Solid phase extraction method for the determination of iron, lead and chromium by atomic absorption spectrometry using Amberite XAD-2000 column in various water samples

Latif Elci [a,*], Aslihan A. Kartal [a], Mustafa Soylak [b]

[a] *Chemistry Department, Science and Arts Faculty, Pamukkale University, Denizli, Turkey*
[b] *Chemistry Department, Science and Arts Faculty, Erciyes University, Kayseri, Turkey*

Abstract

This work describes a procedure for the separation–preconcentration of Fe(III), Pb(II) and Cr(III) from some water samples using a column-filled Amberlite XAD-2000 resin. The analyte ions retained on the column were eluted with $0.5 \, mol \, L^{-1}$ HNO_3. The analytes in the effluent were determined by atomic absorption spectrometry. Several parameters governing the efficiency of the method were evaluated including pH, resin amount, sample volume, flow rates, eluent type and divers ion effects. The recoveries under the optimum working conditions were found to be as $100 \pm 1\%$ Fe, $96 \pm 1\%$ Pb and $93 \pm 2\%$ Cr. The relative standard deviations and errors were less than 2% and 5%, respectively. The detection limit based on three standard deviations of the blank was found to be 0.32, 0.51 and $0.81 \, \mu g \, L^{-1}$, for Fe, Pb and Cr, respectively. The procedure was applied to the determination of Fe, Cr and Pb in hot spring water and drinking water samples.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Solid phase; Preconcentration; Iron; Lead; Chromium; Hydroxide

1. Introduction

The interest in the determination of trace heavy metal ions, such as iron, lead and chromium in natural waters has increased immensely during the last few decades because of the environmental problems and public health studies.

Among heavy metals, iron in small amounts is an essential element for most life on Earth, including humans and animals. It is well known that an iron deficiency is the most common cause of anemia. On the other hand, too much iron can cause a several health problems. High levels of iron are associated with an increased risk for cancer, heart disease, and other illnesses such as endocrine problems, arthritis, diabetes, and liver disease [1]. A sanitary security limit for iron was restricted to $2 \, mg \, L^{-1}$ by World Health Organization [2]. European Legislation has established a maximum contaminant level (MCL) at $200 \, \mu g \, L^{-1}$ for iron [3].

Lead is extremely toxic even at very low levels. It is known that lead is health-endangering metal for humans and animals and its effects include blood enzyme changes, hyperactivity, and neurological disorders [4]. The maximum allowable Pb in drinking water is restricted to $20 \, ng \, mL^{-1}$, by international regulations on water quality including WHO, EPA, EU and other authorities [5,6]. The standard value for lead as a water pollutant is $0.01 \, mg \, L^{-1}$ in Japan [7].

Chromium(III) is an essential trace element in human nutrition, required for the maintenance of normal glucose, cholesterol, and fatty acid metabolism. Insufficient dietary intake of chromium(III) leads to increases in risk factors associated with diabetes and cardiovascular disease including elevated circulating insulin, glucose, triglycerides, total cholesterol and impaired immune function. On the other hand, water soluble Cr(VI) is extremely toxic and carcinogenic owing to its ability to oxidize other species [8–10]. The Environmental Protection Agency (EPA) of USA has set the maximum level of total chromium allowed in drinking water at $100 \, \mu g \, L^{-1}$ [11]. Chromium is normally presented at very low concentration, such as in the $0.1–0.5 \, \mu g \, L^{-1}$ range, in natural waters [12].

* Corresponding author. Tel.: +90 258 2125552.
E-mail address: elci@pamukkale.edu.tr (L. Elci).

Due to the very low concentrations of iron, lead and chromium in natural water samples as described above, their determinations in those samples demand very sensitive analytical techniques including ET-AAS, ICP-MS, ICP-AES and XRF. However, relative to flame AAS, these techniques have some disadvantages such as its high cost, slowness and greater proneness to matrix interferences as well as their high sensitive advantages. Flame atomic absorption spectrometry (FAAS) is, in principle, a suitable technique because of the low cost and easiness in usage. However, the main two problems for the determination of heavy metal ions by FAAS are the low concentration of analytes as heavy metals and high concentration of main components of real samples [13]. Separation–preconcentration procedures can solve the above main problems and leads to simplified heavy metal determination. A separation–preconcentration method improves the detection limit and selectivity of flame atomic absorption spectrometry [14–16]. Also, the preconcentration procedure is an essential step for the accurate determination of the various metal species by ET-AAS [17,18], ICP-MS [19,20], ICP-OES [21] and XRF [22]. The separation, preconcentration and determination processes of trace metal ions from different matrices, especially water samples, are mainly based on the utilization and application of a number of available techniques. These include solid phase extraction (SPE) [17–22], co-precipitation [16,23], ion-exchange [24] and flotation, etc. [25].

Among preconcentration methods, solid phase extraction has some advantages over other preconcentration methods in view of: (i) ease regeneration of solid phase; (ii) high preconcentration factor; (iii) reusability of the adsorbent; (iv) low consumption of reagents; (v) ease of automation; (vi) ecofriend methods; (vii) ease usage. The most extensively used solid phase extractants are modified C-18 silica [26], activated carbon [27], alumina [28,29] and Amberlite XAD resins [30–32]. It would appear that the most successful and popular applications of SPE are to use Amberlite XAD resins, because of good adsorption properties such as large surface areas and good hydrophobic nature. However, the use of Amberlite XAD-2000 resin in Amberlite XAD resin series is limited in preconcentration studies [33–35]. Amberlite XAD-2000 is a polystyrene–divinylbenzene copolymer having specific surface area: $620 \, m^2 \, g^{-1}$, dipole moment: 0.3, pore size: 4.5 nm and bead size: 20–50 mesh [35]. Because of these important properties, it has selected as a solid phase extractant in this work.

