

## Speciation of Cr(III) and Cr(VI) after column solid phase extraction on Amberlite XAD-2010

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### Abstract

A speciation procedure for Cr(III) and Cr(VI) based on column solid phase extraction on Amberlite XAD-2010 and flame atomic absorption spectrometry combination. Cr(VI) was quantitatively recovered on Amberlite XAD-2010 resin at pH range of 2.0–3.0 as its diethyldithiocarbamate complex, while the recoveries of Cr(III) was below 5%. The influences of the various parameters including amounts of the reagents, eluent type and its volume, sample volume, etc., on the quantitative recoveries were examined. The interference of matrix and coexistent elements for method were studied. The detection limit (corresponding to three times the standard deviation of the blank) and the enrichment factor for Cr(VI) were found to be 1.28 µg/L and 25, respectively. To verify the accuracy of the method, drinking water certified reference material (CRM-TMDW-500) was analyzed and the results obtained were in good agreement with the certified value. The proposed method has been successfully applied to the speciation of Cr(III) and Cr(VI) in water samples and preconcentration of total chromium in environmental samples.

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### 1. Introduction

Transition metals at trace levels play important positive and negative roles in human body [1–4]. As a trace heavy metal, chromium has also important roles in our life [5–7]. Chromium is a major pollutant for environment, usually as a result of some industrial pollution including tanning factories, steel works, industrial electroplating, wood preservation, etc., and artificial fertilizers [8,9]. Chromium species exist mainly in two different oxidation states, Cr(III) and Cr(VI) in the environment. Their biological activity, chemical behavior and influences on the environment are very different. While chromium (III) is necessary specie for the living organisms especially for human, chromium (VI) is toxic specie [10]. Chromium (III) is an essential nutrient, effective in insulin action and thus influences carbohydrate, lipid and protein metabolism. Cr(VI) are known to exhibit carcinogenic properties. Cr(VI) attacks liver, kidney and lungs

[11–14]. Chromium speciation has a prime importance in different branches of natural sciences. The importance of chromium speciation originates from widespread participation of this element in various environmental and biological samples [15]. Speciation of chromium (III) and chromium (VI) has been a long-standing analytical challenge. The selective determination of chromium (VI) is of particular importance because of its toxicity [16]. Due to these importance of Cr(III) and Cr(VI), the accurate and sensitive determinations of these ions are the important part of the analytical chemistry. Except some techniques including electroanalytical methods, direct and simultaneous determination of Cr(VI) and Cr(III) is difficult by the instrumental techniques like flame and graphite furnace atomic absorption spectrometry, inductively coupled plasma-optical emission spectrometry, inductively coupled plasma-mass spectrometry, etc. To overcome these problem, separation–preconcentration techniques solvent extraction [17], coprecipitation [18,19], solid phase extraction [20,21] have been widely used by the researchers for the speciation of Cr(VI) and Cr(III).

Amberlite XAD-2010 is a member of Amberlite XAD adsorption resin family [22–24]. It is poly(styrene-divinyl-

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benzene) copolymer. It has high adsorption capacity like other members of this family [25]. Amberlite XAD-2010 has been used for the solid phase extraction of biomolecules and pharmaceuticals [22,25]. According to our literature survey, Amberlite XAD-2010 is not used for the solid phase extraction of the heavy metals ions.

In the presented work, a speciation procedure for Cr(VI) and Cr(III) based on combination of solid phase extraction and flame atomic absorption spectrometric determinations has been presented.

## 2. Experimental

### 2.1. Instrumentation

The measurements were performed with an atomic absorption spectrometer equipped with single element hollow cathode lamps of Unicam AA-929 using an air-acetylene flame. The wavelength used for monitoring Cr was 357.9 nm.

The pH values of the solutions were measured by a Hanna 211 pH meter using the full range 0–14. A mechanical shaker Nuve SL 350 having speed control was used for batch experiments. Milestone Ethos D closed vessel microwave system (maximum pressure 1450 psi; maximum temperature 300 °C) was used for the digestion of lichen and rock samples.

