

Spectrophotometric determination of nickel in aluminium bronze samples with 1,10-phenanthroline and eosine

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A highly selective liquid-liquid extraction spectrophotometric procedure has been described for the determination of trace amounts of nickel with eosine in the presence of 1,10-phenanthroline. The molar absorptivity and Sandell's sensitivity are found to be $7.1 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ and 0.83 ng/cm^2 respectively. The method has been successfully utilized for the determination of nickel in Al-bronze samples.

Various ternary systems reported for the determination of nickel include (i) mixed-ligand complex formation viz. 1,10-phenanthroline-cadion¹ and rubeanic acid-quinoline², (ii) surfactant sensitized systems viz. chromeazurol S-cetyl trimethyl ammonium bromide (CTAB)³ and xylene orange - CTAB⁴ (iii) ion-association systems viz. 1,10-phenanthroline-rose bengal⁵, 1,10-phenanthroline-eriochrome red B⁶ and 4-chloro-2-nitroso-1-naphthol- crystal violet⁷. Of these, the reactions based on ion-association complex formation are more sensitive than mixed ligand and surfactant sensitized reactions. The reaction based on 1,10-phenanthroline-eriochrome red B is highly sensitive ($\epsilon = 19 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$) but is not selective. This note describes the studies on the interaction of cationic 1,10-phenanthroline complex of nickel with eosine that provides a basis for selective spectrophotometric method for the determination of nickel. This method was found to be useful in the determination of nickel in Al-bronze samples.

Experimental

A microprocessor controlled Hitachi 220 double beam spectrophotometer with 10 mm quartz cells was

used. An ELICO LI-120 digital pH meter was used for pH adjustment. All reagents used were of AR grade unless otherwise stated. All solutions were prepared using doubly distilled water.

Nickel(II) stock solution (1000 ppm) was prepared by dissolving nickel sulphate (1.1935 g) in distilled water and standardized by titrating with EDTA. Working solutions were prepared by suitable dilution. Ammonium acetate buffer (pH 6) was prepared by dissolving ammonium acetate (8.40 g) in doubly distilled water, adjusting the pH to 6 using either HCl or NaOH and diluting to 500 ml. Aqueous solutions of 1,10-phenanthroline (0.2%) and eosine (0.02%) were also prepared.

General procedure

To an aliquot of nickel(II) solution (0-10 μg in 25 ml) 2 ml each of 5% NaF, 5% thiourea, 5% thioglycolic acid, 5% tartaric acid and buffer and 5 ml each of 1,10-phenanthroline and eosine were added and the pH was adjusted to 6 using HCl/NaOH. Chloroform (10 ml) was added and the contents shaken for 2 min. The chloroform layer was collected through a filter paper plug and the absorbance measured at 540 nm against reagent blank.

Procedure for determination of nickel in drinking water/sea water

Aliquots (10 ml) of drinking water/filtered sea water were taken and the pH was adjusted to 6 and subjected to analysis by the same procedure as described above.

Analysis of Al-bronze

Al bronze (0.1 g) was dissolved in 5 ml of conc. HCl and 1 ml of HNO_3 . The resulting solution

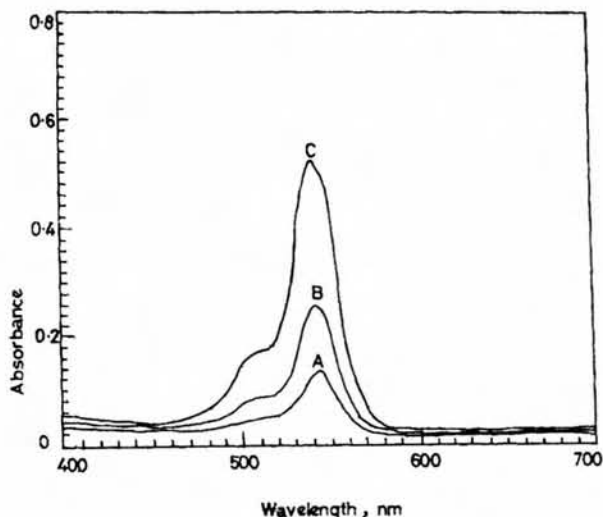


Fig. 1—Absorption spectra of chloroform extract of 2.5, 5.0 and 10.0 μg (curves A, B and C respectively) of nickel(II)-1,10-phenanthroline-eosine against reagent blank (pH 6 ammonium acetate, 1,10-phenanthroline = 5 ml of 0.2%, eosine = 5 ml of 0.02%, shaking time = 2 min, volume of aqueous phase = 25 ml, volume of chloroform = 10 ml).

was diluted to 100 ml with water. Suitable aliquots were taken and subjected to analysis by following the procedure described above.

Results and discussion

Figure 1 shows the absorption spectrum of chloroform extract of red nickel(II)-1,10-phenanthroline-eosine complex recorded for 2.5, 5.0, 10.0 μg of nickel against reagent blank. The ternary ion-association complex has the absorption maximum at 540 nm. The effect of pH was studied on the extraction of 5 mg of nickel in the pH range 4-8. Maximum absorbance was obtained in the pH range 5-7. Hence, all further extractions were carried out from pH 6 ammonium acetate solutions.

