RESIDUES AND TRACE ELEMENTS

Chromium Speciation in Environmental Samples by Solid-Phase Extraction Using Lewatit Ionac SR-7 Resin and Flame Atomic Absorption Spectrometry

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A new method for the speciation, preconcentration, and separation of Cr(III) and Cr(VI) species in different matrixes was developed using SPE combined with flame atomic absorption spectrometry. The procedure is based on the exchange of Cr(VI) ions as CrO_4^{2-} with Cl^- ions on Lewatit Ionac SR-7 ion-exchange resin. After the oxidation of Cr(III) to CrO_4^{2-} ions by concentrated H_2O_2 in basic medium, the procedure was applied to the determination of total Cr. Cr(III) was calculated as the difference between the total Cr and Cr(VI) contents. The influence of the analytical parameters including the pH of the solution, amount of resin, eluent type, sample volume, and flow rates of the sample and eluent solutions were investigated. No considerable interferences were observed from other anions and cations investigated in the Cr speciation. The preconcentration factor was found to be 500. The LOD for Cr(VI), corresponding to three times the SD of the blank, was 0.003 µg/L. The sorption capacity and binding equilibrium constant were calculated as 17.2 mg/g and 2.54 L/mg, respectively. The accuracy of the method was verified by analyzing certified reference materials. The proposed method was applied to the speciation of Cr species in real samples with satisfactory results.

Chromium (Cr) is extensively used either as an alloy or as a trivalent or hexavalent salt in a variety of industrial applications such as in metallurgical, chemical, electroplating, refractory, pigments, tanning, oxidative dyeing, and cooling water towers (1). The importance of Cr speciation is governed by the fact that toxicity and reactivity depend on the chemical form or oxidation state of Cr. Cr(III) is a relatively nontoxic and essential nutrient for humans, and trace amounts of Cr(III) are considered as essential to mammals for the maintenance of normal glucose tolerance factor and lipid and protein metabolism; therefore it is essential for human health (2).

On the other hand, Cr(VI) species are highly toxic and a potential carcinogenic agent due to their high oxidation potential and their relatively small size, which enables them to penetrate through biological cell membranes (3). Cr(VI) inhibits enzymatic sulfur uptake of the cell and is harmful to the lungs, liver, and kidneys. The oxidation of sulfur dioxide and formation of acidic aerosols involved in global acid rain are observed in the air due to Cr particulates (4). Also, Cr(VI) diffuses as CrO_4^{2-} or $HCrO_4^-$ through the cell membranes and oxidizes biological molecules, causing toxic results, such as chronic ulcers and corrosive action in the nasal septum (5, 6). Again, experimental evidence shows that the kinetics of the transformation of Cr(III) to Cr(VI) is rapid enough in presence of even mild oxidants, as the potential necessary to oxidize Cr(III) to Cr(VI) decreases with increase in the pH of the media (7).

Cr species in water mainly exist as CrO_4^{2-} and cationic hydroxo complexes [$Cr(OH)^{2+}$, $Cr(OH)_2^+$, etc.] and organically bound or colloidally sorbed Cr(III) (8). Therefore, it is important to determine the individual species of Cr in natural water, wastewater, or drinking water. In addition, it is necessary to control the level of Cr(VI) in natural and drinking water, where typical concentrations of total Cr are in the range of 0.1–0.5 µg/L (9–12). These facts show that the speciation analysis of Cr, as well as its total determination, is very important for its biological and environmental evaluations.

Various techniques for the determination of Cr(VI) and Cr(III) have been developed in recent years. Spectrophotometric procedures based on the reaction with diphenylcarbazide can determine Cr(VI) in the presence of Cr(III), but they are not sensitive (13). On the other hand, atomic spectrometric methods like flame atomic absorption spectrometry (FAAS), graphite furnace–AAS, inductively coupled plasma (ICP)–atomic emission spectrometry, and ICP/MS cannot distinguish Cr(VI) and Cr(III) species. The most commonly used method is the separation of Cr species by HPLC often coupled with one of the above-mentioned atomic spectrometric detection systems (14–16).