### 2.2. Reagents

All chemicals were analytical reagent-grade (Merck and Fluka) and all solutions were prepared in distilled/deionized water. Cr(III) and Cr(VI) stock solutions were prepared from  $\text{Cr}(\text{NO}_3)_3$  in 0.5 mol L<sup>-1</sup> HNO<sub>3</sub> and K<sub>2</sub>CrO<sub>4</sub> in water, respectively with a concentration of 1000 mg L<sup>-1</sup>. 0.05% (w/v) solution of sodium diethyldithiocarbamate (DDTC) in ethanol was used as a chelating agent. The model and standard solutions of analytes were prepared by diluting from the stock solutions using suitable ratios.

Amberlite XAD-2010 (specific surface area 660 m<sup>2</sup> g<sup>-1</sup> and bead size, 20–60 mesh) and were purchased from Sigma Chem. Co., St. Louis. Trace metal in drinking water standard reference material (CRM-TMDW-500) were obtained from High-Purity Standards Inc.

Buffer solutions were used for pH adjustments, therefore, solutions containing suitable amounts of Na<sub>2</sub>SO<sub>4</sub>–NaHSO<sub>4</sub> for pH 2, HAc–NH<sub>4</sub>Ac for pH 4–6, NH<sub>3</sub>–NH<sub>4</sub>Cl for pH 8–10, and NaOH–Na<sub>2</sub>HPO<sub>4</sub> for pH 12 were prepared in water.

### 2.3. Sampling

Water samples were taken from a tap, which provides drinking water for Karadeniz Technical University and from a stream of Degirmendere River, which supply drinking water to Trabzon city. Polyethylene bottles were used for sample storage and were thoroughly washed with detergent, tap water, HNO<sub>3</sub>, distilled/deionised water, respectively prior to collection of the water samples. Finally, the water samples were acidified with

HNO<sub>3</sub> and filtered through a nitrocellulose membrane with 0.45 μm of pore size.

A moss was collected from Hopa-Artvin, Turkey. A rock sample collected from Kumbet Plateau (Giresun) in Turkey were dried in an oven for 20 h at 105 °C and fine powdered.

### 2.4. Column preparation

A mini-column with 10 cm length and 1.0 cm diameter, having a porous disk and a stopcock, has been used for pre-concentration of the metals. First, XAD-2010 (grounded and sieved to 150–200 μm) resin was washed successively with 1 mol L<sup>-1</sup> NaOH, water, 1 mol L<sup>-1</sup> HNO<sub>3</sub>, water, acetone and water. Before placing 250 mg of Amberlite XAD-2010 into the column, a small amount of glass wool placed in the lower part of the column and after placing the sorbent another layer of glass wool placed in the upper part of the column to prevent loss of the XAD-2010 resin. Then the sorbent was washed with ethanol and 1 mol L<sup>-1</sup> HNO<sub>3</sub>. The resin was thoroughly washed with H<sub>2</sub>O until the effluents were neutral. After each use, the resin in the column was washed thoroughly with water, 1 mol L<sup>-1</sup> HNO<sub>3</sub> and related buffer solution, and then stored in water for further applications.

### 2.5. Procedure of Cr(VI)

Twenty-five micrograms of chromium (VI), buffer solution to give the desired pH between 2 and 10 and 5 mL of DDTC was added to 50 mL model solution. The XAD-2010 column was preconditioned by passing buffer solution. Cr(VI)-DDTC solution was passed through the column at a flow rate of 7 mL/min. After passing of this solution, the column was rinsed twice with 10 mL of water. The adsorbed chelate on the XAD-2010 column was eluted with 7.5 mL portion of 1 mol L<sup>-1</sup> HNO<sub>3</sub> in acetone. The eluent was evaporated over a hot plate to near dryness. The residue diluted to 5 mL with 1 mol L<sup>-1</sup> HNO<sub>3</sub>. The eluent was analyzed by atomic absorption spectrometer.

### 2.6. Oxidation of Cr(III) to Cr(VI) and determination of total chromium

Oxidation of Cr(III) to Cr(VI) has been performed by using the procedure given in literature [26,27]. After adjustment of the pH of the solution pH 10, 10 mL of 3% hydrogen peroxide was added. The amount of chromium (III) in this solution was 25 μg. The solution was heated at 80 °C for 40 min. Then the solution was boiled for 10 min in order to remove any excess of H<sub>2</sub>O<sub>2</sub>. Then test procedure given above was applied to this solution. Chromium level was determined by FAAS.

