Preconcentration and Determination of Ultra Trace Cobalt(II) in Water Samples Using Co(II)-Imprinted Diazoaminobenzene-Vinylpyridine Copolymers

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Cobalt(II) imprinted and non-imprinted copolymers were prepared by metal ion imprinted polymer (MIIP) technique. The copolymers were obtained by co-polymerizing cobalt chloride (or without it), diazoaminobenzene (DAAB) and vinylpyridine (VP) using ethyleneglycoldimethacrylate (EGDMA) as cross-linker in the presence of 2,2'-azobisisobutryonitrile as initiator. The separation and preconcentration characteristics of the copolymers for Co(II) were investigated by batch and column procedures. The results demonstrated that the Co(II) imprinted copolymers had higher adsorption capacity with the value of 205 µmol g^{-1} of dry copolymer, about 3.5 times of and good selectivity for Co(II) compare to non-imprinted copolymers (58.6 µmol g^{-1} of dry copolymer). The distribution ratio (D) values of the Co(II) imprinted copolymers increased for Co(II) with respect to both distribution ratio values of Zn(II), Cu(II), Co(II) and non-imprinted co-polymer. The relatively selective factor (α_r) values of Co(II)/Cu(II), Co(II)/Zn(II), Co(II)/Fe(II), are 36.7, 51.8, 86.7, respectively. The tolerance limit for other elec-trolytes such as NaCl, KBr, KI, NaNO$_3$, Na$_3$PO$_4$, Na$_2$SO$_4$ and Mg(NO$_3$)$_2$ is also remarkably improved with the values of 10-100-fold of the non-imprinted co-polymer. The Co(II) imprinted copolymers can be used at least 20 times with *ca.* 96 % recoveries. Based on the packed columns with Co(II) imprinted copoly-mers, a highly selective solid-phase extraction (SPE) and preconcentration method for Co(II) from dilute aqueous solution was developed. The MIIP-SPE preconcen-tration procedure showed a linear calibration curve within concentration range from 0.13 to 25 µg L^{-1}. The detection limit and quantification limit were 0.05 and 0.13 µg L^{-1} (3σ) for flame atomic absorption spectrometry (FAAS). The relative standard deviation of the eleven replicate determinations was 2.6 % for the deter-mination of 1.0 µg of Co(II) in 100 mL water sample. Determination of Co(II) in certified tap water and rain water demonstrated that the column was good enough for Co(II) determination in matrixes containing components with similar chemical properties such as Cu(II), Zn(II), Co(II).

Key Words: Solid-phase extraction, Metal ion imprinted polymer, Preconcen-tration, Co(II), Flame atomic absorption spectrometry, Water.

INTRODUCTION

Cobalt is an important trace element in nature and can be either essential or toxic for many biological systems depending on its concentration range[1-3]. It is clear that the determination of trace amount of cobalt in biological and environ-mental samples plays an important role in the fields of environmental surveillance, food control, medicine, toxicology and hygiene. Flame atomic absorption spectrometry

(AAS) is a simple and well available technique for the determination of cobalt in real samples. However its main problem is the low sensitivity for trace cobalt at µg L^{-1} level. This limitation can be overcome by the use of a preconcentration procedure. For this purpose, various preconcentration/separation methods including copreci-pitation[4], liquid-liquid extraction[5,6], ion exchange[7] and chelating sorbents[8-11] have been used. Because of possessing the advantages of high recovery, short analysis time, high enrichment factor, low consumption of organic solvents, solid phase extraction (SPE) technique have found increasing application for the preconcentration of trace cobalt and elimination of matrix interference prior to AAS analysis.

