Asian Journal of Chemistry Vol 11, No. 1 (1999), 45–48

Use of 2-Hydroxy-4-Chloro-5-Methylacetophenone Oxime as a Spectrophotometric Reagent for Co(II), Ni(II) and Cu(II): Their Sequential Extraction and Determination in the Mixtures and Alloys

PUNITA S. BHARADWAJ* and H.B. NAIK†
Department of Chemistry
J.P. Arts and Science College, Bharuch-392 002, India

2-Hydroxy-4-chloro-5-methylacetophenone oxime (HCMAOX) has been used for the spectrophotometric determination of Co(II), Ni(II) and Cu(II) at pH 8.4, 7.0 and 3.5 respectively by extraction method. Stoichiometry ratios of these complexes, studied by Yoe and Jones mole ratio methods show metal : ligand ratio in the complex to be 1 : 2. The stability constants of the complexes are found to be 1.27×10^8, 2.68×10^7 and 2.23×10^8 for Co(II), Ni(II) and Cu(II) respectively. The reagent has also been found to give satisfactory results for the analysis of Co(II) and Ni(II) or Cu(II) in synthetic mixtures and Cu(II) and Ni(II) in certain alloys.

INTRODUCTION

The reagent, 2-hydroxy-4-chloro-5-methylacetophenone oxime (HCMAOX) is a versatile chelating agent attracting numerous applications, particularly concerning the gravimetric and spectrophotometric determinations of Cu(II), Ni(II), Co(II) and Pd(II)[1]. In the present work HCMAOX is used as a spectrophotometric reagent for Co(II), Ni(II) and Cu(II) and stability constants of metal complexes are studied. It is also observed that HCMAOX can be used for the quantitative extraction of Co(II), Ni(II) and Cu(II) in chloroform and so we used it for the sequential extraction and determination of copper and nickel and copper and cobalt in synthetic mixtures and certain alloys also.

EXPERIMENTAL

All the pH measurements were carried out on Elico pH meter and absorbances were carried out on Bausch and Lomb's spectrophotometer. All the chemicals used were of AR grade. The 0.05 M stock solution of metal has been prepared by dissolving requisite amount of copper sulphate, nickel chloride and cobalt nitrate and finally standardized.[2]

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*Span Research Centre, Udhna-Surat, India

Stoichiometry and Stability Constants of the Complexes

The reagent HCMAOX forms complexes with Cu(II), Ni(II) and Co(II) which can be extracted in benzene, acetone, chloroform, carbon tetrachloride etc., which facilitate the spectrophotometric study of these complexes. pH of these solutions were adjusted at 3.5, 7.0 and 8.4 for Cu(II), Ni(II) and Co(II) complexes respectively. Digestion at room temperature was carried out for 45 min, 90 min and 2 h for Cu(II), Ni(II) and Co(II) complexes respectively and was extracted in 10 mL of $CHCl_3$ for Cu(II), 15 mL of $CHCl_3$ for Ni(II) and Co(II) complexes. Absorbances were recorded at 400 nm and 420 nm respectively. To determine the stoichiometry Yoe and Jones mole ratio method[3] was studied and stability constants of all the complexes were calculated.

General procedure for extraction and determination of Cu(II), Ni(II) and Co(II)

Transferred an accurately measured aliquot of metal solution containing 12 to 51 ppm of Cu(II) into a separating funnel, added required amount of reagent solution and 5 mL of the buffer solution. Extracted the precipitated complex in 20 mL benzene. Dried the extract with anhydrous sodium sulphate, then measured the absorbances taking benzene as blank. In a similar way, the calibration curves for Ni(II) and Co(II) were also constructed by taking 14 to 59 ppm of Ni(II) and 5 to 24 ppm of Co(II).