After oxidation of Cr(III) to Cr(VI) by using H<sub>2</sub>O<sub>2</sub> in basic media, the method was applied to the determination of the total chromium. The level of Cr(III) is calculated by difference of total chromium and Cr(VI) concentrations.

### 2.7. Analysis of the real samples

Before the analysis, the pHs of the water samples (tap water, river water and CRM-TMDW-500 trace metal in drinking water

certified reference material) were adjusted to 2.5. Then 5.0 mL of 0.05% (w/v) DDTC solution was added. The sample was passed through the column. DDTC chelates adsorbed on column were eluted with 1 mol L<sup>-1</sup> HNO<sub>3</sub> in acetone. The effluent was evaporated to near dryness and made up to 5.0 mL with 1 mol L<sup>-1</sup> HNO<sub>3</sub>. The levels of the investigated analyte ions in the samples were determined by FAAS.

Prior to preconcentration step for solid samples analyzed, moss and rock sample were microwave digested. Digestion conditions for microwave system for the samples were applied as (45 bar) 1 min for 250 W, 1 min for 0 W, 6 min for 650 W, 5 min for 400 W, 8 min for 250 W, vent: 5 min, respectively. Moss (1.00 g) were digested with 6 mL of HNO<sub>3</sub> (65%), 2 mL of H<sub>2</sub>O<sub>2</sub> (30%) in microwave digestion system. Rock sample (0.5 g) were digested with 4.5 mL of HCl (37%), 1.5 mL HNO<sub>3</sub> (65%) and 2 mL HF (39%) in microwave digestion system.

After microwave digestion, the suspension was filtered through a blue band filter paper, and insoluble part was washed with distilled water. And then the volume of the sample was made up to 50.0 mL with distilled water. Blanks were prepared in the same way as the sample, but omitting the sample. The preconcentration procedure given above was applied to the samples. The final volume was 5.0 mL.

### 3. Results and discussion

#### 3.1. Effect of pH

The effect of pH on the retention of Cr(III) and Cr(VI) on to the Amberlite XAD-2010 column has been investigated separately. pH of the solution was adjusted in a range of 2.0–12.0 by using buffer solutions and passed through the column. The retained ions were eluted by 7.5 mL of 1 mol L<sup>-1</sup> HNO<sub>3</sub> solution in acetone. Cr(III) and Cr(VI) have been determined in the eluate by FAAS. As can be seen in Fig. 1 quantitative recovery (>95%) was found at the pH 2.0–4.0 with Cr(VI) while the recovery of Cr(III) is rather low (<5%). This point could make it possible to separate Cr(VI) from Cr(III) at the

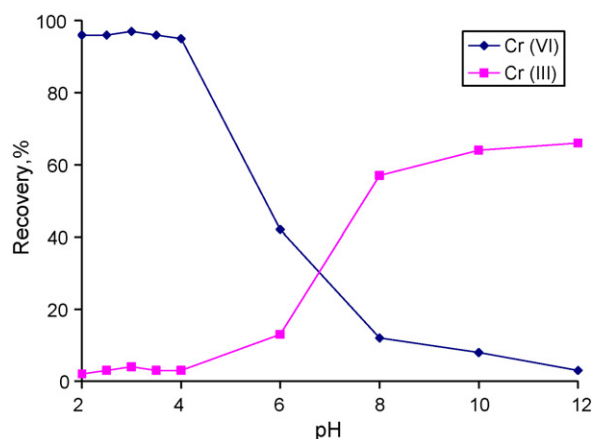


Fig. 1. Effect of pH on the recoveries of chromium species on Amberlite XAD-2010 (N:3).

