Metal Complexes of Mononitrosochromotropic Acid. A Study of the Copper Complex and Its Chelometric Titrations

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It appears that chromotropic acid forms two nitroso derivatives; mononitroso and dinitroso.¹⁾ The dinitrosochromotropic acid has been used by Steigmann²⁾ for the detection of copper, nickel and palladium. Datta³⁾ used this compound for the complexometric and spectrophotometric determination of thorium. The mononitroso derivative has been utilised by various workers for the detection and determination of copper, cobalt and nickel. Since the two nitroso compounds of chromotropic acid give colour reactions with many metals, a thorough investigation of the colour complexes and their probable analytical applications has been undertaken by the present authors.⁵⁾ The following elements were found to give coloured products with mononitrosochromotropic acid: copper, palladium, cobalt, nickel, magnesium, manganese, vanadium, uranium, beryllium, iron(III), chromium, cerium(III), lanthanum, gold, thorium, zirconium, etc. Lead and cobalt(III) form a coloured precipitate. Methods for the detection of most of these and of fluoride ion on the spot plate and filter paper have already been developed.⁶⁾

The present paper will deal with the copper complex of mononitrosochromotropic acid (abbreviated as MNCA) and will make a thorough study of its application in the complexometric determination of copper. This reagent has been used recently by Pande and Srivastava,⁷⁾ and later by Sen and Srivastava,⁸⁾ as an indicator in the titration of copper with EDTA. However, they carried out such titrations only in a pure solution, and the interference in the titration has not been studied in detail. The direct titration of copper with nitrosochromotropic acid carried out by Ansbacher and his co-workers⁹⁾ proved very unsatisfactory to the present authors. The method was also rejected as unsuitable by Conn et al.¹⁰⁾ in their determination of copper in milk. However, in all the works carried out by various workers, nitrosochromotropic acid was present in the solution in which it was prepared and that solution was employed as such, without isolating the pure product. The present authors prepared and isolated the compound in its pure form and used it for the experiments reported on here and earlier. The study of the copper complex by various physico-chemical methods and the spectrophotometric determination of copper with this reagent will be reported on shortly.

Experimental

Reagents and Chemicals.—*Copper Solution.*—A stock solution of A. R. copper sulphate pentahydrate was prepared in water containing a little sulphuric acid and was estimated with EDTA, using PAN as an indicator. The other copper salts were made from reagent-grade salts.

Reagent Solution.—Mononitrosochromotropic acid (MNCA) was prepared as has been reported earlier.⁶⁾ A 0.05% solution in water was used. Other indicator solutions: PAN, a 0.05% solution in ethanol; murexide, a saturated solution in water; pyrocatechol violet, a 0.1% solution in water, and Chrome Azurol S, a 0.4% solution in water.

EDTA. — Disodium dihydrogen ethylenediaminetetraacetate dihydrate (A. R.) was dissolved in water to make 0.05, 0.01 and 0.001 M solutions; it was estimated as usual by means of a standard calcium solution. The other reagents and chemicals used were also of reagent grade.

Apparatus. — A Beckman Model H-2 pH meter was used for the adjustment of the pH of the solutions.

Results

The Reaction of Copper with Mononitrosochromotropic Acid.—MNCA reacts with copper in a weakly acidic or weakly alkaline medium

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to form a violet- or permanganate-coloured soluble complex. The formation of the copper complex with various copper salts has been studied. A few drops of an MNCA solution were added to 0.05 M solutions of different copper salts, which had previously been rendered almost neutral, and then the pH was raised by adding a 0.1 M ammonium hydroxide solution. The colour changes are noted in Table I. It appears that the same complex is formed with various copper salts and that the colour deepens only when the pH is raised.

