposed by Superoxol, evaporated to dryness, and ignited to germanium dioxide as in the method of Johnson and Dennis (*4*). The results are as follows:

	Calcd. %	Found %
Tetrabenzyl germanium	16.62	16.45

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Microdetermination of Carbon

Improvements in Nicloux Method

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The method for microdetermination of carbon developed by Nicloux (*3*) would appear to have many possibilities, particularly in the field of biochemistry, since it is a comparatively rapid and moderately accurate method which can be applied both to organic compounds and to mixtures containing carbonaceous compounds either in the solid state or in solution. In its original form, the Nicloux method had many shortcomings, part of which were chemical and part technical. Boivin (*1*) has so modified the method as to overcome most of the difficulties which arose from faulty combustion and absorption of the resulting carbon dioxide. Various other modifications have been developed, as by Osuka (*4*), and Schadendorff and Zacherl (*5*), both of whom have improved the method of handling carbon-containing solutions, such as urine, etc. From the technical standpoint, the method remained clumsy and difficult to carry out. In this paper, further modifications are reported, aiming at the reduction of these technical difficulties and the simplification of the procedure. These modifications also make possible an increase in the accuracy and decrease the time necessary to carry out an analysis.

Apparatus Used

The apparatus is shown in Figure 1. It is essentially the apparatus used by Boivin, except that instead of having a bulb blown directly in the upper chamber to hold the absorbing caustic solution, a detachable absorption chamber is introduced. The rubber tube at *G* in the Nicloux and Boivin apparatus is replaced by a stopcock, as well as the plunger type of stopcock in funnel *D*. Originally Nicloux used an ordinary stopcock in funnel *D* and later replaced it with the plunger type to prevent entrance of carbon from the stopcock grease. Such a replacement may be desirable but does not seem to be necessary from the authors' experience. In addition to the changes in design, it has been found advantageous to use the microfilters to be obtained from the Central Scientific Co., Chicago, Ill., previously described by Kirk and Schmidt (*2*) for separating the barium carbonate precipitate, instead of centrifuging as in the original method.

Procedure

A sample of dry material containing 2 mg. of carbon is weighed. Unless the percentage content of carbon is very low, this must be carried out on a microbalance, or by dilution of a weighed quantity of the unknown material with a larger weighed quantity of noncarbonaceous solid material and subsequent weighing of a sample of the mixture on an analytical balance. Dry sodium sulfate may serve for such a diluting material if allowance is made for it in adding the reagent later. The dry material is transferred to sample tube *A*. To this is added 0.6 gram of silver chromate and 0.1 gram of anhydrous sodium sulfate. The sample tube is attached to the upper part of the apparatus and 3 ml. of concentrated carbon-free sulfuric acid placed in funnel *D*. The sulfuric acid is rendered free from carbon by heating it under a good vacuum on a boiling water bath with a little chromate. This heating should take place behind a protective glass screen because of a certain risk from explosions. In one case out of a considerable number of such heatings, the reagent exploded with considerable violence. No reference to this hazard has been found in the literature.

If a stopcock is used, as shown here, it should be greased scantily with vaseline. The sulfuric acid apparently does not dissolve or attack the trace of vaseline with which it comes in contact. Another alternative is to use a phosphoric acid mixture as a lubricant, as described by Stevens (*6*).

The absorption cup, *C*, which is made from the bottom of a test tube, is now charged with 0.6 ml. of 2 *N* sodium hydroxide which must be carbonate-free. This is insured by the previous addition of a little barium hydroxide to the sodium hydroxide solution. The cup, inserted in the stopper containing a hole bored partly through, is inserted into chamber *B*. The system is now thoroughly evacuated and closed. In case any leakage develops, a little clear lacquer has been found to be very effective in sealing it without introducing difficulties. This, of course, must never come in contact with the oxidizing reagent, but may be safely applied around the stopper holding the absorption cup. Another possible point of leakage is the stopper through which filament *F* is introduced. De Khotinsky cement will seal this point and is practical for use, since this stopper need never be removed. It is likewise possible, if desired, to seal platinum or tungsten leads directly through the glass, rather than to use a stopper. Such seals are subject to considerable breakage due to heat from the filament.

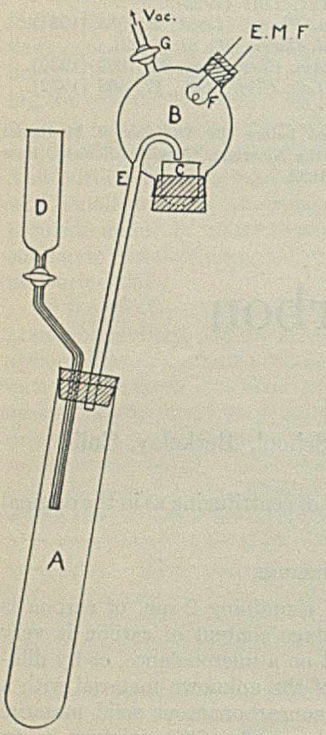

FIGURE 1. DIAGRAM OF APPARATUS

After evacuation, 2 ml. of the carbon-free sulfuric acid are run into *A* from the funnel. The tube is immersed in a boiling water bath for about 20 minutes. A microburner is then applied directly to the tube until the contents turn definitely green, which marks the end of the reaction. The tube is now cooled in a beaker of water and dilute sulfuric acid run in from the funnel until the liquid level is about 0.5 cm. from the end of tube *E*. A current of short duration is now passed through filament *F* by means of a tapping key. The current should be adjusted so as to heat the filament rapidly to a bright red color. A considerable number, fifty or sixty, of these intermittent currents are applied. The consequent heating and cooling of the filament catalyzes the oxidation of the carbon monoxide present to carbon dioxide, and thoroughly circulates the gases over the caustic in cup *C*, producing complete absorption of carbon dioxide.

The procedure thus far has been that recommended by Boivin with the exception of the use of a different absorption apparatus. From this point on, it is decidedly preferable to abandon his method. The removable cup is simply taken out without disturbing the remainder of the apparatus, and the carbonate is precipitated in the cup with a solution of barium chloride. This is stirred thoroughly and immediately poured into a filter previously prepared as described by Kirk and Schmidt (*2*). The solution is sucked through and the precipitate thoroughly washed with water saturated with barium carbonate. Otherwise, either alkali is retained by the asbestos, or carbonate is dissolved. The precipitate is transferred to a test tube by pushing out the asbestos pad from the bottom of the filter with a small stirring rod. The cup and the sides of the filter are rinsed down by means of 0.05 *N* hydrochloric acid solution delivered from a microburet or accurate pipet, and followed by a little water. About 10 ml. of the acid are necessary to insure complete solution of the barium carbonate. A drop of methyl red is now added to the solution in the test tube, and the tube is heated by immersion in a boiling water bath until gas evolution ceases. The excess acid is back-titrated while still hot, using 0.05 *N* sodium hydroxide, and the methyl red as indicator. The acid required to react with the carbonate is found by subtracting the base added from the total acid added, and the number of milligrams of carbon in the sample is obtained by multiplying the milliliters of 0.05 *N* acid by 0.3, since one ml. of 0.05 *N* acid is equivalent to 0.3 mg. of carbon.

A blank must be run on the reagents and, if the sulfuric acid is first heated with silver chromate as recommended by Boivin, this blank should not exceed 0.3 ml. of 0.05 *N* hydrochloric acid. The blank must be subtracted from the amount of acid used in the determination.

For analysis of physiological fluids, this method has been recommended by Boivin (*1*), Osuka (*4*), and Schadendorff and Zacherl (*5*). Urine analysis in particular is difficult on account of its content of volatile carbon compounds which are released in the evacuated chamber without undergoing oxidation. The method of Boivin for urine analysis has been tried and found to give unsatisfactory results. The last work mentioned undoubtedly avoids many of the difficulties of the Boivin technic. The modifications proposed here are equally applicable to any of these methods and will result in an improvement in the method.

RESULTS

Since the general method used is the same as that of Boivin it remains only to show that the modified method gives reliable results and is an actual improvement over the older type of technic. In Table I are listed a series of typical analyses of pure compounds.

TABLE I. TYPICAL ANALYSES OF PURE COMPOUNDS

SUBSTANCE	WT. OF SAMPLE	0.0502 *N* HCl	THEORETICAL C	AMT. OF C OBTAINED
	Mg.	*Ml.*	*Mg.*	*Mg.*
Sucrose	8.45	11.798	3.56	3.539
	7.67	10.743	3.23	3.22
	5.10	7.115	2.14	2.134
p-Amino-benzoic acid	3.20	6.61	1.98	1.983
	3.48	7.02	2.13	2.106
Tyrosine	3.58	6.996	2.135	2.098
	3.36	6.994	2.06	2.097
Glutamic acid	5.31	7.264	2.17	2.179
	5.13	7.10	2.09	2.13

From the results given in Table I it is seen that the method as modified compares very favorably with that of Boivin as regards accuracy when applied to pure compounds. In fact, it is theoretically possible to attain a higher degree of accuracy, since the exposure to the carbon dioxide of the air is reduced, the complete removal of the carbonate from the apparatus is more readily accomplished, and the filtration and washing give more nearly quantitative manipulation of the precipitate than is possible when the centrifuge method is used. In addition to the question of accuracy, the saving of time is considerable, which is particularly important in handling the absorption liquid to keep it free from carbon dioxide of the air. The ease of manipulation is considerably increased, thus making it possible to develop the necessary technic with a minimum of effort.

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Graphical Representation of Mineral Components in Water Analyses

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A GRAPHICAL method for expressing water analyses should depict adequately composition and significant relationships. Previously reported diagrams for representing results of water analyses include those of Tickell (*4*), Reistle (*3*), Collins (*1*), and others.

The method presented herein consists in plotting milliequivalent concentrations of the various ions along the sides of a rectangle in such a manner that its segmentation, form, and size completely describe the dissolved minerals. Referring to Figure 1, the construction of the rectangular diagram from an ionic analytical statement is as follows:

Let *OX* and *OY* be horizontal and vertical coördinate axes, respectively. On *OY* scale off a length, *Oa*, proportional to the magnitude of chloride ion in the water. Starting at *a*, lay off a length, *ab*, proportional to the amount of sulfate. At point *b*, perpendicular to axis *OY* lay off *bc* proportional to the bicarbonate content, or in cases where both bicarbonate and carbonate ions are present together, the equivalent of their sum may be used. Drop from point *c* a perpendicular, *cd*, to axis *OX*. To represent cations, commence at point *b* and lay off *be* proportional to calcium and *ec* plus *cf* proportional to magnesium. If in a sample calcium is greater than bicarbonate, then point *e* will be located on vertical *dc*. The residual length, *fd*, represents the amount of sodium present and may be used in this way to solve graphically for the sodium content of a water or to check the analytical value obtained therefor. In most cases the alkali ions sodium and potassium may be considered entirely as sodium. The lengths *be*, representing calcium, and *ec*, a part of the magnesium, might just as well have been located along the base *od*, except that this part of the diagram as drawn gives the advantage of coincidence to aid in comparisons.

Relationships

A rectangular diagram can readily be drawn on ordinary graph paper and shows at a glance several important characteristics of the water. The perimeter represents the total concentration of minerals in the water; one-half of the perimeter measures the normality of the solution. Relative lengths of segments indicate relative concentrations of the various ions.

The width of the figure shows the so-called temporary hardness, or more properly the carbonate hardness of the water. Segments *be* and (*ec* plus *cf*) indicate relative amounts of calcium and magnesium; their sum represents the total hardness. Incrustants, or noncarbonate hardness, is shown by the length *cf*. If a water sample shows negative hardness, point *f* will lie somewhere along the line *bc*, in which case segment *fc* will geometrically represent the amount of negative hardness.

The sulfate-carbonate ratio, if the water is completely softened by zeolites for boiler feed, is indicated by the ratio of segments *ab* to *bc*, or the slope of the diagonal *ac*.

As it stands, the diagram pairs off cations and anions by assigning them homologous positions. No imaginary compounds are hypotheticated. All graphical relationships arise solely from the choice of appropriate positions for the various ions.

For waters constitutionally similar but varying no matter how widely in total concentration, rectangular diagrams are geometrically similar. Only the size will change.

If a water undergoes change chemically, its diagram will vary in size, shape, or in special cases, merely by segmentation.

Although the width of the diagram for a typical natural water may become relatively small by elimination of bicarbonate through treatment to its solubility limit, the figure will in general retain its height except in cases where sulfate is changed intentionally by addition of some soluble sulfate, or is reduced by barium softening.

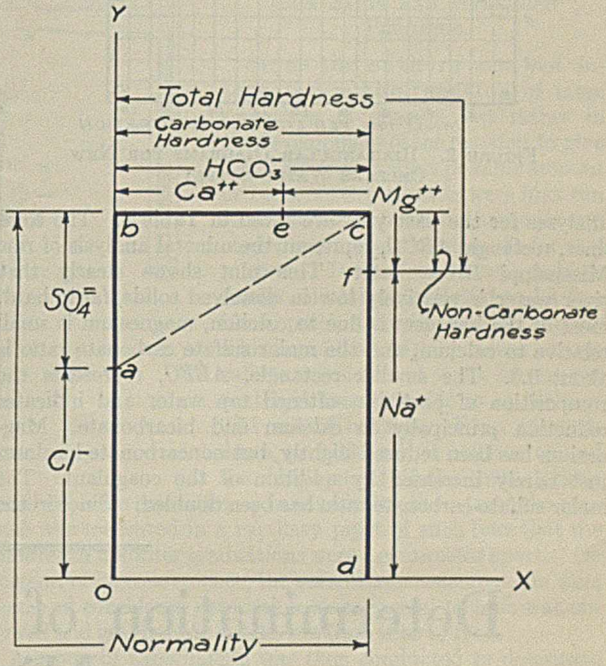

Figure 1. Construction and Some Properties of Rectangular Diagram

In special instances of waters having unusual composition, such as those from some mineral springs, any rarely occurring ions may be included in the diagram in positions occupied by chemically similar ions. For highly siliceous water, the silicate radical should be included in the figure.

In segment *bc* the carbonates have been reduced to equivalent bicarbonate ion mainly because the bicarbonate condition is usually associated with natural waters. If preferred, this detail may be reversed and the carbonate ion plotted instead. If maximum differentiation is desired, the proportion of carbonate and bicarbonate may be indicated by a secondary division along line *bc*. Free carbon dioxide may be appended in the diagram by extending line *bc* across its intersection with the vertical *dc*. Since the ratio of free carbon dioxide to the bicarbonate alkalinity in many waters is an index of the pH, as shown by Greenfield and Baker (*2*), the diagram affords a graphic approximation thereof. When representing acid mine or volcanic waters, the total amount of titratable hydrogen ion should be plotted as a cation, preferably along the upper base, *bc*. Similarly to represent the causticity of boiler waters, the hydroxyl ion should be plotted as a segment along *bc*.

APPLICATIONS

As an illustration of the utility of the rectangular diagram, a specific application of this method to represent the municipal water supply of New Orleans both before and after purification by the lime-iron process is given in Figure 2. Average analyses for the past year are given in Table I. The solid lines, rectangle *ABCD*, represent the mineral analysis of raw Mississippi River water. This plot shows clearly that river water is relatively low in dissolved solids, fairly hard, most of the hardness is due to calcium, magnesium is small relative to calcium, and the molar sulfate carbonate ratio is about 0.5. The smaller rectangle, *AEFG*, represents the composition of partially softened tap water and indicates reduction principally in calcium and bicarbonate. Magnesium has been reduced slightly, but noncarbonate hardness just barely increased by addition of the coagulant. The molar sulfate-carbonate ratio has been doubled. Since in the analyses sodium is obtained by calculation, the difference between the values reported for this ion in river and in filtered waters arises from cumulative errors in sampling, storage, and analysis. It should be noted that free carbon dioxide in river water and residual bicarbonate alkalinity in treated water are plainly indicated in the plot.

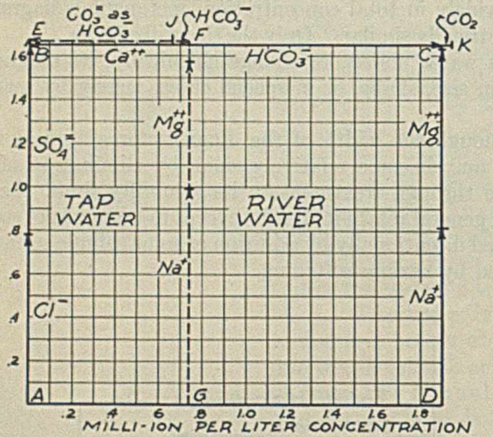

FIGURE 2. RECTANGULAR DIAGRAMS FOR NEW ORLEANS WATER SUPPLY

TABLE I. AVERAGE ANALYSES OF MISSISSIPPI RIVER WATER AND OF NEW ORLEANS TAP WATER FOR 1931

ITEM	$\frac{1}{\text{EQUIV. WT.}}$	RIVER WATER		TAP WATER	
		P. p. m.	*Milli-equiv./liter*	*P. p. m.*	*Milli-equiv./liter*
SiO_2	....	5.9	...	7.8	...
Fe_2O_3 Al_2O_3	....	0.0	...	0.0	...
CATIONS:					
Ca	0.0499	38.6	1.926	16.8	0.839
Mg	0.0822	10.0	0.822	7.1	0.584
Na	0.0435	18.5	0.806	22.8	0.992
ANIONS:					
HCO_3	0.0164	115.9	1.900	45.0	0.738
SO_4	0.0208	41.9	0.872	43.0	0.895
Cl	0.0282	27.7	0.782	27.7	0.782
Solids by analysis (all HCO_3 as CO_3)		201.5		148.1	
Solids by evaporation		221		158	
Incrustants (as $CaCO_3$)		29.4		33.3	
Alkalinity (as $CaCO_3$):					
Methyl orange		95.0		36.9	
Phenolphthalein		0.0		16.4	
Free CO_2		1		0.0	

If all hardness were removed by zeolite treatment, the rectangle *AEFG* would still show the anions in the completely softened effluent, but the sides *EF* and *FG* would now represent sodium.

A single set of related rectangles has thus effectively described the characteristics of a given water and its modifications.

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Determination of Benzene in Solvent Mixtures

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A SIMPLE and rapid method for the detection and estimation of benzene in solvent mixtures, of sufficient sensitivity to be further adapted to the determination of the concentration of benzene vapors in air when of interest from a health standpoint, has been deemed necessary.

This method should make the results attainable immediately in the plant without reverting to the laboratory. There are data available (*7*) to show that concentrations of benzene in air as low as 100 parts per million are objectionable. Since the type of absorption apparatus usually employed for collecting samples of vapors in air handles a liter of air per minute, a 30-minute run would make only about 0.012 ml. of benzene available when the above concentration occurs. Consequently, it was considered necessary to have a method of sufficient sensitivity to detect this small amount.

This discussion will be confined to a survey of possible methods, their relative advantages and disadvantages, and a description of sufficient experimental data covering two methods investigated in the laboratory, one of which fulfils the above requirements rather well and is adaptable where there is as little as 0.010 ml. of benzene available in the liquid phase. In a subsequent work the authors hope to show that this method is also adaptable to the determination of benzene in air.

POSSIBLE METHODS

Four reactions were found in the survey of the literature which gave promise of being applicable.

1. Bromination in presence of anhydrous aluminum bromide (*4*).
2. Nitration with a mixture of concentrated sulfuric and fuming nitric acids (*5*).

3. The "pernitric acid" method (*6*).
4. The oxidation method with hydrogen peroxide in presence of iron salts (*2*).

Bromination. The method of Gustavson (*3*) for the detection of aromatic hydrocarbons in gasoline is based on complete bromination in the presence of anhydrous aluminum bromide. The hexabromobenzene and the pentabromotoluene are crystalline products, whereas the aliphatic bromine compounds are liquids. Because of this, the hexabromobenzene and pentabromotoluene may be filtered off and weighed. Schultz (*4*) has shown that even a few milligrams of benzene or toluene can be determined in air in the presence of ethylene. For the purpose desired, this method is regarded as unsatisfactory by the authors for the following reasons: The necessity of using bromine and aluminum powder was objectionable in field work; washing, drying, and weighing the precipitate are manipulations which are not feasible in field work; and the test for benzene is not specific.

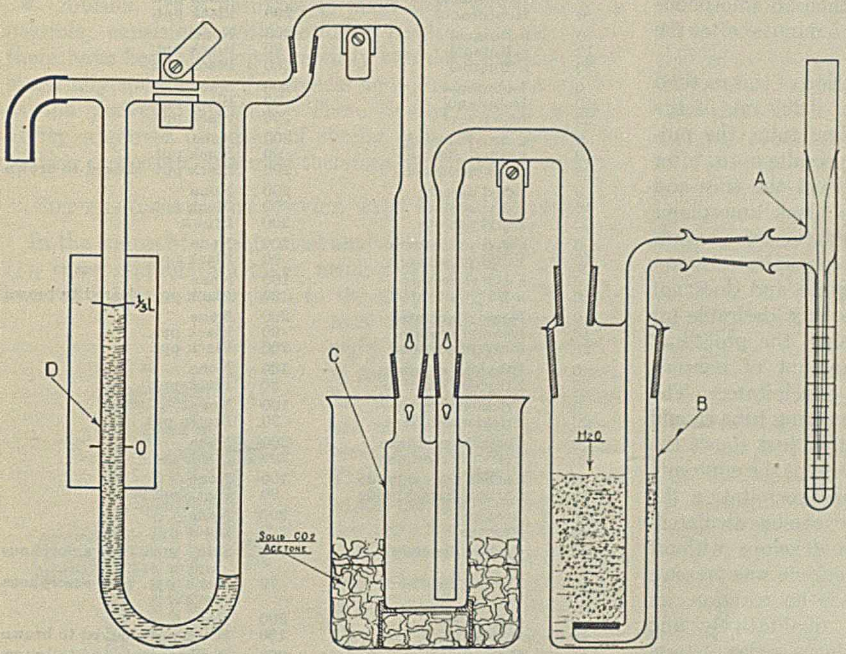

Figure 1

Nitration with Concentrated Sulfuric and Fuming Nitric Acids. This method involves, after the absorption and nitration of the benzene by a mixture of concentrated sulfuric and fuming nitric acids, the steam distillation of the nitration product, *m*-dinitrobenzene. The *m*-dinitrobenzene is quantitatively reduced in an excess of standard titanous chloride, the excess of this reagent being estimated by ferric chloride using potassium thiocyanate as indicator. In the words of the investigator (*5*), "The method is admitted to be somewhat cumbersome and slow, but it is specific for benzene in the presence of many compounds known to be interferences in previously used methods. It will satisfactorily estimate benzene for hygienic purposes in the presence of as much as four times as much toluene as benzene, which is a strong point in its favor." In view of the foregoing, this method does not meet the authors' requirements.

Pernitric Acid Method. This method as used by Trufonow (*6*) is as follows: To 2 ml. of the sample add 4 ml. of an equivolume mixture of 4 per cent sodium nitrite solution and a 3 per cent hydrogen peroxide solution. Shake thoroughly. Add 2 ml. of 2 *N* sulfuric acid and again shake thoroughly. Allow to stand for one minute and remove 3 ml. of lower (aqueous) layer with a pipet. To these 3 ml. add a piece of sodium hydroxide about the size of a small pea. Formation of a distinct brick-red ring at bottom of the test tube indicates presence of benzene.

This method, as well as slight improvements on it, such as use of nitric acid and hydrogen peroxide in place of sodium nitrite, hydrogen peroxide and sulfuric acid mixture and also alcoholic potassium hydroxide in place of solid sodium hydroxide, were tried. The limit of sensitivity was 0.05 ml. of benzene, and in this range one ml. of toluene produced approximately the same color reaction.

This method is regarded as unsatisfactory because the preparation of nitric oxide or its transportation in sufficient amount in the field is relatively inconvenient, and because toluene seriously interferes at the lower limits of sensitivity on the reaction.

Oxidation Method by Means of Iron Salts and Hydrogen Peroxide

Since the authors were not interested in the reaction of large quantities of benzene but rather in the development of the reaction to give a test for the smallest possible amount of benzene, experiments were first run to arrive at the optimum amounts and concentrations of the reagents for this purpose. It was found that a reddish brown coloration developed and a fine black precipitate was formed on the addition of 5 ml. of 0.5 per cent ferrous sulfate solution and 2 ml. of one per cent hydrogen peroxide to as little as 0.01 ml. of benzene. Even amounts down to 0.005 ml. of benzene caused the development of the characteristic reddish brown coloration. In conducting these tests, the benzene was measured in a capillary pipet of such bore that the hundredth milliliter graduations were a centimeter apart. On account of its convenience, the volumetric measurements were used and considered permissible since careful technic was observed and gravimetric checks run from time to time.

A group of experiments was then conducted to determine whether other solvents interfered with this reaction. It was found that most other solvents inhibited the reaction, and that generally the more water-soluble, the smaller the amount necessary to cause interference.

Description of Apparatus. In order to avoid this interference, an apparatus was designed to remove the more water-soluble substances from the solvent mixture. This is illustrated in Figure 1. It consists of a vaporizing tube, *A*, a bubbler type absorption bottle, *B*, and a trap, *C*, immersed in a freezing mixture of solid carbon dioxide in acetone. These units are joined by ground-glass connections. A rubber tube attached to the flowmeter leads to suction. The capillary part of the vaporization tube is graduated to 0.02 ml. and has a capacity of slightly more than 0.3 ml.

Experimental Procedure. One- to three-tenths milliliter of the solvent mixture is placed in the vaporizing tube, and air drawn through the apparatus at the rate of one-third liter per minute. To facilitate vaporization, a capillary is inserted well into the vaporizing tube. The vapors are bubbled through the absorption bottle in which are placed 25 ml. of water. A small amount of pure benzene is run through the apparatus previously in order to saturate the water under these conditions. Most of the benzene and a small portion of the more water-immiscible solvents pass over into the trap which is placed in an acetone–solid carbon dioxide bath. Here the benzene is frozen out of the air stream and deposited. After passing air through the system for 2 minutes, the trap is removed. Five milliliters of 0.5 per cent ferrous sulfate are directed down the inlet tube, followed immediately with 2 ml. of one per cent hydrogen peroxide. Both these reagents should be made up shortly before running the tests. The trap is shaken 2 minutes and the contents poured into a test tube. If benzene is present in amounts of 0.010 to 0.050 ml. in the solvent mixture added to the vaporizing tube, a brown coloration suddenly develops and then an amorphous black precipitate. This may occur in 2 to 5 minutes after the crystals in the trap have melted.

A procedure which assisted in the utilization of this method quantitatively was developed as follows: 0.200 ml. of the solvent mixture is placed in the vaporizing tube, the procedure outlined above is followed, and the results noted after the reaction mixture has been removed from the trap and allowed to stand for 3 minutes. If the black amorphous precipitate is formed, 0.010 ml. or more benzene was present. (Between 0.010 and 0.012 ml., the black precipitate is produced in an exceedingly finely divided state and does not coalesce or readily settle out. Therefore, it is desirable for the one conducting the test to run through the procedure and determine exactly the minimum amount of benzene which, in his opinion, gives the black precipitate.) The total amount of solvent placed in the vaporizing tube should then be decreased until the reaction mixture just shows the black amorphous precipitate. Since 0.010 ml. is the minimum amount of benzene which will produce this precipitation, the percentage of benzene in the solvent mixture can be calculated.

If the characteristic brown coloration develops without the black precipitate, 0.005 ml. or more benzene was present. Both in this case and also when there is no reaction, an indication of the presence of benzene, qualitatively and quantitatively, may be obtained by running a series of tests in which measured amounts of pure benzene are added to the solvent mixture.

Upon the addition of 1 ml. of 2 *N* nitric acid, the black amorphous precipitate will dissolve and the solution may then be diluted with water and compared with standards. This colorimetric method permits greater accuracy in the quantitative estimation of benzene.

If carbon disulfide is present, amorphous sulfur is liberated. This is of course not dissolved on the addition of the nitric acid and should be filtered from the solution. The benzene may then be estimated from the coloration of the filtrate.

Inasmuch as this reaction is decidedly complicated, yielding a mixture of phenol, catechol, hydroquinone, and the black amorphous precipitate mentioned above, it could hardly be expected that the colors of the resultant liquid described in the preceding paragraph would lend themselves to anything more that a rough quantitative estimation, except over a very narrow range such as around 0.010 ml., as described above. For the same reason it is highly important to observe the same technic in all tests. However, the entire estimation takes less than 10 minutes to run, so the number of these estimations can be run rather economically in order to get the desired quantitative accuracy.

Table I shows the results obtained with the reaction on mixtures of benzene and various other solvents. The solvents listed include most of those ordinarily used for industrial operations and having boiling points relatively near that of benzene. Solvents boiling at temperatures appreciably higher than the boiling point of benzene were not included, since they would not be sufficiently vaporized under the experimental conditions to impede the reaction.

TABLE I. EXPERIMENTAL RESULTS

AMT. OF BENZENE *Ml./1000*	OTHER SOLVENTS	AMT. TAKEN *Ml./1000*	REACTION
0	Toluene	200	None
10	Toluene	90	Black ppt.
20	Toluene	200	Black ppt.
0	Xylene	200	None
10	Xylene	90	Black ppt.
20	Xylene	200	Black ppt.
0	Methanol	200	None
10	Methanol	90	Black ppt.
20	Methanol	200	Black ppt.
0	Ethyl alcohol	200	None
10	Ethyl alcohol	90	Black ppt.
20	Ethyl alcohol	200	Black ppt.
0	Isopropanol	200	None
10	Isopropanol	90	Black ppt.
20	Isopropanol	200	Black ppt.
0	*n*-Butanol	200	None
10	*n*-Butanol	90	Black ppt
20	*n*-Butanol	200	Black ppt.
0	Isobutanol	200	None
10	Isobutanol	90	Black ppt.
20	Isobutanol	200	Black ppt.
0	*n*-Amyl alcohol	200	None
10	*n*-Amyl alcohol	90	Black ppt.
20	*n*-Amyl alcohol	200	Black ppt. cleared to brown
0	Ethyl acetate	200	None
10	Ethyl acetate	90	Black ppt.
20	Ethyl acetate	200	Brown
0	Ethyl propionate	200	None
10	Ethyl propionate	90	Black ppt.
0	*n*-Butyl acetate	100	None
10	*n*-Butyl acetate	90	Black ppt. cleared to brown
0	Isoamyl acetate	200	None
10	Isoamyl acetate	90	Black ppt.
20	Isoamyl acetate	200	Black ppt.
0	Ethylene chloride	100	None
20	Ethylene chloride	20	Black ppt.
0	Trichloroethylene	100	None
20	Trichloroethylene	20	Brown ppt.
0	Tetrachloroethane	200	None
20	Tetrachloroethane	200	Black ppt.
0	Carbon tetrachloride	100	None
10	Carbon tetrachloride	90	Black ppt.
0	Acetone	200	None
20	Acetone	200	Black ppt.
0	Carbon disulfide	100	Soln. greenish, amorphous sulfur ppt.
10	Carbon disulfide	90	Black ppt. plus amorphous sulfur
0	Cellosolve	200	None
10	Cellosolve	100	Black ppt. cleared to brown
20	Cellosolve	200	Black ppt. cleared to brown
0	Gasoline	200	None
20	Gasoline	200	Black ppt.
	MIXTURES		
0	Equivolume mixture of all solvents above, except carbon disulfide	200	None
20	Equivolume mixture of all solvents above, except carbon disulfide	200	Brown ppt.
0	Equivolume mixture of toluene and xylene	200	None
20	Equivolume mixture of toluene and xylene	200	Black ppt.
0	Equivolume mixture of 6 alcohols above	200	None
20	Equivolume mixture of 6 alcohols above	100	Black ppt.
0	Equivolume mixture of 3 acetates above	200	None
20	Equivolume mixture of 3 acetates above	200	Black ppt.

