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Column Solid-Phase Extraction with 2-Acetylmercaptophenyldiazoaminoazobenzene (AMPDAA) Impregnated Amberlite XAD-4 and Determination of Trace Heavy Metals in Natural Waters by Flame Atomic Absorption Spectrometry

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Abstract. A column solid-phase extraction (SPE) preconcentration method was developed for the determination of Cd, Co, Cu, Ni and Zn ions in natural water samples by flame atomic absorption spectrometry. The procedure is based on the retention of analytes in the form of 2-acetylmercaptophenyldiazoaminoazobenzene (AMPDAA) complexes on a short column of AMPDAA-XAD-4 resin from buffered sample solution and subsequent elution with hydrochloric acid plus sodium chloride. Important SPE parameters were optimized using model solutions. The loading half-time, $t_{1/2}$, for Cd, Co, Cu and Zn was found to be less than 5 min, and for Ni the value was 12 min. The detection limit for Cd, Co, Cu, Ni and Zn was 0.028, 0.064, 0.042, 0.023 and $0.16\,\mu g\,L^{-1}$, respectively, and the quantification limit was 0.043, 0.11, 0.099, 0.044 and $0.29\,\mu g\,L^{-1}$, respectively. The AMPDAA-XAD-4 resin has good selectivity for Cd, Co, Cu, Ni and Zn over several electrolytes, especially over earth alkaline metals with tolerance limits of $0.05\,mol\,L^{-1}$. The method was validated by analysing a standard reference material (GBW 08301), and it was found that the results agree with those quoted by the manufactures. The developed method was applied to the determination of trace metal ions in tap water and river water samples with satisfactory results.

Key words: Solid-phase extraction; 2-acetylmercaptophenyldiazoaminoazobenzene; Amberlite XAD-4; natural water; flame atomic absorption spectrometry.

As the number of ecological and health problems associated with environmental contamination continues to rise, the determination of trace metals in environmental samples is becoming more and more important. Flame atomic absorption spectrometry (FAAS) has been widely used for the determination of trace metal ions because of the relatively simple and inexpensive equipment required. However, direct determination of metal ions at trace levels by FAAS is limited due to their low concentrations and matrix interferences. In trace analysis, therefore, preconcentration and/or separation of trace elements from the matrix is frequently necessary to improve the detection limit and selectivity for their determination by FAAS. For this purpose, several methods have been proposed and used to separate and preconcentrate trace elements according to the nature of the samples,

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the concentrations of the analytes and the measurement techniques [1]. They include ion exchange [2, 3], coprecipitation [4–6], solvent extraction [7, 8] and adsorption [9, 10]. Among the various preconcentration methods, solid-phase extraction (SPE) is one of the most effective multielement preconcentration methods because of its simplicity, rapidity and ability to attain a high concentration factor. Until now, XAD resins [11–18], activated carbon [19, 20], silica gel [21–23], ion-exchange resins [24, 25], chelating resins [26–29] and various polymers have been used as solid-phase materials.

However, these materials have poor selectivity for heavy metals over earth alkaline metals. According to our knowledge, the triazene reagents have good selectivity and sensitivity for cobalt, nickel, copper and zinc group elements, especially for cadmium and nickel owing to their functional group of "–N=N–" [30, 31]. If they were loaded to a solid phase support and applied to the preconcentration of heavy metals, high selectivity should be obtained.

In the present study, a previously synthesized triazene reagent of 2-acetylmercaptophenyldiazoaminoazobenzene (AMPDAA) [30] was impregnated onto Amberlite XAD-4 resin, and the feasibility of using AMPDAA-XAD-4 resin as a solid-phase extractant for the separation and preconcentration of Cd, Co, Cu, Ni and Zn at trace level was investigated using batch and column procedures. The results showed that the analytes were easily retained in the form of 2-acetylmercaptophenyldiazoaminoazobenzene complexes on AMPDAA-XAD-4 resin from a buffered sample solution and then eluted from the resin column with hydrochloric acid plus sodium chloride. The modified resin AMPDAA-XAD-4 has good selectivity for Cd, Co, Cu, Ni and Zn over earth alkaline metals, and the tolerance limits can reach up to $0.05\,\mathrm{mol\,L^{-1}}$, which is significantly higher than for most of the reported sorbents [11–16]. In the development of the procedure, several parameters relevant to the retention and elution of the analytes were examined. Based on this, a new method for determining these metal ions by flame atomic absorption spectrometry (FAAS) after their preconcentration on a short column packed with AMPDAA-XAD-4 resin was developed and applied to the analysis of tap water, river water and sediment samples. The procedure was validated by standard addition and analysis of a standard reference material (GBW 08301).

