Short communication

The uses of 1-(2-pyridylazo) 2-naphtol (PAN) impregnated Ambersorb 563 resin on the solid phase extraction of traces heavy metal ions and their determinations by atomic absorption spectrometry

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Abstract

1-(2-pyridylazo) 2-naphtol (PAN) impregnated Ambersorb 563 resin was used as solid phase extractor of copper, nickel, cadmium, lead, chromium and cobalt ions in aqueous solutions prior to their atomic absorption spectrometric determinations. The parameters including pH, sample volume, matrix effects were also investigated. The relative standard deviation (R.S.D.) of the combined method of sample treatment, preconcentration and determination with atomic absorption spectrometry is generally lower than 10%. The limit of detection was between 0.21 and 1.4 μg l^{-1}. The results were used for preconcentration of analyte ions from natural water samples. The method was also applied to a stream sediment standard reference material (GBW7309) for the determination of Cu, Ni, Cd, Pb, Cr and Co.
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1. Introduction

Modern instrumental methods including spectrophotometry, ICP-AES, AAS, NAA etc. [1–8] have been used for the determination of traces heavy metal ions in the various media. In these determinations, low concentration levels of and analytes and high levels of matrices are the main problems [9,10]. To solve these problems, solid phase extraction that is the one of the important preconcentration method has been generally used, because of its simplicity and accuracy. Solid phase extractors including activated carbon, chelating resins, titanium dioxide, microcrystalline naphthalene, fullerenes, C-18, diatomaceous earth [11–18] have been also used for this purpose.

The usages of synthetic adsorption resins on the solid phase extraction of traces heavy metal ions are also very popular [10,19–25]. In general, metal

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chelates in the aqueous solutions were adsorbed on the resin and then desorbed with a suitable eluent solution. In these studies, chelate solution has to use each experiment. Another application of solid phase extraction is impregnation. The resin is coated with the excess of chelating agent. These studies have an important advantage: The impregnated resins can be used repeatedly for the retentions of analytes.

Using impregnated resins in the separation/enrichment studies has performed various studies. Copper determinations were performed in natural water samples by using FAAS after preconcentration onto Amberlite XAD-2 loaded with calmagite by Ferreira et al. [25]. Masi and Olsina have been used Amberlite XAD resin coated with 2-(5-bromo-2-pyridylazo)-5-(diethylamino) [26] and 5-phenylazo-8-quinolinol (5-PHAQ) [27] for the preconcentration of rare earth elements and gallium–indium, respectively. Amberlite XAD-2 coated with PAN resin has been used for separation of gallium and indium from ores by Bermejo-Barrera et al. [28]. For the determination and separation of some metal ions in cadmium salts [29] and natural water samples [30], chromotrope 2R coated Amberlite XAD-1180 resin has been used by our working group. Chromium in the natural water samples has been preconcentrated on chromotrope 2R coated Amberlite XAD-1180 and determined by flow injection-flame atomic absorption spectrometry (FAAS) [31]. According to our literature scanning, no studies have been performed for the impregnation of Ambersorb 563 with chelating agents.

In the present work, possible usage of an impregnated PAN/Ambersorb 563 resin on the solid phase extraction studies for the separation and enrichment of some metal ions in natural water samples and a sediment reference material was investigated.

2. Experimental

2.1. Reagents and solutions

Analytical reagent-grade chemicals were employed for the preparation of all solutions. Freshly prepared doubled distilled water, from a quartz still, was used in all experiments. Stock metal ion solutions, 1000 mg l^{-1} (E. Merck, Darmstadt) were diluted daily to obtaining reference and working solutions. The ligand; 1-(2-pyridylazo) 2-naphtol (PAN) (0.2% w/v) was dissolved in water. The stream sediment standard reference material (GBW 07309) was obtained from National Research Centre for Certified Reference Materials (NRCCRM), China.

Ambersorb 563 Resin (Sigma Chem. Co.) was washed successively with methanol, water, 1 M HNO_3 in acetone, water, 1 M NaOH and water, respectively. Ammonium acetate buffers (0.1 M) were prepared by adding an appropriate amount of acetic acid to ammonium acetate solutions to result in solutions of pH 4–6 and ammonium chloride buffer solutions (0.1 M) were prepared by adding an appropriate amount of ammonia to ammonium chloride solutions to result in solutions of pH 8–10.

