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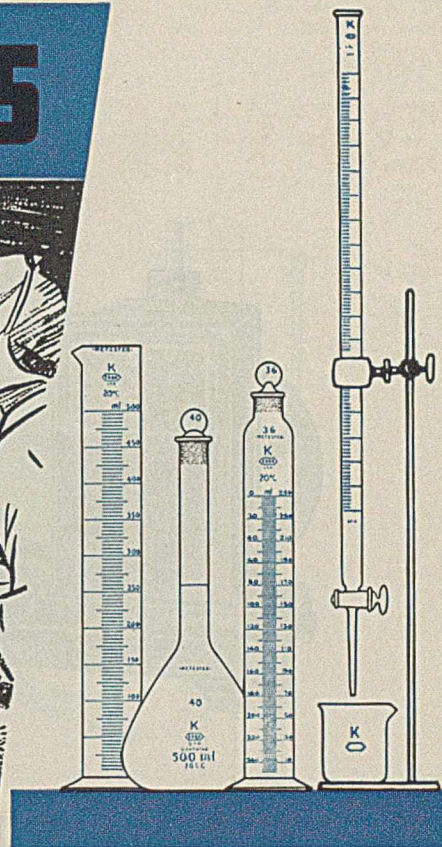
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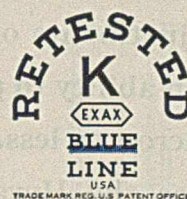


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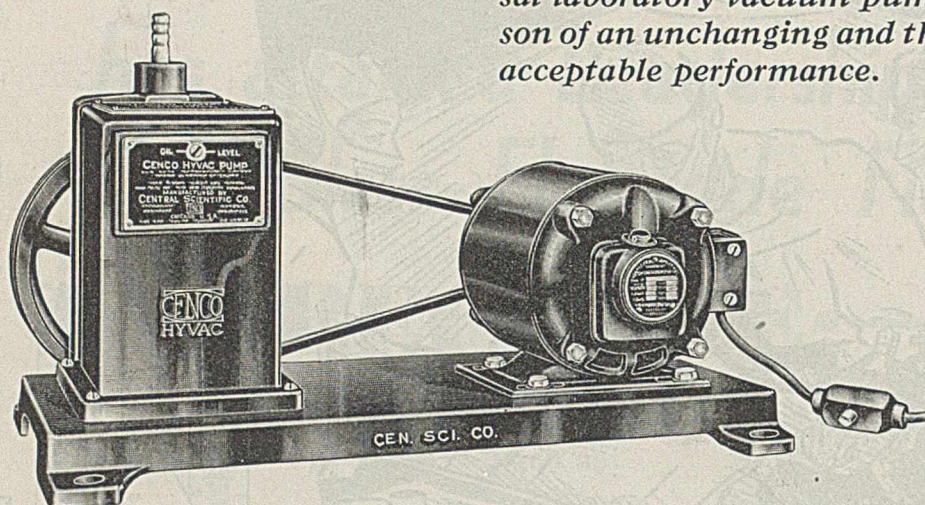
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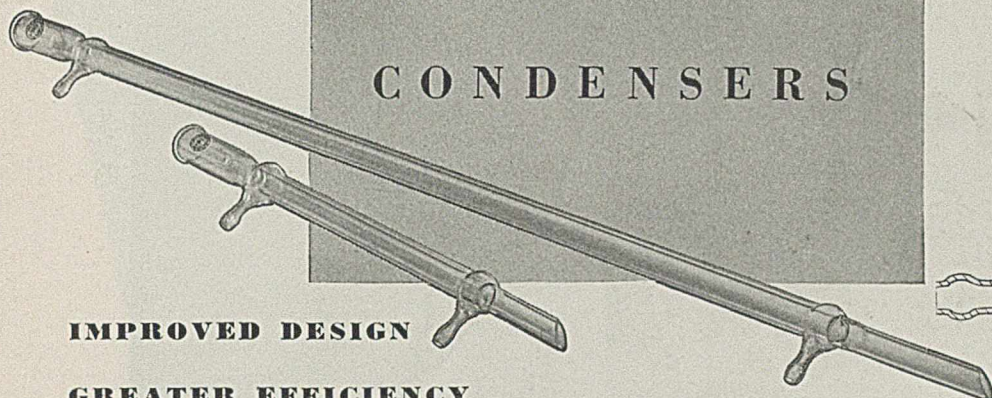
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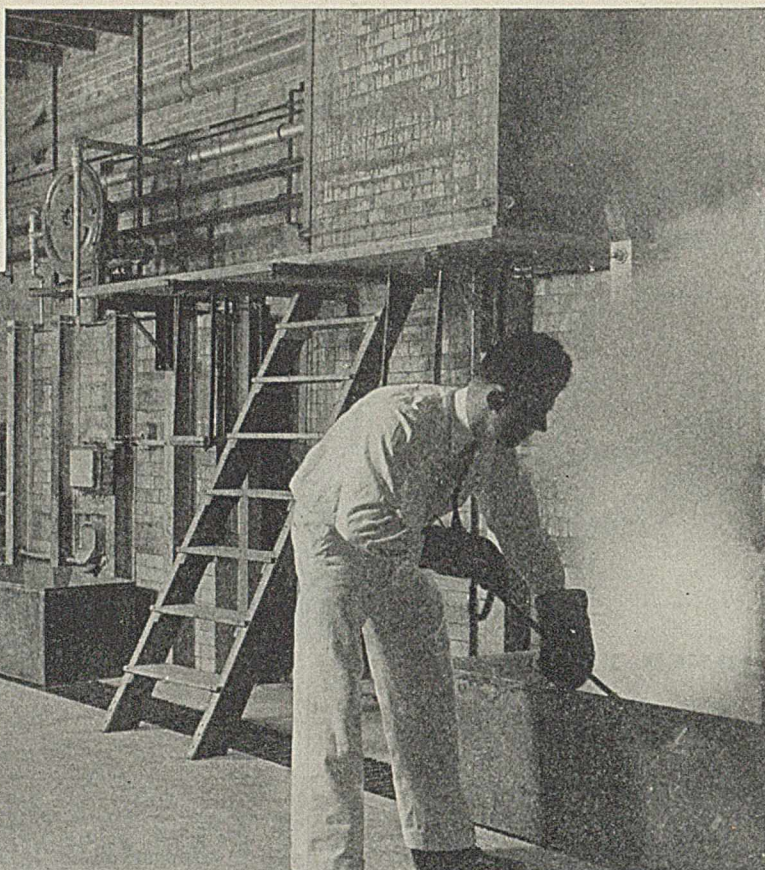


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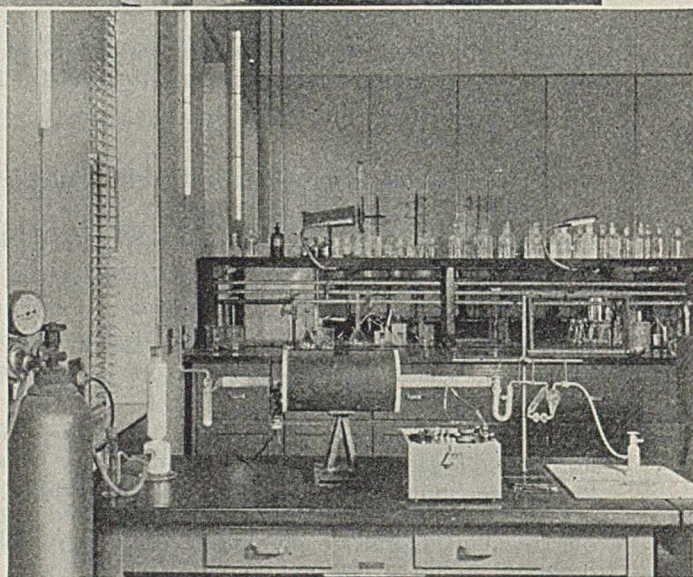
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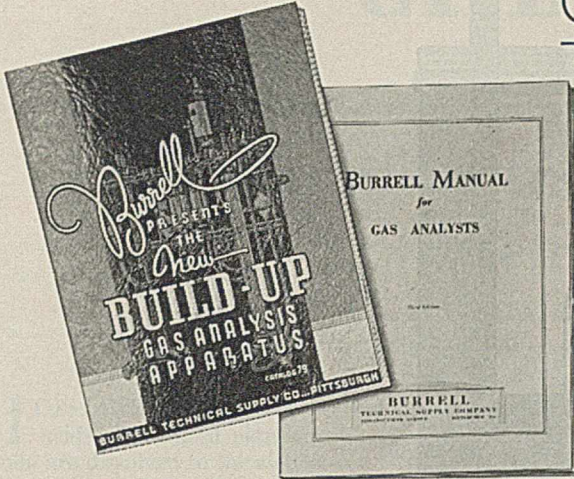
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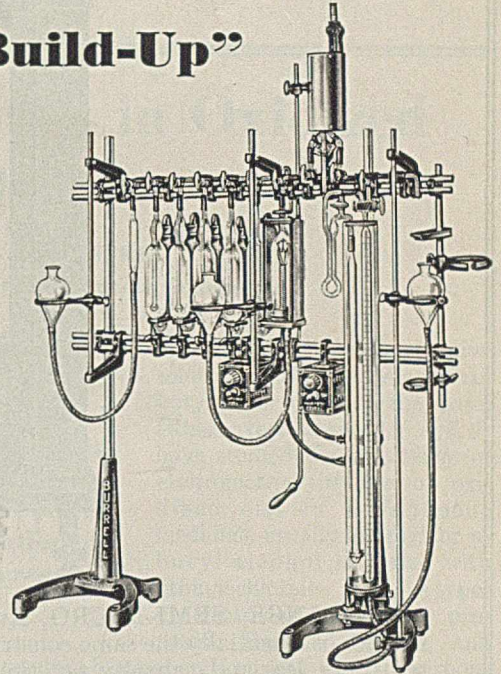
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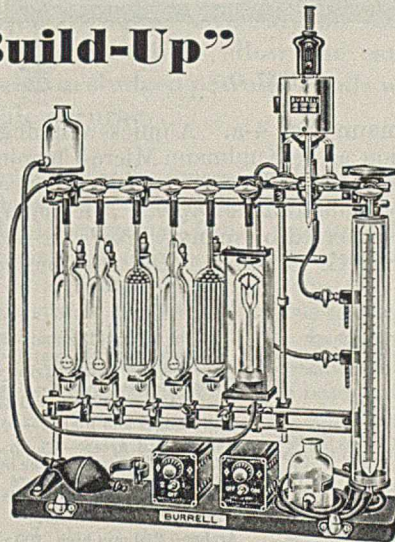
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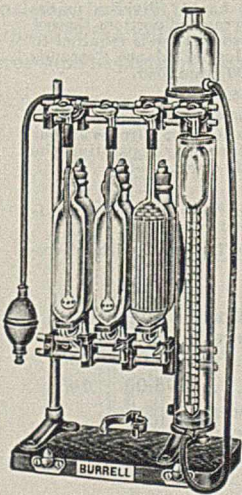
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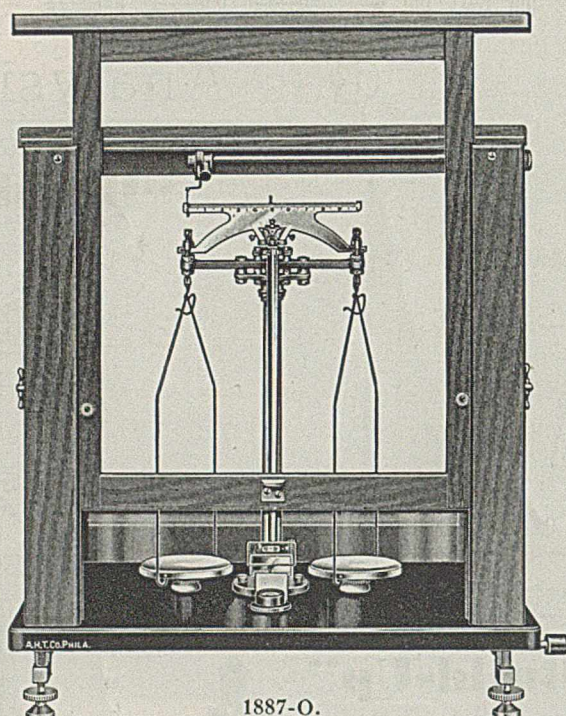
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INDUSTRIAL and ENGINEERING CHEMISTRY

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Electrometric Titration of Acids in Oxidized Petroleum Oils

A. R. RESCORLA, F. L. CARNAHAN, AND M. R. FENSKE

Petroleum Refining Laboratory, The Pennsylvania State College, State College, Pa.

IT IS LIKELY that not all the acids of oxidized petroleum oils are dissolved in the alcohol-water mixture used in the procedure (2) in A. S. T. M. Designation D188-27T, but that instead they are distributed between the solvent and the oil (3). This circumstance makes titration difficult. Furthermore, the deep shade of the mixture being titrated masks the delicate color change of the indicator. Committee D-2 of the American Society for Testing Materials has been active in developing a potentiometric method (1) for the determination of oil acidity under such circumstances that ordinary procedures are not feasible. A thermionic titrimeter or a potentiometer is used to indicate the e. m. f. of an electrode system composed of a calomel half-cell and a platinum indicator electrode; the oil is dissolved in butyl or amyl alcohol or in certain solvent mixtures such as equal parts of butyl alcohol and benzene, lithium

The very weak acids present in oxidized petroleum oils are titrated only with difficulty by most methods. A simple pair of dissimilar electrodes and a direct-reading amplifier with the oil dissolved in a nonaqueous liquid with suitable solvent power and conductivity allow the estimation of acids in sludged petroleum oils with reasonable accuracy.

chloride being present to give solution conductance; sodium butylate is used as the base. Other investigators (3, 5, 7, 8, 9) have studied the possibility of electrometric titration of oxidized oils in nonaqueous mediums, usually isoamyl or *n*-butyl alcohol saturated with lithium chloride. Various types of electrodes have been proposed; Ralston, Fellows, and

Wyatt (5) as a result of Kahlenberg's work (4) used the carbon-platinum pair. Shenk and Fenwick (6) designed a direct-reading amplifier which can be substituted for the potentiometer frequently used in connection with bimetallic electrode systems; this instrument is satisfactory for aqueous or nonaqueous solutions.

In the present investigation, attention has been given to the selection of a suitable electrode pair, an indicating device and a base, but it was especially necessary to develop a nonaqueous mixture of proper solvent and conducting power for use with oxidized oils.

Apparatus

The apparatus used in determining acid contents of oxidized oils is shown in Figure 1. It consists essentially of a pair of electrodes together with a device for amplifying and indicating the very small current furnished by the electrodes to a high-resistance circuit, a buret (graduated in units of 0.05 cc.), and a suitable reaction vessel with provision for stirring. The presence of air did not cause any difficulty. The oil under examination was dissolved in a mixture consisting of equal parts by volume of isoamyl alcohol, benzene, and carbon tetrachloride and saturated with lithium chloride; the base was prepared by dissolving sodium in isoamyl alcohol.

ELECTRODES. Since the hydrogen electrode and other standard electrodes are easily poisoned and rather difficult to use in routine work, the tungsten-platinum pair was selected for this investigation. Of several electrode combinations tested (see Figure 3) the tungsten-platinum gave the largest change in potential at the equivalence point and appeared to be sufficiently rugged. Holt and Kahlenberg (4) previously found this combination suitable for water solutions.

The data in Table I present a comparison of titration results

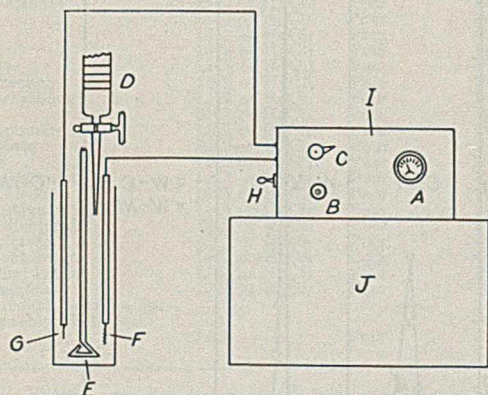


FIGURE 1. ASSEMBLY FOR ELECTROMETRIC TITRATION

- A. Milliammeter
- B. Battery switch
- C. Adjustable rheostat
- D. Buret, 10 cc.
- E. Stirrer, motor not shown
- F. Platinum electrode
- G. Tungsten electrode
- H. Electrode switch
- I. Aluminum box containing tubes 57, 2A3, etc.
- J. Asbestos box containing transformers, etc.

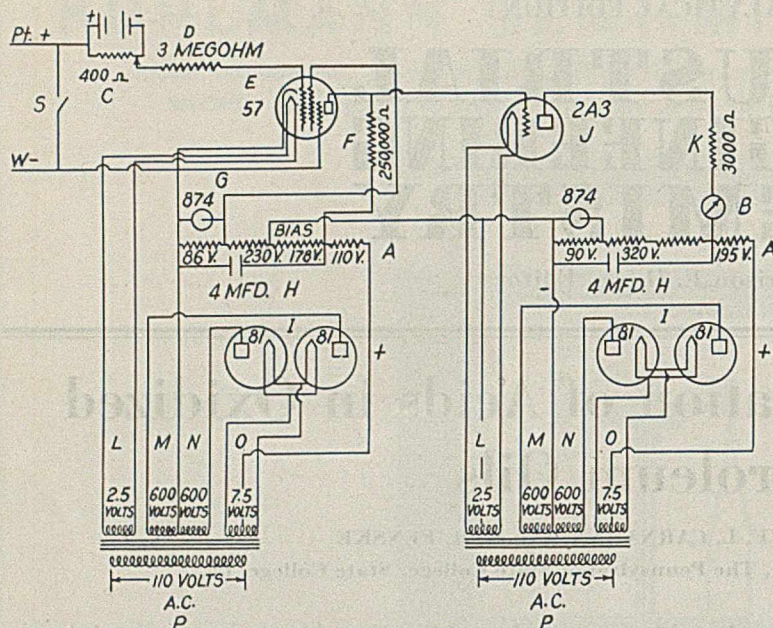


FIGURE 2. WIRING DIAGRAM OF INDICATOR FOR ELECTROMETRIC TITRATION

- A. Voltage dividing resistance, 250,000 Ω
 B. Direct current milliammeter (0 to 50 ma.)
 C. Radio "C" battery (UH 15 B) and resistance
 D. 3-megohm resistance
 E. R. C. A. radiotron tube 57
 F. 250,000 Ω plate resistance
 G. R. C. A. radiotron tube 874
 H. 4-microfarad Sprague oil condenser, 1000 volts
 I. R. C. A. rectifier tube 81
 J. R. C. A. radiotron tube 2A3
 K. 3000 Ω resistance
 L. 2.5-volt tap-off transformer
 M, N. 600-volt tap-off transformers
 O. 7.5-volt tap-off transformer
 P. Power supply to transformer
 Pt. Platinum electrode
 W. Tungsten electrode
 S. Shorting switch for electrodes

obtained with the tungsten-platinum pair to those resulting from the use of platinum-calomel and platinum-silver-silver chloride electrodes; the neutralization number for a particular oil sample is 0.71, 0.73, and 0.77, respectively, for the three electrode combinations.

TITRIMETER. The titrimer consists of a rectifier and an amplifier with electrical circuits as shown in Figure 2.

The No. 81 tubes are full wave rectifiers, each with a 4-microfarad filter to supply voltages for the grid and plate circuits of tubes 57 and 2A3. The voltage imposed on the screen of tube 57 is controlled by a gas-filled voltage-regulator tube designated as 874. It will be noted that the system is arranged to nullify the effect of variations in the source of supply.

The potential over the grid circuit of tube 57 is the algebraic sum of the bias voltage and the voltage across the electrodes. It may be seen from Figure 2 that a voltage change in the grid

TABLE I. COMPARISON AMONG PLATINUM-TUNGSTEN, PLATINUM-CALOMEL, AND PLATINUM-SILVER-SILVER CHLORIDE ELECTRODES IN TITRATING A SAMPLE OF USED OIL

Base Cc.	Pt-W		Pt-Calomel		Pt-Ag-AgCl	
	Ma.	Δ Ma./cc.	Ma.	Δ Ma./cc.	Ma.	Δ Ma./cc.
0	8.0	..	10	..	5.0	..
0.1	8.8	8	10.8	8	6.0	10
0.2	9.2	4	11.0	2	6.5	5
0.3	9.8	6	11.5	5	6.8	3
0.4	10.2	4	11.5	0	7.0	2
0.5	10.5	3	11.8	3	7.2	2
0.6	11.0	5	12.0	2	7.5	3
0.7	11.5	5	13.0	10	8.0	5
0.8	13.0	15	13.2	2	8.8	8
0.9	14.2	12	13.8	6	9.8	10
1.0	15.8	16	15.0	12	11.2	14
1.1	17.0	12	16.5	15	13.8	26
1.2	19.5	25	18.0	15	15.2	16
1.3	21.2	17	19.8	18	16.5	13
1.4	24.0	28	21.8	20	18.5	20
1.5	27.0	30	24.3	25	21.0	25
1.6	29.2	22	26.8	25	23.5	25
1.7	30.2	10	28.5	17	27.0	35
1.8	31.2	10	29.5	10	28.5	15
1.9	32.0	8	30.5	10	30.5	20
2.0	32.2	2	31.0	5	32.5	20
2.1	33.2	7
Neutralization number	0.71		0.73		0.77	

circuit of the 57 tube affects the plate current of this tube. The plate current variation in the 57 tube in turn effects a change in the bias of the grid circuit of the 2A3 tube through a 250,000-ohm resistor. The bias on the 2A3 tube is the algebraic sum of the voltage drop of the plate resistor and the drop across the section of the voltage dividing resistor marked *BIAS*. When the current decreases in the plate of tube 57, the negative bias on tube 2A3 becomes less with a concomitant increase in current. Since this current is indicated directly on the milliammeter, *B*, changes in the potential between the electrodes may be readily followed as the titration proceeds. At the outset of a titration, the plate current of the 2A3 tube is regulated to about 10 milliamperes by adjusting the variable resistance, *C*; with this initial current, the radio tubes function in the most sensitive part of their operating curve during the addition of base.

Experimental

SOLVENT. Electrometric titration methods were first used for acids in turbine oils. Such oils are usually of low viscosity and contain no appreciable amount of sludge or naphtha-insoluble material; it was found that isoamyl alcohol saturated with lithium chloride is a satisfactory solvent medium. However, this solvent is not suitable for more viscous oils or for sludged products. Considerable difficulty was experienced in finding a solvent mixture which would dissolve sludged oils completely and readily and at the same time possess sufficient electrical conductivity. Such good oil solvents as benzene, chloroform, or carbon tetrachloride are poor conductors and apparently not susceptible to improvement.

When a saturated solution of lithium chloride in ethyl alcohol was mixed with various nonconducting oil solvents, the mixture had good conductance but low solvent power. The presence of a conducting salt in many

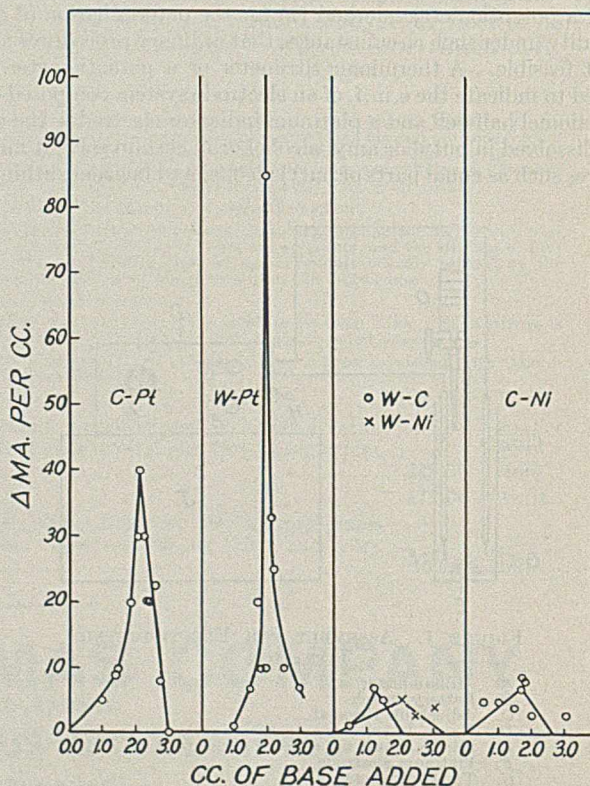


FIGURE 3. INFLECTIONS OBTAINED WITH VARIOUS ELECTRODE PAIRS IN THE TITRATION OF ACIDS IN A USED OIL

cases appears to decrease oil solubility. Table II gives information on some of the solvents tried. At length it was discovered that a mixture composed of equal parts by volume of isoamyl alcohol, benzene, and carbon tetrachloride and saturated with lithium chloride evidences the necessary qualifications. It was found possible to dissolve completely an oil containing 0.4 per cent of sludge in two volumes of this solvent; in titrations six or more volumes of solvent to one of oil were used.

The solvent may be conveniently prepared as follows: The middle 80 per cent of commercial isoamyl alcohol as obtained by simple distillation was refluxed half an hour with an excess of lithium chloride. Volumes of benzene and carbon tetrachloride equal to that of the isoamyl alcohol were then added; the mixture was refluxed for an additional half hour, still in the presence of undissolved lithium chloride. The solvent was filtered from any excess salt and stored in dark glass bottles.

BASE. A base prepared by dissolving sodium in freshly distilled isoamyl alcohol was found to be more satisfactory than one prepared from potassium hydroxide and isoamyl alcohol. The solution was made up every week and kept in dark glass bottles with stoppers; no special arrangements were made to exclude air. Standardization was effected by the use of *c. p.* benzoic acid, using the electrometric titration procedure described later. Except for oils containing more than about 0.2 per cent of sludge (naphtha-insoluble material), the base used was approximately 0.05 *N*; for such oils 0.2 *N* base gave a sharper inflection in the titration. Some of the results may be explained on the basis that 1 cc. of reagent added contains four times as much base, but in other cases the end point with the weaker base can hardly be detected. The situation is shown graphically in Figure 4.

PROCEDURE. The amplifier is set in operation by imposing 110 volts upon the transformers and switching on the "C" bat-

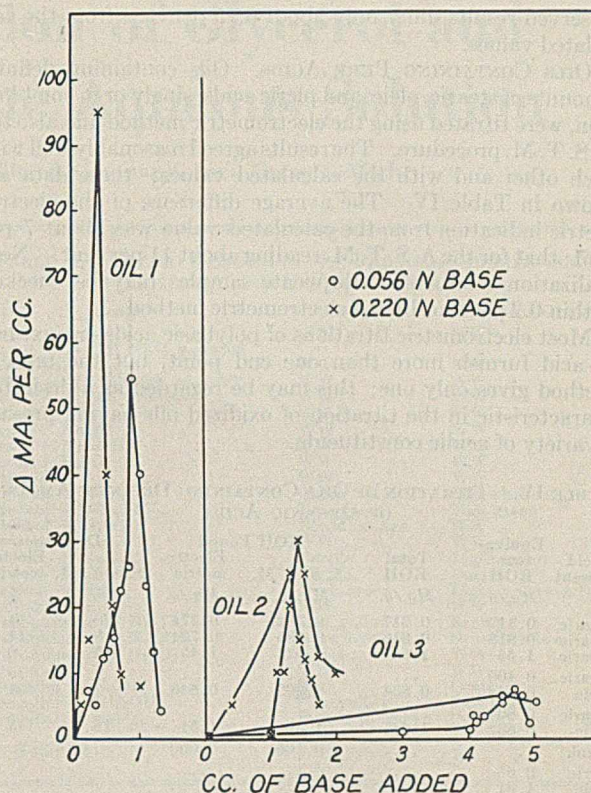


FIGURE 4. INFLECTIONS OBTAINED WITH DIFFERENT CONCENTRATIONS OF SODIUM ISOAMYLATE IN THE TITRATION OF USED OILS

TABLE II. SOLVENTS EXAMINED FOR CONDUCTIVITY AND OIL SOLUBILITY

Solvents	Conducting Salt	Oil Solubility	Conductivity
Isoamyl alcohol	LiCl	Fair	Good
<i>n</i> -Butyl alcohol (10 parts by volume), carbon tetrachloride (1 part)	LiCl	Poor	Good
Ethyl acetate (6 parts), benzene (3 parts), carbon tetrachloride (1 part)	LiCl	Poor	Good
Isoamyl alcohol, benzene, carbon tetrachloride (equal parts)	LiCl	Good	Good
<i>sec</i> -Butyl alcohol	LiCl or HgCl ₂	Poor	Poor
Dioxan	LiCl or HgCl ₂	Poor	Poor
Tetralin	LiCl or HgCl ₂	Poor	Poor
Terpineol	LiCl or HgCl ₂	Poor	Poor
Pentacetate	LiCl or HgCl ₂	Poor	Poor
Chlorobenzene	LiCl or HgCl ₂	Poor	Poor
Tetrachloroethane	LiCl or HgCl ₂	Poor	Poor
Hexalin	LiCl or HgCl ₂	Poor	Poor
Butyl propionate	LiCl or HgCl ₂	Poor	Poor
Butyl acetate	LiCl or HgCl ₂	Poor	Poor
<i>α</i> -Picoline	LiCl or HgCl ₂	Poor	Fair
<i>o</i> -Dichlorobenzene	LiCl or HgCl ₂	Poor	Fair
<i>tert</i> -Amyl alcohol	LiCl or HgCl ₂	Poor	Fair
<i>n</i> -Amyl butyrate	LiCl or HgCl ₂	Poor	Fair
Ethylene dichloride	LiCl or HgCl ₂	Poor	Fair
Benzyl chloride	LiCl or HgCl ₂	Poor	Fair
Methylethyl ketone	LiCl or HgCl ₂	Poor	Good
Methylhexyl ketone	LiCl or HgCl ₂	Poor	Poor
Acetonylacetone	LiCl or HgCl ₂	Poor	Good
<i>n</i> -Butyl alcohol, benzene, carbon tetrachloride (equal parts)	LiCl	Fair	Good

TABLE III. TITRATION OF PURE ACIDS IN SOLVENT

Benzoic acid, gram	0.0225	0.0212
Stearic acid, gram	0.0386	0.0353
Normality of base	0.106	0.106
Base required, calcd. for:		
Benzoic acid	1.75	1.65
Stearic acid	1.30	1.20
Blank	0.50	0.50
Total	3.55	3.35
Base used in titration	3.60	3.30
Difference, per cent	0.14	0.15
Maximum value of Δ ma. per cc. of base	110	100

tery (*C*, Figure 2). Ten minutes are allowed for the tubes to reach equilibrium. In the meantime, the platinum-tungsten electrodes are removed from the 5 *N* hydrochloric acid solution in which they are immersed when not in use, heated red-hot, and allowed to cool before being placed in operating position as shown in Figure 1. An oil sample of approximately 4 grams (weighed to 0.01 gram) is put in a cylindrical glass container about 12.5 cm. (5 inches) tall and 3.75 cm. (1.5 inches) in diameter. To the oil are added 30 cc. of a liquid mixture containing equal volumes of isoamyl alcohol, benzene, and carbon tetrachloride and saturated with lithium chloride.

With the test jar in position as shown in Figure 1, its contents are whirled rapidly by an electric stirrer. The shorting switch (*S*, Figure 2) is opened and the resistance, *C*, is adjusted to allow a current of 10 milliamperes through the system; since the electrodes do not reach equilibrium at once, variation of the resistance is continued until a steady state is attained.

Addition of base to the oil solution is made in 0.1-cc. portions with stirring for 1 minute after each increment before the reading of the milliammeter is taken. The titration is conducted in this manner until a sharp increase in current is noted on adding one of the 0.1-cc. portions of base; further additions produce little change in current. From the data so obtained the increase in milliamperes per cubic centimeter of base added (Δ ma. per cc.) is calculated; the end point of the operation is indicated by a comparatively large value for this term. Correction for any solvent acidity is made on the basis of blank runs. End points may be shown very clearly by plotting Δ ma. per cc. against the amount of base added as has been done in Figure 3; this procedure, however, is not usually necessary, as inspection of the calculated values is sufficient. The time required for each titration is approximately half an hour. The data have been expressed as A. S. T. M. neutralization numbers, milligrams of potassium hydroxide per gram of oil.

Experimental Results

PURE ACIDS. Weighed amounts of benzoic and stearic acids were dissolved in the solvent mixture; electrometric titration was conducted in the usual way. The detailed data are given in Table III; the course of the titration may be followed in Figure 5. The indication of the end point is very clear; the

observed results differ only about 0.15 per cent from the calculated values.

OILS CONTAINING PURE ACIDS. Oils containing definite amounts of stearic, oleic, and picric acids, singly or in combination, were titrated using the electrometric method and also the A. S. T. M. procedure. The results agreed reasonably well with each other and with the calculated values; these data are shown in Table IV. The average difference of the electrometric indication from the calculated value was about 7 per cent; that for the A. S. T. M. reading about 11 per cent. Neutralization numbers on duplicate samples may be checked within 0.2 per cent by the electrometric method.

Most electrometric titrations of polybasic acids or mixtures of acid furnish more than one end point, but the present method gives only one; this may be regarded as a desirable characteristic in the titration of oxidized oils having present a variety of acidic constituents.

TABLE IV. TITRATION OF OILS CONTAINING DEFINITE AMOUNTS OF ORGANIC ACIDS

Acid Present	Equivalent KOH Mg./g.	Total KOH Mg./g.	KOH Found		Deviation	
			A. S. T. M. Mg./g.	Electrometric Mg./g.	A. S. T. M. %	Electrometric %
Stearic	0.317	0.317	0.382	0.274	20	14
Stearic	0.818	0.818	0.885	0.724	8	11
Stearic	1.55	1.55	1.62	1.45	5	6
Stearic	0.400
Oleic	0.434	0.834	0.909	0.846	9	1
Stearic	0.804
Oleic	0.832	1.64	1.39	1.51	15	8
Blank	0.106	0.060
Picric	0.65
Oleic	1.91
Stearic	6.24	8.80	9.54	9.19	8	4

OXIDIZED OILS. Duplicate determinations were run on over a hundred oil samples obtained from engines operated by the Department of Mechanical Engineering. The results were reproducible within 10 per cent; this variation may be attributed to the difficulties of sampling sludged oils, to the less marked end points, and probably to other factors. Figure 5 demonstrates the relative values of Δ ma. per cc. of base added for some oxidized oils and for oils to which benzoic and stearic acid had been added. The smaller rate of change of current at the equivalence point is probably due to the low ionization constants of petroleum acids as compared even to the relatively weak pure acids mentioned.

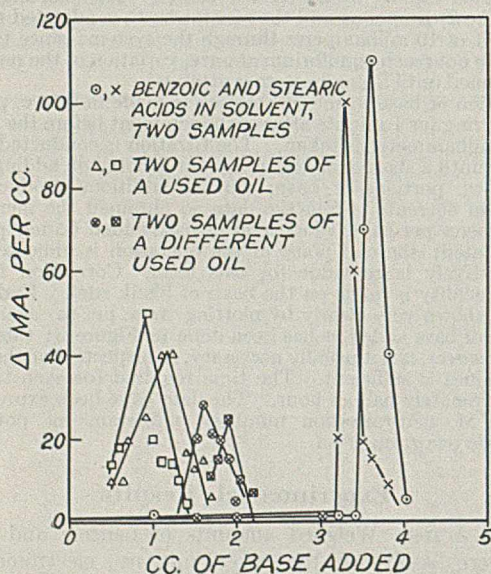


FIGURE 5. COMPARISON OF INFLECTIONS OBTAINED WITH PETROLEUM ACIDS TO THOSE SHOWN BY MIXTURES OF BENZOIC AND STEARIC ACIDS

The neutralization numbers of many of the oxidized oils were found also by the A. S. T. M. method (2); these are generally lower than those determined electrometrically for the same oils, especially when deterioration was extensive. Illustrative data are found in Figure 6. It is considered that the electrometric procedure for used oils is the more reliable, inasmuch as the acids in the sludge are taken into account. Sludge is soluble in the liquid mixture used for electrometric titration but not in the mixture of alcohol and water employed in the A. S. T. M. procedure.

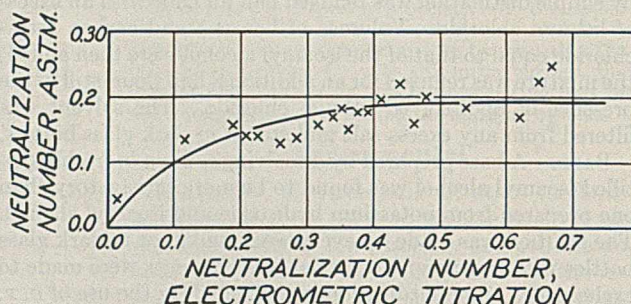


FIGURE 6. COMPARATIVE NEUTRALIZATION NUMBERS OF USED OILS

The acid content of a lubricating oil under service conditions frequently becomes larger along with increases in Conradson carbon residue value, viscosity, and sludge formation, regular curves being obtained when the quantities mentioned are plotted against acidity. In such cases it may be convenient to follow the deterioration of the oil by determining its neutralization number from time to time during the progress of an engine test.

Summary

An electrometric method using tungsten-platinum electrodes has been developed for the estimation of acids in oxidized petroleum oils. The used oil is dissolved in a mixture composed of equal parts by volume of isoamyl alcohol, benzene, and carbon tetrachloride and saturated with lithium chloride. The base is prepared by dissolving sodium in isoamyl alcohol.

Results for pure organic acids dissolved in solvent are reproducible within 0.2 per cent; the average difference of the observed from the calculated values is 7 per cent. Check determinations on used oils have a maximum deviation of 10 per cent.

Acknowledgment

The technical assistance of E. M. Fry, R. H. McCormick, and G. E. Woods in constructing the apparatus and obtaining data is appreciated. This work was a part of the research program of the Pennsylvania Grade Crude Oil Association and is published with its permission and that of the School of Chemistry and Physics of The Pennsylvania State College.

Literature Cited

- (1) Am. Soc. Testing Materials, Rept. Comm. D-2, "Standards on Petroleum Products and Lubricants," p. 25, Sept., 1936.
- (2) *Ibid.*, p. 224.
- (3) Evans, R. N., and Davenport, J. E., *IND. ENG. CHEM., Anal. Ed.*, 8, 287 (1936).
- (4) Holt, M. L., and Kahlenberg, L., *Trans. Am. Electrochem. Soc.*, 57, 361 (1930).
- (5) Ralston, R. R., Fellows, C. H., and Wyatt, K. S., *IND. ENG. CHEM., Anal. Ed.*, 4, 109 (1932).
- (6) Shenk, W. E., and Fenwick, F., *Ibid.*, 7, 195 (1935).
- (7) Seltz, H., and McKinney, D. S., *IND. ENG. CHEM.*, 20, 542 (1928).
- (8) Seltz, H., and Silverman, L., *Ibid.*, Anal. Ed., 2, 1 (1930).
- (9) Wooten, L. A., and Ruehle, A. E., *Ibid.*, 6, 449 (1934).

Qualitative Determination of Glycerol and Ethylene Glycol in Dilute Aqueous Solution

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BECAUSE alkyd resins contain polyhydric alcohols, detecting the nature of the polyhydric alcohol is essential. The customary procedure in analyzing alkyd resins is to determine the weight of phthalic anhydride or other polybasic acids and the weight of fatty acids or other modifiers leaving the glycerol to be determined by difference (5, 6). As long as glycerol was the only polyhydric alcohol used, this determination by difference was allowable though not satisfactory. Today, however, ethylene glycol is available and relatively cheap and therefore we must expect its presence in many alkyd resins. There seem to be no references in the literature to an easy and sensitive qualitative determination of ethylene glycol in dilute aqueous solution. Qualitative tests for glycerol in dilute solutions have been described by Mulliken (3), Gardner (3), and others, but in these tests there is still much to be desired, particularly when it is necessary to distinguish glycerol from ethylene glycol.