Experimental

Apparatus

A Shimadzu AA-6800 atomic absorption spectrophotometer equipped with single element hollow cathode lamps and an air-acetylene burner was used for the determination of metals. The instrumental parameters were those recommended by the manufacturer. The wavelengths (nm) selected for the determination of the analytes were as follows: Cd 228.8, Co 240.7, Cu 324.8, Ni 232.0, and Zn 213.9. A model pHS-3C pH-meter (Shanghai Lida Instrument Factory, China) was used for the pH adjustments. The flow of liquid through the columns was controlled using a model BT00-600M peristaltic pump with eight channels (Baoding Laonger Precision Pump Co. Ltd, China). A model DZD-3 multifunctional shaker (Changzhou Aite Technologies Co. Ltd, China) was used for the equilibration of the kinetics of metal adsorption measurement.

Chemicals and Solutions

$18\,\mathrm{M\Omega\,cm}$ Distilled De-Ionized (DDI) water was purified with a Milli-Q system (Millipore, USA). Unless otherwise stated, all reagents used were of analytical grade and all solutions were prepared with DDI water. Standard labware and glassware was used throughout and repeatedly cleaned with HNO_3 and rinsed with DDI water, according to a published procedure [32].

Stock solutions ($1000\,\mathrm{mg\,L^{-1}}$) of the elements were prepared by dissolving appropriate amounts of nitrate salts in 1.0% (v/v) HNO_3 and further diluting daily prior to use. 2-Acetylmercaptophenyldiazoaminoazobenzene (AMPDAA) was prepared by the previous procedure [30]. Pure HCl and NaCl from Beijing Institute of Chemical Reagents (Beijing, China) were used as eluent.

The standard river sediment sample (GBW 08301) was obtained from the National Research Center for Certified Reference Materials (Beijing, China).

The following buffer solutions were used for the SPE procedures: Na_3PO_4/Na_2HPO_4 buffer for pH 2.0 and 3.0; $NaCH_3COO/CH_3COOH$ buffer for pH 4.0 and 6.0; Na_2HPO_4/NaH_2PO_4 buffer for pH 7.0; $Na_2B_4O_7/NaOH$ buffer for pH 8.0–10.0. XAD-4 resin (Aldrich Milwaukee, USA) was used as the solid-phase extractant. It is a porous styrene-divinylbenzene copolymer with a surface area in the range of $300–400\,\mathrm{m^2\,g^{-1}}$ and 40–60 mesh particle size. This hydrophobic resin can be used in a pH range of 0 to 14. Before use, it was thoroughly washed in the sequence of $4.0\,\mathrm{mol\,L^{-1}}$ HCl, DDI water, $1.0\,\mathrm{mol\,L^{-1}}$ NaOH and DDI water. It was finally washed with 10 mL of methanol and dried in the air.

The preparation of AMPDAA-XAD-4 was modified from Blains' procedure [33] and described as follows: 500 mg of pretreated XAD-4 was suspended in 100 mL of 0.2% (w/v) AMPDAA acetone solution. Then 500 mL of DDI water were added dropwise to the organic solution while gently stirring at room temperature. The impregnated resins were filtered off, rinsed several times with DDI water and stored in a $1.0\,\mathrm{mol\,L^{-1}}$ hydrochloric acid solution. The saturation value of the loaded AMPDAA is $0.865\,\mathrm{mmol\,g^{-1}}$ resin. When AMPDAA-XAD-4 is suspended in DDI water for three days, there is no significant bleeding of AMPDAA. Accordingly, the AMPDAA-XAD-4 resins are suitable for SPE use.

