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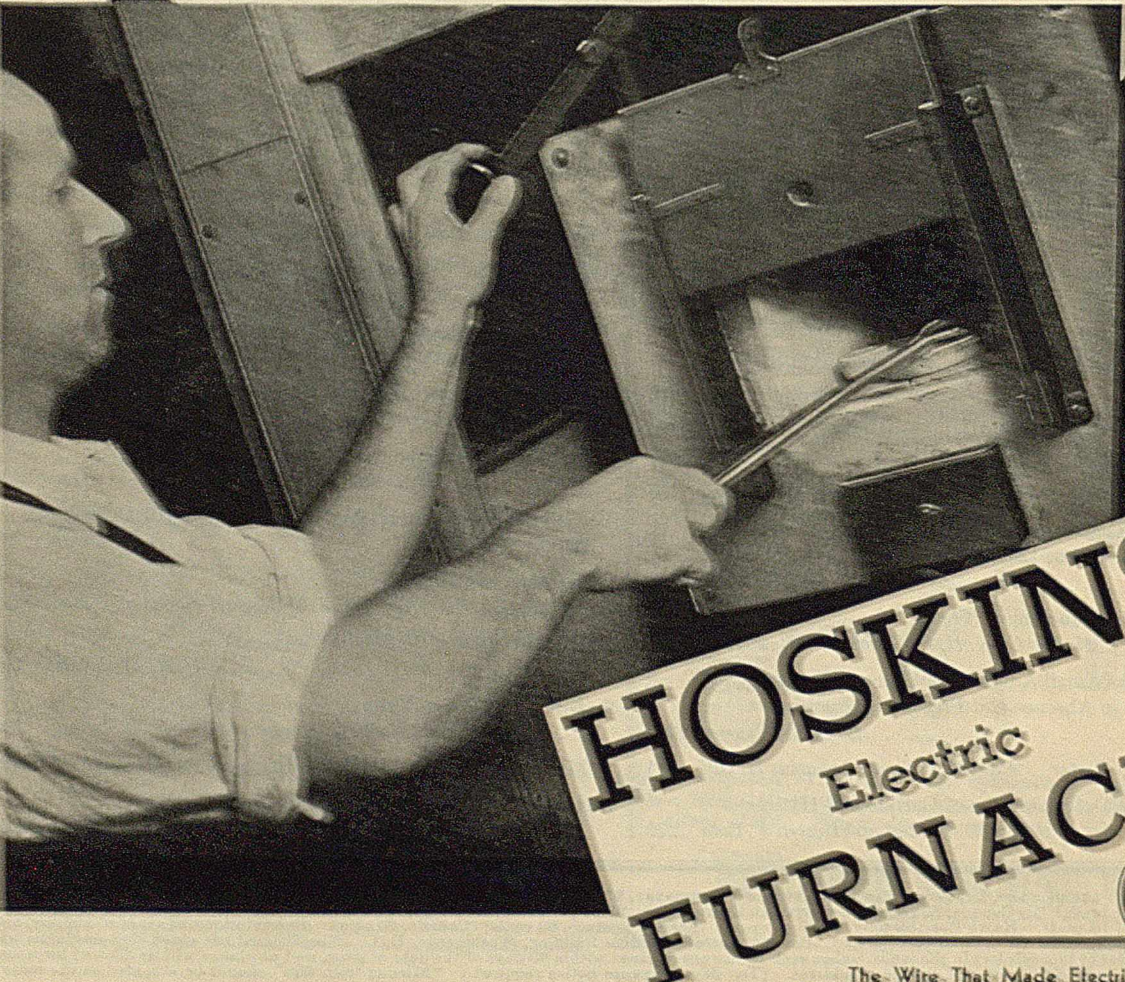

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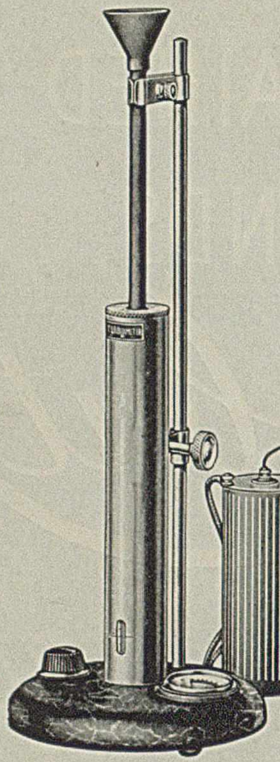


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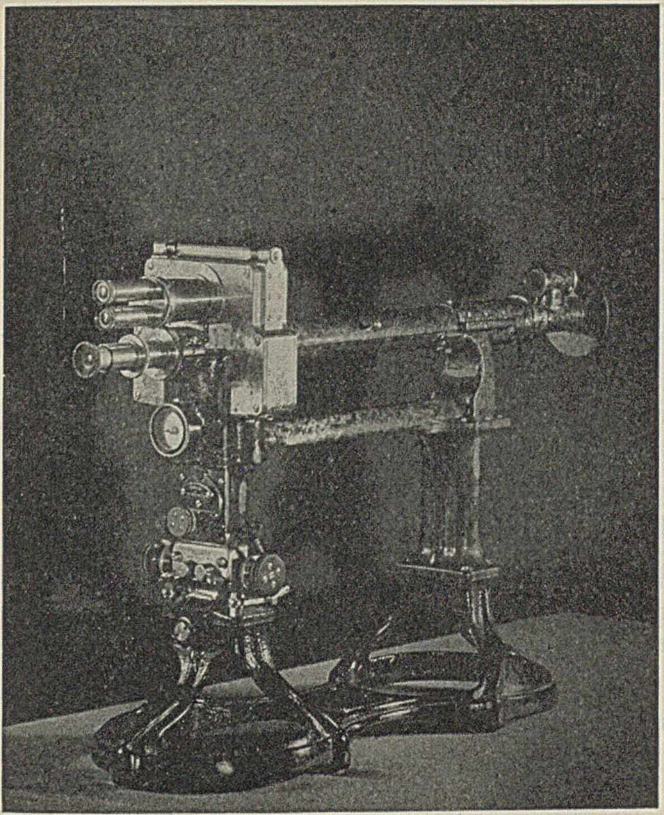

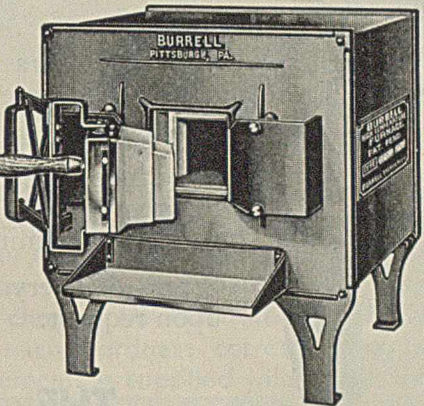
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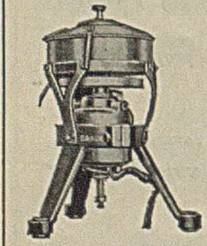

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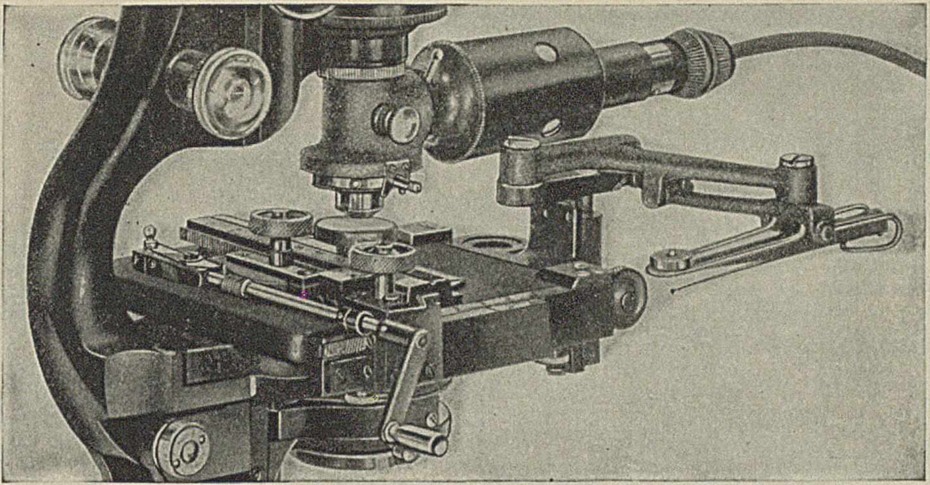

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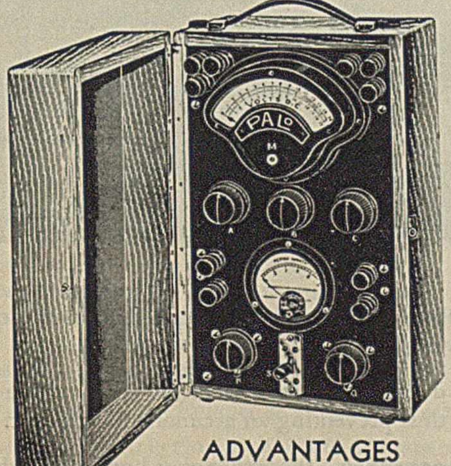

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Viscosity of Petroleum Products

Methods and Apparatus for Viscosity Measurement

E. A. WILLIHNGANZ, W. B. MCCLUER, M. R. FENSKE, AND R. V. MCGREW
Petroleum Refining Laboratory, Pennsylvania State College, State College, Pa.

The probable sources of error encountered in viscometry practice are discussed and methods for eliminating or minimizing these effects are given.

Modified Ostwald pipets designed to minimize the probable sources of error have been constructed, many of which have been in satisfactory use for about 2 years. The pipets are of rugged construction and loss due to breakage is negligible.

Viscosity determinations made by various research workers using different apparatus normally check within 0.2 per cent. The pipets require only 5 cc. of liquid for viscosity determinations. Their application to petroleum work and research in general is indicated.

THE measurement of viscosity by means of capillary tubes dates at least as far back as 1839. In that year, Hagen (*5*) published work anticipating the results obtained by Poiseuille which were published in 1846 (*7*). Because of the completeness of Poiseuille's work, the concept of the laws controlling viscometry flow are generally attributed to him. Since that time, the subject of viscosity has been studied by many investigators. The results obtained substantiate those of Poiseuille in general, although various corrections (usually arising from conditions other than viscous flow) have been proposed. These corrections usually involve drainage, liquid head, kinetic energy, end effects, and surface tension.

Results obtained in capillary viscometers are expressed in terms of absolute or kinematic viscosity. In general, the pressure type of capillary viscometer, in which zero change in liquid head occurs, is preferred for determining viscosities in terms of absolute units. Viscometers similar to the Ostwald type (*6*) are generally preferred when the results are to be expressed in terms of kinematic viscosity.

REDUCTION OF ERRORS IN VISCOSITY MEASUREMENTS

Errors resulting from incomplete drainage may be reduced by making the draining surfaces more nearly vertical, increasing the time of drainage, and decreasing the surface-volume ratio. The nearly horizontal surfaces at the top and bottom of most commercial forms of the Ostwald pipet (Figure 1) are to be avoided. Bingham (*1*) states that the ideal shape of the upper bulb is that produced by placing two cones base to base. The time of drainage may be increased for any given viscosity through pipet design by increasing the capillary length, decreasing the capillary diameter, and increasing the volume of liquid. The last factor also serves to decrease the surface-volume ratio which itself decreases the percentage drainage error. Obviously, the drainage error may be eliminated by measuring the volume of the efflux fluid rather than the volume of the inlet fluid. This is difficult to perform experimentally at various temperature levels except by means of the pressure viscometer (*2*, *3*, *8*).

Most errors in liquid head result from uncertain values of the average head if viscosities are calculated from Poiseuille's law. A second source of error arises from the pipets being at various angles from the vertical during different viscosity measurements. This may be avoided to a considerable extent (Figure 2) by placing one bulb directly over the other (*4*). The degree of this probable error for pipets of different design is shown in Table I. A third source of error results unless precaution is taken to fill the pipet each time with exactly the same volume of liquid. The seriousness of this possible source of error is a function of the size of the lower bulb.

TABLE I. EFFECT OF RELATIVE POSITION OF BULBS ON PERMISSIBLE TILT OF VISCOMETER

ANGLE *A*, FIGURE 1[a]	ANGLE *B*, FIGURE 1[b]
0° 0′	2° 34′
2° 30′	1° 04′
5° 0′	37′
10° 0′	19′
15° 0′	13′
20° 0′	09′

[a] Angle between the vertical and the line joining the centers of the two bulbs.
[b] Angle of tilt which produces an error of 0.10 per cent.

Kinetic energy errors may be minimized greatly through the proper choice of capillary length and diameter and volume of liquid employed. Certain corrections of Poiseuille's law involving $\frac{MU^2}{g}$ have been proposed and experimental data on this effect have been discussed by Grüneisen (4). The relation of kinetic energy correction to viscosity and capillary diameter are given in Figure 3, based both on experimental data and values calculated from $\frac{MU^2}{g}$. Errors amounting to 0.1 per cent are on the upper curve, while errors of 1.0 per cent are on the lower curve. Experimental errors of this nature may be reduced considerably by properly designing pipets for specific purposes, and corrections may be eliminated by calibrating the pipets with liquids of known viscosity throughout the anticipated working range.

End effects are closely related to those produced by kinetic energy effects. These effects may be reduced to a considerable extent by employing capillaries having trumpet-shaped ends. In general, kinetic energy corrections include end effects and end corrections include kinetic energy effects.

Surface tension affects viscosity measurements whenever the diameters of the upper and lower bulbs vary greatly. Corrections for surface tension effects may be neglected if the pipets are calibrated with liquids having surface tensions approximately equal to those of the liquids whose viscosities are to be determined. For work with petroleum fractions, this procedure is entirely satisfactory since the surface tensions of various types of oils having equal viscosities do not vary appreciably.

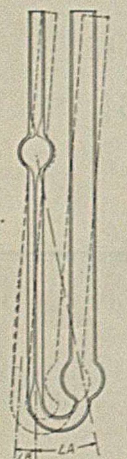

Figure 1. Commercial Form of Ostwald Pipet

Requirements of Viscometer

Any viscometer, regardless of design, should fulfill certain practical requirements. These are as follows:

1. The viscometer should be sufficiently accurate to produce results in terms of relative viscosity within 0.2 per cent.
2. For convenience the time required for determining the viscosity of any liquid should not be less than 200 seconds nor greater than approximately 2000 seconds.
3. Viscosity measurements should avoid manual operation, control, and constant observation.
4. The viscometer should be capable of operating on not more than 5 cc. of liquid.
5. The usefulness of the viscometer should not be limited by temperature.
6. The viscometer should be capable of measuring the viscosity of any product regardless of its viscous characteristics, provided true fluid flow is obtained.
7. The viscometer should be of sufficiently rugged construction so that undue breakage does not occur.

Development of Modified Ostwald Viscometer

A preliminary review of the existing methods for viscosity measurements indicated that precision of measurement with small amounts of liquid could be best attained with instruments employing capillary tubes.

The Ostwald type of pipet was considered more desirable than the pressure type of capillary viscometer for two reasons: (1) the determination of a great number of viscosities per day required a minimum of complicated apparatus; (2) viscometers of the Ostwald type produce results directly in terms of kinematic viscosity which can be converted readily either into the conventional units of Saybolt viscosity or into units of absolute viscosity.

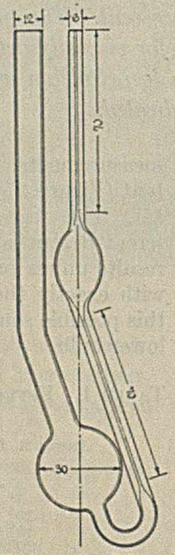

Figure 2. Modified Viscometer Pipet

All dimensions in millimeters.

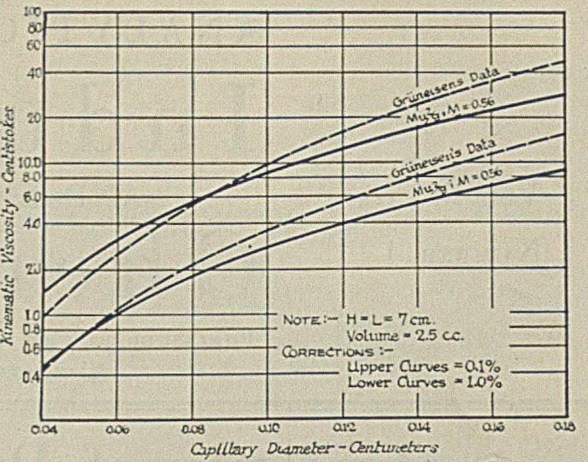

Figure 3. Relation of Kinetic Energy Correction to Viscosity and Capillary Diameter

The modified type of Ostwald pipet (Figure 2) reduces appreciably the first four sources of error, while all five are further minimized by the method of calibration. Drainage errors are reduced by making the upper bulb pear-shaped, assimilating Bingham's recommendation of two cones base to base (1). Variations in liquid head are minimized by placing the upper bulb directly over the lower bulb. Kinetic energy corrections are reduced in so far as practical by the proper relation of capillary length to diameter. End effects are minimized by the trumpet-shaped ends of the capillary. Appreciable differences in bulb diameters do not result in significant errors due to surface tension effects.

Table II. Specifications for Three Series of Viscometers

Viscometer series	100	200	300
Total volume required, cc.	5.0	5.0	5.0
Volume of upper bulb, cc.	2.5	2.5	2.5
Diameter of lower bulb, cm.	2.5	2.5	2.5
Capillary length, cm.	7.0	7.0	7.0
Capillary diameter, cm.	0.07	0.12	0.16
Accurate viscosity range (0.1 per cent error)			
Centistokes	4.6–45	40–100	125–1250
Saybolt seconds	41–200	185–1800	560–5500
Useful viscosity range (0.1 to 1.0 per cent error)			
Centistokes	1.4–45	4.0–400	12.5–1250
Saybolt seconds	33–200	39–1800	68–5500

The method of calibrating viscometers is important in the further reduction of errors and in the elimination of correction factors. The generally accepted method for the calibration of viscometers consists in determining the time of efflux for two liquids of known viscosity (the liquids preferably being more viscous and less viscous, respectively, than the anticipated working range) and expressing the calibration of the viscometer in terms of an equation involving two constants and the time of efflux. The equation does not, however, consider other probable sources of error such as drainage, end effects, etc. The fact that calibration by this method is not desirable is indicated by the results shown in Figure 4. The solid curve (temperature = 100° F., 37.8° C.) represents the actual calibration data obtained, while the dotted line represents the results obtained when the calibration curve is calculated from the kinetic energy correction equation and terminal data are employed. It is indicated that there is a possible error of approximately 1 per cent in the pipet constant, and consequently in viscosity.

Corrections for all sources of error other than liquid head and the negligible effects produced by slight variations in surface tension for oils of equivalent viscosity but of different source and type may be included in the calibration of the viscometer. This is accomplished by calibrating the pipets with several oils of known viscosity which cover not only the maximum and minimum limits of viscosity but also the intermediate range. The time of flow in seconds, divided by the viscosity in stokes or centistokes, is called the pipet constant. A smooth calibration curve results if the pipet constant determined for each different calibrating liquid is plotted against the corresponding time of efflux. A straight line, instead of a curve, usually results if the logarithm of the time of efflux is plotted against the pipet constant. Hence, the correct pipet constant for determining the kinematic viscosity of any unknown liquid is obtained from the plot after the time of efflux for that liquid has been determined. The fact that corrections involving drainage, kinetic energy, end effects, and surface tension (within negligible limits) may be included in the pipet constant is due to the relation of each to the time of efflux. Errors due to differences in surface tension for oils of equal viscosity in pipet of the present design are indicated to be less than 0.05 per cent.

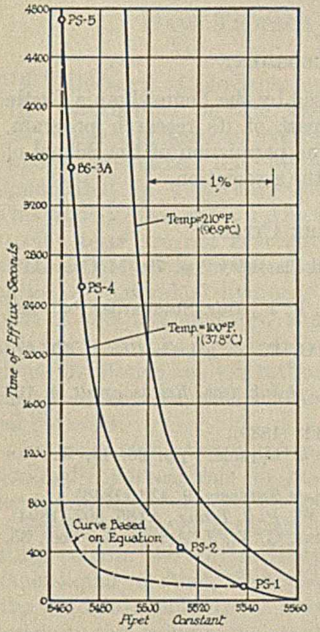

FIGURE 4. CALIBRATION CURVE FOR VISCOMETER 104

Corrections for all major sources of error in viscometry practice other than variations in liquid head are included in the pipet constant by the method of calibration. Significant errors due to variations in liquid head are avoided by filling the pipet with the same amounts of material (either by weighing or more practically by using a volumetric pipet), by placing the upper bulb directly over the lower bulb, and by aligning the pipet vertically within 1° by means of a small plumb-bob.

CONSTRUCTION OF PIPETS

During the past two years, approximately one hundred pipets of the design illustrated in Figure 2 have been made. These pipets have been constructed according to the three classifications of dimensions given in Table II. Series 100 is adapted for determining the 210° F. viscosity of most grades of oil and the 100° F. viscosity of light oils. Series 200 is adapted for determining the 210° F. viscosity of very heavy oils and the 100° F. viscosity of most grades of oil. Series 300 is adapted for determining the 100° F. viscosity of relatively heavy oils.

For viscosity ranges other than those indicated in Table II or for pipets having more particular and specific purposes, reference to Figure 5 will enable capillary diameters to be selected for the case when the capillary length and liquid head is 7 cm. and the volume of liquid flowing through the capillary is 2.5 cc. The middle curve in Figure 5 is based on a minimum time measurement of 200 seconds and the kinetic energy correction data for 0.1 per cent error contained in Figure 3.

Pipets of this design can be fabricated at a reasonable cost.[1] Loss due to breakage is negligible.

ACCESSORY APPARATUS

In making viscosity determinations, the viscometers are supported in water or transparent oil baths which are thermostatically controlled at 100° F. (37.8° C.), 130° F. (54.4° C.), or 210° F. (98.9° C.) within ±0.1° F. A convenient form of thermostat affording complete visibility and low heat loss is shown in Figure 6. Instead of the indicated compressed-air reciprocating motor, an electric motor may be used to drive an efficient stirrer. Cork or rubber stoppers, fitting in the supporting member and slit to facilitate easy removal, serve as suitable supports for the viscometers.

Stopclocks[2] have been found more suitable than stopwatches, since they are of more rugged construction and the minimum times of flow are never less than 200 seconds. Experience with nine stopclocks has led to checking them daily. Changes in room temperature introduce errors in measurement of elapsed time, a change from 70° to 90° F. making an error of approximately 0.3 per cent. Also, the clocks should be used only when wound to the same extent.

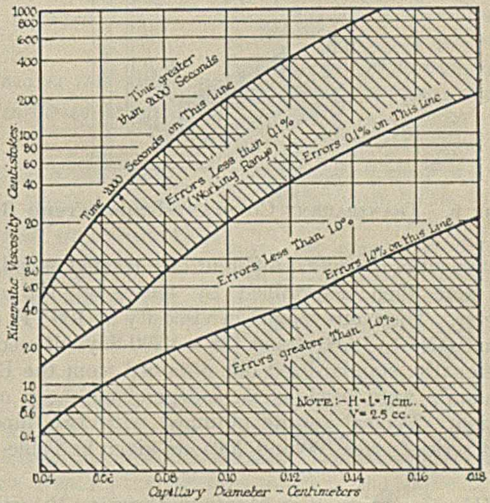

FIGURE 5. CAPILLARY DIAMETERS FOR DIFFERENT VISCOMETERS

CALIBRATION OF PIPETS

The method of calibration and the reasons for adopting this method have been given. Satisfactory calibrating liquids may be secured through the Bureau of Standards when the required accuracy is approximately 1 per cent. Especially standardized oils were made in this laboratory for the calibration of the viscometers used. These oils were made from fractions of petroleum having the required viscosity. Prior to standardization, the fractions were treated with anhydrous aluminum chloride, the sludge separated, the oil washed, and then filtered through activated charcoal. Standardization was accomplished by means of a Washburn precision viscometer[3] made of quartz (*9*).

Accurate viscometer constants were obtained by using distilled water as the calibrating liquid at various rates of shear. A value of 1.005 centipoises (1.008 centistokes) was used for the viscosity of water at the calibrating temperature, 20° C. (68° F.).

---

[1] F. J. Malloy, State College, Pa.

[2] Purchased from Arthur H. Thomas Co., Philadelphia, Pa.

[3] Purchased from the Thermal Syndicate, Brooklyn, N. Y.

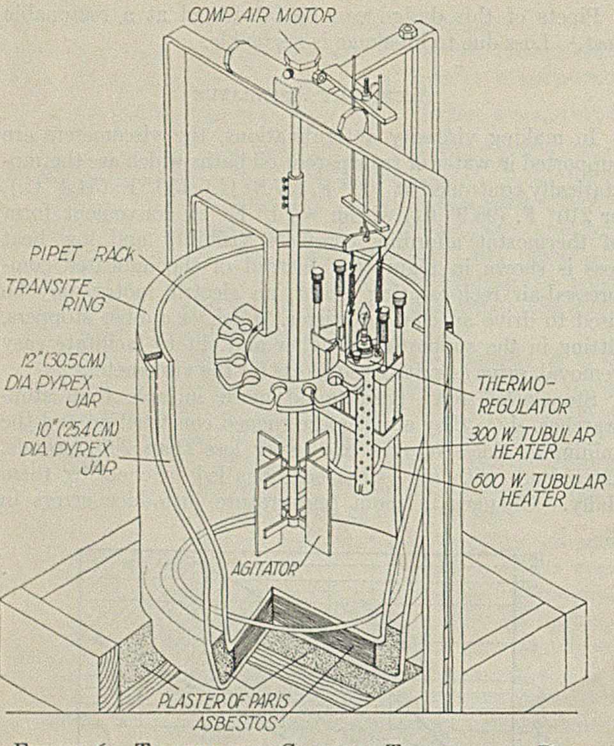

Figure 6. Transparent Constant-Temperature Bath

The viscosities of several different oils, treated as indicated above, were then determined by means of the quartz viscometer. These oils ranged in viscosity at 100° F. (37.8° C.) from 0.0217 to 12.80 stokes (34 to 6200 Saybolt seconds).

Occasionally, standardized oils obtained from the Bureau of Standards were used as an independent check on the calibration. Typical results obtained with two pipets of different series (series 100 and 200) are given in Table III.

Table III. Calibration of Modified Ostwald Viscometers

Standardized Oil	Viscosity of Oil 77° F. (25.0° C.)	Viscosity of Oil 100° F. (37.8° C.)	Pipet 104 Time of efflux	Pipet 104 Pipet constant	Pipet 220 Time of efflux	Pipet 220 Pipet constant
	Centistokes	Centistokes	Seconds		Seconds	
PS 1		2.170	120.1	55.35		
PS 2		8.010	441.3	55.13	29.7	3.722
PS 4		46.53	2546	54.73	172.3	3.703
BS 3A	64.43		3519	54.69	236.8	3.680
PS 5		86.04	4704	54.65	316.3	3.675
PS 6		157.4			579.7	3.681
BS 5	295.3				1088	3.688
PS 7		398.6			1469	3.684
PS 8		1280			4713	3.681

All viscometers were calibrated at 100° F. Experience has shown that the same calibration data may be used for evaluating the pipet constant at 210° F., provided the change in volume of the oil with temperature, resulting in a change in liquid head, is considered. Calculations indicated that the thermal expansion of Pyrex glass between the limits of 100° F. and 210° F. was negligible in its effect on the viscometer. Actual tests showed this to be true.

Practical Operation

Thousands of viscosity determinations have been made at 100° F. (37.8° C.), 130° F. (54.4° C.), and 210° F. (98.9° C.) during the past two years with pipets of this design. Some twenty research workers have used the pipets successfully. It has been found that different operators using different apparatus can check viscosities within 0.2 per cent. Pipets of this modified design are being used by four other petroleum laboratories.

The time required for making accurate viscosity determinations with these pipets is not excessive. During a recent research program it became necessary to determine approximately 4000 viscosities accurately. One research worker averaged 40 viscosities per day.

These viscometers fulfill the practical requirements listed above.

Acknowledgment

This work was largely financed by the Pennsylvania Grade Crude Oil Association as a part of its research program. The paper is published with the permission of the School of Chemistry and Physics and of the association.

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Union Square Hotel, New York, N. Y.

The use of solid carbon dioxide as the source of carbon dioxide gas and as a cooling medium facilitates the determination of tin or the weight of coating on tin plate, by reducing the time required, and by reducing the amount of work required for the determination.

The standard volumetric methods for tin or tin plate require extensive equipment, such as Sellers apparatus, a cylinder of carbon dioxide, and a cooling arrangement where a large number of tin determinations are made. In some laboratories a generator is arranged so that the gases evolved by the dissolving tin can be conducted into a solution of sodium bicarbonate when only a small number of determinations are made at a time. The use of solid carbon dioxide makes it possible to determine tin or the weight of coating on tin plate by using an Erlenmeyer flask, a small watch glass, and a hot plate. No time is required to set up or take down apparatus and any number of determinations can be made at a time. There is no need for a cooling arrangement other than the solid carbon dioxide and the use of solid carbon dioxide reduces the time required for cooling.

The start of the determination is conducted as heretofore up to the point where carbon dioxide is to be passed through the solution. At this point, approximately 0.5 cubic inch of solid carbon dioxide is added to the flask. If it is desired to speed up the work, this may even be crushed into smaller particles. Cooling and purging of the solution take place simultaneously and titration may be commenced when the solid carbon dioxide has about disappeared.

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Analysis of Gaseous Hydrocarbons

A Method for Determining Gaseous Paraffins and Olefins

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A method of hydrocarbon analysis is described, in which by fractional condensation small samples (500 cc. or less) of complex mixtures are separated into composite fractions containing both two and three, and both three and four carbon atoms per molecule. Density determinations of these composite fractions containing paraffins and olefins and the same fractions after the removal of the olefins, by means of a Stock electromagnetic gas-density balance, give data from which the percentage of each hydrocarbon is readily derived.

Pentane and hydrocarbons of higher molecular weight (gasoline) are determined in the same fractionation.

The accuracy of the method has been verified by the analysis of carefully prepared synthetic mixtures of known composition and application made to the analysis of various types of refinery gases. The method is rapid and of low cost of operation and maintenance.

THE work of previous investigators on the analysis of gaseous hydrocarbon mixtures has been summarized in a review (*8*). This study has shown that specific tests are not generally available for the direct determination of individual hydrocarbons in complex mixtures, and that resort must be made to fractional distillation analysis rather than to difference in their chemical behavior.

A precise separation of the individual hydrocarbons in not too complex mixtures can be obtained by means of a fractionating column which utilizes vapor-liquid contact, but the unavoidable hold-up of material in the column makes it necessary to have a sample sufficiently large, usually not less than 4 or 5 liters, to make an error from that source negligible. For the same reason the separation of a very small fraction in a large sample is unsatisfactory. With even the most precise fractionating column, the separation of the individual hydrocarbons in the complex C-4 fraction of highly cracked gases is difficult and time-consuming.

The object of this work was to modify and improve the fractional condensation method of Tropsch and Dittrich (*7*) to a general method for the analysis of mixtures of gaseous paraffin and olefin hydrocarbons, the method being rapid, accurate for the determination of very small samples (less than 0.5 liter of gas), of low cost of operation and maintenance, and suitable primarily for routine analyses in which the composition as ethane, ethylene, propane, propene, butanes, butenes, and pentane and heavier is rapidly determined.

The boiling points of the gaseous hydrocarbons, particularly the simpler ones, depend chiefly upon the number of carbon atoms per molecule and are affected little by differences in structure and unsaturation. For this reason a complex mixture can be more easily separated into fractions containing molecules of the same number of carbon atoms, and with even less difficulty into fractions containing molecules of two and three, and three and four carbon atoms, which can be analyzed by chemical means or by a combination of chemical and physical methods. The latter procedure constitutes the most favorable method for meeting the object of the research.

The mixture of hydrocarbons condensed from the sample at the temperature of liquid nitrogen is distilled into composite fractions containing both two and three, and both three and four carbon atoms per molecule. This fractionation is accomplished without the use of a fractionating column by simple evaporation at controlled low temperatures and correspondingly low pressures and by fractional condensation in a series of glass bulbs cooled to suitable temperatures by liquid nitrogen and by aluminum blocks cooled by this medium. Advantage is taken of the high vapor pressure ratios between the constituents at low temperatures and hence the rates of evaporation, which make possible the selection of temperatures such that the less volatile components present possess in each case a negligible vapor pressure and the more volatile components relatively high vapor pressures. Since these distillation, or condensation, temperatures are maintained fairly constant for the removal of each fraction, the fractionation is effected by varying the pressure rather than the temperature. Very low pressures are employed, 1 mm. or less, which involve correspondingly low temperatures. Two desired advantages accrue from these conditions. The first, and by far the more important, is that the ratio of the vapor pressure of the more volatile component to that of the less volatile component becomes very much greater at low temperatures, and so the separation is distinctly sharper.

Figure 1 shows the per cent ratios of the vapor pressures of hydrocarbons in pairs, curve 1 being the per cent ratio of the vapor pressure of ethane to the vapor pressure of methane at the same temperature. This per cent ratio is not in general the per cent of the more volatile hydrocarbon in the vapor but merely a comparison of the vapor pressures of two hydrocarbons. However, when the two hydrocarbons are present in equal molal proportions in the liquid, the curves do represent the per cent of the less volatile hydrocarbon in the vapor above the liquid and may be interpreted on this basis.

In the first place, the proportion of the less volatile hydrocarbon in the vapor above the liquid increases with temperature in almost a straight-line function. Therefore, the separation of hydrocarbons by fractional condensation improves as the temperature and therefore the pressure are lowered. The curves also give a measure of how the efficiency of separation will change upon a change in temperature.

At a temperature of −100° C., the vapor above a binary mixture of butane and propane of equal molar proportions will contain about 92 per cent of propane, while at a temperature of 0° C. it will contain only about 78 per cent of propane. At very low temperatures the separation is particularly effective in the case of ethane and butane, curve 3, whereas at −100° C. there is only 0.5 per cent of butane in the vapor above a 50-50 per cent mixture. The effect of low temperatures on the ratios is even more pronounced in the case of methane and ethane, curve 1, where at −160° C. there is only about 0.1 per cent of ethane in the vapor above a 50-50 per cent mixture. While the separation of heavier hydrocarbons is not nearly as efficient at correspondingly low temperatures, the trend of the curves indicates that their separation can be made fairly complete by going to very low temperatures.

A second advantage in using very low pressures lies in the fact that the actual amount of the vapor phase over the liquid phase is quite small at the low pressures, and consequently a negligible amount of the vapor phase remains above the liquid at the completion of each distillation, an important consideration where small amounts of gas are used.

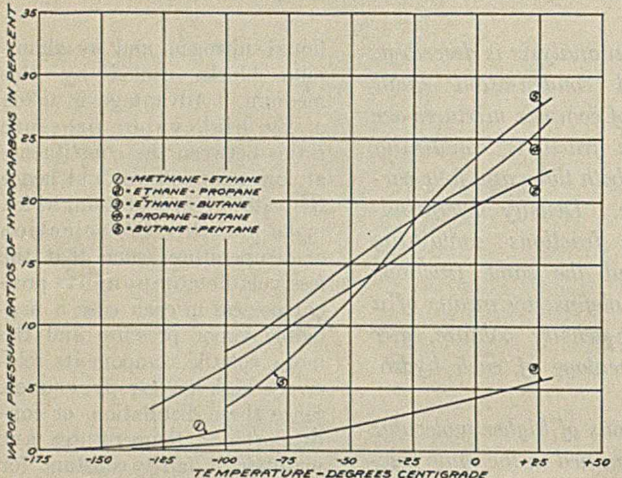

FIGURE 1. PER CENT RATIOS OF HYDROCARBON VAPOR PRESSURES

A number of distillations made in this way would be required to obtain results equal to those from one fractionation in a well-designed column. However, the separation into the above composite fractions may be accomplished in one distillation, as it is necessary only to avoid a separation so imperfect as to allow ternary fractions.

In an earlier method of the same type (*1*, *7*), the most difficult part of the analysis was the analysis of the composite fractions, which may contain as many as four constituents, two paraffins and two olefins. For a simple gas, such as a natural gas containing only the paraffin hydrocarbons, the procedure would be simple, as no fraction would contain more than two constituents, and the measurement of a single physical property, such as density, thermal conductivity, or refractive index by the interferometer, would serve to determine both. However, if the method is to be general, it must be suitable for the analysis of mixtures which may contain any or all of the following gases: hydrogen, carbon monoxide, oxygen, nitrogen, methane, ethane, ethylene, propane, propene, butanes, butenes, and pentane and heavier. The method described has been developed so as to be suitable for the analysis of the hydrocarbon constituents in such complex mixtures.

The hydrogen, carbon monoxide, oxygen, nitrogen, and methane are easily and rapidly removed from the condensable hydrocarbons at the temperature of liquid nitrogen by reducing the pressure to 0.1 mm. or less, and the percentage of each constituent may be obtained by an Orsat analysis on this fraction. Acetylene is removed from the gas before the condensation is made. The vapor pressure of ethane always remains so low at the temperature of liquid nitrogen (−195° C.) that none of it is removed with the last methane distillates. Pentane and heavier hydrocarbons present in the gas mixture are quantitatively condensed from the butanes and the other gaseous hydrocarbons at a temperature of −105° C. and 1 mm. pressure. The fractionation of the remaining hydrocarbons into two composite fractions is made at 1 mm. pressure and at temperatures of −135° to −140° C. and at −195° C.[1] The components of the fractions are as follows:

FRACTION	TEMP. OF CONDENSATION ° C.	CONSTITUENTS
1	−195	Ethane, ethylene, propane, propene
2	−135 to −140	Propane, propene, butane, butene
3	−105	Pentane and higher (gasoline)

The analysis of fractions 1 and 2 is made by density determinations, one on the mixture of paraffins and olefins and a second on the paraffins after the removal of the olefins by concentrated sulfuric acid activated by nickel and silver sulfates. From the change in the density of the fraction on the removal of the olefins the density of these olefins is calculated. Then from the density of the two olefins, the density of the two paraffins, the volume of the olefins, and the volume of the paraffins in the fraction, the volume of each hydrocarbon and the volume per cent of each hydrocarbon in the original sample are calculated.

Fraction 3, consisting of pentane and higher hydrocarbons, is reported as gasoline, since these hydrocarbons are liquids at temperatures below 20° C., either as grams per liter of gas, as volume per cent, or as gallons of gasoline per 1000 cubic feet of gas, each of the calculations being made from the volume and the density of the vaporized fraction. Tables have been prepared for facilitating the evaluation of the specific gravity of the gasoline fraction, and by means of a simple relation the gallons of gasoline per 1000 cubic feet of gas may be calculated.

The density determinations are made with a Stock electromagnetic gas-density balance which permits a determination accurate to 3 parts per 1000 in approximately 2 to 3 minutes. This apparatus has been fully standardized and described by Stock and his co-workers (*3*–*6*).

The gas volumes are determined from the pressure exerted in a known volume of the apparatus at a definite temperature.

DESCRIPTION OF APPARATUS

Figure 2 shows apparatus for the separation of the liquefied gas sample into fractions by fractional condensation at regulated low temperatures and a Stock electromagnetic gas-density balance for determining the specific gravities or molecular weights of the fractions.

The apparatus for the fractional condensation of the gaseous hydrocarbons consists essentially of five U-tubes, *B*, *C*, *D*, *E*, and *F*, which can be cooled to suitable temperatures by liquid nitrogen and by aluminum blocks cooled by liquid nitrogen; an absorption pipet, *V*, for removing olefins from the fractions; calibrated bulbs, *P*, *Q*, and *R* for volume measurements; and a manometer, *Y*, for pressure readings. The temperature of the aluminum block is indicated by means of an iron-constantan thermocouple calibrated at the freezing points of water, mercury, and carbon disulfide, and at the boiling point of liquid nitrogen. The junctions of the iron and the constantan wires with the copper lead wires from the millivoltmeter are maintained at a constant temperature of 100° C. by immersion in steam.

The soda-lime tube and anhydrone drying tubes are constructed so as to eliminate all rubber connections or stoppers and to permit their easy removal for cleaning and refilling. Anhydrone, magnesium perchlorate, is used as the drying agent rather than phosphorus pentoxide, which has been found to remove olefins after it has absorbed some moisture.

The precision manometer, *Y*, permits pressure readings from 0 to 800 mm. of mercury, made accurate to 0.2 mm. by use of a mirror scale and 25-mm. tubing to overcome capillary attraction. The manometer is a modification of the one described by Germann (*2*) improved for the authors' purposes.

The construction of the aluminum blocks *I* and *J* used in cooling the condensation tubes is shown in detail in Figure 3. Table I shows the approximate rate of cooling, rate of heating, and the amount of liquid nitrogen used in cooling the blocks.

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[1] These temperatures are slightly lower than those used by Tropsch and Dittrich, but more suitable for the condensation as shown under Selection of Temperatures for Condensations.

Table I. Cooling and Heating Rates of Aluminum Blocks

			Volume of Nitrogen
	° *C.*	° *C./min.*	*Cc./° C.*
Rate of cooling	0 to −80	28	...
Rate of cooling	0 to −100	25–30	...
Rate of heating	−65 to −60	0.2–0.3	...
Rate of heating	−115 to −100	0.9	...
Rate of heating	−130 to −115	0.9	...
Liquid nitrogen required for cooling	0 to −80	...	1.8
Liquid nitrogen required for cooling	0 to −100	...	1.9–2.1

Preliminary cooling with solid carbon dioxide and acetone lowers the temperature to about −80° C., so that less liquid nitrogen is required. The temperatures required for the condensations are maintained by the occasional addition of small amounts of liquid nitrogen. Alcohol is placed in the blocks around the condensation tubes so as to insure more rapid heat transfer.

The first aluminum block used had only one hole for liquid nitrogen, and, especially when the block was warm, the nitrogen boiled so rapidly that considerable quantities were lost in cooling it, and, if the nitrogen was added in such small amounts as to prevent its being wasted, the time required to cool the block was much too long. With the block shown in Figure 3, the liquid nitrogen passes to the bottom of the Dewar flask and boils up through the many small holes in the rim of the block, permitting rapid cooling with no loss of liquid nitrogen.

The calibrated bulbs *P*, *Q*, and *R*, in addition to serving as known volumes for the measurement of the fractions, permit the entire fractions to be transferred to these bulbs, by condensation in *M*, *N*, or *O*, and vaporized so as to obtain a homogeneous mixture before being passed into the gas balance for the molecular weight determination. If the fractions are allowed to vaporize and pass directly into the balance, the lighter components enter the balance first and cause errors in the molecular weight determinations as high as 10 per cent.

The volumes of *P*, *Q*, and *R* are accurately determined before being sealed into the apparatus and are then used to determine the volume of the balance and the manometer, *Y*, since the volume of the balance and the manometer must always be added to any combination of bulbs *P*, *Q*, or *R*. The volume of *P* is approximately 150 cc., *Q* 200 cc., and *R* 500 cc. The volume of the balance, manometer, and connections to stopcocks 6, 10, and 17 is approximately 250 cc.

The activated sulfuric acid is a mixture, in the proportion 1 to 15, of concentrated sulfuric acid (specific gravity 1.84) saturated with nickel sulfate at room temperature, and concentrated sulfuric acid containing 0.6 per cent of silver sulfate (7).

The Stock gas-density balance operates according to the principle of determining specific gravity by measuring the Archimedic buoyancy produced on a small hollow quartz ball fastened to a scale beam by the influence of the surrounding gases. The scale beam, into which a thin staff magnet has been fused, bears at the other end a second hollow quartz ball serving as counterbalance which is open and whose total surface is approximately equal to the surface of the buoyancy ball, in order to avoid final one-sided loading by absorption of gases. The balance beam rests on steel points in stone pans and is in a glass case closed with a ground cap and having ground connections for introduction of gases. The glass balance housing is suspended in a glass trough which is filled with a temperature bath. An observation microscope makes possible convenient observation of the fine-

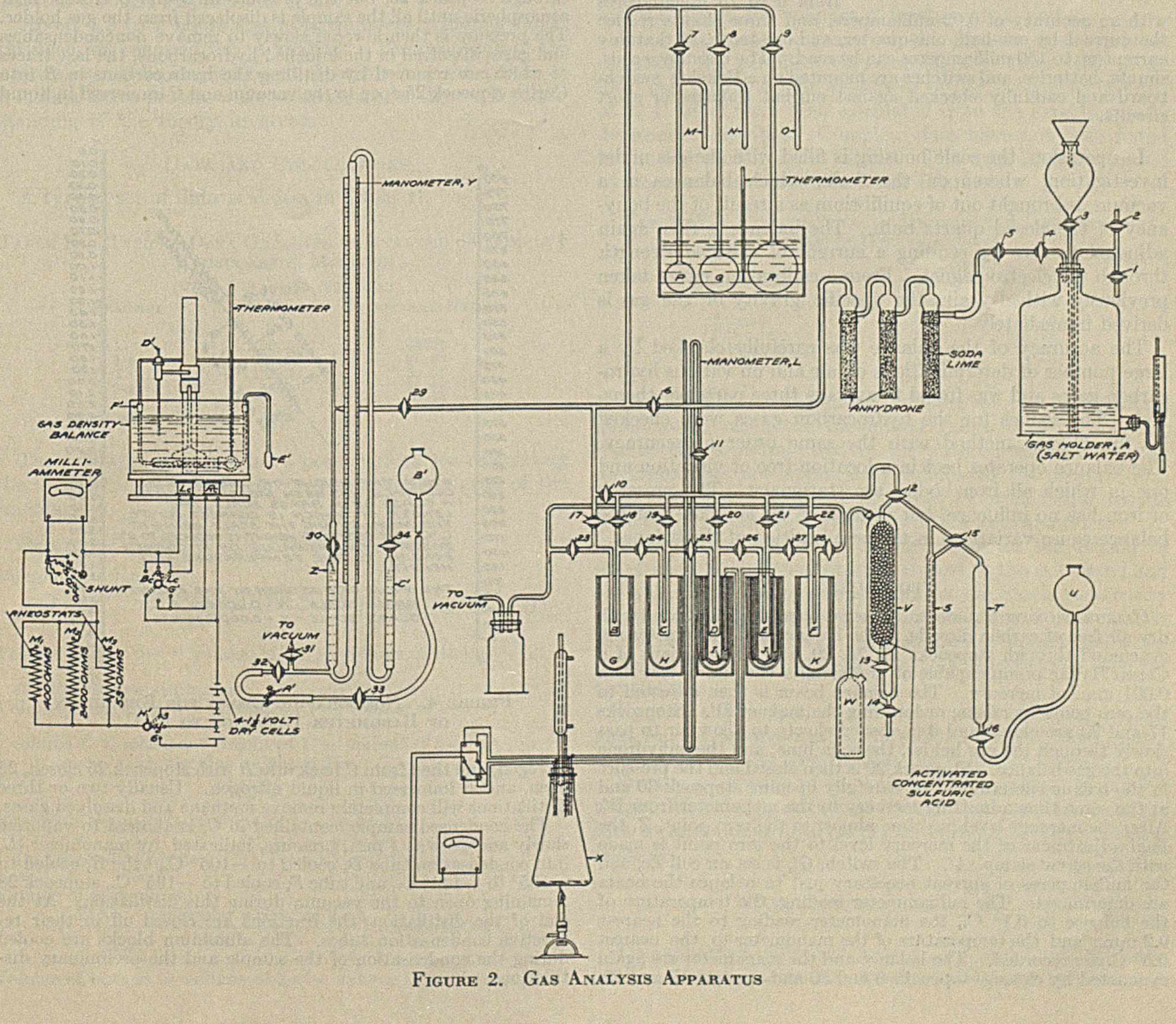


Figure 2. Gas Analysis Apparatus

scale pointer which plays before a fixed counterpointer arranged in the balance frame. Beneath the balance are the electromagnets, *Lc* and *Rc*, free of iron and therefore of hysteresis, for magnetic influencing of the balance.

Water is contained in the bath around the balance and a thermometer indicates the temperature to 0.1° C. The small auxiliary magnet, *D′*, for correcting the zero position of the balance beam (in vacuum) is usually suspended over the center of the balance beam and the adjustments are made by raising or lowering the magnet.

The gas balance is supported on a rigid stand near the manometer and is connected to the manometer and the fractionation apparatus with 8-mm. tubing through a ground-glass joint, *F′*. The arrangement and connection of shunts, resistances, milliammeter, etc., are shown in Figure 2. Switch *G′* permits the left-hand coil, *Lc*, the right-hand coil, *Rc*, or both coils to be used. With the resistances M_1, M_2, and M_3 and the switch *H′*, by which two, three, or four dry cells can be thrown in the circuit, currents from 0.5 to 100 milliamperes can be sent through the coils. The milliammeter reads from 0 to 15 milliamperes with an accuracy of 0.02 milliampere, and three shunts reduce the current by one-half, one-quarter, and one-tenth, so that any current up to 150 milliamperes can be read. The resistance coils, shunts, batteries, and switches are mounted on a Bakelite switchboard and carefully checked against current leakages or short circuits.

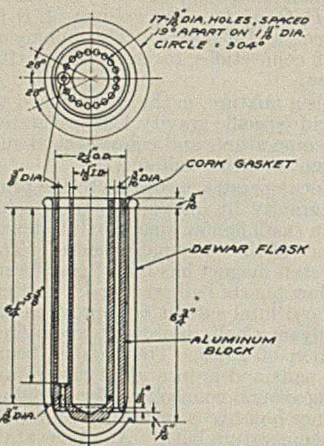


FIGURE 3. ALUMINUM BLOCK FOR COOLING CONDENSATION TUBES

In operation, the scale housing is filled with the gas under investigation, whereupon the scale, which balances in a vacuum, is brought out of equilibrium as a result of the bouyancy of the closed quartz bulb. The balance is then again adjusted to zero by sending a current of suitable strength through the electromagnet. From a calibration curve taken previously with dry air, the specific gravity of the gas is derived immediately.

The accuracy of the balance was carefully checked by a large number of determinations on air and on various hydrocarbon gases and was found to average three parts per thousand. The values for the hydrocarbon gases were checked by the Dumas method with the same order of accuracy. The balance operates best in a location free of vibration and one in which all iron bodies are stationary. The presence of iron has no influence, but changes in its location near the balance cause variations in the zero position of the balance.

PROCEDURE

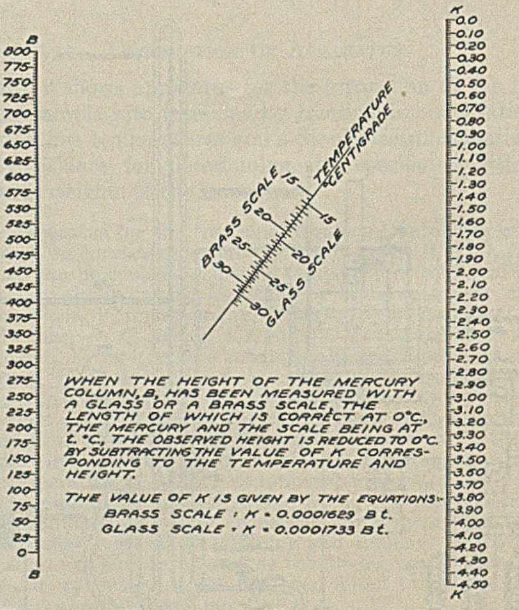
CALIBRATION OF BALANCE. The gas balance is calibrated with dry air free of carbon dioxide. The balance and manometer are evacuated through stopcocks 17, 23, 29, and 30 by means of a Cenco Hyvac pump capable of producing a vacuum of less than 0.001 mm. of mercury. The balance beam is then adjusted to the zero point by raising or lowering the magnet *D′*. Stopcocks 17 and 30 are closed and 6 is opened slowly to allow air to pass slowly through the gas holder, the soda lime, and the anhydrone into the gas balance. Stopcock 29 is then closed and the pressure in the balance determined by carefully opening stopcock 30 and at the same time admitting mercury to the manometer from *B′*. After the mercury level has risen almost to the zero point, *Z*, the final adjustment of the mercury level to the zero point is made with the screw clamp, *A′*. The switch, *G′*, is set on coil *Lc*, and the milliamperes of current necessary just to balance the beam are determined. The milliammeter reading, the temperature of the balance to 0.1° C., the manometer reading to the nearest 0.2 mm., and the temperature of the manometer to the nearest 0.5° C. are recorded. The balance and the manometer are again evacuated by closing stopcocks 6 and 30 and opening 17 and 29. *B′* is lowered, stopcock 33 opened, and, as the mercury level in the manometer falls, stopcock 30 is opened slowly to keep the mercury level near *Z*. When the mercury levels are below *Z* stopcock 33 is closed and 30 opened fully. The evacuation is completed and the operation repeated until at least four determinations have been made for each shunt at pressures distributed over the range of that particular shunt.

The apparent molecular weights, calculated from the temperature and corrected pressure, are plotted as ordinates and the corresponding milliamperes of current as abscissas. The straight line connecting these points should pass through the origin. If the line does not pass through the origin, the zero point has not been properly adjusted.

THE ANALYSIS

The sample for the analysis is measured in gas holder *A* over salt water. The volume of the sample is usually 300 to 500 cc., depending upon the noncondensable gases present. The most suitable quantity is about 200 to 300 cc. of hydrocarbons above methane. The sample may also be measured in the calibrated bulbs *P*, *Q*, or *R* from the pressure and temperature.

The sample is admitted slowly to evacuated condensation tubes *B* and *C* which are cooled by immersion in liquid nitrogen contained in Dewar flasks *G* and *H*. If the pressure, indicated by manometer *L* through stopcock 19, reaches atmospheric, the excess of noncondensables is allowed to pass into the vacuum line through stopcock 25, but the pressure in *B* and *C* is kept near atmospheric until all the sample is displaced from the gas holder. The pressure is then lowered slowly to remove noncondensables and gases dissolved in the liquefied hydrocarbons, the last traces of which are removed by distilling the hydrocarbons in *B* into *C* with stopcock 25 open to the vacuum and *C* immersed in liquid nitrogen, and then from *C* back into *B* with stopcock 25 closed, 23 open, and *B* immersed in liquid nitrogen. Usually two or three distillations will completely remove methane and dissolved gases.



WHEN THE HEIGHT OF THE MERCURY COLUMN, B, HAS BEEN MEASURED WITH A GLASS OR A BRASS SCALE, THE LENGTH OF WHICH IS CORRECT AT 0°C., THE MERCURY AND THE SCALE BEING AT t. °C., THE OBSERVED HEIGHT IS REDUCED TO 0°C. BY SUBTRACTING THE VALUE OF K CORRESPONDING TO THE TEMPERATURE AND HEIGHT.

THE VALUE OF K IS GIVEN BY THE EQUATIONS:-
BRASS SCALE : K = 0.0001629 Bt.
GLASS SCALE : K = 0.0001733 Bt.

FIGURE 4. NOMOGRAPHIC CHART FOR REDUCTION OF BAROMETER READINGS TO 0° C.

The condensed sample, contained in *C*, is allowed to vaporize slowly and pass at 1 mm. pressure, indicated by manometer *L*, into condensation tube *D*, cooled to −105° C., tube *E*, cooled to −135° to −140° C., and tube *F*, cooled to −195° C., stopcock 28 remaining open to the vacuum during this distillation. At the end of the distillation, the fractions are closed off in their respective condensation tubes. The aluminum blocks are cooled during the condensation of the sample and the preliminary distillations.

Fraction 1, containing ethane and ethylene and a part of the propane and propene, is distilled to bulb *M*, *N*, or *O*, depending on its volume, allowed to vaporize into *P*, *Q*, or *R*, and then, with stopcocks 10 and 17 closed, admitted to the gas balance and manometer *Y* for the molecular weight determination. The milliammeter reading, the temperature of the balance, the manometer reading, and the temperature of the manometer are recorded. Stopcock 10 is opened and the gas allowed to pass through stopcock 12 into *S*, forcing the mercury out of condensation tube *S* into buret *T*. Fraction 1 is then condensed in *S* by cooling in liquid nitrogen. If the pressure is not sufficient to force the mercury from *S* into *T*, the fraction is condensed first in *F*, stopcock 10 closed, and the fraction then vaporized. After the fraction, now in *S*, is vaporized into *T*, it is passed into pipet *V*, the portion in *S* being displaced by mercury. As soon as the olefins are absorbed, the remaining paraffins, fraction 1-a, are distilled back into *M*, *N*, or *O*, vaporized, and the molecular weight is determined.

The same procedure is applied to fraction 2 which contains the remainder of the propane and propene and the butanes and butenes. The analysis is complete when fraction 3, the gasoline fraction, is distilled to *M*, vaporized, and the molecular weight determined.

The absorption of the olefins by the activated acid in *V* usually requires 6 to 9 minutes for fraction 1, and 3 to 6 minutes for fraction 2, and the procedure is arranged so that, while the absorption is being made on fraction 1, the molecular weight of fraction 2 is determined, and, similarly, while the olefins are being absorbed from fraction 2, the molecular weight of fraction 3 is determined. When the data on a fraction are complete, the fraction is removed from the apparatus through stopcock 23 or 28.

About 1.5 to 2 hours and approximately 1 liter of liquid nitrogen are required for an analysis. The operation of the apparatus can be learned by an operator in a short time as a manipulative process without necessity for thorough understanding of the theory involved.

DATA AND CALCULATIONS

A typical set of data is shown in Table II.

TABLE II. TYPICAL DATA OBTAINED IN ANALYSIS OF COMPLEX HYDROCARBON MIXTURE

(Volume of sample, 295.5 cc.)

FRACTION	VOLUME	MOLECULAR WEIGHT
	Cc.	
1	96.0	35.90
1-a	57.3	37.23
2	113.2	52.96
2-a	78.3	54.62
3	35.5	72.47
Noncondensable	50.8	...

The following relations have been derived for calculating the volume of each hydrocarbon constituent in each of the fractions:

FRACTIONS 1 AND 1-a. (1) Ethane and propane

$$\text{Volume of ethane} = \left(\frac{45.25 - \text{molecular weight of 1-a}}{14.85}\right) \text{volume of 1-a} \qquad (1)$$

$$\text{Volume of propane} = \text{volume of 1-a} - \text{volume of ethane} \qquad (2)$$

(2) Ethylene and propene

$$\text{Volume of ethylene} = 3\,(\text{volume of 1} - \text{volume of 1-a}) - \left(\frac{\text{volume 1} \times \text{molecular weight of 1} - \text{volume of 1-a} \times \text{molecular weight of 1-a}}{14.02}\right) \qquad (3)$$

$$\text{Volume of propene} = \text{volume of 1} - \text{volume of 1-a} - \text{volume of ethylene} \qquad (4)$$

FRACTIONS 2 AND 2-a. (1) Propane and butane

$$\text{Volume of propane} = \left(\frac{59.87 - \text{molecular weight of 2-a}}{14.62}\right) \text{volume of 2-a} \qquad (5)$$

$$\text{Volume of butane} = \text{volume of 2-a} - \text{volume of propane} \qquad (6)$$

(2) Propene and butene

$$\text{Volume of propene} = 4\,(\text{volume of 2} - \text{volume of 2-a}) - \left(\frac{\text{volume of 2} \times \text{molecular weight of 2} - \text{volume of 2-a} \times \text{molecular weight of 2-a}}{14.02}\right) \qquad (7)$$

$$\text{Volume of butene} = \text{volume of 2} - \text{volume of 2-a} - \text{volume of propene} \qquad (8)$$

With these relations and the data in Table II, the data in Table III are calculated.

TABLE III. DATA CALCULATED FROM MOLECULAR WEIGHT AND VOLUME OF FRACTIONS

HYDROCARBON	FRACTION 1	FRACTION 2	TOTAL	VOLUME PER CENT IN SAMPLE
	Cc.	*Cc.*	*Cc.*	
Methane	..	..	50.8	17.2
Ethane	31.0	..	31.0	10.5
Ethylene	22.5	..	22.5	7.6
Propane	26.3	28.1	54.4	18.4
Propene	16.2	17.1	33.3	11.3
Butanes	..	50.2	50.2	17.0
Butenes	..	17.8	17.8	6.0
Pentane	..	..	35.5	12.0

The volume per cent of each hydrocarbon in the original mixture is calculated from the volumes derived through the above relations and the volume of the original sample, the volumes of propane and of propene being the sum of the volumes of these hydrocarbons in fractions 1 and 2.

The per cent of methane plus noncondensable gases is calculated from the difference in the volume of the sample and the sum of the volumes of fractions 1, 2, and 3.

Since the molar volumes of the gaseous hydrocarbons, especially the paraffins, vary considerably from that of an ideal gas, the molecular weights or rather the weight (grams) of 22.41 liters have been calculated from the experimentally determined densities. Complete data have not been found in the literature for the olefins. The data for the paraffin hydrocarbons are shown in Table IV.

TABLE IV. EXPERIMENTALLY DETERMINED DENSITIES OF PARAFFIN HYDROCARBONS

HYDROCARBON	WEIGHT	
	1 liter	22.41 liters
	Grams	*Grams*
Ethane	1.3564	30.40
Propane	2.0190	45.25
n-Butane	2.6753	59.95
Isobutane	2.6678	59.79

It is clear that the molar volumes of the hydrocarbon gases would reach the theoretical values at zero pressure, but at the pressures used in the authors' experiments the deviation was not appreciably influenced by pressure and they could use the values in Table IV with better results than could be obtained by using the theoretical values.

Since the value given in the literature for the density of ethylene (1.2604 grams per liter) is close to the calculated and the value obtained by the authors on the Stock gas-density balance (2.529 grams per liter) for isobutene is also so close to the calculated value as not to cause any appreciable error in the calculations, the theoretical values have been used for the olefins.

Normal and isobutane are determined together in this analysis, and the average weight of 22.41 liters of these hydrocarbons, 59.87, has been used as the value for butane.

For the calibration of the balance, the apparent molecular weight, *M*, of air is calculated from the pressure and temperature corresponding to a particular current by the following relation:

$$M = 28.98 \times \frac{P}{760} \times \frac{273}{t + 273}$$

The apparent molecular weight, *M*, read from the calibration curve, molecular weight–milliampere relation, is calculated to the molecular weight at 0° C. and 760 mm., M_0, by the relation,

$$M_0 = M \times \frac{760}{P} \times \frac{t + 273}{273}$$

All pressure readings are reduced to 0° C. since at pressures over 100 mm. the expansion of the mercury introduces an appreciable error in the readings. A nomographic chart, Figure 4, has been constructed from which corrections between 15° and 32° C. and to 800 mm. pressure can be read directly.

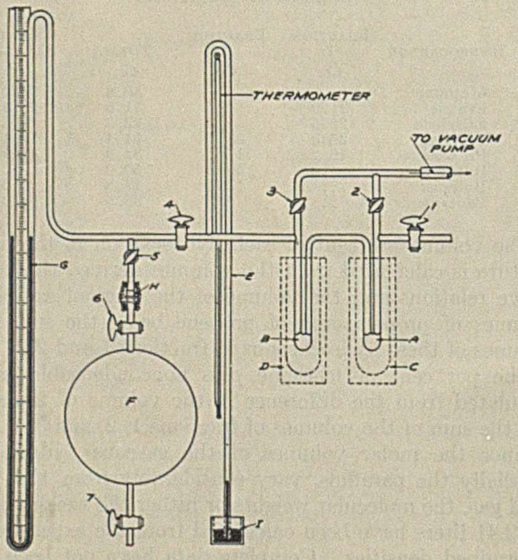


Figure 5. Apparatus for Preparation of Synthetic Gas Mixtures

The volumes of the fractions are calculated from the pressures as read on Y to 0.2 mm., the temperature of the bulbs P, Q, and R to 0.1° C., and the known volume of the apparatus.

Selection of Temperatures for Condensations

The quantitative separation of methane from C-2 hydrocarbons at the temperature of liquid nitrogen (−195° C.) has been well established by a number of investigators, and in this work it has been found unnecessary to provide for the possibility of the presence of C-2 hydrocarbons in the methane fraction.

An inspection of low-temperature vapor pressure data of the gaseous hydrocarbons indicates that at a temperature between −120° and −150° C. the C-4 hydrocarbons should, at pressures of 1 mm. or less, be quantitatively condensed from C-2 hydrocarbons, and similarly, pentanes and heavier from C-4 hydrocarbons at temperatures between −90° and −110° C.

To determine the temperature most suitable for the quantitative separation of C-2 and C-4 hydrocarbons, synthetic mixtures of ethane and isobutane of known composition were fractionated at temperatures between −120° and −160° C. Isobutane was taken for this separation rather than *n*-butane, since isobutane, owing to its lower boiling point, is more difficult to separate. At temperatures between −135° and −140° C. the separation of isobutane from ethane was quantitative. In addition to the measurement of the gas volumes from the fractionation and their comparison with the calculated values, the purity of the fractions was verified by accurate molecular weight determinations. With 50 per cent mixtures, no ethane was condensed at temperatures between −120° and −140° C.; 0.08 per cent was condensed at −145°, 1.2 per cent at −150°, 1.7 per cent at −155°, and 3.1 per cent at −160° C. Similar results were obtained with other ethane-butane mixtures of varying composition.

In similar experiments with *n*-butane–pentane mixtures, the condensation of pentane was −99.1 to 99.7 per cent complete at −100° C. and 100 per cent at −105° C. Accurate molecular weight determinations showed that no butane was present in the pentane fraction. With mixtures containing over about 5 per cent of butanes, a small amount of butane was condensed in the fractionation but was completely removed by a second distillation.

Accuracy of Method

The analysis of a number of complex synthetic hydrocarbon gas mixtures of known composition has shown the method to give values of a high order of accuracy.

The Podbielniak fractionating column was used in the purification of the gaseous paraffin and olefin hydrocarbons. Samples of ethane, ethylene, propane, propene, *n*-butane, and isobutane were obtained from cylinders of the compressed gases and fractionated on the column until a constant-boiling fraction was obtained. Isobutene was prepared from tertiary butyl alcohol and oxalic acid and 1-butene from *n*-butyl alcohol by dehydration over alumina. These butenes were also purified by fractionation on the Podbielniak column.

The apparatus used in the preparation of synthetic gas mixtures is shown in Figure 5. The entire apparatus, including the 5-liter bulb, F, was evacuated through stopcocks 2 and 3; stopcock 4 was then closed. The hydrocarbon was admitted through stopcock 1 and condensed in bulb A which was cooled in liquid nitrogen contained in Dewar flask C. Stopcock 1 was then closed and 3 opened to the vacuum, to remove any air that may have contaminated the sample during storage or in being transferred. Any dissolved air was removed by distilling the hydrocarbons into B, which was cooled in liquid nitrogen contained in D.

The condensed gas, now contained in B, was transferred to F by closing stopcock 3 and lowering D until the pressure in B was near atmospheric, as indicated by manometer E. Stopcock 4 was then opened carefully until the pressure, as shown by manometer G, indicated that the desired amount of the hydrocarbon had been admitted to F. The excess was allowed to vaporize and pass out through stopcock 1 or was removed through the vacuum pump. The absolute pressure of the gases in F was obtained by subtracting the difference in the mercury levels of manometer G from the atmospheric pressure. The volume per cent of each gas was calculated by dividing the pressure exerted by each gas by the total pressure of the mixture, all pressure readings being reduced to 0° C. F was removed from the apparatus through ground joint H and the mixture displaced by mercury or salt water.

This method of preparation of synthetic gas mixtures is rapid and accurate, and excludes the possibility of contamination by air or of any absorption of the gases by salt water, as is usually experienced in other methods for the preparation of these mixtures.

The analysis of one of the synthetic mixtures prepared in this manner is shown in Table V.

Table V. Analysis of Synthetic Mixture

Hydrocarbon	Volume Per Cent of Condensation Analysis			Calculated Volume
	1	2	Av.	%
Methane + air	21.6	21.5	21.6	21.8
Ethane	10.5	10.4	10.5	12.1
Ethylene	10.7	9.7	10.2	10.5
Propane	14.0	15.9	15.0	15.1
Propene	11.7	11.8	11.8	10.9
Isobutane	15.7	14.5	15.1	4.0
n-Butane				10.2
Butenes	10.6	10.7	10.7	10.0
Pentane	5.4	5.4	5.4	5.5

Isobutane and *n*-butane are reported as total butanes, so the values given for *n*-butane correspond to the calculated value of 14.2 per cent.

The method has been applied to the analysis of a number of refinery gases. Typical examples are shown in Table VI.

TABLE VI. ANALYSIS OF REFINERY GASES

HYDROCARBON	SAMPLE 1	SAMPLE 2	SAMPLE 3	SAMPLE 4
Methane + air	0.1	14.8	0.0	0.0
Ethane	3.3	2.5	2.8	4.8
Ethylene	0.2	0.0	1.4	0.0
Propane	24.2	27.1	36.4	30.8
Propene	10.7	0.0	11.1	15.9
Butanes	33.6	52.1	24.6	33.0
Butenes	26.6	0.0	23.7	11.7
Pentane +	1.5	3.5	0.0	3.8

ADVANTAGES OF METHOD

The chief advantages of this method lie in its application to the complete accurate analysis of small samples, less than 0.5 liter, the rapid, routine analysis of all types of gases, and the low cost of apparatus and of operation.

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Estimation of Aldehydes in Rancid Fats

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Statements in the literature suggest that aliphatic aldehydes of medium molecular weight, in particular heptaldehyde and nonaldehyde, are the compounds mainly responsible for the objectionable odor and flavor of oxidized fats.

An investigation of the bisulfite method has therefore been carried out with a view to estimating small quantities of these substances in solution in an oil or fat. Purified heptaldehyde has been employed and the sensitivity of the method increased until the aldehyde content of 1 gram of cottonseed oil (containing approximately 0.1 per cent of the aldehyde) can be determined with an accuracy of the order of 0.001 per cent.

Specimen data are given on the development of aldehydes in oxidizing fats.

THOUGH the theories which have been proposed from time to time to account for the deterioration produced in fats by autoxidation of the unsaturated constituents differ in detail, they all agree in postulating that the first stage in the reaction consists in the addition of molecular oxygen to the double bonds of the unsaturated acids with production of labile peroxides which then further isomerize, decompose spontaneously into, or react with water to form a complex series of products including aldehydes, ketones, and acids of lower molecular weight.

CHEMICAL TESTS FOR RANCIDITY

Various chemical methods based upon the presence of one or other of the above-mentioned decomposition products have been suggested for the detection and estimation of rancidity, of which the peroxide and Kreis tests, and in smaller degree the Schiff and Issoglio tests, are probably the best known.

The peroxide estimation (*11*) has proved itself of particular value in investigating the earliest stages of the oxidation of fats, its sensitivity making possible an investigation of those slow changes during the induction period which lead to rapid oxidation and the accompanying deterioration in odor and flavor. In some cases the peroxide test has been successfully applied in the presence of protein (*10*), thus avoiding the very real difficulty of extracting the fat unchanged from the tissue. In recent work determination of peroxide oxygen appears also to be displacing other less reliable or more cumbersome methods in heat-accelerated tests for the determination of relative susceptibility to oxidation (*9, 17*).

The Kreis reaction, stated by Powick (*13*) to be due to the presence in the fat of a derivative (possibly a glyceryl acetal) of epihydrin aldehyde, has been widely used as a criterion of oxidation rancidity but has recently been adversely criticized in America and in Germany by committees set up to investigate it.

The Schiff test with fuchsin–sulfurous acid for the aldehyde grouping has been applied to the detection of rancidity in fats by Browne (*3*), Fellenberg (*7*), and others, but always in a qualitative or at best a very rough quantitative manner; while determination of the permanganate-reducing power of the steam-volatile or water-soluble products obtainable from a known weight of oil under standard conditions has also found some practical application but is rather empirical in nature.

Much controversy has occurred in the past as to the ability of the various chemical tests to parallel rancidity as judged by odor and flavor. Actually, as Barnicoat (*1*) has recently pointed out in case of the Kreis and peroxide tests, there are no values above which oils and fats in general are invariably rancid and below which they are sweet. The points on the peroxide-oxygen and Kreis curves at which a fat becomes perceptibly rancid depend on the nature of the fat (generally speaking, a low content of acids less saturated than oleic favors the early development of rancidity but this generalization holds better for normal than for high temperatures), and also in some degree on the conditions of temperature and light to which it has been subjected. It has, for example, already been shown (*1, 11*) that the ratio between the rates of peroxide accumulation and development of the Kreis reaction is not constant for a particular fat, but increases with falling and decreases with rising temperature—a result probably attributable to a greater stability of the peroxide at lower temperatures. Similarly the ratio between the observed peroxide and Kreis values is not the same for different oils under similar conditions.

In view of the wide variation in sensitivity to "off" odors and flavors displayed by different individuals, and by the same person at different times, and of the difficulty of fixing standards for odor and flavor, a quantitative chemical test which would correspond more closely to the organoleptic method than do the existing ones would clearly be of considerable value. Such a result would, of course, best be achieved by estimating directly the substance or substances actually responsible for the rancid odor and flavor.

TESTS FOR ALDEHYDES

Among the products of the atmospheric oxidation of fats the aliphatic aldehydes of medium molecular weight immediately stand out as possible sources of the deterioration in odor and flavor, and Scala (*15*) as far back as 1908 expressed the opinion that heptaldehyde and nonaldehyde, and to a smaller extent hexaldehyde and butaldehyde, are actually the substances concerned. More recently Powick (*13*), as the result of an examination of a large series of the compounds which might reasonably be present in an oxidized fat, came to the conclusion that of these only heptaldehyde, and in a smaller degree nonaldehyde, could contribute appreciably to the rancid odor. On the basis of these results it was decided to attempt the estimation of the minute amounts of aldehydes present in oxidized fats.

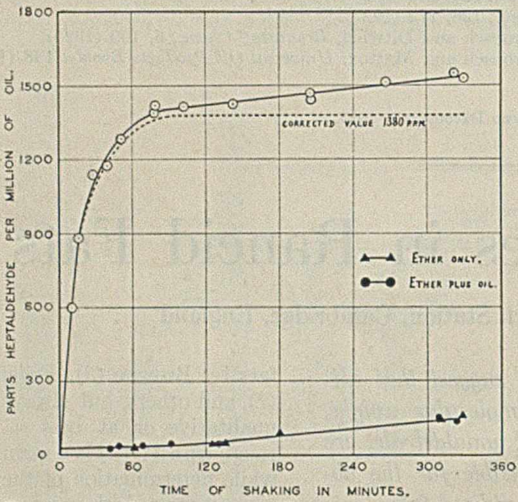

FIGURE 1. ESTIMATION OF HEPTALDEHYDE IN COTTONSEED OIL BY DIRECT TITRATION METHOD, USING ETHER AND 0.1 *N* SODIUM BISULFITE

THE SCHIFF TEST. A series of experiments was therefore carried out with the object of placing the Schiff reaction on a quantitative basis, but neither by Fellenberg's (*7*) technic nor by various modifications of it could quantitative results be obtained. The color produced in the test often appeared to concentrate at the interface between the two phases and attempts to carry out the reaction in a single-phase medium by means of alcohol or glacial acetic acid were not successful. Schibstead (*16*), however, in a paper which has appeared since the above work was carried out, has succeeded in obtaining quantitative results from a modification of the Schiff test. According to this author's technic the fat in petroleum ether solution is shaken with a solution of rosaniline hydrochloride–sulfurous acid in 50 per cent alcohol (which is red), and the color produced in the petroleum ether layer compared with a cresol red standard at pH 8.3. The actual depth of color obtained from a given specimen of fat is dependent upon the concentrations of alcohol, sulfur dioxide, and hydrochloric acid employed, on the proportion of reagent to fat solution, and on the shape of container, manner of shaking, and time and conditions of standing; all of these variables being adjusted so far as possible for maximum color development. Simple aldehydes such as heptaldehyde do not develop any color in the petroleum ether phase, the test apparently being specific for aldehydes of high molecular weight whose condensation products with rosaniline hydrochloride are soluble in petroleum ether. The substances reacting in rancid fats are therefore presumably the glyceride-aldehyde residues which remain after splitting off of the simple aldehydes. Schibstead also states that samples of oleic and linoleic acids which had quite a tallowy odor failed to give any reaction with the reagent.

THE BISULFITE METHOD. As an alternative to the Schiff reagent the bisulfite method for the estimation of aldehydes seemed to offer the best hope of success. Ripper's original method (*14*) improved by Clausen (*4*) has already been used by Clausen and by Friedemann, Cotonio, and Schaffer (*8*) to estimate small amounts of acetaldehyde produced by oxidation of the lactic acid present in tissues, and by Clift and Cook (*5*) for the determination of pyruvic acid and other carbonyl-containing compounds in samples of biological origin. Briefly, the method consists in allowing the solution containing the aldehyde to react with a solution of sodium bisulfite. The excess of the latter is then destroyed by addition of iodine, sodium bicarbonate is added to facilitate dissociation of the aldehyde bisulfite compound, and the combined bisulfite is titrated with standard iodine.

For use with fats the main practical difficulty, apart from the extremely small quantities involved, is that of securing adequate contact between the aqueous reagent and the fat in order that complete extraction may be obtained.

ESTIMATION OF HEPTALDEHYDE

As experimental material solutions of heptaldehyde of known concentrations were made up in the solvent under investigation or in freshly refined cottonseed oil. The commercial product usually analyzed to about 70 to 90 per cent heptaldehyde and was purified via the bisulfite compound before use.

Two or three of the samples thus prepared displayed a rather remarkable instability, the liquid after two or three days becoming turbid through separation of water (?) and of fine needle-like crystals resembling glass wool. During this change the aldehyde content fell from 96–98 per cent to about 15 per cent without, however, any appreciable increase in free acidity, indicating that the reaction involved was one of condensation rather than of oxidation. Suspecting the influence of traces of alkali derived from the anhydrous sodium sulfate (analytical reagent) used or from the glass bottles, the time of drying was reduced to a minimum and the aldehyde stored in small hard glass tubes at −20° C. during the few days elapsing between purification and use. Under these conditions no further trouble was experienced.

HYDROXYLAMINE METHODS. For estimation of the purified aldehyde, modifications of the methods of Bennett and Salamon (*2*) and of Leone and Tafuri (*12*), both employing hydroxylamine, were used. The reagent for the former is prepared by dissolving 5 grams of hydroxylamine hydrochloride in 9 cc. of hot water, adding 80 cc. of 90 per cent alcohol and 0.2 cc. of 0.4 per cent bromophenol blue,[1] neutralizing with alcoholic potassium hydroxide to a greenish blue color, and making up to 100 cc. with 90 per cent alcohol. The aldehyde (1 gram) is added to 20 cc. of this solution and after standing for 20 minutes the liberated hydrochloric acid is titrated with 0.5 *N* alcoholic potassium hydroxide to a clear blue color, the end point being matched with that of a blank determination to which has been added a quantity of alcohol corresponding approximately to the titration obtained. In this way it is possible to obtain much better reproducibility than by attempting to neutralize the reagent exactly before use as recommended in the original method. The purified aldehyde always reacted neutral to bromophenol blue, so that no correction was necessary on this score.

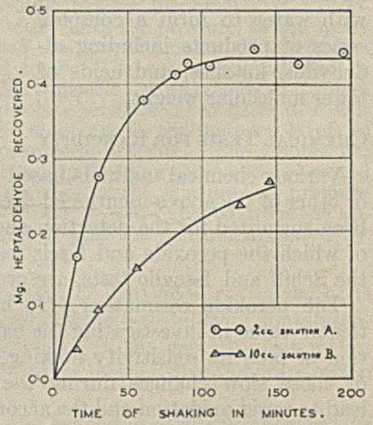

FIGURE 2. EFFECT OF VOLUME OF SOLVENT ON RATE OF EXTRACTION OF HEPTALDEHYDE FROM BENZENE

In the Leone and Tafuri (*12*) method the aqueous hydroxylamine solution employed for the determination of acetaldehyde was found to give low results with heptaldehyde and was therefore replaced by a 5 per cent solution of hydroxylamine hydrochloride in 90 per cent alcohol. Twenty cubic centimeters of this reagent are neutralized to phenolphthalein with 1 *N* alcoholic potassium hydroxide, the aldehyde (1 gram) is added, and after standing for 20 minutes the excess hydroxylamine is titrated to

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[1] The figure of 2 cc. given in the original paper is presumably a misprint, since it is practically impossible to titrate at this concentration.

methyl orange with standard 0.5 *N* sulfuric acid. A blank determination is again carried out, water being added in this case to the experiment to compensate for the smaller quantity of acid required. The results obtained were not quite so reproducible and were usually also somewhat lower than those obtained by the Bennett and Salamon method (Table II).

TABLE I. ESTIMATION OF HEPTALDEHYDE BY BISULFITE METHOD

Specimen	Time of Shaking	Normality of Bisulfite Solution 0.1	0.2	0.5	1.0	2.0	5.0
	Min.						
A	30	..	88.8	92.6	94.1	94.1	..
A	60	..	88.2	93.6	93.3	..	94.6
A	90	..	88.5	92.8	93.9	93.7	..
B	60	..	90.4	94.7	96.6	97.0	..
C	30	85.5	91.0	94.9	96.7	96.6	96.3
D	90	84.8	90.3	94.7	96.2	96.2	96.0
E	30	..	..	94.2	95.7	..	..
E	60	..	..	94.5	96.8	..	..
E	90	..	..	94.9	96.6	..	..
F	60	..	..	95.2	96.0	..	..
G[a]	30	..	..	..	79.8	..	..
G	60	75.4	78.0	78.3	79.5	79.6	80.0
H[a]	60	73.7	76.1	79.1	79.4	..	..

[a] Unpurified specimens.

BISULFITE METHOD. In Table I is given a series of results obtained by the bisulfite method. In this case the aldehyde (0.15 gram) was shaken at approximately 240 cycles per minute with 20 cc. of the bisulfite solution in a constant-temperature room at 20° C. The excess bisulfite was then neutralized with iodine, sodium bicarbonate added, and the combined bisulfite titrated with standard 0.1 *N* iodine. The figures show that no appreciable advantage is to be gained by using concentrations of bisulfite greater than normal, or by shaking for longer than 30 minutes. The values obtained were slightly lower than those given by the hydroxylamine methods.

ESTIMATION OF TRACES OF HEPTALDEHYDE

For the purpose of extracting small amounts of heptaldehyde from a fat the latter was dissolved in a solvent and shaken vigorously with the bisulfite solution in the absence of light. Various solvents were employed in turn, the earlier experiments being carried out with ether, which emulsified readily with the bisulfite, gave more rapid extraction than any other solvent tried, and did not interfere too seriously with the end point of the titration. The blank titration in the absence of added aldehyde or fat was, however, found to increase appreciably with the time of shaking, owing possibly to the production of traces of acetaldehyde, a reaction which is known to occur when ether is allowed to stand in the presence of air, especially in daylight (*6*). In Figure 1 results are given for one of the preliminary experiments in which a solution of heptaldehyde in fresh cottonseed oil (1 gram), ether (5 cc.) and 0.1 *N* sodium bisulfite solution (25 cc.) were used for each estimation. The lower curve, which has been used to correct the values plotted in the upper, shows the increase in the blank titration (calculated as heptaldehyde) during the experiment. Under the conditions here employed extraction of the aldehyde from the fat is apparently complete in 90 to 100 minutes.

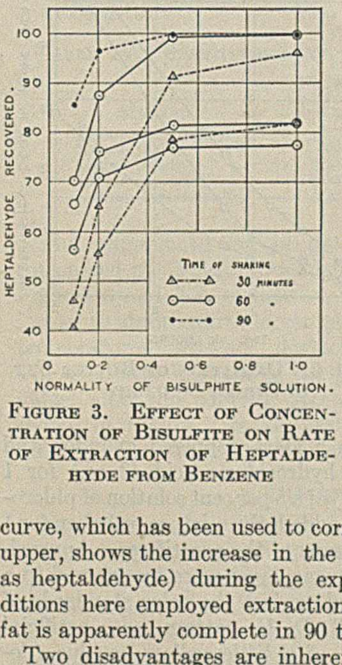

FIGURE 3. EFFECT OF CONCENTRATION OF BISULFITE ON RATE OF EXTRACTION OF HEPTALDEHYDE FROM BENZENE

Two disadvantages are inherent in the above method—namely, the relative instability of the solvent, and the presence of ether and fat in the emulsion to be titrated which makes the end point somewhat difficult to obtain accurately. In later experiments therefore the emulsion obtained after shaking was centrifugalized for 5 minutes and an aliquot portion of the aqueous layer removed for titration. Ether proved unsatisfactory with this technic on account of its volatility and partial miscibility with water, and was replaced by benzene.

The efficiency with which heptaldehyde can be transferred from the benzene to the bisulfite solution will depend upon the volume of benzene employed and the partition coefficient of the aldehyde between benzene and water, as well as the volume and concentration of bisulfite solution and the dissociation constant of the bisulfite compound at the temperature and pH of the reaction. The effect of volume of benzene is shown in Figure 2 in which 2 cc. of solution A of heptaldehyde in benzene or 10 cc. of solution B (one-fifth as strong as A) were shaken with 20 cc. of 0.2 *N* sodium bisulfite at 20° C. for various lengths of time, centrifugalized, and 15 cc. of the aqueous portion titrated. The results show a much slower and less complete extraction in presence of the larger amount of solvent. In subsequent determinations the volume of benzene was therefore fixed at 2 cc. which is sufficient to hold 1 gram of a solid fat in solution.

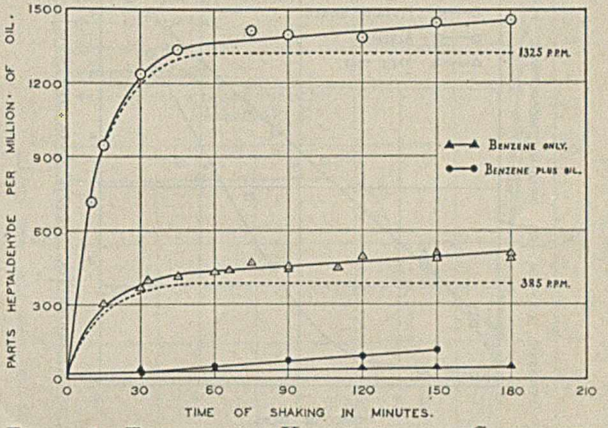

FIGURE 4. ESTIMATION OF HEPTALDEHYDE IN COTTONSEED OIL BY CENTRIFUGE METHOD, USING BENZENE AND 0.5 *N* SODIUM BISULFITE

The figures given in Table I indicate that the rate of combination of heptaldehyde with sodium bisulfite is influenced to a considerable extent by the concentration of the latter employed. In case of the extraction of small quantities of aldehyde from solution in benzene the effect is still more marked. In Figure 3 are collected the results of a series of experiments in each of which 2 cc. of a solution of heptaldehyde in benzene were shaken with 20 cc. of bisulfite solution of various concentrations for 30, 60, and 90 minutes. Several samples of aldehyde were used, the results being expressed as percentage purity of the sample, those below 85 per cent representing crude commercial samples and those above 95 per cent purified specimens. These results show that with the possible exception of 1 *N* and stronger bisulfite solutions 30 minutes' shaking is not sufficient to extract the aldehyde completely. Using 60 or 90 minutes, comparatively little advantage is to be gained by increasing the bisulfite concentration beyond 0.5 *N*. With solutions stronger than normal the estimation becomes difficult owing to fading of the end point when the 0.002 *N* iodine is being used, and the larger quantities of iodine necessary to destroy the excess bisulfite give rise to so much hydriodic acid and sodium bisulfate as to cause considerable frothing during neutralization with bicarbonate. For subsequent experiments 0.5 *N* was therefore adopted as the most suitable bisulfite concentration.

Finally a series of determinations was carried out on 2 cc. of a benzene solution of the aldehyde shaken for 30 minutes at 20° C. with 5, 10, 15, 20, and 25 cc. of 0.5 *N* bisulfite solution, resulting in values of 41.4, 58.0, 70.0, 78.3, and 80.0 per cent for a sample of crude aldehyde which analyzed to 79.7 per cent by the bisulfite method. The figures indicate that a volume of 25 cc. of bisulfite is desirable; in practice, however, owing to the limited capacity of the centrifuge cups used 20 cc. were found more suitable, the slight loss in efficiency being compensated for by a longer time of shaking.

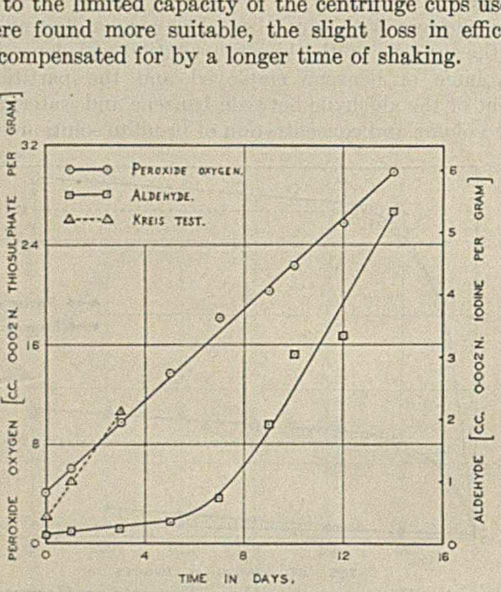

FIGURE 5. OXIDATION OF COTTONSEED OIL IN LAMP LIGHT AT 23° TO 28° C.

RECOMMENDED METHOD. The bisulfite solution is prepared by dissolving 66.2 grams of anhydrous sodium carbonate in approximately 450 cc. of water, saturating with sulfur dioxide, and making up to 500 cc. with a little sulfur dioxide water. A portion of this stock solution is diluted 10 times when required.

A determination is carried out as follows: Approximately 1 gram of the fat is weighed into each of several glass-stoppered bottles (total capacity about 70 cc.), dissolved in 2 cc. of analytical reagent benzene, warming if necessary, 20 cc. of 0.5 *N* bisulfite solution are added, and the mixture is shaken at about 240 cycles per minute at 20° C. in the absence of light. At intervals a bottle is removed, the emulsion poured into a tube, centrifugalized at 2000 to 3000 r. p. m. for 5 minutes, and 15 cc. of the clear aqueous layer are pipetted into a 150-cc. Erlenmeyer flask. Iodine is then run in, first 1 *N*, then 0.05 *N*, and finally 0.002 *N* until the excess bisulfite has been destroyed. Should the end point be slightly overrun, a drop or two of dilute thiosulfate may be added, the end point being adjusted to a definite depth of tint, starch and at least 1 gram of potassium iodide of course being present. Sodium bicarbonate (analytical reagent, 3 grams) is now added and standard 0.002 *N* iodine run in until the same tint is again reached. Towards the end of the titration the color produced by the latest addition of iodine tends to fade more and more slowly, but the true end point is perfectly definite and easy to determine. In this as in the peroxide estimation it has been found preferable to titrate by the aid of a daylight lamp in a darkened room, but this is not, of course, essential.

In Figure 4 are graphed the results of a series of determinations carried out on two solutions of heptaldehyde in fresh cottonseed oil. It can be seen that the blank titration for the benzene alone rises hardly perceptibly (the initial value of about 25 p. p. m. is due to the bicarbonate), but in presence of the oil the increase after 60 minutes becomes rather more marked. When the curves obtained for the aldehyde solutions are corrected for the blank titrations constant values of 1325 and 385 parts per million are obtained, corresponding to 99.2 and 100.3 per cent of the crude aldehyde contents of the two solutions. The specimen of heptaldehyde used analyzed to 98.7 per cent by the Bennett and Salamon method.

In Table II are given analyses of a series of samples of heptaldehyde by the Bennett and Salamon and Leone and Tafuri methods, using in each case approximately 1 gram of material, by the bisulfite method shaking about 0.15 gram of aldehyde with normal or stronger bisulfite for 30 or 60 minutes, and by the same method shaking 1 gram of cottonseed oil or 2 cc. of benzene containing about 0.0004 gram of aldehyde with 0.5 *N* or 1 *N* bisulfite for 60 or 90 minutes. The determinations on the dilute solutions actually correspond more closely to the hydroxylamine figures than do the bisulfite estimations on the aldehyde itself.

TABLE II. ESTIMATION OF HEPTALDEHYDE IN DILUTE SOLUTION BY BISULFITE METHOD

HYDROXYLAMINE METHODS		BISULFITE METHOD		
Bennett and Salamon	Leone and Tafuri	Aldehyde alone	Benzene solution	Cottonseed oil solution
96.3	95.1	94.0	..	..
98.3	96.3	96.3	99.5	..
98.7	97.5	96.5	..	99.2
98.5	97.2	..	99.5	..
97.4	95.9	..	..	97.9
96.4	94.6	..	95.8	..
97.5	96.7	95.6	97.1	..

ALDEHYDE DETERMINATIONS ON OXIDIZED FATS

Aldehyde determinations have as yet been carried out on relatively few natural fats, but preliminary experiments indicate that zero values are obtained from perfectly fresh samples. The method employed in all cases has been that described above, the time of shaking being 60 minutes and appropriate correction being made for the blank titration on the reagents. [Mean values for the blank titration (15 cc.) in the absence of fat were 0.17, 0.20, 0.24, and 0.27 cc. of 0.002 *N* iodine for 30, 60, 90, and 120 minutes' shaking.] With continued shaking perceptibly higher results are obtained (Table III), but the shorter period has been adhered to in order to minimize any danger of aldehyde production during the determination.

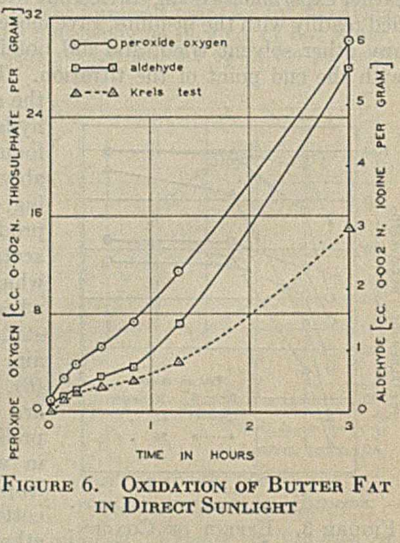

FIGURE 6. OXIDATION OF BUTTER FAT IN DIRECT SUNLIGHT

In Figure 5 data are given for the oxidation of a specimen of cottonseed oil illuminated at 22° C. by a 100-watt lamp at a distance of 3 feet (90 cm.), 20 cc. of the oil being placed in each of a series of flat-bottomed glass dishes 6 cm. in diameter, one of which was removed at intervals for examination. The Kreis test was carried out by dissolving the oil (3 grams) in benzene (6 cc.) in a glass-stoppered cylinder, and shaking with concentrated hydrochloric acid (3 cc.) for 1 minute. Five drops (0.1 cc.) of a 5 per cent solution of phloroglucinol in alcohol were then added, the mixture reshaken for 1 minute and separated by means of the centrifuge. Approximately 2 cc. of the clear aqueous layer were transferred to a 1-cm. glass cell and matched against the color standards of the Lovibond tintometer (B. D. H. pattern, with artificial light attachment). By use of a little yellow or blue (depending on the nature of the fat) in conjunction with the red an accurate match can readily be obtained. The values plotted in Figures 5, 6, and 7 on the same scale as the peroxide oxygen figures are the sums of the red and yellow or red and blue glasses required. In case of samples of fat giving colors deeper than about 10 units on the Lovibond scale the amount of fat used must be reduced and the observed value corrected back to the normal weight.

Figure 6 gives the results of an experiment in which butter fat (20 cc.) was exposed in Petri dishes (15 cm. diameter) to direct sunlight for 3 hours. All the specimens of fresh butter fat examined gave Kreis tests of 0.0R, 0.5Y; which figure has therefore been treated as a blank and subtracted from the subsequent readings.

A second sample of butter fat oxidized under conditions similar to those employed for the cottonseed oil gave the results expressed in Figure 7. In this latter experiment the Schibstead test was carried out exactly as described by the author, the solutions being matched in a Duboscq colorimeter. It is, however, somewhat simpler to calibrate the cresol red standard against the Lovibond color glasses (4.75R, 1.1B in 1-cm. cell), after which the experimental solutions can be matched directly in the tintometer. The color of light transmitted through 1 cm. of the melted butter fat is expressed in Lovibond units and plotted on the same scale as the peroxide oxygen and Kreis values.

Table III. Effect of Time of Shaking on Apparent Aldehyde Content of Oxidized Fats

Fat	Time of Shaking 30 min.	60 min.	90 min.	120 min.
Fresh beef fat[a]	0.0	0.0	0.0	0.0
Fresh butter fat[a]	0.0	0.0	0.0	0.0
Oxidizing butter fat	0.0	0.1	0.1	0.1
Oxidizing butter fat	0.2	0.2	0.2	0.2
Oxidizing butter fat	0.4	0.5	0.6	0.5
Oxidizing butter fat	0.4	0.7	0.7	0.7
Oxidizing butter fat	0.6	0.8	0.8	0.8
Oxidizing butter fat	0.8	1.0	1.2	1.2
Oxidizing butter fat	1.2	1.6	1.6	1.7
Oxidizing butter fat	8.4	10.5	10.6	10.8
Fresh lard[a]	0.0	0.1	0.1	0.1
Oxidizing lard	0.8	1.2	1.6	1.7
Oxidizing lard	1.0	1.5	1.7	1.9
Fresh cottonseed oil[b]	0.0	0.1	0.4	0.4
Oxidizing cottonseed oil	0.1	0.3	0.4	0.4
Oxidizing cottonseed oil	0.3	0.7	0.7	1.0
Oxidizing cottonseed oil	1.6	1.9	2.0	2.3
Oxidizing cottonseed oil	2.3	3.0	3.2	3.3
Oxidizing cottonseed oil	2.8	3.3	3.5	3.5
Oxidizing cottonseed oil	4.8	5.3	5.6	5.6

[a] Laboratory extracted.
[b] Commercial.

Table IV. Standardization of Thiosulfate Solutions

Method	Without Carbonate 0.002 *N*	With Carbonate 0.002 *N*	0.1 *N*
Bichromate (acid)	97.2	97.2	99.6
Iodate (acid)	99.8	99.8	100.0
Iodine (acid)	100.0	100.0	100.0
Iodine (no acid)	100.4	104.2	100.4
Iodine (bicarbonate)	102.9	...	...

The pronounced lag in the appearance of aldehyde in cottonseed oil (Figure 5) as compared with the butter fat in Figures 6 and 7 is of interest in view of the ability of the former to absorb much larger quantities of oxygen at ordinary temperatures without developing perceptible rancidity. The similarity in shape of the peroxide-oxygen, fat aldehyde value, aldehyde content, Kreis test, and bleaching curves shown in Figure 7 is also rather striking. Further work utilizing the aldehyde estimation method is in progress.

Discussion

Dilute thiosulfate solutions are often standardized against 0.01 *N* bichromate prepared by weighing out the exact amount of the dry analytical reagent salt. This method possesses the advantage that the bichromate solution is quite stable, and when precautions are taken in running a blank on the reagents and titrating in the absence of daylight perfectly consistent results can be obtained. It has been found, however, that the values given by the bichromate method are distinctly in error. Further, as can be seen from Table III, the common practice of adding a trace of sodium carbonate (0.1 gram in 5 liters) to thiosulfate solutions for the purpose of preventing precipitation of sulfur can lead to serious inaccuracy with dilute solutions unless the titration against iodine is carried out in presence of acid. It is probably preferable, therefore, whether carbonate has been added or not, to standardize dilute thiosulfate solutions against iodine in the presence of a little acid, the results obtained in this manner agreeing closely with those of the iodate method.

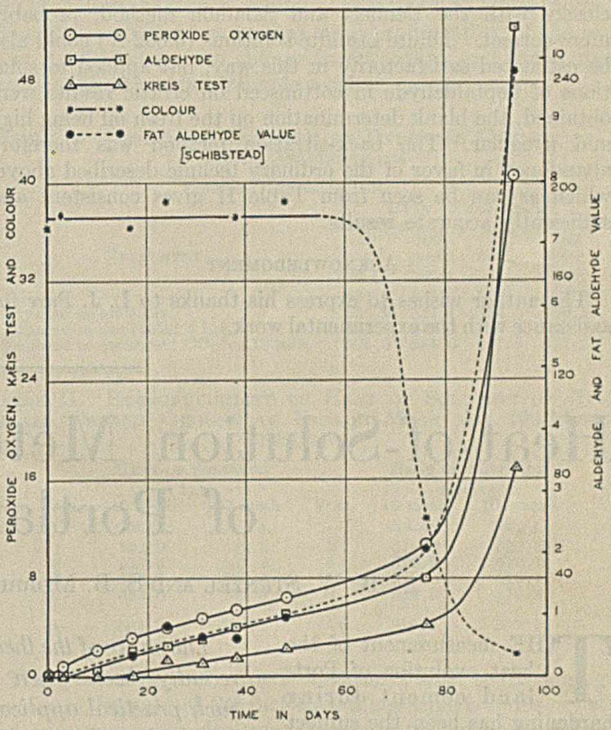

Figure 7. Oxidation of Butter Fat in Lamp Light

Bisulfite Titration. In the determination of small quantities of aldehydes by the Clausen method the combined bisulfite is liberated by addition of sodium bicarbonate and titrated with iodine in the presence of the excess of bicarbonate. If, however, a blank determination is carried out without the aldehyde, and, after addition of the bicarbonate, a known amount of sodium bisulfite is run in and titrated with iodine, an incorrect result is obtained. For example, 25 cc. of a bisulfite solution actually equivalent to 25.7 cc. of 0.002 *N* iodine (standardized by running the bisulfite from the buret into the acidified iodine solution) neutralized only 12.3 cc. of iodine under the conditions of the determination, though by omission of the bicarbonate the figure could be raised to 25.1 cc. By running in the bisulfite approximately 1 cc. at a time and immediately neutralizing with iodine a titration of 25.1 cc. was, however, again obtained even in presence of the bicarbonate. This latter observation probably accounts for the fact that no large error arises in the actual estimation of aldehyde, most of the bisulfite being oxidized as soon as it is liberated.

Two modifications of the standard method were investigated. In the first the bicarbonate was added slowly as a 10 per cent solution. The first 8 or 10 cc. being used in neutralizing the acid present produced practically no liberation of bisulfite, which was however almost completely liberated by the next 1 or 2 cc., the remainder of the bicarbonate being added only at the end of the titration to insure complete reaction. The results obtained were identical with those of determinations in which the solid bicarbonate had been used.

In the second modification, after neutralization of the excess bisulfite a quantity of standard iodine equal to approximately twice that which would be required to oxidize the combined bisulfite was added, followed by the bicarbonate in the usual way, the excess iodine being titrated with thiosulfate solution. A blank determination without the aldehyde sufficed to standardize the thiosulfate. Several determinations carried out by this method on a sample of heptaldehyde (0.15 gram) gave consistent results rather higher than those obtained by the usual technic, and, since they agreed closely with the Bennett and Salamon method, probably more correct. Dilute bisulfite solutions (0.002 *N*) could also be estimated satisfactorily in this way, but applied to solutions of heptaldehyde in cottonseed oil erratic results were obtained, the blank determination on the fresh oil being high and irregular. The back-titration method was therefore abandoned in favor of the ordinary technic described above, which as can be seen from Table II gives consistent and sufficiently accurate results.

ACKNOWLEDGMENT

The author wishes to express his thanks to L. J. Parr for assistance with the experimental work.

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Heat-of-Solution Method in the Calorimetry of Portland Cement

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The study of the thermochemistry of cement has recently been given considerable impetus by such practical application as the specification of heat evolution limits during hardening for cement used in construction of the Boulder Dam. Fundamental to such studies is an accurate calorimetric method and this article indicates the precautions necessary to attain a reasonable accuracy. The method given is especially designed for measuring the heat of hydration of cement at various ages.

Zinc oxide is suggested as a suitable secondary standard for heat capacity determinations.

THE measurement of the heat evolution of Portland cement during hardening has been the subject of numerous investigations during the past two years (*2*, *6*), and has reached the stage of practical application in mass concrete construction. Thus the cement used in the construction of the Pine Canyon Dam[1] (City of Pasadena, Calif.) and of the Boulder Dam has been subject to restrictions of heat development at 7 and 28 days (*3*,*4*).

The heat-of-solution method as proposed by Woods, Steinour, and Starke is probably the most accurate of those used thus far, and although it may be replaced by less expensive methods for routine work, it will undoubtedly continue in use for research and referee tests. For this reason it was thought desirable to make available the results obtained by the authors during the investigations of the heat evolution characteristics of cement furnished for construction of the Pine Canyon Dam, and to point out the sources of error in the method and means of avoiding them. The principle of the method is scientifically sound and requires simply the measurement of the heat of solution of the dry cement and of the hydrated cement in a suitable acid charge, the difference between the two values obtained being the heat of hydration.

The apparatus is shown diagrammatically in Figure 1, being modeled after that of Woods et al. (*6*), and follows the principles of calorimeter design given by White (*5*). It consists essentially of a gold-lined reaction vessel into which the cement to be tested is introduced. The temperature rise is measured by a copper resistance thermometer, and the heat capacity is determined by means of a manganin wire heater coil and a potentiometer. A platinum stirrer is used to maintain a uniform distribution of temperature. The calorimeter is immersed in a water bath which is closely regulated at 30° C. The cement sample is contained in a stoppered glass tube which has a rod and ground-glass valve to permit the introduction of the sample into the acid. The acid charge consists of 1200 grams of nitric acid (normality 2.000 ± 0.002) and 22.5 grams of 48 per cent hydrofluoric acid. Six grams of dry cement and a weight of the hydrated cement which gives approximately the same temperature rise constitute the cement charge.

PROCEDURE

The procedure may suitably be divided into four distinct operations: preparation of the sample for hydration; weighing of the calorimeter sample; operation of the calorimeter; and calculation of results. The principal features of these operations will be discussed here; the detailed procedures must be adapted to the particular apparatus used.

PREPARATION OF THE SAMPLE FOR HYDRATION. The dry cement is mixed with pure water to give a water-cement ratio of 0.40 and is stored for one day at 70° F. (21.1° C.), then at 100° F. (37.8° C.) until the time of test, which is at 7 days' and at 28 days' total elapsed time. This time-temperature curve is of course entirely arbitrary, but lends itself well for laboratory testing and does not differ greatly from that actually found to exist in mass concrete construction. It is

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[1] This structure has recently been renamed the "Morris Dam."

obvious that any curve whatever would be just as arbitrary since the temperatures in the structure itself are not uniform. The effect of different curing temperatures upon the heat of hydration is shown in Figure 6 and will be discussed below.

The water-cement ratio of 0.40 corresponds to that used in mortar compression test specimens but differs from that actually used in the concrete of the dam, which is nearer 0.6. However, the heat development with different ratios may be determined by suitable auxiliary tests, such as are shown in Figure 5.

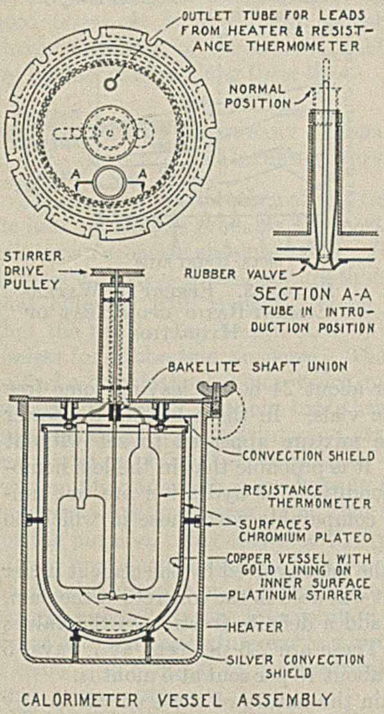

FIGURE 1. DIAGRAM OF APPARATUS

The principal precaution to be observed in preparing the sample is that each container (4-dram homeopathic vials were used) shall contain a truly representative portion of the water-cement mixture. Since there is some tendency for the cement to settle, it is not advisable to pour the mixture from a cup unless thorough stirring is continued during the process. A convenient arrangement is that shown in Figure 2. The manually operated screen stirrer does not beat air into the mixture, as is usually the case with the ordinary propeller type. The stirring is continued while the cork is withdrawn and the vials filled. The reproducibility of different vials from the same pour as shown in Table II indicates that the desired result has been accomplished. It is essential that the hydrated cement be sealed in its containers during storage, so that no water will escape or air be introduced.

WEIGHING PROCEDURE. The dry cement is safely handled in the air when exposure is not longer than that required to weigh the sample by the usual methods.

Two sources of error in preparing the hydrated sample for the calorimeter must be carefully guarded against if reproducible results are to be obtained. The sample will of course have "set" in its container during the hydration period, so that it must be ground before weighing. During the grinding and weighing processes it is exposed to the laboratory atmosphere, and it has been found that undue exposure of this kind causes it to absorb carbon dioxide from the air, resulting in a lowered heat of solution. The magnitude of the effect is shown in Table I and indicates that the exposure must be kept to a minimum, especially when the sample is still quite moist—i. e., at the earlier ages. The most effective means of accomplishing this purpose is to grind the sample as rapidly and as coarsely as the procedure will permit (a 10-mesh sieve size has been found satisfactory). The advantage of using a 10-mesh sieve size instead of the 100-mesh which has usually been specified can be readily seen in that the grinding time is reduced to one-third and the surface area probably to $^1/_{100}$ of the values for the finer grinding. This is clearly indicated in Table II, which shows the results obtained on four different vials from the same pour, each sample being ground first through the 10-mesh and then through the 100-mesh sieve. As has been stated, the effect of exposure is greater at the earlier ages, which is reflected in the 7-day group. The average difference of 1 calorie between the two sets at 7 days has been found consistently in other tests. Thus the magnitude as well as the reproducibility of the results is affected by the change in procedure, and shows the care required to obtain reliable results.

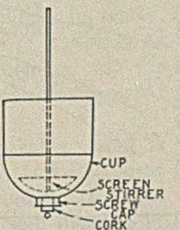

FIGURE 2. MIXING APPARATUS

TABLE I. EFFECT OF EXPOSURE OF HYDRATED CEMENT TO VARIOUS ATMOSPHERES

(Sample: Riverside 19R4)

TREATMENT	HEAT OF SOLUTION 7 DAYS 10 mesh	 100 mesh	 28 DAYS 10 mesh	 100 mesh
	Cal./g.	*Cal./g.*	*Cal./g.*	*Cal./g.*
Normal	535.6	534.7	526.4	525.4
Exposed to air 4 hrs.	525.9	521.7	518.1	510.3
Exposed in desiccator 4 hrs.	535.2	534.2	527.3	525.9
Exposed to saturated CO_2 for 10 min.	502.3	484.0	497.9	477.3

TABLE II. REPRODUCIBILITY OF HEAT OF SOLUTION OF HYDRATED CEMENT GROUND TO PASS 10-MESH AND 100-MESH SIEVES

VIAL	HEAT OF SOLUTION 7 DAYS 10 mesh	 100 mesh	VIAL	HEAT OF SOLUTION 28 DAYS 10 mesh	 100 mesh
	Cal./g.	*Cal./g.*		*Cal./g.*	*Cal./g.*
1	532.9	532.3	2	519.0	520.2
3	533.3	531.2	4	520.9	520.1
5	533.7	533.3	6	519.6	520.1
7	533.5	531.5	8	519.8	519.9
Av.	533.3	532.1	Av.	519.8	520.1

The other source of error is associated with the weighing procedure, because of the fact that the sample is quite moist and loses water rapidly upon exposure to the atmosphere. The usual procedure of differential weighing of the calorimeter sample and the ignition sample successively from the same weighing bottle is subject to considerable error when the sample is moist. This error may be made negligible by use of a suitable technic—e. g., the sum of the calorimeter sample and that for ignition may be roughly weighed into a bottle, then thoroughly rolled in the bottle, and the ignition sample quickly removed in one operation.

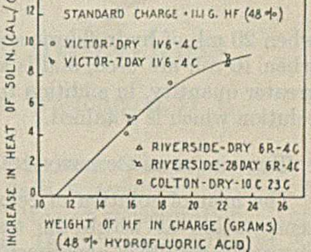

FIGURE 3. EFFECT OF HYDROFLUROIC ACID CONCENTRATION ON HEAT OF SOLUTION

If these precautions are observed, the error in the heat of solution of the hydrated sample will be no greater than that in the dry sample.

CALORIMETER PROCEDURE. The quality of the results of the calorimeter tests depends primarily upon the accuracy of the temperature measurements and heat capacity determinations. The resistance thermometer is carefully calibrated against a Bureau of Standards Beckmann thermometer and suitable calibration charts are made. The heat capacity is determined by introducing a measured quantity of electrical energy and noting the resultant temperature rise. The operating technic will of course be peculiar to each apparatus and need not be given here.

CALCULATION OF RESULTS. A discussion of the calculation of the heat of hydration of the cement from the calorimetric data has been given in the literature (*1*). The required precision makes it necessary to take into account fully all the sources of error which are encountered and to make adequate corrections therefor.

Effect of Hydrofluoric Acid Concentration

The heat of solution of cement is rather sensitive to the concentration of hydrofluoric acid in the charge, so that suitable corrections must be made if the concentration differs materially from the standard. Figure 3 shows the variation of the heat of solution with the amount of hydrofluoric acid used and may be used as a basis for these corrections. The specifications originally prescribed a hydrofluoric acid concentration of 10 ml. of 48 per cent acid per charge, but were later modified to double this quantity because some of the cements showed incomplete solution with the smaller amount of the acid present.

Differential Heat-of-Solution Effect

A correction to the heat of solution must be made when a weight of cement is used in the charge which differs from the standard weight which has been decided upon (6 grams in this case). This arises from the fact that successive increments of cement added to the acid do not give the same heat of solution per gram, and is called the differential heat-of-solution effect. Its magnitude is determined empirically from data such as those plotted in Figure 4. It is evident that this effect is only one-third as great when 20 ml. of hydrofluoric acid are used in the charge than when 10 ml. are used, and is an advantage of the use of the greater quantity, in addition to the more rapid and complete solution which is obtained.

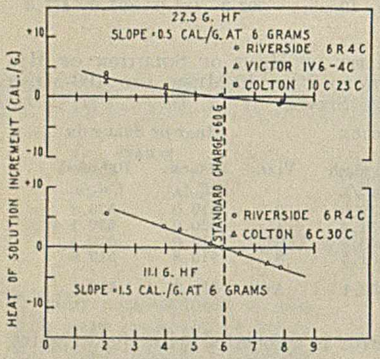

Figure 4. Differential Heat-of-Solution Effect

Heat of solution at 6.0 grams taken as reference point.

Temperature Coefficient of Heat of Solution

The heat of solution of cement also varies with the temperature at which the tests are made. Table III shows the results of experiments made to determine the temperature coefficient of the reaction, which turns out to be about − 0.3 calorie per gram per ° C. in the range from 15° to 30° C. This coefficient will of course apply only to the low-heat cement for which it was determined, but probably does not vary greatly with the chemical compositions ordinarily encountered.

Table III. Temperature Coefficient of Heat of Solution of Cement

Sample	Heat of Solution 17.1° C. Cal./g.	Heat of Solution 29.9° C. Cal./g.	Difference
Victor 1V6-4c	590.0	585.7	4.3
Riverside 6R4	590.4	586.2	4.2

Temperature coefficient = −0.33 cal. per ° C.

Effect of Change in Water-Cement Ratio

Since the water-cement ratio actually used in the concrete of the dam differs from that used in the test specimens, it is important to know what effect upon the heat development is brought about by a change in this ratio. The results of tests on two different cements are shown by the curves in Figure 5. The water-cement ratio was varied from 0.40 (used in the tests) to 1.0. The ratio used in the concrete of the dam was about 0.6 and is indicated by the broken line. Instead of the smooth curves which might be expected, consistently angular graphs are obtained.

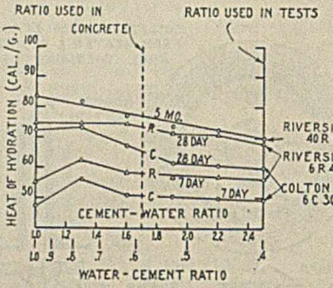

Figure 5. Effect of Water-Cement Ratio upon Heat of Hydration

The irregularities may be due to the fact that it was difficult to maintain the cement in uniform suspension during the curing period. The vials in which the cement was placed were rotated horizontally for 2 days to prevent segregation, but in the case of the higher water contents a portion of the mix acquired a set after about 24 hours, leaving some free water at one end of the vials. In those having the lower water-cement ratios the mixture appeared to set without noticeable segregation. It is probable that in the less homogeneous mixtures the conditions of hydration are not uniform and therefore not comparable with those in which no segregation takes place.

In order to calculate the heat evolved by the cement under the conditions in which it was used in the concrete of the dam, it appears necessary to add a definite fraction to the values obtained in the tests. These are 2.5 per cent at 7 days, 5 per cent at 28 days, and about 10 per cent at 5 months.

It is difficult to explain the nature of these curves in any simple manner; there are evidently a number of complicating factors, such as the hydrolysis of the cement compounds, etc., whose effects cannot be separated by means of the data obtained.

Effect of Change in Curing Temperature

Since the particular time-temperature curve used in curing the test specimens will be different from that to which the concrete in the dam is subjected, it is of interest to know what the general effect is of a change in curing temperature conditions. Figure 6 shows the results obtained with a Riverside low-heat sample for curing temperatures of 70°, 100°, and 212° F. (21.1°, 37.8°, and 100° C.) continuously, as well as the standard of 70° F. for 1 day and 100° F. thereafter. It is significant that while the rates of heat development differ markedly for the different temperatures, yet the ultimate value seems to be nearly the same. This would indicate that the temperature coefficient of the reaction is rather small. It should also be noted that the ultimate value is reached

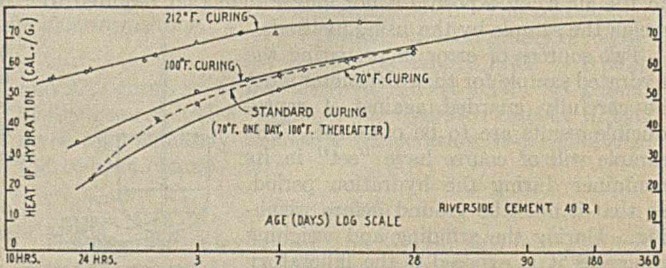

Figure 6. Effect of Curing Temperature upon Heat of Hydration

in less than 14 days by the sample cured at 212° F., whereas those cured at 70° and 100° F. require 6 months or more to reach a maximum. It is clear that when it is desirable to know the ultimate heat developed by the cement, a curing temperature of 212° F. would be advantageous in greatly accelerating the reaction. The results here shown are of course to be considered as preliminary and merely indicative of the possibility of using elevated temperatures for accelerated tests. It is likely that valuable information on the thermochemistry of the cement reactions may be obtained by further studies along these lines.

Zinc Oxide as a Secondary Standard in Heat Capacity Determinations

The electrical calibration of the calorimeter to determine its heat capacity is probably the most reliable method of obtaining an accurate absolute value. However, it is somewhat tedious and gives a temperature-time curve which is unlike that obtained with cement. There is also the possibility that the heater may be attacked by the acid and rendered useless for calibration purposes. Therefore it was desirable to find a chemical substance which might be used as a secondary standard. Calcium oxide has been proposed, but its high reactivity with moisture and carbon dioxide introduces manipulation difficulties, in addition to the precipitation of calcium fluoride which it produces in the acid charge. After some investigation it was found that zinc oxide was suitable for the purpose, being only slightly hygroscopic and giving a highly reproducible heat of solution. The best results are obtained if the zinc oxide is first ignited at about 950° C. for several hours. It goes into solution very rapidly and produces a time-temperature curve which approximates that of a cement, in contrast to the electrical heating which gives a slow temperature rise.

Table IV shows a series of results obtained with the substance and indicates its suitability as a standard of this kind. In one set of comparative tests it was found that both Merck c. p. and Baker c. p. samples gave the same value.

Table IV. Reproducibility of Calorimeter Tests

Heat Capacity of Calorimeter		Heat of Solution				
		Dry cement 6C30		Zinc oxide (c. p., ignited)		
Date	*Cal./° C.*	*Date*	*Cal./g.*	*Date*	*Cal./g.*	
Apr. 17	1165.3	Dec. 20	572.8	May 10	256.65	Lot 1
May 3	1163.5	Dec. 30	572.5	May 10	256.69	
May 19	1162.6	Dec. 31	573.0	May 10	256.70	
June 26	1163.3	Feb. 1	573.8	June 27	256.56	Lot 2
July 26	1164.8	Feb. 7	572.6	July 26	256.75	
Sept. 20	1164.1	Feb. 17	573.1	Sept. 20	256.55	
Dec. 14	1162.5			Dec. 5	256.10	Lot 3
		Av.	573.0	Dec. 5	256.00	
				Dec. 14	256.34	
Av.	1163.7			Av.	256.48[a]	

[a] Using heat capacity 1163.7, average heat of solution is 256.1.

Reproducibility of Results

It was found that by exercise of the precautions given above, the errors could be reduced to those which may be called purely calorimetric—i. e., involving errors due to the calorimeter alone. Tables II and IV show the kind of reproducibility of which the calorimeter is capable and indicate that the probable error in the heat of solution tests is less than one calorie. Such accuracy is quite satisfactory when the number of operations involved is considered, but its price is great care and skill in conducting the operations.

Acknowledgment

The authors are indebted to R. G. Folsom, R. A. Brown, and J. L. Dickinson for their suggestions and skillful work which have made possible whatever advance in cement calorimetry has been made during these investigations.

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Dilution Method for Micro-Kjeldahl Determinations

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THE use of sulfuric acid as a dilution medium in micro-Kjeldahl determinations, where no microbalance is available, is convenient for materials insoluble in water, such as wool and silk, and reduces the time of digestion as compared with that required for water solutions. So far as the writer is aware, this has not been previously suggested in the literature.

Rapid solution occurs, without charring, when wool is heated with concentrated sulfuric acid in a thick-bottomed container, over a hot plate, with frequent shaking to avoid local overheating. A 0.2-gram wool sample will dissolve in 10 cc. of sulfuric acid in 3 to 5 minutes, giving a clear amber solution. Since special volumetric flasks with thick bottoms would be needed to apply a volumetric method, the solution was carried out in this laboratory in 30 cc. dropping bottles. Portions containing 25 drops were then transferred to micro-Kjeldahl digestion flasks, the weights determined by difference, and the catalyst added.

The amount of catalyst may also be regulated by dissolving it in sulfuric acid and using a definite number of drops. Selenium, which was found to give much quicker results with wool than Pregl's $CuSO_4$–K_2SO_4 catalyst, was prepared in 1 per cent solution by strongly heating reduced selenium in concentrated sulfuric acid, until it dissolved to a pale yellow solution. A round-bottomed flask is required. A 1 to 1 ratio of selenium to wool is the optimum concentration. The digestion liquor is clear within 15 minutes, but 25 to 30 minutes should be allowed for complete nitrogen recovery. Hydrogen peroxide is seldom required.

It was also found advantageous to use a volume rule instead of Pregl's[1] time rule for the steam distillation in Parnas and Wagner's micro-Kjeldahl apparatus. Distillation is continued until 10 cc. of distillate have condensed in the receiver. Graduated centrifuge tubes of 50 cc. capacity are satisfactory for collection and subsequent titration and boiling.

Aliquots of the same wool solution checked within 1 part in 160. Typical results were 16.23, 16.11, and 16.18 per cent of nitrogen in a wool blanket composed of two parts of three-eighths blood and one part of one-quarter blood wool, and 16.00, 16.01, and 15.93 per cent of nitrogen in a wool blanket containing one part of one-quarter blood wool and two parts of reworked wool.

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[1] Pregl, F., "Quantitative Organic Microanalysis," 2nd English ed., tr. by E. Fyleman, P. Blakiston's Son & Co., Philadelphia, Pa., 1930.

Modified Hydrogen Evolution Method for Metallic Magnesium, Aluminum, and Zinc

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CHEMICALLY this method is the same as the Meyer hydrogen evolution method (*2*), depending on the measurement of hydrogen gas evolved by metals acting on dilute sulfuric acid. The apparatus and technic used, however, offer a quicker, more convenient, and more accurate way of determining metallic magnesium, aluminum, and zinc than is obtained by the Meyer method.

The glass immersion filter (*3*), which is the essential feature of this method, affords a means of controlling the speed of reaction by allowing acid to be drawn into or driven out of the reaction tube at will by the simple expedient of lowering or raising the leveling bulb. In the same way any accumulation of salts formed by the reaction can be flushed out at regular intervals without danger of losing gas, keeping the surface of the metal constantly exposed to fresh acid. When the evolution of gas is completed, it can easily be drawn into the eudiometer without any difficulty from trapped gas bubbles, which one frequently encounters in the regular method.

The immersion filter used was made of Jena glass, with a fused-in sintered filter disk 3 mm. thick. These tubes are made in three degrees of porosity—coarse, medium, and fine. The tube used was of medium porosity, and was of 30 cc. capacity. The other parts of the assembled apparatus are illustrated in Figure 1.

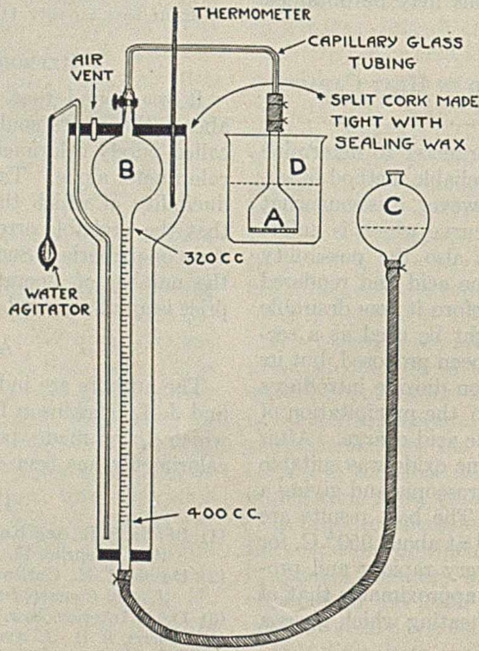

Figure 1. Diagram of Apparatus

The eudiometer tube was especially designed for this method. As illustrated it has a capillary tube on top for entrance of gas, and is graduated in 0.1 cc. between the 320-cc. and 400-cc. mark.

Procedure

The apparatus is assembled preferably in a room with fairly even temperature and no drafts.

All rubber connections are made secure with wire, and eudiometer tube *B* is filled completely with distilled water, saturated with hydrogen. The metal, equivalent to about 360 cc. of hydrogen gas at standard conditions of temperature and pressure, is weighed into the dry immersion filter, *A*. (The eudiometer was calibrated from 320 to 400 cc.) A piece of thick-walled rubber tubing, of 0.188 inch (0.47 cm.) inner diameter and 4 inches (10 cm.) in length, is next connected with the filter. Distilled water saturated with hydrogen is poured rapidly into the filter until it flows over the top of the tubing, at which time a pinchcock is clamped on the rubber tubing, stopping the flow of water through the porous filter and preventing air from entering the tube from the top.

While filling, the slow downward flow of water through the porous disk keeps the finer mesh metals in the bottom of the tube. By using hydrogen-saturated water, preferably at 15° to 20° C., in filling the tube little difficulty is experienced even with very fine magnesium powder of a high degree of purity. A spring-type pinchcock, which can be operated with one hand, is the best to use, leaving the other hand free for pouring. After clamping the pinchcock and making sure the rubber tubing is completely filled with water, the reaction bulb is connected to the eudiometer as shown. About 1 inch (2.5 cm.) of distilled water is poured into beaker *D* around the reaction tube, and the pinchcock is removed.

The reaction can now be started A little concentrated sulfuric acid is poured into beaker *D*, the stopcock on the eudiometer opened, and leveling bulb *C* slightly lowered, so as to draw a little acid into the immersion filter. At first, caution should be used so that the flow of gas is slow, until a gap is formed between the levels of liquid in *B* and *A*. Action is then increased by lowering *C* as required. About two or three times during a determination leveling bulb *C* is raised, and the liquid in *A* partially expelled. On lowering *C* again, fresh acid is drawn in and the reaction continues with renewed vigor. On completion of reaction, leveling bulb *C* is slowly lowered and all remaining gas in *A* and in the tubing is drawn into the eudiometer and after standing 5 minutes is measured in the usual way.

Barometer and temperature readings are closely checked and calculation made according to the formula

$$\frac{PV}{T} = \frac{(P' - v)V'}{T'} \times \frac{1 - (0.00018 \times t)}{1}$$

$\frac{V}{X} \times 100$ = per cent free metal in sample

X = volume of hydrogen, under standard conditions of temperature and pressure, generated by same weight of metal of 100 per cent purity

This method has been used successfully with magnesium samples of various degrees of purity and fineness, and has been found applicable for all grades up to and including 150-mesh material.

Table I. Results of Laboratory Tests

Metal	Modified Gas Evolution Method	Copper Oxide Method(*1*)	Aluminum Chloride Method(*1*)
Magnesium ribbon	99.89	...	...
	99.88	99.87	...
Magnesium 35–80 mesh	98.11	98.30	...
	98.11	98.28	...
	98.16	98.41	...
	...	98.15	...
Magnesium 100-mesh	97.51	97.47	...
	97.68	97.64	...
	...	97.35	...
Magnesium 100-mesh. Sample 120	99.09	98.99	...
	99.20	99.21	...
	...	99.09	...
Magnesium 150-mesh. Sample A	92.40	...	...
	92.41	...	...
	92.33	...	...
Magnesium powder. Sample D. 100-mesh	97.42	97.81	...
	97.67	97.71	...
	97.88	97.50	...
Magnesium powder 5	95.13	95.18	...
	94.85	...	...
Aluminum wire	99.70	...	99.81
	99.73	...	...

Zinc and aluminum (but not aluminum powder) can also be determined in this way. In the case of aluminum, a sodium hydroxide solution is used as a reagent.

Some results obtained at this laboratory by different analysts over a period of about 4 years are given in Table I.

The time required for an analysis of magnesium varied from 2 to 4 hours, depending on the temperature of the room. No heat was applied to speed up the reaction, but could doubtless be used to advantage when the room temperature is very low or when less reactive metals than magnesium are being analyzed.

Acknowledgment

The author wishes to thank J. A. O'Callaghan, T. C. Jenkin, and F. Thames of this laboratory for analytical work done in connection with this method.

Literature Cited

(1) Aluminum Co. of America, Methods.
(2) Scott, "Standard Method of Chemical Analysis," pp. 487-8, D. Van Nostrand Co., N. Y., 1920.
(3) Thomas Co., Arthur H., "Laboratory Apparatus and Reagents," p. 367.

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Furoic Acid as an Acidimetric Standard

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The suitability of furoic acid as a primary standard was suggested by experience gained in purifying the acid for use of its derivatives as bactericides. In these experiments it was necessary to prepare by sublimation from the technical grade an acid of the highest purity. The acid was then titrated with an alkali previously standardized by the Bureau of Standards—Standard Samples No. 39d, benzoic acid, and No. 84, acid potassium phthalate. It was observed that the purified furoic acid could be titrated with the standardized alkali to a high degree of accuracy and that this titration afforded the most rapid and accurate method of determining the purity of the sample of furoic acid, which finally led to the determination of its applicability as a standard.

The method used in studying the applicability of furoic acid was indirect, standardizing the standard alkali by Bureau of Standards samples.

Upon analysis the furoic acid showed the following results:

Melting point	128-9° C.
Moisture	0.25%
Nonvolatile matter	0.02%
Acidity (as furoic acid with phenolphthalein)	99.72%

This sample was purified by crystallization from water. After drying, the melting point was found to be 129.6° C. After subliming the melting point became 131° C.; resubliming gave no change in the melting point, which remained constant at 131° C.

A sample of this purified furoic acid exposed to the regular laboratory conditions for 3 months showed a gain of 0.04 per cent moisture, indicating that it was slightly hygroscopic, but this slight trace of water was readily removed by careful fusion.

The sodium hydroxide solution used was prepared free from carbonates. It was carefully protected from the carbon dioxide of the air by guard tubes and all titrations were performed on the same day in order to avoid possible errors in the titrations due to contamination by carbonates. The apparatus in which the titrations were performed was that of Jackson.[1]

Standardization of Sodium Hydroxide by Benzoic Acid

The first step was to standardize the sodium hydroxide solution by the use of benzoic acid which was fused and cooled before using. The titration was performed according to the directions in Certificate No. 39d for benzoic acid, U. S. Bureau of Standards, using the Jackson titrating apparatus. Various weighings of benzoic acid were taken, 3 drops of a 1 per cent solution of phenolphthalein were added, and the solution was titrated with the approximately 0.1 *N* alkali. The results obtained are shown in Table I.

Table I. Benzoic Acid

(99.98 per cent pure Bureau of Standards Sample No. 39d)

No.	Weight of Sample	NaOH Used	Relative Normality	Corrected Normality
	Gram	*Cc.*		
1	0.3241	25.49	0.10417	0.10415
2	0.3419	26.90	0.10414	0.10411
3	0.2551	20.07	0.10414	0.10411
4	0.3133	24.64	0.10418	0.10415
5	0.2981	23.44	0.10420	0.10417
6	0.3091	24.32	0.10413	0.10410
7	0.2446	19.24	0.10416	0.10413
		Mean of seven determinations		0.10413

Standardization by Potassium Phthalate

The second step was to repeat the standardization by the use of potassium acid phthalate. These titrations were performed as described in Certificate No. 84, U. S. Bureau of Standards, and the results obtained are recorded in Table II.

Table II. Potassium Acid Phthalate

(99.97 per cent pure Bureau of Standards Sample No. 84)

No.	Weight of Sample	NaOH Used	Relative Normality	Corrected Normality
	Gram	*Cc.*		
1	0.2122	9.98	0.10415	0.10411
2	0.2319	10.90	0.10421	0.10417
3	0.3115	14.64	0.10422	0.10418
4	0.2535	11.92	0.10417	0.10413
5	0.2242	10.54	0.10419	0.10415
6	0.3575	16.80	0.10423	0.10419
		Mean of six determinations		0.10415

Standardization of Furoic Acid

Before using, the purified furoic acid was fused in a covered platinum dish over an air bath. The temperature during the fusion did not exceed 142° C. Upon completion of the fusion the acid was cooled in a desiccator. Various weighings were transferred into the titrating apparatus, 25 to 50 cc. of previously boiled distilled water were added, and the apparatus was swept free from carbon dioxide. The sample was allowed to stand until the acid had dissolved and then titrated. The results are shown in Table III.

Table III. Furoic Acid

No.	Weight of Sample	NaOH Used	Normality
	Gram	*Cc.*	
1	0.2927	25.08	0.10417
2	0.2033	17.43	0.10411
3	0.4754	40.73	0.10418
4	0.3000	25.72	0.10411
5	0.3321	28.45	0.10419
6	0.2862	24.52	0.10418
		Mean of six determinations	0.10415

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[1] Jackson, J., *J. Soc. Chem. Ind.*, **53**, 36 (1934).

CONCLUSION

The normalities obtained by the use of benzoic acid and potassium acid phthalate, respectively, show that on the basis of these titrations furoic acid has a purity of 100 per cent and a neutralizing power almost equivalent to benzoic acid. There is no justification for carrying the normality beyond the fourth decimal place without such precautions as correction of weights to *vacuo* and the use of weight burets; however, these figures were carried out to the fifth decimal place to show the relative purity of furoic acid and the close agreement of the results obtained. They indicate that furoic acid can be employed as a standard because of the following advantages: ease of obtaining the acid in a fairly high state of purity, coupled with ease of purification; solubility in water, which is the chief advantage over benzoic acid, as benzoic acid requires the use of alcohol to effect solution; its fairly high molecular weight, permitting large samples; and finally its stability and lack of appreciable hygroscopicity.

RECEIVED March 13, 1934.

Mixed Perchloric and Sulfuric Acids

II. Potassium Ferro- and Ferricyanides as Reference Standards in the Evaluation of Titanous Solutions

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POTASSIUM ferricyanide as a reference standard (*1*, *2*) is the only practical example of a salt of ferric iron suitable for the evaluation of reducing solutions. Its reaction with potassium iodide in acid solution, with or without the addition of zinc, for the liberation of iodine followed by reaction with sodium thiosulfate is an important procedure of iodometry. Potassium ferrocyanide trihydrate can be used as a reference standard for the same purpose. In this case (*4*) a weighed quantity of the salt is oxidized with a slight excess of potassium permanganate. Potassium bromide is added to remove the excess permanganate, followed by hydrazine sulfate to remove bromine. The ferricyanide thus formed is used to liberate iodine from potassium iodide.

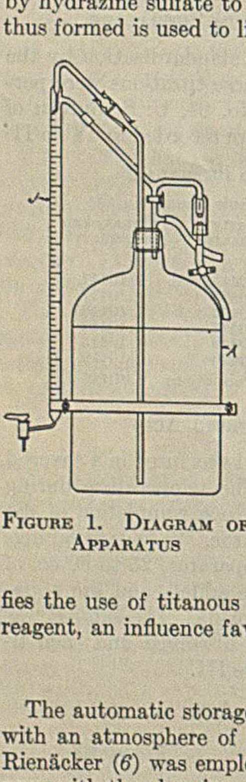

FIGURE 1. DIAGRAM OF APPARATUS

Potassium ferrocyanide has been used in the direct standardization of potassium permanganate (*3*) in sulfuric acid solution, but the reaction for this purpose has no advantage over other methods except the high equivalent weight, and there are several disadvantages.

The ferro- or ferricyanide is decomposed by digestion with mixtures of perchloric and sulfuric acid or by perchloric acid alone. The process serves, therefore, for the determination of ferro- and ferricyanides and has the distinct advantage that insoluble salts can be determined without previous liberation of the iron by digestion with sodium carbonate. Finally, the new process simplifies the use of titanous solutions as a laboratory volumetric reagent, an influence favoring its more general application.

APPARATUS

The automatic storage bottle and buret delivery assembly with an atmosphere of hydrogen as described by Zintl and Rienäcker (*6*) was employed, somewhat modified in accordance with the drawing of Figure 1. The storage bottle, *A*, was of 14 liters capacity and buret *J* a 50-ml. U. S. Bureau of Standards calibrated goose-neck buret modified as shown.

The titration flask is shown in Figure 2. A 300-ml. Erlenmeyer flask, *A*, has the insealed side arm, *B*, of 8-mm. glass tubing terminating on the inside at the bottom of the flask. A 2-inch (5-cm.) extension outside is for connection to a source of carbon dioxide or hydrogen gas. The titration head, *C*, is made from a 100-ml. beaker with a 12-mm. neck sealed in the bottom at *D* for insertion of the buret tip and side arm *E* for washing the inside walls of the reaction flask.

The digestion of samples of potassium ferro- and ferricyanides with either perchloric acid or mixtures of perchloric and sulfuric acids to destroy organic matter required that a cover to the flask be employed to prevent loss by spray. An inverted crucible cover was not satisfactory since drops of cold acid collected on the projection of these lids and, upon dropping into the hot acid of the solution below, caused violent spattering. This difficulty was corrected by a chestnut-shaped cover, *F*, made from short sections of 35-mm. tubing closed flat at one end and with an extension as shown to make contact with the inside top of the 300-ml. Erlenmeyer flasks used for the digestions. Drops of condensed acid from the under side of the cover return to the flask down the side walls and the difficulty of spattering is eliminated.

MATERIALS

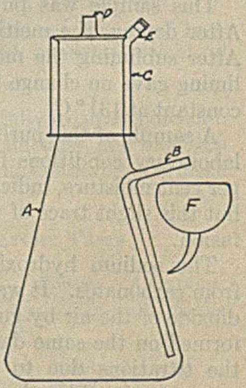

FIGURE 2. TITRATION FLASK AND PROTECTION HEAD

POTASSIUM FERRICYANIDE. As ordinarily purchased from stock, this reagent was found to be sufficiently pure. It was ground to a fine powder and dried at 135° to 140° C.

POTASSIUM FERROCYANIDE. Stock preparations were found to be of a high degree of purity but of indefinite degrees of hydration. The sample from stock was therefore dried over anhydrone at 135° to 140° C. to form the anhydrous salt, or, in some cases, it was found necessary to purify by recrystallization with subsequent drying to the anhydrous form.

TITANOUS CHLORIDE. A stock solution of 20 per cent titanous chloride in hydrochloric acid was diluted to the desired strength after the addition of hydrochloric acid. It was not tested for ferrous iron since with the methods to be employed this impurity has no influence.

PERCHLORIC ACID. The 70 to 72 per cent, C. P. (sp. gr. 1.67) acid free from iron was diluted to 60 per cent (sp. gr. 1.54) for oxidation of ferro- and ferricyanides if used alone. The full strength was used if the oxidations were to be made with the addition of sulfuric acid.

SULFURIC ACID. The regular stock 96 per cent (sp. gr. 1.84) acid was diluted to 75 per cent strength (sp. gr. 1.675).

Perchloric and Sulfuric Acid Mixture. One part by volume of 70 to 72 per cent perchloric acid was mixed with five parts by volume of 75 per cent sulfuric acid.

Ammonium Thiocyanate. A 10 per cent solution of c. p. stock crystals which gave a colorless solution was prepared.

Ferric Alum and Potassium Permanganate. Solutions of approximately 0.1 *N* strength were prepared in the usual manner for stock reagents.

Sodium Oxalate. Bureau of Standards sodium oxalate; dried at 100° C.

Standardization of Solutions

Potassium Permanganate. Weighed samples of sodium oxalate were dissolved in 15 to 20 per cent sulfuric acid and titrated hot by the addition of the potassium permanganate from weighing burets. The results of the standardization were as follows:

	1	2	3	4	5
Sample of $Na_2C_2O_4$, gram	0.1934	0.2306	0.2257	0.1902	0.1966
Weight of $KMnO_4$ solution required, grams	35.318	40.256	40.3525	34.656	35.823
N $Na_2C_2O_4$ per gram of $KMnO_4$, ml.	0.08174	0.08166	0.08183	0.08192	0.08192

Av. 0.08182 ml. of *N* $KMnO_4$ per gram of solution.

Ferric Alum Solution. Weighed portions of the ferric alum solution containing 5 per cent of free sulfuric acid were reduced by a Jones reductor and the ferrous iron titrated using standard potassium permanganate. The solutions were reduced in the cold and titrated with potassium permanganate after the addition of sufficient phosphoric acid to decolorize the iron after oxidation. Weighing burets were used for both solutions. The results follow.

	1	2	3	4
Ferric alum solution, grams	43.013	44.342	44.678	45.1415
$KMnO_4$ solution, grams	74.490	73.533	73.996	74.922
N $Fe_2(SO_4)_3$ per gram of solution, ml.	0.13557	0.13585	0.13568	0.13596

Av. 0.1358 ml. of *N* $Fe_2(SO_4)_3$ per gram of solution.

Titanous Chloride Solution. Weighed portions of standard ferric alum were taken using weighing burets. The samples were treated with 10 ml. of ammonium thiocyanate and titrated with titanous chloride, using the apparatus described and a stream of carbon dioxide. The reagent was added dropwise at the end of the reaction to avoid overtitration as a result of the slow reaction velocity at the end point. Titration was made at room temperature following the directions of Thornton and Chapman (*5*). Hydrogen gas can be used in place of carbon dioxide as shown by the results of cases 1 and 2 following.

	1	2	3	4	5	6
Ferric alum solution, grams	12.0657	9.8760	10.6586	9.6642	9.6783	9.7577
Titanous chloride solution, ml.	59.61	47.85	51.76	46.90	47.05	47.30
Normality of titanous chloride	0.02749	0.02796	0.02796	0.02798	0.02793	0.02801

Av. (results 2 to 5 incl.): titanous chloride = 0.02796 *N*.

A second solution of titanous chloride was similarly prepared and stored under hydrogen. It was found to have the value 0.0550 *N*. It was used to check the efficiency of the hydrogen storage bottle described below.

Oxidation of Potassium Ferro- and Ferricyanides Using Perchloric and Sulfuric Acids

Samples of anhydrous potassium ferro- or ferricyanides of approximately 400 mg. were weighed from a glass-stoppered bottle into clean, dry 300-ml. Erlenmeyer flasks. Perchloric acid (10 ml. of 60 per cent) was added and each flask covered with the cover glasses previously described and heated on the hot plate to just below the boiling temperature for 30 minutes. The reaction mixture first precipitates potassium perchlorate and, as the temperature rises, the yellow solution due to the ferro- or ferricyanide turns dark blue. The decomposition products of this color then turn brown and some spray forms as a result of the oxidation of a small amount of deposited colloidal carbon to carbon dioxide. The digestion need not be done in a draft hood. As the heating is continued, the 60 per cent acid concentrates to 70 to 72 per cent strength and the solution gradually turns light yellow as chlorine is formed from the decomposition of the hot, concentrated perchloric acid. The digested solution, after this 30-minute treatment, is cooled to approximately 100° C. and 20 ml. of water are added. The flask contents are gently boiled for 2 minutes to expel chlorine, cooled, and transferred to the titration vessel and diluted to 100 ml. after the addition of 10 ml. of 10 per cent ammonium thiocyanate. Carbon dioxide is passed in for a few minutes, and the solution titrated with titanous chloride solution in a current of carbon dioxide. The last few drops of the reducing agent are added with a time lapse of one minute between drops.

The required amount of perchloric acid, if thought to involve excessive cost, can be reduced greatly by using an oxidation mixture of sulfuric acid to which is added a small portion of perchloric acid. The boiling point of the mixed acids is higher because of the sulfuric acid present and the oxidation is somewhat more rapid, but the formation of insoluble ferric sulfate requires a little more heating after digestion and dilution to dissolve the ferric sulfate which has been partially dehydrated. The heating does not completely dehydrate the ferric sulfate and it is fairly easily dissolved upon dilution. Sulfuric acid alone for the process was found to be unsatisfactory, the decomposition always being incomplete after 30 minutes' digestion. If the cost is not considered, the perchloric acid alone is to be preferred.

Standardization of Titanous Chloride Using Potassium Ferricyanide

A sample of J. T. Baker's potassium ferricyanide was pulverized and dried 12 hours at 100° C. Weighed samples were digested using 2 ml. of 70–72 per cent perchloric acid plus 8 ml. of 75 per cent sulfuric acid for 30 minutes. The resulting mixture was diluted with a little water and the chlorine expelled by gentle boiling. The samples were diluted to 80–100 ml. and titrated with titanous chloride as previously described. The resultant values are found in Table I.

Table I. $K_3Fe(CN)_6$ as Primary Standard for Evaluation of Titanous Chloride

$K_3Fe(CN)_6$	Volume of Ti^{+++} Solution	Normality of Ti^{+++} Found	Fe^{+++} Present	Fe^{+++} Found	Error Fe
Gram	*Ml.*		*Mg.*	*Mg.*	*Mg.*
0.4926	53.33	0.02806	83.56	83.26	+0.30
0.4842	52.69	0.02792	82.13	82.26	−0.13
0.3967	43.07	0.02798	67.29	67.24	+0.05
0.4463	48.45	0.02798	75.71	75.64	+0.07
0.4633	50.25	0.02801	78.59	78.45	+0.14
0.4087	44.42	0.02795	69.33	69.35	−0.02
		Av. 0.02798			+0.07

Av. value of $TiCl_3$ from previous standardization = 0.02796.

It will be seen from Table I that the standardization of a titanous solution by the new process gives an average accuracy of one part in one thousand using potassium ferricyanide without further purification. The high equivalent weight, 329.19, requires 400 to 500 mg. for each 44 to 54 ml. of 0.028 *N* titanous solution. The process is therefore admirably suited to the standardization of weak solutions which are most frequently employed in titanometry.

Standardization of Titanous Chloride Using Potassium Ferrocyanide

A sample of J. T. Baker's hydrated potassium ferrocyanide was recrystallized from water, pulverized, and dried 12 hours at 135° to 140° C. over anhydrone. Weighed samples of this product were used to standardize the titanium solution as described in the case of the ferricyanide with the results found in Table II.

TABLE II. $K_4Fe(CN)_6$ (ANHYDROUS) AS PRIMARY STANDARD FOR EVALUATION OF TITANOUS SOLUTIONS

(Conditions same as in Table I)

$K_4Fe(CN)_6$	Volume of Ti^{+++} Solution	Normality of Ti^{+++} Found	Fe Present	Fe Found	Error Fe
Gram	*Ml.*		*Mg.*	*Mg.*	*Mg.*
0.4199	40.80	0.02795	63.66	63.70	−0.04
0.4173	40.66	0.02787	63.27	63.48	−0.21
0.3882	37.90	0.02793	58.86	59.17	−0.31
0.4215	41.15	0.02781	63.91	64.25	−0.34
0.4070	39.43	0.02803	61.71	61.56	−0.15
		Av. 0.02792			−0.21

It will be observed that results are obtained which, while not quite as satisfactory as those obtained using potassium ferricyanide, are well within the range of ordinary error—4 parts in 2800 or approximately 0.15 per cent.

INFLUENCE OF TIME UPON REDUCING VALUE OF TITANOUS CHLORIDE

Two solutions of titanous chloride stored under hydrogen in the apparatus described in Figure 1 were tested. The determinations of the first solution were made with potassium ferricyanide by the process described above but without the use of a titration head or stream of carbon dioxide during titration. The results with the second solution were obtained using the titration head and a stream of carbon dioxide. In all cases the standardization was carried out in duplicate or triplicate. The results are found in Table III. The value for the second solution at the beginning of the storage period was obtained, as previously described, using ferric alum standardized by permanganate through sodium oxalate.

TABLE III. INFLUENCE OF TIME OF STORAGE UNDER HYDROGEN UPON REDUCING STRENGTH OF TITANOUS CHLORIDE

Time stored, days	1	2	3	4	5	8	15
Solution 1, normality	0.0551	0.0550	0.0550	0.0550	0.0550	0.0549	
Solution 2, normality	0.02796	....	....	....	....	....	0.02796

No hazardous reactions are described in connection with this paper.

SUMMARY

Potassium ferricyanide has been shown to be an accurate primary standard for ferric iron after oxidation with perchloric acid or perchloric acid and sulfuric acid to liberate its iron either as ferric perchlorate or as the perchlorate plus sulfate. The ferricyanide is stable at 140° C. for dehydration.

Potassium ferrocyanide trihydrate can be dried at 140° C. to form the anhydrous salt and serves as a substitute for potassium ferricyanide.

Potassium ferri- and ferrocyanides have been shown to be capable of standardizing solutions of titanous chloride with an accuracy of one part in one thousand.

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Estimation of Methyl Salicylate, Menthol, and Camphor in Mixtures

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THE literature dealing with the estimation of methyl salicylate, menthol, and camphor in medicinal preparations discloses the difficulties of obtaining accurate results. Menthol and camphor present particular problems owing to their volatility even at room temperature. Methods have been published for the analysis of substances containing one or two of these three ingredients, but none was found which involved the estimation of all three in one sample.

Methyl salicylate is usually determined by the use of alcoholic potassium hydroxide to saponify the ester, the quantity used being determined by titrating the excess alkali (*16*). When other saponifiable substances are present, the salicylic acid formed by saponification is sometimes extracted with ether (*9*).

Menthol, while more difficult to determine, can be satisfactorily estimated by itself by acetylation (*6, 8, 17*).

Camphor in substantial amounts is estimated by polarization in alcohol (*18, 20*) or benzene (*5*) with satisfactory accuracy. In small amounts it cannot be determined with a high degree of accuracy by known methods. Reported methods include precipitation and gravimetric estimation as semicarbazone (*1*), salol camphor (*15*), and the oxime (*2, 14*). Estimation by loss on evaporation from a nonvolatile base is inaccurate if the base is oxidizable (*19*).

Other methods are extraction with carbon tetrachloride and evaporation of the solvent in an atmosphere saturated with camphor (*7*), extraction from aqueous salt solution (*3, 10*) with ether, and extraction from aqueous solution with petroleum ether (*12*). Estimation of camphor by its effect on the surface tension of an aqueous solution has also been proposed (*4, 13*). Results 10 per cent low for camphor are reported in extraction of menthol–methyl salicylate mixtures followed by determination of the methyl salicylate (*11*).

An effort was made to select from these methods those which could be suitably combined in a procedure for analysis of commercial products. The mixtures to which the method was applied were analgesic balms made by well-known manufacturers. These consist of a base of lanolin, petrolatum, or gum solution, in which the methyl salicylate, menthol, and camphor have been incorporated.

PROCEDURE

Weigh about 20 grams of the substance into a flask and steam-distill, using an efficient condenser, till no more oily matter comes over. Usually about 500 cc. of distillate are sufficient.

Rinse the condensing system with 50 cc. of ether and add this to the distillate in a separatory funnel. Extract the distillate with this 50-cc. portion of ether. Repeat with another 50-cc. portion of ether. The aqueous layer still contains some menthol and camphor in solution, because of the solubility of ether in water. Saturate the solution with salt and extract with two more 50-cc. portions of ether. Filter the combined ether extracts through a dry filter paper into a weighed narrow-necked glass-stoppered flask. An iodine flask is suitable. Evaporate the bulk of the ether on a water bath. Remove the remaining ether under a moderate vacuum at room temperature. This minimizes loss of menthol and camphor due to volatilization; 30 minutes to 1 hour in the vacuum desiccator is usually sufficient. As a check on later results weigh the flask and extract. This gives the combined weights of methyl salicylate, menthol, camphor, and any oil that has been distilled over from the base.

Add 25 cc. of approximately *N* potassium hydroxide solution in absolute methyl alcohol to the flask, or to a portion weighed out therefrom if the amount is large. Reflux for 2 hours. To minimize loss during subsequent evaporation it is advisable to keep the volume of alkali solution added low. For this reason *N* instead of 0.5 *N* potassium hydroxide is used and the lower-boiling methyl alcohol is used instead of ethyl alcohol. After refluxing, evaporate the bulk of the methyl alcohol on a water bath, dilute with 50 cc. of water, and titrate with 0.5 *N* hydrochloric acid. Run a blank equal to the amount of alcoholic potassium hydroxide used and titrate. The difference gives the potassium hydroxide used in saponifying the methyl salicylate. Then

$$\text{cc. } 0.5\ N \text{ KOH used} \times 0.07605 \times \frac{100}{\text{wt. of sample}} = \text{per cent of methyl salicylate}$$

After titration transfer the contents of the flask with water to a separatory funnel. Rinse the flask with ether and extract the solution twice with 50 cc. of ether. Then saturate with salt and extract with two more 50-cc. portions of ether as before. Filter through dry filter paper into a dried and weighed narrow-neck, glass-stoppered flask and evaporate off most of the ether on a water bath. As previously, finish evaporation of the ether in a moderate vacuum at room temperature and weigh. This weight gives a check on the amount of menthol and camphor present, with possibly a small amount of oil distilled over from the base. The loss in weight should check with the amount of methyl salicylate determined by saponification.

Add to the flask 10 cc. of acetic anhydride and 1 gram of anhydrous sodium acetate. Reflux gently for 1 hour, cool, and wash into a separatory funnel. Wash two or three times with water, being careful not to shake too vigorously. The addition of salt will assist in preventing formation of emulsions. Then wash with very dilute sodium hydroxide or with 2 *N* sodium carbonate until just alkaline, and finally wash once with distilled water. Drain well and transfer by washing with neutralized absolute methyl alcohol into a dry flask. It is not necessary to perform the tedious drying with calcium chloride usually recommended in the acetylation method for menthol. Saponify the acetylated menthol by heating gently under reflux for 1 hour with 25 cc. of 1 *N* potassium hydroxide in absolute methyl alcohol. Treat a blank of the alcoholic alkali similarly. Cool, dilute with water, and titrate the sample and blank with 0.5 *N* hydrochloric acid. The difference is due to alkali used in saponification of acetylated menthol. Calculate as follows:

$$\text{cc. } 0.5\ N \text{ KOH used} \times 0.0781 \times \frac{100}{\text{wt. of sample}} = \text{per cent of menthol}$$

Subtracting this from the previous weight gives the percentage of camphor plus oil.

To obtain the amount of camphor, extract the contents of the flasks as before with ether. Evaporate the ether in a weighed crystallizing dish on a water bath, and weigh to obtain a value for menthol and camphor. After all the ether is gone, place the dish in an oven at 110° C. Menthol and camphor are volatilized. The residue is oil from the base which was volatile with steam. Calculation, allowing for the menthol determined by saponification, gives the amount of camphor present. An error will be introduced if the sample contains drying oil.

In actual practice it has been found that the amount of oil from the base distilled over was negligible and need only be taken into account for very accurate work. For routine determinations it is therefore not necessary to perform the last extraction and the volatilization of the menthol and camphor.

The method was applied to a synthetic sample with the following results.

	Added %	Found %
Lanoline	76	...
White petrolatum	10	...
Methyl salicylate	10	10.05
Menthol	2	1.87
Camphor	2	2.18

The accuracy of the technic is also confirmed by satisfactory checks when applied to commercial samples, and agreement with the known composition of commercial products.

Discussion

While the above method is necessarily rather long, it is not involved and can be performed in a surprisingly short time. The three ingredients can be determined on the one sample. The base itself can be identified and determined on the residue after steam distillation of the same sample. The objection to using ether as an extracting agent, owing to its solubility in water with consequent solubility of menthol and camphor, is overcome by the use of salt. Ether is the best extraction medium because of its very low boiling point.

By employing the low-boiling methyl alcohol for the saponifications it is possible to evaporate without substantial loss of menthol and camphor. Finally, the troublesome drying of the acetylated menthol is eliminated.

Summary

Available methods for estimation of methyl salicylate, menthol, and camphor do not include mixtures such as occur in analgesic balms. Methyl salicylate may be determined by saponification and checked by the loss in weight of sample resulting. Camphor is then determined by the acetylation method. Camphor and menthol are estimated by volatilization and menthol then obtained by difference. A synthetic sample shows a high degree of accuracy for methyl salicylate and accuracy within 10 per cent for camphor and for menthol.

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Deterioration of Eggs in Storage. The secret of why storage eggs compare unfavorably with fresh eggs has been revealed by scientists of the Department of Agriculture, who have found that an egg deteriorates in storage because it is digesting itself. For years food chemists have suspected that trypsin, one of the enzymes present in the pancreatic juice of the human body, was present in egg white. Recent experiments have shown the existence of this enzyme in egg white.

The search for trypsin in egg white was hindered by the presence of a substance which inhibits further action of the enzyme. Consequently, tests of mixed thick and thin egg white have failed to show the presence of trypsin.

Rapid Method for Determination of Small Amounts of Arsenic

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A method is given for the determination of arsenic by estimating the evolved arsine deposited upon a mercuric-bromide-impregnated diaphragm. It is applicable for estimating minute quantities of arsenic in the presence of impurities such as iron, tin, antimony, or reducible sulfur and phosphorus compounds. Modifying the procedure somewhat makes it possible to determine the arsenic content of many products using an undigested sample.

THE method is essentially a modified Gutzeit procedure, except that the arsine is liberated from the sample in a manner similar to that employed by Smith (*15*) and Taber (*17*) but using smaller quantities. Taber modified Smith's procedure by adopting a larger generator flask to accommodate a larger volume of liquid and fitting to it a condenser so that heat could be applied to the flask to secure proper reduction of the arsenic and a vigorous ebullition of gas. The estimation of arsenic by Taber's distillation method was based upon an iodine titration of the reaction products formed when arsine is passed into mercuric chloride solution.

The method described in this paper differs from that of Taber and the official Gutzeit method in that the evolved arsine is impinged upon an impregnated mercuric bromide diaphragm securely held between two ground-glass joints. The colored disks are then developed in a solution of iodide (*1, 7*) and compared with standards. Earlier workers have employed the principle of stain deposition upon a sensitized paper disk (*2, 3, 4, 11, 12*), but the sensitizing solution used was mercuric chloride. Various devices for securing the diaphragm in place have also been suggested (*6, 8, 9, 13, 14, 16, 18, 19*); some of these were unsatisfactory because they did not enable the operator to obtain a stain with a sharply defined boundary, and others were subject to criticism for reasons related to simplicity of design or ease of manipulation. For minute amounts of arsenic the method is especially applicable, as the entire digest of a sample can be used. With a disk 20 mm. in diameter 0.001 to 0.040 mg. of arsenic trioxide can be directly determined. The analysis can be made in the presence of impurities such as iron, tin, antimony, or reducible sulfur or phosphorus compounds, which tend to affect the evolution rate of arsine or to deposit interfering stains on the mercuric bromide strips used in the regular Gutzeit method.

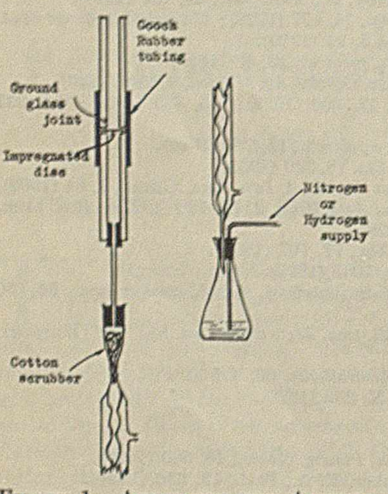


FIGURE 1. APPARATUS FOR ARSENIC DETERMINATION

REAGENTS

HYDROCHLORIC ACID. Make up 50 cc. of 35 per cent arsenic-free hydrochloric acid to 100 cc. with water.

STANNOUS CHLORIDE SOLUTION. Dissolve 40 grams of arsenic-free $SnCl_2 \cdot H_2O$ in concentrated hydrochloric acid and make up to 100 cc. with the same strength acid.

MERCURIC BROMIDE PAPER. Carefully select filter sheets, similar to S & S No. 589 black ribbon paper, for weight and texture, and soak one hour in a saturated alcoholic solution of mercuric bromide. After sensitizing, remove sheets and dry by means of an air blast, and cut in disks of the same diameter as the diaphragm tube. Avoid touching the sensitized disks with the hands as far as possible. Disks should not be used when more than 5 or 6 days old.

ZINC. Cut arsenic-free zinc in pieces about 1 cm. in length (approximately 5 grams). Activate the pieces by covering with hydrochloric acid (1 + 3) containing about 2 cc. of special stannous chloride solution for each 100 cc. of acid. Allow the action to continue for 15 minutes and wash well with distilled water.

POTASSIUM IODIDE SOLUTION. Dissolve 15 grams of potassium iodide in water and dilute to 100 cc.

FERROUS AMMONIUM SULFATE. Use this substance or ferrous sulfate crystals free from arsenic.

CUPROUS CHLORIDE SOLUTION. Dissolve 15 grams of cuprous chloride in 100 cc. of 1 to 1 hydrochloric acid.

CADMIUM IODIDE SOLUTION. Dissolve 20 grams of cadmium iodide in water and dilute to 100 cc.

STANDARD ARSENIC SOLUTION. Dissolve 1 gram of arsenic trioxide in 25 cc. of 20 per cent sodium hydroxide. Saturate the solution with carbon dioxide and dilute to 1 liter with recently boiled water. One cc. of this solution contains 1 mg. of arsenic trioxide. Dilute 40 cc. of this solution to 1 liter, diluting 50 cc. of the resulting solution to 1 liter. One cc. of this latter solution contains 0.002 mg. of arsenic trioxide and is used to prepare standard stains. Prepare fresh dilute solutions at frequent intervals.

APPARATUS AND PROCEDURE

Use an Erlenmeyer flask connected by a two-hole stopper to a Liebig or Allihn condenser. A gas such as nitrogen or hydrogen is introduced through a tube extending below the surface of the contents of the flask. The upper end of the condenser is packed with absorbent cotton, the lower half of which is saturated with the cuprous chloride solution which acts as a scrubber to remove impurities, such as phosphine, stibine (*10*), and hydrogen sulfide, from the evolved arsine. A chamber having a diameter that will accommodate a sensitized diaphragm of a size sufficient to combine with all the arsine is fitted to the condenser. The chamber consists of two thick-walled tubes of the same diameter with ground-glass joints held together by an outside sleeve of Gooch rubber tubing. The impregnated paper is fitted between the two ground joints as pictured in Figure 1.

An aliquot obtained from a sample digested with sulfuric and nitric acid in the usual manner (or the entire digestion in case of small amounts) is placed in a 1000-cc. Erlenmeyer flask with enough distilled water to make about 200 cc. of solution. Then 2 to 3 grams of solid ferrous ammonium sulfate or ferrous sulfate, 10 to 15 drops of stannous chloride solution and 50 cc. of 1 to 1 hydrochloric acid are added. Just before connecting to the condenser, introduce two or three pieces of activated zinc. A continual stream of nitrogen is kept flowing through the system to carry all traces of evolved arsine through the scrubber cotton to the paper diaphragm impregnated with mercuric bromide. The contents of the flask are boiled until all the arsine is evolved, which usually requires about 15 minutes. When the reaction is complete, the disk is removed and developed in cadmium iodide solution. This fixes the stain more permanently to light and water than does potassium iodide and changes the color from yellow to brown. The disk is allowed to remain in the iodide solution until all traces of red mercuric iodide, which immediately forms, have been dissolved. After prolonged use, the cadmium iodide solution turns yellow from the accumulation of complex cadmium mercuric iodides and should be replaced by fresh reagent. The excess reagent is removed from the disk by a water wash followed by a rinse with alcohol, and the disk is then dried between blotters. When dry the stains are compared with standards. The standards are prepared in a similar manner to the unknowns in steps of 0.0025 mg. of arsenic trioxide, keeping them free from excess light exposure. The stains have a tendency to bleach slightly with age and it is desirable to prepare fresh standards frequently, especially in the approximate range of the unknown.

With some modifications the method is applicable to the undigested material, thus shortening the total time of an arsenic determination to 15 to 30 minutes and eliminating the costly procedure of digestion with nitric and sulfuric acids.

From 5 to 100 grams of the undigested sample may be placed directly in the 1000-cc. Erlenmeyer flask together with 100 cc. of 1 to 1 hydrochloric acid, 1 to 2 cc. of stannous chloride solution, 15 cc. of potassium iodide solution, and 1 to 2 grams of solid ferrous sulfate. The activated zinc (three or four pieces) is added, and the flask immediately connected to the condenser unit. The reaction is usually complete after 15 minutes of boiling except that, when using large amounts of sample, a somewhat longer time may be necessary to evolve all the arsine. The scrubber cotton should be saturated with a 15 per cent solution of cuprous chloride in 1 to 1 hydrochloric acid to remove hydrogen sulfide, phosphine, and stibine, if present. In case these gases have not been efficiently removed, the yellow stain imparted to the disk is not changed to brown when immersed in the cadmium iodide solution. When using large samples of some products that contain considerable reducible sulfur or phosphorus compounds, the scrubber cotton may not remove all impurities, and a preliminary treatment is necessary. The sample is heated a short time with an alkaline solution, after which it is slightly acidified with hydrochloric acid and the excess sulfide removed by boiling. The remaining sulfur and reduced phosphorus compounds are oxidized with bromine water, and then the bromine is removed by boiling before adding the sample to the reaction flask.

TABLE I. RECOVERY OF ADDED INORGANIC ARSENIC FROM UNDIGESTED FOOD PRODUCTS

(20-mm. disk)

SAMPLES	As_2O_3–FREE PRODUCT	WEIGHT OF SAMPLE	ADDED As_2O_3	RECOVERED As_2O_3[a]
		Grams	*Mg.*	*Mg.*
4	Apple sauce	20	0.010	0.008–0.011
3	Apple sauce	20	0.020	0.018–0.021
4	Apple butter	20	0.005	0.004–0.006
4	Apple butter	20	0.0075	0.0075–0.009
4	Apple butter	50	0.010	0.009–0.011
15	Canned peaches	50	0.010	0.0075–0.010
1	Canned pears	50	0.010	0.010
2	Canned cherries	50	0.005	0.004–0.005
4	Canned cherries	50	0.010	0.008–0.010
2	Canned apricots	50	0.010	0.009–0.010
3	Canned sauerkraut	20	0.010	0.009–0.011
2	Canned celery	20	0.010	0.010
1	Canned spinach	20	0.010	0.009
1	Apple cider	50 cc.	0.010	0.010
1	Apple cider	50 cc	0.020	0.019
10	Shrimp[b]	10	...	Trace[b]
5	Shrimp	10	0.005	0.005–0.006
5	Shrimp	10	0.010	0.010–0.012
2	Shrimp	10	0.020	0.018–0.022

[a] Maximum spread of results.

[b] These samples all contained arsenic originally which could not be recovered by the disk method except after complete digestion with nitric and sulfuric acids

TABLE II. TESTS ON LYE-PEELED PEACHES

SAMPLE	GUTZEIT METHOD	DISK METHOD	SAMPLE	GUTZEIT METHOD	DISK METHOD
	Mg./gram	*Mg./gram*		*Mg./gram*	*Mg./gram*
83	0.00010	0.00014	52	0.00010	0.00017
173	0.00021	0.00028	89	0.00015	0.00036
130	0.00015	0.00017	54	0.00014	0.00028
85	0.00014	0.00034	136	0.00011	0.00017
175	0.00028	0.00029	137	0.00011	0.00007
132	0.00007	0.00014	183	0.00004	0.00004

DISCUSSION OF RESULTS

Known amounts of added inorganic arsenic were directly recovered from undigested material in such products as fruits, apple sauce, apple butter, cider, sauerkraut, celery, and other vegetables. However, in the case of marine products, such as shrimp, it was not possible to determine the original arsenic content without first thoroughly digesting the sample with nitric and sulfuric acids, although complete recovery was made of inorganic arsenic added to undigested samples of macerated shrimps previously found to give negative results for arsenic by the disk method (Table I). Determinations made of the original arsenic content of various undigested fruit and vegetable products were found to be in good agreement with those obtained by the Gutzeit method on the same samples after digestion. The presence of such substances as waxes, casein binders, oils, soaps, and nicotine bases, which are used in various spray mixtures, were found to be without effect in the determination. One set of data obtained on lye-peeled peaches which had been heavily sprayed with lead arsenate in plot tests made by representatives of the Department of Agriculture of the State of California (*5*) is shown in Table II. The disk method was employed on 50-gram samples of the raw product using a 15-mm. disk, and check analyses were made by the Gutzeit method on one-fifth aliquots of a 210-gram sample digested with nitric and sulfuric acids.

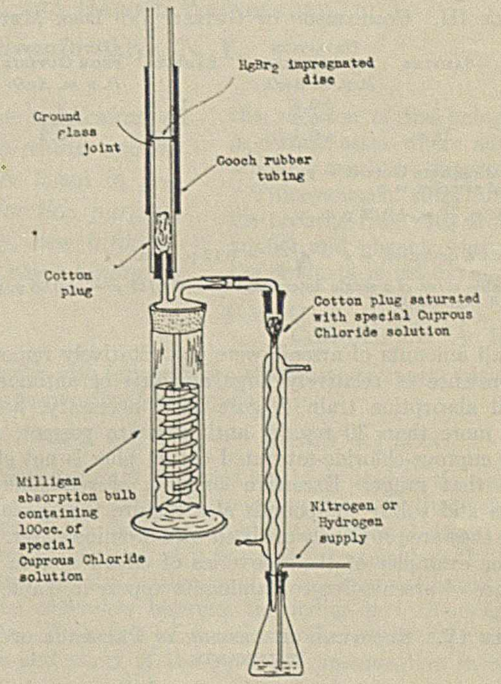
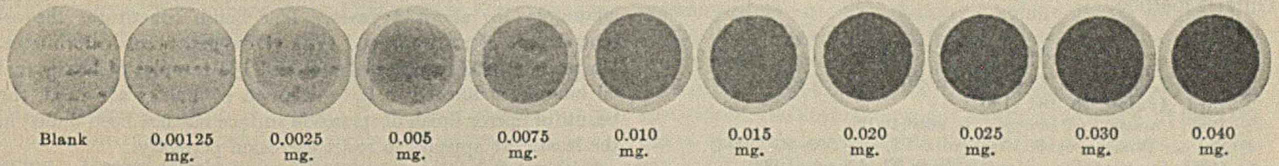


FIGURE 2. SPECIAL APPARATUS FOR ARSENIC DETERMINATION

After using the disk method in this laboratory over the period of a year for the analysis of various products, the



STANDARD ARSENIC STAINS

(20-mm. disk)

method was submitted to an industrial laboratory for use. Using 20-gram samples of undigested material in the disk method with 20-mm. diaphragms, the variation they obtained on fifty-four samples of apple butter (ranging in arsenic trioxide content from 0.1 to 3.0 p. p. m.) compared to the Gutzeit determination run on a digested sample is shown in Table III.

Table III. Comparison of Gutzeit and Disk Methods

Samples	Deviation from Gutzeit	Samples	Deviation from Gutzeit
	P. p. m. As_2O_3		*P. p. m.* As_2O_3
1	+0.3	14	0
8	+0.2	12	−0.1
18	+0.1	1	−0.2

Deviation from Gutzeit = v
No. of samples = n
Mean = $\frac{\Sigma v}{n}$ = +0.04 p. p. m.
Standard deviation = $\sigma = \sqrt{\frac{\Sigma v^2}{n}}$ = 0.12 p. p. m.
Probable error of a single determination = 0.6745 σ = ±0.08 p. p. m. = ±0.0016 mg. As_2O_3

Small amounts of arsenic were quantitatively removed in the presence of relatively large amounts of antimony. A special absorption train (Figure 2) is necessary, however, when more than 30 mg. of antimony are present, as the single cuprous-chloride-saturated cotton plug is not efficient above that range. Excessive amounts of reducible phosphorus and sulfur compounds also require the special train unless they are previously oxidized with bromine water.

Some examples of the recoveries of added arsenic in the presence of arsenic-free contaminants appear in Table IV.

Table IV. Recovery of Arsenic in Presence of Contaminants

Impurity	As_2O_3 Added	As_2O_3 Recovered
Mg.	*Mg.*	*Mg.*
500 Purified antimony trioxide	0.005	0.005
125 Same	0.010	0.011
125 Same	0.010	0.008
250 Same	0.020	0.020
250 Same	0.020	0.022
250 Same	0.020	0.020
250 Same	0.020	0.020
250 Same	0.040	0.038
500 Same	0.005	0.005
250 Sodium thiosulfate	0.005	0.004
250 Copper chloride	0.010	0.010
250 Lead acetate	0.010	0.010
50 Sodium hypophosphate	0.010	0.010

Arsenic was quantitatively removed without previous digestion from dilute solutions of the following organic arsenicals having arsenic in the trivalent as well as the pentavalent form:

	Av. by Gutzeit Method	Av. by Disk Method
	Mg./cc.	*Mg./cc.*
Tryparsamide	0.0025	0.0020
Neoarsphenamine	0.0012	0.0010
Tricacodylates	0.0006	0.0004
Carbasone	0.0030	0.0035
Arsphenamine	0.0010	0.0012

Acknowledgment

The author is indebted to G. S. Bohart of this laboratory for his helpful suggestions concerning this method and also to L. G. Petree for conducting many check determinations by the Gutzeit method.

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Easily Made Gas-Washing Bottle

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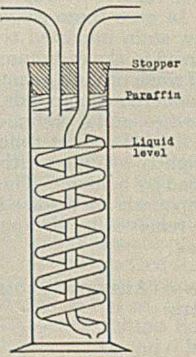

The gas-washing bottle herein described is useful because of its ease of construction and satisfactory performance. The requirements are a 5-foot (150-cm.) section of glass tubing, a glass cylinder, a rubber stopper, and a few grams of paraffin. The glass tubing is bent in the spiral form as shown so that it will fit within the glass cylinder. At the bottom of the spiral, on the under side of the tubing, a hole is blown. This is best done in a hot flame with but gentle pressure, so that the hole will not be too small. When the apparatus is assembled with the paraffin loose within the jar, the jar is inverted and heated so that the paraffin makes a gas-tight seal around the stopper and protects the latter from attack by the liquid.

In operation the gas to be washed passes down to the bottom of the central tube. As it starts up the spiral, liquid enters the tube through the hole so provided. The gas then passes up the spiral as small bubbles, acting as an air lift, the volume of the bubbles and the ratio of liquid to gas depending upon the design of the apparatus and the gas velocity. The gases remain in contact with the liquid from 10 to 40 times as long as they would if allowed to bubble unobstructed to the surface.

In the laboratory of the Philadelphia Quartz Company, this bottle of home-made construction, has, in a period of four years, been found entirely satisfactory. It has been subsequently improved first by specifying a ground-glass stopper and finally by making it of one-piece glass construction.

Received April 14, 1934.

Stainless Steel Bomb in Oxygen Calorimeter

A bomb made of stainless steel (18-8) has been in use in this laboratory for about 3 years. This bomb constitutes the essential part of an improved type of oxygen bomb calorimeter. Up to date 2593 samples of coal and 164 samples of heavy fuel oil have been burned in it. Although no linings are used, the beautiful mirror finish of its inside surface has not been dulled in the least. It appears to resist corrosion perfectly.

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Nature and Constitution of Shellac

VIII. Thiocyanogen Numbers of Resins

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This paper describes how the application of thiocyanogen may be extended to resins, and the many precautions which must be taken in preparing thiocyanogen solutions for this purpose. As a result of this investigation, new information has been obtained regarding steric hindrance and the structure of shellac.

ALTHOUGH some inorganic free radicals have been known for nearly a century, it was not until the last decade that Browne (*7*) first pointed out their similarity in properties. It was in Browne's laboratory that one of us (W. H. G.) first became interested in this field (*9*), and it was there that he recognized the analytical possibilities of free dimeric inorganic radicals. This is the first paper of a series which will describe the use of some of these new reagents in analytical work.

From their close analogy to the halogens Browne used the term "halogenoids" to described the radicals fulminate, cyanate, trinitride, thiocyanate, azidodithiocarbonate, selenocyanate, and tellurocyanate. This term describes them as a group more clearly than "pseudo-halogens," later used by Birckenbach and Kellerman (*6*). Walden and Audrieth (*36*) cite the parallel which this work bears to the now classical investigations which were carried out with organic free radicals.

THIOCYANOGEN

Liebig attempted to prepare free thiocyanogen (*26*) shortly after the discovery of the first halogenoid, cyanogen. A great deal of investigation followed (*11, 23, 27, 33*), but it remained for Söderbäch (*34*) actually to isolate the true free radical in 1920. This was undoubtedly because of the relative lack of stability of this compound, a property shared by some of the others and by many of their inter-halogen derivatives (*9, 12, 17, 20, 35*). In this respect they deviate most from the halogens.

Söderbäch first obtained free thiocyanogen by the action of iodine on an ethereal suspension of silver thiocyanate. He later showed that bromine gave a more complete reaction, pointing out that the solvent, the concentration, and local heat effects had an important influence on the character of the product obtained. This halogenoid may also be prepared by the oxidation of the free acid in ethereal solution with manganese dioxide, but the yield from this reaction is small (*19*). It has been prepared too by the electrolysis of thiocyanates (*21*) and by the interaction of lead tetraacetate and thiocyanic acid (*19*).

Although the tautomeric properties of thiocyanogen (*18, 36*) and its inorganic reactions are of only passing interest to the resin chemist, a number of the organic reactions studied by Kaufmann (*17*) are directly related to the chemistry of resins. With unsaturated members of the C_nH_{2n} series, thiocyanogen forms addition compounds:

$$R{-}CH{=}CHR + (SCN)_2 \longrightarrow RCH\ (SCN)\ CH(SCN)R$$

With unsaturated members of the C_nH_n series it is added only at one of the unsaturated bonds, while with compounds containing a triple bond there is no addition. Similar reactions occur with the unsaturated fatty acids. These reactions, however, are not general, since steric hindrance can prevent the addition of the halogenoid in certain cases where addition products would be expected.

Thiocyanogen substitutes in the benzene ring with aromatic amines and phenols, and one of the products is thiocyanic acid:

$$C_6H_5OH + (SCN)_2 \longrightarrow C_6H_4(OH)SCN + HSCN$$

This acid is also formed when thiocyanogen reacts with mercaptans to give disulfide compounds:

$$RSH + (SCN)_2 \longrightarrow RSSCN + HSCN$$

The first group of reactions has been used in the analysis of oils (*16*) and fats (*37*) to determine quantitatively the amounts of the different unsaturated glycerol esters. For example, in a linseed oil it is possible to calculate the exact percentage of the triglycerides of oleic and linoleic acids from the difference between the iodine and thiocyanogen numbers. Both sets of reactions offer possibilities in the analysis and study of the nature of unsaturation in resins.

ANALYTICAL SOLUTIONS

In the preparation of stable thiocyanogen solutions for analytical use, none of the authors clearly emphasize all the essential precautions, especially when it is intended to extend their use to resins.

Kaufmann (*17*) has shown that the tendency of thiocyanogen to polymerize is less in glacial acetic acid than in any other solvent. This is fortunate, since this liquid is usually one of the best solvents for resins. Kaufmann also points out that traces of moisture on the glass apparatus and exposure to the atmosphere lessen the stability. Dilute solutions (0.05 *M*) were found to give the best results. He prepared his acetic acid by treating it with phosphorus pentoxide and using the fraction distillating at 118° to 120° C. His solution of thiocyanogen was stable for more than a week and he reports that 5 hours' contact of the reagent with the oils is sufficient for complete addition.

Zeleny and Bailey (*37*), who kept their solutions in the dark, found that 17 hours were required in analyzing lard. Barbour (*3*) claims to have obtained a more stable solution by dehydrating his acid solvent with acetic anhydride. Kimura (*22*) adds the bromine during the preparation of the thiocyanogen by dissolving it in carbon tetrachloride. This modification the authors find prevents local overheating. Kimura also uses a 50 per cent excess of thiocyanogen and allows 24 hours for its reaction. Hugel and Krassilchik (*14*) recommend the use of a shaking machine during preparation of the reagent and a rapid filtration for the removal of the lead bromide formed.

Besides incorporating the best features of all these investigators, the authors found it desirable to add a 10 per cent excess of acetic anhydride to the reagent in order to remove any moisture introduced by the resin. They also proved that either chloroform or carbon tetrachloride can be used as solvent for the bromine, but that the bromine solution must be added in very small quantities to the lead thiocyanate suspension and the mixture allowed to become completely decolorized between additions. During this operation, which takes several hours, the reaction mixture should be vigorously agitated.

The purity of the lead thiocyanate is also highly important. One of the best grades that could be purchased in the market did not give satisfactory results. For this reason in all this work, the lead thiocyanate was freshly prepared from recrystallized lead nitrate and sodium thiocyanate, and dried in a desiccator protected from light. It is essential that lead thiocyanate shall be perfectly dry in order to obtain stable solution of thiocyanogen. For the same reason a calcium chloride tube was used above the buret to protect the solution during titrations.

Method of Preparation

The methods of preparation of the reagent and the procedure found practical for resins were as follows:

Acetic Acid. Glacial acetic acid was dehydrated with phosphorus pentoxide. The supernatant liquid was then distilled in a round-bottomed flask which carried a fractionating column attached to a Liebig condenser. All connections were made with corks carefully protected with silver foil. The flask was heated in a 28° Bé. glycerol bath and the acid which distilled between 118.0° to 118.5° C. was collected and received in a suction flask which was protected from atmospheric moisture by means of a phosphorus pentoxide tube attached to the side arm.

This procedure was repeated until the product had a melting point corresponding to 99.5 per cent acetic acid, and showed no reaction with potassium permanganate when 2 ml. of the acid were diluted with 10 ml. of distilled water and 0.1 ml. of 0.1 *N* permanganate was added. As proof of this, the color did not disappear at the end of 2 hours when kept at 24° ± 3° C.

To the pure acetic acid was now added a 10 per cent excess of acetic anhydride and the solution was kept in a stoppered container protected from moisture.

Lead Thiocyanate. About 56 grams of sodium thiocyanate were dissolved in 100 ml. of distilled water, evaporated to one-half the original volume, and allowed to cool. The material which separated was filtered on a Büchner funnel and then recrystallized in a similar manner. The lead nitrate was purified in the same way.

Each salt was then dissolved in 100 ml. of distilled water and lead thiocyanate precipitated by adding the solution of the sodium salt to that containing the lead nitrate. Precipitation was carried out in the cold, since a high temperature causes decomposition of the lead haloid. The precipitated salt was then thoroughly washed with distilled water, filtered, and placed in a desiccator to dry in the dark over phosphorus pentoxide.

A determination of lead as lead sulfate on the dry material gave the following results: found, 64.15 per cent; theory, 64.10 per cent.

Bromine Solution. In 200 ml. of redistilled, water-free carbon tetrachloride 8.4 grams of pure bromine were dissolved. To this were added 300 ml. of the above specially prepared acetic acid solution.

Thiocyanogen Solution. Five milliliters of the bromine solution were then added to a suspension of 30 grams of lead thiocyanate in 300 ml. of the acetic acid, and vigorously shaken until the mixture was practically colorless before adding another portion of bromine. This procedure was followed until all the above bromine solution had been added. The mixture was then rapidly filtered through a dried, fluted filter paper. At this step if traces of moisture are present a pink color is imparted to the paper. This was avoided in all cases.

The solution was then standardized against sodium thiosulfate in the usual manner. The buret containing the thiocyanogen solution was protected from moisture with a tube containing calcium chloride or phosphorus pentoxide.

The above method gives approximately 0.1 *N* solution and retains its strength for about 8 days, as shown by the following: 15 ml. of thiocyanogen required 14.90 ml. of sodium thiosulfate solution initially; on the third day it required 14.90; on the fifth, 14.80; on the sixth, 14.75; and on the eighth, 14.75.

Procedure. Into a dry Erlenmeyer flask containing 20 ml. of the specially prepared acetic acid, 0.2000 gram of ground (30-mesh) resin was introduced, and the contents were warmed on an oil bath at 65° to 70° C. for 15 minutes to insure complete solution. Ten milliliters of pure dry chloroform or carbon tetrachloride were then added and the flask was kept at 22° ± 5° C. for 30 minutes. At the end of this time 25 ml. of the standard solution of thiocyanogen were added and allowed to react in a dark place for 48 hours.

To determine the excess thiocyanogen, 20 ml. of a 10 per cent aqueous solution of potassium iodide were added and the mixture was rapidly titrated with standard sodium thiosulfate. The thiocyanogen absorbed was calculated as centigrams of iodine in order to obtain numbers which could be readily compared with those from Wijs solution.

Thiocyanogen Numbers

Thiocyanogen numbers were determined for three unsaturated carboxylic acids, and for several samples of shellac and rosin. These numbers were compared with those obtained by using Wijs solution (*1*, *2*).

Table I. Thiocyanogen Numbers

Substance	Iodine Number	Thiocyanogen Number
Ricinoleic acid	131.8	84.6
Oleic acid (commercial)	84.3	75.2
Oleic acid (vacuum distilled)	85.6	77.7
Cinnamic acid (pure)	71.0	0.0
Methyl cinnamate	100.6	3.9
Rosin (G)	186.0	105.0
Rosin (G)	199.6	88.5
Rosin (WG)	203.1	101.7
Rosin (I)	197.3	88.4
Rosin (W. W.)	204.4	102.1
Abietic acid (commercial)	180.9	87.0
Shellac (T. N. pure)	18.0	18.4
Shellac (superfine)	19.9	19.8
Shellac (refined bleached)	9.5	9.2
Shellac (bleached)	10.6	11.1
Shellac (L & M)	19.1	18.3
Shellac (U. S. S. A. T. N.)	23.7	20.6
Shellac (U. S. S. A. T. N.)	23.0	20.0
Manila copal	69.84	44.0

As can be seen from Table I, the thiocyanogen value for ricinoleic acid is nearly that for theory, 85.03, but the iodine value is practically one and a half times that required. Ricinoleic acid, 9-octadecene-12-ol-1-acid, contains a hydroxyl group which is removed by but one carbon from the unsaturated bond. It is highly probable that with Wijs solution, the hydroxyl group in this acid is oxidized by the halogen. The literature contains no values for pure ricinoleic acid, but methyl acetyl ricinoleate has the theoretical iodine number, acetylization protecting the hydroxyl group.

The thiocyanogen number for oleic acid is lower than that required by theory, but the iodine number is also below that for a pure sample. The values are, however, the same as those obtained by other investigators (*8*, *25*) for commercial oleic acid. Vacuum distillation does not greatly increase the purity.[1]

The reaction between cinnamic acid and Wijs solution is incomplete, as shown by the very low value, while thiocyanogen is practically without reaction.

The halogenoid numbers for two grades of rosin and of commercial abietic acid are less than half the iodine number determined by the Langmuir method, but it is of interest to note that they are approximately one-half of the theoretical value, 168, for the addition of 4 atoms of halogen by pure abietic acid. It is well known that Wijs solution gives both addition and substitution with this substance (*4*, *5*, *28*, *29*, *31*). Apparently thiocyanogen adds at but one unsaturated bond and from the high degree of hydrogenation of structure of abietic acid, one would expect it to behave as a fatty acid of the $C_nH_{2n-1}O_2$ series.

The two numbers are practically identical for pure shellac. The differences for the U. S. Shellac Association T.N. grades is due entirely to the presence of rosin as shown by calculating the percentage of rosin both by the Langmuir formula (*2*) and by the difference in the two absorption numbers. The results agree within 0.2–0.3 per cent. It would appear, there-

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[1] In the discussion of this paper at Washington, J. S. Long stated that he had obtained similar results, but that when the acid was purified by the method of Lapworth, Pearson, and Mottran, *Biochem. J.*, **19**, 7 (1925), both the thiocyanogen and iodine values correspond to theory.

fore, that there is some theoretical chemical basis for the results obtained by the Langmuir method (*24*). For this reason the Langmuir values should not be treated as purely empirical, when considering them in connection with those of other methods, such as the Hübl method.

The iodine number for the superfine shellac is abnormal for this grade. This sample contained 0.45 per cent of arsenious sulfide, and Rangaswami and Aldis (*32*) have shown that if this adulterant is in a finely divided state, it will increase the iodine number. Apparently it affects both thiocyanogen and iodine numbers equally.

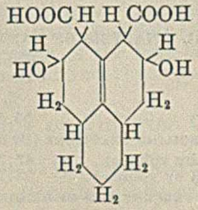
Steric Hindrance

These results bring to light certain other theoretical considerations, such as the effect of steric hindrance (*15*) which investigators are apt to overlook. The authors' values for cinnamic acid present a typical case. It is well known that while chlorine and bromine add quantitatively to this acid, the absorption of pure iodine is very slow. This is caused by the proximity of two strongly negative groups, phenyl and carboxyl, to the unsaturated bond of the acid. In view of these facts, it was not surprising to find that the less reactive thiocyanogen gave no reaction.

If the authors' theory is correct, values for methyl cinnamate should be better than those for the free acid, since the methyl group should decrease the negative character of the carboxyl group. As can be seen from Table I, this is true for the addition of iodine, but the negative groups still prevent the addition of thiocyanogen.

This would explain the behavior of this halogenoid with fatty acids of the $C_nH_{2n-1}O_2$ series where the addition of one molecule of thiocyanogen would prevent the absorption at the second, and hence, as is observed, the thiocyanogen number is one-half of the iodine number.

The consideration of steric hindrance is also of interest from the point of view of postulation of the constitution of shellac, since Harries and Nagel have found that the only isolated unsaturated acid (*10, 13, 30, 31*), shellolic acid, did not absorb bromine (*13*). To account for this they have postulated an internal unsaturated bond in its structure:



The question, then, naturally arises as to why shellac should have an iodine number. It can be readily demonstrated by acetylization that Wijs solution does not replace hydroxyl groups in this resin, so that some other explanation is necessary.

The facts as they are known can be readily explained if cinnamic acid and methyl cinnamate are used for analogy. If we assume that the double bond in shellolic acid is adjacent or close to the carboxyl groups, it is easy to understand why halogens may not be absorbed by the free acid, but if in the structure of shellac these same carboxyl groups form part of the ester linkages, it would be clear why the resin itself showed unsaturation. The large molecules, attached to these acid groups of shellolic acid, should have a marked effect in decreasing their negative character, so that a thiocyanogen number for shellac would not be considered unreasonable.

Conclusions

Halogenoid solutions may be used to give the chemist another method by which to study the nature of unsaturation and the constitution of resins. Because of the difference between the iodine and thiocyanogen numbers of different resins, it may be possible to develop methods for the quantitative determination of some of these resins in varnish mixtures.

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* * *

Detection and Determination of Solvents and Volatile Liquids in Nitrocellulose Lacquers and Lacquer Thinners

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WITHIN the last few years, various new solvents for use in the lacquer industry have made their appearance on the market. Some of these solvents are sold under trade names which afford no certain clue to their actual chemical identity; or they may be encountered as unknown components of finished nitrocellulose lacquers or of the thinners sold with such lacquers.

For the purpose of appraising a solvent, thinner, or lacquer as to probable value and behavior on application or in use, it is often highly desirable to know the identity of the liquid or liquids it contains, as well as the approximate composition of the mixture in case a thinner or lacquer is involved. For this purpose a practical method for the quantitative determination of low-boiling and high-boiling solvents and diluents, followed by their identification, is here presented.

Solvents are distilled from the lacquer at atmospheric pressure, low-boiling partly water-soluble components being taken off first, followed by removal of higher-boiling components after the addition of water. Distillation under reduced pressure may be desirable for the removal of super-high-boiling compounds, but in general is not recommended since it entails the possible loss of volatile components.

Lacquers formulated with the esters of lactic acid require a special procedure which will not be described in this paper.

Quantitative results are obtained by analysis of two fractions—the fraction boiling up to 93° C. and the fraction boiling above 93° C. Components are identified by fractional distillation of the products of alkaline saponification. Identification tests for the more commonly used lacquer solvents and diluents are described. Results obtained by the method described have been found to agree closely with the actual composition of known lacquers and thinners.

QUANTITATIVE DETERMINATION OF ESTERS, ALCOHOLS, AND TOTAL HYDROCARBONS

ANALYSIS OF THINNER. Two hundred and fifty cubic centimeters of thinner are slowly distilled through a good fractionating column until a vapor temperature of 93° C. is reached. At 93° C. all ethyl compounds will have been distilled over. If iso- or secondary butyl compounds are present, small amounts of these compounds may come over with ethyl acetate below 93° C. The volume of distillate is measured and recorded; and esters, hydrocarbons, and alcohols on both distillate and residue are determined as follows:

Esters are determined on both the distillate and the residue by saponifying 2 cc. of sample with 25 cc. of 1 *N* alcoholic sodium hydroxide. The mixture is refluxed for 1.5 hours, and the excess sodium hydroxide titrated against standard acid. Saponifiable matter in the distillate is calculated as ethyl acetate and converted from grams per 100 cc. to per cent by volume of 88 per cent commercial ethyl acetate by dividing by (0.9 × 0.88). Esters in the residue above 93° C. are calculated as butyl acetate and converted from grams per 100 cc. to per cent by volume of 92 per cent commercial butyl acetate by dividing by (0.88 × 0.92).

Hydrocarbons are determined on both the distillate and the residue by mixing 20 cc. of sample with 20 cc. of 80 per cent sulfuric acid (80 cc. of concentrated sulfuric acid plus 20 cc. of distilled water) in a 50-cc. buret which has been sealed off at the lower end. After thorough shaking, the mixture is allowed to stand overnight in an upright position, and the percentage by volume of hydrocarbons is calculated from the volume of the upper layer. Erroneous results will be obtained if the strength of the sulfuric acid deviates more than ±3 per cent from the 80 per cent specified.

Alcohols are determined on both the distillate and the residue by mixing 50 cc. of sample with 200 cc. of water in a 250-cc. graduated cylinder. The percentage of alcohols is determined by decrease in volume of upper layer from the original 50 cc. This determination is approximate only, and is used as a check. In final calculations, alcohols are estimated by difference.

In case the volume of either distillate or residue is insufficient for the determination of alcohols, as outlined above, 10 or 20 cc. of sample may be mixed with an equal volume of distilled water in a 50-cc. buret sealed at one end. If the sample is insufficient for esters, hydrocarbons, and alcohols, determination of the alcohols should be omitted or a larger amount of sample taken for fractional distillation at the start. Alcohols as determined on the distillate below 93° C. should be fairly accurate, but results on the residual portion (above 93° C.) will be somewhat low and merely indicative of the presence or absence of free higher alcohols.

If time is available, a valuable check may be obtained on the values derived above by determining esters, hydrocarbons, and alcohols on the sample as received, following the procedure outlined above. In this case, esters calculated as butyl acetate will be higher than actual, the error being in proportion to the ratio of butyl acetate and ethyl acetate present in the thinner. Very little extra time is required to make these determinations if run simultaneously with tests outlined above.

TABLE I. TYPICAL ANALYSIS OF SAMPLE OF THINNER

	HYDROCARBONS	ESTERS	ALCOHOLS
	%	%	%
As received (by volume)	55.5	28.58	16.0
HIGH- AND LOW-BOILING FRACTIONS (250 CC. DISTILLED)			
Below 93° C. (80 cc., 32% by volume)	47.75	21.32	42
Above 93° C. (170 cc., 68% by volume)	58.75	29.64	12
CONVERTED TO PERCENTAGES OF ORIGINAL THINNER			
Low-boiling	15.28	6.82	13.44
High-boiling	39.95	20.16	8.16
	55.23	26.98	21.60
	26.98		
	21.60		
	103.81		
ALCOHOLS CALCULATED BY DIFFERENCE			
Low-boiling	15.28	6.82	9.90
High-boiling	39.95	20.16	7.89
	55.23	26.98	17.79

Calculating the alcohols by difference is believed to be more accurate, in that it allows for the alcohols which normally are present in the commercial acetates. This analysis agrees fairly closely with results for the material as received, and indicates the following approximate formula, subject to confirmation and identification later:

	%
Hydrocarbons	55.0
Ethyl alcohol	10.0
Ethyl acetate	7.5
High-boiling alcohols	7.5
High-boiling esters	20.0
	100.0

Analysis of Lacquer. After separation of the total volatile constituents from the solids, analysis of a lacquer is identical with that of a thinner, except that the amount of sample available is less, and that it may be advisable, from the point of view of the extra time involved, to omit determinations on sample as received and confine the analysis to examination of low- and high-boiling portions.

For unthinned lacquers of average viscosity, 1030 cc. are poured into a graduated cylinder (the 30-cc. mark is estimated on a 1000-cc. cylinder) and transferred to a 3-liter round-bottomed flask. In this way allowance is made for the lacquer which adheres to the sides of the cylinder and the actual sample taken is 1000 cc. The flask is fitted with two thermometers, one reaching into the lacquer and one to record the vapor temperature in the neck of the flask. The flask is immersed in an oil bath in which a third thermometer is immersed. To avoid the difficult operation of drying the low-boiling alcohols and esters, distillation is conducted slowly and carefully on the water-free lacquer until a vapor temperature of 93° C. has been reached. At this point a cut is made, and, if the lacquer still appears to be fairly liquid, distillation is continued and as much high-boiling (from 93° C. upwards) liquids as possible recovered before stopping the distillation and adding water. However, caution is advised at this point and the temperature of both the oil bath and the liquid lacquer should be carefully watched, so that the oil bath does not go above 150° to 155° C. and the liquid lacquer above 110° C.

When the liquid lacquer temperature has reached 110° C., distillation is discontinued and, as soon as the apparatus is cool enough for handling, 500 cc. of distilled water are added and heat again applied. Distillation is continued until about 1100 cc. of total distillate, dry and aqueous, have been collected. The distillate towards the end should be tested for the presence of solvents by tasting and by collecting a small portion and treating with anhydrous potassium carbonate. In some cases a second portion of 300 cc. of distilled water may be necessary for complete removal of solvents.

When tests show that the solvents have all been extracted, the aqueous distillate, including small amounts used for testing, is dried with potassium carbonate and added to any nonaqueous distillate collected above 93° C. Drying of the high-boiling liquids is much easier and more complete than when low-boiling distillates are present. Determination of alcohols, esters, and hydrocarbons is then made according to the procedure outlined for analysis of thinner. If desirable and time permits, the dried high-boiling liquids can at this point be mixed with the low-boiling portion, and total esters, hydrocarbons, and alcohols determined. However, if this be done, it is desirable to refractionate the mixture up to 93° C., since identification of the low-boiling solvents, assumed to be ethyl alcohol and ethyl acetate, is usually omitted, and identification of the high-boiling solvents is more positive in the absence of the ethyl compounds.

Identification of Volatile Constituents

In the identification of the volatile constituents of a lacquer or thinner, close attention should be paid to distillation temperatures, as much can be learned in this way. Low-boiling naphtha may be detected by initial boiling point, or, in the rare cases in which it is used, acetone may be detected by its boiling point and otherwise confirmed later. The absence of saponifiable matter discovered in the foregoing scheme of analysis would indicate a solvent of the cellosolve type. Cellosolve may be readily identified by its boiling point, water solubility, solvent action on nitrocellulose, and odor after separation from hydrocarbons in the manner to be described. Its approximate percentage by volume may be determined by fractional distillation of the nonhydrocarbon material.

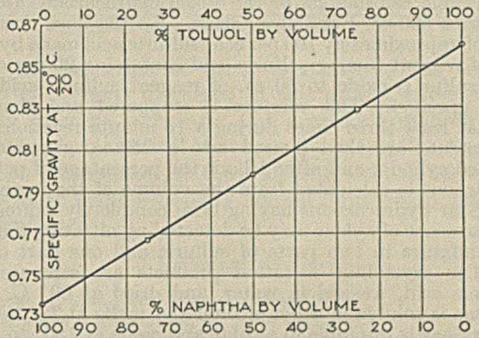

Figure 1

For identification of the solvents and diluents in a standard lacquer or thinner of the alcoholic ester type, 500 or 1000 cc. (depending on the amount of hydrocarbons present) of sample are thoroughly mixed with an equal volume of cold sulfuric acid (80 cc. of concentrated sulfuric acid plus 20 cc. of distilled water). The mixture should be kept cool during mixing to prevent losses by evaporation, or to minimize decomposition due to heating. In some cases the use of 85 per cent phosphoric acid rather than 80 per cent sulfuric acid may be found preferable, but in general the much higher cost of phosphoric acid will make its use in large quantities undesirable. For the quantitative estimation of hydrocarbons in the analysis of lacquers and thinners, cold sulfuric acid has been found to give more accurate results than 85 per cent phosphoric.

In the analysis of a lacquer, if the quantitative determinations and the distillations preceding it tend to show that the low-boiling solvents are ethyl compounds, further treatment of this portion is unnecessary, unless identification of the possible low-boiling hydrocarbons is important. The entire high-boiling portion left after quantitative determinations of hydrocarbons, esters, and alcohols is treated with an equal volume of 80 per cent sulfuric acid. The solvent hydrocarbon–sulfuric acid mixture is allowed to settle in a separatory funnel, and the lower layer of alcohols and esters in sulfuric acid is drawn off. The upper hydrocarbon layer is examined for composition and the presence of naphthas, toluene, and

Table II. Properties of Alcohols Present in Indicated Esters

Ester	Boiling Range or Point ° C.	Refractive Index	$ZnCl_2$–HCl Test	Iodoform Test
n-Butyl acetate	117.7	1.3993	Perfectly clear solution. No upper layer on standing	Negative
Secondary butyl acetate	90–101	1.397	Deep upper layer	Positive in one minute
Fermentation amyl acetate	78–130.5	1.361 to 1.406. Principal fraction from 120° to 130.5° C. is 1.406	No upper layer in any fraction	None in amyl alcohol range. Trace in low-boiling fraction
Amyl acetate from unsaturated hydrocarbons	110–135	Mixture of alcohols is 1.4078. Principal fraction 117° to 119° C. is 1.406. Last fraction 134° to 135° C. is 1.413.	Upper layer in all fractions	Positive test in 5 minutes or less in all fractions
Amyl acetate from saturated hydrocarbons	117–137	1.404 to 1.410. Principal fraction boiling from 120° to 136° C. is 1.410	Upper layer in first fractions fading out above 130° C.	Positive test in fractions below 120° C. Heavy precipitate in 117° to 120° C. fraction. Trace only above 120° C.
Higher alcohols acetate by catalysis, mostly isobutyl acetate	105–130	1.388 to 1.420. Principal fraction boiling from 106° to 112° C. is 1.396	Upper layer in last fraction only	Negative in all fractions

xylene determined by correlation of boiling ranges and specific gravities of naphtha, and toluene and xylene, so that it is easy to detect the presence of the former in admixture with the two latter compounds. Figure 1 gives the specific gravities of mixtures of lacquer diluent naphtha and toluene.

However, in cases where it is important that the actual composition of the hydrocarbons be known, the following method will give very close approximations:

Fifty cubic centimeters of the mixed hydrocarbons are measured into a 500-cc. Erlenmeyer flask. To the flask are added 100 cc. of approximately 100 per cent sulfuric acid made by adding 50 cc. of reagent fuming sulfuric acid containing 20 per cent excess of sulfur trioxide to 50 cc. of reagent sulfuric acid (1.835 specific gravity). This mixture is stoppered and thoroughly shaken at least three times during a 15-minute reaction period. The contents are then poured into a 250-cc. glass-stoppered graduated cylinder and after 1 hour the percentage of petroleum hydrocarbons is calculated from the volume of the upper layer, the coal-tar hydrocarbons having been completely sulfonated.

The presence of xylene may be detected by nitrating the hydrocarbon mixture in two parts of sulfuric and one part of nitric acid. The crystalline nitration products are separated from the excess acid, washed in water, and dried at 60° C. Trinitrotoluene is soluble in ethyl alcohol and melts at 78° to 80° C.; trinitroxylene is insoluble in alcohol and melts at 180° to 182° C.

The sulfuric acid solution of the alcohols and esters is slowly diluted with at least three times its volume of distilled water, precautions being taken to avoid heating the mixture at the start of the dilution. Through a short fractionating column the alcohols and esters are distilled off with water, and the water is removed by salting out with potassium carbonate. The dried mixture may be analyzed for ester and alcohol content by the method given for analysis of thinner, or, if the volume is not large enough, 2 cc. may be taken for ester determination and the alcohols estimated by difference. If these data are desired, it will be necessary to redistill the dried solvents to remove any dissolved potassium carbonate, as this would interfere with the determination of esters by alkaline saponification.

The dried alcohols and esters are now saponified in the following way:

Crushed sodium hydroxide sticks or pellets, equal in weight to one-third of the weight of the alcohols and esters, are dissolved in an equivalent number of cubic centimeters of distilled water with constant stirring to take advantage of the heat generated. After complete solution the liquid is cooled, and a volume of methanol equal to twice the amount of water used is added. This alkaline solution is now added cautiously to the alcohol-ester mixture in a suitable size round-bottomed flask. The mixture is refluxed for 0.5 hour under a good fractionating column, after which the known amount of methanol is distilled off and discarded. The alcohols are then distilled off and the wet fractions dried with potassium carbonate.

Several refractionations may be necessary to divide the alcoholic mixture into its true fractions. At this point, much will be known of the probable identity of the alcohol or alcohols, and 5- to 10-cc. cuts of the apparently pure fraction should be made, using the theoretical boiling point of the suspected alcohol as a guide. These small pure fractions can be used for identification tests, such as refractive index and the zinc chloride–hydrochloric acid test for characterization as primary, secondary, or tertiary alcohol.

The alcohols from the original esters, as well as any high-boiling free alcohols originally present, are now ready for identification, and the following data should be obtained:

1. Volume–per cent distribution of the different fractions present, for use in comparison with the same values for known alcohols or mixtures of alcohols used in the lacquer industry.
2. Refractive indices of all fractions.
3. The zinc chloride–hydrochloric acid test on all fractions for characterization as primary, secondary, or tertiary alcohols. This test, described by Lucas (*1*), has been found very satisfactory in distinguishing between the more commonly used primary and secondary alcohols. The reagent for this test is made by dissolving 136 grams (1 mole) of anhydrous zinc chloride in 105 grams (1 mole) of concentrated hydrochloric acid with cooling. The test is carried out by adding 2 cc. of the alcohol in a vial or test tube to 12 cc. of the zinc chloride–hydrochloric acid reagent, stoppering with a cork, and shaking. Alcohols lower than hexyl are soluble in this amount of the reagent, but tertiary alcohols react so fast that separation of tertiary chloride as an upper layer is noticeable almost at once. If a secondary alcohol is present, the clear solution becomes cloudy in about 5 minutes and, on standing overnight, a distinct upper layer is visible. In the case of a primary alcohol, no change, except a slight darkening, takes place even on long standing. By the use of larger amounts of alcohol and reagent in standard test tubes, such as Nesslers, the method may be made more or less quantitative for mixtures of secondary and primary alcohols by measuring the upper layer formed and comparing its volume with the volume of chloride produced by a known alcohol or mixtures of alcohols.
4. In case positive tests for secondary alcohols are obtained in 3, the iodoform test for secondary alcohols should be made. In addition to isopropyl, which is little used in the lacquer industry, both secondary butyl and secondary amyl alcohols have been found to react with iodine at room temperature in alkaline solution. Two or three drops of the alcohol are dissolved in 10 cc. of 1 *N* sodium hydroxide solution, and 15 or 20 cc. of 0.1 *N* iodine are run with constant shaking. A yellowish white precipitate of iodoform, visible in a minute in the case of the secondary amyls, indicates these alcohols.

CORRELATION OF DATA. With the above data at hand, the nature or source of the alcohols present originally, mostly as esters, may be fairly accurately determined by a process involving elimination and comparison. The esters most commonly used in the lacquer industry are ethyl acetate, secondary butyl acetate, normal butyl acetate, amyl acetate (from fusel oil), secondary amyl acetate by synthesis from unsaturated hydrocarbons, amyl acetate by chlorination of saturated hydrocarbons, and the acetates of synthetic alcohols by catalysis from hydrogen and carbon monoxide (mostly isobutyl alcohol). Cellosolve and its esters will be recognized by special tests referred to above.

Ethyl acetate is universally used in lacquer formulas, is easily separated from the higher-boiling compounds, and its presence as the low-boiling ester is generally assumed in lacquer analysis, unless contradictory behavior of some sort is noticed, in which case identification could be made by well-known methods. The characteristics of the six other types can be summarized as in Table II.

From these data it is possible to recognize with certainty any of the esters of the foregoing list present in a lacquer or thinner. For example, *n*-butyl compounds can be readily identified by the narrow boiling range, the refractive index, the absence of any upper layer in the zinc chloride–hydrochloric acid test, and the negative test for iodoform. Further confirmation may be obtained by determining the melting point of the dinitrobenzoate (*2*, *3*). Secondary butyl alcohol may be identified by its boiling point, its very positive reaction in the zinc chloride–hydrochloric acid and the iodoform tests, and by its characteristic odor. Fermentation amyl alcohol is distinguished by its boiling range and the negative test with zinc chloride–hydrochloric acid in all fractions. Amyl alcohol from unsaturated hydrocarbons is identified by its characteristic odor, and the positive reaction of all its fractions in the zinc chloride–hydrochloric acid and the iodoform tests. This commercial product is made up largely of secondary alcohols in contrast to the amyl alcohols from saturated hydrocarbons, which are largely primary amyl alcohols, and have a higher average boiling point. The latter compounds may be distinguished from fermentation amyl alcohols by the presence of the lower-boiling secondary compounds. The higher alcohols produced from hydrogen and carbon monoxide may be identified by the high isobutyl alcohol content and the negative iodoform test in all fractions.

For more positive identification when necessary, the melting point of the 3,5-dinitrobenzoic acid derivative, referred to above, may be found helpful.

The following method devised by the author has been found to give closely approximate results for the determination of secondary butyl compounds in mixture with normal butyl compounds:

Ten cubic centimeters of thinner, or 10 cc. of the total volatile matter from a lacquer, are carefully weighed into 50 cc. of 1 N aqueous potassium hydroxide solution in a stoppered flask. Refluxing for 3 to 4 hours with frequent shaking, using a long condenser, has been found to yield practically complete saponification of the esters. The saponified mixture is then titrated to neutrality with 0.25 N sulfuric acid solution, and the esters are calculated as a check on previous quantitative determination. The neutral solution is diluted with about 100 cc. of distilled water, and the alcohols are distilled off in about 75 cc. of water. The distillate is made up to 150 cc., thoroughly mixed, and a 25-cc. aliquot pipetted into a 500-cc. flask containing 100 cc. of sulfuric acid (1.35 specific gravity). Fifty cubic centimeters of 1 N potassium dichromate are now run in slowly from a buret with constant shaking and maintenance of the temperature at 10° to 15° C. The mixture is allowed to stand for 30 minutes after the last of the bichromate has been added. It is then diluted to 600 cc. and distilled, 250 cc. of distillate being collected in a flask immersed in a bath of water at 15° C. The 250 cc. of distillate are thoroughly mixed, and a 25-cc. aliquot is pipetted out for determination of methyl ethyl ketone by the Messenger method, as follows:

Fifty cubic centimeters of 1 N potassium hydroxide are measured from a cylinder into a 750-cc. Erlenmeyer flask. The 25-cc. aliquot from the 250 cc. of distillate is added, and 50 cc. of 0.1 N iodine are added from a buret with constant shaking. The mixture is allowed to stand at room temperature for about 20 minutes, after which the excess iodine is titrated with 0.05 N sodium thiosulfate using starch as the indicator. A blank must be run on the reagents, omitting the sample.

The approximate percentage of secondary butyl acetate by weight is calculated as follows:

$$\frac{(\text{cc. of thiosulfate for blank} - \text{cc. of thiosulfate for sample}) \times \text{normality of thiosulfate} \times 60 \times 0.01935 \times 100}{\text{weight of sample (10 cc.)}} = \%\ \text{secondary butyl acetate}$$

For the detection of other mixtures of the six typical groups of solvents discussed in this article, considerable ingenuity may be necessary, but a reliable opinion may be formed by comparison of the suggested properties, the volume-per cent distribution of the different alcohols as to boiling temperature being especially helpful in detecting mixtures or adulterations.

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Determining Flex Cracking in Treads

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A method for comparing the flex cracking properties of tread stocks on standard tires which permits the use of laboratory-mixed batches is presented. The method can be adapted to the testing of the effect of carcass construction, tread design, etc., on flex cracking. Comparative tests on tires of different make can also be made. Laboratory results check with information obtained from the road.

THE initiation and growth of cracks are obviously important factors in the service rendered by tire treads. Several machines have been designed to give comparative data on the flex resistance of various compounds, but in the experience of the present authors, none of the available methods for flex cracking comparisons are satisfactory, since predictions based upon them are not confirmed by road tests. As a result, a great deal of time and money has been wasted in developing compounds in the laboratory only to meet with failure on the road.

Any new method should permit a fairly accurate means of estimating the tendency towards initiation of cracks and a quantitative measure of cracks and cuts once formed. In addition, it should be adapted to studying the effect on cracking of various compounding ingredients such as age resisters, of varying such physical properties as modulus, hardness, etc., of cure, methods of mixing, tread design, tread contour, etc. The method should also permit the use of either laboratory- or factory-mixed stock. Before the present work was completed, it was found possible to make fairly accurate studies of various construction details of the tire carcass on tread cracking as well as to compare the products of various manufacturers.

Definite knowledge on formation of cracks due to flexing is necessary. On the other hand, in many types of service, tires are subjected to the action of sharp objects, such as cracked stones, which will cut the tread. Such cuts are not always harmful. If there is a tendency to grow, however, the cut will, in time, extend to the carcass and serious trouble result. Some tread designs will pick up stones, which may cut the undertread before they are expelled. Here again, in many cases, if the cuts do not grow to any extent, very little harm is done.

DESCRIPTION OF TEST

Obviously, the only way to test a tread that would answer all the above qualifications would be on a tire. A 7.00-18, 6-ply tire was used exclusively for the preliminary work on laboratory-mixed batches. Other sizes varying from a 5.25-18, 4-ply, to a 10.50-22, 12-ply, have been satisfactorily used.

One standard and three experimental sections can be tested on a single tire. The raw materials for the four batches, except the particular items to be tested, are always taken from the same lot. If possible, the major portion of the batches are mixed in a master batch in the factory. The batches, generally 10 pounds, are mixed on a 24-inch laboratory mill. The stock is sheeted off about 0.125 inch thick, and while still warm is cut and plied up to approximate the shape of the mold described in the next paragraph. Care must be taken not to trap air between the plies.

The plied-up stock is now ready to be molded. The mold used is merely a flat plate, machined out to a cavity which in cross section equals the contour and gage of a tubed 7.00 tread. The length of the cavity is about 3 inches greater than one-fourth that of a 7.00-18 tread. A standard sheet-metal cover is used. The

TABLE I. VARIATION IN AGING PERIOD[a]

DAYS IN AGING OVEN	CRACK GROWTH INDEX	NUMBER OF FLEX CRACKS
None	100	0
2	144	0
5	268	39
7	330	71
9	403	109
21	830	186

[a] Both crack growth index and number of independently formed flex cracks vary with the increase in time in the aging oven.

TABLE II. LIMITS OF TEST

PART 1. VARIATION IN LENGTH OF CRACKS IN A GIVEN SECTION[a]

UNAGED COMPOUND		LENGTH OF CRACKS IN INCHES[b] Gr. 1	Gr. 2	Gr. 3	Gr. 4	AVERAGE CRACK GROWTH	CRACK GROWTH INDEX	NUMBER OF FLEX CRACKS
						%		
A		0.37	0.43	0.40	0.36			
		0.39	0.41	0.38	0.42			
		0.46	0.41	0.41	0.41			
	Av.	0.41	0.42	0.40	0.40			
	% increase	64	68	60	60	63	100	None
B		0.35	0.35	0.35	0.38			
		0.35	0.36	0.33	0.34			
		0.35	0.33	0.34	0.33			
	Av.	0.35	0.35	0.34	0.35			
	% increase	40	40	36	40	39	62	None
AGED COMPOUND								
A		0.72	0.83	0.75	1.02			
		0.90	0.88	0.74	1.06			
		1.03	0.81	0.81	0.98			
	Av.	0.88	0.84	0.77	1.02			
	% increase	252	236	208	308	251	100	107(large)
B		0.70	0.69	0.64	0.81			
		0.80	0.74	0.65	0.76			
		0.73	0.54	0.56	0.65			
	Av.	0.74	0.66	0.62	0.74			
	% increase	196	164	148	196	176	70	61(small)

PART 2. VARIATION FROM TIRE TO TIRE

Test no.	CRACK GROWTH INDEX[c] Unaged	Aged
1	68	84
2	76	75
3	83	..
4	86	80
5	89	96
6	65	83
Av.	78	83

[a] Of two sections, the one with the larger average growth will generally show the greater variation from cut to cut within the section. Three cuts were placed in each of four grooves.

[b] Original length of each crack, 0.25 inch.

[c] On basis of standard as 100.

Actual percentage growth of both compounds on some tires was considerably greater than on others, but variation of crack growth index of the experimental on the basis of the standard as 100 is not extreme.

TABLE III. COMPARISON OF GROWTH OF CRACKS IN MOLDED AND EXTRUDED TREADS FROM SAME BATCH[a]

COMPOUND	UNAGED Molded	UNAGED Extruded	AGED Molded	AGED Extruded
	%	%	%	%
R	51	52	276	272
S	53	55	245	240

[a] Variation shown is no greater than would be expected from two halves of a tire with a single tread.

TABLE IV. ACCELERATOR COMPARISONS[a]

ACCELERATOR	BUREAU OF STANDARDS MACHINE: UNAGED Crack growth index	UNAGED No. of flex cracks	HOT ROOM Crack growth index	HOT ROOM No. of flex cracks	AGED Crack growth index	AGED No. of flex cracks	ROAD DATA Crack growth index
A	100	0	100	1	100	186 large	100
E	53	0	68	0	23	5 very small	67
F	41	0	...	.	...	...	62
B	40	0	36	0	24	97 very small	56
G	39	0	...	.	...	...	47

[a] All stocks were cured to optimum conditions as judged by cure analysis.

TABLE V. AGE RESISTER COMPARISONS

AGE RESISTER[a]	BUREAU OF STANDARDS MACHINE: UNAGED Crack growth index	HOT ROOM Crack growth index	AGED Crack growth index	AGED No. of flex cracks	ROAD DATA Crack growth index
A	100	100	100	90 large	100
C	93	..	86	66 large	98
B	81	..	60	74 small	90
D	76	82	72	26 small	89
E	78	78	83	32 small	79
F	77	62	70	66 very small	76
G	133	134	148	67 large	..

AMOUNT OF AGE RESISTER ON 100 RUBBER[b]	AGED Crack growth index
0.75	100
1.00	72
1.50	36

[a] Small amount of age resister.

[b] Increasing amount of age resister. Choice of age resister as well as amount used is of extreme importance in development of a tread stock.

TABLE VI. COMPARISON OF CARBON BLACKS FROM VARIOUS SOURCES[a]

BLACK	BUREAU OF STANDARDS MACHINE Crack growth index aged	ROAD DATA Crack growth index
B	82	80
C	79	88
D	102	97
A	100	100
F	116	113
E	104	116

[a] All batches were mixed in the factory under standardized conditions. The blacks were equally well dispersed. The laboratory data place the black in the same order as the road except that E and F are reversed.

mold and cover are heated in a press to approximately the temperature of the stock as it comes from the mill.

A sheet of parchment paper is placed on each side of the built-up tread slab. The slab is then placed in position in the mold, and the mold placed in a press and cooled under pressure.

The standard and three experimental sections are cut to one-fourth the length of a 7.00-18 tread. The sections are spliced to form a full tread, built into a tire, cured, and are ready for test.

As samples from factory-mixed batches can be used as well as laboratory batches, all desired variations in factory processing can be studied. By using laboratory-mixed batches, it is possible to obtain information on materials available only in small quantities. The use of both factory- and laboratory-mixed batches permits the study of all available materials. Factory-mixed experimentals are checked against factory-mixed standard and laboratory-mixed experimentals against laboratory-mixed standard.

Molded treads have been checked against extruded treads and found to be equal in resistance to cracking. In testing this point, the stock in a given test was from the same factory batch. Part of the batch was held out for the preparation of two molded sections and the rest extruded in the regular way. These two molded sections were spliced to make half a tread. The other half was taken from the extruded ribbon. Crack growth on the extruded and molded tread from the same batch was identical.

After the tire has been cured, a series of 12 cuts is made with a special tool in the tread design in each of the stocks at definite points, relative to the design. The blade of the knife is approximately 0.031 inch thick and is exactly 0.25 inch long. The knife is fitted with a shoulder so that the blade cannot penetrate the surface more than 0.016 inch. The cut formed is 0.25 inch long by 0.016 inch deep. After the tire has been run, the length of the cuts is measured. The increase over 0.25 inch multiplied by four gives the percentage increase. The average increase of the 12 cuts in a given section is used on the crack growth percentage for the section.

After the cuts have been made, the tire is mounted and inflated as desired, generally using loads and inflations recommended by the Tire and Rim Association. The tire is then run on a Bureau of Standards test wheel at 45 miles per hour 2000 miles at room temperature, the tire is removed, and the increase in length of the cuts is recorded. Examination may reveal independently formed flex cracks with some tread compounds.

In the first part of the work on this problem, the tires, after the original 2000 miles, were replaced on the machine, using the same

TABLE VII. TESTS RUN ON 9.75-22 TIRES

	BUREAU OF STANDARDS MACHINE				
	UNAGED		HOT ROOM		
COMPOUND	Crack growth index	No. of flex cracks	Crack growth index	No. of flex cracks	ROAD DATA[a]
C[b]	100	36	100	Very numerous (not counted)	Cracked badly
D	43	7	31	36	No cracking

[a] Results from tires in service in various parts of the country. Half-and-half tread tires.

[b] It was necessary to remove some of the tires from service because of excessive cracking in section C.

TABLE VIII. FLEX-CRACKING COMPARISON OF AGE RESISTERS ON BUREAU OF STANDARDS MACHINE AND ON CRUSHED STONE ROADS[a]

			STONE ROAD			
	BUREAU OF STANDARDS MACHINE		UNAGED		AGED	
AGE RESISTER	Unaged	Aged	In grooves	Radial in side-wall	In grooves	Radial in side-wall
M	1	90 large	14	3	70	69
N	9	66 v. small	5	1	31	5

[a] Average number of flex cracks of four tires on both road and Bureau of Standards machine. The tires were run 6000 miles.

TABLE IX. EFFECT OF CURE VARIATION[a]

	UNAGED		AGED	
CURE	Crack growth index	No. of flex cracks	Crack growth index	No. of flex cracks
A (optimum cure)	100	0	100	290
B (over-cure)	114	0	122	475

[a] Corresponding road data are not available.

TABLE X. TREAD DESIGN COMPARISON

	BUREAU OF STANDARDS MACHINE		
	CRACK GROWTH INDEX		
TREAD DESIGN	Unaged	Aged	ROAD DATA Crack Growth Index
A	100	100	100
B	40	62	77
C	88	79	[a]
D	100	100	[a]
E	102	136	[a]
F	126	92	[a]
G	149	164	[a]

[a] Crack growth index relationship of the aged tires not the same as on the unaged tires. Facilities did not permit testing on the road.

TABLE XI. VARIED THICKNESS OF UNDERTREAD[a]

	UNAGED		AGED	
UNDERTREAD	Crack growth index	No. of flex cracks	Crack growth index	No. of flex cracks
Thick	100	0	100	77
Thin	178	0	183	245

[a] Comparison given merely to show how much cracking can be varied using same compound.

TABLE XII. EFFECT OF DIRT AND GRIT ON TREAD CRACKING

	NUMBER OF FLEX CRACKS	
TREAD	Unaged	Hot room
X	7	10
Y[a]	Very numerous (not counted)	Very numerous (not counted)

[a] Three per cent of grit from black and dirt from various places in the factory added to tread Y. Test used as example in a campaign against dirt.

initial load and inflation, and were run an additional 1500 miles. In this second phase, however, the temperature of the room was maintained at 46° C. (115° F.). Crack growth percentage and number of independent flex cracks were again recorded.

As the work progressed, it was found that the test was not drastic enough and it became necessary to develop an aging procedure. The tires, after running the initial 2000 miles, are removed from the rim and hung on a truck which is placed in an oven maintained at 82° C. (180° F.). The tires are left in the oven for 16 hours and are then removed for 8 hours. This cycle is repeated seven times. It is felt that the alternate heating and cooling is more nearly like natural aging than continued heating would be. The tires are then run for 1500 miles at room temperature as described above. This modified test brings out enormous differences between various stocks both in growth of cracks and flex cracks. However, some tires are still tested in the hot room as a check.

The method has been checked by hundreds of tests in the field. In the field tests, half tread tires were built. Tests were run on the test cars, mileage accounts, and the regular commercial accounts, and in various sections of the United States. Without exception, stocks that show low crack growth, and few if any flex cracks after the aging period, will perform better on the road as far as cracking is concerned than those that show a larger number of cracks and greater crack growth on the indoor test.

A still further check on the laboratory procedure is to age tires with half-and-half treads for 7 days, as described, without previously running them on the wheel. If such tires are then run on a gravel or crushed stone road, the cracking tendencies will check the results obtained on the indoor machine although percentage relationship will vary. Furthermore, such tires have all the appearance of having been run for a season or so in a region where crushed stone roads predominate.

For the most part, it is unnecessary to run more than one tire where the standard stock is on the same tire as the experimentals. Where comparisons are to be made from tire to tire, however, it is always advisable to run parallel tests.

EXPERIMENTAL DATA

In Tables I to XII, the basic compounds are the same in any given table although the compounds are not the same from table to table. Percentage relationships from comparisons run on the road and in the laboratory are not exact but for the most part are close approximations and are almost invariably in the same direction.

Comparisons of increase in length of the cuts are carried under the heading "Crack Growth Index." In all cases, the growth of the cuts in the standard section or tire is considered as 100. Values less than 100 mean that the cracks grew less than the standard, while those larger than 100 indicate greater growth. The number of independent cracks formed is listed under "Flex Cracks." In most cases, the approximate size of the independent cracks is indicated. Where flex cracks are not shown on road test tires, none were in evidence.

Where data are listed under the heading "Hot Room," it is to be understood that the tires have first been run at room temperature. "Aged" tires have been run at room temperature first. All percentages are calculated from the original 0.25-inch cut and are listed in whole numbers.

No attempt has been made to compare the results obtained with those from various flexing machines available in the laboratory. Furthermore, it is not the interest of the authors to show how to compound to obtain maximum resistance to tread cracking.

Except where definitely indicated as "Road" the data are from tires run on the Bureau of Standards machine.

CONCLUSIONS

A practical method of studying tread cracking in the laboratory which gives data comparable with field service results has been presented. The method is not a costly one and permits the investigation of a large number of factors that have a bearing on crack growth and flex cracking.

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FORMATION OF IODINE PENTAFLUORIDE. Iodine pentafluoride is formed when iodine is brought into contact with fluorine, but is invariably in admixture with the heptafluoride. According to O. Ruff [*Chem.-Ztg.*, 58, 449 (1934)] compounds with a lower proportion of fluorine could not be detected. In the presence of oxygen, however, or when the pentafluoride was exposed to moisture, iodine oxyfluoride (IOF_3) could be detected.

Determination of Small Amounts of Glucose, Fructose, and Invert Sugar in Absence and Presence of Sucrose

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The method depends upon the oxidation of potassium ferrocyanide to potassium ferricyanide by ceric sulfate after the ferricyanide has been reduced by the sugars in alkaline solution. The end point of the titration is obtained by using alphazurine G as the indicator. This dye is very sensitive in acid solution to any excess of ceric sulfate, but is not affected as long as any ferrocyanide remains in the solution.

The proposed method was developed and used with pure sugar solutions. In addition, its accuracy was examined when certain buffers and other impurities were present in the reduction mixture. Chlorides and tartrates have practically no effect on the reduction of the ferricyanide by invert sugar, while acetate and citrate buffers slightly affect the reduction. The influence of these buffers may be measured and proper correction made.

IN CONNECTION with a study of the hydrolysis of very dilute sucrose solutions by invertase, it was necessary to make many determinations of the small amounts of invert sugar (0.5 to 2.0 mg.) which were formed. The methods given in the literature as standard for invert sugar determination were examined and found either inconvenient or inaccurate for making many routine determinations. Colorimetric methods were discarded because of the difficulty in manipulation and in preparing standards of the same composition as the unknown sugar solution. In the case of the copper reduction methods, the minute amounts of cuprous oxide could not be measured easily with sufficient accuracy. The Hagedorn-Jensen (*3*) method, while sufficiently precise, requires very careful manipulation. In that method, alkaline potassium ferricyanide is added to the reducing sugar and the unused ferricyanide is determined by iodine-thiosulfate, the amount of ferricyanide reduced by the sugar being then obtained by difference. Very careful measurements must be made of the volume of ferricyanide added to the reduction mixture, since small errors are apt to double in the final determination of the volume of ferricyanide used; and, in addition, the thiosulfate solution requires frequent standardization.

The present method is comparable to the Hagedorn-Jensen method in accuracy and has the advantage of being a direct method, requiring no great skill in manipulation, and using solutions which are very stable. It determines the reducing sugar by oxidation in alkaline solution with potassium ferricyanide, also employing a modification of the method originally suggested by Gentele (*2*). The ferrocyanide formed in the reaction is titrated, after acidifying with sulfuric acid, with a standard solution of ceric sulfate. Furman and Evans (*1*) have shown that ferrocyanide can be oxidized quantitatively by ceric sulfate. Because of the small quantities of reducing sugars in the reduction mixtures, the amounts of ferrocyanide and ceric sulfate were not sufficient to give sharp color changes at the end point in such titrations. This difficulty is met by the use of an inside indicator, alphazurine G, which is extremely sensitive in acid solution to the least excess of ceric sulfate.

Materials and Solutions

Alphazurine G. This dye was a product of the National Aniline Co. It is listed in the Color Index[1] as No. 712 and is supposed to have the same composition as the following: Neptune Blue, BG, Badische Co.; Brilliant Acid Blue V, Bayer Co.; and Azure Blue V, Kalle Co. Its color change in the presence of ceric sulfate as oxidant is from yellowish green to brown and is very distinct and marked when viewed under a white light, such as is given by a 100-watt stereopticon bulb in an ordinary study lamp. (Alphazurine G is suitable as an indicator for either day or night work, since the color change is accentuated by a white light.) The brown color is not permanent, lasting about 3 minutes when pure potassium ferrocyanide is titrated and from 0.5 to 3 minutes if sugar oxidation products are present in the solution. The color change is so pronounced that it can be detected by any one who has observed it a few times in practice, even with an excess of half a drop (a drop being about 0.015 cc.) of 0.01 *M* ceric sulfate.

Five drops of a 0.4 per cent water solution of the dye as obtained from the National Aniline Co., without further purification, were usually used in each titration. Its stability was tested by titrating definite volumes of potassium ferrocyanide solution with ceric sulfate solution, using solutions of alphazurine G which had been prepared at various times during a period of over 3 years. Practically no difference could be noted.

The oxidation products of the sugars apparently have no effect on the ceric sulfate in this titration. Potassium permanganate may be used to titrate the reduction mixture obtained when reducing sugars are oxidized by alkaline potassium ferricyanide, using alphazurine G as indicator, in the same manner as ceric sulfate. The color change of the indicator is not as good as with ceric sulfate; hence, potassium permanganate was used only with pure glucose in the standardization of the ceric sulfate. The color change of the indicator when potassium ferrocyanide solution is titrated is just as good with permanganate as with ceric sulfate.

Ceric Sulfate. A stock solution of ceric sulfate was prepared from cerous oxalate and standardized against Bureau of Standards sodium oxalate, according to directions given by Willard and Young (*6*). About 6 liters of approximately 0.01 *M* ceric sulfate were prepared by diluting 750 cc. of the stock solution of ceric sulfate (0.08122 *M*) and 300 cc. of concentrate sulfuric acid to 6 liters. This dilute solution was standardized against Bureau of Standards glucose by comparison with results obtained when standard potassium permanganate was used to titrate the ferrocyanide formed in the reduction mixture, and against pure potassium ferrocyanide.

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[1] Published by the Society of Dyers and Colourists, 30 Pearl Assurance Buildings, Bradford, Yorkshire, England.

In standardization of ceric sulfate solution against glucose the procedure detailed below was followed. The sugar sample contained 1.5 mg. of glucose in 100 cc. Some reduction mixtures, after acidifying with sulfuric acid, were titrated with ceric sulfate, others with standard potassium permanganate. The concentration of the potassium permanganate as determined by titrating against Bureau of Standards sodium oxalate was 0.00931 *N*.

TABLE I. STANDARDIZATION OF CERIC SULFATE AGAINST GLUCOSE

DATE	CERIC SULFATE SOLUTION REQUIRED	0.00931 *N* POTASSIUM PERMANGANATE REQUIRED
	Cc.	*Cc.*
Nov. 14, 1932	4.09	4.47
Dec. 19, 1932	4.085	....
March 18, 1933	4.08	....

The concentration of the ceric sulfate, calculated by comparison with the permanganate values, using an inverse proportion—X : 0.00931 :: 4.47 : 4.085—was 0.01018 *N*.

In standardization of the ceric sulfate solution against pure potassium ferrocyanide, Baker's C. P. analyzed, the sample of potassium ferrocyanide, $K_4Fe(CN)_6.3H_2O$, was accurately weighed, dissolved in water, and diluted to 250 cc. This solution was then poured into a buret and 15 cc. were withdrawn as used into a 400-cc. beaker, diluted to about 95 cc., and acidified with 5.7 cc. of 4.3 *M* sulfuric acid. It was titrated at once with the ceric sulfate solution, using 5 drops of alphazurine G, 0.4 per cent, as indicator. Some titrations were made with standard potassium permanganate as the oxidant and alphazurine G as the indicator.

TABLE II. STANDARDIZATION OF CERIC SULFATE AGAINST POTASSIUM FERROCYANIDE

DATE	POTASSIUM FERROCYANIDE	CERIC SULFATE SOLUTION Found	CERIC SULFATE SOLUTION Calculated[a]	0.00931 *N* $KMnO_4$ SOLUTION Found	0.00931 *N* $KMnO_4$ SOLUTION Calculated[a]
		Cc.	*Cc.*	*Cc.*	*Cc.*
Dec. 20, 1932	0.3622 gram in 250 cc. at room temp.	5.135	5.09	5.56	5.52
Mar. 5, 1933	0.3691 gram in 250 cc. at 20° C.	5.24	5.07	..	..

[a] Calculated for 15 cc. of a constant weight of 0.36 gram of potassium ferrocyanide in 250 cc.

From the above data, the concentration of the ceric sulfate by comparison with the permanganate values—X : 0.00931 :: 5.52 : 5.08—was calculated as 0.01013 *N*. Assuming that the potassium ferrocyanide is pure $K_4Fe(CN)_6.3H_2O$, the concentration of the ceric sulfate was found to be—X : 0.003409 :: 1000 : 338.6 or 0.01006 *N*.

Since the ceric ion undergoes a decrease of 1 in valence when used as an oxidant, normal solutions will be the same as molar and the above concentrations may be expressed as 0.01018 *M*, 0.01013 *M*, and 0.01006 *M*. This 0.01 *M* ceric sulfate solution used in most of the experiments has remained stable for over 4 months. The 0.002 *M* solution of ceric sulfate used in the modified method was prepared by diluting 100 cc. of the 0.01 *M* ceric sulfate to 500 cc. at 25° C.

BUFFER SOLUTIONS. The pH values of the buffer solutions were determined electrometrically.

POTASSIUM FERRICYANIDE. Merck's C. P. crystals were used without further purification. Eight grams of the crystals were weighed, dissolved in water, and diluted to 1 liter at 20°. This solution was poured into a Pyrex bottle, the outside of which had received two coats of black paint, and was kept in a dark room. When required, the solution was withdrawn by means of a pipet and transferred to a buret which was also kept in a dark room except when the ferricyanide was being withdrawn. Under these conditions, the potassium ferricyanide solution remained stable for at least 6 weeks.

FRUCTOSE. The fructose was prepared from cane sugar by the method of Jackson, Silsbee, and Proffitt (*4*), and recrystallized from alcohol until a 2 per cent solution gave a reading of −4.23° at 25° C. using a 200-mm. tube and mercury light (5461 Å.). According to Vosburgh (*5*), the rotation value of a 2 per cent pure fructose solution under the same conditions is −4.18°.

GLUCOSE. Bureau of Standards, standard sample 41.

SUCROSE. Bureau of Standards, standard sample 17.

DESCRIPTION OF METHOD

The following procedure provides for the reduction of alkaline potassium ferricyanide by amounts of glucose, fructose, and invert sugar varying from 0.5 to 2.0 mg. in a total volume of 125 cc. and the titration of the ferrocyanide formed with ceric sulfate, using alphazurine G as the indicator.

Five cubic centimeters of potassium ferricyanide solution (8 grams per liter) were placed in a flat-bottomed 125-cc. Pyrex flask containing 15 cc. of water and 5 cc. of sodium carbonate solution (140 grams of $Na_2CO_3.H_2O$ per liter). The flask and its contents were allowed to stand at 25° for 4.5 minutes. A 100-cc. sample of the sugar solution was added by means of a pipet 1.5 minutes before placing in the bath at 80° C. (Sugar solutions at approximately 25° C. were used to make up the sugar sample to a volume a little greater than 100 cc. so that 100 cc. contained the required amount of sugars.) A small glass stirring rod was inserted in the reduction mixture, which was stirred and then covered with a small glass funnel, the stem of which had been removed. The reduction mixture was placed in a water bath kept at 80° C. and stirred for 1 minute, usually beginning about 10 seconds after placing in bath. After 30 minutes, it was removed to a 25° bath, allowing 30 seconds for making the change, and after about 5 seconds was stirred for 1 minute and left for 4.5 minutes. (The entire procedure required 35 minutes.)

After cooling, the mixture was poured into a 400-cc. beaker. The flask was rinsed three times with 5-cc. portions of distilled water which also were added to the beaker. The contents of the beaker were next acidified with 5.7 cc. of 4.3 *M* sulfuric acid and then titrated with 0.01 *M* ceric sulfate, using a Folin microburet to which a jet tube had been attached which delivered drops of approximately 0.015 cc. The ceric sulfate was added in a rapid succession of drops, with constant shaking, to within about 0.1 cc. of the end point. Five drops of a 0.4 per cent alphazurine G solution were added and the titration was continued by adding the ceric sulfate a drop or fraction of a drop at a time, shaking after each addition, until the color changed from yellowish green to brown.

The titration with ceric sulfate is apparently an extremely rapid reaction and hence permits the ceric sulfate to be added slowly or rapidly without affecting results.

DETERMINATION OF GLUCOSE, FRUCTOSE, AND INVERT SUGAR. Different amounts of sucrose may be used, as the slight effect on the ferricyanide appears in the blank and can be measured. In order to have the proper concentration of sugars, it was found convenient to prepare the solutions as follows:

At 25° C. 40 cc. of the glucose solution contained 1 mg. of glucose.

The fructose solution was prepared in the same way as the glucose solution.

Exactly 0.25 gram of glucose and 0.25 gram of fructose were dissolved in water and diluted so that 20 cc. contained 1 mg. of invert sugar.

The sucrose solution was prepared so that 1 cc. contained 2 mg. of sucrose.

The sugar solutions were often prepared approximately 24 hours before being used.

The volume of 0.01 *M* ceric sulfate in Table III, obtained by subtracting the blank for the reagents from the mean of many determinations, represents definite values for the weights of the sugars as given, under the conditions of the reduction. An accuracy of 0.3 to 0.4 per cent was readily attained with 1 mg. of these reducing sugars. Sucrose does not seem to affect the reduction, since the increase in the amount of ceric sulfate solution required when sucrose is present is fairly constant and is approximately 0.02 cc. for 18 mg. of sucrose. The reduction of the potassium ferricyanide by the invert sugar is practically constant and equivalent under the conditions of the reduction to about 0.545 cc. of the 0.01 *M* ceric sulfate solution per 0.2 mg. of invert sugar.

TABLE III. DETERMINATION OF GLUCOSE, FRUCTOSE, AND INVERT SUGAR BY PROPOSED METHOD

WEIGHT OF SUGAR PER 100 CC.		0.01 M CERIC SULFATE REQUIRED	
Glucose	Sucrose	Volume	Calculated for 0.2 mg. of invert sugar
Mg.	*Mg.*	*Cc.*	*Cc.*
0.5	0	1.365	...
1.0	0	2.735	...
2.0	0	5.44	...
0.5	18	1.385	...
1.0	18	2.75	...
2.0	18	5.47	...
Fructose			
0.5	0	1.37	...
1.0	0	2.75	...
2.0	0	5.48	...
0.5	18	1.395	...
1.0	18	2.78	...
2.0	18	5.50	...
Invert sugar			
0.5	0	1.37	...
1.0	0	2.745	...
1.2	0	3.28	0.535
1.4	0	3.83	0.550
1.6	0	4.37	0.540
1.8	0	4.915	0.545
2.0	0	5.46	0.545
0.5	18	1.395	...
1.0	18	2.765	...
1.2	18	3.305	0.540
1.4	18	3.855	0.550
1.6	18	4.40	0.545
1.8	18	4.94	0.540
2.0	18	5.475	0.535

The sodium carbonate and potassium ferricyanide solutions need not be accurately measured into the reduction flask. The sulfuric acid was added to the reduction mixture from a measuring pipet which was filled to the mark and then allowed to empty. Variation of 1 cc. in the amount of acid gave no noticeable effect.

Practically no effect on the results was noted when the temperature of the bath fluctuated from 80° to 79° C.

The alkali had no effect on the sugars when the order of adding the sugar sample and the potassium ferricyanide was reversed. The sugar solution may be allowed to stand as long as 10 minutes in contact with the alkaline solution before adding the potassium ferricyanide solution and continuing with the reduction.

The volume of the reduction mixture can be varied from 125 to 100 cc. without affecting the results to any extent.

A decrease in the amount of reduction was noted when the reduction mixture was allowed to remain in the cooling bath at 25° C. for 9.5 minutes instead of the usual 4.5 minutes. The alkaline mixture seemed much more susceptible to change than when acidified.

Sugar solutions mixed with sodium carbonate, potassium ferricyanide, and acetate buffer solutions showed practically no change when allowed to stand for 5 minutes, and only a trace of an effect was observed when they stood for 10 minutes. This makes it unnecessary to follow rigidly the direction for adding the sugar sample and the potassium ferricyanide solution to the reduction flask.

MODIFIED METHOD

When amounts of reducing sugar approximating 0.1 mg. are to be determined, a ceric sulfate solution more dilute than 0.01 M should be used in order to obtain comparable accuracy. However, when a very dilute ceric sulfate solution is used, the sharpness of the indicator change is affected because of the large volume (about 150 cc.) of the titration mixture. In order to overcome this difficulty the method was modified by selecting 20 cc. as the volume of the reduction mixture and carrying out the reduction in a special tube. This gives a reduction mixture of less than 40 cc. for titration and 0.002 M ceric sulfate solution may be used.

This modified method was applied to the determination of amounts of glucose as small as 0.05 mg. The color change of the alphazurine G is not as permanent as with the 0.01 M ceric sulfate, but with care it can be distinguished very sharply with 1 drop of 0.002 M ceric sulfate solution. An accuracy of less than 0.8 per cent may be easily attained in the determination of these small amounts of glucose. (For details about this modified method, the reader is referred to the author's thesis.)

Obviously, this modified method may be used with amounts of reducing sugar in the range of the previous method (from 0.5 to 2.0 mg.). However, it is not readily applicable in a series of experiments where the volume of the sugar sample is varied greatly in order to maintain the amount of reducing sugar within fixed limits—determination of invert sugar between 2.5 and 10 per cent of the hydrolysis when sucrose solutions varying from 0.02 to 2.0 per cent in concentration are hydrolyzed with invertase.

INFLUENCE OF POSSIBLE INTERFERING SUBSTANCES

Since sugar solutions usually contain buffers or other foreign substances, the accuracy of the determination was examined when certain of these substances were present. By adding such a substance to the reduction flask, carrying out the reduction in the presence of definite weights of sugars, and then subtracting the blank for the reagents including the foreign substance, the total effects of the sugars and foreign substance in terms of cubic centimeters of ceric sulfate are obtained. By comparing these results with the values in Table III for the corresponding weights of the sugars, any influence of the foreign substance is readily apparent.

Impurities apt to be present in sugar solutions which are able to influence the reduction of alkaline ferricyanide (or affect the titration of the ferrocyanide with ceric sulfate and alphazurine G) must either be removed or their effect measured and proper correction made.

CHLORIDES AND TARTRATES. These substances were found to be without effect on the reduction of ferricyanide when as much as 10 cc. of 0.1 M potassium chloride or sodium tartrate was added to the reduction mixture.

ACETATE AND CITRATE BUFFERS. Both acetate[2] and citrate buffers with pH values of 3.5 and 4.5 increase the reduction of potassium ferricyanide by invert sugar and this increase is not given by the blank for the reagents (including the buffer). Furthermore, this increase seems to be proportional to the amount of invert sugar present. The citrate buffer at pH 5.75 likewise gives an increase in the reduction, but this increase is practically taken care of by the blank and does not affect the reduction of the ferricyanide by the sugar.

TABLE IV. INCREASE IN CERIC SULFATE REQUIRED IN PRESENCE OF BUFFER SOLUTIONS[a]

WEIGHT OF SUGAR		EXCESS 0.01 M CERIC SULFATE REQUIRED				
		ACETATE BUFFERS		CITRATE BUFFERS		
Invert sugar	Sucrose	pH 4.4	pH 4.59	pH 3.5	pH 4.5	pH 5.75
Mg.	*Mg.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*
0.5	18	0.02	0.015	...	...	0.005
1.0	18	0.045	0.045	0.035	0.040	0.005
1.2	18	0.055	0.080	...	...	0.020
1.4	18	0.070	0.090	...	...	0.010
1.6	18	0.080	0.100	...	...	0.015
1.8	18	0.090	0.110	...	...	0.020
2.0	18	0.100	0.135	0.110	0.115	0.025

[a] In each case 10 cc. of buffer were measured into reduction flask and the reduction carried out in the regular way, total volume of reduction mixture being 125 cc.

PROBABLE APPLICATIONS

The proposed method provides for the determination of small amounts of reducing sugars and because of its simplicity, accuracy, and stability of solutions, may find application in both physiological and general sugar chemistry. By increasing the concentration of the potassium ferricyanide and ceric sulfate solutions, the range of the method as given in Table III may be considerably extended (unpublished data). The period of heating and temperature may be varied to suit specific conditions. Thirty minutes and 80° C.

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[2] Two acetate buffer solutions were used: one at pH 4.59 and one at pH 4.4. The one at pH 4.59 was made from sodium acetate and acetic acid and the one at pH 4.4 from sodium hydroxide and acetic acid. The experiments using the buffer at pH 4.4 were run several months after those with the buffer at pH 4.59 and all solutions had been remade except the ceric sulfate. Three citrate buffers with pH values of 3.5, 4.5, and 5.75 were used. These buffers were made from solutions of citric acid, sodium hydroxide, and hydrochloric acid.

were selected because preliminary experiments indicated that the maximum effect of the reducing sugars with little reduction of sucrose was attained under these conditions.

The use of alphazurine G as an indicator for ceric sulfate may find application in the analytical determination of various compounds. Titrations with ceric sulfate and alphazurine G as indicator give constant results with ferrous sulfate, hydroquinone, and potassium ferrocyanide. In the case of potassium ferrocyanide, the results are practically unaffected by phosphoric acid, malic acid, succinic acid, and ethyl alcohol.

ACKNOWLEDGMENT

The writer wishes to express his sincere appreciation to John M. Nelson, Department of Chemistry, Columbia University, for the kindly criticism and encouragement given during the progress of this work. It has been a true pleasure and inspiration to be under his guidance and for his friendly interest and coöperation the author is deeply grateful.

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The Mackey Oil Tester

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INDUSTRY annually suffers large losses from spontaneous combustion. Despite the seriousness of the hazards encountered in the use of unsaturated oils, satisfactory methods of predetermining the action of such oils have not yet been developed.

Ordinarily, a questionable oil is tested by exposing it to the air on fibers in a heated bath. The temperature rise within a specified time is used as an indication of the degree of hazard of the oil. In the Mackey tester, which is used to the greatest extent, 14 grams of the oil are intimately worked into 7 grams of cotton. This material, with a thermometer in the middle, is then put into a wire gauze and the whole inserted in a combustion chamber, which is merely a water-jacketed container of specified size kept at 100° C. in which arrangement for a continuous current of air is provided by means of tubes inserted in the cover. Any oil which shows a temperature of over 100° C. at the end of 1 hour or over 200° C. at the end of 2 hours is arbitrarily considered as dangerous; results thus obtained seem to agree with practice.

In order to study the action of the tester, samples were carefully prepared in identical manner and subjected to the test. Figure 1 shows a typical curve. Between the times of 95 and 120 minutes there is a temperature rise of 98° or 3.9° C. per minute.

TABLE I. TESTS WITH CORN OIL

TEMPERATURE AT END OF First hour	Second hour	MAXIMUM TEMPERATURE	TIME TO REACH MAXIMUM
° C.	° C.	° C.	Min.
95	185	205	100
97	180	202	93
100	175	192	100
96	173	178	110
96	170	190	100
96	170	174	110
105	173	190	100
99	140	152	100
95	180	198	100
95	183	198	103
96	171	187	100
95	190	207	110
95	190	206	100
99	165	182	100
104	200	225	100
104	182	203	100

Considerable discrepancies are frequently encountered in the temperature of the samples when duplicates are tested, as is illustrated by the results of the tests on corn oil. No matter how carefully the oil is dispersed through the cotton, there is some difference between the samples. Moreover, factors such as the depth at which the thermometer is inserted, its position in relation to the center of the wire cylinder, the condition of the cylinder itself, whether new or covered with an oily film, and the height of the water bath—all cause variable results, that frequently cause the rise in temperature to vary by as much as 10 minutes. In the case of the oil in Figure 1, this would mean a temperature difference of 39° C. on the steep part of the curve. It may thus happen that a dangerous oil may be considered safe and *vice versa*.

In making these tests, if the oil is not extremely inflammable, a maximum temperature is reached after a quick rise. If the temperatures of the samples are observed only at the suggested times of 1 and 2 hours, it may well happen that the maximum may have been passed and a low temperature would be recorded. A dangerous oil would thus be passed as safe.

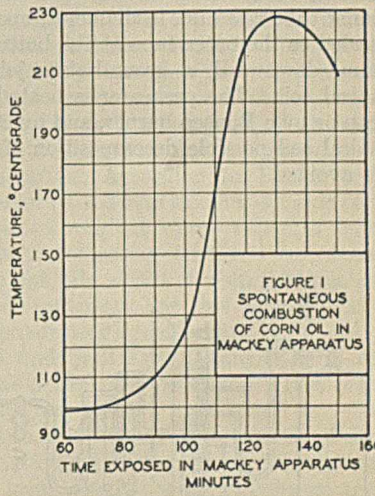

FIGURE 1
SPONTANEOUS COMBUSTION OF CORN OIL IN MACKEY APPARATUS

In order to make this test more reliable, some standard other than the arbitrary "not over 100° in the first or over 200° C. at the end of the second hour" should be considered. In the many tests conducted, it has been found that the time required to reach a maximum temperature gives better checks and is of much more value in determining the future action of an oil than the usual standard. The actual maximum temperature is of some value in appraising an oil, but considerable discrepancies occur in the numerical values.

It is apparent that the ruling factor to be considered in judging the safety of an oil is the time required to attain the maximum temperature, and not merely the temperature at the expiration of 1 or 2 hours.

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Microanalytical Determination of Carbon and Hydrogen

A Simplified Method

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SINCE the introduction of organic microchemical methods at New York University (*1*) in 1925, the interest in these procedures has widened considerably (*21*, *33*), notably at the University of Pittsburgh, Coal Research Institute, Pittsburgh, Merck's Research Laboratory, Rockefeller Institute, College of Physicians and Surgeons, Columbia University, Loyola College, Baltimore, and elsewhere. A simplified method for the microdetermination of carbon and hydrogen is described below, incorporating numerous improvements.

Apparatus

In the simplified apparatus the use of air has been eliminated from the combustion train and the gasometer is replaced by the use of a reduction valve on the oxygen tank, *a*, and a Pregl precision stopcock (*28*). Traces of organic matter and hydrogen found in many sources of oxygen are eliminated by passing the gas through a preheater, *b*, devised by Böck and Beaucourt (*5*) and modified by Whitman (*36*). It consists of two quartz tubes, one inside the other, the outer one, which is filled with coarse copper oxide or platinum asbestos, being 100 mm. long and 10 mm. in diameter. The inner tube is 3 mm. in diameter, open at the upper end and sealed to the outer tube at the bottom, thence extending 40 mm. downward, a ground-glass joint attaching it to the spiral coil. The preheater is heated by an electric heating cap or by a Bunsen burner, and by cooling the oxygen in the spiral coil possible decomposition of the rubber connections is avoided.

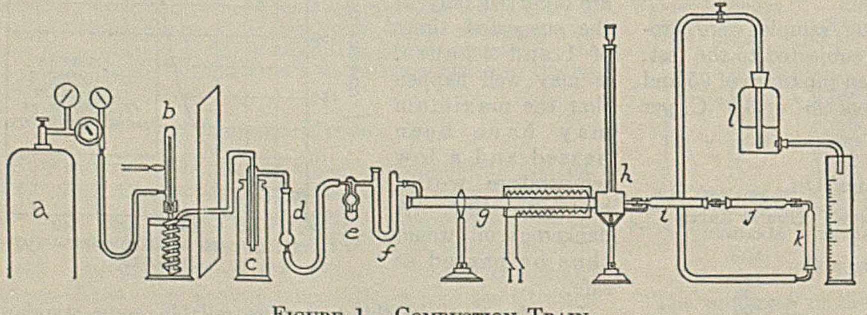

Figure 1. Combustion Train

a. Oxygen tank
b. Preheater
c. Pressure regulator
d. Ascarite tube
e. Bubble counter
f. Drying tube
g. Combustion tube
h. Heating mortar
i. Water-absorption tube
j. Carbon dioxide–absorption tube
k. Drier
l. Mariotte flask

The pressure regulator, *c*, is the usual one described by Pregl (*28*). The side-arm outlet is bent at right angles directly into an ascarite absorption tube, *d*, which also removes moisture, preventing dilution of the alkali in the bubble counter.

The bubble counter, *e*, and drying tube, *d*, are larger than those used by Pregl (*29*). Having a total length of 150 mm. and a diameter of 12 mm., the anhydrone filling needs replacement less often. By connecting the capillary glass arm of the drying tube directly with the side arm of the combustion tube, Pregl's (*29*) capillary tubes and rubber connections are eliminated.

The combustion tube, *g*, is of quartz, 50 cm. long, with a side arm (*24*) of capillary glass of the same dimensions as the arm of the bubble counter. It is filled with the Universal filling devised by Pregl (*30*) and closed by a tight-fitting cork, removable for the introduction of the sample without disconnecting the oxygen stream.

As constant-temperature device, *h*, for the lead superoxide, the improved mortar according to Verdino (*34*) is employed using *p*-cymene as the constant-boiling liquid. A copper rod, protruding from the mortar, heats the capillary constriction on the water absorption tube. The permanent filling is heated by Flaschenträger's (*13*) electric furnace, and a Bunsen burner serves as the movable burner.

Pregl absorption tubes with a hollow ground-glass stopper and well-fitting copper wires suggested by Boetius (*8*) and modified by Whitman (*27*), to reduce the absorption of moisture and carbon dioxide during weighing time, are used. The water absorption tube, *i*, is filled with a coarse and fine layer of anhydrone, previously treated with carbon dioxide, with thick cotton plugs on each side of the layers. The carbon dioxide absorption tube, *j*, contains a 10-mm. layer of anhydrone and is otherwise filled completely with ascarite. They are connected head to head, the water absorption tube next to the combustion tube, with specially impregnated seamless rubber tubing.

The Boyle-Mariotte flask, *l*, is similar to Pregl's (*31*) except for a stopcock on the gas inlet tube, as employed by Lieb. A drier, *k*, filled with anhydrone, attaches it to the absorption tubes.

A similar Mariotte flask is kept in the balance room, serving as an aspirator (*27*) to rinse the oxygen-filled absorption tubes with air while they are cooling to balance room temperature. The air is purified by passing it through a gas wash bottle containing sulfuric acid to remove organic matter, and a purifying tube containing ascarite and anhydrone is connected with the wash bottle. The free end of the water absorption tube is connected with the purifying train and the carbon dioxide absorption tube to the drier of the Mariotte flask, so that the air flows in the same direction as the oxygen during the combustion, bringing the temperature of the absorption tubes quickly down to balance room conditions.

Procedure

1. The capillary ends of the ascarite tube are cleaned with cotton, the copper wires inserted, and the tube is wiped according to Pregl's directions, placed on the rack for 10 minutes, transferred to the balance, and 5 minutes later weighed to 0.01 mg. It is reweighed after 5 minutes. The anhydrone tube is wiped and weighed in the same manner.

2. After removal of the copper wires, the absorption tubes are connected head to head by a rubber tubing 20 mm. long, another 15 mm. long being attached to the anhydrone tube, the rubber tubings having been moistened previously with a trace of glycerol. The absorption tubes are then attached to the combustion train, the anhydrone tube adjoining the latter, and the ascarite tube next to the drier of the Mariotte flask, the side arm of which is always in a horizontal position.

3. The cork stopper of the combustion tube is removed, the substance quickly introduced to within 50 mm. of the oxidation filling, and the tube immediately closed. Then the stopcock to the Mariotte flask is opened.

4. As soon as the gas flow is normal (5 cc. per minute), a small flame is applied 30 mm. from the sample, slowly increased until it envelops the combustion tube, and then gradually moved toward the sample, observing whether the substance sublimes, distills, or decomposes, the distillate or sublimate slowly being driven toward the heated oxidation filling. If it decomposes with charring, it is heated strongly directly under the substance until no black residue remains. The combustion is carried out with 75 cc. of oxygen and should take about 15 minutes, after which it is repeated to burn off all traces of charring, requiring only about 5 minutes.

5. The gaseous products are washed out with 75 cc. of oxygen in 15 minutes, then the stopcock of the Mariotte flask is closed, the absorption tubes are detached and immediately attached to the air filter, and the entire train is connected to the aspirator and washed with 50 cc. of air at the rate of 10 cc. per minute.

By employing two sets of absorption tubes and utilizing the waiting time during the analysis, while washing out the gaseous products, for wiping and weighing the second set, the time for an analysis may be reduced to about 35 minutes.

Discussion

The use of an extra combustion tube for a precombuster, as previously used, incurred the possibility of overheating the rubber connections at the end, but this danger is eliminated by the preheater described above.

Improvements in the Pregl pressure regulator and advice on the treatment of rubber tubing are given by Weygand (*35*). A new pressure meter is also described by Friedrich (*14*). A newer method of treating rubber tubing with strong potassium hydroxide and steaming out has been found effective (*16*).

The original form of the bubble counter was replaced by a few authors with a similarly functioning arrangement. Boetius (*6*) uses a bubble counter having on each side a special removable tube, one filled with ascarite, the other with phosphorus pentoxide–pumice stone mixture.

Pregl's combustion tube has been retained by most authors except Flaschenträger (*12*), whereas Avery, Brackenbury, and Maclay (*2*) suggest the use of copper and silver tubes with water-jacketed ends. Müller and Willenberg (*24*) simplified the handling by devising a side-arm inlet for the combustion tube.

Boetius (*6*), Weygand (*35*), and Lindner (*22*) tested extensively the materials used by Pregl for the filling of the combustion tube. Boetius (*7*) shows in numerous experiments a gradual lessening of the water content of the lead superoxide and Friedrich (*15*) finds that this substance gradually takes up carbon dioxide and gives it off again in the combustion of substances containing nitrogen, halogen, and sulfur. Haas and Rappaport (*17*) suggest cerium dioxide for copper oxide–lead chromate as filling, contending that the tube is better protected. Kirk and McCalla (*20*) use catalytic manganic oxide, and Friedrich (*16*) has devised a catalytic combustion method, permitting the easy removal of the lead superoxide, a platinum foil serving as the catalyst. Niederl (*25*) calls attention to the danger of not having present sufficient oxygen for the complete oxidation, when using this method. In a succeeding article Friedrich (*14*) separates the thermal decomposition of the substance and the oxidation of the decomposition products using the catalyst only for the last, but it seems that combustion would be difficult for substances which char. Attempts have been made to replace the lead superoxide by metallic copper or silver. Lindner suggests air for the actual combustion and nitrogen for the transport gas, but even partial use of air would oxidize the copper and necessitate frequent renewals. Avery, Brackenbury, and Maclay (*2*) use a metal tube allowing the insertion of a copper coil for the combustion of substances containing nitrogen. Niederl and Whitman (*27*) use nitrogen exclusively by mixing the sample with copper oxide and employing a combustion tube filling similar to the micro-Dumas.

Investigations of the weighing errors of absorption tube are summarized by Hernler (*18*) and include the observations of Schoorl (*32*), Friedrich (*15*), Brunner (*10*), and Meixner and Krocker (*23*). Blumer (*4*) and Flaschenträger (*12*) constructed tubes with side-arm exits which could be closed by movable glass stoppers. Mercury for a liquid seal was adopted by Kemmerer and Hallett (*19*) and improved by Cornwall (*11*). Friedrich describes two kinds of mechanically self-sealing tubes (*14*). All these absorption devices have been found of little advantage, as the difficulty of handling (wiping) such tubes increases, while on account of prevented temperature-pressure equalization no greater constancy is observable.

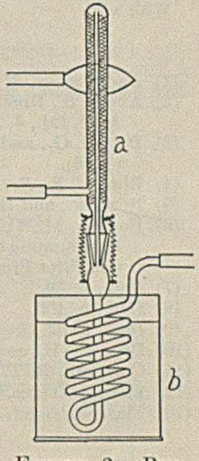

Figure 2. Preheater

a. Preheater tube
b. Condenser

At first moistened soda lime and calcium chloride, as recommended by Pregl (*28*), were used in the absorption tubes which, however, required refilling every six or seven analyses, and ascarite, capable of absorbing up to ten times as much carbon dioxide, was substituted for the soda lime. But when the tube was aspirated, it increased in weight about 0.02 mg. for every 100 cc. of air or oxygen, equivalent to over 0.04 mg. increase for 175 cc. of oxygen and 50 cc. of air used in an analysis and due to the difference in vapor pressure of calcium chloride and ascarite. According to Baxter and Starkweather (*3*) a liter of air passed over calcium chloride and sodium hydroxide contained residual water vapor of 0.36 and 0.16 mg., respectively, indicating that 100 cc. of air dried over fused calcium chloride would give up 0.02 mg. of moisture on passing over ascarite. For this reason anhydrone, a more efficient dehydrating agent, was used.

According to Willard and Smith (*37*), anhydrone is as efficient a drying agent as phosphorus pentoxide. It is neutral, porous, and stable towards heat up to 250° C. Its vapor pressure is 0.000 mm. at 0° C. and it is capable of absorbing water up to 30 per cent of its weight. Kirk and McCalla (*20*) reported using ascarite and anhydrone and Boetius (*9*) ascarite and phosphorus pentoxide. A change in the absorption of the combustion products is described by Niederl and Meadow (*26*). The absorption of carbon dioxide takes place in a filter tube and is gravimetrically determined as barium carbonate.

In previous attempts to eliminate the use of air in the combustion, Müller and Willenberg (*24*) and later Kirk and McCalla (*20*) weigh the absorption tubes filled with oxygen instead of air. Later experiments on absorption tubes which are not self-sealing show that they cannot be brought to constant weight when filled with oxygen, and self-sealing tubes, as mentioned before, do not allow for the equalization of pressure and temperature of the contained oxygen or air to balance room conditions. Table I shows the decrease in weight of the absorption tubes on standing, due to the replacement of oxygen by air, comparing also the increase in weight when filled with air due to the absorption of moisture and carbon dioxide, with and without wires in the capillaries.

TABLE I. CHANGE IN WEIGHT OF ABSORPTION TUBES

(Measured in 0.001 mg.)

	ANHYDRONE Minutes			ASCARITE Minutes		
	15	45	90	15	45	90
Filled with oxygen						
Without wires	−47	−104	−168	−23	−76	−125
With wires	− 9	− 41	− 88	−13	−37	− 82
Filled with air						
Without wires	+ 3	+ 11	+ 19	+ 3	+ 6	+ 13
With wires	+ 2	+ 4	+ 9	+ 1	+ 4	+ 8

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Determination of Selenium and Arsenic by Distillation

In Pyrites, Shales, Soils, and Agricultural Products

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INVESTIGATION of an animal disturbance (known locally as alkali disease), which was traced to vegetation grown in certain soil areas, rendered urgent the development of a rapid and accurate method for the detection and estimation of selenium in both organic and inorganic materials. The methods outlined below are an extension and improvement of a distillation method described by Robinson (*7*) during the progress of the work.

The principles of the distillation method are outlined by Noyes and Bray (*6*). Selenium can be separated from all the other elements except arsenic and germanium by distillation with concentrated hydrobromic acid. The selenium must be in, or be converted into, the hexavalent condition before distillation in order to insure its distillation with the acid. In most cases this conversion may be accomplished by the use of bromine. The excess of bromine distills at a low temperature and the hydrobromic acid then reduces the selenium to the quadrivalent condition. In this form it readily distills along with hydrobromic acid.

When a distillation method is applied to soils and other insoluble materials difficulties due to bumping and frothing may be encountered. Bumping may be greatly minimized by the introduction of short pieces of capillary tubing, sealed at one end. In the case of soils, at least, frothing is diminished or wholly prevented by the use of a sufficient excess of bromine.

In the distillate, selenium may be precipitated quantitatively by reduction by sulfur dioxide and hydroxylamine hydrochloride. The selenium may be estimated either gravimetrically or by the colorimetric procedure of Cousen (*2*). In either case reprecipitation is essential to free the precipitate from sensible quantities of impurities.

Arsenic is quantitatively distilled along with the selenium and may be determined in the filtrate from the first selenium precipitation. If present in but small quantities it is best determined by one of the modifications (*3*, *9*) of the cerulean blue molybdate method of Denigès (*4*).

In general, the procedures described below are very sensitive and may be used for any material with such modifications as may be necessary. The method as developed for soils is perhaps the most sensitive used in soil analysis. One part of selenium in ten million parts of soil may be easily detected and by use of the integration procedure described below, quantities as small as one part in a billion may be isolated.

APPARATUS

A distilling apparatus is graphically described in Figure 1. The still is conveniently made of Pyrex glass and rubber connections must be avoided. Measuring flasks and Nessler jars of 25 cc. capacity are also required.

REAGENTS

All reagents should be free from selenium. Blank determinations should be made on all reagents.

1. Hydrobromic acid, 40 to 48 per cent, capable of being completely decolorized with sulfur dioxide.
2. Bromine.
3. Solution of 1 cc. of bromine in 10 cc. of hydrobromic acid.
4. Hydroxylamine hydrochloride.
5. Sulfur dioxide as compressed gas in cylinders.
6. Five per cent solution of gum arabic in water.
7. A suspension of asbestos which will not lose weight when washed with strong hydrobromic acid.

Procedure for Soils

The air-dried sample should be well mixed and passed through a 2-mm. sieve.

Weigh out 50 grams of the air-dried soil and transfer to the distilling flask. Add 10 cc. of solution 3, a few cubic centimeters at a time, with shaking. If carbonates are present, add the mixture to the contents of the flask slowly and with constant shaking to avoid loss by frothing. Add, in all, 10 to 50 cc. of solution 3, the quantity depending on the quantity of organic matter present. There must be an excess of bromine over that required to saturate the organic matter in the soil. After sufficient bromine in solution 3 has been added, add enough hydrobromic acid to bring the total quantity of this reagent up to 75 to 100 cc. The larger quantity is used on soils containing much calcium carbonate or on very basic soils. Connect the still with the adapter just below the surface of 2 to 3 cc. of bromine water in the receiver flask and apply heat gradually. One or two grams of bromine should distill over in the first few cubic centimeters of distillate. If insufficient bromine has been added to produce this quantity of bromine, more must be added. A somewhat greater excess of bromine does no harm, but too great an excess is to be avoided because of the formation of too much sulfuric acid later. When danger of frothing is passed, apply increased heat and collect from 30 to 50 cc. of distillate. Make a second, or even third, distillation with intervening additions of hydrobromic acid and bromine, unless it is certain from experience that all the selenium is in the first distillate. Remove the distillate and pass in sulfur dioxide until the yellow color due to bromine is discharged. Add 0.25 to 0.5 gram of hydroxylamine hydrochloride, stopper the flask loosely, put on the steam bath for an hour, and allow to stand overnight at room temperature. If selenium is present it will appear as a characteristic pink or red precipitate. If much selenium is present it will shortly turn black.

Collect the precipitated selenium on an asbestos pad in a porcelain crucible, and wash slightly with hydrobromic acid containing a little hydroxylamine hydrochloride. Dissolve the selenium on the pad by passing through 10 to 15 cc. of solution 3 in small quantities and wash into a 25-cc. measuring flask if the quantity is small and is to be estimated colorimetrically. If over 0.5 mg., filter into a small beaker, precipitate as before, gather on an asbestos pad as before, and wash with hydrobromic acid containing a little hydroxylamine hydrochloride and then with water. Prepare a tare in a similar manner. Dry at 90° C. for 1 hour, place in a vacuum desiccator, and exhaust the air while the crucibles are still hot. Cool 0.5 hour. Allow the air to enter the desiccator, cool an additional half-hour, and weigh against a tare. Check the weight by drying again. If the quantity is small and is to be estimated colorimetrically, add 1 cc. of a solution containing 5 per cent gum arabic and precipitate the selenium by sulfur dioxide and hydroxylamine hydrochloride. Prepare comparison solutions containing known quantities of selenium in exactly the same manner and allow them to stand overnight. Shake the standard and test solutions and compare the depth of color in Nessler jars. This comparison is best carried out in sunlight. It is difficult to match solutions containing more than 0.5 mg. of selenium in 25 cc. and the color comparison is most satisfactory when 0.01 to 0.1 mg. is present.

Procedure for Pyrites and Other Sulfides

Grind the sample to pass a 100-mesh sieve. Weigh out 10 grams of the sample. Pour 100 cc. of concentrated nitric acid into a 300-cc. quartz or porcelain dish and place the dish on the steam bath. Add small portions of the pyrites into the dish by tapping from a spatula, stir thoroughly between portions, and add more when brown fumes cease to come off. Add 25 to 50 cc. more nitric acid when half the material has been added. When the reaction appears to be complete, add 15 cc. of concentrated sulfuric acid and evaporate until all nitric acid is expelled. Add a few drops of 30 per cent hydrogen peroxide and stir vigorously. When the peroxide is decomposed add 75 cc. of concentrated hydrobromic acid and bromine and distill as under directions for soils. The mixture bumps badly.

Procedure for Water

Measure from 1 to 10 liters of water, and add sufficient sodium peroxide to make the liquid definitely alkaline. Evaporate to dryness. Take up with 100 cc. of concentrated hydrobromic acid and 1 to 5 cc. of bromine, depending upon the quantity of organic matter present, and proceed as under directions for soils.

Procedure for Vegetable Matter

With vegetation the procedure must be modified according to the quantity of selenium present. The most satisfactory procedure for material of unknown character is as follows:

Stir 100 grams of well ground and mixed vegetation into a concentrated solution of 25 grams of magnesium nitrate, and add 5 grams of magnesium oxide. Dry the mass over a water bath and finally in an oven at 105° C. Ignite the dried material slowly in a muffle until the ash is a uniform gray color.[1] After ignition, triturate the ash with 100 cc. of concentrated hydrobromic acid and 2 cc. of bromine, transfer it to a distilling flask, distill as suggested for soils, and estimate the selenium in the distillate.

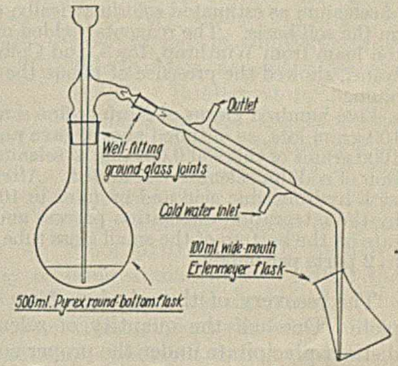

Figure 1. Distilling Apparatus

In case the quantity of selenium exceeds 2 parts per million it is preferable to use a procedure devised by A. Van Kleeck in this laboratory. The procedure is as follows:

Digest 1 to 5 grams of the material with sulfuric acid as in the Kjeldahl process, using a suitable catalyst. Instead of digesting in a Kjeldahl flask, carry out the process in the distillation apparatus previously described (Figure 1). Conduct the issuing gases through bromine water which is kept continuously supplied with an excess of bromine. When the digestion is complete, cool the flask and cautiously add an equal volume of water and then the distillate, together with 100 cc. of concentrated hydrobromic acid, through the funnel of the distilling apparatus. Distill the mixture, as in the case of soils, and estimate the selenium. If more than 5 grams of vegetation must be digested in order to secure a measurable quantity of selenium, this procedure becomes very tedious, but it nevertheless seems to be the most accurate yet devised. The oxidation of vegetation, preliminary to distillation, may also be effected by digestion with 30 per cent hydrogen peroxide to which has been added 0.5 gram of soil and a few drops of nitric acid.

Procedure for Animal Tissue

Cut flesh, skin, etc., into small pieces and drop into cold 30 per cent hydrogen peroxide. When danger of frothing has ceased, warm on the steam bath, add a little nitric acid, and when decomposition is nearly complete, add about 5 per cent of the weight of the sample of magnesium nitrate. Evaporate to dryness and char at a low temperature. The animal tissues may also be digested by the Kjeldahl process as a preparation for distillation if the selenium content is sufficiently large. Distill and proceed as under "Soils."

Sensitiveness of Method

By the use of what may be termed an integration distillation process (the cohobation of the alchemist) the selenium from a large quantity of soil may be concentrated into a very small volume of distillate. A charge of 50 to 100 grams of soil or plant ash is distilled and the distillate is poured back

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[1] Beath (*1*) and his associates at the University of Wyoming use a procedure which they ascribe to Taboury (*8*) but with a very important modification. The material is digested with a solution of sodium hydroxide, dried, and ignited to a gray ash. During this ignition a very voluminous swelling occurs, accompanied by crust formation which makes the procedure difficult. Ignition without the addition of a fixative is accompanied by large losses of selenium. Even with this addition the loss of some selenium remains possible.

into the still with a fresh sample of soil with additional hydrobromic acid and bromine, and the process repeated.

Fifty grams of Cecil sandy loam from Statesville, N. C., were treated with 75 cc. of 42 per cent hydrobromic acid and 2 cc. of bromine, and distilled until the volume of the distillate measured was about 50 cc. One hundred grams of a fresh sample of the soil were introduced into the flask, the distillate from the first lot was poured into the distilling flask, 75 cc. of hydrobromic acid and 2 cc. of bromine were added to the mixture in the flask, and the contents distilled until the volume of the distillate was again about 50 cc. One hundred grams more of the soil were put in the distilling flask and the operation repeated as above. The residual soil from each distillation was, of course, thrown away. In this manner the selenium in 250 grams of soil was concentrated into a distillate of about 50 cc. This was further concentrated in a small still to about 10 cc. This distillate, when treated to precipitate the selenium, showed the presence of about 0.02 mg. of selenium as estimated colorimetrically, or 0.08 part per million, on the soil basis. The reagents yielded no blank test. Carrington loam from Winthrop, Iowa, and Colby silt loam from Hays, Kans., showed the presence of about the same quantity of selenium.

Five hundred grams of Norfolk fine sandy loam treated in five 100-gram lots, as outlined above, gave no test for selenium. To 1000 grams of this soil 0.002 mg. of selenium in the form of a solution of sodium selenate was added. After drying, it was treated with hydrobromic acid and bromine in 10 lots of 100 grams each by the integration distillation process and a distinct red precipitate on the bottom of the small glass tube resulted, corresponding to 2 parts per billion.

The recovery of the selenium from the soil appears complete. One-half the quantity of selenium used will give a distinct precipitate under the proper conditions and less than one-tenth as much will give a distinct yellow color when treated, in volumes of 5 cc. or less, by Cousen's (*2*) method, as used in the determination of selenium in glass. The method appears capable of detecting one part of selenium in a billion of soil, and probably with care and patience one part in ten billion can be detected. The limits of detection would be the patience of the analyst in making the number of distillations necessary. Large quantities of the reagents can be prepared free from selenium by redistillation, so there should be no danger of contamination from this source. In carrying out the successive distillations air-dry soils should be employed and no water added to the receiving flasks. This precaution is essential in order to avoid dilution of the successive distillates.

ACCURACY OF METHOD

It appears that selenium is quantitatively recovered, by the distillation process, from material properly prepared for distillation. Quantities of selenium as small as 0.01 mg. may be satisfactorily determined colorimetrically. For quantities greater than 0.5 mg. the degree of accuracy with which the precipitated material can be determined depends primarily on the accuracy of the balance employed. When ignition methods are employed there is, of course, a possibility of loss of selenium, despite the fact that added sodium selenate may be quantitatively recovered from wheat and similar materials. Complete combustion of wheat, without the addition of any fixative, reduces the quantity of selenium recovered. In an earlier publication (*7*), it was stated that, in the absence of tellurium, the distillation procedure could be eliminated, and determination made directly upon the leachate from the ash. Unless a second precipitation is made the results so obtained are too high, owing to contamination with silica and possibly other materials.

In the treatment of soils and shales and ignited organic matter some difficulty has been caused by failure to add sufficient bromine to insure an excess.

The agreement of duplicates and of different analysts on the same sample is shown in Table I for two materials, selected because representative of a long series of shales, soils, and grains.

TABLE I. AGREEMENT OF DUPLICATES AND OF DIFFERENT ANALYSTS BY DISTILLATION METHOD

ANALYST	SHALE, B-2885	PIERRE CLAY LOAM, B-391	WHEAT
	P. p. m.	*P. p. m.*	*P. p. m.*
H. C. Dudley	32–35	10–12	15–15[a]
W. O. Robinson	38–40	11–14	14[b]–17[c]
K. T. Williams	38–40	10–11	14[a]–16[a]

[a] Oxidation by Kjeldahl process.
[b] Ignition with magnesium nitrate.
[c] Oxidation with hydrogen peroxide.

DETERMINATION OF ARSENIC

In the process of isolation of selenium any arsenic present in the sample distills over with the hydrobromic acid and is converted into arsenic acid by the bromine present in the receiver. Reduction by sulfur dioxide and hydroxylamine does not precipitate the arsenic, which is present quantitatively in the first filtrate from the selenium precipitate. It is thus separated from all other elements save germanium. A quantitative separation of all the arsenic from mispickel was effected by one distillation when the mispickel was treated as recommended for pyrites. Arsenic may be determined in the filtrate from the selenium determination after evaporation with concentrated nitric acid, essentially as recommended by Deemer and Schricker (*3*) for the determination of arsenic in plant ash. By the use of the integrated distillation procedure the detection and estimation of arsenic may be made as sensitive as is the case with selenium.

The same procedure may be followed for concentration of germanium into the distillate where it appears in the filtrate after removal of selenium. In the solution it may be determined by the methods suggested by Noyes and Bray (*6*) or Hillebrand and Lundell (*5*). In the present investigation, no attempt has as yet been made to apply the procedures suggested to the determination of germanium. The procedure suggested for arsenic was followed in the case of a sample of Cecil clay loam from North Carolina, and 21 parts per million found.

The method described, with appropriate modifications, has been applied to the determination of selenium in several thousand analyses in this laboratory and has been found eminently satisfactory. These analyses include the estimation of selenium in sulfide ores, shales, soils, water, a wide range of vegetation and grains, blood, hoofs, bones, and a wide variety of animal tissues. The quantities found have ranged from minute fractions of a part per million to as high as 0.38 per cent.

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Determination of Total Carbon in Soils by the Wet Oxidation Method

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The apparatus presented obviates the necessity for glass seals to prevent contamination of the sample by the disintegration of rubber connections. A novel but efficient interception of the fumes from the oxidizing solution allows complete absorption of the carbon dioxide. The use of a measured quantity of absorbing solution permits a single titration with phenolphthalein as the indicator with the elimination of the methyl orange titration except when desired as a check. Twelve units occupy but 6.5 feet of desk space.

THE need of a rapid method for the determination of carbon is apparent when a large number of samples are to be analyzed. In the investigations under way at this station experimental plots are sampled periodically and are analyzed for carbon to obtain an index of the changes in the organic matter content of the soils as influenced by the crop management.

The methods for the determination of carbon in soils are well known. The carbon, regardless of form or source, is converted into carbon dioxide which in turn is determined by gravimetric, titrimetric, or gasometric methods. The furnace or dry combustion method is ordinarily employed and consists of the oxidation of the carbon by oxygen at a high temperature. A mixture of sulfuric and chromic acids has been used extensively for this purpose in the so-called wet combustion method. The fact that the two methods give comparable results has been established by Ames and Gaither (*1*) and White and Holben (*11*); the former found it necessary to boil the solution in order to obtain complete oxidation of the carbon, while the latter introduced the use of an absorption tube containing constant-boiling sulfuric acid to intercept the fumes from the boiling solution, thus insuring complete absorption of the carbon dioxide. Other workers, Cameron and Breazeale (*3*), Brown (*2*), Hardy (*4*), Heck (*5*), and Schollenberger (*8*), have studied the wet oxidation method as applied to soils. A variation of the method is that of Robinson (*7*) in which the sulfur dioxide evolved in the Kjeldahl digestion of soil was used as a measure of the carbon content. The results were low as compared with those obtained by the furnace method; therefore a factor was used to correct for the deficiency. Some modification is necessary when the method is applied to materials containing chlorides. Normal soils do not contain these in appreciable quantities; consequently the apparatus as presented does not take these into account.

Brown used the soil residues following the determination of carbon by the wet oxidation method for the determination of nitrogen. The results were in fair agreement as compared with those obtained by the Gunning method. The apparatus presented was developed with the idea of saving time and materials. However, the speed with which the carbon determination can be made, coupled with the difficulties involved in the removal of the excess sulfuric acid before making the Kjeldahl distillation, made this procedure unnecessary and undesirable.

White and Holben point out the danger of contamination of the sample by the charring and disintegration of rubber stoppers through contact with the fumes from the oxidizing solution. They used the Knorr apparatus in which glass seals instead of rubber stoppers are employed. It has been found in this laboratory that contamination from the source mentioned is very appreciable after a few determinations are made. This objection, coupled with the cost of equipment using glass seals, led to the abandonment of the type of apparatus ordinarily used and the development of a unit that can be prepared at a low cost. It is very compact, easy to operate, and in addition retains the features necessary for accuracy. Rubber stoppers can be used safely. The incoming oxygen prevents the fumes from reaching the stopper of the Kjeldahl flask, while the interception of the fumes by the glass wool protects the smaller stopper. The necessity of using a condenser to return the acid and water to the oxidizing solution is eliminated. The fumes are intercepted in a novel but efficient way which allows the complete absorption of the liberated carbon dioxide.

CONSTRUCTION OF APPARATUS

OXYGEN LINE. This consists of 0.375-inch (0.94-cm.) copper tubing into which the individual 0.125-inch (0.3-cm.) copper outlets are soldered at intervals of 6.25 inches (15.6 cm.). Glass tees and rubber tubing have been used but are more difficult to support.

MODIFIED BUNSEN VALVE (Figure 2). A 3-inch (7.5-cm.) piece of glass tubing is fitted at each end with a rubber stopper carrying a short piece of glass tubing. The valve consists of a 1-inch (2.5-cm.) piece of thin-walled, red rubber tubing in which a smoothly cut slit, 0.125 to 0.188 inch (0.31 to 0.47 cm.) long, is made. The valve is attached to the glass tubing of one of the stoppers and the free end plugged with a short piece of glass rod, the mounted valve being enclosed in the 3-inch (7.5-cm.) glass tube.

ABSORPTION TUBE. Pyrex, heavy-walled tubing of an outside diameter equal to the average inside diameter of 800-cc. Kjeldahl flasks is used. A length equal to that of the neck of the flask is constricted to approximately 1 cm. at one end. This is packed with glass wool to within 1 inch (2.5 cm.) of the open end, care being taken to leave no channels. If packed too firmly the gases from the oxidation flask will be forced back into the main line in spite of the Bunsen valve and will be distributed among the units of lower resistance. The wool has to be changed after approximately one hundred determinations, as it disintegrates under prolonged acid digestion.

DELIVERY TUBE. This is made from 10-mm. Pyrex combustion tubing. The added strength of the heavy wall is necessary to prevent excessive breakage.

CARBON DIOXIDE ABSORPTION TOWER. This is a modified Truog (*10*) tower. The lower end is constricted to insure the formation of a stream of small bubbles and to retain the short pieces of glass tubing which are not removed during the washing process.

OPERATION OF APPARATUS

Sulfuric acid is boiled in each unit for 10 to 15 minutes to saturate the glass wool preparatory to operation. This suffices for the life of the wool. An amount of sample sufficient to produce 0.1 to 0.3 gram of carbon dioxide is added to *G*, care being taken to prevent any of the sample from adhering to the neck of the flask. Three to five grams of potassium dichromate are added to the dry sample and *G* is clamped loosely in position. Approximately 60 cc. of concentrated sulfuric acid are now added from a flask with wash-bottle fittings, using compressed air or oxygen. The entire assembly, including the measured quantity (100 cc.) of sodium hydroxide in flask *K* which has previously been attached to stopper *J*, is connected to flask *G* at *E*. The oxygen inlet tube *A* which is attached to the main line (not shown) is of sufficient length to allow the assembly to hang on a universal clamp attached to the upper part of the rod before making the connection and while the apparatus is not in use.

It is best to regulate the flow of oxygen, or air, for each unit before heating is commenced. This is done by means of the screw-clamp on *A*. The upward or downward adjustment of the absorption tower is made at this time; this is made easier by lubricating the openings in stopper *J* with glycerol, as recommended by Heck. The flow of oxygen is now shut off at the tank, spring clamp *C* is placed on the rubber tube between the valve and glass inlet tube *D*, and slow heating is begun. Slow boiling is continued for 15 minutes and then *C* is clamped on *D* and oxygen is forced through all the units simultaneously with sufficient force to maintain a rapid flow of bubbles in the absorption towers.

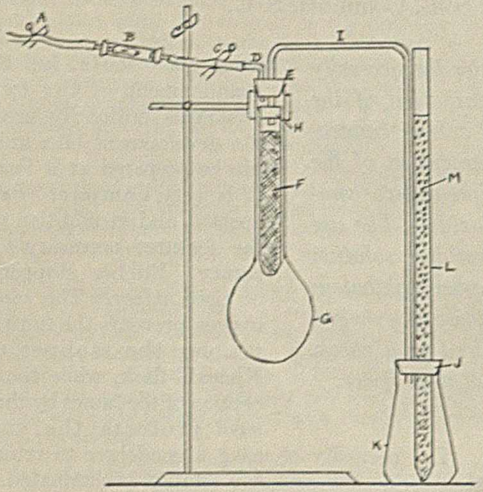

FIGURE 1. DIAGRAM OF APPARATUS

A. Rubber tube leading to main oxygen line with screw pinch clamp
B. Modified Bunsen valve
C. Spring pinch clamp
D. Inlet tube for oxygen
E. No. 7 rubber stopper
F. Tube with glass wool
G. Kjeldahl digestion flask, 800 cc.
H. Rubber stopper for *F* attached to *I*
I. Delivery tube
J. No. 10 rubber stopper
K. Erlenmeyer flask, 500 cc.
L. Absorption tower
M. Glass tubing as beads

When the oxidation is complete (30 to 45 minutes) the oxygen is shut off, *C* is clamped on the rubber inlet tube, the absorption flasks are loosened, and heating is discontinued. The apparatus is elevated with one hand and the tower flushed with approximately 150 cc. of water, the last 20 cc. being used to wash the outside of the tip of the tower. The entire apparatus is now clamped in an elevated position and left until cool.

Twelve units can be operated satisfactorily from one tank of oxygen, using a pressure regulator. Air under constant pressure and free from carbon dioxide can be used. Drawing air through the apparatus is not recommended, as the vacuum produced decreases the absorptive capacity of the glass wool.

DETERMINATION OF CARBON DIOXIDE

A comprehensive survey of the literature on the determination of carbon dioxide is given by Partridge and Schroeder (*6*).

There are two titrimetric procedures ordinarily used when the carbon dioxide is dissolved in a solution of either sodium or potassium hydroxide. One is to titrate with a standard acid using phenolphthalein and methyl orange as the indicators, the former indicating the complete neutralization of the base and the conversion of the carbonate to bicarbonate; the latter indicating the conversion of the bicarbonate to a salt, carbon dioxide, and water. In the other procedure a measured quantity of base is used to absorb the carbon dioxide, the carbonate is precipitated as barium carbonate, and the solution titrated to the phenolphthalein end point. A like quantity of base is titrated to the same end point and is termed the blank. The difference between the titrimetric value of the blank and sample solution is proportional to the amount of carbon dioxide absorbed from the sample. Heck terms this a "single" titration, while Schroeder calls it the Winkler titration. This use of a measured quantity of base to absorb the carbon dioxide from a sample, with a like quantity as a blank, makes unnecessary the titration of the solutions beyond the phenolphthalein end point, even though the carbonate is not precipitated as barium carbonate. The titrimetric value of the blank minus that of the sample solution gives a difference that is proportional to the amount of the carbon dioxide absorbed, as is the case in the Winkler titration. This difference, numerically, is twice that for the Winkler titration if the same strength acid is used in both cases; it follows that the carbon equivalent of the acid in the first case is one-half that used in the Winkler method. This difference is also equal, numerically, to the amount of acid required to titrate the sample solution from the phenolphthalein end point to the methyl orange end point, providing the blank has also been titrated to the same end point to determine the amount of carbonate it contains. In this procedure one titration serves as a check on the other. This technic has been used for several years in this laboratory and has been found reliable.

Truog has given a discussion of the difficulties involved in the so-called double titration. Schroeder (*9*) gives a critical discussion of the conditions pertaining to an accurate analysis of a mixture of base and carbonate. The phenolphthalein end point is quite definite, however, if the solution is agitated by a mechanical stirrer so that the operator's attention can be centered on the color change. Mechanical stirring is also an aid should the methyl orange titration be made.

The complete absorption of carbon dioxide from a rapidly flowing stream of oxygen and this gas requires a fairly strong solution of sodium hydroxide. Ames and Gaither, and Brown used a 4 per cent solution for this purpose. This method employs 100 cc. of an approximately 0.5 *N* solution. The titration of a large excess of unused base is exceedingly laborious if an acid sufficiently dilute to insure an accurate end point is used alone. To obviate this difficulty it is necessary to know the approximate carbon content of the sample.

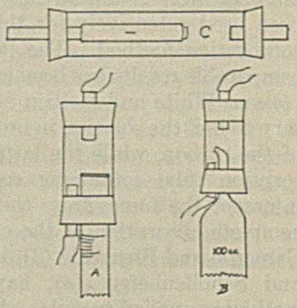

FIGURE 2. DETAILS OF APPARATUS

A. Top section of buret (three-way stopcock)
B. Top section of automatic pipet modified to deliver solution under pressure
C. Modified Bunsen valve

A measured quantity of approximately 2.5 *N* acid, sufficient to neutralize most of the base unused by the carbon dioxide, is added from a buret to the sample solution accompanied by stirring or vigorous rotation of the flask. The solution is then titrated to the phenolphthalein end point with the weaker acid. To another 100-cc. portion of the base a like amount of strong acid is added and titrated in the same way; this is termed the blank. The difference obtained by subtracting the titrimetric value of the sample solution from the blank is then multiplied by the carbon equivalent of the titrating acid. The accuracy of this procedure is determined by that with which the solutions are measured. The chance for error is enhanced by the considerable variation in the strengths of the solutions used. A satisfactory and rapid procedure is to use an automatic pipet to dispense the sodium hydroxide and a buret with a three-way stopcock for the strong acid. Each is so equipped (Figure 2) that the entire contents can be forced out with carbon dioxide–free air under pressure; the air being allowed to flow through each for an instant to sweep the tips free of solution. The titrations of duplicate blanks with a 0.166 N acid show that a combination of the factors involved results in an average error of 0.3 mg. of carbon.

It is not necessary to have the approximately 0.5 N sodium hydroxide free from carbonate. Neither it nor the strong acid needs to be standardized. The saving in time is considerable and is enhanced if large quantities are prepared at one time, as is desirable for routine work. A considerable saving of the standard acid is accomplished in the use of the single titration if the proper amount of strong acid is used for establishment of the blank.

Table I. Comparison of Dry Combustion and Wet Oxidation Methods

Substance Analyzed	Total Carbon Wet oxidation	 Dry combustion
	%	%
Soluble starch	36.86	36.89
Potassium acid phthalate	44.64	44.45
Soil 188[a]	2.01	1.98
Soil 199[a]	2.04	2.05
Soil 4	1.00	0.99
Soil 7B	0.39	0.40
Soil 4C	0.58	0.58

[a] Samples furnished by E. C. Shorey, Bureau of Chemistry and Soils, Washington.

Analytical Data

Although the apparatus was developed for the determination of carbon in soils, it has been used to determine its adaptability to a limited number of other materials. The apparatus needs modification for use with some organic materials, as the reaction with the oxidizing solution is very vigorous. As presented it is best adapted to materials of medium to low carbon content. A comparison of results obtained by the dry combustion and wet oxidation methods is made in Table I.

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Received April 2, 1934. Presented before the Division of Agricultural and Food Chemistry at the 87th Meeting of the American Chemical Society, St. Petersburg, Fla., March 25 to 30, 1934. Contribution from the laboratory of the Soil Fertility Division, Sandhill Experiment Station, U. S. Department of Agriculture and S. C. Experiment Station coöperating. W. M. Quattlebaum, Jr., was associated with the author when the method was developed and credit is due him for much valuable assistance.

Constant-Head Gas Scrubber for Small Pressure Drops

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In the analysis of combustible gases by thermal conductivity, it is often necessary to eliminate one or more constituents by combustion and subsequent removal of the combustion products. In such a process, particularly if oxygen or air is added for combustion, constant gas flows are essential. To obtain constant rates of flow, the pressure drop through the apparatus must remain unchanged. It is, furthermore, desirable to have as small a gas volume and pressure drop throughout the apparatus as is consistent with satisfactory operation.

Of the combustion products, water offers no difficulties in removal. Furnas (*1*) has described a gas bubbler which is suitable for carbon dioxide removal by caustic solutions but which has the disadvantage of the possibility of a change in liquid head due to dilution from absorption of moisture and from the carbon dioxide reaction. During the construction of an apparatus for continuous analysis of helium (*3*), now in use in the Amarillo Helium Plant of the U. S. Bureau of Mines, the need arose for a carbon dioxide scrubber to fulfill the requirements outlined above. Such a scrubber has been designed which gives entire satisfaction, and which may find application in similar work.

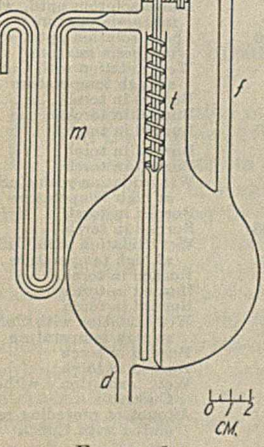

Figure 1

The gas scrubber, constructed on the principle of the Milligan (*2*) absorber, is shown in Figure 1. It is made from a 500-cc. round-bottomed flask by sealing a manometer tube *m* to the neck of the flask about 1 cm. below the stopper bottom. The absorbing solution is filled and drained conveniently through tubes *f* and *d*, sealed to the side and bottom of the flask. The gas enters through capillary tube *c* and is scrubbed free from carbon dioxide as it passes upward through the liquid around the spiral which fits snugly in tube *t*. The spiral is formed from a 2-mm. glass rod wound around the gas inlet tube and fused to it, at each end and in the middle, to secure the rod in place. The gas, as it breaks into bubbles at the entrance to the spiral, creates a lifting effect which causes fresh solution from the bottom of the flask to rise in tube *t* and pass around the spiral so that a fresh absorption surface is continually presented to the gas. Increase in pressure head, due to dilution, is eliminated by overflow from manometer tube *m*, by which a constant level is maintained in the flask. The residual gas leaves the flask through capillary tube *e*.

The scrubbing surface of the spiral is equivalent to a column of solution approximately 20 cm. long. Complete removal of carbon dioxide has been accomplished, using 20 per cent sodium hydroxide solution, from 1.5 liters per hour of gas containing 70 per cent carbon dioxide, for 24- to 30-hour periods. The rate of gas flow is limited by the size of the spiral. The dimensions, as given, provide for a maximum flow of about 3 liters per hour.

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Application of Enclosed Torch to Estimation of Arsenic in Foods

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The method of the Association of Official Agricultural Chemists (*1*) for the determination of traces of arsenic in foods provides for the destruction of organic matter by wet combustion with nitric and sulfuric acids. Wet ashing, properly conducted, gives concordant results and good recoveries on most food products. In applying it to dried shrimp and cod liver oil, however, the authors experienced certain difficulties, which, together with the long time required for the digestion, led them to try combustion in the enclosed torch devised in this laboratory (*7*) for the estimation of iodine in foods.

Method

The apparatus is set up and handled exactly as for the estimation of iodine (*7*). It was found, however, that 1 or 2 cc. of nitric acid in each absorber could be substituted for the sodium hydroxide, with equally efficient absorption and the advantage that less acid is required in the later treatment.

After combustion, the water and ash of the cup are transferred to a beaker, the cup and flask rinsed with very dilute nitric acid, and the rinsings added to the beaker together with the contents of the absorption bottles. The combined solutions are evaporated to small volume, then 5 to 20 cc. of sulfuric acid are added, the beaker is covered with a watch glass, and the solution evaporated to fumes. The concentration to small volume before addition of sulfuric acid insures oxidation and expulsion of chlorine, a precaution that is of particular importance in analysis of sea food or other products rich in salt. In a properly conducted combustion there should be no darkening with sulfuric acid, but if darkening does occur, a few drops of nitric acid will clear the solution. From this point the solution or an aliquot of suitable size is treated as provided in the official method.

It was found that while a larger proportion of arsenic than of iodine stays in the combustion chamber, absorption in the washing bottles is not so efficient, so that in some cases the addition of a third washing bottle is desirable. On account of its larger orifice, the Friedrichs wash bottle is very much less efficient than the Milligan in this case, even though the two bottles are alike in principle. Table I gives data from experiments with both types of bottles.

Importance of Oxidation

Usual directions for wet digestion do not stress sufficiently the necessity for constantly maintaining oxidizing conditions. Whenever charring of the sample takes place, arsenic may be reduced from the pentavalent to the trivalent state. According to Rushton and Daniels (*5*) the vapor pressure of arsenious oxide is practically negligible below 250°, and increases to 32 mm. at 275° and 144 mm. at 338° C., the boiling point of sulfuric acid. Appreciable losses might therefore be expected if the digest were heated to vigorous fuming while any reduced material was still present. Analysts generally avoid this danger by keeping the temperature relatively low, with frequent additions of nitric acid, until satisfied that oxidation is complete and arsenic consequently in pentavalent form.

Occasionally substances are encountered which are very difficult to oxidize completely by the wet method, or which contain compounds which interfere with the evolution of arsine in the generator. Fats and oils require long treatment at high temperatures and correspondingly greater amounts of nitric acid. With acid-digested tobacco, Gross (*2*) experienced difficulty which he attributed to the presence of pyridine, and was able to get better recoveries if the arsenic was precipitated by magnesia mixture before marshing, thus separating it from the pyridine. Pyridine is obtained on dry distillation of many proteins, however, and Sörensen and Anderson (*6*) have noted that if nitrogen determinations yield lower values by the Kjeldahl than by the Gunning-Arnold method, the sample contains either ring-like nitrogenous compounds such as pyridine or piperidine which are not decomposed, or substances which yield these compounds on closure of the ring; hence the difficulty encountered by Gross in working with tobacco might occur in many foods rich in protein.

Table I. Distribution of Arsenic in Different Parts of Absorption Train
(10 grams dried shrimp)

	Nitric Acid Used in Absorbers	Sodium Hydroxide Used in Absorbers
	%	%
Combustion chamber	52.83	51.95
1st Friedrichs bottle	4.20	6.43
2nd Milligan bottle	41.69	40.58
3rd Friedrichs bottle	1.28	1.04
	100.00	100.00
	P. p. m.	*P. p. m.*
Total As_2O_3	157.1	154.0

Table II. Recovery of Arsenic from Dried Shrimp

Sample	Weight Taken	As_2O_3 Added	As_2O_3 Found	Recovery of Added As_2O_3	Remarks
	Grams	*Mg.*	*Mg.*	%	
107	10		No stain		Wet oxidation at low temperature
	20		No stain		Wet oxidation at low temperature
	10	1.0	No stain	None	Wet oxidation at low temperature
	10		Trace		Above solution pptd. with magnesia mixture
	20		Trace		Above solution pptd. with magnesia mixture
	10	1.0	1.03	103	Above solution pptd. with magnesia mixture
	10		0.72		Wet oxidation with $CuSO_4$ at high temperature
	10		0.73		Burned in torch
	10		0.725		Burned in torch
	10	1.0	1.69	97	Burned in torch
108	10		0.275		Burned in torch
	10		0.289		Burned in torch
	10		0.288		Wet oxidation with $CuSO_4$ at high temperature
102	10		0.109		Burned in torch
	10	1.0	1.090	98	Burned in torch
	20		0.215		Wet oxidation with $CuSO_4$ at high temperature
113	10		0.048		Burned in torch
	10		0.049		Burned in torch
	10		0.045		Burned in torch
	20		0.097		Wet oxidation with $CuSO_4$ at high temperature
117	10		0.900		Burned in torch
	10		0.980		Burned in torch
	10		0.470		Wet oxidation without $CuSO_4$
	10		0.988		Aliquot of preceding redigested with $CuSO_4$

Application of Torch Method

The authors digested a sample of dried shrimp by the official method, but failed to recover more than traces of arsenic, either with or without precipitation with magnesia mixture. When 1 mg. of arsenic trioxide was added to 10

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[1] Associate biochemist, U. S. Bureau of Fisheries.

grams of dried shrimp before digestion, none was recovered by direct marshing of an aliquot, but 1.03 mg. after precipitation with magnesia mixture. The authors concluded that the arsenic of the shrimp was not liberated by the digestion, and that some substance, possibly pyridine, was present in the digest and inhibited the evolution of added arsenic, until removed by separation. This same sample of shrimp, when burned in the torch, yielded duplicate values of 73 and 72.5 parts per million of arsenic trioxide. When digested with acid at higher temperature and with the addition of copper sulfate as a catalyst, as suggested by Maechling (*4*), 72 parts per million were recovered.

A sample of pipe tobacco yielded 17.4 parts per million of arsenic trioxide by wet oxidation, and 24.8 parts after precipitation with magnesia mixture, confirming the observation of Gross. Another sample of tobacco gave 28.0 when treated according to Gross, and 27.4 when burned in the torch. The results shown in Table III indicate that the method can be applied to various kinds of dried vegetable matter.

TABLE III. ARSENIC RECOVERED FROM MISCELLANEOUS FOODS BY ENCLOSED TORCH COMBUSTION

SAMPLE	DESCRIPTION	As_2O_3 RECOVERED Dry basis	 Fresh basis
		P. p. m.	*P. p. m.*
753	Carrot tops	0.34	0.046
1265	Carrot tops	0.16	0.024
856	Cabbage (S. C.)	0.35	0.038
837	Cabbage (S. C.)	0.12	0.008
796	Cabbage (N. Y.)	0.04	0.003
493	String beans (S. C.)	0.32	0.052
794	String beans (Ga.)	0.29	0.025
388	String beans (S. C.)	0.20	0.020
812	Spinach (Va.)	0.59	0.084
857	Spinach (S. C.)	0.94	0.116
A	Dried kelp	88.0	...
B	Dried kelp	97.0	...

The authors also found the torch applicable to the burning of cod liver oil, the oil (usually 5 cc.) being pipetted onto a 6-inch (15-cm.) piece of No. 3 dental cotton roll, the roll enclosed in a segment of Visking sausage casing to prevent loss of oil by contact with the side of the feed tube of the apparatus, and the roll burned. To insure that the roll turns with the feed plate, the bottom of it is split and the two halves are pressed down on the pins of the plate. Twenty samples of American cod liver oil analyzed by this method gave values ranging from 1.9 to 6.7 parts per million of arsenic trioxide (*3*). Duplicate analyses of cotton rolls, to which had been added 10 γ of arsenic dissolved in alcohol, yielded identical results of 10.4 γ. No detectable stain was obtained from the cotton alone.

CONCLUSION

The method is applicable to products which contain sufficient combustible matter to burn freely in a current of oxygen. Consequently it can hardly have wide application in the estimation of spray residues on vegetables, which would have to be dried and ground before burning, except as a check on acid digestion. Its principal advantages, when applied to dried material or oils, are economy in time and reagents and the elimination of acid fumes from the air of the laboratory. Dry samples ranging in size from 5 to 100 grams can be burned continuously in one operation, at a rate of 1 to 3 grams per minute. The amount of oil that can be burned in one operation is limited to that which a cotton roll will absorb without leaking when subjected to the heat of the torch.

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Determination of Base Exchange in Soils with Copper Nitrate

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THE determination of the total base-exchange capacity and the amounts of the various exchangeable bases in soils is important in many soil and agronomic investigations. The results of such determinations have been applied with singular success in the study of morphological and genetical problems pertaining to soils; the study of soil acidity and its related problem, soil liming; the investigation of the availability of plant food cations and their retention when applied as fertilizers; and finally the problem of adequately explaining the development of so-called alkali soils. It is evident that a simple, accurate, and rapid method for the determination of the base-exchange capacity of soils and the amounts of the various exchanged bases should be available to the soil investigator.

By the term "base exchange" is meant the exchange or replacement of the adsorbed cations of the soil by some other cation. Those cations which have been replaced or removed are known as the exchanged or replaced bases. Theoretically any salt can be used to supply the replacing cation, provided it will form an aqueous solution of sufficiently high concentration and be highly ionized. In laboratory practice the soil is usually leached with solutions of one of the following salts: sodium chloride, potassium chloride, ammonium chloride, or ammonium acetate, or with 0.05 *N* hydrochloric acid. Each of these substances as a source of cations has certain inherent objections. When sodium or potassium salts are used as the replacing agents, it is impossible to determine the amounts of these elements in the replaced bases. Another serious objection is that exceedingly small quantities of the replaceable bases, a few milligrams, must be determined in the presence of a high concentration of the replacing agent, usually several grams, or some special method must be used in order to remove these salts, such as volatilization in the case of ammonium salts with possible mechanical losses, or evaporation with nitric acid, which is tedious, disagreeable, and expensive when many determinations are to be carried out, as previously pointed out (*2*). Also it is important to note that all the methods so far proposed and used require for the estimation of the base-exchange capacity a subsequent replacement from the soil of the adsorbed replacing cation and its quantitative determination in the second leachate. This latter objection is not so serious when the ammonium ion is used as the replacing agent since its quantity can be determined by distillation with magnesium oxide. However, when many determinations are undertaken, this operation requires considerable time and attention.

To eliminate these objections, the authors propose the use of copper nitrate to supply the replacing cation, and the determination of the base-exchange capacity by the electrolytic deposition of copper in the leachate. The electrolytic separation of the copper serves two purposes—namely, the calculation of the base-exchange capacity of the soil and, most important of all, the removal of the replacing cation from the leachate, leaving a solution which can then be used for the determination of the replaced bases, after concentration to small volume to remove excess nitric acid set free during electrolysis.

METHOD

The method consists in using 250 ml. of approximately 0.3 *N* copper nitrate for leaching 10 grams of soil. The soil is ground to pass a 40-mesh sieve and is then allowed to stand in contact with 125 ml. of the solution for 24 hours. The solution and soil are transferred to a prepared Gooch crucible and leached with the remaining 125 ml. of solution. The soil is then washed with 80 per cent alcohol until the washings are free of copper. This requires about 100 ml. Alcohol is used to wash out the unadsorbed copper ions instead of water, since the latter causes hydrolysis of the adsorption complex with subsequent low values for the base-exchange capacity. The leachate and washings are made up to 500 ml. and an aliquot of this is analyzed for copper and the replaced bases. An aliquot of the original copper nitrate solution is also analyzed for its copper content. The subtraction of the former value from the latter gives the amount of copper adsorbed by the soil, and when expressed in milliequivalents per 100 grams of soil represents the base-exchange capacity of the soil.

For the determination of copper the authors have used with satisfactory results the electrolytic apparatus sold by the Fischer Scientific Company, and also a set-up consisting of storage battery, suitable resistors, ammeter, and voltmeter. The authors have obtained the best results by using 1 to 1.5 amperes and 5 volts. Each determination requires about 45 minutes. Using these conditions, a dense adherent film of copper was obtained which did not flake off through stirring or washing. After removal of the copper the solution was concentrated to convenient volume and the calcium and magnesium were determined by the usual methods.

The authors have also determined the amount of copper ions adsorbed by the soil by replacing these adsorbed copper ions by leaching with 0.1 *M* hydrochloric acid, and electrolytically determining the copper in this leachate.

As a check upon the accuracy of this new method, they have also determined the base-exchange capacity, and the exchangeable calcium and magnesium ions, using the standard neutral ammonium acetate method (*4*). Since the concentrations of replaceable sodium and potassium in the soils reported are exceedingly low, their values were not determined.

RESULTS

In Table I is reported a comparison of the values obtained for base-exchange capacity and for replaceable calcium and magnesium by using the neutral ammonium acetate method and the copper nitrate method upon six soil profiles. Soils 1 to 5, inclusive, are forest soils of the Caddo Series and soil 6 is a Sharkey silty clay loam. The results in all cases are the average of duplicate determinations. It is evident that the two methods yield values which check within the limits of experimental error for base-exchange capacity, and also for the amounts of replaceable calcium and magnesium. The data also show that the amount of copper adsorbed by the soil from the copper nitrate solution can be displaced by hydrogen ions, and that the copper so replaced is equal to the amount of copper lost from the cupric nitrate solution used in the original leaching of the soil.

TABLE I. COMPARISON OF BASE-EXCHANGE CAPACITY OF SIX SOIL PROFILES

	BASE-EXCHANGE CAPACITY[a]			REPLACEABLE[a] CALCIUM		REPLACEABLE[a] MAGNESIUM	
SOIL	Ammonium acetate method	Copper adsorbed by soil	Copper recovered from soil	Ammonium acetate method	Copper nitrate method	Ammonium acetate method	Copper nitrate method
1A	7.58	7.45	7.23	4.68	4.46	2.24	2.52
1B	9.91	10.68	10.61	5.45	5.18	1.75	1.48
1C	32.75	32.70	32.60	23.20	23.85	3.23	3.50
2A$_1$	12.36	12.57	12.44	4.55	4.46	2.11	2.57
2A$_2$	3.43	3.46	3.45	3.21	3.21	1.16	1.07
2B	8.69	8.33	8.22	7.31	7.31	2.61	2.55
2C	21.45	21.40	20.90	15.95	16.55	3.27	3.59
3A	2.22	2.51	2.23	2.31	2.14	Trace	Trace
3B	12.80	12.73	12.84	6.51	6.86	3.41	3.19
3C	15.70	15.87	15.88	10.17	10.67	3.24	3.32
4A	5.92	6.29	6.30	4.61	4.91	Trace	Trace
4B	19.50	19.50	18.92	14.59	14.25	1.86	1.62
4C	14.51	13.89	13.90	12.17	12.11	0.96	0.97
5A	5.70	5.97	6.02	3.56	3.72	1.07	1.03
5B	9.70	9.28	9.14	6.05	6.21	1.65	1.73
5C	14.90	14.45	14.26	10.25	10.38	2.11	2.29
6A	24.01	24.05	24.01	16.30	16.50	2.33	2.38
6B	11.19	11.16	11.08	9.26	9.10	1.61	1.69
6C	36.10	35.75	35.72	19.26	19.36	2.82	2.82

[a] Milliequivalents per 100 grams of soil.

Previously it was generally agreed that base exchange in soils could be represented by stoichiometrical relationships, but later work has shown that within narrow limits it is a function of the hydroxide-ion concentration of the replacing solution, and also that these cannot be differentiated from the exchangeable cation (*1*, *3*). The results reported here, while not offering conclusive proof, indicate very clearly that stoichiometrical relationships do hold for base exchange in soils.

CONCLUSIONS

A rapid and accurate method for the determination of the base-exchange capacity of soils is proposed, which results in considerable saving in time when compared to the standard ammonium acetate method and eliminates some objections which have been raised to the older methods.

A 0.3 *N* solution of copper nitrate is used to replace the adsorbed bases, the decrease in copper content of replacing solution being used as a measure of the total exchange capacity of the soil. The removal of the copper from the leachate by electrolysis results in a solution which can be used, after evaporation to small volume to remove the excess nitric acid, for the determination of the replaced bases.

If desired, a check upon the accuracy of the base-exchange capacity can be obtained by leaching the adsorbed copper from the soil by means of dilute hydrochloric acid and estimating the amount of copper in this leachate by electrolysis. The replacement of the adsorbed bases of soils by copper ions is quantitative and can be represented by stoichiometrical values.

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Determination of Citrate

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A relatively simple procedure is presented for estimating citrate in a solution containing as little as 1 mg. in a 5-ml. sample. The procedure consists principally in oxidizing citric acid by means of potassium permanganate in the presence of mercuric sulfate. The insoluble precipitate formed is determined gravimetrically. The analysis may be completed in 3 to 4 hours. A study of the conditions required in the determination and of some possible sources of interference is made.

FOR investigations requiring large numbers of citrate determinations, such as the study of decomposition of citrates by microörganisms, a relatively simple and rapid method for estimating citrate is desirable. The most general methods available for the determination of citric acid are: (*a*) acetone formation (*1, 6, 15*); (*b*) pentabromoacetone formation (*5, 8, 9, 11, 12*); (*c*) mercuric sulfate complex formation (*2, 4, 13, 14*); (*d*) enzymatic dehydrogenation (*12*); and (*e*) esterification (*10*). These methods have their peculiar limitations, some in the large quantity of material required for a determination or the excessive time necessary for complete analysis; some in the appreciable volatility and solubility of the analytical precipitate, the limited number of concurrent determinations feasible, the delicate control needed, or the complicated apparatus demanded.

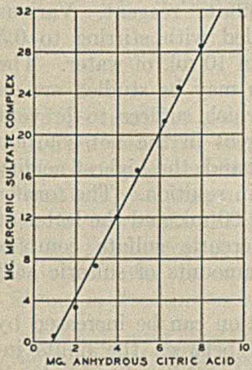

Figure 1. Relation between Citric Acid and Mercuric Sulfate Complex

The mercuric sulfate method was selected for its rapidity and convenience. A detailed study of some of its limitations, including the effect of temperature, acidity, and rate of oxidation on the amount of mercuric complex produced, was made. It was found that control of volume during oxidation and the use of centrifuge tubes rather than Gooch crucibles increase accuracy and speed. Interference from aconitic acid has been established, but moderate amounts of formate, acetate, succinate, malate, tartrate, lactate, and phosphate do not interfere.

Experimental Procedure

The method consists in precipitating citric acid with barium acetate in dilute alcoholic solution to separate it from interfering substances. The precipitated citrate, which is soluble in acid, is then oxidized by permanganate in the presence of mercuric sulfate, yielding a very insoluble precipitate. This is determined gravimetrically and compared with the weight of a precipitate formed from known amounts of citrate treated in the same way.

Materials and Apparatus. The following solutions are prepared:

1. A fresh solution of analyzed anhydrous citric acid (*3*) containing 2 mg. of citric acid per ml.
2. Ten per cent barium acetate.
3. Saturated barium hydroxide.
4. Fifty per cent alcohol with one per cent barium acetate.
5. Eighty-five per cent phosphoric acid.
6. A solution of mercuric sulfate, made by dissolving a suspension of 50 grams of mercuric oxide in 500 ml. of water by the gradual addition of 200 ml. of 96 per cent sulfuric acid and diluting to 1000 ml.
7. One per cent potassium permanganate.
8. Fifty per cent alcohol.

Heavy-walled Pyrex glass centrifuge tubes of 15 ml. capacity, numbered, weighed, and marked at 10 ml. are used. A copper stand holds the centrifuge tubes in a water bath and a special stirrer is used when permanganate is added to each in turn. The stirrer is made from a 25-cm. length of 3-mm. glass rod, fitted with a glass bearing and rubber stopper as holder. The upper end is bent to a small hook and weighted. The lower end is bent to a short spiral small enough to enter the centrifuge tubes, with a 2-cm. tip to prevent the stirrer from sticking in the cone. This stirrer when mounted is operated by a string in the hand of the analyst. Graduated 1-ml. pipets are used to measure the mercuric sulfate and phosphoric acid solutions. Potassium permanganate is added from a 10-ml. buret having a rubber connection with a glass pearl and a bent tip. This type of buret permits more accurate control of the rate of addition of the reagent than the type with a glass stopcock. A silver or platinum wire is used for stirring the precipitate in the wash liquid.

Procedure. For known quantities of citric acid, six centrifuge tubes containing 1 to 5 ml. of the standard solution are a convenient series. To each is added 1 ml. of 10 per cent barium acetate and four drops of saturated barium hydroxide. The precipitation of the barium salt is completed by the addition of two volumes of 95 per cent alcohol. After standing 10 minutes, the precipitate is centrifuged for 5 minutes and is washed three times by centrifuging with 3 ml. of 50 per cent alcohol containing 1 per cent barium acetate. After the precipitate is well drained (10 minutes at 30° C.), it is dissolved in a mixture of 3 ml. of water and 0.16 ml. of phosphoric acid. For 5 minutes this solution is placed in a boiling water bath to insure complete elimination of the alcohol.

To the hot solution is added 1 ml. of the mercuric sulfate reagent. After the precipitate has settled, the solution is diluted with water to 10 ml., centrifuged, and decanted through a filter into a small beaker. Eight ml. of the filtrate are transferred to a weighed 15-ml. centrifuge tube, and 0.2 ml. of mercuric sulfate reagent and 1 ml. of water are added. The tube is placed for 1 minute in a water bath at 85° C., a drop of 3 per cent hydrogen peroxide is added, and with continuous stirring, 1 per cent potassium permanganate is added at a rate not exceeding one drop in 10 seconds until a faint pink color persists for 10 seconds. One drop of hydrogen peroxide is added. After 1 minute the stirrer is rinsed off, and the tube cooled and centrifuged for 5 minutes. Upon decanting the supernatant liquid, the precipitate is stirred with 3 ml. of 50 per cent alcohol and centrifuged again. Washing is repeated three times. During the process a slight scum occasionally escapes from precipitation; but the combined scum from eight such tubes weighs less than 0.2 mg. After draining for 5 minutes, the tube is wiped off and dried at 100° C. for an hour, or in a vacuum oven for half an hour. No change in weight occurs on standing overnight. The weights of precipitate, multiplied by 10/8 to correct for the fraction of the original solution taken, when plotted against the known amounts of citric acid, form a straight line between 1 and 10 mg. of acid (Figure 1).

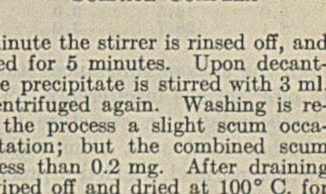

Figure 2. Effect of Temperature on Yield of Mercuric Sulfate Complex

The same procedure applies to the determination of citrate in some mixtures of organic materials. Certain precautions are necessary in this case, however, and these are discussed after some sources of error are considered.

Studies of Interference

By the precipitation of the barium salt, interference due to chloride ions has been avoided. Phosphate has not been found detrimental. Although Gowing-Scopes (*4*) has reported that the precipitate is dissolved by prolonged exposure to hydrogen peroxide, no interference from this source has been found in the present procedure. The small amount of peroxide introduced does not alter the weight of precipitate appreciably until the period of contact is many times that given in the procedure.

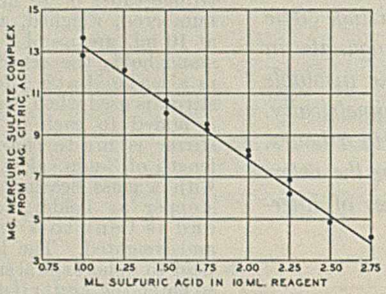

Figure 3. Effect of Acid Concentration on Yield of Mercuric Sulfate Complex

Studies on the effect of formate, acetate, and succinate on the amount of mercuric sulfate complex formed are summarized in Table I. No interference was observed.

Table I. Absence of Interference by Succinate, Acetate, and Formate

	Mercuric Sulfate Complex
	Mg.
8.0 mg. anhydrous citric acid	29.1
+ 2 mg. sodium succinate	29.0, 28.2
+ 2 mg. each of sodium acetate and succinate	29.1, 28.3
+ 2 mg. each of sodium formate, acetate, and succinate	28.6, 28.7

While U. S. P. lactic acid yielded a rather large precipitate with this procedure, distilled lactic acid and pure zinc lactate did not. A study of the influence of tartaric and malic acids on the yield of the precipitate from citric acid showed that no appreciable error was introduced within the range selected. The results of these studies are summarized in Table II. The maximum error is equivalent to about 0.4 mg. citric acid.

Table II. Effect of Tartaric and Malic Acids on Citrate Determination

Anhydrous Citric Acid	Mercuric Sulfate Complex	Tartaric Acid Added	Mercuric Sulfate Complex	Malic Acid Added	Merucric Sulfate Complex
Mg.	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*
1.9	2.9	3.0	3.4	3.0	3.3
5.0	16.5	3.0	16.4	3.0	16.5
8.1	28.7	3.0	30.4	3.0	29.9

Of the various substances studied, only one has been found to offer serious interference. This is aconitic acid, which is closely related in structure to citric acid. This material, whether used as a commercial c. p. chemical, or whether further purified, yielded a precipitate when subjected to the same procedure as citric acid. (See Table III.)

Table III. Mercuric Complex Obtained from Aconitic Acid

c. p. Aconitic Acid (d. 192°)	Mercuric Sulfate Complex	Recrystallized Aconitic Acid (Water)	Mercuric Sulfate Complex
Mg.	*Mg.*	*Mg.*	*Mg.*
8.5	5.9	7.9	5.9
7.0	5.6	5.9	4.0

Effect of Temperature

Since the product of oxidation in this procedure is presumably acetone dicarboxylic acid, the objection may be raised that the known instability of this acid at elevated temperatures may cause erratic deviation in the results. Since this acid may be kept for months at 7° C. but is almost instantly decomposed at 100°, the rate of decomposition evidently varies with the temperature. The yield of mercuric sulfate complex might therefore increase as the temperature is lowered from 100°. Experimental study has shown that this is not the case. The amount of precipitate remained practically constant between 70° and 100°, and therefore no error due to changes in temperature will be encountered when the temperature is kept above 70° C. Below 70° the amount of precipitate decreases (Figure 2). An explanation for this may be found partly in the observation of Kuyper (*7*) that oxidation of citric acid is more complete at lower temperatures, and partly in the fact that, while oxidation and complex formation occur practically instantaneously at elevated temperatures, the rate becomes slower at the lower temperatures, and the easily oxidized product is subjected to further oxidation before it is removed as an insoluble precipitate.

Effect of Acidity

The effect of varying the acid concentration in the oxidation has been studied by changing the amount of sulfuric acid added with the mercuric sulfate reagent. Various amounts of sulfuric acid were added with stirring to 0.5 gram of mercuric oxide suspended in 10 ml. of water. The limits between which this variation may be studied are on the one hand the lowest acidity which suffices to prevent spontaneous hydrolysis of the reagent in the hot solution before oxidation, and on the other hand, the highest acidity at which the reagent may be held in solution. The former was found to lie between 0.75 and 1.00 ml. and the latter at about 2.75 ml. The yield of mercuric sulfate complex decreased linearly with increasing amounts of sulfuric acid (Figure 3).

The sensitivity of the determination can be increased by diminishing the acid concentration between the limits indicated. The reagent made by using 1.0 ml. of sulfuric acid permits detection of half as much citrate as can be found by the usual method using 2.0 ml. This may be of particular importance where small amounts of material are to be analyzed.

Discussion of Results

The method for analysis of citric acid by the mercuric sulfate procedure as modified here can be used for samples containing 1 to 10 mg. of citric acid in 1 to 5 ml. of solution. By using half the amount of sulfuric acid in the reagent, as little as 0.1 mg. per ml. can be found. This modification has not seemed desirable for larger quantities because the precipitate assumes a dark appearance during the extended period of oxidation.

The volume of the solution from which the barium salts are precipitated does not materially influence the result within the indicated limits. The results of Täufel and Mayr (*15*) show that, in the presence of an excess of the precipitating agent, the solubility of barium citrate in 50 per cent alcohol is sufficiently low to allow an accuracy of 0.1 per cent.

No interference was encountered from formic, acetic, succinic, malic, lactic, or tartaric acids in amounts comparable with the citric acid present. Where much larger amounts of substances precipitable by barium acetate are present, it is necessary to use larger amounts of the reagent. To test this possibility, the supernatant fluid from the precipitation of an unknown mixture of barium salts should be treated with more reagent before it is discarded. It is necessary to neutralize the sample if much strong acid is present, since the precipitation of the barium salt is most complete in a neutral or slightly alkaline medium.

Interference by aconitic acid requires a qualitative test for the absence of this material in the unknown mixture in order to determine the applicability of the method. The pink or blue coloration of acetic anhydride at 100° C. (*16*) is of some value in detecting aconitic acid. The absence of this coloration indicates absence of aconitic acid.

The rate of oxidation should be not greater than one drop of potassium permanganate solution in 10 seconds, since more rapid oxidation gives low results. The use of other oxidizing agents or more dilute permanganate was not found advantageous in the present procedure. For the smaller quantities in particular, the addition of manganous sulfate has proved useful, but this has not been essential for the successful application of the method within the sample range considered here. All the oxidative methods apply to the citrate ion; trimethyl citrate and citric triamide, for example, give no evidence of citrate content by the permanganate procedures unless they are first hydrolyzed.

ACKNOWLEDGMENT

Acknowledgment is made of the helpful criticism of M. Kunitz and the technical assistance of B. Prytz.

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A Large-Size Modified Soxhlet for Hot Extractions

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THE need for a modified Soxhlet extractor intermediate between the large-size Soxhlets ordinarily used for quantitative determinations and the very large extractors described by Cameron (*1*), Drake and Spies (*2*), and McCay (*4*) but more refined than that described by Liston and Dehn (*3*) led the authors to design the extractor shown in Figure 1. This extractor is especially useful where the material is fibrous in structure or is to be given a hot extraction.

The apparatus consists of three parts like the ordinary Soxhlet: the condenser *A*, the extractor body, *C*, and the receiving flask which fits at *D*. Condenser *A* consists of a 12-inch (30-cm.) Allihn condenser having the delivery tube bent and cut as shown. The flask (not shown) is a 2-liter flat-bottom flask having a No. 30 standard taper joint to fit at *D*. The body of the extractor, *C*, is 16 inches (40 cm.) in length (over-all) and carries a No. 50 standard taper joint, *B*, at the top and a No. 30 standard taper joint, *D*, at the bottom. The vapor tube, *G*, having a vent, *V*, at the top, carries the siphon tube *E*, fastened at points *H* to give it strength and protected by the shield, *F*. *F* is vented at *I* and carries 6 or 8 holes, *J*, at the bottom. The body is 5 inches (12.5 cm.) in diameter and 10.5 inches (26 cm.) in height (exclusive of joints). Shield *F* is 2 inches (5 cm.) in diameter. The volume of liquid required to cause siphoning (extractor empty) is 1900 cc.

This extractor overcomes the chief difficulty found in most Soxhlets—imperfect siphoning—by the use of the large siphon shield *F*. This shield, besides protecting the siphon tube, acts as a reservoir so that the siphon is always in contact with liquid, the reservoir being so large that the solvent has considerable time to drain from the sample into the reservoir before the reservoir is emptied. For best results siphon tube *E* should be flattened at the top and constricted at the bottom as advised by Cameron (*1*).

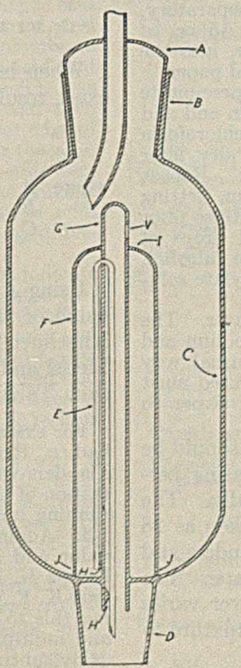

FIGURE 1

The fact that the vapor tube, *G*, passes through the liquid in the extractor means that only constant-boiling solvents, or those which have a very short boiling range, may be used because the liquid in the reservoir is always hot and refluxing will occur to such an extent that no extraction will take place if the solvent has a wide boiling range. However, by placing a chimney around the body of the extractor in such a manner that little heat is lost by radiation, extraction at a few degrees below the boiling point of the solvent will take place when a constant-boiling solvent is used. Since siphoning is clean and rapid, very good hot extractions can be carried out in this manner. If low-boiling solvents are used and exceptionally rapid extractions are desired, it would no doubt be advantageous to replace condenser *A* by one of the type described by Cameron (*1*).

The extractor described above has been used mainly for the alcohol extraction of cotton linters, although other solvents have been employed. With this solvent excellent results have been obtained over a period of 6 months.

ACKNOWLEDGMENT

The authors wish to acknowledge the assistance of Otto Greiner & Company, of Newark, N. J., who made this extractor from Pyrex glass to specifications.

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Determination of Butter Fat in the Presence of Coconut Oil

A Modified Kirschner Procedure

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The regular Kirschner test[1] for the determination of butter fat in the presence of coconut oil has a number of inherent disadvantages which limit its usefulness. It calls for a second distillation of the fatty acids and depends upon the use of silver sulfate, which is not very soluble or quick in its action.

The modification to be described reverses the regular procedure in that it avoids the second distillation and operates directly upon that portion of the fatty acids precipitated by silver. Also, the use of silver nitrate as the silver salt insures quick and clean precipitation. This process has been in use for many years in this laboratory in controlling the composition of oleomargarine which contained 10 per cent of butter fat and a similar amount of coconut oil. The authors' modification of this method (called the Kirschner-Flanders procedure) is as follows:

Modified Method

The Reichert-Meissl determination is carried out as usual, using glycerol soda for the saponification. The distillation is best conducted on an electric heater capable of close regulation, as the time of distilling 110 cc. must be 30 ± 0.5 minutes for good results.

The 110 cc. of distillate are titrated in a 300-cc. Erlenmeyer flask with 0.1 *N* sodium hydroxide, using phenolphthalein indicator and running to a distinct end point. This gives the Reichert-Meissl number, which should be corrected by a blank titration found by carrying through the heating and distillation on the glycerol soda solution alone.

Add 5 cc. of 10 per cent silver nitrate solution to the neutralized Reichert-Meissl distillate. Let it stand 30 minutes with occasional rotatory shaking. (The flask should be stoppered.) Filter on a 9-cm. paper (Whatman No. 41). Let filter drain (do not wash precipitate). Transfer precipitate to a separatory funnel with cold water and also rinse out flask into separatory, using as little water as possible. Rinse flask with 15 cc. of 0.1 *N* sulfuric acid and pour the acid over the filter, into the separatory. Rinse filter with a little water and discard paper.

Stopper the separatory and shake vigorously till precipitate is dissolved. Rinse the flask with 15 cc. of chloroform and add to separatory. Shake well and let stand until the chloroform clears. Draw chloroform layer carefully through a dry filter (Whatman No. 4) into a 150-cc. Erlenmeyer flask. Repeat extraction twice with 10-cc. portions of chloroform, letting stand a few minutes each time before drawing off. Rinse filter with 25 cc. of additional chloroform. Add 3 or 4 drops of phenolphthalein indicator made up with absolute alcohol. Titrate directly in chloroform with 0.1 *N* sodium ethylate solution to strong end point.

The titration is carried out in the absence of water. The standard sodium ethylate is prepared from cleaned sodium and absolute alcohol and may be standardized in the usual way against standard hydrochloric acid. The chloroform used must be washed, if not neutral, and filtered through dry paper to remove water.

For practical use the figures as shown in Table I should be plotted on plain cross-section paper, with increasing percentages running vertically and titrations horizontally. The Reichert-Meissl value of the pure butter fat is taken as 28 and is drawn as a straight line. The Kirschner-Flanders and Reichert-Meissl values yield curves of similar shape. The proportion of the volatile acids precipitated by silver varies from 81 per cent at 10 per cent coconut oil in the mixture to 76 per cent when pure coconut oil is used.

The authors' experience with this method has been principally on oleomargarine containing 10 per cent of butter fat and from 6 to 15 per cent of coconut oil. Under these conditions it has given results very close to the true value for butter fat and approximate values for the coconut oil. In this range fairly close results for the butter fat may be secured on mixtures of butter fat with coconut oil by subtracting the Kirschner-Flanders titration from the Reichert-Meissl and dividing the result by 28.

Table I. Pure Butter Fat and Coconut Oil Alone

	Butter Fat		Coconut Oil	
	Reichert-Meissl	Kirschner-Flanders	Reichert-Meissl	Kirschner-Flanders
%				
100	28.0	4.0	7.8	6.0
90	..	3.5	7.6	5.85
80	..	3.0	7.2	5.6
70	..	2.5	6.85	5.4
60	..	2.05	6.4	5.1
50	..	1.6	6.0	4.8
40	..	1.2	5.5	4.5
30	..	0.8	4.8	4.0
20	..	0.5	3.9	3.2
10	..	0.25	2.7	2.1
5	..	0.1	1.8	0.8

Table II. Results with Varying Amounts of Butter Fat and Coconut Oil

Fat Mixture						
Butter fat	Coconut oil	Reichert-Meissl[a]	Kirschner-Flanders[a]	Kirschner[a]	Butter Fat by Kirschner	Butter Fat by Kirschner-Flanders
%	%				%	%
50	50	17.7	5.6	12.6	55.4	48.6
40	40	15.1	5.2	10.1	44.7	39.7
30	30	11.6	4.2	7.6	33.6	29.3
20	20	8.4	3.2	5.0	22.1	20.7
15	15	6.3	2.6	3.7	16.4	14.6
10	10	4.8	2.0	2.5	11.7	10.9
5	5	2.7	1.0	1.2	5.3	6.6
80	20	23.6	5.8	19.7	87.1	73.2

[a] Cc. 0.1 *N* sodium hydroxide.

When larger percentages of butter fat are involved more exact results may be secured by the following formula:

$$\%\ \text{butter fat} = \frac{(A - B) + C \times 100}{28}$$

where A = Reichert-Meissl value
B = Kirschner-Flanders value
C = correction for part of Kirschner-Flanders due to butter fat

Using $A - B$ as an approximation for the Reichert-Meissl value of the butter fat present we find the corresponding Kirschner-Flanders value for pure butter fat on the Reichert-Meissl and Kirschner-Flanders curves, which can be plotted from Table I.

For example, a mixture containing butter fat and coconut oil had a Reichert-Meissl value of 17.7 cc. and a Kirschner-Flanders value of 5.6 cc.: $A - B = 12.1$. Using this approximation of the R. M. value for the butter fat present we find by running up to the R. M. line a corresponding K. F. value of 1.3. Adding this to 12.1 we get 13.4. By using this corrected value and again referring to the R. M. line we find it would have a K. F. of 0.2 higher, or 1.5. This is the value C, or the true K. F. value corresponding to the butter fat present. Adding this to $A - B$ or 12.1, we get 13.6, which divided by 28 and multiplied by 100 gives 48.6 per cent.

By subtracting the K. F. number from the total R. M. value we have taken off not only that portion of the acids from coconut

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[1] Assoc. Official Agr. Chem., Methods of Analysis, 3rd ed., p. 324 (1930).

oil which were precipitated by silver, but also those from butter fat. This is not serious when the percentage of butter fat is in the neighborhood of 10 per cent, but becomes serious when larger percentages are present. By means of the approximate value $A - B$, we may determine what the K. F. was and add it as a correction.

Table II gives results obtained on several samples containing varying amounts of butter fat and coconut oil. Results by the regular Kirschner method are given for comparison, also the percentages of butter fat indicated by dividing these results by the average factor 22.6.

A very interesting set of curves showing the relation between the Reichert-Meissl, Kirschner-Flanders, and Kirschner values may be secured by plotting all the values given in both tables on the same sheet of cross-section paper.

A consideration of the curves obtained would indicate that the method should be most useful on mixtures containing up to 30 per cent of butter fat and from 10 to 40 per cent of coconut oil. The lower range might be extended by the addition of just enough of the silver salt of the fatty acids to saturate the solution in which the precipitation is to be made. On the Kirschner-Flanders curve this would appear to be the equivalent of 5 per cent of coconut oil. This the authors have never tried, but offer the suggestion for what it is worth.

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Columbium in Steel

Determination in 18-8 Chromium-Nickel Steel and in Low-Titanium Steel

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The use of columbium in steel is increasing rapidly, and a simple gravimetric method for its determination in alloy steels is available. Weiss and Landecker (*2*), in a summary of the properties of columbium and tantalum, stated that they could be separated from solution by perchloric acid, quantitatively, and in an easily filterable form. It was found that fuming with perchloric acid also gave an easily filterable product.

Procedure

Columbium. Two grams of alloy steel (0.8 per cent columbium, 18 per cent chromium, 9 per cent nickel) were dissolved in about 25 cc. of dissolving solution (750 cc. hydrochloric acid, 250 cc. nitric acid, 1000 cc. water) in a 400-cc. beaker. After the steel had been completely disintegrated, 20 to 25 cc. of 70 per cent (technical) perchloric acid were added; the heating was continued until red chromic acid formed and then 5 minutes longer. The contents of the beaker were cooled and diluted to 100 cc. with water, the chlorine was boiled out, and the precipitate was filtered off on a No. 40 Whatman paper.

The paper was washed six times with hydrochloric acid (1 to 10) and once with water to remove excess acid. The paper was transferred to a tared platinum crucible, the paper charred, and the crucible ignited, cooled, and weighed. This gave columbium pentoxide plus silica. About 5 cc. of 1 to 5 sulfuric acid and 3 to 4 drops of hydrofluoric acid were added. The crucible was heated (150° to 200° C.) to fumes of sulfuric acid, and then till practically all acid had been evaporated. The upper edge of the crucible was heated in the flame of a Meeker burner (because of danger of spitting), and increasing portions of the crucible were ignited to drive off more acid; finally the residue in the crucible was heated to about 900° C. to drive out the last traces of acid. Columbium pentoxide remained. Silica was obtained by difference.

The residue on the filter paper was black, which might indicate lower oxides or the carbide of columbium. To determine carbon, a sample of steel was fumed in perchloric acid, filtered off on a small Gooch crucible, and washed with hydrochloric acid and then with water. The crucible was dried at 110° C. and placed in a carbon furnace apparatus; the carbon was determined and found to be 0.05 per cent. It is possible that lower oxides of columbium were present. Hydrofluoric acid changes the residue to the higher oxide of columbium.

Redigestion of the black precipitate on the paper with a mixture of nitric and perchloric acids is of no help. However, if hydrofluoric acid is added to the original dissolving solution, the residue from the perchloric acid treatment will be light yellow but will contain some silica. Such treatment of the steel would have no advantages.

In the removal of the silica by hydrofluoric acid, sulfuric or nitric acids may be used, but in decided excess to prevent partial volatilization of columbium as the fluoride. The residue must be ignited strongly to remove the last traces of the acid radical present. The oxide is yellow when hot and nearly white when cold. The oxide may easily be removed from the crucible by fusion with phosphate.

If the steel is dissolved in hydrochloric acid (1 to 2), cooled, and cupferron added, columbium, some iron, silica, and carbides are found on the filter paper. When the paper is returned to the beaker, treated with 10 cc. of nitric plus 10 cc. of perchloric acid, fumed, and then treated as in the usual procedure, all the columbium will be found in the residue.

Titanium. It has been shown (*1*) that titanium originally present in a steel sample can be dissolved out with perchloric acid. Weiss and Landecker (*2*) found that titanium causes tantalum and columbium to react differently after fusion than if titanium were absent. A steel containing both columbium and titanium was not available. However, a 1-gram sample containing columbium and a 1-gram sample containing 0.30 per cent titanium were mixed and run for columbium. The residue indicated that the perchloric acid had taken up all the titanium, and left the columbium. It has been found that perchloric acid will hold at least 12 mg. of titanium in solution.

Tantalum. Tantalum is expected to react in the same manner as columbium but no samples of tantalum in steel have been received.

The data obtained are as follows:

	1 g. Steel Treated with HNO_3–HF in Pt Crucible		2 g. Steel Treated with HF–H_2SO_4 by Cupferron Method
Crucible, SiO_2, Cb oxide, grams	19.8545	19.8443	25.0994
Same, after HF treatment, grams	19.8441	19.8341	25.0958
Crucible, grams	19.8318	19.8219	25.0715
SiO_2–Cb_2O_5, gram	0.0227	0.0224	
SiO_2, gram	0.0104	0.0102	
Cb_2O_5, gram	0.0123	0.0122	0.0243 (2 g.) 0.0122 (1 g.)
Si, %	0.49	0.48	...
Cb, %	0.86	0.85	0.85

	1 g. Cb + 1 g. Ti (0.30%) Steels Mixed
Crucible + oxides, grams	16.0461
Same, after HF treatment, grams	16.0264
Crucible, grams	16.0143
Remainder, gram (shows no Ti)	0.0121

	C in a 2-g. Residue
2 g. CO_2, gram	0.0038
1 g. CO_2, gram	0.0019
Carbon, %	0.05

Literature Cited

(1) Silverman, Louis, *Chemist-Analyst*, **23** (July, 1934).
(2) Weiss and Landecker, *Chem. News*, **101**, 2, 13, 25 (1910).

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Determination of Malic Acid in Plant Tissue

Simultaneous Determination of Citric and Malic Acids

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Malic acid, when oxidized by potassium permanganate in the presence of potassium bromide, is converted into a bromine compound that is volatile with steam. This substance combines with dinitrophenylhydrazine in acid solution to yield a product insoluble in water which can be filtered off and dissolved in pyridine. The pyridine solution, when diluted with water and made alkaline with sodium hydroxide, promptly develops a blue color suitable for spectrophotometric measurements, strictly proportional to the quantity of malic acid taken over the range 0.1 to 2.5 mg., and stable for several hours. The same product is formed from both optically active and inactive malic acid.

A method, based upon this reaction, has been developed to determine the malic acid content of dried leaf tissue, or of extracts from leaves, and has been applied to tobacco leaf. Preliminary experiments have shown that it can readily be adapted to the investigation of the malic acid content of muscle, blood, and urine, and also to the determination of aspartic acid after this has been deaminized with nitrous acid.

MALIC acid is one of the most widely distributed organic acids found in plants, and frequently occurs in relatively high concentration in them. A method for its accurate determination is therefore a matter of considerable importance in plant physiology; unfortunately, however, none of the methods that have been proposed hitherto are suitable for the estimation of small quantities.

Methods that depend upon precipitation of the acids as lead or barium salts (*4, 5, 9*), with subsequent preparation and fractional distillation of the esters, can be successfully applied only to large quantities of material. The method most commonly used in recent years is based upon the high optical rotation of malic acid in the presence of uranium (*2*) or of molybdenum (*1*) salts. This method is specific only in the absence of other optically active acids; furthermore, the possibility that *dl*-malic acid may sometimes be present in plant tissues (*8*) introduces an element of uncertainty into the result as a measurement of the total quantity of malic acid present.

The method described in the present paper depends on the observation that malic acid, when treated with potassium permanganate in the presence of potassium bromide under the proper conditions, is converted into a bromine compound that is volatile with steam. This substance yields an extremely insoluble condensation product when heated with dinitrophenylhydrazine in acid solution. The ratio between the amount of this product and of the malic acid submitted to oxidation is constant, and the quantity can be easily estimated by dissolving the product in pyridine, diluting with water, and making the solution alkaline with sodium hydroxide. The intense blue color formed is in every way suitable for measurement in a Pulfrich spectrophotometer.

The specificity of this reaction with respect to the common organic acids is remarkable. A quantity of 0.2 mg. of malic acid gave a distinct orange precipitate after heating the oxidation product with an acid solution of dinitrophenylhydrazine, but 25 mg. each of acetic, lactic, fumaric, succinic, pyruvic, tartaric, maleic, glycollic, and glyoxylic acids failed to give any precipitation when oxidized and treated in the same way. Citric acid is converted into pentabromoacetone by the oxidation procedure employed, and this substance yields a precipitate with dinitrophenylhydrazine. No difficulty is thereby presented, however, since pentabromoacetone, if present, is readily removed from the oxidation mixture by extraction with petroleum ether. This solvent does not extract the oxidation product of malic acid.

Products that yield precipitates with dinitrophenylhydrazine are formed when carbohydrates or certain amino acids are subjected to oxidation with potassium permanganate. But no such compound is formed from either malic or citric acid, unless potassium bromide is also present during the oxidation; consequently it is possible to estimate malic acid in the presence of these interfering substances if two parallel oxidations are conducted, one with and one without bromide, and the resulting solutions are extracted with petroleum ether to remove pentabromoacetone. The difference in the yields of dinitrophenylhydrazine derivative then represents with considerable accuracy the quantity of malic acid present, inasmuch as the bromide has no effect upon the oxidation of the carbohydrates. It is generally more convenient, however, to eliminate the amino acids and carbohydrates as a preliminary step by extracting the organic acids with ether from the material under investigation.

Although considerable study has been given to the nature of the oxidation product of malic acid, a detailed explanation of the chemical reactions that occur has not yet been obtained. It seems better therefore at present to describe the reaction from an entirely empirical point of view.

Reagents

Sulfuric acid, 50 per cent: a mixture of equal volumes of concentrated acid and water.

Potassium bromide, 1 M: 11.9 grams diluted to 100 cc.

Potassium permanganate, 1.5 N: 47.4 grams diluted to 1000 cc.

Bromine water: saturated aqueous solution.

Sulfuric acid, 2 N: 28 cc. of concentrated acid diluted to 500 cc.

Hydrogen peroxide, 3 per cent: ordinary commercial product.

Petroleum ether: boiling point, 35° to 50° C.

Sodium sulfide, 4 per cent: 4 grams of crystalline sodium sulfide diluted to 100 cc., prepared fresh every 2 to 3 days.

Hydrogen peroxide (halogen-free): 4 grams of sodium peroxide dissolved in 50 cc. of water, cooled, and faintly acidified to Congo red with 50 per cent sulfuric acid (7 to 8 cc. required); prepared fresh every week.

Silver nitrate, 0.02604 N: 4.4231 grams of pure silver nitrate diluted to 1000 cc. 1 cc. = 1.0 mg. of citric acid.

Ammonium thiocyanate, 0.02604 N; 1.98 grams diluted to 1000 cc. and standardized against the silver nitrate.

Ferric ammonium sulfate (ferric alum): 30 grams dissolved by warming with 100 cc. of water.

Dinitrophenylhydrazine: 5 grams of Eastman's dinitrophenylhydrazine are ground in a mortar with several successive portions of a mixture of 200 cc. of concentrated hydrochloric acid with 800 cc. of water. The whole is then transferred to a beaker and boiled for 1 to 2 minutes with vigorous stirring; after being cooled, the solution is diluted to 1000 cc. with water and filtered through hard paper. The reagent is filtered again just before using.

Sodium sulfite, 20 per cent: 20 grams of crystalline sodium sulfite diluted to 100 cc., prepared fresh every 2 to 3 days.

Pyridine: Eastman's pyridine (pract.) is redistilled.

Sodium hydroxide, 5.0 *N:* 200 grams of c. p. sodium hydroxide diluted to 1000 cc.

Preparation of Organic Acid Fraction

Two grams of the dried and powdered tissue are acidified to pH 1 with sulfuric acid, mixed with 3.5 grams of asbestos, and extracted with ether according to the technic of Pucher, Vickery, and Wakeman (*7*). The organic acids are transferred to aqueous alkali and the solution is made to 100 cc. If extracts of tissue are employed, a portion equivalent to 2 grams of the tissue is evaporated to a sirup (not to dryness), acidified to pH 1 with sulfuric acid, and mixed with the asbestos; the mixture is then extracted with ether in the same way.

Oxidation of Malic and Citric Acid

An aliquot part of the organic acid fraction that contains 0.2 to 2.0 mg. of malic acid (5 cc. are usually sufficient) is diluted to 20 cc. with water, and 3 cc. of 50 per cent sulfuric acid are added. The mixture is boiled gently for 8 to 10 minutes to expel traces of ether, cooled, and 1 cc. of bromine water is added. After 5 minutes the solution is filtered with gentle suction through asbestos in a Gooch crucible into a beaker marked at 35 cc.; interfering impurities are thereby removed. The precipitate is washed with small quantities of water until the filtrate reaches 35 cc., when 2 cc. of 1 *N* potassium bromide are added. The temperature of the solution is then adjusted to 20° to 22° C. and 5 cc. of potassium permanganate previously brought to the same temperature are added. The mixture is allowed to stand in a water bath at 20° to 22° C. for 10 minutes with occasional stirring, and is then chilled to 5° to 10° C. and decolorized with 3 per cent hydrogen peroxide added dropwise with vigorous stirring.

Removal of Pentabromoacetone

The oxidation mixture contains the pentabromoacetone derived from any citric acid present; this is removed by extraction with petroleum ether according to the technic described by Pucher, Vickery, and Leavenworth (*6*). The petroleum ether is washed once with 3 cc. of water and the citric acid equivalent to the pentabromoacetone may be determined as described below.

Determination of Malic Acid

The aqueous solution together with the 3 cc. of wash fluid from the petroleum ether is diluted to 100 cc. and a 25-cc. aliquot is transferred to a 300-cc. Kjeldahl flask. About 25 cc. of water and a few angular quartz pebbles are added. To insure the destruction of hydrogen peroxide about 0.5 cc. of potassium permanganate is then added and the solution is decolorized by the addition of 2 cc. of sodium sulfite solution. The flask is fitted with the distillation tube described by Folin and Wright (*3*). A 250-cc. wide-mouth Erlenmeyer flask charged with 10 cc. of freshly filtered dinitrophenylhydrazine solution and 20 cc. of water is used as a receiver; the end of the distillation tube is dipped beneath the surface of the reagent in the receiver and the flame of a microburner is applied to the flask. Distillation is continued at a rapid rate without cooling the receiver until the volume of solution remaining in the Kjeldahl flask has been reduced to somewhat less than 10 cc. A mark previously placed on the flask with a wax pencil at the 10-cc. point is of assistance. The distillation requires from 12 to 15 minutes. The distillation tube is then rinsed off and the receiver is cooled to room temperature.

The orange precipitate is transferred as completely as possible with water to a small (No. 2) Gooch crucible furnished with an asbestos mat, and is then dried for a short time at 100° to 110° C. Meanwhile the receiver is thoroughly drained, and the last traces of precipitate are taken up in hot pyridine used in several successive portions but not more than 3 to 4 cc. in all. The pyridine washings are transferred to a 25-cc. volumetric flask. The crucible is then fitted into a rubber stopper carried on a cylindrical funnel which is attached to a test tube equipped with a side arm and marked at 20 cc. Boiling pyridine is added in small portions to the crucible, and the contents are gently triturated with a glass rod, after which suction is applied and the pyridine is drawn through each time; three or four washings are usually sufficient to dissolve and transfer all the precipitate to the test tube. The pyridine solution is then added quantitatively to the 25-cc. flask used for the rinsings of the receiver. After being cooled to room temperature the solution is made to volume with pyridine and mixed; it is then allowed to settle or is filtered, if necessary, through soft paper to remove shreds of asbestos.

Either a 2-cc. or a 5-cc. aliquot part of the pyridine solution is transferred to a 100-cc. flask and 50 cc. of water are added, followed by 5 cc. of 5 *N* sodium hydroxide. The solution is then diluted to the mark and the blue color is read in a Pulfrich spectrophotometer using color filter S-57 and a cell length that gives readings between 30 and 80 per cent. In general a 1-cm. or a 3-cm. cell is suitable. The extinction coefficient is calculated and the malic acid equivalent is read from a calibration curve constructed as described in the next section.

The method is satisfactory for the estimation of from 0.1 to 2.5 mg. of malic acid in the 25 cc. of pyridine. If more than 2.5 mg. are found the distillation should be repeated on a smaller aliquot part of the oxidation mixture, but if less than 25 cc. are employed it is necessary to add 1 or 2 cc. of 50 per cent sulfuric acid before distilling, and in any case the aqueous volume in the Kjeldahl flask must be from 40 to 50 cc.

Construction of Calibration Curve

Pure commercial *dl*-malic acid is recrystallized twice from water and dried to constant weight in a vacuum desiccator; exactly 200 mg. of the product are dissolved and diluted to 100 cc. with 1 *N* sulfuric acid. This solvent preserves the malic acid indefinitely.

A 5-cc. aliquot (10 mg.) is oxidized under the conditions described; the oxidation mixture is made to 100 cc. omitting the extraction with petroleum ether, and aliquot parts are distilled into the dinitrophenylhydrazine reagent. Readings of the blue color are obtained using both 2- and 5-cc. aliquots of the pyridine solution, and the extinction coefficients are plotted against the number of milligrams of malic acid in the aliquot of pyridine taken. Several determinations should be made of each point and these should agree within 5 per cent of each other. The average values should give a straight line.

Table I. Calibration Data for Determination of Malic Acid with Pulfrich Spectrophotometer

(Light filter S-57)

Extinction Coefficient K	Malic Acid *Mg.*
0.030	0.016
0.039	0.020
0.047	0.024
0.060	0.032
0.078	0.040
0.116	0.060
0.156	0.080
0.200	0.100
0.315	0.160
0.395	0.200
0.473	0.240
0.628	0.320

Table I gives the data of the calibration curve obtained in this laboratory. It represents the average of a large number of closely agreeing determinations obtained in several different ways: (1) From 0.1 to 5.0 mg. of malic acid were separately oxidized and the extinction coefficient was obtained with and without steam distillation of the product of oxidation. When distillation was omitted the dinitrophenylhydrazine was added and the mixture was heated for 10 minutes in a boiling water bath. (2) Ten milligrams of malic acid were oxidized and the resulting solution was diluted to 100 cc.; of this 0.5- to 25-cc. aliquots were analyzed both with and without distillation. (3) Similar experiments were conducted in which from 0.3 to 6.4 mg. of citric acid were added before oxidation, and the pentabromoacetone was subsequently removed by extraction with petroleum ether. In all cases five and usually ten readings of the spectrophotometer were taken and averaged, and readings were usually obtained with two cells of different lengths. In these observations the extinction coefficient observed for a given quantity of malic acid never varied more than ±8 per cent, and duplicate determinations usually agreed within ±3 per cent. Consistent results were obtained whether the oxidation products were distilled or not, and the presence of citric acid during the oxidation had no effect.

The data in Table I give the extinction coefficient, K, for the number of milligrams of malic acid represented by the 100-cc. volume of blue solution upon which readings are taken. The calculation of the result of an analysis is made as follows:

Grams of malic acid in 2 grams of tissue = mg. of malic acid in

$$Py \times \frac{25}{Py} \times \frac{100}{Ox} \times \frac{100}{Fr} \times \frac{1}{1000}$$

where Py = aliquot of the 25 cc. of pyridine solution
Ox = aliquot of the 100 cc. of oxidation mixture
Fr = aliquot of the 100 cc. of organic acid fraction

To convert into percentage the result is multiplied by 50.

If preferred, calibration curves may be so drawn as to give the malic acid content of the entire 25 cc. of pyridine when a 2-cc. aliquot and a 5-cc. aliquot are taken. The data for these curves may be derived by multiplying the data in column 2 of Table I by 12.5 and 5, respectively.

DISCUSSION

The oxidation of malic acid with potassium permanganate must be conducted with careful attention to the temperature. In a series of experiments carried out at various temperatures with known amounts of malic acid, the yield of product, as measured by the blue color of the alkaline solution of its dinitrophenylhydrazine derivative, was 66 per cent at 9° C., 100 per cent at 19° and at 26° C., 70 per cent at 32° C., and 32 per cent at 40° C. Experience showed that an oxidation temperature within the range 20° to 22° C. gave consistent results and this condition was therefore adopted.

The yield of product is also influenced by the amount of potassium bromide added, being considerably depressed if only 1 cc. of N bromide is added instead of 2 cc. A further moderate excess of bromide, however, did not influence the results. Variations in the amounts of sulfuric acid and of permanganate were without material influence, provided excess of both were present, but the conditions recommended with respect to these reagents have been found advantageous and should be observed.

The removal of the excess of permanganate after the oxidation was found to present some difficulty. Ferrous sulfate was not satisfactory because oxidation mixtures prepared with this reagent gave a large blank when heated with dinitrophenylhydrazine. Sulfites were satisfactory if malic acid alone was to be determined, but if citric acid was present the pentabromoacetone was partly converted into substances that could not be removed with petroleum ether and that subsequently increased the apparent yield of malic acid. Hydrogen peroxide was satisfactory if carefully used. Undue excess must be avoided since, if present under the conditions adopted, a dinitrophenylhydrazine compound soluble in pyridine is produced which increases the amount of blue color observed. The addition of a small amount of permanganate to the solution before distillation provides for the removal of any ordinary excess of peroxide, and the subsequent addition of sulfite removes the excess of permanganate together with any bromine that may have been liberated.

The distillation of the oxidation product with steam effects an important purification of the substance and eliminates the necessity for blank determinations, at least in connection with the determination of malic acid in the leaf tissue the authors have chiefly employed. Before the possibility of this step had been appreciated, it had been necessary to conduct parallel oxidations on equal aliquots of the oxidation mixture, one with and one without potassium bromide. The blank determination usually amounted to the equivalent of from 0.2 to 0.4 per cent of malic acid in the tobacco leaf tissue, but was undoubtedly due to the presence of some other substance. Blanks of a similar order of magnitude were secured when tissue was analyzed from which all the malic acid had been removed by thorough extraction with hot water. This difficulty was completely avoided by the steam distillation of the oxidation product.

Another blank, although of very small magnitude, was eliminated by the aliquoting of the oxidation mixture. The reagents alone give a small but constant blank equivalent to from 0.025 to 0.04 mg. of malic acid in the entire pyridine solution when the whole of the oxidation mixture is distilled; a similar blank is obtained if organic acids are present but potassium bromide is omitted. The amount of color is unreadable, however, if an aliquot of 50 cc. or less of the oxidation mixture is employed, and does not influence the accuracy of the determination of even as little as 0.1 mg. of malic acid. The blank determination in the oxidation mixture does assume importance, however, when tissues very low in malic acid are studied. Such preliminary experiments as the authors have carried out with blood, urine, or muscle extracts have shown that a control oxidation in the absence of bromide is necessary in these cases.

The selection of the proper aliquots to use must be founded on experience. The method is best adapted to the determination of quantities of malic acid not exceeding 2.5 mg. Larger amounts yield a precipitate with dinitrophenylhydrazine that is difficult to manage by the technic described.

The oxidation product of malic acid is stable for many days in sufficiently acid aqueous solution at room temperature, but is unstable in alkali. The pyridine solution of the dinitrophenylhydrazine derivative can be kept for several days if necessary without change. The blue color produced by the addition of alkali is fully developed at once and does not change appreciably for at least 2 hours.

SIMULTANEOUS DETERMINATION OF CITRIC ACID

The citric acid equivalent of the pentabromoacetone removed by extraction with petroleum ether is best determined by the method recently described by Pucher, Vickery, and Leavenworth (*6*). Certain refinements of this method have been developed to deal with the small quantities of citric acid encountered when the chief object is the estimation of the malic acid.

The petroleum ether extract, obtained as already described, is washed three additional times with 3 cc. of water to remove inorganic halides, the washings being discarded. A 3-cc. quantity of 4 per cent sodium sulfide solution is added to the funnel and, after vigorous shaking, the aqueous layer is drawn off into a 50-cc. Erlenmeyer flask. The petroleum ether is then treated a second time with 3 cc. of sodium sulfide, and is washed three times with 3 to 4 cc. of water, the aqueous solutions being all received in the same flask. To this 2 cc. of 2 N sulfuric acid are added, a few angular quartz pebbles are dropped in, and the solution is boiled gently for 3 minutes to expel hydrogen sulfide. It is then cooled to room temperature, and sufficient 1.5 N permanganate is added to produce a red color (0.8 to 1.0 cc. usually) permanent for 15 to 20 seconds. The color is discharged by the addition of a small excess of halogen-free hydrogen peroxide, and 2 cc. of concentrated nitric acid, 3 cc. of standard silver nitrate, 1 cc. of ferric alum indicator solution, and 3 to 4 cc. of ether are added. The flask is shaken vigorously to coagulate the silver bromide, and the solution is titrated with thiocyanate from a microburet to a faint salmon-pink color. Multiplication of the number of cubic centimeters of silver nitrate used by the factor 1.12 gives the number of milligrams of citric acid in the aliquot of the organic acid fraction taken. If the solution should chance to contain in excess of 3 mg. of citric acid the first drop of thiocyanate will produce a red color. In these circumstances additional silver nitrate is added and the titration is completed in the usual way.

RECOVERY OF MALIC ACID

Table II gives the data of analyses of a solution of pure malic acid. The values of the extinction coefficient as observed in cells of two lengths are shown, and the malic acid equivalent to the average of these is given as closely as it could be read from the calibration curve.

TABLE II. RECOVERY OF MALIC ACID

(Light filter S-57)

MALIC ACID TAKEN	*K* 1-cm. cell	*K* 3-cm. cell	MALIC ACID FOUND	RECOVERY
Mg.			*Mg.*	%
0.20	0.032	0.031	0.20	100
	0.029	0.031	0.20	100
0.50	0.079	0.077	0.50	100
	0.082	0.081	0.51	102
	0.074	0.075	0.48	96
1.00	0.153	0.152	0.97	97
	0.168	0.158	1.03	103
	0.158	0.155	1.00	100

In Table III are data on further analyses; the first five determinations were made on solutions that were subjected to the complete procedure—that is, the malic acid was extracted with ether in the customary way and every successive step was carried out. The next group of determinations was on aliquots of a standard solution to which 25 mg. of a mixture of oxalic, lactic, pyruvic, succinic, tartaric, maleic, glycollic, and fumaric acids in approximately equal amounts had been added. The last determinations were conducted in the presence of 6.4 mg. of citric acid.

TABLE III. RECOVERY OF MALIC ACID

MALIC ACID TAKEN	MIXTURE OF OTHER ACIDS TAKEN	CITRIC ACID TAKEN	MALIC ACID FOUND	RECOVERY
Mg.	*Mg.*	*Mg.*	*Mg.*	%
2.00	..	...	2.10	105
4.00	..	...	4.00	100
100.0	..	...	104.0	104
100.0	..	...	101.0	101
100.0	..	...	106.0	106
0.0	25	...	0.00	...
0.0	25	...	0.03	...
1.0	25	...	1.00	100
1.0	25	...	1.08	108
0.1	25	...	0.09	90
0.1	25	...	0.11	110
2.0	..	6.4	1.96	98
2.0	..	6.4	2.04	102

Table IV illustrates the recovery of malic acid added to tobacco leaf tissue. The malic acid content of each sample of the tissue was first ascertained by the present method; additions of malic acid were then made, and the complete analysis was conducted. The results are expressed in milligrams per 2 grams of tissue and show excellent recoveries and close reproducibility.

TABLE IV. RECOVERY OF MALIC ACID ADDED TO DRY TOBACCO LEAF TISSUE

(Figures are milligrams per 2-gram sample)

ADDED	ORIGINALLY PRESENT	FOUND	RECOVERED	RECOVERY
Mg.	*Mg.*	*Mg.*	*Mg.*	%
80.0	20.8	103.5	82.7	103
80.0	15.0	91.2	76.2	95
100.0	26.4	135.0	108.6	109
100.0	26.4	124.0	97.6	98
100.0	26.4	126.0	99.6	100
100.0	26.4	130.0	103.6	104
100.0	26.4	123.0	96.6	97
2.0	26.4	28.3	1.9	95
4.0	26.4	30.4	4.0	100

As a further test of the reliability of the present method, a number of samples of tobacco leaf tissue were analyzed for malic acid by the polarimetric method of Dunbar and Bacon (*2*), as modified by Vickery and Pucher (*9*). The results in Table V show a satisfactory agreement between the two methods. The oxidation method in all but one case gave slightly higher results. The data illustrate the wide differences in malic acid content that may be encountered in this tissue, and provide evidence that little, if any, optically inactive malic acid occurs in the tobacco plant.

TABLE V. COMPARISON OF OXIDATION AND POLARIMETRIC METHODS FOR MALIC ACID

SAMPLE	OXIDATION METHOD	POLARIMETRIC METHOD
	%	%
Fresh leaf I after extraction with water	0.00	0.00
Fresh leaf F.L. after extraction with water	0.10	0.00
Cured leaf 584	1.02	0.95
Cured leaf 594	4.76	4.00
Cured leaf 582	0.88	0.86
Partially cured leaf I	3.04	2.88
Partially cured leaf H	4.08	3.93
Partially cured leaf A	8.14	8.34
Partially cured leaf E	6.48	6.20
Fresh leaf F.L.	9.64	9.53

The oxidation method to determine malic acid has been chiefly employed in this laboratory in the study of tobacco leaf and stem tissue. Preliminary experiments with other plant tissues have given equally satisfactory results, however, and there seems no reason to suppose that the method cannot be generally applied. Successful analyses have also been conducted on blood, urine, and muscle extracts, and experiments with aspartic acid have shown that this amino acid can be accurately determined, if deaminized with nitrous acid previous to the oxidation.

ACKNOWLEDGMENT

The expenses of this investigation were shared by the Connecticut Agricultural Experiment Station and the Carnegie Institution of Washington.

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RECEIVED April 12, 1934. The fourth paper of a series under the general title "Determination of the Acids of Plant Tissue."

Preparation of Sintered Pyrex Glass Filters

SIR: Attention of research workers was called in your Analytical Edition of March 15, 1934, to the preparation of fritted glass filters by an article on page 154 of that issue by Kirk and his coworkers at the University of California. Unfortunately, Kirk neglected to mention that the filters he described are covered by patents throughout the world and, in the United States, by Patent 1,620,815 issued to Herschkowitsch and Prausnitz and by them assigned to this company. Obviously your readers should be appraised of this fact for their protection and our own.

JENA GLASS WORKS, SCHOTT & GEN.

JENA, GERMANY
MAY 28, 1934

Volumetric Estimation of 5-Bromo-2-Furoic Acid with Standard Bromate

Elizabeth E. Hughes and S. F. Acree, Bureau of Standards, Washington, D. C.

In a preceding article (*4*) the authors described the equipment, technic, and conditions for allowing furfural to react quantitatively with one molecule of bromine from standard bromate within 5 minutes at 0° C. with errors less than 0.5 per cent. The method is especially useful in the analysis of farm wastes for pentosan content. The usual procedure (*1*) is to distill the fibers with 12 per cent hydrochloric acid and determine the volatilized furfural with phloroglucinol, thiobarbituric acid, or with excess bromine by the method of Powell and Whittaker (*5*). The errors, even with empirical corrections, may be 2 to 4 per cent. The technic of the bromination method cited above is more nearly accurate and takes much less time.

In an attempt to apply this method to the analysis of products of bromination and oxidation of furfural, the present investigation was undertaken to see whether 5-bromo-2-furoic acid can be determined quantitatively both by titration with standard alkali and by addition of molecular equivalents of bromine.

Experimental Procedure

The 5-bromo-2-furoic acid was first described by Hill and Sanger (*3*) with melting point of 184° to 186° C. It is isomeric with a monobromo derivative having the bromine in the 3 or β position with melting point of 128° to 129° C. The acid used in these experiments was kindly made for the authors by J. A. V. Turck by the method of Gilman and Wright (*2*), and was a white crystalline substance melting at 184° to 186° C. The purity based upon acidity by titrating with 0.1 *N* or 0.02 *N* sodium hydroxide using phenolphthalein as indicator was 100 per cent (±0.1 per cent). The solubility in water was determined as approximately 2.5 mg. per ml. at ordinary room temperatures.

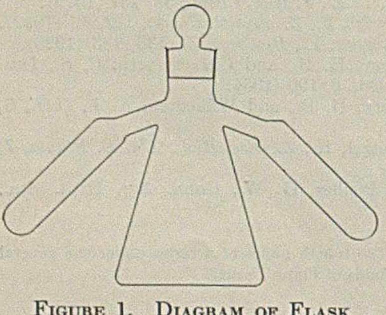

Figure 1. Diagram of Flask

For these experiments the solution of the acid was prepared by dissolving 2 grams of the acid in 1 liter of boiling water which was kept warm until solution was complete, then cooling to room temperature. An aliquot portion of the solution was transferred to the body of a special side-arm titration flask (Figure 1) containing 200 ml. of 3 per cent hydrochloric acid (prepared by diluting 1 part of 36 to 38 per cent concentrated hydrochloric acid with 11 parts of water). In one side arm were placed 25 ml. of 0.1 *N* aqueous solution of potassium bromate containing 50 grams per liter of potassium bromide. In the other side arm were placed 10 ml. of an aqueous solution of 10 per cent potassium iodide. A second flask was similarly prepared but omitting the 5-bromo-2-furoic acid. The flasks were sealed by placing a drop of phosphoric acid on the ground-glass stopper; the flask and contents were allowed to come to constant temperature. The experiments at 0° C. were made with the flasks suspended in an ice bath for the short time periods and placed in an ice box maintained at 0° C. for the longer ones. Experiments at 21° C. were conducted in a constant-temperature room. The temperatures mentioned above are subject to fluctuations of not more than 2° C.

The potassium bromate solution was introduced from the side arm into the acidified 5-bromo-2-furoic acid by tilting and the solutions were mixed by swirling the flask gently. The reaction was allowed to proceed for definite time periods, at the end of which the potassium iodide was added. At ordinary laboratory temperature about 10 minutes seems to be ample duration for the reaction. The contents were shaken vigorously and the liberated iodine titrated with 0.1 *N* sodium thiosulfate using starch indicator (0.5 grams of soluble starch in 250 ml. of boiling water).

Table I. Reaction of 5-Bromo-2-Furoic Acid with Bromine

Time of Reaction	Weight of Sample 103 mg.	85 mg.	50 mg.	62 mg.	46 mg.	26 mg.
	Per cent of theoretical amount found 21° C.			0° C.		
Sec.						
30	61.7	63.2	...	...	...	...
Min.						
1	81.6	83.8	...	...	...	...
2	92.3	95.7	99.0	...	...	...
3	...	...	...	63.1 65.9	...	52.4
4	97.7	98.9	100.0	...	...	...
5	...	...	...	...	...	86.3
6	99.0	99.8	100.1	...	...	...
8	99.8	100.0	100.1	...	...	...
10	100.0	100.2	100.1	...	92.8	93.6
20	100.1	100.6	100.5	98.3	(85.3)	97.8 99.3
30	100.0	100.5	100.6	...	...	...
40	...	...	...	...	99.6	99.8 99.7
60	100.0	100.6	102.3	...	(93.7)	98.5 100.6
90	...	...	...	100.6 (75.8)	...	99.9 100.7
Hrs.						
2	101.1	...	...	...	100.1 (97.8)	...
5	...	...	...	...	...	103.4
18	...	...	...	103.3	101.9 100.5	102.9
20	101.2	102.1	...	...	...	...
Days						
3	103.0	...	...	...	...	...
7	105.2	...	...	...	...	...

The results at 0° and 21° C. are shown in Table I and Figure 2 and express the extent of the reaction with respect to time. The addition of 2 moles of bromine to 1 of 5-bromo-2-furoic acid is represented by 100 per cent. The number of milliliters of 0.1 *N* thiosulfate required for the blank less that required for the sample multiplied by 0.004775 gives the number of grams of 5-bromo-2-furoic acid.

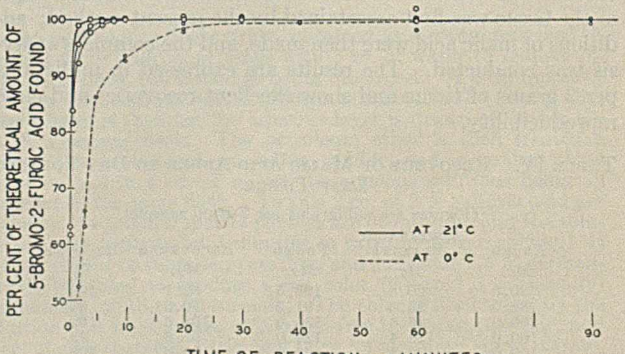

Figure 2. Reaction of 5-Bromo-3-Furoic Acid with Bromine

DISCUSSION OF RESULTS

Table I and Figure 2 show the rate of addition of bromine under specified conditions upon which basis the percentage of the theoretical amount found is calculated. It is found that bromine adds so rapidly to 5-bromo-2-furoic acid that, in contrast to furfural (*4*), it is not practical to stop the reaction short of two molecular equivalents of the halogen. Over a period of several hours and days the tetrabromide addition product of the normal reaction apparently loses hydrobromic acid very slowly to form more double bonds and the bromine used in subsequent reaction may reach 0.1 mole or more. According to the mass law and verified in Table I and Figure 2, the percentage of normal and of further reaction with the same amount of bromine for a given short time period should increase with decrease in size of sample.

At 0° C. the results are not always reproducible, as shown by the percentages given in parentheses. Experiments to be reported later show a small photochemical effect which is not, however, responsible for the discrepancies in the analyses, especially at 0° C. At 21° C., however, the results are concordant and the reaction, regardless of the size of the sample, is complete within 8 to 30 minutes.

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Continuous Determination and Recording of Carbon Dioxide Content of Gas Mixtures

Apparatus Used in the Bureau of Mines Helium Plant

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In designing an apparatus to give a continuous record of the carbon dioxide content of helium-bearing natural gas processed in the Amarillo Helium Plant of the Bureau of Mines, three methods were investigated. One, described by White, based on conductance measurements, was selected as being most suitable for the application desired. A modification of this method, which improves its operation and adaptability in plant installation, is briefly described. The apparatus, as modified, has given satisfactory service in a plant installation for recording concentrations of carbon dioxide from 0.1 to 1.0 per cent in sweet natural gas.

THE determination of carbon dioxide in gas mixtures by absorption in alkaline media has occupied the attention of a large number of investigators since Dalton originated the method. The literature has been adequately reviewed, most recently by Thomas (*9*) and by Martin and Green (*3*). The latter authors also classify and discuss briefly the methods which have been used. An improvement in pH measurement has been published by Wilson, Orcutt, and Peterson (*11*), who describe a potentiometric method for determination of carbon dioxide.

At the Amarillo Helium Plant of the Bureau of Mines the need arose for an accurate apparatus to record continuously and automatically the carbon dioxide content of helium-bearing natural gas. The average carbon dioxide content of the unprocessed gas is about 0.7 per cent, and the hydrogen sulfide content less than 0.002 per cent. The other constituents vary somewhat, depending upon the proportion of the total flow produced from each of the government's gas wells and upon temperature conditions in the pipe line. Because of this low concentration of carbon dioxide and variation in other constituents the gasometric methods and those based on physical properties of the gas could be eliminated at once in considering the known continuous, recordable processes. Three types of electrolytic methods offered possibilities and were investigated.

MEASUREMENT OF CARBONATE-BICARBONATE EQUILIBRIA

FIRST METHOD. Two variations of a method depending upon measurement of the equilibrium between carbonate and bicarbonate salts of the alkalies or alkaline earths, as affected by the partial pressure of carbon dioxide in equilibrium with the solution, have been developed. The earlier process determined the equilibrium by colorimetric measurement of the pH of the solution. The relatively low accuracy inherent in this method has been improved upon by the use of the glass electrode to determine the pH potentiometrically (*11*), adding rapidity and simplicity to a method which has advantages in being independent of gas flow.

Continuous measurements of the pH of a solution are practicable only with the quinhydrone and antimony electrodes.[1] The latter has the advantage of not requiring the addition of any reagents for the measurement but offers some difficulties in preparation and calibration for use with alkaline solutions which are in motion and are not in contact with air. The quinhydrone electrode has a limited range because of decomposition and oxidation which occur in the system when subjected to alkaline solutions. It has been applied without success in an attempt to measure carbonate-bicarbonate equilibria (*11*). This type of electrode is not suitable for use in unbuffered solutions, but since a decided change in pH will be caused by a trace of carbon dioxide in a perfectly neutral salt it seemed desirable to make some very brief tests of the pH in unbuffered solutions. The results of this limited study were not satisfactory, showing excessive drifting of the

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[1] After completion of the experimental work on which this paper is based, an article by Vickers, Sugden, and Bell appeared in *Chemistry & Industry*, 51, 545 (1932), reporting an apparatus for the continuous recording of pH in which a glass electrode is used.

potential, as would be expected, and slow attainment of equilibrium.

Second Method. A continuous record of the carbon dioxide content of a gaseous mixture has been obtained by Gordon and Lehmann (2), who used a recording alternating current milliammeter to measure the electrolytic conductance of a barium carbonate-bicarbonate solution in equilibrium with carbon dioxide. To determine the operating characteristics of this method and its adaptability to the immediate requirements an apparatus was constructed similar to that used in the work of the authors mentioned above. The recommended gas flow and temperature of operation were employed, but a smaller volume (15 cc.) of saturated barium carbonate was used, since it was believed that equilibrium in the apparatus would be attained more quickly. The measuring circuit consisted of an alternating current indicating milliammeter in series with the conductance cell and with a 110-volt, 60-cycle source of current.

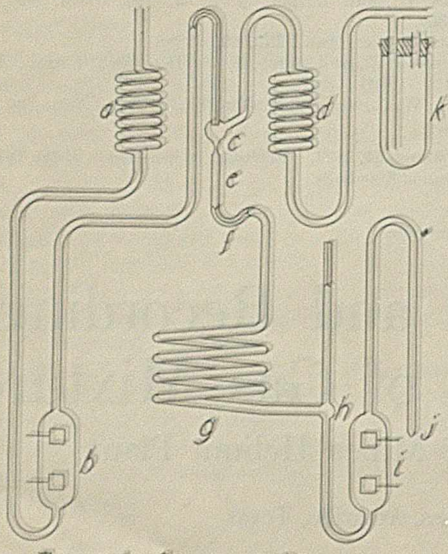

Figure 1. Schematic Diagram of Apparatus

Gordon and Lehmann (2) found the time lag of their apparatus to be of the order of one minute at 50° C. In the apparatus constructed for preliminary tests in this laboratory the time to reach equilibrium, which is an indication of the usefulness of the apparatus, was 10 to 20 minutes, depending upon the carbon dioxide concentration. Although the device is simple, the method was not considered suitable because of the time lag.

Measurement of Neutralization of a Hydroxide by Electrical Conductivity

Third Method. The third type of electrolytic method investigated was a direct measurement of the change in conductance of a solution of an alkaline or alkaline earth hydroxide accompanying the formation of a carbonate. A brief theoretical discussion of the method has been given by Smith (6).

Martin and Green (3) state that the method was devised by Cain and Maxwell (1), although Taylor and Taylor (8) give priority to Rideal and Taylor (4) by stating that in 1918 they "published the first account of gas analysis on the electrolytic principle." It has been useful in determining small percentages of carbon dioxide by cumulative absorption at constant gas flow, measuring the rate of change of conductivity. A recording instrument has been employed by Thomas (9) in measuring the conductivity of a sodium hydroxide solution used for the continuous absorption of carbon dioxide from a measured volume of air, and by Spoehr and McGee (7) with barium hydroxide. Both developments were designed to measure atmospheric carbon dioxide.

White (10) has developed an ingenious apparatus suitable for the analysis of various percentages of carbon dioxide as well as a number of other gases. His device is a simplification of the carbon monoxide recorder described by Taylor and Taylor (8) who developed, and applied for a patent on, a fluid proportioning device. The novelty of their apparatus consisted in this method of securing accurate mixtures of gas and reagent. A disadvantage of both devices is the use of direct current for the conductance measurements, making recording of the measurements not readily applicable, and introducing the possibility of error from polarization of the electrodes. A modification of White's apparatus was constructed and found to operate satisfactorily with natural gas containing 0.7 per cent carbon dioxide and with atmospheric carbon dioxide. It was not so satisfactory with the gas which had passed through the carbon dioxide–removal system of the Amarillo Helium Plant, possibly because of minute traces of other soluble constituents in the gas, which contained only a trace of carbon dioxide. The modified apparatus differs from that of White's in three particulars:

1. Two conductivity cells are used, relative measurements being made with a Wheatstone-bridge circuit.
2. Alternating current is used for the conductivity measurements.
3. The apparatus operates under a small pressure differential.

A schematic diagram of the apparatus is shown in Figure 1.

Description of Apparatus

The absorbing solution of 0.025 *N* potassium hydroxide is siphoned at a constant-pressure head from a 20-liter reservoir (not shown) through temperature-equalizing coil *a* into reference cell *b*. The solution then drops at a predetermined rate into bulb *c*, trapping a sample of gas, which enters through coil *d* in tube *e*. Goose-neck *f* is adjusted so that each drop will halt, making it necessary for a succeeding drop to form and push the sample of gas and the preceding drop down into absorption coil *g*. The gas and liquid separate at *h*, the solution, after absorption of the carbon dioxide, passing into measuring cell *i* and being discharged from the siphon at *j*. Trap *k* maintains constant pressure on the apparatus with an excess gas flow. As constructed in this laboratory, the entire apparatus is operated in a large Dewar vessel used as a water thermostat.

For convenient plant installation 110-volt, 60-cycle current is used, from which are obtained 6 volts for the Wheatstone-bridge conductance-measuring circuit. The use of two cells allows relative measurements to be made of the change in conductance due to the absorption of carbon dioxide, and partially compensates for variations in temperature, voltage, and concentration. A Leeds & Northrup potentiometer recorder was adapted (6) for use in recording the carbon dioxide concentration. Two ranges are available: one from 0 to 1.0 per cent and a low range from 0 to 0.2 per cent of carbon dioxide. The range of the recorder is conveniently changed by means of a double-pole, double-throw switch which changes the galvanometer and slidewire shunts of the recorder. A wiring diagram is given in Figure 2.

Calibration of Apparatus

Two methods are available for calibration. White recommends an empirical calibration for mixtures containing 5 per cent or more of the gas sought, or in cases where absorption is incomplete. When the sample contains less than 2 per cent of the soluble constituent a calibration from conductance data is said to be capable of great accuracy. The latter method of calibration was undertaken for the purpose of determining the capacity and probable range of the apparatus, the effect of variations in operating conditions, and as a guide in the design of the electrical circuit before construction was completed. This calibration followed White's procedure for obtaining the volume of the drop and the volume of gas aspirated per drop, a and b, respectively, in his notation. After obtaining the number of moles of dry gas m pumped per stroke, the method is somewhat different.

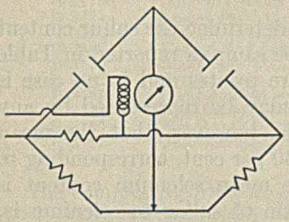

FIGURE 2. WIRING DIAGRAM

Experimental values for a, b, and m were 0.0993 cc., 0.958 cc., and 3.34×10^{-5} moles, respectively, at 25° and 670 mm. An equation, specific for the apparatus, correlating conductivity and carbon dioxide concentration under any conditions facilitates calibration. This is derived as follows:

$$m = \frac{0.958 \times 273\ (P - p)}{22420 \times 760 \times T}$$

$$N_{K_2CO_3} = n = \frac{0.958 \times 273\ (P - p) \times 138.21 \times 1000 \times P_{CO}}{22420 \times 760 \times T \times 0.0993 \times 69.105 \times P}$$

$$n = \frac{0.3091\ (P - p)P_{CO_2}}{TP}$$

where P = pressure in mm.
p = vapor pressure in mm.
P_{CO_2} = partial pressure of carbon dioxide in mm.
T = absolute temperature
$n = N_{K_2CO_3} = N - N_{KOH}$ in gram equivalents per liter
$N = N_{KOH}$ at 0 per cent carbon dioxide

The specific conductance k of any mixture is

$$\begin{aligned} k &= 0.253\ (N - n) + 0.1205\ n \\ &= 0.253 \left[N - \frac{0.3091\ (P - p)P_{CO_2}}{TP} \right] \\ &\qquad + 0.1205 \left[\frac{0.3091\ (P - p)P_{CO_2}}{TP} \right] \\ &= 0.253N - \frac{0.041\ (P - p)P_{CO_2}}{TP} \end{aligned}$$

To determine the effect of the variables in the equation, it was differentiated with respect to P, T, and N and the differential equations integrated to obtain the pressure, temperature, and concentration coefficients. The first two coefficients are negligible, but the latter is considerable, indicating that care must be exercised in preparing a carbon dioxide-free potassium hydroxide solution, unless the two cells are identical so that compensation will be perfect.

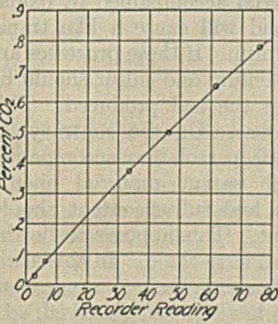

FIGURE 3. CALIBRATION DATA

The calibration from conductance data was obtained only as a guide during construction, and in the arrangement of the electrical circuit of the recorder. For use in plant operation an empirical calibration was made by using standard samples of natural gas containing various percentages of carbon dioxide. The concentration of carbon dioxide was determined by absorption in barium hydroxide with subsequent titration, using thymolphthalein as the indicator, as recommended by Schollenberger (*5*). The calibration data, using standard samples, are plotted in Figure 3. A comparison of curves plotted from empirical and calculated data showed a constant percentage deviation, indicating systematic errors in the calibration from conductance data. Although the relation between conductance and concentration of carbon dioxide is a straight line, resistance, the reciprocal of conductance, is a hyperbolic relation; hence, the curves are hyperbolic.

OPERATION OF APPARATUS

As mentioned by White (*10*), the apparatus is somewhat fragile, but, securely mounted and enclosed in a cabinet, it has proved satisfactory for industrial process control. The attention required is limited to renewal of the potassium hydroxide solution at weekly intervals and occasional checking of the gas-aspirating device and the zero point. Excessive vibration will interfere with a steady rate of gas sampling and must be avoided.

The lag of the apparatus was determined to be approximately 3 minutes, which may be reduced, if desirable, by increasing the rate of flow of the reagent. There should be no possibility of incomplete absorption with the low carbon dioxide-content gas at any rate of flow possible with the apparatus. The spiral absorber has been shown (*3*) to be a highly efficient scrubbing device, and, moreover, the absorbent is but 25 per cent exhausted at the maximum of the range of carbon dioxide. To check the completeness of absorption, however, a qualitative test was made, by passing the gas from the apparatus through a barium hydroxide solution, which showed complete absorption in the apparatus.

The apparatus whose calibration was described by White was stated to have a sensitivity of about one volume of carbon monoxide (or carbon dioxide) in ten thousand of the mixture in the range 0 to 2 per cent. This degree of precision was not required in the apparatus which has been described. In the range 0 to 1 per cent carbon dioxide, the recorder is easily sensitive to one division, or about 0.01 per cent. The analyses of the gas samples which determined the calibration were readily reproducible to 0.01 per cent. Some unaccountable factors may also affect the precision of measurement, but an assumed accuracy of one part in five thousand is considered to be well within the limits of error.

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SOLID CARBON DIOXIDE IN GERMANY. Germany, like European countries generally, lags far behind the United States in the use of this product. High cost, climatic conditions, absence of extremely hot weather, and smaller consumption of ice cream and iced foodstuffs generally, coupled with transportation difficulties, have retarded development. Manufacture, nevertheless, is making steady gains. The Mannesmannroehren-Werke is constructing a plant at its limestone works in Neandertal, utilizing the carbon dioxide gas produced in burning lime.

Occurrence of Selenium in Pyrites

KENNETH T. WILLIAMS AND HORACE G. BYERS, Bureau of Chemistry and Soils, Washington, D. C.

THE work of Kurt W. Franke, state chemist of South Dakota, which traced the causes of a certain animal disturbance, locally known as alkali disease, to the vegetation grown upon certain definite soil areas, and the subsequent detection in the Bureau of Chemistry and Soils of selenium in the vegetation of these areas has led to a series of investigations upon selenium. In the course of these investigations the presence of selenium has been traced from plant to soil and from soil to its parent shales.

Among the shales known to contain selenium is the Pierre shale, in certain sections of which occur nodules of iron pyrites. One of these nodules, collected by one of the writers, was found to contain 205 parts per million of selenium. This is a greater concentration of selenium than has been found in any other portion of the shale, some hundreds of samples of which have been examined in this laboratory. This fact, coupled with the known occurrence of selenium in chamber sulfuric acid made by roasting pyrites, and the historical fact that selenium was discovered, in 1817, in the sulfuric acid chambers in which the sulfur dioxide used was derived from certain copper pyrites *(2)*, made it of interest to determine how general the association of sulfur and selenium in pyrites may be. There was also the added incentive that over the area of soils known to be derived from the Pierre shale, the presence of selenium in both soil and vegetation had been determined to be of general occurrence.[1] These soils all occur in arid or semi-arid areas. If selenium occurs in pyrites in general, the fate of the selenium in humid areas, as contrasted with its disposition in arid areas is of striking interest in relation to the whole selenium problem. Initial data were secured through the analyses by W. O. Robinson of the samples indicated in Table I.

TABLE I. SELENIUM IN SELECTED SAMPLES OF PYRITES

SAMPLE	SOURCE	SELENIUM CONTENT
		P. p. m.
Concretionary pyrite	Fischer's Gully, Nebr.	205
Massive pyrites	Brigham, Utah	15
Crystals of pyrite	Saratoga, Colo.	10
Crystals of pyrite	Isle of Elba	Trace
Mispickel	Paris, Me.	Trace

With these facts in mind, T. D. Rice, of the Soil Survey, was requested to locate a number of sources of pyritiferous materials in the humid area of the eastern portion of the United States. In 1917 a survey of available pyrite sources was published by Smith *(4)*, and through this a number of the sources of pyrite listed below were located and samples collected by Rice and Byers.

Other samples were secured from a pyritiferous clay deposit near Bay Springs, Miss. A sample of concretionary pyrite was secured by S. A. Swenson from the Selma chalk of Alabama, and samples of pyrite and of limonite pseudomorphs after pyrite through the courtesy of W. H. Sage of the Alberene Company of Schuyler, Va. In addition to the pyrite samples a number of samples of soil and of other materials presumably derived from materials of pyrite content were also secured.

These samples were all examined quantitatively for their selenium content by the appropriate one of the methods outlined by Robinson, Dudley, and Williams *(3)*. The results obtained are given in Table II. Where only whole number values are given, the accuracy does not exceed 2 parts per million.

No attempt has been made to determine the sulfur content of the pyritiferous material of the samples reported in Table II. The ores were far from pure pyrites and in no case is there any guarantee that they may be represented by any definite formula. It is probable, however, that the mean sulfur content is not more than 40 per cent, corresponding to 400,000 parts per million. The mean selenium content is 59.0 parts per million. The ratio of sulfur to selenium is, therefore, of the order of 6×10^3. The mean ratio of sulfur to selenium in the earth's crust is, according to Clark and Washington *(1)*, about 10^6. Both these quantities are of course a rough approximation, but even so, it is evident that in this series of minerals there is a very marked concentration of selenium.

TABLE II. SELENIUM CONTENT OF PYRITE AND ASSOCIATED MATERIALS

LAB. NO.	TYPE OF MATERIAL	LOCATION	SELENIUM CONTENT
			P. p. m.
B-3179	Marcasite in black clay	Bay Springs, Miss.	0.3
B-3183	Marcasite in clay	Bay Springs, Miss.	0.6
B-3174	Concretionary pyrite in Selma chalk	Livingstone, Ala.	8
B-3192	Pyrite	Pyriton, Ala.	75
B-3196	Pyrite	Bremen, Ga.	8
B-3197	Pyrite	Draketown, Ga.	50
B-3199	Pyrite	Villa Rica, Ga.	45
B-3202	Pyrite	Dallas, Ga.	250
B-3203	Pyrite	Marietta, Ga.	110
B-3204	Pyrite	Marietta, Ga.	150
B-3205	Pyrite	Marietta, Ga.	180
B-3207	Pyrite	Ball Ground, Ga.	80
B-3169	Pyrite	Crouse, N. C.	10
B-3170	Pyrite (partially decomposed)	Crouse, N. C.	55
B-3171	Pyrites	Crouse, N. C.	50
B-3209	Pyrrhotite	Ducktown, Tenn.	5
B-3210	Chalcopyrite	Ducktown, Tenn.	10
B-3211	Pyrite	Ducktown, Tenn.	1
B-3212	Pyrite	Mineral, Va.	15
B-3213	Pyrite	Mineral, Va.	65
B-3215	Pyrite	Madison, Va.	0
B-3216	Pyrite	Dumfries, Va.	125
B-3464	Pyrite in serpentine	Schuyler, Va.	75
B-3465	Pseudomorphs after pyrites	Schuyler, Va.	45
		Av.	59

It would appear, therefore, that in the hydrolysis of pyritiferous material to produce soil, the selenium content, when conditions are not favorable for removal of both sulfur and selenium, should be higher than in soils derived from other sources. It is to be expected that the processes which convert pyrites to limonitic material accompanied by oxidation of the sulfur to sulfuric acid will cause a like transformation of selenium to soluble form. If these processes are accompanied by leaching both selenium and sulfur should be almost completely removed from the soil produced. This should be the case in humid areas. On the contrary, in arid or semi-arid areas where little percolation accompanies soil formation, pyritiferous soil parent material should result in a soil which, along with a high sulfur content, should have appreciable selenium content. This appears to be the case in the soils derived from the Pierre shale. In this shale the selenium content varies between wide limits, a range from traces up to 103 parts per million having been observed. In soils derived from these shales, in an area of present mean annual rainfall of 15 inches, selenium has been found as high as 32 parts per million.

In soils of humid areas selenium has been found only in traces, though it must be confessed that no extensive examinations have as yet been made. A little light is thrown upon the fate of selenium in soil formation under humid conditions by the data given in Table III.

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[1] Unpublished data, Bureau of Chemistry and Soils.

TABLE III. SELENIUM CONTENT OF SECTIONS OF A CLAY BED NEAR BAY SPRINGS, MISS.

LAB. No.	MATERIAL	SELENIUM CONTENT
		P. p. m.
B-3175	Surface soil	0.0
B-3176	Yellow sand (0–6 ft.)	0.0
B-3176a	Limonite scales in sand	0.4
B-3177	Yellow sand (6–20 ft.)	0.1
B-3178	Iron stone cap of clay	0.3
B-3187	Yellow clay beneath cap	0.4
B-3179	Black clay with pyrites	0.3
B-3183	Pyrites scale	0.6
B-3180	Light-colored scale	0.15
B-3182	Weathered black clay	0.15
B-3181	Weathered mixed clay	0.20
B-3185	Concentrated extract of weathered clay	0.01

The samples reported in Table III were obtained from a deposit which is being used as the source of supply of a "medicine." The clay bank has been excavated to a depth of about 50 feet. The over-burden is a yellow sandy clay of a maximum depth of about 25 feet. On parts of this sandy slope small pillars of clay are capped with thin scales of limonitic material. Below the sandy layer is a crust of limonitic material about 2 inches thick. This crust is apparently a partly hydrolyzed pyrite layer. Immediately below this crust is a thin layer of yellow clay. Below the yellow clay is a 3-foot layer of dense black clay containing large numbers of small crystals of marcasite. Below the black clay is a very thin layer of scale consisting largely of marcasite. Below this, and of a thickness not determined, is a deposit of clay somewhat lighter in color than the black clay and containing much smaller quantities of pyrites. The clay layers are used for the preparation of the above mentioned medicine by being allowed to dry and weather, under cover, for a year or more. The weathered material, which contains considerable quantities of ferrous sulfate, is leached with water.

It is unfortunate that this deposit is so low in selenium content, since otherwise it offers a very favorable set of conditions for tracing the course of the selenium in weathering. It is, however, clear that the soil proper is essentially free from selenium, that the weathering produces water-soluble selenium removable by leaching, and that the removal of selenium from the limonitic material does not keep full pace with the removal of the sulfur. This last fact is also indicated by B-3465 of Table II. In this sample nearly all the sulfur is removed while a considerable selenium content remains.

The transfer of selenium by leaching of weathered products, and its relation to sulfur translocation, are also indicated by the presence of selenium in certain shallow wells in the Pierre shale. These waters are high in sulfate content and selenium has been found in quantities as high as 0.07 part per million. The presence of selenium in gypsum deposits in weathered Pierre shale has also been determined in quantities ranging from 5 to 15 parts per million.[2]

A small number of shales were also collected and their selenium content determined in Table IV.

TABLE IV. SELENIUM CONTENT OF ALABAMA SHALES

LAB. No.	MATERIAL	LOCATION	SELENIUM CONTENT
			P. p. m.
B-3191	Dark calcareous shale	3 miles south of Desmopolis	0.6
B-3188	Dark shale	Leeds	0.15
B-3189	Ferruginous shale	Leeds	0.20
B-3190	Dark shale	Leeds	0.15
B-3195	Light shale	Heflin	0.15

GENERAL REMARKS

It would appear from the data above presented, supplemented by a mass of unpublished data on file in this bureau, that selenium is of much greater distribution in soils and vegetation than has heretofore been suspected. It seems probable that in arid and semi-arid areas the presence of selenium is to be expected in every case where the sulfur content of the soil parent material is high and that, where the selenium content permits, the derived soils and their vegetation may contain sufficient selenium to render them potentially dangerous. The mere presence of selenium in soil is not to be considered an indication of an inferior soil. It also seems probable that soils produced in humid areas are not likely to have a pernicious selenium content even though the parent materials are relatively rich in this element.

If the above inferences be warranted, it would appear that investigations of the selenium contamination of soils should be greatly broadened in scope, and that, in particular, they should cover soils which are to be used under irrigation.

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RECEIVED March 24, 1934.

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[2] Unpublished data, Bureau of Chemistry and Soils.

Constant-Feed Buret and Apparatus for Catalytic Dehydration of Alcohols

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IN MANY reactions a constant rate of liquid feed is desirable and it is impossible to obtain an even flow of liquid by means of an ordinary glass stopcock. The apparatus described below will deliver liquid at a constant rate over any desired length of time. It operates on the principle of opposing a constant liquid head to a constant resistance. Somewhat similar devices have been described by Sabatier (*1*) and by Vaughen (*2*).

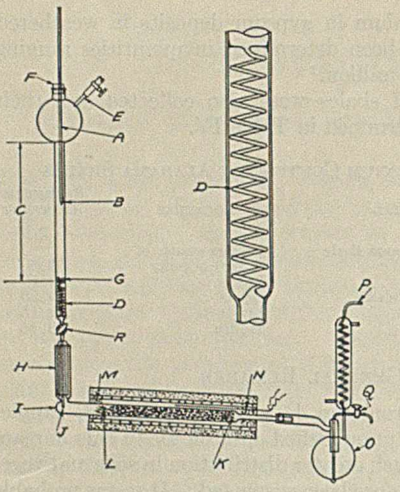
The liquid reservoir of the constant feed-buret is essentially a Mariotte bottle, and the head of liquid can be varied at will by raising or lowering tube *A;* the effective head is at *B*, the lower end of tube *A*, and the range through which the head can be varied depends on distance *C*. The constant resistance is furnished by capillary spiral *D* through which the liquid must travel. The choice of feed rate is wide, depending as it does on two variables, the liquid head and the resistance, the latter being governed by the length and the bore of the capillary.

For an all-round buret capable of delivering from 15 to 60 cc. per hour, the capacity of *A* is 500 cc., the length of *C* is 60 cm., the bore of capillary *D* is 0.25 to 0.5 mm., and the length of the capillary is 40 cm., the vertical height of the spiral being 5 cm. Tube *E* is of convenience in venting the pressure caused by the insertion of stopper *F*, and with liquids which tend to deposit solid matter, it is well to protect the capillary by a small filter plug of cotton, *G*.

CATALYTIC DEHYDRATION OF ALCOHOLS

This apparatus has a general application for catalytic reactions in which a liquid is vaporized and the resulting gas passed over a solid catalyst. It is especially convenient for the dehydration of alcohols over alumina.

The buret is connected to the catalyst tube by means of mercury seal *H*, which is designed along the conventional lines of a mercury seal for a mechanical stirrer. The alumina catalyst is introduced through the open end of the tube at *I*, which is then



sealed. The charging rate is visible at *J*. The catalyst is held in place by a perforated glass partition at *K* and by a plug of glass wool at *L*. Heat loss is cut down by the insertion of asbestos packing at *M* and *N* into the annular space between the catalyst tube and the furnace block. Receiver *O* can be emptied without dismantling the apparatus, by application of pressure at *P* with a bulb aspirator, stopcock *Q* being open and stopcock *R* closed.

In the dehydration of the lower alcohols (ethyl, propyl, and butyl) the gaseous olefin passes out at *P*, water and undecomposed alcohol collecting in receiver *O*, whereas in the case of higher alcohols such as amyl, liquid olefin also condenses in the receiver.

This apparatus can be used for any catalytic reaction in which a vaporized liquid is passed over a solid catalyst at approximately atmospheric pressure—dehydrogenation, dehydration, dehalogenation, etc. Also by the addition of a gas inlet tube at *I*, catalytic reactions can be run in the presence of a gas—oxidation, halogenation, hydrogenation, hydration, etc.

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Received March 26, 1934.

Thiocyanogen Number

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The thiocyanogen number is a very useful method of determining the composition of oleaginous bodies having oleic and linoleic acids or glycerides as constituents.[1] With tests conducted according to the customary procedure, however, it seems to be subject to considerable inaccuracy.

The usual method of analysis requires 25 cc. of thiocyanogen solution equivalent to 25 cc. of 0.1 *N* thiosulfate and 0.2 gram of the oil to be analyzed. Since there must be a 50 per cent excess, only 12.5 cc. are used in the reaction. In the analysis for the iodine number the 25 cc. of Hanus iodine solution are equivalent to approximately 50 cc. of 0.1 *N* thiosulfate. It is apparent, therefore, that the accuracy of the thiocyanogen number is much less than that of the iodine number, when 25 cc. of solution and 0.2 gram are used in the analysis. In order to make the thiocyanogen number as accurate as the iodine number, as it should be, since it must be in conjunction with the iodine number in these analyses, it appears that samples of double in size should be used.

In order to determine the effect of a larger sample, five different samples of olive oil were analyzed with 0.2 gram of sample and 25 cc. of solution and with 0.4 gram and 50 cc. of solution. In both cases, the thiocyanogen solution was added from pipets having glass stopcocks on the outlets, in order to give greater accuracy than could be secured from a buret.

Table I. Results of Thiocyanogen Analyses

Sample 1	2	3	4	5
		0.2 gram 25 cc. used		
78.05	77.07	74.72	72.78	73.17
77.32	76.55	73.21	71.49	73.42
77.36	77.41	72.92	72.63	72.62
74.00	75.98	67.59	74.46	78.36
73.89	73.52	68.11	74.80	82.97
		0.4 gram 50 cc. used		
75.84	75.21	75.49	73.00	75.58
76.28	75.37	75.73	74.60	75.53
75.63	75.69	76.00	74.39	...

A very wide disparity was encountered in the 0.2-gram sample analyses—a difference which is much greater than would ever be secured in an iodine number. It is obvious that these analyses would lead to very inaccurate results in the linoleic and oleic acid determinations since the error is so great. With the 0.4-gram sample and 50 cc. of thiocyanogen solution excellent checks were secured. With the exception of the first analysis of sample 4, all were well within the limits of accuracy of the iodine determination.

It is therefore recommended that the determination of the thiocyanogen number should be made with 0.4-gram sample and 50 cc. of thiocyanogen solution.

Received March 20, 1934.

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[1] Jamieson, G. S., "Vegetable Fats and Oils," p. 345, Chemical Catalog Co., N. Y., 1932.

Solution of Difficultly Soluble Copper Ores

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It has been known since the time of Fresenius that sulfide ores of copper may often be extremely difficult to get into solution for analysis. When treatment with mineral acids and ordinary aqua regia fails to effect solution, the author has found that the acid mixture recommended by Bonilla (*1*) for dissolving nickel metals is very effective. This mixture consists of 40 volumes of 15 *M* nitric acid and 3 volumes of 12 *M* hydrochloric acid. Samples of ore from 0.150 to 3.0 grams are usually dissolved by 43 cc. of the mixture, after boiling for half an hour.

The excess nitric and hydrochloric acids are easily removed by adding 20 cc. of 18 *M* sulfuric acid after the above treatment and heating until the total volume is reduced to 10 cc. This solution can then be diluted with water and the copper determined either iodometrically or electrolytically according to standard procedures.

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Received June 8, 1934

A New Distillation Trap

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AMONG the common laboratory manipulations none can be more troublesome than distillations of foaming and bumping liquids, especially under reduced pressures which fluctuate. To overcome these troubles, various and familar distillation flasks, bulbs, traps, and columns have been devised. Few of these have the desired combination of durability, simplicity in design, efficiency of operation, and general utility, which have been combined in a fairly satisfactory way in the distillation trap illustrated. It is easily constructed and functions very satisfactorily even under a fluctuating house vacuum, in distillations of either foaming or bumping liquids filling the distilling flask into the neck.

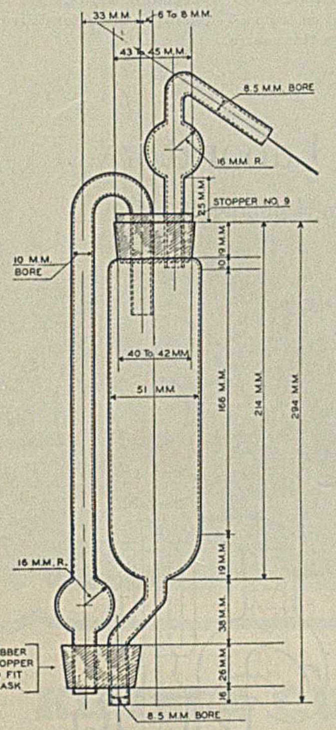

Figure 1. Distillation Trap

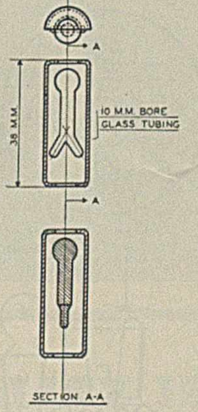

Figure 2. Valve

The valve illustrated by Figure 2, attached by means of fusion or a short piece of rubber tubing to the drain tube of the large safety reservoir, prevents liquids in the distillation flask from ascending into the safety reservoir but allows liquids to drain out of the reservoir and back into the distillation flask.

If desired, the lower bulb identified by dimension 16 M. M. R. in Figure 1 may be omitted without impairing seriously the operation of the trap.

The dimensions specified are those of a trap suitable for a 1- or 2-liter ring-neck flask, and should be increased by 25 to 50 per cent for traps to be used on 3- to 5-liter flasks and probably doubled for traps to be used on 10-liter or larger flasks.

Received April 11, 1934.

Superiodized Sea Water containing more than 500 mg. of iodine in salt form per liter is reported to be obtained by use of a recently patented French process (French Patent 763,083). Iodine-saturated air is continuously pumped into a sea water reservoir stocked with certain marine animals and plants, and through this medium the iodine eventually finds its way into solution in salt form.

A Microburet

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IN THE practice of quantitative spectrographic analysis in this laboratory, it is necessary to measure small volumes of many different solutions with precision and rapidity (*1*, *2*). In the course of routine analytical work, from one to four 0.1-cc. portions of fifty or more different solutions are measured daily. The use of one of the usual forms of microburet or fractional cubic centimeter pipet would require a clean buret or pipet each time a different solution is to be measured. To overcome this difficulty a microburet was designed in which the calibrated portion could be used over and over again without cleaning.

Description of Microburet

Figures 1 and 2 are photographs of the microburet.

Tube *A* is a capillary measuring pipet of 2 cc. capacity, graduated in tenths of a cubic centimeter, each marking encircling the tube and being separated from adjacent graduations by about 0.375 inch (0.94 cm.). The tip end, *B*, of the measuring pipet is attached with a rubber tube to the S-shaped glass tube, *C*. At *D* is attached the delivering tube, *E*, which is a glass tube of 7 mm. outside diameter and 6 inches (15 cm.) long, with its lower end drawn to a tip. The liquid to be measured is drawn into and delivered from this tube, a clean tube being used for each liquid. The tubes are readily removed by detaching them from the rubber tubing connector, *D*, and the bronze spring clip, *F*. Water (tinted with a few drops of red ink) is introduced into the right-hand half of *C* and into the calibrated tube in approximate amount indicated by the levels at *G* and *H*. Level *H* is controlled by varying the position of the top of the air column above it. This is done by varying the position of the roller, *J*, which is arranged to pinch the rubber tube, *K*, against a backing plate at any point, maintaining an air-tight seal continuously. The roller is mounted on a carriage, *L*, actuated parallel to the rubber tube by a long vertically mounted screw, the latter being rotated

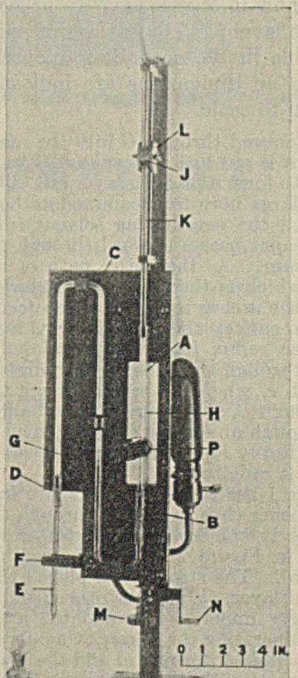

Figure 1

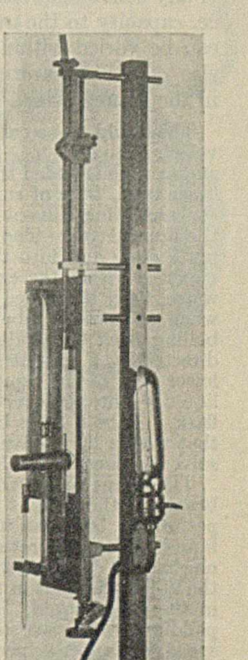

Figure 2

by hand at *M* or *N*. The carriage is designed so that it may be disengaged from the screw for a rapid change of position, the screw being intended for a fine adjustment of the position of the roller.

Tube *K* should be of semi-transparent pure gum rubber, other types of tubing giving trouble due to air leakage at the point of pinch by the roller. The tubing is kept under slight tension in order to enable the roller to move smoothly and produce definite displacements of the water in the graduated tube.

In use the liquid to be measured is drawn into the delivery tube by dipping the tip of the latter into the liquid and moving the roller upward. When a sufficient quantity has been drawn into the tube the roller is moved downward until the level of the water in the calibrated tube is at one of the graduations. The solution adhering to the tip of the delivery tube is touched off, after which the microburet is ready for use. The desired amount of solution is delivered by running the roller downward, the amount of solution delivered being equal[1] to the volume displacement of the water in the calibrated tube. Precise setting of the level of water in the graduated tube is facilitated by the magnifier, *P*, and parallax is avoided by the fact that the graduations completely encircle the tube. The measuring tube is viewed against an illuminated ground glass, as indicated.

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(1) Nitchie, C. C., Ind. Eng. Chem., Anal. Ed., 1, 1–18 (1929).
(2) Nitchie, C. C., and Standen, G. W., *Ibid.*, 4, 182 (1932).

RECEIVED March 1, 1934.

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[1] This is not exactly true, inasmuch as the volume of the air column between the liquid in *E* and the water in *C* is not constant but varies with the height of the column of liquid retained in *E*. Calculation shows, however, that the error in delivering each 0.1 cc. from a 5-mm. inside diameter delivery tube is only about 0.00005 cc. from this source.

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THE extractors shown in Figures 1 and 2 are designed for extractions with immiscible solvents lighter than water. They are self-contained and compact, occupying little table space as they have a minimum of lateral extension. The absence of projecting parts decreases the liability to breakage. Obviously these extractors can be made only by a glass blower, but it may be assumed that apparatus of such permanent usefulness need not be considered an extravagance because it cannot be homemade.

The extractors are made wholly of Pyrex glass and may be of any convenient size; those now in service have about 1000 cc. capacity to the overflow at level *b*. Dimensions of parts can be varied within reasonable limits, depending upon the size of the apparatus; hence no dimensions are indicated in the figures, which are drawn to scale.

The liquid to be extracted is poured through *G* into the main vessel, *C*, to level *a*. The solvent is put into the boiling flask, *A*, and enough is added through *G* to form a floating layer, *ab*. The inner tube, *B*, is of sufficiently large bore to accommodate both the ascending solvent vapor and the overflowing solvent from the upper layer. The solvent vapor passes upward through the ports at *D* and into the condenser. As the entire path of the vapor is within the extractor, which is thereby kept somewhat warm, there is avoided much of the useless refluxing which occurs when an external tube is used to convey the solvent vapor from boiling flask to condenser. The reflux from the condenser is directed by *F* so that it passes through the tube *E*, entering the lower part of the liquid through *e*, whence it rises through the liquid, eventually overflows through *B*, and returns to the boiling flask. Tube *E* must be long enough above the overflow level so that with a light solvent and a heavy liquid a sufficient head of solvent can collect in *E* to expel it rapidly at *e*.

The extractor shown in Figure 1 has tube *E* divided into four branches, the refluxed solvent being thus delivered through the perforated bulbs at four points in the lowermost level of the liquid. The apparatus shown in Figure 2 is provided with a mechanical stirrer and liquid seal. The stirrer is so placed that the upper paddle is in the solvent layer, *ab*, and the other paddles in the lower liquid. Further, the upper paddle and the lower paddles are opposed so that, by operating the stirrer at moderate speed, the upper solvent layer is pushed downward and the lower liquid upward, the sliding interface and the continuous movement within both layers increasing the rapidity and thoroughness of the extraction. The drainage tube, *H*, permits the apparatus to be emptied while assembled.

These extractors once started require no attention and can be operated at a high rate of solvent flow. Those now in use are of substantial construction, and are the work of J. D. Graham, University of Pennsylvania glass blower.

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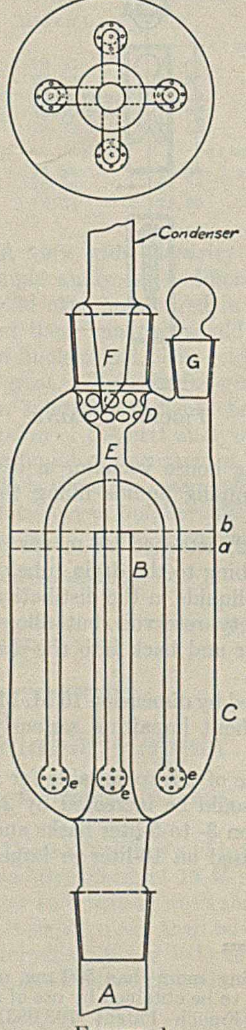


FIGURE 1

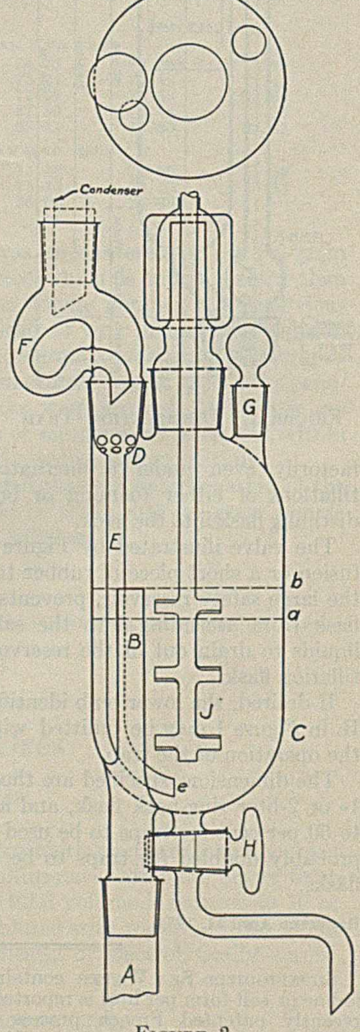
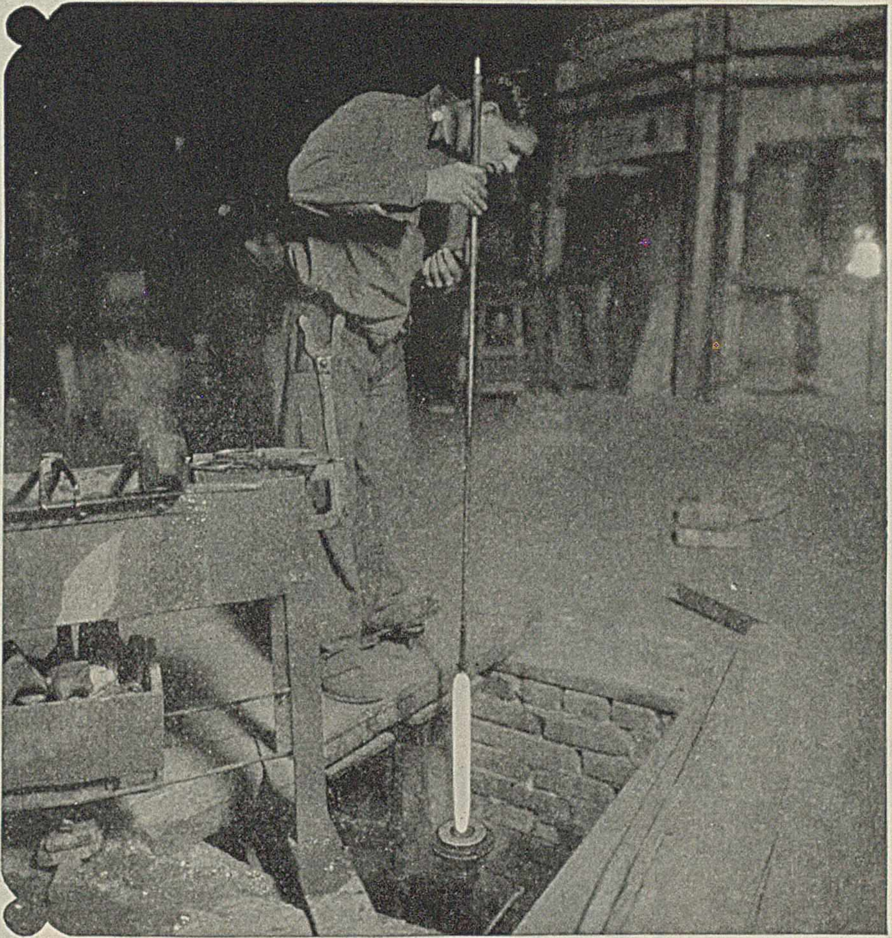
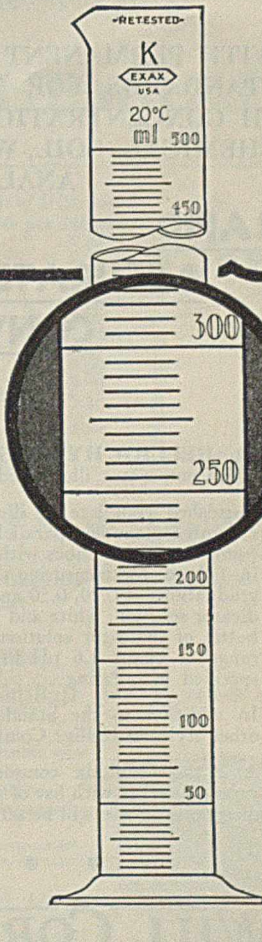


FIGURE 2

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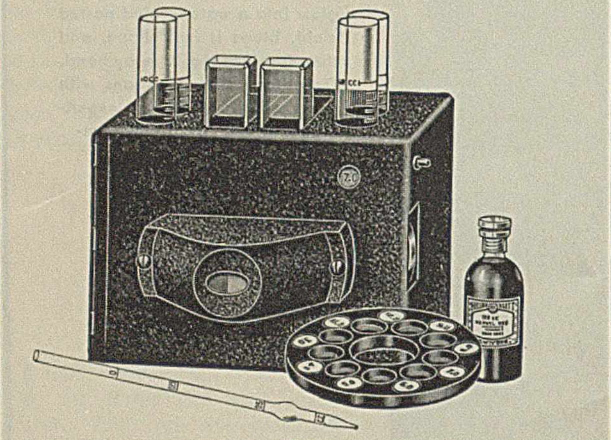

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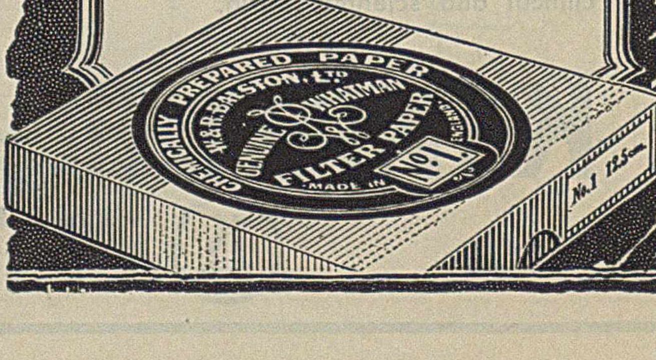

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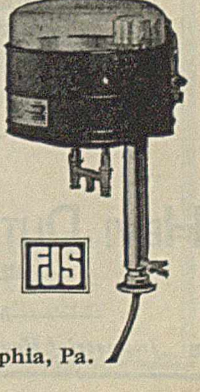

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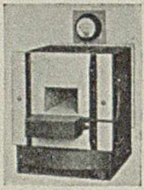

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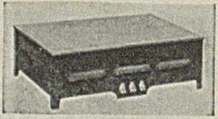

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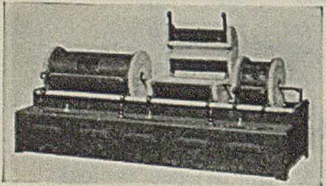

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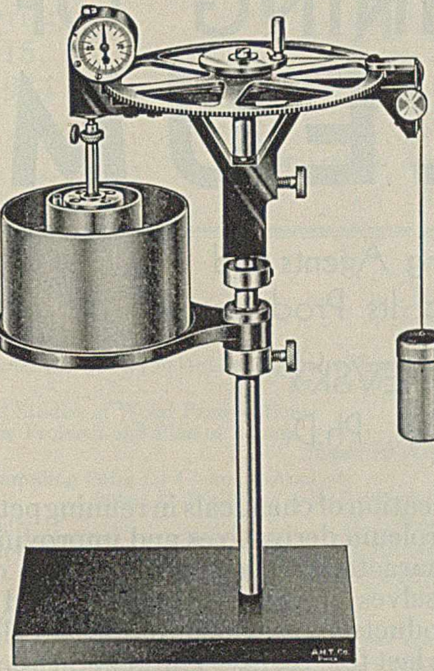

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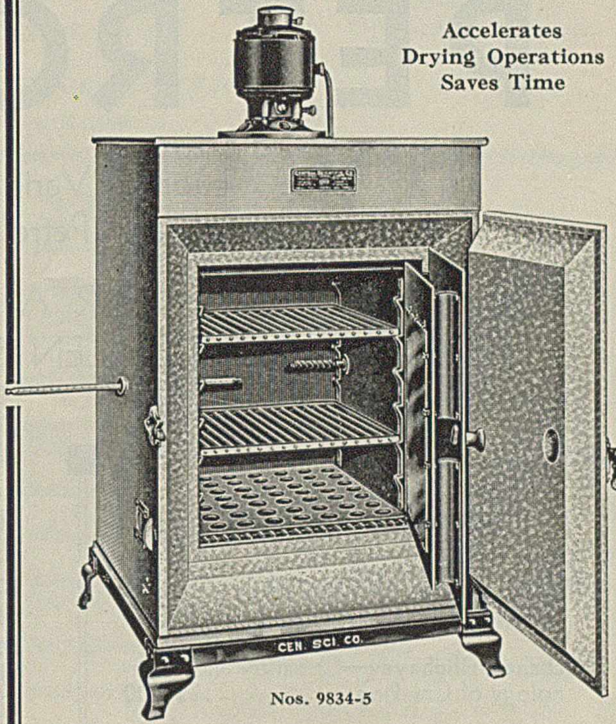

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