Up to now, several kinds of SPE sorbents such as chelating resin[8], C-18 bonded silica[10], polymeric supports[11,12], functionalized silica[13,14], functionalized cellulose[15,16], activated oxide[17,18] and activated carbon[19,20], have been used for the preconcentration and determination of cobalt. Of all the above solid phase extractants, silica gel bonded chelating ligands have gained growing interest in recent years[21,22]. Silica gel used as a solid support for chelating groups possesses some definite advantages[23]. It dose not swell or strain, has good mechanical strength and undergoes heat treat-ment. The synthetic methods of solid phase extractors and preconcentrators are mainly based on the surface modification of the solid supports by either the chemical immobilization or physical adsorption approach[24]. The modified solid sorbents are then used and applied in the fields of normal or selective solid phase extraction of the target species[25,26]. Such variations in the behaviour of the modified solid sorbents are mainly depend on the presence of some active donor atoms or groups such as O, N, S and P into the incorporated organic modifier. However, the selectivity of the modified solid phases toward certain metal ion(s) is attributed to several well-known factors such as the size of the organic modifier, the activity of the loaded surface groups, the type of the interacting donor atom and metal ion and the reported well-known phenomenon of hard-soft acid-bases[27]. Recently, an easy and efficient method was reported for the preparation of silica-based reagents[28,29].

To our best of knowledge, SPE and preconcentration by Co(II)-imprinted diazoamino-benzene-vinylpyridine copolymer packed-bed columns have not been employed for the separation and preconcentration of Co(II) from aqueous solution. This paper reports the synthesis of Co(II) imprinted and non-imprinted copolymers by copolymerizing cobalt chloride (or without it), diazoaminobenzene (DAAB) and vinylpyridine (VP) using ethyleneglycol dimethacrylate (EGDMA) as cross-linker in presence of 2,2'-azobisisobutryonitrile as initiator and its analytical applica-tions for column preconcentrative separation of Cd(II) from natural water.

EXPERIMENTAL

A Varian Model SpectrAA 220 (Mulgrave, Vic., Australia) atomic absorption spectrometer, equipped with a cobalt hollow cathode lamp and an air-acetylene flame was used for cobalt determination. The wavelength used for monitoring Co was 240.7 nm. The flow rates of air and acetylene were set as recommended by the

manufacturer. The pH measurements were carried out by using a Metrohm pH meter (model 780) with a combined pH glass electrode calibrated against two standard buffer solutions at pH 4.0 and 7.0. An Edward vacuum pump was used for filtration purposes. The flow rate of liquid through columns was controlled using a model BT00-600M peristaltic pump (Baoding Laonger Precision Pump Co. Ltd.).

Unless otherwise stated, all water is 18 MΩcm pure water purified with a Milli-Q system (Millipore, USA) and all reagents used were of analytical grade and all solutions were prepared with pure water. Standard labware and glassware used were repeatedly cleaned with HNO_3 and rinsed with pure water, according to a published procedure[30].

Stock solutions (containing Co(II), 1000 mg L^{-1}) of $Co(NO_3)_2 \cdot 6H_2O$ (Fluka) in water were purchased from Aldrich. The prepared cobalt standard solutions were stored in brown glass bottles with TFE-lined closures at 4 ℃ in a dark environment. The reference and working solutions were diluted daily from stock metal solutions. Other metal stock solutions (1000 mg L^{-1}) were prepared by dissolving appropriate amounts of nitrate in 1.0 % (v/v) HNO_3 and further diluted daily prior to use. The pH was adjusted with the following buffer solutions: $H_2C_2O_4/NaHC_2O_4$ for pH 2.0 and 3.0; CH_3COONa/CH_3COOH for pH 4.0-6.0. Na_2HPO_4/NaH_2PO_4 for pH 7.0; $Na_2B_4O_7/NaOH$ for pH 8-11; NaOH for pH 12-14. Diazoaminobenzene (DAAB) was procured from Aldrich (Milwaukee, USA). Azobisiso butyro-nitrile (AIBN) and thylene glycoldimethacrylate (EGDMA) were obtained from Fluka (Switzerland). 4-Vinyl pyridine was purchased from Merck (Darmstadt, Germany).

