

Column chromatographic preconcentration of cobalt and zinc with 3-hydroxy-4-imino-(N-2'-pyridyl)-2-methylnaphthalen-1-one adsorbed on naphthalene and their estimation in vitamin and milk samples

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A sensitive, economical and rapid spectrophotometric method of preconcentration and separation of cobalt and zinc has been developed using a solid chelating resin, 3-hydroxy-4-imino-(N-2'-pyridyl)-2-methylnaphthalen-1-one (HIPMN) supported on naphthalene. Co and Zn are quantitatively determined using this absorbent in a column in the pH range of 4.0-6.0 and 5.8-8.0 respectively with a flow rate of 2 ml min⁻¹. The metal complex and naphthalene are dissolved out from the column with 10 ml of DMF and the absorbance is measured at 568.5 nm and 466 nm for Co and Zn, respectively. Beer's law is obeyed up to 15 mg l⁻¹, for Co and 22 mg l⁻¹ for Zn using this method with a sensitivity of 0.035 µg cm⁻² for Co and 0.032 µg cm⁻² for Zn for log (I₀/I) = 0.001. Atomic absorption spectrometry (AAS) is also used to determine the metal ion concentration.

For the analysis of trace metal ions present in various samples, they first have to be separated and preconcentrated^{1,2}. The simplest technique for preconcentration of metal ions with suitable complexing agent is solvent extraction. But this technique has several disadvantages. The extraction of metal ions that form complexes with complexing agent at high temperature cannot be carried out by liquid extraction^{3,4}. This technique is also inconvenient if emulsion forms between two phases on shaking. Also solvent extraction involves consumption of a lot of expensive and toxic organic solvents. These difficulties can be overcome by extracting metal complexes into molten naphthalene^{5,7}. The main advantage of this technique is that equilibrium distribution in the two phases is attained in a few seconds owing to high temperature used and the metal chelates are dissolved merely by contact with the molten phase. Since the technique employed is carried out at a high tempera-

ture, it cannot be applied for extraction of metal ions that form thermally unstable complexes. This drawback is overcome by a new method, solid-liquid separation after adsorption of metal chelates on microcrystalline naphthalene⁸⁻¹⁴. This method is simple, rapid, sensitive, economical and useful for many metal complexes, which have low solubility in non-aqueous organic solvents.

In the present note, column chromatographic method has been developed for the separation and preconcentration of Co and Zn from large volume of aqueous phase using the title chelating agent adsorbed on naphthalene. This absorbent is easy to synthesize, highly economical and gives 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 AAS after dissolving the naphthalene phase in suitable solvent like dimethylformamide (DMF).

Experimental

For pH measurements, a digital ECIL pH meter 5651A and for estimation of metal ions, UV-vis Shimadzu spectrophotometer and Shimadzu AA-640-13 atomic absorption spectrometer were used. All chemicals used were of analytical grade and were used without purification. The pH was maintained with acetate buffer by mixing required volumes of 0.2 mol l⁻¹ of acetic acid and sodium acetate.

3-Hydroxy-4-imino-(N-2'-pyridyl)-2-methylnaphthalen-1-one (HIPMN) was prepared by reacting 3-hydroxy-2-methyl-1,4-naphthalendione with 2-aminopyridine in ethanol in presence of sodium acetate. The yellow coloured HIPMN was precipitated by adding dil HCl and recrystallized from ethanol (m.p. 186°C). Its purity was checked by TLC and was characterized by IR and ¹HNMR. Vitamin and milk samples were prepared as described before¹⁵.

Preparation of loaded HIPMN-naphthalene

A mixture of HIPMN (3 g), water (10 ml) and acetone (100 ml) was stirred for a few minutes to obtain a clear solution of the chelating agent. Then naphthalene (20 g) mixed with 1.0-1.5 l of distilled water at room

Table 1—Determination of cobalt in vitamin

Sample	Amount of cobalt (mg l ⁻¹)		Recovery (%)	Standard deviation
	Present	Found*		
1	22	21.1	95.9	0.03
2	23	21.2	92.2	0.14
3	21	20.2	96.2	0.05

* mean of three experiments

Table 2—Determination of zinc in milk samples

Sample	Amount of zinc (mg l ⁻¹)		Recovery (%)	Standard deviation
	Present	Found*		
A	56	54	96.4	0.08
B	57	55	96.5	0.16
C	60	57	95.0	0.05

* mean of three experiments

temperature was added to the mixture. The coprecipitated mixture was stirred for 3 h and allowed to stand for 12 h. The supernatant solution was drained off and the mixture was washed twice with doubly distilled water. The final adsorbent obtained was a slurry of HIPMN-naphthalene in water.