Table I. Reactions of MNCA with different copper salts

Copper salt	pH	Colour reactions
Copper sulphate	3.4 8.0	Pale pink Permanganate colour
Copper chloride	4.0 7.8	Pink Violet
Copper nitrate	4.2 8.0	Pink Violet
Copper acetate	5.5 7.8	Bluish violet Violet
Copper ammonium sulphate	5.2 8.4	Pale permanganate colour Violet
Copper ammonium chloride	3.5 6.8	Pink Violet
Copper oxalate	5.4	Violet colour on boiling
Copper citrate	3.4 7.3	Reddish pink Violet
Copper tartrate	3.2 7.8	Pale pink Pale violet
Copper perchlorate	3.8 7.2	Pink Violet
Copper glycinate	—	No colour formation at any pH
Copper iodate	4.4	Pink colour, intensifies on heating

Preliminary Studies of the Stability of the Copper Complex.—To 100 ml. of a 0.1 M copper sulphate solution, a solution of 1 M sodium acetate was added slowly until the pH became 5.6 to 6 and the volume had been diluted to 200 ml. To this mixture 50 ml. of 0.4 M MNCA was added, and the mixture was kept in a water bath at 40°C for 5 min. to complete the reaction. A deep-red-violet copper complex formed in the solution. The complex could not be isolated in the solid state or extracted by any organic solvent.

To 5 ml. of this complex solution, various substances (acids, alkalis, oxidizing agents, reducing agents, protective colloids, alcohols, ketones, amines, amino acids, polyhydroxy alcohols and other organic substances) were added in order to study the stability or instability of the copper complex in their presence. The results indicated are: The copper complex appears to be stable as such for about a week, and it remains stable in the presence of protective colloids, starch, gelatine, etc., for about a fortnight. The mineral acid decomposes it, and it breaks below pH 5. The colour intensifies with ammonium hydroxide, sodium hydroxide and potassium hydroxide, up to a pH of 9. No change is observed with ammonium carbonate. Among the oxidizing agents, a 0.1 M solution of potassium permanganate or dichromate at pH 5.6 to 5.8 discharges the colour of the complex slowly, but in the presence of acid, the decomposition is immediate. Hydrogen peroxide discharges the colour at once. Persulphates and periodates also decompose the complex. The reducing agents (ascorbic acid, hydroxylamine hydrochloride, hydroquinone in an alcoholic solution, sodium sulphite, etc.) break the complex, and the colour changes to yellow. With hydrogen sulphide, a black precipitate of copper sulphide forms. The complex is decomposed by thiosulphate, potassium iodide, ferro- and ferricyanides, and ammonium sulfocyanide, but it does not change with fluorides, molybdates, selenates, ammoniacal potassium iodide, or thiosulphate. The organic solvents, such as alcohols, ketones, esters, chloroform, carbon tetrachloride, and polyhydroxy alcohols, do not change the colour, nor can the complex be extracted in the organic phase. With acetylacetone, the complex breaks and the lower layer becomes blue because of the formation of copper acetylacetonate, while the upper layer becomes orange because of the liberation of the free reagent. Glycine and EDTA displaced copper from its complex.

The Titrimetric Determination of Copper with EDTA Using MNCA as an Indicator.—As the copper complex of MNCA is less stable than the copper-EDTA complex, the direct titration of copper with EDTA, using MNCA as an indicator, is possible. The end-point colour change is from a permanganate or violet colour to a greenish yellow or to an almost colourless state in a dilute solution. The optimum conditions for such titration have been developed from the study of various factors, such as pH, buffer solutions, the temperature, the dilution of the volume and the concentration and age of the indicator solution.