Preparation of cobalt(II) imprinted and non-imprinted copolymers: Diazoaminobenzene (DAAB) (10 mmol) and 10 mmol cobalt chloride was dissolved in 50 mL of methanol and kept for 2 h, then 40 mmol 4-vinylpyridine (VP), 200 mmol ethyleneglycol-dimethacrylate (EGDMA) and 0.4 g azobisiso-butyronitrile (AIBN) were added and dissolved in a ultrasonic water bath for 15 min. The polymerization mixture was flushed by bubbling N_2 for 10 min, sealed and heated at *ca.* 60 ℃ with stirring for 30 h. The solid formed was ground in a mortar and dried in constant temperature vacuum oven at 70 ℃ for 2 h. The resulting copolymers were grinded and screened, of which the 30-54 μm size were selected as experimental sorbents. The selected particles were treated with 1:4 (v/v) methanol/water for 10 h and then the mixed solution of 0.1 mol L^{-1} HCl and 0.5 mol L^{-1} thiourea till to remove all of Co(II) linked to the copolymer. Cobalt(II) imprinted copolymer was cleaned with pure water and then dried in a vacuum oven at 65 ℃ for 48 h. In the same way, non-imprinted copolymers were also prepared without cobalt chloride added. The repeated unit of Co(II) imprinted copolymers complex with Co(II) are shown in **Scheme-I**.

Batch procedure: In 100 mL polyethylene bottles, previously cleaned with detergent, pure water, dilute nitric acid and pure water in sequence, added 5 mL pH 8.0 buffer solution except for pH effect test with pH 1.0-12.0 buffer and 45 mL 2.0 $\times 10^{-7}$ mol L^{-1} metal ion solution except for sorption capacity measurement with the metal ion concentration of 0.05 to 5.0 $\times 10^{-5}$ mol L^{-1} and immersed 50 mg Co(II)
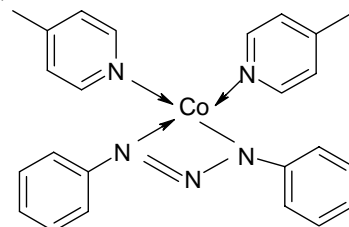
Scheme-I: Repeated unit of Co(II) imprinted copolymers complex with Co(II)

imprinted copolymer with shaking at 25 ºC. At pre-fixed time, an aliquot of the supernatant was separated and the metal ions were determined by FAAS or titration. The adsorbed copolymer was eluted with 0.1 mol L^{-1} of HCl + thiourea and the desorbed Co(II) was measured with complex titration or FAAS. The adsorption capacity, the distribution ratio, the selectivity factor of Co(II) with respect to Cu(II), Zn(II), Co(II) and the relative selectivity factor were calculated as the following equations:

$$Q = \frac{(C_0 - C_e)V}{W} \tag{1}$$

$$E = \frac{C_0 - C_e}{C_e} \tag{2}$$

$$D = \frac{Q}{C_e} \tag{3}$$

$$\alpha = \frac{D_{Co}}{D_M} \tag{4}$$

$$\alpha_r = \frac{\alpha_i}{\alpha_n} \tag{5}$$

where Q represents the adsorption capacity (μmol g^{-1}), C_0 and C_e are the initial and equilibrium concentration of Co(II) (μmol L^{-1}), W is the mass of copolymers (g) and V is the volume of metal ion solution (l), E is the extraction percentage (%), D is the distribution ratio (mL g^{-1}), α is the selectivity factor, D_{Co} and D_M represent the distribution ratios of Co(II) and Cu(II), Zn(II) or Co(II), respectively. α_r is the relative selectivity factor, α_i and α_n represent the selectivity factor of imprinted copolymer and non-imprinted one.

