

A novel solid phase extraction procedure on Amberlite XAD-1180 for speciation of Cr(III), Cr(VI) and total chromium in environmental and pharmaceutical samples

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Abstract

Due to the toxicity of chromium, species depend on their chemical properties and bioavailabilities, speciation of chromium is very important in environmental samples. A speciation procedure for chromium(III), chromium(VI) and total chromium in environmental samples is presented in this work, prior to flame atomic absorption spectrometric determination of chromium. The procedure is based on the adsorption of Cr(III)–diphenylcarbazone complex on Amberlite XAD-1180 resin. After oxidation of Cr(III), the developed solid phase extraction system was applied to determinate the total chromium. Cr(III) was calculated as the difference between the total Cr content and the Cr(VI) content. The analytical conditions for the quantitative recoveries of Cr(VI) on Amberlite XAD-1180 resin were investigated. The effects of some alkaline, earth alkaline, metal ions and also some anions were also examined. Preconcentration factor was found to be 75. The detection limits (LOD) based on three times sigma of the blank ($N: 21$) for Cr(VI) and total chromium were 7.7 and 8.6 $\mu\text{g/L}$, respectively. Satisfactory results for the analysis of total chromium in the stream sediment (GBW7310) certified reference material for the validation of the presented method was obtained. The procedure was applied to food, water and pharmaceutical samples successfully.

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Keywords: Speciation of chromium; Amberlite XAD-1180; Solid phase extraction; Environmental samples; Pharmaceutical samples

1. Introduction

Speciation information of heavy metal ions is very important for their toxicity and biological role of a particular elements vary greatly depending on its chemical form [1]. Speciation studies of heavy metal ions are generally focused on chromium, arsenic, antimony, etc. The toxicity of chromium depends on the chemical properties and bioavailability of the species, which are related to their characteristics and concentrations [2].

Chromium(III) is known to be an essential trace nutrient involved in the mechanism of the action of the pancreatic hormone insulin and/or glucose metabolism [3]. On the other hand, Cr(VI) is toxic for biological systems especially for human. Chromium(VI) is water soluble and extremely irritating and

toxic to human body tissue owing to its oxidizing potential and permeability of biological membranes [4]. The major toxic effects of Cr(VI) are chronic ulcers, dermatitis, corrosive reaction in nasal septum and local effects in lungs [5]. Owing to the high oxidation potential and the ease penetrate from biological membranes, Cr(VI) compounds are approximately 100 times more toxic than Cr(III) salts [6,7]. The US EPA has set the concentration of 0.1 mg L^{-1} of total chromium for drinking water as “maximum contaminant level goals”. World Health Organization states that the guideline values of 50 $\mu\text{g L}^{-1}$ of Cr(VI) [8]. Due to these factors, accurate and facile determinations of both valence forms in environmental samples take an important role in the analytical chemistry.

Direct determinations of chromium species in the real samples are difficult and limited with some instrumental techniques. For the determination of chromium species by flame atomic absorption spectrometry, sample pretreatment procedures especially separation–preconcentration techniques have been used

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H₄L: 1,5-Diphenylcarbazine

H₂L: Diphenylcarbazone

Scheme 1. Reaction between chromium(VI) and diphenylcarbazine.

by the researchers around the world [9–14]. Solid phase extraction is also found very important place in the speciation studies of chromium due to its simplicity, selectivity, flexibility, economic and environment-friendly, sampling in the field, safety, ease of automation and absence of emulsion. Activated carbon, polymeric resins, chelating resins, etc. are widely used on the speciation studies of chromium [15–20]. Diphenylcarbazine gives reaction with chromium(VI) in mineral acid medium and Cr(III)–diphenylcarbazone complex occurs (Scheme 1).

In the presented study, a solid phase extraction procedure for the speciation of chromium(III) and chromium(VI) on Amberlite XAD-1180 adsorption resin has been established. The analytical parameters including amounts of ligand, eluent type, and sample volume were investigated for the quantitative recoveries. The procedure was applied to the environmental, food and pharmaceutical samples.

