

Scientific paper

Chromium Speciation Using an Aminated Amberlite XAD-4 Resin Column Combined with Microsample Injection-Flame Atomic Absorption Spectrometry

Erkan Aksoy,¹ Şükrü Gökhan Elçi,¹ Ali N. Siyal² and Latif Elçi^{1,*}¹ Chemistry Department, Faculty of Science and Arts, University of Pamukkale, 20020, Denizli, Turkey² Institute of Advance Research Studies in Chemical Science, University of Sindh, Jamshoro, Pakistan

* Corresponding author: E-mail: elçi@pau.edu.tr

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Abstract

Amberlite XAD-4 resin (AXAD-4) was chemically modified to an aminated Amberlite XAD-4 (AAXAD-4) resin and characterized by infrared spectroscopy. AAXAD-4 resin was used as an efficient solid phase for the preconcentration and speciation of Cr(III) and Cr(VI) ions by column technique. The concentration of chromium species was determined by microsample injection system-flame atomic absorption spectrometer (MIS-FAAS). Selective retention of Cr(III) ions was achieved at pH 8.0 and eluted using 1.0 mL of 3.0 mol L⁻¹ HCl and 1.0 mL of 2.0 mol L⁻¹ NaOH, successively, at the flow rate of 5.0 mL min⁻¹. The maximal sorption capacity of AAXAD-4 resin for Cr(III) ions was found to be 67.0 mg g⁻¹. The limit of detection (LOD) and limit of quantitation (LOQ) for Cr(III) ions were found to be 0.041 and 0.131 µg L⁻¹, respectively, with preconcentration factor (PF) of 375 and relative standard deviation (RSD) of 3.75% (n = 11). The method was validated using certified reference materials (CRMs) and successfully applied to the real samples, spiked with Cr(III) and Cr(VI) ions.

Keyword: Aminated Amberlite XAD-4 resin; column; solid-phase; chromium speciation; MIS-FAAS

1. Introduction

Speciation of chromium is still one of most important long-standing analytical challenges due to its impact on environmental chemistry, ecotoxicology, clinical toxicology and food industry. Among several redox states, chromium exists mostly in the trivalent Cr(III) and hexavalent Cr(VI) redox states with contrasting chemical, biological and toxicological properties. While water insoluble Cr(III) is an essential ion for mammals, water soluble Cr(VI) is a human carcinogen, mutagen and toxin due to its high oxidation potential and relatively small size. Compounds of Cr(VI) are 10 to 100 times more toxic than those of Cr(III).^{1,2} Cr(III) and Cr(VI) also cause dermatologic allergy during contact. Thus, US EPA and WHO recommend the threshold value for total chromium as 100 µg L⁻¹ for drinking water and 50 µg L⁻¹ Cr(VI) as tolerance level, respectively.^{3,4}

The toxicity of metals strongly depends on their oxidation states rather than their total concentrations.⁵ Therefore, metallic species have become a prime task for analytical chemists for years.⁶ Various techniques, such as flame atomic absorption spectrometry (FAAS), graphite furnace

atomic absorption spectrometry (GF-AAS), inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma optical emission spectrometry (ICP-OES), thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS) and electrothermal atomic absorption spectrometry (ET-AAS), have been routinely used for the determination of total chromium.⁷ Unfortunately these techniques cannot differentiate Cr(III) from Cr(VI) ions. For the speciation and preconcentration of chromium species, several methods based on solid-phase extraction (SPE),^{8–11} coprecipitation,^{12–14} cloud point extraction¹⁵ and liquid phase microextractions^{16–18} have been developed. Among these, SPE has advantages such as easy operation, smallest consumption of toxic solvents, recycling of solid phases and high selectivity.^{19,20} For speciation of chromium species, activated carbon,²¹ silica gel,²² sawdust,²³ chelating resins^{11–18,23–25} and Amberlite XAD resin series have been used as solid phase.^{25–27} Amine group was incorporated on the polymeric matrix of Amberlite XAD-4 resin. This modified resin was used as effective solid phase for SPE speciation and preconcentration of chromium species.

2. Experimental

2. 1. Apparatus

A Perkin-Elmer flame atomic absorption spectrometer (AAAnalyst 200) equipped with a chromium hollow cathode lamp, an air-acetylene flame atomizer and hand-made microinjection system was used for chromium determination. The instrumental parameters were established as recommended by manufacturer: wavelength, 357.9 nm; lamp current, 30.0 mA; slit width, 0.7 nm; acetylene flow, 2.0 L min⁻¹ and air flow, 17.0 L min⁻¹. As reported in the previous study, a 100 µL volume (for all sample and standard solutions) was injected manually into a micropipette tip of the microinjection system connected to the nebulizer of FAAS.¹³ The pH of solution was carefully measured using a digital pH meter (Hanna 211, Germany). ATR-IR spectrometer (UATR Spectrum Two from PerkinElmer) was used for recording ATR spectra. The reverse osmosis system (Human Corp., Seoul, Korea) was used to obtain ultrapure (UP) quality water (resistivity, 18.2 MΩ cm⁻¹).