The Effect of pH and Buffer Solutions.—The titration of copper with EDTA has been carried out at various pH values in order to study the effect of hydrogen ion concentration in the titration employing this indicator. The effect of using different buffer solutions in fixing the pH has also been examined. One millilitre of a copper solution was mixed with 2 ml. of buffer solution, and the volume was diluted to about 30 ml. and 4 drops of an indicator solution (0.02%) were added. The

TABLE II. EFFECT OF pH AND BUFFER IN THE EDTA TITRATION OF COPPER
1 ml. of 0.1 M $CuSO_4$, taken 10 ml. of 0.01 M EDTA

Buffer used	pH	EDTA, reqd. ml.	Remarks on end point
Sodium acetate-hydrochloric acid	3.4	4.2	Pink colour changes to pale yellow end point not sharp
	4.5	6.3	
	5.0	7.2	
Sodium acetate	5.2	8.0	Red-violet to light green, fairly sharp
	5.56	9.1	
	5.86	9.95	Sharp end point
	6.30	9.96	Sharp end point
	6.51	10.02	Sharp end point
	6.60	10.05	Sharp end point
Ammonium acetate - acetic acid	5.2	8.60	Reddish pink to pale yellow, not sharp
	5.4	8.85	
Pyridine	5.6	8.82	Pink to greenish yellow, sharp end point
	6.1	9.20	
	6.8	9.95	Violet to greenish yellow, sharp end point
	7.0	10.10	Violet to greenish yellow, sharp end point
Ammonium chloride - ammonia	6.6	9.85	Pink to pale yellow, sharp end point
	7.0	9.90	
	7.2	10.01	Permanganate to pale yellow, sharp end point
	7.6	10.05	
	7.8	9.98	
	8.1	10.10	
	8.6	10.20	End point not sharp
	9.4	10.32	End point not sharp
Triethanolamine	7.4	10.12	Bluish violet to almost colourless, fairly sharp end point
	8.0	10.15	
	8.6	10.18	End point not sharp
	9.0	10.25	
	10.2	10.55	

mixture was then titrated with 0.01 M EDTA in the cold. Some of the results of this titration have been recorded in Table II and represented in Fig. 1.

The results indicate that pH range from 6.8 to 7 with a pyridine - hydrochloric acid buffer was suitable for the titration of copper. A sharp colour transition was obtained. Triethanolamine gave a little higher result, and the colour change at the end point was also not very sharp. An ammonium chloride - ammonia buffer gave good results from pH 7 to 8. A very sharp end point from a permanganate colour to pale yellow was obtained with this buffer. The titration at lower pH values, from 5.8 to 6.5, may also be carried out with a sodium acetate buffer, the end point colour transition is then sharp but not as good as that obtained with an ammonium chloride - ammonia buffer. Other buffers were not found suitable.

The Effect of Temperature.—Titration at different temperatures from 10 to 66°C showed that the complex is stable up to 40°C and that the titrations may be made at room temperature without any loss of accuracy.

The Effect of the Concentration of the Indicator.—In order to examine whether the concentration of the indicator solution has any effect on the titre value and on the sharpness of end point, titrations were carried out with different amounts of the indicator in 50 ml. of the titrant. It was seen that, in an ammonium chloride - ammonia buffer, when a few drops of a 0.05% indicator solution were gradually added to the pale blue copper solution, the blue colour gradually faded, the solution became almost colourless and then turned a pale permanganate colour, and, at the end point with EDTA, the colour changed to pale yellow or became nearly colourless. However, with a large ammount of indicator, the colour is deep yellow or orange, and with a larger amount of copper, the end point colour is a greenish-yellow. Too great an excess of the indicator obscures the end point. Good results are obtained with 0.2 to 0.5 ml. of a 0.05% indicator solution for a solution containing about 6 mg. of copper. The same results were