2. Experimental

2.1. Reagents

All chemicals used in this study were of analytical reagent grade and were used without further purification. Deionised water (Millipore Elix[®] 5 UV resistant 14 MΩ cm⁻¹) was used for all aqua dilutions. All the plastic and glassware equipments were cleaned by soaking in dilute HNO₃ (1 + 9) and were rinsed with deionised water prior to use. 1,5-Diphenylcarbazine solution (5 × 10⁻³ mol L⁻¹) was prepared daily by dissolving appropriate amount of 1,5-diphenylcarbazine (Merck) in ethanol. Cr(VI) and Cr(III) stock solutions (1000 mg L⁻¹) were prepared from K₂CrO₄ and Cr(NO₃)₃·9H₂O. Stock solutions of diverse elements were prepared from high purity compounds.

Amberlite XAD-1180 is an aromatic type adsorbent, based on crosslinked polystyrenic matrix. It was purified by washing with methanol, water, 1.0 mol L⁻¹ nitric acid in acetone, water, 1.0 mol L⁻¹ NaOH, water and acetone sequentially, in order to eliminate the contamination of trace metal ions, other inorganic and organic compounds.

2.2. Instruments

A Varian AA240 model flame atomic absorption spectrometer was used for determination of chromium. The operating parameters of instruments for chromium were set according to the manufacturer recommendation. These conditions were given Table 1. For measuring pH values in the aqueous phase, WTW 330i model glass-electrode was employed. Ohaus EP214C model analytical balance was used for all mass measurements and Milestone Ethos D closed vessel microwave system (max-

Table 1
Conditions for flame atomic absorption spectrometer

Parameters	Cr
Wavelength (nm)	357.9
Slit width (nm)	0.2
Lamp current (mA)	7.0
Flow rate of acetylene (L min ⁻¹)	2.9
Flow of air (L min ⁻¹)	11.0

imum pressure 1450 psi, maximum temperature 300 °C) was used for microwave digestion.

A short glass column with an inner diameter of 10 mm and a length of 100 mm, equipped with porous frits, was filled up to a height of about 20 mm with a suspension of 700 mg Amberlite XAD-1180 resin in water.

2.3. Model studies for Cr(IV)

The procedure was tested by using model solutions. Model solutions containing 5 μg of Cr(VI) were prepared in 50 mL of 0.5 mol L⁻¹ sulfuric acid. One millilitre of 1,5-diphenylcarbazine (5 × 10⁻³ mol L⁻¹) was added to the model solutions. After waiting 10 min for complex formation, the model solutions were gravitationally passed through a column at a flow rate of 2 mL min⁻¹. The retained Cr(III)–diphenylcarbazone complex was eluted by 8–10 mL of 1 mol L⁻¹ HNO₃ in acetone with a flow rate of 2 mL min⁻¹. The flow rates were controlled by a stopcock of the column. The effluent was collected in a small glass beaker and carefully evaporated to 0.5–1 mL on a hot plate adjusted ca. 30–40 °C on a hood. The residue was diluted to 2 or 5 mL with 1 mol L⁻¹ HNO₃ solution. Chromium concentrations in the final solutions were determined by using flame atomic absorption spectrometry.

2.4. Procedure for total chromium

Total chromium was determined after oxidizing Cr(III) to Cr(VI) by the addition of K₂S₂O₈ in an acidic medium. Oxidation procedure was performed according to literature [21]. 0.5 mL of K₂S₂O₈ (1%, w/v) solution, one drop of AgNO₃ (0.01%, w/v) and 0.5 mL concentrated H₂SO₄ were added into 100 mL beaker containing 50 mL of the spiked solution of 5 μg mL⁻¹ Cr(III). The beaker was covered with a watch glass and heated without boiling (≈65 °C) for about 45 min to complete oxidation and then boiled to reduce excess of K₂S₂O₈. Then the method described in Section 2.3 was applied. The concentration of Cr(III) was calculated by subtracting the content of Cr(VI) from total chromium content.