Batch Procedure

Batch experiments were carried out under the following conditions: 500 mg AMPDAA-XAD-4 was suspended in 250 mL of feed solution containing 5.0 mg each of Co, Cu, Ni, Zn and 10 mg of Cd prior to adjusting to pH 7.0. Then the mixture was shaken at room temperature for the required time and at predetermined intervals. Aliquots of 5.0 mL solution were taken out for analysis. The concentration of metal ions in the supernatant solution was determined, and the amount of metal ions loaded on the resin phase was calculated by mass balance (in µg g^{-1} resin).

SPE–FAAS Procedure

The polytetrafluoroethylene (PTEE) column (100 mm × 10 mm) was covered with a fritted glass disc. A total of 500 mg of AMPDAA-XAD-4 resin was slurried in water and then poured into the column. A small amount of glass wool was placed on the disc to prevent loss of the resin beads during sample loading. It was washed successively with water, HCl and water. The column was preconditioned by passing a blank solution prior to use. After each use, the resin in the column was washed with a large volume of water and stored in water for the next experiment. The acidic effluent was collected in a PTEE tube.

The performance of the column method was tested with the model solution before its application to the samples. A total of 25 mL of the model solution containing 5 µg each of Co, Cu, Ni and Zn, and 10 µg of Cd was buffered to the desired pH. It was impregnated to the top of the preconditioned column and passed through at a flow rate of 2 mL min^{-1}. The column was washed with 5–10 mL of blank solution prepared with the corresponding buffer solution. The retained metal ions were eluted with 8.0 mL of 1 mol L^{-1} HCl + 1 mol L^{-1} NaCl and 2 mL of DDI water. The 100 µL of effluent was directly injected for determination by FAAS.

Sampling Procedure

The sediment reference material (GBW 08301 China) was treated according to a previously published procedure [18].

Tap water samples taken from our research laboratory were analyzed without pretreatment.

The surface river water samples were collected from a dirty region of Sanggan River (Datong, China) and Fen River (Taiyuan, China) in September 2003. To oxidize organic matter such as humic acid, the sample was digested by oxidizing UV-photolysis in the presence of 1% H_2O_2 using a low pressure Hg-lamp which was integrated in a closed quartz vessel [34]. The digested samples were immediately filtered through a Millipore cellulose nitrate membrane, pore size 0.45 µm, acidified to pH 3 with hydrochloric acid and stored in pre-cleaned polyethylene bottles.

Results and Discussion

Adsorption Characteristics

To determine the loading capacity and loading rate of Cd, Co, Cu, Ni and Zn for AMPDAA-XAD-4, batch experiments were conducted. The equilibration times were 24 h for the former and predetermined intervals for the latter. The adsorption capacities of AMPDAA-XAD-4 for Cd, Co, Cu, Ni and Zn are 180, 100, 95, 170 and 60 µmol g^{-1}, respectively. The loading half-time ($t_{1/2}$) defined as the time needed to reach 50% of the resin's total loading capacity was estimated from the curves (Fig. 1). From the kinetics of Cd, Co, Cu, Ni and Zn uptake, it was observed that AMPDAA-XAD-4 exhibited good kinetic characteristics with an equilibrium time of about 60 min for 95–100% sorption, except for Ni. Moreover, the time of 50% sorption was less than 5 min for Cd, Co, Cu, Zn, and 10 min for Ni. The faster uptake of these metal ions on AMPDAA-XAD-4 probably reflects their better accessibility to the ligand sites in the impregnated resin. For Ni, it is mainly influenced by temperature (described below).

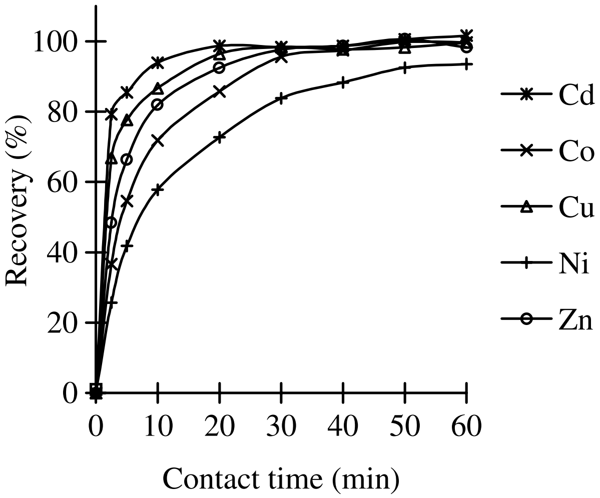

Fig. 1. Kinetics of metal ion adsorption on AMPDAA-XAD-4. Other conditions: 500 mg AMPDAA-XAD-4; 5.0 mg each of Co, Cu, Ni, Zn and 10 mg of Cd in 250 mL; pH 7.0; room temperature