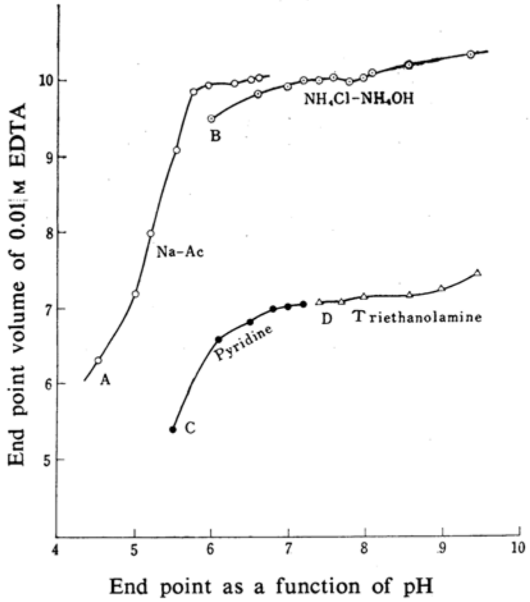

Fig. 1. The end point as a function of pH in the EDTA titration of copper. EDTA, 0.01 M

Curve A: 0.1 M $CuSO_4$ 1 ml., using sodium acetate buffer
Curve B: 0.1 M $CuSO_4$ 1 ml., using ammonium chloride-ammonia buffer
Curve C: 0.1 M $CuSO_4$ 0.7 ml., using pyridine buffer
Curve D: 0.1 M $CuSO_4$ 0.7 ml., using triethanolamine buffer

obtained with a sodium acetate or pyridine buffer.

The Effect of the Dilution of Volume.—Titration was carried out by varying the volume of the titrant without changing the amount of indicator or copper. A 50 ml. volume gave good results. With a larger amount of copper, for instance, more than 10 mg., the volume should be about 100 ml. or larger.

The Age of the Indicator Solution.—The solution of the indicator is not very stable. A solution, once prepared, may be used for only a week with little loss of accuracy. It is desirable that the titrations always be carried out with solutions which are not older than two or three days, and such solutions should always be kept in amber-coloured bottles.

The Effect of Ketonic Solvents in the Titrant.—The sharpness of the end point of the titration has been found to improve slightly in the presence of some ketones, like acetone, diacetone alcohol or ethyl methyl ketone. The addition of about 10 ml. acetone per 50 ml. of volume was found to give good results.

Procedures Recommended for Pure Copper Solution.—a) Take 10 ml. of a nearly copper solution containing about 6～10 mg. copper in a 250 ml. conical flask, and add 2 ml. of 1 M ammonium chloride solution and 5 drops of 2 M ammonium hydroxide, 10 ml. of acetone and 4 drops of 0.05% indicator solution. Dilute the mixture to 50 ml. Adjust the pH to 7.2 to 7.4 with one or two more drops of ammonia. The solution then assumes a permanganate colour. Titrate in the cold with 0.01 M EDTA until the colour sharply changes to pale yellow. This method may be used for the determination of 2 to 30 mg. of copper in a solution.

b) To the above copper solution, add 1 ml. of pyridine and 4 drops of the indicator. Dilute to 50 ml. with water. The pH should be 7; if it is below, add 1 or 2 drops of a dilute pyridine solution (0.2%) in order to raise it to 7. The colour of the solution is violet. Titrate with EDTA. At the end point the colour changes from bluish-violet to greenish yellow or becomes almost colourless. This method is useful for the estimation of 2 mg. to 20 mg. of copper.

c) To an almost neutral copper solution, add 2 ml. of a sodium acetate solution, 10 ml. of acetone and 4 drops of the indicator. Dilute to 50 ml. with water. Adjust the pH to 6.2～6.6 with a few drops more of a sodium acetate solution and titrate it as before with EDTA until the colour changes from red-violet to light green. From 2 to about 60 mg. of copper may be determined by this method with accuracy. With more than 60 mg. of copper, the end point passes through a series of colour changes, from red-violet to blue-violet, bluish grey, grey, and, finally, yellowish green. Here the end point is a bit long-drawn and not sharp.

Some typical results of titrations in the lower range are recorded in Table III. The titration of copper was also carried out side by side by following the prescribed procedures but using other indicators (viz. PAN,[11] murexide,[12] pyrocatechol violet[13] and Chrome Azurol S[14]) for the sake of comparison. The results indicate that the new indicator, mononitrosochromotropic acid, is satisfactory, being as effective as the standard indicators mentioned above.