The 1,10-phenanthroline and eosine concentrations necessary for the formation of ternary ion-association complex was studied by varying the concentrations from 1.0 to 8.0 ml of 1,10-phenanthroline and 1.0-8.0 ml of eosine in a final aqueous phase volume of 25 ml. It was found that constant and maximum absorbance was obtained from 4-8 ml of 0.2% 1,10-phenanthroline or 0.02%

Table 1. Interference studies

Interferents	Remarks
Hg, Na, K, Tl(I), Ba, Ca, Mg, Be(II), Pb(II), Pd(II), Cu(II), Mn(II), Al(III), As(III), Sb(III), Bi(III), Fe(III), La(III), Pt(IV), Zr(IV), Th(IV), Nb(V), U(VI), Mo(VI), W(VI), SCN^- , $\text{S}_2\text{O}_3^{2-}$, PO_4^{3-} , $\text{B}_4\text{O}_7^{2-}$, SO_3^{2-} , CrO_4^{2-} , F $^-$, Br $^-$, I $^-$ & oxalate	No interference at 200 fold level
Zn(II) & Cd(II)	No interference* at 1 fold level
CO(II)	Interferes at all levels

eosine. Hence, 5 ml each of 0.2% 1,10-phenanthroline and 0.02% eosine were used for further studies. Of the various solvents, the ternary complex was found to extract only in chloroform and hence this solvent was chosen for further studies. Further, it was found that by shaking 25 ml of aqueous phase with 10 ml of chloroform for periods ranging from 1 to 5 min resulted in constant and maximum absorbance of the chloroform extract and hence 2 min was chosen. The effect of aqueous phase volume was studied in the range 10 to 25 ml. The absorbance of the chloroform extract was independent of the phase volume; 25 ml of the aqueous phase was chosen. The order of addition of reagents was not found to be critical.

The ratios of nickel with 1,10-phenanthroline and eosine were established by both mole ratio and continuous variation methods. The molar ratios of nickel, 1,10-phenanthroline and nickel to eosine were found to be 1:3 and 1:2 respectively by the above methods. Hence, the ternary ion-associate that is extracted into chloroform was evidently formed by the ion-association of 2 molecules of anionic dye, eosine with tris(phenanthroline) nickel(II) primary cationic complex.

The effect of 1000 μg amounts each of several cations and anions on the determination of 5 μg of nickel was carried out by following the developed procedure. The results are summarized in Table 1.

The recoveries obtained by the standard addition of 1,2 and 4 μg of nickel in drinking water and sea water samples by the proposed method were found to be good, indicating that the developed method can reliably be used for the analysis of nickel in polluted sea water and tap water samples (after separation from cobalt).

Analysis of Al-bronze sample

Al-bronze certified reference material was subjected to analysis by the developed spectrophotometric method. The results obtained by the present method for nickel (4.41 ± 0.4) agree well with certified (4.75%) ion- chromatographic (IC) (4.84%) and AAS (4.40%) values.

Conclusions

The present method based on the extraction of ternary ion-association complex; nickel - 1,10-phenanthroline- eosine, into chloroform though less sensitive than 1,10-phenanthroline-eriochrome red B, is of comparable or better sensitivity than

1,10-phenanthroline-rose bengal and 4-chloro-2-nitroso-1- naphthol-crystal violet and other surfactant sensitized, mixed ligand and most of the binary reagents. In addition, the present procedure is highly selective in the presence of various masking agents compared to other ternary systems and could reliably be used for the determination of nickel in Al-bronze samples.

References

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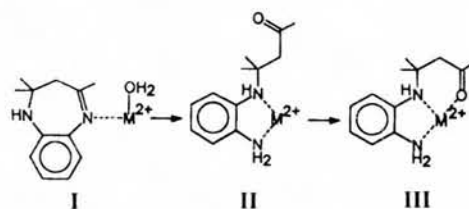
Errata

1. Paper entitled, "Structure and metal binding of a 1H-1, 5-benzodiazepine", *Indian J Chem*, 38A (1999) 553-557:

On page 555, the captions for Figs 1 and 2 have been interchanged inadvertently. The correct captions are:

Fig. 1—The "ball and stick" representation of the solid state conformation of the seven-membered heterocyclic ring in L.

Fig. 2—50% Probability displacement ellipsoid plot of L showing the labelling of the nonhydrogen atoms. Further, on page 556, in Scheme 1, there is a misprint in Structure II of Scheme 1. The correct Scheme 1 should now read as,



Scheme 1

2. Paper entitled, "Kinetics and mechanism of oxidation of hydroxylamine by 12-tungstocobaltate(III) ion in acetate buffer", *Indian J Chem*, 38A (1999) 541-546. On page 541, in the equation in the 2nd line of the abstract, U may be read as W.

On page 543, at the bottom of the left hand column in Eqs 2 and 3, the equal signs should be replaced by the signs of equilibrium.

On page 543 again in Table 1, the column headings of 2nd to 5th column have been shifted. The correct column headings are shown below:

pH/Temp ($^{\circ}\text{C}$)	25	30	35	40	45
	$10^2 k_2 (\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$				