The repeated use time was also tested by batch procedures. The equilibration time was 24 h. The elution operations were carried out by shaking the resin with 50 mL of suitable eluent for 1 h to ensure complete equilibration. The operating capacity was calculated from the loading and elution tests. The results from both tests agreed within 2–5% error for all the five metal ions up to 10 cycles of repeated experiments. The resin shows better reusability and stability towards these metal ions.

Effect of pH

The effect of the pH on the retention of metal ions on the AMPDAA XAD-4 resin column was studied by applying the proposed SPE–FAAS procedure at different pH values. The results (Fig. 2) indicate that the quantitative recovery (≥95%) pH ranges are as follows: 7–10 for Cd and Ni, 7–9 for Co, 6–8 for Cu and 7–8 for Zn. Consequently, pH 7 was used in further experiments.

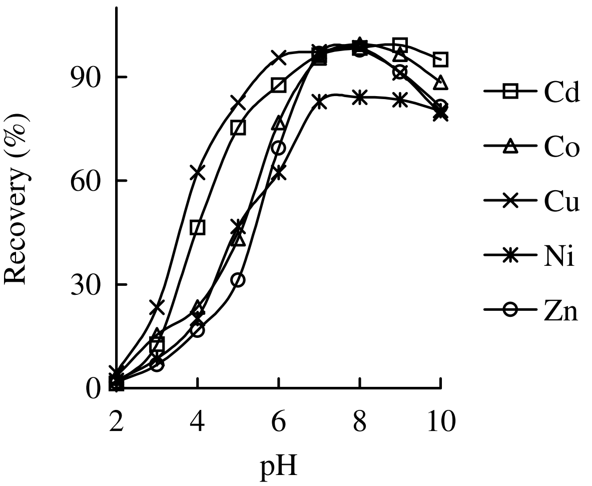

Fig. 2. Recovery of metal ions at different pH values. Other conditions: 500 mg AMPDAA-XAD-4; 25 mL 5 µg each of Co, Cu, Ni and Zn, and 10 µg of Cd; flow rate, 2 mL min^{-1}; eluent, 8.0 mL of 1 mol L^{-1} HCl + 1 mol L^{-1} NaCl and 2 mL DDI water; room temperature

Table 1. Effect of temperature on retention of metal ions on AMPDAA XAD-4 (n = 3)

Temperature (°C)	Sorption (%)				
	Cd	Co	Cu	Ni	Zn
5	95	88	92	61	93
10	96	93	96	73	95
20	98	97	98	84	97
30	99	99	98	92	99
40	101	99	99	96	98

Effect of Temperature

The temperature effect was investigated using the batch procedure and shaking for 1 h at different temperatures ranging from 5 °C to 40 °C. The results (Table 1) show that the temperature has little effect on the adsorption of Cd, Cu and Zn on AMPDAA-XAD-4 (adsorption increases by 7%), moderate effect on Co (adsorption increases by 11%) and a significant effect on Ni (adsorption increases by 35%). For convenient operation, room temperature (20 °C) was chosen for further experiments.

Effect of AMPDAA-XAD-4 Amount

To test the effect of resin amount on quantitative retention of analytes, different amounts of AMPDAA-XAD-4 (ranging from 200 to 800 mg) were added to the column. The procedure was applied to the model solutions by using these columns. Quantitative recoveries for all the examined analytes were obtained in the range of 300–700 mg of impregnated resin. Quantitative retention was not obtained with amounts of resin smaller than 300 mg. On the other hand, resin amounts larger than 700 mg prevented elution of the quantitatively retained metal ions by 8.0 mL of 1 mol L^{-1} HCl + 1 mol L^{-1} NaCl + 2 mL DDI water. Accordingly, the column was filled with 500 mg of AMPDAA-XAD-4 resin in further experiments.