ACKNOWLEDGMENT

The authors wish to express their appreciation to Eimer and Amend, New York, N. Y., for the helpful suggestions in designing the apparatus shown in Figure 1.

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RECEIVED June 10, 1932.

New Aliquot and Filter Devices for Analytical Laboratories

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In these laboratories large numbers of mechanical analyses of soils have to be made as a part of the service routine. It is desirable to make these as rapidly as is possible, consistent with accurate results. In this work there have been developed recently two devices which have materially speeded up the process and diminished errors due to the personal equation. These devices are of general utility wherever processes of similar type are employed in routine procedure, and may therefore be of general interest.

Suspension Aliquot Device with Depth Control

In the course of a mechanical analysis by the pipet method (*1*), three aliquots are taken using a Lowy pipet, which is lowered into the suspension to the proper depth. In ordinary routine, suspensions of eight soil samples are placed in sedimentation cylinders for pipetting. The samples are pipetted with a regular time interval between them. This means the depth at which the aliquot is taken is the same for the set of eight samples. It was with this idea in mind and in an effort to eliminate errors in lowering the pipet to the correct depth that the following device was developed. It makes possible the lowering of the pipet definitely to any prearranged depth and repeating the operation any number of times without a change in setting.

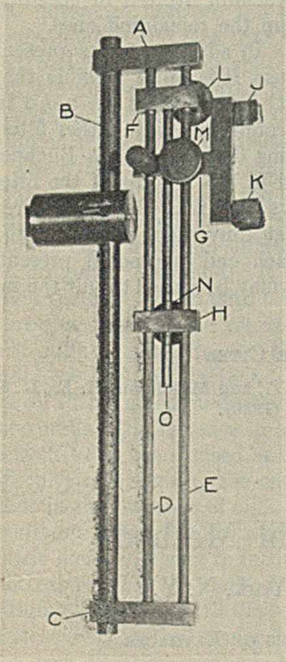

Figure 1. Suspension Aliquot Device

From Figure 1 it will be seen that the device consists of a frame, *A*, *B*, *C*, supporting two parallel rods, *D* and *E*, which serve as rails. Upon them three parallel blocks, *F*, *G*, *H*, slide. *G* is provided with clips, *J* and *K*, with which the pipet is secured firmly. *F* and *H* serve as limits, limiting the travel of *G*. *L*, *M*, and *N* are thumb wheels used in securing the position of *F*, *G*, and *H*. *O* is a calibrated rod used in adjusting the distance between *F* and *H*—i. e., depth of pipetting.

For smooth operation, a good mechanical construction is necessary. Blocks *F*, *G*, and *H* should have good bearing surfaces, and if rods *D* and *E* are in alignment, no jamming or chattering of *F*, *G*, or *H* should result. Any shaking of *G* would result in undue disturbance of the suspension.

In operating, the procedure is as follows: The pipet is inserted in clips *J* and *K* provided on *G*. *N* is loosened and the upper edge of *H* is set against the scale on *O* at the desired depth of pipetting. *N* is tightened and requires no further attention until a new depth is used. The pipet tip is brought directly over the suspension. *M* is loosened and *G* allowed to descend until the tip of the pipet touches the top of the suspension. *F* has also descended with its lower face in contact with the upper face of *G* (Figure 2). *L* is tightened and *G* allowed to descend again until its lower surface is in contact with the upper surface of *H*. At this point the pipet has reached the desired depth and the aliquot is taken. When this has been done, *L* is released and *G* is raised as far as it will go, carrying with it *F* and its associated parts. When the pipet is clear of the suspension, *M* is secured and the pipet is removed from *J*, *K*. The time consumed in the complete operation, exclusive of filling the pipet, usually does not exceed 10 seconds.

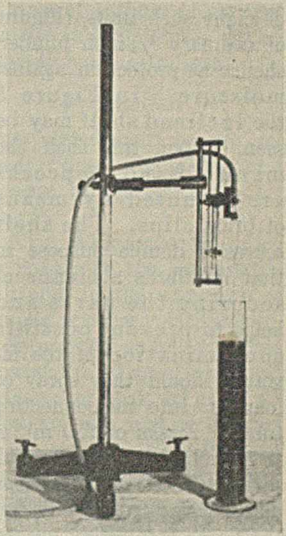

Figure 2. Suspension Aliquot Device in Place

Over a period of 15 months the device has proved to be accurate, rapid, trouble-free, and labor-saving. Its cardinal advantage lies in the feature whereby, once set for a particular depth, the accuracy of this most important factor is insured throughout the series of samples.

New Filter Rack

In the analysis of a large number of samples by the pipet method (*1*), a considerable amount of filtering is necessary. The filtering is done by means of Pasteur-Chamberland filter tubes, using the laboratory vacuum, and the filtrates are saved for evaporation and determination of soluble material. To aid in this work, a filter rack was developed. Figure 3 shows this device as used in this laboratory, connected to the filters shown in the foreground. Figure 4 shows the

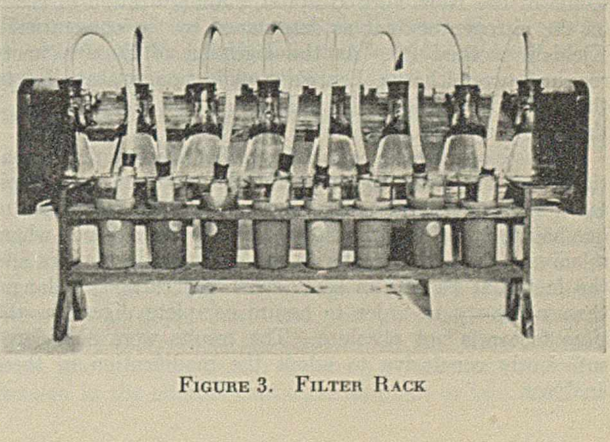

Figure 3. Filter Rack

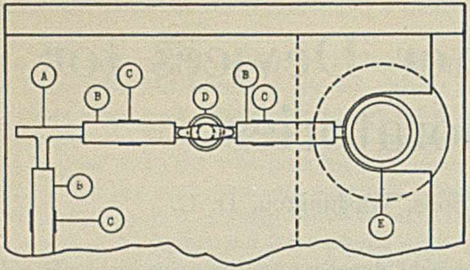

Figure 4. Top View of Unit of Rack
A, glass T; *B*, rubber tubing; *C*, clamp; *D*, stopcock; *E*, suction flask

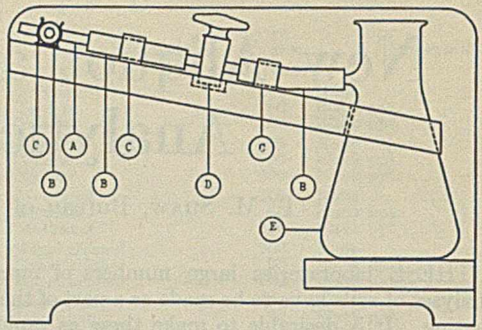

Figure 5. Side View of Unit of Rack
A, glass T; *B*, rubber tubing; *C*, clamp; *D*, stopcock; *E*, suction flask

top view of one of the units, and Figure 5 is a side view of the same unit. As now constructed, the rack is composed of eight such units (Figure 6). The frame is constructed of ordinary ³/₄-inch lumber finished with a heavy coat of shellac as protection against moisture. In Figure 5 the inclined shelf may be seen. Upon this shelf the manifold and stopcocks are mounted by means of brass clips. The shelf serves a double purpose in that it affords a means of securing the parts and helps to prevent possible contamination of the filtrates should they spray or foam up into the connecting tubes. Flasks of 250 ml. capacity are used, and since 200 to 700 ml. of filtrate are required, the flasks have to be emptied several times. This is accomplished easily, as the filters are disconnected from the flasks and removed in a group, leaving the flasks completely accessible from the front and in position to be disconnected with an ease comparable to that of breaking an electrical connection by means of the conventional attachment plug. After emptying, the flasks are replaced in the same manner. Since the rubber connections are securely fastened and in individual units, the analyst is spared the confusion attached to the usual tangle of loose tubing, glass T connections, and flasks. The individual stopcocks afford several conveniences: The rack may be used for less than the usual number of samples by simply turning off the unused units, or, if a few samples filter before the others of the group, they may be cut out and all of the vacuum utilized in speeding up the remaining ones.

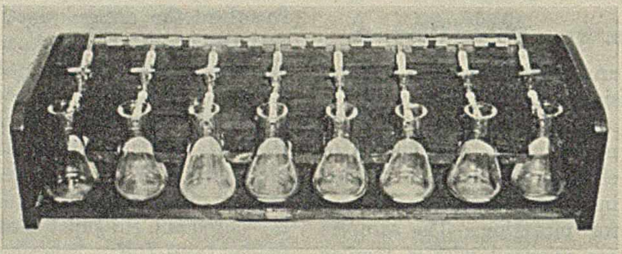

Figure 6. Filter Rack of Eight Units

In addition to its present use, it is quite possible that the rack may be used in connection with other filtering devices such as Büchner funnels, conventionally mounted in the mouths of the filter flasks. Uneven distribution of vacuum may easily be cleared up by inserting additional T's at convenient places in the manifold; one connection at each end is used at present. The number of units in the rack may be varied to suit the individual need of the user.

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Selenium in Determination of Nitrogen by Kjeldahl Method

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Lauro (*2*), from results on cereal extracts, has suggested the use of selenium in place of copper sulfate as a catalyst to reduce the time of digestion in Kjeldahl nitrogen determinations. In the aqueous extracts used in the Allergy Clinic of the New York Hospital, standardization is based on the nitrogen content as determined by the conventional Kjeldahl method (*1*). As the digestion of these extracts required several hours, Lauro's modification was applied to their standardization. It will be evident from Table I that these extracts are of wide variety.

Analyses of extracts, on which parallel nitrogen determinations were run using copper sulfate and amorphous precipitated selenium, showed checking results with a decrease of one-half to two-thirds the time necessary for digestion where selenium was used. Owing to the variation in burners and the fact that heating in some cases was carried on longer than necessary in order to assure complete digestion, the time factor is not absolute. The results were considered sufficiently conclusive to adopt the modification in these analyses.

Table I. Analyses of Extracts

Extract	Copper Sulfate		Selenium	
	Mg. N/cc.	*Min.*	*Mg. N/cc.*	*Min.*
Date	0.53		0.55	
			0.53	
Pumpkin	0.17		0.18	
Potato flour	0.07	180	0.06	120
	0.04			
Horse epithelium	0.26	150	0.27	75
Green pepper	0.88	300	0.86	150
Guinea pig epithelium	1.26	165	1.26	90
Pumpernickel	0.58		0.56	
Birch pollen	0.43	140	0.42	50
Ash pollen	0.58	140	0.60	75
Oak pollen	0.92	175	0.94	135
Poplar pollen	1.00	170	1.00	85
Plantain pollen	0.43	215	0.45	135
Ragweed pollen 1	0.39	180	0.37	90
Ragweed pollen 2	0.98	170	0.99	95
Ragweed pollen 32	0.62	165	0.63	90
Timothy pollen 31	0.31	170	0.32	90
Timothy pollen 32	0.40	135	0.40	60
Cashew nut	3.73	180	3.72	150
Urine 1	7.29	75	7.26	35
Urine 2	9.85		9.90	

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Determination of Sulfuric Anhydride in Sulfonated Oils

New Titration Method

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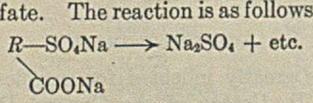
A new titration method is outlined, based upon the absorption of alkali when the sulfonated oil is ashed. It is more rapid than the old acid-boiling titration method, particularly where many analyses are to be run at the same time. The new method yields better check results and requires fewer reagents. The values for organic sulfur are higher, indicating either more complete decomposition or the presence of true sulfonic acids. The method, however, does not determine the organic sulfur in sulfonated mineral oils or other nonsaponifiable oils or salts. It is suggested that it may also be used as a qualitative test for sulfonation.

ONE of the most important determinations in the analysis of sulfonated oils is the amount of organically combined sulfuric anhydride. This may be in the form of a sulfate—that is, a sulfonic acid ester—or a true sulfonic acid. The former is characterized by the formula $R—O—SO_3H$ and the latter by $R—SO_3H$, where R represents the fatty radical. An essential difference between the two compounds is the fact that the sulfonic acid esters split off sulfuric acid when heated with mineral acids, whereas the true sulfonic acids are stable under such conditions.

The writer (*3*) in 1917 proposed a volumetric method, now widely used in practice, for the determination of organically combined sulfate in sulfonated oils of the ester type, which eliminated two barium sulfate determinations required in the old gravimetric method. It is based upon the principle that when the oil is boiled with mineral acids, one molecule of the neutralized sulfonated oil liberates one molecule of sodium acid sulfate, according to this formula: $R—O—SO_3Na + H_2O \longrightarrow ROH + NaHSO_4$. The method consists in heating the oil with a given quantity of standardized sulfuric acid and determining the increase in acidity after boiling. Some objections have been raised against the method because of the difficulty in observing the end point, since the titrations are made in the presence of oil. It has also been stated that the results are somewhat low when compared with the acid gravimetric method, owing to incomplete decomposition. Finally it is claimed that the method is inapplicable in the presence of sodium acetate since all the sodium is not completely titrable in presence of methyl orange, the indicator used.

A new titration method, hereafter called "ash-titration" method, is outlined below which is based upon the principle that when the completely neutralized sulfonated oil is ashed, the organically combined sulfate is quantitatively converted into sodium sulfate. The reaction is as follows:



$$R—SO_4Na \longrightarrow Na_2SO_4 + \text{etc.}$$
$$\searrow COONa$$

It will be noticed that one mole of sodium hydroxide or its equivalent combined with the carboxyl group corresponds to one mole of sodium sulfate. Since the former can be accurately determined, it follows that the organically combined sulfate can readily be estimated. The method consists in ashing a mixture of the oil and excess standardized caustic, and finding the loss in titrable alkali after ignition. The loss in alkalinity—i. e., the difference between the alkali added plus the fixed alkalinity of the sample and the alkali found after ignition—is calculated to organically combined sulfate according to the following formula: one mole KOH $\approx$ one mole SO_3. This relationship, instead of two moles of potassium hydroxide being equivalent to one mole of sulfate, holds true since the sulfuric acid in the oil is already half neutralized.

PROCEDURE

Two determinations are required: "fixed alkalinity," and "decrease in alkalinity after ashing."

FIXED ALKALINITY (A_F). This refers to the nonvolatile alkali and, in the absence of ammonia or other volatile alkali, it is determined as follows: Ten grams of the oil are dissolved in 50 cc. of water in a 250-cc. Erlenmeyer flask, 50 cc. of 25 per cent neutral salt solution added, and the mixture titrated to an approximate end point in the presence of 5 drops of methyl orange (1 per cent solution, dissolved hot, cooled, and decanted). The contents are transferred to a separatory funnel, the flask rinsed with 3- to 15-cc. portions of ether, which are added to the separatory funnel, and the mixture made distinctly acid with standardized solution. After shaking and separating, the lower layer is drawn off into a 250-cc. beaker. The ether layer is washed with 15-cc. portions of the salt solution until the wash water is neutral to methyl orange, first rinsing the flask with them. The combined water layers are warmed to expel ether, two drops of methyl orange are added, and the titration completed, approaching the end point with acid. The result is calculated to milligrams of potassium hydroxide per gram of sample and denoted by A_F.

In the presence of ammonia, the fixed alkalinity is determined in the following manner: Five grams of the oil are dissolved in 100 cc. of water in a 400-cc. beaker, 25 cc. of 0.5 N sodium hydroxide are added, and the solution boiled until wet litmus paper no longer indicates ammonia. The rest of the procedure is according to the above. The fixed alkalinity in this case is given by the difference in the alkalinity after boiling and the amount of alkali added, and is readily calculated according to the following formula (acid and alkali used in titration, in milligrams of potassium hydroxide):

$$\text{Fixed alkalinity } (A_F)\text{, mg. KOH per gram} = \frac{\text{total acid} - \text{total alkali}}{\text{sample}}$$

In this connection it is to be observed that the change in the presence of methyl orange at the neutral point when titrating with acid is from a yellow color to a faint orange. The following method for noting this change accurately is suggested: Titrate to an approximate end point, leaving the solution slightly but distinctly on the alkaline side, and transfer about 30 cc. into a 100-cc. beaker (beaker 1). Continue with the titration in the original beaker, adding one or two drops of the acid at a time, and transfer after each addition 30 cc. of the solution into another 100-cc. beaker (beaker 2). If upon comparing beakers 1 and 2 there is no change in color, contents of the latter are poured back into the original beaker and the titration continued until a change is just noted. Beaker 1 is now carefully titrated until it just matches beaker 2. Very slight change in the color of the solution is readily detected by this procedure, whereas over-titration is likely by the usual method.

DECREASE IN ALKALINITY AFTER ASHING. Five grams of the oil in a 30-cc. platinum or porcelain evaporating dish are mixed with an equal quantity of 1 N sodium hydroxide, using a small glass rod for stirring. The solution is evaporated to dryness either in an oven or over a free flame, the residue heated until it catches fire, allowed to burn gently, and the ash ignited for about 10 minutes, or until the carbon is nearly consumed. The stirring rod is now removed and wiped with moistened ashless filter paper, the latter is added to the oil, and the stirring rod is put in the beaker in which the titration is to be made. The residue is again heated until the filter paper is ashed, and then oxidized with 3 to 5 drops of 30 per cent neutral hydrogen peroxide. The ash is now heated to a dull red heat, covering the dish to prevent loss by spattering. If not practically free from carbon, the treatment with peroxide is repeated. After cooling, the dish is covered with water in a 250-cc. beaker and brought to a boil. It is now titrated in the presence of methyl orange with 0.5 N sulfuric acid, then about 0.5 cc. excess added, and boiled about 5 minutes to expel carbon dioxide. Half normal caustic is now added until slightly but distinctly alkaline, the dish and small stirring rod removed, and the titration finished as given under Fixed Alkalinity. The combined sulfate is given by the following formula, where Al represents total milligrams of alkali and Ac the amount of acid added or used during the titration:

$$\text{Combined } SO_3, \% = \left(\frac{Al - Ac}{\text{sample}} + A_F\right)\frac{8}{56.1}$$

DISCUSSION

Where the fatty acids in the oil have been neutralized with ammonia only, the oil will evidently contain no titrable fixed alkali. Moreover, part or all of the organically combined sulfate may have been neutralized with ammonia. In that case, upon boiling with caustic soda the ammonium sulfonate is converted into the sodium salt, with the liberation of ammonia and absorption of fixed alkali that can no longer be determined by titration. The fact that the fixed alkali is absorbed by the sulfonic group in this manner is indicated by a negative result obtained by means of the alkalinity formula, which should be carefully retained for use in subsequent calculations.

The writer finds that sodium acetate may be titrated with a fair degree of accuracy with thymol blue as the indicator. The pH (*1*) of 0.2 molal sodium acetate is 8.3, the same concentration of acetic acid is 2.86, and the color change of thymol blue is 1.2 to 2.8 (red to yellow). Since the pH of acetic acid is above the pH of the color change of thymol blue, it can exert only a very slight effect on the indicator. Hence NaAc may be titrated with thymol blue the same way as soap is titrated in the presence of methyl orange. However, the end point in the former case is not so sharp as might be desired.

The least accurate factor in the method is the titration, which may vary by as much as 0.1 cc. of half normal solution, or 2.8 mg. This affects the result on a one-gram sample by 2.8 × 8/56.1, or 0.4 per cent sulfate. By increasing the size of the sample taken for analysis, the error is correspondingly reduced. With a 5-gram sample, the accuracy of the method is approximately 0.1 per cent sulfate, which is about the variation found in the data given below. It must also be evident that errors due to mechanical losses are smaller the less the excess of alkali added to the oil, the losses being a minimum or zero where there is no excess alkali present at all. It seems that excess alkali is not required in order to get accurate results. A number of tests were made with excess alkali varying from zero to an amount equivalent to twice the sulfate content, with practically identical results.

EXPERIMENTAL RESULTS

A number of analyses for organically combined sulfate in commercial sulfonated products by the old and new titration methods are given in Table I.

TABLE I. ORGANICALLY COMBINED SULFATE IN SOME COMMERCIAL SULFONATED OILS AND SALTS

SAMPLE	DESCRIPTION	ORGANICALLY COMBINED SO_3 Old method	New method	
		%	%	%
1	Sulf. olive oil	4.90	5.28	5.29
2	Sulf. castor oil	5.09	5.41	5.47
3	Sulf. castor oil[a]	3.30	3.41	3.39
4	Sulf. neat's-foot oil[b]	1.87	2.08	2.01
5	Sulf. cod oil[c]	3.44	3.51	3.49
6	Sulf. oil[d]	8.92	9.48	9.48
7	Silk finishing oil	4.82	5.09	5.00
8	Silk soaking oil	1.97	2.10	2.14
9	Sulf. mineral oil[e]	..	Neg.	Neg.
10	Isobutyl naphthalene sodium sulfonate[e]	..	Neg.	Neg.

[a] Completely neutralized with caustic soda.
[b] Contained 0.88% NH_3, mostly as ammonium sulfonate.
[c] Contained 1.45% NH_3, mostly as ammonium sulfonate.
[d] Highly sulfonated oil of foreign manufacture.
[e] Large amounts of sulfide formed on ashing.

ADVANTAGES OF THE NEW METHOD

The ash-titration method offers the following advantages over the old acid-boiling titration method: It is more rapid, particularly where many such analyses are made simultaneously, gives better check results, and requires fewer reagents. Moreover, the results are consistently higher, indicating either more complete decomposition than by the acid-boiling methods (titration and gravimetric), or the presence of true sulfonic acids. In this connection it is interesting to note that De Groote, Keiser, Wirtel, and Monson (*2*) report that the values for organically combined sulfate determined by the Parr bomb were much greater in some cases than results obtained by any method depending on decomposition by boiling, even for excessive periods, with mineral acid, such as concentrated hydrochloric acid. A sample of a true sulfonic acid of a saponifiable oil not being available at short notice, this phase was not further investigated. It was found, however, that the new method is not applicable to sulfonic acids that are not saponifiable, for example, sulfonated mineral oils, naphthalene sulfonic acid, etc. By taking a small sample for analysis, such as one gram, the method is sufficiently rapid to be used as a qualitative test for organically combined sulfate.

ACKNOWLEDGMENT

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Identification of Common Carbohydrates

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THOUGH some two hundred tests (*9*) for glucose, including different reagents with modifications of conditions, etc., are found in the literature, no one of these is exclusively characteristic for glucose and, indeed, no one physical constant will identify it. Some of the common carbohydrates, such as levulose, starch, mannose, glycogen, and cellulose, can be identified by a single test, but most of the others require two or more tests for reliable identification.

This study was undertaken to develop new tests for certain carbohydrates, to determine the extent of application of old tests, and to formulate a system of identification, based largely on color reaction, of the carbohydrates given in the table. Also an unsuccessful search was made to find a characteristic test for glucose.

A number of conditions have contributed to confusion in the identification of carbohydrates. First, numerous tests have been applied to individual carbohydrates,[1] but most frequently they have not been applied to all common carbohydrates, hence cannot be held to be characteristic. For example, nitroprusside (*14*), permanganate (*1*, *2*), ferricyanide (*3*, *6*), chromate (*7*, *12*, *13*), etc., have been used for glucose, and hydrochloric acid (*10*, *15*) has been applied to levulose. The effects of these and other reagents on many carbohydrates are indicated in Table III.

Another cause of confusion has been the multiplicity of reagents applied and assumed to be characteristic, especially as applied to glucose and levulose. Many are modifications of the same reagent—there are six modifications of Seliwanoff's, ten of Nylander's, and ninety of Fehling's reagents.

Table I. Group Identification of Fructose, Sucrose, Raffinose, and Inulin (F)

In Dil. HCl	Time Heated at 100° C. Min.	Elapsed Time Reading Min.	Colors of (F)	Colors of Other Carbohydrates
$TiCl_4$	2–5	5–20	Deep amber	Agar-agar faintly yellow
Phloroglucinol	20–30	5–20	Fructose, red-brown; others, deep amber	All colors deepened by NH_4OH
Orcinol	15–20	5–20	Raffinose amber; others, yellow	With NH_4OH (F) amber; glycogen, violet-red
Resorcinol	2–5	5–20	Cherry-red	Dextrin, maltose, glycogen, faintly yellow
Benzidine	2–5	5–20	Yellow-amber	Rhamnose, agar-agar, maltose faintly yellow
$SnCl_2$	2–5	5–20	Amber to deep red	

Finally, some of the tests given are characteristic for impurities in the material tested. For example, cobaltous chloride (*11*, *13*) was claimed to be a test for sucrose; we find that it is characteristic for levulose only.

Table II. Reagents

	Reagent	Solvent	Amt. of Reagent %	Time Heated at 100° C. Min.	Elapsed Time Reading Min.	Remarks
a	Water	^{a}				Cellulose insoluble
b	I + KI	H_2O	3	..	..	Heat to expel free iodine; cool
c	Nylander's^b	8% NaOH	6	1	1–5	Reagent catalyzed with $AuCl_3$; (+) bk. ppt's.; (wh) white ppt's.
d	Disch's	^{c}		30	30+	Pentoses brown; hexoses, etc., blue
e	Orcinol	^{d}		1	1–5	See Table III
f	Phloroglucinol	^{e}		1	1–5	See Table III; boiling gives ChR with pectin, gum arabic, and gum tragacanth
g	Na_2CrO_4	H_2O	10	1	1–60	Simple sugars green; pectin, red solution
h	Sodium nitroprusside	H_2O	1	1+	?	Add NH_4OH and heat; (+) green while hot; arabinose green without NH_4OH
i	$KMnO_4$	H_2O	0.1	..	1–60	(+) immediate decolorization; (*) decolor. in 1 hr.
j	Fehling's^f	H_2O		..	60	
k	$K_3Fe(CN)_6$	H_2O	0.5	1	1–5	$+FeCl_3$; brown, negative; greens, positive; maltose, blue
l	Picric acid	H_2O	Sat.	1	1–5	$+NH_3$; nos. indicate depth of colors (red)
m	H_3PO_4	H_2O	85	1	1–60	Yellow to amber to brown to black; nos. = depth of colors
n	$HClO_4$	H_2O	60	1	1–60	Yellow to amber to brown to black; nos. = depth of colors
o	H_2SO_4	H_2O	50	1	1–60	Yellow to amber to brown to black; nos. = depth of colors
p	HCl	H_2O	20	1	1–60	Yellow to amber to brown to black; nos. = depth of colors
q	KOH^g	H_2O	5	1	1–60	Nos. = depth of color; pectin, yellow
r	$(NH_4)_2MoO_4$	H_2O	5	..	60	Add carbohydrate, then $^1/_2$ the vol. conc. H_2SO_4. Nos. = depth of color; rhamnose, green
s	HNO_3	H_2O	25	..	..	Evap. $^2/_3$ for mucic acid
t	H_2SeO_3	50% H_2SO_4	10	1	1–60	Nos. = depth of red
u	Ni_2O_3	^{h}		..	..	Nos. = relative speeds of decolorization of Ni_2O_3
v	Heroine	H_2SO_4	1	..	15	Mostly ambers to brown-blacks^i
w	Codeine	H_2SO_4	1	..	15	Mostly rose to brown-blacks^g
x	$AgNO_3$	Dil. NH_4OH	1	1	1–60	(+) black ppt. or silver mirror; some give brown solution
y	*p*-Tolylhydrazine	Dil. HCl	1	..	1–60	Boiling gives for (+) dichromate color; levulose and sucrose give color and ppts.
z	Table I					

[a] Mono-, di-, and trisaccharoses are sweet and soluble in cold water. Polysaccharoses, except cellulose, dissolve in hot water. Starch, pectin, glycogen, and gum tragacanth dissolve in hot water to give opalescence and foam. Gum arabic gives clear solution and foam. Dextrin and inulin give clear solutions but no foam.

[b] Nylander's reagent: 2 grams of bismuth subnitrate and 4 grams of Rochelle salt dissolved in 100 grams of 8% NaOH.

[c] Prepare 10% solution of diphenylamine in alcohol and add 1 volume to 4 volumes of acetic acid and 5 volumes of HCl (*4*).

[d] To 5 cc. of saturated aqueous solution of orcinol, add 50 cc. of HCl and dilute to 90 cc.

[e] To 0.2 gram of phloroglucinol in 10 cc. of alcohol, add 50 cc. of HCl and dilute to 90 cc. Solution of orcinol or of phloroglucinol in dilute HCl will indicate carbohydrates containing levulose. See Table I.

[f] Fehling's reagent: (1) solution of 36.44 grams of $CuSO_4.5H_2O$ in water diluted to 500 cc.; (2) solution of 125 grams of KOH and 173 grams of sodium potassium tartrate in water diluted to 500 cc.

[g] Usually called Moore's test.

[h] Prepare solutions (*a*) 10 grams of $NiSO_4.7H_2O$ in 1000 cc. of H_2O, and (*b*) 4.8 grams of $K_2S_2O_8$ and 6 grams of KOH in 1000 cc. of H_2O. Use equal parts and let stand—black Ni_2O_3 precipitates. Carbohydrates decolorize this.

[i] With varied times and temperatures carbohydrates give changing colors. A check with a known carbohydrate is revealing and desirable. Perhaps in these reactions, formaldehyde is split off, because colors closely follow Kobert's (*5*, *8*) test for codeine, etc.

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[1] The application of the following reagents, given in the literature as characteristic for glucose, were applied to other carbohydrates and were found to be reactive with many other carbohydrates: mercuric, lead, uranium, vanadium, zinc, ferric, and tin salts; the cresols, naphthols, menthol, thymol, diresorcinol, and nitroso-β-naphthol; dyes such as methylene blue, alizarine red, saffranine, and indigo carmine; amino compounds such as the naphthyl amines, the hydrazines, benzidines, and the phenylene diamines, HBr and HI.

