

Speciation of Cr(III) and Cr(VI) in environmental samples by solid phase extraction on Ambersorb 563 resin

Ibrahim Narin^a, Yavuz Surme^b, Mustafa Soylak^{c,*}, Mehmet Dogan^d

^a Erciyes University, Faculty of Pharmacy, 38039 Kayseri, Turkey

^b Nigde University, Faculty of Art and Science, Department of Chemistry, 51200 Nigde, Turkey

^c Erciyes University, Faculty of Art and Science, Department of Chemistry, 38039 Kayseri, Turkey

^d Hacettepe University, Faculty of Science, Department of Chemistry, 06532 Ankara, Turkey

Received 9 November 2005; received in revised form 16 December 2005; accepted 20 December 2005

Available online 25 January 2006

Abstract

A simple and sensitive method for the speciation, separation and preconcentration of Cr(VI) and Cr(III) in natural water, soil and sediment samples was developed. Cr(VI) has been separated from Cr(III) and preconcentrated as Cr(III)–diphenylcarbazone complex by using Ambersorb 563 resin and determined by spectrophotometric method at 540 nm. Effect of analytical parameters such as sulfuric acid concentration, ligand volume, type of elution solution, sample volume, amount of resin and foreign ions were investigated. The presented procedure was successfully applied for the chromium speciation in various environmental samples with successfully results.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Speciation; Chromium; Ambersorb 563; Solid phase extraction; Spectrophotometric determination

1. Introduction

In environmental samples, chromium is one of the pollutants. Chromium exists in the environment as chromium(III) and chromium(VI) oxidation states. As oxidation states, the chemical properties of these species are different. Chromium is an indispensable nutrient element for the carbohydrates and lipids metabolism. While chromium(III) is considered to be essential nutrition and for the maintenance of normal glucose tolerance, chromium(VI) can have acute and chronic toxic, including carcinogenic effect [1,2]. Chromium is a major water pollutant, usually as a result of some industrial pollution including tanning factories, steel works, dyeing or chromium plating, wood preservation, etc. and artificial fertilizers [3,4]. For this reason, determination of chromium in environmental samples as natural water, waste water samples and soil samples has become very important. The US EPA has set the concentration of 0.1 mg L⁻¹ of total chromium for drinking water as “maximum contaminant level goals”. WHO states that the guideline values of 50 µg L⁻¹

of Cr(VI) [5]. Because of these importances of the chromium species, their accurate and facile determinations are an important point in the chemistry.

Various analytical techniques have been used for determination of chromium including spectrophotometry [6,7], atomic absorption spectrometry (AAS) [6,7], inductively coupled plasma atomic emission spectrometry (ICP-AES) [7–10], high performance liquid chromatography [11], etc. Due to the levels of chromium species in the natural and waste water samples are generally at µg L⁻¹ and high matrix contents of the samples, a separation/preconcentration technique is necessary, prior to determination of chromium by an instrumental technique [12–16]. Diphenylcarbazide (DPC) gives very sensitive color reaction with Cr(VI) in mineral acid medium and Cr(III)–diphenylcarbazone (Cr(HL)₂⁺) complex occurs [17].

Ambersorb adsorption resins are synthetic carbonaceous adsorbents. They are partial pyrolyzed resin of sulfonated styrene/divinylbenzene polymer. They have good adsorption properties: high surface area, porosity, durability, uniform pore distribution and high surface area. They have been used for the separation, preconcentration and isolation of organic substances from various media especially natural waters and sediments [15–18]. Ambersorb 563 has been used for preconcentration

* Corresponding author. Tel.: +90 352 4378802; fax: +90 352 4378802.
E-mail address: soylak@erciyes.edu.tr (M. Soylak).

of traces heavy metals in some studies of our working group [13,19–21].

In presented study, the conditions for the sorption of chromium(III)–diphenylcarbazone complex on Amborsorb 563 resin for speciation of Cr(III) and Cr(VI) in environmental samples have been investigated.

2. Experimental

2.1. Reagents

Otherwise stated analytical-grade acetone, acids and other chemicals used obtained from Merck, Darmstadt. Doubly distilled water was used for the preparation of the reagent solutions. 1,5-diphenylcarbazide solution ($1 \times 10^{-4} \text{ mol L}^{-1}$) was prepared daily by dissolving appropriate amount of DPC (Merck) in ethanol. Cr(VI) and Cr(III) stock solutions (1000 mg L^{-1}) were prepared from K_2CrO_4 and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$.

Amborsorb 563 is carbonaceous resin (20–50 mesh, part no. 10430-U) that was purchased from Supelco (Bellefonte, PA, USA). 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 trace metal ions and other inorganic and organic contaminants in the resin.