The aim of this work was the development of a solid phase extraction procedure for preconcentration of lead, iron and chromium based on the use of a column-filled Amberlite XAD-2000 resin as a solid phase extractant, prior to flame atomic absorption spectrometric determination.

2. Experimental

2.1. Materials and solutions

All chemicals used in this work, were of analytical reagent grade and were used without further purification. Ultra-pure (UP) quality water ($18.2 \, M\Omega \, cm^{-1}$) obtained using a reverse osmosis system (Human corporation, Seoul, Korea) was used throughout to prepare all solutions. All the plastic and glassware were cleaned by soaking in dilute HNO_3 (1 + 9) and were rinsed with distilled water prior to use. The standard and working solutions of Fe(III), Pb(II), Cr(III), Cu(II), Cd(II) and Ni(II) were prepared daily, through the appropriate dilutions of a $1000 \, mg \, L^{-1}$ stock solution of the respective analyte (atomic absorption grade, Carlo Erba). Hydrochloric and nitric acid solutions used as eluents were prepared by direct dilution with UP water from the concentrated solutions (Merck Darmstadt, Germany). EDTA solutions ($0.01–0.1 \, mol \, L^{-1}$) as eluent were prepared from solid $Na_2H_2Y \cdot 2H_2O$ (Merck Darmstadt, Germany) in UP water. NaOH solution was prepared from solid NaOH (Merck Darmstadt, Germany) with the water.

Acetate buffer solutions for pH 4, 5 and 6 were prepared by mixing of appropriate volumes of $1 \, mol \, L^{-1}$ acetic acid (Merck, Darmstadt) and $1 \, mol \, L^{-1}$ sodium acetate solutions (Merck, Darmstadt). For pH 7, a 250 mL of phosphate buffer was prepared by adding of $1 \, mol \, L^{-1} \, H_3PO_4$ to 0.4 g NaOH. Ammonium/ammonia buffer solutions pH 8, 9 and 10 were prepared by mixing of appropriates amounts of $0.1 \, mol \, L^{-1}$ ammonia (Merck, Darmstadt) and $0.1 \, mol \, L^{-1}$ ammonium chloride solutions (Merck, Darmstadt). pH of the buffer and the buffered solutions were controlled with a digital pH meter (Hanna pH 211 model).

Amberlite XAD-2000 resin having 0.25–0.48 mm particle size from Sigma (RT 1-0393) was grounded to 0.1–0.2 mm and washed with the procedure reported previously [36]. 1,5-Diphenylcarbazide (DPC) solution, 0.05%, was prepared by dissolving the required amount of DPC in ethyl alcohol immediately before use.

2.2. Instrumentation

A Perkin-Elmer model AAS 700 atomic absorption spectrometer was used in the determination of metals in standard solutions and in the eluents during preconcentration studies. All measurements of metal concentrations investigated in the optimization studies of solid phase extraction were carried out in air/acetylene flame. Instrumental parameters for metal determination were those provided by the manufacturer. The spectral lines of Fe 248.3 nm, Pb 283.3 nm, Cr 357.9 nm, Cu 324.8 nm, Cd 228.8 nm and Ni 232.0 nm were selected for the absorbance measurements. The spectral slit widths of Fe, Pb, Cr, Cu, Cd and Ni were set to 0.2, 0.7, 0.7, 0.7, 0.7 and 0.2 nm, respectively.

The determination of iron in the eluent obtained with SPE for the water samples was carried out by Flame AAS. Lead and chromium in the eluent were determined using A Perkin-Elmer AAnalyst 700 Atomic Absorption Spectrometer equipped with an electrothermal atomizer HGA 800, an autosampler AS-70 and a deuterium-lamp background correction system.

Uncoated graphite furnaces (Perkin-Elmer, Germany, part no.: B0070699) were used as an atomizer. All measurements were performed in the peak area mode. Operating parameters of graphite furnace for the determination of lead and chromium by GFAAS was programmed according to the manufacturer recommendations (Table 1).

Table 1
Graphite furnace program for the determination of Pb and Cr by GFAAS

Steps	Temperature (°C)/ramp time (s)/hold time (s)	
	Lead	Chromium
Drying 1	100/5/20	100/5/20
Drying 2	140/15/15	140/15/15
Pyrolysis	850/10/20	1650/10/20
Atomization	1650/0/5	2500/0/5
Cleaning	2600/1/3	2600/1/3

Gas flow (argon) was set to $0\,mL\,min^{-1}$ for atomization step and $250\,mL\,min^{-1}$ for the other steps.

2.3. Sampling

The water samples were collected from four different stations in Denizli. One of four samples was drinkable from Caybasi, the others were hot spring water from Pamukkale, Karahayit and Kaklik cave. The distance between Karahayit and Pamukkale is almost 5 km. Karahayit water is known as red-water by local public because of red-brown appearance sourced its high iron content and drunk by some of visiting people. Kaklik cave is almost 25 km to Pamukkale. The fantastic cotton castles created by Kaklik cave and Pamukkale (open area) waters likes to each other as appearance.

The water samples were collected in polyethylene bottles washed with detergent, pure water, dilute HNO_3 and pure water, respectively. Before the analysis, the samples were filtered through a cellulose membrane filter (Millipore) of pore size $0.45\,\mu m$.

2.4. Column

The glass column, having a stopcock and a porous disk, was 10 cm long and 1.0 cm in diameter. A small amount of glass wool was placed on the disc to prevent loss of the resin beads during sample loading. Then, 500 mg of Amberlite XAD-2000 resin was slurried in water, and then poured into the column. The resin was preconditioned under optimum pH. The bed height of resin in the column was approx. 20 mm. It was washed successively with water, acetone and water, respectively. It was conditioned with 10–15 mL of pH 9 buffer. The resin bed was washed with plenty of distilled water until neutral pH and subsequently reused.

