Study on solid phase extraction and graphite furnace atomic absorption spectrometry for the determination of nickel, silver, cobalt, copper, cadmium and lead with MCI GEL CHP 20Y as sorbent

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ABSTRACT

A solid phase extraction and graphite furnace atomic absorption spectrometry (GFAAS) for the determination of nickel, silver, cobalt, copper, cadmium and lead with MCI GEL CHP 20Y as sorbent was studied. Trace amounts of chromium, nickel, silver, cobalt, copper, cadmium and lead were reacted with 2-(2-quinolinil-azo)-4-methyl-1,3-dihydroxidobenzene (QAMDHB) followed by adsorption onto MCI GEL CHP 20Y solid phase extraction column, and $1.0\,mol\,L^{-1}$ HNO_3 was used as eluent. The metal ions in 300 mL solution can be concentrated to 1.0 mL, representing an enrichment factor of 300 was achieved. The recoveries of analytes at pH 8.0 with 1.0 g of resin were greater than 95% without interference from alkaline, earth alkaline and some metal ions. When detected with graphite furnace atomic absorption spectrometry, the detection limits in the original samples were $1.4\,ng\,L^{-1}$ for Cr(III), $1.0\,ng\,L^{-1}$ for Ni(II), $0.85\,ng\,L^{-1}$ for Ag(I), $1.2\,ng\,L^{-1}$ for Co(II), $1.0\,ng\,L^{-1}$ for Cu(II), $1.2\,ng\,L^{-1}$ for Cd(II) and $1.3\,ng\,L^{-1}$ for Pb(II). The validation of the procedure was performed by the analysis of the certified standard reference materials, and the presented procedure was applied to the determination of analytes in biological, water and soil samples with good results (recoveries range from 89 to 104%, and R.S.D.% lower than 3.2%. The results agreed with the standard value or reference method).

1. Introduction

In spite of great improvements in sensitivity and selectivity of modern instrumental analysis, difficulties still lie in the analysis of trace heavy metals because of both their low abundance levels in the samples and the high complexity of the sample matrices [1,2]. Hence, preliminary concentration and matrix-removal steps are frequently required to guarantee the accuracy and precision of the analytical results.

Various preconcentration techniques including solvent extraction, coprecipitation, cloud point extraction, ion-exchange, solid phase extraction and electroanalytical techniques [3–7] have been used for the enrichment and separation of heavy metals at trace levels in various environmental samples around the world.

Solid phase extraction is an attractive separation-preconcentration technique for heavy metal ions with some important advantages (simplicity, flexibility, economic, rapid, higher enrichment factors, absence of emulsion, low cost because of lower consumption of reagents, more importantly environment friendly). Various solid phase extraction materials have been successfully used for the preconcentration and separation of heavy metal ions at trace levels [8–12].

2-(2-Quinolinil-azo)-4-methyl-1,3-dihydroxidobenzene (QAMDHB) is a spectrophotometric reagent for the heavy metal ions studied. It can react with chromium, nickel, silver, cobalt, copper, cadmium and lead at room temperature rapidly [13,14]. The aim of the present work is to show the possibility of the usage of MCI GEL CHP 20Y polymeric resin as adsorbent for the separation and preconcentration of heavy metal–QAMDHB chelates. The optimum analytical conditions for the quantitative recoveries of

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chromium, nickel, silver, cobalt, copper, cadmium and lead ions on MCI GEL CHP 20Y adsorption resin were investigated.

2. Experimental

2.1. Apparatus

A PerkinElmer Model A Analyst 600 graphite furnace atomic absorption spectrometer (GFAAS) equipped with a Model AS-800 autosampler (Norwalk, CT) was used with monoatomic hollow cathode lamps. A Beckman Φ-200 pH meter was used for the pH measurements. All analytical procedures were carried out in a Hitachi Model ECV-843 BY clean bench (Hitachi, Japan). A Fei Yue DS-200 closed vessel microwave system (maximum pressure 2000 psi, maximum temperature 450 °C) was used for samples digestion.

2.2. Reagents and material

The certified standard reference materials (rice GBW08458 and human hair GBW08126) were obtained from Chinese Standards Center. The standard values of Cr, Ni, Ag, Co, Cu, Cd and Pb were determined by atomic absorption spectrum (AAS), atomic fluorescence spectrum (AFS), neutron activation analysis (NAA), inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-atomic emission spectrometry (ICP-AES) and ion chromatography (IC) method.

