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THE DETERMINATION OF SULPHUR IN PETROLEUM OILS

For the determination of sulphur in gasoline and kerosene there are satisfactory methods of burning almost any desired quantity in a lamp and converting any sulphur, whether free or combined, into sulphuric acid. This is titrated with standard alkali or weighed as barium sulphate. For less volatile oils one of the various bomb methods is usually employed. Not more than 0.6 to 0.8 g of the oil can be burned in a determination, so that if it contains only a few hundredths of a per cent of sulphur, the volume of N/10 alkali used in the titration, or the weight of barium sulphate found, is quite small. The bomb method is therefore not entirely satisfactory for determining the percentages of sulphur in highly refined oils, or for investigations in which the amount of sulphur must be followed closely.

The method here described has been found accurate, and although a determination takes longer than one by means of the bomb, it has some advantages. Only ordinary laboratory equipment is needed, as much as 2.5 g of oil can be burned at a time, and several determinations can be run simultaneously. The method is not applicable to gasoline, which is lost by evaporation during the preliminary treatment, but it can be used for kerosene and all petroleum products up to asphalt; if the

latter will melt on the steam-bath.

The procedure was described in a preliminary paper (J. Ind. & Eng. Chem., vol. 12, pp.483-5 and 613; 1920), and later in Bureau of Standards Technologic Paper No.177, which is out of print. The description in the latter is the more complete because it tells how to apply a correction for the error caused by the occlusion of salts by the precipitated barium sulphate.

METHOD

According to the suspected percentage of sulphur in the material, weigh from 0.5 to 2.5 g in a 100-cc porcelain crucible, add a measured volume of concentrated nitric acid which has been saturated with bromine, and at once cover the crucible with a watch-glass. For weights of oil up to 1.8 g, 5 cc of the acid is enough; for greater weights of oil use 8 cc of the acid. When rather volatile oils, or those which smell of hydrogen sulphide, are analyzed, the crucible should be kept covered as much as possible during the weighing, and each portion of oil should be treated with nitric acid as soon as its weight is known, and not be left until the duplicate portion is weighed.

Place the covered crucible on the side of a steam-bath and digest for 30 minutes or more. Unless the contents show signs of foaming over, then heat in direct contact with the steam for two or two and one-half hours. Remove the crucible from the bath and add cautiously in small portions 10 or 13 g

of anhydrous sodium carbonate if 5 cc of nitric acid was used, or 16 to 18 g if the volume of acid was 8 cc. Lift the watch-glass a little and by means of a spatula or small scoop throw some of the carbonate against the side of the crucible, about half way down. In this way the soda is introduced so as to coat the wall of the crucible all around, and with little danger of loss by foaming over. With some oils it is necessary to start the reaction, after two or three portions of soda have been added, by slightly tilting the crucible. When all of the soda has been added, rinse the cover into the crucible with a little hot water, and at once thoroughly mix the contents by means of a glass rod about 13 cm long and 4 mm thick. Spread the pasty mass around on the wall of the crucible half or two-thirds of the way to the top. Leave the rod in the crucible, which is placed on a steam-bath or in an oven at about 100°C until the contents are dry. Then place the crucible in an inclined position on a wire triangle and start the ignition over a low flame. When more than a gram of oil has been taken for a determination, there is a tendency for it to burn too briskly, but this can be controlled by judicious use of the stirring rod, with which the burning portion is scraped away from the rest. When part of the mass has burned nearly white, work more of the unburned material 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. Towards the end of the ignition the flame can be increased

somewhat, but it is rarely necessary to heat the crucible to redness. Each ignition requires about 20 minutes. It is not safe to make ignitions in a muffle because the reaction can not be controlled and many determinations will be lost by spattering, even with covered crucibles.

According to the amount of oil taken and its action on the nitric acid, the mixture of sodium salts after the ignition varies from granular to pasty when hot. In the latter case it is easier to burn all of the carbonaceous matter. After cooling, the crucible, placed upright in a 400-cc beaker, is filled just to the brim with water. After the bits of the melt on its upper part have dissolved, tilt the crucible on its dide, cover the beaker and digest on a steam-bath. When all has dissolved from the bottom of the crucible, remove the latter from the beaker by means of the glass rod and rinse it inside and out with a little hot water. Filter the solution to remove specks of carbon, bits of glass rod, etc., wash the first beaker and pour the washings through the filter. Two washings of the beaker, with enough water each time to fill the 7-cm filter-paper, will suffice. The filtrate and washings are caught in a beaker of suitable capacity -- 250 cc when the smaller amounts of nitric acid and soda were used, and 400 cc when the larger. The beakers should be marked at the 175-cc, or 280-cc levels, respectively.