2.5. General procedure for preconcentration

The performance of column method was tested with model solution prior to its application to waste water samples. For this, 25 mL of the model solution containing $20\,\mu g$ Fe(III), Pb(II) and Cr(III), $5\,\mu g$ Cu(II), Cd(II) and Ni(II) was buffered to desired pH. Four milliliters of 0.05% m/v DPC solution was added to form the metal–DPC chelates. After 5–10 min, the solution was loaded to the column. The flow of sample solution through the column was gravitationally performed at range of $1.0–2.5\,mL\,min^{-1}$. The flow rate of solution was controlled by use a stopcock of column. After passage of the solution fin-

ished, the column was washed with an aqueous solution adjusted to the working pH. Then, the retained metals were recovered from the column by the aid of 5–10 mL of $0.5\,mol\,L^{-1}$ HNO_3 at $1.0\,mL\,min^{-1}$ of flow rate. The metal concentrations in the eluent solution were determined by a flame atomic absorption spectrometer (FAAS).

2.6. Determination of metal ions in water samples

For the preconcentration procedure, pH of the sample, 250 mL, was adjusted to 9 by ammoniacal buffer. Then, the DPC solution was added. After 10 min, the sample was passed through the column at a $2.5\,mL\,min^{-1}$ flow rate. The metal chelates retained through the XAD-2000 column were eluted with 5 or 10 mL of $0.5\,mol\,L^{-1}$ HNO_3. The determination of iron in the eluent solution was carried out by FAAS. Lead and chromium in the eluent were determined by graphite furnace atomic absorption spectrometry (GFAAS).

3. Results and discussion

Some preliminary experiments were carried out in order to investigate quantitative retention of Fe(III), Pb(II), Cr(III), Cu(II), Cd(II) and Ni(II) ions as analytes by Amberlite XAD-2000 resin column in the absence and presence of diphenylcarbazide as a complexing agent.

3.1. Effect of acidity

The influence of the pH of test solutions on the recovery of $20\,\mu g$ Fe(III), Pb(II), Cr(III), and $5\,\mu g$ Cu(II), Cd(II) and Ni(II) from 25 mL solutions was studied in the pH range 4.0–10.0. The pH was adjusted by using $1\,mol\,L^{-1}$ nitric acid or $1\,mol\,L^{-1}$ sodium hydroxide. The recoveries of analyte ions are fewer than 20% in the pH range 4.0–10.0.

The above experiment was repeated using the buffer solutions, instead of $1\,mol\,L^{-1}$ nitric acid or $1\,mol\,L^{-1}$ sodium hydroxide solutions. The results shown in Fig. 1 indicate that the Pb(II) and Cr(III) ions can be retained quantitatively at pH 9.0. The retention for Fe(III) was quantitative in the
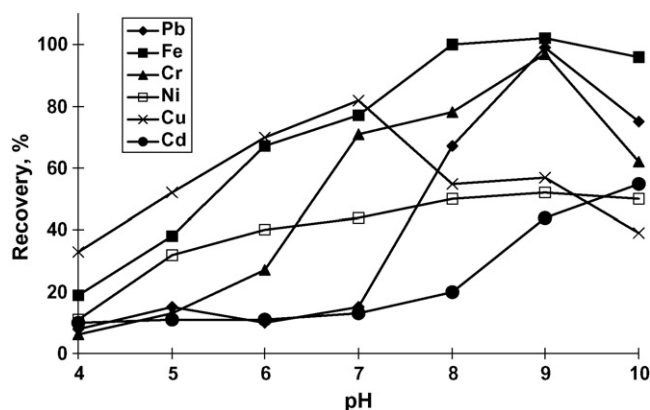

Fig. 1. Effects of the pH of sample on the retention of Fe(III), Pb(II) and Cr(III) without adding diphenylcarbazide by aid of buffer solution.

pH range of 8–10. Especially, due to the low solubilities of Fe(OH)$_3$ ($K_{sp} = 1.6 \times 10^{-39}$), PbO ($K_{sp} = 8.0 \times 10^{-16}$) and Cr(OH)$_3$ ($K_{sp} = 1.6 \times 10^{-30}$), it may be explained that Fe(III), Pb(II) and Cr(III) can be retained as hydroxides by the column. Also, the formation of Cu(II), Cd(II) and Ni(II) hydroxides is expected under the same conditions. However, because of the formation of soluble amine complexes of these ions by ammonia coming from the buffers used in the pH range 8.0–10.0 (ammonium/ammonia buffers), it may be offered that these elements are not quantitatively retained. On the other hand, the pronounced decrease in the recovery of Fe(III) in presence of phosphate buffer (pH 7) is probably because of the formation of soluble Fe(III)–phosphate complexes in aqueous solutions. The decreases on the recoveries of Pb(II) and Cr(III) ions in solutions having pH < 9 may be due to the possible decomposition of their hydroxides. In addition, because of the possible formation of hydroxo-complexes of Pb(II) and Cr(III) at pH −10, their recoveries are under 95%. Fe(III) does not form the stable complexes with hydroxide ion. Therefore, there is no important decrease in the recovery for Fe(III) at pH 10. After these findings, the study was continued for Fe(III), Pb(II) and Cr(III) at pH 9.

3.2. Effect of sample volume on retention

The recoveries of the analytes from sample solutions in different volumes were evaluated using the test solutions buffered to pH 9. Fe(III) and Cr(III) up to 100 mL and, Pb(II) up to 50 mL were quantitatively recovered (Table 2). According to this result, the preconcentration factors of Fe(III), Cr(III) and Pb(II) for 5 mL of eluent were 20, 20 and 10, respectively.