2.5. Applications

Wastewater sample collected from Bor Organized Industrial Region was filtered from 0.45 μM cellulose nitrate filter. For determination of Cr(VI); 10 mL of wastewater was diluted 10-fold with deionized water, than this solution was acidified with 2.7 mL of concentrated H₂SO₄. After cooling for 30 min at room

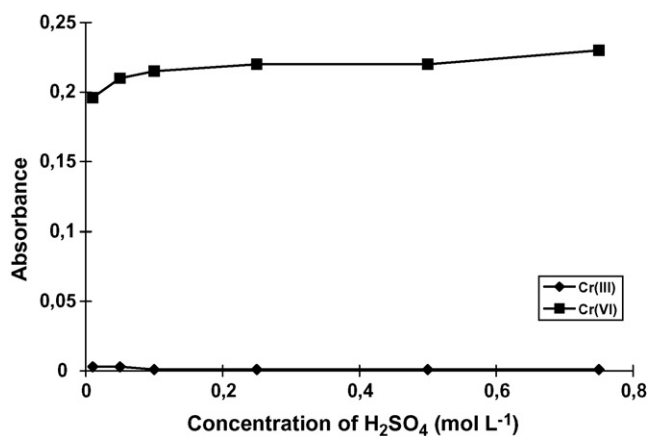


Fig. 1. The influences of concentration of sulfuric acid on the recoveries of Cr(VI) and Cr(III) ($N: 4$).

temperature, the speciation procedures given above were applied to this solution.

Hundred milligrams stream sediment standard reference material (GBW 07310) was decomposed in 10 mL of aqua regia and the solution was evaporated to dryness. Ten to fifteen millilitres of 1 mol L⁻¹ HNO₃ was added to the residue. The suspension was filtered through a blue band filter paper, and insoluble part was washed with deionized water. Then the preconcentration procedure given above was applied to the final solutions for the total chromium. The same procedure was applied to the blank solution.

Another application of the presented method was performed for the analysis of chromium contents of Solgar Chromium Picolinate Vegetable Capsules [22–24]. Fifty milligrams Solgar Chromium Picolinate Vegetable Capsules was decomposed with 3 mL of concentrated HNO₃, 9 mL of concentrated HCl and diluted to 50 mL with distilled water. Then the preconcentration procedure given above was applied to the final solutions. The same procedure was applied to the blank solution.

In order to the microwave digestion of lentil sample, 0.5 g of sample was mixed with 6.0 mL of concentrated HNO₃ and 2.0 mL of H₂O₂ in microwave digestion system. Digestion conditions for microwave system of the samples were applied as 2 min for 250 W, 2 min for 0 W, 6 min for 250 W, 5 min for 400 W, 8 min for 550 W, vent: 8 min. After digestion, the volume of the solution was filled up to 25.0 mL with deionized water. Blanks were prepared in the same way as the sample. Then preconcentration procedure given in Section 2.3 was applied.

3. Results and discussion

3.1. Optimization of the procedure

According to literature [25,26], Cr(III)–diphenylcarbazone complex is formed at the sulfuric acid media. The influences of concentration of sulfuric acid on the recoveries of Cr(VI) and Cr(III) onto Amberlite XAD-1180 resin were investigated between ranges of 0.01–0.75 mol L⁻¹ sulfuric acid. The results were depicted in Fig. 1. Cr(III) in the all working range of sulfuric acid were not recovered and Cr(VI) recoveries were increased

