

Preconcentration and solid phase extraction method for the determination of Co, Cu, Ni, Zn and Cd in environmental and biological samples using activated carbon by FAAS

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Abstract

2-[[1-(2-Hydroxynaphthyl) methylidene] amino] benzoic acid (HNMAA) was synthesized for solid phase extraction (SPE) to the determination of Co, Cu, Ni, Zn and Cd in environmental and biological samples by flame atomic absorption spectrophotometry (FAAS). These metals were sorbed as HNMAA complexes on activated carbon (AC) at the pH range 5.0 ± 0.2 and eluted with 6 ml of 1 M HNO₃ in acetone. The effects of sample volume, eluent volume and recovery have been investigated to enhance the sensitivity and selectivity of proposed method. The effect of interferences on the sorption of metal ions was studied. The concentration of the metal ion detected after preconcentration was in agreement with the added amount. The detection limits for the metals studied were in the range of 0.05–0.82 $\mu\text{g ml}^{-1}$. The proposed system produced satisfactory results for the determination of Co, Cu, Ni, Zn and Cd metals in environmental and biological samples.

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1. Introduction

Nowadays determination of trace metals in environmental samples is essential. Because of these metals have been used in various industries. Various techniques have been reported for the determination of trace metals in environmental samples. Flame atomic absorption spectrometry (FAAS) has been widely used for the determination of trace metal ions. However, direct determination of metal ions at trace levels by FAAS is limited due to their low concentrations and matrix interferences [1]. In trace analysis, therefore, preconcentration leads to simplified trace metal determination. Several methods of preconcentration include solvent extraction [2,3], adsorption [4,5], membrane extraction [6], coprecipitation [7–9], ion-exchange [10,11]. But, solid phase extraction (SPE) is multielement preconcentration methods because of its sim-

plicity, rapidity and ability to attain a high concentration factor.

Activated carbon has been widely used for many purposes due to its ability [12–17], to adsorb organic compounds and organic metal complexes. Enrichment of trace metals using activated carbon has been carried out with very high preconcentration factors in different matrices [18–28]. The standard method for determination of trace metals in environmental samples involves the use of ammonium pyrrolidine dithiocarbamate for complex formation, followed by extraction of the metal complex with methyl isobutyl ketone (MIBK) [29] and subsequent determined by flame atomic absorption spectrometry. The disadvantages of above reported techniques are the large amount of solvent required and time consuming.

Hence, there is a need to develop simple, sensitive reagent that requires less solvent preconcentration method for the determination of metal ions in various environmental matrices. In the present study, 2-[[1-(2-hydroxynaphthyl) methylidene] amino] benzoic acid (HNMAA) was synthesized and impregnated onto activated carbon for the preconcentration of Co, Cu, Ni,

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Zn and Cd in environmental and biological samples. The metals determination was performed by FAAS.

2. Experimental

2.1. Apparatus

Flame Atomic Absorption Spectrometer (Perkin-Elmer Model AAnalyst100) was used to determine metal concentrations using an air/acetylene flame. The instrumental parameters were those recommended by the manufacturer were represented in Table 1. The SPE was performed using 25 ml polyethylene tubes and frits. A digital pH meter (Elico Li 129 model) was used for all pH measurements.

2.2. Reagents

All reagents and solvents were standard analytical grade and used without further purification. Double distilled water has been used for all reagents preparation. Working standard solutions of Co, Cu, Ni, Zn and Cd (Merck Chemicals, Mumbai, India) were prepared by stepwise dilution of $1.0 \mu\text{g ml}^{-1}$. Sodium acetate buffer solution was prepared by adding an appropriate amount of acetic acid to sodium acetate solution until pH 5.0 was attained.