Analysis of Cupronickel and Cuprocobalt

A known volume of the solution containing copper and nickel or copper and cobalt was taken into the beaker. 10-fold excess of reagent is required for complete precipitation of Cu(II) complex with HCMAOX. Added 10 mL of buffer solution of pH 3.5. After digestion, extracted the Cu-complex in 20 mL $CHCl_3$ with one 10 mL and two 5 mL portions with shaking for 30 sec. Dried the combined extract with anhydrous sodium sulphate and measured the absorbance at the respective wavelengths. Then pH of the aqueous solution was raised to 7.0–7.5 or 8.4 with 0.1N NaOH for nickel and cobalt respectively. 25-fold excess of reagent was required for complete precipitation of nickel and cobalt. After digestion for half an hour and cooling, extracted the Ni and Co complexes in 20 mL $CHCl_3$ in four portions of 5 mL each and measured the absorbances at their respective wavelengths. In the same way copper is determined in brass and bronze and copper and nickel simultaneously can be determined in german silver.[4] Weigh about 100 mg. of sample and dissolve it in nitric acid (1 + 1). Add 5 mL of concentrated hydrochloric acid and evaporate the solution nearly to dryness on a water bath, then repeat this treatment to remove the bulk of the nitric acid. Take up the residue in water and dilute to volume in 100 mL standard measuring flask. Take an aliquot of sample solution and work up as described before.

RESULTS AND DISCUSSION

Spectrophotometric study of all the three complexes confirms 1 : 2 (metal : ligand) ratio. The values of stability constants calculated from mole ratio method are given in Table-1 .

TABLE-1

Complex	E_m	E_s	α	K_s
$Cu(C_9H_9O_2NCl)_2$	0.2218	0.2076	0.06402	2.23×10^8
$Ni(C_9H_9O_2NCl)_2$	0.3872	0.3600	0.07025	2.68×10^7
$Co(C_9H_9O_2NCl)_2$	0.5229	0.4881	0.06655	1.27×10^8

From the study of effect of pH, it was studied that copper is extracted completely at pH 3.6–10.0 and nickel at pH 7.0–8.0 and cobalt at 8.4. This differnece between the pH values for extraction of these complexes has been exploited for their sequential extraction and determination of Cu(II), Ni(II) and Co(II) in synthetic mixtures and copper and nickel in certain alloys. Copper and nickel and copper and cobalt can be determined sequentially by using their calibration curves and by exploiting the difference between the pH values. It is observed that nickel or cobalt is not extract at all at pH < 4.0, whereas copper is extracted completely at pH 3.5–4.0. So nickel and cobalt can be extracted thereafter after raising the pH and adding required amount of reagent. Typical results for synthetic mixtures are given in Table-2 and 3 which shows that the amount determined by proposed procedure agree reasonably well with the amount taken.

TABLE-2
SEQUENTIAL DETERMINATION OF COPPER AND NICKEL

Taken ppm		Found ppm		Error in ppm		Error %	
Cu^{2+}	Ni^{2+}	Cu^{2+}	Ni^{2+}	Cu^{2+}	Ni^{2+}	Cu^{2+}	Ni^{2+}
12.70	+11.74	12.57	+11.60	0.13	0.14	1.02	1.19
25.40	+29.35	25.32	+28.62	0.08	0.73	0.31	2.40
19.06	+11.74	19.00	+11.80	0.06	0.06	0.31	0.51
25.40	+29.35	26.05	+30.08	0.65	0.73	2.50	2.40

TABLE-3
SEQUENTIAL DETERMINATION OF COPPER AND COBALT

Taken ppm		Found ppm		Error in ppm		Error %	
Cu^{2+}	Co^{2+}	Cu^{2+}	Co^{2+}	Cu^{2+}	Co^{2+}	Cu^{2+}	Co^{2+}
12.70	+11.78	12.80	+11.78	0.10	—	0.78	—
19.06	+1178	18.42	+12.08	0.64	0.30	3.30	2.50
25.40	+11.78	24.78	+11.31	0.62	0.47	2.40	3.90
25.40	+17.68	25.73	+17.38	0.33	0.30	1.20	1.69

DETERMINATION OF COPPER IN BRASS AND BRONZE
(Mean of five separate analyses)

Sample	% of Copper reported	% of Copper found
Brass	59.20	58.46
Bronze	88.40	88.90

In a similar way copper and nickel in german silver, found by proposed procedure (Cu 70.25 ± 0.5%, Ni 23.68% ± 0.5%) agree reasonably well with that found by standard method.[5]

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(*Received*: 9 June 1998; *Accepted*: 4 September 1998) AJC- 1565