was formed, which, instead of sinking, floated away from the electrode in straight lines on the surface of the solution. This hydride was also produced electrolytically by Sir Humphrey Davy.

With lead electrodes, in a solution of sodium phosphate, some hydrogen phosphide was produced along with the lead precipitate.

With borax and lead electrodes, the lead precipitate was formed very rapidly; and when the negative electrode was held close to the side of the glass beaker, a bright reddish-brown stratum of liquid was seen to be continually formed at the surface of the electrode. This disappeared almost instantly after moving away from the electrode, but was continually formed as long as the current was strong enough to produce the lead precipitate. The addition of acetic acid did not prevent this formation.

Sodium thiosulphate gave a deposit of sulphur at the positive pole, confirming the theory that in the thiosulphates one atom of sulphur is electro-negative, and takes the place of an atom of oxygen in the sulphates.

With sodium sulphite, sulphur dioxide was liberated at the positive plate.

Strontium nitrate, instead of giving the lead powder, gave a blue flame around the point of the lead cathode.

These results seem to indicate the possibility of obtaining, by the use of high electromotive force and high current density in electrolysis, products of an entirely different nature from those of ordinary electrolysis.

A METHOD FOR DETERMINING SULPHUR IN ROASTED SULPHIDE ORES.*

BY HARRY F. KELLER AND PHILIP MAAS.

Numerous methods have been proposed for the estimation of sulphur in materials containing it in the form of sulphides not decomposable by hydrochloric acid. New methods, as well as modifications of older ones, are contin-

* Read at the stated meeting of the Chemical Section, held January 18, 1895.

ually devised; analysts do not seem satisfied with the existing processes, and it must be admitted that a method which is both accurate and expeditious, still remains a desideratum.

The great majority of methods now practiced consist in oxidizing—either in the dry way or wet way—the sulphur to sulphuric acid, and estimating the latter gravimetrically or by titration.

The method we are about to describe is likewise based on this principle, and is a combination of well-known reactions. What we claim for it is that it is specially adapted for the determination of the sulphur in roasted copper ores and cupriferous pyrites.

The conversion of the sulphur into an alkaline sulphate is effected by fusion with potassium hydrate and sodium peroxide, and the amount of sulphur is then ascertained in the usual manner—gravimetrically, when accuracy is the principal object—by the Wildenstein method, when rapidity is aimed at.

The details of the process are as follows: Five to six grams of caustic potash (pure by alcohol) are fused in a nickel crucible and heated until the excess of water is expelled. The size of the flame is now reduced so that the contents of the crucible just remain liquid, and 5 grams of the finely powdered material introduced in small portions. A gram of sodium peroxide is then added while the heat is gradually increased to redness, and this is maintained for a few minutes. After cooling, the fused mass is dissolved in water, and the solution filtered with the aid of a pump. The undissolved residue is washed four or five times with hot water.

The colorless* filtrate is acidified with hydrochloric acid (8-9 c.c., sp. g. 1.2) and boiled to expel carbonic acid.

If the estimation is to be made gravimetrically, the sulphate of barium is precipitated from the boiling liquid in the usual manner. In case, however, titration is resorted to, the liquid is made alkaline with ammonia (about five c.c.,

* Before filtering the liquid is often colored purple by a small amount of ferrate of potassium; a blue color in the filtrate indicates that too much potash was used.

sp. g. '9). A slight excess of standard barium chloride solution is added from a burette, and the excess measured with an equivalent solution of dichromate of potassium. A distinct yellow color of the liquid marks the end of the reaction. After a little practice it is generally easy to strike this point, though it will sometimes happen that the precipitate does not settle rapidly. In such doubtful cases, portions of the liquid should be filtered off. Care should also be taken that the liquid does not become too dilute. It is convenient to prepare the standard solutions of such strength that one c.c. is equivalent to '005 grams of sulphur, *i. e.*, indicates one per cent. in a sample weighing '5 grams.

The solution of barium chloride is prepared by dissolving 38.109 grams of the crystallized salt to a liter, while the dichromate solution should contain 23 grams of the salt per liter.

To test the accuracy of our method, a considerable number of determinations were made of the sulphur in a typical roasted copper ore from Montana.

By oxidation with nitric acid and with aqua regia the percentage of sulphur in this material had been found to be 7.095 and 7.14, respectively.

Somewhat lower results were obtained by fusion with caustic potash and potassium chlorate, a method which had been used by one of us to control the working of a lead ore roasting furnace. The figures varied from 6.78 per cent. to 6.92 per cent.

Our first attempts to oxidize the ore by means of sodium peroxide were not successful. By using 10 grams of potash and 3.5 grams of peroxide, figures much lower than those before given resulted.

The oxidation was evidently incomplete. When bromine water was added to the solution of the fused mass, 6.82 per cent. of sulphur was obtained.

To our surprise a higher percentage was also found when less of the peroxide was employed. Thus with 10 grams of potash and 1 gram of peroxide the determinations averaged 6.8 per cent.

The large excess of alkali employed in these fusions in-

variably caused the solution of some copper, which renders titration impossible. Our next step, therefore, was to reduce the amount of potash.

When 5 grams of hydrate and 1 gram of peroxide were taken, the filtered solution of the fused mass was entirely free from the blue tint produced by the copper, and it is seen from the following figures that the oxidation of the sulphur was complete :

(1)	6.71	per cent. S.
(2)	6.82	" "
(3)	6.79	" "
Average	6.77	" "

Volumetric estimations gave the following results :

(1)	6.74	per cent. S.
(2)	6.86	" "
(3)	6.89	" "
(4)	7.14	" "
(5)	6.97	" "
Average	6.92	" "

Another series of determinations, in which a preparation of potash marked *puriss pro analys.** was used, yielded :

(1)	6.70	per cent. S.
(2)	7.09	" "
(3)	6.71	" "
(4)	6.85	" "
(5)	6.79	" "
(6)	7.00	" "
Average	6.85	" "

A final series in which the directions given in this paper were strictly adhered to, resulted as follows :

(1)	6.90	per cent. S.
(2)	6.75	" "
(3)	7.15	" "
(4)	7.05	" "
(5)	7.05	" "
(6)	7.10	" "
(7)	7.14	" "
Average	7.05	" "

The time required for the volumetric assay does not exceed thirty minutes.

*A correction of .35 per cent. was necessary in this case, the potash being less free from sulphur than that labelled "pure by alcohol."