Column procedure: The stopcock of the glass column (100 mm in length and 10 mm in diameter) was covered with a fritted glass disc. A total of 500 mg of copolymers was slurred in water and then poured into the column. A small amount of glass wool was placed on the disc to prevent loss of the copolymer beads during sample loading. It was treated successively with 1.0 mol L^{-1} HCl and pure water. The column was preconditioned by passing a blank solution and then a solution containing 1.0 μg of Co(II) in a volume of 100 mL was passed through the column at a flow rate of 0.5 mL min^{-1} (controlled by a peristaltic pump) after adjusting pH

8.0. The column was washed with 15 mL pure water and the adsorbed Co(II) was eluted with 8 mL of 0.1 mol L^{-1} of HCl + thiourea and 2mL pure water and 100 μL eluent were injected to determine by FAAS.

Sample preparation: The certified tap water and rain water sample were prepared according to the previous procedure[15]. The surface tap water and rain water samples, collected from dirty region of Varamin in 2007. The Caspian sea water samples were Mhmoodabad. To oxidize organic matter such as humic acid, the tap water and rain water, sea water samples were digested by an oxidizing UV photolysis in the presence of 1 % H$_2$O$_2$ using a low pressure Co-lamp which was integrated into a closed quartz vessel[23,24].

A 100 mL of the above samples were percolated through the column packed with 500 mg of copolymers. The adsorbed analytes were eluted and analyzed according to the column procedure.

RESULTS AND DISCUSSION

Adsorption capacity of copolymers for Co(II): Adsorption of Co(II) from aqueous solution was investigated in batch experiments with shaking for 24 h. As can be seen in Fig. 1, the amount of Co(II) adsorbed per unit mass of poly-Co(II)-DAAB-VP increased with the initial concentration of Co(II) increase. In order to reach the 'saturation', the initial Co(II) concentrations were increased till the plateau values (adsorption capacity values) were obtained. The average maximum adsorption capacity of Co(II) imprinted copolymer (205 μmol g^{-1} dry copolymer) was about 3.5 times of non-imprinted one (58.6 μmol g^{-1} dry copolymer) for three replicate measurements.
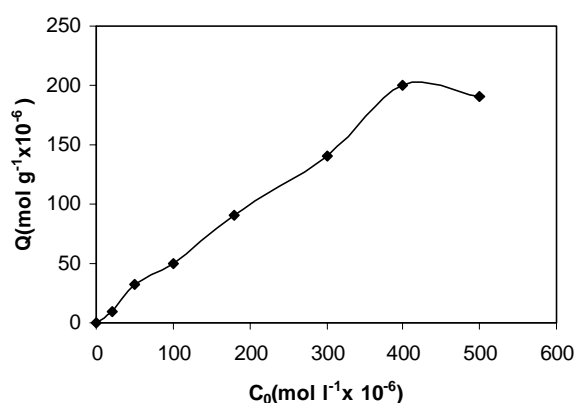

Fig. 1.   Effect of Co(II) initial concentration on the adsorption quantity of Co(II) imprinted copolymers. Other conditions, 50 mg of Co(II) imprinted copolymers; V 50 mL; pH 8.0; shaking time 24 h; temperature 25 ºC

Effect of pH: The effect of varying pH values on Co(II) uptake was investigated using the batch procedure with shaking for 1 h. It can be seen from Fig. 2, the

sorption quantity of Co(II) increases with the increase of pH values. The sorption quantity is very low owing to the protonation of Co(II) imprinted copolymers below pH 3.0, but the sorption capacity is increasing rapidly. After pH 5.0, the increasing rate is relatively very slow, the sorption capacity is near the maximum capacity at pH 8.0. So, pH 8.0 is chosen for this experiment.
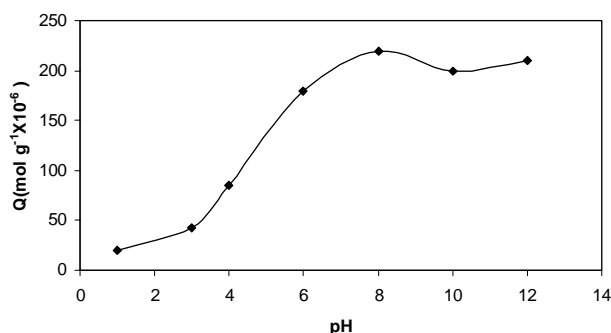