The Micro Titration of Copper.—Microgram quantities of copper may be determined with EDTA, using MNCA, with a fair degree of accuracy. The minimum quantity of copper that may be titrated by this procedure is about 7 μg.; with a lesser amount, a sharp

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TABLE III. EDTA TITRATION OF COPPER IN PURE SOLUTION

Indicator used	Cu taken mg.	pH adjusted with	pH	EDTA, 0.01 M		End point colour
				Reqd. ml.	Theo. ml.	
MNCA	8.472	NH_4Cl-NH_4OH	7.4	13.30	13.33	Permanganate to pale yellow
	2.118	NH_4Cl-NH_4OH	7.2	3.34	3.33	
	4.236	Pyridine	7.0	6.67	6.67	Bluish-violet to greenish-yellow
	2.118	Pyridine	6.8	3.35	3.33	
	8.472	Na-acetate	6.4	13.35	13.33	Red-violet to light green
	2.118	Na-acetate	6.2	3.32	3.33	
PAN	4.236	Acetate buffer	5.0	6.65	6.67	Red-violet to yellow
	2.118	Acetate buffer	5.0	3.30	3.33	
Murexide	8.472	NH_4Cl-NH_4OH	10.0	13.36	13.33	Yellowish-green to violet
	2.118	NH_4Cl-NH_4OH	10.0	3.32	3.33	
Pyrocatechol violet	8.118	Acetate buffer	5.6	3.30	3.33	Blue to yellow
	4.236	Acetate buffer	5.6	6.62	6.67	
Chrome Azurol S	8.472	Na-acetate	6.5	13.29	13.33	Blue to light-green
	2.118	Na-acetate	6.5	3.30	3.33	

TABLE IV. MICRO TITRATION OF COPPER

Cu taken μg.	Cu found μg.	Diff. μg.	Cu taken μg.	Cu found μg.	Diff. μg.
41.31	41.33	0.02	12.71	12.76	0.05
31.78	31.75	0.03	9.54	9.59	0.05
25.42	25.40	0.02	6.36	6.43	0.07
15.89	15.84	0.05	3.18	3.38	0.20

TABLE V. TITRATION OF COPPER IN THE PRESENCE OF ORGANIC SUBSTANCES

0.1 M $CuSO_4$ solution, taken 0.5~5 ml. of 0.01 M EDTA

Substances added	Amount ml.	Buffer used	pH	EDTA, 0.01 M reqd.	Remark
Pyridine	1	—	7.0	5.0	Sharp end point
Quinoline	0.5	NH_4Cl-NH_4OH	7.6	4.88	End point not sharp
Pyperidine	0.5	—	7.8	5.0	Sharp end point, violet to greenish yellow
Urea (5%)	2	Na-acetate	6.4	4.92	Sharp end point
Glycine (1%)	2	NH_4Cl-NH_4OH	7.2	—	Complex does not form
Monoethanolamine	0.5	—	7.6	4.7	Not sharp
Diethanolamine	0.5	—	8.0	4.87	Not sharp
Triethanolamine	0.5	—	8.0	4.98	Sharp end point
Ethylene glycol	1	Na-acetate	6.4	4.98	Sharp end doint
Propylene glycol	1	Na-acetate	6.2	4.92	Sharp
Glycerol	1	Na-acetate	6.4	4.95	Sharp
Diacetone	2	Na-acetate	6.4	5.0	Sharp
Ethyl methyl ketone	2	Na-acetate	6.1	5.1	Sharp
Tricresylphosphate in acetone (1%)	2	Na-acetate	5.8	4.8	Fairly sharp
Tri-*n*-butylphosphate in acetone (1%)	2	Na-acetate	6.4	5.1	Fairly sharp
Dibutylphthalate in acetone (1%)	2	Na-acetate	6.2	4.95	Fairly sharp

end point is not obtained. Some of the results of this titration carried out by following the procedure given below are recorded in Table IV.