2. 2. Reagents and Solutions

Analytical grade chemicals and UP water were used throughout the study. Stock solutions of Cr(III) and Cr(VI) were prepared using high-purity Cr(NO₃)₃ · 9H₂O (Sigma-Aldrich, St. Louis, MO, USA) and K₂Cr₂O₇ (Merck, Darmstadt, Germany), respectively. The working and reference solutions were prepared daily by diluting the stock solutions. Amberlite XAD-4 resin was purchased from Alfa Aesar (Germany). The pH was adjusted using CH₃COOH/CH₃COONa buffer to pH 3-6, a solution of equal volume of 1.0 mol L⁻¹ HCl and 1.0 mol L⁻¹ NaOH solutions for pH 7 and NH₄NO₃/NH₃ buffer for pH 7.5–10.

2. 3. Sampling

The bottled drinking and mineral water samples were purchased from a local market in Denizli, Turkey. The waste water samples were collected from outlet of the wastewater treatment plant in Denizli, Turkey. The fountain water was taken from Incilipinar, Denizli, Turkey. The waste water samples were immediately transported to the laboratory and filtered with 0.45 µm cellulose nitrate membrane (Sartorius, GmbH, Germany) under vacuum to remove suspended materials and then analysed by the proposed procedure within 24 h.

2. 4. Chemical Modification of Amberlite XAD-4 resin

Amberlite XAD-4 resin (polystyrene divinyl benzene) was chemically modified by the reported procedure.^{26,27} 5.0 g of Amberlite XAD-4 resin was put into 250

mL round bottom flask and a nitrating mixture of 10 mL of concentrated HNO₃ and 25 mL of concentrated H₂SO₄ was added. The system was stirred for 1 h at 60 °C. Reaction mixture was poured into an ice-cold water and filtered. The nitro derivative was washed repeatedly with cold water until acid was rinsed out and air-dried. The nitro group was reduced to amino derivative by refluxing with 40 g of SnCl₂ and 60 mL of 2.0 mol L⁻¹ HCl in 100 mL of ethanol. The amino product (AAXAD-4) was treated thoroughly with 2.0 mol L⁻¹ sodium hydroxide to decompose the tin-amine complex, followed by 1.0 mol L⁻¹ HCl in order to remove the excess stannous chloride. Finally, the product was washed with excess water and dried at 75 °C in drying oven for 24 h. The final resin product was confirmed by infrared spectroscopy.

2. 5. Preparation of SPE Column

A purchased empty Chromabond column SPE cartridge tube (3 mL) from Macherey-Nagel, Düren, Germany, was packed with 185 mg of aminated resin (ground). Glass wool was used to pack both ends of the column to avoid the loss of the resin during experiments. The flow rate of the sample solution was controlled with Chromabond vacuum manifold. The SPE column was decontaminated by washing with acetone, 1.0 mol L⁻¹ HCl, 1.0 mol L⁻¹ NaOH and water, respectively. For adjusting pH of the resin to 8, NH₄NO₃/NH₃ buffer was passed through the column.

2. 6. Speciation and Preconcentration Procedure

The model solutions in the range of 10–750 mL including 5–10 µg Cr(III) or Cr(VI) were adjusted to pH 8 and passed through the column. Cr(III) ions were retained on the resin and Cr(VI) ions were passed as effluent. Cr(III) ions were eluted by sequential use of 1.0 mL of 3.0 mol L⁻¹ HCl and 1.0 mL of 2.0 mol L⁻¹ NaOH at the flow rate of 5.0 mL min⁻¹. The Cr (III) ions in the eluent were determined by MIS-FAAS. The recovery of Cr(III) ions was quantitatively achieved. The total concentration of chromium was determined by the same procedure after the reduction of Cr(VI) to Cr(III) ions using reported reducing mixture of 0.5 mL of ethanol and 0.5 mL of concentrated H₂SO₄.²⁹

3. Results and Discussion

3. 1. Characterization

The modification of Amberlite XAD-4 resins was characterized by infrared spectroscopy. In supporting information, ATR-IR spectra of unmodified Amberlite XAD-4 resin (Figure S1), nitro derivative (Figure S2) and amino derivative (Figure S3) are given. By comparing

spectra (Figure S1 and S2), the additional strong peaks in Figure S1 spectrum at 1525 and 1347 cm^{-1} , respectively, correspond to the asymmetric and symmetric stretching vibrations of N=O bond in nitro derivative.²⁸ By comparing spectra in Figure S2 and Figure S3, appearance of two characteristic peaks at 3359 and 3217 cm^{-1} in Figure S3 spectrum corresponds to N-H bond in amino derivative (primary amine). The spectral information revealed that Amberlite XAD-4 resin was successfully converted to amino derivative.

