Potassium Thiocarbonate (PTC) as a Masking Agent and as a Metal Indicator in EDTA-Titrations*[1]

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A number of reagents have already been on record in a literature[1] for preventing interference due to adverse ions in the titrimetric determination of metals with EDTA. Among the sulphide precipitants, use has been suggested of thioacetamide,[2] thiourea,[2] and trithiocarbonic acid[1] for the selective precipitation of one metal against the other. In this investigation, the results of masking[3] action of PTC (potassium thiocarbonate) for copper(II) ions against EDTA in complexometric titrations are reported. Evaluation of some metal ions in their binary mixtures containing copper(II) as one of the constituents, the other being zinc(II), nickel(II), cobalt(II), manganese(II) calcium(II) or magnesium(II) without their separation is found to be fairly accurate. Furthermore, PTC as a metal-indicator in EDTA titrations is found to be suitable for the estimation of nickel(II) directly and that of calcium(II) and magnesium(II) indirectly.

Masking Action of PTC against EDTA. Copper on reaction with sufficient excess of PTC forms a soluble complex, anion,[4] $Cu(CS_3)_2^{2-}$, of higher stability than that of the Cu-EDTA complex in solutions at high pH. Whereas, the thiocarbonates of other metals have lower order of stability constants as against that of their EDTA-complexes. This relative difference in the stability of the thiocarbonate and EDTA complexes of copper enables PTC to inhibit (mask) copper(II) against EDTA, thereby affording titrimetric evaluations of other metals without prior separation of copper(II) from solutions.

As compared to the solubility product of copper thiocarbonate ($CuCS_3$), those of zinc(II), nickel(II), cobalt(II), manganese(II), calcium(II) and magnesium(II) thiocarbonates are of much higher orders.[5] Consequently PTC is found to be very effective in releasing copper(II) from its EDTA complex, while the other metal-EDTA complexes remain unaffected in solution. Copper is released in the form of a dense and pure precipitate of its thiocarbonate subsequently forming the soluble complex anion $[Cu(CS_3)_2]^{2-}$ with excess PTC and a corresponding amount of EDTA is released in solution. Under optimum conditions of pH and concentrations of constituents metals in their binary mixtures, efficient end points are obtainable during back titrations of EDTA released from Cu-EDTA complex.

Evaluation of Some Binary Mixtures of Metal Ions. First, the total amount of EDTA required in the complexometric titration of binary mixture of metal ions is determined using a suitable metal indicator. Copper(II) being one of the constituent metal is then released from the Cu-EDTA complex with PTC and the corresponding amount of the released EDTA is back titrated to evaluate the amount of copper. The amount of the other metal constituent is determined from the difference in the total EDTA and the released EDTA corresponding to copper. Besides this releasing action of PTC concerning copper(II), interference due to copper as a minor constituent, is obviated by masking copper(II) with excess PTC. The complex anion, $[Cu(CS_3)_2]^{2-}$, thus formed enables accurate determination of major constituent metals through direct or indirect EDTA titrations without separation of Cu(II) from solution.

Experimental

Reagents. *EDTA Solution* (0.05 M). It was prepared by dissolving disodium salt of ethylenediamminetetraacetic acid (Merck, G. R. grade) into double distilled water and standardised against standard zinc solution using Eriochrome Black T as an indicator.

Potassium Thiocarbonate Reagent (1 M). It was prepared and standardised as reported earlier.[6,7] Working solution (0.1 M) was obtained freshly by dilution.

Standard Solutions of Metal Ions. They were prepared by dissolving metal salts (AnalaR, B. D. H. or G. R., Merck) in double distilled water and standardised by the usual methods.

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*[1] Presented at the Joint convention of the Indian Chemical Society and the Chemical Research Committee, CSIR, New Delhi, held at Aligarh Muslim University, Aligarh, December, 1965.

1) W. Pilz, *Monatshe., Chem.*, **83**, 1291 (1952); *Chem. Abstr.*, **47**, 4243 (1953).

2) F. J. Welcher, "The Analytical Uses of Ethylenediamine Tetraacetic Acid," D. Van Nostrand Co., Inc., New York (1958).

3) K. N. Johri and K. Singh, *Curr. Sci.*, **34**, 582 (1965).

4) K. N. Johri and K. Singh, *ibid.*, **34**, 78 (1965).

5) K. N. Johri, "Chemical Analysis Without H_2S Using Potassium Trithiocarbonate," Asia Publishing House, Bombay (1963).

6) K. N. Johri and K. Singh, *Indian J. Chem.*, **3**, 158 (1965).

7) K. N. Johri and K. Singh, *Analyst*, **90**, 745 (1965).

Indicator Solution. A 0.1% aqueous solution of Pyrocatechol Violet was prepared.

Buffer Solution. It was prepared by mixing equal volumes of 1 M ammonium chloride and 1 M ammonia solution (pH 10).

Procedure. For each evaluation 100 m*l* solution containing not more than 30 mg of total metal ions was taken and to this 10 m*l* of the buffer solution added, followed by the addition of 3—5 drops of the pyrocatechol Violet indicator solution. Standard EDTA solution (0.05 M) was run into until the original greenish blue colour changed to reddish-purple. Next, 5 m*l* of 0.1 M PTC was added and the released EDTA was back-titrated against standard (0.02 M) magnesium solution. In the case of calcium, Murexide indicator was used and back-titration was carried out with standard (0.02 M) calcium solution while pH was adjusted to 12 by using sodium hydroxide solution. In the case of manganese, small amount of hydroxylamine hydrochloride was also added to prevent the oxidation of Mn(II).

