

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.

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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,

nickel, etc., goes to increase or decrease the percentage of alumina found.

Among the direct methods for determining alumina, the best known and most used are the alkali method and the thiosulphate method of Wöhler. Neither of these succeed satisfactorily when only traces of alumina are present with iron. Neither the potassium cyanide method nor the basic nitrate method of Beilstein and Luther seem to have become popular. These methods, as well as many others that have been worked out, either require special expensive platinum apparatus or much attention to detail to obtain the correct conditions. In short, the present direct methods for estimating alumina are laborious, and too uncertain in their accuracy to pay for the heavy labor entailed, and consequently have not as yet displaced the simple though somewhat uncertain indirect method.

A method for the direct determination of alumina in presence of other substances commonly occurring with it, which is accurate, simple and rapid, would seem to be of great practical value, especially to those chemists connected with the iron ore industry, with cement and other clay industries, as well as in general mineral analysis.

While engaged in trying to modify the old alkali process so as to make it more satisfactory, experiments were carried on with a view of finding some reagent which would quantitatively precipitate alumina without precipitating iron. Recourse was taken to the organic bases for a suitable reagent for this purpose.

The well-known ammonium base, phenylhydrazine, which has proved of such great value in establishing the chemistry of the sugars, was found to be the most satisfactory of the many organic bases tried for the precipitation of alumina. As a base it is somewhat weaker than ammonia. It precipitates aluminum from its solutions quantitatively as the hydroxide without a trace of the precipitate being redissolved in excess of the precipitant. Phenylhydrazine is, moreover, a strong reducing agent, quickly reducing iron from the ferric to the ferrous state, thus playing a double rôle of usefulness in the separation of iron from alumina.

METHOD OF ANALYSIS.

A convenient sample to be analyzed is weighed out and

obtained in solution preferably as the chloride in the usual way. To a convenient bulk of solution, 200 to 300 cc. heated to near the boiling-point, dilute ammonia is added slowly as long as the precipitate formed just redissolves with readiness. A neutral, saturated solution of ammonium bisulphate¹ is added, drop by drop, with stirring to this hot and nearly neutral solution, until it becomes colorless, showing the complete reduction of the iron. To the hot solution now smelling strongly of sulphur dioxide, one or two cc. of phenylhydrazine are added. If this amount of phenylhydrazine causes a permanent precipitate, then a few drops more of phenylhydrazine are added to insure complete precipitation of the alumina. If one to two cc. of phenylhydrazine do not produce a permanent precipitate, it is economical, after adding this amount of phenylhydrazine, to add dilute ammonia carefully, drop by drop, to a just perceptible permanent precipitate, and then complete the precipitation by adding a few drops more of phenylhydrazine. The precipitate, consisting of aluminium hydroxide and aluminum phosphate, is filtered out on an ordinary filter and washed with warm water containing a small amount of phenylhydrazine bisulphite. This washing solution is prepared as follows: To a few cubic centimeters of phenylhydrazine in a beaker, a saturated water solution of sulphur dioxide is added gradually until the precipitate of phenylhydrazine sulphite, which at first separates out in crystals, is redissolved to a yellow solution. If, after a few minutes, an odor of sulphur dioxide is perceptible, a few drops of phenylhydrazine are added to neutralize this excess of sulphurous acid. This concentrated solution of phenylhydrazine bisulphate, if well stopped, will keep indefinitely. Five to ten cc. of this to 100 cc. of water is an efficient strength of solution for washing the precipitate of alumina. The washing with this warm solution is continued until the washings give no test for iron with ammonium sulphide. A drop or two of phenylhydrazine is added to the filtrate with stirring to see if the precipitation has been complete. If chlorides of metals other than iron be present, the washing must be continued until the washings are free from chlorine. The presence

¹ (This solution of ammonium bisulphite is made by passing sulphur dioxide into a cooled solution of ammonia (1 : 1) until the solution becomes yellow. It serves the purpose here, not only of reducing the iron, but the excess of sulphurous acid unites with the phenylhydrazine added, to form a salt which acts as a most efficient agent for keeping the iron reduced and thus prevents its precipitation with the alumina.)

of chlorides of volatile bases will do no harm in the ignition of alumina.

