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SULPHUR IN PETROLEUM OILS

BY

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SULPHUR IN PETROLEUM OILS

By C. E. Waters

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I. INTRODUCTION

Crude petroleum, from whatever source, contains sulphur. In the early days of the industry in this country, little or no attention was paid to this. The Pennsylvania oils contained but small amounts of this element, and the lighter distillates held lower percentages of sulphur than the crudes from which they were obtained. If this had not been so, the petroleum oils would no doubt have come into popular favor much more slowly than they did. Not only do oils which contain much sulphur have a disagreeable odor, but the products of their combustion are irritating and corrosive.

When the Canadian oil fields, and soon afterward those in Ohio and the adjacent States, were tapped, the removal of the comparatively large amounts of sulphur they contained became at once a refinery problem of the first importance. It is an interesting coincidence that Frasch, who years later developed the process by which the immense deposits of sulphur in Louisiana and Texas are worked, devised the first commercially successful method of removing sulphur from petroleum.

II. ORIGIN OF SULPHUR IN PETROLEUM

Several different sources of the sulphur and sulphur compounds which occur in petroleum have been suggested.[1] If the theory that the oil is derived from decayed animal remains be accepted, no other source of the sulphur need be sought, because this element is an essential constituent of all proteids.

It has been suggested that gypsum and other sulphates may be reduced by the oil. The sulphides thus formed could, according to the conditions, yield hydrogen sulphide or free sulphur. A portion of the latter might be deposited in the rocks. Again, oil percolating through these rocks might take up sulphur which was deposited in earlier ages.

III. FORMS IN WHICH SULPHUR OCCURS

1. FREE SULPHUR

Free sulphur has been found in numerous Roumanian[2] oils, as well as in some from California[3] and Texas.[4]

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[1] Steuart, J. Soc. Chem. Ind., **19**, p. 989, 1900; and Naphta, **10**, p. 27, 1902; Peckham, Proc. Amer. Phil. Soc., **37**, p. 137, 1898; Engler, Fortschritte naturw. Forschung, **1**, p. 297; Mabery, Petroleum, **1**, p. 516; **2**, p. 319; Höfer, Erdöl u. s. Verw., Ed. 2, pp. 82 and 141; Höfer, Sitzber. k. Akad. Wiss. Wien, Math.-Nat. Kl., III, Abt. 1.

Nearly all of the data on the occurrence of sulphur in petroleum, as well as many literature references, were obtained from Engler-Höfer, Das Erdöl, **1**, pp. 463 to 479.

[2] Bourqoui, Chem. Rev. Fett-Harz-Ind., **8**, p. 210, 1901; Kissling, Chem.-Ztg., **26**, p. 492, 1902.

[3] Peckham, Proc. Amer. Phil. Soc., **36**, p. 108; 1897.

[4] Richardson and Wallace, Eng. Min. J., **73**, p. 352, 1902; and J. Soc. Chem. Ind., **21**, p. 316, 1902; Thiele. Chem.-Ztg., **26**, p. 896, 1902.

2. HYDROGEN SULPHIDE

Hydrogen sulphide is produced by the decay of organic matter, particularly under anaerobic conditions, and it is a frequent constituent of volcanic gases and occurs dissolved in subterranean waters. It is not surprising, therefore, that it is found in crude petroleum from many sources.[5]

Petroleum which contains free sulphur or organic sulphur compounds gives off hydrogen sulphide when heated, sometimes even at moderate temperatures. This appears to be somewhat at variance with what seems to be a well-established fact that the higher-boiling distillates contain a higher percentage of combined sulphur than the more volatile ones.

3. ORGANIC SULPHUR COMPOUNDS

It is very difficult to separate from crude petroleum any of its constituent hydrocarbons in pure form. Because of the ease with which many of them break down when heated, it is even more difficult to isolate and identify individual sulphur compounds, or even classes of compounds. However, members of more than one class of compounds have been identified. The evidence is not always as convincing as one could wish, for some of the compounds have been detected in distillates or found in the residues from crude oil. The ease with which hydrogen sulphide is formed by heating the oil shows that changes must take place in the organic sulphur compounds to some extent. No doubt those who have done most work in this field realize most fully the difficulties and limitations.

(*a*) Thiophene and some of its homologs apparently occur in some crudes, and their presence in certain light distillates has been proved by means of the indophenine reaction.[6]

(*b*) The Thiophanes are an interesting class of compounds which were obtained from the acid tar of a Canadian petroleum.[7] Although little is known of their structure, the empirical formula, $C_nH_{2n}S$, and their chemical behavior seem to show that they contain a polymethylene ring. They react readily with bromine,

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[5] Vender, Riv. scient. industr., **27**, p. 14, 1895; and Chem.-Ztg. Rep., **19**, p. 61, 1895; Nawratil, Dingl. pol. J., **246**, p. 423, 1882; Bolley, Ibid., **169**, p. 124, 1863; Mabery, Proc. Amer. Acad., **31**, pp. 17 and 43, 1894; Richardson, J. Frank. Inst., **162**, p. 115, 1906; Thiele, Chem.-Ztg., **25**, pp. 175 and 433, 1901; Richardson and Wallace, J. Soc. Chem. Ind., **20**, p. 690, 1901; Kast and Künkler, Dingl. pol. J., **278**, p. 38, 1890; Peckham, Proc. Amer. Phil. Soc., **36**, p. 108, 1897; Rakusin, Untersuchung des Erdöls, p. 102.

[6] Krämer, Verh. Vereins Beförd. Gewerbe-Fl., **1885**, p. 296; Meyer and Nahnsen, Ber. d. Chem Ges., **18**, p. 217, 1885; Edeleanu and Filiti, Bull. soc. chim., Ser. 3, **23**, p. 384, 1900; Charitschkoff, J. Russ. Phys.-Chem. Soc., **31**, p. 655, 1889, and Chem.-Ztg. Rep., **30**, p. 476, 1906; Girard, Petroleum, **2**, No. 3, 1906, and J. du Pétrole, **1906**, p. 69.

[7] Mabery and Quayle, Proc. Amer. Acad., **41**, p. 89, 1905; and Amer. Chem. J., **35**, p. 404, 1906; Mabery, J. Soc. Chem. Ind., **19**, p. 508, 1900.

but are not unsaturated compounds, because the amount of bromine evolved as hydrobromic acid is equal to that held in combination. By oxidation with alkaline permanganate solution, the thiophanes are converted into the corresponding sulphones, $C_nH_{2n}SO_2$.

The eight thiophanes isolated ranged in composition from $C_7H_{14}S$ to $C_{18}H_{36}S$.

(*c*) ALKYL SULPHIDES, OR THIO ETHERS, $(C_nH_{2n+1})_2S$, have been reported in certain Ohio crudes. Ten members of the series, from methyl sulphide, $(CH_3)_2S$, to hexyl sulphide, $(C_6H_{13})_2S$, were isolated.[8]

Kast and Lagai,[9] who may not have had the same crudes as Mabery and Smith, failed to find any compounds of this series in Ohio oils. On the other hand, Charitschkoff [10] detected alkyl sulphides in naphtha from Grosny.