Table 1

Effect of the type of elution solution on the recovery of Cr(VI) (N:3, eluent volume: 7.5 mL)

Type of elution solution	Recovery (%)
1.0 mol L <sup>-1</sup> HCl	<5
2.0 mol L <sup>-1</sup> HCl	<5
1.0 mol L <sup>-1</sup> HNO <sub>3</sub>	<5
2.0 mol L <sup>-1</sup> HNO <sub>3</sub>	<5
Acetone	32 ± 1
Ethanol	26 ± 1
1.0 mol L <sup>-1</sup> HCl in acetone	80 ± 4
2.0 mol L <sup>-1</sup> HCl in acetone	72 ± 5
1.0 mol L <sup>-1</sup> HNO <sub>3</sub> in acetone	96 ± 3
2.0 mol L <sup>-1</sup> HNO <sub>3</sub> in acetone	91 ± 3

pH range of 2.0–4.0. All further works were performed at pH 2.5.

#### 3.2. Effect of ligand amount

Due to the amounts of chelating agent is one of the important factor for the quantitative recoveries of analyte ions [28–30], the effects of the sodium diethyldithiocarbamate (DDTC) amounts on the adsorption of Cr(VI) on the resin was investigated. The recoveries of Cr(VI) was <10%, when DDTC was not added to the solution. The recovery values increased with the addition of DDTC. The quantitative values were obtained after 2.0 mg (4 mL of 0.05% (w/v)) of DDTC. After this point the recoveries were quantitative in all working range of DDTC. In all further studies, 2.5 mg (5.0 mL of 0.05% (w/v)) of DDTC was used.

#### 3.3. Eluent type and volume

In order to elution of adsorbed Cr(VI) on the XAD-2010, hydrochloric acid, nitric acid, acetone, ethanol and their combinations have been tested as eluent. The results were given in Table 1. It was found that 1.0 mol L<sup>-1</sup> HNO<sub>3</sub> in acetone could be used to elution of the adsorbed Cr(VI) on XAD-2010 column. In all further works, 7.5 mL 1 mol L<sup>-1</sup> HNO<sub>3</sub> solution in acetone was used.

#### 3.4. Effect of amount of Amberlite XAD-2010

The influences of amounts of XAD-2010 on the retention of Cr(VI) were investigated. The results were given in Fig. 2. The recovery values for chromium (VI) were not quantitative till 200 mg of XAD-2010. Quantitative recovery values were obtained in the 200–600 mg range of XAD-2010. In all experiments were performed with 250 mg of XAD-2010.

#### 3.5. Influence of flow rate of sample

The flow rate of the sample solution affects the retention of Cr(VI) complex on the adsorbent and the duration of complete analysis. Therefore, the effect of the flow rate of sample solution was examined under the optimum conditions. The flow rate of

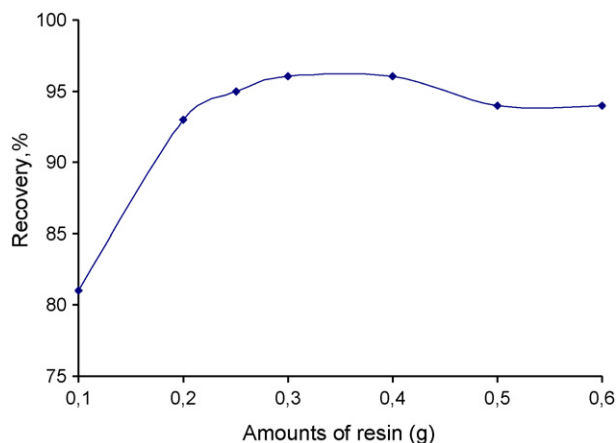


Fig. 2. Effect of resin amount on the recovery of Cr(VI) (N:3).

the sample solution was adjusted in a range  $0.5\text{--}17.0\text{ mL min}^{-1}$  (Fig. 3). It was found that the retention of Cr(VI) was practically not changed up to  $8.0\text{ mL min}^{-1}$  flow rate. Above this value, the recoveries were decreased gradually. For that reason,  $7.0\text{ mL min}^{-1}$  was chosen as the optimum flow rate.

### 3.6. Effect of sample volume

In order to deal with real samples, the maximum applicable sample volume must be determined for the solid phase extraction studies. Fifty to 300 mL of sample solutions containing  $25\text{ }\mu\text{g}$  of Cr(VI) were passed through the column under the optimum conditions. The results are depicted in Fig. 4. The recovery of Cr(VI) was approximately quantitative ( $>95\%$ ) up to 125 mL of sample volume. Above 125 mL, the recovery decreased quickly with increasing volume of sample. The adsorption of chromium ions with 250 mg resin was not affected by sample volume till 125 mL. The highest preconcentration factor was 25 for analyte ions when final volume was 5.0 mL.

### 3.7. Effect of diverse ions

In order to assess the possible analytical applications of the recommended procedure, the effect of some foreign ions

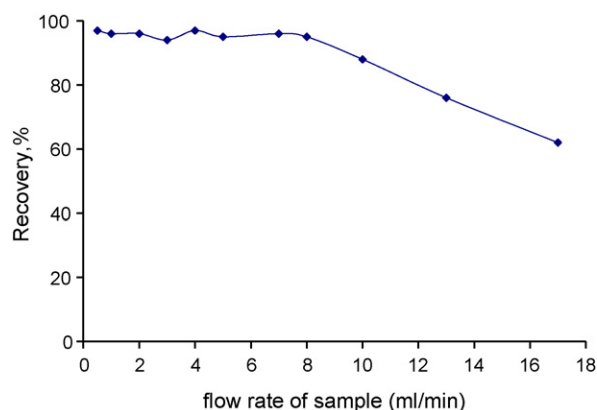


Fig. 3. The influence of flow rate of sample solution on the recovery of chromium (VI) from XAD-2010 (N:3).

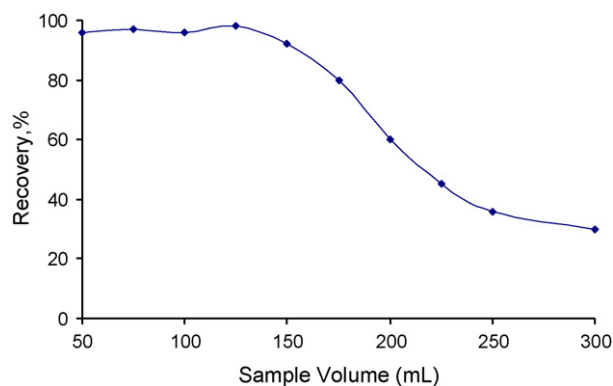


Fig. 4. Influences of sample volume on Cr(VI) retentions (N:3).

Table 2

Influences of some ions on the recovery of chromium (VI) on the XAD-2010 (N:3, V: 50 mL)

Ions	Concentration ( $\text{mg L}^{-1}$ )	Recovery (%)
Na <sup>+</sup>	10,000	96 ± 3
K <sup>+</sup>	1,000	94 ± 5
Ca <sup>2+</sup>	1,000	94 ± 6
Mg <sup>2+</sup>	1,000	97 ± 2
Cl <sup>-</sup>	12,500	96 ± 5
PO <sub>4</sub> <sup>3-</sup>	1,000	93 ± 4
SO <sub>4</sub> <sup>2-</sup>	500	94 ± 4
NO <sub>3</sub> <sup>-</sup>	10,000	96 ± 2
Cu <sup>2+</sup> , Ni <sup>2+</sup> , Cd <sup>2+</sup> , Co <sup>2+</sup> , Pb <sup>2+</sup> , Zn <sup>2+</sup>	10	96 ± 4
Fe <sup>3+</sup> , Mn <sup>2+</sup>	20	94 ± 3
Mixed <sup>a</sup>		92 ± 4

<sup>a</sup> The solution containing ions in this table altogether.

was examined. For this studies,  $25\text{ }\mu\text{g}$  Cr(VI) was taken with different amounts of foreign ions and recommended procedure was followed. The results were given in Table 2. The recoveries for Cr(VI) were not affected when the solution contained sodium, magnesium, calcium, potassium, chloride, sulfate, phosphate, nitrate and various metal ions. The tolerable levels of the some heavy metal ions are suitable for the separation and preconcentration of Cr(VI) in the real samples examined present study, because of the levels of transition metals in these samples are lower than their interferic level.

Table 3

Determination of total chromium in spiked test solutions (N:3, V: 50 mL)

Added ( $\mu\text{g}$ )			Found total chromium ( $\mu\text{g}$ )	Recovery (%)
Cr(VI)	Cr(III)	Total chromium		
0	25	25	24.3 ± 0.7	97
5	20	25	24.0 ± 0.9	96
10	15	25	23.9 ± 0.5	96
15	10	25	24.8 ± 0.4	99
20	5	25	24.2 ± 0.3	97
25	0	25	24.4 ± 0.6	98

Table 4  
Determination of Cr(III), Cr(VI) and total chromium in tap water and river water (N:3, V:125 mL)

Sample	Added ( $\mu\text{g}$ )		Found ( $\mu\text{g}$ )			Recovery (%)		
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Total chromium	Cr(III)	Cr(VI)	Total chromium
Tap water	–	–	N.D. <sup>a</sup>	N.D.	N.D.	–	–	–
	5	10	$4.7 \pm 0.1$	$10.1 \pm 0.2$	$14.8 \pm 0.2$	94	101	99
	10	5	$9.7 \pm 0.3$	$5.1 \pm 0.2$	$14.8 \pm 0.4$	97	102	99
Degirmendere river water	–	–	$3.0 \pm 0.1$	N.D.	$3.0 \pm 0.1$	–	–	–
	5	10	$7.7 \pm 0.2$	$9.4 \pm 0.5$	$17.1 \pm 0.5$	96	94	95
	10	5	$12.6 \pm 0.6$	$4.8 \pm 0.1$	$17.4 \pm 0.6$	97	96	97

<sup>a</sup> Not detected.

### 3.8. Determination of total chromium

In order to determination of total chromium, firstly model solutions that contain different amounts Cr(VI) and Cr(III) were prepared. Then Cr(III) ions in the model solutions were oxidized to Cr(VI) by using  $\text{H}_2\text{O}_2$  in basic media according to procedure given by Demirata [26]. Because of the quantitative recoveries for Cr(VI) were obtained at pH 2.5, the pH of the basic solution was adjusted to pH 2.5 by the addition of  $0.1 \text{ mol L}^{-1} \text{ HNO}_3$  carefully. The pH of this solution was controlled by pH meter. Then the procedure presented was applied to these solutions. The results are given in Table 3. The results show that the proposed method could be applied for the determination of total chromium.

### 3.9. Capacity of XAD-2010 resin

In order to the adsorptive capacity of XAD-2010 resin, batch method was used. 0.1 g Amberlite XAD-2010 resin was added 100 mL of solution containing 1.0 mg of chromium (VI) chelated with DDTC, at pH 2.5. After shaking for 2 h, the mixture was filtered. Two milliliters of the supernatant solution was diluted to 4 mL. Then chromium content was determined by atomic absorption spectrometry. The capacity of sorbent was  $4.40 \text{ mg g}^{-1} \text{ Cr(VI)}$ .

### 3.10. Figures of merit

The detection limit (LOD) of the present work was calculated under optimal experimental conditions after application of the preconcentration procedure to blank solutions. The limit of detection for chromium (VI) based on three times the standard deviations of the blank ( $k = 3$ ,  $N = 20$ ) was  $1.28 \mu\text{g L}^{-1}$ .

The precision of the determination of chromium (VI) was evaluated under the optimum conditions mentioned above. For this purpose, the procedure was repeated 10 times for chromium (VI). It was found that the recovery of Cr(VI) was  $96 \pm 3$  at 95% confidence level.

### 3.11. Applications

The proposed method was applied to the speciation of Cr(VI) and Cr(III) in tap water and river water samples collected from Trabzon. The tap water and river water samples were filtered

Table 5  
The level of total chromium in the standard reference material after application of the presented procedure (N:3, V:50 mL)

Sample	CRM-TMDW-500 <sup>a</sup>
Certified ( $\mu\text{g L}^{-1}$ )	$20 \pm 0.1$
Found ( $\mu\text{g L}^{-1}$ )	$20.3 \pm 0.2$
Recovery (%)	102

<sup>a</sup> Certified reference material trace metals in drinking water.

through  $0.45 \mu\text{m}$  MFS membrane filter. The Cr(VI) and total chromium were determined in unspiked and spiked tap water and river water samples. For this purpose, Cr(VI) and Cr(III) were added to all samples at different amount and proposed method was applied. The obtained results were given in Table 4. As can be seen from Table 4, the method could be applied successfully for the separation, preconcentration and speciation of trace amount of chromium in tap water and river water samples. The accuracy of the results was quite satisfactory. Relative error was lower than 6% for Cr(VI), Cr(III) and total chromium.

