NOTE ON THE PRECIPITATION OF SMALL AMOUNTS OF POTASSIUM AS POTASSIUM SODIUM COBALTINITRITE

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Precipitation of potassium as potassium sodium cobaltinitrite has been one of the common methods used in determining small amounts of that element since 1920, when Kramer, and Kramer and Tisdall (1) described a technique by which the reaction could be applied to blood serum. This method has been studied by a number of investigators and modified in different ways; but all of the practical and theoretical objections to its use have apparently not yet been overcome in a wholly satisfactory manner (2).

The chief difficulty in the way of basing an entirely satisfactory analysis upon this reaction seems to rest upon the property which sodium and potassium possess of forming a series of double nitrites with cobalt; the precipitate formed seems frequently to be a mixture of different members of this series. This fact has made it necessary to adopt a value for the factor used in converting the nitrite determined into its potassium equivalent which does not correspond with accepted definite chemical relationships between the two substances. Furthermore, conditions under which the precipitation is carried out must be carefully standardized, and in many instances the conversion factor be determined for the particular technique used if accurate results are to be obtained.

The author has found simple conditions under which, when potassium is present in amounts between 0.05 and 0.8 mg., a precipitate of apparently definite composition is obtained. Since the acidity of the solution can be varied within rather wide limits, he feels that the technique may be useful in determining small amounts of the element. The proportion between the potassium (controlled by using known amounts of pure K₂SO₄ dissolved in
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water) and the nitrite (determined by titrating the dissolved precipitate with permanganate) corresponds in his experiments with the formula $\text{K}_2\text{NaCo(NO}_3\text{)}_6$ for the volume of 0.02 $\text{mol}$ permanganate used when multiplied by 0.13 gave the number of mg. of potassium present. This formula is one generally accepted as that of one of the particular members of this series of double salts (3). The relative concentrations of potassium, sodium, cobalt, and nitrite ions and the acidity of the solution were the factors which most markedly affected the composition of the precipitate. A number of different methods of regulating these factors was found which gave approximately theoretical results, and the following method was finally adopted as the most satisfactory one.

To centrifuge tubes containing 1 cc. of a solution containing 0.05 to 0.8 mg. of potassium there was added 1 cc. of a solution of sodium acetate (100 gm. of crystalline salt made to 250 cc. with distilled water) followed by 1 cc. of a sodium cobaltinitrite solution described by Kramer and Tisdall (1). The tubes were then set in ice water for between $\frac{1}{2}$ and 2 hours. Acid up to an equivalent of 0.1 cc. of concentrated $\text{HNO}_3$ did not affect the determination, and it was not necessary to take any precautions in adding the reagent, as the latter could be dumped in very rapidly or added very slowly without affecting the results. After removal from the cooling bath the tubes were centrifuged. The precipitate was then washed two or three times, preferably with suitable organic solvents (acetone diluted with 3 parts of water was convenient for the first, and pure acetone for subsequent washings), dissolved, and titrated with 0.02 $\text{mol}$ $\text{KMnO}_4$. Precautions essentially similar to those of Kramer and Tisdall (1) were used to prevent the loss of nitrous acid during titration. In a few instances the results were confirmed by colorimetric analyses carried through by the diazo technique recommended by Bell and Doisy (4).

If desired, the potassium could be freed from interfering organic substances (5) by one of two methods. The washed precipitate first obtained could be treated with 0.1 cc. of concentrated $\text{HNO}_3$ on a boiling water bath and the potassium reprecipitated as described above, or the precipitate could be dried, a small crystal of $\text{Na}_2\text{CO}_3\cdot10\text{H}_2\text{O}$ be added (anhydrous sodium carbonate did not mix well with the precipitate, and when solutions were used loss from bumping was usual) and an alkaline fusion be carried out.
After the latter procedure, the cobalt oxide was dissolved by the aid of heat in 0.1 cc. of a solution containing equal parts of concentrated H₂SO₄ and water, and the potassium reprecipitated as described. Either technique gave satisfactory recovery of potassium, and the alkaline fusion removed large amounts of organic compounds and ammonia added to the fusion mixture.

Results obtained by this technique upon amounts of potassium greater than 1 mg. were rather unsatisfactory. One cause of this was the difficulty experienced in washing and manipulating the large amount of precipitate obtained. If amounts less than 0.05 mg. were present, precipitation took place very slowly, and apparently was complete only after several hours in the cooling bath. In standardizing the method under various conditions, amounts between 0.05 and 0.8 mg. were precipitated as described between 500 and 1000 times with very satisfactory results. Deviations from the mean as great as 2 per cent occurred very rarely, and could be explained in almost every, if not in each, instance by marked variations introduced into the technical procedure for experimental purposes.

Although the formulae of the different compounds of sodium, potassium, cobalt, and nitrite ions are much alike, it seems almost certain that the slight deviations from the calculated value, met with only very rarely, could more properly be attributed to technical errors rather than to variations in the composition of the precipitate; and therefore, that, for the range of potassium values described, a precipitate of constant theoretical composition is given by this method.

BIBLIOGRAPHY

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