The water samples (pure water, well water, tap water and lake water) were collected at Kunming, Yunnan Province, PR China. The soil sample was obtained from Yunnan Academy of Agricultural Sciences, Yunnan Province, PR China.

All solutions were prepared with deionized double-distilled water. Otherwise stated, analytical grade acids and other chemicals used in this study were obtained from Tianjin Chemical Factory, PR China. The calibration curve was established using the standard solutions prepared in 1.0% (w/v) HNO_3 by dilution from 1000 mg L^{-1} stock solutions (Chinese Standards Center, PR China). The calibration standards were also submitted to the preconcentration procedure. QAMDHB (structure in Fig. 1) was synthesized by our laboratory as literature [13,14] and a 0.1% (w/v) solution of QAMDHB was prepared daily in ethanol. Buffer solutions of ammonia–ammonium chloride (0.5 mol L^{-1}, pH 8.0) were prepared by dissolving 0.5 mol (26.8 g) of ammonium chloride in water, adjusted the pH to 8.0 with ammonia and diluted to the volume of 1000 mL.

MCI GEL CHP 20Y was purchased from Mitsubishi Chemical Corporation (Tokyo, Japan). MCI GEL CHP 20Y is an aromatic type adsorbent in the standard grade and is based on cross-linked polystyrenic matrix. Its particle size is 30 μm, and surface area is 560 m^2 g^{-1}. It is a reversed-phase resin widely used in different industrial fields [15]. It was washed successively with methanol, water, 1.0 mol L^{-1} HNO_3 in acetone, water, 1.0 mol L^{-1} NaOH and water, sequentially.
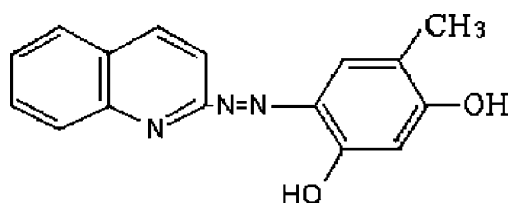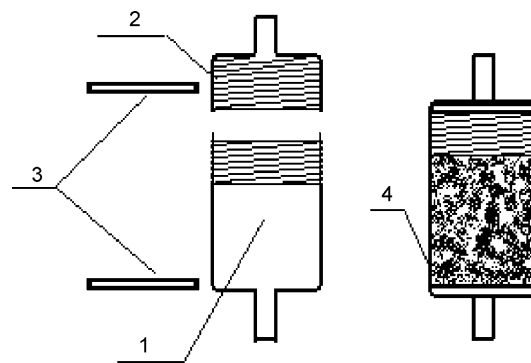

Fig. 1. The structure of QAMDHB.

Fig. 2. The SPE cartridge: (1) tube for fill in the adsorbent; (2) screw cap for sealing the tube; (3) sieve plate; (4) MCI GEL CHP 20Y adsorbent.

2.3. Preconcentration procedure

The teflon column was 2.0 cm long and 1.0 cm in diameter (Fig. 2). The 2.0 μm of sieve plate was placed to prevent loss of the resin beads during sample loading. Then, 1.0 g of MCI GEL CHP 20Y resin was poured into the column. It was washed with water, acetone and water, sequentially. It was conditioned with 10–15 mL of pH 8.0 with ammonia–ammonium chloride buffer. The resin bed was washed with plenty of distilled water until neutral pH and subsequently reused.

The method was tested with model solutions before its application to real samples. 10 mL of buffer solution (pH 10) and 5.0 mL of 0.1% QAMDHB solution were added to 50–300 mL of solution containing 5–40 μg of analyte ions. The column was preconditioned with the buffer solution. Metal–QAMDHB solution was passed through the column at a flow rate of 10 mL min^{-1} using a vacuum aspirator. After passing of this solution, the column was rinsed twice with 10 mL of water. The adsorbed metal chelate on the column was eluted with 1.0 mL of 1.0 mol L^{-1} HNO_3 in the reverse direction. The eluent was analyzed by the graphite furnace atomic absorption spectrometry.