Cr at trace level can be determined after separation and preconcentration by instrumental analysis. Low Cr levels are usually determined by the separation of one specific form by sorption (8, 17), liquid–liquid extraction (18, 19), or coprecipitation (20, 21). In some cases, the preconcentration of selective Cr species (not all Cr species) followed by detection has been carried out using electroanalytical techniques (22–24). Nevertheless, reports on the use of a solid-phase resin for pH-dependent speciation following selective elution of different forms of Cr, viz, Cr(III) and Cr(VI), are scarce (25–32).

Among the various treatment techniques available, the most commonly used is ion exchange. The main advantages of using ion-exchange resins are due to their high chemical and mechanical stability and high ion-exchange capacity and rate. Another advantage is the possibility of selecting the fixed ligand groups and the degree of crosslinking. Anion-exchange resins are generally prepared from synthetic polymers such as styrene–divinylbenzene copolymers, which are aminated and methylated to form strong base anion exchangers (33). The

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removal of Cr(VI) from cooling water and groundwater by an ion exchanger has been investigated by some researchers (34, 35). The separation of metals with similar properties is a most useful analytical application of ion exchange (15, 16). Obviously, the ion-exchange process is a good alternative to other treatment techniques because of its ability to reduce dissolved chromate concentration to nondetectable levels in water treatment plants. The concentrations of the substances that have to be removed are normally in the lower ppm range (36, 37).

In this study, Lewatit Ionac SR-7 anion-exchange resin (a strong basic quaternary ammonium salt) was used for the separation and preconcentration of Cr(VI) species. To the best of our knowledge, Lewatit Ionac SR-7 anion exchange resin has not been used before in the determination of Cr(VI) by FAAS. The Cr(VI) was quantitatively separated from Cr(III) and preconcentrated. Cr(III) concentrations were obtained as the differences between total Cr and Cr(VI). The analytical characteristics of the resin were established, and optimum recovery conditions were determined for Cr(VI). The sorption capacity of the sorbent for Cr(VI) was also studied. The proposed method was applied to determination and speciation of inorganic Cr species in various environmental samples.

Experimental

Instruments

A PerkinElmer Model AAnalyst 800 flame atomic absorption spectrometer (Norwalk, CT) equipped with a deuterium background correction system and an air-acetylene burner was used for the determination of Cr. The wavelength used was 357.9 nm. A spectral bandwidth of 0.7 nm, acetylene flow rate of 1.4 L/min, and nebulizer flow rate of 10.0 mL/min were the working parameters. For measuring pH values in the aqueous phase a Consort (Consort bvba, Turnhout, Belgium) Model C533 pH meter combined with a glass-electrode was used, and a magnetic stirrer (Chiltern, Sydney, Australia) was also used.

Reagents and Standard Solutions

All reagents used were of the highest available purity and at least analytical reagent grade (Merck, Darmstadt, Germany). Deionized water was used for the preparation of the solutions. Cr(III) and Cr(VI) stock solutions (1000 mg/L) were prepared from $Cr(NO_3)_3 \cdot 9H_2O$ and K_2CrO_4 (20), respectively. From these solutions, dilute working solutions were prepared on a daily basis. The oxidation of Cr(III) to Cr(VI) in basic medium was carried out using H_2O_2 as the oxidation agent. Lewatit Ionac SR-7 anion-exchange resin (Marcel Decker, Mannheim GmbH, Germany), which is a strong basic quaternary ammonium salt (Cl^- form), was used for the separation/preconcentration of Cr(VI) species. The following solutions were used for adjusting the pH values of the aqueous solutions: HCl and/or NaOH for pH 1–7. A 3 M HNO_3 solution was used as the ion-exchange column eluent throughout the experiments.