Table III. Effects of Various Reagents on Carbohydrates

	Carbohydrate	a	b	c	d	e	f	g	h	i	j	k	l	m	n	o	p	q	r	s	t	u	v	w	x	y	z
1	Cellulose	–	–	–	Bl	–	–	–	–	–	–	Br	–	–	–	–	–	–	3	–	–	–	R	r	–	–	–
2	Starch	+	+	Wh	Bl	–	–	–	–	*	–	Br	–	–	–	1	–	–	–	–	–	–	–	r	–	–	–
3	Soluble starch	+	+	Wh	Bl	–	–	–	–	–	–	Br	–	rose	–	4	–	–	–	–	5	–	–	–	–	–	–
4	Glycogen	+	+	Wh	Bl	–	–	–	–	+	–	G	–	1	1	1	3	–	3	–	–	1	–	rV	Br	–	–
5	Dextrin	+	+	Wh	Bl	–	Am	–	–	+	+	G	–	–	–	2	–	5	5	–	1	3	–	–	Br	+	–
6	Pectin	+	–	–	Br	–	–	R	+	*	+	G	–	–	1	2	–	Y	–	+	1	1	–	–	Br	+	–
7	Levulose	+	–	+	Bl	Br	Br Bk	+	+	*	+	G	9	9	9	9	9	9	9	–	9	4	Br Bk	Br Bk	+	+	+
8	Mannose	+	–	+	Bl	–	–	+	+	*	+	G	2	1	–	3	1	7	–	–	5	7	V	VP	+	–	–
9	Maltose	+	–	+	Bl	–	Y	+	+	+	+	Bl	2	3	1	5	–	8	6	–	3	9	Am	r	r– Br	+	–
10	Rhamnose	+	–	+	Br	–	Or	+	+	–	+	G	2	2	3	6	–	4	G	–	8	4	orR	R	+	–	–
11	Arabinose	+	–	+	Br	Bl	ChR	+	+	*	+	G	9	1	2	2	–	7	7	–	3	8	r	R	+	–	–
12	Xylose	+	–	+	Br	Bl	ChR	+	+	*	+	G	9	1	–	7	–	7	5	–	7	8	R	R	+	–	–
13	Galactose	+	–	+	Bl	–	Am	+	+	+	+	G	2	1	–	3	–	7	–	+	6	5	–	–	+	–	–
14	Lactose	+	–	+	Bl	–	Am	+	+	–	+	G	2	–	–	3	–	7	6	+	6	2	–	–	+	–	–
15	Raffinose	+	–	–	Bl	Br	Br Bk	–	–	–	–	Br	–	3	2	6	5	–	7	+	8	2	Am Bk	Am Bk	–	+	+
16	Sucrose	+	–	–	Bl	Br	Br Bk	–	–	–	–	Br	–	8	8	8	7	–	8	–	8	2	Br Bk	Am Bk	–	+	+
17	Inulin	+	–	–	Bl	Br	Br	–	–	*	+	G	–	8	7	9	6	–	8	–	5	2	Am	r	–	+	+
18	Glucose	+	–	+	Bl	–	Y	+	+	*	+	G	2	–	–	3	–	8	–	–	2	6	–	–	+	+	–
19	Gum arabic	+	–	Am	Bl Bk	–	–	–	–	+	+	G	–	3	2	6	–	3	2	+	5	1	r	–	–	–	–
20	Gum tragacanth	+	–	Wh	Br Bk	–	–	–	–	+	–	G	–	rose	1	4	–	–	4	+	6	1	R	R	–	–	–
21	Agar agar	+	–	Am	Bl	Br	Br Bk	–	–	–	–	G	–	–	4	4	3	5	8	+	–	–	BrR	vR	–	+	–

Since most reagents used for identifying carbohydrates are not neutral, secondary effects are often produced. With alkalies, yellow to brown colors are developed; with acids, hydrolysis, carmelization, and carbonization result. Under properly controlled conditions of concentration, time, and temperature, these reactions become of great importance in identifying the carbohydrates. For example, if each of the carbohydrates is treated in the cold with 85 per cent phosphoric acid, only fructose blackens in 24 hours; when heated one minute in boiling water, fructose, sucrose, and inulin are indicated. However, if all are heated for a longer time, changes of color from faintly yellow through amber and brown to black result with all carbohydrates. Similar changes of color also result with other acids such as perchloric, sulfuric, hydrochloric, etc. However, under controlled conditions, the different rates of decomposition to yield color become valuable for indicating many of the carbohydrates.

Many of the reagents employed for carbohydrates are oxidizing;[2] toward these levulose shows the greatest ease of oxidation. However, all carbohydrates do not show the same order and rates of oxidation with different reagents. For example, maltose is more easily oxidized by nicklic oxide than galactose; the latter is more easily oxidized by silver nitrate.

With cold solutions, or with solutions heated one minute, and with readings made over extended times, rates of oxidation, hydrolysis, color formations, etc., can be read and their variations indicate the different carbohydrates. Increasing numbers in Table III show increased depth of color for equal times.

To identify some of the carbohydrates, the judgment of color can be confirmed by a repetition of the test on the unknown with another tube containing the suspected known carbohydrate, both materials being treated with the reagent in equal concentrations, temperatures, and times.

One-Test Identification of Certain Carbohydrates

1. Cellulose. Insoluble in hot water.[a]
2. Starch. Blue with iodine.[b] Soluble starch is soluble in cold water.
3. Glycogen. Wine-colored with iodine.[c] Characteristic colors developed when glycogen is heated in dilute hydrochloric acid with certain ortho-diphenolic compounds and solution is made ammoniacal: catechol, deep brown-red; pyrogallol, deep brown; gallic acid, cherry-red; tannic acid, deep wine-red. Indigo colored solution of diphenylhydrazine HCl changed at ordinary temperature to permanganate color.
4. Dextrine (erythrodextrin). Red-violet to red-brown with iodine. With Nylander's reagent, whose alkalinity has been partially neutralized with hydrochloric acid, amber solution to white colloidal precipitate[d] to black.
5. Pectin.[e] Sodium chromate develops color of dichromate. Cold 5% KOH gives bright yellow.
6. Levulose. Heated with dilute cobaltous chloride cooled and treated with little ammonium hydroxide, a violet to purple color[f] is developed. Most of the reagents of Table III indicate characteristic tests for levulose.
7. Mannose. Violet to purple[g] with reagents v and w.
8. Maltose. Blue with reagent k and[h] red-brown with x.
9. Rhamnose. Green[i] with reagent r.

The other carbohydrates require two or more tests for identification; these are indicated in Table III. Table I indicates tests for the levulose-containing carbohydrates, and Table II gives a list of the reagents and their characteristics.

Reagents d, e, f, v, and w indicate pentoses and pentose-containing carbohydrates. Reagent f gives cherry-reds with arabinose and xylose, but when boiled, pectin, gum arabic, and gum tragacanth also give the cherry-red. With v and w arabinose is a red which persists longer than with any of the other carbohydrates.

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[a] Soluble in Schweitzer's reagent; in warm 85% phosphoric acid catalyzed by $ZnCl_2$; in acetic acid and acetic anhydride (4 to 1) catalyzed by H_2SO_4 or by $ZnCl_2$; in 30% $ZnCl_2$ in conc. HCl. Water yields precipitates with these solutions.

[b] Raw and soluble starch are distinguished by cold water. Gum tragacanth and some samples of dextrin contain starch. Blue with iodine is decolorized by boiling and restored by cooling.

[c] Discharged by heat and restored by cooling. Warming with Nylander's reagent salts out colloidal glycogen.

[d] Soluble in cold mixture and reprecipitated by heat.

[e] With sucrose and organic acid it yields a jelly.

[f] Green cobaltous hydroxide with other carbohydrates.

[g] Reagent v more characteristic.

[h] Confirm by other tests of Table III.

[i] Other carbohydrates give blue or colorless solutions.

[2] The term "reducing sugar" has been applied to Fehling's and other reagents. However, it is a misnomer because with some reagents all simple sugars are not oxidized, and with other reagents all carbohydrates and even mannitol are oxidized, as, for example, with nitric acid. Mannitol gives negative tests with most of the reagents of the table.

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Sulfite Digester for Research and Instruction

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Chemical engineering laboratory equipment should be selected on the basis of usefulness. Too frequently, expensive apparatus to be used at best part time is purchased, whereas a slightly modified form would have lent itself to a variety of experiments. Conversely, a special piece may be purchased for a limited but important investigation and then with a few and relatively inexpensive accessories, used for basic studies in class work. In such cases, one can justify the initial expense. This discussion has to do with the design of a special KA 4 metal rotary digester for sulfite pulping studies, and also its use in class work.

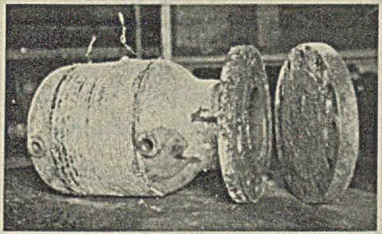

Figure 1. Digester Showing KA 4 Metal Casting

The preparation of sulfite pulp in the laboratory is usually limited to working with heavy glassware and rare-metal containers. Such limitations frequently permit working with only small samples. At the University of Washington, a digester of 25 liters capacity has been in operation for several months, and because of the ease of control and wide limits of operation and application, a detailed description has been prepared. Those interested in such equipment may find use for this apparatus and many can add, no doubt, to its applicability.

In the digestion of wood chips by a solution, variables such as size and composition of chips, temperature, concentration, and composition of solution are usually studied. Uniformity of operating conditions is always desirable. Apparatus for such work should withstand corrosion, allow for simple but accurate control, be of the rotating or tumbling type, and externally heated.

Description of Digester

The digester is shown in Figure 1. The body of KA 4 metal was cast from the pattern of a standard 6-inch steel steam drip pocket. The flanged opening was fitted with stud bolts which, in conjunction with a solid KA 4 metal plug in the bottom, were used for mounting the casting in a steel drum. The side openings intended for gage cocks in the drip pocket were used for thermometer well, pressure gage, sampling, and blow-down fittings. The apparatus was given a 24.6 kg. per sq. cm. (350 lb. per sq. in.) hydrostatic test. Figure 2 shows the mounting of the casting in the steel cylindrical drum which rotates at right angles to its axis. The sprocket, chain drive, and commutator rings for electrical heating are evident. Two steel digesters similar to the one described are installed and all may be rotated from a main drive at 4.7 r. p. m.

The speed of rotation is not so great but that temperatures and pressures may be read without stopping the apparatus. Three electrical resistance coils, which are used for heating, are connected through three commutator rings, and hence no switches need be on the rotating drum. There is little danger of heating interruptions due to shorting with this arrangement.

Operation

Before use of this digester for sulfite pulping studies, two series of heating rates were obtained. One was made with the KA 4 digester insulated only with the electrical packing normally placed around the heating elements and in running position. The other was obtained after packing "85 per cent magnesia" between the digester and the steel carriage. In these runs 18 kg. (39.6 lb.) of water were heated. The results, given in Figure 3, show that 0.56 kw. maintained a constant temperature of 132° C. (270° F.) before and 146° C. (295° F.) after packing with 85 per cent magnesia. The usual maximum temperatures used in the sulfite cooking process are 143° to 149° C. (290° to 300° F.). The additional insulation had little effect upon the rate of temperature rise to 149° C. (300° F.) when 2.07 and 1.12 kw. were used.

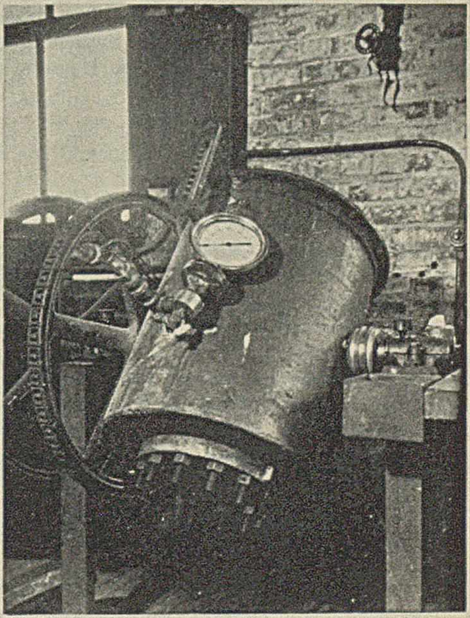

Figure 2. Assembly of Digester

Experiment in Rate of Heating

Charges may be heated having heat capacities other than that equivalent to 18 kg. of water, and then the heating

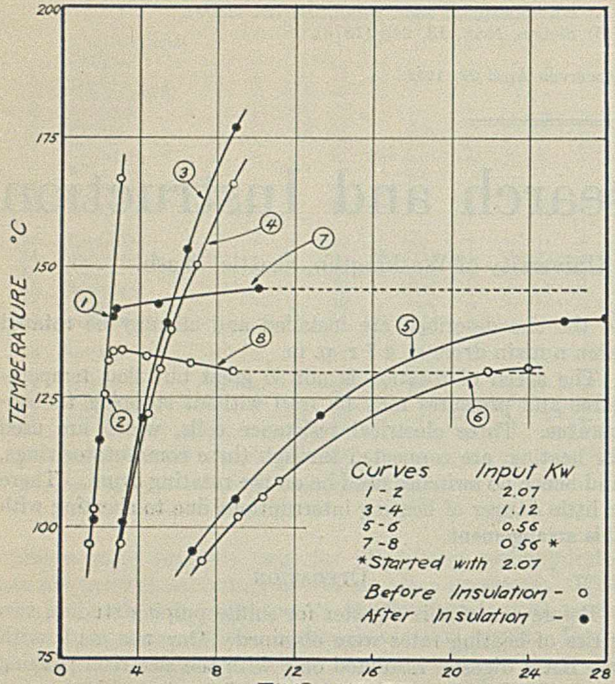

Figure 3. Digester Heating Rates

time required to bring to a given temperature is desirable. A method for such calculations is given below.

Assuming that each temperature represented on the 2.07-kw. input curve of Figure 3 gives the average temperature of the metal digester and the water, the total heat loss, Q_2, in lagging and radiation up to a given time, Θ hours, is given by:

$$\frac{(1000)(2.07)(3600)\Theta}{4185} = \left[\frac{(22.7)(454) + w}{1000}\right](T - T_r) + Q_2 \quad (1)$$

$$\frac{(1000)(2.07)(3600)\Theta}{1055} = (22.7 + w)(T - T_r) + Q_2 \quad (1a)$$

The total heat capacities in Calories per ° C. or B. t. u. per ° F. of the metal parts and of the water are (22.7) (454)/1000, or 22.7 and w, respectively, depending on the units. Equation 1 is for metric and 1a for English units. Room temperature, T_r, is taken as 25° C. (77° F.), while T represents the average temperature of the water. Corresponding values of time and temperature have been taken from curve 1 of Figure 3, and Equation 1 solved for Q_2. Values of Q_2 so calculated have been plotted against $T - T_r$ on log-log paper and result in the equation:

$$Q_2 = 2.45\,(T - T_r)^{1.35} \text{ in metric units}$$
$$Q_2 = 4.40\,(T - T_r)^{1.35} \text{ in English units}$$

where T_r is the room temperature and Q_2 is expressed in Calories or B. t. u., respectively. Substituting this value of Q_2 in Equation 1 and simplifying,

$$\Theta = (0.00578 + 0.00000056\,w)(T - T_r) + 0.000137(T - T_r)^{1.35} \quad (2)$$

$$\Theta = (0.00321 + 0.000141\,w)(T - T_r) + 0.000622(T - T_r)^{1.35} \quad (2a)$$

where Θ represents the hours required to heat a charge of w grams or pounds of water from 25° to T° C. (77° to T° F.).

In Figure 4, Equation 2 has been solved for values of w equal to 5 and 10 Calories per ° C. (11.0 and 22.0 B. t. u. per ° F.) corresponding to charges of 5 and 10 kg. (11.0 and 22.0 lb.) of water. Experimental results for such charges are also indicated in Figure 4. The maximum error introduced in calculating by means of Equation 2 the time required to heat 10 kg. (22.0 lb.) of water from 25° C. (77° F.) to any temperature below 149° C. (300° F.) is illustrated by selection of the temperature 164° C. (327° F.). The error for this temperature is 9.0 minutes, or 6 per cent. Similar calculation for a charge of 5 kg. (11.0 lb.) of water shows the same error.

Measurement of Heat Losses

When the temperature of the digester charge becomes steady, and after allowing for the energy required for any change taking place, the electrical input will be equivalent to the heat losses. Measurement of such losses can be accomplished easily with the usual electrical meters. Since heat leaves the steel jacket by radiation and convection, the quantitative determination of either loss separately is rather complicated, and simplifying expressions have been suggested. Although the transfer of heat by radiation from a body is proportional to the fourth power of its absolute temperature, the net exchange between two bodies at approximately room temperature, having a small temperature difference, may be approximated closely by assuming it proportional to only the temperature difference as in heat transfer by conduction. Heat transfer due to radiation and convection may be estimated from the equation

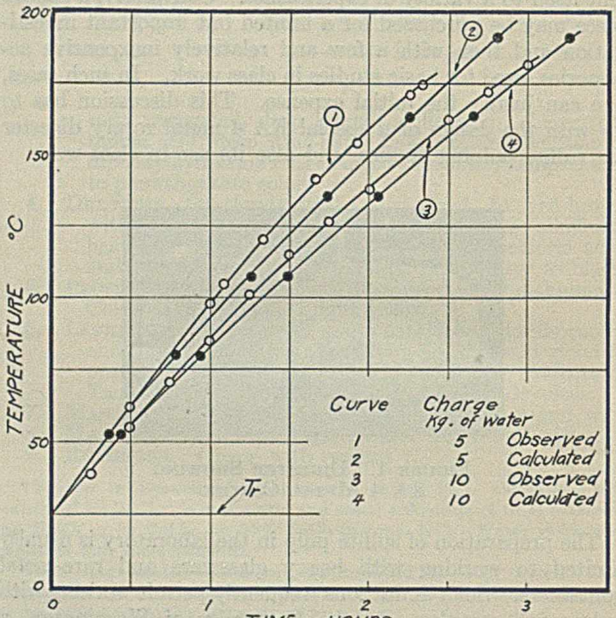

Figure 4. Comparison of Calculated and Observed Heating Rates

$$\frac{Q}{\Theta} = (hc + hr)A\,\Delta T \quad (3)$$

where $\frac{Q}{\Theta}$ = heat transferred per unit of time
$hc + hr$ = gas film + radiation coefficient
A = area of hot body
ΔT = temperature difference

The application of this equation in work with the digester can be exemplified by measuring the heat input required for maintaining steady charge temperatures and recording the temperature of the steel-jacket surface and of the room. An input of 0.56 kw. (481 Calories per hour) was found to maintain the temperature of the charge at 146° C. (295° F.). The skin temperature of the steel jacket averaged 45° C.

(113° F.) and that of the room 25° C. (77° F.). The value of $(hc + hr)\ A$, using Equation 3, is found to be 24.1 Calories per hour per ° C. (53.2 B. t. u. per hour per ° F.).

Heat capacities of solutions and mixtures, in particular those used in the pulping industries, can be determined by the use of Equation 1.

Chemical Preparations

Undergraduate laboratory courses in industrial chemistry have many uses for rotating autoclaves. The preparation of wood pulp is but one of the digestion processes which familiarize the student with important phases of the chemical industry. Other processes, especially those peculiar to geographical location, suggest themselves.

The object of this paper has been to show that expensive research equipment can be also used for undergraduate instruction in industrial chemistry and chemical engineering. The intensive and general application of apparatus can justify the installation of equipment developed for special investigations.

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Estimation of Thallium after Oxidation with Bromine

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Of THE reagents employed for the oxidation of thallium, bromine has received little attention, although its action is rapid and complete. Sponholz (*3*) recommended it for the volumetric estimation of thallium, using the color of excess bromine to indicate when the reaction was complete. In the description of this method he called attention to the necessity of frequent standardization of the bromine solution. The difficulties of such a volumetric procedure are quite obvious. If, however, the oxidized solution is treated with an alkali hydroxide in slight excess, the immediate and complete precipitation of thallic hydroxide is effected.

The delicacy of this reaction was first tested qualitatively, and it was found that in a volume of 10 cc., 0.1 mg. of thallium could be detected by the dark coloration of the thallic hydroxide, a delicacy which was rarely exceeded by such reagents as potassium iodide, chloroplatinic acid, or sodium cobaltinitrite. Sodium peroxide proved to be much less satisfactory as a means of detection. This test cannot be made in the presence of such elements as iron, manganese, cobalt, or nickel which give similar color changes due to oxidation.

Quantitatively the results were as follows: A solution of thallous nitrate was made up and standardized by oxidizing four portions of 10 cc. each with potassium ferricyanide in the presence of potassium hydroxide (*1*, *2*), filtering off the thallic hydroxide on a weighed asbestos felt, and weighing the oxide after bringing it to constant weight at a temperature of 150° to 200° C. The mean of four closely agreeing results gave 0.1345 gram of thallic oxide.

Portions of 10 cc. each of this same solution were oxidized with bromine water in slight excess, the oxidized solutions precipitated, with or without gentle warming, with sodium or ammonium hydroxide, and the precipitates filtered off, heated, and weighed in the same manner as the precipitate from the ferricyanide treatment described above. Four closely agreeing results, ammonium hydroxide having been used as the precipitant, gave as a mean 0.1334 gram of thallic oxide; and another four, sodium hydroxide having been employed as the precipitant, gave a mean of 0.1344 gram of thallic oxide.

The method was rapid, easy of manipulation, and certainly, when sodium hydroxide was used, of satisfactory accuracy. Obviously, those elements whose hydroxides are insoluble in excess of sodium or ammonium hydroxide must be absent when this method is applied. This necessitates the previous removal of thallium from most of the other elements, a procedure not unusual before the application of many gravimetric processes to the estimation of a single element.

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An Improved Flask for Van Slyke Protein Analysis

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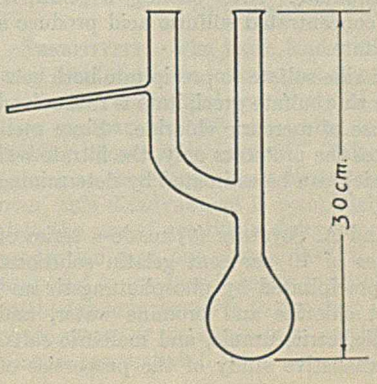
THE flask shown has been found to be an improved form for hydrolysis of proteins according to Cavett's modified Van Slyke nitrogen distribution method (*1*). It consists of a 300-ml. Kjeldahl flask to which has been attached a side neck, in the manner of a Claissen flask. Several operations are performed in the flask, saving time and increasing accuracy. The protein sample is hydrolyzed, the hydrochloric acid is distilled off, the ammonia nitrogen is determined, and the total nitrogen in the humin fraction is determined, all in the same flask on the same sample.

The advantages of this Kjeldahl-Claissen flask over the 250-ml. distilling flask recommended in the original method, are: (1) The double neck prevents foam from bubbling over into the standard acid during the ammonia determination. (2) The additional strength of the Kjeldahl flask makes it more suitable for the Kjeldahl digestion, etc.



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Detection of Gelatin in Dairy Products

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A method for the detection of gelatin in dairy products, especially for sour cream and cultured milks, is presented. Basic lead nitrate is used as a protein precipitant and calcined charcoal is used to adsorb the pseudo-gelatins formed in the souring process. The details of the method and its comparison with other methods as to sensitivity and applicability are given. It is found less sensitive but more definite than the official or Stokes method.

GELATIN has for many years been used as a thickening agent in dairy products. In ice cream it has of course been accepted because it improves the texture as well as the standing qualities of this product. However, in milk and cream and like products, its use has generally been frowned upon because of a tendency to use it to conceal inferior products.

The method mainly used for its detection in dairy products in the past has been that of Stokes (*10*), which will be described in detail later. This method, however, in the case of slightly soured milk or slightly soured sweet cream, and especially in the case of sour cream, fails to give a decisive result in the absence of gelatin. This necessitates either a laboratory rule-of-thumb method, such as the density of turbidity before considering a test positive, or a resort to a test distinguishing between a gelatin-picrate precipitate and a pseudo-gelatin-picrate precipitate such as the Seidenberg method (*8*). This test, besides being laborious, does not always differentiate between the aforementioned types of precipitate.

In view of these facts, the authors have developed a method from their experience with other thickeners (*3*) which will completely satisfy the condition of giving no precipitate in the case of a dairy product in which gelatin is absent and a heavy precipitate or a marked turbidity for every dairy product containing gelatin, including sour cream. Furthermore, this method needs no laborious confirmatory tests.

The properties of gelatin as a colloid have been discussed so frequently in the literature that there is no need for a further discussion along these lines here. However, there are many other properties of gelatin so little known and yet so pertinent to its detection that it would be wise to review them. Moreover, there are a few methods used for the estimation of gelatin which are also used for its detection which will be reviewed.

Trillat (*12*) estimated gelatin in gums and alimentary substances by weighing the precipitate produced by formaldehyde.

Henzold (*2*) boiled the material supposed to contain gelatin in water and filtered. The filtrate is boiled with excess 10 per cent potassium dichromate. After cooling, if gelatin is present, a few drops of concentrated sulfuric acid produce a white, flocculent precipitate.

Greifenhagen (*1*) used zinc sulfate to precipitate both gelatin and proteoses. The zinc sulfate precipitate is redissolved and reprecipitated by use of mercuric chloride. Since mercuric chloride precipitates the proteoses only, the filtrate will contain only gelatin, which can be estimated by determining the nitrogen.

A. and L. Lumiere and A. Seyewitz (*6*) made a series of studies of the properties of 10 per cent gelatin solutions. They found that it is precipitated by phosphotungstic and phosphomolybdic acids, chlorine and bromine water, and ferric, manganic, vanadic, ceric, uranic, and mercuric salts. They made a rather exhaustive study of the properties of concentrated solutions of gelatin.

Steinizer (*9*), in a study of the properties of gelatin and glue in comparison with other proteins, noticed that lead acetate solution did not precipitate gelatin, whereas it did precipitate chondrins and mucins.

Straub (*11*) states that if gelatin solution is shaken for 20 to 30 minutes with a few cubic centimeters of thionin solution, a dark blue color results, whereas if agar-agar is treated the same way, a violet coloration is obtained.

Liesegang (*5*) found that if 40 per cent tertiary potassium phosphate and 10 per cent cupric chloride are allowed to diffuse into gelatin gel, the green tertiary cupric phosphate does not result, but a deep violet transparent color. A water-gelatin solution may be used as well, but tertiary potassium phosphate causes a precipitate of gelatin. However, in 1914 (*4*) he pointed out that tricalcium phosphate and cupric chloride gave a violet color without turbidity instead of a green precipitate in the presence of gelatin in solution.

STOKES METHOD

The official method given in the methods of the A. O. A. C. for the detection of gelatin in milk and milk products is the Stokes (*10*) method. This is performed in the following manner: To 10 cc. of milk or cream or milk product, add an equal volume of acid mercuric nitrate solution (mercury dissolved in twice its weight of nitric acid and this solution diluted to 25 times its volume with water). Shake the mixture, add 20 cc. of water, shake again, allow to stand 5 minutes, and filter. If much gelatin is present, the filtrate will be opalescent and cannot be obtained clear. To a portion of the filtrate contained in a test tube, add an equal volume of saturated aqueous picric acid solution. A yellow precipitate will be produced in the presence of any considerable amount of gelatin, whereas smaller quantities will be indicated by a cloudiness. In the absence of gelatin, the filtrate will remain perfectly clear.

Acid mercuric nitrate is added to the milk product in order to precipitate all the proteins except gelatin. In the souring process certain decomposition products are formed whose exact nature is unknown. Patrick (*7*) found that these substances had properties very similar to gelatin, and called them "pseudo-gelatins." They are not completely precipitated by acid mercuric nitrate, and they give a precipitate with picric acid and with tannic acid. Consequently, the Stokes method is indeterminate for milk and sweet cream on the verge of souring, and fails completely for sour cream. Furthermore, acid mercuric nitrate itself will, if present in large excess, cause a turbidity in the presence of picric acid, and a turbidity will develop on standing even if the acid mercuric nitrate is not in excess.

SEIDENBERG METHOD

Seidenberg (*8*) developed a method to distinguish between the precipitate produced by gelatin and that produced by pseudo-gelatin. His method is as follows: After performing the Stokes test, shake the solution and precipitate in a large test tube very thoroughly, allow to stand, decant off the clear liquid, and collect the precipitate on a filter. Wash with water containing 2 to 3 drops of ammonia per 100 cc. until the washings are slightly alkaline to litmus, then with water alone until they are neutral. Transfer the precipitate or the precipitate and filter to a small beaker, add 10 to 20 cc. of water, heat to boiling, and filter hot into a test tube. The filtrate will contain the gelatin-picrate but not the protein. Cool and test for gelatin by adding an equal volume of the picric acid solution.

This method was advocated for sour creams, but failed to solve the problem completely because sometimes on samples known to contain gelatin, a positive test for gelatin with picric acid was not obtained after subjecting the sample to the Seidenberg treatment.

Basic Lead Nitrate Method

In view of the limitations of both the Stokes and Seidenberg methods, the authors have devised and developed an entirely new method for the detection of gelatin in dairy products. This method is based on the separation of gelatin from the other proteins in the milk product and then the subsequent identification of gelatin. This is done first by the use of a protein precipitant, and second by the use of an agent to adsorb the pseudo-gelatins and proteoses. The protein precipitant is basic lead nitrate and the adsorbing agent is calcined charcoal. The basic lead nitrate consists of two solutions added separately to the solution or mixture to be clarified.

Solution 1: lead nitrate, 250 grams to 500 cc.
Solution 2: sodium hydroxide, 25 grams to 500 cc.

To 10 cc. of milk or milk product, add 3 cc. of lead nitrate solution and stir, add 3 cc. of sodium hydroxide solution and stir, add 5 cc. of water and stir, add 0.1 gram of calcined charcoal and stir thoroughly, allow to stand for 5 minutes, and filter. To 3 cc. of the filtrate add 2 drops of concentrated nitric acid and then a few drops of freshly or recently prepared 5 per cent tannic acid solution. In the presence of gelatin there is a white or brownish voluminous precipitate. In the absence of gelatin the solution remains perfectly clear. As a confirmatory test, add to a portion of the filtrate (no addition of nitric acid is now necessary) an equal volume of freshly filtered saturated aqueous picric acid solution. In the case of considerable quantities of gelatin, there is a heavy precipitate of gelatin picrate. In the case of smaller quantities, there is a turbidity which develops within 2 minutes. In the absence of gelatin, the filtrate will remain perfectly clear even on standing. For the tannic acid test the addition of nitric acid is essential, for otherwise tannic acid will always give a precipitate. For the picric acid test there is no need to use acid. The addition of acid in this case reduces the sensitivity of the test, because gelatin picrate is somewhat soluble in nitric acid.

Basic Lead Acetate Method

As an alternative method to the one given above, the authors suggest the following. It will not give as good results as the previous method, but nevertheless is better for sour creams than the Stokes method. It is based on the same principle as the preceding one, but uses dry basic lead acetate instead of basic lead nitrate solution as the protein precipitant. The adsorbing agent used is the same. The dry basic lead acetate may be made in the manner given in the methods of the A. O. A. C. or in any sugar handbook.

