

Spectrophotometric determination of copper(II), nickel(II), iron(III) and cobalt(II) using indane-1,2,3-trione trioxime in aqueous medium

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Received 12 September 1988; revised 6 January 1989; accepted
16 March 1989

Indane-1,2,3-trione trioxime (ITT) forms water soluble complexes with copper(II), nickel(II), iron(III) and cobalt(II) in the presence of potassium periodate in sodium acetate - acetic acid buffer medium. The formation of the water soluble complexes has been used to develop a direct spectrophotometric method for the determination of these metal ions. The compositions and stability constants of the complexes formed have also been determined.

Indane-1,2,3-trione trioxime (ITT) has been earlier used by us for the spectrophotometric determi-

nation of palladium(II)¹ and cobalt(II)². In continuation of our earlier work, we report here the use of ITT for the spectrophotometric determination of copper(II), nickel(II), iron(III) and cobalt(II). A direct spectrophotometric method for the determination of cobalt(II) with ITT in aqueous medium has already been reported earlier². Work on the influence of potassium periodate on Co(II)-ITT system is included in this note.

Experimental

The synthesis and characterization of indane-1,2,3-trione trioxime and the instruments used in the present study have been described elsewhere^{1,2}. A solution of the reagent (1×10^{-2} M) was prepared in 30% aq DMF medium.

Stock solutions of copper(II), nickel(II), iron(III) and cobalt(II) were prepared and standardised titrimetrically³. The experimental solutions were obtained by suitable dilution of the stock solution. Hydrochloric acid - sodium acetate and acetic acid buffers were used in the present study.

Table 1 — Physico-chemical and analytical characteristics of complexes

Characteristic	ITT complexes of				
	Copper(II)	Nickel(II)	Iron(III)	Cobalt(II)*	Cobalt(II)†
Absorbance maximum ($\lambda_{\max}$ nm)	320	320	305	400	320
Optimum pH range	3.0-6.0	5.0-7.0	4.0-7.0	5.0-6.0	4.5-7.5
Mole of reagent required per mole of metal ion for full colour development	10	5	5	20	20
Molar absorptivity ($L \text{ mol}^{-1} \text{ cm}^{-1}$)	7.64×10^3	8.75×10^3	7.87×10^3	2.67×10^4	5.32×10^4
Sandell's sensitivity ($\mu\text{g cm}^{-2}$)	0.0083	0.0067	0.0075	0.0022	0.0011
Beer's law validity range (ppm)	0.51-4.57	0.35-4.93	0.45-4.01	0.12-1.65	0.047-0.94
Optimum concentration range (ppm)	1.52-4.32	1.06-3.52	0.89-3.57	0.236-1.88	0.094-0.850
Composition (M:L) of complex by Job's and Mole ratio methods	1:1	1:1	1:1	1:1	1:3
Standard deviation†	0.0042 ^a	0.0044 ^b	0.0042 ^c	0.0048 ^d	0.00588 ^e
Relative standard deviation	1.31%	1.44%	1.31%	0.99%	1.45%

*In the presence of potassium periodate

†Reference 2.

^aIn the determination of (a) 2.54 ppm of copper, (b) 2.11 ppm of nickel, (c) 2.23 ppm of iron, (d) 1.06 ppm of cobalt, (e) 0.45 ppm of cobalt

General procedure for the determination of copper(II), nickel(II) and iron(III)

The samples for the analysis were prepared in 25 ml standard flasks taking 10 ml of buffer (pH 4.5 for Cu, pH 5.5 for Ni, pH 5.0 for Fe), the metal ion solution (Cu 12-112 μg , Ni 9-123 μg , Fe 11-100 μg) and 2 ml of the ligand (ITT) solution ($1 \times 10^{-2} \text{ M}$), and the volume was made up to the mark with distilled water. Absorbances were measured at 320 nm for Cu and Ni and at 305 nm for Fe against reagent blank. The amounts of metal ions present in unknown samples were read from a corresponding calibration graph prepared similarly.

Recommended procedure for the determination of cobalt(II)

To an aliquot containing 2.8 - 53.0 μg of cobalt(II) were added 10 ml of the buffer (pH 5.5), dimethylformamide (2.5 ml), potassium periodate (4 ml, 0.4%) and the ligand (1.5 ml, 10^{-2} M) solution. Total volume was made upto 25 ml by dilution with distilled water and its absorbance measured at 400 nm (after 30 min), against a reagent blank prepared under identical conditions. The calibration graph was prepared similarly.

Results and discussion

The complexation reactions were studied in detail with a view to finding optimum conditions for the determination of copper(II), nickel(II), iron(III) and cobalt(II). The optimum conditions and important physico-chemical characteristics of complexes are summarized in Table 1.

The colour reaction between cobalt(II) and ITT in sodium acetate - acetic acid buffer (pH 5.5) medium has been used for the direct spectrophotometric determination of cobalt in aqueous medium². In the present study we have studied the interaction between cobalt(III) and ITT using periodate as an oxidising reagent. ITT gives a brownish coloured complex species (λ_{max} , 400 nm) with cobalt(II) in the presence of potassium periodate. The analytical characteristics of this brown coloured species are compared with the coloured species formed between cobalt(II) and ITT in Table 1.