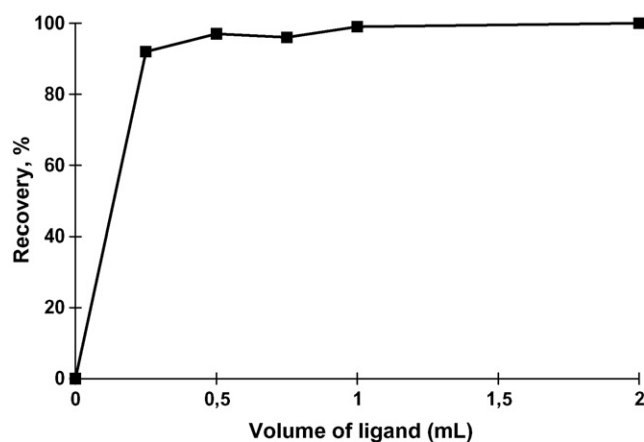


Fig. 2. The influences of ligand on the recoveries of Cr(VI) ($N: 4$).

with increasing sulfuric acid concentrations. Quantitative values for Cr(VI) were obtained using more concentrated acid than 0.10 mol L⁻¹ sulfuric acid. These results showed the possibility of separation of Cr(VI) from Cr(III). All other studies were performed with 0.5 mol L⁻¹ sulfuric acid.

In the solid phase extraction studies, amount of ligand is an important factor for the quantitative recoveries of the analytes [27–30]. Due to this point, the influences of the amount of 1,5-diphenylcarbazide on the recoveries of Cr(VI) on Amberlite XAD-1180 were investigated under optimal conditions. The results were given in Fig. 2. No recoveries were obtained without ligand. The recovery values increased with the increasing amounts of 1,5-diphenylcarbazide and reached to quantitative value 0.5 mL of 5×10^{-3} mol L⁻¹ 1,5-diphenylcarbazide. Chromium(VI) was quantitatively recovered in 0.5–2.0 mL of 5×10^{-3} mol L⁻¹ 1,5-diphenylcarbazide. All further investigations were carried out 1 mL of 5×10^{-3} mol L⁻¹ 1,5-diphenylcarbazide.

In order to desorb retained chromium(III)–diphenylcarbazone complex on the Amberlite XAD-1180 column, effect of various eluting agents were searched. For that purpose, 10 mL of each eluent was used for desorption. These results were given in Table 2. The recovery values were not quantitative with diluted mineral acids. Mineral acid solutions in acetone were examined. Quantitative recovery values for chromium(III)–diphenylcarbazone complex from XAD-1180 were obtained following eluting agents: 1 mol L⁻¹ HNO₃ in acetone, 2 mol L⁻¹ HNO₃ in acetone and 2 mol L⁻¹ HCl

Table 2
Influences of various eluents ($N: 4$)

Eluent	Recovery (%)
1 mol L ⁻¹ HNO ₃	9 ± 1
2 mol L ⁻¹ HNO ₃	<5
1 mol L ⁻¹ HCl	<5
2 mol L ⁻¹ HCl	<5
1 mol L ⁻¹ HNO ₃ in acetone	99 ± 4
2 mol L ⁻¹ HNO ₃ in acetone	95 ± 6
1 mol L ⁻¹ HCl in acetone	85 ± 2
2 mol L ⁻¹ HCl in acetone	97 ± 5

Mean ± S.D.

Table 3
Effect of sample volume on the recovery of Cr(VI) on XAD-1180 ($N: 4$)

Sample volume (mL)	Recovery (%)
30	99 ± 4 ^a
50	104 ± 3
100	112 ± 0
150	100 ± 4
200	88 ± 1

^a Mean ± S.D.