To 10 cc. of milk or milk product, add 1 gram of basic lead acetate and stir. Add 15 cc. of water and stir, add 0.1 gram of calcined charcoal and stir thoroughly, allow to stand for 5 minutes, and filter. To 3 cc. of the filtrate add 3 cc. of water, 2 drops of concentrated nitric acid, and then a few drops of freshly or recently prepared tannic acid. A heavy voluminous white or brownish precipitate shows the presence of gelatin. To another portion of the filtrate add an equal volume of water and 2 to 3 drops of concentrated nitric acid, and then add an equal volume of freshly filtered saturated aqueous picric acid solution. A heavy precipitate of gelatin picrate or a pronounced turbidity which develops in 2 minutes shows the presence of gelatin. In the absence of gelatin the filtrate will remain clear for at least 10 minutes. The main drawback of this method is that after adding picric acid, a crystalline precipitate settles out on standing if the filtrate from the basic lead acetate treatment is not diluted. However, this precipitate is markedly different from gelatin picrate or pseudo-gelatin picrate, and consequently can easily be distinguished.

Experiments on Adsorbing Agent

In order to determine the best adsorbing agent for the pseudo-gelatins a series of experiments were run with various adsorbents and clarifying agents. The results of these are given in Table I.

Table I. Experiments to Determine Adsorbing Agent

(All results considered after 2 minutes)

	Picric Acid		Tannic Acid	
Adsorbent	Sour cream without gelatin	Sour cream with gelatin	Sour cream without gelatin	Sour cream with gelatin
Fuller's earth	Clear soln.	Ppt.	Faint ppt.	Heavy ppt.
Magnesium carbonate	Turbid	Turbid	Ppt.	Heavy ppt.
Calcined charcoal	Very clear soln.	Ppt.	Very clear soln.	Heavy ppt.
Kaolin	Turbid	Ppt.	Heavy ppt.	Heavy ppt.
Pumice	Ppt.	Ppt.	Heavy ppt.	Heavy ppt.
Blood charcoal	Clear soln.	Turbid	Faint ppt.	Heavy ppt.
Alumina cream	Ppt.	Ppt.	Heavy ppt.	Heavy ppt.

These tests were performed in the following manner: Sour cream known not to contain gelatin was subjected to the basic lead nitrate treatment substituting in each case 0.1 gram of the adsorbents given in Table I. Columns 1 and 3 show the results with picric and tannic acids. Then sour cream known to contain gelatin was again tested by the basic lead nitrate method, substituting in each case 0.1 gram of each adsorbent. These results are shown in columns 2 and 4. It can be seen at a glance that calcined charcoal adsorbs the pseudo-gelatins the most, and gelatin itself the least, making it ideal for use in this test. The authors found that decolorizing carbons were better adsorbents to use in this test than carbons used for physiological or pigment purposes. Of these types of decolorizing carbons, Eimer and Amend's calcined charcoal, Darco, and Norit were found to be about equally efficacious as the adsorbing agent.

Comparison of Methods

Sensitivity. The basic lead nitrate method will give a good test for gelatin for one part of gelatin in 2000 of the milk product. The actual sensitivity of this reaction is greater than one part in 2000 but, owing to the addition of the adsorbing agent, it is lowered. This is compensated by obtaining an exceedingly clear filtrate and negative test. Moreover, this disadvantage is completely balanced by the fact that the use of gelatin in dairy products requires a greater proportion than one part in 2000 if the effect the gelatin is supposed to produce is really to be obtained. However, the method is only sensitive to one part in 400 for such products as ice cream or ice cream mix, particularly if these products contain egg material.

Table II. Comparison of Methods for Applicability

(All tests considered after standing 2 minutes)

Method	Reagent	Sweet Cream		Sour Cream	
		Without gelatin	With gelatin	Without gelatin	With gelatin
Stokes	Picric acid	Very faintly cloudy	Heavy turbidity	Turbid	Heavy turbidity
	Tannic acid	Heavy ppt.	Heavy ppt.	Heavy ppt.	Heavy ppt.
Basic lead acetate	Picric acid	Very faintly cloudy	Marked turbidity	Very faintly cloudy	Marked turbidity
	Tannic acid	Clear soln.	Heavy ppt.	Clear soln.	Heavy ppt.
Basic lead nitrate	Picric acid	Perfectly clear soln.	Turbid	Perfectly clear soln.	Turbid
	Tannic acid	Perfectly clear soln.	Heavy ppt.	Perfectly clear soln.	Heavy ppt.

In order to make certain as to whether this method would detect any type of gelatin, twenty samples of gelatin of various grades and types, one sample of glue, and one sample of isinglass were respectively incorporated with sour cream, or milk or cultured milks which had previously been found not to contain gelatin. Subjecting these prepared samples to the basic lead nitrate test yielded a positive test for gelatin for every type of gelatin or glue used. These tests were performed on sour cream samples containing 0.25 per cent gelatin.

A further series of experiments was run to determine whether time would alter the sensitivity of this test. This set of experiments at the same time reproduced plant conditions, for a dairy product to be tested for gelatin seldom comes directly to the analytical laboratory from its original source, hence time elapses before the test for gelatin is made.

To three samples of sour cream which had been found not to contain gelatin by the basic lead nitrate method three samples of gelatin were added. For each cream and each sample of gelatin, a 0.25 and 0.5 per cent mixture of gelatin in cream was made. These six prepared samples were tested for gelatin over a period of one month at various intervals. They continued to give a decisive test for gelatin throughout the entire period.

Practically every type of dairy product that might contain gelatin was tested by this method to determine whether it would apply in every case. The following products were tested: milk, sweet cream, sour cream, sweetened condensed milk, unsweetened condensed milk, and cultured milks. Ice cream samples were also tested and in every case gave a positive test for gelatin, as might be expected from the fact that nearly all ice creams contain gelatin. For unsoured ice cream and ice cream mix, the amount of adsorbent added and the length of standing time must be strictly adhered to in order to obtain results.

Applicability. The basic lead nitrate method was rigidly tested for complete and practicable applicability in three ways. First, it was compared with the Stokes method. This was done in the following manner: The Stokes method we know works for sweet creams. Consequently, a sweet cream known not to contain gelatin was tested by the Stokes, the basic lead nitrate, and the basic lead acetate methods. To a portion of this cream which was found negative for gelatin by all three methods, some gelatin was added, the sample was again tested by all three methods, and all three gave a positive reaction. Then that portion of the sweet cream to which no gelatin was added was allowed to sour. This soured cream was now tested for gelatin by all three methods. The Stokes test was now indeterminate because of a turbidity, the basic lead acetate method gave a very faint turbidity, whereas the basic lead nitrate method yielded a perfectly clear negative result. Gelatin was now added to the remainder of the soured cream and was again tested by all three methods. The results of this experiment are given in Table II.

It may be seen in the table that the Stokes method gives a positive gelatin test with a soured sweet cream containing no gelatin. It may also be seen that the tannic acid test for gelatin cannot be used in conjunction with the Stokes method.

The second test of the basic lead nitrate method was performed in the following manner: Samples of cream and cultured milks containing and not containing gelatin were submitted to three chemists. These chemists did not know which samples contained the gelatin and which did not contain it. By the use of this method every sample of cream or of cultured milk with gelatin and those without it were reported correctly by each of the three.

The third test of this method was performed by subjecting various grades of gelatin and glue and isinglass to the test. These results have been discussed in the above text.

Discussion

The basic lead nitrate method is one which, in so far as the picric acid reaction for gelatin is concerned, is less sensitive than the Stokes method, but which far surpasses the Stokes test in the following particulars:

1. It gives a perfectly clear blank or negative result in the absence of gelatin for sour cream and cultured milks, as well as for any other dairy product, for the reactions with tannic acid and picric acid.
2. The filtrate can be tested by one reagent—namely, tannic acid—and confirmed by another reagent—namely, picric acid.
3. It is easy to perform and dispenses with the Seidenberg addition to the Stokes test.

Acknowledgment

The authors wish to express their thanks to Reginald Miller, chief chemist, for his aid and coöperation in this work.

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Determination of Carbon in Fermented Liquors

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In studies involving the dissimilative changes of carbohydrates by microörganisms, it is desirable to control the analytical results by comparing the total carbon found by analysis in the medium, or in any fraction, with that represented by the various end products. Frequently, in fermentation studies, no attempt is made to account for the carbon in this manner, and it will be found by computation that the difference between the total carbon in the medium and the carbon accounted for in the final dissimilative products may range from 5 to 50 per cent of the carbon in the medium at the start of fermentation. There is difficulty when an organism produces relatively large amounts of gum, as this may contain sufficient carbon to endanger seriously any deductions concerning the scheme of dissimilation, unless taken into consideration. The advantages of a convenient and accurate method for the routine determination of total carbon in the medium are apparent. A determination of total carbon frequently saves considerable time when a fraction of the fermented medium is being examined, such as the neutral distillate or the nonvolatile acid residue. A determination of the carbon will immediately indicate whether all of the carbon is accounted for by the products isolated from the fraction. Other carbon products may have remained in the fraction and may thus have been overlooked.

Grey (*5*) was one of the first to apply this idea to the examination of fermented liquors. His method failed to effect complete combustion, although valuable information as to the nature of the organic compounds present could be obtained by it.

Friedemann and Kendall (*4*) and, independently, Heck (*6*) have developed the method based on the oxidation of the carbon to carbon dioxide by chromic acid. Friedemann and Kendall pointed out the necessity of maintaining a high concentration of acid during the oxidation by keeping the volume of water at a minimum. The carbon dioxide was absorbed by 0.5 *N* sodium hydroxide solution in a Truog tower (*7*), and the excess sodium hydroxide was titrated after the carbon dioxide had been precipitated by barium chloride. The method gives excellent results on solutions of pure organic compounds, but suffers because of the necessity of running a blank along with each determination. Considerable difficulty may be encountered in the titration when small amounts of carbon are being determined.

The impracticability of running a blank in actual practice is evident. Chlorides are usually present in culture media and are oxidized by hot chromic acid. A blank run does not always give a true indication of the amount of sulfuric acid fumes which may be absorbed.

A further necessity of running a blank results from the fact that very few samples of phosphoric acid can be found which do not contain carbon in some form. Quite often as much as 10 to 30 mg. of carbon has been found to be present in 30 cc. of phosphoric acid. Heck (*6*) avoided part of these difficulties by introducing a fume trap at the top of the reflux condenser.

The chief difficulty to be overcome, however, in the adaptation of any method for carbon determination to fermentation studies, is the necessity of maintaining a high acid concentration. Quite often the carbon-containing compounds are present in such low concentrations that it is necessary to use as much as 200 cc. of the solution in order to obtain appreciable quantities of carbon dioxide. Oxidation with chromic acid is not complete in the presence of the quantity of water sometimes required (*4*).

Of the strong oxidizing agents, the only ones worthy of consideration under the circumstances are the chlorates, persulfates, and probably certain of the peroxides which act catalytically, such as silver peroxide. Of these, the chlorates are practically precluded because of their explosive tendencies, and because of the large quantities of chlorine which may be evolved. The peroxides either decompose too rapidly in water or are too expensive.

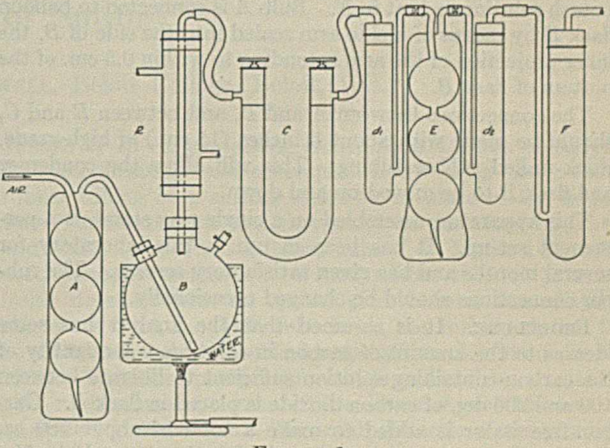

Figure 1

The only reference to persulfate oxidation of carbon which was found in the literature is that of Franz and Lutze (*3*). According to these authors, certain compounds, such as acetates, carbohydrates, and glycerol, can be quantitatively oxidized in dilute solution at 70° C. in the presence of three times the theoretical quantity of potassium persulfate. The available oxygen from potassium persulfate may be calculated from the equation $K_2S_2O_8 + H_2O \longrightarrow 2KHSO_4 + O$. The oxidations were carried out in the presence of 100 cc. of water. The carbon dioxide was absorbed in potash bulbs and weighed. The presence of chlorides vitiated the results. The method as recorded by these authors has certain disadvantages which may be easily overcome.

Method for Carbon Determination

Aside from accuracy and rapidity, two requirements must be met if a routine method for the determination of carbon in fermentation liquors is to be successful.

1. The presence of water in quantities up to 200 cc. must not be objectionable.
2. The method must be applicable in the presence of mineral chlorides, and chlorine-, sulfur-, and nitrogen-containing compounds.

The method as described below has met these requirements satisfactorily.

Method. The oxidation is carried out in the presence of

180 to 200 cc. of carbon-free water by means of potassium persulfate. The carbon dioxide either may be absorbed in Bowen potash bulbs and weighed, or determined by any of the volumetric methods. In the present procedure, the carbon dioxide is weighed. Ordinary distilled water is freed from carbon and carbon dioxide by adding about 10 grams of potassium persulfate to 500 cc. of water, and distilling in the presence of a little silver nitrate as catalyst.

APPARATUS. The apparatus used is shown in Figure 1. The oxidation takes place in the 200-cc. balloon flask, *B*. The reflux condenser, *R*, need not be more than 10 inches (25 cm.) in length. The U tube, *C*, is filled with 12-mesh calcium chloride, with a few large pieces on top of the arm next to the condenser. The small calcium chloride tubes, d_1 and d_2, are also filled with 12-mesh calcium chloride, with larger pieces of the chloride placed next to the potash bulbs—i. e., in the bottom of each tube. The carbon dioxide is absorbed in the Bowen potash bulb, *E*. The bulb is filled with a 65 per cent solution of potassium hydroxide. The potash bulb, *E*, and the two calcium chloride tubes, d_1 and d_2, are weighed as a unit, and should be designed accordingly. The final tube, *F*, is also filled with 12-mesh calcium chloride.

The initial potash bulb, *A*, is filled with the same strength potash solution as that in *E*. Bulb *A* is connected to balloon flask *B* by means of a side arm sealed into the side of *B*, the inner projection of the arm extending to within 0.5 cm. of the bottom of flask *B*.

The connections between *A* and *B*, and between *R* and *C*, should be made with about 6 inches (15 cm.) of high-grade, thick-walled rubber tubing. This will allow the condenser and flask *B* to be moved up and down.

This apparatus, assembled on a single ring stand, is a permanent set-up. It has been in use in this laboratory for several months and has given satisfactory service. The rubber connections should be changed occasionally.

PROCEDURE. It is assumed that the analyst has some idea as to the amount of carbon in solution. A quantity of the carbon-containing solution sufficient to liberate between 100 and 200 mg. of carbon dioxide is placed in flask *B*. Carbon-free water is added to make a total of about 180 cc. From 5 to 10 grams of powdered potassium persulfate (depending on the amount of carbon and hydrogen to be oxidized) are added, and the flask is rotated to dissolve as much of the reagent as possible. From 5 to 10 cc. of 4 per cent silver nitrate solution are then added, and the apparatus is properly connected. No oxidation occurs in the cold, and it is good practice to pass air through the apparatus for a few minutes to remove the carbon dioxide. Bulb *E*, with its calcium chloride tubes d_1 and d_2, is then detached, carefully wiped dry, and weighed. The static charge generated on the tube by friction of the towel should be discharged by grounding.

After again connecting the potash bulb to the train, oxidation flask *B* is immersed in water at a temperature of 70° to 80° C. No air is passed through at this time.

As the solution in *B* becomes warm, a black deposit of silver peroxide forms, and at about 70° C. a lively evolution of oxygen gas commences.

The reaction should be maintained at 70° C. until the solution clears up and the evolution of gas has stopped. Usually 15 to 25 minutes are required. Flask *B* is now removed from the water bath and the contents brought to a gentle boil. Air is started through the apparatus at the rate of about 5 bubbles per second. The boiling and aëration are continued for 15 minutes. During the oxidation, the rate of evolution of the gas can be controlled by the temperature, and should not be allowed to exceed 3 or 4 bubbles per second, as there is danger of incomplete oxidation if the oxidant is decomposed too rapidly. Potash bulb *E* is then removed and weighed with the usual precautions.

If chlorides or combined chlorine is present, enough silver nitrate is added to give about 0.2 gram excess over that required to precipitate the chlorine.

It can be seen from the equation $K_2S_2O_8 + H_2O \longrightarrow 2KHSO_4 + O$, that the solution becomes acid during the process, and consequently there is no difficulty in driving all the carbon dioxide out of the solution. In the presence of silver nitrate the reaction follows a different path, but the end products are the same.

DISCUSSION AND EXPERIMENTAL RESULTS

In view of the objections raised by Cain (*2*) and others against the gravimetric method for the determination of carbon dioxide, it seems desirable to offer a few remarks in defense of its use under the present circumstances, at the same time admitting its limitations.

In Table I are shown results from a series of blank tests which indicate the errors to be expected due to gain or loss of moisture by the potash bulb. The length of time during which air was passed through the apparatus is indicated in each experiment. In each case the time exceeded that of an actual experiment. The water in flask *B* was kept at boiling temperature, but no reagents were present. Table II shows the results of blanks run on the reagents and water.

TABLE I. BLANKS OBTAINED BY PASSING AIR THROUGH APPARATUS

TIME	GAIN IN WEIGHT
Min.	*Mg.*
30	0.0
45	0.2
45	0.5
60	−0.3
60	0.0
120	0.0
120	0.5

TABLE II. BLANK DETERMINATIONS MADE ON REAGENTS[a]

$K_2S_2O_8$	GAIN IN WT. OF POTASH BULB
Grams	*Mg.*
5.0	0.4
5.0	0.5
7.5	1.5
7.5	1.0
10.0	0.7
10.0	2.0

[a] 0.2 gram of silver nitrate present in 180 cc. of water in each case.

From Tables I and II it can be seen that an error of 2.5 mg. may be expected. This error becomes serious in cases where less than 50 mg. of carbon dioxide are evolved and, in some cases, even where 100 mg. of carbon dioxide are obtained. When the aim is to check the carbon balance in fermentation processes, and when as much as 150 mg. of carbon dioxide can easily be obtained, the accuracy is sufficient. The time required for detaching the potash bulb and weighing it for each experiment is short.

The carbon dioxide–absorbing efficiency of Bowen potash bulbs when filled with 65 per cent potassium hydroxide is perfectly satisfactory. Table III shows results on pure sodium bicarbonate and sulfuric acid. The rate of bubbling air through the apparatus is indicated in the first column. Dilute potash solutions are to be strictly avoided.

TABLE III. EFFICIENCY OF ABSORPTION OF CARBON DIOXIDE[a]

BUBBLES PER SECOND	CO_2 CALCD.	CO_2 FOUND
	Gram	*Gram*
1	0.0880	0.0875
2	0.0880	0.0880
5	0.0880	0.0882
5 to 10	0.0880	0.0877

[a] 200 grams of 0.1 *M* sodium bicarbonate present in each case.

Oxidation flasks of less than 200 cc. should not be used. The solubility of potassium persulfate is approximately 5 grams per 100 cc. of water. If the reagent is not in solution, the liberation of nascent oxygen occurs at the solid surface and the oxidizing efficiency is low.

Table IV. Results of Analyses

Substance	CO_2 Calcd.	CO_2 Found	Recovery
	Mg.	*Mg.*	%
Acetic acid	176	175	99.4
Propionic acid	132	130	98.5
Butyric acid	176	173	98.3
Chloroacetic acid[a]	88	83	94.3
Thiourea	44	43	97.7
Ethyl alcohol	150	150	100
Succinic acid	176	173	98.3
Dextrose	150	150	100
Dextrose + NH_4Cl	100	99	99.0

[a] Eastman's c. p. chloroacetic acid used; could not be further purified.

The results of analyses made on solutions containing representative compounds obtained by fermentation of carbohydrates are shown (chloroacetic acid and thiourea are also included in Table IV). From Table IV it can be seen that the presence of sulfur, nitrogen, and chlorine has no serious effect.

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Sulfur Content of Foods

Modification of Turbidimeter for Determination of Small Quantities of Sulfur

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The necessity for an accurate knowledge of the mineral constituents of our common foodstuffs has increased in recent years. So far as the present authors have been able to find, the data on the sulfur content of foods are fragmentary and are based on different methods of analysis. Sherman (*5*) has compiled a table listing the sulfur content of many foods. The data are gathered from various sources and the methods used are undoubtedly varied. It is the purpose of this paper to describe a modification of the sulfur turbidimeter adapted to the determination of small quantities of sulfur in foods and biological material following oxidation of the sample with nitric and perchloric acids according to the method of Toepfer and Boutwell (*6*), and to give the sulfur content of a number of our common foods as determined by this method.

The earlier work (*1*, *6*) from this laboratory was carried out with the old model of the sulfur photometer. The present authors have used a modification of the new model of the Burgess-Parr turbidimeter. The new instrument offers advantages over the old in simplicity, accuracy, and speed, but it requires from 4 to 6.5 mg. of sulfur in a volume of 200 cc. in order to obtain suitable readings. In the case of materials low in sulfur, this would often require too large a sample for oxidation. The authors have modified the instrument so as to make it suitable for use with a working volume of 25 cc. containing from 0.7 to 1.3 mg. of sulfur. This modification was accomplished by using black hard rubber tubing of a smaller diameter in place of the larger tubes furnished with the instrument as described by Parr and Staley (*3*). The stationary tube *C*, in Figure 1 in their description, is replaced by a hard rubber tube of 13 mm. inside diameter with an optical glass bottom immediately above the light *L*. This tube holds the turbid solution to be examined and is suitable for use with a volume of 20 to 25 cc. The inner plunger tube, *P*, is replaced by a smaller hard rubber tube of 8 mm. outside diameter, also fitted with an optical glass bottom. The small diameter of the plunger tube gives a small field for comparison but adds to the sharpness of the end point. Suitable metal collars are used to hold the smaller tubes in place in the instrument. This modification is of especial value for work on materials low in sulfur. It has made possible an accurate determination of sulfur in a sample one-sixth to one-seventh as large as would have been necessary if the original instrument had been used. This modification is recommended for the turbidimetric determination of sulfur in urine (*1*).

The accuracy of the results secured with the modified turbidimeter is shown by the ability to reproduce the calibration curve of the instrument between the optimum range of 0.7 to 1.3 mg. of sulfur with an average error of about

Table I. Results Illustrating Use of Modified Turbidimeter

	Sulfur 1			Sulfur 2			Sulfur 3		Red Radishes			Apple		
Wt. of sample, grams	0.3163			0.5565			0.5060		25.81			82.5		
Volume (made up to), cc.	500			200			250		100			50		
Aliquot taken, cc.	20			7			14		15			10		
Turbidimeter reading	I	II	III	I	II	III	I	II	I	II	III	I	II	III
	86	84	84	67	67	67	64	65	67	69	67	61	60	61
	87	84	83	64	65	67	64	63	64	69	68	61	61	60
	85	83	85	65	67	71	63	65	66	69	67	61	62	62
	85	84	84	65	67	68	65	65	65	69	68	60	60	61
	85	82		65	67	68			65			64		
				64		68						61		
Mean	85.6	83.4	84.6	65	66.8	68.1	64	64.9	65.3	69	67.5	61.3	60.9	61
Average	84.5			66.6			64.5		67.3			61.07		
Sulfur found, grams	0.00078			0.00095			0.00099		0.00097			0.00101		
Sulfur present, grams	0.000783			0.000945			0.00099							
Error, grams	−0.000003			+0.000005			0.00000							
Sulfur found, %	6.165			4.93			3.53		0.025			0.012		
Sulfur present, %	6.188			4.84			3.53							
Error, %	0.32			1.6			0.00							

1 to 2 per cent. This represents the limit of accuracy in reading the instrument and applies in any determination. The earlier papers (*1*, *6*) from this laboratory show the ability to recover added sulfur by this method and a comparison of the turbidimetric results with those obtained by the standard gravimetric methods.

TABLE II. SULFUR CONTENT OF FOODS

MATERIAL	SULFUR %	MATERIAL	SULFUR %
Apple (crab)	0.018	Meat (cont'd)	
Apple (Rome beauty)	0.012	Ham (pig)	0.130
Asparagus	0.065	Heart (pig)	0.125
Banana	0.013	Kidney (pig)	0.155
Barley	0.137		
		Lamb chop	0.174
Beans (lima, dry)	0.187	Pork liver	0.266
Beans (navy, dry)	0.250	Pork loin	0.242
Beans (shell)	0.070	Steak (round)	0.202
Beans (soy, dry)	0.290	Shoulder (pork)	0.174
Beans (string, yellow)	0.017	Veal chop	0.069
Beets (red)	0.017	Milk (condensed)	0.126
Beets (sugar)	0.015	Milk (whole)	0.028
Bread (bran)	0.011	Molasses	0.032
Bread (white)	0.011	Muskmelon	0.031
Bread (whole wheat)	0.104	Mustard seed	1.175
Cantaloupe	0.031	Nut meats (hickory)	0.166
Cabbage	0.046	Nut meats (English walnut)	0.135
Carrot	0.016	Oats	0.160
Cauliflower	0.056	Oatmeal	0.233
Celery	0.025	Orange (California)	0.014
Cheese (American Kraft)	0.198	Parsnip	0.036
Cherries (maraschino)	0.041	Peach	0.005
Chocolate (bitter)	0.196	Peanut	0.208
Cocoa	0.236	Pear	0.016
Coffee (bean)	0.131	Peas (dried)	0.154
Corn (yellow, maize)	0.120	Peas (green)	0.031
Corn (sweet, dried)	0.131	Plums (purple)	0.004
Corn (sweet, green)	0.051	Plums (red)	0.005
Corn (gluten)	0.607	Potato (early Ohio)	0.049
Cornflakes	0.114	Potato (sweet)	0.017
Cracker (white)	0.094	Prunes	0.022
Cucumber	0.009	Pumpkin	0.018
Egg (total)	0.167	Pepper	0.035
Egg (yolk)	0.108	Radish (white)	0.019
Egg (white)	0.169	Radish (red)	0.025
Egg plant	0.036	Raisins (seedless)	0.046
Garlic	0.506	Rice (white)	0.136
Grapes (with skins)	0.012	Shredded Wheat	0.164
Hemp seed	0.291	Spinach	0.030
Honey	0.004	Spinach (New Zealand)	0.045
Horse radish	0.221	Squash (Table Queen)	0.029
Jelly (grape)	0.006	Squash (summer)	0.053
Kohlrabi	0.036	Sirup (Karo)	0.029
Lettuce (southern)	0.013	Tapioca	0.012
Lettuce (northern)	0.016	Tea	0.217
Meat		Tomato	0.017
Calves' liver	0.225	Wheat	0.145
Brain (pig)	0.113	Wheat flour (40% gluten)	0.470

TREATMENT OF SAMPLE

It is desirable to have sufficient sulfur in the oxidized sample to make possible check determinations. In the course of this work three sets of readings were taken on each sample, so it was necessary to have from 3 to 5 mg. of sulfur in each sample oxidized. The samples used varied in weight from 0.5 gram for materials high in sulfur to 120 grams for materials such as honey which contain little sulfur. The per cent of sulfur in all cases is reported on the wet basis or on the condition in which the sample was offered in the market for food consumption. This was done in order to obtain a more representative sample of the material. It is difficult in many cases to dry a sample of food high in moisture and then obtain a satisfactory sample for analysis. Volatile compounds other than water may be lost at the temperature of the drying oven or even at low temperatures. Peterson (*4*) has shown a 10 to 20 per cent loss of the volatile sulfur in rutabagas and cabbage on drying the green material in the oven. The figures presented in this paper do not represent the sulfur content of these foods in general, but only the sulfur content of the particular sample analyzed. Only when a large number of samples grown in different localities and under different conditions have been analyzed will it be possible to state the average sulfur content of any foodstuff.

OXIDATION OF SAMPLE

The method of oxidation was essentially that described in an earlier paper (*6*). The sample was weighed in its natural condition and was introduced into an 800-cc. Pyrex Kjeldahl flask and digested on the steam bath with 50 cc. of concentrated nitric acid until solution took place. The flask was then transferred to a digestion rack and boiled very gently until the evolution of nitrogen dioxide ceased. If violent bumping occurred, 15 cc. of fuming nitric acid were added. As a rule, this caused sufficient oxidation to prevent further bumping. After the evolution of nitrogen dioxide had stopped, the solution was boiled until nearly all the nitric acid had been distilled off. Then 10 cc. of 70 per cent perchloric acid were added and the boiling continued until approximately one cc. of solution was left. In some cases further treatment with perchloric acid was required. The oxidation up to this point requires from 4 to 6 hours depending on the type of material and the size of the sample. The excess of nitric and perchloric acids was destroyed by adding 10 cc. of concentrated hydrochloric acid and again evaporating to near dryness. The remaining acid was neutralized by adding dilute ammonium hydroxide and boiling to remove the excess of ammonia. The solution was made slightly acid with hydrochloric acid and filtered into a 50-cc. volumetric flask. The correct hydrogen-ion concentration for the subsequent precipitation of barium sulfate was obtained by making the solution alkaline with ammonium hydroxide and then just acid to litmus with hydrochloric acid. The solution was then made up to volume.

A blank determination was made for the sulfur present in the reagents used by running a determination on a solution containing 5 mg. of sulfur. This correction averaged 0.00006 mg. of sulfur.

USE OF MODIFIED TURBIDIMETER

The turbidimeter readings using the modified instrument were obtained by running a suitable aliquot of the solution prepared as above into a 25-cc. volumetric flask. Three cubic centimeters of a solution containing 240 grams of sodium chloride and 15 cc. of concentrated hydrochloric acid per liter were added and the whole diluted to 25 cc. The solution was transferred to a 50-cc. Erlenmeyer flask, 0.1 gram of solid sized barium chloride added, and the solution shaken for about one minute. Turbidimetric readings were taken within the following 5 minutes as described in the bulletin (*2*) furnished with the instrument. Practice in reading the instrument is essential and frequent checking of the calibration curve is recommended. The instrument should be calibrated by each operator. In the determination of sulfur in urine this same procedure should be substituted for that previously described (*1*) if the modified turbidimeter is used.

Results illustrating the use of the modified turbidimeter are given in Table I. The data in the "sulfur found" column were obtained from the calibration curve of the instrument. The figures given under the "sulfur" heads represent data on analyzed samples of known sulfate content. No oxidation was involved in their analysis. In no case did the operator know the sulfate content of these samples until after the analysis was complete.

In Table II the sulfur content of ninety-six foodstuffs is given. The results in both Tables I and II are corrected for the blank determination.