The order of addition of reagents (metal ion, buffer and reagent) has no effect on the absorbance of complexes. The complex formation is instantaneous and the complexes are stable for 2 hr. In the case of Co(II) metal ion, a period of 30 min is required for full colour development, which remains constant for ~ 2 hr. The order of addition of reagents (buffer, cobalt(II), DMF, peri-

Table 2—Effect of diverse ions on the determination of copper, nickel, iron and cobalt

Ion added	Tolerance limit (ppm)			
	Copper	Nickel	Iron	Cobalt
Fluoride	2850	2800	—	1140
Chloride	350	350	350	350
Bromide	400	160	160	160
Sulphate	800	800	950	800
Nitrate	620	620	600	620
Oxalate	352	352	70	352
Thiosulphate	600	2320	48	96
Thiourea	400	160	30	160
Thiocyanate	1240	50	50	25
Citrate	180	7	3	14
Tartrate	1240	50	50	25
EDTA	40	2	1	1
Cadmium(II)	900	900	900	2
Lead(II)	410	410	415	8
Thorium(IV)	190	190	185	185
Zinc(II)	130	131	130	3
Manganese(II)	110	120	330	2
Tungsten(VI)	37	15	220	147
Molybdenum(VI)	910	12	19	192
Zirconium(IV)	18	18	36	73
Iron(III)	235*	120*	—	24*
Copper(II)	—	*3 [†]	2.5 [†]	0.3
Chromium(III)	2 [†]	3 [†]	—	—
Vanadium(V)	9*	3*	3	1
Rhodium(III)	10	21	21	0.2
Iridium(III)	20	15	20	2
Osmium(VIII)	2	6	6	0.6
Gold(III)	2	2	2	2
Palladium(II)	1	1	1	0.7
Platinum(IV) [§]	13	7	5	4
Aluminum(III)	110	150	216	5
Mercury(II)	10	40	40	80

*In the presence of 1520 ppm of fluoride

[†]In the presence of 22 ppm of hypo

[‡]In the presence of 40 ppm of tartrate

[§]In the presence of 300 ppm of oxalate

—Seriously interferes

odate and ITT) has no effect on the absorbance of reaction mixture provided DMF is added prior to the addition of the reagent solution.

Effect of foreign ions

Interference due to associated ions in the determination using ITT was examined. The tolerance limit in ppm was taken as the amount of foreign ion required to cause $\pm 2\%$ error in the absorbance. The tolerance limits, (in ppm) for various foreign ions in the determination of copper (2.54

Table 3—Analysis of alloy samples

Alloy sample	Concn. of metal(II) in sample $\times 10^4$ (<i>M</i>)	Volume (ml) Metal(II) = Cu(II)	Metal Found* (%)	Error (%)
NBS.NKK-1021 ^a	2.00	3.0	2.75	+1.25
		4.5	2.67	-1.84
		6.0	2.76	+0.25
NBS SRM 856 ^b	2.05	3.0	4.05	+1.50
		4.5	3.97	-0.50
		6.0	4.02	+0.75
NTPC Ball bearing material ^c	2.10	3.0	4.57	+1.76
		4.5	4.55	+1.11
		6.0	4.48	-0.42
Metal(II) = Ni(II)				
NTPC Ball bearing material ^c	2.05	3.0	10.20	+2.00
		4.0	9.92	-0.80
		5.0	10.15	+1.50

*Average of five determinations

^a5.56% Si, 0.99% Fe, 2.72% Cu, 0.20% Mn, 0.29% Mg, 0.03% Cr, 0.14% Ni, 1.76% Zn, 0.04% Ti, 0.10% Sn, 0.18% Pb, 0.007% V, 0.01 Zr, 0.01% Si, 0.01% Sb.

^b0.03% Zn, 0.02% Ti, 0.18% Si, 0.29% Fe, 1.49% Mg, 0.006% V, 0.21% Pb, 0.084% Ni, 0.211% Cr, 0.61% Mn, 3.99% Cu.

^c10% Ni, 15% Cr, 65% Fe, 4.5% Cu, 2% Mn.

ppm), nickel (2.35 ppm), iron (2.35 ppm) and cobalt (0.943 ppm) are presented in Table 2. Interference due to iron in the determination of copper, nickel and cobalt could be minimised by using fluoride as the masking reagent. Tartrate, oxalate and hypo were used for masking interference of chromium(III), platinum(IV) and copper(II) respectively (Table 2). Cobalt(II) seriously interferes in the determination of copper(II), nickel(II), iron(III). Small amounts of nickel(II) (16 μ g in Cu system, 6 μ g in Fe system and 5 μ g in Co system) and ruthenium(III) (18 μ g in Cu and Ni systems and 25 μ g in Fe system), however, did not interfere.

Analysis of alloys

A sample of alloy steel (0.25 g) was dissolved in aqua-regia (15 ml) by warming and the solution evaporated to dryness. The residue was dissolved in hydrochloric acid (10 ml) and the resulting solution concentrated to ~5 ml, diluted to ~50 ml with doubly distilled water and made upto 100 ml. Suitable aliquots of sample containing metal ion (Cu or Ni) were analysed according to the standard procedure using sodium fluoride (1520 ppm) for masking iron. The results are presented in Table 3.

Except cyclohexane-1,2,3-trione trioxime^{4,5}, trioximes have not been used as analytical reagents for the spectrophotometric determination of metal

ions. Since most of the spectrophotometric methods^{6,7} for the determination of copper(II), nickel(II) and iron(III) using oximes involve an extraction step, an attempt is made for the determination of these metal ions in aqueous medium. The extraction procedures are known to be expensive, time consuming and laborious. The present method offers the advantages of simplicity, rapidity, reasonable sensitivity without the need for heating or extraction. Thus indane-1,2,3-trione trioxime has been found to be a useful spectrophotometric reagent for the title metal ions over the existing ones.

Acknowledgement

One of us (DMR) is thankful to the CSIR, New Delhi for the award of a senior research fellowship.

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