To evaluate the retention of Fe(III), Cr(III) and Pb(II) from larger sample volumes, the effect of diphenylcarbazide (DPC) on their retention was investigated. In presence of DPC, the effect of pH was firstly examined on the retention. The results given in Fig. 2 indicate that the retentions of Fe(III), Pb(II) and Cr(III) were quantitative at pH 9, but the retentions of Cu(II), Cd(II) and Ni(II) were not quantitative. The results obtained for Fe(III), Pb(II) and Cr(III) in presence and absence
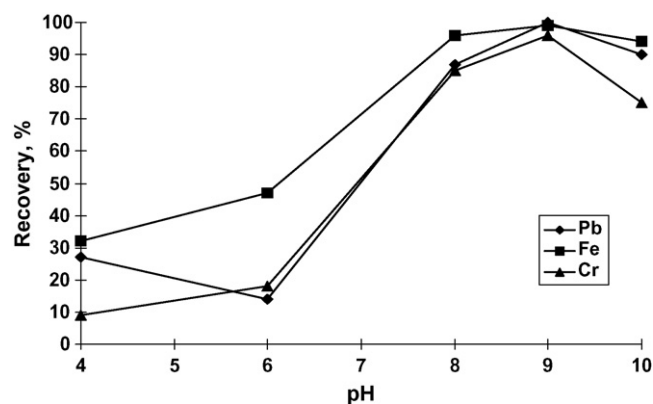
Fig. 2. Effects of the pH of sample on the retention of Fe(III), Pb(II) and Cr(III) with adding diphenylcarbazide by aid of buffer solution.

of DPC like each other. However, the sample volumes, which it was obtained quantitative recoveries, increased to 250 mL for Fe(III) and Cr(III), and 500 mL for Pb(II) in presence of DPC (Table 2). So, by adding DPC prior to passing of sample solution through the resin, the preconcentration factors obtained for Fe(III), Cr(III) and Pb(II) were found to be 50, 50 and 100, respectively.

A complex between diphenylcarbazide and chromium(III) does not form, while the formation of Fe(III)–DPC and Pb(II)–DPC chelates is expected [37,38]. In this work, the retained Fe(III), Pb(II) and Cr(III) in presence of DPC are eluted easily with 0.5 mol L^{-1} HNO$_3$ solution. It could be concluded that the retention factors obtained here for analytes are rather the result of precipitation of metal hydroxides in experimental conditions than formation of chelates. However, the results show that the interaction between DPC and Amberlite XAD-2000 resin particles influences positively retention properties of the resin. It may be due to synergic effect. Because, the sample volume reached in presence of DPC is larger than the volume obtained in absence of DPC (Table 2). In addition, the recoveries for Pb and Cr in presence of DPC are slightly bigger than the recoveries in absence of DPC at pH 8 and 9 (Figs. 1 and 2). After the findings above, all the further preconcentration studies were carried out by using DPC at pH 9.

Table 2
Effect of sample volume on retention of Fe(III), Pb(II) and Cr(III) in presence or absence of diphenylcarbazide

Sample volume (mL)	Recovery (%) in presence of diphenylcarbazide (n = 3)			Recovery (%) without diphenylcarbazide (n = 3)		
	Fe(III)	Pb(III)	Cr(III)	Fe(III)	Pb(III)	Cr(III)
25	101	103	102	99	100	94
50	100	100	90	98	94	92
100	106	92	94	94	79	93
150	–	–	–	82	50	85
200	–	–	–	88	50	86
250	100	98	97	–	–	–
400	83	95	79	–	–	–
500	86	97	84	–	–	–
600	75	77	77	–	–	–
750	86	85	64	–	–	–
1000	64	46	50	–	–	–

(–) not worked.

Table 3
Effect of different eluents on the recoveries of Fe(III), Pb(II) and Cr(III) (eluent volume: 10 mL, $n = 3$)

Eluent	Recovery (%)		
	Fe(III)	Pb(II)	Cr(III)
Acetone	25 ± 1	32 ± 1	13 ± 1
1 mol L^{-1} HNO$_3$ in acetone	100 ± 2	98 ± 2	96 ± 2
1.5 mol L^{-1} HNO$_3$	100 ± 1	100 ± 1	96 ± 3
1 mol L^{-1} HNO$_3$	103 ± 2	93 ± 1	98 ± 1
0.5 mol L^{-1} HNO$_3$	102 ± 3	103 ± 2	102 ± 1
1.5 mol L^{-1} HCl	100 ± 2	100 ± 2	96 ± 1
0.01 mol L^{-1} EDTA	13 ± 1	94 ± 1	<5
0.05 mol L^{-1} EDTA	17 ± 1	100 ± 2	<5
0.1 mol L^{-1} EDTA	12 ± 1	93 ± 2	<5

Table 4
Effect of different salts and ions on preconcentration (pH 9, $n = 3$)

Ions	Added as	Tolerance limits (mg L^{-1})		
		Fe(III)	Pb(II)	Cr(III)
Na$^+$	NaNO$_3$	5000	5000	5000
Ca^{2+}	Ca(NO$_3$)$_2$	2000	2000	1500
Mg^{2+}	Mg(NO$_3$)$_2$	2000	2000	1250
K$^+$	KCl	2000	2000	2000
Cl$^-$	NaCl	3000	3000	3000
CO$_3$$^{2-}$	Na$_2$CO$_3$	2000	1500	1000
HCO$_3$$^-$	NaHCO$_3$	2000	1500	1250
SO$_4$$^{2-}$	Na$_2$SO$_4$	3500	3250	3000

3.3. Elution

The effect of different solutions on the elution of Fe(III), Pb(II) and Cr(III) retained by the Amberlite XAD-2000 resin column is given in Table 3. Fe(III), Pb(II) and Cr(III) retained on Amberlite XAD-2000 column in presence of DPC could be completely eluted with 0.5 mol L^{-1} HNO$_3$ or more concentrated HNO$_3$. Also, the analytes were completely eluted with 1.5 mol L^{-1} HCl, 1 mol L^{-1} HNO$_3$ in acetone and pure acetone. On the contrary to many other papers, it was not necessary to extract the analytes with 1 mol L^{-1} HNO$_3$ in acetone or pure acetone where the eluent was evaporated to near dryness at 35 °C and diluted with HNO$_3$ prior to the determination of Fe(III), Pb(II) and Cr(III) by AAS [31]. So the analysis time of the proposed procedure is shorter than that of those procedures. On the other hand, while lead is eluted with EDTA solution in the concentration range of 0.01–0.1 mol L^{-1}, iron and chromium were not eluted quantitatively.