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Comparative Efficiencies of Gas-Washing Bottles

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DECISION as to the efficiency of various types of gas-washing bottles is an apparently simple matter, but one which proves quite complex on thorough investigation. Friedrichs (*2*), in 1919, showed that of the various devices known at that date, only the gas washers built on the spiral-pattern principle could insure complete absorption. Since that time, apparatus with sintered-glass filter disks have been developed. In a paper by Sieverts and Halberstadt (*5*) it was shown that besides the length of passage in which gas and liquid are in contact with each other, the size of the gas bubbles distributed within the liquid is also of decided importance. These results are referred to in a recent paper by Friedrichs (*3*). He employed mixtures of sulfur trioxide and air, both wet and dry, and tested the absorption with eleven different patterns of gas washers.

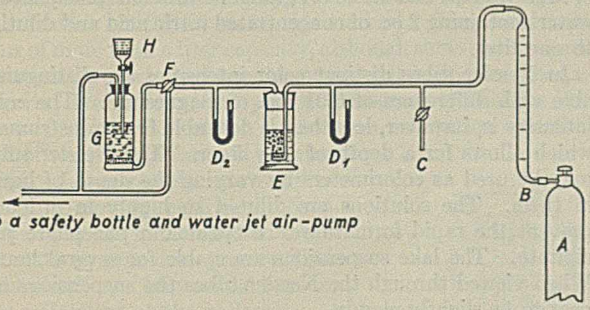

FIGURE 1. MODIFIED APPARATUS

Unfortunately these experiments cannot be compared with former ones because it is well known that wet sulfur trioxide is likely to form a nebula in air and that these nebulas behave quite differently from real gases. It is difficult to absorb them in liquids, but easy to retain them by the action of filters. This is clearly shown by Friedrichs' results. When using a moist mixture of air and sulfur trioxide, a glass-filter gas washer and a spiral gas washer filled with glass grains are most efficient, and have approximately the same effect. When using the dry mixture, the spiral gas washer filled with glass grains gives the same efficiency, owing to the considerable thickness of the filtering layer. On the other hand, the glass-filter gas washers of Schott and Gen. are less efficient because the nebulas are produced only in the thin filter disk in which the gas comes into contact with the liquid, but they are still capable of comparison with the best apparatus without glass filters.

Rhodes and Rakestraw (*4*), who also studied these problems, came to the conclusion that the spiral gas washers of Greiner and Friedrichs and the pattern 101 of Schott and Gen. (apparently G1 porosity) gave about the same good results. They employed air containing 13.4 and 5.1 per cent of carbon dioxide, with velocities of flow up to 16 cc. per second—i. e., about 60 liters per hour. They mention that for the glass-filter gas washers, a comparatively higher pressure must be used.

The following experiments were made in accordance with the last-mentioned paper. The gas mixture, contained in a steel cylinder, *A* (Figure 1), was passed through a flowmeter (Rotamesser), then through a gas washer, *E*, filled with a solution of potassium hydroxide (1 to 2), and through a three-way stopcock, *F*, to a glass-filter gas washer, 101 G3, containing a clear solution of barium hydroxide, *G*. The outlet from this led to a water-jet pump. On either side of the gas washer being tested there was placed a mercury manometer D_1, D_2. The differences in height between these two manometers are given in Table I as "resistance of the gas washer."

The gas washer containing the solution of barium hydroxide was constructed in the following manner: The usual ground-glass stopper was replaced by a double-bore rubber stopper carrying an outlet delivery tube and a glass-filter dropping funnel, *H*. With the three-way stopcock, *F*, closed, clear filtered barium hydroxide could be drawn into the bottle from this funnel. After every experiment, the filter and the gas-washing bottle were cleaned with hydrochloric acid and carefully washed with distilled water. Then a fresh portion of 75 cc. of barium hydroxide was introduced in the same manner.

The results of these experiments are shown in Table I.

TABLE I. RESULTS OF EXPERIMENTS WITH DIFFERENT TYPES OF APPARATUS

TYPE	HT. OF LIQUID COLUMN	AV. RESISTANCE OF GAS WASHER	VELOCITY GIVING REACTION WITH $Ba(OH)_2$ WITHIN 5 MIN. 17% CO_2	3% CO_2	0.67% CO_2
	Mm.	*Mm. Hg*	*L./hr.*	*L./hr.*	*L./hr.*
Drechsel	65	10	20	20	20
	95		20	20	20
Greiner and Friedrichs	(200 cc. KOH) length of way about 880 mm.	10	60	60	60
Schott 83 G1	65	20	30	45	45
	95		30	45	60
Schott 101a G1	40	25	30	45	60
	65		45	45	75
	95		60	60	75
	140		60	75	80
Schott 101 G3	40	90	60	75	100
	60		75	90	100

From these data it may be concluded that the Greiner and Friedrichs gas-washing bottle, as also found by Rhodes and Rakestraw, is useful for very many purposes. In certain cases, however, the glass-filter gas washers proved to be superior, since with this type the lower the concentration of the gaseous component to be absorbed, the greater the permissible velocity. The spiral gas washer can, in all cases, be employed only up to a certain maximum velocity (60 liters per hour) independent of the gas concentration. A possible relationship might be found if the height of the liquid in the spiral washer were varied; in this case, a shorter length of the liquid column should suffice for a more dilute gas. Now with increased flow velocity, the resistances of the gas washers become of less importance. When using finer glass filters (G3), a type which was not available to Rhodes and Rakestraw, this effect becomes even more apparent.

In this connection, it is worth calling to attention a paper by Brückner (*1*), who made use of a gas washer, pattern 101a, with a glass filter G1, for the determination of minimal concentrations of ammonia in illuminating gas. As compared with previous experiments with older types of gas washers, he could increase the flow velocity up to sixty times the previous quantity (1500 liters per hour).

The filling of the spiral gas washer of Greiner and Friedrichs with glass grains, after the example of Friedrichs, proved to be impossible in the model used, because in this case the gas passed through the filter from top to bottom, and at high velocity the glass grains were blown out of the interior chamber.

ACKNOWLEDGMENT

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Rapid Determination of Small Amounts of Magnesium in Presence of Phosphates

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THE most commonly used micromethod for determining magnesium in biological fluids or ash consists in precipitating the magnesium as magnesium ammonium phosphate from the filtrate of a calcium determination and determining the phosphorus colorimetrically (*2*, *5*).

Bečka (*1*) described a method based upon the formation of a lake by magnesium with Titan yellow. The method presented here does not require the time needed to perform a determination by the first method nor as many preparations as the second. It is suitable especially for laboratories in which such magnesium determinations are not a routine matter.

The determination is based upon the formation of a lake by magnesium with curcurmin (*3*) in the presence of sodium hydroxide, and its colorimetric comparison with standards prepared simultaneously. The phosphates affect the color of the lake suspension but, if the standard solution also contains dissolved tricalcium phosphate, the color intensities are comparable and in proportion to the amount of magnesium present. Variations in the relatively large amounts of calcium phosphate added in no way affect the color intensities of the standard solution. This fact and a difference in color shade suggests the formation of a magnesium-curcurmin-phosphate lake. The lake suspensions may be made more stable by the addition of starch glycerite solution (*4*). The removal of iron if present in too large quantities is also provided for.

PROCEDURE. Pipet an aliquot of the ash solution (containing about 2 cc. of concentrated nitric or hydrochloric acid per liter) which is equivalent to 0.02 to 0.04 mg. of magnesium into a 50-cc. Nessler tube or volumetric flask. Dilute to about 40 cc., and add 2 cc. of starch glycerite solution (prepared by shaking some of the jelly with water and filtering) and 4 drops of a 1 per cent alcoholic solution of curcurmin. Since it is important that the unknown and standard solutions receive the same amount of curcurmin, this should be added with a pipet made for the purpose from a capillary tube. Mix contents thoroughly and add 5 cc. of 4 *N* sodium hydroxide. Mix again, dilute to mark, and mix.

One or several standard solutions are treated simultaneously in the same way. A standard solution containing 0.02 mg. of magnesium per cc. is prepared by dissolving 0.203 gram of $MgSO_4 \cdot 7H_2O$ and 0.1 to 0.4 gram of tricalcium phosphate in water containing 2 cc. of concentrated nitric acid and diluting to one liter.

In Nessler tubes distinct color intensities are distinguishable with differences of 0.01 mg. of magnesium. The color intensity is, however, less than is desirable for an instrument which allows for a depth of only 5 cm. The Nessler tubes may be used as colorimeters by varying the depth of liquid in them. The solutions are diluted so highly in order to prevent the rapid formation of a tricalcium phosphate precipitate. The lake suspensions are stable for several hours. When viewed through the Nessler tubes the suspensions appear to be slightly cloudy.

If iron is present in sufficient quantity so that an appreciable colored suspension is formed upon adding the sodium hydroxide and diluting, it may be removed as follows: Titrate a separate aliquot with dilute sodium hydroxide to the neutral point of methyl red (pH 4 to 5). Add the same amount of sodium hydroxide to the aliquot to be used and filter or centrifuge out the precipitate. At that pH, the magnesium phosphate is still soluble.

When borates are present in excess of 0.6 mg. (as the oxide) magnesium-free blanks are affected slightly. The color intensities of blanks varying in boric oxide concentration from 1.4 to 8 mg. were the same. Two lake solutions were made up according to the directions given above containing 0.03 mg. of magnesium and 0.6 mg. of tricalcium phosphate. One of them contained in addition 6 mg. of boric oxide. The color intensities of both solutions were apparently the same. The slight effect, if any, of borates when present in larger amounts than 0.6 mg. can be eliminated in two ways. A solution containing 2 mg. of boric oxide may be added to each of the standard aliquots, or the sample aliquot may be evaporated to dryness with hydrochloric acid and methyl alcohol to remove the boric acid and the residue taken up with a little hydrochloric acid and water and transferred to the reaction vessel.

By this method a synthetic milk ash solution calculated to contain 0.54 mg. of magnesium was found by taking seven colorimeter readings in comparison with a standard containing 0.45 mg. of magnesium to contain 0.52 mg. A partially ashed food composite has 0.40 per cent of magnesium by this method and 0.42 per cent by the modified method of Denis (*2*).

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The Baro-Buret

III. Application to Gas Density Determinations

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GAS density determinations are of prime importance in the determination of molecular weights for the establishment of new gaseous compounds, the analysis of gaseous mixtures, the study of diffusion and viscosity, and in many other investigations. A rapid, yet accurate, method for the easy determination of gas densities from small samples would be of value.

Early gas density determinations were unsuccessful owing to the lack of suitable containers, pumps, and the means for accurately measuring volume, pressure, and temperature. With the introduction of gas balloons and the modern vacuum pumps, rapid strides have been made in the "balloon" methods of density determination. Morley (*16*), Rayleigh (*18*), and Germann (*6*) undoubtedly made some of the most valuable modern contributions to this method. They used balloons of more than a liter capacity, although some more recent investigators have used smaller ones. All balloon methods, however, are tedious, and present numerous difficulties because of contraction of the balloons on exhaustion and the need of weighing globes and counterpoises. Large samples are required which are slow to reach equilibrium. Corrections are numerous and measurements at pressures greater than atmospheric are impossible because of the fragility of the balloons.

Of other methods for determining gas densities by buoyancy (*5*, *12*), by balancing a column of gas against a column of air (*1*), or by dynamic methods (*9*, *13*), it may be said that in general large volumes of the gas are required, cumbersome manipulatory details are involved, and the results are not entirely satisfactory.

Volumeter methods (*11*, *15*), in which the volume of a known weight of gas is determined, generally require large samples and give difficulty in the measurement of pressure, volume, and temperature.

Measurements of gases in balloons, followed by adsorption or condensation in small weighing tubes, have been made by several workers (*7*, *8*, *17*) of which the recent work of Maass and Russell (*14*) probably provides the most accurate simple method. Errors and corrections due to weighing a large balloon were eliminated by first measuring the gas in a balloon, and then condensing it in a small glass ampoule which was sealed off and weighed. The tube was reopened to allow volatilization of the gas and then reweighed. Although a simple U-manometer was used to measure pressure, an accuracy of 0.05 per cent is claimed with the possibility of 0.01 per cent accuracy using a cathetometer. By modifying this method, the pressure, volume, and temperature of a much smaller sample may be measured in the baro-buret and the weight of the sample determined by adsorption and weighing in a glass tube filled with charcoal, as indicated in Figure 1. The use of the baro-buret in gas evolution methods has previously been described (*3*).

Baro-Buret Method

Advantages. The baro-buret is a simple instrument with the following distinct advantages:

1. It is rapid and easy to use.
2. It requires only a small sample.
3. It may be adjusted to give optimum conditions of volume and pressure (*2*).
4. It is possible to make several readings on the same sample.
5. It requires few corrections.
6. It is accurate.

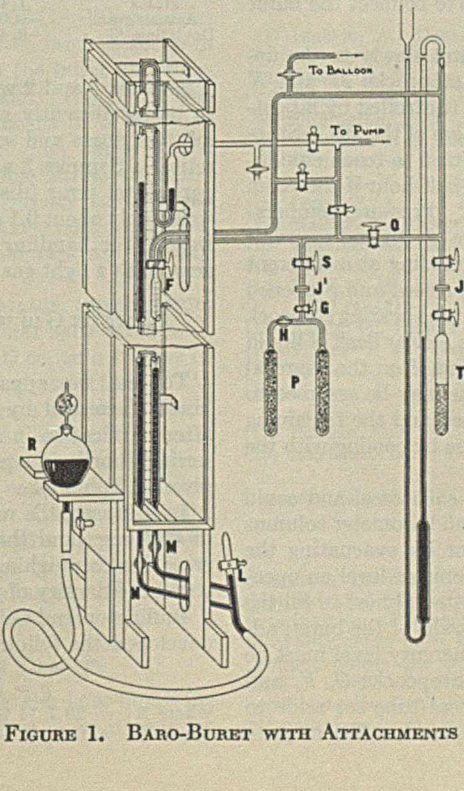

Figure 1. Baro-Buret with Attachments

The one disadvantage is that the determinations are made at room temperature rather than at 0° C.

Apparatus. To the baro-buret, described in previous articles (*2*, *3*), there are attached by means of capillary tubing, the flat joints *J* and *J'*, the manometer, the storage balloons, and the vacuum pump connections as shown in Figure 1. All stopcocks are hollow-blown and provided with clamps to permit operating under pressure. Tube *T* permits transfer of the condensed gas from the generating unit to the baro-buret, and by using two such transfer tubes at the flat joints, *J* and *J'*, purification of the gas within the apparatus itself may be accomplished by fractionation. The purified gas may be taken into the buret from the transfer tube directly, or from the storage balloons. If pressures greater than atmospheric are desired, the gas must be taken directly from tube *T*, since the balloons will not stand a pressure greater than atmospheric. Raising the mercury level in the buret to increase pressure after introduction of the gas is not satisfactory, since some gas "lies down" between the mercury and the walls of the buret and erroneous results are obtained.

The charcoal tube, *P*, is initially prepared by evacuating and then heating to 250° C. in an electric furnace while still connected to the pump. After cooling to room temperature, the tube is wiped carefully with a moist lintless cloth, dried with a silk cloth, and placed in the outer balance case. A counterpoise heavier than the tube itself is similarly moistened, dried, and placed in the balance case. The following day, the tube is weighed and then attached to the apparatus.

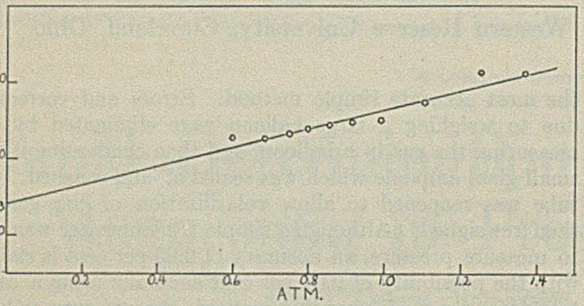

FIGURE 2. LIMITING DENSITY OF CCl_2F_2

OPERATION. With the charcoal tube connected to *J'* as shown, the capillary system and entire buret are evacuated and rinsed several times with small amounts of the gas under observation. If the gas reacts with the stopcock grease, it should be allowed to stand in the system for some time to permit saturation of the lubricant. The system is then evacuated as highly as possible with a good vacuum pump, care being taken to remove gas from both sides of stopcock *F*. Stopcock *Q* is then closed and *F* opened to connect the buret with the balloon or transfer tube.

The gas is permitted to enter the buret slowly to the desired volume at the desired pressure, stopcocks *M* and *N* both being open. The pressure may be controlled by adjusting reservoir *R* previous to the introduction of the gas. Stopcock *F* is then closed and the gas permitted to reach equilibrium with the surroundings (about one-half hour if the room is at reasonably constant temperature). Pressure, temperature, and volume readings are then made (*2*, *3*), and reservoir *R* lowered, if desired, to give a second reading at a different pressure. Stopcocks *M* and *N* are then closed and *F* opened to the charcoal tube, *P*. The arm of the tube bearing stopcock *H* has previously been surrounded with a Dewar flask of liquid air or other refrigerant. Stopcocks *G* and *H* on the charcoal tube are opened. When most of the gas may be assumed to have been adsorbed, stopcock *H* is closed and the remaining gas adsorbed in the other arm of the tube by cooling with the refrigerant.

Complete adsorption was secured in each case, and could be determined by balancing the buret and barometer columns of mercury after opening *M* and *N*, or by evacuating the capillary system and checking the manometer level on opening stopcock *Q*. The mercury is permitted almost to fill the buret. (If gas appears sticking to the walls of the buret, adsorption has been incomplete and the mercury level must be lowered to free the entrapped gas.) Stopcocks *G*, *F*, and *S* are closed, *H* opened, and the charcoal tube set aside to reach room temperature. If *H* is not opened, sufficient pressure may develop to blow out the stopcock plug or break the tube. The charcoal tube and counterpoise are then wiped with a moist lintless cloth, dried with a silk cloth, and allowed to stand in the outer balance case overnight before weighing.

Several runs may be made in the same day by using additional charcoal tubes. Measurement and adsorption require only about an hour or so per tube (two readings), provided the room temperature is reasonably constant. Several charges of the same or different gases may be added one on top of the other in the same charcoal tube. Care should be taken that the gases on warming to room temperature do not develop pressure sufficient to blow out the stopcock plugs or break the tubes.

EXPERIMENTAL WORK. To test the validity and accuracy of the baro-buret for gas density determinations, oxygen was used because at room temperature the gas is far from the critical temperature and corrections for the slight deviation are available. Electrolytic oxygen, kindly furnished by the Ohio Chemical and Manufacturing Company, was further purified by six fractionations with liquid air at pressures between one and two atmospheres. The results are given in Table I.

Two readings of pressure, volume, and temperature were made on samples 3 and 4, with the mean deviations, −0.13 and −0.20 per cent. The observed pressure was multiplied by 1.0016 to correct for the deviation of oxygen (*10*) and was further corrected for *g*, the gravity constant, and the density of the mercury at the experimental temperature. *Ln* was then calculated by the perfect gas law.

TABLE I. DENSITY DETERMINATION OF OXYGEN

	1	2	3	4	Av.
Wt. of tube before charge, grams	5.14375	9.95142	2.54243	3.78430	
Wt. of tube after charge, grams	5.04099	9.85086	2.40826	3.66921	
Wt. of oxygen, gram	0.10276	0.10056	0.13417	0.11509	
Vol. observed, cc.	96.61	98.40	99.78	98.33	
T observed, abs.	293.91	293.78	295.14	295.49	
p observed, mm. of Hg	613.1	584.6	776.2	676.8	
p cor. to 0° C., atm.	0.8040	0.7666	1.0176	0.8853	
Ln, experimental, grams	1.4215	1.4320	1.4257	1.4248	
Theoretical, grams	1.4279	1.4279	1.4279	1.4279	1.4279
Actual, gram	−0.0064	+0.0041	−0.0022	−0.0031	−0.0019
Deviation, %	−0.44	+0.29	−0.15	−0.22	−0.13

Samples 1 and 2 were weighed on a balance which proved to be insufficiently accurate for this type of work, but the mean of these and several others is fairly close to the theoretical. Samples 3 and 4 check well within the limits of experimental error (discussed later). Since 100 cc. of oxygen weigh only about 0.1 gram, an inexact weight (due to balance, weights, or handling of charcoal tube) introduces a greater error with a light gas like oxygen than with a heavy gas.

TEST ON GAS WITH CRITICAL POINT ABOVE ROOM TEMPERATURE

To test the apparatus further, dichlorodifluoromethane, kindly furnished by the Kinetic Chemicals, Inc., was used after purification in a special fractionating device, to be described shortly in a paper from this laboratory. Results are given in Table II.

In this case, the weighings were probably accurate to 0.03 or 0.04 mg., and the greater weight of sample reduced the error due to weighing. Pressure readings were corrected for *g* and the density of mercury.

Buffington and Gilkey (*4*), who worked with the same gas, developed the following equation of state:

$$p = RT\,(V + B)/V^2 - A/V^2$$

where $A = 23.7\,(1 - 0.305/V)$
and $B = 0.59\,(1 - 0.622/V)$

The units are atmospheres, degrees Centigrade absolute, and liters per gram-mole.

Table II. Density Determinations of CCl_2F_2

	1	2	3	4	Av.
Wt. of tube before charge, grams	3.88277	2.49756	9.02133	3.78603	
Wt. of tube after charge, grams	3.37222	1.98644	8.51426	3.28067	
Wt. of CCl_2F_2, gram	0.51055	0.51112	0.50707	0.50536	
Vol. observed, cc.	99.72	99.94	100.61	99.94	
T observed, abs.	294.82	297.42	297.62	298.02	
p observed, mm. of Hg	763.4	772.0	760.7	764.4	
p cor. to 0° C., atm.	1.0009	1.0117	0.9969	1.0017	
L_{23}° C., atm. (experimental)	5.0932	5.0781	5.0818	5.0811	5.0835
Deviation, actual, gram	+0.0097	−0.0054	−0.0017	−0.0024	+0.0001
From mean, %	+0.20	−0.10	−0.03	−0.05	+0.01

Table III shows the results of calculating the data given in Table II by this equation.

Table III. Calculation of Data by Equation

V	T	p Obsvd.	p Calcd.	$\frac{p(\text{Obsvd.}) - p(\text{Calcd.})}{p(\text{Obsvd.})} \times 100$
Gram-moles	*K*	*Atm.*	*Atm.*	
23.61	294.82	1.0009	1.0070	−0.6
23.64	297.42	1.0117	1.0145	−0.3
23.99	297.62	0.9969	1.0020	−0.5
23.91	298.02	1.0017	1.0065	−0.5

Thus we find the errors −0.6, −0.3, −0.5, and −0.6 per cent, showing that the values check the equation to about 0.5 per cent, the accuracy claimed by the authors. By this method of calculation, the greatest deviation from the mean is about 0.2 per cent, a value corresponding to that obtained in Table II.

Since the gas is known to deviate greatly and no accurate equation is available, no attempt was made to calculate the weight of a normal liter. Hence the values for the weight of a liter are given at 23° C. and one atmosphere calculated by the perfect gas law, which introduces but a very slight error.

Corrections and Errors

The observed pressure in any experiment with this apparatus must be multiplied by the correction for g (1.0004 at this laboratory) and by the ratio of the densities of mercury at the experimental temperature and at 0° C. When deviation corrections are known, they should be used as above in the case of oxygen. Errors inherent in the buret and thermometers were eliminated by calibration. The buret was calibrated in place with mercury by means of a stopcock with a fine tip placed just above M. The buret should always be checked in this way, since some burets are made for convex downward menisci, whereas mercury has a convex upward meniscus. The pressure corrections outlined above, together with those for buret and thermometer, are the only corrections required.

In any determination using this apparatus, certain errors are unavoidably present. On the particular baro-buret used, readings of volume could be made to 0.05 cc. on a volume of 100 cc., of pressure to 0.4 mm., of temperature to 0.1° C., and of weighings to 0.04 mg. on a 0.1-gram sample, giving a maximum error of about 0.20 per cent for a light gas (oxygen) and a somewhat smaller error for a heavier gas. (Additional errors might, however, be introduced if care were not taken in the handling of the charcoal tubes). The errors should be self-compensating and a mean should be very accurate. Individual error could be reduced by using a cathetometer and mirror scale to read pressures and volumes, and an error of not over 0.1 per cent should be easily secured.

Determination of Limiting Density

To determine the possibility of using the baro-buret for determining molecular weights of small samples of gas by the limiting density method, a set of readings was made between pressures of 0.6 and 1.4 atmospheres. All readings were made on the same sample of gas and the results are shown in Table IV.

Table IV. Calculation of Limiting Density

(Wt. of CCl_2F_2 sample, 0.20879 gram)

V Cor.	D_{23}°c.	p Cor.	D/p
25° C.	*Grams/liter*	*Atm.*	
29.75	7.01815	1.36959	5.12428
32.51	6.42233	1.25195	5.12986
37.25	5.60511	1.10492	5.07287
41.72	5.00455	0.99085	5.05076
45.24	4.61516	0.91440	5.04720
48.43	4.31117	0.85459	5.04472
52.10	4.00749	0.79530	5.03897
56.39	3.70261	0.73567	5.03298
60.76	3.43631	0.68362	5.02664
69.52	3.00331	0.59731	5.02806

Readings of volume were made at temperatures between 25° and 30° C. and corrected to 25° C. by the perfect gas law. Pressures were corrected as in the earlier tables. D is the weight in grams of one liter of the gas at pressure p.

Figure 2 is intended to show that the straight line through the calculated limiting density (4.9433) passes through the average value of the points, rather than to establish the limiting density. The accuracy needed to establish the molecular weights of a gas could be secured by averaging several such determinations.

Discussion and Conclusion

The baro-buret has been shown to provide a rapid and accurate means for the determination of gas densities using a small sample. The apparatus is comparatively easy to build and use. Few corrections are necessary.

When the apparatus is used to determine molecular weights to assist in identifying unknown compounds, the possibility of deviation from the perfect gas law must be kept in mind. By taking readings at several pressures, with each sample the molecular weight can be readily determined by the method of limiting densities (*15*) and only one set of weighings is required.

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Chemists in the Bureau of Chemistry and Soils have demonstrated that hydrochloric acid and sulfuric acid cause the deterioration of paper. When chlorine compounds are used in bleaching paper pulp, hydrochloric acid may form in the finished product unless the pulp is washed clean. Alum is generally used in sizing paper and if present in excessive quantities will cause deterioration of the finished product. The paper must be virtually free from acid or it will not endure.

Glass and Quartz Filters for Handling Gases

A Review

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Glass filter apparatus with porous glass filter disks sealed into solid glass walls have been shown to be extremely useful for many laboratory operations where gases are to be treated. These are briefly reviewed here and a copious bibliography refers to many investigations using this technic. Applications discussed include mercury traps, explosion safety valves, dust filters, and gas-liquid reaction vessels. High-velocity gas flow in such apparatus is especially characteristic of glass filter apparatus, and this is important in gas analysis where small quantities of an impurity in large volumes of gas are to be determined, in air-conditioning for textile tests, in flotation experiments, and in physiological and biochemical work.

GLASS filters for separating solids from liquids have been in use for some years, and a number of American investigators have published researches involving their application since the first notice of them (*47*) appeared. In the meantime, the wider use of this convenient form of apparatus has been considerably extended by the development of many unique applications, particularly in Germany. Since the researches dealing with these have most largely appeared in German publications, and since the use of filters of this kind in working with gases presents many novel features of special convenience to investigators in this field, it has been thought desirable to review briefly here the progress that has been made along this line. The appended bibliography provides references to methods of applying the new technic in many lines of investigation.

Glass filters are made of ground and sifted glass powder fritted in suitable molds (without any added binder) into porous disks of glass (*5, 32*) which may be fused into any desired shape of solid glass of the same coefficient of expansion. By selecting the glass used, any desired qualities of chemical or temperature resistance may be had. Ordinary soft glass or special glasses, such as Jena G20 resistance glass, and even fused quartz (*27*) may be used, and it is possible to use special jointing glasses to permit fusing filter disks to other glasses (such as Pyrex) forming the apparatus where necessary. Many standard forms of apparatus embodying such filters are shown in the accompanying illustrations (courtesy Fish-Schurman Corp., 230 East 45th St., New York, N. Y.).

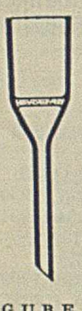


Figure 1. Glass Filter for Mercury Purification

Some Uses of Glass and Quartz Filters

During the past ten years or so an increasing amount of work has been done with gases in large and complicated vacuum apparatus, and in connection with this several interesting applications of glass filters have been devised. Whereas coarse-grained filters will allow mercury to pass through, retaining dirt, dust, and solid amalgams (Figure 1), fine-grained glass filters will retain mercury even against a pressure of one atmosphere. Making use of this peculiarity, Stock (*44, 62*) was one of the first to include a glass filter in his apparatus for interrupting gas flow. Stock's device (Figure 2) may be used as a safety valve in a vacuum line by placing a vessel of mercury under the lower stem. A single filter of this kind (Figure 3) may be similarly used as a gas valve by placing a layer of mercury on top of the filter disk, thus allowing gas to pass one way but not the other. Hein (*22, 23, 46, 69*) proposed that similar devices (Figure 4) be used as a pressure regulator connected to the top bulb of a Kipp apparatus, especially for generating carbon dioxide in elementary microanalysis after Pregl.

Glass filters may be used advantageously as diffusion membranes, since the diffusion rate of any particular filter is constant and depends upon the porosity as established by the grain size of the glass of which the filter disk is made. Membranes of this kind may form an integral part of gas flow measuring devices (*13*). Similarly, such membranes have been used by Bennewitz and Neumann (*3*) for preventing uneven flow of gas to their catalyst in studies of the impulses in heterogeneous catalysis. Martienssen (*18*) has utilized this property of glass filters in a device for detecting the presence of an explosive mixture in the air of coal mines by using them as membranes to separate the reaction chamber containing an electrically heated platinum wire from the outer air. The device operates on the same principle as the Davy safety lamp, but is safer since the glass filter cools the flame more thoroughly than a wire gauze and thus prevents its outward passage.

Figure 2. Double Mercury Trap after Stock

Similarly glass filters fused into glass tubes may be used to advantage as safety valves to prevent gas explosions in laboratory work (*49, 50*). When an explosive gas mixture is passed through a tube, like that shown in Figure 5, into the small end and is ignited at the wide end, even a coarse filter will prevent the explosion from going beyond it. This is much more effective than the use of copper gauze, and ordinary glass filters will withstand the temperature of the flame of an explosive mixture of illuminating gas with air. A quartz tube with a quartz filter are necessary on account of the higher temperature if oxygen replaces air. The flame moves from the open end to the filter, and there surface combustion (after Bone) may be seen. Even with the most explosive mixture of hydrogen and oxygen the filter is not damaged, but when a white heat is reached, the gas back of the filter ignites at the hot surface. This apparatus lends itself to the determination of the explosive characteristics of air-petroleum mixtures, among others.

Figure 3. Single Filter Mercury Safety Valve

Using this principle, Grote of the Edeleanu G. m. b. H., Berlin, was able to devise a method of making Heslinga's (*64*) determination of sulfur in liquid fuels easy and convenient.