Acidify the filtrate with hydrochloric acid (2:1) and add 3 (or 5) cc in excess. A 2-mm strip of congo red paper is used as outside indicator, but in most cases the sudden

clearing up of a slight turbidity (aluminum hydroxide from attack of the crucible during the ignition) is almost as good a sign. The neutralization proceeds more safely if part of the acid required is placed in the covered beaker into which the filtrate flows. About 15 (or 25) cc can be put into the beaker. After all of these operations the total volume of the solution should not exceed 175 (or 280) cc. If it is not that much, make up to the required amount by adding water. Heat on the steam-bath and then add 10 (or 16) cc of a solution of barium chloride which contains 10 g of the crystallized salt in 100 cc. Continue the digestion on the steam-bath until the solution clears. Next day filter off the precipitate, wash, ignite and weigh it, and either calculate the corresponding weight of sulphur, or read it from the graph described further on.

It is well known to chemists, but a fact generally ignored in the determination of sulphur, that barium sulphate always occludes some of the salts which are in the solution from which it is precipitated. In working out the details of the method just described it seemed best to keep down the volume of the solution in order to lessen the error due to the slight solubility of barium sulphate. Some oils low in sulphur yield only a few milligrams of precipitate, and the error would not be negligible. As the amount of sodium carbonate could not be decreased without running the risk of having the ignition proceed too rapidly, it was realized that the barium sulphate precipitate would be quite impure. The

correction to be applied was determined as suggested by Johnston and Adams (Jour. Amer. Chem. Soc., vol. 33, pp.829-845; 1911), by adding known amounts of sodium sulphate to the other reagents as in an actual analysis, and finding the difference between the calculated weight of barium sulphate and that of the precipitate. The error was found to be practically 5 per cent for weights of precipitate up to 300 mg. The deviations from this are too slight to be considered. Of course this correction is to be applied only when the conditions of acidity and concentration of sodium salts are as described above. A precipitate weighing 200 mg is equivalent to 190 mg of pure barium sulphate, or to 26.1 mg of sulphur. Hence the factor for calculating the sulphur content of the precipitate is 0.1305, which is 95 per cent of the usual factor 0.1374. By means of the accompanying graph the corrected weight of sulphur can be read directly from the weight of barium sulphate found.

The following table shows how the procedure is changed according to the weight of sample taken for a determination. For the great majority of oils the amounts in the first column are ample.

Weight of sample	0.5-1.8 g	1.8-2.5 g
Vol. nitric acid-bromine ..	5 cc	8 cc
Weight of sodium carbonate	10-11 g	16-18 g
Excess hydrochloric acid(2:1)	3 cc	5 cc
Vol. of solution before adding barium chloride ..	175 cc	280 cc
Vol. of barium chloride sol.	10 cc	16 cc

Of the reagents used, the sodium carbonate is most likely to contain sulphur compounds that will affect the analysis. A blank, using the full amount for a determination, should be run on each new supply of it.

SUGGESTIONS

The soda need not be weighed, but can be measured with sufficient accuracy in a small procelain crucible, or in a small, graduated glass tube. The "bulking value" of different samples of soda depends upon the size and porosity of the grains. It is a simple matter to find out what volume 11 (or 17) g of each new lot of it occupies.

The flame over which the ignition is made should be free from sulphur. Instead of using city gas, it is best to feed the Bunsen burner with a mixture of air and the vapors of petroleum ether. A convenient arrangement can be made by placing a layer of large glass beads, about 4 cm deep, in a Drechsel gas-washing bottle, and covering the beads with 3 or 4 cm of petroleum ether. Air blown through the bottle from the laboratory compressed air system or other suitable source will carry over enough of the vapor to maintain a good flame. If the bottle has been used for a long time without emptying out the "heavy ends" of the ether, it may have to be set in a beaker or can of warm water. Usually, however, the flame tends to be smoky at first, until the evaporation chills the ether and lessens its volatility. In extreme cases it may be necessary to add some mineral spirits (turpentine substitute)

to the ether, if the bottle has been cleaned recently, so that the air-vapor mixture will be poor enough to give a blue flame. The size of the flame should be adjusted at the burner, and not by regulating the air supply.

The gummed labels which mark the beakers will remain on indefinitely, in spite of many washings, if they are moistened on both sides when applied, allowed to dry thoroughly, and then waterproofed by warming over a small flame and rubbing with a piece of paraffin.

The close agreement that can be expected of duplicate analyses is shown by the following figures. These were selected only to show a wide range in sulphur content, and not because of their concordance.

