Preconcentration and Separation of Metal Ions Using Chelating Adsorbents Based on Naphthalene

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N-(2′-Pyridyl)-2-hydroxybenzamide (NPHB) supported on naphthalene has been used for the preconcentration and separation of cobalt and nickel ions. Further, a simple, convenient and rapid spectrophotometric method has been developed for the estimation of these ions. Co(II) and Ni(II) can be quantitatively determined using this adsorbent in a column in the pH range of 5.0 to 6.5 and 6.0 to 7.0 respectively with a flow rate of 2 mL min^{-1}. Metal ions were detected spectrophotometrically at a wavelength of 434 nm for Co(II) and 455 nm for Ni(II). Beer's law is obeyed up to 15 mg L^{-1} for Co(II) and 17 mg L^{-1} for Ni(II) using this method with a sensitivity of 0.037 μg/cm^2 for Co(II) and 0.030 for Ni(II). The concentration of metal ions has also been determined by means of atomic absorption spectrometry.

Key words: Cobalt, Nickel, Naphthalene, N-(2′-Pyridyl)-2-hydroxybenzamide.

INTRODUCTION

Various methods have been used and developed for the preconcentration and analysis of several metal ions[1–3]. Amide group containing reagents have been used as potential extractants for the separation and determination of many metal ions[4, 5]. In the present paper, we have used the column chromatographic method using N-(2′-pyridyl)-2-hydroxybenzamide (NPHB) adsorbed on naphthalene as a solid phase for the separation and preconcentration of Co(II) and Ni(II) from large volume of aqueous phase. This adsorbent is easy to synthesize, does not involve the use of large amounts of organic solvents, thus is highly economical, rapid and gave a preconcentration factor of 15 and more for these metal ions. The adsorbed metal in the column cannot be eluted out even on washing with water and can be estimated spectrophotometrically or by atomic absorption spectroscopy (AAS) after dissolving the naphthalene phase in suitable solvent like dimethyl formamide (DMF).

EXPERIMENTAL

All chemicals used were of analytical grade. pH was maintained by acetate buffer by mixing required volumes of 0.2 mol L^{-1} of acetic acid and sodium

acetate. A digital pH-meter 5651-A and Shimadzu AA-640-13 atomic absorption spectrometer were used. Mixture of NPHB (3 g), water (10 mL) and acetone (100 mL) was stirred to obtain a clear solution and add to this naphthalene (20 g) with 1.0–1.5 L of distilled water. The coprecipitated mixture was stirred for 3 h and allowed to stand overnight. The supernatant solution was drained off and the mixture was washed twice with double distilled water. The final adsorbent is a slurry of NPHB-naphthalene in water.

Glass columns were packed with NPHB-naphthalene slurry to a height of 10 mm. Then 10 mL (10 ppm) solution of metal ions, maintained at the required pH with acetate buffer, was passed through the column at a fixed flow rate. The metal ions-NPHB complex was determined by dissolving the naphthalene adsorbent in 10 ml of DMF. The time required for the system to attain equilibrium condition was determined at a definite pH by placing fixed amount of metal ions in a conical flask and shaking with fixed amount of chelating naphthalene. The supernatant solution was separated off at different time intervals (from 2–30 min) and metal in it was determined by AAS. The difference in original metal ion concentration and the metal ions in supernatant gave the metal ions adsorbed.

RESULTS AND DISCUSSION

A fixed strength of metal ion solution was adjusted to definite pH and then passed through a column filled with fixed amount of chelating naphthalene at a definite flow rate. The adsorbent was dissolved in 10 mL of DMF and absorption spectrum of NPHB-metal complex was recorded against DMF and reagent. It was observed that the NPHB-Co(II) complex and NPHB-Ni(II) complex gave absorption maxima at 434 and 455 nm, whereas the absorption of reagent was negligible. Retention of metal on the column packed with NPHB-naphthalene slurry was studied as a function of pH in the range 3.0–10.0 and the metal ion concentration determined by AAS. It was observed that the retention of Co(II) was constant and maximum in the pH range 5.0–6.5, while for Ni(II) this range was 6.0 to 7.0. An addition of 2–10 ml of buffer caused no variation in the retention of metal ions. The time required for the adsorption of metal ions and attainment of equilibrium condition by the chelating naphthalene was determined by batch method. The time taken for the system to reach equilibrium was 15 min for Co(II) and 18 min for Ni(II). The effect of flow rate of metal ion solution was studied between 0.5–5.0 mL min^{-1} and 2 mL min^{-1} was found to be the most suitable. Effect of different amounts of chelating naphthalene on adsorption was studied by using the column filled with different amounts (0.02–0.16 g) of chelating naphthalene. It was observed that the percentage retention of Co(II) was best found when 0.10 g of chelating naphthalene was employed while for Ni(II) this amount was 0.12 g.