2.2. Instruments

A Shimadzu 160 double beam UV–vis spectrophotometer with 10 mm quartz cells was used for the determination of chromium at 540 nm. pH measurements were made with a WTW level 1 digital pH meter. In the aching procedure of sediment and soil samples an Elektro-Mag 1813 model laboratory oven was used.

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 300 mg of Amborsorb 563 resin in water.

2.3. Procedure for Cr(VI)

For the optimization of column separation and preconcentration method, 2 mL $1 \times 10^{-4} \text{ mol L}^{-1}$ DPC added into 30 mL of 0.05 mol L^{-1} sulfuric acid solutions containing $0.5 \mu\text{g}$ of Cr(VI). Total volume of the model solution was 30 mL. After waiting 10 min for complex formation, the solution was passed through the column at the 2 mL min^{-1} flow rate. The adsorbed diphenylcarbazone complex of chromium(VI) on the column was eluted with 5 mL of acetone. Absorbance of the solution was measured by UV–vis spectrophotometer at 540 nm.

2.4. Procedure for total chromium

Total chromium was determined after oxidizing Cr(III) to Cr(VI) by the addition of $\text{K}_2\text{S}_2\text{O}_8$ in acidic medium. For this purpose, 0.5 mL of $\text{K}_2\text{S}_2\text{O}_8$ (1%, w/v) solution added and one drop of AgNO_3 (0.01%, w/v) and 0.5 mL concentrated H_2SO_4 were added into 100 mL beaker containing 50 mL of the spiked solu-

tion $5 \mu\text{g mL}^{-1}$ Cr(III). The beaker was covered with a watch glass and heated without boiling ($\approx 65^\circ\text{C}$) for about 45 min to complete oxidation and to reduce excess of $\text{K}_2\text{S}_2\text{O}_8$. Then the method described in Section 2.3 was applied was applied. The concentration of Cr(III) was calculated by subtracting the content of Cr(VI) from total chromium content.

2.5. Application to the real samples

Waste water sample is filtered from $0.45 \mu\text{m}$ cellulose nitrate filter. For determination of chromium(VI), 10 mL of waste water diluted 10-fold with deionized water than this solution is acidified with 5.0 mL $1.0 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$. After cooling for 30 min at room temperature, the speciation procedures given above were applied to this solution.

The procedure was also applied for the sediment and soil samples. For this purpose, the samples dried in an oven at 105°C and homogenized with a sieve. Then 0.3000 g sediment or soil sample was weighed and transferred into porcelain crucible. The samples were burned in an oven at 450°C for 3 h and the resulting inorganic residues dissolved with 5 mL of concentrated HNO_3 [22]. These solutions boiled until dryness and 3 mL of concentrated HNO_3 added again. The final solution was transferred to 50 mL volumetric flasks and diluted with deionized water. Then the procedure given above was applied to this solution.

3. Results and discussion

3.1. Effect of acidity

The effects of acidity of the aqueous solution on the retention of Cr(VI) and Cr(III) on to the Amborsorb 563 resin were investigated between ranges of 0.01 – 0.10 mol L^{-1} sulfuric acid. As can be seen in Fig. 1, the quantitative recovery ($>95\%$) was found as 0.05 mol L^{-1} sulfuric acid concentration and for the higher concentrations the recovery of Cr(VI) was quantitative

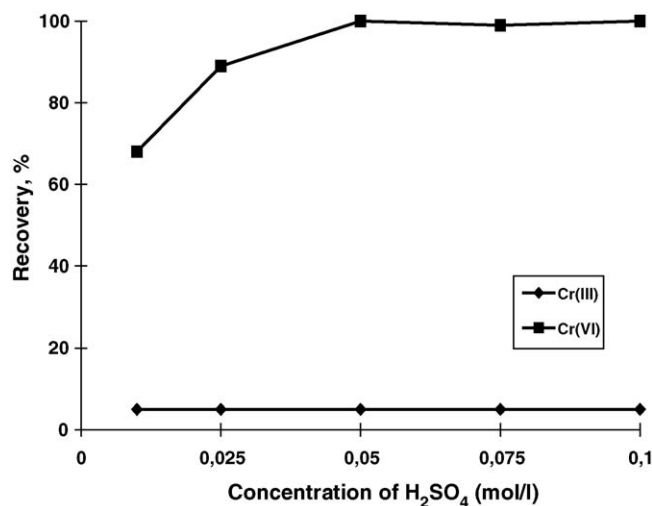


Fig. 1. Effect of sulfuric acid concentration on the recoveries of Cr(VI) and Cr(III) on Amborsorb 563 ($N=4$).