As a result, in order to elution of the three analytes from the column at the same time, 0.5 mol L^{-1} HNO$_3$ solution was selected as an eluent. The needed volume of 0.5 mol L^{-1} HNO$_3$ was found to be 5 mL to obtain quantitative recovery for the analyte ions.

3.4. Effect of flow rate on retention and recovery

The effect of flow rates of sample and eluting solutions from the column on the retention and recovery of Fe(III), Pb(II) and Cr(III) ions was studied. It was found that the sample solution flow rates in the range of 1–2.5 mL min^{-1} had no significance

influence on the quantitative retention of Fe(III), Pb(II) and Cr(III) by the XAD-2000 column. On the other hand, quantitative elution of Fe(III), Pb(II) and Cr(III) ions from the column was achieved in a flow rate range of 1.0–5.0 mL min^{-1}, using 5 or 10 mL of 0.5 mol L^{-1} HNO$_3$. At higher flow rates (after 5 mL min^{-1}), the larger volumes of 0.5 mol L^{-1} HNO$_3$ is necessary to obtain the quantitative recoveries of Fe(III), Pb(II) and Cr(III).

3.5. Resin amount and reusability

The influences of amounts of Amberlite XAD-2000 on the retention of Fe(III), Pb(II) and Cr(III) were examined in range of 250 and 600 mg under the optimized working conditions. The recovery values for Fe(III), Pb(II) and Cr(III) were not quantitative up to 400 mg of XAD-2000. Quantitative recovery values were obtained in the 400–600 mg range of XAD-2000. Accordingly, 500 mg of XAD-2000 resin in the all experiments were used.

The column-filled 500 mg XAD-2000 can be reused over 500 cycles of adsorption–desorption without any significant change (less than 5%) in the retention of Fe(III), Pb(II) and Cr(III).

3.6. Effect of diverse ions

To detect potential interference on the preconcentration of Fe(III), Pb(II) and Cr(III) ions, various salts and ions were added to 50 mL of a solution containing 5.0 µg of Fe(III), Pb(II) and Cr(III) ions and the preconcentration procedure was applied. The tolerance limit (relative error; ±<5%) is given in Table 4.

The tolerance limits in Table 4 and the quantitative recoveries of various Fe(III), Pb(II) and Cr(III) spikes in Table 6 show that

Table 5
Content of hot spring waters and drinking water

Stations	Temperature (°C)	Conductivity (mS cm^{-1})	pH	Cations (mg L^{-1})				Anions (mg L^{-1})		
				Na$^+$	K$^+$	Ca^{2+}	Mg^{2+}	HCO$_3$$^-$	Cl$^-$	SO$_4$$^{2-}$
Pamukkale (Jandarma) [39]	35.5	2550	6.06	48.76	50.7	1923	378.60	1195.60	17.75	2910.70
Karahayit [39]	55	3750	5.85	60.49	69.81	452	15.55	1244.40	28.40	3688.30
Kaklik [40]	23.5	2000	6.85	–	–	286.17	110.62	–	31.6	–
Caybasi[a]	14	468	7.28	–	–	72	61	–	–	172.80

(–) not determined.
[a] The results obtained in our lab.

the presence of Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^- at high concentrations has no significant effect on the retention performance of Amberlite XAD-2000 column. On the other hand, the contents of Na^+, K^+, Mg^{2+}, Ca^{2+}, HCO_3^-, Cl^- and SO_4^{2-} of the analysing water samples given in Table 5 were less than the tolerance limits in Table 4. Thus the procedure is highly selective and may safely be applied for the determination of Fe(III), Pb(II) and Cr(III) in salinity water samples such as spring hot waters.

3.7. Method validation and analytical performance

The validation, preconcentration factors, relative standard deviations and limits of detection, for Amberlite XAD-2000/hyroxide solid phase extraction supported with DPC-FAAS system to determine Fe(III), Pb(II) and Cr(III) were investigated as performance criteria.

The validation of present method was evaluated using a spiking water sample. The recoveries of analytes spiked into one of analysing water samples, Karahayit, were studied; satisfactory results were obtained as shown in Table 6. Good agreement was obtained between the added and recovered analyte contents using the experimental procedure. The recovery values calculated for the standard additions were always higher than 95%, thus confirming the accuracy of the procedure and the absence of matrix effects. Also, the high tolerance limits for diverse ions confirm the accuracy of the procedure. R.S.D.% values for the determination of analytes in the spiked sample were in range of 1.2–5.2%.

The preconcentration factors for Fe(III), Cr(III) and Pb(II) according to 5 mL eluent and the workable maximum sample volumes were calculated as 50, 50 and 100, respectively.

