

COMPLEXOMETRIC ESTIMATION OF MICROGRAM AMOUNTS OF COPPER USING E.D.T.A.

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Microgram amounts of copper can be determined by titration against a standard EDTA solution using pyridine and potassium thiocyanate as an indicator at pH 5.2. Bromobenzene is used to enhance the sharpness of the end point. At the end point the colour change is from green to colourless which can be readily detected visually. As little as 25 μg of copper in 25 ml. solution can be estimated. Citrate, pyrophosphate, thiosulphate and oxalate interfere. In the presence of interfering cations modified procedures such as masking, solvent extraction and Lead Collector separation procedure give accurate results.

Introduction

A number of methods have been used for the titrimetric determination of copper with EDTA.¹ They employ some indicator and give satisfactory results upto milligram quantities of copper. Ansbacher, Remington and Culp² have employed modified Biazzo's method for the colorimetric determination of copper. In this method copper (II) is precipitated by means of pyridine (Py) and thiocyanate as a green inner-complex of the composition, $[\text{Cu}(\text{Py})_2(\text{CNS})_2]$. The precipitate is extracted with bromobenzene from the aqueous phase and concentration of copper determined colorimetrically. Accurate results are obtained for 50-150 μg of copper. It was thought of interest to investigate the copper (II), pyridine and thiocyanate reaction for estimating microgram amounts of copper by a titrimetric method using EDTA (disodium salt) with a view to develop a rapid, convenient and accurate volumetric method for the said purpose.

Principle of the Method.—Copper forms a green coloured complex with pyridine and thiocyanate (CNS) which reacts with EDTA at $\sim 90^\circ\text{C}$. giving a light blue solution. Hence, copper can be titrated against EDTA using pyridine and potassium thiocyanate as an indicator. The use of bromobenzene gives a sharp end point as in this solvent copper-pyridine-thiocyanate complex is highly soluble and trace amounts of unreacted copper-complex gives intense colour in bromobenzene. The titration is continued to the point till bromobenzene layer becomes colourless.

Experimental

Reagents.—All reagents used were either A.R. grade or extra pure (E. Merk).

Standard Copper (II) Solution.—A stock solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, of 99.89 purity,³ was prepared by

dissolving 8.4337 g. of the salt in 1-litre distilled water. Solutions of desired concentrations varying from 1000 μg to 1 μg Cu/ml. were obtained by diluting an aliquot of the stock solution with water.

Standard EDTA (Disodium Salt) Solution.—A stock solution of EDTA of about 0.005 M was prepared and standardised against Calcium Carbonate using Eriochrome Black T indicator.⁴ Solutions ranging from 1×10^{-3} to 5×10^{-6} M in strength were prepared by diluting the stock solution.

HCl-Acetate Buffer of pH 5.2.—It was prepared by mixing 200 ml. of N-Na Ac and 40 ml. of N-HCl and making the volume to 1 litre with distilled water.

Potassium Thiocyanate.—A 10% solution (w/v) of KCNS was prepared.

Colorimeter: For photometric titrations Karl Kolb "Lichtelektrisches Kolorimeter Modell VI" with a cell of 1 ml. capacity was used.

EFFECT OF PH

Effect of pH on the detectability of copper is shown in Table 1. The optimum pH for this determination is 5.2.

PROCEDURE IN ABSENCE OF INTERFERING SUBSTANCES

A known volume of copper solution containing 5 to 3000 μg copper was taken in a conical flask (50 ml.) and different volumes of pyridine and 10 percent KCNS solution were added, followed by buffer solution of pH 5.2. The volume of solution was made upto 25 ml., heated to 90°C . and standard EDTA was added from a micro burette until the green colour precipitate had almost completely disappeared. Bromobenzene (0.5-1 ml.) was added and the titration continued till bromobenzene layer had become colourless. The end point was noted visually and photome-

trically using bromobenzene in one ml. capacity cell and a blue filter (430 m μ). The results are reported in Table 2.

It is evident that the optimum concentration of pyridine and 10% KCNS for detecting complete reaction between copper and EDTA solution is 0.4% and 16% (by volume), respectively.

TABLE 1.—THE EFFECT OF pH ON THE DETECTABILITY OF COPPER.

pH	Copper detectable (μ g)
1.5	1.5
2.0	1.25
3.6	0.65
5.2	0.45
5.9	0.80
6.8	1.40
7.4	2.00

TABLE 2.—RESULTS IN THE ABSENCE OF INTERFERING ELEMENTS.