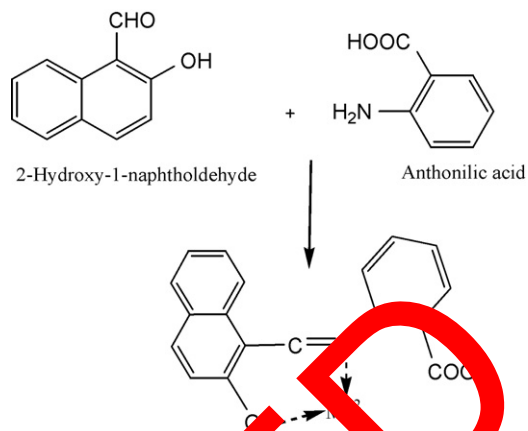
2.3. Synthesis of 2-{[1-(2-hydroxynaphthyl) methylidene] amino} benzoic acid

2-Hydroxy-1-naphthaldehyde (0.138 g, 1 mmol) and anthranilic acid (0.137 g, 1 mmol) were dissolved in diethyl ether and the mixture was stirred at room temperature for 24 h. The solvent was removed on a rotary evaporator to get red colored Schiff's base HNMABA, which was recrystallized in ethanol. Scheme of the reagent preparation was shown in Scheme 1.

Table 1

Instrumental conditions for the determination of cobalt, copper, nickel, zinc and cadmium with HNMABA impregnated on activated carbon using SPE

Flame: acetylene–air (1 min)	
Acetylene	2.0
Air	15
Hollow cathode lamp: monochrome photonics L 233 lamp	
Lamp current	12 mA
Slit width	0.5 nm
Burner height	7 mm
Wave length (nm)	
Cobalt	240.7
Copper	324.8
Nickel	232.0
Zinc	213.9
Cadmium	228.8
Measurement mode	Background correction
Detection limits ($\mu\text{g ml}^{-1}$)	
Cobalt	1.09
Copper	0.75
Nickel	1.72
Zinc	1.10
Cadmium	3.82



Scheme 1. Synthesis of 2-{[1-(2-hydroxynaphthyl) methylidene] amino} benzoic acid.

2.4. Metals preconcentration procedure

2.4.1. Batch method

An aliquot of 10 ml of sample solution containing $0.1 \mu\text{g ml}^{-1}$ of each metal (Co(II), Cu(II), Ni(II), Zn(II) and Cd(II)) was taken in a 250 ml glass stoppered bottle. Before taking these aliquots pH was previously adjusted to a value. Then 0.1 g of activated carbon impregnated with HNMABA was added to the bottle and the mixture was shaken for 30 min. After filtration, the substrate was eluted with 6.0 ml of 1 M HNO_3 in acetone. The concentration of metal ion in the eluate was determined by FAAS.

2.4.2. Column method

AC loaded with 2-{[1-(2-hydroxynaphthyl) methylidene] amino} benzoic acid (1.0 g) was packed in a glass column (1.0 cm \times 10 cm) and treated with 1 M HNO_3 in acetone [30] washed with double distilled water until the AC was free from acid. A suitable aliquot of the solution containing Co(II), Cu(II), Ni(II), Zn(II) and Cd(II) was passed through the column, after adjusting its pH to an optimum value at a flow rate of $0.5\text{--}3.0 \text{ ml min}^{-1}$. The column was washed with double distilled water in order to remove free metal ions. The eluate of the metal ions from the AC was carried out by 1 M HNO_3 in acetone. The eluate was collected in 25 ml calibrated flask and made up to the mark with double distilled water. Finally, this aliquot was aspirated into the nebulizer of FAAS for the determination of Co(II), Cu(II), Ni(II), Zn(II) and Cd(II) in various environmental and biological samples.

2.4.3. Determination of metal ions in water samples

The optimized preconcentration method (AC-HNMABA) was used applied to preconcentrate Co(II), Cu(II), Ni(II), Zn(II) and Cd(II) ions in water samples collected from the industrial areas (Gajulamanyam) and Gram Panchayaty taps (Chandragiri), followed by their determination with by FAAS. The estimation of all these metal ions concentration was made with and without (referred as direct determination) standard addition (S.A.) by passing 1000 ml of water sample (spiked with 50–100 μg of each of the five metal ions in the case of standard

addition method) through the column packed with 1.0 g of matrix after adjusting the pH to an optimum value and determining the metal ion as described in the recommended column procedure. The elution was made with 1 M HNO_3 in acetone was used. The results obtained are given in Table 6 and reflect the suitability of the preconcentration column method using AC-HNMABA for water analysis. The concentrations reported in Table 6 as estimated by standard addition method are the values obtained by subtracting the amount of metal added for spiking from the total metal recovered. The closeness of results of direct and standard addition method indicates the reliability of present results of good agreement were obtained between the direct and standard addition methods indicating the reliability of the proposed method for metal analysis in water samples.

2.4.4. Determination of Co in pharmaceutical samples

Solid phase extraction with using AC-HNMABA coupled with FAAS method of determination was applied to determine cobalt in pharmaceutical samples. The contents of vitamin B_{12} as Cobalt in four ampoules for injection were decomposed in a 50 ml round-bottom flask by heating with a 5.0 ml mixture containing concentrated nitric and sulfuric acids (10:1) on a hot plate until near dryness [31]. A drop wise addition of concentrated nitric acid was needed to obtain a colorless residue. The residue was neutralized with a dilute sodium hydroxide solution, and was then diluted to an appropriate volume (50 ml). The cobalt contents were analyzed using 2.0 ml of the solution by the recommended procedure. A standard method using Nitro-PR salt has also been used [32] as a reference method. The results are given in Table 5.

2.4.5. Determination of Zn in a milk sample

A sample of powdered milk (1.0 g) was placed in a beaker containing mixture of concentrated sulphuric acid (10 ml) and nitric acid (4 ml) till a clear solution was obtained. It was allowed to cool and most of the acid was neutralized with sodium hydroxide. The pH was adjusted to optimum value and the volume was made up to 500 ml. The concentration of zinc was estimated by passing the solution through the column packed with HNMABA loaded AC. The metal ion was eluted from the column using 6 ml of 1 M nitric acid in acetone and determined using FAAS. The average (three determinations) amount of zinc was found to be $38.55 \mu\text{g g}^{-1}$ (R.S.D. $\sim 4.28\%$). The reported value of zinc in the milk sample is $38.4 \mu\text{g g}^{-1}$. The determination of zinc in a powdered milk sample was performed in triplicate. The results obtained ($38.0 \mu\text{g g}^{-1} \pm 4.28\%$) were in good agreement with those reported for this sample ($38.0 \mu\text{g g}^{-1}$), which indicates the suitability of this method for zinc determination in this kind of matrix.

3. Results and discussion

3.1. Effect of pH

pH is an important parameter, because it significantly affects the metal-AC-HNMABA complex formation. The effect of pH and complexation of metal ions with AC-HNMABA was studied

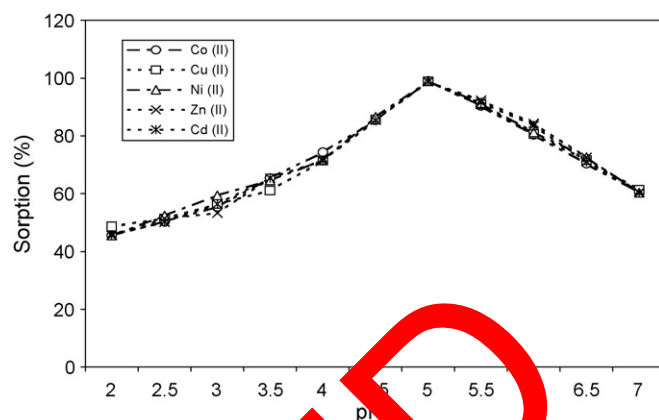


Fig. 1. Effect of pH.

by adding $100 \mu\text{g}$ of each element individually in 150 ml doubly distilled water and determined by complexing with AC-HNMABA in the pH range of 2.0–7.0 as shown in Fig. 1. The results indicate maximum recovery was obtained at $\text{pH } 5.0 \pm 0.2$ for all the elements. So, $\text{pH } 5.0 \pm 0.2$ was selected as further investigation.