Table 1
Influences of various eluents on the desorption of chromium–diphenylcarbazone complex from Ambersorb 563 resin (eluent volume: 5.0 mL, $N=4$)

| Eluent type | Recovery (%) |
|---------------------------------|--------------|
| 1 M HCl | <5 |
| 2 M HCl | <5 |
| 1 M HNO ₃ | <5 |
| 2 M HNO ₃ | <5 |
| Acetone | 98 ± 1 |
| Ethanol | 82 ± 4 |
| 1 M HCl in acetone | 90 ± 1 |
| 2 M HCl in acetone | 91 ± 2 |
| 1 M HCl in ethanol | 72 ± 2 |
| 2 M HCl in ethanol | 76 ± 1 |
| 1 M HNO ₃ in acetone | 67 ± 2 |
| 2 M HNO ₃ in acetone | 30 ± 2 |
| 1 M HNO ₃ in ethanol | 60 ± 1 |
| 2 M HNO ₃ in ethanol | 54 ± 1 |

while the recovery of Cr(III) is rather low (<5%). These results showed the possibility of separating Cr(VI) from Cr(III). In further studies, the acidity of the model solutions was adjusted to 0.05 mol L⁻¹ with sulfuric acid.

3.2. Effect of ligand

The effect of volume of ligand solution on the retention of Cr(VI) on Ambersorb 563 was investigated between ranges 1–10 mL of 1×10^{-4} mol L⁻¹ DPC on the kept other parameters constant. Chromium(VI) was quantitatively recovered

Table 2
Effect of sample volume on the recovery of Cr(VI) on the Ambersorb 563 resin ($N=4$)

| Sample volume (mL) | Recovery (%) |
|--------------------|--------------|
| 25 | 101 ± 2 |
| 50 | 102 ± 4 |
| 100 | 101 ± 1 |
| 150 | 98 ± 2 |
| 200 | 91 ± 3 |
| 250 | 90 ± 4 |

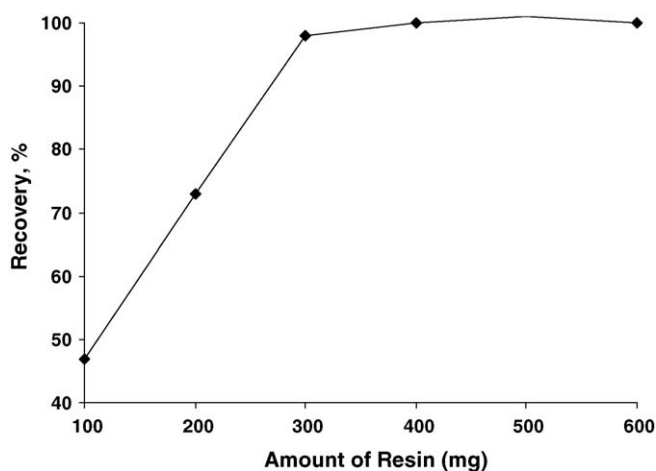


Fig. 2. Effect of Ambersorb 563 amount on the recoveries of Cr(VI) ($N=4$).

in 1.0–10.0 mL of DPC. For all subsequent works, 2 mL of 1×10^{-4} mol L⁻¹ DPC solution was used.

3.3. Elution

The influence of the eluent type was tested by using various eluents including hydrochloric acid, nitric acid, acetone, ethanol and their combinations. The results were given in Table 1. Chromium(VI) was quantitatively desorbed from the Ambersorb 563 column only with acetone. The volume of the acetone as eluent was also tested. The recoveries of chromium(VI) were quantitative 5.0–15.0 mL of acetone. In all further works, 5 mL of acetone was used.

3.4. Effect of sample volume

In order to obtain high preconcentration factor, the sample volume is one of the important analytical parameter. The influences of sample volume on the recoveries of Cr(VI) complex on the Ambersorb 563 resin was investigated between ranges of 25–250 mL. The results were given in Table 2. The recovery was quantitative till 150 mL of the sample volume. The highest preconcentration factor was 30, when the adsorbed complex was eluted with 5.0 mL acetone.

3.5. Effect of resin amount

The influences of amounts of Ambersorb 563 on the retention of Cr(VI) were investigated. The results were given in Fig. 2. The recovery values for chromium were not quantitative till 300 mg of Ambersorb 563. With more than 300 mg of the resin quantitative recovery values were obtained.

3.6. Effect of interfering ions

The influences of possible matrix ions in the environmental samples and some transition metals were also examined. The effect of potential interfering ions on the determination of

Table 3
Tolerable levels of interfering ions for the retention of Cr(VI) on Ambersorb 563 resin ($N=3$)

| Ions | Concentration (mg L ⁻¹) | Salt added | Recovery (%) |
|-------------------------------|-------------------------------------|-------------------------------------------------|--------------|
| Na ⁺ | 5000 | NaCl | 97 ± 4 |
| K ