Asian Journal of Chemistry Vol. 21, No. 5 (2009), 3781-3787

Preconcentration of Some Trace Elements in Natural Waters as Their 8-Hydroxy Quinoline Chelates Using Amberlite XAD-4 Resin

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In this paper we have developed a simple and reliable method for the determination of Fe, Ni, As, Sn, Co and Mn ions in natural water samples by inductively coupled plasma optical emission spectrometry (ICP-OES), using solid phase extraction. The procedure is based on the retention of analytes in the form of 8-hydroxyquinoline (8-HQ) complexes on a mini column of XAD-4 resin and subsequent elution with nitric acid. The influence of various analytical parameters including the amount of solid phase, pH, elution factors (concentration and volume of eluting solution), volume of sample solution and amount of ligand on the extraction efficiency of analytes was investigated. The average relative standard deviations of the determinations were below 7 %. The limit of detection (3S, n = 12) for analytes were found in the range of 0.02-1.2 µg L^{-1}. The method was applied to the analysis of trace elements in some natural waters.

Key Words: Solid phase extraction, Amberlite XAD-4, Inductively coupled plasma-optical emission spectroscopy, 8-Hydroxyquinoline.

INTRODUCTION

Direct determination of trace elements in extremely low concentration by atomic absorption and inductively coupled plasma emission in many cases is difficult. This is not only due to the insufficient sensitivity of the methods, but also to the matrix effect. To accomplish this task many methods such as solvent extraction, co-precipitation, electro-deposition and solid phase extraction can be applied[1,2].

Solid phase extraction techniques are quite popular since they offer a number of important advantages over other preconcentration methods. One of these benefits is that sorbent material can be packed into mini-columns or cartridges which provide sufficient adsorption capacity for many applications[3].

Numerous substances have been proposed and applied as solid phase extraction sorbents, such as activated carbon[4], octadecyl bonded silica membrane disk[5,6], silica-gel[7], polyurethane foam[8], chelex 100, *etc*. Amberlite XAD resin family have also

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been used for the preconcentration of trace metal ions from various media such as natural water samples, urine, geological samples, *etc*. The family divided into two main groups: polystyrene-divinyl benzene resins including XAD-1, XAD-2, XAD-4, XAD-16, XAD-1180 and XAD-2000 and polyacrylic acid ester based resins including XAD-7, XAD-8 and XAD-11. One of the main advantages of polymeric adsorbent is their capability of extracting a large number of elements over a wide pH range[9-12]. Amberlite XAD-4 is a non-ionic cross linked polymeric adsorbent which derives its adsorptive properties from its patented macro reticular structure, high surface area and the aromatic nature of its surface. This structure gives Amberlite XAD-4 polymeric adsorbent excellent physical, chemical and thermal stability[13-20].

In this work, a simple and sensitive separation/preconcentration method have been established prior to ICP-OES determination of some trace metal ions in natural water samples. It involves complexation of the metal ions with 8-hydroxyquinoline followed by adsorption on Amberlite XAD-4 resin.

EXPERIMENTAL

An Optima 2100 DV inductively coupled plasma optical emission spectrometer (Perkin-Elmer Instruments, Shelton, CT, USA) was used for metal determination. The operation conditions and the analytical wavelengths are summarized in Table-1. Sample solution was driven through the columns with a multi-channel Heidolph PD 5001 peristaltic pump. The pH values were controlled with a Mettler Toledo MA235 pH meter (Mettler Toledo Instruments CO. LTD, Shanghai, China) supplied with a combined electrode. A self-made polytetrafluoroethylene (PTFE) mini-column (50 × 5 mm i.d.), packed with XAD-4, was used for separation/preconcentration.

TABLE-1
INSTRUMENTAL AND OPERATING CONDITIONS FOR ICP-OES MEASUREMENTS

Parameters	
RF power (watts)	1300
Nebulizer gas flow rate (L min^{-1})	0.8
Auxiliary gas flow rate (L min^{-1})	0.2
Plasma gas flow rate (L min^{-1})	15
Sample flow Rate (mL min^{-1})	1.5
Wavelength (nm)	Fe 238.204, Ni 221.648, As 193.696, Sn 235.485, Co 238.892, Mn 257.610

