

SPECTROPHOTOMETRIC STUDY OF COMPLEXATION EQUILIBRIA OF Ni(II) WITH AMMONIUM-(2'-AMINO-3'-HYDROXYPYRIDYL-4'-AZO) BENZENE-4-ARSONATE AND DETERMINATION OF Ni(II) IN COMMONLY AVAILABLE HYDROGENATED OILS*

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The composition, molar absorptivity and stability constant for the complex of Ni(II) with ammonium-(2'-amino-3'-hydroxypyridyl-4'-azo)benzene-4-arsonate (metal-ligand ratio 1 : 2, ionic strength $\mu = 0.1$ M, Na_2SO_4) were determined from the absorbance curves using graphical methods. The optimum conditions for spectrophotometric determination of Ni(II) with this reagent were determined. The complexation at different pH was studied in water-ethanol and water-dimethyl formamide media. Ni(II) was determined in commonly available hydrogenated oils using modified wet oxidation method of Reitz *et al.* (1960) and also by the procedure of Price *et al.* (1960). The results obtained by these two methods have been compared.

Keywords: Ammonium (2'-Amino-3'-hydroxypyridyl-4' azo)benzene-4-arsonate (AHP-4A); Nickel (II); Spectrophotometry

INTRODUCTION

SEVERAL reagents for the spectrophotometric determination of Ni(II) have been reported (Marczenko, 1976) of which heterocyclic azo-dyes constitute an important class of chromogenic reagents with high photometric sensitivities (Sandell & Onishi, 1978; and Shibata, 1972). Ammonium-(2'-amino-3'-hydroxypyridyl-4'-azo) benzene-4-arsonate (AHP-4A), a water soluble pyridinol azo dye has already been successfully used in the spectrophotometric determination of cyanide ions using mercury (II) complex by indirect method (Varma *et al.*, 1979). In the present communication, the complexation equilibria of AHP-4A with Ni(II) have been studied in aqueous, in 30 per cent ethanol and in 30 per cent dimethylformamide (DMF) media. Characteristics of the complex have been investigated using graphical methods and the metal determined spectrophotometrically.

EXPERIMENTAL

Reagents

Stock solution of Ni(II) was obtained by dissolving nickel ammonium sulphate in double distilled water and standardised by conventional method.

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AHP-4A Solution : AHP-4A was synthesised (Varma *et al.*, 1979) by condensing 2-amino-3-hydroxypyridine (Aldrich) with diazotised *p*-arsanilic acid (Koch-Light) and neutralising with aqueous ammonia. The purity of the reagent was checked by tlc.

NaOH and H₂SO₄ have been used for pH adjustments. A hexamine-nitric acid buffer of pH 6.7 was prepared.

All other reagents (Na₂SO₄·7H₂O) used were of analytical grade.

Apparatus

A Unicam SP-600 spectrophotometer with 10 mm glass cells was used for absorbance measurements. A Beckman pH meter (model Expandomatic SS-2) was used for pH measurements. A Rotofix-2800 centrifuge was used for separating the supernatant liquid.

Recommended Procedure

To a suitable aliquot containing 3.5–21.0 μg of nickel, add excess of AHP-4A (2.8 ml of 5×10^{-4} M) followed by 1 ml of 1 M Na₂SO₄ (to maintain the fixed ionic concentration ($\mu = 0.1$ M) and 2.0 ml of hexamine-nitric acid buffer of pH 6.7. Dilute to 10 ml and record the absorbance at 540 nm against a reagent blank. Determine the amount of unknown Ni(II) in the given sample from pre-calibrated curve, drawn under similar conditions.

RESULTS AND DISCUSSION

Addition of AHP-4A to an aqueous solution of Ni(II) results in the formation of a water soluble, red coloured complex which is stable for at least 8 hours.

Effect of pH : The effect of alkalinity or acidity reveals that the maximum complexation occurs in the pH range of 6.0–7.0 (Fig. 1). Low absorption at pH 5.0 and 10.8 may be attributed to the formation of protonated and hydroxy species of the complex respectively.

Effect of Solvents

The complexation was studied in 30 per cent ethanol and in 30 per cent DMF at different pH and at a constant ionic strength, $\mu = 0.1$ M. It was, however, noticed that the presence of these solvents stabilised the colour and the absorbance increased slightly. The pH range of maximum complexation narrows down (becomes sharp) in 30 per cent DMF. However, in ethanol, it remains unaffected.