3.2. Effect of sample volume

The effect of sample volume on the elution of Co, Ni, Zn and Cd was studied by taking different volumes of various samples, 200, 300, 400, 500, 600 and 700 ml. The extraction was carried out as described in the earlier procedure. In all cases the recovery obtained was higher than 98.5% for all these elements. However, the efficiency of recovery slightly decreases when the sample volume was more than 60 ml. Hence, 600 ml of water sample was chosen for the present study.

3.3. Effect of flow rate of sample volume

The degree of metal ion sorption on AC-HNMABA was studied by varying the flow rate of the metal ion solution (sample solution). The optimum flow rate for loading all these metal ions was $0.5\text{--}3.0 \text{ ml min}^{-1}$. As flow rate increases beyond 3.0 ml min^{-1} , there was a decrease in the percentage of sorption of metal ions. Hence, 3.0 ml of sample solution was chosen for further investigation. The obtained results were represented in Fig. 2.

3.4. Total sorption capacity

A volume of 150 ml solution containing $100 \mu\text{g}$ of each metal ($\text{pH } 5.0 \pm 0.2$) was placed in contact with 0.5 g of AC-HNMABA at constant stirring (rpm) during 24 h and the sorption capacity of the AC-HNMABA was determined by column method. The solid matrix was filtered and washed with double distilled water. Then the sorbed metal ions were eluted with 6.0 ml of 1 M HNO_3 in acetone and determined by FAAS to calculate sorption capacity of the column. The results obtained are reported in Table 2 (discuss above results). The batch method was also used to determine the sorption capacity and similar

Table 2
Analytical parameters

Experimental parameters	Metal ions				
	Co(II)	Cu(II)	Ni(II)	Zn(II)	Cd(II)
pH range	5.0	5.0	5.0	5.0	5.0
Flow rate (ml min ⁻¹)	0.5–1.5	1.0–3.0	2.0–3.0	0.5–2.5	1.5–2.5
Sorption capacity (μmol ⁻¹ g)	223	465	259	195	98
Average recovery (%)	99.6	97.8	98.7	99.0	97.2
Standard deviation	0.048	0.036	0.020	0.029	0.037
Relative standard deviation (%)	4.390	3.780	2.279	2.750	4.018

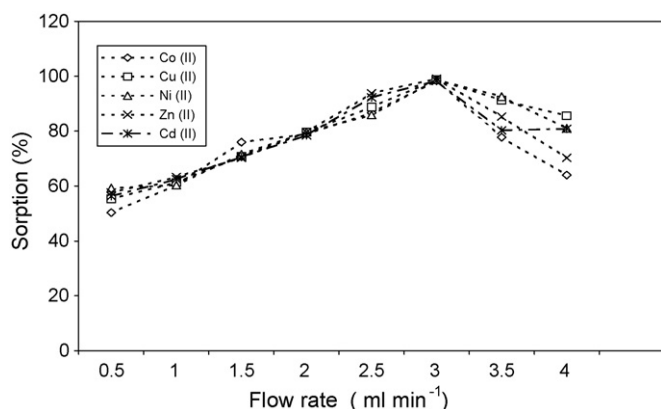


Fig. 2. Effect of flow rate on sorption capacity of metal ions.

results were obtained. It was found to be nearly same variation ($\pm 5\%$) by the two methods.