Heretofore in attempting to determine whether glycerol or ethylene glycol is present, many tedious procedures have had to be overcome. The main detectable differences between glycerol and ethylene glycol have been in their physical properties. Differences between these two polyhydric alcohols in aqueous solutions have been determined by comparison of such physical properties as specific gravity (1), refractive index (4), boiling point (2), freezing point, etc. In actual practice, however, there is usually so much water present that concentrating the solution of a polyhydric alcohol involves as much difficulty and tediousness as the regular manufacturing process for concentrating glycerol (9). This excess of water in the analytical sample is due to the fact that the resin sample has first to be acidified after the saponification so as to precipitate out fatty acids, phthalic acid, or other polybasic acids. After this separation a steam distillation (?) is necessary to separate the polyhydric alcohol from the salts, which are formed by acidification of the saponified sample.

The literature has been searched for a qualitative colorimetric method for determining glycerol and ethylene glycol in dilute solution; such a method would save the trouble of concentrating the distillate. A test has been described by Mulliken (3) which is essentially as follows: One drop of glycerol is dissolved in 2 cc. of cold water, and 5 drops of 1 per cent aqueous solution of pyrogallol and 2 cc. of concentrated sulfuric acid are added. Upon shaking and heating quickly to boiling, the boiling being held 20 to 25 seconds before cooling, a coloration appears in a 15-cm. (6-inch) test tube upon dilution to 20 cc. with strong alcohol. The coloration is a purplish red, which fades in a very few minutes on standing. The authors have found that this purple coloration is also observed when using ethylene glycol in place of glycerol. In both tests, the purple coloration turns to a light brown upon standing. In the case of ethylene glycol the color seems to fade somewhat faster than that of glycerol, but unfortunately this is not a distinguishing test.

Experimental

Using Mulliken's work as a starting point, the authors have carried the work further, using homologs of phenol under both acid and alkaline conditions. A summary of the results is shown by Table I.

TABLE I. COLOR REACTIONS OF PHENOLIC BODIES WITH GLYCEROL AND ETHYLENE GLYCOL

Reaction	Glycerol	Ethylene Glycol
Phenol	WW ^a	WW ^a
Phenol + NaOH (25% aqueous solution)	WW	WW
Phenol + NH ₄ OH (sp. gr. 0.90)	WW	WW
Phenol + H ₂ SO ₄ (concd.)	WW	WW
Cresol	WW	WW
Cresol + NaOH	WW	WW
Cresol + NH ₄ OH	WW	WW
Cresol + H ₂ SO ₄	WW	WW
Catechol	WW	WW
Catechol + NaOH	Green	Light brown
Catechol + NH ₄ OH	Pale green	Pale green
Catechol + H ₂ SO ₄	Blood orange	WW
Resorcin	WW	WW
Resorcin + NaOH	Purple	Light green
Resorcin + NH ₄ OH	Purple	Purple
Resorcin + H ₂ SO ₄	Dark green	Light yellow-green
Hydroquinone	WW	WW
Hydroquinone + NaOH	Pale yellow	Brown
Hydroquinone + NH ₄ OH	Brown-yellow	Brown-yellow
Hydroquinone + H ₂ SO ₄	WW	WW
Pyrogallol	WW	WW
Pyrogallol + NaOH	Red	Orange
Pyrogallol + NH ₄ OH	Pale yellow	Pale yellow
Pyrogallol + H ₂ SO ₄	Purple to brown	Purple to light brown

^a Water-white.

Table I, while it shows the possibilities of color differences between glycerol and ethylene glycol, is subject to variations if certain specific proportions and conditions are not observed. Catechol appears to give the most reliable and satisfactory color differences, especially when in an acid medium.

Chemicals

The catechol (Eastman Kodak Company No. 604) had a melting point of 103° to 104° C. The other phenols were also from the Eastman Kodak Company.

The glycols were from the Carbide and Carbon Chemicals Company and possessed the following properties:

	Specific Gravity	Refractive Index
Ethylene glycol	1.1176 @ 15/15° C.	1.4311 @ 20° C.
Diethylene glycol	1.1185 @ 20/20° C.	1.4475 @ 20° C.
Triethylene glycol	1.122-1.127 @ 20/20° C.	
Propylene glycol	1.0381 @ 20/20° C.	

The trimethylene glycol was obtained from the Procter & Gamble Company and had the following properties:

Specific gravity	1.0603
Ash, %	0.002
Titer	2.0
Moisture, %	1.6
Purity, %	96.0
Color	14 Yellow 2 Red

The glycerol c. p. had a specific gravity of 1.265 at 15° C.

The sulfuric acid c. p., specific gravity 1.84 (A. C. S. specifications), was from Baker & Adamson. Ammonium hydroxide was Baker's c. p. grade (sp. gr. 0.90). Sodium hydroxide was Merck's c. p. (A. C. S. specifications).

Procedure

The best conditions for the color determination of glycerol appear to be as follows:

Place the following ingredients in a 15-cm. (6-inch) test tube in the order given: (1) 3 ml. of the solution to be tested, (2) 3 ml. of 10 per cent aqueous solution of catechol (freshly prepared, since such solutions color with age even if kept in a dark bottle), and (3) 6 ml. of concentrated sulfuric acid.

Heat the tube (gently) for about 30 seconds.

If glycerol is present, a blood-orange coloration will quickly appear at about 140° to 145° C. The color so produced is stable over a period of many days, unlike Mulliken's test which changes color after a few minutes.

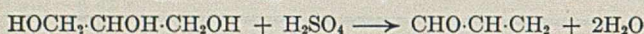
With ethylene glycol, diethylene glycol, and ethyl alcohol, no color is formed. With other polyhydric alcohols, distinctive colors (see Table IV) are produced, which may serve as a means of identification.

It is important not only that the order of mixing be followed as above, but also that the tube containing the solution to be tested and the catechol solution be well shaken before the addition of the concentrated sulfuric acid. Merely mixing the three materials and then shaking and warming produces unreliable results—i. e., in the case of ethylene glycol, a very faint pink color may be observed instead of the water-white condition which is obtained when the correct order of procedure is followed. In the case of glycerol, however, merely mixing and warming the three materials do not interfere with the characteristic blood-orange coloration.

Since the test for ethylene glycol is negative (water-white color), a confirmatory test is desirable. This may be accomplished by color differences obtained through the use of polyhydroxy phenols in the presence of sodium hydroxide (see Table I).

Interfering Substances

Since a concentration approaching 50 per cent of sulfuric acid is employed in the color test for glycerol, it seemed possible that the glycerol might be dehydrated to form acrolein:



However, substituting acrolein for glycerol in the test, a purple flocculent precipitate is formed which is readily distinguished from the blood-orange color of glycerol.

Aldehydes, in general, give color reactions with catechol and sulfuric acid (see Table II).

The presence of any of these aldehydes would tend to interfere with the test for glycerol, but with the exception of acrolein the chances of their being present are fairly remote. This test with catechol and sulfuric acid, since it produces a flocculent purple precipitate with acrolein and obscures the blood-orange glycerol color, serves as the basis for a good color test for determining acrolein in the presence of glycerol.

TABLE II. COLOR REACTIONS OF ALDEHYDES BY THE CATECHOL-SULFURIC ACID METHOD

No.	Aldehyde	Color
A-1	Acrolein	Purple flocculent precipitate
A-2	Formaldehyde	Purple turning to brown
A-3	Acetaldehyde	Purplish red
A-4	Benzaldehyde	Red-orange

Concentration Range

The test, as outlined above, was tried out at various concentrations in an attempt to establish the lower limit of sensitivity for the concentration of the polyhydric alcohol. It was found to be extremely sensitive, as is shown by Table III.

Since it works so well on glycerol in the presence of ethylene glycol, the test was studied to see what other color differences might be observed if the constitution of the alcohol was varied from monohydric to hexahydric. These color differences are shown in Table IV.

A number of other compounds which were not phenolic were also tried for color differences. The most interesting color differences which were observed are shown in Table V.

Discussion

It seems possible by means of a series of dilutions of the unknown and by comparison with a color standard to obtain

TABLE III. EFFECT OF MOLAR CONCENTRATION ON COLORIMETRIC DETERMINATION OF GLYCEROL IN AQUEOUS SYSTEMS

Molar Concentration	Parts per 1000	Percentage Glycerol	Color
1	92	9.2	Blood-orange
0.5	46	4.6	Blood-orange
0.25	23.0	2.30	Blood-orange
0.125	11.5	1.15	Blood-orange
0.0625	5.75	0.575	Blood-orange
0.03125	2.875	0.2875	Blood-orange
0.015625	1.4375	0.14375	Light pink ^a
Ethylene Glycol			
1	62	6.2	Water-white
0.5	31	3.1	Water-white
0.25	15.5	1.55	Water-white
0.125	7.77	0.777	Water-white
0.0625	3.88	0.388	Water-white
0.03125	1.94	0.194	Water-white
0.015625	0.97	0.097	Water-white

^a 0.0156 M would indicate the limit of this colorimetric test. The last full deep red coloration is at double this molar concentration—i. e., 0.03125 M.

TABLE IV. COLOR DIFFERENCES FOR ALCOHOLS VARYING IN THE NUMBER OF HYDROXYL GROUPS

No.	—OH Groups	Alcohol	Color
A	1	Ethyl alcohol	Water-white
B	2	Ethylene glycol	Water-white
C	2	Diethylene glycol	Water-white
D	2	Propylene glycol	Faint pink
E	2	Triethylene glycol	Faint pink
F	2	Trimethylene glycol	Dark brown
G	3	Glycerol	Blood-orange
H	4	Pentaerythritol	Dark purple-red
I	4	Erythritol	Faint pink
J	6	Mannitol	Red-orange
K	6	Sorbitol (neutral)	Blue
L	6	Sorbitol (H ₂ SO ₄)	Faint pink

TABLE V. COLOR DETERMINATION OF GLYCEROL AND ETHYLENE GLYCEROL WITH SUBSTANCES OTHER THAN STRAIGHT PHENOLS

		Glycerol	Ethylene Glycol
R-3	<i>p</i> -Aminobenzoic acid + H ₂ SO ₄	Dark brown	Light brown to orange
R-9	<i>n</i> -Dichlorosuccinic acid + EtOH	Straw yellow	Water-white
R-10	<i>n</i> -Dichlorosuccinic acid + EtOH + H ₂ SO ₄	Dark brown	Pale straw
R-21	National Scarlet R salt + NaOH	Orange	Yellow
R-22	National Scarlet R salt + H ₂ SO ₄	Yellow	Pink
R-24	National Red G salt + NaOH	Yellow-orange	Yellow
R-25	National Red G salt + H ₂ SO ₄	Yellow-pink	Pink
R-31	National Blue BN salt + H ₂ SO ₄	Green-yellow	Pink-yellow
R-32	National Orange GC salt	Yellow	Yellow-orange

semiquantitative results for the glycerol content. The authors are working on this possibility and hope to make the facts available soon.

Summary

A color test using catechol and sulfuric acid for the qualitative determination of glycerol in the presence of ethylene glycol is described which is sensitive to concentrations approaching 0.0156 M (or 1 part in 700).

The test may also be applied in the detection of other polyhydric alcohols which give specific color reactions with the reagents.

The compounds which produce the most color differences between glycerol and ethylene glycol are the polyhydroxy phenols.

Aldehydes, if present, interfere with the catechol-sulfuric acid test for glycerol.

The test may also be applied in the detection of acrolein in the presence of glycerol.

Acknowledgment

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Literature Cited

- (1) Bossart and Snoddy, *IND. ENG. CHEM.*, 19, 506-10 (1927).
- (2) Carr, Townsend, and Badger, *Ibid.*, 17, 643 (1925).
- (3) Gardner, "Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors," 7th ed., p. 957, Washington, 1935.
- (4) Hoyt, *IND. ENG. CHEM.*, 26, 329 (1934).
- (5) Kappelmeier, *Farben-Ztg.*, 40, 1141 (1935); *Paint, Oil Chem. Rev.*, pp. 20-4 (June 10, 1937).

- (6) Kavanaugh, *IND. ENG. CHEM., Anal. Ed.*, 8, 397 (1936).
- (7) Lawrie, "Glycerol and the Glycols," pp. 144-50, New York, Chemical Catalog Co., 1928.
- (8) Mulliken, "Identification of Pure Organic Compounds," Test No. 816, p. 169, New York, John Wiley & Sons, 1904.
- (9) Rogers, "Industrial Chemistry," 4th ed., Vol. II, Chapter XXXI, New York, D. Van Nostrand Co., 1926.

RECEIVED September 23, 1937. Presented before the Division of Paint and Varnish Chemistry, Organic Plastics Section, at the 94th Meeting of the American Chemical Society, Rochester, N. Y., September 6 to 10, 1937.

Determination of Butenes in Refinery Gases

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PUBLISHED methods for the analysis of hydrocarbon gases are notably inadequate in the case of the group containing four carbon atoms. This is to be expected when it is realized that no fewer than seven compounds occur in this group (Table I) six of which are usually found in gases from cracking operations; yet the total boiling range of the group is only some 15° C. (27° F.).

In general, there are only three methods available in the literature for the analysis of the C-4 hydrocarbons: bromination, reactions with sulfuric acid, and direct low-temperature fractionation. These are further subdivided into specific methods varying concentrations or reagents, methods of fractionation, and times of contact. The only thing all three possess in common is definite unreliability. Most of them have been based on relatively few experiments, using particular types of gases for which they may or may not be satisfactory. Even in the few cases where relatively pure gases were used, the mixtures were made with air or other inert gas, and in most cases the authors admit that inclusion of butanes, diolefins, or other olefins will spoil the results.

Perhaps the most used, but certainly not the best of the methods, depends on the selective absorption of isobutene in 62 to 64 per cent sulfuric acid followed by absorption of the normal butenes in 87 per cent acid. For low concentrations of isobutene such as are usually found, the method has been more or less discredited even by those responsible for its development (10), but is still used because no better one is available and at least an approximate measure is obtained in most cases.

Work done in this (9) and other laboratories over the past several years has indicated the unreliability of selective acid absorption. As a final test before this work was started, a "butene concentrate" was submitted to four laboratories to see if their variations of the sulfuric acid method would give reproducible results. The results obtained by six methods gave a spread on the "standard" sample greater than the amount of isobutene present and even the individual methods varied as much as 7.0 per cent on the basis of total gas on check samples.

Methods depending on the production of dibromides, separation by fractional distillation, and determination of the individual olefins by prolonged low-temperature fractional distil-

lation, after regeneration by zinc (3, 5), are also of doubtful value as far as results are concerned, not to mention the size of samples and excessive times required. It has been the author's experience that it is almost impossible to distill the dibromides without some decomposition even at low pressures. The regeneration of butenes by zinc has been shown to result in mixtures in all cases (13) and the low-temperature fractional distillation of iso- and 1-butene, boiling less than 1° C. apart, even at extremely slow rates, would require an efficiency far greater than that exhibited by ordinary laboratory columns (7).

The best of all the bromide methods (2) is that based on measurement of the reaction rates of the pure dibromides with potassium iodide in methyl alcohol. Even this is only accurate to 2.0 per cent, according to the authors, and fails when isobutene is present.

The proposed method calls for the separation of two cuts by exact low-temperature fractional distillation (8). The first, containing isobutane, isobutene, and 1-butene, is subsequently hydrogenated (9) over a nickel catalyst to obtain the total unsaturation of the cut and the isobutene is then determined separately by reaction with anhydrous hydrogen chloride gas. The second, containing all the *n*-butane and 2-butenes, is also hydrogenated for total unsaturation and the residual gas is condensed into a bulb and treated with bromine at low temperatures. The dibromides are subsequently left as a residue on warming the mixture and are determined by measurement of the refractive indices. All the steps except the last are accurate to ± 0.15 per cent at least. Thus far no reason has been found for determining the individual 2-butenes with an accuracy greater than 3.0 per cent, of which the method is capable. If more accurate determination is desired the method of Dillon, Young, and Lucas (2) can be used, but in that case a much larger sample is needed. 1,3-Butadiene, if present, will be found with the iso- and 1-butenes and should be determined separately (4, 11) and the calculations corrected accordingly.

Apparatus

The low-temperature fractional distillation apparatus (7, 8) and the hydrogenation unit (9) have been described in previous papers.

The apparatus for the addition of hydrogen chloride is shown in Figure 1. It consists of two 50-ml. rebuilt distillation flasks, *A* and *A'*, with individual check valve manometers, *B* and *B'*, joined through a gold-plated stopcock, *C*. Two other gold-plated stopcocks, *D* and *E*, connect the apparatus to the distillation or introductory unit, *F*, and to the hydrogen chloride generator, *G*, respectively. The entire apparatus is of Pyrex glass except as shown in the sketch.

Gold-plated stopcocks are essential for the apparatus; no other cocks will hold the vacuum and the hydrogen chloride vapors under the condition of the analysis. They require only a thin film of vaseline or Burrell stopcock grease. Other lubricants,

TABLE I. FOUR-CARBON HYDROCARBONS

	B. p. ° C.
Isobutane	-12.2
Isobutene	-7.6
1-Butene	-6.8
1,3-Butadiene	-4.7
<i>n</i> -Butane	+0.4
<i>trans</i> -2-Butene	+0.5
<i>cis</i> -2-Butene	+3.2

such as Aircro HyVac and Cellogrease or compounds containing rubber, cannot be used, since they also react with the hydrogen chloride, causing leaks and giving poor results. Care should be exercised not to scratch the gold-plating, which is very soft, and any tendency on the part of the stopcock to "drag" should be corrected immediately by relubrication.

The bulbs are carefully calibrated to the nearest 0.1 ml. by displacing air from a calibrated buret. Manometers are read to the nearest 0.5 mm. The apparatus should be held at as constant a temperature as possible and protected from drafts.

The hydrogen chloride generator is a 45-cm. (18-inch) drying tower filled with calcium chloride in the drying section, except for a 2.5-cm. (1-inch) layer of barium chloride crystals on the top. Glass-wool plugs are placed at both ends of the drying section.

Fifty grams of c. p. ammonium chloride crystals are added dry to the bottom section and the dropping funnel is inserted with a rubber stopper as shown. Both the top and bottom stoppers closing the openings of the drying tower are sealed in place with sealing wax, after which the whole assembly is tested to make sure that it is vacuum-tight. When ready for use, approximately 25 ml. of concentrated c. p. hydrochloric acid are added through the funnel to the evacuated scrubber and then c. p. concentrated sulfuric acid is added slowly, drop by drop, allowing time for reaction, until the pressure is brought to atmospheric as shown by the manometer, *B'*. The generator is then ready for use.

The generator described above is completely safe if the instructions are followed. After once the pressure has been built to atmospheric, it is usually sufficient to add 2 to 3 drops of acid each time hydrogen chloride is removed for an analysis. At the end of the day's runs any excess pressure is vented carefully through the acid-inlet stopcock and the generator is ordinarily connected to the bulb, *A'*, with *C* closed, so that the manometer can act as a safety valve if necessary. The general reaction is so fast and complete that pressure is developed only immediately after addition of the acid.

With the generator filled with dry hydrogen chloride and cock *E* closed, the remainder of the apparatus is evacuated as completely as possible. Stopcock *C* is then closed and a pressure of about 450 or 500 mm. (maximum) of hydrogen chloride is built up in *A'* by cracking cock *E* slightly. *E* is then closed and the pressure read on the balanced manometer, *B'*, using a constant reference point (900 mm.) for the leg connected to bulb *A'*.

Gas is admitted to bulb *A* from the distillation or scrubbing unit, *F*, until the pressure reaches a maximum of 400 mm. (absolute), at which point *D* is closed and the pressure is read on *B*.

Both mercury bulbs are then lowered so that the open leg stands at about 100 mm. on the manometer and *C* is opened, connecting *A* and *A'*. Bulb *A* is then immersed in liquid air or carbon dioxide-gasoline until the contents of both bulbs are condensed in *A*.

If complete condensation occurs (in the presence of no non-condensables) the gas is allowed to revaporize immediately, but if only partial condensation occurs, pressure is again allowed to build up by warming the bulb with the hands. Then the gases are again recondensed. This is necessary to sweep unreacted gas into the bulb where it can be condensed. In the special case where isobutene is determined on the original sample, if too small a pressure reduction is obtained on immersion in liquid nitrogen,

owing to extra large amounts of hydrogen or air in the sample, it will be necessary to eliminate the noncondensables by distillation.

After the gases are condensed, the liquid nitrogen is removed and the solid hydrogen chloride allowed to melt. The bulb is then immersed in water at approximately 37.78° C. (100° F.), and the contents are completely vaporized. After the bulb again comes to room temperature both manometers are set back to the reference points and the new readings are taken. The contraction in volume is a direct measure of the amount of isobutene present.

A typical calculation is shown:

Barometer	= 755.5 mm.
Reference point on manometers	= 900.0 mm. (zero 144.5)
Original reading, HCl	= 627.5 mm.
Original reading, sample	= 572.5 mm.
Final reading, both manometers	= 524.5 mm.

Absolute pressures:		
627.5	572.5	524.5
144.5	144.5	144.5
HCl = 483.0	Sample = 428.0	Final = 380.0

$$\text{HCl} - \frac{483.0 \times 80.5 \text{ (volume of bulb)}}{755.5} = 51.5 \text{ ml.}$$

$$\text{Sample} - \frac{428.0 \times 82.7 \text{ (volume of bulb)}}{755.5} = 46.8 \text{ ml.}$$

$$\text{Final} - \frac{380.0 \times 163.2 \text{ (combined volumes)}}{755.5} = 82.0 \text{ ml.}$$

$$51.5 + 46.8 - 82.0 = 16.3 \text{ ml. contraction}$$

$$\frac{16.3}{46.8} \times 100 = 34.8 \text{ per cent isobutene}$$

The product of the reaction between isobutene and hydrogen chloride boils well above room temperature and under ordinary conditions would condense out in the apparatus. For this reason maximum pressures have been established and are given above. Even with pure isobutene and the given pressures no condensation will occur, but by going above these pressures high results may be obtained.

Experimental

For the purpose of this work an accuracy of ± 0.1 per cent of the individual components was desired, with the exception of the isomeric 2-butenes. It was realized that in order to attain such accuracy it would be necessary to separate the four-carbon group from the remainder of the gas by accurate low-temperature fractional distillation. This step had previously been worked out to the desired accuracy (?). However, the succeeding step of separating the four-carbon group into two groups had not been worked out completely for gases containing olefins.

By synthesizing known mixtures of pure hydrocarbons, as in previous work (7, 9), it was found that making the distillation cuts at the mid-temperature point between iso- and *n*-butanes, as is usually done in such analyses, did not give good results. Cutting at the mid-temperature point between 1-butene and *n*-butane also gave poor results. However, if the distillation was cut at a point midway between these two cut points much better results were obtained in every case.

SEPARATION BY DISTILLATION. Preparation of the gases isobutane, butane, and 1-butene has been described in previous papers (7, 9).

Isobutene was prepared by dehydration of redistilled tertiary butyl alcohol over oxalic acid and then fractionated and treated the same as 1-butene.

1,3-Butadiene was prepared by the method of Kistiakowsky (6), then scrubbed, dried, and refractionated to constant boiling point and vapor pressure. The boiling point was the same (-4.5° to -4.6° C.) as that obtained by Kistiakowsky for his best sample. There is some evidence to indicate that this is not pure 1,3-

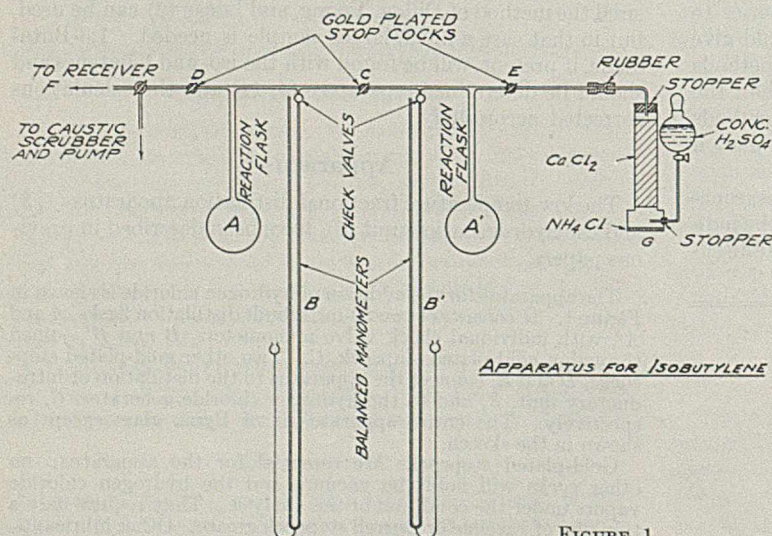


FIGURE 1

butadiene but a constant-boiling mixture. However, this has not been definitely proved as yet, mainly because of the general unreliability of methods for the determination of 1,3-butadiene.

Mixed 2-butenes were prepared by dehydrating a mixture of primary and secondary alcohols with 60 per cent sulfuric acid according to the method of Young and Lucas (12). The resulting butenes were fractionated as well as possible into two cuts corresponding to the *cis* and *trans* isomers, which were then brominated at about 0° C. (32° F.). After washing with caustic and drying, the dibromides were twice fractionated at low pressures and the butenes regenerated by zinc in ethyl alcohol. Subsequent refractionation at low temperatures indicated that pure *cis* and *trans* isomers could not be produced by this method, but the resulting mixes were satisfactory for testing the reproducibility of the refractive indices using the method indicated.

As in previous work, all synthetic mixtures were made to accurately known composition by blending by condensation in a calibrated and carefully evacuated all-glass system (9).

For the majority of the work on the separation of the groups by low-temperature fractional distillation, four-component mixtures were used consisting of isobutane, isobutene, 1-butene, and *n*-butane. Typical results on mixtures of this type are shown in Table II, using the average cut point of -4.5° C. (+23.9° F.) described above. The first three components of the mixtures correspond to the first cut and the *n*-butane corresponds to the second cut.

TABLE II. SEPARATION BY DISTILLATION

Run No.	Butane		Deviation %
	Synthesized %	Found %	
1	24.9	24.6	-0.3
2	31.1	30.8	-0.3
3	26.6	26.7	+0.1
4	38.1	38.0	-0.1
5	29.0	29.1	+0.1

DETERMINATION OF ISOBUTENE. When it had been definitely determined that the isobutane, isobutene, and 1-butene could be separated from the *n*-butane and 2-butenes, it was still necessary to develop a method for separating the iso- and 1-butenes. This was simplified by the hydrogenation method previously worked out, which allows the determination of the combined butenes within an accuracy of 0.1 per cent (9). It was then necessary only to determine either 1-butene or isobutene accurately in order to make possible the calculation of the individual components in this group of three hydrocarbons. The only method found which would give the required separation depends on the use of dry hydrogen chloride gas. It is based on an observation by Coffin, Sutherland, and Maass (1) that isobutene reacts instantaneously when hydrogen chloride is passed through a liquefied butene mixture, while the other butenes are unaffected. So far as can be determined, these authors never worked out an analytical method based on the observation.

The method developed in this work is essentially simple. It requires only that a measured volume of dry hydrogen chloride be mixed with a measured volume of hydrocarbon gas containing isobutene and the resulting mixture be condensed and then revaporized. The contraction in volume is a direct measure of the isobutene present according to the reaction:



The reaction is specific, so far as the author has been able to determine, for isobutene. Tests made with pure ethylene, propylene, 1-butene, mixed 2-butenes, 1,3-butadiene, butanes, and acetylene have not shown any reaction with hydrogen

chloride when alone or mixed. In the presence of isobutene, no reaction other than that due to isobutene has taken place. Some typical results are shown in Table III.

TABLE III. DETERMINATION OF ISOBUTENE

Components Present	Isobutene	
	Actual %	Found %
Isobutene	100.0	100.0
1-Butene	None	None
Isobutene, 1-butene	34.8	34.8
Isobutene, 1-butene	42.3	42.0
Isobutene, 1-butene	42.3	42.4
Isobutene, 1-butene	66.3	66.3
1,3-Butadiene	None	None
Isobutene; 1,3-butadiene ^a	28.7	28.2
Isobutene; 1,3-butadiene	45.6	45.5
Acetylene	None	None
Mixed 2-butenes	None	None
(Iso- and 1-butenes)		
(Iso- and <i>n</i> -butanes)		
1	19.7	19.6
2	32.7	32.8

^aExtremely small sample. Possible error in synthesis.

The total time per analysis averages less than 15 minutes. The reaction is instantaneous and the time required is taken up mostly by allowing the bulbs to come back to temperature before the final readings are made.

In those analyses where only the isobutene is required, it can be determined directly on the original gas with the same degree of accuracy, providing no pentenes or higher homologs are present having tertiary carbon linkages. However, in that case, the gas should be freed from hydrogen sulfide by soda lime and dried by calcium chloride.

DETERMINATION OF 2-BUTENES. The combined 2-butenes are easily determinable in the presence of *n*-butane to 0.1 per cent, by hydrogenation of the cut as outlined above. The actual determination of the individual *cis* and *trans* isomers, however, is not as easy and, as far as can be determined at the present time, is not necessary for most petroleum gases. For purposes of estimation, the following method has been worked out. It allows an accuracy of 3.0 per cent in only a few minutes' time, which is good compared to the estimated accuracy of other more exact methods (2) which take much longer and require much larger quantities of gas.

Total unsaturation of the butane cut is determined as usual and the residual gas in the distillation receiver is then recondensed into a bulb using liquid nitrogen. This is best accomplished by having a stopcock sealed to one of the receivers with a male interchangeable ground-glass joint sealed to it, forming an L-joint pointing downwards. The female joint is then sealed off at the lower end, making a closed-off bulb which can be detached from the apparatus. At the beginning of the analysis this bulb is completely evacuated and closed off, or the bulb is calibrated into the apparatus and the cock is normally left open.

Once the butane-butenes are condensed, the stopcock is closed and the joint disconnected, while the tube is kept cold. About 5 drops of pure liquid bromine are then added slowly from a 1-ml. pipet and the reaction is allowed to take place at as low a temperature as possible. No evidence of hydrobromic acid has been detected when the brominations were carried out at low temperatures. No attempt is made to brominate completely all the butenes present.

As soon as all the bromine has reacted, the tube is set aside and allowed to come to room temperature. It is then put in a boiling water bath and the last trace of butane is completely eliminated. After cooling, the tube is held in a 25° C. water bath for a few minutes and the refractive index is determined as accurately as possible at that temperature by an Abbé refractometer. Only 2 drops of liquid are required and a reproducibility of one in the fourth decimal place can readily be attained. This corresponds to an accuracy of 3.0 per cent using the constants (2) for the dibromides of

	Refractive Index at 25° C.
Meso-2,3-dibromobutane (from <i>trans</i>)	1.5092
Racemic-2,3-dibromobutane (from <i>cis</i>)	1.5125

and assuming that the laws of mixtures hold.

As a check on the validity of this last assumption, mixtures were made of the impure 2-butenes prepared above. Dibromides prepared from the two materials designated as *cis* and *trans* and their known percentage mixtures as gases, both alone and in the presence of normal butane, gave results typical of those shown in Table IV. For most of the cases the results were within the limit of one in the fourth place on the refractive indices; however, in about 10 per cent of the runs the error was two in the fourth place. In a few cases, where the original mixture was in doubt, the results were much worse than these.

TABLE IV. CHECK RESULTS

	Refractive Index at 25° C.	<i>cis</i> -2-butene	
		Synthesized %	Found %
Original C ^a	1.5120	..	85.0
Original T ^b	1.5098	..	19.0
52% C + 48% T	1.5110	53.3	54.5
31% C + 69% T	1.5104	39.5	36.5
76% C + 24% T	1.5115	69.1	69.5

^a *Cis*.
^b *Trans*.

Summary

A new method is presented for the determination of individual components normally occurring in refinery and cracked petroleum gases. By its use, the individual four-carbon hydrocarbons, with the exception of the individual isomeric 2-butenes, can be determined within an accuracy of better than ± 0.15 per cent. No larger gas samples are required than are now used for low-temperature fractional distillation, and the time required is but very little more than for this step alone.

A new gas-reaction analytical method for the determination of isobutene with anhydrous hydrogen chloride has also been developed as a part of the general scheme of analysis, which allows the determination of isobutene in the presence of any other normally gaseous olefin with an accuracy of 0.1 per cent. Twenty to thirty milliliters of gas are normally used and the total time per determination is 15 minutes or less.

Acknowledgment

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Literature Cited

- (1) Coffin, Sutherland, and Maass, *Can. J. Research*, **2**, 267 (1930).
- (2) Dillon, Young, and Lucas, *J. Am. Chem. Soc.*, **52**, 1953 (1930).
- (3) Frey and Huppke, *IND. ENG. CHEM.*, **25**, 54 (1933).
- (4) Gooderham, *J. Soc. Chem. Ind.*, **56**, 32T (1937).
- (5) Hurd and Goldsby, *J. Am. Chem. Soc.*, **56**, 1812 (1934).
- (6) Kistiakowsky, Ruhoff, Smith, and Vaughan, *Ibid.*, **58**, 146 (1936).
- (7) McMillan, *J. Inst. Petroleum Tech.*, **22**, 616 (1936).
- (8) McMillan, U. S. Patent 2,005,323 (1936).
- (9) McMillan, Cole, and Ritchie, *IND. ENG. CHEM., Anal. Ed.*, **8**, 105 (1936).
- (10) Marcovitch and Moore, *Natl. Petroleum News*, **23**, No. 41, 33-8 (1931).
- (11) Tropsch and Mattox, *IND. ENG. CHEM., Anal. Ed.*, **6**, 404 (1934).
- (12) Young and Lucas, *J. Am. Chem. Soc.*, **52**, 1964 (1930).
- (13) Young and Winstein, *Ibid.*, **58**, 441 (1936).

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Electrometric Titration of Dichromate Glycerol Samples

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FOR control purposes in soap and glycerol manufacture glycerol is usually determined through the oxidation of a prepared sample by an excess of potassium dichromate in the presence of an excess of sulfuric acid. The most common procedure is to titrate the excess of the dichromate solution, after oxidation is completed, with ferrous sulfate solution using potassium ferricyanide as an external indicator on a spot plate. Randa (5) has recently described a method in which the dichromate solution after oxidation is made to volume and used to titrate standard ferrous sulfate solution, using diphenylamine as internal indicator.

For a number of years in the Procter & Gamble laboratories, the excess dichromate after oxidation has been titrated in the oxidation flask without any transfer or further treatment other than cooling. Ferrous sulfate is used for the titration with an electrometric setup as internal indicator. As far as the authors have been able to learn, the electrometric method has not been used in other laboratories for the titration of the excess dichromate in glycerol determinations, although such a setup has been in use for dichromate-ferrous sulfate titrations in other laboratories, such as some of those of the steel industry (2).

In 1922 electrometric titration of practically all routine glycerol samples replaced the use of the spot plate in one of the company laboratories. In the first setup a platinum electrode

and calomel half-cell were used with *N* potassium chloride. The ferricyanide spot plate was used only for checkup. In 1935 a bimetallic electrode setup was placed in use in one of the laboratories and the calomel cell was eliminated. Plati-

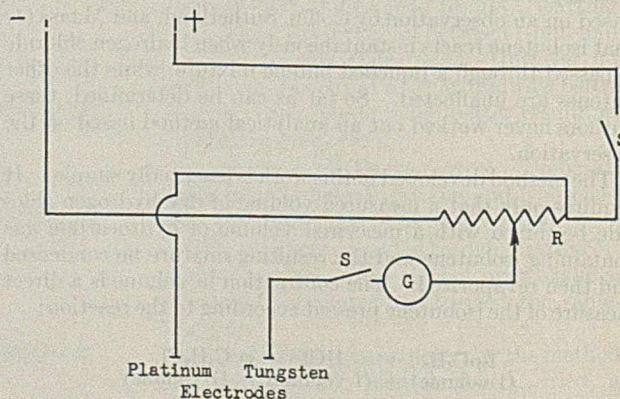


FIGURE 1. WIRING DIAGRAM

S. Double-pole, single-throw switch
R. Potentiometer
G. Galvanometer
Batteries (4 dry cells in series)

num and nickel electrodes (1) were used. The nickel electrode was changed monthly, and a few months later was replaced by a tungsten electrode (6, 7).

The platinum-tungsten setup is now in use in practically all of the company laboratories and an electrometric apparatus in all. Figures 1 and 2 show the photograph and the wiring diagram of the preferred bimetallic electrode apparatus.

The cabinet is of oak with a black Formica base, and is closed at the back with double wooden doors. The lines for ferrous sulfate solution, distilled water, and motor are carried through the back of the cabinet. All exposed metal clips and parts are chromium plated. The motor and the ring supporting the flask are carried on a rod in the interior of the cabinet. At the upper left (Figure 2) is the Weston galvanometer, model 699, sensitivity 2 microamperes per scale division. Below the galvanometer is the adjusting knob of the potentiometer, Yaxley Manufacturing Company, 1000 ohms. The knob below the potentiometer controls a three-armed distilled water spray for washing the electrodes and stirrer. The support for the flask is movable, so that the flask may be raised or lowered from position. In some installations the support is attached to the water valves, so that the spray operates when the ring is pushed to the left. The toggle switches are shown at the lower left: a single-pole single-throw at the left for the motor, and a double-pole single-throw for the galvanometer circuit. The funnel, stainless steel or Monel, is connected to the drain. The electrodes are 20-gage platinum or tungsten wire sealed into glass tubing. The exposed electrode wires are approximately 5 mm. The tubing of the electrode is mercury-filled. The stirrer is made of a glass rod and fastened in a chuck on the motor shaft. The motor is model 3 (Eastern Engineering Corporation) with rheostat for regulating the speed.

Procedure

While the general procedure of the dichromate oxidation of glycerol is well known, an outline of the preparation of the solutions and details of oxidation and titration may be desirable.

STANDARD DICHROMATE SOLUTION. The dichromate solution is pipetted into the oxidation flasks with a 25-ml. Lowy automatic pipet (or for special samples a 10-ml. Lowy automatic pipet holding exactly two-fifths as much as the 25-ml. pipet). The strength of the dichromate solution is made so that the 25-ml. pipet will deliver 1.864 (4) grams of $K_2Cr_2O_7$, which is equivalent to 0.25 gram of glycerol. The weight of potassium dichromate in grams required for 1 liter at 25° C. is determined by multiplying 74.56 by the ratio of 25 to the volume delivered by the pipet at 25° C. The dichromate is dissolved in distilled water, 150 ml. of concentrated sulfuric acid are added, and the solution is made to 1 liter at 25° C. The strength of the solution is checked against standard dry powdered dichromate by weighing 1.864 grams of the latter, and dissolving in 75 ml. of distilled water and 15 ml. of concentrated sulfuric acid. The ferrous sulfate titrations of a pipetful of the dichromate solution and of the standard dichromate must check within 0.05 ml. of ferrous sulfate solution or the dichromate solution must be adjusted.

FERROUS SULFATE SOLUTION. Five kilograms of reagent grade ferrous ammonium sulfate are dissolved in about 10 liters of distilled water, 1800 ml. of concentrated sulfuric acid are added, and the volume when cooled to room temperature is made up to 16 to 17 liters.

Details of Analysis of a Sample

The details described in the following paragraphs apply to a sample of c. p. glycerol requiring no preliminary purifica-

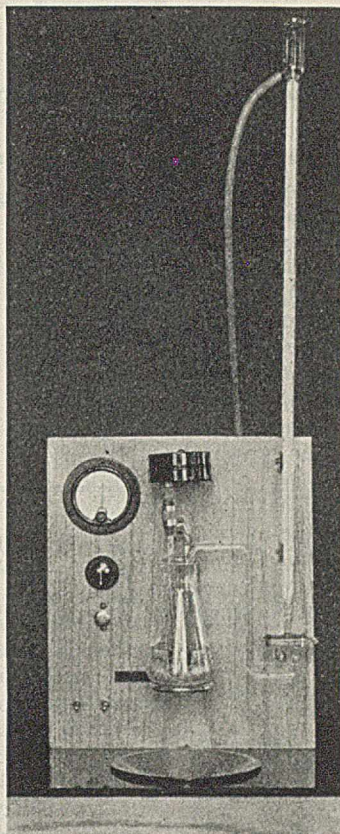


FIGURE 2. PHOTOGRAPH OF APPARATUS

tion. The procedures of oxidation and titration are identical for other samples.