All chemicals used were of analytical-reagent grade. Deionized water was used throughout. Multi-element standard (various concentrations) and model solution were prepared by dilution of single element 1000 mg L^{-1} stock solutions. Nitric acid, hydrochloric acid, methanol and ammonia solutions were purchased from Merck. Amberlite XAD-4 (surface area, 750 m^2 g^{-1} and bead size, 20-50 mesh) were obtained from Fluka. Column experiments were performed with micro-particles prepared by crushing XAD-4 resins in a mortar, subsequently sieving into fractions. Fractions were cleaned thoroughly washed in the sequence of 1.0 mol L^{-1}

NaOH, deionized water, 2.0 mol L^{-1} HNO_3 and deionized water. It was finally washed with methanol and dried in the air. 8-Hydroxyquinoline (from Fluka) solution, (0.5 mol L^{-1}) was prepared in 2.0 mol L^{-1} hydrochloric acid.

XAD-4 column preparation: An 400 mg of XAD-4 resin (100-150 mesh) was introduced into a mini-column (50 × 5 mm i.d.) plugged with a small portion of glass wool at both ends. 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.

General procedure: The performance of proposed column was tested with model solution prior to its application to real water samples. A 100 mL of the model solution containing 2 µg each of Fe, Co, Mn and 10 µg Ni, As and Sn prepared and 200 µL of 8-hydroxyquinoline solution was added to form the metal-complexes. The pH was adjusted to desired value with addition appropriate volume of nitric acid and ammonia solution. The sample solution was passed through a cleaned and conditioned column at a flow rate of 6.0 mL min^{-1} by using a peristaltic pump. After loading further washing with buffer solution served to remove any sample still present in the column. Finally, the metal-complexes retained on the mini-column were eluted with 2.0 mol L^{-1} nitric acid solution. The eluted trace elements were measured by ICP-OES. The column could be used repeatedly after regeneration with 2.0 mol L^{-1} nitric acid solution, deionized water, methanol and deionized water, respectively.

Sample collection: Samples used for the developing of the analytical procedure were collected from Darband River in the north of Tehran, Iran and Karaj River in the city of Karaj, Iran.

All samples were collected in pre-cleaned high density polyethylene bottles. Collected samples acidified at pH lower than 2.0 by adding concentrated nitric acid in order to avoid metal adsorption on to the inner bottles walls then samples were filtered through a 0.45 µm polycarbonate membranes nucleopore filter.

RESULTS AND DISCUSSION

Effect of pH on the metal complexes formation: The pH value plays an important role in the complexation of 8-hydroxyquinoline with metals which form uncharged chelate complexes. This is because 8-hydroxyquinoline is an ampholyte, forming oxinium (8-hydroxy quinoliniun) ion by protonation of N in acid solutions and oxinate ion in basic solutions[21]. Most of the divalent and trivalent elements react with the oxinate form and the establishment of optimum pH values for the different elements is necessary.

In order to evaluate the effect of pH, the pH values of the sample solutions were adjusted in the range of 2-12 before the proposed method was applied. Each pH value was tested more than three times. The data corresponding to each element is shown in the Fig. 1. It can be seen that most of the studied metals are largely formed/retained at pH = 8. Quantitative recoveries were obtained in the pH range of (6-12) for Ni, Fe, Co, Sn while Mn and As are efficiency complexed and retained at pHs within (8-9.5). Therefore, the optimum pH was 8 for most of the studied metals.

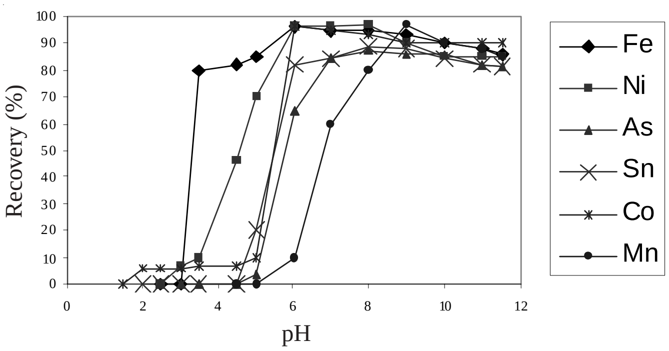

Fig. 1. Effect of pH on the recovery of Fe, Ni, As, Sn, Co and Mn

Effect of volume and concentration of nitric acid for elution: The eluent volume and concentration are other important factors which are studied in this paper. For these, different nitric acid solutions were tested in order to obtain optimum volume and concentration of eluent. Two nitric acid solutions, 2.0 and 4.0 mol L^{-1}, were simultaneously studied for eluting volumes between 2.5-10 mL. Result has shown those efficient metals elutions are reached under 5-10 mL nitric acid volume when using 2.0 mol L^{-1} nitric acid as eluting solution. Similar results have been obtained by using 4.0 mol L^{-1} nitric acid. Therefore, the lowest nitric acid concentration (2.0 mol L^{-1}) and the lowest nitric acid volume (5 mL) were chosen for most of the studied elements.