Column Preparation

The ion-exchange resin was washed successively with 1 M HNO_3, 1 M NaOH, ethyl alcohol, and deionized water and then dried in an oven at about 60°C; 0.5 g portions resin, as a suspension in water, were packed into glass columns (100 mm length × 10 mm id; Erciyes University, Kayseri, Turkey). The resin bed height in the column was approximately 1.5 cm. The column was washed thoroughly with 30 mL deionized water and then conditioned with 20 mL aqueous solution with a pH of 3.

General Preconcentration Procedure for Cr(VI)

The method was tested by using model solutions prior to application to the real samples. For this purpose, the pH of test solutions (25 mL) including 20 μg Cr(VI) was adjusted to 3 using HCl and/or NaOH solution. The column was conditioned by passing 20 mL of 1 M HCl and/or NaOH solution (pH 3) through the column, and then the test solutions were passed through it at a flow rate of 2 mL/min. The Cr(VI) ions retained on the resin were eluted with 25 mL of 3 M HNO_3 solution. The concentration of the Cr(VI) in the eluate was determined by FAAS.

Determination of Total Cr

In order to determine the total Cr, 25 mL portions test solutions containing 20 μg of both Cr(III) and Cr(VI) were prepared. In order to oxidize the Cr(III) ions to Cr(VI) ions in the test solutions, 10 mL of 3% (w/v) H_2O_2 in the basic medium (pH 12) was added to the test solution and then heated on a hot plate adjusted to 80°C for 40 min (38). Then the solution was boiled for 10 min to remove any excess H_2O_2. The solution was allowed to cool at room temperature for 30 min. After this step, the pH of the solution was adjusted to 3, and its volume made up to 25 mL with deionized water. The described preconcentration procedure was applied, and total Cr was determined by FAAS. The concentration of Cr(III) in samples was calculated by subtracting the concentration of Cr(VI) from the total Cr concentration.

Applications

The presented procedure for the speciation of Cr(III) and Cr(VI) species was applied to various real samples. Tap water, electroplating wastewater, wastewater, sediment, and soil samples were used. The tap water samples were taken from our laboratory and analyzed without pretreatment. The wastewater samples were collected in prewashed polyethylene bottles from various plants located in the Kayseri Organized Industrial Region. All water samples, except for the tap water, were filtered through a cellulose membrane filter (EMD Millipore Corp., Billerica, MA) of 0.45 μm pore size and analyzed as described in the *General Preconcentration Procedure for Cr(VI)* section above.

A 0.1 g aliquot of soil and/or certified reference material (BCR 701 lake sediment) was put into a 100 mL beaker. A mixture of 9 mL HCl (37%, w/w) and 3 mL HNO_3 (65%, w/w) was added to the soil and/or sediment sample, and this mixture was digested by heating on a hot plate adjusted to 200°C; 0.25 g sediment was decomposed by fluxing with Na_2O_2. After completing the fusion, the mass was allowed to cool slowly, and the solid material was dissolved in 5 mL water. The obtained solution was filtered through a blue ribbon filter paper (Whatman, Florham Park, NJ) and diluted to 50 mL with deionized water. After diluting 10 mL of this solution to 100 mL, the pH was adjusted to 3. Blanks were analyzed in the same way but without sample. Then the separation/preconcentration procedure was applied to the

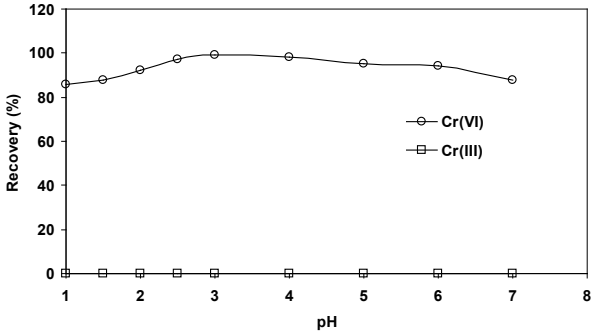


Figure 1. Effect of pH on Cr(III) and Cr(VI) recoveries (*n* = 3).

obtained solutions. Afterwards, the final measurement volume was 2 mL, and the measurement was performed by FAAS.

