

COMPLEXOMETRIC ESTIMATION OF SOME TRANSITION ELEMENTS (HAVING $3d^5$ TO $3d^9$ ELECTRONIC CONFIGURATION) USING LANAS AS VISUAL METALLOCHROMIC INDICATOR

by R. C. CHADHA, B. S. GARG and R. P. SINGH, *Chemistry Department, University of Delhi, Delhi-110 007*

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2-(2'-Lepidyl azo)-1-naphthol-4-ammonium sulphonate (LANAS) has been used successfully as metallochromic indicator in complexometric estimation of Mn (II), Fe (II), Co (II), Ni (II) and Cu (II). Recommended procedures, effect of pH , temperature, range of metal ion concentration for accurate determination have been given. Masking agents have been used successfully to mask some of the common metal ions. Statistical evaluations of the titration procedures have also been carried out.

INTRODUCTION

HETEROCYCLIC azo dyes introduced recently (Anderson & Nickless, 1967) find extensive use in analytical chemistry for micro-determination of metal ions spectrophotometrically (Flaschka & Barnard, 1972) or complexometrically (Flaschka & Barnard, 1964; Schwarzenbach, 1960; and Welcher, 1961). Only very few water soluble heterocyclic azo dyes have been used so far as analytical reagent. In the present communication 2-(2'-lepidyl azo)-1-naphthol-4-ammonium sulphonate (LANAS) (I) has been introduced.

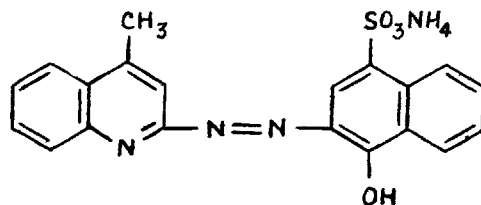


FIG. I

LANAS has been prepared in our laboratory and characterised by elemental analysis, and I. R. spectroscopy (Chadha *et al.*, 1976). The purity of the ligand has been checked by thin layer chromatography. LANAS forms violet to blue complexes with Mn(II), Fe(II), Ni(II), Co(II) and Cu (II) which are completely discharged to the original colour of the LANAS (yellow) by adding EDTA solution. This has been made the basis for the complexometric estimation of these metal ions.

EXPERIMENTAL

Reagents

EDTA Solution — A stock solution (0.1 M) of disodium salt of EDTA (BDH, AR) was prepared by dissolving requisite quantity of the salt in doubly distilled water

and it was standardised with standard magnesium sulphate, using erio-*T* as indicator. The stock solution was diluted from time to time in order to get the working solutions.

Metal ion solutions — The 0.1M solutions of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) were prepared by dissolving requisite quantities of analytical grade manganese sulphate, ferrous ammonium sulphate, cobalt sulphate, nickel ammonium sulphate and copper sulphate in acidulated double distilled water. Solutions were standardised wherever necessary, complexometrically and subsequent dilutions were made as and when desired.

LANAS solution — 0.01% (w/v) solution of LANAS was prepared in double-distilled water and stored in corning glass bottle.

Buffer solution — Sodium acetate/acetic acid/HCl buffers were prepared by mixing 0.2M sodium acetate and 0.2M acetic acid/HCl in different proportions (Ju. Lurie, 1975). Similarly $\text{KH}_2\text{PO}_4/\text{NaOH}$ buffers were prepared by mixing 0.2N KH_2PO_4 and 0.2N NaOH. Hexamine/ HNO_3 or pyridine / HNO_3 buffers were prepared by adjusting the pH of hexamine or pyridine with dilute nitric acid (Sommer & Janoscova, 1974).

Recommended Procedure

To the metal solution containing 0.32 to 25.0 mg of manganese(II) or 0.28 to 8.38 mg of iron(II) or 3.0 to 9.43 mg of cobalt(II), or 0.296 to 5.87 mg of nickel (II) or 0.127 to 20.0 mg of copper(II), add 2 to 3 drops of 0.01% (w/v) LANAS solution (except in the case of iron(II) where 6 drops are added), add the requisite buffer 2 to 3 ml (Table I) to bring the required pH. Raise the volume to 20 ml and titrate the contents under the given conditions with standardised EDTA solution till the end point is reached. For titration in hot media, indicator should be added after heating the solution.