2.4. Sample preparation

For biological samples, 0.25 g of sample was weighted accurately into the 25 mL teflon high-pressure microwave acid-digestion bomb to which, 3.0 mL of concentrated nitric acid and 3.0 mL of 30% hydrogen peroxide was added. The bombs were sealed tightly and then positioned in the carousel of the microwave oven. The system was operated at full power for 6.0 min. The digest was evaporated to near dryness. The residue was dissolved with 10 mL of 1% nitric acid and the preconcentration procedure given above was applied to the samples.

For water samples, the samples were immediately acidified by adding several drops of nitric acid and filtrated with 0.45 μm filter. Then the preconcentration procedure given above was applied to the samples.

For soil samples, 0.1 g of sample was weighed into a 25 mL of teflon high-pressure microwave acid-digestion bomb to which, 2.0 mL of concentrated nitric acid and 1.0 mL of hydrofluoric acid were added. The bombs were sealed tightly and then positioned in the carousel of the microwave oven. The system was operated at full power for 20 min. The digested material was evaporated to incipient dryness. Then, 10 mL of 1% nitric acid was added and heated close to boiling to leach the residue. After cooling, the preconcentration procedure given above was applied to the samples.

Table 1
Operating conditions for GFAAS

	Co	Ni	Cu	Ag	Cd	Pb
Lamp settings wavelength (nm)	242.5	232.0	324.8	328.1	228.8	283.3
Spectral band width (nm)	0.2	0.2	0.7	0.7	0.7	0.7
Lamp current (mA)	30	25	15	10	6	10
Furnace temperature (°C)						
Drying 1 (ramp 1 s, hold 5 s)	110	110	110	110	110	110
Drying 2 (ramp 5 s, hold 15 s)	130	130	130	130	130	130
Ashing (ramp 10 s, hold 30 s)	700	600	700	500	350	600
Atomizing (ramp 0 s, hold 5 s)	2400	2300	2000	1700	1500	1600
Clean-up (ramp 1 s, hold 3 s)	2450	2450	2450	2450	2450	2450

2.5. GFAAS analysis

The GFAAS analysis condition is listed in Table 1. For samples analysis, a 10 µL aliquot of the samples or standard solution was injected into the graphite cuvette for the GFAAS determination. No matrix modifier was used. The atomic absorption signals were measured with the Zeeman background corrector in operation. The measurement was repeated three times and the obtained signals were averaged.

2.6. ICP-MS analysis

The ICP-MS analysis was carried out on a Plasma Quad-3 ICP-MS instrument (Micromass Corporation, UK) as described according to the literature [16]. The operating conditions were as following: frequency (MHz) 40.68; R.F. power (kW) 1.2; sampling depth (mm) 12; gas flow (Ar, principal $15 \, L \, min^{-1}$, intermediate $1.2 \, L \, min^{-1}$, carrier $1.06 \, L \, min^{-1}$); dwell time (ms) 100; replicate accumulation 20; channel width 3; replicate measurements 3.

3. Results and discussion

3.1. The influences of pH on sorption

For solid phase extraction of the heavy metal ions based on chelation, the pH of the aqueous solution is one of the main factor for quantitative recoveries of the analytes [9,13]. Due to this important point, the influences of pH were investigated at the pH ranges 2–10 with model solutions keeping the other parameters constant. The recovery values of the analyte metals were shown in Fig. 3. The optimum pH range for quantitative recoveries of Cr(III), Ni(II), Ag(I), Co(II), Cu(II), Cd(II) and Pb(II) as
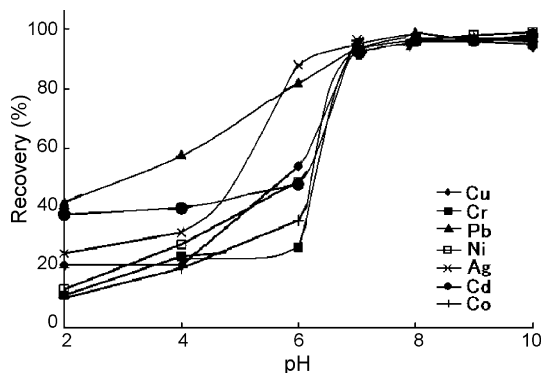
Fig. 3. Influences of pH on the recoveries (ligand: QAMDHB; amounts of analytes: 10 µg Cu, 20 µg Cr, 20 µg Pb, 10 µg Ni, 10 µg Ag, 5 µg Cd, 10 µg Co; eluent: $1.0 \, mol \, L^{-1}$ HNO_3).

QAMDHB chelates on MCI GEL CHP 20Y resin is 6.8–10.0. All subsequent studies were carried out at pH 8, and buffer solutions of ammonia–ammonium chloride (pH 8.0) was recommended to control the pH.

3.2. The influences of ligand amount on the recoveries

In order to determine the amounts of QAMDHB required for quantitative recoveries for chromium, nickel, silver, cobalt, copper, cadmium and lead ions, the proposed method was applied. Changing the QAMDHB amounts (0.1% solution) at the range of 0–10 mL, the recoveries were not quantitative without QAMDHB, and the recovery values of the analyte metal ions increased with increasing amounts of QAMDHB added. The recovery reaches a constant value with at least 2.5 mL of 0.1% QAMDHB solution used. On this basis, studies were carried out at QAMDHB amounts of 5.0 mL. This amount of QAMDHB is enough for the separation and preconcentration procedure because of the very low level of the investigated metal ion concentrations in real samples.

3.3. Effects of the resin amount

Also the amounts of solid phase extraction material are another important factor on the column studies for the quantitative recoveries of metal chelates [17,18]. The effect of the amount of MCI GEL CHP 20Y on the sorption of metal ions at pH 8.0 was examined in the range of 0.3–1.5 g. The results demonstrated that, quantitative recoveries (>95%) of the working elements were observed when the resin was used above 0.6 mg. Therefore, in the proposed procedure, 1.0 g of MCI GEL CHP 20Y resin is recommended.

3.4. Solid phase extraction

In order to study the adsorptive capacity of SP-850 resin, batch method was used. To 0.1 g resin was added to 50 mL of solution containing 1.0 mg of metal ion at pH 8.0 and QAMDHB existed. After shaking for 1.0 h, the mixture was filtered. Ten milliliters of the supernatant solution was diluted to 100 mL and the analyte ions were determined by graphite furnace atomic absorption spectrometry. This procedure was repeated for each analyte ions, separately. The capacity of 1 g of MCI GEL CHP 20Y was found 18 mg for chromium, 14 mg for nickel, 25 mg for silver, 20 mg for cobalt, 24 mg for copper, 12 mg for cadmium and 18 mg for lead.

The influence of flow rate on the adsorption of analyte ions was also studied. Flow rate in the range of $2–20 \, mL \, min^{-1}$ had no significant effect on the recoveries of the investigated elements. All subsequent experiments for this study were performed at $10 \, mL \, min^{-1}$ flow rate.
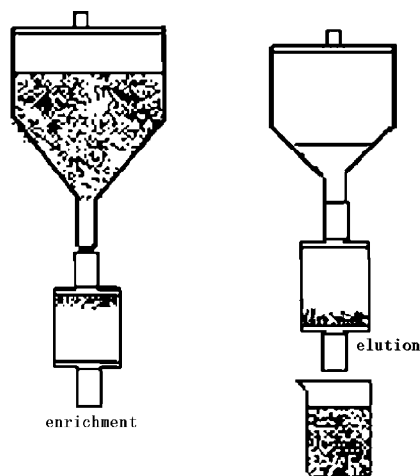
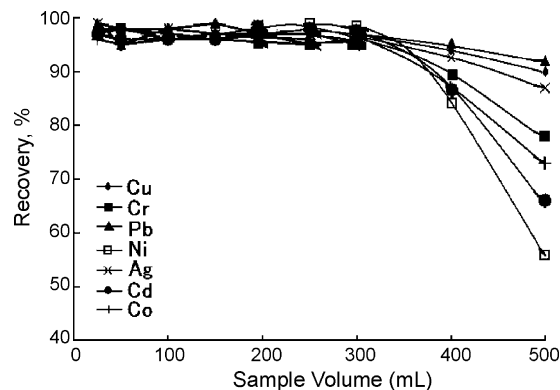**Fig. 4.** Eluting the metal ions in the reverse direction.

Fig. 5. Effect of the sample volume on the recoveries of analyte ions from the MCI GEL CHP 20Y column (pH: 8.0; ligand: QAMDHB; amounts of analytes: 10 μg Cu, 20 μg Cr, 20 μg Pb, 10 μg Ni, 10 μg Ag, 5 μg Cd, 10 μg Co; eluent: 1 mol L^{-1} HNO$_3$).