3. 2. Effect of pH

The pH is an important parameter that strongly influences the retention of metal species on the surface of the resin. Thus, the effect of pH between 2 and 9 on the adsorption of Cr(III) and Cr(VI) ions was studied separately. For optimization, 50 mL of model solutions at pH from 2 to 9 was passed through the column individually. The adsorbed Cr(III) and Cr(VI) ions were eluted by sequential use of 2.5 mL of 3.0 mol L^{-1} of HCl and 2.5 mL of 2.0 mol L^{-1} of NaOH and determined by MIS-FAAS. At pH

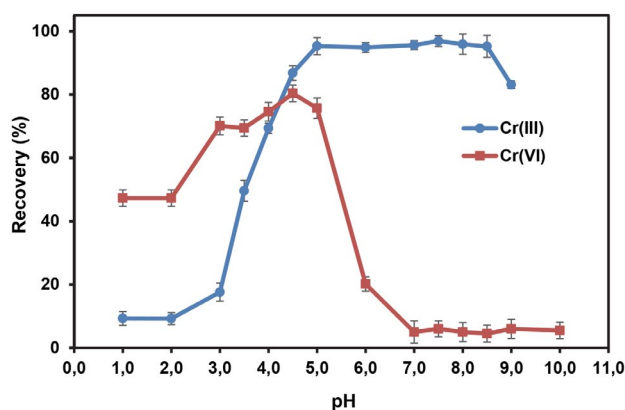


Figure 1. Effect of pH on recoveries of 1.0 $\mu\text{g L}^{-1}$ Cr(III) and 1.0 $\mu\text{g L}^{-1}$ Cr(VI) ions from 50 mL sample solution ($n = 3$).

7 through 9, the recoveries of Cr(III) and Cr(VI) ions were $\geq 95\%$ and $\leq 10\%$, respectively, as shown in Figure 1. Therefore, pH 8 was selected as the best point for the separation of Cr(III) and Cr(VI) ions. Very low uptake of Cr(VI) ions at pH 7 through 10 can be explained as amino group of AAXAD-4 resin became negatively charged in alkaline medium and possessed electrostatic repulsion with CrO_4^{2-} ions that caused a decrease in the uptake of Cr(VI) ions. At low pH values, Cr(III) exists as its kinetically non-reactive aqua-complex $\text{Cr}(\text{H}_2\text{O})_3^{3+}$ that leads to its low uptake due to possible electrostatic repulsion between $\text{Cr}(\text{H}_2\text{O})_3^{3+}$ and protonated amino group of AAXAD-4 resin. As pH was increasing, the coordinated water molecules were replaced by the more reactive hydroxide ions, transforming the former complex ($\text{Cr}(\text{H}_2\text{O})_3^{3+}$) to a more active form ($\text{Cr}(\text{H}_2\text{O})_2(\text{OH})^{2+}$ or $\text{Cr}(\text{H}_2\text{O})(\text{OH})_2^+$), which leads to comparatively better interaction with amino group ($-\text{NH}_2$) of AAXAD-4 resin.³¹

3. 3. Effect of Eluents

The effects of type, volume and concentration of eluents were tested for the quantitative desorption of Cr(III) ions from the column. Figure 1 clearly indicates the percentage decrease in recoveries below pH 3 for the uptakes of Cr(III) ions by AAXAD-4 resin. Thus, 5.0 mL of HCl with concentration range from 1.0 through 7.0 mol L^{-1} was tested to elute the Cr(III) ions. The recovery of Cr(III) was not achieved quantitatively up to 7.0 mol L^{-1} HCl as shown in Table 1. At $\text{pH} > 8.5$ (Figure 1) the uptake of Cr(III) ions decreased due to the conversion of $\text{Cr}(\text{OH})_3$ to highly soluble tetrahydroxo complex ($\text{Cr}(\text{OH})_4^-$). Thus, 5.0 mL of NaOH with concentration range from 1.0 through 4.0 mol L^{-1} was tested to elute the Cr(III) ions. The quantitative recovery of Cr(III) ions was not achieved until up to 4.0 mol L^{-1} NaOH (Table 1). Based on these results, a consecutive use of 2.5 mL of 3.0 mol L^{-1} HCl and 2.5 mL of 2.0 mol L^{-1} NaOH solutions was tested for desorption of Cr(III) ions and resulted in quantitative recovery