The apparatus (*10*) is shown in Figure 6. The quartz tube is 520 mm. long and is fitted with a diaphragm having an opening 5 mm. in diameter and two coarse quartz filter disks. The sample, in a porcelain dish or open glass ampoule, is placed in the left end of the tube and compressed air or oxygen is supplied. The first filter disk serves as a safety valve to prevent backfire, and the second serves as the combustion surface. The oxidation products, containing carbon dioxide and sulfur dioxide, are conducted through the glass absorption vessel (fitted with a glass filter disk to insure complete absorption) containing a known quantity of hydrogen peroxide, and the sulfuric acid formed is then titrated in the usual way. This method has been used and approved by a number of investigators (*56*) and seems likely to be adopted as standard in Germany.

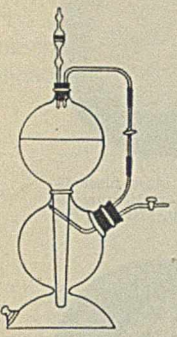


FIGURE 4. KIPP GAS GENERATOR WITH HEIN'S MERCURY SAFETY VALVE ON TOP

Many investigators have used glass filters for separating solids from gases even at elevated temperatures (*25*, *33*, *51*, *54*, *55*), and since different porosities are to be had to meet different conditions, they have proved highly practical for a variety of researches. By proper selection of porosities, high gas velocities can easily be obtained without sacrifice of efficiency. The apparatus shown in Figure 7 has been proposed for the determination of tar in illuminating gas (*6*, *34*), and has been used with considerable success for this purpose. A measured flow of gas passes first over cotton wool to remove coarse droplets, then over a coarse glass filter to remove tar mist, and finally over a finer glass filter to insure complete separation.

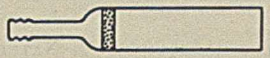


FIGURE 5. EXPLOSION SAFETY VALVE

An interesting method of analyzing aluminum and its alloys using glass filters has been developed by Jander (*29*, *30*). The apparatus is shown in Figure 8. A stream of dry hydrochloric acid gas coming from the left hand side is passed over the metal shreds in the porcelain boat and thence through a coarse-pored glass filter in front of the glass fitting and on to the absorption apparatus. If magnesium is present in the sample, magnesium chloride may be removed from the gases before they reach the filter by applying the Cottrell electrical precipitator principle. This is done by sealing a molybdenum wire into the tube to serve as one electrode, and placing a metal band around it to serve as the other. The high voltage applied across these electrodes flocculates the magnesium chloride and prevents its passage through the glass filter. Aluminum oxide present in the sample does not combine with the hydrochloric acid under these conditions and may be determined separately from the metallic aluminum which passes the filter as the volatile chloride along with silicon tetrachloride. The temperature of the process may be 200° to 350° C., depending upon the metals present. A simpler apparatus for microanalysis and micropreparations (Figure 9) has been developed by Soltys (*60*).

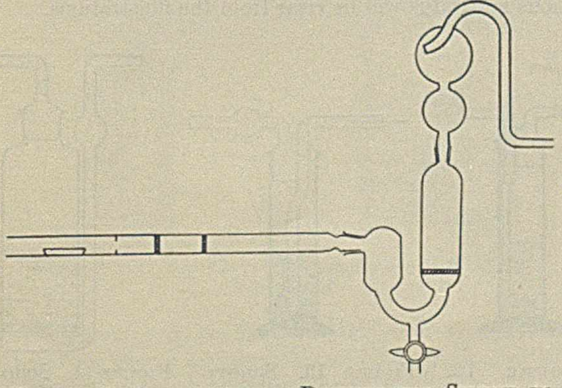


FIGURE 6. APPARATUS FOR DETERMINING SULFUR IN LIQUID FUELS AFTER GROTE

In all glass apparatus where reactions are to be carried out between solids and gases, glass filters are very convenient. Mittasch (*43*) has used this technic in studying the decomposition of ammonia over metallic iron, and Huettig (*26*) applied it to the catalytic slitting of methanol by zinc oxide.


FIGURE 7. DOUBLE GLASS FILTER FOR TAR DETERMINATION AFTER BRÜCKNER

One of the most important applications of glass filters is in securing intimate contact between gaseous and liquid phases, a technic principally developed in Germany. In the United States, Edgar and Calingaert (*11*) used a glass filter tube in determining the sulfur content of gases from combustion of gasoline, and Degering (*8*) proposed a similar device as an efficient gas-liquid reaction tower.

DETERMINATION OF PORE SIZES AND SIZE OF BUBBLES

In applications of this kind, the value of glass filters depends upon their ability to break the gas stream up into tiny bubbles while allowing it to pass at relatively high velocity. On this account, a method of estimating pore size and its relation to bubble size in different filters and with different liquids is valuable. Bechhold (*1*) showed that the pressure drop occurring at a gas-liquid interface is directly proportional to the capillary constant of the liquid and inversely proportional to the pore diameter. His formula was rediscovered by Einstein and Muehsam (*12*), and measurements of the kind have been widely used for determining maximum and average pore diameters for different filtering materials (*24A*, *53*). A simplified form of the Bechhold equation (*48*) will serve for practical laboratory use as follows:

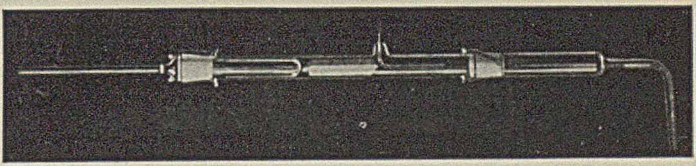


FIGURE 8. GLASS FILTER TUBE AFTER JANDER FOR ANALYSIS OF ALUMINUM ALLOYS

$$2r = \frac{4\pi \cdot b \cdot 10^4}{p \cdot 10^6 \cdot 1.033}$$

where $2r$ = diameter of pore emitting bubbles, microns
b = barometric pressure, mm. of mercury
π = capillary constant of liquid employed
p = manometric pressure drop, mm. of mercury
$1.033 \cdot 10^6$ = pressure of one atmosphere, dynes

Later Bechhold (*2*) and Schnurmann (*54A*) showed that this equation is not strictly correct, and that some variation

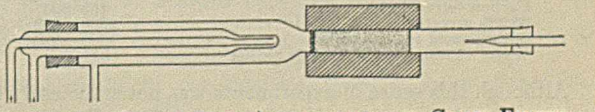
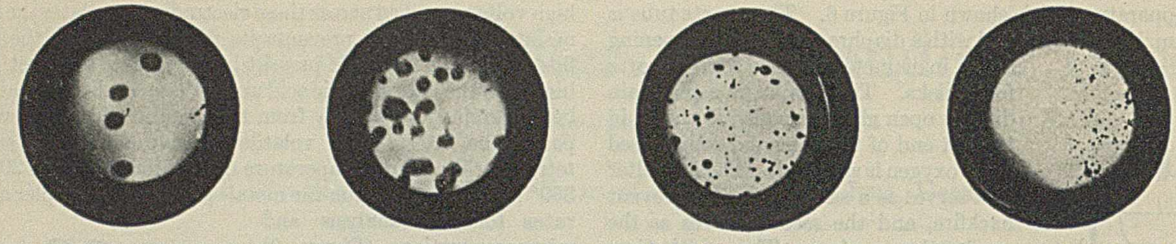


FIGURE 9. SUBLIMATION APPARATUS WITH GLASS FILTER AFTER SOLTYS

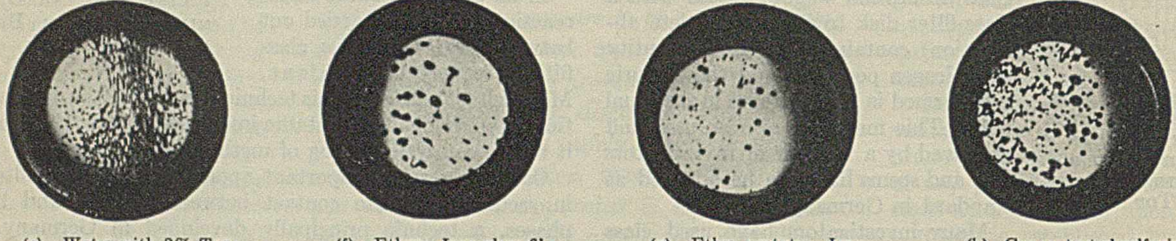


(a) Water over 20-micron platinum foil (pinhole diameter, 243 microns; pressure drop, 16 mm. Hg)

(b) Jena glass filter G1 (pore diameter, 120 microns; pressure drop, 18 mm. Hg)

(c) Jena glass filter G2 (pore diameter, 45 microns; pressure drop, 42 mm. Hg)

(d) Jena glass filter G4 (pore diameter, 10 microns; pressure drop, 170 mm. Hg)



(e) Water with 2% Turkey red oil; Jena glass filter G2 (pressure drop, 30 mm. Hg)

(f) Ether; Jena glass filter G2 (pressure drop, 14 mm. Hg)

(g) Ethy acetate; Jena glass filter G2 (pressure drop, 16 mm. Hg)

(h) Concentrated sulfuric acid; Jena glass filter G2 (pressure drop, 38 mm. Hg)

FIGURE 10. PHOTOGRAPHS OF AIR BUBBLES IN LIQUIDS ($^3/_4$ NATURAL SIZE)

was found between the values of $2r$ for a porous diaphragm when different liquids are used, as well as with two immiscible liquids brought together across it.

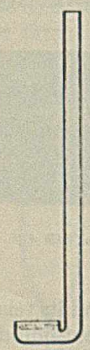


FIGURE 11. GLASS FILTER GAS-DISTRIBUTING TUBE

The size of bubbles produced by a porous diaphragm is not the same as the pore size, but is always larger than the capillary diameter (*42*) and depends on the nature of the liquid used (*2*, *54A*). To take this into account, Halberstadt and Prausnitz (*19*) have devised a method of studying the bubbles themselves depending upon photographing them as they rise between the parallel walls of a kind of inverted cuvette. This investigation is of sufficient interest to justify rather careful consideration here. Its principal conclusions may be summarized as follows:

Different pore sizes of glass filters require different pressures; the smaller the pores, the higher the pressure. Plotting the gas bubble size against pressure drop for glass filters of different pore diameters yields a hyperbolic curve when either water or ether is used. There is a distinct optimum of distribution contact between gas and liquid for pore diameters between 14 and 34 microns. A further decrease in pore diameter only slightly decreases the size of gas bubbles, but requires a considerably higher pressure.

Using a glass filter of medium porosity (Jena G2; average pore diameter 34 microns), the size of the gas bubbles formed in different liquids varies widely. The following bubble diameters were measured under these conditions, using the same glass filter:

LIQUID	BUBBLE DIAMETER *Microns*
Water	490–1240
Ether	270–1650
93.6% alcohol	450–1660
Ethyl acetate	480–740
Carbon tetrachloride	450–800
88.2% glycerol	2330–2890
Sulfuric acid (concentrated)	1060–1330
Water containing 2% Turkey red oil	350–500

Although this series of experiments was not sufficiently extensive to relate the physical constants of the liquids completely to the bubble size, yet it is obvious that the addition of a surface-active substance like Turkey red oil exerts a profound influence in reducing bubble diameter, and that such additions may therefore be most valuable for increasing the gas surface developed with any specified diaphragm. A coarse filter working with a low pressure drop will form small bubbles where the nature of the reaction desired permits the addition of such materials. Figure 10 shows some of the photographs (three-fourths natural size) of bubbles taken at pressures sufficient to allow the whole filter surface to pass gas, together with a similar photograph for comparison purposes showing the bubbles from a perforated platinum foil.

APPLICATION OF GLASS FILTERS

Glass filters, used for a variety of operations requiring the intimate contact between a gas and a liquid, have been built into many different types of apparatus (Figures 11 to 18, inclusive), and for use in these are available with pore diameters from 1.5 to 250 microns. The most popular pore sizes are 120 and 45 microns. The principles of construction of the various apparatus will be clear from the illustrations.

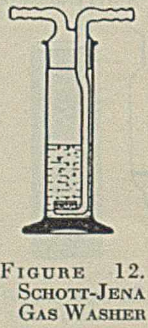


FIGURE 12. SCHOTT-JENA GAS WASHER

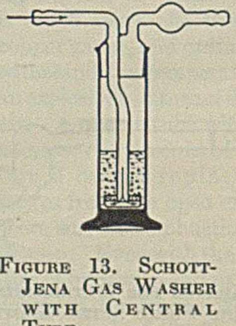


FIGURE 13. SCHOTT-JENA GAS WASHER WITH CENTRAL TUBE

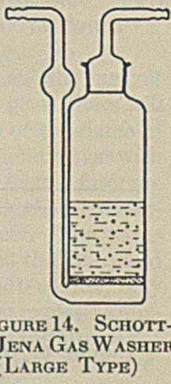


FIGURE 14. SCHOTT-JENA GAS WASHER (LARGE TYPE)

The application of these various forms to particular problems has been developed by a number of investigators; Heinrich and Petzold (*24*) for sulfur determinations; Slotta and Heller (*59*) for organic hydrogenations; Gehlen (*17*) for the reaction between nitric oxide and alkaline hydrosulfite;

Sieverts and Halberstadt (*58*) for oxygen absorption; Vorlaender and Gohdes (*66*) for nitric oxide absorption; Berl (*4*) for general gas analysis; Tschopp (*65*) in microanalysis; Pfyl and Schmitt (*45*) and Heiduschka (*20, 21*) in the determination of nicotine in cigarette smoke; Strobl (*63*) in Orsat apparatus to replace platinum foil proposed by Shepherd (*57*); Brückner (*6A*) for determining ammonia in illuminating gas; Koelliker (*37*) for detecting minute traces of impurities in the atmosphere; Loeffler (*40*) and Dietrich (*9*), tandem glass filters for determining benzene in air.

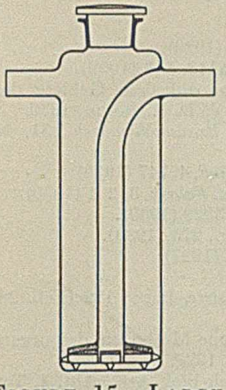


FIGURE 15. LARGE GAS WASHER AFTER KOELLIKER AND DWILLING

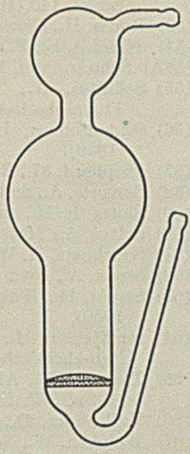


FIGURE 16. GAS WASHER FOR PHYSIOLOGICAL CARBON DIOXIDE DETERMINATION AFTER KNIPPING

The methods used by Brückner (*6A*) and Koelliker (*37*) are particularly interesting, since by utilizing the efficiency of glass filters at high gas velocities, they have developed a technic for detecting and determining extremely minute traces of impurities. Using a gas-washing bottle as shown in Figures 13 (*31*), 14, or 15, they draw a large measured volume of gas through the absorbent solution at velocities as great as 50 liters per minute, obtaining excellent results.

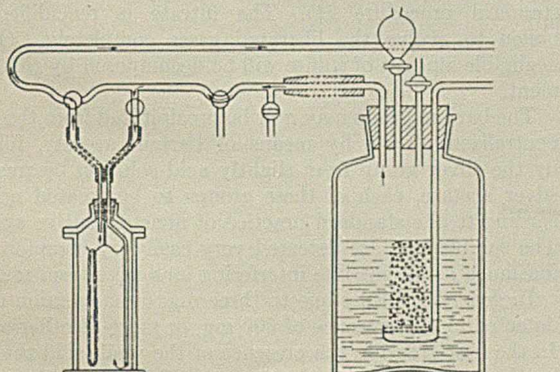


FIGURE 17. AIR-CONDITIONING APPARATUS AFTER WELTZIEN

At low gas velocities the Friedrichs (*16*) screw type gas scrubber has been shown by Sieverts and Halberstadt (*58*) to be about equal to a coarse-pore G (Figure 1) glass filter, but these investigators have shown that as velocity is increased or a finer glass filter, G3, used, the latter is more efficient. With glass filters the pressure required to break down the initial film to allow the gas to pass looms large in the total pressure where low velocities are used, as by Friedrichs (*15*) in sulfur trioxide absorption and by Rhodes and Rakestraw (*52*) in absorbing carbon dioxide at low velocities. Fischer and Hess (*14*) also worked at low velocities in absorbing sulfur trioxide. However, at high velocities Koelliker and Dwilling (personal communication) have shown that the resistance to flow introduced by the narrow tubes and abrupt curves of the Friedrichs apparatus may become as great as that of the glass filter. Using the apparatus shown in Figures 14 and 15 at gas velocities as great as 120 liters per minute, they have found that the pressure drop in the latter type (Figure 15) at this velocity is comparable with that obtained by Rhodes and Rakestraw (*52*) in the former type (Figure 14) at a velocity of only one liter per minute. Obviously with velocities as great as 120 liters per minute through a filter 60 mm. in diameter available at a pressure of less than 400 mm. of water column, many new possibilities in the treatment of large volumes of gases are available.

FIGURE 18. YEAST AËRATION VESSEL AFTER KLUYVER

Utilizing this high-velocity characteristic Knipping (*7, 36*) has devised an apparatus for determining carbon dioxide produced by a person during hard labor (Figure 16). An enclosed air volume (with oxygen added as needed) of only 3.2 liters is circulated at a rate of 40 liters per minute to the subject with continuous removal of carbon dioxide. A somewhat similar arrangement for treating an enclosed volume of air to secure continuously a definite humidity for textile tests has been developed by Weltzien (*67, 68*). In this (Figure 17) air from the enclosed space whose humidity is to be controlled is pumped through aqueous sulfuric acid of a known vapor tension at high velocity.

In bacteriological work, Kluyver (*35*) uses a conical vessel with medium pores, G3 filter (Figure 18), for aërating yeast cultures. Kraeber (*38*) uses a similar but cylindrical vessel in flotation experiments. Large technical glass filters may be had in diameters up to 610 mm., and these are already finding considerable use in industry for such operations as forcing corrosive gases into solutions (*28*) and in numerous other operations.

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Notes on Systematic Qualitative Analysis of Anions

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Although many qualitative systems of cation analysis have been developed, up to the present time there is no generally accepted scheme for the anions in which each of the various groups is separated consecutively from one sample. It is believed that the following method of group separation makes this possible. The first group removes all those ions which ordinarily interfere with the clean-cut use of the well-known group precipitants in a consecutive system, so that the well-known groups then fall naturally into the remainder of the scheme. There is no overlapping of the groups, inasmuch as each group reagent provides complete separation. A system has been developed (*3*) which includes thirty-one anions.

One gram of the unknown substance (in solution unless acid-soluble) is neutralized with 6 N acetic acid in a stoppered Erlenmeyer flask fitted with a thistle tube and strips of lead acetate, starch-iodide, and potassium chromate papers held by the stopper, and a delivery tube dipping into baryta or lime water. The delivery tube should have a small bulb blown in it to contain slightly moistened potassium permanganate crystals to prevent sulfur dioxide from reaching the baryta water (*2*). Three milliliters excess acetic acid are added to the solution through the thistle tube and the mixture is heated to 65° C. for one minute, which will liberate hydrogen sulfide, chlorine from hypochlorite, sulfur dioxide from thiosulfate but not from sulfite (unless over 150 mg. of sulfite are present), and carbon dioxide. These gases are detected, if present, by the means provided in the above description. A special thiosulfate test is advisable, and Eastman Formula HT-1 will detect one mg. (*1*).

Two milliliters of 6 N ammonium hydroxide are added through the thistle tube followed by nickel acetate to precipitate sulfide, if present, completely, and the cyanogen group (cyanide, ferrocyanide, and ferricyanide), which may be filtered off and the individual ions separated according to standard procedure (*4*). The filtrate is reacidified and boiled to evolve the liberated gases completely. Only a negligible amount of sulfite will be decomposed by this treatment.

The barium group may now be precipitated from the above neutralized filtrate by means of barium acetate, followed by the silver group from slightly acid solution by means of silver acetate, each of these groups to be treated now according to the standard practice of nonconsecutive systems. The soluble ions are detected very easily by common tests, inasmuch as all possible interfering ions have been removed.

In general, at least one to three mg. of each anion can be detected in the presence of 300 mg. or more of other anions. In the first group in the presence of the weak acid there will not be sufficient reaction between sulfide and sulfite to prevent the detection of each at the usual point. This method of group separation makes possible quick and accurate detection of the negative ions.

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Functional Relationship between Ash Content and Electrical Conductance of Cane Sirups and Molasses

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An empirical formula has been developed for predicting the ash percentage in cane sirups and molasses from conductance measurements in the presence of hydrochloric acid, phosphoric acid, and potassium hydroxide, but without the addition of sucrose to the sample.

The formula was developed, on the basis of the statistical technic of multiple regression, out of the interrelations existing among the conductance values corresponding to the percentage of chemical ash. The error in the ash percentage calculated by this method is but 3 parts in 93, whereas the permissible error in the chemical method is about 3 parts in 50.

IT HAS been shown in previous papers (*1*, *7*) that the ash content of various kinds of sugar-cane products, such as raw and refined sugars, raw and refinery sirups, and molasses, can be determined by means of conductivity measurements. A specific equation was proposed for each type of product, and in this way the differences among the samples due to their heterogeneous geographical origins, which brought about a variability in the composition of the nonsugar impurities, and their subsequent processing, can be appropriately taken into consideration. The following conductometric formula was developed for determining ash in both raw and refinery sirups and molasses (*2*) under the condition that 4.5 grams of pure sucrose are added to each 0.5 gram of sugar product before making up to 100 ml. of total volume:

$$\%\ \text{ash} = 0.019137\,K - 0.002249\,K_2 - 0.00121\,K_3 + 3.07$$

where K is the specific conductance × 10^6 of the solution prepared as above; K_2 that of a solution made by adding 5 ml. of 0.25 N potassium hydroxide to 200 ml. of the above solution; and K_3 that of a solution made by adding 5 ml. of N orthophosphoric acid to 200 ml. of the above solution.

The sucrose was added for the purpose of preparing a synthetic raw cane sugar solution. In this way it was hoped possibly to relate the analysis of sirups and molasses directly with the method of determining ash conductometrically in raw cane sugars (*5*, *6*).

For routine work, the omission of sucrose from each solution would be advantageous, and so conductometric determinations were made, without the addition of sucrose, on 149 samples of molasses and sirups which had remained in the laboratory from the previous work. Aside from the fact that 0.5 gram of the sample alone was taken for each 100 ml. of solution, no changes were made in the experimental procedure (*1*–*7*).

The formula which was found to hold under these conditions is as follows:

$$\%\ \text{ash} = 0.01556\,K - 0.001125\,K_1 - 0.000623\,K_2 - 0.000219\,K_3 + 3.083$$

The meaning of the various K's is the same as in the first formula; K_1 represents the specific conductance × 10^6 of the solution obtained by adding 5 ml. of 0.25 N hydrochloric acid to 200 ml. of the solution of the product, as specified above.

The new formula indicates that four conductivity determinations must be made in order to calculate the ash percentage. The reason for this will be explained below. It will be remembered that conductometric ash determinations in raw sugars require only two conductance measurements (*4*). The formula in question was readily derived by simple graphic and arithmetic methods. But when it was later found that in the case of sirups and molasses at least three conductivity determinations are necessary, the derivation of the required formula proved to be a laborious task. It was therefore decided to have recourse to statistical methods, and the cooperation of one of the present writers was invited. The formulas given in the later papers of this series were calculated by him on the basis of experimental results. The methods by which the formulas were derived will undoubtedly prove of interest, and they are therefore briefly explained here.

Statistical method has developed a numerical measure of the relationship existing between two variables on the assumption of linearity. By linearity is meant that the equation relating one variable to another is of the nature:

$$x = by + c$$
$$y = dx + f$$

where x and y are deviations from the means of the X and Y distributions, respectively.

The multiplying factors, d and b, are known as the "beta weights." The square root of the cross product of the two beta weights is defined by the worker in statistical mathematics as the correlation coefficient. In the case in which a variable is completely a function of another variable, the product of the two betas is equal to one and the correlation coefficient is obviously ±1. There are, however, many instances when, owing to lack of precision in measurements or lack of complete functional relationship among variables, a variable is not completely determined by a weighted measure of another. Such deviations from complete prediction give rise to correlation coefficients other than ±1. The predictability on the basis of correlations less than one varies approximately as the square root of $1 - r^2$, where r is the correlation coefficient. Whenever complete predictability is impossible upon the basis of the data, we have two equations as above. The b is defined as

$$r_{xy}\frac{\sigma_x}{\sigma_y}$$

where r_{xy} is defined as the correlation coefficient measuring the relationship between variable x and variable y, and σ_x is defined as the square root of the mean of the sum of the squares of the deviations around the mean of the X variable. σ_y, similarly, is defined as the square root of the mean of the sum of the squares of the deviations around the mean of the Y variable. Mathematically,

$$r_{xy} = \frac{\Sigma xy}{N\sigma_x\sigma_y}$$

where σ_x and σ_y have the same meaning as before, and the Σxy refers to the cross product of the deviation from the mean of the X variable with the deviation from the mean of the Y variable, summating from sample to sample over all samples, and N refers to the number of cases or population.

When the problem is simply the prediction of one variable from another, the calculation of the single correlation coefficient relating the two and the computation of the sigmas is all that is necessary to the development of a prediction formula, or, as it is known in statistics, a regression equation. The regression equation thus obtained is developed under the assumption that all measurements have the same reliability. By reliability is meant the degree to which confidence can be placed in a single measurement of the variable. For instance, it is assumed in this paper that the average of a duplicate chemical determination of sugar ash is so accurate that any redetermination of the same sugar ash for the same sample will yield the same result. This, obviously, is not true except within certain experimentally and statistically determinable limits. The formula

$$r_{xy} = \frac{\Sigma xy}{N\sigma_x\sigma_y}$$

makes for a cumbersome computational technic. There are various computational forms which will yield the same result. The formula used for computing the correlation coefficient for this particular paper is

$$\frac{\frac{\Sigma XY}{N} - \left(\frac{\Sigma X}{N}\right)\left(\frac{\Sigma Y}{N}\right)}{\sqrt{\frac{\Sigma X^2}{N} - \left(\frac{\Sigma X}{N}\right)^2}\sqrt{\frac{\Sigma Y^2}{N} - \left(\frac{\Sigma Y}{N}\right)^2}}$$

where X and Y refer to the actual value of X and of Y, and X^2 and Y^2 to the squares of such values.
Then

$$\frac{\Sigma X}{N} = \text{arithmetic mean of } X$$

$$\frac{\Sigma Y}{N} = \text{arithmetic mean of } Y$$

and

$$\sqrt{\frac{\Sigma X^2}{N} - \left(\frac{\Sigma X}{N}\right)^2} = \sigma_x$$

and

$$\sqrt{\frac{\Sigma Y^2}{N} - \left(\frac{\Sigma Y}{N}\right)^2} = \sigma_y$$

For example, our data sheets show for chemical ash and K the following three sample observations:

SAMPLE	CHEMICAL ASH (X)	K (Y)
354	7.31	474.7
355	6.96	443.5
356	6.71	426.2

The sum of such terms as (7.31 × 474.7) and (6.96 × 443.5) and (6.71 × 426.2) will yield ΣXY. The sum of such terms as 7.31, 6.96, and 6.71 will yield ΣX, and the sum of such terms as 474.7, 443.5, and 426.2 will yield ΣY. The sum of such squares as $(7.31)^2$, $(6.96)^2$, and $(6.71)^2$ will be ΣX^2. The ΣY^2 will be the addition of terms like $(474.7)^2$, $(443.5)^2$, and $(426.2)^2$. The manipulation of these terms will yield the needed correlation coefficient.

The above computations, as has been pointed out, are sufficient for obtaining a regression equation predicting one variable from another. When, however, the predictability of one variable from only one other leaves too large a margin of error, it is possible to make use of multiple regression, by which technic the regression equation predicting a criterion variable from a dependent variable is improved by utilizing the relationships that may exist between the criterion and some other dependent variable or variables.

When the number of variables, including the criterion, is greater than two, the number of correlation coefficients that must be computed to obtain a multiple regression equation is equal to

$$\frac{n(n-1)}{2}$$

where n refers to the total number of variables. In developing the equation reported in this paper, five variables are used: ash (the criterion variable), K, K_1, K_2, and K_3, where the K's are the conductometric readings as previously defined. Hence, ten correlations must be computed among these five variables. Table I gives the correlation coefficients obtained between ash and the conductometric readings. Such correlation coefficients are known as zero order correlation coefficients, since no attempt is made to eliminate the effect of other variables from any of the reported correlation coefficients.

TABLE I. ZERO ORDER CORRELATION COEFFICIENTS BETWEEN CHEMICAL ASH AND EACH SPECIFIED CONDUCTOMETRIC READING

	ASH	K	K_2	K_3	K_1
Ash		0.9861	0.5974	−0.3318	−0.5486
K			0.6493	−0.2342	−0.4574
K_2				−0.0431	−0.1090
K_3					0.9092

On the assumption that the conductometric readings and the determination of chemical ash are perfectly reliable, it is possible to set up a formula for the solution of the multiple regression equation predicting chemical ash from the conductometric readings, which is the problem of this paper. The data needed for setting up the normal equations to yield the beta weights are the correlation coefficients and the sigmas of each variable. After the weights have been determined, it is a simple matter to determine the constant term. For this, in addition, we need the arithmetic mean of each variable. Table II gives the necessary sigmas and means for the complete solution of the problem.