TABLE I

Titration conditions for different metal ions

Metal ion	pH	Optimum concentration mg/20 ml	Buffer	Colour change	Temperature °C	Standard deviation
Manganese (II)	7.0-7.7	0.32 to 25.0	Pyridine/ HNO_3	B—O	15 to 80	0.0071
Iron (II)	3.09-4.5	0.28 to 8.38	HAc/Ac	B—O	50 to 90	0.0064
Cobalt (II)	3.0-5.2	3.0 to 9.43	HAc/Ac	B—O	10 to 70	0.0026
Nickel (II)	3.09-5.0	0.296 to 5.87	HAc/Ac	B—O	40 to 80	0.0038
Copper (II)	2.8-5.40	0.127 to 20.0	HAc/Ac	B—YO	0 to 95	0.0037

B = Blue; O = Orange; and YO = Yellow Orange

RESULTS AND DISCUSSION

The titrations in the case of manganese (II), cobalt(II) and copper(II) can be performed at a room temperature whereas in the case of iron(II) and nickel(II), these are carried out in hot media. In the case of copper(II), a small amount of DMF increases the sharpness of the end point and dissolves coloured solid particles of copper-LANAS complex.

Effect of Diverse Ions

In order to ensure the utility of the titration procedures, effect of various diverse ions has been studied in detail in the estimation of 1.10 mg of manganese, 1.117 mg of iron(II), 1.179 mg of cobalt, 1.174 mg of nickel and 1.271 mg of copper. The results of the studies are summarised below. The tolerance limits in ppm are given in brackets.

Determination of Manganese (II)

Fluoride, chloride, iodide, bromide, sulphite, thiosulphate nitrate, borate, acetate, thiourea and tartrate (5000); thiocyanate (3000), nitrite, ascorbic acid and oxalate (100); citrate, hydroxyl amine, calcium(II) (2000); cyanide (0.5 ml of 4%); chromate (70); magnesium and chromium(III) (300); platinum metals (50 ppm each) and silver(I) (700). The following cations have been masked in amounts in ppm by the anion given in parentheses :

Cobalt(II) (600, CN'), nickel(II) (300, CN'), mercury (II) (900, I' and CN'), copper (II) (300, CN'), lead (II) (20, SO_4^{2-}), tin (II) (50, F'), aluminium (III) (100, F') and bismuth (III) (300, Cl').

Phosphate, iron(II), zinc(II) and cadmium(II) interfere seriously and could not be masked.

Determination of Iron(II)

Bromide, iodide sulphite, chloride, borate, nitrate and barium(II) (5000); fluoride, oxalate, molybdate and silver(I) (350); thiosulphate, thiocyanate and tartrate (2500); phosphate and ascorbic acid (1700); (hydroxylamine and thiourea (750); tin(II) and platinum metals (75); calcium (2000) and chromium(III)(250). The following cations have been masked in amounts in ppm by the anions given in parentheses ; bismuth (300, Cl'), aluminium(III) (150, F'), mercury(II) (900, I'), lead (II) (10, SO_4^{2-}). Nitrite, cyanide and some other transition elements interfere and could not be masked.

Determination of Cobalt (II)

Fluoride, bromide, iodide, chloride (5000); thiosulphate, nitrate, thiocyanate, citrate, borate (4000); sulphite (400); oxalate and calcium(II) (2000); thiourea (800); phosphate (470); ascorbic acid (2650); magnesium and molybdate (200), platinum metals (50) and silver (I) (700). The following ions have been masked in amounts in ppm by the anions given in parentheses : copper(II) (200, $\text{S}_2\text{O}_8^{2-}$); lead (II) (10, SO_4^{2-}); cadmium(II) (336, I') bismuth (150, Cl'), aluminium(III) (300, F'), mercury(II) (200, I') and tin (II) (100, F'). The common transition metal ions, Fe(II), Mn (II),

Ni(II), Zn(II), Ga(III) etc. interfere. Cyanide and nitrite also interfere seriously. Interference due to nitrite could be avoided successfully by adding ascorbic acid. Thiosulphate in large amounts imparts green colour to the solutions.