Table 1. Effect of type, concentration and volume of eluents on the recovery of 1.0 $\mu\text{g L}^{-1}$ Cr(III) ions in 100 mL sample from the column ($n = 4$)

Eluents	Recovery \pm RSD, %
5.0 mL 1.0 mol L^{-1} HCl	44.7 \pm 0.8
5.0 mL 3.0 mol L^{-1} HCl	51.7 \pm 2.1
5.0 mL 5.0 mol L^{-1} HCl	67.2 \pm 1.0
5.0 mL 7.0 mol L^{-1} HCl	69.1 \pm 1.2
5.0 mL 1.0 mol L^{-1} NaOH	26.2 \pm 1.4
5.0 mL 2.0 mol L^{-1} NaOH	38.4 \pm 1.3
5.0 mL 4.0 mol L^{-1} NaOH	40.2 \pm 1.1
2.5 mL 3.0 mol L^{-1} HCl and then 2.5 mL 2.0 mol L^{-1} NaOH	97.9 \pm 1.2
2.0 mL 3.0 mol L^{-1} HCl and then 2.0 mL 2.0 mol L^{-1} NaOH	95.1 \pm 1.2
1.0 mL 3.0 mol L^{-1} HCl and then 1.0 mL 2.0 mol L^{-1} NaOH	96.3 \pm 2.1
0.5 mL 3.0 mol L^{-1} HCl and then 0.5 mL 2.0 mol L^{-1} NaOH	78.7 \pm 1.1
0.25 mL 3.0 mol L^{-1} HCl and then 0.25 mL 2.0 mol L^{-1} NaOH	48.5 \pm 1.1

ery. The volume of eluent solutions was further decreased to 1.0 mL of 3.0 mol L⁻¹ HCl and 1.0 mL of 2.0 mol L⁻¹ NaOH (to obtain high preconcentration factor) and resulted in quantitative recovery of Cr(III) ions (Table 1). Thus, a consecutive use of 1.0 mL of 3.0 mol L⁻¹ HCl and 1.0 mL of 2.0 mol L⁻¹ NaOH solutions was selected as the best elution solvent for the desorption of Cr(III) ions in further experiments.

3. 4. Effect of Sample Volume

Another strategy to concentrate analyte at very low concentration is to increase the volume of sample. Therefore, the effect of sample volume on the retention of Cr(III) was studied. The recovery of Cr(III) ion was achieved quantitatively ($\geq 95\%$) up to the sample volume of ≤ 750 mL as shown in Figure 2. Thus, the PF was calculated to be 375 as the ratio of maximal sample volume (750 mL) to minimal eluent volume (2.0 mL). Considering time factor, the volume of real samples for analysis was fixed to 100 mL.

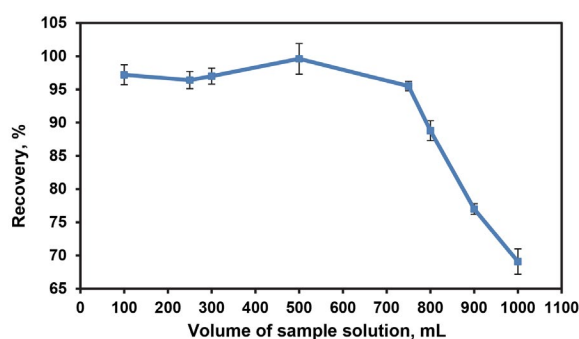


Figure 2. Effect of sample volume on retention of 1.0 µg L⁻¹ Cr(III) ions by the column at pH 8 (n = 4).

3. 5. Effect of Flow Rate of Eluent and Sample Solution

In order to decrease the preconcentration time, the flow rates of sample and eluent solutions were optimised

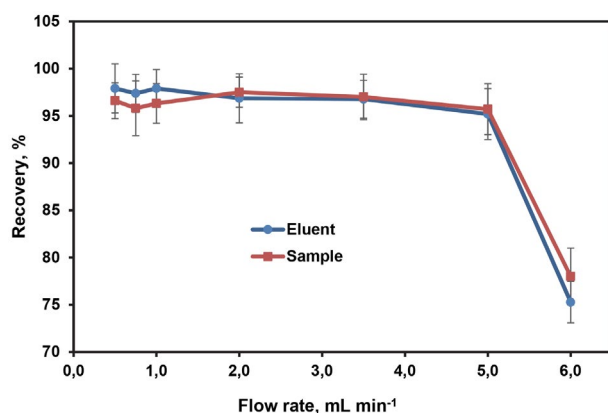


Figure 3. Effect of flow rate of eluent and sample solutions on the recovery of 1.0 µg L⁻¹ Cr(III) ions from 25.0 mL samples (n = 4).

in the range of 0.5–6.0 mL min⁻¹. The results (Figure 3) demonstrated that the quantitative retention and percentage recovery of Cr(III) ions were achieved at the flow rate of 5.0 mL min⁻¹ of sample solution and eluent as well.