TABLE II. MEANS AND SIGMAS OF CHEMICAL ASH AND CONDUCTOMETRIC READINGS[a]

	MEAN	STANDARD DEVIATION
Ash	9.2658	2.0327
K	592.5953	125.5153
K_2	1447.6308	120.0157
K_3	1561.1677	131.5440
K_1	1594.7046	180.9855

[a] These values represent figures obtained from original data. When equation derived from them was used for calculation of ash content, 17 cases fell outside of arbitrarily adopted limits of variability of ±0.30%. These samples were redetermined, and in every case errors in manipulation were causes of discrepancies between chemical ash and calculated ash. Final corrected values were used in compiling Table III which shows percentage of cases where conductometric ash checked with chemical ash within certain limits of error. It would be possible to repeat statistical analysis using corrected values, and thus obtain a still better equation. As it is, first approximation is very good, and it seems unnecessary to repeat laborious statistical calculations for slightly higher precision which might thus be obtained

The formulas necessary for the calculation of the requisite beta weights are given below where the sigmas have the same meaning as before, where r's represent the correlation coefficient between the variables indicated by the subscripts, and where B_{12}, B_{13}, B_{14}, and B_{15} are the beta weights to be determined.

$$r_{\text{ash}\,(K)} = 1.000\,\frac{\sigma_K}{\sigma_{\text{ash}}}\,B_{12} + r_{(K)\,(K_2)}\,\frac{\sigma_{K_2}}{\sigma_{\text{ash}}}\,B_{13} + r_{(K)\,(K_3)}\,\frac{\sigma_{K_3}}{\sigma_{\text{ash}}}\,B_{14} + r_{(K)\,(K_1)}\,\frac{\sigma_{K_1}}{\sigma_{\text{ash}}}\,B_{15}$$

$$r_{\text{ash}\,(K_2)} = r_{(K_2)\,(K)}\,\frac{\sigma_K}{\sigma_{\text{ash}}}\,B_{12} + 1.000\,\frac{\sigma_{K_2}}{\sigma_{\text{ash}}}\,B_{13} + r_{(K_2)\,(K_3)}\,\frac{\sigma_{K_3}}{\sigma_{\text{ash}}}\,B_{14} + r_{(K_2)\,(K_1)}\,\frac{\sigma_{K_1}}{\sigma_{\text{ash}}}\,B_{15}$$

$$r_{\text{ash}\,(K_3)} = r_{(K_3)\,(K)} \frac{\sigma_K}{\sigma_{\text{ash}}} B_{12} + r_{(K_3)\,(K_2)} \frac{\sigma_{K_2}}{\sigma_{\text{ash}}} B_{13} + 1.000 \frac{\sigma_{K_3}}{\sigma_{\text{ash}}} B_{14} + r_{(K_3)\,(K_1)} \frac{\sigma_{K_1}}{\sigma_{\text{ash}}} B_{15}$$

$$r_{\text{ash}(K_1)} = r_{(K_1)\,(K)} \frac{\sigma_K}{\sigma_{\text{ash}}} B_{12} + r_{(K_1)\,(K_2)} \frac{\sigma_{K_2}}{\sigma_{\text{ash}}} B_{13} + r_{(K_1)\,(K_3)} \frac{\sigma_{K_3}}{\sigma_{\text{ash}}} B_{14} + 1.000 \frac{\sigma_{K_1}}{\sigma_{\text{ash}}} B_{15}$$

If we had used as a measure of each variable its deviation from its own mean, we should be able to write the formula directly in deviation form, which would give the deviation of the criterion (chemically determined ash) from its own mean. This, however, was not done. Hence it is necessary to calculate the correction which will give the actual rather than the deviational ash. This is given by substituting in the following equation:

$$C = \text{mean ash} - (B_{12}\,\text{mean}_K + B_{13}\,\text{mean}_{K_2} + B_{14}\,\text{mean}_{K_3} + B_{15}\,\text{mean}_{K_1})$$

where C is the correctional term to be applied. The required formula then is

$$\widetilde{\text{Ash}} = B_{12}S_K + B_{13}S_{K_2} + B_{14}S_{K_3} + B_{15}S_{K_1} + C$$

where $\widetilde{\text{ash}}$ refers to the value of ash to be predicted from the knowledge of the conductometric readings for any given sample. S_K, S_{K_1}, etc., refer to the conductometric readings for a given sample. The degree to which faith can be placed in this formula is indicated by its standard error of estimate, which is a measure of the probable deviation of the predicted value of chemically determined ash from actual determinations of it in all the samples considered. The standard error of estimate is

$$\sigma_{\text{ash}}\sqrt{1 - R^2_{0\cdot1234}}$$

where 0 refers to the chemically determined ash and 1234 refer respectively to K, K_2, K_3, K_1, and where

$$R_{0\cdot1234} = \frac{B_{12}\sigma_1 r_{01} + B_{13}\sigma_2 r_{02} + B_{14}\sigma_3 r_{03} + B_{15}\sigma_4 r_{04}}{\sigma_0}$$

where 0, 1, 2, 3, and 4 have the same meaning as above.[1]

Sixty-eight per cent of all cases will lie between plus or minus the standard error of estimate. Ninety-nine per cent of the cases will lie between three times plus or minus the standard error of estimate. (The standard error of estimate for this problem is 0.08).

TABLE III. COMPARISON BETWEEN CHEMICAL ASH AND ASH CALCULATED FROM CONDUCTOMETRIC DETERMINATIONS

CHECKING WITHIN	PER CENT OF CASES
%	
0.05	20.1
0.10	40.9
0.15	59.7
0.20	77.9
0.25	89.9
0.30	100.0

The relationship as explained above is true only if the variables are perfectly reliably determined. It is improbable that the average between two chemical determinations of ash, which are used as the criterion in this problem, is as reliable as the composite of four conductometric readings.

Table III gives the percentage of cases in which the conductometric ash checked with the chemical ash within specified limits. In order to save space, the complete experimental data are not presented, but the writers will be glad to furnish them to any one interested.

The agreement between the chemical and the conductometric ash is not quite so good as may be expected from statistical theory, because, as stated above, the prediction holds only if the variables are perfectly reliably determined, which is not the case in experimental work of this character.

It is obvious that knowing the correlation coefficients, one can obtain any regression equation predicting the criterion from the knowledge of any one or any two or three of the conductometric readings taken together. Sample formulas in the deviation form are

$$\%\ \text{ash} = 0.9799K - 0.01115K_1$$
$$\%\ \text{ash} = 0.96212K - 0.10674K_3$$
$$\%\ \text{ash} = 1.0482K - 0.0752K_2$$

The multiple correlation coefficients of these equations are, respectively, 0.9922, 0.9921, 0.9943, whereas the multiple correlation for the equation which we have decided to use is 0.99931.

The formula using the variables K, K_2, and K_3 is as follows:

$$\text{Ash} = 0.016028K - 0.000693K_2 - 0.001518K_3 + 3.14$$

This formula is less reliable than the one we have used. It will yield the value of the ash in 68 per cent of the cases with an error of ±0.256. All the cases will be included between the limits of ±0.768.

The discrepancy between the previous formula, requiring only three conductance determinations to yield reliable results, and the new one based on four, is attributable to the addition of sucrose in the former case. This addition affects the correlations among the various conductance readings through a change in the variability and mean of each conductance criterion in the presence of the alkali or either of the acids used.

The correlation coefficients among the ash and conductivity values are given in Table IV, which may be compared, relation for relation, with Table I.

TABLE IV. ZERO ORDER CORRELATION COEFFICIENTS BETWEEN CHEMICAL ASH AND EACH SPECIFIED CONDUCTANCE CRITERION IN PRESENCE OF ADDED SUCROSE

ASH	K	K_2	K_3	K_1
K	0.9886	−0.5929	0.9177	−0.3419
K_2		−0.4338	0.9457	−0.2259
K_3			−0.3853	0.9469
K_1				−0.1803

The K_2 values were positively related with ash and K in the series without added sucrose, but are negatively related when sucrose is added. Other changes in relationship occur, indicating that the addition of large amounts of sucrose affects the various conductometric criteria quite differently.

The means and standard deviations of the series with added sucrose are given in Table V, which may be compared with the corresponding Table II, showing the data for the series without added sucrose.

TABLE V. MEANS AND SIGMAS OF CHEMICAL ASH AND CONDUCTOMETRIC READINGS

(Series with added sucrose)

	MEAN	STANDARD DEVIATION
Ash	9.1443	1.9863
K	529.7843	111.6370
K_2	1475.1193	165.5589
K_3	1098.7388	98.3436
K_1	1418.0075	115.9811

It is apparent from a comparison of the two tables that the principal difference is in the effect of sucrose on the K_3 reading and to a lesser degree on the K_1 reading. In these two readings, the means and variabilities are significantly reduced.

The maximum deviations of the calculated ash values from those obtained by incineration are ±0.30 per cent (see Table

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[1] $R_{0\cdot1234}$ is known as the multiple correlation coefficient and represents the correlation between the variable to the left of the decimal point in the subscript—i. e., ash—and the best weighted composite of the variables to the right of the decimal point in the subscripts which are the conductometric determinations. It also is the correlation between actual ash values and predicted ash values.

III). The highest ash content among all the samples was 14.34 per cent, and the lowest 4.84 per cent. The average for the entire series was 9.27 per cent. The maximum error for an average low-purity product amounts thus to 3 parts in 93, which is much better than the permissible error in the chemical method.

It is undoubtedly possible to attain higher precision in the conductometric ash determinations than in those which form the basis of the comparison—namely, the less accurate and more difficultly reproducible values obtained by incineration. The real meaning of this apparent paradox is that the reproducibility and reliability of the conductance measurements introduce greater consistency among themselves than is to be found among the chemical ash determinations. A striking example is the following application of the above idea: Suppose a sugar of 0.01 per cent ash content were treated with a purified carbon to see whether or not the ash would be reduced by this treatment, and that the carbon actually removed 10 per cent of the total ash. It is at once apparent that in such a case the incineration method would have to furnish data much beyond its order of accuracy, or else excessive quantities of sugar would have to be ashed. On the other hand, a previous knowledge of the changes in the various conductance values as they are related to changes in ash content would at once furnish an insight into the changes produced by the carbon treatment, even though these changes are exceedingly slight. Moreover, only a small quantity of sample would be required.

Acknowledgment

The writers wish to thank John E. Mull of this laboratory for his kind assistance in making the conductance determinations in the presence of phosphoric acid.

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Graphical Method for Converting Atomic Per Cent into Weight Per Cent

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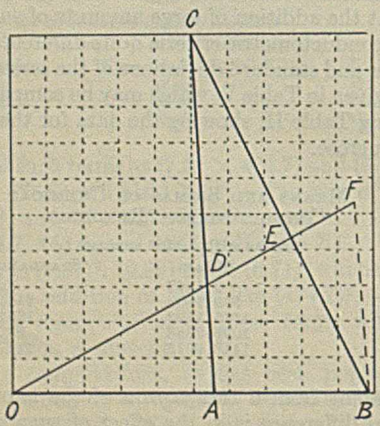
The following method for converting atomic per cent into weight per cent, and vice versa, seems not to be generally known, and as the numerical calculation is relatively tedious, it seems to be worth communicating.

The theorem of Menelaos states: If *OF* intercepts the sides of a triangle *ABC*, the product of the three quotients of the intercepts of each side is

$$\frac{OA}{OB}\cdot\frac{BE}{CE}\cdot\frac{CD}{DA} = 1$$

This is easily proved by making $BF \parallel AC$, when two pairs of similar triangles give

$$BF = \frac{DA.OB}{OA} = \frac{CD.BE}{CE}$$



If we have two substances with the atomic (molecular) weights A and B, mixed in the proportions of atomic per cent *a* and *b* ($a + b = 100$), which is weight per cent *p* and *q* ($p + q = 100$),

$$\frac{\mathrm{A}a}{\mathrm{A}a + \mathrm{B}b} = \frac{p}{100}$$

This formula will be used for the numerical calculation. It can be transformed into

$$\frac{\mathrm{A}a}{\mathrm{B}b} = \frac{p}{q}, \quad \text{or}$$

$$\frac{\mathrm{A}}{\mathrm{B}}\cdot\frac{a}{b}\cdot\frac{q}{p} = 1$$

Now, it is clearly seen how Menelaos' theorem is to be used. On a coördinate paper the atomic weights of the two components are set off on the line *OAB*. The point *C* is chosen arbitrarily, but 100 or 200 mm. from *OB*. If the triangle *ABC* is completed, the two new sides are divided in per cent by the coördinate net.

Let *AD* signify *p;* i. e., weight per cent of the component A. Then the extension of *OD* to *E* gives $BE = a$; i. e., atomic per cent of A. *CD* and *CE* are the corresponding quantities for the component B.

But the formula can also be written

$$\frac{\mathrm{A}}{\mathrm{B}}\cdot\frac{q}{p}\cdot\frac{a}{b} = 1$$

and then *BE* may signify *q* and *AD*, *b*. The corresponding quantities *p* and *a* for A are in this case *CE* and *CD*.

One has only to remember that the intercept nearest to the plotted atomic weight is weight per cent of this component, and that the projection on the other side of the triangle is the corresponding atomic per cent.

The line *OE* will of course not be drawn, but a rule or the edge of a paper will be put through *O* and the known percentage.

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Measuring Microscope for Rubber Specimens

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A microscope provided with a six-times micrometer eyepiece and objectives of 32 and 48 mm. focal length is suitable for measuring the cross-sectional dimensions of rubber test specimens. The width of specimens is usually greater than that of the die with which they were cut. The thickness of soft compounds as determined by the microscope is greater than that indicated by a gage of the plunger type.

A MICROSCOPE of low power, equipped with a micrometer eyepiece, affords a convenient and practical means for accurately measuring the dimensions of rubber test specimens, and at the same time permits the inspection of specimens for defects. The equipment here described was designed particularly for measuring the width of the familiar dumb-bell shaped tensile test strips. At the present time no convenient and accurate gage is available for this purpose, and it is common practice to assume that the width of the specimen is the same as the die with which it was cut. The same equipment has been found satisfactory for determining the thickness of test strips, and is generally applicable for the measurement of dimensions up to about 6.4 mm. (0.25 inch).

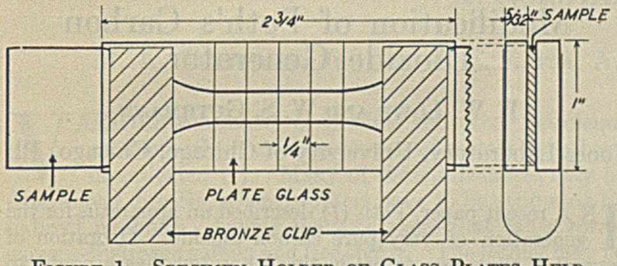

Figure 1. Specimen Holder of Glass Plates Held Together with Bronze Clips

This use of the microscope embodies no original features. The method and equipment, however, are here described in some detail, since they may be of interest to investigators who may have occasion to make accurate mechanical measurements on rubber.

It is not the purpose of the present discussion to make a critical comparison of dimension-measuring devices employed in connection with test specimens of rubber. Some comparative measurements are cited which indicate that the microscope affords an improvement in accuracy over existing methods, but consideration is not given here to the general subject of the probable errors in rubber testing.

The Microscope

The microscope is of low power in order that a relatively wide field of view may be obtained. It consists of a standard microscope body fitted with a six-times micrometer eyepiece and objectives of 48 and 32 mm. focal length. With the former objective and a tube length of 160 mm., the field of view is 9.3 mm. in diameter, and the magnification 13 diameters; with the latter objective, the field is 5.4 mm. in diameter and the magnification 24 diameters. The equipment includes a mirror and a mechanical stage.

The micrometer eyepiece is a standard eyepiece on the diaphragm of which is cemented a glass disk ruled with a scale 10 mm. in length which is ruled in 100 subdivisions. The eyepiece is provided with a focusing eye-lens in order to accommodate the micrometer scale to the eye of the observer. When an object is viewed under the microscope, the scale appears to be superimposed on it and dimensions may be read directly from the scale. A conversion factor is, of course, employed to convert the observed number of scale divisions to the desired units. The micrometer eyepiece is more convenient than a filar micrometer for work where a very high order of accuracy is not necessary, since the use of the latter requires the setting of cross-hairs on one edge of the specimen, and the moving of them to the other edge.

Specimen Holders

Suitable specimen holders greatly facilitate the manipulation of samples on the mechanical stage, and insure the samples lying flat without distortion. Two holders for dumb-bell shaped test strips are shown in Figures 1 and 2. One consists of two microscope slides held by spring bronze clips which are attached to the glass by de Khotinsky cement. The clips are so adjusted that an ordinary rubber test strip is held snugly between the slides. The other holder consists of two thick glass slides near whose ends grooves are cut so that the slides with a specimen between them may be held together with rubber bands. The rubber bands do not project above the surface of the glass, since they would interfere with the free movement of the holder by the mechanical stage. Both specimen holders are so designed that measurements may be made on either side of a sample without removing it from the holder. The slides are ruled so that measurements may be made at definite intervals along the length of specimens under observation.

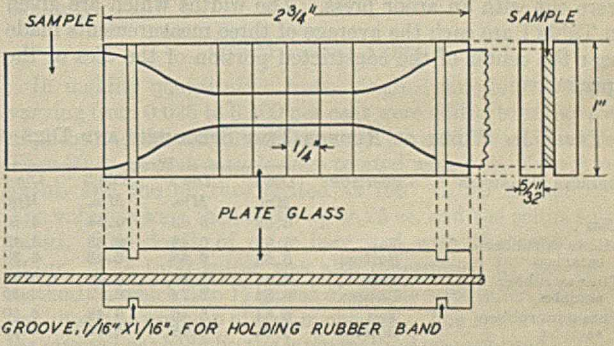

Figure 2. Specimen Holder of Glass Plates Held Together with Rubber Bands

Method of Making Measurements

The scale of the micrometer eyepiece is conveniently calibrated by comparison with a stage micrometer which is ruled on a glass slide. The calibration factor is dependent on the length of the draw tube of the microscope, and consequently may be adjusted to a convenient number by the proper setting of the draw tube. In the case of the equipment described herein, the calibration factor for the 32-mm. objective ranges from 0.0373 mm. per scale division for a 150-mm. tube length, to 0.0470 mm. for a tube length of 170 mm., and has the convenient value, 0.0400 mm. per scale division, when the tube length is adjusted to 161.7 mm.

In making measurements, the specimen under examination is mounted in a holder and located in the middle of the microscope field with the proper focus, at which the scale and the surface of the specimen appear in the same plane and show no relative displacement as the eye is moved from one side of the eyepiece to the other. The eyepiece is then rotated so as to bring the scale across the specimen in the direction in which measurement is desired. If the edges of the specimen are clean-cut, readings may be estimated to 0.1 scale division, although a reading to 0.5 scale division, which may be made almost at a glance, is equivalent to a precision of 0.5 per cent if the object covers the full scale. If the sample has been placed symmetrically in the holder, a length of several centimeters may be brought into the field by lateral motion of the mechanical stage. This permits the cut edges to be scrutinized for irregularities, and facilitates the making of measurements at a number of points along a strip.

The microscope may be readily employed for examining and measuring the dimensions of a die. It is only necessary to remove the stage and mirror and mount the die in the field of vision. The difficulty of focusing sharply on the edges of the die may be obviated by placing a glass slide across the die and bringing the lower surface of the glass into focus by observing marks on it.

ILLUSTRATIVE MEASUREMENTS

Measurements of the width of the constricted portion of several dumb-bell shaped dies and of specimens cut with them were made by means of the microscope. The specimens were prepared from three rubber compounds having different degrees of hardness: a pure gum compound, a compound containing 24 per cent of titanox pigment by volume, and one containing 20 per cent of micronex by volume. The hardness values, as determined by the Shore instrument, were 48, 60, and 75, respectively. The dies employed were taken at random from those in routine use, and the samples were cut with an arbor press. The widths which are given in Table I are each the average of three measurements made near the center of the constricted portion of the dies or the specimens.

TABLE I. WIDTH OF RUBBER TEST SPECIMENS AND DIES

OBJECTS MEASURED	POSITION	WIDTH Die 1	Die 2	Die 3	Die 4
		Mm.	*Mm.*	*Mm.*	*Mm.*
Dies		6.58	6.43	6.54	6.45
Micronex rubber samples	Top	6.68	6.44	6.48	6.48
	Bottom	6.68	6.48	6.48	6.38
Titanox rubber samples	Top	6.64	6.46	6.48	6.48
	Bottom	6.84	6.74	6.72	6.55
Pure gum rubber samples	Top	6.64	6.46	6.49	6.50
	Bottom	6.82	6.68	6.69	6.58

The results indicate that the specimens are on the average wider than the die with which they were cut, the upper side being about the same width as the die, but the lower side being appreciably wider in the case of the softer compounds. The mean of the top and bottom widths was in several instances as much as 0.10 to 0.15 mm. greater than the width of the die, hence the possible error which might arise from this source would be of the order of 2 per cent if the width of the test specimen were assumed to be the width of the die. This estimate leaves out of consideration the fact that the edges of specimens cut with a die are usually somewhat concave. At the time of measurement, however, it is possible to make qualitative observation of the degree of concavity.

Measurements of thickness were made with the microscope on some of these same specimens, mounted on edge in a slot in a wooden block. A comparison of the values found with the thickness as indicated by a dial gage of the plunger type is given in Table II. This gage was provided with a contact foot 6.4 mm. (0.25 inch) in diameter, and was actuated by a load of 85 grams (3 oz.). In the case of the soft, pure gum stock, the thickness indicated by the microscope was of the order of 2 per cent greater than the thickness indicated by the gage, as would be expected from the evident compression by the contact foot. In the case of the stiffer stocks, the measurements by the microscope and the gage were in reasonably close agreement. In some instances the thickness indicated by the gage was somewhat the greater. This may have been owing in part to bloom and dust particles on the surface of the specimens.

TABLE II. COMPARATIVE MEASUREMENTS OF THICKNESS

SPECIMEN		THICKNESS By microscope	By plunger type gage
		Mm.	*Mm.*
Pure gum	1	2.13	2.08
	2	2.06	2.02
	3	2.08	2.05
	4	2.07	2.04
Titanox	1	1.40	1.40
	2	1.34	1.35
	3	1.41	1.42
	4	1.32	1.33

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Modification of Poth's Carbon Dioxide Generator

E. W. LOWE AND W. S. GUTHMANN

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IN A recent paper, Poth (*1*) described an apparatus for the generation of very pure carbon dioxide. Operation of several of these generators in this laboratory has brought to light several undesirable features: (1) The pressure at which the carbon dioxide is delivered varies considerably, owing to the rise and fall of the acid in tube *C* of Figure 1; (2) the apparatus is rather fragile, exhibiting a tendency to break at point *D* because of strains in the glass, and at *B* and *C* because of jars and strains which occur in handling; (3) a cup-like mass of crystals forms at point *A* during continuous operation of the generator, causing accumulation of acid and resulting in erratic operation; (4) the lack of a reservoir at *E* allows mercury to be drawn from trap *F* into the sulfuric acid bulb in case of a large drop in temperature.

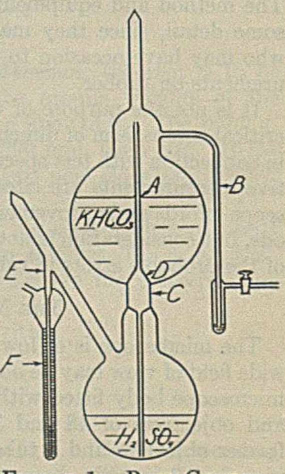

FIGURE 1. POTH GENERATOR

To eliminate these defects in an otherwise excellent piece of apparatus, a number of modified generators have been constructed and tried out. The one which has proved most satisfactory is shown in Figure 2. The two large bulbs are made from 1- and 2-liter flasks. Spout *L* is best made from tubing of 2 mm. inside diameter, and should not be more than 1 cm. from bend to tip. Tube *N* should have an inside diameter of 5 or 6 mm. Bulb *O* should have an outside diameter of about 30 mm., and trap *R* should have a depth of 14 or 15 cm. and a capacity of at least 20 cc.

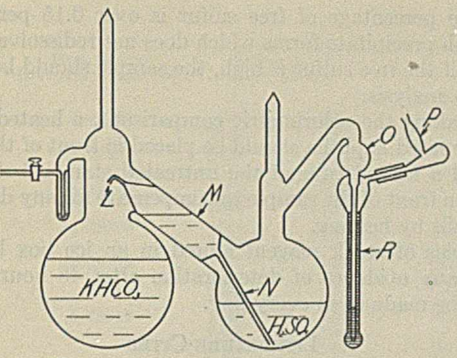

Figure 2. Modified Generator

of mercury. The apparatus, if reasonably well built, will stand fairly rough treatment. It needs no mounting other than two cork rings as support for the two large bulbs, and is easily carried about, using neck *M* as a handle. A safety trap, *P*, is provided to prevent loss of mercury in case a considerable amount of carbon dioxide blows through the pressure regulator, *R*.

This generator is charged and operated in exactly the same manner as the Poth apparatus, except that, owing to the relatively large volume of chamber *M*, 200 cc. of water and 200 cc. of concentrated sulfuric acid are placed in the smaller bulb, instead of 170 cc. of each, as recommended by Poth.

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Detection and Determination of Free Sulfur in Petroleum Distillates

A Colorimetric Method

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Various substances in gasoline and other petroleum products which cause corrosion of metals have been investigated (*1*). Many of these substances may be determined directly, whereas others have to be estimated by indirect methods. Among the substances that cause corrosion are hydrogen sulfide and free sulfur. The former may be determined directly and rapidly by well-known analytical methods, but for the determination of the latter, the direct methods are long and tedious and are seldom used. The copper strip test, an indirect method, is used more frequently.

In searching for a reaction which could be used as the basis of a direct qualitative and quantitative method for the determination of sulfur and which would be both rapid and accurate, the Halphen method for the detection of cottonseed oil was studied. Sulfur is one of the reagents in this test. Since this seemed to offer the necessary basis, an obvious modification of this reaction was tried for the detection and determination of free sulfur in naphthas.

Procedure

Reagent. Mix 80 cc. of refined unbleached cottonseed oil, 80 cc. of freshly distilled carbon disulfide, and 8 cc. of pyridine, and place in a glass-stoppered bottle. This mixture should be made fresh every day and kept cool in the dark when not in use, as it decomposes upon standing.

Standard Solutions. Prepare odorless, purified naphtha by distilling over metallic sodium. Dissolve one gram of sulfur in 1000 grams of naphtha and prepare solutions of sulfur containing 0.010, 0.025, 0.050, 0.075, and 0.100 gram of sulfur in 100 grams by suitable dilutions with sulfur-free naphtha. It must be cautioned that standard solutions of sulfur in purified naphtha are not stable and that in some cases, at least, corrosive naphtha becomes noncorrosive on aging.

Procedure. Place 20 cc. of the oil to be tested in an oil-sample bottle, add 4 cc. of the sulfur reagent, and heat for 30 minutes at 100° C. The standard solutions with which the oil is to be compared should be treated similarly and run simultaneously. At the same time, heat 20 cc. of the oil to be tested and one of the standards to which no reagent has been added to insert in the comparator to correct for any color that may be developed from the heat on the oils. After heating for 30 minutes, add sufficient water-white gasoline to the sample to bring the volume to 25 cc., and compare with the color developed by the standards which have been treated similarly.

Quantitative Tests

In making quantitative tests, weighed amounts of sulfur varying from 0.025 to 0.100 per cent were added to sulfur-free naphtha and the mixture shaken until the sulfur was dissolved. Then 20 cc. of each sample were treated with 4 cc. of stock reagent, and the mixture heated at 100° C. for 30 minutes. The volumes were then made up to 25 cc. and the colors compared. The depth of color increased with the content of sulfur. The total sulfur was also determined by the lamp method, in which 5 to 12 grams of sample were taken, depending upon the amount of sulfur present. The sulfur found in the original naphtha by the lamp method was subtracted from the total sulfur in the solution to obtain the free sulfur. The results are shown in Table I.

Table I. Relation between Free Sulfur in Naphtha as Found by Combustion and by Colorimetric Method

	S Added to 100 Grams of Naphtha	S by Color	Total S by Lamp	Free S by Lamp	Diff. between S by Color and Lamp
	Gram	%	%	%	%
1	None	None	0.003	None	
2	0.010	0.0095	0.012	0.009	+0.0005
3	0.025	0.026	0.027	0.024	+0.002
4	0.050	0.050	0.052	0.0495	+0.000
5	0.075	0.0745	0.078	0.075	−0.0005
6	0.100	0.103	0.104	0.101	+0.002

These tests showed that the results by the colorimetric method agree with both the quantity of sulfur added and the free sulfur found by the lamp method.

Tests were made to ascertain whether other sulfur compounds would interfere with the reaction. The compounds of sulfur used were hydrogen sulfide, mercaptans, sulfuric esters, organic sulfides, disulfides, sulfonic acids, and sulfones in concentrations varying from 0.1 to 3.0 per cent in the naphtha. They were treated with the reagent by the process described above, but in no case did pink or red color develop. The modified Halphen method can therefore also be used for the qualitative detection of free sulfur in light petroleum distillates.

Discussion

In making these tests, it was found that excessive dilution of the standards after the color had developed gave low results. In no case should the standard be diluted with water-white naphtha to more than one and one-half times its original volume in making the comparisons.

If the percentage of free sulfur is over 0.15 per cent, a brownish precipitate forms which does not redissolve readily. Hence, if the free sulfur is high, the sample should be diluted prior to analysis.

In making the colorimetric comparisons, a heated tube of the untreated naphtha should be placed in front of the standard and a heated tube of the untreated standard should be placed in front of the sample to compensate for any darkening of the oils by heating.

Samples of stock reagent stored in an ice box have not shown any evidence of deterioration after 48 hours, but it should be made fresh every day.

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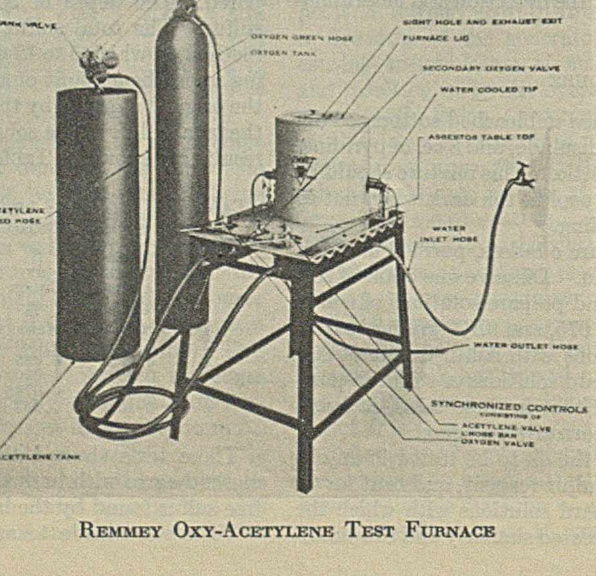
Remmey Oxy-Acetylene Test Furnace for Coal Ash Fusion Point Determination

F. H. Fish, F. M. Taylor, and J. L. Porter, Virginia Polytechnic Institute, Blacksburg, Va.

THE introduction of the Remmey furnace (*4*) to the ceramic industry and its subsequent success in this field has led to the investigation of its possible use for coal ash fusion determinations. Acetylene and oxygen are the fuels used with this furnace. The entire weight of the apparatus exclusive of oxygen and acetylene tanks is about 150 pounds (68 kg.), and it can be moved from one place to another without damage to the furnace or any of its connections. It is sturdily constructed and built to withstand temperatures as high as 3320° F. (1827° C.) (Cone 37). The floor space needed is approximately $3^1/_3$ square feet (0.3 sq. meter) and must be near a supply of water for the circulating cooling system.

The furnace is placed on a metal table with an asbestos top. Regulators on the oxygen and acetylene tanks are set to deliver the gases at 16 and 10 lb. per sq. in. (1.12 and 0.7 kg. per sq. cm.) pressure, respectively, to the connecting hose which leads to the synchronized valves of the furnace. These valves are attached to the front of the table and are so connected that when one valve is opened or closed the other valve is opened or closed a corresponding amount. From the synchronized valves the gases enter a mixer attached to the under side of the table and then pass into the firebox through the water-cooled tips of the burner. Between the synchronized valves is a secondary oxygen valve which is used only in starting. An excess of oxygen is needed only at the start of a run or in special cases where a highly oxidizing atmosphere is desired at all times.



Remmey Oxy-Acetylene Test Furnace

The mixed gases enter the furnace at a tangent to the inner wall and consequently take a rotary motion around the center post on which the plaque and test cones are placed.