Procedure.—To a solution containing about 10 to 100 μg. of copper, add 0.5 ml. of 0.5 M ammonium chloride, 2 drops of 0.5 M ammonium hydroxide, and 1 drop of a 0.02% indicator. Dilute to 10 ml. with warm water (40°C). The pH is now between 7 to 7.4. Now titrate with 0.001 M EDTA until it changes from a pink to a colourless state. The end point is

Table VI. Titration of copper in presence of masking agents
0.1 M Copper solution, taken 0.5~5 ml. of 0.01 M EDTA

Masking agent	Amount ml.	pH	EDTA, 0.01 M ml.	Remark
Citric acid (10%)	4	7.4	4.94	Blackish end point in excess
Tartaric acid (10%)	5	7.4	4.97	Permanganate to yellow, sharp
Oxalic acid (10%)	2	7.6	4.96	Pale greenish yellow end point
Ascorbic acid (2%)	2	—	—	Complex does not form
Glycollic acid (2%)	2	—	—	Complex does not form
Sulfosalicylic acid (5%)	2	7.2	—	Complex does not form
Hexamine (20%)	2	6.6	5.0	Yellowish green, sharp
Triethanolamine	0.5	8	4.98	Almost colorless
Hydroxylamine hydrochloride (2%)	2	—	—	Complex does not form
Thiourea in NH_4OH (1%)	2	7.4	4.95	Not sharp
Sodium fluoride (10%)	2	7.2	5.05	Sharp end point
Ammonium fluoride (10%)	3	7.4	4.98	Sharp end point
Ammonium bifluoride (10%)	3	7.4	4.97	Sharp end point
Disodium hydrogen phosphate (10%)	5	7.6	5.10	Fairly sharp
Potassium cyanide (2%)	3	7.2	—	Copper is masked
Potassium iodide in ammonia (5%)	3	7.4	4.98	Fairly sharp
Sodium thiosulfate in ammonia (2.5%)	5	7.8	4.94	Fairly sharp
Potassium fluoride and potassium tartrate (1 : 1) in ammonia (2%)	5	7.8	5.15	Fairly sharp

The p. c. in the above solutions indicate the amount in gram dissolved in 100 ml. of water or ammonia (5 M).

sharp. The titration may also be made by using a sodium acetate buffer, the pH is adjusted to 6.4 by adding a 0.2 M sodium acetate solution drop by drop, and the titration is carried out as before.

Titration in the Presence of Various Organic Substances.—It was observed that the copper complex of MNCA was stable in the presence of many organic compounds. The titration of copper with EDTA has been carried out in mixtures containing various organic amines and other complexing agents in order to examine whether the copper present in the solution becomes available to MNCA and, subsequently, to EDTA for its complexometric titration. The results of such titrations, under the conditions stated, are given in Table V. In the case of quinoline, 0.5 ml. of it was dissolved in a mixture of 15 ml. acetone and 10 ml. ethanol, the copper solution added, and the pH of the mixture raised to 7.4 with 2 ml. ammonium chloride and a few drops of 1 M ammonium hydroxide the mixture was then diluted to 50 ml. and titrated as before with EDTA.

The Effect of Masking Agents.—In order to examine the effect of masking agents on the indicator-copper complex and the possibility of using them as masking agents for the elimination of the interference of various metal ions, titrations of copper in the presence of some well-known masking substances have been carried out. The results are recorded in Table VI. It may be seen that a number of such complexing agents do not interfere with the titration, but that those which form strong complexes with copper itself, such as potassium cyanide and glycine, cannot be used. The copper-indicator complex does not form in the presence of those reducing agents which may also be used as masking agents, such as ascorbic acid, hydroquinone and hydroxylamine.