Effect of Flow Rate

Since the retention of elements on an adsorbent depends on the flow rate of the metal solution, the influence of the sample solutions' flow rate on the retention of the trace metals was investigated under the optimum conditions. From Fig. 3, it can be seen that retentions of Cd, Co, Cu and Zn as AMPDAA complexes were almost independent of flow rates from 2 to 12 mL min^{-1}. Flow rates slower than 2 mL min^{-1} were not studied so as to avoid long analysis times. At flow rates above 4.0 mL min^{-1}, the decreased retentions of Ni can be interpreted as a result of slow adsorption (see Fig. 1).

Effect of Eluent Type and Volume

To obtain quantitative recovery, the effect of the eluent types on preconcentration was investigated using

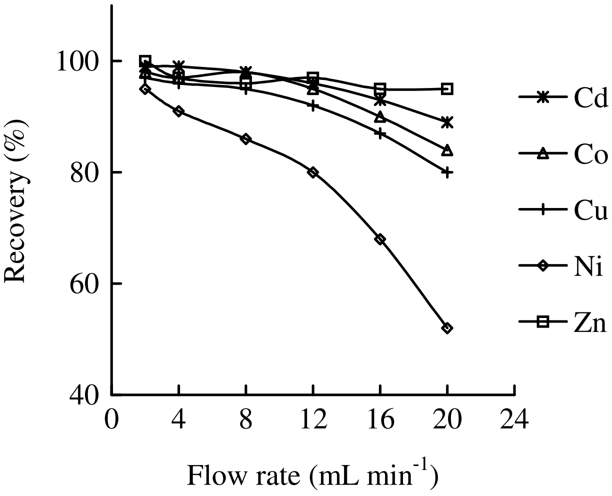

Fig. 3. Recovery of metal ions at different flow rates. Other conditions: 500 mg AMPDAA-XAD-4; 25 mL 5 µg each of Co, Cu, Ni and Zn, and 10 µg of Cd; flow rate, 2 mL min^{-1}; eluent, 8.0 mL of 1 mol L^{-1} HCl + 1 mol L^{-1} NaCl and 2 mL DDI water; pH 7.0; room temperature

Table 2. Effect of eluent types on retention of metal ions on AMPDAA XAD-4 (n = 3)

Eluent type	Recovery (%)				
	Cd	Co	Cu	Ni	Zn
1 mol L^{-1} HNO_3	90	82	95	92	96
1 mol L^{-1} HCl	96	93	96	93	95
1 mol L^{-1} HCl + 1 mol L^{-1} HNO_3	98	97	98	97	99
1 mol L^{-1} HCl + 1 mol L^{-1} NaCl	98	97	97	95	98

various eluting solutions. The volume of eluent was 10 mL. The results are shown in Table 2. Recoveries were less than 95% for Cd, Co and Ni with 1 mol L^{-1} HNO_3 and for Co and Ni with 1 mol L^{-1} HCl. Quantitative recoveries were obtained with 1 mol L^{-1} HCl + 1 mol L^{-1} HNO_3 and 1 mol L^{-1} HCl + 1 mol L^{-1} NaCl for all five metal ions. Since HNO_3 has the ability to oxidize AMPDAA, 1 mol L^{-1} HCl + 1 mol L^{-1} NaCl was used as eluent in all further experiments. The effect of the eluent volume on the recoveries was also evaluated. As can be seen from Fig. 4, the recoveries of metal ions approach quantitative values when 8.0 mL 1 mol L^{-1} HCl + 1 mol L^{-1} NaCl + 2 mL water is used.

Effect of Sample Volume

In order to deal with real samples containing very low concentrations of trace metal ions, the maximum applicable sample volume must be determined. Therefore, the effect of the sample volume on the recoveries was studied by SPE using increasing volumes of metal ion solution and keeping the total amount of metal ion uptake constant at 10 µg for Co, Cu, Ni, Zn and 20 µg for Cd. Table 3 indicates that the retention of all the metal ions examined is not affected by sample volumes of up to 800 mL. After 800 mL of sample volume, recovery values of less than 95% for Cu, Ni and Zn were obtained. In this study, therefore, the final solution volume was 10 mL, and the concentration factors were 80 for five metal ions.