Make a 2 ± 0.001 -gram sample to volume in a 500-ml. flask. Pipet a 50-ml. aliquot into a 250-ml. wide-mouthed Erlenmeyer flask containing a 25-ml. pipetful (at 25° \pm 0.5° C.) of the standard dichromate solution. Add 15 ± 1 ml. of concentrated sulfuric acid. Cover the flask at once with a watch glass.

The samples are usually handled in batches. With each batch prepare at least two blanks by using the same amounts of dichromate solution, sulfuric acid, and water as for the samples. Titrate one blank before and the second after the samples. Use the average of the blank titrations in calculating the glycerol content. Immerse the flasks containing the samples and blanks in a steam bath and hold them at a temperature of 90° to 100° C. for 2 hours. At the end of 2 hours cool the flasks and contents by immersion in cold water until a temperature of 25° to 40° C. is reached.

Remove the watch glass from a flask and place the flask in position on the apparatus with both electrodes and stirrer in the solution and the tip of the buret extending well into the neck of the flask. Close the circuits and bring the galvanometer reading to zero by adjustment of the rheostat. Begin titration slowly with ferrous sulfate solution and observe the galvanometer needle closely. When within 1 to 2 ml. of the end point the needle is deflected sharply to one side, but immediately returns to the zero position. Add the ferrous solution more slowly. When almost at the end point, a short time should be allowed after each addition to allow the needle to move back. At the end point the needle swings over to the side of the scale and remains there. Open the circuits, read the buret, and remove the flask for the next titration. Press the button and flush the electrodes and stirrer as the flask is being removed. After the final titration wash off the electrodes and stirrer and allow the electrodes to stand in distilled water. The glycerol content of the sample is calculated from the difference between blank and sample titrations.

The tungsten electrode should be cleaned about every 6 weeks by dipping for a few seconds into fused sodium nitrite held just slightly above its fusion temperature.

Care must be taken to use sufficient sulfuric acid to give an equivalent of, at least, 1.230 specific gravity (3). The excess of dichromate after heating must be such that a back-titration of at least 9 ml. of ferrous sulfate solution is obtained. For some samples of low glycerol content of 100-ml. aliquot, 30 ml. of sulfuric acid and 10 ml. of dichromate are used.

Summary

The method is very rapid and accurate with a sharp, positive end point, and can readily be operated under varying conditions of lighting by any analyst who can read a buret—even by one who is color-blind.

Literature Cited

- (1) Atanasiu, I. A., and Velculescu, A. I., *Bul. Chim. Soc. Romane Chim.*, 35, 85-90 (1934).
- (2) Kelley, G. L., Adams, J. R., and Wiley, J. A., *J. IND. ENG. CHEM.*, 9, 780-2 (1917).
- (3) Kellner, J., *Z. deut. Ol u. Fett-Ind.*, 41, 751-2 (1921).
- (4) Langmuir, A. C., *J. IND. ENG. CHEM.*, 3, 679-86 (1911).
- (5) Randa, E., *Oil & Soap*, 14, 7-10 (1937).
- (6) Shenk, W. E., and Fenwick, F., *IND. ENG. CHEM., Anal. Ed.*, 7, 194-7 (1935).
- (7) Willard, H. H., and Fenwick, F., *J. Am. Chem. Soc.*, 44, 2504-16, (1922).

Extraction of Gossypol with Different Ethers

Causes of Varying Results

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VARIOUS lots of ethyl ether (U. S. P. grade, not for anesthesia) differ in their ability to extract gossypol from cottonseed meal (2). The influence of factors affecting results in the method of estimation has been studied (2), but the cause of the varying results obtained with the extraction with different lots of ether has heretofore remained obscure. It was essential that consistent results be obtained in the study of the nature of the bond between gossypol and the processed meal in "bound" gossypol which is not readily extracted (unpublished work) but is slowly broken down in the presence of water (3).

Ethers from two sources were used, designated as *B* and *G*. The results reported are in most instances the average of triplicate or quadruplicate determinations obtained by a modified method (in press). Various lots of ether were used at different times; some of these contained peroxide which oxidizes gossypol solutions, especially if alkaline (1).

Table I presents the results of the extraction of gossypol from three samples of cottonseed meal with U. S. P. ethers from two sources, both with and without peroxides. The ether containing peroxides extracted appreciably less gossypol, in one instance as low as 0.006 per cent, while the same ether with the peroxides removed extracted 0.102 per cent, almost equal to the 0.112 per cent extracted by the *G* ether which did not contain peroxides.

TABLE I. GOSSYPOL EXTRACTED WITH U. S. P. ETHERS

Cottonseed Meal	Date	Source of Ether ^a	Gossypol, %
2117	12/17	<i>B</i> 1 year old	0.081
		<i>B</i> (with peroxides)	0.063
2118	12/17	<i>B</i> 1 year old	0.051
		<i>B</i> 2 years old	0.056
	1/2	<i>B</i> 2 years old	0.052
		<i>B</i> (with peroxides)	0.037
1578	5/16	<i>B</i> (with peroxides)	0.006
		<i>B</i> (peroxides removed)	0.102
		<i>G</i> (no peroxides)	0.112

^a *B*, from J. T. Baker Chemical Co., ordered in 50-pound steel drums; *G*, from General Chemical Company, ordered in 30-pound steel drums.

TABLE II. RECOVERY OF GOSSYPOL (50 MG.) REFLUXED WITH ETHER WITH OR WITHOUT PEROXIDES

Date	Treatment of Ether	Gossypol, Mg.	Recovered, %
3/28	Reagent ether	48.0	96.0
	<i>B</i> , purified	46.7	93.6
	<i>G</i> (drum), no peroxides	46.6	93.3
	<i>B</i> , with marked peroxides	34.8	69.6
	Control (not refluxed)	46.9	93.8
4/8	<i>B</i> , purified	46.0	92.0
	<i>B</i> , with peroxides	39.7	79.4
	Control (not refluxed)	48.2	96.4
	<i>B</i> , purified plus acetaldehyde	45.7	91.4

Since the presence of peroxides in the ether appeared to give low results, 50 mg. of purified gossypol were refluxed with a highly purified ether (reagent), a purified *B* ether, a peroxide-free *G* ether, and two *B* ethers containing peroxides (Table II). In every instance where peroxides were absent 91.4 per cent or more of gossypol was recovered; where they were present, materially less gossypol (69.3 and 79.4 per cent) was obtained. It is evident that the presence of peroxides and not aldehyde in the ether caused the destruction of gossypol.

Table III indicates that a purified ether free from peroxides extracted less gossypol (0.085 per cent) from meal 1578, than

TABLE III. RESULTS WITH PURIFIED OR PEROXIDE-FREE ETHERS

Cottonseed Meal	Date	Ether	Gossypol, %
1578	6/20	<i>G</i> (drum), peroxide-free	0.108
		<i>B</i> , purified	0.085
		<i>B</i> , purified plus 10 ml. of alcohol	0.106
		<i>B</i> , purified	0.103
2216	2/4	<i>G</i> (drum), peroxide-free	0.123
		Purified ether plus 10 ml. of alcohol	0.092
2217	2/10	Purified ether plus 10 ml. of alcohol	0.096
		Purified ether plus 10 ml. of alcohol	0.101
2217	2/10	Purified ether plus 10 ml. of alcohol	0.101
		Purified ether plus 10 ml. of alcohol	0.098

the *G* ether (0.108 per cent) from the drum which was peroxide-free. When 10 ml. of alcohol per determination were added to the purified *B* ether (Table III), almost the same amount of gossypol, 0.106 per cent, was extracted as with the *G* ether. A similar difference is shown with meal 1578 (Table I). Likewise, a purified ether with 10 ml. of alcohol added extracted more gossypol from meal 2217 (Table III) than the *B* ether with 1 per cent of alcohol added (Table IV). The addition of 10 ml. of alcohol to the purified ether extracted 0.092 and 0.101 per cent of gossypol from meals 2216 and 2217, respectively. This was later confirmed by repeating the extractions, giving 0.096 and 0.098 per cent.

The peroxide-free *G* ether from the drum extracted more gossypol than the purified ether. The addition to the purified ether of 10 ml. of alcohol per determination increased the yield. The high results from the extractions on meal 1578 made on July 1 with *B* purified ether and with peroxide-free *G* ether are exceptional. This set of extractions was made during an extremely hot spell; the unusually high room temperature probably facilitated the rate of extraction so that it proceeded more rapidly than usual. Therefore, all extractions thereafter were made at 45° C., the receiving flasks being kept in a thermoregulated water bath, with the Soxhlet extractors containing the charge surrounded on all sides and top with a detachable box of pressboard fitted closely on the top of the water bath. This expedited the rate of extraction, making it more uniform for all determinations, and also yielded more uniform results.

Since purified ether extracted more gossypol when alcohol was added (Table III) and since ethyl ether (U. S. P. grade, not for anesthesia) may contain as much as 4 per cent of alcohol and water, sufficient alcohol was added to the peroxide-free *B* ether from the drum to modify the *B* ethers to contain, respectively, 1, 2, 2.5, 3, and 3.5 per cent of alcohol, including that already present (Table IV). The *B* ether without the addition of alcohol had previously extracted less gossypol. The results show that 1 per cent of alcohol was not effective but that 2 to 3.5 per cent aided the extraction of gossypol in yielding higher results.

The peroxide-free ethers from the drums (Table V) vary in their ability to extract gossypol, the *G* ether being superior. The *G* and *B* ethers differ in their density, being 0.724 and 0.722, respectively. An analysis of these ethers showed the water and alcohol content to be appreciably higher in the *G* ether which extracted the greater percentage of gossypol. The percentage of alcohol, ether, and water was readily determined by means of a buret, thermometer, and pycnometer, using the method of Marquoyrol and Goutal (4) as modified by Smisniewicz and Zielinski (5).

TABLE IV. GOSSYPOL EXTRACTED WITH ETHER CONTAINING VARIOUS AMOUNTS OF ALCOHOL

(Cottonseed meal, 2217; B ether, drum, peroxide-free, composition modified)

Alcohol, %	1	2	2.5	3	3.5		
Gossypol, %	0.085	0.094	0.098	0.101	0.092	0.096	0.100

TABLE V. EFFECT OF COMPOSITION OF ETHER ON AMOUNTS OF GOSSYPOL EXTRACTED (Cottonseed meal 2217)

Date	Source of Ether	Density	Composition			Gossypol Ex-tracted %
			Alco-hol %	Water %	Ether %	
2/17	B (drum), peroxide-free	0.722	0.3	0.70	99.0	0.089
	G (drum), peroxide-free	0.724	2.4	1.02	96.55	0.108
3/3	B (drum)	0.077
	B, modified to G	0.726	2.3	1.2	96.5	0.099
	G (drum)	0.090
3/7	B (drum)	0.094
	B modified to G	0.726	2.3	1.2	96.5	0.107
	G (drum)	0.107
3/18	B	0.083
	B modified to G	0.726	2.5	1.05	96.45	0.096
	G	0.096

The extraction of gossypol from meal 2217 was made with the G and B ethers and later with this B ether modified to the same composition as that of the G ether with a density of 0.724, by the addition of the proper amount of alcohol (95 per cent alcohol by volume, the composition of which was carefully determined) and by water. The modified B ether extracted somewhat more gossypol (0.099 per cent) than the G ether (0.090 per cent) but not quite as much as the 0.108 per cent which the G ether extracted on February 17. The B ether was again modified on March 7 and March 18 to the same composition as the G ether. In both instances the modified ether extracted as much gossypol as the G ether, all having the same composition. The modified peroxide-free ether which extracted the optimum amount of gossypol at a constant temperature of 45° C. contained 2.3

to 2.5 per cent alcohol (by weight) and 1 to 1.2 per cent of water, having a density of 0.724 to 0.726 at 15.6° C.

Summary

In the estimation of gossypol from cottonseed meal it is necessary to use ethyl ether free from peroxides, the presence of which causes low results.

Ether which was purified to remove peroxides did not extract as much gossypol as the peroxide-free G ether taken from the drum. This was due to the presence of the relatively larger quantities of alcohol and water in the ether from the drum, since the greater part of these constituents were removed during purification. When the composition of the purified ether was modified to that of the G ether, both extracted the same quantity of gossypol from cottonseed meal.

Conclusion

It is concluded that a peroxide-free ether containing 2.3 to 2.5 per cent of alcohol (by weight) and 1 to 1.2 per cent of water, having a density of 0.724 to 0.726 at 15.6° C., is necessary for the optimum extraction at 45° C. of gossypol from cottonseed meal containing approximately 22 per cent of moisture and with 5 ml. of water added to the ether in the receiving flask.

Literature Cited

- (1) Carruth, F. E., *J. Am. Chem. Soc.*, **40**, 661 (1918).
- (2) Halverson, J. O., and Smith, F. H., *IND. ENG. CHEM., Anal. Ed.*, **5**, 29, 320 (1933).
- (3) *Ibid.*, **6**, 356 (1934).
- (4) Marqueyrol, M., and Goutal, E., *Mém. poudres salpêtres*, **19**, 368-80 (1917).
- (5) Smisniewicz, T., and Zielinski, R., *Przemysl Chem.*, **16**, 35 (1932).

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Revised Method for the Estimation of Gossypol in Cottonseed Meal

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THE published method (2) for the estimation of ether-soluble gossypol has been considerably modified. Because of the difficulties encountered in working with gossypol, the revised method is described here in detail.

Moisten a charge (120 grams) of cottonseed meal ground to pass through a 40-mesh sieve with 27.5 ml. of water in a large mortar. Remove the pasty meal which adheres to the mortar and pestle and incorporate it with that part which is not sufficiently wet to form a paste. Pass the moist meal through a 20-mesh sieve and return the wet lumps to the mortar for further grinding. Mix a portion of the meal which most readily passed through the sieve with the wet meal resulting from the crushed lumps and sieve as before. Repeat this process until the whole charge has passed through the sieve, then return it to the mortar and mix thoroughly.

Take a 2-gram charge of the mixed moistened sample for the determination of moisture, which should be about 22 per cent. Divide the remaining portion into equal parts by weight by counterbalancing and immediately transfer to the thimbles (43 by 123 mm.) of two Soxhlet extractors. Extract 72 hours with peroxide-free ether containing 2.3 to 2.5 per cent of alcohol and 1 to 1.2 per cent of water by weight (yielding an ether of 0.724 to 0.726 density at 15.6° C., 3, 4), also adding 5 ml. of distilled water to the ether in each receiving flask.

NOTE. To prepare peroxide-free ether shake 3.5 liters of ether and 0.25 liter of distilled water with portions of a saturated solu-

tion of sodium bisulfite until Jorissen's vanadic acid color test (1) shows that all peroxides are reduced. Then wash the ether three times with 0.35 liter of distilled water, draining off each time. Finally wash with 0.35 liter of a solution of 5 per cent sodium hydroxide to neutralize any residual bisulfite and free sulfur dioxide. Drain off the alkali solution, dehydrate with calcium chloride, and distill the ether in the presence of a stick of sodium hydroxide. Determine the composition (3, 4) and modify by adding the proper amounts of alcohol and water. Ether of this composition may also be prepared by adding alcohol and water, by weight, directly to peroxide-free reagent ether.

The joints of the Soxhlet extractor should be tight to prevent loss of ether. The depth of ether in the receiving flask during the process of extraction should not decrease to less than 3.5 cm. (1.5 inches). The extraction is conducted at a constant temperature of about 45° C. in a water bath regulated by a thermostat. The extractors are enclosed on the top and sides above the water bath with pressboard, holes being cut in the top for passing the condensers through to the extractors.

When the process of extraction is completed, remove the thimbles, and collect the ether in the extractors until 25 to 30 ml. of the extract remain in each receiving flask. Remove the receiv-

ing flasks and filter the extracts through crucibles in which a layer of Hy-Flo-Supercel (from the Johns-Manville Co.) is placed over a layer of ignited asbestos. The filtrates are received in 200-ml. Erlenmeyer flasks placed under bell jars; in a hole in the top of each jar a cork stopper is inserted for the stem of the Gooch holder and a glass tube to which suction is applied. Wash the flasks and Gooch crucibles with ether, combining the washings with the filtrates.

Remove the ether in each Erlenmeyer flask rather completely under reduced pressure by inserting in the flask a one-hole rubber stopper and applying suction. Hasten the removal of the ether by rotating the flask in a pan of hot water not exceeding 50° C. Discontinue when the "rapid boiling" stops. Add 75 ml. of petroleum ether (Skelly solve F) and 5 ml. of ethylene glycol to each flask. Mix by rotating the flask and let stand overnight. Filter through a Gooch crucible (prepared as above) in order to remove the material precipitated by the petroleum ether. Wash the precipitate with a small amount of petroleum ether, receiving the washings in the filtrate. In order to prevent further precipitation of the insoluble material by the decrease in temperature and the addition of the washings during the process of filtration, place the flasks containing the filtrates in a pan of water at about 35° C.

In order to precipitate the gossypol as a dianiline compound, add 2 ml. of aniline and shake thoroughly. Digest 1 to 1.25 hours by placing the flasks in pans of hot water (50° to 55° C.)

not over 2 cm. (0.75 inch) deep, exercising care not to exceed 60° C. When the digestion is completed, add sufficient petroleum ether, if necessary, to make a total volume of 50 to 60 ml. If the volume should fall to approximately 25 ml. before the digestion is completed, add an equal volume of petroleum ether (Skelly solve B or F). Lightly stopper the flask and let stand overnight. When the precipitate is small (10 to 15 mg.), let stand 36 hours or longer.

Filter through a tared Gooch crucible and wash the precipitate of dianiline gossypol with petroleum ether (Skelly solve B or F). Follow with four washings of water, then with 5 ml. of 95 per cent alcohol, and finally with a few milliliters of petroleum ether. Dry the precipitate to constant weight at 100° C. Multiply the weight of dianiline gossypol by 0.775 to obtain the equivalent weight of gossypol.

Literature Cited

- (1) Baskerville and Hamor, *J. IND. ENG. CHEM.*, 3, 387 (1911).
- (2) Halverson, J. O., and Smith, F. H., *Ibid.*, Anal. Ed., 5, 29 (1933).
- (3) Marquayrol, M., and Goutal, E., *Mém. poudres salpêtres*, 19, 368-80 (1917).
- (4) Smisniewicz, T., and Zielinski, R., *Przemysl Chem.*, 16, 35 (1932).

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Determination of Chromium in Chromite

A New Procedure Employing a Mixture of Phosphoric, Sulfuric, and Perchloric Acids

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THE determination of chromium in chromite has until now been made following solution of the sample after a sodium peroxide fusion (1). The highly refractory nature of chromite ores eliminates the possibility of solution following acid treatment with 72 per cent perchloric acid, 95 per cent sulfuric acid, or mixtures of both. The nearest approach to a suitable single acid is concentrated perchloric acid, but it would be desirable to be able to increase the temperature at which it could be used and simultaneously to increase the solubility of chromic acid, which forms an insoluble protective coating on the surface of the undissolved ore. Using a mixture of phosphoric and sulfuric acids, solution of all available types of chromite ores is rapid. The conditions for the subsequent oxidation of chromium in this mixed acid solution of the sample are described here. The resulting complete method is very rapid, accurate, and economical.

The complete analysis of chrome ores has been described by Cunningham and McNeill (1). The determination of chromium follows solution after fusion with sodium peroxide. The determination of iron and aluminum can be made after solution in a mixture of sulfuric and perchloric acids, or for samples not soluble by such treatment, after fusion in a mixture of sodium carbonate and borax. Willard and Thompson (5) recommend sirupy phosphoric acid as a solvent for refractory materials such as iron ore and bauxite, but this procedure was found to be unsuited to the solution of chromite. Smith and Getz (2) have used phosphoric acid as a solvent for ferrochrome, followed by the addition of perchloric and sulfuric acid for the oxidation of chromium. A somewhat similar process has been described by Smith and Smith (4) for the determination of chromium in stainless steel after solution in a mixture of sulfuric and perchloric acids.

TABLE I. ANALYSIS OF BUREAU OF STANDARDS CHROME REFRACTORY 103

Sample Gram	0.05019 N FeSO ₄ Required	Cr ₂ O ₃ Found	Error
	ML	%	Cr ₂ O ₃ %
0.1132	32.99	37.07	+0.10
0.1526	44.30	36.91	-0.06
0.1843	53.47	36.88	-0.09
0.1285	37.36	36.96	-0.01
0.1568	45.80	36.97	0.0
0.1576	45.70	36.88	-0.09
0.1936	55.94	36.73 ^a	-0.24 ^a
0.1441	41.95	37.02	+0.05
		Av. 36.96	0.05

^a Excluded from the averages.

Materials Used

The chromite solvent consists of a mixture of 8 parts of 95 per cent sulfuric acid and three parts of 85 per cent phosphoric acid. The oxidizing solution is made up with 2 parts of 72 per cent perchloric acid and one part of distilled water. A standard 0.05 N solution of ferrous sulfate and a standard 0.05 N solution of ceric sulfate are prepared and standardized by procedures often previously described. Ferroin (*o*-phenanthroline ferrous ion), a 0.025 M solution, is used as the indicator. Finely ground crystals of potassium permanganate, dilute (1 to 3) hydrochloric acid, and dilute (1 to 1) sulfuric acid are also required.

Special Laboratory Apparatus

The technic employed in the solution of samples, oxidation of chromium, and subsequent preparation for titration is greatly simplified by use of a few special items of laboratory equipment which have been described in a previous paper (2). While the determinations can be carried out successfully without the modified Rodgers ring burner and digestion flask

still head therein described, the work is much simplified by their use.

Analyzed Samples for Evaluation of Procedure

The Bureau of Standards chrome refractory No. 103 was the most valuable analyzed sample available. A sample of chromite ore having a complete, accurate analysis was supplied through the courtesy of H. H. Willard. A series of chromite ores was furnished by E. J. Lavino and Co., Norristown, Pa., with the works analysis for Cr_2O_3 given through the kindness of G. E. Seil. Other samples were supplied by the Chromium Mining and Smelting Corporation, Sault Ste. Marie, Ontario. The samples were from such varied sources

part of the hexavalent chromium is reduced. Add 3 drops of ferroin indicator and titrate to complete reduction of chromium, as indicated by the appearance of a definite pink coloration. About 0.05 ml. of the ferrous sulfate is required after the first appearance of an orange color in the blue-green reduced solution. From the measured volume of standard ferrous sulfate required, the per cent of chromic oxide present may be calculated. The potassium permanganate is used in this procedure to eliminate the effect of hydrogen peroxide, known to result (3) during oxidations using perchloric acid at or near 200° C.

Analyses

For the following analyses the ceric sulfate was found as the mean of 9 consecutive comparisons with Bureau of Standards $\text{Na}_2\text{C}_2\text{O}_4$ to be 0.03541(1) *N* with an average deviation from the mean of one part in a thousand. The ratio of ceric sulfate to ferrous sulfate was 50/35.28, giving a ferrous sulfate normality of 0.05018(6) *N*.

BUREAU OF STANDARDS CHROME REFRACTORY 103. Eight consecutive analyses of chrome refractory 103 (corrected for its content of 0.08 per cent of vanadium) were carried out and the results are given in Table I. The certificate value for this sample is 36.97 per cent Cr_2O_3 . The average of the absolute errors shows that the determinations agreed with the certificate value to within less than 2 parts per thousand.

To check the extent to which the finely ground samples of chromite ore adsorb moisture upon standing, three analyses of undried sample 103 were made and 36.75, 36.78, and 36.79 per cent of chromic oxide were found. This indicates the importance of drying before sampling.

CHROMITE FROM COMMERCIAL SOURCES. To test further the general applicability of the new process to samples of chromite from a wide variety of sources, 12 additional samples were analyzed and the results are given in Table II. The values shown are the average of 3 to 4 individual determinations of each ore.

The complete analysis of sample 10 was: Cr_2O_3 , 26.58; SiO_2 , 22.04; FeO , 14.93; Al_2O_3 , 9.01; MgO , 21.38; SO_3 , 0.38; *P*, 0.39; loss on ignition, 4.77 per cent. The beneficiated sample, No. 12, was found to be the most resistant of all to the solvent action of mixed phosphoric and sulfuric acids.

Summary

A new and rapid method for the solution of all types of chromite ore, using a mixture of phosphoric and sulfuric acids, is described. The chromium, after solution in mixed phosphoric and sulfuric acids, is oxidized, using concentrated perchloric acid at 215° C., followed by treatment for a brief time with potassium permanganate.

In the determination of hexavalent chromium, standard ferrous sulfate is used with ferroin as indicator.

The new process was used for the analysis of 13 samples of chromite and chrome refractories from a wide variety of sources and no exceptions to its applicability were found. The method is rapid, accurate to within less than 2 parts per thousand, and not costly.

Literature Cited

- (1) Cunningham and McNeill, *IND. ENG. CHEM., Anal. Ed.*, 1, 70 (1929).
- (2) Smith and Getz, *Ibid.*, 9, 378 (1937).
- (3) Smith, McVickers, and Sullivan, *J. Soc. Chem. Ind.*, 54, 369T (1935).
- (4) Smith and Smith, *Ibid.*, 54, 185T (1935).
- (5) Willard and Thompson, *IND. ENG. CHEM., Anal. Ed.*, 3, 399 (1931).

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TABLE II. DETERMINATION OF Cr_2O_3 IN COMMERCIAL SAMPLES OF CHROMITE

Source	Sample No.	No. of Duplicate Analyses Averaged	Cr_2O_3 Found %	Average Deviation from Average	Cr_2O_3 Present %	Difference Cr_2O_3 %
E. J. Lavino	1	3	32.56	0.01
	2	4	31.88	0.06
	3	4	33.35	0.02	33.39	-0.04
	4	4	30.96	0.04	30.86	-0.10
	5	4	30.90	0.02	30.88	-0.02
	6	3	31.79	0.02
	7	2	31.44	0.02
	8	3	31.64	0.03
	9	3	31.92	0.05
University of Michigan	10	3	26.63	0.06	26.58	+0.05
Canadian	11	3	27.12	0.04
Canadian (beneficiated)	12	5	25.72	0.10

that the new procedure is probably applicable to any chromite ore that may be encountered. The samples had a range of 26 to 37 per cent of chromic oxide, 8 to 22 per cent of silica, and 16 to 22 per cent of magnesium oxide. The beneficiated sample supplied by the Canadian firm was low in Cr_2O_3 and high in calcium oxide.

Detailed Procedure

Grind samples to pass a 100-mesh sieve and dry 2 hours at 105° to 110° C. Transfer weighed 100- to 150-mg. samples from a weighing bottle to a clean, dry 500-ml. Erlenmeyer flask. Add 10-ml. of chromite solvent and swirl flask vigorously at once to get the sample in suspension and prevent a strong tendency to form a cake and stick to the bottom of the flask. Adjust the refluxing still head in the neck of the flask and heat to gentle boiling temperature, continuing the swirling motion for 5 to 15 minutes or until the sample is seen to be entirely dissolved. Allow to remain on the burner without swirling 5 minutes longer. Samples which are not all dissolved in the time given should be ground finer. The solution at this point is grayish green in color and only a very small amount of insoluble silica is found suspended in the solution. In swirling the hot flask, a laboratory metal clamp is conveniently employed.

Allow the contents of the flask to cool for a minute and add through the still head 12 ml. of the oxidizing solution. Place a small Anschütz thermometer, suspended from a small platinum wire, within the solution in the flask, retaining the refluxing still head in position. Heat to 215° C. during a 5-minute interval. The droplets of condensed acid on the flask walls should all be undergoing rapid reflux down the flask walls at the end of this period. Remove the flask and contents from the source of heat and add 60 to 70 mg. of powdered potassium permanganate, after partially removing the still head and allowing the flask contents to cool to 210° C. Readjust the still head and swirl the flask contents to disperse the permanganate. With continued swirling of the flask contents, dip the flask into cold water. After 8 to 10 seconds add 125 ml., cautiously at first, of distilled water, pouring it through the refluxing still head. Remove and rinse the still head and thermometer. Rinse the flask walls and add 25 ml. of dilute (1 to 3) hydrochloric acid and a Filter-Cel boiling chip.

Heat to a gentle boil and continue to boil 5 minutes after disappearance of potassium permanganate and manganese dioxide to remove the chlorine. Cool to ordinary temperature, and add 40 ml. of dilute (1 to 1) sulfuric acid. Titrate, using a standard solution of approximately 0.05 *N* ferrous sulfate, until the greater

Modified Distillation Method for Moisture

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A SERIOUS defect of the distillation method for the determination of moisture is the difficulty in removing all the condensed water adhering to the inner wall of the condenser tube (3, 4). This defect may be corrected by introducing into the condenser a very small amount of some volatile substance which will dissolve both the water and the immiscible liquid adhering to the inner wall of the condenser tube, but will allow them to separate again in the receiver tube.

TABLE I. USE OF ETHANOL IN THE DISTILLATION METHOD FOR THE DETERMINATION OF MOISTURE

Sample	Amount of Sample		Water Collected		Drops of Alcohol	
	Trial 1	Trial 2	Trial 1	Trial 2	Trial 1	Trial 2
	Ml.	Ml.	Ml.	Ml.		
Water	1	1	1.0	1.0	2	2
	2	2	2.0	2.0	2	2
	4	4	4.0	4.0	5	2
	6	6	6.0	6.0	2	2
	8	8	8.0	8.0	2	5
	10	10	10.0	9.97	2	5
	Grams	Grams				
Soap powder (official method)	20.0	20.0	2.14	2.16	2	2
Soap powder (modified method)	20.0	20.0	2.20	2.20	2	2

Experimental

The volatile substance used was 95 per cent ethanol and the immiscible liquid, xylene. Since the solubility data in the literature (2, 6) on the system ethanol-xylene-water are not accurate enough for the very small concentrations of ethanol used in this work, determinations were made to test the accuracy of the modified method.

The Dean-Stark distilling tube receiver (5) was calibrated against the pipet used for measuring the water into the boiling flask. A known volume of water was added to a definite quantity of xylene in a 500-ml. boiling flask. The flask was attached to the distilling tube receiver and heated for 1 hour at a rate giving approximately 5 ml. of reflux per minute and then for 3 hours at double that rate. Two drops of ethanol were then added through the top of the condenser, causing violent ebullition and refluxing. When these had ceased, boiling was continued for 5 minutes. If drops of water still remained in the condenser tube the ethanol treatment was repeated, using 3 drops. The source of heat was then removed, the apparatus allowed to cool, and the volume of the aqueous distillate read.

The use of 5 drops of ethanol produced no readable increase even when the water volume was only 1 ml. Determinations made with the addition of larger quantities of ethanol, never exceeding more than 3 drops at a time, showed that a total of 30 drops caused no readable increase in the volume for 10 ml. of aqueous distillate, but did cause an increase for volumes of 4 ml. or less.

Both 100- and 50-ml. quantities of commercial xylene were used, but since there was no difference in the results obtained, only the values for the 50-ml. quantities are reported in Table I. The table also reports results obtained in the analysis of a sample of soap powder by both the official method (1) and the modified method described below.

Discussion

The slow rate of boiling for the first hour prevents the aqueous condensate from being carried back to the boiling

flask through mechanical action of the returning xylene. For samples yielding less than 4 ml. of water, the total boiling time is usually about 2.5 hours, but for those yielding 6 to 10 ml. of water, about 3.5 hours is the shortest possible time for complete dehydration. Under ordinary laboratory conditions distillations performed without interruption at the boiling rates and for the periods specified in the modified method will give complete dehydration in 4 hours, even when the aqueous condensate amounts to 10 ml. A longer time is required if the distillation is interrupted before completion.

The use of ethanol as an indicator to show when dehydration of the sample is complete should not be attempted, on account of the danger of using too much and causing a serious error in the reading as a result of the solvent action of ethanol on xylene and water. The ethanol should not be added until dehydration of the sample is complete.

The xylene after serving for two determinations should be freed from ethanol by washing three times with one-tenth its volume of water, and dried before further use.

When the condenser has been cooled properly during the distillation, one addition of ethanol, 2 drops, is sufficient. If on account of insufficient cooling a large section of the condenser tube shows drops of water, the second portion, 3 drops, must be used also. The ethanol must not be added in a single 5-drop portion, since the violent boiling that results is likely to eject condensate from the top of the condenser.

If after the first portion of ethanol is introduced additional water is deposited on the condenser tube, the dehydration of the sample has not been complete. Careful observance of the rates and periods of boiling specified will give complete dehydration.

Modified Method

Prepare and weigh the sample for distillation in the usual manner. Boil continuously for 1 hour at a rate of approximately 5 ml. of reflux per minute and for 3 hours at double that rate. Without interrupting the boiling, now add through the top of the condenser 2 drops of 95 per cent ethanol. After the violent ebullition and refluxing have ceased, continue boiling for 5 minutes. Should drops of water still remain on the inner wall of the condenser tube, prolong the boiling and give a second treatment with ethanol, using 3 drops. After the violent action has stopped, maintain the boiling for 5 minutes, then remove the source of heat, allow the apparatus to cool, and read the volume of aqueous distillate.

Summary

In the distillation method for determining moisture, the introduction of a very small quantity of ethanol removes water adhering to the inner wall of the condenser tube, thus increasing the accuracy of the method.

The ethanol should be added only after dehydration of the sample is complete.

Ethanol should not be used as an indicator to show when dehydration of the sample is complete.

Rates and periods of boiling are specified which will give complete dehydration of the sample.

Boiling must be uninterrupted throughout the analysis.

The experimental work in this paper is restricted to the Dean-Stark method, with xylene as the immiscible liquid.

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Literature Cited

- (1) Assoc. Official Agr. Chem., "Official and Tentative Methods of Analysis," 4th ed., p. 58 (1935).
- (2) Bonner, W. D., *J. Phys. Chem.*, **14**, 738 (1909).
- (3) Cone, R. M., and Davis, L. H., *IND. ENG. CHEM., Anal. Ed.*, **9**, 220 (1937).

- (4) Dean, A. L., *U. S. Forest Service Circ.* 108 (1908).
- (5) Dean, E. W., and Stark, D. D., *J. IND. ENG. CHEM.*, **12**, 486 (1920).
- (6) Holt, A., and Bell, N. M., *J. Chem. Soc.*, 105, 633 (1914).

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Rapid Saponification of Esters by Potassium Hydroxide in Diethylene Glycol

An Aid in Identification and Analysis

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THE saponification of an ester is usually the first step in its identification or analysis. For the purpose of identification, as in quantitative analysis, the reaction preferably is carried out in an aqueous solution of sodium or potassium hydroxide (5); the resulting alcohol and organic acid are then identified through a suitable derivative. For the purpose of obtaining quantitative data—i. e., determining the saponification equivalent—a standard alcoholic solution of sodium or potassium hydroxide (or ethoxide) is used. The reaction proceeds much more rapidly in alcohol than in water, partly because both reactants are soluble, and partly because the unknown ester may be transposed to the ethyl ester, as in an alcoholic solution of sodium ethoxide (1, 6). In the case of fats, the solvent sometimes employed is glycerol.

TABLE I. SAPONIFICATION TIME AT REFLUXING TEMPERATURE

Ester	Time
Benzyl acetate	Very short ^a
Butyl acetate	30 sec.
Butyl oleate	2 min.
Butyl phthalate	2 min.
Butyl propionate	1 min.
Ethyl acetate	Very short ^a
Ethyl acetoacetate	Very short ^a
Ethyl benzoate	1 min.
Ethyl malonate	Very short ^a
Ethyl <i>m</i> -nitrobenzoate	1 min.
Ethyl salicylate	Very short ^a
Olive oil	1.5 min.

^a Completely reacted when refluxing temperature was reached.

There are some undesirable features in the usual procedures which it is desirable to eliminate. In the qualitative examination of esters, these are: extreme slowness of the reaction in water solution, especially if the ester is quite insoluble, difficulty in obtaining a derivative of the resulting alcohol, because of contamination with water; and difficulty in obtaining a pure derivative of the resulting alcohol when, because of the insolubility of the ester, the saponification has been done in alcoholic solution. In the quantitative examination of esters, the undesirable features are: slowness of the reaction, necessitating long refluxing with possibility of loss through volatilization; poor keeping quality of the standard solution, necessitating elaborate precautions against decomposition, or else frequent preparation; and possible transposition of the unknown ester to the corresponding ethyl ester, with a possible resultant loss because of increased volatility.

The use of diethylene glycol (β,β' -dihydroxyethyl ether) as the solvent, replacing water, alcohol, and glycerol, is advantageous for several reasons: Diethylene glycol readily dissolves potassium hydroxide; the solution is stable, and

darkens very slowly; diethylene glycol is a better solvent for fats and for many esters than glycerol; it is an industrial hydroxide pellets. Following the addition of 10 drops of water, the mixture is heated over a small flame until the potassium hydroxide has dissolved. The mixture is cooled if the ester to be tested is volatile. The ester is added, 1 ml. if a liquid, 1 gram if a solid, or double these amounts if the substance is known to be of high molecular weight. The neck of the flask is now closed with a cork stopper carrying a thermometer of suitable temperature range. The side arm is fitted with a cork stopper of suitable size to connect the flask to a small water-cooled condenser. The flask is heated over a small flame, during which time the contents of the flask are mixed by shaking. When only one liquid phase, or one liquid and one solid phase, remains in the flask, the flask is connected to the condenser and the alcohol is carefully distilled.

Procedure for Qualitative Identification of Esters

In a 10- or 25-ml. distilling flask (preferably the former) are placed 3 ml. of diethylene glycol and 0.5 gram of potassium hydroxide pellets. Following the addition of 10 drops of water, the mixture is heated over a small flame until the potassium hydroxide has dissolved. The mixture is cooled if the ester to be tested is volatile. The ester is added, 1 ml. if a liquid, 1 gram if a solid, or double these amounts if the substance is known to be of high molecular weight. The neck of the flask is now closed with a cork stopper carrying a thermometer of suitable temperature range. The side arm is fitted with a cork stopper of suitable size to connect the flask to a small water-cooled condenser. The flask is heated over a small flame, during which time the contents of the flask are mixed by shaking. When only one liquid phase, or one liquid and one solid phase, remains in the flask, the flask is connected to the condenser and the alcohol is carefully distilled.

When done carefully, this procedure generally yields sufficient alcohol to prepare at least two solid derivatives such as the 3,5-dinitrobenzoate (3), the nitrophenyl urethane (8), or others.

The residue left in the distilling flask is either a solution or a suspension of the potassium salt of the acid portion of the ester in diethylene glycol. Derivatives of this salt may be prepared as follows:

About 10 ml. of water and 10 ml. of ethyl alcohol are added to the diethylene glycol solution; then a drop of phenolphthalein solution and 6 *N* sulfuric acid, drop by drop, are added until just acid. The resulting solution is set aside for a few minutes to allow as complete precipitation of the potassium sulfate as possible. This precipitate is separated by filtration and the clear filtrate is divided into two equal parts. One portion may be treated with *p*-nitrobenzyl bromide (7), and the other with *p*-phenylphenacyl bromide (2) or other suitable reagent. This procedure will generally yield two solid derivatives with melting points of use in identifying the acid constituent of the ester.

Discussion of the Qualitative Procedure

The method has been found to be very rapid and entirely satisfactory for a large number of esters. A good separation of the alcohol part of the ester from ethylene glycol is possible,

even when the boiling point of the alcohol is as high as 200° C.—for example, benzyl alcohol. If the ester yields a glycol or a polyhydric alcohol on saponification, the identification of the alcohol part of the ester is not possible, although identification of the acid can still be made. The rapidity with which the saponification takes place is shown in Table I.