TABLE 1. RESULTS OF EVALUATION OF BINARY MIXTURE

Copper, mg		Other metal ion taken mg	Other metal ion found mg
Taken	Found		
7.50	7.56	Ni(II)/15.46	15.50
10.00	10.05	Zn(II)/13.86	13.92
8.25	8.18	Mn(II)/15.25	15.34
5.00	5.04	Co(II)/7.00	7.05
9.50	9.54	Mg(II)/17.72	17.60
6.50	6.46	Ca(II)/20.54	20.38

Discussion

The results are accurate while dealing upto 10 mg of copper ions. In the presence of larger amount of copper ions, the thiocarbonate reagent required for masking copper as the complex thiocarbonate is large which affects the end point. Direct determination of nickel(II), cobalt(II), zinc(II), manganese(II), calcium(II) and magnesium(II) was easily carried out in the presence of about 10 mg of copper masked with PTC at high pH. It is also possible to evaluate the above metals in the presence of micro quantities of lead(II), cadmium(II) and bismuth(III) which are rendered ineffective by forming insoluble thiocarbonate with PTC and not affecting the end point in EDTA titrations.

PTC as an Indicator in EDTA-Determination of Nickel(II) Ions. Nickel(II) forms a water soluble blood-red thiocarbonate complex, anion $[Ni(CS_3)_2]^{2-}$. The dissociation constant was reported[8] as 1×10^{-9}. This complex of nickel is stable only at high pH but is decomposed through acidification. The stability of Ni-EDTA complex is fairly higher than that of its thiocarbonate complex. Therefore, on adding PTC solution to the Ni-EDTA complex at high pH, no coloured complex is formed. Alternatively, on adding EDTA to the thiocarbonate complex of nickel when buffered at pH 10—11, the red colour of the nickel thiocarbonate complex is discharged. On account of this it has been possible to determine nickel directly by titration with EDTA while using PTC as indicator, provided the titration is carried out in a well buffered alkaline solution. The results of titrimetric determination of nickel with EDTA, using PTC as the indicator are given in the Table 2.

TABLE 2. DETERMINATION OF NICKEL WITH EDTA USING PTC AS INDICATOR

Nickel, mg		Difference, mg
Taken	Found	
5.27	5.25	−0.02
11.22	11.29	+0.07
14.05	14.11	+0.06
17.13	17.08	−0.05
22.44	22.65	+0.21

Experimental

Reagents. *EDTA Solution* (0.02 M). It was prepared as stated above.

Standard Solution of Nickel, 0.05 M. It was prepared by dissolving $NiSO_4\cdot7H_2O$ in double distilled water and standardised by precipitation with dimethylglyoxime.

Indicator Solution. A 1% freshly prepared aqueous solution, obtained by diluting a stock solution (**1 M**) of potassium thiocarbonate.

Buffer Solution. As specified above.

Procedure. To each 50 m*l* solution containing 5—20 mg of nickel, was added 5—10 m*l* of the buffer solution, followed by 2—3 m*l* of 1% aqueous solution of the thiocarbonate indicator. A purple red precipitate or blood red colour appeared. Titration was carried out with standard (0.02 M) EDTA solution run dropwise with constant shaking until the original colour changed to yellowish green.

$$1\ \mathrm{m}l\ 0.1\ \mathrm{M}\ \mathrm{EDTA} \equiv 5.87\ \mathrm{mg\ Ni}.$$

Interfering Ions. All those metal ions yielding precipitates of thiocarbonate[5] or hydroxides at high solution

TABLE 3. DETERMINATION OF CALCIUM AND MAGNESIUM USING PTC AS INDICATOR

Calcium, mg		Magnesium, mg	
Taken	Found	Taken	Found
10.32	10.29	12.45	12.49
15.25	15.33	17.12	16.98
25.50	25.35	23.36	23.42
29.48	29.32	30.12	30.26

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[8] J. Bankovskis and A. Ievins, Latvijas PSR, *Zinatnu Akad. Vestis.*, No. 3, 123 (1957); *Chem. Abstr.*, 5193b (1958).

pH interfere. Among the anions phosphate and oxalate interfere.

Determination of Calcium and Magnesium by Back Titration With Nickel Ions Using Potassium Thiocarbonate as an Indicator. To each 100 m*l* solution containing upto a maximum of 30 mg of calcium or magnesium was added 0.1 M EDTA solution in known excess. Ten millilitres of the ammonium chloride-ammonia buffer of pH 10 and 1 m*l* of 1% PTC solution were added and the solution titrated against standardised nickel sulphate (0.05 M) solution.

Some of the results are given in Table 3.

Sodium thiocarbonate (STC) when used in place of potassium thiocarbonate gives identical results, whereas the use of ammonium thiocarbonate as masking agent is less efficient. Ammonium thiocarbonate is not suitable as an indicator due to its low stability as a non-fixed salt of thiocarbonic acid.

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