3. 6. Adsorption Capacity

The adsorption capacity of the resin is a significant parameter that determines the minimal quantity of adsorbent required for quantitative uptake of analyte from a sample solution. Based on a previous report in reference³¹, the capacity experiments were conducted. Buffered at pH 8.0 in room temperature, 10 mL of model solutions containing Cr(III) in the concentration range of 0.5–400 mg L⁻¹ were equilibrated with 10 mg AAXAD-4 up to 24 h to saturate amino groups. The adsorption isotherm (Figure 4) was plotted as concentrations of Cr(III) ions against adsorbed amount of Cr(III) ions per gram of AAXAD-4 resin. The adsorption capacity of Cr(III) ions was found to be 67.0 mg g⁻¹ as a value at which the adsorbed amount of Cr(III) ions remained constant although the concentration of Cr(III) was increased.

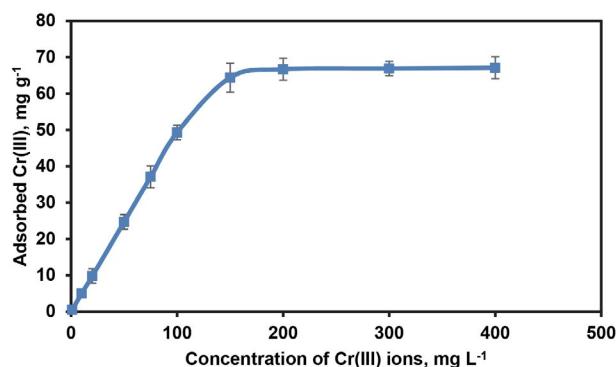


Figure 4. Adsorption isotherm for Cr(III) ions. Conditions: 10 mg adsorbent, 0.5–400 mg L⁻¹ Cr(III), Saturation time: 24 h and pH = 8.0 (n = 3).

3. 7. Sorption Competition of Coexisting Ions with Cr(III) Ions

Environmental water samples contain many heavy metal ions and some common alkali and alkaline earth metals as coexisting ions. For this reason, the effect of present coexisting ions on the preconcentration of Cr(III) needs to be evaluated at optimal conditions. For this purpose, 20 mL of model solution containing 1.0 µg L⁻¹ of Cr(III) ions was spiked with possible interfering ions and subjected to the column according to the proposed method. The Cr(III) ions were quantitatively recovered in the presence of coexisting ions at tolerance limits, taken as a relative error $\leq \pm 5\%$. It can be seen from Table 2 that the presence of main cations and anions cause an insignificant

Table 2. The influence of the common coexisting ions on recovery of 1.0 $\mu\text{g L}^{-1}$ Cr(III)

Coexisting ions	Tolerance limits of the ions, mg L^{-1}
Na ⁺ & K ⁺	40000
Ca ²⁺ & Mg ²⁺	250
CH ₃ COO ⁻	8000
Cl ⁻	60 000
H ₂ PO ₄ ⁻	10 000
SO ₄ ²⁻	1000
CO ₃ ²⁻	3000
Zn ²⁺ , Ni ²⁺ , Mn ²⁺ & Pb ²⁺	50
Cu ²⁺ , Hg ²⁺ , Fe ²⁺ & Fe ³⁺	10

influence on the retention of Cr(III) ions onto AAXAD-4 resin. This shows us that AAXAD-4 resin is highly selective for Cr(III) ions for the analysis of various real water samples.

3. 8. Cr(III) Determination in Presence of Cr(VI) and Determination of Total Chromium Amount

The applicability of the proposed method was tested in presence of Cr(VI) ions for the determination of Cr(III) ions. For testing, the synthetic aqueous solutions including various mixtures of Cr(III) and Cr(VI) ions at different concentration levels were passed through the column at optimal conditions. Cr(III) ions were quantitatively separated and retained while Cr(VI) ions were almost completely passed through the column. This was observed by analyzing the effluent. The recoveries of Cr(III) ions were achieved quantitatively as shown in Table 3. In further study, the usability of the method for the determination of total chromium amount was also tested. Total chromium was determined after the reduction of Cr(VI) ions to Cr(III) ion by adding a mixture of 0.5 mL of concentrated H₂SO₄ and 0.5 mL of ethanol to 50 mL of sam-

ple solution containing Cr(VI) and Cr(III) ions at different concentration levels (Table 3).²⁹ The recovery of total chromium was also achieved quantitatively as shown in Table 3.