The accuracy of the proposed separation/preconcentration method was examined by determination of total chromium in certified reference drinking water materials (CRM-TMDW-500). The results are given in Table 5. The results show that this system provided analytical data within the ranges of the certified values.

The proposed preconcentration method was applied to determination of chromium in environmental sample. The results were given in Table 6.

Table 6  
The level of chromium species in environmental after application of the presented procedure (N:3)

Sample	Concentration ( $\mu\text{g L}^{-1}$ )	
	Chromium (III)	Chromium (VI)
Tap water	BDL <sup>a</sup>	BDL
River water	$24.0 \pm 0.7$	BDL

Sample	Concentration ( $\mu\text{g L}^{-1}$ ) (total chromium)
Moss ( $\mu\text{g g}^{-1}$ )	$1.2 \pm 0.1$
Rock ( $\mu\text{g g}^{-1}$ ) <sup>b</sup>	$14.7 \pm 0.6$

Uncertainty at 95% confidence limit.

<sup>a</sup> BDL: below the detection limit.

<sup>b</sup> Total chromium content of rock was determined as  $15.68 \mu\text{g/g}$  (R.S.D.: <5%) by ACME Analytical Lab. (ISO 9002 Accredited Co.) in Canada.

#### 4. Conclusion

The speciation procedure presented for Cr(III) and Cr(VI) is simple, facile and economic for their speciation and preconcentration. Amberlite XAD-2010 resin can be used all throughout the works without any loss in recovery values. The procedure presented is comparable for the procedure in the literature [16–21] with quantitative recovery values and lower detection limit for chromium speciation.