TABLE II. SAPONIFICATION DATA OF ESTERS

Name of Ester	Saponification Equivalent		Mean Found 1 and 2	Average Deviation from Mean %	Theoretical Value	Error of Mean %
	No. 1	No. 2				
Isoamyl acetate	135.2	135.9	135.5	0.26	130	+4.4 ^a
Isobutyl acetate	116.1	115.7	115.9	0.17	116.1	-0.17
n-Butyl acetate	116.8	116.4	116.6	0.17	116.1	+0.43
Ethyl acetate	88.39	88.63	88.51	0.14	88.06	+0.51
Ethyl benzoate	149.2	148.9	149.1	0.10	150.08	-0.6
Ethyl malonate	79.89	80.21	80.05	0.20	80.04	+0.012
Ethyl p-nitrobenzoate	192.1	192.5	192.3	0.10	195.08	-1.3 ^b
Ethyl phthalate	111.9	111.8	111.85	0.045	111.06	+0.70
Ethyl salicylate	165.6	166.4	166.0	0.24	166.08	-0.05
Ethyl succinate	86.88	86.48	86.68	0.23	87.05	-0.44
Methyl cinnamate	162.1	161.4	161.8	0.22	162.08	-0.12
Methyl oxalate	59.56	59.23	59.38	0.27	59.02	+0.61

^a Ester probably contained some isoamyl alcohol.

^b Ester was shown to contain some free acid.

Saponification Equivalent of Esters

The pieces of equipment necessary are 125-ml. glass-stoppered Pyrex conical flasks, an ordinary 20- or 25-ml. pipet, and a buret. Because diethylene glycol is very viscous, it is desirable to open the tip of the pipet to an inside diameter of 2 to 3 mm., in order to facilitate drainage. The pipet need not be calibrated, since a blank is run on the reagent. It is important that the conditions under which the solution is delivered, especially the temperature and the time of drainage, should be the same for both the analysis and the blank.

The reagents are aqueous 0.5 *N* hydrochloric acid and 1 *N* potassium hydroxide in diethylene glycol. The acid is standardized against aqueous sodium hydroxide, which in turn is standardized against recrystallized potassium acid phthalate using phenolphthalein. The reagent is made by weighing about 60 grams of c. p. potassium hydroxide pellets into a 500-ml. flask, adding 250 ml. of ordinary technical diethylene glycol, and heating to effect solution. A thermometer should be used for stirring and the temperature should be kept below 130° C.; otherwise a dark yellow color, which is troublesome during the titration, develops. As soon as the solid has dissolved, the hot solution is poured into 750 ml. of diethylene glycol in a glass-stoppered reagent bottle. The liquid is thoroughly mixed and allowed to cool. This solution keeps well, but the color deepens slowly. After 5 months the yellow color is sufficient to make the end point difficult to distinguish, but the titer has changed less than 0.1 per cent.

The procedure used in the determination of the saponification equivalent is as follows:

The desired volume (20 to 25 ml.) of the ethylene glycol solution of potassium hydroxide is delivered into a dry 125-ml. glass-stoppered conical flask. The flask is weighed, a suitable quantity (1 to 3 grams) of the ester is added, the stopper is replaced, and the flask is reweighed. The ester is mixed with the solvent by a rotary motion of the flask and contents. While the stopper is firmly held in place, heat is applied slowly and gently by means of a small flame, so that a temperature of 70° to 80° C. is reached within 2 to 3 minutes. The liquid is agitated by a whirling motion during the heating. At this point, the flask is shaken vigorously, the liquid is allowed to drain, and the stopper is carefully loosened to allow air to escape. The stopper is replaced and the temperature is raised to 120° to 130° C. In the case of very high-boiling esters, the stopper is removed and a thermometer inserted.

After 3 minutes at this temperature, such refractory esters as dibutyl phthalate are completely saponified. Lower boiling esters (see below for exception) are entirely reacted at 100° C. The flask and contents are cooled to 80° to 90° C. and the stopper is removed and washed with distilled water. The rinsings are allowed to drain into the flask. The liquid is diluted by the

addition of about 30 ml. of distilled water, phenolphthalein is added, and titration is made with 0.5 *N* hydrochloric acid. A blank is run by pipetting an equal volume of the reagent into a second 125-ml. flask, adding about the same amount of water, and titrating with the standard acid, using phenolphthalein. The saponification equivalent is calculated in the usual way.

Discussion

The principal sources of error are loss by volatility and incompleteness of reaction. Fortunately, most volatile esters are easily saponified. If the flask is kept firmly stoppered, the saponification of volatile esters usually is quantitative by the time the stopper is first removed. Even at room temperature the reaction may proceed fairly rapidly—for example, when two samples of ethyl acetate were weighed out and titrated, within the 8 to 10 minutes elapsed time the extent of saponification was 56 and 57 per cent, respectively. Less volatile esters—for example, ethyl benzoate—although oftentimes less reactive, give quantitative results, because saponification proceeds rapidly at 120° to 130° C. without material loss of ester, but tertiary butyl acetate saponifies slowly and is rather volatile. By the

standard procedure, this ester is only about 50 per cent hydrolyzed, and even when held at 90° to 95° C. for 15 minutes the results are about 8 per cent low.

Table II gives the values obtained for twelve common esters, which had been highly purified. The average per cent deviation of duplicate determinations from the mean shows the good degree of reproducibility offered by this method. The general good agreement of the measured and theoretical values for these esters demonstrates the satisfactoriness of the method.

A few determinations of saponification numbers were made on ordinary oils to indicate the applicability of this general method to the determination of saponification numbers of fats and oils. Although this phase of the work was not extensively investigated, sufficient work was done to show that saponification numbers within the accepted range were readily obtained. These results are shown in Table III.

TABLE III. SAPONIFICATION DATA OF OILS

	Saponification Number Found		Accepted Range
	197.5	199.3	
Olive oil	197.5	199.3	185-196
Castor oil	180.0	180.4	175-183

Summary

Esters and fats may be saponified rapidly and quantitatively by potassium hydroxide in diethylene glycol. The procedure does not give quantitative results with a volatile inert ester such as tertiary butyl acetate. The reaction is of value in qualitative analysis, because in general the alcohol (unless a di- or polyhydric alcohol) can be isolated easily and in a reasonably pure state and also because the derivative of the acid can be prepared in the reaction mixture.

Literature Cited

- (1) Gibby and Waters, *J. Chem. Soc.*, 1932, 2643.
- (2) Judefind and Reid, *J. Am. Chem. Soc.*, 42, 1043 (1920).
- (3) Malone and Reid, *Ibid.*, 51, 3424 (1929).
- (4) Matignon, Moreau, and Dode, *Bull. soc. chim.*, [5] 1, 1313 (1934).
- (5) Mulliken, "Identification of Pure Organic Compounds," Vol. 1, p. 111, New York, John Wiley & Sons, 1904.
- (6) Pardee and Reid, *J. IND. ENG. CHEM.*, 12, 129 (1920).
- (7) Reid, *J. Am. Chem. Soc.*, 39, 124 (1917).
- (8) Shriner and Cox, *Ibid.*, 53, 1601 (1931).

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Estimation of Riboflavin

A Simple Fluorescent Method

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IT IS WELL established that riboflavin (also known as vitamin B₂, lactoflavin) emits a yellowish green fluorescence under ultraviolet light. Cohen (3, 4) and Supplee (10) have described methods for utilizing this property to assay for the content of riboflavin. The present method differs from that of the other workers in its greater simplicity from the operator's standpoint, requiring only inexpensive fluorescent standards.

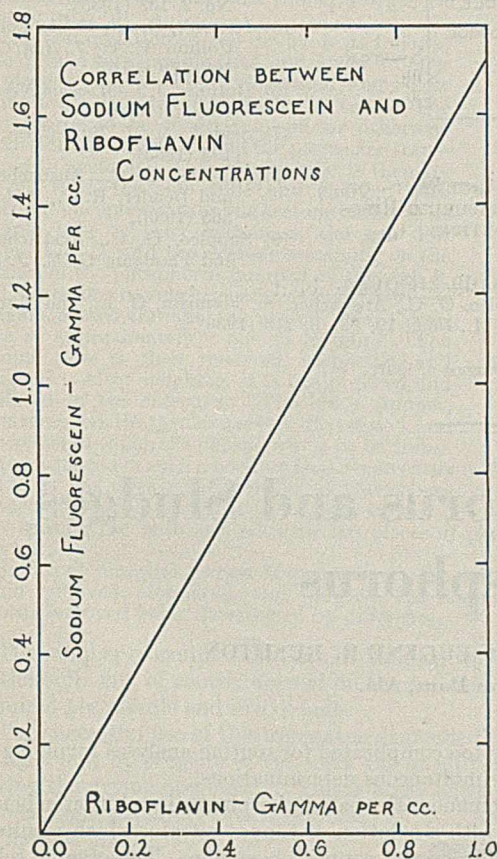


FIGURE 1

In order to prepare a sample for the fluorescence analysis a clear solution must be obtained and extraneous coloring materials as well as fluorescing substances other than riboflavin must be removed. A procedure that has given good results with dairy products is as follows:

Reflux a weighed sample of the solid product three times with methanol acidulated with acetic acid, in the presence of carbon dioxide and in the absence of light, washing the residue with fresh methanol between extractions. Add a volume of acetone equal to the combined methanol extracts and refrigerate overnight at -17.78°C . (0°F .) to precipitate flocculent impurities. Filter and condense filtrate *in vacuo*, adding enough water to ensure removal of the organic solvents and to leave the riboflavin in aqueous solution. Make this final solution up to a definite volume and assay. If any turbidity is present, it must be removed by filtration, or if of fatty origin it may be removed by ether extraction.

This method is also applicable to liquid samples, but no refluxing is required. The methanol carries the riboflavin

into solution and the acetone precipitates out extraneous matter from the methanol.

Another procedure for extracting the riboflavin content for analysis is as follows:

Reflux a weighed sample three times with methanol in the presence of carbon dioxide and in the absence of light. Adsorb the riboflavin from the methanol on British fuller's earth, using approximately 10 grams of earth for each 453.6 grams (1 pound) of original sample, assuming the potency in riboflavin to be of the order of whey powder or dried yeast. Centrifuge and wash the earth, then elute with a mixture consisting of pyridene 1, methanol 1, water 4. Thirty-six cubic centimeters of mixture are required per gram of adsorbate. A second elution should also be made on the earth. Filter the combined eluates, condense *in vacuo*, and remove the colloidal fuller's earth by adding methanol and filtering. Add water and condense the filtrate further to remove organic solvents. Then make the liquid up to volume and assay. A control should also be made by eluting the British fuller's earth and following through as above, deducting any fluorescence value deriving from the earth itself and reagents.

Other procedures which might be used wholly or in part for purifying riboflavin-containing samples for the fluorescence assay are those of Booher (2), Seidell (7), Itter, Orent, and McCollum (5), Supplee, Ansbacher, and Bender (8), Bisbey and Sherman (1), and Supplee, Ansbacher, and Flanigan (9).

In the authors' method sodium fluorescein (Eastman Kodak Company) in an aqueous solution of 0.001 per cent is used for making up the fluorescent standards, and the fluorescence of the unknown aqueous solution, purified so as to contain only riboflavin as the fluorescing agent, is compared with the sodium fluorescein standards under ultraviolet light. The fluorescein standards are calibrated by means of a solution of synthetic riboflavin (Winthrop Chemical Company).

By reference to Table I and Figure 1 the correlation between the fluorescence intensity of sodium fluorescein and riboflavin in water may be seen. This curve was obtained from the observations of three independent observers.

The fluorescein standards are made up in terms of 0.1 to 1.0 gamma of riboflavin per cc. Higher concentrations are difficult to match, owing to the high intensity of the fluorescence and the green component of the sodium fluorescein. The purified unknown solution is diluted so that it falls into the range of 0.1 to 1.0 gamma per cc. and the various dilutions are multiplied by the dilution factor to obtain the flavin concentration.

In making the assay, various dilutions of the unknown sample are made up to 50 cc., placed in French square bottles of 60-cc. (2-ounce) capacity, and compared under ultraviolet light with the fluorescein standards contained in similar

TABLE I. CORRELATION BETWEEN RIBOFLAVIN AND SODIUM FLUORESCIN CONCENTRATIONS

Riboflavin Gamma/cc.	Sodium Fluorescein Gamma/cc.	0.001% Sodium Fluorescein Made to 50 Cc. Cc.
0.1	0.17	0.85
0.2	0.34	1.70
0.3	0.51	2.55
0.4	0.68	3.40
0.5	0.86	4.30
0.6	1.03	5.15
0.7	1.20	6.00
0.8	1.37	6.85
0.9	1.54	7.70
1.0	1.72	8.60

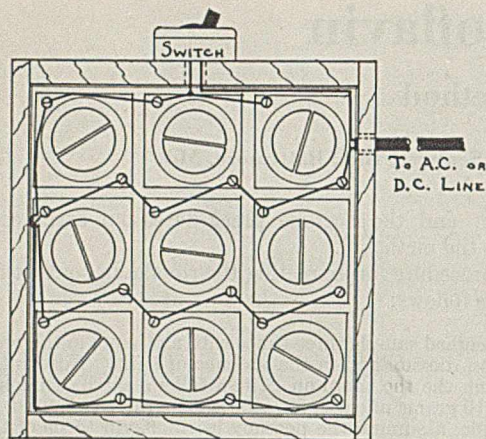


FIGURE 2. ULTRAVIOLET SOURCE FOR RIBOFLAVIN DETERMINATION. TOP VIEW

bottles. Glass or cork stoppers may be used, but rubber stoppers must not be used, as enough solution of rubber takes place to impart a blue fluorescence to the solutions.

The ultraviolet light is obtained from nine Blue Glow (argon mixed gas) lamps (General Electric Vapor Lamp Company, Hoboken, N. J.) mounted in a box similar to that described by Rorimer (6), either of wood or metal, and wired as shown in Figure 2. The filter used is the 16.25-cm. (6.5-inch) square Corning glass, Violet Ultra, No.

586 (Corning Glass Works, Corning, N. Y.) which transmits a rather monochromatic beam at 3650 Å.; it was chosen because very little blue and other visible light can pass through. The filter constitutes the lid of the box and a determination is made by placing the sodium fluorescein standard, together with the riboflavin unknown, on the glass filter with lamps underneath, as shown in Figure 3.

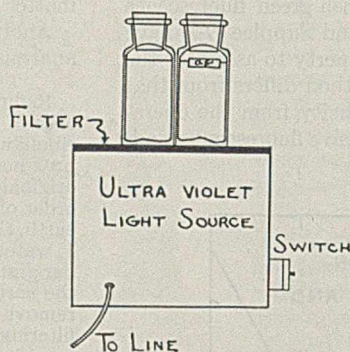


FIGURE 3. ARRANGEMENT OF EQUIPMENT FOR MEASURING RIBOFLAVIN CONTENT

- (1) Bisbey, B., and Sherman, H. C., *J. Biol. Chem.*, **112**, 415 (1935).
 (2) Booher, L. E., *Ibid.*, **102**, 39 (1933).
 (3) Cohen, F. H., *Arch. néerland. physiol.*, **20**, 167 (1935).
 (4) Cohen, F. H., *Rec. trav. chim.*, **54**, No. 2, 133 (1935).
 (5) Itter, S., Orent, E. R., and McCollum, E. V., *J. Biol. Chem.*, **108**, 579 (1935).
 (6) Rorimer, J. J., *Museum News*, **13**, No. 15 (1936).
 (7) Seidell, A., *J. Biol. Chem.*, **100**, 195 (1933).
 (8) Supplee, G. C., Ansbacher, S., and Bender, R. C., *Ibid.*, **110**, 365 (1935).
 (9) Supplee, G. C., Ansbacher, S., and Flanigan, G. E., *J. Dairy Sci.*, **19**, 215 (1936).
 (10) Supplee, G. C., Ansbacher, S., Flanigan, G. E., and Hanford, Z. M., *Ibid.*, **19**, No. 3, 215 (1936).

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Analysis of Crude Phosphorus and Sludges Containing Phosphorus

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THE analysis of phosphorus produced from rock phosphate by the electric furnace method has presented a number of problems. The crude phosphorus, condensed from the furnace gas by a water spray, contains water, oxides of phosphorus, rock dust, silica, and other impurities. For control purposes and for the study of furnace operation it was necessary to determine the phosphorus content of samples ranging from nearly pure phosphorus to aqueous sludges containing very little phosphorus.

It was necessary to develop methods for the handling and weighing of samples, separation of the phosphorus from water and insoluble residues, and determination of the phosphorus extracted. A search of the available literature failed to reveal a method meeting the requirements. Most of the published work was based on solution of the phosphorus in a suitable organic solvent, followed by oxidation to the orthophosphate and determination of the latter by conventional methods.

Buehrer and Schupp (1) described phosphorus determinations employing the reaction between phosphorus and hydriodic acid with subsequent titration of the iodine liberated. The oxidation alone required 4 hours, and the time required for the total analysis was probably 7 or 8 hours. The appa-

ratus was too complicated for routine analyses involving four or more simultaneous determinations.

Christomanos (2) treated phosphorus in solution in benzene or ether with a solution of copper nitrate, which resulted in the precipitation of copper phosphide. The organic solvent was removed by evaporation and the phosphorus was converted to orthophosphoric acid by oxidation with bromine and nitric acid, from which point the analysis proceeded by the standard gravimetric method. It was this method of treatment that was thoroughly checked and incorporated in the complete analysis described below.

Preparation of the Samples

In the case of aqueous phosphorus sludges, the sample is shaken thoroughly and transferred to four 40-ml. heavy-duty centrifuge tubes which are then centrifuged for 10 minutes at 2500 r. p. m. The volumes of supernatant liquid and solids are determined, the liquid is discarded if not wanted for further analysis, and the solids are rinsed with water out of the tubes into a small beaker. Four tubes are taken in order to obtain sufficient solid matter for the phosphorus extraction.

In the case of crude solid phosphorus, the sample is granulated by melting it under water in a large beaker or stoppered flask, followed by cooling in running water while vigorously stirring the melt.

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SAMPLING PURE PHOSPHORUS. In the course of the development of a method for the analysis, it was necessary to handle and weigh many samples of pure phosphorus. The apparatus shown in Figure 1 was devised for this phase of the work.

The glass tube, *C*, is provided with a solid rubber stopper at the bottom. Through the two-hole rubber stopper at the top pass delivery and exit tubes for an inert gas. The side tube supports by means of a one-hole rubber stopper, a sample tube, *A*.

The manipulation of the device is as follows: The Y-tube with sample tube and lower stopper in place is supported by a ring stand, and a flow of inert gas is started through the tube. The phosphorus to be weighed is cut or otherwise subdivided under water and the pieces are transferred to acetone. The sample tube is then removed from the side tube and charged with pieces of phosphorus from the acetone bath. The sample tube is then reinserted, the gas flow stopped at *D*, and the acetone remaining on the surface of the phosphorus pumped off through *E*.

The acetone having been removed, the inert gas is again passed through the system under pressure of approximately 1 cm. of mercury. The sample tube is then removed, stoppered, and weighed. After weighing, it is unstoppered and replaced in the side arm. The lower stopper, *B*, is removed, the regular gas exit, *E*, is closed, and the vessel to which the phosphorus is to be transferred is placed in such a position that it can easily be flooded with the inert gas during the transfer of phosphorus. The transfer is accomplished by rotating the sample tube about its long axis, thus raising the bulb and allowing the pieces of phosphorus to run out.

Sufficient material having been removed, the sample tube is again removed, stoppered, and weighed, the amount of phosphorus removed being determined by difference.

The number of samples that can be handled with one filling of the bulb will, of course, depend on the amount of material required per sample and size of bulb.

The successful use of this apparatus demands that there be a slight flow or pressure of the inert gas at all times, except during the drying operation. This is easily accomplished by connecting a gas safety tube or bubbler in the gas line.

Determination of Water and Benzene-Insoluble Residue

APPARATUS AND REAGENTS. The extraction apparatus is shown in Figures 2 and 3 and is a modification of the apparatus described by Dean and Stark (3) for the analysis of soap and vegetable products. The flask, water trap, and condenser are connected by standard taper ground joints. The flask is heated in a water bath consisting of a cylindrical can of 16-gage sheet copper 22.5 cm. (9 inches) high and 15 cm. (6 inches) in diameter, provided with a 600-watt immersion heater fixed parallel to and 2.5 cm. (1 inch) above the bottom.

The reagents employed are: copper nitrate solution, 25 per cent by weight;

benzene, c. p.; nitric acid, 15 *N* saturated with bromine.

METHOD. Three layers of filter paper are fitted into the bottom of a Gooch crucible. A perforated porcelain plate fitting inside the crucible is also provided and all are weighed in a closed weighing bottle. The sample is washed into the crucible and the excess water is removed by gentle suction, leaving the material moist enough to prevent its igniting. The sample is covered with the perforated plate, the crucible returned to the weighing bottle and reweighed.

This weight less the tare represents the weight of the wet sample. A covering of benzene is poured on the sample and the crucible is set in the neck of an extraction flask containing about 150 ml. of benzene. Assembly of the apparatus is completed as shown in Figures 2 and 3 and the sample is extracted for about 2 hours, the time depending on the nature and amount of sample. At the end of the extraction period the flask and contents are cooled to room temperature, the crucible is removed, dried at 105° C., and weighed in the original weighing bottle. The weight, after subtracting the tare, is the amount of benzene-insoluble matter. The water introduced with the sample is collected and

measured in the graduated trap below the condenser. From this volume the dry weight of the sample is found and this gives the basis for percentage calculations.

Oxidation and Determination of Phosphorus

The benzene is transferred from the extraction apparatus to a 250-ml. volumetric flask, the apparatus is washed with benzene, and the washings are added to the flask. Benzene is added to make 250 ml., the contents of the flask are thoroughly mixed, and two aliquots of 10 ml. each are transferred to 20-ml. portions of 25 per cent copper nitrate solution in 100-ml. Erlenmeyer flasks. The flasks are stoppered and shaken vigorously at 2-minute intervals for 10 minutes, the stoppers and sides of the flasks are washed down with water, 50 ml. of hot water are added, and the mixture

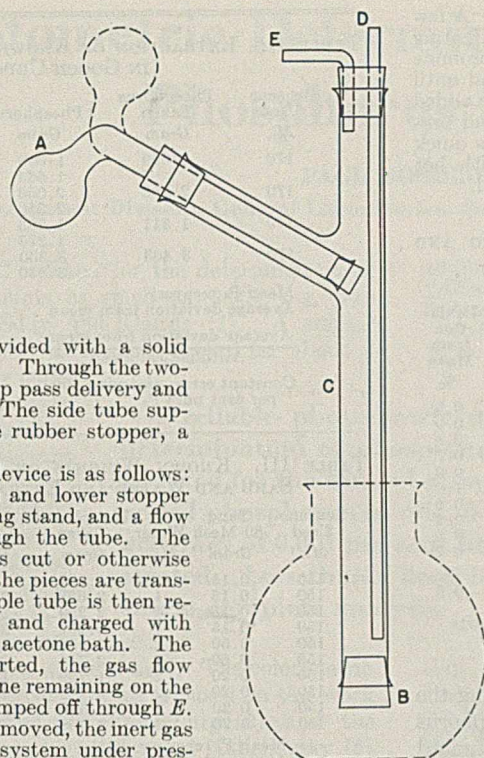


FIGURE 1. PHOSPHORUS DRYING AND WEIGHING APPARATUS

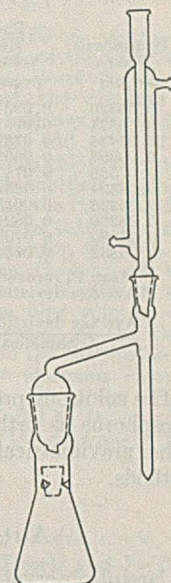


FIGURE 2. EXTRACTION APPARATUS

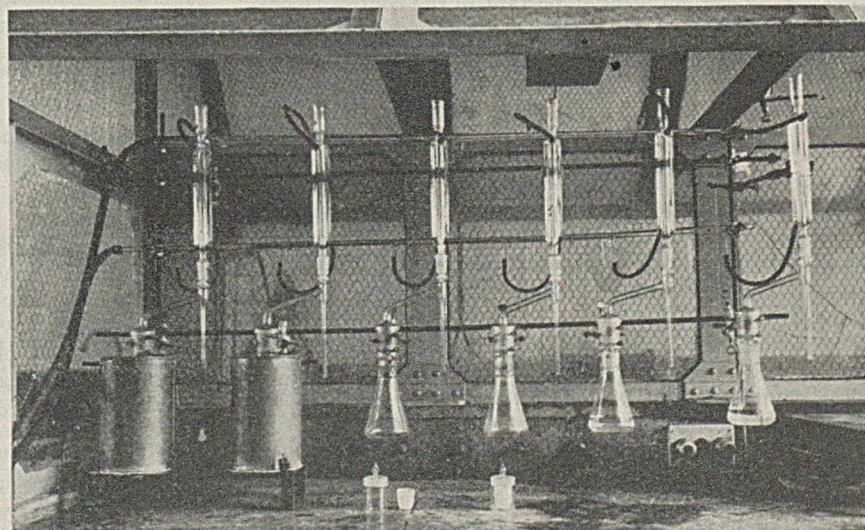


FIGURE 3. PHOSPHORUS EXTRACTION APPARATUS

is heated at about 100° C. until all benzene is expelled. A few glass beads are added to the flask to prevent bumping. Heating is then stopped, 5 ml. of 15 *N* nitric acid saturated with bromine are added cautiously, and the mixture is allowed to stand until action ceases; then about 7 ml. more of this reagent are added and the mixture is boiled until all fumes of nitric acid and bromine are expelled. The solution is then filtered through a quick filter into 250-ml. beakers, with thorough washing with hot water. The volume at this stage should be about 100 ml.

TABLE I. COMPARISON OF ANALYSES BY VOLUMETRIC AND GRAVIMETRIC METHODS

(Solutions from treatment of phosphorus by copper nitrate)

Phosphorus Taken Gram	Phosphorus Recovered Volumetrically		Deviation from Mean %	Phosphorus Recovered Gravimetrically		Deviation from Mean %
	Gram	%		Gram	%	
0.09320	0.09315	99.9	1.3	0.09312	99.9	0.9
0.09524	0.09510	99.8	1.2	0.09513	99.9	0.9
0.07424	0.07370	99.3	0.7	0.07342	98.9	0.1
0.09308	0.08991	96.6	2.0	0.09154	98.3	0.7
0.07356	0.07110	96.7	1.9	0.07217	98.1	0.9
0.08324	0.08321	99.9	1.3	0.08323	100.0	1.0
0.06236	0.06116	98.1	0.5	0.06122	98.2	0.8
0.08260	0.08213	99.4	0.8	0.08164	98.8	0.2
0.07080	0.07003	98.9	0.3	0.06966	98.4	0.6
0.06832	0.06657	97.4	1.2	0.06813	99.7	0.7
Mean P ₄ recovery	98.6			99.0		
Average deviation from mean	1.1			0.6		
Average deviation from mean	About 11 parts			About 6 parts		
Arithmetical mean	in 1000			in 1000		

The solutions prepared as described above, containing the phosphorus as orthophosphate, are analyzed for phosphorus either gravimetrically or volumetrically according to standard methods.

Autoignition of Solutions

Careful observations were made of the solutions of phosphorus in benzene regarding their tendency toward autoignition. It was found that while nearly saturated solutions smoked increasingly with increase in temperature, there was no autoignition. Where a solution was allowed to evaporate spontaneously, the phosphorus did not burn until the benzene had evaporated. When pieces of elemental phosphorus were taken from immersion in benzene and in acetone, complete evaporation of the solvent seemed necessary before ignition took place. A film of benzene or acetone definitely inhibits autoignition.

Comparison of Gravimetric and Volumetric Methods

The saving of time being important in the control laboratory, gravimetric and volumetric methods were run on ten samples of pure phosphorus dissolved in benzene and treated with copper nitrate, bromine, and nitric acid as described above. The results are given in Table I.

Accuracy of the Method

Samples of phosphorus; phosphorus, sand, and water; and phosphorus, precipitated silica, and water were analyzed according to the above procedure, the analyses being completed by the gravimetric method. The data are given in Tables II, III, and IV.

The results indicate that a solution of phosphorus in benzene can be digested under a reflux condenser for a period of at least 90 minutes without loss of phosphorus and that the procedure is suitable for the extraction of phosphorus from sludges and crude material. Samples containing as much as 2.6 grams of phosphorus were analyzed with fair accuracy and precision.

In practice, six determinations are run at one time, requiring about 6 hours for a complete analysis.

TABLE II. EXTRACTION OF KNOWN WEIGHTS OF PHOSPHORUS IN GOOCH CRUCIBLES

Benzene Used ML.	Phosphorus Taken Gram	Phosphorus Recovered		Deviation from Mean %
		Gram	%	
170	1.699	1.698	99.8	1.3
		1.663	97.8	0.7
170	2.062	2.050	99.4	0.9
		2.050	99.4	0.9
170	1.311	1.283	97.8	0.7
		1.273	97.0	1.5
170	3.403	3.350	98.5	0.0
		3.330	97.9	0.6
Mean P ₄ recovery				98.5
Average deviation from mean				0.8
Average deviation from mean				About 8 parts in 1000
Arithmetical mean				
Constant error, assuming 100 per cent pure P ₄				1.5 parts in 100

TABLE III. KNOWN WEIGHTS OF PHOSPHORUS MIXED WITH SAND AND WATER AND EXTRACTED IN CRUCIBLES

Benzene Used ML.	Sand 80-Mesh Gram	Water ML.	Phosphorus Taken Gram	Phosphorus Recovered		Deviation from Mean %
				Gram	%	
150	0.15	1	1.963	1.963	100.0	0.5
150	0.15	1	2.628	2.632	100.1	0.4
150	0.15	1	2.259	2.271	100.5	0.0
150	0.15	1	2.407	2.399	99.7	0.8
150	0.50	2	1.932	1.956	101.2	0.7
150	0.50	2	2.318	2.346	101.2	0.7
150	0.20	2	1.739	1.779	102.3	1.8
150	0.20	2	2.189	2.204	100.7	0.2
150	0.20	2	2.307	2.306	99.9	0.6
150	0.20	2	2.568	2.566	99.9	0.6
Mean P ₄ recovery				100.5		
Average deviation from mean				0.63		
Average deviation from mean				About 6 parts in 1000		
Arithmetical mean						
Constant error				5 parts in 1000		

TABLE IV. KNOWN WEIGHTS OF PHOSPHORUS, PRECIPITATED SILICA, AND WATER EXTRACTED IN CRUCIBLES

Benzene Used ML.	Pre-precipitated		Phosphorus Taken Gram	Phosphorus Recovered		Deviation from Mean %
	Silica Gram	Water ML.		Gram	%	
150	0.20	Nil	2.331	2.395	100.6	0.7
150	0.20	2	2.330	2.323	99.7	0.2
150	0.20	2	1.856	1.881	101.3	1.4
150	0.20	2	2.327	2.324	99.9	0.0
150	0.20	2	1.839	1.837	99.9	0.0
150	0.20	2	2.081	2.070	99.5	0.4
150	0.20	2	1.559	1.576	101.1	1.2
150	0.20	2	2.065	2.022	97.9	2.0
150	0.20	3	1.770	1.767	99.8	0.1
150	0.20	3	1.708	1.699	99.5	0.4
Mean P ₄ recovery				99.9		
Average deviation from mean				0.64		
Average deviation from mean				About 6 parts in 1000		
Arithmetical mean						
Constant error				1 part in 1000		

For the work for which the above procedure was developed, the final determination of phosphorus by the volumetric method was satisfactory, resulting in a great saving of time.

Summary

An apparatus is described for the separation of crude phosphorus and phosphorus-bearing sludges into phosphorus, water, and benzene-insoluble residue.

A method is given for determining phosphorus in crude phosphorus and phosphorus-bearing sludges, as well as a technic for handling and weighing small samples of pure phosphorus.

Literature Cited

- (1) Buehrer and Schupp, *J. Am. Chem. Soc.*, 49, 9 (1927).
- (2) Christomanos, *Z. anorg. Chem.*, 41, 305-14 (1904).
- (3) Dean and Stark, *J. IND. ENG. CHEM.*, 12, 486 (1920).

Photometric Determination of Added Phosphorus in Oils

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A PHOTOELECTRIC method for the determination of phosphorus in amounts as small as 0.001 mg. was recently published by Eddy and DeEds (1). A similar method has been employed in this laboratory for about a year for the control of the addition of phosphorus compounds to mineral oils, and its reliability and ease of application warrant its being reported.

The organic phosphorus in oil solution is changed to inorganic phosphate in aqueous solution by the simple and rapid procedure of igniting the sample in a crucible with zinc oxide, followed by solution in dilute sulfuric acid. The colorimetric method chosen after a number of trials is based on the work of Zinzadze (6) and Farber and Youngburg (2), and the electric colorimeter developed by Story and Kalichevsky (5) has been employed throughout with consistent success.

Standard Solutions

10 N SULFURIC ACID. Add 450 cc. of c. p. phosphorus- and arsenic-free concentrated sulfuric acid (sp. gr. 1.84) to 1150 cc. of distilled water, mix, and cool. Titrate the solution and dilute with the calculated amount of water (5 to 10 cc.) to exactly 10.0 N.

MOLYBDATE REAGENT. Place 64 grams of ammonium heptamolybdate in a 1-liter volumetric flask, add 300 to 400 cc. of distilled water and 500 cc. of 10 N sulfuric acid, dissolve, and make to 1 liter. This solution keeps for at least 3 months.

STANNOUS CHLORIDE SOLUTION. Make a stock solution by placing 5 grams stannous chloride dihydrate (A. C. S. Standard) in a small glass-stoppered brown bottle, adding 25 cc. of concentrated c. p. hydrochloric acid, and shaking until dissolved. This stock solution should be renewed each 2 weeks. Each day pipet out 1 cc. of the stock solution and make to 100 cc. for use. The diluted solution deteriorates in 12 to 15 hours.

STANDARD PHOSPHATE SOLUTION. Dissolve 4.3917 grams of c. p. monobasic potassium phosphate in 50 cc. of 10 N sulfuric acid and 500 cc. of distilled water. Add a few crystals (not over 0.1 gram) of potassium permanganate as preservative, and make to 1 liter. Pipet out 100 cc. of this solution and make to 1 liter; the resulting solution contains 0.1 mg. of phosphorus per cc. By again diluting 100 cc. to 1 liter, make a solution containing 0.01 mg. of phosphorus per cc.

Procedure

Weigh the sample (1 gram) into a small Coors crucible with an accuracy of 0.1 mg. and cover the oil with an approximately equal weight of zinc oxide.

Place the crucible and contents in a tilted position on a clay triangle, heat with a large luminous flame until the oil has been burned up slowly, then ignite until the crucible is entirely free from carbon. Allow the crucible to cool a little and place in a 250-cc. beaker, dumping out the contents by tapping the crucible against the side of the beaker. Cover with distilled water and add approximately 10 cc. of 10 N sulfuric acid.

Heat on a hot plate with occasional stirring until solution is complete and then remove the crucible with washing. Transfer the solution to a volumetric flask and make up to 250 cc. Of this solution pipet 25 cc. (0.1 of original sample) into a 100-cc. volumetric flask and make to about 50 cc. with distilled water. Make alkaline by adding 20 per cent sodium carbonate solution drop by drop until the solution is turbid, owing to the appearance of zinc hydroxide. Add 10 N sulfuric acid drop by drop until the solution clears on the addition of the last drop, swirling after the

addition of each drop (2,4-dinitrophenol, 6, may be used as a yellow to colorless indicator here if a more apparent end point is desired).

To the faintly acid sample in a little less than 60-cc. volume, add 10 cc. of 10 N sulfuric acid followed by 10 cc. of the molybdate reagent. Wash down the sides of the flask until the contents are about 90 cc. and mix by swirling. While swirling, add 5 cc. of the diluted stannous chloride solution (1 cc. of stock solution diluted to 100 cc.), noting the time at which it is added, make to 100 cc., close with a glass stopper, and mix.

Fill a 2.5-cm. (1-inch) cell used in the electric colorimeter with a part of the blue solution and read the intensity of the transmitted light in the colorimeter exactly 10 minutes after the addition of the stannous chloride. From the scale reading so obtained and the weight of the sample, the percentage of phosphorus can be calculated by means of an equation determined by prior calibration of the colorimeter with standard phosphate solution.

Ashing

Other substances may be used in place of zinc oxide, but none seems to equal it in all respects. Howk and DeTurk (3) have used calcium carbonate in the ashing of plant material, but calcium compounds cannot be used here because the subsequent colorimetric method is carried out in sulfuric acid solution. The alkali carbonates can be used, but they require longer ignition and are more difficult to remove from the crucible than zinc oxide. Magnesium nitrate has been used as an ashing material for biological serums by Roepke (4), but the presence of magnesium ion has a decided influence on the color to be produced later and the amount of magnesium nitrate used must be exactly the same each time. Nitrates interfere with the formation of the color unless they are completely eliminated by decomposition during the ignition.

Zinc ion, in the small amounts used, has only a negligible effect on color development, and pure grades of zinc oxide are available. The formation of yellow zinc peroxide when the oxide is heated makes this material an active agent in the oxidation process and the voluminous nature of the oxide lends itself particularly well for ashing purposes.

Operation of Colorimeter

The colorimeter has been described elsewhere (5) and only brief directions for its use need be given here. The constant ammeter reading is obtained with the scale at zero and from this figure the blank is subtracted to obtain a corrected ammeter reading. The cell containing the blue solution is introduced and the scale is moved until the ammeter records the corrected reading. The scale reading at this point is then related to the amount of phosphorus in the solution.

The blank is determined by taking a sample of phosphorus-free oil through exactly the same procedure as is applied to an unknown. The resulting 100 cc. of solution should be practically water-white if the reagents are free from phosphorus. On introducing a cell containing this solution into the colorimeter, with the scale remaining at zero, a deflection of the ammeter pointer will be noted. This difference in

TABLE I. EXPERIMENTAL DATA

Phosphorus Mg.	Scale Reading	Phosphorus Calculated by Equation 1 Mg.	Absolute Error Mg.
0.001	2.5
0.002	2.4
0.003	3.1	0.0001	0.0029
0.004	5.9	0.0035	0.0005
0.005	6.7	0.0045	0.0005
0.006	7.4	0.0054	0.0006
0.007	8.4	0.0065	0.0005
0.008	9.2	0.0076	0.0004
0.009	10.1	0.0086	0.0004
0.010	10.9	0.0096	0.0004
0.011	12.0	0.0109	0.0001
0.012	12.8	0.0119	0.0001
0.013	13.8	0.0131	0.0001
0.014	14.5	0.0140	0.0000
0.015	15.3	0.0150	0.0000
0.016	15.9	0.0157	0.0003
0.017	16.9	0.0169	0.0001
0.018	18.1	0.0184	0.0004
0.019	18.2	0.0185	0.0005
0.020	19.9	0.0206	0.0006
0.021	20.7	0.0215	0.0005
0.022	21.1	0.0220	0.0000
0.023	21.8	0.0229	0.0001
0.024	22.6	0.0239	0.0001
0.025	23.9	0.0254	0.0004
0.026	25.2	0.0270	0.0010
0.027	24.7	0.0264	0.0006
0.028	26.0	0.0280	0.0000
0.029	26.9	0.0290	0.0000
0.030	27.0	0.0292	0.0008
0.031	28.4	0.0309	0.0001
0.032	29.6	0.0324	0.0004
0.033	30.1	0.0330	0.0000
0.034	31.7	0.0350	0.0010
0.035	31.7	0.0350	0.0000
0.036	32.4	0.0358	0.0002
0.037	33.4	0.0370	0.0000
0.038	34.6	0.0385	0.0005
0.039	34.7	0.0386	0.0004
0.040	36.2	0.0404	0.0004
0.041	36.7	0.0411	0.0001
0.042	37.0	0.0414	0.0006
0.043	37.8	0.0425	0.0005
0.044	38.0	0.0426	0.0014
0.045	38.6	0.0434	0.0016
0.046	37.7	0.0423	0.0037
0.047	39.3	0.0442	0.0028
0.048	39.3	0.0442	0.0038

the ammeter readings when the colorimeter is empty and when it contains a cell filled with the blank solution is the blank. When the blank is applied, the corrected ammeter reading so obtained is actually the reading the ammeter would have if the colorimeter contained the blank solution in the cell.