The Study of Interference by Diverse Ions in the Titration. — As the EDTA titration of copper is best carried out in a weakly alkaline medium, many cations (e. g., zinc, nickel, cobalt, calcium, magnesium, barium, lead, cadmium and the rare earths) interfere in the process. When the titration is done in an acetate buffer at pH 5.8 to 6.4, small amounts of calcium, barium and magnesium may be tolerated, and the addition of a little ammonium fluoride improves results. The interference of iron(II) and aluminium may be removed by using triethanolamine, sodium or ammonium fluoride in both ammoniacal and sodium acetate solutions. Mercury(II) may be masked by an ammoniacal potassium iodide solution. The addition of oxalic acid removes the interference of zirconium. The method is effective when copper is separated from the mixture of cations containing tartaric acid with thioacetamide or hydrogen sulphide and the EDTA titration is applied. Silver and alkali metals do not interfere. Table VII shows some of the results.

TABLE VII. EFFECT OF FOREIGN IONS ON TITRATION OF COPPER
Copper taken (0.1 M solution), 1~10 ml. of 0.01 M EDTA

Ions present	Quantity mg.	Buffer used	Masking agent	EDTA, reqd.
Na	28.42	NH_4Cl-NH_4OH	—	10.04
K	20.16	NH_4Cl-NH_4OH	—	10.02
Ag	7.2	NH_4Cl-NH_4OH	—	9.93
Hg(II)	6.51	NH_4Cl-NH_4OH	KI in NH_4OH	9.95
Fe(III)	6.60	—	Triethanolamine	10.11
		Na-acetate	NaF	10.05
Al	4.33	Na-acetate	Triethanolamine	10.14
		Na-acetate	NaF	9.98
		Na-acetate	Ammonium fluoride	10.06
		NH_4Cl-NH_4OH	Tartaric acid	10.13
Mg	5.82	Na-acetate	—	9.97
Ca	7.56	Na-acetate	—	10.09
Sr	10.06	Na-acetate	—	10.06
Zr	4.32	Na-acetate	Oxalic acid	10.10

Discussion and Summary

The copper complex of mononitrosochromotropic acid (MNCA) forms in a weakly acidic or a weakly basic solution, and the colour of the complex in solution deepens as the pH is raised (from pH 5 to 5.4 it is pink, from 5.4 to 6.6 it is red-violet, from 6.6 to 7.2 the colour is permanganate-violet, and at higher values pH up to 8.5, it is blue-violet). The complex decomposes at higher pH values. The same copper complex appears to form in all the above pH ranges. The complex is stable in the presence of many inorganic substances, but it is decomposed by oxidising and reducing agents and also by substances that form stronger complexes with copper. The copper complex, however, could not be extracted with any of the organic solvents commonly employed in solvent extraction methods. MNCA may be successfully used as an indicator in the complexometric titration of copper with EDTA.

The titrations carried out with this indicator, side by side with other indicators for copper, indicated that the new indicator may be placed in the same group as murexide, PAN, pyrocatechol violet or Chrome Azurol S with regard to the sharpness of the end point, colour contrast, accuracy, and precision in the titration of copper. The titration may be performed at different pH ranges using different buffer solutions: with sodium acetate at pH 5.8 to 6.5, with pyridine at pH 6.8 to 7, and with ammonium chloride and ammonia at pH 7 to 8. The change in the end point colour is from reddish-violet, bluish-violet or permanganate-violet to pale greenish yellow. Copper may be titrated in the macro range from 2 to 60 mg. of copper and in the micro-range down to 7 μg. by using this indicator.

The effect of various complexing agents, polyhydroxy alcohols, amines, amino acids and other masking agents, etc., on the EDTA titration of copper has also been studied; a number of them do not appear to interfere. The cations that form EDTA complexes in the same pH range as copper interfere in the titration, however. Iron and aluminium may be masked by triethanolamine or sodium fluoride, mercury(II), by ammoniacal potassium iodide, and zirconium, by oxalate. The alkali and alkaline earth metals do not interfere.

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