The desorption of the retained analyte metal ions from column was examined using various elution solutions. The quantitative recoveries (>95%) were obtained for the investigated elements with 1.0 mL of 0.5–3.0 mol L^{-1} HNO$_3$, 2.5 mL of 0.4–3.5 mol L^{-1} HCl, 3.0 mL of 1.0–3.5 mol L^{-1} H$_2$SO$_4$ and 3.0 mL of 1.0–2.5 mol L^{-1} HClO$_4$. The maximum enrichment factor was achieved when 0.5–3.0 mol L^{-1} HNO$_3$ was selected as eluent. Therefore, 1.0 mol L^{-1} HNO$_3$ was selected as eluent in this experiment.

Experiments have shown that it is easier to elute the retained metal ions in the reverse direction in comparison to the forward direction (only 1.0 mL of eluent was needed when eluted in reverse direction. However, 8 mL of eluent was needed when eluted in forward direction). Thus, it is also recommended to invert the column before elution (Fig. 4).

3.5. Effect of the sample volume

The effect of the sample solution volume on the metal sorption on MCI GEL CHP 20Y was studied by passing 20–500 mL volumes through MCI GEL CHP 20Y column at a 10 mL min^{-1} flow rate. The results were given in Fig. 5. The adsorption of the metal ions was not affected by sample volume when the volume is below 300 mL. However, the percent of analytes sorption decrease when the volume is above 300 mL. The recoveries of analytes decrease probably due to the excess analytes loaded over the column capacity with increasing sample volume above 300 mL. The adsorbed metals can be eluted with 1.0 mL of 1.0 mol L^{-1} HNO$_3$ and a preconcentration factor of 300 is achieved by this technique.

3.6. Effect of foreign ions

In order to evaluate the possibility of selective recovery of analyte ions in the presence of alkaline, earth alkaline metals and major anions of the real samples, the procedure has been performed with 50 mL solutions containing such ions. Quantitative recoveries (>95%) for 5000 mg L^{-1} of NaCl, for 2000 mg L^{-1} of Mg^{2+}, for 1000 mg L^{-1} of K^{+}, Ca^{2+}, SO$_4$$^{2-}$, 100 mg L^{-1} for Zn^{2+}, 50 mg L^{-1} for Al^{3+} were obtained. These tolerable levels of foreign ions were enough for the quantitative separation of analyte ions from the matrix of the real samples.

3.7. Calibration graphs and detection limits

Under the GFAAS analysis conditions, regression equations of metal ions were established based on the standard samples injected and their absorption signals. The results were shown in Table 2. The detection limits in the original samples (before applying the preconcentration procedure) were obtained based on three times the standard deviations of the blank. The results were also shown in Table 3.

3.8. Recovery of spikes from the samples

In order to estimate the accuracy of the procedure, different amounts of the investigated metal ions were spiked in water, soil and biological samples. The resulting solutions were submitted to the preconcentration procedure. Good agreement was obtained between the added and found analyte content using the recommended procedure. The recovery values for the analyte ions were in the range of 89–104%. These values were quantitative and it shows that the presented method can be applied for the separation/preconcentration of analyte ions. The relative standard deviation for the analyte ions (7 repeat determinations) were below 3.2%.

Table 2
Regression equation and detection limit

Metal ions	Regression equation[a]	Linearity range (μg/L)[a]	Coefficient, r	Detection limit (ng L^{-1})[b]
Cr	$A = 0.0346C$ (μg/L) + 0.0385	0.015–120	0.9992	1.4
Ni	$A = 0.0268C$ (μg/L) − 0.0476	0.012–190	0.9995	1.0
Ag	$A = 0.0214C$ (μg/L) − 0.0285	0.010–120	0.9994	0.85
Co	$A = 0.0314C$ (μg/L) + 0.0462	0.015–160	0.9992	1.2
Cu	$A = 0.0252C$ (μg/L) + 0.0287	0.012–180	0.9991	1.0
Cd	$A = 0.0287C$ (μg/L) + 0.0418	0.010–110	0.9990	1.2
Pb	$A = 0.0315C$ (μg/L) + 0.0226	0.012–150	0.9993	1.3

[a] In the preconcentrated solution.

[b] In the original samples before applying the preconcentration procedure.