Fig. 2.   Effect of pH on sorption of Co(II) on Co(II) imprinted copolymers. Other conditions, 50 mg of Co(II) imprinted copolymers; $C_{Co(II)}$ 2.0×10^{-7} mol L^{-1}; V 50 mL; shaking time 2 h; temperature 25 ºC

Kinetics of Co(II) sorption: To determine the rate of loading Co(II) on the copolymers, batch experiments were carried out. The Co(II) concentration in suspensions was analyzed in 5 min interval. Fig. 3 shows that an equilibration time of *ca.* 1 h was required for 96 % sorption. Although the time ($t_{1/2}$) of 50 % sorption was less than 20 min, but it was longer than that obtained with the ordinary resins such as the modified Amberlite XAD series[31-33] this is derived from the high degrees of crosslinking.
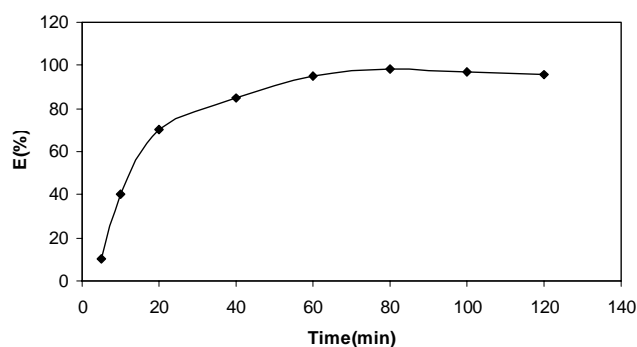

Fig. 3.   Kinetics of Co(II) sorption on Co(II) imprinted copolymers. Other conditions, 50 mg of Co(II) imprinted copolymers; $C_{Co(II)}$ 2.0×10^{-7} mol L^{-1}; V 50 mL; pH 8.0; temperature 25 ºC

Effect of temperature: The temperature effect experiments were carried out in the range of 10-50 ºC in consideration of the evaporation of cobalt species in real

analysis. The results showed that the adsorption of Co(II) with the imprinted co-polymer was slightly dependent on temperature with the adsorption capacity decreased 14 % due to the adsorption process were exothermal and the elution time was shortened 16 %. In this experiment, temperature 25 ºC were chosen for easy control.

Cobalt(II) imprinted copolymers stability tests: To test the copolymers stability, it was subjected to several loading and elution batch operations. The elution operations were carried out by shaking the copolymers with 25 mL of 0.1 mol L^{-1} of HCl + thiourea 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 % difference up to 20 cycles of repeated experiments. The Co(II) imprinted copolymers show good reusability and stability towards Co(II).

Effect of flow rate: The flow rate of the Co(II) solution through the packedbed column is a very important parameter for the time controls of adsorption and analysis. Using the column procedure, the effect of flow rate on sorption of Co(II) was investigated. The results show that the flow rate has more influence on the sorption of Co(II). Cobalt(II) can be adsorbed quantitatively by Co(II) imprinted copolymers at a flow rate below 1.0 mL min^{-1}. Above 1.0 mL min^{-1}, the recovery was less than 96 %, as shown in Fig. 4, it need longer time using Co(II) imprinted copolymers than using the ordinary copolymers to get equilibrium with the copolymers bed[31-33]. So, the flow rate of 0.5 mL min^{-1} was chosen for column procedures.
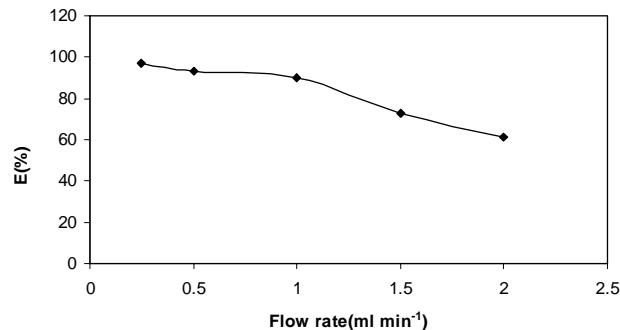