In the operating conditions chosen above, the precision of the system was evaluated using $0.2\,\mu g\,L^{-1}$ Fe(III), Pb(II) and Cr(III) in 100 mL test solution. The relative standard deviations ($N = 6$), for the recoveries of Fe(III), Pb(II) and Cr(III) was found to be 1.2%, 0.8% and 1.8%, respectively. On the other hand, the relative standard deviations ($N = 6$) calculated for the analysis of

Table 6
Analysis of Karahayit red water sample spiked analytes by proposed procedure (sample vol.: 25 mL, $n = 3$)

Analyte	Added (µg)	Found (µg)	R (%) $x \pm s$ ($n = 3$)	R.S.D. (%)
Fe(III)	–	2.50	–	–
	5	7.75	104.7 ± 5.4	5.2
	10	13.06	104.5 ± 3.7	3.5
	20	24.97	103.2 ± 1.2	1.2
Pb(II)	–	Nd	–	–
	5	4.45	95.2 ± 1.4	1.5
	10	9.90	99.0 ± 3.1	3.0
	20	13.60	93.0 ± 2.6	2.7
Cr(III)	–	Nd	–	–
	5	4.63	92.6 ± 4.0	4.3
	10	8.90	98.3 ± 2.6	2.6
	20	19.00	95.0 ± 1.4	1.5

Nd: not detected.

Table 7
Comparative data from some recent studies on off-line SPE/FAAS system based on use of Amberlite resins

Preconcentration system	Analytes	Flow rate (mL min⁻¹)	Eluent/volume (mL)	PF	Detection limit (µg L⁻¹)	R.S.D. (%)	Refs.
Amberlite XAD-4/DDTC	Cu, Fe, Pb, Ni, Cd, Bi	10	Acetone/10	150	15 for Fe; 19 for Pb	<9	[31]
XAD–2000/1-(2-pyridylazo)-2-naphthol (PAN)	Cr(III), Cu(II), Ni(II), Pb(II)	10	1 mol L⁻¹ HNO₃ in acetone	250		<8	[33]
XAD-2000/DDTC	Mn, Fe, Co, Cu, Cd, Zn, Pb, Ni	20	1 mol L⁻¹ HNO₃ in acetone/7.5	100	0.35 for Fe; 0.45 for Pb	1.7–5.6	[41]
Amberlite XAD-16/1,5-diphenylcarbazone;	Cr(VI) and Cr(III)	1.5	0.05 mol L⁻¹ H₂SO₄ in methanol/10	25	45	<1	[42]
Amberlite XAD-4/Agrobacterium tumefaciens	Fe(III),Co(II), Mn(II), Cr (III)	2	1 mol L⁻¹ HCl/10; 1 mol L⁻¹ HCl in acetone/10 for Cr(III)	25	3.6 for Fe and Cr	2–3	[43]
Amberlite XAD-16/DMABA	Zn(II), Mn(II), Ni(II), Pb(II), Cd(II), Cu(II), Fe(III), Co(II)	5	1–4 mol L⁻¹ Cl/HNO₃/10–25; 1 mol L⁻¹ HNO₃ for Pb	450 (Fe); 250 (Pb)	0.67–3.92; 0.67 (Pb), 2.52 (Fe)	2.1–4.4	[44]
XAD-2000/hyroxide + DPC	Fe, Pb, Cr	5	0.5 mol L⁻¹ HNO₃/5	50–100	0.32–0.81	0.4–1.1 for FAAS; 1.2–9.2 for GFAAS.	This work

PF: preconcentration factor, DMABA: 2-{[1-(3,4-dihydroxypheny)methylidene]amino}benzoic acid, DDTC: diethyldithiocarbamate, and DPC: diphenylcarbazide.

Table 8
Determination of Fe(III), Pb(II) and Cr(III) in water samples ($n = 6$, sample volume: 250 mL, final volume: 5 mL)

Sample	Concentration ($\mu g\,L^{-1}$) $x \pm ts/\sqrt{n}$			R.S.D. (%)		
	Fe(III)[a]	Pb(II)[b]	Cr(III)[b]	Fe(III)	Pb(II)	Cr(III)
Pamukkale	90 ± 1	0.67 ± 0.01	0.19 ± 0.01	1.1	1.4	5.0
Karahayit	104 ± 1	4.14 ± 0.20	0.37 ± 0.03	0.9	4.6	7.0
Kaklik cave	190 ± 2	2.06 ± 0.30	0.60 ± 0.02	1.0	8.8	3.2
Caybasi	240 ± 1	2.58 ± 0.50	0.48 ± 0.03	0.4	9.2	5.9

[a] Flame AAS.
[b] Graphite furnace AAS.

water samples were varied in range of 0.4–1.1% for Fe(III) with FAAS, in range of 1.4–9.2% for Pb(II) and in range of 3.2–7.0% for Cr(III) with GFAAS (Table 8).

The detection limits based on three times the standard deviation of the blank ($N = 20$) for the combination of the proposed preconcentration procedure and flame atomic absorption spectrophotometric measurement were found to be 0.32, 0.51 and 0.81 $\mu g\,L^{-1}$ for Fe(III), Pb(II) and Cr(III), respectively.

For comparative purposes, the performance characteristics of the proposed method and other selected off-line SPE/FAAS systems based on use of Amberlite resins reported in the literature are given in Table 7. The proposed procedure shows good detection limits and precision with reasonable eluent volume, flow rate and preconcentration factor over other SPE off-line preconcentration methods.

3.8. Application of the proposed procedure

The proposed preconcentration procedure has been applied to the water samples. The results are given in Table 8. The relative standard deviations of the determination were lower than 10%.

4. Conclusion

The results of the present investigations in this paper demonstrate the usability of Amberlite XAD-2000/hydroxide system supported with DPC for selective preconcentration of Fe(III), Pb(II) and Cr(III) from high salinity water such as hot spring waters. The accuracy of the results was verified by analyzing the spiked water sample and the model solutions. The recoveries of Fe(III), Pb(II) and Cr(III) from the spiked water sample and the model solutions including diver ions up to the high tolerance limit were almost quantitative (>95%), it is evident for the reliability of the proposed method for the analysis of high salinity waters like hot spring water and the drinking water.