Effect of resin amount: The quantitative retention is not obtained by the smaller amount of resin than the optimum amount and the excess amount of resin also prevents the elution of the quantitative retained chelates by a small volume of eluent. To test the resin amount for quantitative retention of analytes, the column was filled with different amounts of Amberlite XAD-4 (200- 700 mg). The procedure was applied to the model solutions given above by use of these columns. The quantitative recoveries for all the examined analytes were obtained in range of 300-600 mg resin. As a result in all experiments 400 mg of XAD-4 was used.

Effect of sample volume: In order to explore the possibility of enriching low concentration of the metal ions from large volumes, the influences of the sample volume on the recoveries of the investigated metal ions were examined and maximum applicable sample volume was determined. The recoveries of the metal ions from different volumes of aqueous model solution containing the same amounts of the metal ions were tested in the range of 50-800 mL. The results were given in Table-2. The recoveries were found to be stable up to 400 mL of sample volume. The highest preconcentration factor was found to be 80 according to 5 mL of the final solution.

TABLE-2
EFFECT OF THE SAMPLE VOLUME ON RECOVERIES (%)
OF THE INVESTIGATED METAL IONS (n = 5)

Volume of sample (mL)	Fe	Ni	As	Sn	Co	Mn
50	101.7	101.8	91.6	94.2	102.7	98.6
100	102.2	101.0	86.5	89.4	103.2	100.8
200	99.4	99.5	87.7	91.3	100.7	101.4
400	104.1	97.9	94.3	92.6	100.4	99.0
600	90.6	92.6	86.0	90.4	86.7	86.8
800	84.0	73.3	78.0	81.3	78.4	75.1

Effect of ligand concentration: The concentration of 8-hydroxyquinoline as a chelating agent were also studied. The influence of the 8-hydroxyquinoline concentration on the recovery of the metals was investigated in the range of 10-400 µL, 0.5 mol L^{-1} 8-hydroxyquinoline solution using the aforementioned model solution. The results are given in Fig. 2. These results indicate that the recoveries of the metal ions increased with increasing concentration of added 8-hydroxyquinoline. The quantitative values were obtained after 5×10^{-5} mol L^{-1} of 8-hydroxyquinoline. After this point the recoveries were quantitative in all working range of 8-hydroxyquinoline. On this basis, studies were carried out at an 8-hydroxyquinoline concentration of 5×10^{-5} mol L^{-1}.

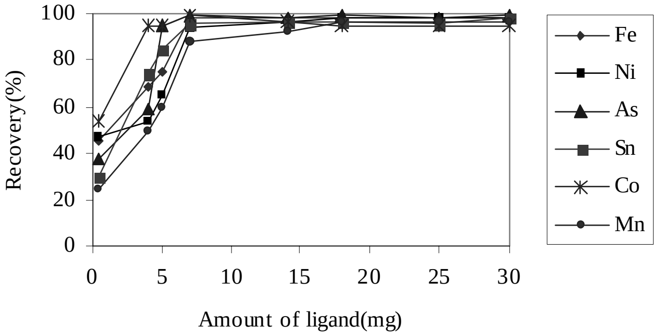

Fig. 2. Effect of amount of ligand on the recovery of Fe, Ni, As, Sn, Co, Mn

Effect of matrix ions: One of the challenging principles in preconcentration method is the elimination of interfering ions. The matrix related problems in river water analysis are alkali and alkaline earth metals (in the chloride form).

These matrices can cause some interference problems in the analysis of trace metals by ICP-OES. Fortunately, the method used here rejects more than 99 % of the interfering ions. The recoveries of interfering ions (Na, Mg and Ca) were less than 1 % in the preconcentration solution. The low values obtained might be due to the washing of the column with ammonium acetate solution before elution, the poor affinity of the 8-hydroxyquinoline for Na, Mg and Ca ions and the strong mobility of these metals, so their organic complexes are very weak or could not be found. The interferences effects resulting from the presence of major elements are very limited in present method which makes it suitable for the determination of metals in a complex matrix such as sea water.

