[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

SULPHIODIDE OF LEAD.

BY VICTOR LENHER.

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ACCORDING to Humefeld (*J. prakt. Chem.*, **7**, 27) Reinsch (*J. prakt. Chem.*, **13**, 130) and Parmentier (*Compt. rend.*, **114**, 299) there exists a chlorsulphide of lead and an analogous bromsulphide of a cinnabar red color, obtained by adding hydrogen sulphide to a solution of lead chloride in hydrochloric acid, or to the corresponding bromide in hydrobromic acid.

As lead iodide dissolves readily in potassium iodide with the formation of the double iodide $PbI_2,2KI$, and with excess of potassium iodide $PbI_2,4KI$, it was found that when working with this salt an iodosulphide of brick-red color and rapidly changing composition was formed when its solution was treated with hydrogen sulphide.

The precipitate formed, when hydrogen sulphide is added to a solution of the double iodide in potassium iodide, is brick-red in color, rapidly changing, on further addition of that reagent, successively through dark red to brown, and finally the black sulphide is obtained which careful examination showed to be free from iodine. Cold water saturated with hydrogen sulphide was added to a strong solution of lead iodide in a saturated solution of potassium iodide; the red precipitate which was obtained was rapidly filtered by means of a suction apparatus, washed with a saturated solution of potassium iodide to remove any PbI_2,KI which possibly may have separated by the dilution; it was then washed with cold water till the reaction for iodine entirely disappeared; absolute alcohol was then added to displace the water, followed by carbon bisulphide to remove any sulphur, after which absolute alcohol was again added and the precipitate dried by drawing cold air over it.

When $PbI_2,4KI$ is diluted with water, yellow PbI_2,KI separates. The red sulphide was examined very carefully for potassium but none was found.

As the tendency of the substance to decompose into lead sulphide and lead iodide was so great, only small quantities were prepared at one time.

The lead was determined by treatment with nitric acid, followed by a few drops of sulphuric, and was weighed as sulphate. The sulphur was determined only after much trouble, as all attempts to oxidize it caused sulphur to separate. The method employed was treatment with a hot solution of sodium carbonate, which completely converted it into lead sulphide, carbonate, and sodium iodide. This was brought upon a Gooch crucible, washed with water, followed by a little dilute acetic acid to remove the carbonate, again washed with water, after which it was treated with nitric and sulphuric acids, and weighed as lead sulphate.

The iodine was estimated by covering the iodosulphide with an excess of a decinormal solution of silver nitrate; decomposition was then effected by means of nitric acid, and the excess of silver titrated with a decinormal ammonium thiocyanate solution, using ferric alum as an indicator. Analysis gave the reults:

Lead.	Iodine.	Sulphur.
49.06	49.97	1.51
50.16	49.81	1.98
.....	50.24	2.21
.....	50.33	2.17

The results approximate the composition of $PbS,4PbI_2$ which requires:

Lead.	Iodine.	Sulphur.
49.20	48.77	1.53

Hydrogen sulphide gas passed through a saturated solution of $PbI_2,4KI$ in the cold, also gave a brick-red precipitate which, treated in the manner described in the previous experiment, gave on analysis, 49.98 per cent. of iodine.

This method for the preparation of the iodosulphide is very unsatisfactory, as it rapidly darkens even in presence of large excess of the iodide, and from the fact that only a small fraction of a per cent. of product can be obtained.

Various colored products were obtained in the investigation, containing lead from 49.06 per cent. to the normal sulphide, and iodine in a similar manner from 50.84 per cent. to a sulphide entirely free from it. All of these but the one approximating, $PbS,4PbI_2$, were inconstant in composition and more or less rapidly decomposed into lead sulphide and lead iodide, as might be expected from the knowledge of the chlor- and bromsulphides; the iodosulphide is readily decomposed by heat, acids, and alkalies; and even long exposure to light decomposes it.

ON THE DETERMINATION OF SMALL QUANTITIES OF PHOSPHORIC ACID BY THE CITRATE METHOD.[1]

BY E. G. RUNYAN AND H. W. WILEY.

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THE results obtained by analysts in different parts of the world in precipitating phosphoric acid directly by magnesia mixture, in presence of citric acid or its salts, show that this process may safely take the place of the molybdenum method with all standard tricalcium phosphates or their preparations. We have observed in our work the most satisfactory agreement between this method and the molybdenum method of the Association of Official Agricultural Chemists. This statement, however, holds true only when the phosphoric acid is present in considerable quantities, at least in excess of five per cent. With smaller quantities of phosphoric acid we have observed that the citrate method leads to results which are decidedly inferior to those obtained by the molybdenum process.

The principle of the citrate method may be stated as follows: In the presence of a considerable excess of ammonium citrate a solution of a magnesium salt, made alkaline by ammonia, will precipitate the phosphoric acid as ammonium magnesium phosphate. The iron and alumina which may be present in the solution will not be precipitated under the above circumstances either as hydroxides or as phosphates. The ammonium magnesium phosphate can be subsequently separated by filtration, converted into magnesium pyrophosphate and weighed. An examination of the

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[1] Read before the Washington Section, April 11, 1895.