The method was also applied to the standard reference materials SPS-WW2 Batch 108 wastewater and BCR 701 lake sediment. A 5 mL amount of electroplating wastewater, 10 mL wastewater sample, and 100 mL of other water samples were used for the speciation of Cr(III) and Cr(VI). The preconcentration procedure was applied to the aqueous samples. The final measurement volume was 2 mL.

Results and Discussion

Effect of pH on Recovery of Cr(III) and Cr(VI)

The effect of sample pH on the retention of Cr(III) and Cr(VI) ions was investigated using a column containing the resin. The pH of each test solution was adjusted with 1 M HCl/ and/or 1 M NaOH solution (if necessary) in the range of pH 1–7. The retained Cr(VI) ions were eluted with 25 mL of 3 M HNO_3 solution. The eluate solution was evaporated to near dryness and then diluted to 10 mL with 1 M HNO_3. The concentration of the Cr(VI) ions was determined by FAAS. The effect of pH on the recoveries of Cr(III) and Cr(VI) ions is given in Figure 1. The recoveries of Cr(VI) were quantitative in the pH range of 2–6, while Cr(III) was not quantitatively recovered at all pH values. These results show that the two Cr species were quantitatively separated in the pH range of 2–6. In all the subsequent studies for the separation/preconcentration of Cr(III) and Cr(VI) species, pH 3 was used as optimum.

Effect of Type, Concentration, and Amount of Eluent

For the elution of retained Cr(VI) ions on the ion-exchange resin, dilute acid solutions of different amounts and concentrations were tested by using 25 mL aliquots of the model solutions containing 20 µg of Cr(VI) ion at pH 3. The studies were performed with 5, 10, and 25 mL portions of 1, 2, and 3 M HCl and HNO_3 solutions. The results are given in Table 1. For all further studies, 25 mL of 3 M HNO_3 was chosen as eluent due to its quantitative recovery results.

Effect of Flow Rate

Flow rate is an important parameter to obtain quantitative retention of the analyte on the ion-exchange resin. The flow rates of the test solutions were controlled by using the stopcock of the column. The effects of the flow rates of the sample and eluent solutions on the recoveries were investigated in the range of 1–10 mL/min. Quantitative recoveries of Cr(VI) were obtained at the sample flow rate of 8 mL/min (Figure 2). Further studies were performed at a flow rate of 8 mL/min.

Table 1. Effect of amount and concentration of HCl and HNO_3 solutions on the recovery of the analyte[a]

Concn and amount of eluent	Volume, mL	Recovery, %[b]	
		Cr(III)	Cr(VI)
3 M HNO_3	10	—[c]	84 ± 2
3 M HNO_3	25	—	99 ± 3
2 M HNO_3	25	—	35 ± 1
1 M HNO_3	25	—	7 ± 1
3 M HCl	25	—	94 ± 2
2 M HCl	10	—	34 ± 1
2 M HCl	25	—	90 ± 2

[a] Sample volume 25 mL, pH 3.

[b] Average ± SD, *n* = 3.

[c] Below LOD.

The effects of the eluent flow rates on the recoveries were investigated in the range of 1–10 mL/min. Quantitative recoveries of Cr(VI) were obtained between the eluent flow rates of 1 to 2 mL/min (Figure 3). Further studies were performed at a flow rate of 2 mL/min for the elution process.

Effect of Resin Amount

The effect of the amount of resin on the recovery of Cr(VI) ions was investigated at the flow rate of 8 mL/min for the sample solution. The results are shown in Figure 4. The recovery values increased with the increasing amounts of the resin used and reached a quantitative value (about 100%) from 0.5 to 0.75 g of resin. In all subsequent studies, the glass column was filled with 0.5 g of resin.