Analytical performance of the method: The analytical performance of the method can be shown for the results obtained from ICP-OES measurements. The accuracy of the procedure was confirmed by the recoveries of spiked two water samples (100 mL of river water) with analyte quantities of 2, 4, 6 µg for Fe, Co, Mn and 10, 20, 40 µg for Ni, As, Sn. The recovery values are presented in the Table-3. As can be seen, good recoveries were reached for all elements which confirmed the accuracy of the procedure. The limit of detection given by LOD = 3 (SD) were calculated, where SD is the standard deviation of (n = 12) measurements of blank. After preconcentration factor of 80, limit of detections for Fe, Ni, As, Sn, Co and Mn were 0.06, 0.12, 0.66, 1.2, 0.02 and 0.08 µg L^{-1}, respectively.

TABLE-3
AVERAGE RECOVERY AS PERCENTAGE FOR ADDED ANALYTES TO KARAJ AND DARBAND RIVER WATER SAMPLES (n = 5)

	Added (µg)	Karaj river		Darband River	
		Found (µg)	R (%)	Found (µg)	R (%)
Fe	0	17.02 ± 0.12	-	3.073 ± 0.10	-
	2	19.30 ± 0.19	101.9	5.945 ± 0.41	103.6
	4	21.24 ± 0.80	102.5	7.970 ± 0.17	103.1
	6	23.84 ± 1.23	103.6	10.050 ± 0.44	103.7
Co	0	11.70 ± 0.62	-	3.710 ± 0.27	-
	2	13.50 ± 0.74	98.5	5.870 ± 0.05	96.2
	4	16.02 ± 1.30	98.0	7.930 ± 0.43	97.9
	6	17.84 ± 0.55	100.2	9.880 ± 0.15	97.7
Mn	0	N.D.	-	0.126 ± 0.20	-
	2	1.86 ± 0.17	93.0	2.050 ± 0.10	96.4
	4	3.84 ± 0.21	96.0	3.970 ± 0.15	96.2
	6	5.71 ± 0.36	95.2	6.020 ± 0.07	98.3
Ni	0	4.02 ± 0.09	-	3.710 ± 0.27	-
	10	14.13 ± 0.57	100.8	13.680 ± 0.30	99.8
	20	24.65 ± 1.51	102.6	24.010 ± 0.82	101.2
	40	43.83 ± 2.43	99.5	43.780 ± 0.64	100.1
As	0	N.D.	-	N.D.	-
	10	8.43 ± 0.20	84.3	8.900 ± 0.70	89.0
	20	17.92 ± 0.09	89.6	18.130 ± 0.61	91.0
	40	37.02 ± 1.70	92.5	37.920 ± 1.36	95.0
Sn	0	1.6	-	N.D.	-
	10	10.2 ± 0.49	88.0	8.640 ± 0.80	86.4
	20	18.4 ± 1.32	85.2	18.470 ± 1.40	92.3
	40	39.1 ± 0.67	94.0	38.300 ± 0.43	95.7

The repeatability of over-all procedure (solid phase extraction and ICP-OES) was assessed by analyzing a same river water sample three times. The average relative standard deviation (RSD) was lower than 7 %, respectively.

Conclusion

In this study we used XAD-4 resin as a sorbent material for separation and preconcentration of trace metals Fe, Ni, As, Se, Co and Mn (8-hydroxyquinoline complexes) from aqueous solution. The procedure is simple but requires clean instrument and high purity reagents. For this purpose a previous washing step with 2.0 mol L^{-1} HNO_3, is required to avoid contamination from the XAD-4 adsorbent packing material. Preconcentration of trace metals and elimination of matrix effects were successfully achieved which is one of the advantages of the method. So the proposed procedure can be extended to the determination of the investigated metal ions in the various samples having high salt contents as sea waters, urine and dialysis solutions. In addition, the sample volume required for this method is low when comparing to other methods and XAD-4 columns can be reused for several times without losing of analytical performances. At last, the proposed method demonstrated good sensitivity, precision and accuracy for all the analytes.

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(*Received*: 6 July 2008; *Accepted*: 17 February 2009) AJC-7251