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INSTRUMENTATION, METHODOLOGY,
AND TECHNICAL DEVELOPMENTS

Determination of Some Trace Heavy Metals in Some Water Samples by FAAS After Their Preconcentration Using DETA

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ABSTRACT

Diethylenetriamine, DETA polymer was used as a preconcentration of cobalt, iron and nickel prior to their determination by flame atomic absorption spectrometry (FAAS). Both batch and column methods were used for the separation and concentration of above metals. These metals were quantitatively retained on the proposed adsorbent at pH 2, then were quantitatively eluted with 2 M hydrochloric acid or nitric acid. The recoveries of metal ions were greater than 98%. Detection limits (3 δ) were 1.5 g/L for Co, 2.1 g/L for Fe and 1.9 g/L for Ni. The relative standard deviations for the determinations were found to be 1.0–8.8%. The effect of Na on the preconcentration of trace metals has also been investigated. The method was applied to tap, ground and lake water samples.

Key Words: Diethylenetriamine; Preconcentration; Co; Mn; Ni; Atomic absorption spectrometry.

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INTRODUCTION

The excellent performance of the atomic absorption spectrometry, AAS as a precise and rapid analytical tool, allows the fast acquisition of data on samples introduced into a flame. One of the attractive characters of the AAS technique is its ease of operation.[1,2] Flame atomic absorption spectrometry (FAAS) is a well-established, extremely valuable technique for the determination of trace amounts of metals. However, because of low concentration and/or matrix interference, the direct determination of trace concentrations by FAAS is limited. It is necessary therefore to employ preconcentration and separation techniques.

In trace element analysis, the preconcentration and separation technique of analytes from the matrix is frequently necessary to exchange the sensitivity and precision of their determination.[3] Various methods of preconcentration and separation procedures,[4] such as electrodeposition, coprecipitation, solvent extraction, evaporation and freeze drying can be used prior to the atomic absorption spectroscopic measurements. Among these techniques used in trace element determination, sorption is one of the most widely used within recent years.[5,6] Polymers having chelating groups are being widely used for this purpose.[7–9] The lower quantity of reagents required is frequently quoted as an advantage. A further advantage is that the solid phase is packed into a column and can thus be used repeatedly. In another technique called batch procedure, the solid phase collector is placed directly into the solution matrix. The formed matrix can subsequently be eluted with minimum volume of solvent. In this way, it is possible to achieve high enrichment or concentration factors with good separation from the matrix, especially for natural water samples.[2,10] The problem of good sorption and slow desorption of the analytes has been treated in a number of papers and widely varying solutions have been proposed.[11,12]

Separation and preconcentration methods utilizing the sorption of trace heavy metals on solid surfaces like Amberlite XAD resins,[13–15] activated carbon,[16,17] chelating resins,[18,19] ion-exchange resins[20,21] and C18[22,23] have often been used. Polymer supported organic compounds are playing an important role in many applications.[24–28] Some of these organic compounds, specially those serving as chelating agent can be used as polymer-supported materials in waste water treatment as well as selective sensing and separation of some heavy metal ions.

The DETA polymer has recently been used for preconcentration of some metal ions.[28,29] This paper presents, the use of a DETA (diethylenetriamine) polymer for the preconcentration and separation of Co(II), Fe(II) and Ni(II) prior to their determination by FAAS. The procedure was fast, the recoveries quantitative ($>98\%$) with low RSD values. The elements added to tap, ground and lake water could be accurately found with quantitative recovery.

MATERIALS AND METHODS

Reagents and Solutions

The preparation of DETA (diethylenetriamine) polymer is described by Bıçak and Şenkal.[30] Before use the polymer was treated with concentrated nitric acid and

hydrochloric acid washed-out with water to remove contaminations prior to use. All chemicals used were analytical grade. Standard stock solutions (1000 mg/L) of Co(II), Fe(II), and Ni(II) were prepared by dissolving appropriate amounts of metals or compounds. Reference solutions were prepared daily by further dilution with distilled water.

Apparatus

A Unicam Model 929 AA flame atomic absorption spectrometer with deuterium lamp and air-acetylene burner was used for the determination of the analyte. The hallow cathode lamps were operated for cobalt at 15 mA, for iron and nickel at 20 mA. The wavelength for cobalt, iron, and nickel were set to 240.7 nm, 248.3 nm and 232.0 nm, and spectral slit widths to 0.2 nm respectively. All pH measurements were made with Orion 720 A Model pH-meter and combination glass electrode.

Procedure for Batch Method

Ten milliliters of a standard metal solutions (1 mg/L Co, Fe and Ni) and 0.1 g of DETA polymer were adjusted to a preselected value by the use of 0.1 M HCl or NaOH in a small beaker. The mixture was shaken for 1 to 10 min, then the resin was separated by centrifuging and metals were washed-out by means of 10 mL of 2 M hydrochloric acid or nitric acid. The concentration of cobalt, iron, and nickel was measured using a flame atomic absorption spectrometer.

Procedure for Column Method

A glass column (0.7 cm i.d.) was filled with 0.3 g of DETA. The height of filling became about 1.3 cm. The pH of a studied solution (e.g., standard solutions of analytes, samples and blanks) was adjusted to pH 2 and was passed through the column at a flow rate of about 2.5 mL/min, which was found to be optimum. Samples, blanks and standards were treated in the same way with the only exception that the volume of the real samples passed through the column were increased depending on their metal concentration. Cobalt and iron were eluted from the column with 10 mL of 2 M hydrochloric acid and nickel with 10 mL of 2 M nitric acid. The DETA column was regenerated by washing with concentrated nitric acid and hydrochloric acid and then distilled water at least three times which was enough to remove all contaminations in the column material if the washing water passing through the column still contained trace elements the washing procedure repeated.

RESULTS AND DISCUSSION

To obtain quantitative recovery of metal ions on the DETA polymer, batch and column methods were optimized for various analytical parameters such as pH,

sample volume, eluent type and eluent volume. The percentage of metal adsorbed on DETA was calculated from the amounts of metal in the starting sample and the amounts of metal eluted.

Effect of pH on Retention

The retention of each metal ions on a DETA polymer was determined at different pH values by the batch method as described before. The results are shown in Fig. 1. Nickel was retained quantitatively on DETA at pH $\geq$ 1 and cobalt and iron at pH $\geq$ 2. Therefore quantitative recoveries ($>$98%) for Co, Fe and Ni were found in the pH range 2–8.

Effect of Shaking Time

For quantitative recovery ($>$98%), a shaking time of more than 4 min is required. Therefore 5 min is selected as optimum for all experiments. The analytes were eluted from the DETA by shaking in suitable solutions, typically nitric acid and hydrochloric acid in various concentrations. The elements were almost completely eluted with 2 M hydrochloric acid and quantitative recoveries were obtained. Nickel was not recovered at all by hydrochloric acid but could be completely eluted with 10 mL, 2.0 M nitric acid.

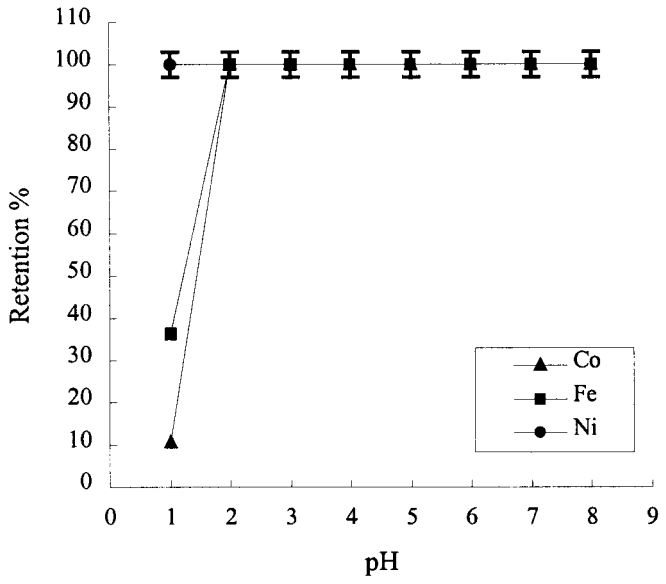

Figure 1. The effect of pH on the retention of the analytes.

Column Technique

The glass column was packed with 0.3 g of DETA. It was treated with concentrated hydrochloric acid and nitric acid and washed with double distilled water until free from acid. 10 mL portions of test solutions (1.0 mg/L) were taken. The pH of the solutions was varied and adjusted in the range 2.0–8.0. The retention and elution of the metal ions from the solutions were studied by the recommended procedure given earlier. At pH 2 the three elements studied were quantitatively retained in the column when the flow rate is slower than 2.5 mL/min. Flow rates of >2.5 mL/min reduce the extraction capacity. The elution studies were performed by using different acids at different flow rates. Although 2.0 M hydrochloric acid gave up to 98.0% recovery for cobalt and iron. Nickel could not be quantitatively eluted (Table 1). For the elements studied, 2.0 M hydrochloric acid solution was found to be most satisfactorily at an elution rate of 2.5 mL/min which is quite an effective elution rate. The detection limits for Co, Fe and Ni based on three times the standard deviations of the blank were 1.5, 2.1 and 1.9 g/L ($N=10$) respectively.

The effect of changes in the volume of sample solution passed through the column investigated for 250–1000 mL of sample. The data in Table 2 indicate that there is little change in the recoveries over this range. Therefore,

Table 1. Effect of eluents on the recovery of the elements using column procedure ($N=3$; DETA: 0.3 g; pH: 2; sample volume: 10 mL; eluent volume: 10 mL).

	Recovery[a] (%)		
Eluent	Co	Fe	Ni
HCl, 2.0 M	98.2 ± 2.0	98.0 ± 1.0	78.7 ± 1.1
HCl, 4.0 M	88.2 ± 2.3	96.0 ± 1.5	89.2 ± 2.0
HCl, 6.0 M	86.6 ± 2.0	53.3 ± 2.8	63.0 ± 2.6
HNO_3, 2.0 M	56.7 ± 1.7	75.9 ± 1.6	98.3 ± 1.5
HNO_3, 4.0 M	52.2 ± 2.0	79.5 ± 2.1	81.0 ± 1.7
HNO_3, 6.0 M	99.0 ± 2.0	77.5 ± 2.3	73.0 ± 2.6

[a]Mean value $\pm$ standard deviation.

Table 2. Effect of sample volume on the recovery of trace elements using the column procedure (DETA: 0.3 g; pH: 2; eluent volume: 50 mL; eluent: 2 M hydrochloric acid).

Sample volume (mL)	Concentration of element (g/mL)	Recovery[a] (%)		
		Co	Fe	Ni
250	0.4	98.2 ± 1.8	99.0 ± 1.4	79.8 ± 2.5
500	0.2	96.0 ± 2.2	99.4 ± 1.0	80.2 ± 1.1
1000	0.1	97.4 ± 1.7	98.2 ± 1.6	76.5 ± 2.0
1000	0.05	95.0 ± 2.3	96.4 ± 3.0	70.5 ± 1.6

[a]Mean value $\pm$ standard deviation.

higher concentration factors may be easily achieved with decrease in the elution volume and increase in the sample volume. When using the column technique, the results are much reproducible because the experiments are performed with the same polymer, so some of the uncertainties in the batch method, which cannot be controlled, e.g., uncertainties in the weighing and adjusting the volumes are removed.

Recovery in NaCl

In order to determine the analytes in brine solutions 170 g of Co, Fe and Ni were added to 0.5% m/v NaCl solution. After adjusting the pH 2, the solutions were passed through the DETA polymer column and the analytes were subsequently eluted with 2.0 M hydrochloric acid or nitric acid. The flow and elution rates were about 2.5 mL/min in every case. The effect of sodium chloride on the determination of cobalt, iron and nickel is shown in Table 3. Each metal was recovered satisfactorily in the presence of sodium chloride, which shows that the proposed method could be used for the determination of trace metals in heavy matrix, e.g., sea-water.

Application

The proposed method was used for the analysis of tap and ground water samples using column technique (Table 4). As can be seen from the results in the Table the analyte elements added to samples are satisfactorily recovered. Cobalt, iron and nickel concentrations of blanks are quite low and negligible. In addition the method was applied to the determination of these three metal ions in lake water sample (RSD < 2.1–8.8%). Water sample was collected from the lake of Terkos in İstanbul which is ore of the water reservoirs in İstanbul. The sample was filtered with a filter paper and the pH was adjusted to about 2.0. One liter of sample was passed through the column containing 0.3 g of DETA at a flow-rate of 2.5 mL/min and eluted with 10 mL of 2.0 M hydrochloric acid and a nitric acid. The element contents were measured by FAAS. The analytical results are shown in Table 5.

Table 3. Effect of sodium chloride on the determination of cobalt, iron and nickel using the column procedure ($N = 3$; DETA: 0.3 g; pH: 2; sample volume: 250 mL; eluent volume: 10 mL; eluent: 2.0 M hydrochloric acid for Co and Fe; 2.0 M nitric acid for nickel).

Sample	Found[a] (g)	Recovery[a] (%)
170 g Co in 5% NaCl	168.3 ± 2.9	99.0 ± 1.7
170 g Fe in 5% NaCl	167.5 ± 2.5	98.5 ± 1.5
170 g Ni in 5% NaCl	167.3 ± 2.1	98.4 ± 1.2

[a]Mean value ± standard deviation.

Table 4. The recovery of elements in spiked water samples using the column procedure ($N = 3$; DETA: 0.3 g; pH: 2; sample volume: 250 mL; eluent volume: 10 mL; eluent: 2.0 M hydrochloric acid for Co and Fe; 2.0 M nitric acid for nickel).

Element	Tap water[a] (g/L)	Ground water[a] (g/L)	Added[b] (g/L)	Recovery[a] (%) of added amounts	
				Tap water	Ground water
Co	24.1 ± 0.3	26.3 ± 0.4	100	99.4 ± 1.3	98.7 ± 1.7
Fe	48.8 ± 0.9	52.0 ± 0.6	100	98.5 ± 2.5	97.4 ± 2.6
Ni	10.8 ± 0.2	8.5 ± 0.1	100	94.6 ± 4.7	95.6 ± 4.5

[a]Mean value ± standard deviation.
[b]Concentration in the solution.

Table 5. Results of analysis lake water samples from İstanbul/Turkey using column procedure ($N = 5$, DETA: 0.3 g; pH: 2; sample volume: 1000 mL; eluent volume: 10 mL; eluent: 2.0 M hydrochloric acid for Co and Fe; 20 M nitric acid for nickel).

Station no.	Metal concentration[a,b] (g/L)		
	Co	Fe	Ni
1	BLD	18.9 ± 0.4	7.3 ± 0.5
2	BLD	22.0 ± 1.4	3.4 ± 0.3
3	3.9 ± 0.5	23.3 ± 1.7	4.0 ± 0.3
4	BLD	22.7 ± 1.5	8.5 ± 0.4
5	21.6 ± 0.4	31.3 ± 1.4	10.4 ± 0.4

[a]Mean value ± standard deviation.
[b]BLD = below the limit of detection.

CONCLUSIONS

The described preconcentration method provides reproducible and correct results. The study indicates that the DETA (diethylenetriamine) polymer is an appropriate collector for the determination of trace elements in different samples after preconcentration. The preconcentration with DETA is expected to be easily combined with AAS and other methods. This technique is fast, simple and sensitive. Only 0.3 g of the polymer is needed and repeated use is possible.

ABBREVIATIONS

AAS	Atomic absorption spectrometry
DETA	Diethylenetriamine
FAAS	Flame atomic absorption spectrometry
BLD	Below limit of detection

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