The precipitate together with the filter is placed in a platinum crucible, dried and the filter charred at a low temperature. After the filter is completely burned, the ignition is continued at a bright red heat to constant weight. Care is taken to weigh quickly with the cover on the crucible, since both the phosphate and oxide of aluminum are very hygroscopic. A second ignition and weighing is always necessary. This precipitate of alumina carries all the phosphorus pentoxide so that the weight of alumina is found by subtracting the weight of phosphorus pentoxide found in a separate sample.

Chromium is quantitatively precipitated by phenylhydrazine, and may thus be separated from iron with great readiness. Neither calcium, magnesium, manganese, cobalt, or nickel is precipitated.

GRAVIMETRIC METHOD FOR IRON.

If a gravimetric estimation of the iron is desired, it has been found to be most expedient to add ammonium sulphide to the filtrate in case there is no other metal present that will be precipitated by this reagent. The sulphide of iron thus formed is filtered out, and without washing is redissolved in dilute hydrochloric acid. From this hydrochloric acid solution the iron is estimated in the usual way with ammonia after oxidation with nitric acid. It may under some circumstances be desirable to separate the iron and alumina by means of ammonia or as basic acetate, to get rid of other metals before attempting their specific separation by means of phenylhydrazine.

SEPARATION AND ESTIMATION OF PHOSPHORIC ACID.

Since the aluminum hydroxide precipitated with phenylhydrazine carries all the phosphorus pentoxide with it that is present in the solution, this method may be conveniently used for its separation. If the alumina present in the mineral is not sufficient to carry all the phosphoric acid as the normal phosphate, an excess of a known solution of aluminum chloride is added. The alumina is then separated by the above method. If only the phosphoric acid is desired, this precipitate may be dissolved in nitric acid and the phosphoric acid may be deter-

mined in the usual way. Or the precipitate may be ignited and weighed, thus giving the combined weight of alumina added, of alumina in the mineral and of phosphoric acid in the mineral.

RESULTS ON KNOWN MIXTURES.

Mixtures were made by Prof. Campbell's private assistant which were strictly unknown to the operator, and were subjected to the above method of analysis with results as recorded in the following table:

	Weight of iron taken. Gram.	Al ₂ O ₃ taken. Gram.	P ₂ O ₅ taken. Gram.	P ₂ O ₅ + Al ₂ O ₃ taken. Gram.	P ₂ O ₅ and Al ₂ O ₃ found. Gram.	Gain or loss. Gram.
(1)	0.7023	0.00664	0.00077	0.000741	0.000735	0.00006
(2)	0.2020	0.1343	0.00022	0.13452	0.1343	0.00022
(3)	0.059934	0.0105	0.00576	0.01581	0.0162	0.00039
(4)	0.3339	0.0966	0.01072	0.10732	0.1066	0.00072
(5)	0.6604	0.030	0.00577	0.03577	0.03570	0.00007
(6)	0.551	0.05152	0.01073	0.06225	0.06220	0.00005
(7)	0.527	0.0219	0.01073	0.03263	0.0330	0.00037
(8)	0.564	0.0644	0.00822	0.07262	0.0719	0.00072

A solution was prepared by dissolving one gram of calcium carbonate, 0.200 gram magnesium carbonate, 0.571 gram of ferric oxide, and one gram of manganous chloride, in hydrochloric acid. To this solution, 0.09016 gram aluminum oxide, and 0.05234 gram of phosphorus pentoxide was added. The combined weight of alumina and phosphorus pentoxide taken was therefore 0.1425 gram. The weight found was 0.1428 gram.

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THE DETERMINATION OF ANTIMONY IN ORES.

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THE object of this paper is not to present new methods, but on the other hand the application of some very old ones which have been agreed upon by the buyers and sellers for determining antimony in ores, and which after trial have been proved to give more closely agreeing and satisfactory results than those formerly obtained by the many more widely used volumetric and gravimetric methods. In addition such observations and innovations in using these methods will here be mentioned as have been made by the writer in an experience of a year or so in analyzing the Mexican ores for the large exporters.