3. 9. Analytical Performance of the Proposed Method

The accuracy and validation of proposed method was confirmed by analysing different CRMs such as industrial wastewater (BCR-715), drinking water (TMDW-500) and lyophilised water (BCR-544) for the determination of Cr(III) ions and total chromium. It was checked by Student's t-test whether the difference between the certified value and the found value was significant. The results shown in Table 4 indicated that there is not a significant difference between certified and found values.

After preconcentration of Cr(III) ions, the linear equation was $A = 5.5259X + 0.0008$ and $r^2 = 0.9995$ for 600 mL with concentration range of 2–12 $\mu\text{g L}^{-1}$ of Cr(III) ions. Before preconcentration, the linear equation was $A = 0.0191X + 0.0021$ and $r^2 = 0.998$ within the concentration range of 0.2–5.0 $\mu\text{g mL}^{-1}$ of Cr(III) ions. Theoretical PF was calculated to be 289 as the ratio of slope of linear equation after preconcentration to the slope of linear equation before preconcentration close to the experimental PF of 300, indicating the retention and elution of the analyte was quantitative with recovery of 96%. The sensitivity was found to be 5.53 $\mu\text{g L}^{-1}$ from the slope of the calibration curve.³² The reproducibility of the overall preconcentration method in terms of RSD was calculated to be 3.75% ($n = 11$) at the concentration of 0.5 $\mu\text{g L}^{-1}$ Cr(III) ions. LOD (blank + 3 σ) and LOQ (blank + 10 σ , where σ is RSD of blank analysis, $n = 20$) are defined by IUPAC and were calculated accordingly.^{33,34} The LOD and LOQ of Cr(III) ions were found to be 0.041 and 0.131 $\mu\text{g L}^{-1}$, respectively. AAXAD-4 resin was successfully reused more than 250 times without significant loss in its performance.

Table 3. Test of proposed method for the determination of 1.0 $\mu\text{g L}^{-1}$ Cr(III) in presence of Cr(VI) ions and determination of total chromium (Sample volume: 50 mL & $n = 4$)

Added, μg Cr(III)	Cr(VI)	Found, μg , mean \pm SD				Recovery, %		
		Cr	Cr(III) ^a	Cr(VI) ^b	Cr ^c	Cr(III)	Cr(VI)	Cr
5	5	10	4.74 \pm 0.5	4.85 \pm 0.06	9.48 \pm 0.16	95 \pm 10	97 \pm 1	95 \pm 2
5	10	15	4.79 \pm 0.14	9.86 \pm 0.30	14.28 \pm 0.13	95 \pm 3	99 \pm 3	95 \pm 1
5	20	25	5.25 \pm 0.12	19.64 \pm 0.24	24.15 \pm 0.41	105 \pm 2	98 \pm 1	97 \pm 2
5	30	35	5.01 \pm 0.06	30.07 \pm 0.37	33.37 \pm 0.34	100 \pm 1	100 \pm 1	95 \pm 1
10	5	15	9.40 \pm 0.33	5.05 \pm 0.10	14.49 \pm 0.24	94 \pm 3	101 \pm 2	97 \pm 2
20	5	25	18.97 \pm 0.34	4.88 \pm 0.13	23.85 \pm 0.52	95 \pm 2	98 \pm 3	95 \pm 2
30	5	35	28.39 \pm 0.68	5.03 \pm 0.10	33.84 \pm 0.84	95 \pm 2	101 \pm 2	97 \pm 2

Cr(III)^a: Found amount of Cr(III) ions in presence of Cr(VI) ions.

Cr(VI)^b: Total amount of Cr(VI) ions by subtracting Cr(III) amount from total amount of Cr added.

Cr^c: Total amount of Cr determined after reducing Cr(VI) to Cr (III) ions in sample solutions

Table 4. Analysis of some certified reference materials (n = 3, final vol.: 2 mL)

Analytes		Certified reference materials/sample volume/concentrations		
		BCR-715 industrial waste water/5mL/ $\mu\text{g mL}^{-1}$	CRM TMDW-500 drinking water/ 50mL/ $\mu\text{g L}^{-1}$	BCR-544 Lyophilised water, 50mL/ $\mu\text{g L}^{-1}$
Total Cr	Certified	1.00 ± 0.09	20.0 ± 0.1	49.6 ± 1.4 ^b
	Found	1.05 ± 0.02	19.1 ± 0.4	47.5 ± 1.4
	Recovery,%	105	95.5	95.6
	t _{test} value	4.3(ns)	3.9(ns)	2.6(ns)
Cr(III)	Certified	–	–	26.8 ± 1.0
	Found	0.56 ± 0.02	9.7 ± 0.1	25.4 ± 1.1
	Recovery,%	–	–	94.8
	t _{test} value	–	–	2.2(ns)
Cr(VI)	Certified	–	–	22.8 ± 1.0
	Found	0.49 ± 0.02 ^a	9.4 ± 0.3 ^a	22.1 ± 0.9 ^a
	Recovery,%	–	–	96.9
	t _{test} value	–	–	1.4(ns)

^a Calculated from found total Cr and Cr(III) concentrations. ^b Calculated from the certified Cr(III) and Cr(VI),

^c Significance of t-test (n = 3) at 95% confidence level, t_{critical} = 4.30; ns: Not Significant.

3. 10. Application of the Developed Method

The proposed method was applied successfully on different real water samples for the determination of Cr(III) ions and total chromium. The samples were analysed before and after spiking with Cr(III) ions and

Cr(VI) ions. The recoveries of Cr(III) ions from the samples were achieved quantitatively as shown in Table 5. The total chromium levels of Incilipınar drinking fountain water and outlet water of waste water plant (Denizli, Turkey) samples do not pose a risk for public health.

Table 5. Determination of Cr(III) and Cr(VI) in various water samples (sample volume: 100 mL, n = 4).

Samples	Added, $\mu\text{g L}^{-1}$		Found, $\mu\text{g L}^{-1}$			Recovery,%	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI) ^a	Total Cr ^b	Cr (III)	Cr(VI)
Nestle bottled drinking water	–	–	n.d.	n.d.	n.d.	–	–
	20	20	20.72 ± 0.79	19.29 ± 2.02	40.01 ± 1.86	104 ± 4	96 ± 10
	40	20	40.81 ± 1.75	20.31 ± 1.81	61.12 ± 0.46	102 ± 4	102 ± 9
	20	40	21.18 ± 1.39	38.11 ± 1.74	58.29 ± 1.05	106 ± 7	93 ± 4
Pure bottled drinking water	–	–	n.d.	n.d.	n.d.	–	–
	20	20	19.10 ± 0.22	20.59 ± 1.14	39.69 ± 1.12	96 ± 1	103 ± 6
	40	20	39.36 ± 1.21	20.49 ± 1.42	59.85 ± 0.76	98 ± 3	102 ± 7
	20	40	19.55 ± 0.76	39.74 ± 1.20	59.29 ± 0.93	98 ± 4	99 ± 3
Mineral water	–	–	n.d.	n.d.	n.d.	–	–
	40	40	42.13 ± 1.99	37.21 ± 3.29	79.34 ± 4.90	105 ± 5	93 ± 8
	80	40	79.48 ± 2.66	41.22 ± 3.24	120.70 ± 3.05	99 ± 3	103 ± 8
	40	80	41.40 ± 0.31	78.45 ± 4.58	119.85 ± 4.57	104 ± 1	98 ± 6
İncilipınar drinking fountain water	–	–	1.14 ± 0.07	0.79 ± 0.11	1.93 ± 0.08	–	–
	20	20	21.22 ± 0.63	19.69 ± 1.11	40.91 ± 0.91	106 ± 3	98 ± 6
	40	20	41.11 ± 1.39	19.89 ± 1.74	61.00 ± 1.05	103 ± 4	99 ± 9
	20	40	20.91 ± 1.00	40.26 ± 1.44	61.17 ± 1.04	105 ± 5	101 ± 3
Outlet water of waste water plant (Denizli)	–	–	6.45 ± 0.12	1.22 ± 0.54	7.67 ± 0.53	–	–
	20	20	19.60 ± 0.65	21.26 ± 1.08	40.86 ± 0.86	98 ± 3	106 ± 5
	40	20	40.90 ± 0.97	20.25 ± 1.58	61.15 ± 1.25	102 ± 2	101 ± 8
	20	40	20.02 ± 0.87	41.10 ± 1.26	61.12 ± 0.91	101 ± 4	103 ± 3

^a Calculated from found total Cr and Cr(III) concentrations.

^b Total amount of Cr determined after reducing Cr(VI) to Cr (III) ions in sample solutions

3.10. Comparison

Analytical performance of the proposed method was compared with recently reported methods. In comparison, LOD and PF of reported method are better than those of reported methods shown in Table 6.