The analytical performance is not significantly different to those achieved by other methods described in the literature. However, Amberite XAD-2000 resin in the system investigated in this work has a superior reusability and stability with adsorption–desorption cycles over 500. The acid concentration required for desorption is low with the present resin.

The preconcentration time is the main disadvantage of the proposed method, especially according to flow procedure, and it is about 45 min for 100 mL of sample volume and 5 mL of eluent, with 2.5 and 1 mL min^{-1}, respectively.

References

[1] C. Niederau, R. Fischer, A. Purschel, W. Stremmel, D. Haussinger, Long-term survival in patients with hereditary hemochromatosis, Gastroenterology 110 (1996) 1107–1119.
[2] WHO, Rolling revision of the WHO guidelines for drinking water quality, Nutrient minerals in drinking-water and the potential health consequences of long-term consumption of demineralized and remineralized and altered mineral content drinking-waters, (2003).
[3] European Community, Directive 98/83/EC on the quality of water intended for human consumption, (1998).
[4] E.M. Erfurth, L. Gerhardsson, A. Nilsson, L. Rylander, A. Schutz, S. Skerfving, Effects of lead on the endocrine system in lead smelter workers, Arch. Environ. Health 56 (2001) 449–455.
[5] World Health Organization (WHO), 53th Report of Joint FAO/WHO Expert Committee on Food Additives, WHO Technical Report Series 896, Geneva, Switzerland, 2000.
[6] US Environmental Protection Agency, Drinking Water Regulations; maximum contaminant level goals and national primary drinking water regulations for lead and copper, Federal Register 53 (1988) 31516.
[7] Eurepean Commission Directive 98/83/EC, 1998, Brussels, Belgium.
[8] Environmental Quality Standards for Water Pollution, Ministry of the Environment, Japan, http://www.env.go.jp/en/water/wq/wp.html.
[9] J.O. Nriagu, E. Nieboer, Chromium in the Natural and Human Environment, Wiley, New York, 1988.
[10] M. Ghaedi, E. Asadpour, A. Vafaie, Sensitized spectrophotometric determination of Cr(III) ion for speciation of chromium ion in surfactant media using alpha-benzoin oxime, Spectrochim. Acta Part A 63 (2006) 182–188.
[11] http://www.epa.gov/OGWDW/mcl.html.
[12] W. Som-Aum, J. Threeprom, H. Li, J.M. Lin, Determination of chromium(III) and total chromium using dual channels on glass chip with chemiluminescence detection, Talanta 71 (2007) 2062–2068.
[13] L.H.J. Lajunen, Spectrochemical Analysis by Atomic Absorption and Emission, The Royal Society of Chemistry, Cambridge, 1991, p. 220.
[14] M. Karve, R.V. Rajgor, Solid phase extraction of lead on octadecyl bonded silica membrane disk modified with Cyanex302 and determination by flame atomic absorption spectrometry, J. Hazard. Mater. 141 (2007) 607–613.
[15] N. Pourreza, R. Hoveizavi, Simultaneous preconcentration of Cu, Fe and Pb as methylthymol blue complexes on naphthalene adsorbent and flame atomic absorption determination, Anal. Chim. Acta 549 (2005) 124–128.
[16] M. Soylak, N.D. Erdogan, Copper(II)–rubeanic acid coprecipitation system for separation–preconcentration of trace metal ions in environmental samples for their flame atomic absorption spectrometric determinations, J. Hazard. Mater. 137 (2006) 1035–1041.
[17] R.A. Gil, S. Cerutti, J.A. Gásquez, R.A. Olsina, L.D. Martinez, Preconcentration and speciation of chromium in drinking water samples by coupling of on-line sorption on activated carbon to ETAAS determination, Talanta 68 (2006) 1065–1070.

[18] A. Ceccarini, I. Cecchini, R. Fuoco, Determination of trace elements in seawater samples by on-line column extraction/graphite furnace atomic absorption spectrometry, Microchem. J. 79 (2005) 21–24.

[19] F. Séby, S. Charles, M. Gagean, H. Garraud, O.F.X. Donard, Chromium speciation by hyphenation of high-performance liquid chromatography to inductively coupled plasma-mass spectrometry—study of the influence of interfering ions, J. Anal. At. Spectrom. 18 (2003) 1386–1390.

[20] D. Rekha, K. Suvardhan, J. Dilip Kumar, P. Subramanyam, P. Reddy Prasad, Y. Lingappa, P. Chiranjeevi, Solid phase extraction method for the determination of lead, nickel, copper and manganese by flame atomic absorption spectrometry using sodium bispiperdine-1,1′-carbotetrathioate (Na-BPCTT) in water samples, J. Hazard. Mater. 146 (2007) 131–136.

[21] J. Otero-Romaní, A. Moreda-Piñeiro, A. Bermejo-Barrera, P. Bermejo-Barrera, Evaluation of commercial C18 cartridges for trace elements solid phase extraction from seawater followed by inductively coupled plasma-optical emission spectrometry determination, Anal. Chim. Acta 536 (2005) 213–218.

[22] K. Suvardhan, D. Rekha, K. Suresh Kumar, P. Reddy Prasad, J. Dilip Kumar, B. Jayaraj, P. Chiranjeevi, Novel analytical reagent for the application of cloud-point preconcentration and flame atomic absorption spectrometric determination of nickel in natural water samples, J. Hazard. Mater. 144 (2007) 126–131.

[23] X. Mao, H. Chen, J. Liu, Determination of trace amount of silver by atomic-absorption-spectrometry-coupled flow injection on-line coprecipitation preconcentration using DDTC–copper as coprecipitate, Microchem. J. 59 (1998) 383–391.