The blank should detect and make correction for minor changes in the reagents or the colorimeter and give warning of error when major changes occur. It is wise to determine the blank at the beginning of each work day, although experience has shown that it changes only when fresh reagents are made up or those in use deteriorate.

The colorimeter must be turned on about 15 minutes before use, as it requires about this time to warm up to equilibrium. Readings of the millimeter should be made to one-fourth division and of the colorimeter scale to one-tenth division.

Calibration

Using standard phosphate solution, known amounts of phosphorus (0.01, 0.02, and 0.03 mg. are suggested) can be placed in 100-cc. volumetric flasks, and diluted with water, reagents added and color developed, and the scale reading corresponding to these amounts of phosphorus determined. Essentially a straight line can then be drawn through these points and the equation of this line can be used to calculate the amount of phosphorus from the scale reading.

For these known samples of standard phosphate the color is developed as follows: The samples are diluted with distilled water to about 50-cc. volume and then 10 cc. of 10 N sulfuric acid, 10 cc. of molybdate reagent, and 5 cc. of stannous chloride solution are added in the order given. The

intensity of the light transmitted is read 10 minutes after the addition of the stannous chloride. The color begins to develop within 3 minutes and in about 6 minutes has reached a maximum intensity which is maintained for about 30 minutes.

A blank must also be used in connection with the standard phosphate samples for calibration and in general it will differ from the blank obtained on a sample of phosphorus-free oil which is ignited and then carried through the procedure. The calibration blank is run using a 50-cc. sample of distilled water to which are added the sulfuric acid, molybdate reagent, and stannous chloride solution. Again the scale is left at zero and the deflection of the ammeter pointer caused by the introduction of the cell containing the blank solution into the colorimeter is called the blank. It is used in the same way as pointed out above.

With the two colorimeters now in use, the following equations were determined empirically, constants being rounded off:

$$\text{Mg. of phosphorus} = \frac{\text{scale reading} - 3}{820} \quad (1)$$

$$\text{Mg. of phosphorus} = \frac{\text{scale reading} - 1}{1000} \quad (2)$$

To give the per cent of phosphorus in the oil these equations become:

$$\text{Per cent of phosphorus} = \frac{\text{scale reading} - 3}{8.2 \times \text{mg. of sample taken}} \quad (3)$$

$$\text{Per cent of phosphorus} = \frac{\text{scale reading} - 1}{10 \times \text{mg. of sample taken}} \quad (4)$$

In Equations 3 and 4 the milligrams of sample taken do not refer to the weight of the oil ignited, but to an aliquot of this weight. This aliquot is determined by the amount of the standard volume of solution taken after ignition. This permits taking several different aliquots of the solution until one falling in the correct range is obtained.

Table I gives the experimental data obtained in the calibration of the first colorimeter and the calculation of Equation 1. It includes the values calculated from the scale readings by means of Equation 1 to indicate the degree of applicability of this equation.

Discussion

As can be seen from Table I, the straight-line function holds only when the phosphorus in the sample lies between 0.005 and 0.04 mg., but if the sample is chosen so that the amount of phosphorus taken lies between these limits, the method is applicable and accurate to 0.001 per cent. Thus, the directions given apply to oils containing 0.005 to 0.04 per cent of phosphorus. If the oil (or other organic substance) contains only 0.001 per cent of phosphorus, this can be detected accurately by taking a 1-gram sample which would contain 0.01 mg. of phosphorus. Furthermore, by careful dilutions, substances containing much larger quantities of phosphorus may be analyzed by this method. Preliminary results indicate that pure organic compounds containing up to 10 per cent of phosphorus are susceptible to analysis by this method with an accuracy approaching 0.1 per cent.

An outstanding advantage possessed by this method is that the time required for a complete analysis as outlined is less than 1 hour. If several samples are carried through together, which is easily effected in practice, the time required is reduced to 0.5 hour per sample.

The final acidity of the colored solutions as prepared in this method is 1.5 N. The necessity for this high concentration of acid is obvious from experimental results given in Table II. Farber and Youngburg (2), employing an almost identi-

cal procedure, have the final acidity of their colored solutions adjusted to be only 1 *N*, and in a similar colorimetric method Zinzadze (6) uses a final acidity of 0.35 *N*. The Zinzadze method employs molybdenum trioxide in place of the ammonium heptamolybdate used here.

TABLE II. EXPERIMENTAL DATA

Sample	Scale Reading	Acid Normality
Blank	76.5	0.5
Blank	25.0	0.75
Blank	9.3	1.0
Blank	1.2	1.25
Blank	0.2	1.5

Interfering Substances

The interference of other substances in the development of the color in the methods based on the reduction of phosphomolybdate have been discussed by Zinzadze (6). The means employed here for overcoming the influence of small

amounts of ferric iron in the sample, taken from Zinzadze's work, is as follows: Immediately following the addition of the 10 *N* sulfuric acid to the sample and before the addition of the molybdate reagent, 5 cc. of 16 per cent sodium metabisulfite solution are added and the flask is heated at about 100° C. for 1 hour. This procedure will take care of at least 0.2 mg. of iron.

Acknowledgment

The author wishes to acknowledge the coöperation of B. W. Story and C. W. Brown of this laboratory in the development of this method.

Literature Cited

- (1) Eddy and DeEds, *IND. ENG. CHEM., Anal. Ed.*, 9, 12 (1937).
- (2) Farber and Youngburg, *Ibid.*, 4, 107 (1932).
- (3) Howk and DeTurk, *Ibid.*, 4, 111 (1932).
- (4) Roepke, *Ibid.*, 7, 78 (1935).
- (5) Story and Kalichevsky, *Ibid.*, 5, 214 (1933).
- (6) Zinzadze, *Ibid.*, 7, 227 (1935).

RECEIVED August 16, 1937.

Determination of Chlorides and Bromides

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IT HAS been shown (2) that silver nitrate may be titrated with potassium iodide, using ceric ammonium sulfate and starch as indicators. As this method has never been applied to the determination of chlorides and bromides, it was considered desirable to learn its degree of accuracy as compared with the thiocyanate and the gravimetric methods. Pure potassium chloride and bromide were used for the analyses.

The procedures employed were essentially those given by Kolthoff and Sandell (1) as the Volhard method for chlorides. The directions were made more specific wherever it was considered advisable.

Analytical Procedure

PROCEDURE 1. Add 5 ml. of 6 *N* nitric acid to 25 ml. of 0.03658 *N* potassium chloride solution, and then 25 ml. of 0.1 *N* silver nitrate. Stir to coagulate the precipitate, filter, and wash the precipitate of silver chloride with 60 ml. of 1 *N* nitric acid. To the combined filtrate and washings add 3 ml. of 0.5 per cent starch solution and 0.1 ml. of 0.1 *N* ceric ammonium sulfate solution. Titrate the silver with 0.1 *N* potassium iodide solution to the appearance of a permanent blue-green color. Subtract 0.1 ml. from the buret reading as an indicator blank.

The same procedure was followed in analyzing a 0.08 *N* potassium bromide solution.

PROCEDURE 2. Add 15 ml. of 6 *N* nitric acid to 25 ml. of 0.03658 *N* potassium chloride solution, and then 25 ml. of 0.1 *N* silver nitrate. Dilute to the mark in a 100-ml. volumetric flask, mix thoroughly, filter through a dry filter, and reject the first portion of filtrate. Titrate 50 ml. of the subsequent filtrate with 0.1 *N* potassium iodide solution as previously described.

The same procedure was followed in analyzing a 0.08 *N* potassium bromide solution.

Volhard methods 1 and 2 are similar to procedures 1 and 2, respectively, except that the silver is titrated with a standard solution of potassium thiocyanate in the presence of ferric alum as indicator. A 0.03658 *N* potassium chloride solution and a 0.08 *N* potassium bromide solution were analyzed by these methods.

Finally, the solutions of potassium chloride and of potassium bromide were analyzed by a gravimetric method, precipitating and weighing silver chloride and silver bromide, respectively.

TABLE I. EXPERIMENTAL RESULTS

Method	Cl in KCl,	Br in KBr,
	%	%
Procedure 1	47.67	67.46
	47.57	67.43
	47.67	67.43
	Av. 47.64	Av. 67.44
Procedure 2	47.40	67.61
	47.51	67.47
	47.40	67.54
	Av. 47.44	Av. 67.54
Volhard 1	47.68	67.48
	47.68	67.48
	47.68	67.48
	Av. 47.68	Av. 67.48
Volhard 2	47.62	67.40
	47.52	67.46
	47.42	67.46
	Av. 47.52	Av. 67.44
Gravimetric	47.56	67.42
	47.50	67.46
	47.52	67.44
	Av. 47.53	Av. 67.44

Summary

A method for determining chlorides and bromides is described, which compares favorably with the standard Volhard method and the gravimetric method. Iodides may be determined similarly, it being unnecessary to remove the precipitated silver iodide prior to titration. In the reverse titration, running silver nitrate into the iodide solution, the end point appeared too soon, introducing an error of about 1 per cent. This has been ascribed to adsorption of iodide ions by the silver iodide. The advantages of the new method lie in the ease of preparation of standard solutions and in their stability.

Literature Cited

- (1) Kolthoff and Sandell, "Textbook of Quantitative Inorganic Analysis," p. 544, New York, Macmillan Co., 1936.
- (2) McNabb and Bloom, *IND. ENG. CHEM., Anal. Ed.*, 8, 167 (1936).

RECEIVED July 8, 1937.

Determination of Gold and Silver

By Recovery of Minute Amounts from Solution

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THE marked increase in activity in the recovery of gold from its ores and from various other sources accentuates want of improved methods of determination and recovery. This paper presents a study of the formation and effectiveness of semicolloidal mercurial residues in the recovery and determination of minute amounts of gold and silver from solution. Elaboration and modification of experimental procedure as reported by Yasuda (4) and earlier by Scheibler (3) have been developed.

A new collector of gold and silver from solution has been produced by adding to a gold- and silver-bearing solution ammonium hydroxide followed by mercurous salt solution.

TABLE I. RECOVERY OF GOLD AND SILVER FROM DILUTE SOLUTIONS OF GOLD CHLORIDE AND SILVER NITRATE

Volume of Solution	Gold Added	Silver Added	Gold Recovered	Silver Recovered
L.	Mg.	Mg.	Mg.	Mg.
2	0.62	6.306	0.618	6.082
40	0.62	3.29	0.60	3.06
40	0.015	...	0.014	...
40	0.015	...	0.015	...
10	0.079	...	0.075	...
10	1.80	...	1.74	...
10	0.0795	24.09	0.072	23.50
10	0.0159	24.85	0.012	24.80
10	1.54	...	1.49	...
10	0.385	16.22	0.375	15.75
40	0.08	...	0.08	...
40	0.015	...	0.014	...
40	0.26	10.46	0.22	8.65 ^a
10	2.18	62.80	2.03	56.02 ^a
40	0.19	10.47	0.18	8.05 ^a
40	11.17	116.70	9.60	105.90 ^a
10	0.86	22.66	0.83	18.09 ^a

^a The last five runs using H₂SO₄ show a somewhat lowered silver recovery.

The black, somewhat gelatinous, mercury-mercuric amino salt residue thus formed replaces from solution and occludes noble metals as it settles through the solution.

Suggested Procedure

The following procedure has proved applicable to the determination and recovery of gold and silver in minute amounts from solution:

Two-, 10-, or 40-liter bottles (the 40-liter bottles being acid carboys) are nearly filled with water containing known or unknown amounts of gold and silver in solution. About 10 grams of clean powdered magnesium are added when taking 10-liter samples of solution. One hundred milliliters of 0.1 *M* mercuric chloride are introduced per 10 liters of water, and 100 ml. of concentrated hydrochloric acid are added per 10 grams of magnesium. The bottles are shaken, but the chemical action produces good agitation.

A fine gray precipitate of mercury-mercurous chloride settles to the bottom of the container in a few hours and includes in itself gold and silver from solution. Most of the clear solution may be siphoned off, allowing some water to remain with the residue in the bottom of the bottles. A little swirling motion and the residue is readily suspended in this water and may be easily obtained in a small filter paper. The residue is not voluminous, as but 2.7 grams of mercuric chloride are used per 10 liters of solution.

When making runs on 2 liters of solution, about one-half the quantity of chemicals suggested above is used. In using 40-liter carboy samples, two to three times the quantity of chemicals for 10-liter runs are used.

After partially drying the residue in the filter paper, about 10 grams of granular lead are scattered over the residue; the filter paper is folded up with the residue and lead therein, and placed on a large assay cupel. Ten grams more of granular lead are placed

over and with the residue on the cupel. After cupellation in a small electric muffle furnace, a silver-gold bead is obtained and is weighed on a balance sensitive to 0.002 mg. Parting silver from gold with nitric acid, annealing the gold, and weighing the gold bead follow.

To determine the accuracy of the method, runs were made on several gold and silver solutions of known strength. Solutions were made by dissolving weighed amounts of pure gold in aqua regia and of silver in nitric acid and diluting with a large volume of water in bottles of 2, 10, and 40 liters' capacity. Reagents as detailed above were added, causing the fall of mercury-mercurous chloride through the solutions; residues were assayed as described. Results are shown in Table I.

The main source of error in carrying out this experimental procedure is in the cupellation process which follows the filtering of the mercurial residue. Normal cupellation losses are somewhat enhanced as the mercury vapors leave the residue-lead mixture. Good results have been obtained by allowing the residue to dry in the filter paper, removing it, and intimately mixing it with cupellation lead. A layer of the granular lead is spread on the cupel and the residue with lead mixture placed upon it. A covering of granular lead is also used. The wadded-up filter paper, if much residue remains upon it, may also be included in the cupellation mixture.

If the residue is large, or if greater accuracy is desired, the mercurial residue with its gold and silver content may be given a fusion or scorification to obtain a lead button for cupellation. The runs of Table I are those without use of scorification or fusion for added accuracy.

Gold solutions containing as little as 0.015 mg. of gold in 40 liters of solution were assayed. Obtaining 0.01 mg. of gold from 40 liters of solution is recovery and determination of one part of gold in four billion parts of water. Blank runs on reagents showed an almost indiscernible trace of gold.

Reducing agents for the production of a mercury-mercurous chloride cloud differ greatly in effectiveness. Stannous chloride, in proper concentration, added to mercuric chloride solution gives a good gray precipitate which collects most of the noble metals as it settles, but settling is very slow. Powdered zinc, iron, or lead does not react rapidly enough with dilute acid to produce a good mercuric chloride reduction with concomitant agitation of the solution. The use of magnesium powder plus hydrochloric acid as the reductant is decidedly preferable. Sulfuric acid may be substituted for hydrochloric acid.

Recovery of Colloidal Gold

To verify recovery of colloidal as well as ionic gold from solution by the mercury-mercurous chloride collector, nu-

TABLE II. RECOVERY OF GOLD FROM COLLOIDAL STATE

Reagent to Produce Gold Colloid	Volume of Solution	Gold Added	Gold Recovered
	L.	Mg.	Mg.
Tannic acid	10	0.550	0.525
	10	0.630	0.600
	10	0.945	0.915
	2	0.62	0.62
	10	0.62	0.618
Stannous chloride	2	1.19	0.95
	2	0.60	0.53
	10	0.16	0.15
	10	0.16	0.147
Ferrous sulfate	10	0.25	0.23
	10	0.22	0.20
	10	3.86	3.67

merous runs were made on gold colloids of known gold content. Both organic and inorganic reducing agents were used to produce the gold colloids. When the colored gold colloid was diluted with much water to test recovery from very dilute solution, the colloidal color disappeared. The method is applicable to gold recovery from colloidal solution even though solutions may be much too dilute to give colloidal color (Table II).

Semicolloidal Mercury—Mercuric Amino Salt Collector

Good recovery of gold and of silver from dilute ionic or colloidal solution may be obtained by addition of ammonium hydroxide followed by some mercurous nitrate solution.

TABLE III. RECOVERY OF GOLD AND SILVER FROM SOLUTION
(Using HgNO_3 with NH_4OH to form collector)

Volume of Solution L.	Gold Added Mg.	Silver Added Mg.	Gold Recovered Mg.	Silver Recovered Mg.
10	1.40	32.37	1.30	25.4
40	0.40	20.90	0.38	16.25
10	12.95	12.80
10	1.025	0.98
10	0.31	0.285
10	2.00	25.1	1.90	24.7
10	0.45	18.9	0.43	16.7
10	1.15	32.9	1.07	32.3
10	0.57	8.9	0.51	7.8
10	1.63	21.8	1.49	19.8
40	33.45	133.0	30.93	115.5 ^a
40	38.36	32.9

^a The total quantity of gold and silver in these runs was added in three separate additions, the residue being reprecipitated between additions to test ability of a mercurial residue containing 5 grams of mercury to become progressively enriched.

Mercury—mercuric amino nitrate precipitate forms as a black cloud, settles through the solution, replaces gold and silver from solution, and occludes in itself these noble metals. The residue may be obtained after decanting or siphoning most of the supernatant liquid, followed by filtration. This residue, after partial drying and with test lead added to it, may be assayed for noble metal content, by the cupellation process described for the mercury—mercurous chloride residue.

The mercury—mercuric amino salt collector recovers the noble metals from basic solution. Use of mercurous salt and ammonium hydroxide is cheaper and more convenient than the use of mercuric chloride, magnesium, and hydrochloric acid for formation of a given amount of collector. The precipitate formed is more gelatinous and can be readily suspended again after settling. This latter point is important, since recovery of gold and silver from several solutions may be additionally occluded by use of one mercurial residue.

Proof of noble metal recovery from solution by use of this mercurial collector is evidenced by results recorded in Table III. In preparing the collector for recovery of the auric ion from 10 liters of water, 15 to 20 ml. of concentrated ammonium hydroxide and 30 ml. of a 10 per cent mercurous nitrate solution were used. This gave a convenient amount of residue which gave good gold recovery. The assay procedure used is accurate to about 0.01 mg. of gold and 1.0 mg. of silver.

Control Test for Silver-Ion Concentration in Water Sterilization

The use of silver in water sterilization is gaining in consideration and importance. Brandes (1) and Kirkpatrick (2) give the concentrations of silver ion used as between 0.05 and 0.6 mg. per liter or 50 and 600 mg. per 1000 liters or metric ton of sterilized water.

The experimental procedures developed have been proved

to be accurate to about 1.0 mg. in recovering silver from 40 liters of dilute silver salt or colloidal silver solution, which is equivalent to 25 mg. per metric ton, the lower limit in the amount of silver ion suggested in the water sterilization. The method should be applicable, then, in control testing for silver-ion content in sterilized water. To verify this, varying amounts of silver ion, in the same concentration range used in water purification, were added to 40 liters of water in acid carboys. A semicolloidal mercurial collector fall was produced, as previously described, the residue from which was subjected to cupellation (Table IV). A high percentage of the silver added to the 40-liter carboys was recovered. The average silver loss in the listed runs was 0.64 mg., a goodly portion of which was due to absorption of silver by the cupels and volatilization during cupellation. This average loss is equivalent to but 0.016 mg. per liter, which is well under the lower limit of silver-ion concentration per liter used in water sterilization.

The last four runs recorded in Table IV are typical check runs for silver content on 40-liter samples from a pool of a million liters' capacity in which tests were made on bactericidal action of dilute solution of silver salts. Use was made of ammonium hydroxide and mercurous nitrate to form the collector. The applicability of the procedure to evaluate silver-ion concentration of solutions in the silver-ion concentration range used in water sterilization is proved.

Further Applications

These methods of determining gold and silver by recovery from solution may be applied in geochemical analysis of mine waters, in control assay of certain ore leach solutions, in estimating the gold content of sea water, and in a wet assay procedure for siliceous gold ore. The presence of cyanide in a solution containing gold and silver somewhat inhibits the

TABLE IV. DETERMINATION OF SILVER CONCENTRATION OF SOLUTIONS IN CONCENTRATION RANGE USED IN WATER STERILIZATION

Silver Ion Added Mg.	Silver Recovered Mg.	%	Equivalence of Original Solution Mg./l.
4.70	3.95	84.0	0.1175
10.13	9.62	94.9	0.25325
13.28	12.83	96.6	0.3320
21.12	20.76	98.3	0.5280
26.43	25.95	98.18	0.6608
6.045	5.29	87.6	0.1511
12.83	11.91	92.8	0.3208
17.10	16.67	97.4	0.4276
28.82	27.82	96.9	0.7205
30.72	29.85	97.1	0.7680
38.59	37.66	96.0	0.9548
3.29	3.06	93.3	0.0823

Av. Ag loss per 40 liters 0.64

0.0160

recovery of these noble metals by the methods under consideration.

The economic aspect of recovery of gold from dilute solution by a settling of a semicolloidal mercurial precipitate presents the problem of recovery of the mercurial reagents. When the residue is large, as from treatments of much gold-bearing solution, a retort with condenser can be used to recover mercury and its salts as well as the gold and silver. The use of a soluble mercurous salt plus ammonium hydroxide in producing the mercurial collector seems to have the best commercial possibilities. A few trial runs verify the ability to build up gold content in a mercury—mercurous amino salt residue of 2-gram mercury content by reprecipitating the collector residue through several 40-liter samples of gold-bearing water.

Summary

Improved methods of determining and recovering gold and silver from dilute solutions are presented. As little as 0.01 mg. of gold or 1.0 mg. of silver is recoverable from solution in 40 liters of water, which is recovery of one part of gold in four billion and one part of silver in forty million parts of water.

Gold and silver are quantitatively recoverable from colloidal solution by the procedure outlined.

A procedure is applied to making control determinations of silver-ion concentrations as used in water sterilization. Gold

content of sea water, mine water, and certain ore leach solutions may be estimated by methods described.

Literature Cited

- (1) Brandes, C. H., *IND. ENG. CHEM.*, 26, 962 (1934).
- (2) Kirkpatrick, *Chem. & Met. Eng.*, 41, 373 (1934).
- (3) Scheibler, C., *Ber.*, 2, 295 (1869).
- (4) Yasuda, M., *J. Chem. Soc. Japan*, 2, 321 (1927).

RECEIVED July 6, 1937. Presented before the Division of Physical and Inorganic Chemistry at the 90th Meeting of the American Chemical Society, San Francisco, Calif., August 19 to 23, 1935.

A Noncorrodible Circulating Device

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DURING the progress of work in this laboratory a non-corrodible device that would circulate a liquid was needed.

The apparatus shown in Figure 1 meets the requirements. It is made of glass and operates as described here:

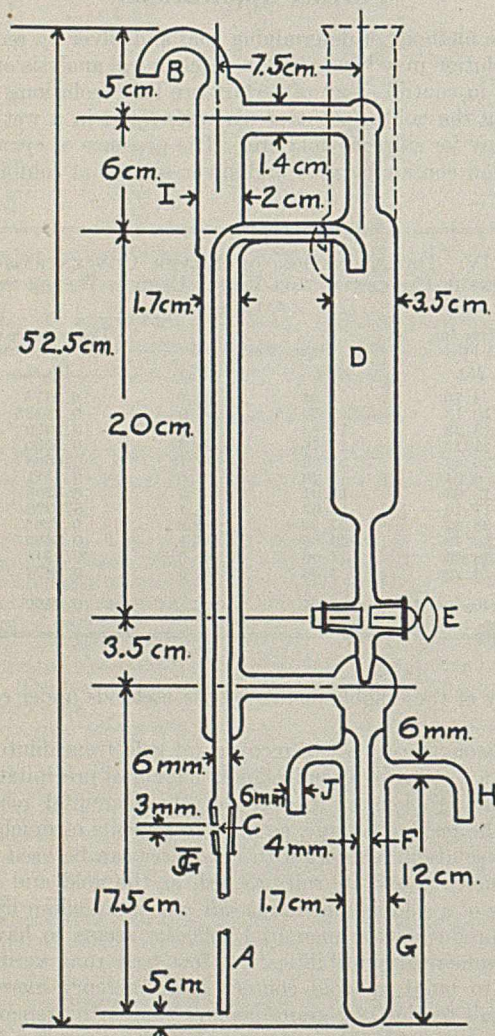


FIGURE 1. DIAGRAM OF APPARATUS

The lower end of tube *A* is placed in the liquid to be circulated and the suction from an ordinary laboratory water aspirator is applied at *B*. The outlet tubes, *H* and *J*, are closed readily by placing the fingers over the ends or by stopcocks. Thus the apparatus is partially evacuated and the liquid rises in tube *A* until it reaches the air inlet, *C*, where the solid column of liquid is broken. The alternate bubbles of air and liquid empty into reservoir *D*. The liquid then passes down through stopcock *E* and tube *F* into well *G*. When the level rises above the lower end of *F*, *H* and *J* are opened. The liquid continues to rise in *G* and then flows out at *H*.

When reservoir *D* becomes full, the excess liquid flows out the top into the large tube, *I*, which in turn empties into *G*. This prevents the liquid from rising high enough to be drawn out of suction tube *B*. However, the suction must remain moderate, so that the rate of inflow will not exceed the combined rates of outflow. The rate of flow from *H* may be regulated either by the amount of suction applied or by stopcock *E*. When the suction is regulated so that the flow becomes steady, the lift requires no further adjustment.

A stopcock or piece of rubber tubing with a screw clamp, placed on delivery tube *H*, may be used to regulate the outflow. In this case it is necessary to provide overflow *J* in such a position that the liquid will return to the original container.

The air inlet *C* may be readily adjusted if the tubes at this point make a ground joint. It is entirely satisfactory to insert a T-tube at this point and regulate the air flow by means of an attached piece of rubber tubing and screw clamp.

The dimensions of the apparatus may be varied to meet any particular need.

The following limits of operation can be obtained with the apparatus of the dimensions in Figure 1:

The pressure difference at *B* may vary between 7 and 31 mm. The rate of delivery at *H* may be as high as 215 ml. of water per minute when the air inlet, *C*, is 1.5 mm. above the level of the liquid being raised. Water can be raised from a level 30 cm. below *C*. For raising liquids a greater distance, it is necessary to lower the position of *C*. Best results are obtained when *C* is close to the liquid surface.

The use of this apparatus with some modification of the well, *G*, as a sampling device for solutions or suspensions is suggested. By altering the shape and dimensions of *D* as indicated by the dotted lines, a filter medium can be inserted. This would make it possible to remove suspended material from the liquor.

The device has been used in this laboratory to circulate the electrolyte through an electrolytic cell. The height of the main reservoir gave sufficient head to keep a steady flow of liquid at all times, and the safety outlet permitted the setup to be left for hours at a time without attention.

RECEIVED August 9, 1937.

A Piezometer Ring

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THE static pressure of a moving liquid in a pipeline may be measured by a manometer attached to a small opening in the pipe wall, the plane of the opening being parallel to the direction of flow. Such a connection, however, may give faulty readings owing to the disturbance of the flow by unremoved burrs at the base of the drilled hole or by the protrusion of the tap beyond the inner wall surface. The readings may not be simply a measure of the static head, but may include a fraction of the velocity head should the stream be diverted up the tap by a sharp downstream edge of the drilled hole.

To avoid these possible errors and to ensure greater precision where small static pressure differences are concerned, the form of piezometer ring shown in Figure 1 was constructed in the authors' laboratory and found to be very satisfactory.

The improvised piezometer consists of two reducing couplings, one nipple, and a short piece of pipe threaded on one end for a tap. It is constructed as follows:

The upstream section of pipe is threaded to receive one of the reducing couplings, into which is screwed a tapped nipple as shown in Figure 1. The downstream pipe is threaded and the second coupling is put on. Now the two sections of pipe are joined by screwing the second coupling onto the remaining end of the nipple. The threaded lengths are gaged so that the opening between the upstream and downstream lengths of pipe is not more than 0.0625 inch. The split between the two sections

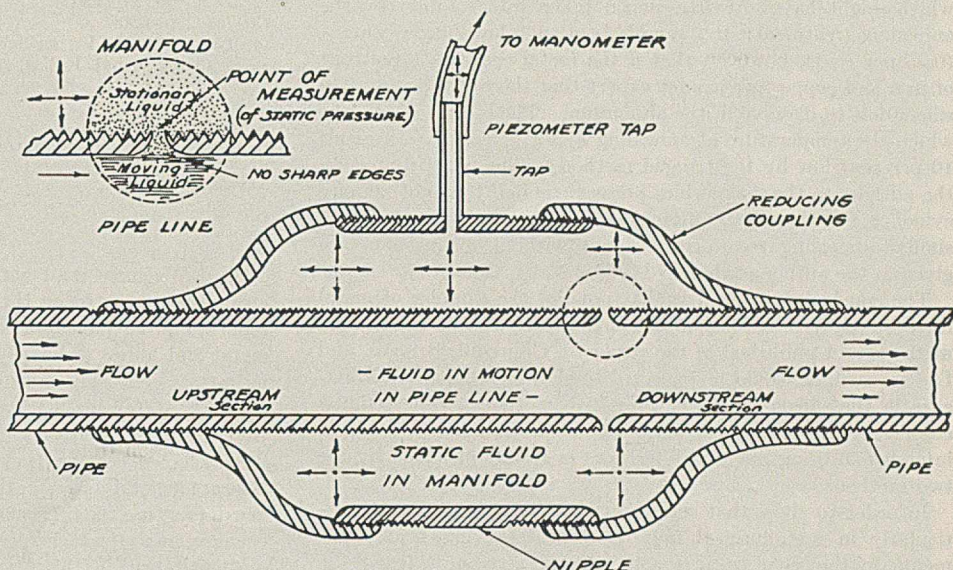


FIGURE 1. PIEZOMETER RING

is the most important part of the ring, as it is the point at which the pressure is measured. To avoid the effect of velocity head on the manometer, the tap in the nipple must be upstream from the static split. The inner edges of the split must be rounded to reduce the friction loss, to encourage flow through the pipe, and to prevent divergence of the flow into the manifold.

The improvised piezometer ring described is constructed from fittings which may be purchased from any dealer in pipe fitting supplies and can be put together with the minimum of shop equipment. It has been used successfully for the determination of the friction loss of pipes and pipe fittings.

RECEIVED August 26, 1937

Determination of Silicon in Aluminum—Correspondence

SIR: Churchill, Bridges, and Lee published in the May 15, 1937, number of *INDUSTRIAL AND ENGINEERING CHEMISTRY* (4) a paper on the above subject containing a number of results which were obtained during an official examination by the A. S. T. M. of my methods published in the *Analyst* (1, 2, 3). Some published comments on these results seem to be necessary to clear up certain difficulties and misunderstandings which, as it appears from this paper from the Aluminum Company of America Laboratories, seem still to exist in America.

In my first paper (1), I pointed out that the tri-acid process recommended by the A. S. T. M. tended to give low results due to the loss of silicon as silicon hydride. In my second paper (2), I gave the actual results for the determination of silicon hydride lost from various classes of metal during solution in different acids and in soda. In my third paper (3), I gave full details of an accurate method for the determination of graphitic silicon in the residue from acid attack.

The main point brought out by my results was that with

aluminum containing as principal impurities iron and silicon only, and in the chill cast condition—i. e., rapidly cooled—some of the silicon was in solid solution in the aluminum unless the iron content of the metal was abnormally high. When the metal was dissolved in mixed acids a part of this silicon in solid solution in the aluminum went off in the form of silicon hydride and was lost from the analysis.

To bring out this important error clearly it is advisable to take metal with high silicon (say 1.5 per cent) and low iron (say 0.10 per cent) and anneal it at about 570° C. for 24 hours and quench in cold water.

Also, since such metal has a tendency to aging and this is accelerated by any heating up during the turning or milling of the sample for analysis, special precautions must be taken to keep the metal cool and analyze it immediately after quenching.

Unfortunately in the A. S. T. M. investigation they did not appreciate these rather complicated metallurgical points and

carried out the comparison between the soda and tri-acid processes on what appears to have been, from the figures given in Churchill's paper, a series of copper-iron alloys (nominal composition stated to be 1 per cent iron, 1 per cent copper, etc., in each case). Further in Table I of that paper there is only one sample, 3S (for which actual figures of annealing are given), which might have any free silicon taken into solution by the annealing treatment; this sample is of such low silicon content (0.25 per cent), however, that if the metal contains 1 per cent of iron and copper, we cannot expect that there will be any free silicon left to dissolve in the aluminum. The sample 51SW, for which the temperature of annealing is not given, gives a result 10 per cent low by the tri-acid method. This is attributed by the authors to the magnesium present, though I cannot see any evidence for this assumption since no results for metal with similar annealing treatment W, but without magnesium, are given in the author's table.

The conclusion reached is that none of the samples of metal used for the A. S. T. M. comparison between the soda and tri-acid methods and published in the paper by Churchill, Bridges, and Lee are such as would be expected to show a pronounced difference in the silicon figure by these two methods. The samples chosen are in fact unsuitable for such a comparison where it is intended to bring out the differences in results obtained by the two methods.

In order to show that serious errors can be introduced, particularly in metallurgical investigations involving heat treatments, by the use of tri-acid method, I will give here a few of the most striking results from my papers. I believe I am justified in pointing out that probably as a result of the publication of my papers, there has been a big change since 1933 in the composition of the tri-acid mixture recommended by the A. S. T. M., by which the proportion of nitric acid has been increased three times compared with the other acids. This is undoubtedly a change in the right direction, but the mixture still requires testing out on metal heat-treated, as I have suggested, before it can be considered a satisfactory method for reference analysis.

LOW RESULTS BY TRI-ACID METHOD FOR SILICON

Metal	Silicon		Iron %
	Tri-Acid %	Soda %	
E	0.14	0.18	0.30
K	0.20	0.23	0.33
V	0.28	0.34	0.31
R	0.38	0.40	0.32
C.S	0.57	0.69	0.32
A	0.46	0.58	0.31
B	1.70	2.07	0.35

Other impurities, copper, manganese, etc., were less than 0.02 per cent in the above metal.

All samples were annealed at 550° C. for 24 hours and quenched in cold water. The samples were then immediately milled up for analysis, being kept cool, below 100° F., during the milling operation.

The tri-acid mixture used was as follows:

675 cc. 1.84 H ₂ SO ₄	} and	A. S. T. M. mixture Sept., 1933, schedule	{	1200 cc. 25% H ₂ SO ₄
338 cc. 1.42 HNO ₃				(by volume)
338 cc. 1.16 HCl				200 cc. 1.42 HNO ₃
3150 cc. water				600 cc. 1.20 HCl

The results given in my table (2) show a mean loss for the tri-acid method as compared with the soda method of 18.6 per cent of the total silicon. It must be once more emphasized that losses of this order will be found only for metal which has been annealed at a high temperature, 550° to 570° C., so as to bring all the silicon into solid solution. The loss is due to the formation of silicon hydrides which go off during the solution of the metal in acid mixture.

In conclusion, it appears that this is a case where a thorough re-examination of methods is needed. The A. S. T. M. represents perhaps the highest standard of scientific testing in the

world and the maintenance of this standard depends on a willingness to examine and if necessary, as in this case, to re-examine evidence relating to errors or faults in the standard methods.

Literature Cited

- (1) Callendar, L. H., *Analyst*, 57, 500 (1932).
- (2) *Ibid.*, 58, 81 (1933).
- (3) *Ibid.*, p. 580.
- (4) Churchill, H. V., Bridges, R. W., and Lee, M. F., *IND. ENG. CHEM., Anal. Ed.*, 9, 201 (1937).

L. H. CALLENDAR

THE CHLORIDE ELECTRICAL STORAGE COMPANY LIMITED
RESEARCH LABORATORIES, EXIDE WORKS
CLIFTON JUNCTION, NEAR MANCHESTER, ENGLAND
August 5, 1937

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SIR: We have read with interest Dr. Callendar's comment on our recent paper on the determination of silicon. The work reported in our paper was done on samples representative of the metal and alloys ordinarily encountered here in commerce and industry. The temperatures we used for annealing were incorrectly stated in two instances as 300° and 500° F., whereas they actually were 300° and 500° C. These temperatures were selected because they represent the range of temperatures that are generally used in the aluminum industry in this country. We did not use the higher temperature specified by Dr. Callendar because analytical chemists rarely encounter metal which is quenched from as high a temperature as 550° C., and which they immediately analyze lest aging occur.

Following Dr. Callendar's suggestions, additional analyses were made, the main details of which are summarized below:

Sample	Thermal History	Method of Decomposition	Si %	Fe %
A	Heated 24 hours at 570° C. and quenched	Tri-acid NaOH	0.93 1.01	0.06
A	Heated 24 hours at 300° C. and quenched	Tri-acid	1.02	..
B	Heated 24 hours at 555° C. and quenched	Tri-acid NaOH	1.51 1.65	0.15
B	Heated 24 hours at 300° C. and quenched	Tri-acid	1.64	..
C	Heated 24 hours at 555° C. and quenched	Tri-acid NaOH	5.05 5.19	0.64
C	Heated 24 hours at 300° C. and quenched	Tri-acid	5.19	..

The above data confirm Dr. Callendar's position that the tri-acid method, when applied to some aluminum alloys which have been heated at 550° C. and above, quenched therefrom, and immediately analyzed, may yield low results. This is extremely interesting, since the data in our paper show no such effect when metal has been heated at 500° C. instead of the higher temperature specified by Dr. Callendar.

It now becomes apparent that our limitation of the inapplicability of the tri-acid method to aluminum alloys containing magnesium silicide should be broadened to include aluminum alloys which have been heated and quenched from a temperature of about 550° C. This broadening of the scope of inapplicability makes doubtful the use of the tri-acid method as a fundamental umpire method for use on aluminum samples of unknown thermal history. As a practical control and inspection method for commercial aluminum and aluminum alloys, the tri-acid method will yield satisfactory results, since ordinarily the thermal exposure of such metal does not go above 500° C. We stated in our paper that the sodium hydroxide method is applicable to all types of aluminum alloys. We now concur with Dr. Callendar's suggestion that the basic umpire method for the analysis of aluminum alloys should embrace the sodium hydroxide method of decomposition.

H. V. CHURCHILL, R. W. BRIDGES, AND M. F. LEE

ALUMINUM COMPANY OF AMERICA
NEW KENSINGTON, PA.
October 7, 1937



Courtesy, Leo K. Yanowski

Flavo Cobaltic Silicotungstate Crystals

Direct Microdetermination of Oxygen in Organic Substances by Hydrogenation

Analysis of Pure, Volatile Compounds Containing Carbon, Hydrogen, and Relatively Low Percentages of Oxygen

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

A micromethod, based on ter Meulen's hydrogenation procedure, has been developed for the direct determination of oxygen in volatile organic compounds containing only carbon, hydrogen, and oxygen. A study was also made of the blank determination involved in this method. It was found that, in the analysis of pure compounds which distill or sublime, results can be obtained which agree with theory to within

± 0.1 per cent, provided a more or less empirical blank value is deducted. If the manipulative blank value is deducted the results all tend to be low, which indicates that a hidden compensative error is involved in the method. The same technic when applied to sucrose, which leaves a voluminous deposit of carbon in the boat, has so far yielded results which are consistently low.

THE purpose of this paper is to describe a micromethod for the direct determination of oxygen in organic substances based on ter Meulen's hydrogenation process. The principle of this method consists in distilling, subliming, or pyrolyzing the sample in a current of hydrogen and passing the products over a cracking catalyst, heated to about 1000°C . The products thence pass, along with the hydrogen, over a methanation catalyst, maintained at 350°C ., where hydrogenation occurs and the oxygen present in the sample is converted to water which is collected in an absorption tube and weighed.

Previous papers from this laboratory (4) have described the development of an oxidation method for the direct, simultaneous microdetermination of carbon, hydrogen, and oxygen in organic substances. This oxidation method is based on the determination of the oxygen content of the combustion products (carbon dioxide, water, sulfur trioxide, and nitrogen peroxide), together with the gaseous "oxygen consumed" during the combustion. The relative advantages and disadvantages of the hydrogenation versus the oxidation method have been previously pointed out (5). When work was started on the oxidation method, the hydrogenation method, in its state of development at that time, did not look promising as the basis for a general microprocedure because the presence of elements such as halogens, nitrogen, and sulfur complicated the apparatus and the procedure, and the determination of the oxygen content of the samples was not particularly direct. In the interim, however, there have been some noteworthy improvements made in this method, particularly by Russell and co-workers (12), as well as by ter Meulen (8) and Goodloe and Frazer (1), which have greatly simplified the method. These improvements mainly concern the use of improved methanation and cracking catalysts and also more suitable absorption agents for the water formed by the hydrogenation of the oxygen in the sample. In its improved state the method appeared sufficiently attractive to warrant an attempt to convert it into a micro-method. Indeed, during the course of the present investigation, a paper appeared by Hennig (2) describing a similar hydrogenation method for the direct microdetermination of oxygen in pure compounds containing carbon, hydrogen, and oxygen with a maximum error of ± 0.4 per cent. More than a year after the present work had been finished a

paper appeared by Lindner and Wirth (7) completely describing a volumetric microdetermination of oxygen in organic compounds (containing, besides carbon, hydrogen, and oxygen, also nitrogen, sulfur, and halogens), which is likewise based on the ter Meulen hydrogenation process. A preliminary notice concerning the development of a micro-method, apparently similar to the one described here, was also recently published by Unterzaucher and Bürger (13).

Apparatus

The apparatus is illustrated in Figure 1. Electrolytic hydrogen, taken from a high-pressure cylinder, was transferred to a large gasometer and stored over distilled water. The hydrogen passed from the gasometer through a Pregl precision screw clamp, *A*, to a Pregl pressure regulator, *B*; the gas emerged under a pressure corresponding to about a 10-cm. column of water. From here the gas passed through a large glass-stoppered U-tube, *C*, containing first an equal mixture of soda lime and Ascarite (8- to 20-mesh); Ascarite alone was found unsatisfactory as it soon became sufficiently wet to clog the U-tube and prevent passage of the hydrogen. The remainder of the U-tube was filled with Drierite (10- to 20-mesh anhydrous calcium sulfate, kindly furnished by the manufacturer, W. A. Hammond, Yellow Springs, Ohio, to whom the author wishes to express his thanks. The plain material was used which contained no indicator). The gas then entered a preheater, *D*, which contained platinized asbestos heated to about 400°C . by means of an electrical heater. The gas was cooled by passage through the immersed glass spiral, entered the bubble counter, *E*, containing 50 per cent potassium hydroxide solution, and then passed into the small U-tube, filled just like the large one, and through the three-way stopcock and into the side arm of the hydrogenation tube. All rubber connections in the purifying train were made with paraffin-impregnated tubing. After passing through the hydrogenation tube, the gas entered a Pregl microabsorption tube filled with Drierite, thence into a protection tube, similarly filled, and then into the Mariotte bottle.

The quartz hydrogenation tube was 65 cm. long and had an internal diameter of 8 mm. and 1-mm. wall. To the exit end was sealed a 1-mm. capillary, 3 cm. long. The portion of the hydrogenation tube adjacent to the exit capillary, and with only the capillary protruding, was heated with a small electrical Nichrome-wound furnace (catalyst furnace) 18 cm. long and 7.5 cm. in diameter. Directly against this was a second, similarly constructed high-temperature furnace (cracking furnace) 18 cm. long and 12 cm. in diameter. The catalyst furnace surrounded the portion of the hydrogenation tube which contained the methanation catalyst, while the cracking furnace heated that part of the tube which contained the cracking catalyst. The furnaces were calibrated throughout their entire length using a chromel-alumel thermocouple and the temperatures related to readings

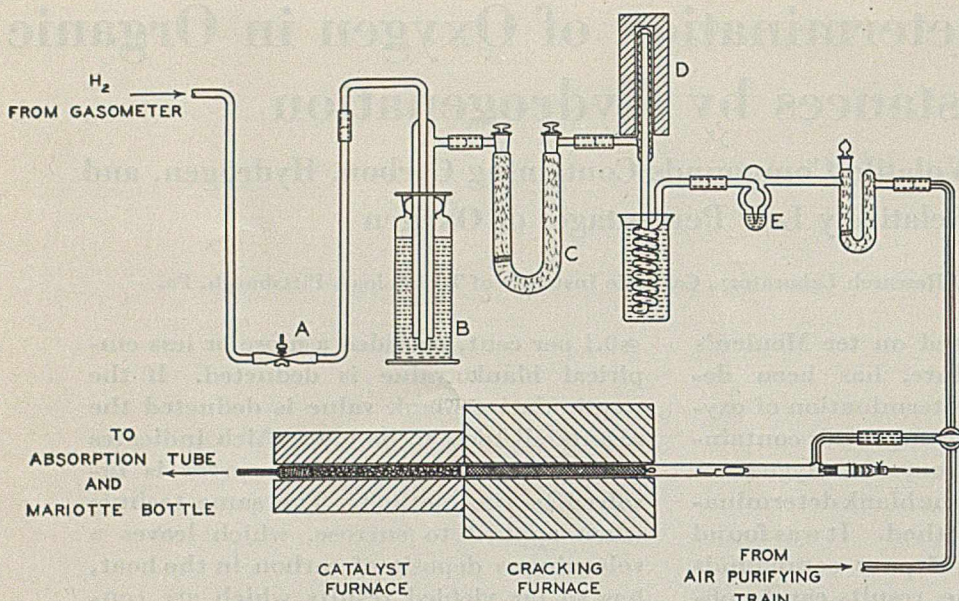


FIGURE 1. DIAGRAM OF APPARATUS

made on a pair of ammeters. By means of slide-wire resistances the furnaces could be adjusted to any desired temperature. The samples were weighed into platinum microboats and were heated by means of a Bunsen burner and wire gauze roll just as in a Pregl carbon-hydrogen determination.

The Hydrogenation Tube Filling

The clean, dry hydrogenation tube was fitted with an asbestos resistance plug, about 2 mm. long, which was placed in the capillary outlet just adjacent to where the latter was sealed to the hydrogenation tube proper. The density of this plug was adjusted so that, with hydrogen flowing through the heated hydrogenation tube under a pressure of 10 cm. of water, the gas flow rate was about 5 cc. per minute as measured with the Mariotte bottle. In adjusting the density of this plug all air must be absent from the tube, since the viscosity of air is considerably higher than that of hydrogen. A 3-cm. layer of compressed nickel wire (No. 35 B & S gage) was then pushed into the tube, followed by three tight-fitting pieces of circular nickel gauze, cut from 200-mesh nickel gauze, which prevent the finely divided catalyst from getting into the end of the hydrogenation tube.

A 14-cm. layer of 2 per cent thoria-nickel oxide was next added, which was prepared according to the directions of Russell and Fulton (12). Their statement was confirmed to the effect that, using this catalyst, the oxygen present in the sample is found only as water. In several experiments an Ascarite-soda lime tube was connected with the Drierite tube, but its increase in weight never exceeded that found in a blank determination. To reduce the amount of catalyst in the tube and to permit easy gas flow, the oxides were mixed with 2- to 3-mm. lengths of 1-mm. glass rod. The 14-cm. layer contained about 2.5 grams of the mixed oxides which yielded about 2.0 grams of active thoria-promoted nickel after reduction. A single piece of circular 200-mesh nickel gauze held the loosely packed catalyst in place. This entire portion of the tube filling occupied 17 cm. and was surrounded by the catalyst furnace. The next portion of the tube filling consisted of the cracking catalyst (6, 9, 10) which was merely a roll of 200-mesh nickel gauze, 17 cm. long. This was made to fit into the tube rather loosely and was held in cylindrical form by means of fine nickel wire ties spaced at about 4-cm. intervals; it also had a nickel wire loop at one end to permit easy removal from the tube. This nickel wire roll filled the portion of the tube which was heated by the cracking furnace. After the nickel gauze roll was prepared it was oxidized in a Bunsen flame and then reduced in a hard-glass combustion tube, heated to dull redness, with hydrogen passing through it, and allowed to cool in the stream of hydrogen. The compressed nickel wire and the circular nickel gauze pieces were treated similarly.

Microabsorption Tube Filling

The single absorption tube was filled with 10- to 20-mesh Drierite in the usual way, the absorption agent being held in

place with small cotton tampons at each end of the tube. Preliminary wiping, aeration, and weighing experiments made with this tube showed satisfactory constancy and reproducibility of weight (± 0.003 mg.).

Procedure

CONDITIONING THE HYDROGENATION- AND ABSORPTION-TUBE FILLINGS. The mixture of thoria-nickel oxide was reduced, *in situ*, by passing hydrogen through the filled hydrogenation tube continuously for several days, the temperature of the catalyst furnace being maintained at 400° C. During the last day of the reduction the nickel gauze roll was also heated to about 1000° C. by connecting the cracking furnace, and the

absorption tube and Mariotte bottle were attached so as to condition the absorption tube filling.

ACTUAL DETERMINATIONS. After at least 72 hours' continuous reduction of the mixed oxides at 400° C., manipulative blank determinations (described below), made with the catalyst heated at 350° C., yield constant and reproducible values which show no further tendency to diminish appreciably. The apparatus is then ready for use in the actual determinations.

Hydrogen is started through the apparatus from the gasometer. The two electric furnaces and the preheater are turned on, the catalyst furnace being set at 350° C. and the cracking furnace at 1000° C. After one hour they attain the required temperatures and the absorption tube is attached to the hydrogenation tube, by means of the usual heavy-walled paraffin-impregnated rubber tube, and connected with the protection tube and Mariotte bottle, and hydrogen is passed for 30 minutes at the rate of 5 cc. per minute. At the end of this interval the absorption tube is removed, taken to the balance room, and placed in an aeration apparatus, similar to that devised by Niederl (11) but containing Drierite as the drying agent, and 50 cc. of air are drawn through it at the rate of about 10 cc. per minute to displace the hydrogen. Then the absorption tube is removed from the aeration apparatus, wiped, stoppered with tight-fitting pins, allowed to stand next to the balance for 10 minutes, placed in the balance and weighed at the end of an additional 10 minutes.

Just after the start of the 5-minute aeration period the weighed sample is introduced into the hydrogenation tube and placed near the end of the tube just beyond the side arm connection, so that it is not heated by radiation from the cracking furnace. During the insertion of the sample the gas flow through the pressure regulator and purifying train is speeded up considerably, by opening the precision screw clamp, so that a rapid stream of hydrogen issues from the open hydrogenation tube and thus inhibits the entrance of air. Immediately behind the boat containing the weighed sample is placed a small quartz plug, provided with a loop so that it can be easily pulled out of the hydrogenation tube. This plug fits the hydrogenation tube fairly snugly but should be capable of being pushed forward and backward without resistance. The purpose of the plug is to increase the velocity of the hydrogen behind the sample and thus hinder any backing up of the sample. When the quartz plug was not used it was found that even with gas velocities of 5 cc. per minute there was a tendency for some compounds to distill backward through the Bunsen flame, countercurrent to the hydrogen stream. The passage of hydrogen is continued during the remainder of the aeration, wiping, waiting, and weighing periods, a total of about 30 minutes. In the event that any air was admitted to the hydrogenation tube during insertion of the sample, it, together with the air present in the sample and in the boat, would be removed

and swept out of the hydrogenation tube before the absorption tube is reattached.

In all the published procedures (except that of Hennig, ²), the weighed sample is introduced into the hydrogenation tube while a rapid stream of hydrogen issues from the open tube and after the absorption tubes have been attached. The assumption is made that no air enters the hydrogenation tube during this procedure. However, any oxygen which enters the tube during this operation will be converted to water, so that there is an excellent opportunity here for the appearance of a compensative error. While such errors may be negligible in macro- or semimicroprocedures, they can assume considerable magnitude in a micromethod. One can readily calculate that the volume of air present in a microboat contains approximately 0.1 mg. of oxygen which would form 0.11 mg. of water on hydrogenation. This was confirmed experimentally. In preliminary attempts to adopt the macro-technic of inserting the sample into the open hydrogenation tube, after the absorption tube had been attached and with an exit flow of hydrogen of 185 cc. per minute, the blank values were in excess of 0.1 mg. It is also difficult accurately to standardize such a procedure with the hydrogenation tube being opened for a minimum period of time. It is therefore imperative, in a micromethod, to conduct a sweeping operation to remove any air which inadvertently entered the hydrogenation tube as well as that present in the boat and adsorbed on the sample, before attaching the absorption tube. Hennig (²) also found it advisable to adopt such a procedure in his micromethod.

After the absorption tube has been weighed it is attached to the hydrogenation tube and connected with the Mariotte bottle. Before starting the flow of water from the Mariotte bottle, the sample and quartz plug are pushed forward in the hydrogenation tube to a distance of 3 to 4 cm. from the cracking furnace. This is done, without permitting air to enter the hydrogenation tube, as follows:

The rubber stopper in the end of the hydrogenation tube (Figure 1) is provided with a tight-fitting glass tube about 5 cm. long which acts as a sleeve. Through this is inserted a snug-fitting glass rod of sufficient length to permit the boat and quartz plug to be pushed forward nearly as far as the cracking furnace. A tight-fitting, impregnated rubber tube, about 5 cm. long, fits over the glass sleeve and also fits snugly over the glass rod; to make a gas-tight connection the rubber tubing is wired around the glass rod with fine copper wire. When the sample and quartz plug are to be pushed forward, this wire is removed; a small amount of hydrogen issues from the annular space between the glass rod and the rubber tube but there is little likelihood of any air or moisture entering the hydrogenation tube, except that adsorbed on the glass rod, since the hydrogen is issuing under pressure. The sample and quartz plug are pushed forward the desired distance and the glass rod is pulled back to its original position and the rubber tube rewired around it. The Mariotte bottle is then started, the gas flow adjusted to 5 cc. per minute, and the remainder of the procedure is carried out exactly like a Pregl carbon-hydrogen determination except that it is done more slowly and carefully.

The first passage of the Bunsen burner usually requires 40 to 50 minutes and the second 5 to 10 minutes. The hydrogen continues to pass so as to sweep the products through the hydrogenation tube and into the absorption tube. During this sweeping period the next sample is weighed out. When 400 cc. of water have been collected from the Mariotte bottle, which requires 75 to 80 minutes, the absorption tube is removed and brought to the balance room, aerated, wiped, and weighed as before. After the start of the aeration period the boat and quartz plug are removed from the hydrogenation tube and the new sample and quartz plug are introduced in preparation for the next analysis.

BLANK DETERMINATIONS. To determine whether or not the catalyst has been sufficiently reduced, it is necessary to make a series of blank determinations. It is also necessary to make blank experiments in order to determine the weight

of water which must be deducted from the final weight of water obtained in an actual determination, since water is continuously being formed by reduction of nickel oxide present in the catalyst as well as from any oxygen (and moisture) in the air inadvertently admitted to the hydrogenation tube during the introduction of the sample. For all blank and actual determinations the methanation catalyst was maintained at 350° C.

In the present investigation the manipulative blank determinations were made exactly simulating an actual determination—that is, the hydrogenation tube was opened, the quartz plug and boat from the previous combustion were removed, and the quartz plug and an empty boat were inserted. The hydrogenation tube was then stoppered and swept with hydrogen for the same length of time as in an actual determination, the weighed absorption tube was attached, the quartz plug and boat were pushed forward, and the same volume of hydrogen was passed through the heated hydrogenation tube as in an actual determination; then the absorption tube was removed and weighed. The gain in weight of the absorption tube represents the manipulative blank value.

All previous investigators have determined a so-called "blank value" by passing hydrogen, at a more or less definite rate of flow, through the heated hydrogenation tube for a given length of time, usually 0.5 hour. The increase in weight of the absorption tube during this period is considered the blank value; if an actual determination required 1.5 hours, then three times the blank value was deducted from the weight of water absorbed during the analysis.

ter Meulen (⁹) claims to have eliminated the blank value entirely by using a very small amount (0.1 gram) of 10 per cent thoria-nickel catalyst. The use of this small amount of catalyst has the disadvantage of necessitating its frequent

TABLE I. BLANK DETERMINATIONS

Month (1936)	Technic	Hydrogen Cc.	Time Min.	Blank Values	
				Mg. H ₂ O	
February	a	300	71	0.020	
		300	71	0.013	
				Mean	0.016
February	b	300	72	0.036	
		300	74	0.034	
		300	71	0.036	
		300	68	0.049	
		300	70	0.044	
		300	70	0.051	
				Mean	0.042
February	c	400	75	0.062	
March	a	400	75	0.024	
March	b	400	82	0.050	
March	c	400	81	0.042	
		400	80	0.035	
				Mean	0.038
May	c	400	80	0.054	
August	c	400	80	0.085	
		400	80	0.080	
		400	80	0.079	
				Mean	0.081

NOTE: a, Hydrogen passed through unopened tube; no heating with movable burner; b, manipulative blank determination except no heating with movable burner; c, complete manipulative blank determination, including heating with movable burner.

renewal. Hennig (²), in his micromethod, using a nickel-pumice catalyst, pointed out that the blank value obtained by passing hydrogen over the catalyst at the rate of 3 to 5 cc. per minute for 0.5 hour should not exceed 0.010 to 0.015 mg. of water. No blank correction was applied to his results, which explains why three out of the four analyses he cites are from 0.15 to 0.39 per cent high.

In order to get some information on this question of blank values, a considerable number of blank determinations were made during the course of the work. It was felt that previous investigators had not devoted sufficient study to the determination of blank values and that blank values, as applied up to this time, might easily compensate for errors made in the actual determinations. Three different technics were used in these determinations, so that a comparison could be made of the results, which are indicated in Table I.

Scrutiny of Table I reveals the fact that the increase in weight of the absorption tube, following a complete manipulative blank determination (technic *c*) is 2 to 3 times that obtained using the technic of previous investigators (technic *a*), where the same volume of hydrogen is merely passed through the heated hydrogenation tube, which is not opened (for the removal of the boat left from the previous analysis, and for the introduction of the boat for the next analysis), nor subjected to heating as in an actual determination. With the very unfavorable factor ($\frac{O_2}{2 H_2O} = 0.888$) involved in this determination, a difference in blank values of this magnitude causes an appreciable difference in the final calculated result.

It was found that if the manipulative blank values were deducted from the weight of water obtained in actual determinations, the final results were always too low. However, if the blank value obtained using technic *a* was deducted, the results were satisfactory. It would therefore appear that a compensative error of some sort is involved in this method and that the "blank value," as determined by other investigators using macro- or semimicroprocedures, fortuitously yielded correct results due to a compensation of errors. In other words, the blank value which must be applied in order to get satisfactory results is a more or less empirical correction factor. This conclusion agrees with the findings of Lindner and Wirth (7). The blank value which they apply to their results is also of a more or less empirical nature. Calculated to the same total volume of hydrogen that was used in the present work (350 or 400 cc.), the magnitude of their blank value is practically identical to that used here (see Table II).

The results shown in Table I also indicate that the magnitude of the blank is directly proportional to the volume of hydrogen passed through the hydrogenation tube. If the hydrogenation tube is opened for the introduction of the boat, the blank value is increased by a factor of 2 to 3. Heating the front end of the hydrogenation tube with a movable burner during the blank determination (technic *c*) causes no appreciable increase over that obtained when the hydrogenation tube is not so heated (technic *b*), all other conditions being identical. In the procedures involving an opening of the hydrogenation tube a marked difference is observed in the blank values as determined at different times of the year; this is presumably a function of the humidity of the atmosphere, since the blank values are highest during the humid summer months.

Results

The results obtained on six pure compounds, with oxygen contents ranging from 4 to 26 per cent, are given in Table II. Generally, in selecting the size of the sample to be analyzed, the larger the oxygen content the smaller the weight of sample taken. It is observed that the mean accuracy of this method is about ± 0.10 per cent.

Cholesterol was chosen as one of the test substances because ter Meulen (9) reported that it sometimes causes difficulty due to the production of a solid hydrocarbon, formed

during passage of the sample over the incandescent asbestos which was used as the cracking agent. This hydrocarbon resists decomposition even at elevated temperatures and, on entering the absorption tube, increases its weight and causes high results. The sample used here was obtained from

TABLE II. RESULTS OF ANALYSES

Substance	Weight of Sample Mg.	Weight of Water Mg.	Oxygen	
			Found %	Difference from theory %
Benzoic acid (26.22% O)	4.575	1.373 ^a	26.27	+0.05
	5.094	1.521 ^a	26.17	-0.05
	4.785	1.431 ^a	26.19	-0.03
	5.141	1.533 ^a	26.14	-0.08
	4.696	1.404 ^a	26.17	-0.05
Anthraquinone (15.38% O)	6.457	1.140 ^b	15.34	-0.04
	8.300	1.448 ^b	15.23	-0.15
	6.371	1.145 ^b	15.61	+0.23
Methyl- β -naphthyl ether (10.12% O)	8.217	0.956 ^b	10.06	-0.06
	7.394	0.877 ^b	10.23	+0.11
	9.076	1.047 ^b	10.00	-0.12
<i>p</i> -Cyclohexyl phenol (9.08% O)	8.160	0.870 ^b	9.20	+0.12
	7.868	0.824 ^b	9.02	-0.06
	7.805	0.826 ^b	9.10	+0.02
Benzalacetophenone (7.69% O)	8.309	0.769 ^b	7.95	+0.26
	8.483	0.757 ^b	7.66	-0.03
	8.848	0.802 ^b	7.80	+0.11
Cholesterol (4.14% O)	9.777	0.493 ^b	4.25	+0.11
	9.116	0.465 ^b	4.29	+0.15

^a Deduct blank of 0.020 mg. of water for 350 cc. of hydrogen passed.

^b Deduct blank of 0.025 mg. of water for 400 cc. of hydrogen passed.

Merk and dried in vacuum over phosphorus pentoxide for several days. The results obtained confirm ter Meulen's statement to the effect that a nickel cracking catalyst performs satisfactorily in this respect.

It was found that after making the above analyses and then removing the nickel gauze roll, a thin deposit of carbon was present on the nickel which covered but about 1 cm. of its length. All the above compounds readily volatilize out of the boat and leave only traces of carbon on the interior of the hydrogenation tube so that practically all the carbon, not converted into methane, is present on the nickel gauze roll.

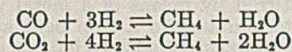
Attempts to Analyze Sucrose

Applying the technic developed on the compounds listed in Table II to a pure sample of sucrose gave results which were consistently low by 0.5 to 1.0 per cent. In a majority of cases the results were low even before deducting a blank. ter Meulen (10) and Inaba and Abe (8) mention no difficulties encountered in the analysis of sucrose, while Russell and Fulton (12) state that strong heating of the carbonaceous residue, left after carbonization of the sucrose, is necessary; they applied the full flame of a blow torch to the bare quartz hydrogenation tube. Each of the above authors has reported only a single analysis on sucrose. Goodloe and Frazer (1) also obtained low results in the analysis of sucrose; they ascribed their failure to obtain satisfactory results to an inactive catalyst. It may also be significant that the results reported for sucrose by Lindner and Wirth (7) and Unterzaucher and Bürger (13) are all low (-0.33, -0.11, and -0.26 per cent).

Following the suggestion of Russell and Fulton, a variety of methods for strongly heating the carbonaceous residue, left after pyrolysis of sucrose, were tried. These included strong heating of the bare quartz hydrogenation tube with a Bunsen burner, a blast lamp, an oxygen blast lamp, a pair of oxygen blast cross fires, and finally an electric split-type furnace which maintained the tube around the boat at 1100° C. All these attempts failed to improve the results and all, except the last method, soon seriously damaged the quartz

tube. If oxygen is retained in the residual carbon it does not appear to yield to these increasingly strenuous heat treatments. The carbonaceous residue is undoubtedly active, so that it did not seem feasible to remove it from the hydrogenation tube in order to make a carbon analysis, since it would probably rapidly adsorb both oxygen and moisture from the atmosphere.

In the analysis of a substance such as sucrose, which has a high oxygen content and which readily loses water on heating, it was thought that perhaps carbon monoxide or dioxide was lost by the reversal of the following equilibria caused by the sudden appearance of considerable amounts of water:



It was experimentally proved that this was not the case, at least for the carbon dioxide reaction. In several analyses an Ascarite-soda lime tube, placed after the Drierite tube, showed no increase in weight over that of a blank determination, so that no carbon dioxide escaped. To get experimental evidence concerning the reversal of the carbon monoxide reaction it would be necessary to determine very small amounts of carbon monoxide in the presence of large quantities of hydrogen, which is difficult. It also did not appear likely that carbon monoxide would escape reduction, since the literature indicates that carbon monoxide is converted to methane, under conditions similar to those used here, more easily than is carbon dioxide. Hence, if carbon dioxide does not escape reaction it is not likely that carbon monoxide would escape. An increase in the rate of hydrogen flow to 10 cc. per minute, using a total of 800 cc., also failed to improve the results. The investigation of sucrose, and other substances which behave similarly on pyrolysis in hydrogen, is being continued and will be reported later.

After a number of sucrose samples have been analyzed, the deposit of carbon in the hydrogenation tube, which renders visibility difficult, is removed as follows:

The glass plug and boat and also the nickel gauze roll are removed. If the nickel gauze contains a deposit of carbon it is burned off in a strong Bunsen flame. The whole gauze is oxidized by heating in a Bunsen flame and then reduced in a stream of hydrogen by heating to dull redness in a hard-glass combustion tube. The hydrogen in the quartz hydrogenation tube containing the carbon deposit is then displaced by nitrogen. The nitrogen (water-pumped) is taken from a high-pressure cylinder and passed through a Pregl pressure regulator, a bubble-counter U-tube, filled like the one in the hydrogen purifying train, and then is passed into the end of the hydrogenation tube, the connection being made with a rubber stopper. During this procedure the hydrogen is completely shut off at the three-way stopcock and the catalyst furnace is at room temperature while the cracking furnace is heated. When the hydrogen is all displaced by nitrogen, air is admitted from the gasometer and passed into the hydrogenation tube through the three-way stopcock after emerging from the air purifying train, which is identical to that used for the hydrogen except that no preheater is used. By heating the portion of the tube containing the carbon deposit with a Bunsen burner and wire gauze the carbon is readily removed. The cracking furnace is then allowed to cool, hydrogen is passed to displace the air, the nickel gauze roll is reinserted, and then both furnaces are reheated, the methanation catalyst being heated to 400° C. during the reduction of any nickel oxide which might have formed during the burning-out process. After reduction overnight, or longer, the temperature of the catalyst furnace is reduced to 350° C., and if the blank determination is satisfactory the apparatus is ready for use.

Acknowledgments

The author wishes to express his appreciation to B. B. Scott for designing the electrical furnaces used in this investigation and to J. A. Thompson for their construction.

Literature Cited

- (1) Goodloe, P., and Frazer, J. C. W., *IND. ENG. CHEM., Anal. Ed.*, 9, 223-5 (1937).
- (2) Hennig, H., *Chem. Fabrik*, 9, 239-41 (1936).
- (3) Inaba, T., and Abe, Y., *J. Soc. Chem. Ind., Japan*, 39, 91B (1936).
- (4) Kirner, W. R., *IND. ENG. CHEM., Anal. Ed.*, 6, 358-63 (1934) 7, 363-5 (1935); 7, 366-8 (1935); 8, 57-61 (1936).
- (5) *Ibid.*, 6, 358-63 (1934); 8, 57-61 (1936).
- (6) Lacourt, A., *Bull. soc. chim. Belg.*, 43, 73-92 (1934).
- (7) Lindner, J., and Wirth, W., *Ber.*, 70, 1025-38 (1937).
- (8) Meulen, H. ter, *Rec. trav. chim.*, 53, 118-25 (1934); *Bull. soc. chim.*, (5) 2, 1692-4 (1935).
- (9) Meulen, H. ter, *Rec. trav. chim.*, 53, 118-25 (1934).
- (10) *Ibid.*, 41, 509-14 (1922); *Bull. soc. chim.*, (5) 2, 1692-4 (1935).
- (11) Niederl, J. B., and Whitman, B., *Mikrochemie*, 11, 287, 295-6 (1932); Niederl, J. B., and Roth, R. T., *IND. ENG. CHEM., Anal. Ed.*, 6, 272 (1934).
- (12) Russell, W. W., and Fulton, J. W., *Ibid.*, 5, 384-6 (1933); Russell, W. W., and Marks, M. E., *Ibid.*, 6, 381-2 (1934); 8, 453-5 (1936); Marks, M. E., *Ibid.*, 7, 102-3 (1935).
- (13) Unterzaucher, J., and Bürger, K., *Ber.*, 70, 1392 (1937).

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The Determination of Acetyl, Especially in O-Acetyl Compounds

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IN A RECENT communication (1) the writer presented a general method for the determination of acetyl, based upon the principle of an alkaline, alcoholic hydrolysis of an acetyl compound, followed by acidification and distillation of the liberated acetic acid. For the distillation the alkali was neutralized with enough strong magnesium sulfate solution containing sulfuric acid, so that the reaction mixture had a volume of 20 cc. This was steam-distilled at constant volume until 50 cc. of distillate were obtained. The acetic acid which came over under these conditions represented 95.7 per cent of the total acetic acid formed by the hydrolysis of the acetyl compound.

The procedure gives satisfactory results, but if it is carried out as previously outlined, except that the distillation of the liberated acetic acid is conducted at such a rate that the reaction mixture is concentrated to approximately 15 cc. during the collection of the 50 cc. of distillate, the entire quantity of acetic acid is found in the distillate. This procedure is simpler and more conveniently conducted than if the distillation is carried out at constant volume; the use of an arbitrary factor is eliminated and the results are as accurate as those obtained by the former method.

In the new procedure a blank must be run upon the reagents for a given set of conditions, as was recommended in the case of N-acetyl compounds.

Literature Cited

- (1) Clark, E. P., *IND. ENG. CHEM., Anal. Ed.*, 8, 487 (1936).

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The Kauri Butanol Test for Solvent Power. II

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A microprocedure for the determination of kauri butanol solvent power has been developed and the solvent powers of a number of hydrocarbons have been determined. A method for correlating the solvent power results with the structure of the hydrocarbons has been worked out which provides an additional tool for the analysis of hydrocarbon mixtures.

THE kauri butanol test is a procedure primarily used for evaluating the diluting or solvent power of solvents of petroleum origin to be used as thinners for paints and varnishes. This test was officially adopted by the Paint and Varnish Superintendents' Club of the Philadelphia District (4). The term "solvent power" was originally used by Kiehl (3). According to that author, solvent power is the amount of a given solvent that can be added to a standard kauri gum solution in butanol to produce a definite turbidity, as compared with the amount of c. p. benzene used in a similar titration and arbitrarily taken as 100 per cent standard.

In a previous paper (1) an improved method for standardizing kauri butanol solutions was proposed by the authors. Subsequent study of the data obtained in the course of this work suggested that the differences in solvent power among the various hydrocarbons used in the standardization of the kauri butanol solutions might be correlated with chemical structure. Additional work has, therefore, been carried out in the hope of obtaining a definite relation between kauri butanol solvent power and the structure of hydrocarbons. The results of this work are summarized herein and show that with the exception of a few compounds, a correlation can be established which may become a very useful tool for qualitative and even quantitative analyses of hydrocarbon mixtures.

Micromethod for Determining Solvent Power

Pure hydrocarbons, some of which are rare and expensive to prepare, were employed to carry out this work. Since the regular procedure to determine solvent power involves a great waste of material, an alternative method was evidently desirable. A microprocedure was therefore developed whereby the solvent powers could be determined on samples of less than 1 cc. with fair accuracy.

TABLE I. STANDARDIZATION OF THE KAURI SOLUTION BY THE MICROMETHOD

Compound	Kauri Solution Used Gram	Compound Titrated Cc.	Kauri Butanol Value	Solvent Power
c. p. Benzene	0.2236	1.25	111.8	100.0
	0.1962	1.10	112.8	100.0
			Av. 112.3	100.0
n-Heptane	0.2234	0.34	30.4	25.4
	0.2275	0.35	30.8	25.4
			Av. 30.6	25.4

Beard, Shipp, and Spelshouse (2) have shown that the kauri butanol value of a solvent is directly proportional to the amount of kauri solution used. In developing a micro-method, it was therefore only necessary to use a smaller sample of solvent, reduce the amount of the standard kauri solution proportionally, and carry out the titration with a microburet. However, the use of the prescribed end point (blurred appearance of a 10-point print paper when viewed through the liquid in the titrating vessel) was found to be

impractical. A much sharper end point is obtained at the start of permanent turbidity.

In practice, the determination is carried out in a 5-cc. flat-bottomed test tube held by a metal plate placed over a small crystallizing dish containing water kept at the specified temperature (25° C., 77° F.). In the course of titration, the liquid in the test tube is stirred by means of a metal wire (iron, aluminum, or copper) terminating in a loop bent at a right angle to the stem. A 1-cc. buret divided into 0.01 cc. is used for the titration.

From 0.2 to 0.4 gram (instead of 20 grams as in the regular procedure) of the standard kauri solution is accurately weighed into the test tube; the latter is then inserted through the metal cover into the water bath kept at 25° C. (77° F.) and the solvent is added drop by drop from the buret to the point of permanent turbidity. The volume of the solvent used is read from the buret. The measured volume of solvent must then, of course, be converted to the amount which would have been necessary in the regular procedure using 20 grams of standard kauri solution. This can be accomplished by the simple proportion:

$$X = 20 S/W$$

where X = kauri butanol value
 W = weight of standard kauri solution used in grams
 S = cc. of solvent used in the titration

The procedure used in computing results can be best illustrated by describing the standardization of the kauri solution for microwork. With 0.2236 gram of the kauri solution, 1.25 cc. of c. p. benzene were required to produce a permanent turbidity. Therefore, 20 grams of this kauri solution would

require $\frac{20 \times 1.25}{0.2236} = 111.8$ cc. of benzene. Similarly, it was

found that 0.2234 gram of the same kauri solution required 0.34 cc. of *n*-heptane, equivalent to 30.4 cc. of *n*-heptane for 20 grams. The two values, 111.8 and 30.4, are called the kauri butanol values of benzene and *n*-heptane, respectively. Previous work (1) had shown that if the solvent power of c. p. benzene was arbitrarily given a value of 100, the solvent power of *n*-heptane would be found to be 25.4 (provided the proper

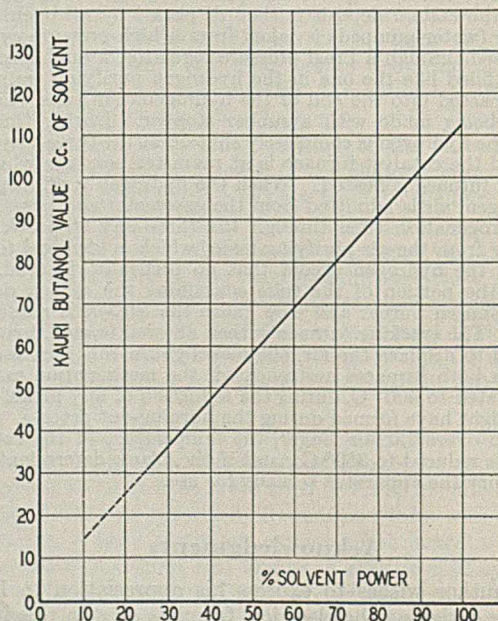


FIGURE 1. SOLVENT POWER CURVE OF KAURI BUTANOL STANDARD SOLUTION

TABLE II. COMPARISON OF RESULTS OBTAINED WITH THE MICRO- AND STANDARD METHODS

Hydrocarbon	Kauri Solution Used Gram	Hydrocarbon Titrated Cc.	Kauri Butanol Value	Solvent Power		Difference %
				Micro-method %	Standard method %	
<i>n</i> -Octane	0.2376	0.35	29.4	24.3	24.5	-0.8
Trimethylpentane	0.2226	0.335	30.1	24.7	24.6	+0.4
<i>n</i> -Tetradecane	0.2221	0.26	23.4	18.6	18.9	-1.6
Methylcyclohexane	0.2157	0.63	58.4	50.5	50.7	-0.4
Ethylbenzene	0.2339	1.14	97.5	86.5	87.6	-1.3
<i>n</i> -Butylbenzene	0.2278	0.91	79.8	70.1	70.1	0
Decahydronaphthalene	0.2159	0.76	70.4	61.6	60.5	+1.8

grade of kauri gum was used in preparing the standard solution). It is therefore only necessary to plot the kauri butanol values of *c. p.* benzene and *n*-heptane against their respective solvent powers and draw a straight line between these two points in order to obtain the standardization curve of the particular kauri solution used for this work. The curve as obtained from the data given in Table I is shown in Figure 1.

Comparative results of solvent power by the micro- and regular procedures on several hydrocarbons are given in Table II, and show that the microprocedure gives results with maximum deviations of under ± 2 per cent from the regular procedure, an accuracy which is deemed to be sufficiently good for a test of this nature.

Solvent Power of Hydrocarbons

The solvent powers of a number of hydrocarbons were determined, using the micro-method when necessary. Some of the compounds were purchased from supply houses, while others were synthesized in the laboratory. In order to allow for differences in room temperatures when carrying out the tests and put the results on a comparable basis, the densities of the various hydrocarbons were obtained at room temperature with a 2-cc. pycnometer calibrated against water at 4°C. Solvent power results can then be expressed on a weight basis by multiplying volume results by respective densities.

TABLE III. SOLVENT POWER OF PARAFFIN HYDROCARBONS

Hydrocarbon	Formula	Number of Carbon Atoms	Solvent Power	Density	Solvent Power by Weight
<i>n</i> -Pentane	C ₅ H ₁₂	5	33.8	0.624	21.1
Isopentane	C ₅ H ₁₂	5	28.8	0.617	17.7
<i>n</i> -Hexane	C ₆ H ₁₄	6	26.5	0.660	17.5
2-Methylpentane	C ₆ H ₁₄	6	25.0	0.654	16.5
<i>n</i> -Heptane	C ₇ H ₁₆	7	25.4	0.684	17.4
<i>n</i> -Octane	C ₈ H ₁₈	8	24.5	0.707	17.3
Isooctane	C ₈ H ₁₈	8	24.3	0.704	17.2
Trimethylpentane	C ₈ H ₁₈	8	24.7	0.722	17.8
Diisoamyl	C ₁₀ H ₂₂	10	24.5	0.730	17.9
Dodecane	C ₁₂ H ₂₆	12	18.7	0.751	14.0
<i>n</i> -Tetradecane	C ₁₄ H ₃₀	14	18.6	0.767	14.3
<i>n</i> -Hexadecane	C ₁₆ H ₃₄	16	14.3	0.777	11.1

The results are given in Tables III to VI. It is, of course, realized that the list of the hydrocarbons tested is not very comprehensive, representing only a few compounds chosen from the best known series. These hydrocarbons are merely cited as examples, in order to show the possibilities inherent to the method and illustrate the procedure used in computing the solvent powers of the various types of hydrocarbons.

The results in Table III show that the solvent powers of paraffin hydrocarbons decrease with increasing number of carbon atoms. The solvent power results have been plotted against the number of carbon atoms in Figure 2, and an average straight line has been drawn through the various points. From the equation of this line

$$y + 0.6x = 22 \quad (1)$$

where x is the number of carbon atoms and y represents the solvent power (by weight), the solvent power of any paraffin hydrocarbon can be calculated.

The solvent power of a few olefins is given in Table IV.

The results show that the introduction of a double bond definitely increases the solvent power of saturated hydrocarbons. Since the solvent power of paraffins decreases with increasing molecular weights, the data indicate that the effect of the double bond must increase with increasing molecular weight. In other words, between two hydrocarbons of the same number of carbon atoms alike in structure, except that one has a double bond and the other no double bond, it has been found that the former will have higher solvent power. In view of the fact that purity of the olefin samples tested was questionable, no mathematical correlation has been tried.

TABLE IV. SOLVENT POWER OF OLEFIN HYDROCARBONS

Hydrocarbon	Formula	Number of Carbon Atoms	Solvent Power	Density	Solvent Power by Weight
Hexene	C ₆ H ₁₂	6	33.6	0.683	23.0
Octylene	C ₈ H ₁₆	8	36.5	0.722	26.4
Diisobutylene	C ₈ H ₁₆	8	35.2	0.719	25.4
Diisoamylene	C ₁₀ H ₂₀	10	35.8	0.773	27.7
Triisobutylene	C ₁₂ H ₂₄	12	32.3	0.758	24.5

Table V gives the solvent power of representative naphthenes of the cyclohexane series. The values show that the solvent powers of the naphthenic hydrocarbons of the cyclohexane series decrease with increasing length of the paraffinic side chain. It would seem logical to expect that the solvent power of any hydrocarbon in this series should consist of the sum of the ring solvent power "effect" plus the paraffinic solvent power "effect." These various effects should also be proportional to the number of carbon atoms of each type. For example, methylisopropylcyclohexane possesses 6 naphthenic and 4 paraffinic, or a total of 10 carbon atoms. The naphthenic effect should therefore be equal to $\frac{6}{10}$ of the solvent power of the original ring and the paraffinic effect to $\frac{4}{10}$ of that of the paraffin having the corresponding number of carbon atoms, or butane, in this case. Therefore, the solvent power of any hydrocarbon in the cyclohexane series should be:

$$S = 42.1 \left(\frac{6}{P+6} \right) + y \left(\frac{P}{P+6} \right) \quad (2)$$

where

S = solvent power by weight

42.1 = solvent power of cyclohexane

P = number of paraffinic carbon atoms

6 = number of naphthenic carbon atoms

y = solvent power of the paraffin having P carbon atoms

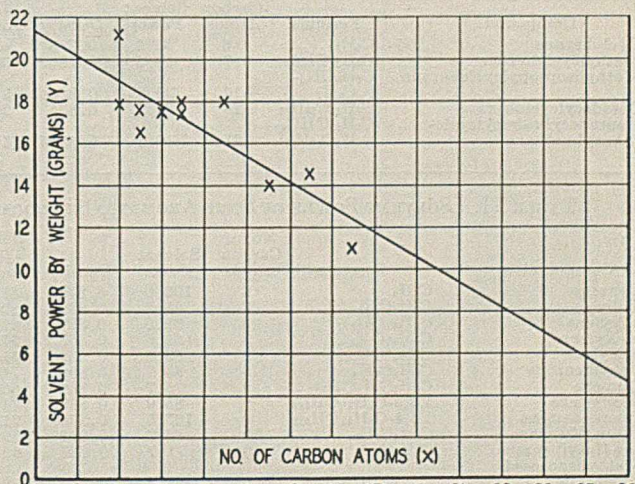


FIGURE 2. SOLVENT POWER OF PURE PARAFFIN HYDROCARBONS
Equation for curve: $y + 0.6x = 22$

The value of y can be computed from Equation 1 or obtained directly from the curve in Figure 2.

The curve represented by Equation 2 has been plotted in Figure 3. There are also plotted in Figure 3 experimental values, shown as small circles, of the solvent powers of five hydrocarbons. The calculated and experimental values are given in Table V. The agreement is good when allowance is made for inaccuracies in the method and the possible presence of impurities in some of the compounds.

In the same way the solvent powers of aromatic hydrocarbons have been calculated and compared with experimental values. The calculations were made using Equation 2, introducing 87.8, the solvent power of benzene, in place of 42.1, the solvent power of cyclohexane. The values are shown in Table VI and the curve in Figure 4.

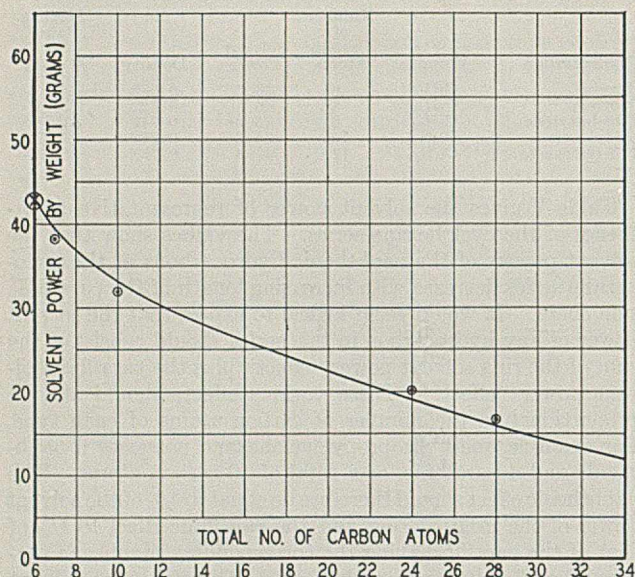


FIGURE 3. SOLVENT POWER OF NAPHTHENIC HYDROCARBONS, CYCLOHEXANE SERIES

Comparison of actual with calculated values
Actual determinations ●

Curve plotted from equations: $S = 42.1 \left(\frac{6}{P+6} \right) + y \left(\frac{P}{P+6} \right)$

TABLE V. SOLVENT POWER OF SOME NAPHTHENIC HYDROCARBONS

Compound	Formula	No. of Carbon Atoms	Solvent Power	Density	Solvent Power Times Density Found	Solvent Power Times Density Calculated
Cyclohexane	C_6H_{12}	6	54.3	0.775	42.1	42.1
Methylcyclohexane	$C_7H_{14}CH_3$	7	50.5	0.764	38.6	39.1
Methylisopropylcyclohexane	$C_8H_{16}CH_2-CH_2-CH_3$	10	39.3	0.820	32.2	33.1
Octadecylcyclohexane	$C_{24}H_{48}C_{18}H_{37}$	24	24.2	0.834	20.4	18.9
Heptadecyl- <i>n</i> -butylcyclohexylmethane	$C_{28}H_{56}C_{17}H_{34}$	28	19.8	0.8395	16.6	15.9

TABLE VI. SOLVENT POWER OF SOME AROMATIC HYDROCARBONS

Compound	Formula	No. of Carbon Atoms	Solvent Power	Density	Solvent Power Times Density Found	Solvent Power Times Density Calculated
Benzene	C_6H_6	6	100.0	0.878	87.8	87.8
Toluene	C_7H_8	7	93.7	0.882	82.6	78.4
<i>o</i> -Xylene	$C_8H_{10}(CH_3)_2$	8	99.0	0.879	87.0	71.1
<i>m</i> -Xylene	$C_8H_{10}(CH_3)_2$	8	89.6	0.863	77.3	71.1
<i>p</i> -Xylene	$C_8H_{10}(CH_3)_2$	8	82.5	0.861	71.0	71.1
Ethylbenzene	$C_8H_{10}C_2H_5$	8	85.7	0.868	74.4	71.1
Cumene	$C_9H_{12}CH(CH_3)_2$	9	75.7	0.864	65.2	65.2
Mesitylene	$1,3,5-C_6H_3(CH_3)_3$	9	85.9	0.863	74.2	65.2
Pseudocumene	$1,3,4-C_6H_3(CH_3)_3$	9	105.5	0.870	91.8	65.2
<i>n</i> -Butylbenzene	$C_{10}H_{14}C_4H_9$	10	68.7	0.862	59.2	60.5
<i>tert</i> -Butylbenzene	$C_{10}H_{14}C_4H_9$	10	71.7	0.867	62.2	60.5
Methylisopropylbenzene	$C_{10}H_{14}C_3H_7$	10	68.3	0.857	58.5	60.5
<i>tert</i> -Amylbenzene	$C_{11}H_{16}C_5H_{11}$	11	66.0	0.874	57.7	56.5
Octadecylbenzene	$C_{24}H_{32}C_{18}H_{37}$	24	37.0	0.906	32.6	30.4

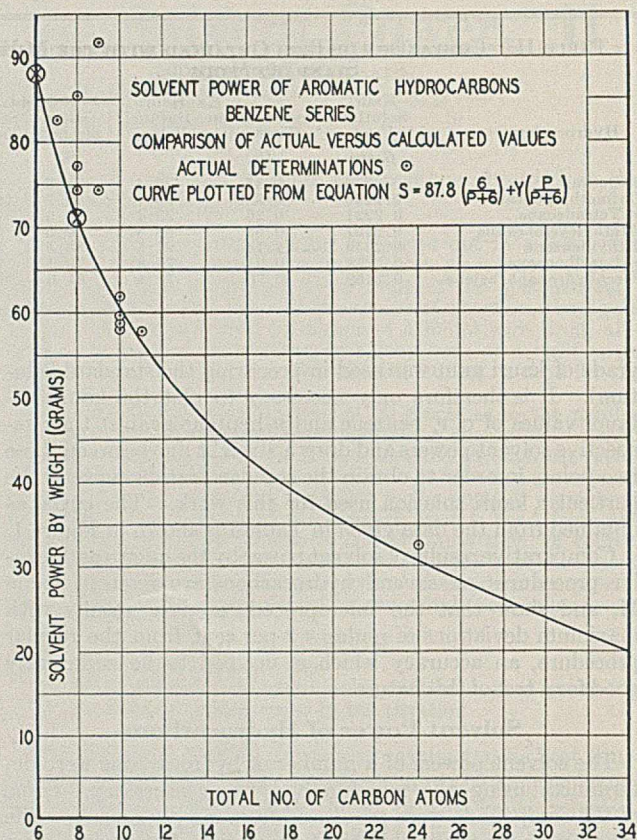


FIGURE 4. SOLVENT POWER OF AROMATIC HYDROCARBONS, BENZENE SERIES

A comparison of the calculated with the experimental values shows, with some exceptions, fair agreement. These exceptions are principally *o*- and *m*-xylenes, pseudocumene, mesitylene, and, to a lesser extent, toluene. It should be noted that the calculated and experimental data for the symmetrical xylene are practically identical. In view of the fact that some of the above compounds were known to be very pure, it is felt that these discrepancies may be due to the disturbing effect of the first substituted methyl group. This

explanation does not appear illogical, inasmuch as the first member of hydrocarbons in a given series often exhibits physical properties which are not in line with those of other hydrocarbons of the same series. The data on the naphthene and benzene hydrocarbons show that, in general, the solvent power of the compounds is affected by total length of the paraffinic chains, not the number of positions replaced in the ring.

Applications of the Procedure

From the above results and discussion it is evident that, given the solvent power of the first member of a hydrocarbon series, it is possible to calculate, or at least obtain a fair idea of the solvent power of other hydrocarbons of the same series. Conversely, the solvent power of an unknown hydrocarbon should give a clue to its composition and structure, thus providing an additional constant.

The method is rapid (about 20 minutes per determination) and very useful in hydrocarbon analysis, such as the examination of commercial hydrocarbon solvents. The method will give valuable indications when used in conjunction with other

physical constants, such as boiling point, etc., in the examination of narrow cuts consisting of isomeric and azeotropic mixtures. Thus the presence of large amounts of *o*-xylene in a close xylene cut can be readily detected. The method is also useful in determining efficiencies of fractionating columns by determining the solvent powers of the cuts obtained by the fractionation of close-boiling binary hydrocarbon mixtures.

Acknowledgment

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Literature Cited

- (1) Baldeschwieler, E. L., Troeller, W. J., and Morgan, M. D., *IND. ENG. CHEM., Anal. Ed.*, 7, 374 (1935).
- (2) Beard, L. C., Shipp, V. L., and Spelshouse, W. E., *Ibid.*, 5, 307 (1933).
- (3) Kiehl, J. R., *Am. Paint Varnish Mfrs. Assoc., Circ.* 319, 585-96 (1927).
- (4) Stewart, J. R., *Ibid.*, *Circ.* 378, 143-53 (1931).

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Determination of Small Proportions of Sulfur By a Modification of the A. S. T. M. Lamp Method

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Refinements of the standard lamp method are described which extend its range to the analysis of 0.0001 per cent of sulfur, in liquids or gases. Purified air for combustion, and turbidimetric estimation of sulfur as barium sulfate, permit high accuracy and reproducibility.

THE determination of the sulfur content of volatile organic compounds by A. S. T. M. method No. D90-34T, which consists in burning a weighed sample in a lamp and determining the acidity of the products of combustion, is subject to large errors when the material being analyzed contains less than 0.01 per cent of sulfur. There are two important sources of error. The first is the impurities in the relatively large volume of air used for combustion. The effect on the analysis of sulfur dioxide or hydrogen sulfide in the air is obvious; but nonsulfurous substances, such as fumes of acids or ammonia, may also pass into the absorber liquid and influence the final titration. The second source of error, which cannot be neglected in the analysis for small proportions of sulfur, is the formation of small amounts of acids in the flame: nitric acid by oxidation of atmospheric nitrogen, and organic acids by incomplete combustion of organic materials.

It is, of course, possible to apply corrections for impurities in the air by running blank samples; but since variations in air flow through individual lamps or fluctuations of flames may destroy the uniformity of the conditions, it seems preferable not to have to rely on blank determinations when high accuracy is desired. Therefore, in this modification of the standard method, purified air is used for combustion of the sample. The effect of nonsulfurous acids formed in combustion is eliminated by determining sulfur as barium sulfate.

Methods using purified air have been described (1, 2, 3), but the apparatus involved have not been convenient when large numbers of routine analyses were required. The arrangement described below, which uses purified air in a special lamp, permits the combustion of volatile liquids, including those that tend to burn with smoky flames in the standard A. S. T. M. apparatus; the equipment can also be adapted to the analysis of gases or liquefied gases under pressure. The products of combustion are absorbed in a solution of sodium hypobromite; after precipitation of the sulfate from the absorbing solution by barium chloride, barium sulfate is determined turbidimetrically. It has been found possible to analyze accurately for proportions of sulfur as low as 0.0001 per cent.

Apparatus and Reagents

THE AIR-PURIFICATION SYSTEM. The air for combustion is purified by heating it to a high temperature and then scrubbing with hypobromite and caustic solutions. It is

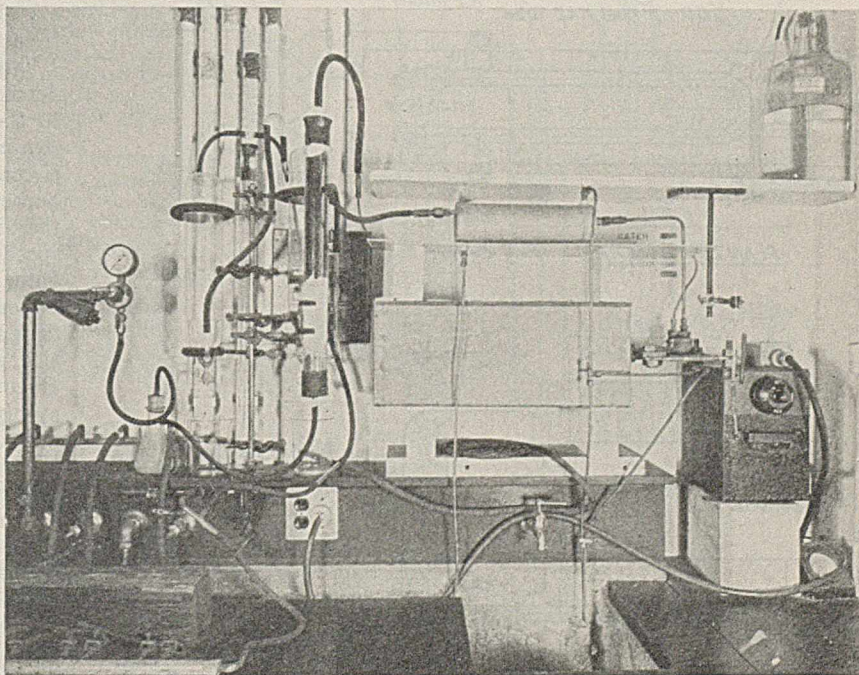


FIGURE 1. EQUIPMENT FOR PURIFYING AIR

first passed through a tube containing cotton and a layer of activated charcoal and then through a stainless steel tube heated by electrical resistance; the exit half of the tube is filled with coarse quartz chips. The exit air should have a temperature of about 500° C.; for a battery of ten lamps, the air required will be sufficiently heated if the surface of the center portion of the tube is kept at approximately 800° C. The temperature of the tube may be estimated roughly from the brightness of the metal observed through a peephole in the insulation, or an optical pyrometer may be used. The heated air is water-cooled in a small copper-coil condenser and finally led into two large cylindrical scrubbers equipped with fritted-glass plates (20- to 25-mesh); the first scrubber contains a 2 per cent solution of sodium hypobromite (stock absorbing liquid) and the second 5 per cent sodium hydroxide. Details of the tube furnace are shown in Figures 1 and 2.

Merely scrubbing the air without preheating it is not sufficient to remove sulfurous impurities completely. With the equipment described, however, blank determinations made by passing the purified air over platinum in a hot tube and into an absorber showed that 5 hours' running produced a negligible turbidity (as barium sulfate). Consequently, no correction for sulfurous impurities in the air is necessary, and inaccuracies resulting from variations in air flow through the individual lamps are obviated.

THE BURNER. The burner (Figure 3) consists of two coaxial glass tubes, which extend upward to the same height to form the burner tip, and are sealed together at the bottom. A side inlet into the outer tube admits the air which, when needed, supports the combustion at the base of the flame, and a small hole near the seal joining the tubes permits the pressure to equalize between the sample flask and the combustion chamber.

For use with gases and liquefied gases a Bunsen microburner is used; it is connected to the source of purified air by means of a short piece of metal tubing soldered to the air inlet at the bottom of the burner. A metal cylinder 3 cm. in length and

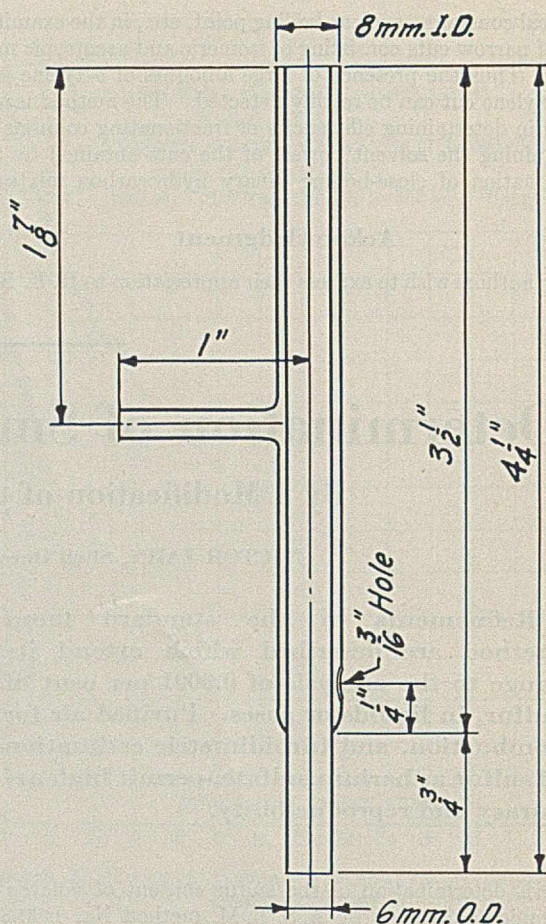


FIGURE 3. BURNER

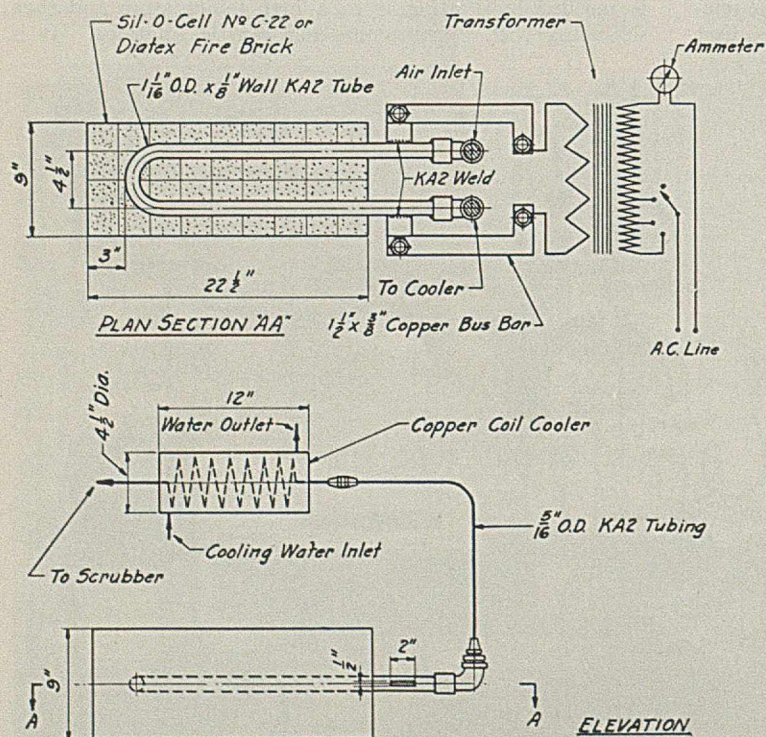


FIGURE 2. DETAIL OF RESISTANCE FURNACE

1.5 cm. in diameter is soldered to the base of the burner to support the cork by which the burner is sealed to the chimney. Such a burner may be seen in Figure 7, in the lamp at the extreme left of the battery.

THE CHIMNEY. The chimney is shown in detail in Figure 4. The inner chamber is similar to the conventional chimney, but the new design includes an outer cylindrical chamber, which is constricted at the bottom and sealed to the burner by a cork stopper, and a side inlet at the top which admits purified air to the annular space between the essential chimney and the outer chamber.

Cork stoppers seal the burner to the sample flask below and the chimney above. In operation, most of the air enters the assembled lamp (Figure 5) through the upper inlet, and passes evenly downward through the annular space and into the chimney, from which it sweeps the products of combustion into the absorber.

THE ABSORBER. The usual A. S. T. M. absorbers may be used. A modified design, however, with a fritted-glass plate (30- to 35-mesh) sealed near the bottom (Figure 6), instead of glass-bead packing, permits gases from the combustion chamber to pass through more steadily and minimizes flickering. A Kjeldahl connecting bulb with a single straight tip serves as a spray trap.

REAGENTS. A solution of 2 per cent c. p. sodium hydroxide and 2 per cent c. p. bromine in distilled water is used as absorbing liquid. Fifteen milliliters of this stock solution plus 10 to 15 ml. of distilled water are used in each absorber.

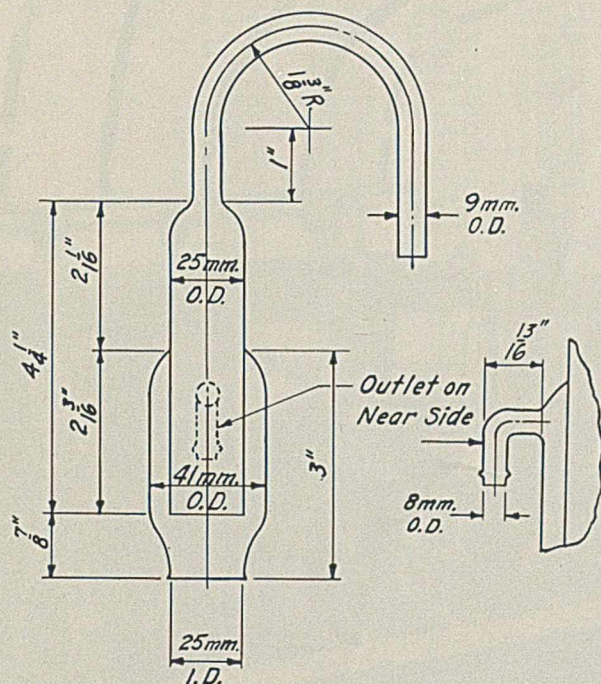


FIGURE 4. CHIMNEY

The turbidimetric determination of sulfur requires 1 *N* hydrochloric acid; 20 per cent solution of c. p. sodium hydroxide; alcohol-glycerol solution, containing 67 per cent by volume of denatured ethyl alcohol (Formula 3A) and 33 per cent of glycerol U. S. P.; and c. p. barium chloride crystals, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, 20- to 30-mesh.

Procedure

COMBUSTION. Four strands of sulfur-free cotton wicking are threaded into the inner tube of the burner. The wick is primed with the liquid to be tested, cut off evenly, flush with the top of the tube, and drawn down 1 or 2 mm. so as not to leave any protruding filaments. For volatile materials like acetone, it may be necessary to draw the wick down 15 to 20 mm. in order to obtain a flame of proper size.

The arrangement in use at present (shown in Figure 7 in partial view) consists of a battery of ten lamps connected to a manifold that distributes air at constant pressure to each lamp through separately regulated inlets to burner and chimney. In putting a battery of lamps into operation, it is best to start with the lamps in place and sufficient air flowing through the manifold to supply all the lamps and the constant-pressure release valve, but with all the pinchclamps on the rubber tubing to the burners closed. One lamp at a time is then removed from its chimney, lighted with an alcohol lamp, adjusted, and put back into the neck of the chimney. The entire battery can readily be set in operation within a few minutes.

Any further adjustment is made after the lamps have been lighted by changing the rate of air flow to the burner or to the chimney. The steadiest flames are obtained with the system under slight pressure with no suction on the absorber, and with only the air needed for good combustion passing through the burner. The rest of the air needed for an analysis enters the system through the chimney; in this way the flame is not cooled below the ignition temperature for less combustible substances by the current of primary air, nor disturbed by too rapid flow of air through the lamp, and the danger of extinguishing the flame is minimized. No suction is required

for burning liquid samples, but suction on the absorber may be used in starting the combustion of gases or liquefied gases with the microburner described above.

The amount of sample burned is determined by the loss in weight of the lamp and sample flask, as in the standard method. According to the proportion of sulfur present, approximately the following amounts of sample should be burned:

Sulfur %	Weight of Sample Burned Grams
0.0001 and less	10 or more
0.0002 to 0.0006	10
0.0007 to 0.0015	5
0.0016 to 0.006	4
0.007 to 0.015	2

TURBIDIMETRIC DETERMINATION. After the sample is burned, the absorber liquid is made ready for the determination of sulfate with a Betz-Hellige turbidimeter (5). This instrument compares the intensity of light scattered laterally by a solution containing barium sulfate with that transmitted by the solution. The intensity of the transmitted light may be altered by means of a precision slit, so that the illumination from the separate beams may be balanced. The liquid from the absorber, with the washings from absorber, spray trap, and chimney, is transferred to an Erlenmeyer flask, acidified with 15 ml. of 1 *N* hydrochloric acid, boiled to remove carbon dioxide and excess bromine, and concentrated to about 25 ml. It is then made slightly alkaline to phenolphthalein with a 20 per cent solution of sodium hydroxide, and exactly neutralized with 1 *N* hydrochloric acid, after which 3 ml. more of the acid are added, and the solution is filtered through Whatman No. 42 filter paper into a 50-ml. volumetric flask and made up to the mark with distilled water.

The contents of the flask are transferred to the 20-mm. optical cell of the turbidimeter and 10 ml. of the alcohol-glycerol solution are stirred into the solution with a rubber-tipped glass rod; the initial turbidity, if any, is then determined. In accurate work, samples showing initial turbidity should be discarded and the analysis repeated; however, it is possible to correct the final results for initial turbidity. After the standard measure (supplied with the turbidimeter) of barium chloride crystals has been added to the solution, the turbidity is determined as described in (5).

When the absorber liquid contains more than 0.6 mg. of sulfur, it is usually more accurate to take a carefully measured aliquot,

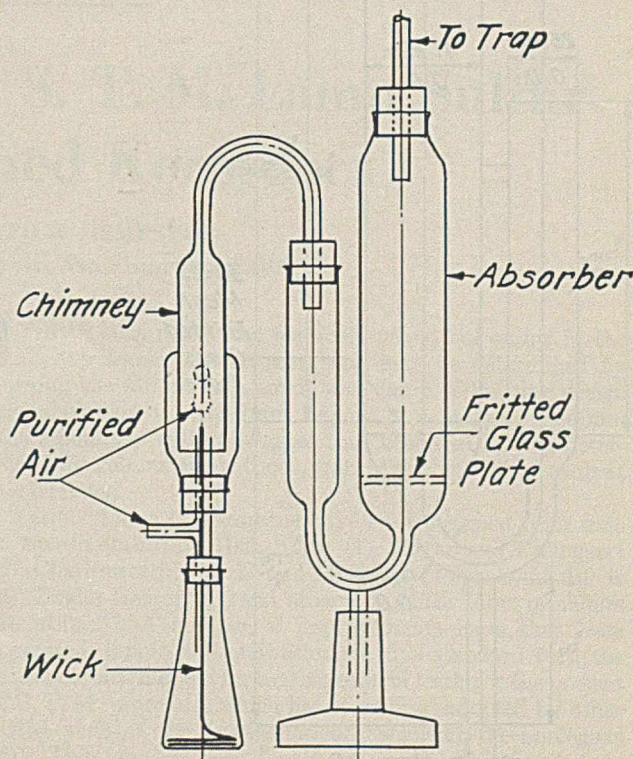


FIGURE 5. ASSEMBLY

say one-half or one-fifth, of the 50 ml. of solution, dilute it to 50 ml., and use the 20-mm. cell, than to use the smaller cell. But errors in dial reading are then multiplied by the reciprocal of the aliquot. If, however, the 10-mm. cell is used, 25 ml. of the 50 ml. of original solution are used and 5 ml. of alcohol-glycerol are added. The clear filter is, of course, necessary. Otherwise the procedure is exactly as described.

Blank determinations are made in the turbidimeter on all the reagents, including those used in the preparation of the reference curves, in the amounts used in the analysis and the proportions of sulfur so found are deducted from the total amount found in the final turbidimetric determination of the sample. Blank determinations made on the purified air, by passing it through the absorber liquid for the time taken to burn a sample and with about the same velocity as in the analysis, must be negative.

The colloid-protecting alcohol-glycerol solution substituted for the salt-acid solution (5), in the final treatment of the absorber liquid before precipitation, appears to improve the sensitivity of the turbidimetric determination to very small amounts of sulfate. Furthermore, it minimizes particle growth of the barium sulfate suspension during adjustment of the turbidimeter; the protected suspension is sufficiently stable that turbidimeter

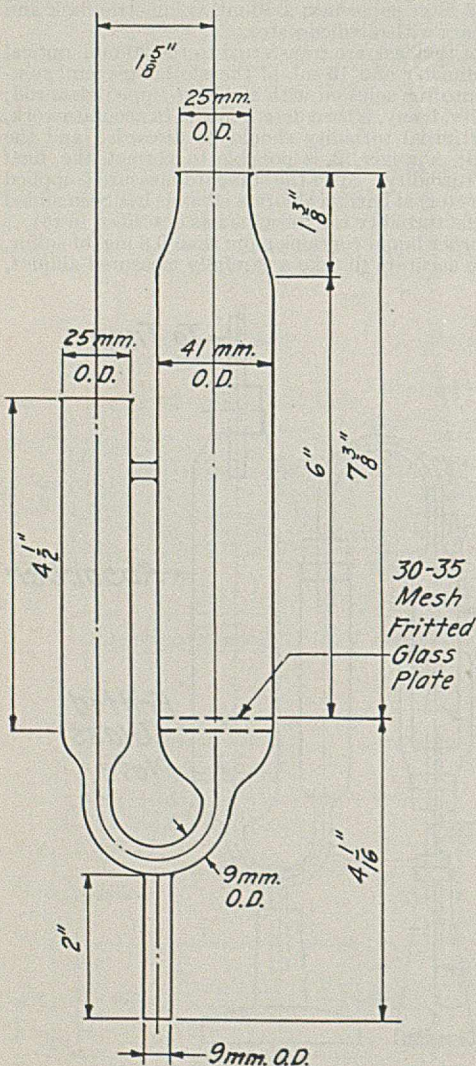


FIGURE 6. ABSORBER

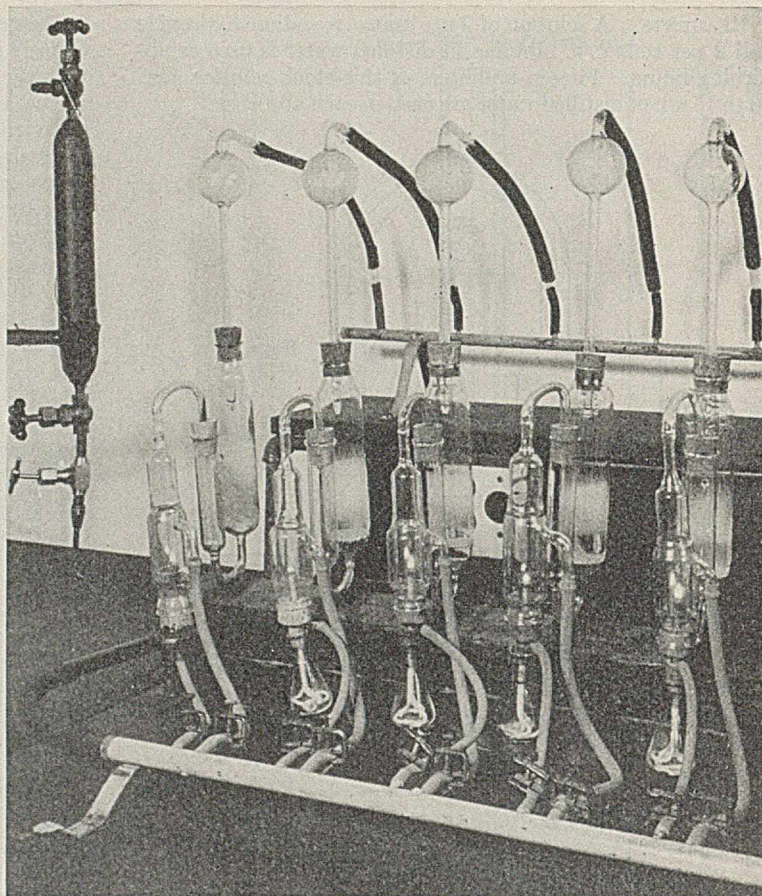


FIGURE 7. LAMPS IN OPERATION

readings taken over the interval from 3 to 12 minutes after precipitation show little variation.

REFERENCE CURVES FOR THE TURBIDIMETER. Because of modifications which have been made in the turbidimetric procedure, a set of reference curves relating dial setting to milligrams of sulfur in the sample should be prepared for each turbidimeter; the data for the curves should be found by a procedure as nearly as possible like that for analysis. A curve for each of the following ranges is necessary:

Range	Sulfur Mg.	Filter	Cell Mm.
I	0 to 0.08	Gray	20
II	0 to 0.26	Milk	20
III	0 to 0.6	Clear	20
IV	0 to 1.8	Clear	10

The additional reagents needed are c. p. sodium sulfate, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$; and a solution of 1 N c. p. sodium chloride containing 200 ml. of 1 N hydrochloric acid per liter. The solution must be filtered until zero turbidity is obtained.

Two standard sodium sulfate solutions are made up, one containing 0.1 mg. of sulfur per ml. and the other 0.2 mg. per ml., both of which must be checked by gravimetric analysis. The first solution and a 1 to 10 dilution of it are used for the data in ranges I to III; the second is used with the 10-mm. cell to determine range IV. Fifteen milliliters of the acid sodium chloride solution are measured into a 50-ml. volumetric flask, the proper amount of standard sodium sulfate solution is added, and the solution is made up to 50 ml. with distilled water. For determinations in the first three ranges the whole solution is transferred to the 20-mm. cell, 10 ml. of alcohol-glycerol are added, and the precipitation and reading are made as previously described. For range IV, 25 ml. of the contents of the volumetric flask are put in the 10-mm. cell, 5 ml. of alcohol-glycerol are added, and the described procedure is followed. Obviously the milligrams of sulfur found from a curve prepared in this way for

TABLE I. DETERMINATION OF SULFUR

Sam- ple	Sulfur Added to Hydrocarbon %	Individual Determinations							Mean of Determinations %	Sulfur Present in Sample %	Standard Deviation %
		%	%	%	%	%	%	%			
1	None	0.00020	0.00022	0.00019	0.00018	0.00019	0.00020	0.00020 (by analysis)	0.000017
2	0.0001	0.00021	0.00029 ^a	0.00020	0.00023	0.00022	0.00033	0.00030	0.000025
3	0.0003	0.00030	0.00031	0.00033	0.00030	0.00035	0.00050	0.00050	0.000029
4	0.0005	0.00036	0.00036	0.00031	0.00030	0.00037	0.00070	0.00070	0.000042
5	0.001	0.00044	0.00048	0.00046	0.00052	0.00051	0.00119	0.00120	0.000051
6	0.002	0.00051	0.00049	0.00054	0.00049	0.00054	0.00217	0.00220	0.000010
7	0.005	0.00066	0.00065	0.00067	0.00073	0.00073	0.00514	0.00520	0.000010
8	0.010	0.00065	0.00068	0.00072	0.00079	0.00077	0.0102	0.0102	0.000012
		0.00120	0.00119	0.00118	0.00118	0.00123	0.00125	0.00123	0.0102	0.0102	0.00010
		0.00119	0.00119	0.00119	0.00115	0.00118	0.00119	0.00115	0.0102	0.0102	0.00010
		0.00222	0.00223	0.00222	0.00221	0.00215	0.0102	0.0102	0.00012
		0.00218	0.00198	0.00231	0.00198	0.00224	0.0102	0.0102	0.00012
		0.0050	0.0052	0.0052	0.0052	0.0051	0.0052	0.0051	0.0102	0.0102	0.00012
		0.0051	0.0051	0.0051	0.0050	0.0052	0.0052	0.0053	0.0102	0.0102	0.00012
		0.0101	0.0103	0.0101	0.0101	0.0100	0.0102	0.0103	0.0102	0.0102	0.00012
		0.0103	0.0103	0.0100	0.0102	0.0102	0.0101	0.0103	0.0102	0.0102	0.00012

^a Result discarded on Chauvenet's criterion (4). This value is not included in the mean.

range IV and the 10-mm. cell will be the amount contained in the 50-ml. sample.

Accuracy and Precision of Results

The method was tested by analyzing a hydrocarbon of low, unknown sulfur content, and the same hydrocarbon containing varying, known, added amounts of sulfur as dimethyl disulfide. A series of ten or more analyses was made at each of eight different sulfur concentrations; the results of the individual determinations are given in Table I.

The precision of the method may be judged from the last column, which shows the standard deviation for each series of analyses; the value given is, in each case, within 20 per cent of that for an infinite number of determinations.

In establishing the accuracy of this method of analysis, it was necessary to use the method itself to find the original sulfur concentration of the hydrocarbon used as diluent; consequently, the systematic error of the result for Sample 1

cannot be stated, although it may be assumed to be low from the accuracy with which the added amounts of sulfur in the other samples were determined. The means of the determinations and the percentages of sulfur in the samples are presented in adjacent columns. The systematic errors are small; when the standard errors at the various concentrations are calculated on the basis of four individual analyses, the systematic errors are not statistically significant.

Literature Cited

- (1) Edgar and Calingaert, *IND. ENG. CHEM., Anal. Ed.*, 2, 104 (1930).
- (2) Engler, *Chem.-Ztg.*, 20, 197 (1896).
- (3) Jackson and Richardson, *J. Inst. Petroleum Tech.*, 7, 27 (1921).
- (4) Mellor, "Higher Mathematics for Students of Chemistry and Physics," 3rd ed., p. 563, New York, Longmans, Green and Co., 1909.
- (5) Sheen, Kahler, and Ross, *IND. ENG. CHEM., Anal. Ed.*, 7, 262 (1935).

