

proceeds but the unmistakable blue can easily be seen after a few trials.

Working by this method I have obtained duplicates within 0.05 per cent. which is certainly accurate enough for all practical purposes. My results have also checked the gravimetric methods very closely.

CHEMICAL LABORATORY OF THE
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THE DETERMINATION OF SULPHUR IN BITUMENS.¹

BY S. F. AND H. E. PECKHAM.

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THE paper read by Mr. E. H. Hodgson, which appeared in the November (1898) number of this Journal, was read by us with great interest. It is evidently intended to be a description of a fair comparative test of the value of the several methods used for the determination of sulphur in the different varieties of bitumen examined.

We wish to call attention to a number of unrecognized, or at any rate unmentioned conditions, which, in our opinion, rendered the results, given by Mr. Hodgson, variable, and to some extent unreliable.

Of the specimens selected for analysis, it is to be said, that the two specimens called "Trinidad Lake" and "Trinidad Lake refined" are very peculiar substances. They, in common with all other Trinidad pitch, consist of a mixture of bitumen, mineral matter, organic matter that is not bitumen, and a considerable proportion of ferric and aluminic oxides, that are combined with organic radicals to form complex salts. There are sound reasons for believing that some of the sulphur is free, some of it in combination with iron as pyrites, in an extremely minute state of division, and some of it in combination as thio-salts, in which it performs a linking rather than saturating function.

There can be no question that the action of nitric acid on this complex mixture of various substances results in the formation, not only of sulphuric oxide, but of other oxides of alumina and iron, that will almost certainly form double barium salts with sulphuric acid, that are nearly or quite as insoluble as pure ba-

¹ Read at the June Meeting of the New York Section.

rium sulphate, and consequently follow, or accompany the barium sulphate, even to the final weighing.

Many years ago one of us precipitated alumina as a double barium and aluminum sulphate, from a solution of potash alum. The potash alum had been mixed, dry with barium chloride, and, as is remembered, with the potash alum largely in excess, as a puzzling problem in qualitative analysis. On attempting to dissolve the mixed salts, a barium alum or double sulphate of barium and aluminum remained undissolved. This reaction indicates why it is of importance that the oxides of iron and alumina should be removed from the solution before the barium chloride is added.

The specimen denominated "Trinidad crude" and further described as "crude asphalt from Hadley's diggings, about one mile from Trinidad Lake; it is known as 'iron pitch,' being the hardest asphalt found in Trinidad," is not asphalt at all, but is a residue from the natural distillation of the pitch by jungle fires. It is found in small masses, and in small quantity, all over the deposit, both within and without the lake, and is uniformly rejected as rubbish. It has been subjected to such a temperature that all of the water has been expelled, and the whole mass melted and brought to a condition of semifluidity. Apparently the sulphur is in part expelled, and that which remains is evidently brought into such a condition that the nitric acid process fails to produce the reaction essential to the formation of double salts, as the results of the analyses by the four processes used by Mr. Hodgson are essentially alike. The results obtained from Cuban, Alcatraz, and California asphaltum are evidently subject to the same criticism as the Lake pitches, in a less degree.

The deflagration method, as described in Mr. Hodgson's paper, is not the method used by the authors. We never used a porcelain crucible; first, for reason of its form, and second, for reason that the fluxes used will react with the porcelain, making it impossible to determine the iron, alumina, and silica in the assay.

We have modified to a slight degree our method of procedure, as experience has suggested, until finally we have weighed out such an amount of the assay as will represent about five-tenths gram of bitumen. This is very thoroughly mixed with fifteen grams each of pure and dry sodium carbonate and potassium

nitrate. The salts are first thoroughly pulverized and mixed in an unglazed porcelain mortar. Two-thirds of the mixture are then removed to a sheet of glazed paper. The assay is then mixed in the mortar with the flux in the most thorough manner and then removed to a second sheet of glazed paper. The mortar is then carefully rinsed with the remaining flux in two successive portions. The whole of the flux and assay are then brought to a uniform mixture on the glazed paper. The mixture is then placed, small portions at a time, into a two-ounce platinum crucible, heated to dull redness. No fusion with a blast-lamp is necessary, as the assay is in quiet fusion when the last portion has deflagrated. A large excess of flux lessens the violence of the combustion and also lessens the liability to loss by spattering.

The contents of the crucible are then dissolved by allowing it to remain covered with water in a beaker, preferably over night. When the solution is complete, the crucible is washed off and the contents of the beaker rendered acid with hydrochloric acid. The solution is then evaporated to dryness over a water-bath, the silica dehydrated, moistened with hydrochloric acid, treated with water and the silica filtered off, ignited, and weighed. The solution is rendered alkaline with ammonia, boiled until the excess of ammonia is removed, and the precipitate of iron and alumina dried and weighed as usual. The iron may be found in another portion with potassium permanganate and the alumina determined by difference. Lime may be determined as oxalate if desired.

The solution, freed from silica, iron, alumina, and lime, is brought to a boil, acidulated with hydrochloric acid, and the sulphuric acid precipitated with barium chloride, added in small portions at a time from a pipette. This method for the determination of sulphur is susceptible of great accuracy, if *conducted with care*. It requires great care from the beginning to the end. Mr. Hodgson's results do not indicate great care,—they are not sufficiently concordant.

We have not found the slightest difficulty in bringing out concordant results to the second place of decimals, and sometimes to the third. The method has also been proved presumably correct, by reason of determinations made by first estimating the

sulphur in a very pure asphalt and then in the same asphalt to which a weighed quantity of pure sulphur had been added dry. The results showed the amount of sulphur in the pure bitumen plus the amount of pure sulphur added.

Dr. William C. Day, of Swarthmore College, has lately used this method for determining sulphur in the natural and artificial gilsonites that he has had under examination. He has kindly given me the results that he has obtained in several analyses of these substances, which fully illustrate of what the method is capable in skilful and sympathetic hands. We give his results below.

UTAH GILSONITE.

	Weight taken. Grams.	BaSO ₄ obtained. Gram.	Sulphur. Per cent.
I	2.7111	0.0474	0.0024
II	2.1651	0.0390	0.0025
III	2.1017	0.0388	0.0027

FISH AND WOOD ASPHALT.

I	2.0218	0.0136	0.0009
II	1.9988	0.0114	0.0008

WOOD ASPHALT.

I	1.9753	0.0134	0.0009
II	1.3777	0.0095	0.0009

FISH ASPHALT.

I	2.0402	0.0287	0.0019
II	1.9954	0.0276	0.0019

INDIAN TERRITORY ASPHALT.

I	2.1676	0.2216	1.40
II	2.2410	0.2238	1.37

These results are sufficiently concordant for any purpose, and are given in preference to our own, although we have found no difficulty in obtaining equally satisfactory figures, both with pure bitumens and mixtures of bitumens with pure sulphur.

This method is simple, reasonably rapid, and accurate, does not require complex and expensive apparatus and, what is especially to be noted, furnishes a ready means for the determination in the same solution of other constituents of most solid bitumens, the correct estimation of which is often of the greatest importance.

It is to be further noted that in these analyses about two grams, more or less, are taken for an assay. These materials are all exceptionally low in sulphur. It is therefore necessary to take a larger portion than is usually found advisable in the use of this process, and when so much of the asphalt is burned it becomes absolutely necessary to use a larger proportion of the flux, otherwise some of the assay will escape oxidation.

Note.—In the discussion that followed the reading of this paper, it was claimed that mercaptans and similar constituents of bitumens could not be oxidized by this method. It has not yet been shown that mercaptans and similar sulphur compounds exist as constituents of crude bitumens in such amount as to be worthy of consideration in this connection. This method is not recommended as superior to the method of Carius in ultimate research, but is recommended for the determination of sulphur in solid and semisolid bitumens for practical purposes.

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A NEW METHOD FOR THE DIRECT DETERMINATION OF ALUMINA IN PRESENCE OF IRON, MAN- GANESE, CALCIUM, AND MAGNESIUM.

BY WILLIAM H. HESS AND E. D. CAMPBELL.

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THE method most commonly used for the determination of alumina in presence of iron, manganese, calcium, magnesium, and phosphoric acid, is the indirect method in which the iron, alumina, and phosphoric acid are obtained together as a combined precipitate with ammonia. The alumina is taken as the difference obtained by deducting the weight of phosphorus pentoxide and ferric oxide as determined in separate samples. While the determinations of phosphoric acid, as well as the volumetric estimation of iron are satisfactory, an error may be introduced by careless ignition of the mixed oxides, since ferric oxide may be more or less converted to magnetic oxide (Fe_3O_4), with loss of oxygen; while in the calculations all the iron is figured as ferric oxide. Any error arising from careless ignition, from failure to perfectly wash the precipitate, or from an imperfect separation of other substances present as calcium, zinc,