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THE DETECTION OF BARIUM, STRONTIUM AND CALCIUM.

BY STANLEY R. BENEDICT.

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THE distinctive features of the following method for the detection of the alkaline earth metals may be briefly summarized as follows: (1) In contradistinction to most, if not all other, methods, it provides for the removal of barium without the use of chromate or dichromate, thus giving colorless solutions for the subsequent detection of strontium and calcium. (2) It entirely avoids the somewhat troublesome operation of filtering solutions containing the precipitated sulphates of calcium, barium or strontium. (3) The method is very rapid, the manipulation simple, and the results positive. The precipitates dealt with filter perfectly clear without difficulty.

The reagents used are saturated potassium iodate solution, dilute hydrochloric acid, ammonium oxalate, and saturated ammonium sulphate solution.

As preliminary to an outline of the method, it may be well to mention the following facts, upon which it is based.

Barium iodate, while somewhat soluble in water, is practically insoluble in an excess of potassium iodate solution of proper concentration, even in the presence of a certain amount of hydrochloric acid. Barium is therefore completely precipitated from its solutions by an excess of potassium iodate, in presence or absence of dilute hydrochloric acid, the filtrate yielding absolutely no turbidity with sulphate or chromate solutions.

Strontium iodate is more soluble in water than is the corresponding barium compound. Like the barium salt it is completely precipitated from neutral or slightly ammoniacal solutions upon addition of a considerable amount of iodate solution, the precipitation taking place somewhat more slowly than with the barium compound. Unlike the barium salt however, strontium iodate is quite soluble in dilute hydrochloric acid, and strontium is therefore only incompletely, if at all, precipitated by an iodate from its solutions which have been acidified with dilute hydrochloric acid.

Calcium iodate is more soluble than either the barium or strontium compound, and is only incompletely, if at all, precipitated from neutral, acid or ammoniacal solutions, upon addition of an excess of iodate solution.

The precipitated iodates of all these metals form bulky, granular precipitates which filter clear very rapidly.

An outline for the procedure for the identification of calcium, strontium and barium follows.

A portion (2-3 cc.) of the solution to be tested is acidified with one-half its volume of 5N hydrochloric acid, and to the liquid thus obtained, its own volume of a saturated solution of potassium iodate is added. If a precipitate forms *at once*, barium is present. If no precipitate forms, barium is absent. If a precipitate forms slowly, either barium is present in low concentration or strontium is present in considerable amount. In such a case the presence or absence of barium should be confirmed by the addition of a few drops of dichromate solution to the original solution. This confirmation is rarely necessary.

Having established the presence or absence of barium, the solution is agitated and allowed to stand for one-quarter to one-half a minute. The precipitate is filtered off, and to a portion of the filtrate (not the first portion through the filter) is added a little more than an equal volume of a saturated solution of ammonium sulphate. The solution is then heated to boiling. A white precipitate, permanent on boiling, consists of strontium sulphate and indicates strontium.

To another portion of the original solution is added two volumes of a saturated potassium iodate solution, the mixture agitated and allowed to stand one-half to one minute and filtered. To the filtrate is added some ammonium oxalate solution (one-half volume of the ordinary reagent). The solution is now warmed to boiling. The formation of a white precipitate (consisting of calcium oxalate), either in the cold or upon warming, indicates calcium.

The directions given above apply to neutral or faintly ammoniacal solutions of the chlorides of calcium, strontium and barium. In the ordinary course of a qualitative analysis the precipitated carbonates should be dissolved in a little hydrochloric acid and the resulting solution evaporated to dryness, warming gently to expel free acid. The residue from this evaporation should be

dissolved in 6 to 10 cc. of water, and this solution used for the analysis. The portion to be tested for calcium may be treated with a drop of ammonium hydroxide solution to insure the absence of free acid.

In the use of the above method, particular attention should be given to the following points: The potassium iodate solution used as a reagent must be fully saturated. This reagent is conveniently prepared by using enough of the dry salt to make a $N/2$ solution and allowing it to stand some hours, with occasional shaking. If it is desired to dissolve the salt more quickly by heating to boiling, the warm solution must be cooled to ordinary temperature and agitated before use.

In adding the reagents, particularly the iodate and hydrochloric acid solutions, the amounts added must correspond quite closely with what is called for in the directions given above. The adequacy of these directions has been tested by their employment in analyses of some forty mixtures by myself and others, in the laboratory of the University of Cincinnati. The results obtained were entirely correct.

I desire to express my sincere thanks to Dr. J. F. Snell, whose continued encouragement and suggestions have been invaluable, in this, as in my previously published work.

THE DETERMINATION OF TOTAL ARSENIC ACID IN LONDON PURPLE.

By EDWARD G. MAHIN.

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MOST methods now in use for the determination of arsenic acid, present, when applied to London purple, certain serious difficulties, to avoid which was the object of the work outlined in the present paper. The Association of Official Agricultural Chemists recommends the method stated briefly as follows:¹

Two grams of the sample are dissolved in 80 cc. of water and 20 cc. of hydrochloric acid at about 70°, one-sixth of this solution is treated with 50 cc. of hydrochloric acid and 3 grams of potassium iodide and allowed to stand, by which means all of the arsenic is reduced to the state of arsenious acid. The free iodine is removed by the addition of $N/10$ sodium thiosulphate; the

¹ U. S. Dept. Agr., Bur. Chem., Cir. 10, p. 4.