3.5. Preconcentration efficiency

The efficiency of the AC-HNMABA column for the sorption of metals was studied by using 450 mg of AC-HNMABA in comparison with 450 mg of AC for preconcentration of metals in a model solution. Starting with 40 μg of each metal in 50 ml of solution, the quantity of unretained metals in the filtrate was determined by FAAS. The percentage sorption of the metals retained on the sorbents was calculated from the difference between the starting amount of each metal (mg) (N_s) and the amount of metal (mg) left in the filtrate (N_f). The AC-HNMABA can retain metal ions while the untreated AC cannot quantitatively retain Co, Cd, Ni and Zn. Evidently, the preconcentration of the metals with the untreated AC is not suit-

able for Co, Cd, Ni and Zn. Therefore, AC-HNMABA seems to be a better sorbent in simultaneous sorption of the studied elements at pH 5.0 ± 0.2 .

3.6. Preconcentration and recovery of metal ions

Enrichment factor was determined by increases the dilution of metal ion solution, increasing metal dilution while keeping the total amount of loaded metal ion fixed at 15 μg for Cd and 20 μg for Co, Cu, Zn or Ni and applying the recommended column procedure. The preconcentration factors for Co(II), Cu(II), Ni(II), Zn(II) and Cd(II) are 175, 310, 100, 299 and 246, respectively, are shown in Table 3.

3.7. Method evaluation

The proposed column preconcentration solid phase extraction method was critically evaluated with regard to reproducibility, accuracy and detection limit.

3.7.1. Reproducibility

To test the reproducibility of proposed column solid phase extraction method, four repetitive analysis cycles of each sample were run. A %R.S.D. in the range 0.6–6.0 were obtained as shown in Tables 5 and 6.

3.7.2. Accuracy

The accuracy of the proposed column preconcentration solid phase extraction method was evaluated by comparing the results with those obtained by the reported method [33]. The results shown in Tables 5 and 6 reveals that the good correlation between the two methods indicative of present method is more sensitive than the reported method in the literature [33].

Table 3
Enrichment factor for the determination of Co, Cu, Ni, Zn and Cd with HNMABA impregnated on activated carbon using SPE in various water, pharmaceutical and milk samples

Metal ion	Total volume (ml)	Concentration (ng ml ⁻¹)	Final volume	Recovery	Preconcentration factor ^a	Preconcentration factor [33]
Co(II)	2500	8.0	15	98.2	175	167
Cu(II)	3000	6.7	10	98.3	310	300
Ni(II)	1000	20.0	10	98.3	100	100
Zn(II)	3000	5.0	10	98.6	299	300
Cd(II)	2500	10.0	10	97.6	246	250

^a Present method.

Table 4
Tolerance limit of electrolytes

Foreign species	Metal ion				
	Co(II)	Cu(II)	Ni(II)	Zn(II)	Cd(II)
NaCl (mol l^{-1})	0.150	0.500	0.150	0.300	0.090
NaBr (mol l^{-1})	0.035	0.085	0.025	0.015	0.075
NaNO ₃ (mol l^{-1})	0.015	0.550	0.460	0.060	0.180
Na ₃ PO ₄ (mol l^{-1})	0.030	0.100	0.020	0.085	0.010
(NH ₄) ₂ SO ₄ (mol l^{-1})	0.200	0.690	0.255	0.070	0.150
NaI (mol l^{-1})	0.145	0.050	0.090	0.220	0.020
Ca(II) (mol l^{-1})	0.150	0.300	0.220	0.280	0.075
Mg(II) (mol l^{-1})	0.160	0.700	0.500	0.500	0.020
Humic acid ($\mu\text{g ml}^{-1}$)	7.0	26.0	16.0	9.0	13.0
Ascorbic acid (mmol l^{-1})	0.560	0.380	0.655	0.215	0.750
Citric acid (mmol l^{-1})	0.460	1.100	0.115	0.150	0.800
EDTA (mmol l^{-1})	0.007	0.005	0.002	0.004	0.009
Tartaric acid (mmol l^{-1})	0.325	0.055	0.220	0.515	0.300

3.7.3. Detection limits

Under optimized conditions the detection limits for the determination of metal ions using column preconcentration solid phase extraction method was presented in Table 1.

3.8. Effect of electrolytes and cations

The effect of electrolytes NaCl, NaF, NaNO₃, Na₂SO₄ and Na₃PO₄, NaI and other foreign species on the sorption of Co(II), Cu(II), Ni(II), Zn(II) and Cd(II) onto AC-HNMABA matrices were studied. According to [33] a species is considered to interfere when it lowers the recovery of metal ions more than 2.5% in comparison to the value observed in its absence. Each reported tolerance/interference is in the preconcentration and not the determination by AAS, as checked with the help of reagent matched standard solutions. The tolerance limits of various foreign species in the sorption of all the metal ions were studied

Table 6
Determination of metal ions in water samples

Sample collected	Method	Metal ion ($\mu\text{g ml}^{-1}$)				
		Co (R.S.D.)	Cu (R.S.D.)	Mn (R.S.D.)	Zn (R.S.D.)	Cd (R.S.D.)
River water ^a	Direct	12.8 ± 1.9	19.7 ± 1.2	6.2 ± 3.2	3.4 ± 3.2	4.0 ± 6.0
	S.A.	13.0 ± 1.2	20.1 ± 0.8	6.4 ± 3.0	3.1 ± 5.8	4.3 ± 3.5
Tap water ^b	Direct	14.6 ± 0.9	24.6 ± 1.3	12.8 ± 1.4	14.6 ± 1.6	7.2 ± 2.6
	S.A.	14.9 ± 1.2	24.4 ± 0.6	13.4 ± 1.2	14.5 ± 0.8	7.0 ± 1.6

Direct, recommended procedure is directly applied; S.A., standard addition method; R.S.D. (%), for four determinations.

^a River water collected near Renigunta industrial area.

^b Collected tap water from Chandragiri Gram panchayats.

Table 7
Comparison of the present method with the reported methods

Reagent	Instrumentation	Detection limits ($\mu\text{g ml}^{-1}$)	References
Diethyldithiocarbamates	FAAS	4–23	[25]
Chloromethylated polystyrene-PAN	FAAS	1–8	[26]
Pyrrolidine dithiocarbamate	FAAS	19–28	[27]
2-Aminoacetylthiophenol	ICP-AES	10–58	[28]
Present method	FAAS	0.75–3.82	Present method

Table 5
Determination of cobalt in B₁₂ vitamin ampoules

Sample	Cobalt found ^a ($\mu\text{g ml}^{-1}$); R.S.D. (%; $n = 4$)	Cobalt found ^b ($\mu\text{g ml}^{-1}$); R.S.D. (%; $n = 4$)
1	44.9 ± 1.2	45.3 ± 2.4
2	46.8 ± 0.9	46.7 ± 1.5

^a Present method.

^b Standard method using Nitroso-R salt [32].

(Table 4). These values indicate that sorption on AC-HNMABA is not much sensitive to foreign species.

4. Applications

To evaluate the applicability of the preconcentration and solid phase extraction of metal ions, it was applied to the determination of Co(II), Cu(II), Ni(II), Zn(II) and Cd(II) in pharmaceutical, water and milk samples. The analytical data summarized in Tables 5 and 6 suggest that the percentage of the recovery of metal ions ranges from 98.50 to 99.82% which is more reliable and sensitive than the metal reported in the literature.

It is evident from the data in Table 7 that the proposed method is rapid, economical and more sensitive.

5. Conclusion

The sorption capacities of the present method are compared with those of other chelating matrices. It shows in some cases (particularly those having Amberlite XAD-2 as support) higher capacities in comparison to others may be obtained in terms of metals with very few exceptions. A simultaneous preconcentration method for Co(II), Cu(II), Ni(II), Zn(II) and Cd(II) from aqueous solutions on using an activated carbon impregnated

with 2-[[1-(2-hydroxynaphthyl) methyldene] amino} benzoic acid column and batch methods were developed. The results obtained shows that the proposed method can be applicable for the determination of trace metal ions in variety of environmental and pharmaceutical samples with low detection limit, high accuracy and precision.

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