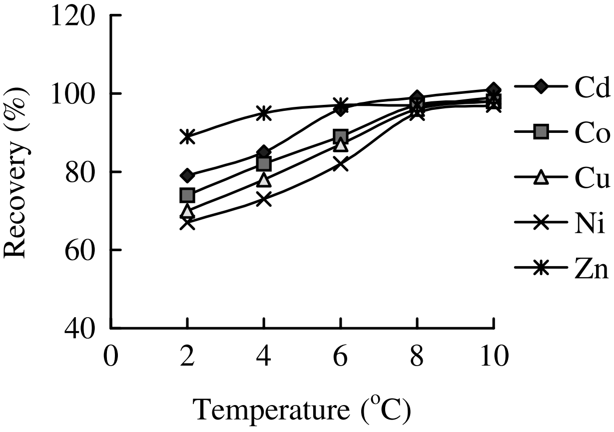

Fig. 4. Effect of eluent volume on retention of metal ions on AMPDAA XAD-4. Other conditions: 500 mg AMPDAA-XAD-4; 25 mL 5 µg each of Co, Cu, Ni and Zn, and 10 µg of Cd; flow rate, 2 mL min^{-1}; eluent, 1 mol L^{-1} HCl + 1 mol L^{-1} NaCl; pH 7.0; room temperature

Table 3. Effect of sample volume on retention of metal ions on AMPDAA XAD-4 (n = 3)

Sample volume (mL)	Recovery (%)				
	Cd	Co	Cu	Ni	Zn
100	97	98	99	97	98
200	98	97	103	104	96
400	96	98	97	99	98
600	100	96	97	98	97
800	102	95	95	98	96
1000	97	92	89	97	93
1200	96	89	80	95	85
1400	94	83	69	93	72

Selectivity for Matrix Ions

The effect of NaCl, KBr, KI, $NaNO_3$, Na_2SO_4, Na_3PO_4 and cations Ca and Mg on the sorption of all five metal ions was studied. The results in Table 4

Table 4. Tolerance limits of electrolytes (n = 3)

Metal ions	Electrolytes or metal ions (mol L^{-1})							
	NaCl	KBr	KI	$NaNO_3$	Na_2SO_4	Na_3PO_4	Ca	Mg
Cd	0.05	0.05	0.005	0.10	0.01	0.001	0.05	0.05
Co	0.05	0.05	0.05	0.10	0.05	0.01	0.05	0.05
Cu	0.10	0.05	0.005	0.10	0.10	0.001	0.10	0.05
Ni	0.10	0.10	0.05	0.10	0.10	0.005	0.10	0.05
Zn	0.10	0.10	0.05	0.10	0.10	0.005	0.10	0.05

Table 5. Determination of Cd, Co, Cu, Ni and Zn in a certified sample (GBW 08301)

Analyte	Found by present method (µg g^{-1})[a]	Certified value (µg g^{-1})
Cd	2.3 ± 0.05	2.45 ± 0.3
Co	15.1 ± 1.8	16.5 ± 1.5
Cu	48.9 ± 3.4	53 ± 6
Ni	30 ± 3	32[b]
Zn	247 ± 11	251[b]

[a] Uncertainties expressed as 95% confidence interval with n = 3.
[b] Reference value (less accurate than certified value).

Table 6. Determination of Cd, Co, Cu, Ni and Zn in water samples (n = 3)

Origin of sample	Method	Metal ions concentration (µg L^{-1})				
		Cd	Co	Cu	Ni	Zn
Tap water	Direct[a]	0.65 ± 0.12	0.23 ± 0.04	8.33 ± 1.10	0.95 ± 0.21	14.55 ± 1.62
	SA[b]	1.47 ± 0.04	1.12 ± 0.06	17.01 ± 0.44	1.86 ± 0.08	23.84 ± 1.43
Fen River	Direct[a]	0.73 ± 0.06	7.58 ± 0.83	66.42 ± 2.08	4.52 ± 0.81	8.71 ± 1.22
	SA[b]	1.62 ± 0.14	17.22 ± 1.14	74.41 ± 2.54	13.40 ± 1.64	17.63 ± 1.70
Sanggan River	Direct[a]	0.81 ± 0.03	10.60 ± 1.19	70.15 ± 2.02	5.53 ± 0.32	7.66 ± 0.52
	SA[b]	1.78 ± 0.02	19.82 ± 0.75	78.04 ± 2.43	15.20 ± 0.71	16.93 ± 0.41

[a] Recommended procedure applied directly.