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A Modification of the A. S. T. M. Lamp Sulfur Method for Refined Kerosenes

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The lamp method for the determination of sulfur in petroleum oils, A. S. T. M. Designation D90-34T, has been modified to obtain a considerably greater degree of accuracy on refined kerosenes. It may be used with improved accuracy on other refined oils for which the foregoing A. S. T. M. method is suited. Data are given to show that it is essential to use purified air during burning, a greater amount of sample must be burned, hydrogen peroxide is preferred as an absorbing medium, and if accurate, reliable results are to be obtained, the total sulfur after absorption must be determined by gravimetric means.

IT HAS been recognized for many years that sulfur in the lighter fractions from petroleum may be determined by burning the sample in a small wick lamp of varying design and absorbing the resultant vapors in a suitable medium. The amount of sulfurous gases thus absorbed is then determined by volumetric methods, from which the sulfur content is calculated.

Various forms of apparatus have been designed from time to time, notably by Richardson (7), Edgar and Calingaert (2), Charlesworth, Harris, and Linder (1), Espach and Blade (4), Engler-Heuser (3), and others, in which these principles are utilized. A number of improvements have thus been suggested, but in the establishment of a standard test, the most practical method for routine control testing is the present A. S. T. M. procedure which has since been adopted by other bodies such as the Institution of Petroleum Technologists (5). This test has been found deficient in certain respects by various laboratories; the lamp needs a simple device for

flame adjustment, complete absorption in the sodium carbonate of products of combustion is questioned, and the end point with methyl orange is sometimes difficult to determine, particularly if the lamp has smoked. These factors become of increasing importance as the sulfur content of kerosene is reduced by the application of refining agents. In fact, recent investigations in the authors' laboratories have shown that the A. S. T. M. method is definitely unsuitable for the determination of the actual total sulfur content of a highly refined kerosene of the order of 0.010 per cent or less. Inasmuch as accurate data were required on such stocks, it was imperative that modifications be introduced.

Development of Modified Method

In developing the modified lamp sulfur method for kerosenes described below, several important factors had to be considered.

PURIFICATION OF THE AIR USED. The present A. S. T. M. procedure gives no recognition of the fact which has been stressed by many investigators, that the condition of the air in the laboratory which is used for the burning process has an important bearing on the results. It is true that a blank determination using alcohol is prescribed, but this is indefinite, in that the air used is not measured and frequently the blank obtained is too great to allow results to be determined accurately on highly refined kerosenes. To overcome this difficulty, all the air supplied to the flame in the modified method was purified by passing through a Davis canister for organic vapors and acid gases, which complies with Bureau of Mines Code OC-4 and contains soda lime and activated charcoal. Other equipment was tried but did not prove so practical or efficient. The use of purified air, as shown in Table I, definitely established that determinations made even in the best atmosphere are subject to appreciable error.

These results were obtained by burning one sample of kerosene on 4 successive days in a room in which the atmosphere was believed to be uncontaminated by sulfur compounds; appreciable differences are to be noted.

It may be of interest in this connection to note the magnitude of error produced by a small amount of carbon tetrachloride vapor in the air. It has been customary in this laboratory to run a standard consisting of duplicate samples of a kerosene which normally runs 0.010 per cent sulfur by the A. S. T. M. method. One day a small amount of carbon tetrachloride was spilled from a fire extinguisher in the room

TABLE I. A. S. T. M. METHOD

Laboratory Air %	Purified Air %
0.0113	0.0096
0.0097	0.0082
0.0121	0.0089
0.0084	0.0088

where sulfurs are burned. The blanks showed approximately 0.04 per cent "sulfur" on that particular day. To make sure that the carbon tetrachloride was the cause of the discrepancy, a small amount of it was purposely sprayed on the floor on another day with similar effects.

SIZE OF SAMPLE, LAMP, AND CHIMNEY. When determining sulfur on highly refined kerosenes, it is necessary to burn at least 20 grams of sample, preferably within a period of 6 to 8 hours. This is difficult with the present A. S. T. M. equipment, for the prescribed lamp, wick, and flame are too small. It was necessary therefore to develop a new lamp containing a larger wick, and after many trials two wicks burning in two glass wick tubes inserted through the same cork were decided upon, a wide-mouthed extraction flask of 150-ml.

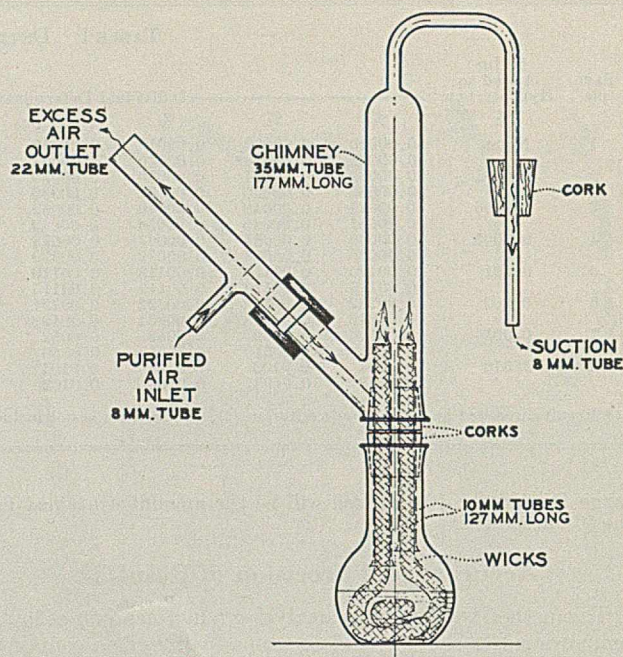


FIGURE 1. CHIMNEY-LAMP ASSEMBLY

capacity being used as the sample container. This equipment necessitated the use of a larger chimney of modified design as shown in Figure 1 to accommodate the larger cork holding the wick tubes, and to allow entrance of purified air. The extra heat generated by the two larger flames, even using humidified air, tends to evaporate the absorbing medium over a period of 6 to 8 hours' burning. It was therefore necessary to immerse the first absorber in a water bath which was kept cool with a small amount of ice; the second absorber which is also required need not be cooled.

ABSORBING MEDIUM. After investigating the comparative merits of sodium carbonate and hydrogen peroxide as absorbing media for sulfur trioxide, it was decided to use the latter reagent in both absorbers. It was found to give complete oxidation and absorption of the sulfuric oxides produced, thus avoiding the use of bromine, and it introduces less silica into the absorbent by contact with the glass over the burning period, than when sodium carbonate is used. However, only the highest grade of hydrogen peroxide must be employed and a blank determination must be made.

VOLUMETRIC vs. GRAVIMETRIC DETERMINATION OF SULFUR AFTER BURNING. The present A. S. T. M. procedure uses volumetric means for determination of the sulfur in the used absorbent. This is reproducible in itself, but on determining sulfur as barium sulfate by microgravimetric means on the same used absorbent, it was found that only a portion of the so-called "sulfur" calculated from the titration is actually sulfur. By way of illustration, one sample of highly refined kerosene gave 0.0077 per cent "sulfur" by titration and only 0.00167 per cent sulfur by microgravimetric determination. The titration in this case was 3.17 ml. of 0.0624 N sodium hydroxide, 41.3 grams of sample being burned. This gravimetric figure of 0.00167 per cent accounts for only 0.69 ml. of the 3.17-ml. titration, leaving 2.48 ml. or 78 per cent of the titration not accounted for. Tests indicate that nitrates are present in considerable proportion, and it is believed that various aliphatic or unsaturated acids are present. In view of these findings, it was essential to resort to microgravimetric means for determining the total sulfur.

DETERMINATION OF SULFATE. Experiments were made with sodium rhodizonate as an indicator for barium. It was

not found sufficiently sensitive for use with such small quantities of sulfate as were present in used solutions.

Further experiments were then made by adding an excess of sodium sulfate and evaporating the solution to dryness. All the sulfate was thus converted to bisulfate and the volatile acids (such as nitric acid) should be driven off. However, nitric acid was only slightly volatilized under these conditions, even when the residue was heated at 105° C. for half an hour.

SOURCES OF ERROR. The possibility that sulfur trioxide mist might be incompletely absorbed by the aqueous hydrogen peroxide solutions was considered. A sintered-glass filter disk was placed behind the second absorber; after 7 hours' absorption, no acidity to methyl orange was detectable, which indicated that complete adsorption had taken place.

Some investigators have reported that some sulfur compounds are preferentially adsorbed by a cotton wick. This possibility was studied by burning four samples with cotton and then with glass-wool wicks, the following results being obtained:

Sample	Sulfur	
	Cotton wick <i>P. p. m.</i>	Glass-wool wick <i>P. p. m.</i>
1	16.7	18.6
2	15.0	16.7
3	32.9	38.0
4	196.0	193.0

In most cases the glass wool gave slightly higher results, but the difference is probably within experimental error.

In order to check the modified method on a sample of known sulfur content, a highly refined kerosene of 4.5 parts per million total sulfur was blended with *n*-butyl sulfide (Eastman Kodak Company) to produce a sample of 14.9 parts per million total sulfur. Duplicate results on this sample by the modified method were 15.2 and 14.0 *p. p. m.*,

which is considered satisfactory accuracy. Espach and Blade (4) found that the sulfur in all the compounds which they tested was completely burned if present in amounts not more than 0.10 per cent or 1000 *p. p. m.*

Experimental Results

The data in Table II have been obtained on four sulfur dioxide-treated kerosene distillates, each of which was submitted to increased acid treatment as indicated. Samples E-1 and E-2 represent a highly refined kerosene before and after distilling. The volumetric figures are those obtained by titration of the used absorbent before a gravimetric determination was made.

Discussion

Inspection of the foregoing data indicates that the gravimetric results are reproducible to a satisfactory degree, considering the small amounts of actual sulfur being determined. Differences between stocks are made apparent which are not disclosed by the A. S. T. M. procedure. In general the smaller the sulfur content the greater is the discrepancy between volumetric and gravimetric determinations.

When testing samples such as distillates and poorly-refined kerosenes which contain larger amounts of sulfur, it is not necessary to burn as large a sample as specified in the modified method.

The procedure for precipitation and ignition of barium sulfate is adapted from that described by Pregl (6).

Apparatus

BURNER. The fount is a 150-ml. wide-mouthed extraction flask. Two 2.5-cm. (1-inch) flat cotton wicks are rolled lengthwise and pulled by means of a wire through two Pyrex tubes, 10 mm. outside diameter, standard wall, 127 mm. long, flared at the bottom. The tubes pass through two corks, the lower one of which fits the neck of the flask, the upper one fitting into the chimney.

CHIMNEY. A Pyrex glass tube 35 mm. outside diameter, 177 mm. long. At the top it narrows down to an 8-mm. tube which in the shape of an inverted "U" makes the connection with the first absorber. A side tube about 22 mm. outside diameter, 50 mm. long, is attached to the chimney as near to the bottom as possible, pointing upward at an angle of 45°. Another tube of the same diameter, about 100 mm. long, is attached by 0.19-cm. (0.75-inch) rubber tubing to the side tube, as an extension of the latter. A tube 8 mm. outside diameter, 30 mm. long, is sealed perpendicularly into this extension tube at a point 30 mm. from its lower end.

ABSORBER. Two regular A. S. T. M. sulfur absorbers with spray traps are used in series connected by glass and rubber tubing, the rubber connections being made as short as possible. Rubber stoppers are used, except for the connection between the chimney and the first absorber which is made with a cork. The large chambers of the absorbers are filled with "resistant glass" rods about 10 mm. long.

AIR PURIFIER. The air supply to the burner is taken from the compressed air line and is purified by passage through a plug of cotton and a 2000-ml. Davis canister for use in organic vapors and acid gases. It is then passed through a humidifier consisting of a sulfur absorber containing distilled water, then through a spray trap, and finally into the side tube of the chimney.

Other requisites are: a flowmeter to indicate rate of passage of air through the absorbers; a glass jar, approximately 12 cm. in diameter, 23 cm. high, for cooling bath for first absorber; vacuum line, balance and weights accurate to 0.05 mg. at 2-gram load, and balance, accurate to 0.1 gram at 200-gram load. Neubauer microcrucibles of porcelain, with integral porous bottom; a filter flask of 125-ml. capacity with rubber tube, pinchcock for suction by mouth; glass and rubber tubing collar for holding Neubauer microcrucible; platinum crucible cover, wire triangle, gas burner, small crucible tongs; small wash bottles to deliver fine streams of 0.03 *N* hydrochloric acid and 95 per cent alcohol, respectively. Graduated pipets, 5 and 1 ml.; stirring rods, 4 by 120 mm.; rubber policeman to fit 4-mm. stirring rods; beakers, graduated cylinders, and funnels. A wire hook to adjust height of wicks, made from a piece of stiff wire such as a paper clip. The end is filed to a flat point and bent at right angles about 3 mm. from the point to make a hook.

TABLE II. COMPARATIVE DATA

(A. S. T. M. and modified lamp sulfur methods)

Sample	Treatment	A. S. T. M.			
		Method D90-34T %	Volumetric %	Modified Method Gravimetric %	<i>P. p. m.</i>
A	SO ₂ -treated distillate 0.16 # 15 F ^a	0.040	0.0360	0.0335	335.0
		0.014	0.0085	0.00326	32.6
		0.013	0.0088	0.00355	35.5
A-20	0.20 # 15 F	0.014	0.0080	0.00315	31.5
		0.013	0.0087	0.00329	32.9
		0.013	0.0080	0.00280	28.0
A-24	0.24 # 15 F	0.011	0.0087	0.00273	27.3
		0.012	0.0073	0.00270	27.0
		0.010	0.0077	0.00245	24.5
B	SO ₂ -treated distillate 0.20 # 15 F	0.026	0.0230	0.0197	197.0
		0.012	0.0070	0.00167	16.7
		0.014	0.0095	0.00186	18.6
B-25	0.25 # 15 F	0.012	0.0067	0.00165	16.5
		0.010	0.0077	0.00150	15.0
		0.012	0.0066	0.00170	17.0
B-35	0.35 # 15 F	0.014	0.0070	0.00152	15.2
		0.012	0.0065	0.00128	12.8
		0.015	0.0066	0.00128	12.8
C	SO ₂ -treated distillate 0.16 # 15 F	0.025	0.0176	0.0139	139.0
		0.012	0.0066	0.00166	16.6
		0.011	0.0076	0.00157	15.7
C-20	0.20 # 15 F	0.012	0.0071	0.00143	14.3
		0.015	0.0064	0.00147	14.7
		0.013	0.0078	0.00180	18.0
C-25	0.25 # 15 F	0.012	0.0072	0.00130	13.0
		0.013	0.0072	0.00160	16.0
		0.012	0.0067	0.00160	16.0
D	SO ₂ -treated distillate 0.20 # 15 F	0.023	0.0181	0.0125	125.0
		0.013	0.0068	0.00170	17.0
		0.014	0.0065	0.00163	16.3
D-25	0.25 # 15 F	0.014	0.0077	0.00190	19.0
		0.012	0.0069	0.00160	16.0
		0.013	0.0074	0.00160	16.0
D-35	0.35 # 15 F	0.012	0.0072	0.00150	15.0
		0.012	0.0065	0.00120	12.0
		0.010	0.0062	0.00132	13.2
E-1	Before distilling	0.010	0.0062	0.00091	9.1
		0.011	0.0063	0.00091	9.1
E-2	After distilling	0.013	0.0058	0.00045	4.5
		0.010	0.0061	0.00045	4.5

^a Fuming sulfuric acid, 15% SO₃.

Reagents

Merck's reagent Superoxol, approximately 30 per cent H_2O_2 ; sodium hydroxide or sodium carbonate solution, approximately 0.06 *N*; barium chloride solution, approximately 0.06 *N*; nitric acid solution, approximately 0.06 *N*; hydrochloric acid, approximately 0.03 *N*; sulfuric acid, concentrated; standard sulfuric acid solution, 0.0624 + 0.0002 *N*; alcohol, pure, 95 per cent; methyl orange indicator, 1 gram per liter of water.

Procedure

Place in the fount about 75 to 100 ml. of the kerosene to be tested. Use new wicks and tamp the tops of the wicks lightly with the wire hook so that the surfaces are flat and dense, and are depressed about 2 or 3 mm. below the tops of the glass tubes. Weigh the assembled burner, and charge each absorber with 1 ml. of reagent Superoxol and about 25 ml. of distilled water. Place the first absorber in the cooling bath, connect the absorbers with one another, and connect the chimney to the first absorber and the second absorber to the vacuum line. Connect the spray trap of the air humidifier to the small tube which is sealed into the extension of the side tube of the chimney.

Start the air blowing through the air purifier and start the suction through the absorbers. Immediately light the burner with a gas flame and place it in the chimney so that the tops of the wicks are slightly above the point where the side tube enters the chimney. The bottom of the chimney must be tightly closed by the cork fitting around the wick tubes. Adjust the suction so that the flames do not smoke; if necessary, tamp the wicks with the wire hook to reduce the height of the flame or pull the wicks up with the hook to increase the height of the flame. Adjust the amount of air passing through the purifier so that a slight excess escapes through the extension of the side arm of the chimney; this can be tested by stopping the opening momentarily with the finger. If an excess of air is escaping, the flames will be depressed, and if the amount of purified air is insufficient the flames will be elongated. Add ice to the cooling bath when necessary to keep the solution from evaporating in the first absorber, and replenish the water in the air humidifier when necessary.

After 6 to 8 hours' burning weigh the burner, rinse the spray traps into the absorbers, and transfer the solutions from the absorbers to a 250-ml. beaker. Neutralize the solution to methyl orange with 0.06 *N* sodium hydroxide or sodium carbonate, then make definitely acid with about 10 ml. of 0.03 *N* hydrochloric acid, cover with a ribbed watch glass, and evaporate to dryness on an asbestos-covered hot plate at a temperature which will just boil the liquid (or dispense with the watch glass and hasten the evaporation by blowing gently with purified air). Allow the residue to bake for 5 to 10 minutes on the hot plate to dehydrate the silica, and then digest for 5 minutes with a little water acidified with hydrochloric acid. Filter through a 7-cm. No. 42 Whatman paper into a 100-ml. beaker, washing the 250-ml. beaker four times with small portions of hot acidified water, then washing the filter three times. Heat approximately to boiling and add slowly with stirring 5 ml. of 0.06 *N* barium chloride (if more than 2 mg. of sulfur is expected use more barium chloride). Cover and boil gently until the volume is about 10 ml.

After at least 1 hour of digestion decant the liquid through an ignited and weighed Neubauer microcrucible, suction for the filtration being produced by the mouth and maintained by the pinchcock on the suction tube. Rinse the sides of the beaker with a fine stream (1 or 2 ml.) of 0.03 *N* hydrochloric acid. Stir the precipitate with a policeman and pour the mixture down the policeman into the crucible. Rub the sides of the beaker with the policeman, rinse, and transfer to the crucible, repeating until the precipitate appears to be completely transferred to the crucible. (Do not let the tip of policeman touch the surface of the liquid in the crucible, as the precipitate will run by capillarity up the stirring rod.) Now rinse the sides of the beaker with 1 or 2 ml. of alcohol; a few particles of precipitate will probably collect on the surface of the alcohol, for alcohol apparently does not wet barium sulfate. Transfer the alcohol to the crucible, repeat the rinsing with 0.03 *N* hydrochloric acid and then with alcohol until no appreciable amount of precipitate is seen on the surface of the alcohol. Then wash the precipitate in the crucible four times with 0.03 *N* hydrochloric acid, dry the outside of the crucible with filter paper, and set it on a platinum crucible cover supported on a wire triangle. Heat gently with a gas burner until the moisture has evaporated, then heat until the bottom of the crucible is red and any organic matter is completely burned off. Allow the crucible partly to cool on the platinum cover, then place it on a flat piece of porcelain such as an inverted spot plate. After cooling at least 10 minutes weigh accurately (estimating to 0.01 mg.).

STANDARDS. With each group of samples, one or more standards should be run containing the same amount of sulfuric acid as is expected in the samples. Each standard is made up from the 0.0624 *N* sulfuric acid (containing 1 mg. of sulfur per ml.), 2 ml. of Superoxol, and the same amount of alkali and water as was used for the samples. The standard is just neutralized to methyl orange by addition of 0.06 *N* nitric acid. It is then made definitely acid with hydrochloric acid and carried through the same procedure as the samples.

CALCULATIONS. Convert the milligrams of barium sulfate to milligrams of sulfur by multiplying by 0.1373. Subtract the milligrams of sulfur actually present in the standard from the amount found and subtract this correction from the milligrams of sulfur found in the sample.

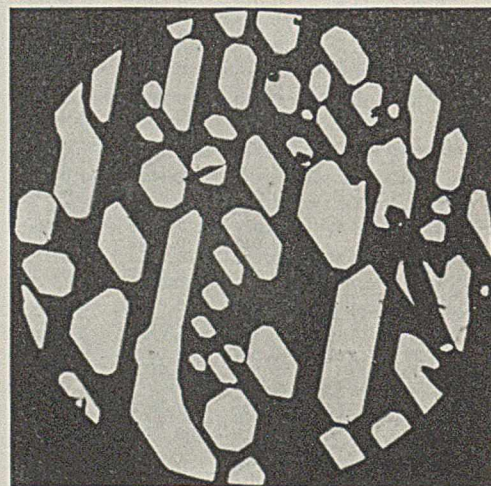
$$\frac{\text{Corrected weight of sulfur in mg.}}{\text{Weight of sample burned in grams}} \times 1000 = \text{parts per million of sulfur}$$

NOTE ON CLEANING NEUBAUER MICROCRUCIBLES. The precipitate is removed by filling the crucibles with water and swabbing them with a rubber policeman. After rinsing thoroughly with distilled water, they are dried on filter paper and ignited to redness on the platinum cover before weighing. Occasionally it may be necessary to dissolve out the barium sulfate by passing some concentrated sulfuric acid through the crucibles. The pores should then be filled up by filtering some freshly precipitated barium sulfate on the crucibles before they are again used for a determination.

Literature Cited

- (1) Charlesworth, S. I., Harris, A. W., and Linder, C. P., U. S. Patent 1,892,329 (1932).
- (2) Edgar, G., and Calingaert, G., *IND. ENG. CHEM., Anal. Ed.*, 2, 104 (1930).
- (3) Engler-Heuser, *Z. angew. Chem.*, 1895, 285.
- (4) Espach, R. H., and Blade, O. C., *Bur. Mines Tech. Paper* 513 (1931).
- (5) Inst. Petroleum Tech., "Standard Methods for Testing Petroleum and Its Products," 3rd ed., Serial Designation G-4, p. 147, London, 1935.
- (6) Pregl, F., "Quantitative Organic Microanalysis," 2nd English ed., pp. 139-46 (1930).
- (7) Richardson, A. W., English Patent 211,925 (1924).

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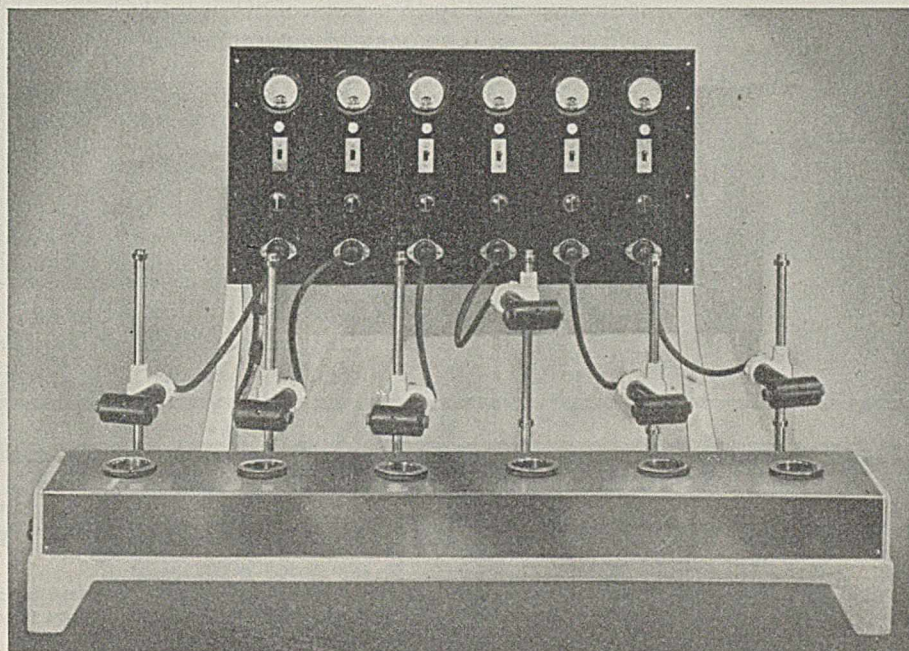
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ETCH FIGURES ON A SINGLE MICROCRYSTAL OF $Ag_2Cr_2O_7$

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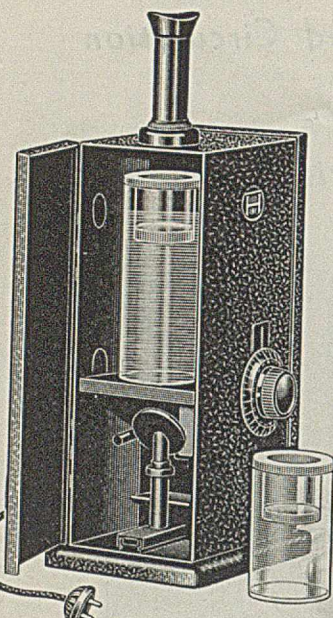
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* *Turbidimetric Determination of Sulfate in Water, Betz-Hellige Method*: Sheen, R. T., Kahler, H. L., and Ross, E. M., *Ind. & Eng. Chem., Anal. Ed.*, Vol. 7, page 262 (7/15/35)—Reprint furnished on request.



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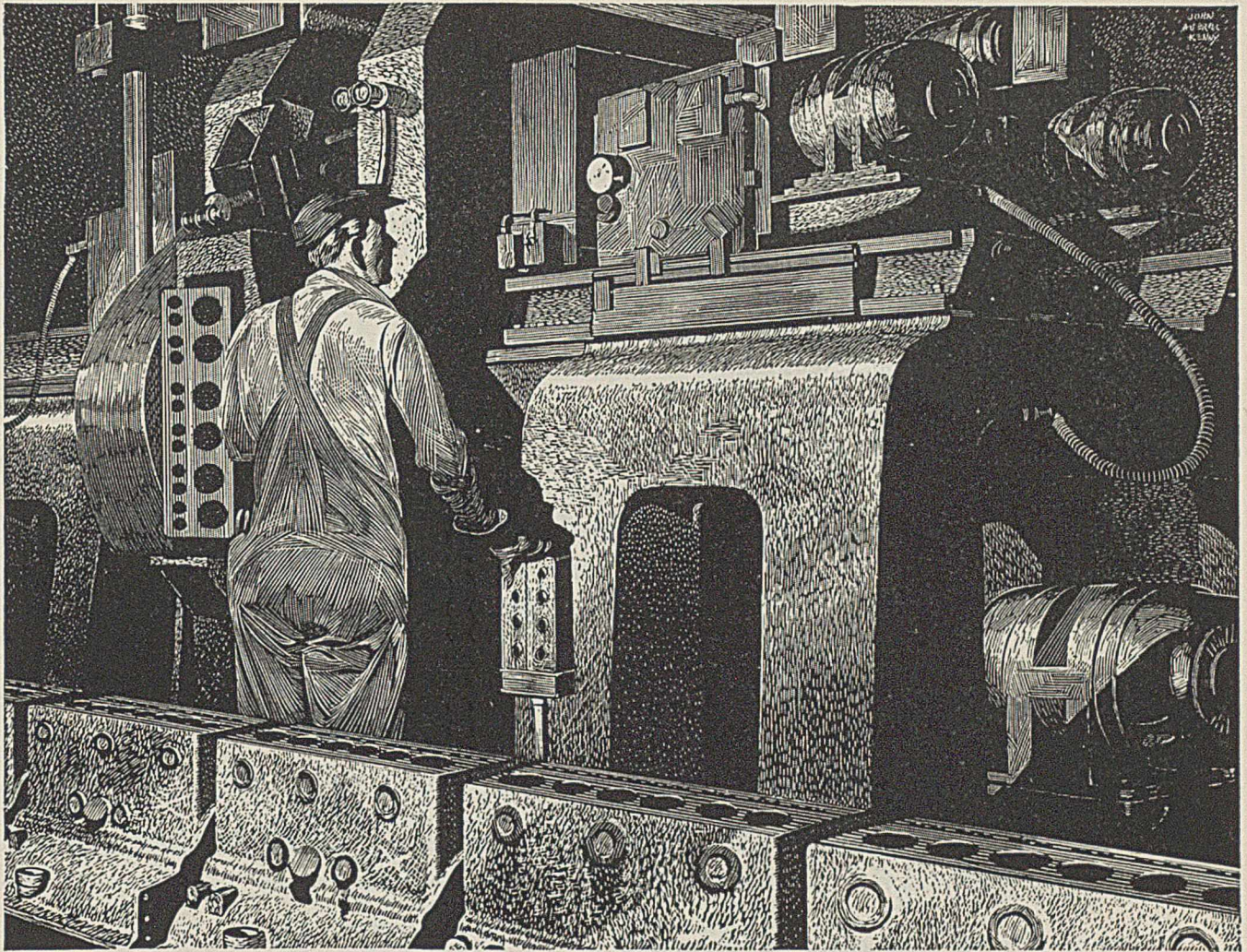
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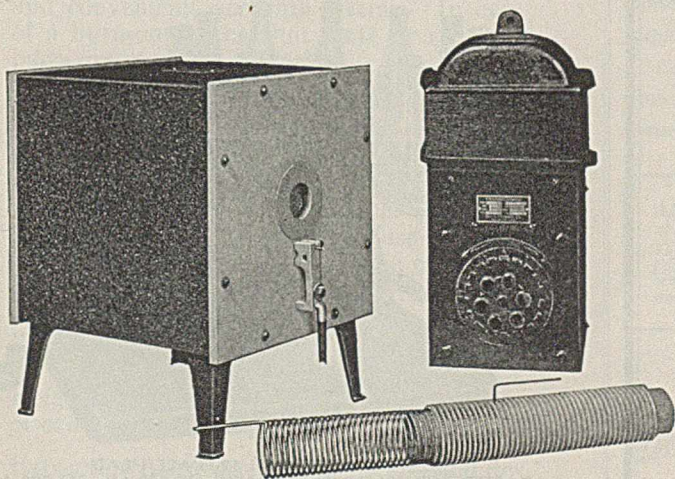
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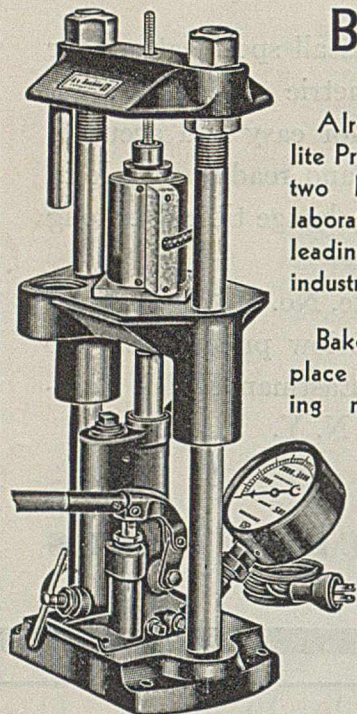
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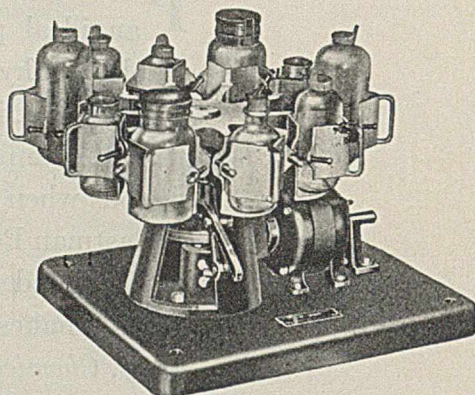
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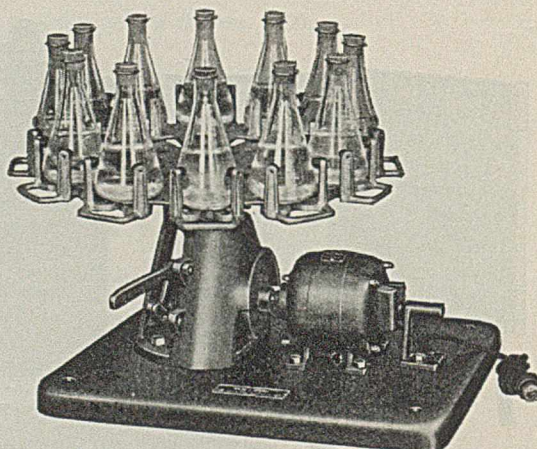
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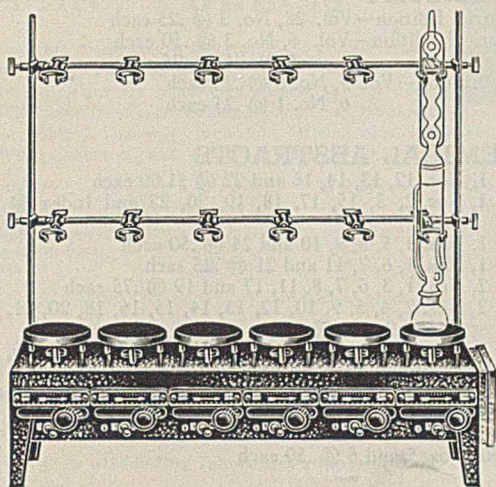
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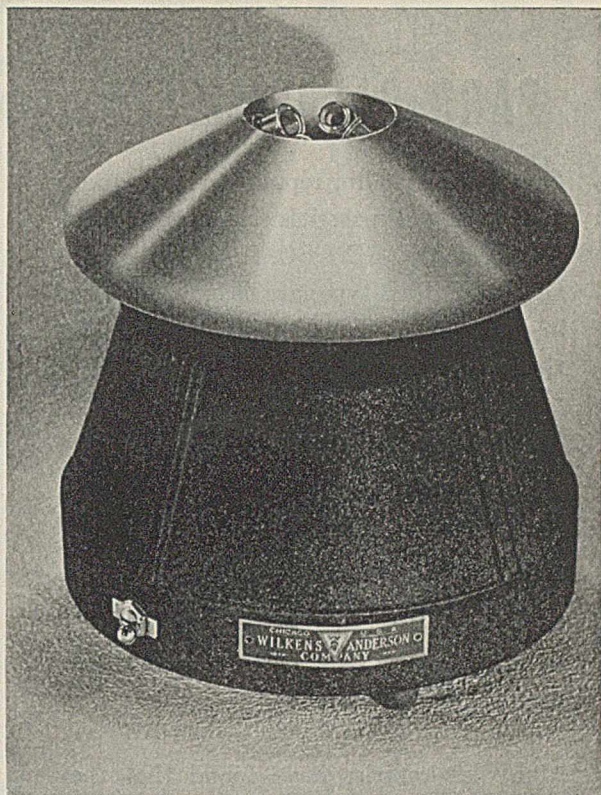
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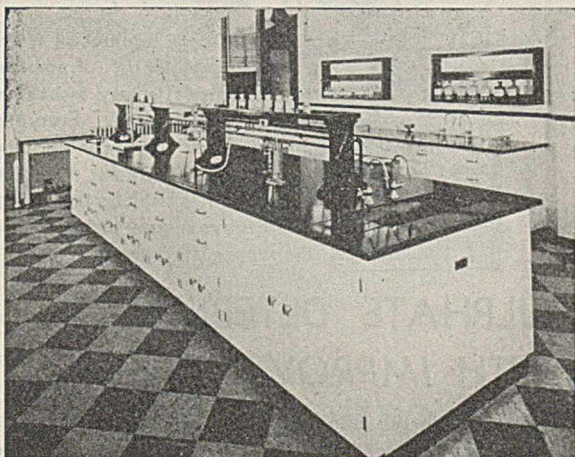
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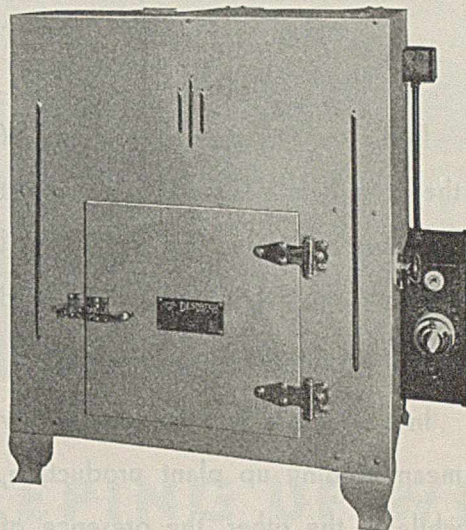
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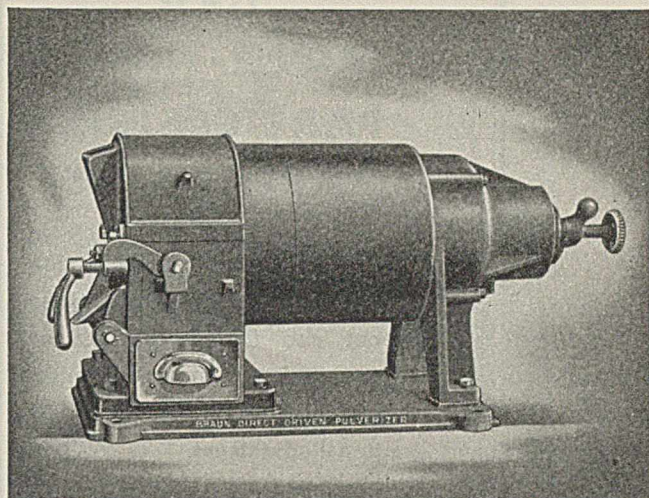
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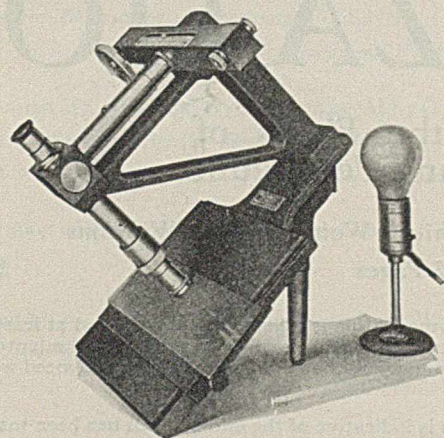
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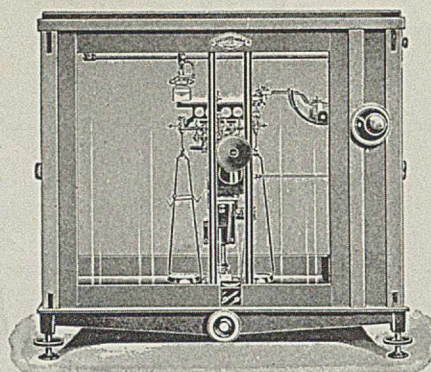
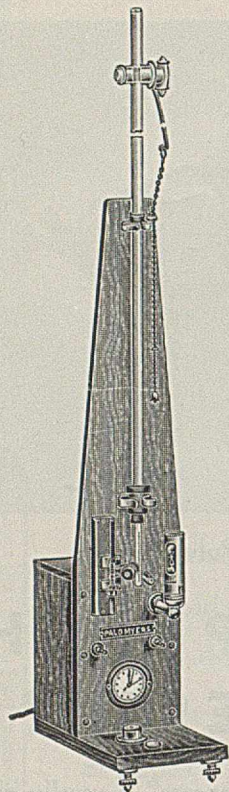
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By Robert E. Burk, Howard E. Thompson, Archie J. Weith and Ira Williams

A. C. S. Monograph No. 75

312 Pages

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IN this work the vast and rapidly growing literature in the field of polymerization is collected, arranged, and at least partially digested. The partnership of theory and application is stressed. It is a book which should be well adapted for the new recruit in polymerization research who wishes a balanced summary of the field and for the experienced worker who wishes to chart his course anew.

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