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INDIRECT COMPLEXOMETRIC METHODS

Part III*. Determination of Thiocyanate and Ferrocyanide

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ABSTRACT

A convenient method for the estimation of thiocyanate ion is developed in which this ion is precipitated with known excess of copper sulphate after reduction to cuprous state and after reoxidation, the unreacted cupric ion is determined using EDTA. Similarly ferrocyanide is estimated by precipitation either as the cupric ferrocyanide or lead ferrocyanide and back-titrating the excess of the cation (cupric or lead) with EDTA. This method is found to have advantage over the earlier methods of estimation of these ions.

THE procedure of quantitative precipitation of an anion as its insoluble salt in the presence of an excess of a suitable cation and determination of the unconsumed cation by a complexometric method would appear to be a simple and obvious one. However a search through the literature showed that this principle has only been rarely exploited in practice. Attention in this direction seems to have been focussed largely in the case of only sulphate ion¹. In the course of our investigations on the determination of anions by indirect EDTA methods, we had earlier shown that the sulphide ion² and the oxalate ion³ may be conveniently determined in this way. These methods, while admittedly indirect and somewhat more tedious than the conventional procedures, have the advantage that they are applicable under conditions where the conventional methods fail. In the present communication, we describe two convenient EDTA methods for the determination of thiocyanate and ferrocyanide.

MATERIALS AND METHOD

Approximately 0.1 M EDTA solutions were prepared and standardised by established procedures⁴.

These solutions were diluted suitably. Standard aqueous solutions of thiocyanate and ferrocyanide were prepared from BDH Analar Grade potassium thiocyanate and potassium ferrocyanide. Standard 0.01 M solutions of copper sulphate and 0.1 M lead nitrate were prepared using BDH Analar salts. These solutions were standardised independently by the usual procedures⁴. A buffer solution of pH 10 was prepared as specified⁵. As indicator for the complexometric titrations, murexide or Eriochrome Black T solutions, were prepared according to reported specifications⁶. Saturated sulphurous acid solution was freshly prepared by bubbling sulphur dioxide into distilled water. All other reagents used were of analytical grade.

PROCEDURE

(i) Determination of Thiocyanate :

Aliquots of copper sulphate solution (20 ml) were measured into a 400 ml beaker and diluted to 100 ml with distilled water. To these, 2 N hydrochloric acid (2 ml) and sulphurous acid (slight excess; 30 ml) were added. The mixture was heated to about 90° C and a measured aliquot (10 ml) of the thiocyanate solution was added dropwise, with stirring, from a burette. The

* For Part II, see reference 3.

precipitate formed was allowed to stand hot for 2 hours after which it was filtered and washed with dilute sulphurous acid solution. The filtrate and the washings were combined and boiled to expel the excess of sulphur dioxide. To this, conc. nitric acid (2 ml) was added and boiled to ensure that the entire cuprous ion was reoxidised back to the Cu (II) state. The solution was then cooled and the excess acid neutralised (pH7) carefully with sodium hydroxide solution. The buffer solution was then added dropwise until the precipitate formed redissolved completely to give a deep blue solution. Care was taken to avoid the addition of excess of the buffer⁵. Murexide indicator (2 drops) was added and the solution was titrated with standard EDTA solution until the colour changed from yellow (green in the presence of free cupric ions) to deep violet. Blanks were run concurrently. It was observed that no blank correction was necessary.

(ii) *Determination of Ferrocyanide :*

(a) *Using copper sulphate.*—The procedure was exactly similar to the one mentioned above for the determination of thiocyanate except that there was no need for the addition of sulphurous acid and the consequent reoxidation later.

(b) *Using lead nitrate.*—Measured aliquots of the standard lead nitrate solution (30 ml) were taken in a 400 ml beaker and diluted to 50 ml with distilled water. The solution was heated to about 90° C and a measured aliquot (5 ml) of the ferrocyanide solution was added dropwise, with stirring, from a burette. The precipitate formed was allowed to settle, then filtered and washed with water. To the combined filtrate and washings, tartaric acid (2 g) and the buffer solution (5 ml) were added. In case turbidity appeared, a little more tartaric acid has to be added. The solution was titrated with EDTA using Eriochrome Black T as the indicator until the colour changed from violet to clear blue. Blanks were also run concurrently and no blank correction was found necessary.

RESULTS AND DISCUSSION

The results of typical experiments are given in Table I.

As the experiments were carried out using Analar samples and yielded concordant values, no standard deviation was calculated.

It is seen from the results (Table I) that the present method has reasonably good precision and accuracy. The methods depend on the fact that the solubilities of cuprous thiocyanate, copper ferrocyanide and lead ferrocyanide are sufficiently low so that quantitative precipitation may be

assumed. The solubility products of cuprous thiocyanate, copper ferrocyanide and lead ferrocyanide are 4.8×10^{-15} , 1.3×10^{-16} and 3.5×10^{-15} respectively.

TABLE I

Anion determined	Amount of anion taken (in m moles per litre)	Amount of anion found (in m moles per litre)	No. of experiments done
Thiocyanate	100	100.2	3
Ferrocyanide (using copper sulphate)	10	9.96	4
Ferrocyanide (using lead nitrate)	100	100.0	4

It may be mentioned that, although good redox titrimetric methods are available for the determination of the anions mentioned above, these methods are highly susceptible to interferences either in the presence of other possible reductants or of interfering anions in the system. For example, although ferrocyanide can be estimated conveniently by permanganometric procedure, such a procedure will fail in the presence of other reductants. The presence of reductants which do not get precipitated by Pb^{2+} or Cu^{2+} will not possibly cause any interference in the present method. Similarly, the excellent argentimetric method available for the estimation of thiocyanate will be complicated if chloride or bromide is present and these halide ions do not cause any interference in the present method.

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