There is but one opening in this furnace when assembled. A hole 0.75 inch (2 cm.) in diameter, directly over the plaque, serves as a sight hole as well as an outlet for exhaust gases. With the aid of dark glass such as is used by acetylene welders, the operator is able to observe the test cones with no difficulty. The heat from the furnace is not noticeable and makes possible the use of this apparatus in any chemical laboratory without discomfort to other employees.

Procedure

In this investigation two series of tests were carried out. Series A, consisting of thirteen samples, was carried out in June, 1932, with J. L. Porter as operator. Series B, consisting of twelve samples, was carried out in August, 1931, with F. M. Taylor as operator.

In carrying out Series A, none of the melting points or softening temperatures were known until after the results were reported to the Bureau of Mines. In Series B, the fusion temperatures were known to the operator at the time the tests were made.

The ash cones were prepared as directed in Technical Paper 8 of the Bureau of Mines (*6*). Ready-made plaques were

Table I. Results with Series A

	Bur. Mines Identification No.	Gas Furnace Method: Fusion temp. (Bur. Mines)		Gas Furnace Method: Difference		Remmey Furnace Method: Fusion temp.		Remmey Furnace Method: Cone No.	Remmey Furnace Method: Difference	
		° F.	° C.	° F.	° C.	° F.	° C.		° F.	° C.
1	A-78161	1996	1091			1975	1079	0.03		
		2008	1098	12	7	1975	1079	0.03	0	0
2	A-78101	2124	1162			2065	1129	1–2		
		2152	1178	28	16	2080	1138	2+	15	9
3	A-78442	2199	1204			2150	1180	5		
		2219	1215	20	11	2160	1182	5+	4	2
4	A-78099	2277	1247			2218	1214	7+		
		2284	1251	7	4	2225	1218	7–8	7	4
5	A-78369	2367	1297	Max. 25	14	2282	1250	9		
		2347	1286							
		2372	1300	Min. 5	3	2291	1255	9–10	9	
6	A-78257	2448	1342	Max. 14	8	2300	1260	10		
		2458	1348							
		2444	1340	Min. 4	2	2295	1257	10 −	5	3
7	A-78256	2552	1400	Max. 29	16	2462	1350	13		
		2541	1394							
		2523	1384	Min. 11	6	2450	1343	13 −	12	7
	A-78151	2611	1433	Max. 5	3	2426	1330	12–13		
		2610	1432							
		2615	1435	Min. 1	1	2450	1343	13 −	24	13
9	A-78436	2689	1476			2565	1407	15 −		
		2678	1470	11	6	2570	1410	15	5	3
10	A-75590	2752	1511			2705	1485	18		
		2790	1532	38	21	2720	1493	18+	15	8
11	A-77864	2806	1541			2690	1477	18 −		
		2793	1534	13	7	2705	1485	18	15	8
12	A-76869	3015	1657			2912	1600	26–27		
		3000	1649	15	8	2921	1605	27	9	5
13	A-75479	2962	1628			2935	1613	28 −		
		2993	1645	31	17	2939	1615	28	4	2
				Av. 17	9			Av.	9.5	5

purchased from the manufacturers of the Remmey furnace. The plaques are approximately $2^{11}/_{16}$ inches (6.84 cm.) in diameter, with a hole three-sixteenths inch (0.5 cm.) in diameter in the center, 0.125 inch (0.02 cm.) thick. There are places for twenty Standard pyrometric cones (small size) about 0.125 inch (0.02 cm.) from the edge of the plaque. The cost of these plaques is about 12 cents each, but the convenience of having the plaque ready for use and the fact that each plaque can be used for more than one ash fusion is a great saving in time. A temperature of over 3000° F. (1649° C.) has no effect on the plaque.

The furnace was started according to directions supplied with each furnace by the manufacturer. The directions for the change in the valves were closely followed until the inside of the furnace came to a red heat. A pyrometer was inserted in the top of the furnace before Series A was run, and the settings recorded, so that a rise of not more than 20° C. per minute could be maintained when within the fusion point range of any cone. For example, it was found that when the valves were set at 44 on the scale, a rise of 18° C. was maintained, falling in rate of rise slowly until about 1800° F. (983° C.) was reached. Then the setting was advanced by fives gradually until the higher temperatures were reached.

Table II. Averages with Series A

	Av. Temp. (Bur. Mines)		Av. Temp. (Remmey)		Difference		Error
	° F.	° C.	° F.	° C.	° F.	° C.	%
1	2002	1095	1975	1079	− 27	−16	−1.35
2	2138	1170	2073	1134	− 65	−36	−3.04
3	2209	1210	2158	1181	− 51	−29	−2.30
4	2281	1249	2222	1216	− 59	−33	−2.58
5	2362	1294	2287	1253	− 75	−41	−3.17
6	2450	1343	2298	1259	−152	−84	−6.20
7	2539	1393	2456	1347	− 83	−46	−3.26
8	2612	1434	2438	1336	−174	−98	−6.65
9	2684	1473	2568	1409	−116	−64	−4.32
10	2771	1521	2713	1489	− 58	−32	−2.09
11	2800	1545	2698	1481	−102	−64	−3.62
12	3008	1651	2917	1603	− 91	−48	−3.02
13	2978	1636	2937	1614	− 41	−22	−1.37
				Av.	− 84	−47	−3.34

Table III. Results with Series B

	Bur. Mines Identification No.	Gas Furnace Method: Fusion temp. (Bur. Mines)		Gas Furnace Method: Difference		Remmey Furnace Method: Fusion temp.		Remmey Furnace Method: Cone No.	Remmey Furnace Method: Difference	
		° F.	° C.	° F.	° C.	° F.	° C.		° F.	° C.
1	A-54455	2053	1123			2057	1125	1		
		2025	1106	28	17	2025	1107	0.01 −	32	18
2	A-54442	2170	1187			2200	1204	7 −		
		2176	1191	6	4	2210	1210	7	10	6
3	A-70080	2269	1243			2260	1238	8–9		
		2244	1229	25	14	2260	1238		0	0
4	A-70849	2314	1268			2350	1288	11–12		
		2331	1278	17	10	2337	1281	11+	13	7
5	A-54454	2376	1302			2462	1350	13		
		2413	1323	37	21	2462	1350		0	0
6	A-70837	2491	1366			2534	1390	14		
		2484	1362	7	4	2500	1371	13–14	34	19
7	A-70035	2520	1382			2534	1390	14		
		2498	1370	22	12	2525	1385	14 −	9	5
8	A-71082	2547	1397			2570	1410	15		
		2550	1399	3	2	2570	1410		0	0
9	A-54439	2601	1427			2642	1450	16		
		2590	1421	11	6	2650	1454	16+	8	4
10	A-54451	2649	1454			2680	1471	17+		
		2649	1454	0	0	2685	1474		5	3
11	A-54449	2674	1468			2705	1485	18		
		2671	1466	3	2	2705	1485		0	0
12	A-71081	2907	1597			2900	1593	26 −		
		2885	1585	22	12	2900	1593		0	0
				Av. 15	8			Av.	9	5

Just as the test cone had slumped down into a spherical mound the furnace was shut off and a portion of the top plate removed so as to stop the heating of the cones suddenly. The fusion temperature was taken from the cone which had leaned to a position where the tip had touched the plaque.

In Series A, where none of the fusion temperatures were known, one run had to be made to find the approximate fusion temperature. This was done by mounting the test cone on a plaque with at least five different Standard cones. The color of the ash cone gave an indication of whether the ash would have an exceedingly low melting point or not. This aided somewhat in deciding whether to put in the cones at the lower or higher end of the range. After the approximate temperature was found, two check runs were made on each ash cone using the Standard cones which had a fusion point close to the ash cone.

TABLE IV. AVERAGES WITH SERIES B

	Av. Temp. (Bur. Mines)		Av. Temp. (Remmey)		Difference		Error
	° *F.*	° *C.*	° *F.*	° *C.*	° *F.*	° *C.*	%
1	2039	1115	2041	1116	2	1	+0.10
2	2173	1189	2205	1207	32	18	+1.50
3	2256	1236	2260	1238	4	2	+0.18
4	2322	1272	2344	1284	22	12	+0.95
5	2394	1312	2462	1350	68	38	+2.84
6	2488	1367	2517	1381	29	14	+1.16
7	2509	1376	2530	1388	21	12	+0.84
8	2549	1398	2570	1410	21	12	+0.82
9	2596	1424	2646	1452	50	28	+1.93
10	2649	1454	2683	1473	34	19	+1.28
11	2673	1467	2705	1485	32	18	+1.20
12	2896	1591	2900	1593	4	2	+0.14
				Av.	26.6	14.7	+1.08

In Series B, the softening temperatures as determined by the Bureau of Mines by the gas furnace method (*1*) were known, and no preliminary test had to be run. The fusion temperature was then obtained, usually in two successive runs.

DISCUSSION

Since heating up the cone to red heat does not affect the final fusion temperature, this furnace needs to be cooled only to around 1500° F. (816° C.) before the next run is started. The time consumed in cooling the furnace to this temperature is comparatively short. Twelve fusions may be run in a working day of eight hours if this method is followed.

The temperature attained in one determination in this investigation was 2900° F. (1593° C.). To make this run, 60 cubic feet (1.7 cubic meters) of oxygen and 25 cubic feet (0.7 cubic meter) of acetylene were consumed when the furnace was started at room temperature. This represents a cost of $1.10 for fuel. When the plaque was placed in the furnace at about 1500° F. (816° C.), it required 36 cubic feet (1 cubic meter) of oxygen and 17 cubic feet (0.5 cubic meter) of acetylene to reach the same fusion point. This represents a fuel cost of only 70 cents for the test. When starting from room temperature, the secondary oxygen valve is opened until the furnace reaches dull red heat and much more oxygen is used. When the furnace is already hot, no excess oxygen has to be supplied.

A particular advantage of the oxy-acetylene method is its suitability for places where no manufactured or natural gas is available. Another advantage is evident in the heat insulation. This is better than is usually provided for commercial gas furnaces. No attempt is made to compare the cost of the oxy-acetylene method with the A. S. T. M. method, for no manufactured or natural gas was available.

In the comparison of the gas-furnace and the micropyrometer methods (*2*) and the comparison of the gas-furnace and De Graaf electric coal ash fusion furnace (*5*), reducing atmospheres were used and were considered necessary if comparable results were to be obtained. The gases from this furnace were analyzed several times, but in each case atmospheric oxygen could not be excluded, owing to cracks in the wall next to the gas nozzle.

Table I gives the number of each sample for Series A as recorded at the Bureau of Mines, the fusion temperatures by each method, the differences in temperature for duplicate runs, and the average difference in duplicate runs by each method. Table II gives the two results obtained by each method, the error in the temperature recorded by the Remmey method (assuming the Bureau of Mines temperature average to be correct), the percentage error in each of thirteen samples, and the average percentage error. Tables III and IV give corresponding data for Series B.

CONCLUSIONS

It is regrettable that the operator of Series A did not run several samples with known fusion points before the series was started, or at least before the series was reported. This undoubtedly would have brought both series nearer together, for it is apparent that in the plaques in Series A the ash cones were not carried to the same degree of softness as in Series B.

A sample of coal ash with known fusion point must always be used in establishing the appearance of the ash cone at what is to be called the fusion temperature. The fact that all results in Series A were below, and all those in Series B were above the results obtained in the gas-fired furnace, although checking closely within themselves, emphasizes the need of further work by some one person who has both methods available and who is accustomed to reading the fusion temperatures by both methods. Another series of tests should be run by the same person by both methods so that the condition of the ash cone at fusion temperature as defined in Technical Paper 8 of the Bureau of Mines will be identical in both methods. Since no gas for use as fuel is available at this station, the above suggestion cannot be carried to completion at the Virginia Polytechnic Institute.

Table V gives the numbers and corresponding fusion temperatures of the cones available for such tests.

TABLE V. STANDARD PYROMETRIC CONE EQUIVALENTS

Cone No.	P. C. E.[a]		Cone No.	P. C. E.[a]	
	° *F.*	° *C.*		° *F.*	° *C.*
0.03	1975	1080	16	2642	1450
0.02	2003	1095	17	2669	1465
0.01	2030	1110	18	2705	1485
1	2057	1125	20	2768	1520
2	2075	1135	23	2876	1580
3	2093	1145	26	2903	1595
4	2129	1165	27	2921	1605
5	2156	1180	28	2939	1615
6	2174	1190	29	2984	1640
7	2210	1210	30	3002	1650
8	2237	1225	31	3056	1680
9	2282	1250	32	3092	1700
10	2300	1260	33	3173	1745
11	2327	1275	34	3200	1760
12	2390	1310	35	3245	1885
13	2462	1350	36	3290	1810
14	2534	1390	37	3320	1825
15	2570	1410			

NOTE: Cones 19, 21, 22, 24, and 25 not made. The average difference between cones in this series of 35 is 33° F. or 18° C.

[a] Pyrometric Cone Equivalent (P. C. E.) of cones manufactured by Standard Pyrometric Cone Company, 1445 Summit St., Columbus, Ohio.

ACKNOWLEDGMENT

The authors wish to express their appreciation to A. C. Fieldner and H. M. Cooper of the Bureau of Mines, Pittsburgh, who furnished the ash samples and the fusion temperatures which they obtained by the Bureau of Mines method, to the Ceramic Engineering Department of the Virginia Polytechnic Institute for their assistance and use of their equipment and laboratory in this investigation, and to O. C. Burkhart for his assistance in preparing the cones for Series A.

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Improved Distillation Trap

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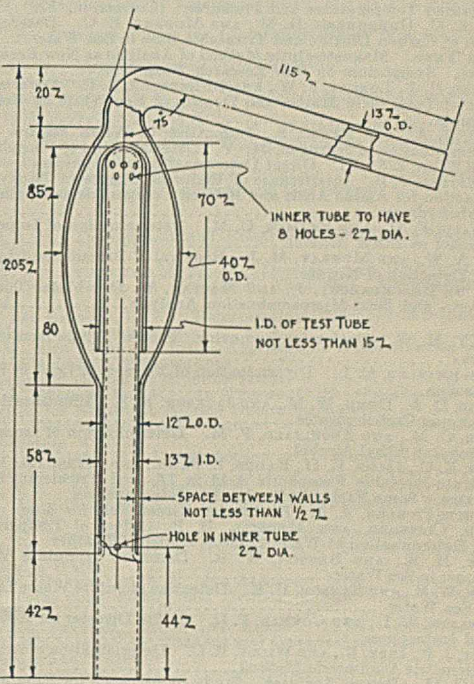
The diagram represents a trap for use as a connecting bulb in Kjeldahl distillations which has been found superior to the ones in common use. It was originally used in a still for conductivity water and is now employed by the writer wherever an efficient distillation trap is required. It has the advantage of operating entirely without spattering and of efficiently removing fine spray from the vapors. The apparatus is easily made.

In operation, vapors pass up the inner tube, through the side holes at the end, and are deflected down through the wet narrow annular space between the inner tube and cap. The vapors again change direction at an angle of 180 degrees and pass out between the wet walls of the cap and bulb. Condensed liquid returns to the boiling flask through a hole at the bottom of the inner tube near its seal to the outer tube. The space between the walls of the inner and outer tubes, around and above this hole, must be sufficiently narrow to hold by capillarity a column of water which will prevent steam blowing through it.

The dimensions given are satisfactory, but may be varied rather widely except that the space between the inner and outer tubes must not be too wide, nor the return hole too large, and the exit holes at the end of the inner tube must be large enough to allow passage of the vapors at a low pressure to prevent blowing through the return hole. Traps with practically any desired efficiency may be made by simply lengthening the inner tube and cap.

This apparatus may be obtained from Arthur H. Thomas Company, Philadelphia, Pa.



Received July 26, 1932

An Identification Test for Oxalic Acid

Earle R. Caley, Frick Chemical Laboratory, Princeton University, Princeton, N. J.

Since several carboxylic acids form more or less insoluble calcium salts, the usual calcium oxalate precipitation test for oxalic acid is not an especially distinctive means for identifying the acid, and may lead to confusion in certain instances. The following specific precipitation reaction for free oxalic acid is based upon the fact that sodium oxalate is a sparingly soluble salt, whereas the normal sodium salts of practically all other known carboxylic acids are freely soluble in water.

Dissolve 0.10 gram of the solid organic acid in 2.0 cc. of cold water and add 1.0 cc. of approximately 6 N sodium hydroxide solution. Shake the mixture vigorously for 1 or 2 minutes. The separation of a white crystalline precipitate indicates oxalic acid.

The proportions of weights and volumes given were those found to give the optimum results in a series of experiments bearing on this point. Any marked deviations from these details may vitiate the test. The weights and volumes may, of course, be reduced in proper proportion in case a sample as large as 0.10 gram is not available for examination.

This reaction is not of value for the detection of oxalic acid in mixtures, but is intended solely as a simple identification test for the free acid in order to distinguish it readily from other solid, water-soluble, carboxylic acids. Tests made on a number of such acids using this procedure yielded negative results even when samples larger than 0.10 gram were taken. Among those examined were the following representative ones: citric, crotonic, glycollic, maleic, malic, malonic, mandelic, succinic, and tartaric. As far as the writer has been able to determine, the only carboxylic acid that will give a precipitate in the above test is dihydroxytartaric acid. However, it is not likely that confusion could arise from this source in view of the unstable character of this acid and the special means required to obtain it.

Received September 8, 1932.

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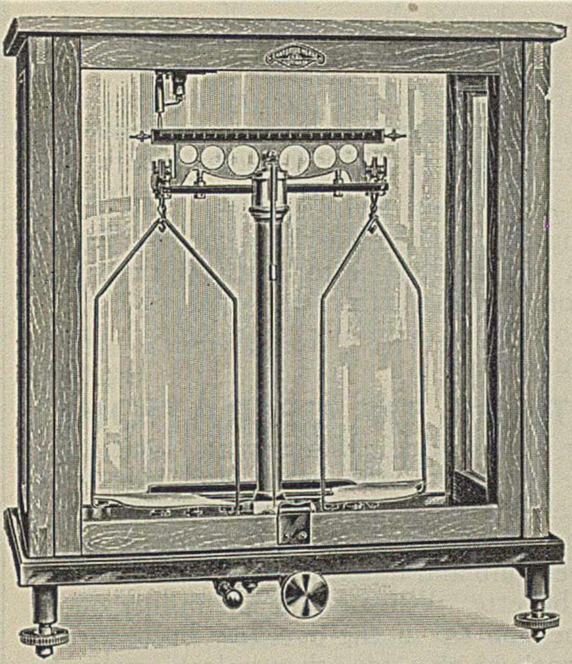

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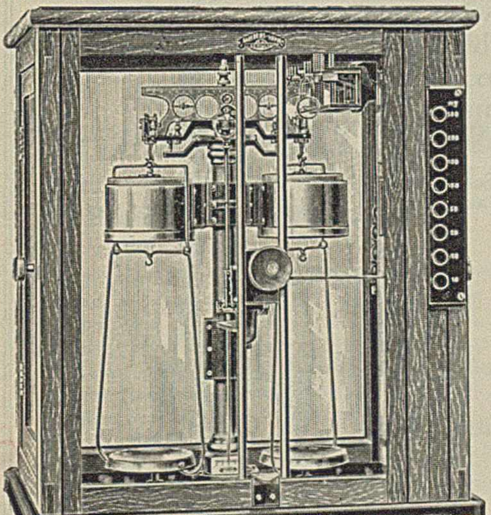

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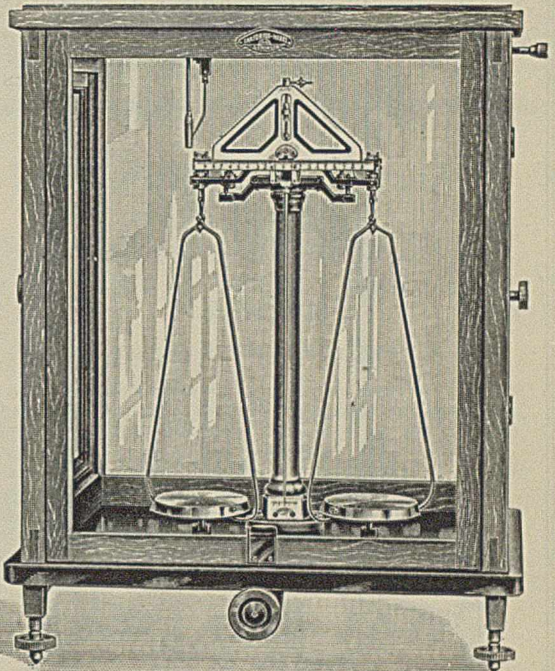

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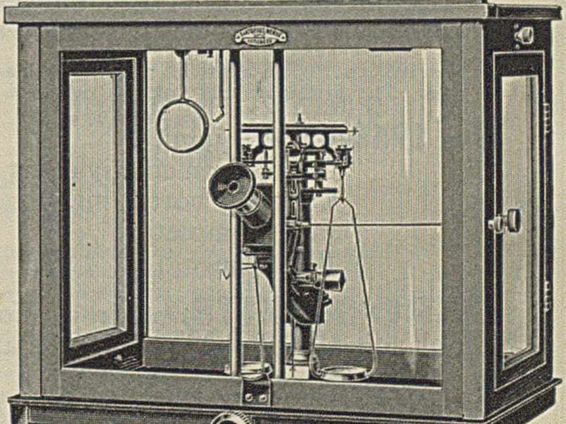

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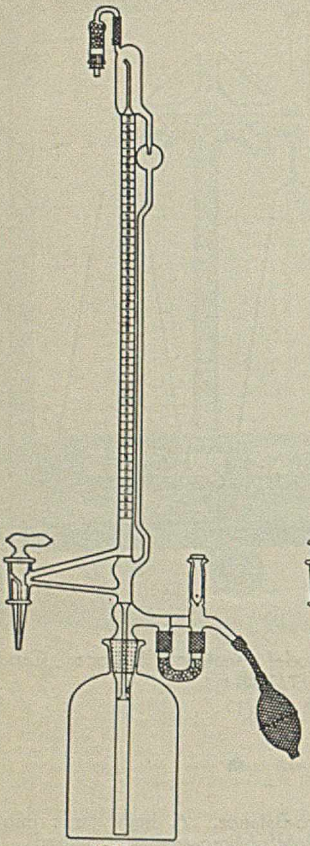
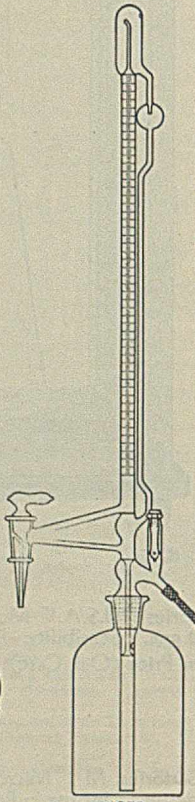


1955



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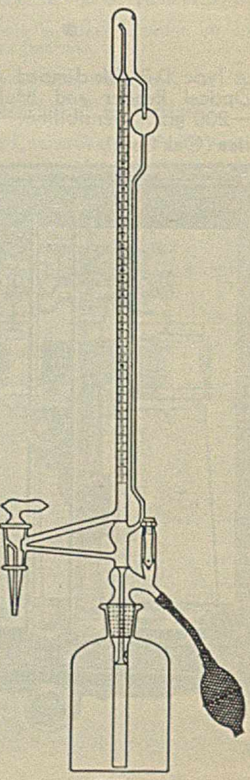

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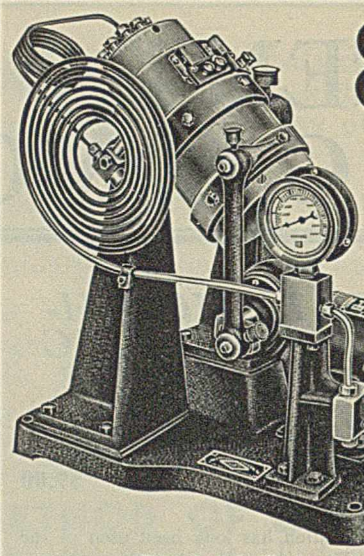

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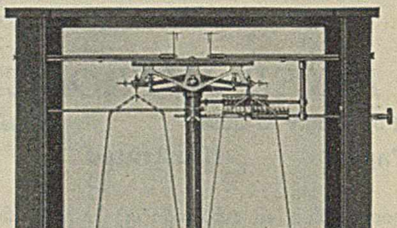

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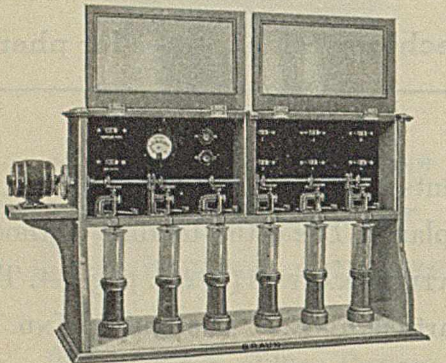

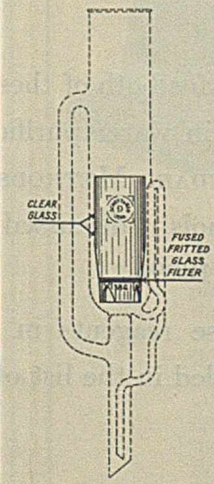
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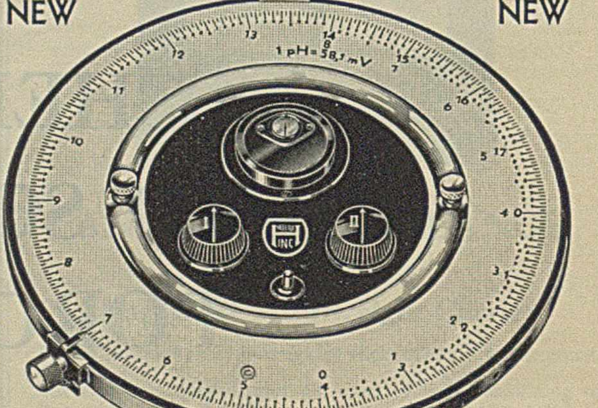
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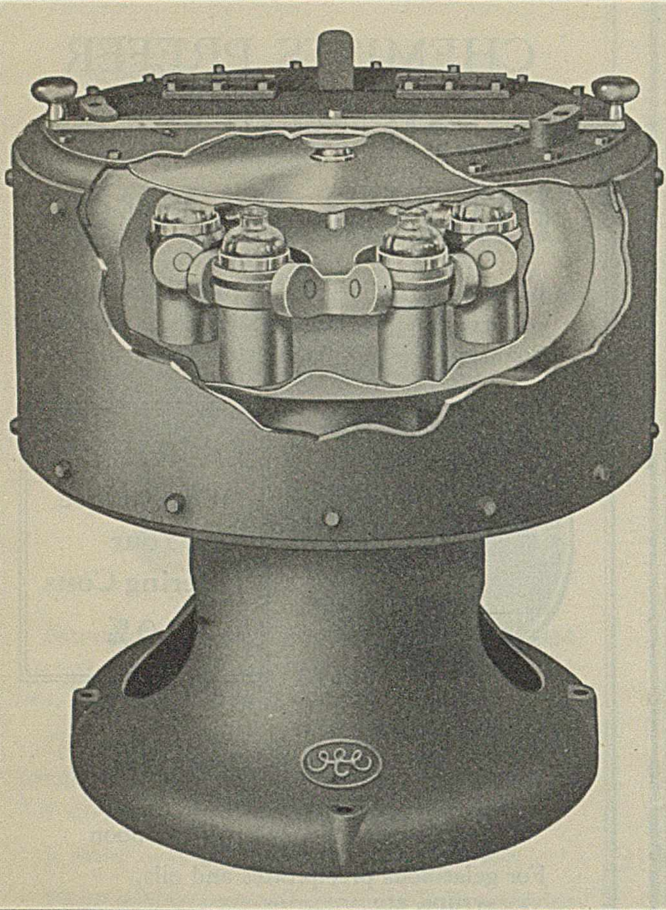

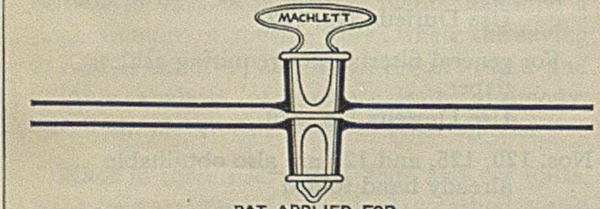
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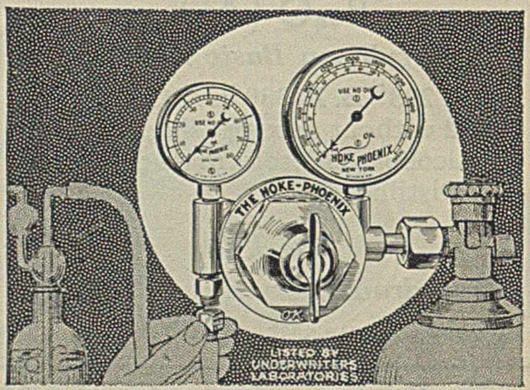
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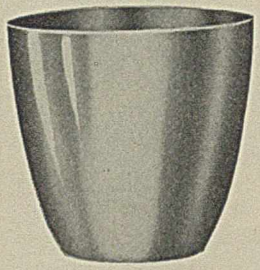

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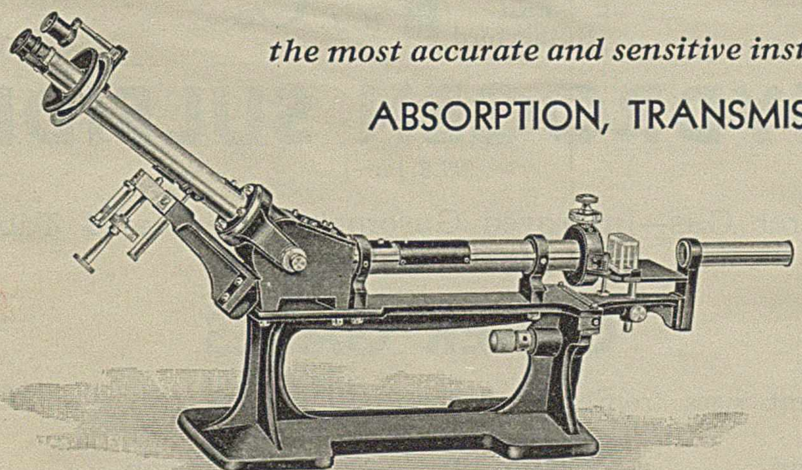

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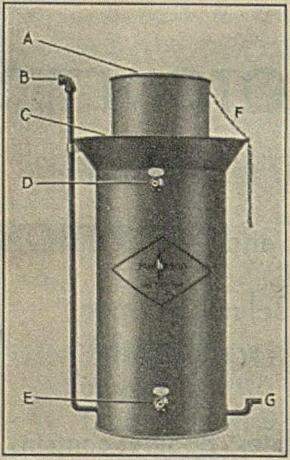
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