Effect of Sample Volume

The effect of sample volume on the retention behavior of Cr(VI) ions on the resin was investigated. For this purpose, 25–1500 mL of the test solutions containing 20 µg of Cr(VI) ions was passed through the column under the optimum conditions. The results are shown in Figure 5. The recovery of Cr(VI) was quantitative

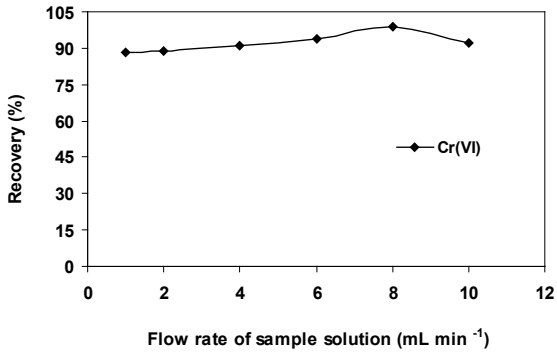


Figure 2. Effect of flow rate of sample solution (*n* = 3).

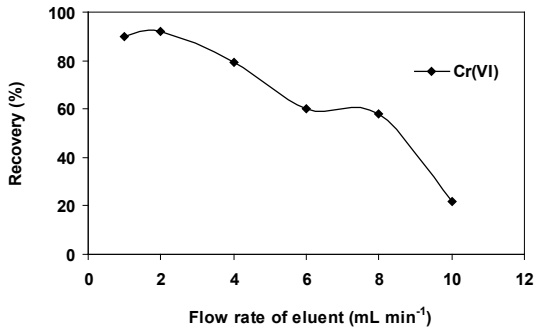


Figure 3. Effect of flow rate of eluent (*n* = 3).

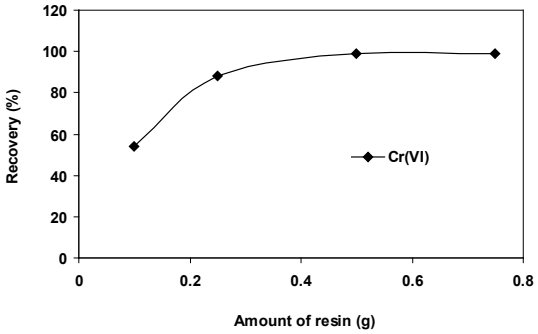


Figure 4. Effect of the amount of the resin on the recovery of the Cr(VI) ions (*n* = 3).

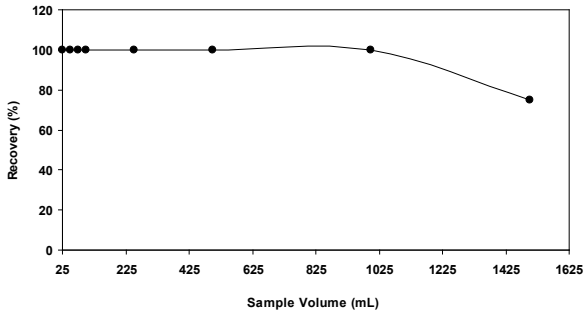


Figure 5. Effect of sample volume on the recoveries of the Cr(VI) ions (*n* = 3).

up to 1000 mL of the test solutions. The preconcentration factor (PF) is calculated by the ratio of the highest sample volume and the lowest final volume (2 mL). In this work, the highest PF was 500 for a sample volume of 1000 mL, although the recovery values for Cr(VI) decreased slowly from 1000 to 1500 mL of the test solution.

Effect of Matrix Ions on Recovery

For the application of the recommended SPE procedure to real samples, the effects of some interfering ions on the recovery of Cr(VI) ions were investigated. To a 25 mL aliquot of the test solution containing 20 µg of Cr(VI), interferent ions at different concentrations were individually added, and then the proposed method was applied. The recovery values obtained and the concentrations of the interfering ions are shown in Table 2. The recoveries for Cr(VI) were at least 94%. Therefore, none of the investigated foreign ions had an interfering effect on the recommended SPE procedure at the levels studied.