[24] P. Pohl, B. Prusisz, Determination of Ca, Mg, Fe and Zn partitioning in UHT cow milks by two-column ion exchange and flame atomic absorption spectrometry detection, Talanta 71 (2007) 715–721.

[25] K. Cundeva, T. Stafilov, Flame atomic absorption spectrometric determination of zinc after colloid precipitate flotation with hydrated iron(III) oxide and iron(III) tetramethylenedithiocarbamate as collectors, Talanta 44 (1997) 451–456.

[26] S.R. Segade, J.F. Tyson, Determination of methylmercury and inorganic mercury in water samples by slurry sampling cold vapor atomic absorption spectrometry in a flow injection system after preconcentration on silica C_{18} modified, Talanta 71 (2007) 1696–1702.

[27] S. Cerutti, M.F. Silva, J.A. Gasquez, R.A. Olsina, L.D. Martinez, On-line preconcentration/determination of cadmium in drinking water on activated carbon using 8-hydroxyquinoline in a flow injection system coupled to an inductively coupled plasma optical emission spectrometer, Spectrochim. Acta 58B (2003) 43–50.

[28] M. Ghaedi, E. Asadpour, A. Vafaie, Simultaneous preconcentration and determination of copper, nickel, cobalt, lead and iron content using a surfactant coated alumina, Bull. Chem. Soc. Jpn. 79 (2006) 432–436.

[29] M. Ghaedi, M.R. Fathi, F. Marahel, F. Ahmadi, Simultaneous preconcentration and determination of copper, nickel, cobalt and lead ions content by flame atomic absorption spectrometry, Fresen. Environ. Bull. 14 (2005) 1158–1163.

[30] K. Suvardhan, K.S. Kumar, D. Rekha, B. Jayaraj, G.K. Naidu, P. Chiranjeevi, Preconcentration and solid-phase extraction of beryllium, lead, nickel, and bismuth from various water samples using 2-propylpiperidine-1-carbodithioate with flame atomic absorption spectrometry (FAAS), Talanta 68 (2006) 735–740.

[31] A. Uzun, M. Soylak, L. Elci, Preconcentration and separation with Amberlite XAD-4 resin; determination of Cu, Fe, Pb, Ni, Cd and Bi at trace levels in waste water samples by flame atomic absorption spectrometry, Talanta 54 (2001) 197–203.

[32] P.K. Tewari, A.K. Singh, Preconcentration of lead with Amberlite XAD-2 and Amberlite XAD-7 based chelating resins for its determination by flame atomic absorption spectrometry, Talanta 56 (2002) 735–744.

[33] I. Narin, M. Soylak, L. Elci, M. Dogan, Separation and enrichment of chromium, copper, nickel and lead in surface seawater samples on a column filled with Amberlite XAD-2000, Anal. Lett. 34 (2001) 1935–1947.

[34] C. Duran, H.B. Senturk, A. Gundogdu, V.N. Bulut, L. Elci, M. Soylak, M. Tufekci, Y. Uygur, Determination of some trace metals in environmental samples by flame AAS following solid-phase extraction with Amberlite XAD-2000 resin after complexing with 8-hydroxyquinoline, Chin. J. Chem. 25 (2007) 196–202.

[35] C. Duran, M. Soylak, V.N. Bulut, A. Gundogdu, M. Tufekci, L. Elci, H.B. Senturk, Speciation of Cr(III) and Cr(VI) in environmental samples after solid phase extraction on Amberlite XAD-2000, J. Chinese Chem. Soc. 54 (2007) 625–634.

[36] L. Elci, M. Soylak, M. Dogan, Preconcentration of trace metals in river waters by the application of chelate adsorption, Fresen. J. Anal. Chem. 342 (1992) 175–178.

[37] S. Balt, E. Van Dalen, The reactions of diphenylcarbazide and diphenylcarbazone with cations. Part IV. Cations of Mn, Fe, Co, Ni, Cu, Zn, Cd, Sn and Pb, Anal. Chim. Acta 29 (1963) 466–471.

[38] S. Balt, E. Van Daien, The reactions of diphenylcarbazide and diphenylcarbazone with cations. Part V. Extraction dissociation constants of the carbazone complexes, Anal. Chim. Acta 30 (1964) 434–442.

[39] S. Simsek, G. Gunay, H. Hatip, M. Ekmekci, Enviromental protection of geothermal waters and Travertines at Pamukkale, Geothermics 29 (2000) 557.

[40] L. Nazik (Project advisory), Kaklik Mağarasi Arastirma Raporu (in Turkish), T.C. Maden Tetkik ve Arama Genel Mudurluğu, Ankara, Turkey, 2000.

[41] V.N. Bulut, A. Gundogdu, C. Duran, H.B. Senturk, M. Soylak, L. Elci, M. Tufekci, A multi-element solid-phase extraction method for trace metals determination in environmental samples on Amberlite XAD-2000, J. Hazard. Mater. 146 (2007) 155–163.

[42] A. Tunceli, A. Rehber, Speciation of Cr(III) and Cr(VI) in water after preconcentration of its 1,5-diphenylcarbazone complex on Amberlite XAD-16 resin and determination by FAAS, Talanta 57 (2002) 1199–1204.

[43] S. Baytak, A.R. Turker, The use of *Agrobacterium tumefaciens* immobilized on Amberlite XAD-4 as a new biosorbent for the column preconcentration of iron(III), cobalt(II), manganese(II) and chromium(III), Talanta 65 (2005) 938–945.

[44] G. Venkatesh, A.K. Singh, 2-{[1-(3,4-Dihydroxyphenyl) methylidene]amino}benzoic acid immobilized Amberlite XAD-16 as metal extractant, Talanta 67 (2005) 187–194.