Table 3
Determination results of certified standard biological samples

Samples	Standard value (μg/g)	By this method (μg/g)	R.S.D.% (n = 5)	Recovery%[a] (n = 5)
Rice (GBW08458)	Ag (0.127), As (0.285), B (64.5), Bi (0.342), Ca (2900), Cd (0.218), Ce (1.25), Co (4.71), Cr (3.76), Cu (10.2), Fe (54), Hg (0.086), Mg (360), Mn (22.5), Mo (0.735), Ni (3.83), Pb (0.852), V (2.86), Zn (13.2)	Ag (0.118), Cd (0.224), Cr (3.67), Cu (9.64), Hg (0.068), Ni (3.74), Pb (0.848)	≤3.2	91–98
Human hair (GBW08126)	Ag (–), As (0.121), B (38.4), Bi (0.825), Ce (0.643), Cd (0.528), Co (6.25), Cr (0.816), Cu (11.2), Fe (123), Hg (0.142), Mg (136), Mn (68.2), Ni (5.61), Pb (1.06), Sn (1.24), Se (0.0412), V (3.86), Zn (18.7)	Ag (–), Cd (0.534), Cr (0.86), Cu (12.4), Hg (0.133), Ni (5.64), Pb (1.10)	≤3.0	89–96

[a] The amount (μg) of metal ions added: Ag (0.01), Cd (0.02), Cr (0.02), Cu (0.05), Hg (0.01), Ni (0.02) and Pb (0.01).

Table 4
Determination results (μg/L) of the sample with this method

Components	Water samples (μg/L)				Soil sample (μg/g)	R.S.D.% (n = 7)	Recovery%[a] (n = 5)
	Pure water	Well water	Tap water	Lake water			
Ag	9.28	11.3	20.5	39.7	2.13	2.8	93–98
Ni	20.6	28.1	45.7	14.2	9.04	3.0	94–106
Hg	1.7	3.30	4.08	12.6	2.62	3.2	92–103
Cu	24.2	35.9	31.6	91.1	28.1	2.8	93–104
Cr	20.6	23.6	34.8	50.1	11.6	2.7	94–102
Cd	2.86	6.02	14.3	31.3	5.11	3.1	93–104
Pb	6.5	20.7	15.8	42.8	9.36	2.9	92–97

[a] The amount (μg) of metal ions added: Ag (0.01), Cd (0.02), Cr (0.02), Cu (0.05), Hg (0.01), Ni (0.02) and Pb (0.01).

Table 5
Determination results (μg/L) of the sample with ICP-MS method

Components	Samples (μg/L)				Soil sample (μg/g)	R.S.D.% (n = 7)
	Pure water	Well water	Tap water	Lake water		
Ag	9.08	12.9	22.4	37.4	2.31	3.5
Ni	22.8	29.7	44.1	13.8	9.28	3.2
Hg	1.89	3.12	4.2	13.5	2.42	3.4
Cu	25.1	37.1	29.8	90.8	29.3	3.6
Cr	19.3	22.8	35.4	48.7	12.8	3.8
Cd	2.95	6.26	14.7	32.8	5.26	3.7
Pb	6.38	19.9	17.6	44.2	9.45	3.6

3.9. Application to real samples

The solid phase extraction procedure presented for chromium, nickel, silver, cobalt, copper, cadmium and lead ions were applied to water, biological and soil samples. The results (deducted the reagents blank) for biological samples were given in Table 3, for water and soil samples were given in Table 4. For water and soil samples, a standard method using ICP-MS according to literature [16] had also been used as reference method and the results are shown in Table 5.

4. Conclusion

The developed method is successfully employed for analysis of water, soil and geological materials after successful validation. The developed method have the following advantages: the method is economic. Instead of the use of fresh solvent as an extracting phase for each sample, the reusability of MCI GEL CHP 20Y was as high as greater than 200 cycles without any loss in its sorption behavior. The elution was easily performed with $1.0 \, mol \, L^{-1}$ HNO_3, and the metal ions in 300 mL solution can be concentrated to 1.0 mL, representing an enrichment factor of 300 was achieved. The analytical performance of the method is comparable with other separation-preconcentration methods. The limits of detection of analyte ions are superior to those of some preconcentration/separation techniques for analyses [3,4,19–23]. The matrix effects with the method were reasonably tolerable. Also the method is relatively rapid as compared with previously reported procedures for the enrichment of traces metal ions.

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