The alkyl sulphides yield crystalline addition products with mercuric chloride.

(*d*) ALKYL HYDROSULPHIDES, OR MERCAPTANS, apparently occur in the distillates from Baku oil.[11]

(*e*) CARBON BISULPHIDE has been detected in petroleum ether (boiling point 50 to 80°C), but not in kerosene.[12] Compounds of the general formula, $C(C_nH_{2n+2})S$, have been obtained from certain Canadian petroleums.[13] They are apparently alkyl derivatives of carbon bisulphide.

(*f*) SULPHONIC ACIDS, RSO_3H, are said to cause the turbidity which is sometimes observed when distillates are allowed to stand for a long time.[14] They can be removed by vigorous agitation with a solution of caustic alkali.

(*g*) ALKYL SULPHATES.—Perhaps most of the compounds commonly called sulphonic acids are in reality alkyl sulphates, $(C_nH_{2n+1})_2SO_4$, which are formed when the oils are treated with sulphuric acid during refining. The saturated hydrocarbons do not react with the acid, but the unsaturated ones can form these esters by direct addition. For instance,[15]

$$2C_nH_{2n} + H_2SO_4 = (C_nH_{2n+1})_2SO_4.$$

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[8] Mabery and Smith, Ber. d. Chem. Ges., **22**, p. 3303, 1889; and Amer. Chem. J., **13**, p. 232, 1890.

[9] Dingl. pol. J., **284**, p. 69, 1892; **292**, p. 116, 1894.

[10] J. Russ. Phys.-Chem. Soc., **31**, p. 655, 1899; Chem.-Ztg. Rep., **21**, p. 203; Chem. Centrbl., **1899**, II, p. 920.

[11] Kwjatkowsky, in Höfer, Erdöl u. s. Verw., 2d ed., p. 82.

[12] Hager, Dingl. pol. J., **183**, p. 165; 1867.

[13] The reference given by Höfer could not be verified, or the statement traced to its source.

[14] Veith, Dingl. pol. J., **277**, p. 567: 1890.

[15] Vohl, Dingl. pol. J., **216**, p. 47, 1875; Heusler and Dennstedt, Z. angew. Chem., **17**, p. 264, 1904; Heusler, Ber. d. Chem. Ges., **28**, p. 498, 1895.

The true sulphonic acids, which have their sulphur directly combined with carbon, can not be hydrolyzed by boiling with water or with dilute acids or alkalies. By careful fusion with caustic alkali the sulphonic group can be replaced by hydroxyl, as in one commercial process for the manufacture of phenol:

$$C_6H_5SO_3H + KOH = C_6H_5.OH + KHSO_3.$$

The alkyl esters, on the other hand, can be hydrolyzed with comparative ease by boiling with dilute acids or alkalies:

$$(C_nH_{2n+1})_2SO_4 + H_2O = 2C_nH_{2n+1}.OH + H_2SO_4.$$

When heated, these esters break down and give sulphur dioxide and carbon, among other products. These are formed even at the moderate temperatures reached in determining the Maumené number.[16]

IV. IDENTIFICATION AND SIGNIFICANCE OF SULPHUR COMPOUNDS

With the possible exception of the "sulphonic" acids, there seems to be no attempt made to determine the nature and amount of the sulphur compounds in routine laboratory practice. The difficulty, or even impossibility, rather than a lack of interest, is probably responsible for this. The oil chemist must feel that not only the total amount of sulphur, but also the nature of the compounds in which that element occurs, influence the behavior of oils. This is particularly true of lubricating oils which are subjected to service conditions favorable to deterioration. Heating in contact with air naturally comes first to mind because of the ease with which so many sulphur compounds are oxidized.

A conclusive decision as to the real influence of sulphur compounds upon the behavior of lubricating oils can be made only by comparing a sulphur-free oil with the same oil to which definite amounts of known sulphur compounds have been added. It does not appear probable that such tests can be made in the near future. However, it might be desirable to collect data on oils that have deteriorated badly in service in order to learn whether they contain higher percentages of sulphur than other oils which have stood up longer under the same conditions.

In this connection it may be pointed out that sulphur and sulphur dioxide cause an increase in the amount of asphaltic matter which is formed when oils are heated in the air.[17]

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[16] See footnote 15, and also Waters, B. S. Tech. Papers, No. 73, p. 12; 1916.

[17] Holde and Eickmann, Mitth. kgl. Materialprüfungsamt, **1907**, p. 145; and Z. angew. Chem., **20**, pp. 1263 and 1923, 1907; Waters, B. S. Tech. Papers, No. 4, p. 9, 1911; and J. Ind. and Eng. Chem., **3**, p. 814, 1911; Southcombe, J. Soc. Chem. Ind., **30**, pp. 261–264, 1911.

Work done recently at this Bureau shows that of four oils which had "carbonization values," or percentages of asphalt formed by oxidation, of 0.02 or less, none contained more than 0.08 per cent of sulphur. Of five oils which had carbonization values of 0.34 or more, all contained at least 0.29 per cent of sulphur. From these few figures it would appear that no oil which contains much sulphur will have a low carbonization value.

Transformer oils are regarded as undesirable if they contain more than a very small proportion of sulphur, because this element is believed to attack the wires and also to increase the tendency to form sludge.

In specifications for fuel oils the maximum permissible percentage of sulphur is generally stated, because of the corrosive effect of the products of its combustion. This is even more important for kerosene, because the oxides of sulphur are irritating and may bleach fabrics in the home, as well as corrode metal objects. The kerosene itself usually has a disagreeable odor when it contains more than a very low percentage of sulphur compounds.

Sometimes the presence of sulphur is desirable, as in flotation oils and some cutting oils. In the first case it is essential that the particles of ore cling to the oil drops in order to become separated from the gangue. The metallic sulphides more easily become oily than the other minerals. This oiling effect is helped by the presence of sulphur, perhaps by its action on particles or surface films of oxide which are thus changed to sulphide.

The principal reason for using a cutting oil is to lubricate the chips so that they can slide off the tool easily. It has been claimed that sulphur causes the oil to cling better to the metal by forming a film of sulphide. If this be true, the film is of extreme tenuity, because the metal shows little sign of tarnishing, as a rule.

V. DETECTION OF SULPHUR AND ITS COMPOUNDS

1. COPPER TEST

Free sulphur, hydrogen sulphide, and perhaps other sulphur compounds, in oils can be detected by the formation of a dark spot of copper sulphide when two or three drops of the oil are left on the polished metal for a sufficient length of time. The "copper dish" test for gasoline is based upon this reaction. It is generally believed that the degree of darkening depends upon the amount of sulphur present. This is not true. A topped Mexican crude, which contained 4.05 per cent of sulphur, and which gave off streams of hydrogen sulphide when heated in a test tube, did not perceptibly darken copper in 72 hours. Even when a strip of the metal was partly immersed in the oil and kept at 295 to 300° C for 2 hours, the lower portion was only slightly tarnished. The end of the strip which was not under the oil was, however, much blackened and covered with a varnish-like coating, which was probably formed by partial oxidation of the oil.

