NOTE

Spectrophotometic Determination of Ni(II) with Isovanillin Thiosemicarbazone

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A new spectrophotometric method using isovanillin thiosemicarbazone (IVTSC) is proposed for the determination of Ni(II) at microgram level. IVTSC reacts with Ni(II) at pH 9 to form a yellow coloured complex which was extracted in *n*-butanol which shows maximum absorption at 400 nm. The molar absorptivity and Sandell's sensitivity were calculated to be 6.4060×10^3 L mol^{-1} cm^{-1} and 0.000109 $\mu g\ cm^{-2}$ respectively. The stoichiometry of the complex was found to be 1 : 2.

Key Words: Spectrophotometric determination, Nickel(II), Isovanillin thosemicarbazone.

Thiosemicarbazones have been widely used as analytical reagents in spectrophotometry[1-3] and fluorometry and also as visual indicators for a wide variety of metals. Their analytical applications have been reviewed[4-6] and the structure of the metal complexes investigated. They act as chelating agents by bonding through sulphur atom and the hydrazine nitrogen atom. The reagent isovanillin thiosemicarbazone (IVTSC) is prepared by reacting isovanillin with thiosemicarbazone[7]. A new spectrophotometric method for determination of Ni(II) using IVTSC is developed. The proposed method is very selective and sensitive and has been applied for the determination of Ni(II) in synthetic and real samples.

The stock solution of Ni(II) was prepared by dissolving equivalent 100 mg in double distilled water and standardized by a known method[8]. The 0.1% reagent solution was prepared in methanol. Absorbance and pH measurements were carried out on a Shimadzu UV-Vis 2100 spectrophotometer with 1 cm quartz cells and a digital pH-meter with combined glass electrode respectively.

Procedure: To an aliquot of solution containing Ni(II) known amount of 0.1% IVTSC was added. The pH of the solution was adjusted by adding 2 mL of buffer and volume was made to 10 mL by using distilled water. The distribution studies were carried out at 25°C, except for the effect of temperature. In a 60 mL separating funnel the aqueous phase was equilibrated with 10 mL (2 × 5 mL) of *n*-butanol for 60 s. The yellow coloured organic extract was collected in a 10 mL standard volumetric flask and made up to mark with *n*-butanol. The absorbance

of extracted Ni-IVTSC complex was measured at 400 nm against reagent blank. The amount of Ni(II) in organic phase was determined from the calibration curve, while the amount of Ni(II) in aqueous phase was determined by a known method[8].

The extraction of Ni(II) (100 μg) was carried out at different pH (2 to 12). The extraction was found to be quantitative at pH 9. The influence of shaking time for the extraction was studied for 30–120 s. The quantitative extraction of Ni(II) was achieved after 30 s with IVTSC and the complex was stable for 48 h.

Influence of diluents: Various solvents such as *n*-butanol, chloroform, ethyl acetate, ethyl methyl ketone, methyl isobutyl ketone, carbon tetrachloride, toluene, hexane were tried to achieve maximum extraction of nickel. The extraction of nickel was quantitative with IVTSC when both were dissolved in aqueous solution taking *n*-buatnol as diluent.

Effect of reagent concentration: The minimum amount of the reagent required for the colour development of a 6 ppm Ni(II) was found by varying the reagent concentration from 0.1 mL to 2 mL of 0.1% methanolic solution of IVTSC. It was found that 1.0 mL of 0.1% IVTSC is sufficient for the extraction of 0.6 ppm of Ni(II).

Nature of extracted species: The nature of extracted species was ascertained from the plot of log D *vs.* log R from aqueous media (Fig. 1), where log D is the
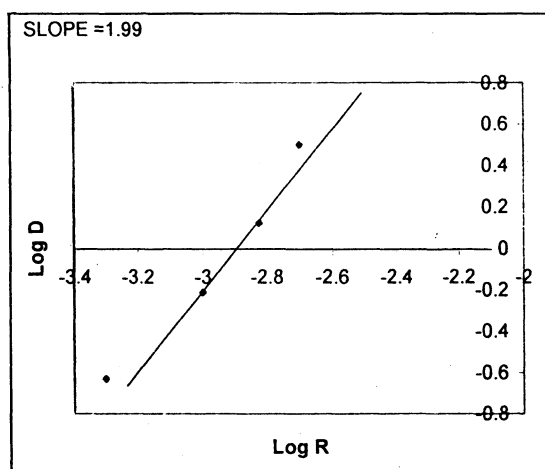

Fig. 1. Stoichiometric ratio of metal to reagent complex of Ni(II) with IVTSC in *n*-butanol from aqueous media

distribution coefficient of the complex and log R is the concentration of the reagent. The slope of the graph is 1.99 for IVTSC. Thus stoichiometry ratio of metal to ligand was found to be 1 : 2 with the reagent. The probable mechanism is therefore

$$Ni^{2+}_{aq} + nX_{org} \rightleftharpoons Ni \cdot nX_{org}$$
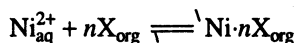
where X stands for IVTSC and $n = 2$ for the system.

Beer's law and sensitivity: Calibration graph for Ni(II) was constructed under the optimum conditions. The graph obeys Beer's law from the range of

1 μg to 60 μg for nickel. Molar absorptivity and Sandell's sensitivity were calculated to be 6.4060×10^3 L mol^{-1} cm^{-1} and 0.000109 μg cm^{-2} respectively.

Influence of diverse ions on the percentage extraction of Ni(II): An inteference study showed that large number of cations and anions offer no interference. The tolerance limit was set at the amount of foreign ions required to cause +1.0% error in the recommended procedure. The presence of various salts of alkali and alkaline earth metals does not show any effect on the absorbance value of Ni : IVTSC complex.

Applications: Various commercial samples and synthetic binary mixtures containing Ni(II) were analyzed according to the recommended procedure and the results were compared to those obtained by standard method. The proposed method also facilitates to determine Ni(II) from commercial samples. The results are shown in Table-1.

TABLE-1

SEPARATION OF Ni(II) WITH IVTSC FROM VARIOUS SYNTHETIC
AND COMMERCIAL SAMPLES

Sr. No.	Sample	Nickel Found	
		DMG method	Present method
1.	Synthetic mixtures		
	(a) Ni (10), V (10)	10.0 μg	10.02 μg
	(b) Ni (5), Cr (5)	5.01 μg	4.98 μg
	(c) Ni (5), Zr (5)	5.02 μg	5.00 μg
	(d) Ni (10), Th (10)	9.90 μg	10.10 μg
2.	Hydrogenated Oil	0.0014 %	0.0013 %
3.	High speed steel alloy	3.95 %	3.93 %
4.	Brass	0.55 %	0.52 %
5.	Cupro-nickel alloy	22.20 %	22.18 %

Conclusion: The proposed method is found to be competitive as compard to other standard methods. The extraction time required is very little i.e. only 30 s and the complex is stable for 48 h. The results show good agreement with the standard method.

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