Determination of Nickel (II)

Fluoride and sulphite (5000); bromide and nitrite (2000); nitrate, tartrate, bromate (3500); thiosulphate, thiocyanate borate and chromate (2500); phosphate, oxalate and thiourea (1500); citrate, molybdate (500); ascorbic acid (850); silver(I) (700); barium(II) (4200); platinum metals (50); tellurium and arsenic (1500). The following ions have been masked successfully in amounts in ppm by anions given in parentheses; copper (II) (125, $S_2O_8^{2-}$) cadmium(II) (28 I'), bismuth(III) (252, Cl') and aluminium (III) (150, F'). Cyanide, zinc(II), manganese(II), lead(II), iron(II) interfere and could not be masked.

Determination of Nickel(II) in presence of copper and lead(II)

Since cyanide interfere seriously in the estimation of nickel(II), and copper(II) can be readily masked with thiosulphate or thiourea, the fact has been utilised in the determination of nickel(II) in presence of copper(II) and lead(II). The procedure adopted is as follows:—

To a suitable aliquot containing nickel(II) 1.174 mg, copper and lead (II) in varying amounts, add 5 to 10 ml of acetate buffer ($pH=3.09$ to 5.0), heat the contents to boiling followed by the addition of a few drops of LANAS solution. Add excess EDTA (known volume) and subsequently titrate immediately with standard nickel(II) solution till blue colour is obtained. To the second aliquot, add thiosulphate or thiourea (1 to 3 ml of 1% w/v), allow it to stand for a few minutes and titrate with standard EDTA solution till orange colour is obtained. This gives the amount of lead and nickel(II). To the third aliquot having a few drops of LANAS, add 4% KCN solution dropwise till blue colour is discharged, raise the pH to 7.0 with hexamine buffer and titrate with standard EDTA solution. This value gives the amount of lead(II) only. From the different total titre values, amount of nickel (II) is obtained. The results of the titrations are summarised in Table II.

TABLE II

Determination of nickel(II) in presence of copper(II) and lead (II)

Amount of nickel (II) (mg)	Ni:Cu:Pb ratio	Amount of nickel (II) Found (mg)	% Error
1.174	1 : 1 : 1	1.177	+0.25
1.174	1 : 2 : 2	1.71	-0.25
1.174	1 : 2 : 1	1.171	-0.25
1.174	1 : 2 : 4	1.180	+0.51
1.174	1 : 1 : 5-3	1.177	+0.25

Determination of Copper (II)

Fluoride, bromide, thiocyanate, citrate, ascorbic acid (4000); nitrate, tartrate, phosphate, hydroxylamine (3000), iodide, nitrite, sulphite, barium (II) and calcium(II) (2500); borate (100); oxalate (200); chromate and magnesium(II) (300), palladium and other platinum metals (50).

The following ions have been masked in amounts in ppm by the anions given in parentheses ; cadmium(II) (20, I'), lead (II) (300, SO_4^{2-}), mercury(II) (1000, I'), tin(II) (1200, F'), aluminium(III) (1100, F') and bismuth(III) (200, Cl'). Cyanide, urea, thiosulphate and some other metals ions viz. zinc(II), nickel(II), cobalt(II), iron(II), gallium(III), indium(III) interfere and could not be masked. The determination of manganese has been possible even in the presence of calcium (a 40 times) and magnesium (~ 4 times) in pH range 7.0 to 7.7. Since cyanide does not interfere in this determination, it has been successfully employed in masking some of the transition metal ions. The estimation of this in the presence of aluminium has been possible as fluoride could be used successfully for masking aluminium(III) ions. Very few metallochromic indicators are used for the complexometric determination of iron(II). LANAS has been successfully used for the estimation of iron(II). Since large quantities of reducing agents such as ascorbic acid and hydroxyl amine hydrochloride do not interfere, it is possible even to determine iron(III) after reduction with these reducing agents. The determination of cobalt(II) in the presence of copper(II) or cadmium(II) (~ 5 to 6 times) when present in a mixture is possible by adding $\text{S}_2\text{O}_3^{2-}$ or \bar{I} masking agents respectively. By using thiosulphate and cyanide as masking agents, the estimation of nickel(II) in the presence of copper(II) and lead(II) can be successfully carried out.

In the case of copper(II) determination, method described has the added advantage that copper(II) can be titrated in lower pH range where alkaline earth metals ions do not interfere and thus the method can be successfully employed for the estimation of copper(II) in presence of alkaline earth metals.

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