Percentages of Sulphur Found

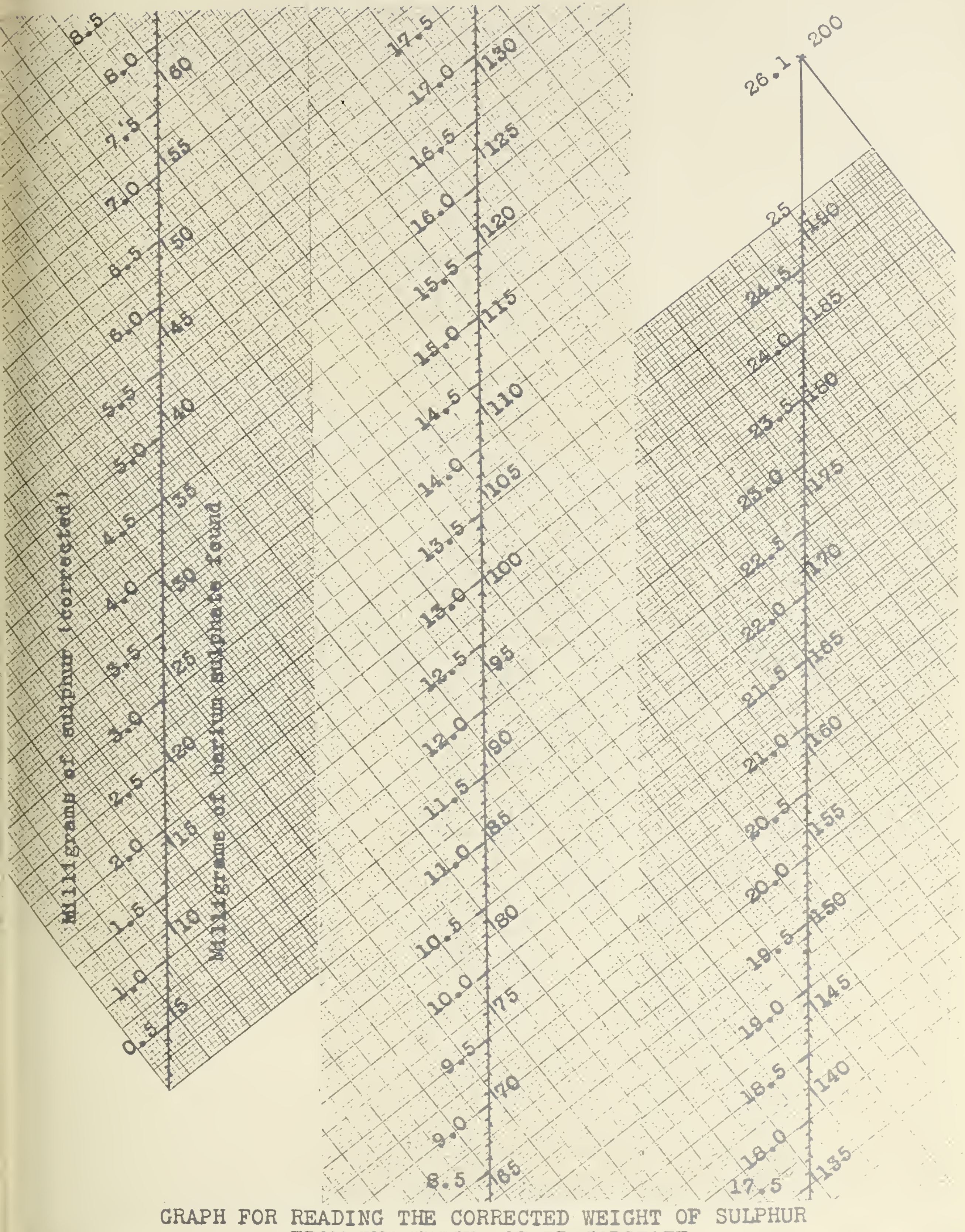
Kerosenes			
0.03	0.01	0.06	0.10
0.02	0.02	0.07	0.10
0.03	0.02	0.07	

Cutting Oils			
0.85	1.65	3.21	9.23
0.85	1.65	3.29	9.29

Lubricating Oils					
0.007	0.08	0.34	0.49	0.85	1.97
0.007	0.09	0.34	0.47	0.86	2.03

Asphalts		
0.35	1.13	6.10
0.37	1.20	6.03

The first two analyses made by the method, in 1920, were on a topped Mexican crude oil. The results were 4.04 and 4.02 per cent.



GRAPH FOR READING THE CORRECTED WEIGHT OF SULPHUR
FROM THE WEIGHT OF PRECIPITATE

Negative 5630