#### References

- [1] Y.K. Rui, H.X. Zhang, J. Guo, K.L. Huang, B.Z. Zhu, Y.B. Luo, Heavy metals content in transgenic soybean oil from Beijing market, *Agro. Food Ind. Hi-Tech.* 17 (2006) 35–36.
- [2] A.S. Souza, G.C. Brandão, W.N.L. dos Santos, V.A. Lemos, E.M. Ganzarolli, R.E. Bruns, S.L.C. Ferreira, Automatic on-line pre-concentration system using a knotted reactor for the FAAS determination of lead in drinking water, *J. Hazard. Mater.* 141 (2007) 540–545.
- [3] C. Arpa, S. Bektas, Preconcentration and determination of lead, cadmium and nickel from water samples using a polyethylene glycol dye immobilized on poly(hydroxyl-ethylmethacrylate) microspheres, *Anal. Sci.* 22 (2006) 1025–1029.
- [4] 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.
- [5] D. Bantrjee, A.K. Das, Application of xanthine functionalized resin in speciation of chromium in natural water, *J. Indian Chem. Soc.* 83 (2006) 479–484.
- [6] M. Soylak, R. Saraymen, M. Dogan, Investigation of lead, chromium, cobalt and molybdenum concentrations in hair samples collected from diabetic patients, *Fresen. Environ. Bull.* 4 (1995) 485–490.
- [7] S. Saracoglu, M. Soylak, L. Elci, On-line solid phase extraction system for chromium determination in water samples by flow injection-flame atomic absorption spectrometry, *Anal. Lett.* 35 (2002) 1519–1530.
- [8] I. Narin, M. Soylak, K. Kayakırlmaz, L. Elci, M. Dogan, Speciation of Cr(III) and Cr(VI) in tannery wastewater and sediment samples on Amber-sorb 563 resin, *Anal. Lett.* 35 (2002) 1437–1452.
- [9] O. Yamaguchi, M. Ida, Y. Uchiyama, S. Hanehara, A method for the determination of total Cr(VI) in cement, *J. Eur. Ceram. Soc.* 26 (2006) 785–790.
- [10] P.M. Outridge, A.M. Scheuhammer, Bioaccumulation and toxicology of chromium: implications for wildlife, *Rev. Environ. Contam. T.* 130 (1993) 31–37.
- [11] M.J. Marqués, A. Salvador, A. Morales-Rubio, M. de la Guardia, Chromium speciation in liquid matrices: a survey of the literature, *Fresen. J. Anal. Chem.* 367 (2000) 601–613.
- [12] W.H. Ma, R.X. Cai, Z.X. Lin, Studies on adsorption properties of chromium (VI) on the nanometer-size TiO<sub>2</sub> powders surfaces using on-line flow-injection analysis, *Chem. J. Chin. U.* 19 (1998) 1566–1569.
- [13] J. Wang, B. Jia, L.P. Guo, Q.P. Lin, The determination of chromium in feeds by flame atomic absorption spectrophotometry, *Spectrosc. Spect. Anal.* 25 (2005) 1142–1144.
- [14] A.K. Shanker, C. Cervantes, H. Loza-Tavera, S. Avudainayagam, Chromium toxicity in plants, *Environ. Int.* 31 (2005) 739–753.
- [15] M. Mohammadhosseini, M.S. Tehrani, M.R. Ganjali, Preconcentration, determination and speciation of chromium (III) using solid phase extraction and flame atomic absorption spectrometry, *J. Chin. Chem. Soc. Taip.* 53 (2006) 549–557.
- [16] S.A. Steiner, M.D. Porter, J.S. Fritz, Ultrafast concentration and speciation of chromium (III) and (VI), *J. Chromatogr. A* 1118 (2006) 62–67.
- [17] S. Abliz, J.D. Wang, Horshida, Speciation analysis of chromium (VI) and chromium (III) in water sample using flame atomic absorption spectrometry with TOA-benzene extraction separation system, *Spectrosc. Spect. Anal.* 25 (2005) 2082–2084.
- [18] J. Ueda, H. Satoh, S. Kagaya, Determination of chromium (III) and chromium (VI) by graphite-furnace atomic absorption spectrometry after coprecipitation with hafnium hydroxide, *Anal. Sci.* 13 (1997) 613–617.
- [19] L. Wang, B. Hu, Z.C. Jiang, Z.Q. Li, Speciation of Cr-III and Cr-VI in aqueous samples by coprecipitation/slurry sampling fluorination assisted graphite furnace atomic absorption spectrometry, *Int. J. Environ. An. Ch.* 82 (2002) 387–393.
- [20] K. Kargosha, M. Noroozifar, Simultaneous flow-injection speciation of Cr(III) and Cr(VI) by solid-phase reactors and spectrophotometry, *Asian J. Spectrosc.* 8 (2004) 101–109.
- [21] M. Tüzen, M. Soylak, Chromium speciation in environmental samples by solid phase extraction on Chromosorb 108, *J. Hazard Mater.* 129 (2006) 266–273.
- [22] <http://www.sigmaaldrich.com/sigma/product%20information%20sheet/xad7pis.pdf>.
- [23] 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.
- [24] 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.
- [25] W. Landgraf, N.H. Li, J.R. Benson, Polymer microcarrier exhibiting zero-order release, *Drug Deliv. Tech.* 3 (2003) 1–12.
- [26] B. Demirata, Speciation of Cr(III) and Cr(VI) by means of melamine-urea-formaldehyde resin and FAAS, *Microchim. Acta* 136 (2001) 143–146.
- [27] J.E.T. Andersen, Introduction of hydrogen peroxide as an oxidant in flow injection analysis: speciation of Cr(III) and Cr(VI), *Anal. Chim. Acta* 361 (1998) 125–131.
- [28] I. Narin, Y. Surme, M. Soylak, M. Dogan, Speciation of Cr(III) and Cr(VI) in environmental samples by solid phase extraction on Ambersorb 563 resin, *J. Hazard. Mater.* 136 (2006) 579–584.
- [29] D.Y. Sarica, A.R. Türker, E. Erol, On-line speciation and determination of Cr(III) and Cr(VI) in drinking and waste water samples by reversed-phase high performance liquid chromatography coupled with atomic absorption spectrometry, *J. Sep. Sci.* 29 (2006) 1600–1606.
- [30] M. Ghaedi, F. Ahmadi, H. Karimi, S. Gharaghani, Preconcentration and extraction of copper on activated carbon using 4-amino-2, 3-dimethyl-1-phenyl-3-pyrazoline or 4-(4-methoxybenzylideneimine) thiophenole, *J. Korean Chem. Soc.* 50 (2006) 23–31.