2.2. Instrument

The instrumental detection system used was a Perkin–Elmer Model 3110 flame atomic absorption spectrometer. The operating parameters for analyte metals were those recommended by the manufacturer. Atomic absorption measurements were conducted in air/acetylene flame. All measurements were carried out without background correction. A pH meter, Nel pH-900 Model glass-electrode was employed for measuring pH values in the aqueous phase.

A short glass column with an inner diameter of 10 mm and a length of 100 mm, equipped with porous frits, was filled up to a height of about 25 mm with a suspension of 500 mg PAN impregnated Ambersorb 563 resin in water. Prior to use, the resin was preconditioned with buffer solution. After each experiment, the column was rinsed with water and stored for the next experiment.

2.3. Preparation of PAN impregnated Ambersorb 563 resin

The preparation of PAN impregnated Ambersorb 563 resin is based on procedure reported by

Saracoglu et al. [29]. Ambersorb 563 (1.0 g) resin was added to 2 ml of PAN solution and diluted to 20 ml with water using continuous stirring for 20 min. Afterwards the PAN/563 resin was filtered off, washed with water and dried over night at 110 °C. The amount of PAN deposited on the Ambersorb 563 resin was estimated by spectrophotometric measurements from the residual amount of a PAN in the solution. It was found that 74.6% of PAN was retained on the PAN/563 resin.

2.4. Test procedure for preconcentration

The method was tested with model solutions before its application to the natural waters. Four millilitre of buffer solution (to result in the desired pH between 2 and 10) were added to 50 ml of solution containing 5–20 μg of the each working element. The column was preconditioned with the buffer solution. Buffered metal solution was passed through the column at a flow rate of 5 ml min^{-1}. The sample solution was permitted to flow through the column under gravity. After passing of solution, the column was rinsed twice with 10 ml of water. The adsorbed metals on the column were eluted with 5–10 ml portion of 1 M HNO$_3$ at a flow rate of 5 ml min^{-1}. The eluate was analysed for metals by FAAS.

2.5. Procedure for the stream sediment SRM sample

A 50 mg amounts of a stream sediment reference material (GBW7309) sample was decomposed with 15 ml of aqua regia and the solution was evaporated to dryness. This process was repeated twice. 10 ml of distilled water was added to the residue. The suspension was filtered through a blue band filter paper, and the insoluble part was washed with distilled water. Then the preconcentration procedure given above was applied to the final solutions. The same procedure was applied to the blank solution.

2.6. Procedure for natural waters

Before the analysis of water samples, the samples were filtered through a cellulose membrane filter (Millipore) of 0.45 μm pore size. For the preconcentration, the pH of 250 ml of the sample was adjusted to 9 with buffer solution. Then the preconcentration procedure given above was applied to the final solutions.

3. Result and discussions

The optimised conditions for the enrichment procedure were established using 30–50 ml of deionised water containing 5–20 μg of each element and submitting these solutions to the preconcentration procedure. Parameters such as pH of the aqueous solution, eluent solution concentration, eluent solution volume, sample and eluent flow rates etc. were investigated.

3.1. Effect of the pH on the retentions of metal ions

pHs effects on preconcentration of metal ions on PAN impregnated Ambersorb 563 resin were examined in the range of 4–10. The results are presented in Fig. 1. The recovery depended on the pH of the sample solution, which was nearly constant in the pH range of 8.5–9.5 for the all
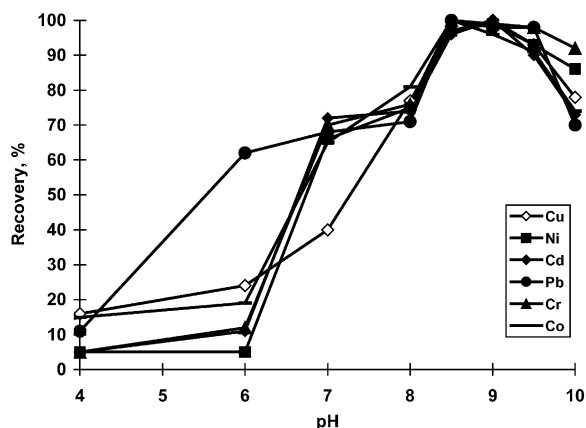

Fig. 1. pH dependence of the recoveries of the metal ions ($N = 3$).

analyte ions. In all subsequent studies were performed at pH 9 by using ammonia/ammonium chloride buffer solution.

The effect of the volume of the ammonia/ammonium chloride buffer solution at pH 9 was investigated. The quantitative recoveries were obtained in the buffer volume range of 2–20 ml. In all further works 10 ml of the ammonia/ammonium chloride buffer was used.

3.2. The effect of eluent type

The effects of various eluents on the recoveries of the analyte ions from PAN impregnated Ambersorb 563 were also investigated. Quantitative recoveries for the analytes were obtained with 10 ml of 1 M HNO_3 in acetone. The recoveries were less than quantitative for the other eluting solutions such as acetone, 1 M HCl, 1 M HNO_3 etc. The effect of the eluent volume was also studied by using 1 M HNO_3 in acetone as eluent. Quantitative recovery values were obtained for all analyte ions in the range of 2–25 ml of eluent volume. All further studies 10 ml of 1 M HNO_3 in acetone was used as eluent.

The effect of number of usage of the PAN impregnated Ambersorb 563 resin on the recoveries of analyte ions were also studied. The PAN coated Ambersorb 563 resin can be used in the preconcentration experiments for 50-times. After 50-times, the new 500 mg resin was filled to the glass mini column.

3.3. The effect of sample volume

For the preconcentration of trace elements in natural water samples, the method used must have high preconcentration factor. To obtain high preconcentration factors, sample volume is an important factor. The effect of the sample volume on the recoveries of analyte ions was also investigated in the range of 50–500 ml. The results are depicted in Fig. 2. The recovery values of copper, nickel, cadmium, lead, chromium and cobalt were very efficient ($ > 95\%$) in the sample volume range of 50–250 ml. The preconcentration factor was 125 when eluent volume is 2 ml.
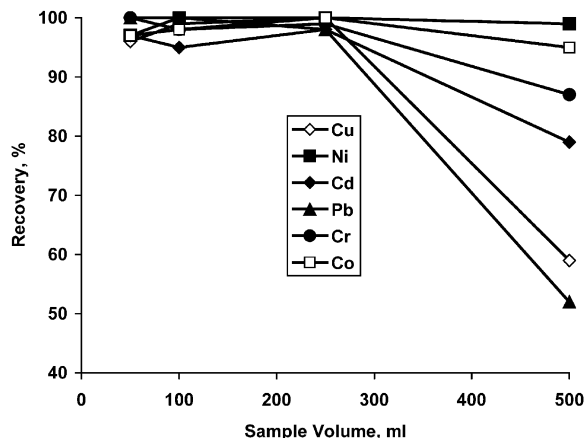

Fig. 2. Effects of sample volume on the recoveries of analyte ions ($N = 3$).

3.4. Sample and eluent flow rates

Sample and eluent flow rates are important parameters to obtain quantitative retention and elution of analyte ions, respectively. The retentions for copper, nickel, cadmium, lead, chromium and cobalt were virtually quantitative for sample flow rates up to 5 ml min^{-1}. Variation of the elution flow rate in the range of 1.0–7.0 ml min^{-1} has no effect on the elution efficiency. In consequence, 5 ml min^{-1} was selected as flow rate for sample loading and sample elution from the trap.

3.5. Interferences

In order to evaluate the feasibility of the PAN/Ambersorb 563 preconcentration method for natural water analysis, the influences of the matrix ions of the natural waters (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, PO_4^{3-}) and some metal ions (Al^{3+}, Zn^{2+}, Fe^{3+} etc.) on the recoveries of analyte ions on PAN coated Ambersorb 563 resin were also investigated (Table 1). Quantitative recovery values were obtained for the analyte ions. The results are desired in view of applications to the natural water samples with the high salt content.

Table 1
Effect of the matrix ions on the recovery of metal ions (100 ml volume, $N = 4$)

Ion	Added as	Concentration (mg l^{-1})	Recovery (%)					
			Cu	Ni	Cd	Pb	Cr	Co
Na^+	NaCl	10 000	98	101	90	101	103	99
K^+	KCl	2000	93	97	98	98	97	95
Ca^{2+}	$CaCl_2$	1000	99	96	98	96	102	96
Mg^{2+}	$MgCl_2$	1000	95	96	96	98	97	96
Fe^{3+}	$FeCl_3$	20	99	98	99	103	104	104
Al^{3+}	$Al_2(SO_4)_3$	50	103	95	97	105	103	100
Zn^{2+}	$ZnSO_4$	25	96	96	97	101	98	99
Mn^{2+}	$MnSO_4$	75	101	97	95	98	97	94
PO_4^{3-}	Na_3PO_4	50	98	96	95	96	94	96
SO_4^{2-}	$(NH_4)_2SO_4$	2000	95	98	95	96	95	95
Cl^-	NH_4Cl	50 000	100	100	96	98	98	101

3.6. Analytical performance of the method

The accuracy of the results was verified by analysing the concentration after addition of known amounts of analytes into a 250 ml of tap water sample. Good agreement was obtained between the recoveries of analyte for spiked and control samples using the experimental procedure for copper, nickel, cadmium, lead, chromium and cobalt. The recovery values calculated for the standard additions were quantitative, thus confirming the accuracy of the procedure and the absence of matrix effects.

The analytical performance of the procedure can be calculated for the results from FAAS measurements. The reproducibility of the preconcentration and separation method was evaluated by passing 50 ml of solution containing 5–20 μg of each analyte ion through the Ambersorb 563 column and repeating this procedure ten-times. The relative standard deviation (R.S.D.) were below 10%.

The detection limits of the investigated elements based on three-times the standard deviations of the blank ($k = 3$, $N = 20$) on a sample volume 100 ml for copper, nickel, cadmium, lead, chromium and cobalt were 0.67, 0.23, 0.23, 1.4, 0.50 and 0.21 μg l^{-1}, respectively. The detection limits of the analyte ions can be decreased by one order of magnitude by increasing the sample volume.

3.7. Applications of the proposed method

The developed method was applied a stream sediment standard reference material (GBW7309) for the determination of copper, nickel, cadmium, lead, chromium and cobalt. The results, based on the average of four replicates, are tabulated in Table 2, which show that the results are in good agreement with the certified values.

The application of the proposed method was also performed for the determination of analyte ions in the various tap waters from Kayseri City and some mineral water samples including high salt contents that were bottled in the sources at the various locations in Turkey. For this purpose, the procedure given in Section 2 was applied to all samples. The results are given in Table 3. The results have been calculated by assuming 100% recovery of the working elements. The R.S.D.

Table 2
Results of the analysis a stream sediment standard reference material (GBW7309)

Element	Certified value (μg g^{-1})	Our value (μg g^{-1})
Cu	32	35 ± 3
Ni	32	30 ± 2
Cd	0.26	0.8 ± 0.1
Pb	23	22 ± 1
Cr	85	89 ± 6
Co	14	16 ± 1

Table 3
Concentration of the analyte ions in various natural samples ($N = 4$, sample volume: 250 ml, final volume: 2 ml)

Concentration* ($\mu g\ l^{-1}$)

Sample	Cu	Ni	Cd	Pb	Cr	Co
Tap water-1	BDL	1.8 ± 0.1	1.6 ± 0.1	21 ± 1	BDL	BDL
Tap water-2	BDL	1.9 ± 0.1	BDL	2.1 ± 0.2	BDL	BDL
Tap water-3	BDL	1.9 ± 0.1	BDL	2.1 ± 0.2	BDL	BDL
Tap water-4	BDL	2.6 ± 0.1	BDL	BDL	BDL	BDL
Tap water-5	BDL	4.2 ± 0.2	BDL	BDL	BDL	BDL
Bottled mineral-1	BDL	1.6 ± 0.2	BDL	2.8 ± 0.2	BDL	BDL
Bottled mineral-2	4.4 ± 0.2	6.5 ± 0.4	1.3 ± 0.1	16 ± 3	7.7 ± 0.1	5 ± 1
Bottled mineral-3	4.3 ± 0.3	2.0 ± 0.4	BDL	9.5 ± 0.1	BDL	BDL
Bottled mineral-4	4.9 ± 0.3	6.7 ± 0.9	BDL	18 ± 2	8.3 ± 0.9	5.5 ± 0.4
Bottled mineral-5	3.6 ± 0.3	9.4 ± 0.7	1.8 ± 0.1	20 ± 2	5.2 ± 0.4	5.6 ± 0.4

BDL, below the detection limit. *, $P = 0.95$, $x \pm ts/\sqrt{N}$.

($N = 4$) with related to the determinations were found to be lower than 10%.

4. Conclusion

The procedure was characterised by good reproducibility and accuracy. The recoveries of impurities were virtually quantitative (95–100%). A column filled with Ambersorb 563 impregnated with PAN works very well for the preconcentration and separation of analyte ions and can certainly be employed for other analytes in other samples.

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