Table 2. Influence of some foreign ions on the recoveries of Cr(VI)[a]

Ions	Added as	Concentration, mg/L	Recovery, %
Na^+	$NaNO_3$	500	100 ± 1[b]
K^+	KNO_3	1000	102 ± 2
Ca^{2+}	$Ca(NO_3)_2{\cdot}4H_2O$	1000	94 ± 2
Mg^{2+}	$Mg(NO_3)_2{\cdot}6H_2O$	500	100 ± 4
Cl^-	NaCl	4000	101 ± 2
SO_4^{2-}	Na_2SO_4	400	103 ± 3
NO_3^-	$NaNO_3$	1000	96 ± 1
PO_4^{-3}	H_3PO_4	400	99 ± 3

[a] pH 3, eluent 25 mL of 3 M HNO_3, sample volume 25 mL.

[b] Average ± SD, *n* = 3.

Effect of Oxidation Agent

In order to oxidize Cr(III) to Cr(VI), test solutions containing 20 µg of Cr(III) were prepared. A 10 mL volume of 3% (w/v) H_2O_2 was added to the test solution at pH 10 and then heated on a hot plate adjusted to 80°C for 40 min (38). The solution was allowed to cool at room temperature for 30 min. After this process, the pH of the solution was adjusted to 3 and its volume made up to 25 mL with deionized water. The described preconcentration procedure was applied, and total Cr content was measured by FAAS. The concentration of Cr(III) in samples was calculated by subtracting the concentration of Cr(VI) from the total Cr concentration. The recovery for Cr(VI) was found to be about 99%.

Analytical Performance of the Method

For quantitative analysis, a calibration curve for Cr(VI) was constructed by spiking standards directly into deionized water, and the proposed method was applied under the optimum conditions. The equation of the calibration curve obtained after applying the preconcentration procedure was:

$$A = 0.0393\ C_{Cr} - 0.0033$$

where A is absorbance and C_{Cr} is Cr(VI) concentration. Linearity, after applying the preconcentration procedure, was observed over the range of 1–12 mg/L with a determination coefficient (r^2) of 0.9995. The LOD based on 3 s was 3 ng/L, where S = SD. In the calculation of the LOD value of the method, a 500-fold preconcentration factor was taken into consideration. The precision of the method was found to be 2% RSD by analyzing wastewater samples (*n* = 6).

The recovery studies for Cr(VI) were performed using tap water, wastewater, and soil samples. Known amounts of Cr(VI) were spiked into the sample solutions in order to estimate the accuracy of the presented procedure (Table 3). Good agreement

Table 3. The results of the accuracy test for the determination of Cr(VI) in various samples

Sample	Added	Found	Recovery, %
Tap water, mg/L	—	—	—
	5	4.93 ± 0.06[a]	99
Well water, mg/L	—	—	—
	5.0	4.92 ± 0.01	98
Soil, mg/g	—	—	—
	5.0	4.98 ± 0.13	100

[a] Average ± SD, n = 3.

Table 4. The determination of total Cr by the proposed method in the two certified reference materials

	SPS-WW2 Batch 108 Wastewater, µg/L		BCR 701 Lake sediment, µg/g	
Element	Certified value	Found	Certified value	Found
Cr	1000 ± 5[a]	990 ± 5	62.5 ± 7.4	62.8 ± 2.8

[a] Average ± SD, n = 3.

was achieved between the added and the obtained Cr(VI) contents using the recommended procedure.

Sorption Capacity

The sorption isotherm of the resin for Cr(VI) was studied by the column method. The sorption capacity of the chelating resin was obtained by using the Langmuir equation (39) based on the following expression:

$$\frac{C}{n} = \frac{1}{n_m K} + \left(\frac{1}{n_m}\right) \times C$$

where C (mg/L) is the concentration of Cr(VI) in the solution at equilibrium and n (mg/g) is the amount of retained Cr(VI)/g of the resin at equilibrium. A breakthrough curve was prepared by plotting the concentration (mg/L) versus the mg of Cr(VI) retained/g of the resin. The sorption capacity (n_m) and the binding equilibrium constant (K) were obtained from the slope and the intercept of the regression plot (by the least squares method), respectively. The pH value of the test solutions (25 mL) containing Cr(VI) at increasing concentrations (10–2000 mg/L) was adjusted to 3, and then the proposed method was applied.