Fig. 4.   Effect of flow rate on the adsorption of Co(II). Other conditions, 500 mg of 30-54 μm Co(II) imprinted copolymers; $C_{Co(II)}$ 5.0×10^{-7} mol L^{-1}; V 100 mL; pH 8.0; temperature 25 ºC

Maximum sample volume, enrichment factor and elution breakthrough volume: The enrichment factor was studied by recommended column procedure using increasing volume of Co(II) solution and keeping the total amount of Co(II) loaded constant to 1.0 μg. The maximum sample volume can be up to 2000 mL with 96 % recovery. The eluent type was also studied in column procedure. The results show that 6 h was needed using 2.0 mol L^{-1} HCl or HNO_3 for 96 % recovery, whereas, 0.5 h was sufficient using 0.1 mol L^{-1} of HCl + thiourea. So, 8.0 mL 0.1 mol L^{-1} of HCl + thiourea and 2 mL pure water was used as eluent in all further experiments. Therefore, the highest enrichment factor of 200 can be obtained.

Selectivity of copolymers for matrix ions: The effect of the electrolytes commonly coexisted with Co(II), such as NaCl, KBr, KI, NaNO$_3$, Na$_3$PO$_4$, Na$_2$SO$_4$, Ca(NO$_3$)$_2$ and Mg(NO$_3$)$_2$ on the sorption of Co(II) was studied using the batch procedure with shaking 1 h. The results (Table-1) show that the selectivity of Co(II) imprinted copolymers for Co(II) over the investigated electrolytes was greatly improved with the tolerance limits 10-100-fold of the non-imprinted ones, indicating that the Co(II) imprinted copolymers can be suitably used as sorbent for Co(II) in high concentration of electrolytes. The reported tolerance limit is defined as the ion concentration causing a relative error $< \pm 5$ %.

TABLE-1
TOLERANCE LIMITS OF ELECTROLYTES (n = 3)

Copolymers	Electrolytes (mol L^{-1})							
	NaCl	KBr	KI	NaNO$_3$	Na$_3$PO$_4$	Na$_2$SO$_4$	CaSO$_4$	MgSO$_4$
Non-imprinted	0.01	0.01	0.005	0.01	0.001	0.005	0.05	0.05
Imprinted	0.05	0.05	0.010	1.00	0.050	0.050	1.00	1.00

Competitive adsorption of Co(II)/Cu(II), Co(II)/Zn(II), Co(II)/Fe(II), from their binary mixture was also investigated in batch procedure. The distribution ratio values of Co(II) imprinted copolymers show increase for Co(II), while decreasing significantly for Zn(II), Cu(II), Co(II) (Table-2). The α_r values for Co(II)/Cu(II), Co(II)/Zn(II), Co(II)/Fe(II), are 36.7, 51.8, 86.7, respectively. This means that Co(II) can be determined even in the presence of Cu(II), Zn(II), Fe(II). In order to further check the selectivity of the method for Cu(II), Zn(II), Fe(II) solution containing Co(II) and other metal ions were prepared and analyzed by the proposed procedure. Studies with 1.0 μg L^{-1} of Co(II) showed that the concentration of 25 μg L^{-1} Zn(II), Cu(II), Fe(II), did not interfere with Co(II) determination after the MIIP-SPE and preconcentration procedure.