4. Conclusion

In this work, a modified AAXAD-4 resin column was evaluated for the speciation of Cr(III) and Cr(VI) ions, providing for selective preconcentration of Cr(III) at high pH. Besides its good selectivity between Cr(III) and Cr(VI) ions, it also has some characteristics such as good stability under working conditions, fast sorption and desorption kinetics, large adsorption capacity and good tolerance to coexisting ions. The used SPE system could recover more than 95% of Cr(III) from aqueous solution at pH=8. The feasibility of speciation at $\mu\text{g L}^{-1}$ levels make it an efficient sorbent for Cr(III). By com-

paring AAXAD-4 minicolumn SPE with MIS-FAAS, the developed method was successfully applied for chromium speciation in various water samples with low LOD, high PF, good accuracy and repeatability. Because of its simplicity, low cost and safety, it could be adopted for routine use for the speciation of Cr(III) and Cr(VI) ions.

5. Conflict of Interest

Authors declare that they do not have any conflict of interest with anyone.

6. Acknowledgement

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Table 6. Comparison of proposed method with reported methods for speciation of Cr(III) and Cr(VI) ions based on SPE

Resins/Techniques	Speciation Modality	Sample V, mL	LOD, $\mu\text{g L}^{-1}$	PF	RSD, %	Refs #
Amberlite XAD-16 loaded with salicylic acid/on-line column	Cr(III) sorption/ Cr(VI) reduction	10	0.10	79	1.2	11
Silica gel modified by <i>N,N'</i> -bis-(α -methyl salicylidene)-2,2-dimethyl-1,3-propa- nediimine/ column	Cr(III) sorption/ Total Cr By GFAAS	0.024 500	50	3.1	22	
Amberlite XAD-16 modified with α -benzoin oxime/on-line column	Cr(III) sorption/ Cr(VI) reduction	10	0.14	76	1.03	24
Maleic acid-functionalized XAD sorbent/column	Cr(III) sorption/ Cr(VI) reduction/	6000	150	300	0.2	35
Cr(VI) reduction C-18 bonded phase silica/ SPE disks	Cr(VI) sorption/ Cr(III) oxidation	1500	20	150	11.2	36
Dowex M 4195 chelating resin/column	Cr(VI) sorption/ Cr(III) oxidation	250	1.94	31	<10	37
MWCNTs-D2EHPA/ batch	Cr(III) sorption Cr(VI) reduction	300	50	60	<10	38
(MAD) chelating resin/column	Cr(III) sorption/ Cr(VI) reduction	2000	0.01	200	1.2	39
Poly(1,3-thiazol-2-yl-methacrylamide)-co-4-vinyl pyridine-co-divinyl benzene / column	Cr(VI) sorption/ Cr(III) oxidation	150	2.4	30	3.2	40
Chromium(III)-cochineal red A chelate/filter	Cr(III) sorption/ Cr(VI) reduction	800	1.4	94	<5	41
Diphenylcarbazone-incorporated resin/column	Cr(III) sorption/ Total Cr by GFAAS	–	30	–	3.2–3.7	42
Aminated XAD-4 / column	Cr(III) sorption/ Cr(VI) reduction	750	0.041	375	3.75	This work

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Povzetek

S kemično modifikacijo smo Amberlite XAD-4 smolo (AXAD-4) pretvorili v aminirano Amberlite XAD-4 (AAXAD-4) smolo in jo okarakterizirali z infrardečo spektroskopijo. AAXAD-4 smolo smo uporabili kot učinkovito trdno fazo za predkoncentracijo in speciacijo Cr(III) in Cr(VI) ionov s kolonsko tehniko. Koncentracijo kromovih zvrsti smo določili z mikrovzorčevalnim injekcijskim sistemom in plamenskim atomskim absorpcijskim spektrometrom (MIS-FAAS). Selektivno retencijo Cr(III) ionov smo dosegli pri pH 8,0 in elucijo z 1,0 mL 3,0 mol L⁻¹ HCl ter 1,0 mL 2,0 mol L⁻¹ NaOH zaporedoma pri pretoku 5,0 mL min⁻¹. Maksimalna sorpcijska kapaciteta AAXAD-4 smole za Cr(III) ione je bila 67,0 mg g⁻¹. Meja zaznave (LOD) za Cr(III) ione je bila 0,041 µg L⁻¹, meja določitve (LOQ) 0,131 µg L⁻¹, medtem ko je bil predkoncentracijski faktor (PF) 375 in relativni standardni odklik (RSD) 3,75% (n = 11). Metodo smo validirali s certificiranimi referenčnimi materiali (CRM) in jo uspešno uporabili za analizo realnih vzorcev z dodanimi Cr(III) in Cr(VI) ioni.