The retention capacity of the chelating naphthalene was determined by dissolving 350 mg of metal ion in 50 mL of distilled water. 10 mL of the above

solution was adjusted to required pH and diluted to 20 mL. This solution was equilibrated with 0.5 g of slurry. The amount of metal in the supernatant was determined by AAS. The maximum capacity was found to be 4.5 mg of Co(II) per g of chelating naphthalene and 4.0 mg of Ni(II) per g of chelating naphthalene. The preconcentration of metal ions and its effect on adsorption behaviour was studied by using varied volumes of aqueous phase (from 20–200 ml). Adsorption for Co(II) and Ni(II) was quantitative when the volume did not exceed 150 mL. Thus a preconcentration factor of 15 was achieved under specified conditions. In order to check the stability of metal chelating naphthalene DMF, the absorbance of eluted metal ion complex solution was recorded at different time intervals. Results have shown that the metal chelate in the naphthalene-DMF was stable upto 20 h. Effect of various electrolytes such as sodium chloride, potassium chloride, potassium nitrate was investigated and it was found that they had no effect on the adsorption of metal ion. Effects of various solvents such as chloroform, DMF, acetone, ethanol were investigated by dissolving the metal chelate-naphthalene. Best results were found with DMF. The interference of various ions in the estimation of metal ions was investigated. Sample solutions containing various amounts of various salts were prepared and effects of different cations and anions were studied. Results indicated that not much deviation in absorbance is recorded when the ions are added in specified amount.

Metal ion solution in the concentration range 2–28 mg L^{-1} maintained at definite pH was passed through the column and the metal chelate-naphthalene was eluted from the column with DMF and their absorbance recorded. Calibration graphs for metal ions were drawn and under optimum conditions, Beer's law was found to be obeyed up to 15 mg L^{-1} for Co(II) and 17 m gL^{-1} for Ni(II).

Determination of cobalt in vitamin and nickel in steel solutions

The sample solution prepared adjusted to the required pH was passed through the chelating naphthalene and the metal complexed chelating resin was dissolved in 10 mL of DMF and the amount of metal ions was determined using AAS. Results are reported in Tables 1 and 2 and recovery is obtained with 96 and 94.5% for Co and Ni respectively.

TABLE-1
DETERMINATION OF COBALT IN VITAMIN

Sample	Amount of cobalt (mg L^{-1})		Recovery (%)	RSD (%)
	Found*	Present		
1.	20.2	21	96.2	0.05
2.	21.1	22	95.9	0.03
3.	21.2	23	92.2	0.14

* Each value is the mean of five simultaneous determinations.

TABLE-2
DETERMINATION OF NICKEL IN ALLOY

Sample	Amount of nickel (mg L^{-1})		Recovery (%)	RSD (%)
	Found*	Present		
1.	1.19	1.24	94.0	1.07
2.	11.30	11.48	93.5	1.24
3.	20.20	20.23	96.0	1.38

* Each value is the mean of five simultaneous determinations.

Conclusion

Using this new chelating adsorbant, cobalt and nickel can be quantitatively estimated. This solid phase extraction has high sorption efficiency and has may advantages over conventional methods of trace analysis. The proposed adsorbent is widely applicable for the measurements of the trace amount of cobalt in commercial samples. Finally we conclude that this method is economical, interference free and highly sensitive and does not need expensive instruments for the analysis of trace amounts of cobalt and nickel.

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