Although the copper test can not be relied upon to show the presence of all sulphur compounds in oils, it is a delicate means of detecting free sulphur and hydrogen sulphide. A series of solutions was made by dissolving recrystallized sulphur in a white, medicinal oil which did not darken copper and which was found to contain too little sulphur to detect by analysis. The strongest solution contained 0.100 per cent of free sulphur. By suitable dilution, samples containing down to 0.0001 per cent, or 1 : 1 000 000, of sulphur were prepared. On each piece of freshly sandpapered, washed and dried piece of copper was placed two or three drops of oil. A blank test was run to check the original oil as well as the air of the laboratory. With 0.10 to 0.050 per cent of sulphur the copper was blackened in a few minutes, with 0.033 to 0.017 per cent the copper was perceptibly darker in 30 minutes, and with 0.01 per cent inside of an hour. When left in contact with copper for 20 hours, oil containing as little as 0.0002 per cent of sulphur, or 2 : 1 000 000, caused a just perceptible darkening of the metal. At the final dilution no action could be detected.

Similar tests were made with oil into which hydrogen sulphide had been passed for a few minutes. This solution, which instantly darkened copper, contained 0.037 per cent of sulphur, equivalent to 0.039 per cent of hydrogen sulphide. A portion of this was diluted to 100 volumes and then three or four times to 10 volumes each. The results of the tests with hydrogen sulphide are given in Table 1.

TABLE 1.—Copper Test for Hydrogen Sulphide

Dilution	Sulphur	Parts per million	Odor	Action on copper in 20 hours
Volumes	Per cent			
100	0.00037	3.7	Strong	Slight.
1 000	.000037	.37	Positive	Doubtful.
10 000	.0000037	.037	Very faint	None.
100 000	.00000037	.0037	None	Do.

It is evident that the copper test is much less delicate than the sense of smell.

2. SODIUM TEST

If the oil is not too volatile, but can be heated to 250 to 300° C without boiling out of the test tube, the sodium test can be applied. A test tube containing a few cubic centimeters of the oil is clamped in an inclined position over a flame which is regulated so that the oil is near its boiling point. A clean piece of sodium, 2 or 3 mm in diameter, is dropped in before the heating begins. After half an hour or longer, the oil is allowed to cool and is then poured off. The blackened lump of sodium is rinsed off with benzene, and dissolved in a few drops of water or 50 per cent alcohol. To the alkaline solution there are now added a few minute particles of sodium nitroprusside. If any sodium sulphide is present, the solution becomes pink to reddish purple, according to the amount. When only traces of sulphur are present, care must be taken not to mask the reaction by adding too much nitroprusside. Hydrogen sulphide does not produce a colored compound, so that the solution must not be acidified.

Attempts to utilize the sodium method for the determination of sulphur were unsuccessful, because duplicate results varied too widely.

VI. DETERMINATION OF SULPHUR

1. METHODS EMPLOYING OXIDIZING AGENTS.

(*a*) Carius Method.[18]—Although capable of giving highly accurate results, few chemists employ it when another can be used. It is not only troublesome and dangerous, but it has the disadvantage that only a few decigrams of material can be used in a determination. It is hardly applicable to oils low in sulphur. Even with oils that contain high percentages, there is danger of getting low results, owing to incomplete decomposition of the oil. Even when no more oily drops are to be seen, the oxidation may not be complete, as will be discussed more fully further on.

In the discussion of the Graefe method (see p. 14), some results obtained by the procedure of Carius are given.

(*b*) Nitric Acid Digestion.—An obvious simplification of the Carius method is to digest the oil with fuming or concentrated nitric acid at atmospheric pressure, in a Kjeldahl flask or other suitable apparatus. There is no danger of explosions, and when the oil is low in sulphur, a large enough amount to yield a convenient weight of barium sulphate can be taken for analysis.

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[18] Liebig's Ann., **116**, p. 1, 1860; **136**, p. 129, 1865; Ber. d. chem. Ges., **3**, p. 697, 1870.

But the oxidation of the oil proceeds very slowly, so that it may require 2 or 3 days to completely decompose as many grams. In order to hasten the reaction, potassium chlorate has been used.[19] According to the last authors cited, the results on California oils agree well with those obtained by the Carius method.

In this laboratory the use of chlorate was abandoned some years ago because it was found that permanganate hastened the oxidation of the oil. This is due to the formation of manganese peroxide, which spreads through the acid and comes into intimate contact with the oil.

The addition of a few drops of bromine, before the nitric acid is poured into the flask, seems to accelerate the reaction. At any rate it lessens the danger of losing hydrogen sulphide, if the oil contains any.

About a year ago it was found that, although duplicate determinations of the sulphur content of two Mexican oils agreed closely, when the nitric acid-permanganate method was used, yet the results were far too low. By the method described farther on, one of the oils was found to contain 1.83 per cent of sulphur.[20] The other, a topped Tampico crude, contained 4.05 per cent. Analyses by the method just described gave the following results for the two oils: First sample, 0.81, 0.80, 0.81, 0.87, 0.81, and 0.90 per cent; second sample, 2.17, 2.27, and 2.21 per cent.

It was noticed that even when all of the sample appeared to be decomposed, there was always some turbidity and usually oily drops separated out when the contents of the flask were washed into a beaker. This was due to the formation of nitrocompounds which were easily soluble in nitric acid but much less so in water. Although but slightly soluble in water, it was not possible to extract the nitroproduct with any reasonable amount of ether, and it was volatile with steam. The oily product dissolved in sodium-carbonate solution, with which it formed a dark brown salt; it was reprecipitated by acidifying the solution.

The nitrocompounds contained a considerable percentage of sulphur.[21] Failure to decompose the oil completely during the

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[19] Kast and Lagai, Dingl. pol. J., 284, p. 71, 1892; Gilpin and Schneeberger, Amer. Chem. J., 50, pp. 65–66, 1913.

[20] This was a topped crude mixed with mineral seal. It was distributed for cooperative analysis by F. R. Baxter, chairman of the subcommittee on sulphur, committee D–2, American Society for Testing Materials. With his permission data taken from his report have been used in the preparation of this paper.

[21] According to Kast and Lagai (see footnote 19) the "resin" formed by the action of nitric acid and chlorate contains no sulphur.

digestion with acid and permanganate, together with its volatility and solubility, explains why low results for sulphur were obtained. The close agreement between the results actually found is in part accidental, in part due to working with nearly the same amounts of oil and reagents each time, and to stopping the digestion as soon as all oily drops disappeared.