TABLE-2
SELECTIVITY PARAMETERS OF COPOLYMERS FOR Co(II)

Metal ions	D$_i$	D$_n$	α_i	α_n	α_r
Hg(II)	1570	384	–	–	–
Cu(II)	34	156	73	2.68	36.7
Zn(II)	28	233	84	1.89	51.8
Fe(II)	35	406	75	1.05	86.7

D = Distribution ratio; α = Selectivity factor.

Accuracy and precision of the MIIP-SPE and preconcentration method: The opposed method was calibrated with a series of Co(II) standards having concentrations up to 25 μg L^{-1}. Calibration graphs obeyed the equation A = 3.02×10^{-2} C + 3.51×10^{-3} (r = 0.999), where A is the absorbance integrated area and C is the cobalt concentration in μg L^{-1}. The linear calibration curve within concentration range from 0.13 to 25 μg L^{-1}. The detection limit (3σ) and the quantification limit (10σ),

defined as by IUPAC[30,35,36] were found to be 0.05 and 0.13 µg L^{-1} for 100 mL samples, respectively, which are lower than the published methods[34,37]. The relative standard deviation of the 11 replicate determinations was 2.6 % for the determination of 1.0 µg of Co(II) in 100 mL water sample. The developed column preconcentration method was validated by ICP analysis (Table-3).

TABLE-3
DETERMINATION OF Co(II) IN TAP, SEA AND RAIN WATER
SAMPLES AND RELATIVE RECOVERY OF SPIKED Co(II)
IN TAP, SEA AND RAIN WATER SAMPLES

Sample	Concentration of Co(II) mean ± SD[a] (ng L^{-1})	Added Co(II) (µg^{-1})	Found Co(II) mean ± SD[a] (ng L^{-1})	ICP-AES	Relative recovery (%)
Tap water1[b]	15.6 ± 0.4	5.0	20.7 ± 0.4	20.2 ± 1.6	96
Sea water[c]	6.8 ± 0.5	5.0	11.5 ± 0.4	11.3 ± 1.6	98
Rain water[d]	7.2 ± 0.9	5.0	11.3 ± 0.6	11.7 ± 1.3	95
Tap water2[e]	n.d.[f]	10.0	9.8 ± 0.9	9.7 ± 1.2	96

[a]Standard deviation (n = 3); [b]From drinking water system of Tehran, Iran; [c]Caspian sea water, Iran; [d]Rain water (Tehran, 26 January, 2007); [e]Tap water (Varamin, taken after 10 min operation of the tap); [f]Not detected.

Application of the method: The proposed method was then applied for the determination of Co(II) in tap water, rain water and sea water samples. Meanwhile, the standard addition method was applied to check the selectivity of the imprinted copolymers for Co(II) against matrix elements. The recoveries were in the range of 94-105 %, demonstrating that the interference species in the matrix were eliminated after the MIIP-SPE and preconcentration procedure. The results given in Table-3 indicate the suitability of the present Co(II) imprinted copolymers for preconcentration of Co(II) from natural water samples.

Conclusion

The Co(II) imprinted and non-imprinted copolymers were prepared by thermal copolymerization with cobalt chloride (or without it), diazoaminobenzene (DAAB) and vinylpyridine (VP) using ethyleneglycol dimethacrylate (EGDMA) as cross-linker in the presence of 2,2'-azobisisobutryonitrile as initiator. Quantitative enrichment of cobalt(II) from very dilute aqueous solutions containing sub-microgram cobalt was achieved with Co(II) imprinted copolymers packed columns. The most important characteristics of the Co(II) imprinted copolymers is its excellent selectivity towards Co(II) over Cu(II), Zn(II), Fe(II), in spite of their similar chemical properties with Co(II) and other alkali and alkali earth metals which normally coexist with Co(II) in natural water compare to non-imprinted copolymers. But the Co(II) imprinted copolymers have some drawbacks such as long equilibration and elution time in comparison to the ordinary resins. This may make it difficult to be put into practical use and should be a subject of further investigations.

ACKNOWLEDGEMENTS

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