Table 4
Tolerable levels of concomitant ions for the retention of Cr(VI) on Amberlite XAD-1180 resin ($N: 3$)

Ions	Salt added	Concentration (mg L ⁻¹)	Recovery (%)
Na ⁺	NaCl	10000	100 ± 6 ^a
K ⁺	KCl	2500	94 ± 1
Ca ²⁺	CaCl ₂	250	96 ± 4
Mg ²⁺	MgCl ₂	100	95 ± 2
Cl ⁻	NH ₄ Cl	2500	102 ± 4
Cr ³⁺	Cr(NO ₃) ₃	25	102 ± 3
Pb ²⁺	Pb(NO ₃) ₂	25	99 ± 2
Cu ²⁺	Cu(NO ₃) ₂	25	98 ± 2
Fe ³⁺	Fe ₂ (SO ₄) ₃	25	103 ± 3

^a Mean ± S.D.

in acetone. The recovery values were approximately at the same level for these solutions. In all further studies, 10 mL of 1 mol L⁻¹ HNO₃ in acetone was used.

To get high preconcentration factor, sample volume is an important point [31–34]. The effect of the volume of model solutions on the recoveries of Cr(VI) on the Amberlite XAD-1180 were also investigated with using the sample volume range of 30–200 mL. The results were summarized in Table 3. Quantitative recoveries for Cr(VI) were obtained with the sample volume range of 30–150 mL. The preconcentration factor was calculated by the ratio of the highest sample volume (150 mL) and the lowest final volume (2 mL). The preconcentration factor was found to be 75.

3.2. Effect of diverse ions

In order to assess the possible analytical applications of the recommended speciation–preconcentration procedure on Amberlite XAD-1180, the effect of some foreign ions which interfere with chromium(VI) ion or/and often accompany analyte ions in various real environmental samples was examined with the optimized conditions. The results were summarized in Table 4. The recoveries of chromium(VI) in these studies were

Table 5
Determination of total chromium in spiked test solutions ($N: 3$)

Added Cr(III) (μg)	Added Cr(VI) (μg)	Total chromium (μg)	Found, total chromium (μg)	Recovery (%)
5.0	0	5.0	5.2 ± 0.1 ^a	104 ± 2
5.0	2.5	7.5	7.4 ± 0.4	99 ± 5
7.5	0	7.5	7.1 ± 0.1	95 ± 2
7.5	2.5	10.0	10.4 ± 0.1	104 ± 2

^a Mean ± S.D.

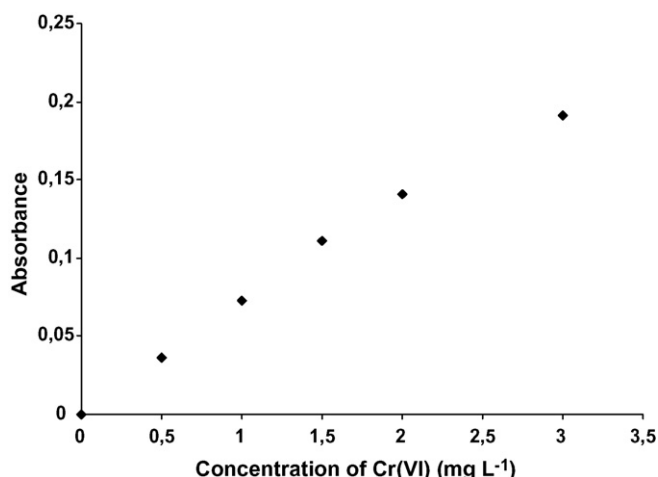


Fig. 3. Calibration graph for Cr(VI) obtained presented speciation system.

higher than 95%. As it is seen in Table 4, large numbers of performing ions, have no considerable effect on the determination of Cr(VI).

3.3. Determination of total chromium in model solutions

In order to determinate total chromium, test solutions that contained different amounts of chromium(III) and chromium(VI) were prepared. Then the oxidation of chromium(III) to chromium(VI) in the test solutions were performed by the procedure given by Skoog et al. [21] and the procedure explained in Section 2.3 was applied to these solutions. The results were given in Table 5. Quantitative recovery values were obtained for these solutions and a good agreement was found between the added chromium(VI) and measured chromium(VI) amount. The recoveries of chromium(VI) were between 95 and 104%. The results show that the proposed method can easily be applied for the determination of total chromium in aqueous solutions.