Composition and Sensitivity

The composition of the complex, as found by Job's method of continuous variations and molar ratio method, is 1 : 2 (metal : ligand). The stability constant of Ni(II)-(AHP-4A) complex at $\mu = 0.1$ M, as calculated from molar ratio plot is 3.31×10^{11} (at 30°). Beer's law is followed up to 2.2 ppm. The optimum concentration range of Ni(II) which can be reproduced accurately is 0.35–2.1 ppm. The molar absorption coefficient as calculated from Beer's law is 2.75×10^4 l

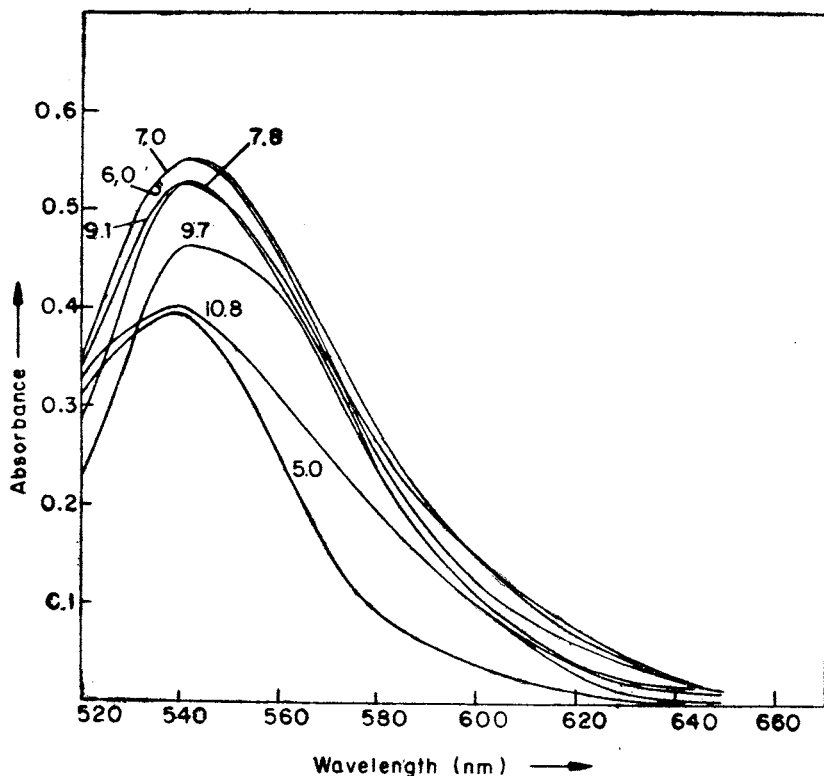


FIG. 1. Absorption spectra of Ni(II)-(AHP-4A) complex at different pH values.

mole⁻¹ cm⁻¹, at 540 nm and Sandell's sensitivity is 0.0021 μg of Ni(II) cm⁻² for an absorbance of 0.001.

Effect of Diverse Ions

The interference due to foreign ions was studied by taking 1.2 ppm of Ni(II). The alkaline earths, Be²⁺, Ba²⁺, Ca²⁺, Sr²⁺, lanthanides, UO₂²⁺ (precipitated and centrifuged), V(V), Mn(II), Cr(III) do not interfere, so did NO₃⁻ (10000 ppm), F⁻, Cl⁻, Br⁻, I⁻, SO₃²⁻, NO₂⁻ (more than 5000 ppm each), BO₃³⁻, C₂O₄²⁻ (800 ppm each), tartrate (600 ppm), thiourea (400 ppm), S₂O₃²⁻ (250 ppm), citrate (25 ppm). Hg²⁺ (20 ppm, masked with S₂O₃²⁻), Pd²⁺ (10 ppm, masked with NO₂⁻) and Fe³⁺ (40 ppm, masked with F⁻).

Zn²⁺, Cu²⁺, Co²⁺, Fe²⁺, Os (VIII) interfere seriously, so do CN⁻, S²⁻ and EDTA.

Determination of Ni(II) in Hydrogenated Oils

Procedure A : Take 20 g of the sample in a Erlenmeyer flask and subject it to wet oxidation process of Reitz *et al.* (1960). After digestion with concentrated nitric acid (in small lots of 5 ml each), cool the whole mass in ice and filter through a

pad of glass wool (Handa, 1974). Raise the total volume to 100 ml. Take 2.0 ml of diluted solution and neutralise with sodium hydroxide to bring the pH around 5.5, add in excess of AHP-4A and adjust the pH to 6.7 with hexamine-nitric acid buffer. Measure the absorbance at 540 nm against reagent blank. Run a solution blank also. Determine the amount of Ni(II) in the hydrogenated vegetable oil from the pre-calibrated curve.

Procedure B (Price et al., 1960) : To a 20 g of the sample, add 20 ml of CCl_4 and 20 ml of 10 per cent HNO_3 . Warm it slightly and centrifuge. Aspirate the upper layer and evaporate to dryness. Add water and few drops of 0.1 M HCl. Reduce the volume to 2.0 ml and dilute to 100 ml. Take 2.0 ml of diluted solution and determine the amount of Ni(II) using the recommended procedure.

Known amounts of Ni(II) were also added to 20 g of the sample and Ni(II) contents were determined following the recommended procedure. The recovery of the total amount of Ni(II) using AHP-4A was found to be quite satisfactory.

The recovery data of the two methods have been compared with dimethyl glyoxime in Table I.

TABLE I
Results of analysis of Ni(II) in commonly available hydrogenated vegetable oils
(amounts in $\mu\text{g}/\text{gm}$ of the sample, average of three readings)

Sample	Present method		DMG method		% error	
	Procedure		Procedure		Procedure	
	A	B	A	B	A	B
I	13.4	13.6	13.3	13.4	0.7	1.5
II	8.5	8.7	8.4	8.6	1.2	1.2
III	8.2	8.3	8.1	8.2	1.2	1.2

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