General procedure

A funnel-tipped glass tube, fitted with cotton wool, was used as a column. The HIPMN-naphthalene slurry (0.12 g) was placed over the cotton wool to a height of 10 mm. A 10 ml aliquot of metal ion solution (10mg l⁻¹) was adjusted to the required pH by adding 5 ml of acetate buffer and the final volume was made upto 20 ml and passed through this column at a fixed flow rate. The metal ions, complexed to HIPMN were determined after dissolving the naphthalene adsorbent in 10 ml of DMF. All the experiments were carried out in triplicate to check the precision of the method.

Results and discussion

A 10 ml solution (1x10⁻³mol l⁻¹) of metal ion was adjusted to definite pH and the final volume was made upto

20 ml. It was then passed through a column filled with 0.12 g of chelating naphthalene at a definite flow rate. The adsorbent was dissolved in 10 ml of DMF and absorption spectra of HIPMN-metal complex was recorded against DMF and reagent blank. It was observed that the HIPMN- Co complex gave absorption maximum at 568.5 nm and the HIPMN-Zn gave absorption maximum at 466 nm whereas the absorption of the reagent was negligible. All absorbance measurements were made at 568.5 nm for Co and 466 nm for Zn. The retention of metal on the column packed with HIPMN-naphthalene slurry was studied as a function of pH in the range 2.0-9.0 and the metal ion concentration was determined by AAS. It was observed that the retention of Co was maximum in the pH range 4.0-6.0 while for Zn this range was 5.5-8.0. All further studies were carried out at pH 5.0 for Co and pH 6.0 for Zn. No variation in the retention of metal ion was observed on addition of 2-10 ml of buffer, thus 5 ml of buffer was used throughout the study.

The time required for the system to attain equilibrium condition was determined by batch method. The time taken for the system to reach equilibrium was found to be 20 min both for Co and Zn.

The effect of flow rate of metal ion solution was studied between 0.5 and 5.0 ml min⁻¹. Adsorption was quantitative and reproducible in this range. The flow rate was maintained at 2 ml min⁻¹ throughout the investigation.

The effect of different amounts of chelating naphthalene on adsorption was studied by the column technique. The column was filled with different amounts (0.02-0.16 g) of chelating naphthalene was used and it was observed that the percentage of metal ion retained was found best with 0.12 g of the chelating naphthalene was employed. Thus 0.12 g of the HIPMN-naphthalene was used for further investigations.

The retention capacity of the chelating naphthalene was determined by the batch method. The maximum capacity was found to be 4.5 mg of Co per g of chelating naphthalene and 5.0 mg of Zn per g of chelating naphthalene. In order to check the stability of metal-chelate in naphthalene-DMF, the absorbance of eluted metal ion complex solution was recorded at different period of time intervals. The results show that the absorbance of metal chelate in the naphthalene-DMF was constant upto 20 h.

The effect of various electrolytes such as sodium chloride, potassium chloride and potassium nitrate was investigated. It was found that none of the electrolytes caused any improvement in the amount of metal ions adsorbed. Various solvents, such as chloroform, DMF, acetone, ethanol were used to dissolve the metal chelate-naphthalene. It was seen that best results were obtained with DMF. Different volumes of DMF were used to dissolve the metal chelate-naphthalene. It was found that 10 ml of DMF was sufficient to dissolve it under specified conditions.

Effect of diverse ions

The interference of various ions in the estimation of metal ions was investigated. Sample solutions containing different amounts of various salts were prepared and the effect of different cations and anions was studied following the recommended procedure. An error of $\pm 2\%$ in the absorbance was considered tolerable. Results indicate that not much deviation in the absorbance was recorded when the ions were added in specified amount.

Beer's Law

Metal ion solution in the concentration range 2-28 mg l⁻¹ maintained at definite pH was passed through the column and the chelating naphthalene was eluted from the column with DMF and their absorbance recorded.

Calibration graph for metal ions were drawn and under optimum conditions and Beer's law was found to be obeyed upto 15 mg l⁻¹ for Co and 22 mg l⁻¹ for Zn with a sensitivity of 0.035 $\mu\text{g cm}^{-2}$ for cobalt and 0.032 $\mu\text{g cm}^{-2}$ for zinc for $\log(I_0/I) = 0.001$.

Preconcentration of metal ion

The volume of aqueous phase was varied from 20 to 200 ml and its effect on adsorption behaviour was studied. Adsorption for Co and Zn was quantitative when the aqueous volume did not exceed 150 ml. Thus a preconcentration factor of 15 was achieved under specified conditions.

Determination of Co in vitamin and Zn in milk samples

The sample solution 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. The results are given in Tables 1 and 2. Results show that both Co and Zn can be quantitatively estimated in various commercial samples using HIPMN-naphthalene as adsorbent with a recovery is found to be 96%.

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