3.4. Calibration curve

Using the optimized conditions of preconcentration, calibration curve (Fig. 3) was prepared for Cr(VI), (0–0.25 μg mL⁻¹). Linear equations were as follows;

$$\text{Cr(VI)}A = 0.0374C - 0.0389 \quad r^2 = 0.9965 \quad (N : 6)$$

where A is absorbance and C is concentration of chromium(VI) (μg mL⁻¹).

Table 6
Determination Cr(III), Cr(VI) and total chromium in two water and a red lentil samples ($N: 3$)

Sample	Added Cr(III) (μg)	Added Cr(VI) (μg)	Found, Cr(VI) (μg)	Found, total chromium (μg)	Found Cr(III) (μg)	Recovery (%)
Tap water	0	0	BDL	BDL	BDL	–
	0	10	9.6 ± 0.5^a	–	–	96 ± 5
	5	5	4.9 ± 0.2	10.0 ± 0.2	5.1	100 ± 2
Bottled mineral water	0	0	BDL	BDL	–	–
	0	10	10.4 ± 0.1	–	–	104 ± 1
	5	5	4.9 ± 0.2	10.4 ± 0.6	5.5	104 ± 6
Red lentil	0	0	–	BDL	–	–
	7.5	7.5	–	14.8 ± 0.7^a	–	99 ± 5

–, not determined; BDL, below the detection limit.

^a Mean \pm S.D.

Table 7
The level of total chromium in the certified reference materials after application of the presented procedure ($N: 3$)

Sample	Certified value	Our value	RSD (%)
Stream sediment (GBW7310) certified reference material	$136 \mu\text{g g}^{-1}$	$140 \mu\text{g g}^{-1}$	5.1
Solgar chromium picolinate vegetable capsules	$200.0 \mu\text{g capsule}^{-1}$	$207.8 \mu\text{g capsule}^{-1}$	5.7

3.5. Limit of detection

The detection limit (LOD) of the present work was calculated under optimal experimental conditions after application of the preconcentration procedure to blank solutions. The detection limit of chromium(VI) and total chromium based on three times the standard deviations of the blank ($N: 21$, $X_L = X_b + 3s$, X_L : limit of detection, X_b : blank value) was 7.7 and $8.6 \mu\text{g L}^{-1}$, respectively.

3.6. Applications of the presented procedure

The presented speciation procedure was applied to the speciation of chromium in a tap water from Kayseri, a bottled mineral water from Beypazarı, Ankara and microwave digested lentil sample from Kayseri. Various amounts of chromium species were also spiked to these samples. Then the procedures given in Section 2 were applied. The results were given in Table 6. A good agreement was obtained between the added and measured analyte amounts. These results confirmed the validity of the proposed method. The presented method could be applied successfully for the speciation of trace amounts of chromium in real samples.

The method was applied to Stream sediment (GBW7310) certified reference material and Solgar Chromium Picolinate Vegetable Capsules for total chromium. The results were given in Table 7. The results were in good agreement with the certified values for chromium. The proposed speciation method was also applied to determination of chromium in the tannery wastewater sample from the Organized Industrial Region of Bor-Nigde. The results were given in Table 8.

Table 8
The level of chromium species in wastewater from Organised Industrial Region of Bor-Nigde ($N: 4$)

	Concentration ($\mu\text{g L}^{-1}$)
Chromium(III)	442 ± 116
Chromium(VI)	974 ± 82

Uncertainty at 95% confidence limit.

4. Conclusion

A facile, sensitive speciation procedure has been established in the presented work for the speciation of chromium prior to its atomic absorption spectrometric determination. The procedure was successfully applied to the environmental and pharmaceutical samples. No interferences were observed from the various foreign ions. Proposed method has been successfully applied to determination of total chromium levels for Stream sediment (GBW7310) certified reference material.

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