Cu taken (μ g)	Pyridine (ml.)	KCNS 10% (ml.)	EDTA		Cu found (μ g)	Error %
			Molarity	ml.		
5.0	1.0	1.0	5×10^{-6}	13.50	4.3	14
5.0	0.1	4.0	"	14.00	4.5	10
10.0	0.1	4.0	"	29.58	9.4	6
10.0	0.5	1.0	"	28.32	9.0	10
10.0	1.0	4.0	"	28.64	9.1	9
25	0.1	4.0	5×10^{-5}	7.87	24.7	1.2
50	0.1	4.0	"	15.50	49.2	1.6
50	0.5	0.5	"	16.50	52.4	4.8
100	0.1	4.0	"	32.00	101.7	1.7
200	0.1	4.0	5×10^{-4}	6.25	198.7	0.65
200	0.1	3.0	"	6.30	200.3	0.15
500	0.1	4.0	"	15.71	499.93	0.07
1000	0.1	4.0	"	30.18	978.5	1.25
3000	0.1	4.0	5×10^{-3}	9.72	3090	3.0
Photometric titrations						
100	0.1	4	1×10^{-3}	1.62	101.7	1.7
25	0.1	4	5×10^{-4}	0.78	24.77	0.88
5	0.1	4	5×10^{-5}	1.43	4.52	9.4

pH=5.2, Total volume of solution in the titration flask=25 ml.

The results obtained at this concentration are fairly accurate.

Reproducibility.—Ten solution samples containing 100 μ g Cu each were analysed visually and the average value of the 5×10^{-4} M EDTA used for 100 μ g Cu was 3.155 ml. against the calculated value of 3.147 ml., showing a standard deviation of about 0.0027. The results indicate that the method is accurate and reproducible.

INTERFERENCES

Determination of copper in presence of other ions were done in order to study their interference effect. The results are shown in Table 3.

Alkali metals, alkaline earths, Hg⁺² and As₂O₃ do not interfere. A certain amount of F₃-PO₄⁻³, tartarate, Ag⁺ and Au⁺³ are permissible. Citrate, pyrophosphate, thiosulphate and oxalate interfere. Among the cations NH₄⁺ ion and Pb, Bi, Co, Ni and other metallic ions which react with EDTA show much interference.

MODIFIED PROCEDURES IN THE PRESENCE OF INTERFERING CATIONS

(a) *Fluoride Masking.*—Al, Mn and Ni ions were masked by adding 15 ml. of 2% KF solution to the copper solution and the titration conducted as usual. The results are shown in Table 4.

(b) *Solvent Extraction.*—Interference due to Pb, Bi, Sn, Ag, Cd and Au can be removed by solvent extraction with bromobenzene. Mn, Fe⁺³ and Zn can be removed by fluoride masking followed by solvent extraction. Cobalt interferes even when present in low concentrations of 25 μ g.

(c) *Lead Collector Separation.*—Cobalt interference may be removed by Lead Collector separation method.⁵

TABLE 3.—COPPER ESTIMATION IN THE PRESENCE OF INTERFERING SUBSTANCES.

No.	Cu taken (μg)	Interfering substance		Cu found (μg)	Error %
		Name	mg. taken		
1.	1000	Na ₃ PO ₄ (in presence of HCl)	200	984	1.6
	1000		80	991.5	0.85
	200		20	101.6	0.53
2.	500	Sod. fluoride	800	494.0	1.2
	500		75	500.0	0.0
	200		400	198.96	0.53
3.	500	Pot. tartarate (in presence of HCl)	200	495.0	1.0
	200		200	194.0	3.0
4.	500	Pot. citrate	50	487.5	2.5
5.	500	Sod. oxalate	20	120.0	80.0
6.	500	Na ₂ P ₂ O ₇	50	100.0	76.0
7.	500	Na ₂ S ₂ O ₃	1.3	175.0	65.0
8.	100	(alkali and alkaline earth metals)	1000	100.0	0.0
	500		1000	500.0	0.0
9.	100	As ₂ O ₃	1000	100.0	0.0
10.	100	NH ₄ Cl	500	93.8	6.2
11.	100	Hg ⁺²	50	100.0	0.0
12.	100	Au ⁺³	10	104.0	4.0
13.	100	Ag ⁺	20	101.8	1.8
14.	—	(Pb, Bi, Sn, Co, Ni, Zn, Mn, and Fe).	—	Interfere	—

TABLE 4.—DETERMINATION OF COPPER AFTER MASKING INTERFERING ELEMENTS.

Interfering elements	Amount taken (μg)	Copper (μg)		Error %
		Taken	Found	
Al	5×10^4	100	100.5	0.5
Mn	2×10^4	100	100.8	0.8
Ni	1×10^4	100	95	5.0

Discussion

Table 2 and Table 3 show that copper (II) in concentration range $25\mu\text{g}$ — $3000\mu\text{g}/25\text{ ml.}$ at pH 5.2 can be determined accurately by the volumetric method using EDTA as a titrant and 0.1 ml. pyridine and 4 ml. 10 percent KCNS as an indicator in presence of bromobenzene. The end point can be easily detected visually, as photometric titrations give no better results than the visual method.

Copper can be determined by the normal procedure in presence of alkali metals, alkaline earth metals, Hg⁺² and As₂O₃. Modified procedures give accurate results in presence of interfering cations. Interference of Al, Mn and Ni can be removed by masking; solvent extraction pro-

cedure is used in presence of Pb, Bi, Sn, Ag, Cd and Au. Masking cum solvent extraction procedure is successful in case of Zn, Mn and Fe. In the presence of cobalt copper can be determined by adopting lead collector separation method.

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