[b] Standard addition method (spiked with 1.0 µg L^{-1} solution for analyte concentrations below 1.0 µg L^{-1} and with 10 µg L^{-1} for analyte concentrations above 1.0 µg L^{-1}).

show that the tolerance limits of the investigated electrolytes or cations can reach up to 0.05 mol L^{-1}, which is much higher than most of the reported sorbents [11–16]. This is because AMPDAA has an “–N=N–” functional group that has a strong affinity to Cd, Co, Cu, Ni and Zn and less of an affinity to the investigated electrolytes. In the preconcentration process, Cd, Co, Cu, Ni and Zn were retained on the column, and most of the electrolytes were still in solution. The interferences caused by the investigated electrolytes, especially the earth alkaline metals, were greatly reduced so that accurate determination results were obtained. The reported tolerance limit is defined as the ion concentration causing a relative error $<\pm 5\%$. The tolerance limits are higher than the concentrations of Na^+, K^+, Ca^{2+}, Mg^{2+} and Cl^- in river water [35].

Validation of the Method

A reference material (GBW 08301) was used for SPE–FAAS validation by the SPE–FAAS procedure given above. As seen in Table 5, the results were compared with the certified values using a *t*-test at 95% confidence limits [36]. Good agreement was obtained between the estimated content by the proposed method and the certified values for Cd, Co, Cu, Ni and Zn. These results also indicate that the developed preconcentration method for Cd, Co, Cu, Ni and Zn is not affected by potential interferences from the major matrix elements of the analyzed water sample containing Al_2O_3 (13.82%), Fe_2O_3 (5.08%), P_2O_5 (0.18), MgO (0.84%), CaO (0.37%), Na_2O (0.56%), and K_2O (2.32%).

The reproducibility of the SPE FAAS procedure was measured using model solution. The relative standard deviations (n = 10) were 3.1% for Cd, 6.2% for Co, 6.5% for Cu, 9.7% for Ni, and 3% for Zn. The detection limit and the quantification limit, defined as by IUPAC [33–39] were found to be 0.028, 0.064, 0.042, 0.023, 0.16 µg L^{-1}, and 0.043, 0.11, 0.099, 0.044, 0.29 µg L^{-1}, respectively.

Applications

The preconcentration procedure given above was used for tap water, Fen River and Sanggan River samples. For analysis, the sample containing 800 mL each of the tap water and of the treated river water was buffered to the desired pH. Meanwhile, the standard addition method was applied. Table 6 shows that the results for Cd, Co, Cu, Ni and Zn were satisfactory.

Conclusion

AMPDAA impregnated Amberlite XAD-4 resin shows excellent adsorption characteristics for Cd, Co, Cu, Ni and Zn. The selectivity of the loaded resin towards these metal ions gives a matrix with very low levels of alkali, especially of earth alkaline elements with tolerance limits of 0.05 mol L^{-1}. AMPDAA-XAD-4 has a large adsorption capacity which is superior (2 to 50-fold) in comparison to 1-(2-pyridylazo)-2-naphthol [12, 13], salicylic acid [14] and pyrocatechol violet [15] loaded Amberlite XAD-2; N,N-bis(2-hydroxyethyl)glycine [16] loaded Amberlite XAD-4; pyrocatechol violet loaded activated carbon [20]; calixarene tetrahydroxamate [21], salicylaldoxime [22] and *o*-vanillin [23] immobilized silica gel; 8-hydroxyquinoline-5-sulfonic acid loaded cellulose [40]. Only 500 mg of the resin is needed. The adsorption rate is very fast with a loading half time, $t_{1/2}$, of less than 10 min. Besides, it can be repeatedly used at least 10 times.

Therefore, it is considered that the proposed method based on AMPDAA-XAD-4 resin is economical and eco-friendly and applicable to the preconcentration of trace heavy metals in tap, river, lake, sea and waste water. No doubt the proposed procedure could be combined with other instrumental determination techniques and utilized for on-site preconcentration and determination of trace heavy metals.

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