Table 5. Speciation of Cr(III) and Cr(VI) and total Cr in various water samples

Water samples	Cr(III), mg/L	Cr(VI), mg/L	Total Cr, mg/L
Electroplating wastewater	19 ± 4[a]	4.13 ± 0.12	23 ± 6
Wastewater (boric acid)	54.1 ± 5	0.032 ± 0.003	70 ± 7
Wastewater (H_2SO_4)	63.3 ± 5	0.25 ± 0.02	77 ± 8
Tap water	—[b]	—	—
Water (inlet of Kaski)[c]	0.73 ± 0.01	1.24 ± 0.01	1.97 ± 0.02
Water (outlet of Kaski)	0.32 ± 0.01	0.130 ± 0.001	0.450 ± 0.002
Sample, µg/g			
Soil	—	—	—
Sediment	—	—	1425 ± 35

[a] Mean ± SD, n = 3.

[b] Below the LOD.

[c] Kaski is the name of the wastewater treatment plant for Kayseri.

The sorption capacity of the resin for Cr(VI) was found to be 17.2 mg/g, and the binding equilibrium constant was calculated to be 2.54 L/mg. The results showed that the resin had a quite high sorption capacity for Cr(VI).

Application to Real Samples

The method was applied to the certified reference materials in order to verify its accuracy. Table 4 shows the results for the certified reference materials, SPS-WW2 Batch 108 wastewater, and BCR 701 lake sediment. Our data showed excellent agreement with the certified values. The proposed method was also successfully applied to both the determination of total Cr and, if possible, its speciation in environmental samples (Table 5).

Comparison with Other SPE Methods

The data from the presented method were compared with those of recently reported methods for the speciation of Cr (Table 6). Some of the parameters obtained are comparable to those reported by other methods. The resin exhibits much higher sorption capacity than the earlier equivalents systems. Both the PF and the LOD of the method for Cr(VI) are better than those obtained by the other methods. The other advantage of the method is the

Table 6. Comparison of the method with some recent studies on Cr speciation reported in the literature

Method	System	Technique	pH	DL,[a] µg/L	RSD, %	PF	Reference
SPE	Diaion HP-2MG/APDC	GFAAS	3.5	0.03 for Cr(VI)	9 for Cr(VI)	—	28
Ion exchange	Natural water, hair, and food samples	FAAS	5.5	4.16 for Cr(III)	2.56 for Cr(III)	—	40
SPE	Dowex M 4195 chelating resin	FAAS	2	1.94 for Cr(VI)	<10 for Cr(VI)	31	41
Cloud point extraction	2-HNAT/Triton X-100	FAAS	8	0.18 for Cr(III)	2.13	58	42
Cloud point extraction	DDTC/Triton X-114	HPLC	7	3.4 for Cr(III) 5.2 for Cr(VI)	4.1–4.6	65 for Cr(III) 19 for Cr(VI)	43
SPE	Chelating resin	FAAS	3	0.01 for Cr(III)	1.2	200	44
Ion exchange	Lewatit Ionac SR-7 anion-exchange resin	FAAS	3	0.003 for Cr(VI)	2	500	This work

[a] DL = Detection limit.

acidic working medium (pH 3), which prevents precipitation of Cr(III) as hydroxides. In addition, the application of this method is simpler and takes less time than the other methods.

Conclusions

An anion-exchange resin was applied for the speciation of inorganic Cr species in various samples. Cr(VI) was quantitatively retained in the wide pH range of 2–6, while Cr(III) remained in the solution. Mutual separation and speciation of Cr(III) and Cr(VI) were attained at pH 3; 0.5 g of the anion-exchange resin was used throughout the experiments without any loss in recovery values of Cr(VI). High sorption capacity (17.2 mg/g), high PF (500), and low LOD (3 ng/L) are the main advantages of the proposed method. This method is also fairly rapid, low cost, and uses fewer chemicals. The proposed method was successfully applied to the speciation of Cr in various solid/liquid samples.

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