In one determination with nitric acid and permanganate, the digestion was carried on in an all-glass apparatus so constructed that permanganate could be added from time to time. The escaping gases were passed through a solution of permanganate. This soon became decolorized by the oxides of nitrogen, but no sulphate was found in it. In this determination the oil was boiled for 25 hours with the acid, and permanganate was added from time to time. The percentage of sulphur found in the acid was 2.21, as against 2.17 and 2.27 in Kjeldahl flasks.

Goetzl,[22] in a similar experiment with fuming nitric acid, passed the escaping gases through caustic potash solution and found no sulphur.

He also heated fuel oil with fuming nitric acid, until it was all oxidized, then evaporated off the acid, extracted the solid mass with concentrated soda solution, acidified, and filtered off the "bituminous" matter which separated. The amount of sulphuric acid found in the filtrate was too low, but he seems to have missed the point that part of the sulphur is held in the nitrocompounds of which the residue is largely composed. As shown above, and confirmed by Goetzl's statement, this forms a salt with soda and is precipitated by hydrochloric acid.

(*c*) ROTHE METHOD.[23]—The oil is digested in a flask with fuming nitric acid to which a little magnesium oxide has been added. After the acid has boiled for a time it is evaporated off, then more is added and the digestion is continued. This treatment is repeated a few times and finally any oil which remains is burned off with the aid of the magnesium nitrate. The residue in the flask is taken up with hydrochloric acid and water, the solution is filtered, and barium sulphate is precipitated.

The method has not been tested in this laboratory. It has been used elsewhere for the analysis of vulcanized rubber, although it is stated that duplicate results on compounds containing about 7.5 per cent of sulphur may be expected to differ by 0.2 or 0.3 per cent, and they may differ by 0.5 per cent.[24]

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[22] Z. angew. Chem., 18, pp. 1528 to 1531; 1905.

[23] Described by Holde in Examination of Hydrocarbon Oils, English translation, pp. 40-41.

[24] Delft Rubber Inst. Communications, Part V, p. 144; 1917.

On the other hand Holde says that the method gave satisfactory results at the Materialprüfungsamt with oils containing no naphtha or illuminating oil.[25] None of these light fractions had been analyzed at the time he wrote.

(*d*) ESCHKA METHOD.—Originally devised for the determination of sulphur in coal,[26] the method has been applied also to the analysis of asphalt and oils. The sample is mixed with sodium carbonate and magnesium oxide and ignited in a crucible. The residue is treated with bromine water and nitric acid to oxidize all sulphur compounds to sulphuric acid, which is then precipitated as barium sulphate.

It has not seemed worth while to try the method, because of the certainty of losing sulphur as hydrogen sulphide or as volatile organic compounds. This seems to be confirmed by cooperative analyses of three samples of oil.[27] One was a heavy red oil known to contain sulphonic acids, the second a topped Mexican crude mixed with mineral seal, and the third a "300" oil which had been vulcanized by heating with sulphur. The last had a strong odor of hydrogen sulphide.

In one laboratory where Eschka's method was used, the results for the Mexican oil were 1.33 and 1.74 per cent. Five determinations at this Bureau gave from 1.80 to 1.85 per cent.

Two laboratories which used the Eschka procedure for the red oil found from 0.28 to 0.41 per cent. This Bureau found 0.51 to 0.59 in 8 determinations.

The figures on the vulcanized oil, as found in three laboratories, varied from 0.91 to 1.19 per cent; at this Bureau from 1.24 to 1.37 per cent in 8 analyses.

The method used by the Bureau is described further on.

(*e*) SODIUM PEROXIDE METHOD.—In recent years sodium peroxide has been used to a great extent for the determination of the halogens and sulphur. In 1895 Edinger employed it for the estimation of sulphur in volatile organic compounds.[28] The method has not been used for petroleum oils in this laboratory.

2. METHODS INVOLVING COMBUSTION IN OXYGEN OR AIR.

(*a*) SAUER METHOD.[29]—The sample of oil is slowly heated in a combustion tube while oxygen and carbon dioxide are supplied from opposite ends at such a rate that the oil vapors burn at a

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[25] The Examination of Hydrocarbon Oils, English translation, p. 40.

[26] Oesterr. Ztschr. Berg- u. Hüttenwesen, **22**, p. 111; Z. anal. Chem., **13**, p. 344, 1874.

[27] See footnote 20, and Goetzl. Z. angew. Chem., **18**, p. 1258; 1905.

[28] Z. anal. Chem., **34**, p. 362; 1895.

[29] Z. anal. Chem., **12**, pp. 32–36; 1873.

constriction at the middle of the tube. The oxides of sulphur are absorbed in bromine water and barium sulphate is finally precipitated. Even with constant attention it is difficult to keep the flame where it should be and to prevent explosions in the tube, or else the escape of unburned oil. If the oil is low in sulphur, so large a sample must be taken that an analysis requires a long time.

DENNSTEDT METHOD.[30]—The chief feature of the Dennstedt procedure for the combustion of organic substances is the use of a catalyzer in the tube ahead of the boat containing the sample. Platinized quartz or a disk of the sheet metal is commonly used. When determinations of sulphur in oils were first made at this Bureau, the Dennstedt method, with platinized quartz, was used. Because only the sulphur was to be determined, the products of combustion were passed through a Meyer bulb tube containing sodium-hypobromite solution. After repeated trials the method was abandoned because, in spite of constant attention, it was almost impossible to prevent explosions or the escape of unburned gases. Another reason was the long time spent in making a combustion. About two working days was required to burn a 3 g sample. This included the time necessary to heat the catalyzer to redness, to cool the furnace at the end of the first day, and for all the other incidental operations.[31]

(*c*) GRAEFE METHOD.[32]—A small quantity of oil on absorbent cotton is burned in a large (7 l.) bottle of oxygen, in which is some sodium-hydroxide solution to absorb the oxides of sulphur. After the combustion the bottle is rinsed out, the solution is warmed with bromine and acidified, before adding barium chloride. Owing to the great heat developed, only about 0.3 g of oil can be burned, so that the method is not applicable to material low in sulphur.

Two fuel oils were analyzed by the Graefe and Carius methods in the laboratory of the Texas Co., and by a new procedure at this Bureau. Four determinations were made on each oil by each of the first two methods, and but two each by the new one.

The values by the new method were 0.54 and 0.53 per cent for one oil, and 0.76 and 0.77 per cent for the other. By the Carius method the figures varied from 0.62 to 0.65 and from 0.82 to 0.88,

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[30] Ber. d. chem. Ges., **30**, pp. 1590–1597; 1902.

[31] In determining nitrogen in petroleum by a combustion method Mabery (J. Amer. Chem. Soc., **41**, p. 1697; 1919) found that "1 g of oil requires two or three hours in safe operation."

[32] Z. angew. Chem., **17**, p. 616; 1904. See also Hempel. Ibid., **5**, p. 393; 1892.

respectively; by the Graefe procedure, 0.56 to 0.66 and 0.84 to 0.89 per cent of sulphur.

In commenting on these analyses, the chemist of the Texas Co. said that he regarded the results of the three methods as in satisfactory agreement for oils which contained over 0.50 per cent of sulphur.

(*d*) LAMP METHOD.—The sulphur content of kerosene can be determined by burning it in a lamp and drawing the products of combustion through suitable absorption apparatus containing hypobromite solution.[33] The oil must burn with an ample supply of air and without a smoky flame. The air must be free from sulphur compounds. In some unpublished work by the author it was found that reducing gases are present in the products of combustion, and in greater amount the lower the flame. The lamp method for sulphur requires a rather low flame to prevent excessive heating of the absorption apparatus, so that the danger of losing organic compounds containing this element must be borne in mind.

Lubricating oils can be burned in a lamp if they are first mixed with light solvents.[34] According to Conradson, the sulphonic acids remain behind on the wick and can be determined separately. In this connection it should be mentioned that Heusler and Dennstedt claim that the charring of the wick is largely due to the presence of neutral alkyl esters of sulphuric acid. When they break down this acid is formed.[35]

(*e*) BOMB CALORIMETER METHOD.—As early as 1899 the bomb calorimeter was used for the determination of sulphur in oils.[36] Since then it has come to be the procedure most generally employed and the one in which most confidence is placed. The oil is burned in oxygen under high pressure, in a bomb calorimeter which contains a few cubic centimeters of water or of soda solution, or some sodium peroxide.

Even this apparently ideal procedure has certain disadvantages, apart from the cost of the apparatus. Not much more than 1 g of oil can be burned at a time and if the percentage of sulphur is low, very little barium sulphate will be obtained. If a lead gasket is used, it will be appreciably attacked by the oxides of sulphur, which will cause low results. Owing to the high tem-

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[33] Heusler, Z. angew. Chem., **1895**, p. 285; Engler, Chem.-Ztg., **20**, p. 197, 1896.

[34] Albrecht, Diss. Karlsruhe, p. 37, 1907; Conradson, J. Ind. and Eng. Chem., **4**, p. 842, 1912; and 8th. Int. Cong. Appl. Chem., **27**, p. 19.

[35] Z. anorg. Chem., **17**, pp. 264–5; 1904.

[36] Filiti, Bull. soc. chim., Ser. 3, **21**, p. 338, 1899; and Z. anal. Chem., **39**, p. 727, 1900.

perature of the combustion, some of the sulphur is burned only to the dioxide. If the bomb is opened too soon this can be tasted in the escaping gases. Under some conditions sulphur trioxide is absorbed slowly by water. A current of air carrying it can be bubbled through water without losing all of its cloudiness.

In the cooperative work referred to above (see p. 13) the three oils were analyzed by the bomb method in several laboratories. The extreme percentages of sulphur were:

	Per cent.
Mexican oil	1. 52 to 1. 90
Red oil	. 39 to . 53
Vulcanized oil	. 89 to 1. 22

One laboratory alone reported five determinations on the red oil which ranged from 0.42 to 0.53 per cent, while eight results for the vulcanized oil varied from 0.89 to 1.19 per cent.

The results obtained at this Bureau are given in the discussion of the Eschka method (see p. 13).

3. MISCELLANEOUS METHODS

In this section are described some attempts to find methods for total sulphur or for the differentiation of the sulphur compounds.

(*a*) Heating with Sodium.—Although heating with sodium to a comparatively high temperature seems to be a reliable way to test for the presence of sulphur, it could not be depended upon for quantitative data. The sodium was treated with water after the oil was removed with benzene, then bromine water and hydrochloric acid were added, the solution was filtered and finally barium sulphate was precipitated. The results varied greatly.

Metallic calcium under the same conditions appeared to remove no sulphur.

(*b*) Heating with Copper and Copper Oxide.—Many experiments were made in which the oil was heated with copper powder or with the partially oxidized metal. The powder was prepared by sifting zinc dust into a solution of copper nitrate. The copper was thoroughly washed, finally with alcohol, and dried at a moderate temperature. For some of the tests this powder was heated until it became covered with oxide. The procedure was the same as for sodium, except that the residue, after washing with benzene, was dissolved in dilute hydrochloric acid containing bromine. Considerable sulphur was removed from the oil by this treatment, but the results rarely checked one another.

(*c*) Lead Peroxide.—This reagent was found to remove very little sulphur when heated with oils. In this case the residue was extracted with sodium-carbonate solution, as recommended by Dennstedt, or with sodium hypobromite.

(*d*) SODIUM HYPOBROMITE AND HYDROXIDE.—These reagents were used in attempts to remove at least a definite part of the sulphur from the Mexican oil which contained 1.83 per cent of sulphur. A solution of hypobromite, made by adding 1.5 cc of bromine to 50 cc of a cold, 5 per cent caustic soda solution, was shaken with 2.2 to 2.3 g of oil at frequent intervals for three and one-half hours. The mixture was then warmed on the steam bath for one and one-half hours and allowed to stand over night. The aqueous layer was separated and acidified. The addition of barium chloride produced merely traces of precipitate, although the smallest sample taken contained enough sulphur to yield over 290 mg of barium sulphate.

A 5 per cent solution of caustic soda, when heated on the steam bath with the oil and frequently shaken for several hours, extracted only insignificant amounts of sulphur. In this case bromine was added before the hydrochloric acid and barium chloride.

(*e*) DIGESTION WITH PERMANGANATE.—When 0.5 g samples of the Mexican oil which contained 4.05 per cent of sulphur were digested on the steam bath with a strong solution of potassium permanganate for several hours some sulphur was oxidized. In two determinations the amounts of barium sulphate were equivalent to 0.30 and 0.37 per cent, respectively, of sulphur. There is no way, at present, of deciding whether this represented a general attack upon all of the sulphur compounds in the oil, or whether only a particular group of such derivatives was oxidized.

(*f*) DIGESTION WITH HYDROCHLORIC ACID.—This work was done chiefly in order to detect esters of sulphuric acid—the "sulphonic acids," as they are often called. Ten-gram samples of the heavy red oil (see p. 13), which contained about 0.55 per cent of sulphur, were digested on the steam bath with hydrochloric acid of three dilutions, from 1:2 to 2:1. Other portions were boiled with 1:5 acid and still others heated with 1:4 acid in sealed tubes. These were hung inside of a steam bath for several hours. In nine determinations the amounts of sulphuric acid found varied from 0.063 to 0.105 per cent, which corresponds to 0.020 to 0.034 per cent of sulphur.

In the analysis of turkey red oil and other "sulphonated" oils, the usual procedure is to boil with hydrochloric acid. In our tests digestion on the steam bath gave results a few thousandths of a per cent higher than those obtained by boiling or by heating in sealed tubes. It is not necessary to boil if the flasks are frequently shaken.

Besides the red oil, the two Mexican oils were also tested. The negligible amounts of sulphuric acid obtained from 10 g samples were equivalent to only 0.001 and 0.004 per cent of sulphur, respectively.

(*g*) HYDROGENATION.—An attempt was made to remove sulphur by heating oil with hydrogen in the presence of a catalyzer. In the first test an engine oil which contained 0.85 per cent of sulphur was used. The apparatus was so arranged that a bulb holding the oil and the catalyzer was heated in an air bath made of an iron crucible with a perforated cover of asbestos board. A slow current of hydrogen bubbled through the oil, passed through a glass tube which was long enough to cool it, and escaped through a Volhard flask containing sodium-hypobromite solution.

The first catalyzer used was made by igniting nickel oxide in hydrogen. The reduced metal was pyrophoric, so that it changed back to oxide before it was mixed with the oil.

At first 3.225 g of oil, with 0.01 g of catalyzer, was heated for two and one-half hours at 320 to 330° C. The hypobromite solution yielded only 0.0023 g of barium sulphate out of a possible 0.1996 g. The same lot of oil was then heated to a much higher temperature, with the thermometer removed, for three hours, after which 0.0043 g more sulphate was obtained. The total of 0.0066 g corresponded to 3.3 per cent of the sulphur in the oil.

Because the topped Mexican crude which contained 1.83 per cent of sulphur gave off streams of hydrogen sulphide when heated, it was tested in the way just described. In five hours' heating, 1.9908 g yielded only 0.0017 instead of a possible 0.2653 g of barium sulphate. When a 7 mm circular disk of platinum foil was used as a catalyzer, 1.7984 g of oil gave 0.0046 g of sulphate.

In the experiments at the higher temperatures the thermometer was removed from the bath when 360° was approached and the flame was increased until the oil vapors condensed 5 or 6 cm above the cover. Only traces of oily distillate were carried over into the hypobromite.[37]

4. NEW METHOD FOR SULPHUR

(*a*) PRELIMINARY WORK.—In a sense all of the methods tested intermittently as opportunity offered since 1908, may be looked

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[37] After this work was finished it was learned that Goetzl (Z. angew. Chem., 18, p. 1529; 1905) attempted to determine the sulphur content of fuel oil by distilling off hydrogen sulphide. The amount of this gas which was set free was not proportional to the quantity of oil distilled off.

upon as leading up to the one finally hit upon. Early in 1910 a series of comparative tests was made of variations of the Henriques method for the determination of total sulphur in rubber. According to the original procedure the rubber is digested with nitric acid, the excess of which is evaporated off. The residue is then oxidized by heating with a mixture of soda and saltpeter. The melt is dissolved in hot water, the solution filtered, acidified and treated with barium chloride. It was found that under certain conditions some sulphur, apparently that in the free state, escaped oxidation by the nitric acid and was lost when the latter was evaporated off. There was no such loss of sulphur when the rubber was treated at the start with nitric acid saturated with bromine.[38]

This success in retaining all of the sulphur in rubber goods led to the use of bromine for the preliminary attack of oils by the nitric acid-permanganate method. At that time, and indeed up to 1919, it was not thought worth while to try the procedure of Henriques for oils, because of the belief that much of the sulphur would be lost by volatilization in organic compounds. This is true if the oil is not first attacked by nitric acid, but it is now known that the nitrocompounds which are formed yield salts when treated with sodium carbonate, and the sulphur is retained.

An oil which six determinations by the nitric acid-permanganate method showed to contain from 0.80 to 0.90 per cent of sulphur, was incorporated with a mixture of soda and saltpeter and carefully ignited. The result was 1.37 per cent. When fused in the same way after treatment with nitric acid and bromine, five determinations gave values from 1.80 to 1.85 per cent. These were the first obtained by the method to be described. A proportionately close agreement is what has come to be expected of beginners in rubber analysis, because there are no complications in the technic.

(*b*) DESCRIPTION OF NEW METHOD.—A preliminary paper describing the method has already been published.[39] The directions here given have been changed but little.

Weigh from 0.5 to 2.0 g of oil in a 100 cc porcelain crucible, add 5 cc of concentrated nitric acid which has been saturated with bromine, and at once cover with a watch glass. When rather volatile oils, or those which smell of hydrogen sulphide are ana-

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[38] Waters and Tuttle, B. S. Bulletin, 8, pp. 445-453, 1911; B. S. Scientific Papers No. 174; J. Ind. and Eng. Chem., 3, Oct., 1911. See also Tuttle and Isaacs, B. S. Tech. Papers, No. 45, 1915.

[39] Waters, J. Ind. and Eng. Chem., **12**, pp. 482-485 and 612, 1920.

lyzed, the crucible should be covered during the weighing, and each sample should be treated with the acid at once, and not be left until the series of weighings is finished. Place on the steam bath, but not in direct contact with the steam, and digest for 30 minutes or more, with an occasional gentle swirling of the contents of the crucible. Unless the mixture threatens to foam up to the cover, the crucible may now be heated by the direct steam for two or three hours. If there is much foaming, which happens but seldom, the digestion at moderate heat must be continued longer.

Remove the crucible from the bath, and when its contents have cooled somewhat, add cautiously, in small portions, 10 or 12 g of anhydrous sodium carbonate. This is conveniently measured in a 15 cc crucible, rather than weighed. The first portions of soda often remain on top of the oily layer, so that the crucible must be tilted or swirled slightly to start the reaction. When about half of the soda has been added, rinse the watch glass with 1 or 2 cc of warm water and leave it off. Pour in the rest of the soda. With a glass rod, about 3 mm thick and 12 cm long, thoroughly mix the contents of the crucible and spread the pasty mass around on the sides and half to two-thirds of the way to the top. The rod is left in the crucible, which is then placed on the steam bath, or in an air bath at 100° C.

When its contents are dry enough, the crucible is placed in an inclined position on a wire triangle and the ignition is started over a low flame. When more than 1 g of oil has been taken, there is a tendency for it to burn too briskly, but this is easily controlled by judicious use of the stirring rod which scrapes the burning portion away from the rest. When part of the mass has burned white, more is worked into it, and so on until all of the organic matter is destroyed. It is necessary to hold the crucible with tongs during this operation. Toward the end of the ignition the flame may be increased somewhat, but it is rarely necessary to heat the crucible to redness. With care a good crucible should last for many determinations. Of two which were used for 17 determinations each, and were still in almost perfect condition, one crucible lost just 100 mg, and the other 1.1 mg less.

If a suitable muffle is available, the ignitions can be made at a temperature not above 550°. The glass rod should be removed and the crucible covered with a watch glass. The principal difficulty is that the oil may start to burn at some point and the whole mass begin to glow in a few seconds. In this case the cover may be blown aside and loss by spattering occur. Under proper conditions, several ignitions can be made at one time.

According to the amount of oil taken, the mixture of sodium salts resulting from the combustion varies from granular to pasty when hot. After cooling, place the crucible upright in a 400 cc beaker and fill it with distilled water. After a short time lay it on its side, cover the beaker and digest on the steam bath. When the salts have dissolved, remove and rinse the crucible. Filter the solution to remove specks of carbon, bits of the glass rod, etc. Acidify with concentrated hydrochloric acid, using Congo red paper as indicator, and add 2 cc of acid in excess. The neutralization proceeds more safely if nearly the required amount of acid is put in the covered beaker into which the solution is filtered. It is safe to use 10 cc of acid for this, but the exact amount can not be stated, because the total amount of carbonate and nitrite to be neutralized depends on how much oil was taken. The acidified filtrate and wash water should have a volume of about 175 cc. Heat on the steam bath, add 10 cc of barium-chloride solution (containing 100 g of crystallized salt in 1 l), and digest on the bath until the supernatant liquid is clear. If possible delay the filtration until the next day.

A blank should be run with every new lot of reagents. An ignition is made just as if oil were present, because the flame may contain enough sulphur to be corrected for. Even when the correction amounts to several milligrams almost no precipitate may be seen before the solution has stood for several hours.[40]

It is needless to describe how the barium sulphate is filtered off, washed, and ignited.

(*c*) CRITICISM OF NEW METHOD.—It is an advantage that several determinations can be started at one time. The digestions and filtrations for these can be carried on simultaneously. An ignition requires 15 to 25 minutes. (Rubber is so completely broken down that less time is spent in this part of the procedure.) Oil is but slightly decomposed by the treatment with acid, and most of it is driven off in clouds of vapor during the first part of the ignition, and it appears as if much of the sulphur were escaping also. The concordance of duplicate results and their sub-

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[40] It is not necessary to have the solution boiling when the barium chloride is added, or to digest the precipitate with the boiling solution. Hillebrand (Analysis of Silicate and Carbonate Rocks, Bull. 700, U. S. Geol. Surv., p. 232) says "at boiling heat or on the steam bath." It is much more convenient to use the steam bath, and there is no danger of loss by bumping; also, as pointed out by Hillebrand. there can be no contamination by sulphur from the flame.

stantial agreement with analyses by the bomb method are evidence that there can be little or no loss.

In discussing the bomb method a few comparative figures were given. The following were obtained in the analysis of five fuel oils in which the sulphur had been determined by the Bureau of Mines laboratory at Pittsburgh.[41] Each oil was analyzed twice by the new method. The figures in parentheses are the values obtained by the bomb method at the Bureau of Mines. The percentages of sulphur were: 3.67, 3.70 (3.17); 4.01, 4.03 (3.98); 1.13, 1.12 (1.01); 0.36, 0.36 (0.29); 0.18, 0.17 (0.13).

Whatever the faults of the new method, it gives results at least as high as those by the bomb. It has been criticized as too bothersome, yet it does not require the same meticulous attention to details as when the bomb is used. For 10 years it has been used at this Bureau for the analysis of rubber, and even in the hands of beginners has given good results. For oils it may well be employed in laboratories which do not have sufficient work of this kind to justify the expense of a bomb calorimeter.

(*d*) SOURCES OF ERROR.—The most obvious way in which incorrect results can be obtained—failure to convert all of the sulphur into sodium sulphate—appears not to be a fault of this method. It has, however, one serious fault in common with all of the other procedures in which salts or oxides of metals are used to effect or facilitate the oxidation of the sulphur compounds in the oil. This is the occlusion of the salts of these metals by the barium-sulphate precipitate. Even when barium chloride is added to water which contains only sulphuric acid, the precipitate is not pure, but is contaminated by more or less chloride, and the results are too high. If soluble sulphates, particularly those of sodium, potassium, or ammonium, are present, there is a considerable amount of occlusion and during the ignition of the precipitate a complication of reactions, with the net result that the values found are too low. On the other hand, the presence of nitrates causes errors in the opposite direction. Finally, the amount of dissolved barium sulphate which is lost in the filtrate and washings depends on their volume and on the quantity of free acid, other than sulphuric.[42]

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[41] They were obtained through the interested cooperation of E. W. Dean and N. A. C. Smith, the latter in the Washington laboratory of that Bureau.

[42] For an interesting discussion of the determination of sulphur as barium sulphate, see the following papers; Allen and Johnston, J. Am. Chem. Soc., **32**, pp. 588–617, 1910; Johnston and Adams, Ibid., **33**, pp. 829–845, 1911.

(*e*) CORRECTION FOR OCCLUSION.—By adapting to the present purposes a suggestion made by Johnston and Adams in the paper just cited, data were obtained which show the necessary corrections of weights of barium sulphate up to 0.200 g. In order to have definite amounts of sulphur, a solution of pure sodium sulphate which was dried at 200° C before weighing out, was prepared. By taking various aliquot portions of this solution, weights of barium sulphate from 3 to 200 mg were obtained. Without going into all the details, the procedure was as follows: To check the purity of the sodium salt an aliquot portion was diluted to 175 cc, acidified with 2 cc of concentrated hydrochloric acid, heated on the steam bath and precipitated with 10 cc of the usual barium-chloride sulution. The results were in satisfactory agreement with those calculated.

In an actual determination of the sulphur in oil, the aqueous solution of the melt contains sodium carbonate, nitrate, nitrite, and sulphate. When this is acidified, the carbonate and nitrite are decomposed, so that finally only chloride, nitrate, and sulphate are present. The amount of chloride depends indirectly upon the weight of oil taken. This is true also of the residual nitrate. In order to have approximately the same conditions as when amounts of oil varying from 0.5 to 2.0 g were burned, portions of sodium carbonate equal to those used in an analysis were dissolved and treated with 2, 3, or 4 cc of concentrated nitric acid. Then to the solution was added hydrochloric acid until there was 2 cc in excess beyond the neutral point. The desired aliquot portion of sulphate solution was added, the volume made up to 175 cc, and barium sulphate precipitated as usual. Next day the precipitates were filtered off and finally weighed. Blanks were run under the same conditions, only with the sodium sulphate left out. The small amounts found in the blanks were used as corrections for the larger weights of barium sulphate.

No matter how much sodium sulphate was taken, the weights of barium sulphate found, after being corrected for the impurities in the reagents, were greater than those calculated from the weights of sodium sulphate. The differences between the weights found and those calculated were the corresponding corrections for occlusion and solubility. On plotting these corrections against the weights of barium sulphate found, it was seen that a straight line running from the origin to a point with the coordinates 10 and 200 mg represented the facts with sufficient accuracy. In other words, the net error amounted to 5 per cent of the weight of the precipitate. The variations from this straight line were so slight as to be of no significance in the analysis of oils. The most surprising fact was that changing the volume of nitric acid caused so little difference in the amount of occlusion.

With a 1 g sample, 200 mg is equivalent to 2.75 per cent of sulphur and the corrected weight, 190 mg, to 2.61 per cent. Under other conditions of volume, acidity, etc., the corrections, and the errors if these are neglected, might be very different.

An easy way to find the weights of sulphur corresponding to the amounts of barium sulphate found is by means of a graph. Figure 1 is such a graph drawn from the data obtained in the determinations of the occluded salts. Each centimeter on the axis of abscissas represents 10 mg of barium sulphate. On the axis of ordinates each centimeter represents 1 mg of sulphur. After correction, 200 mg of barium sulphate becomes 190 mg, which corresponds to 26.1 mg of sulphur. From the point represented by the coordinates 200 and 26.1 draw a straight line to the origin. For any weight of sulphate up to 200 mg the weight of sulphur can be read off directly, and its percentage calculated. If the same weight of oil, say 1 g, is taken for analysis each time, the percentages, instead of the weights of sulphur can be laid off on the axis of ordinates; thus instead of 26.1 mg there would be 2.61 per cent. It is not always desirable to use so little or so much as 1 g of oil, and it may be advisable to make one calculation rather than to delay long enough to make an exact weighing if the oil is losing hydrogen sulphide. For these reasons it seems preferable to lay off the ordinates as first stated.

An example from an actual analysis is given: 0.5053 g of oil yielded 0.0722 g of barium sulphate. The sodium carbonate was so poor that the correction for it was 0.0085 g. This subtracted from the first weight gave 0.0637 g. On the graph 63.7 mg of barium sulphate is seen to be equivalent to 8.3 mg of sulphur. This divided by 0.5053 gives 1.64 per cent. The percentage calculated without the graph is 1.66, an amply satisfactory agreement.

After the manuscript of the present paper was completed, and a few days before a preliminary paper was published in the Journal of Industrial and Engineering Chemistry (May, 1920, pp. 482 to 485), it was learned that an almost identical method was published 15 years ago. This earlier paper seems to have been entirely overlooked or ignored by oil chemists. Goetzl

(Z. angew. Chem., 18, pp. 1528 to 1531; 1905) used the following procedure for the determination of sulphur in "liquid fuel": In a roomy platinum crucible treat 2 or 3 g of oil with 4 cc of fuming nitric acid. The crucible, covered with a watch glass, is allowed to stand over night and then warmed gently on a water bath. The acid is evaporated off and the oily nitrated mass is mixed with sodium carbonate and potassium nitrate. More of the fusion mixture is spread over the top and the whole is ignited. The subsequent operations need not be described.

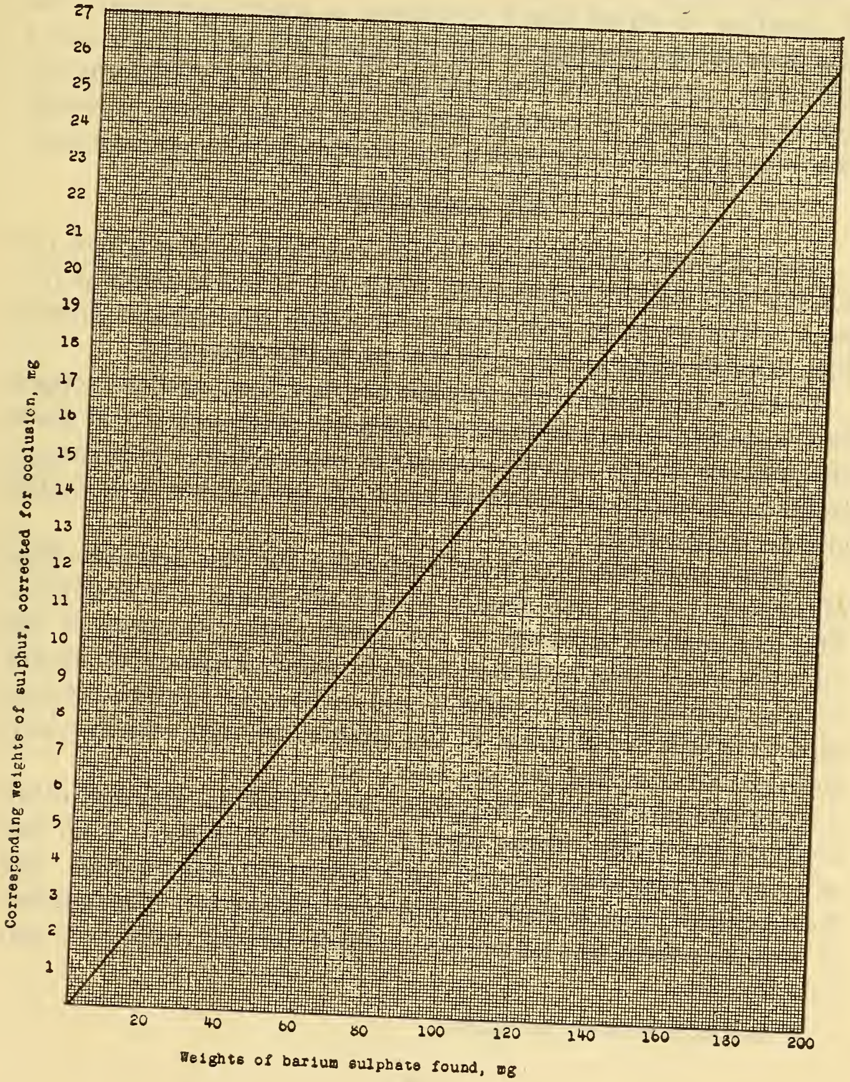

FIG. 1.

Kerosene and naphtha contain so little sulphur that 10 g samples were taken for analysis. The method was used for coal, lignite, peat, organic substances, etc.

As in the majority of papers on the determination of sulphur, no mention of errors due to occlusion is made by Goetzl. He also does not say whether or not the ignition is to be made over a full flame, although he does advise the use of a mushroom-top burner. Heating to redness would rapidly destroy a porcelain crucible, and fortunately such a high temperature in not necessary.

VII. SUMMARY

Short accounts are given of theories concerning the origin of the sulphur and sulphur compounds which are found in crude petroleum. The forms of combination in which the element occurs, their identification and significance are briefly discussed.

Tests for the detection of sulphur are described, and the copper test is shown to be one of great delicacy. Although it will show the presence of very minute amounts of free sulphur or of hydrogen sulphide, it may be of no value when all the sulphur is in stable organic compounds.

Various methods that have been used for the determination of sulphur in oils, and finally a new procedure, are described. The new method is based on the preliminary treatment of the oil with nitric acid saturated with bromine, followed by fusion with a mixture of sodium nitrate and carbonate. Certain sources of error which are inherent in the method and the way in which they can be corrected for, are taken up.

Data obtained by the analysis of certain oils by this and other methods are given. From these it appears that there is no loss of sulphur when oil is treated with nitric acid and bromine, and then ignited with sodium nitrate and carbonate. The method is recommended for laboratories which do not have a bomb calorimeter.

WASHINGTON, May 28, 1920.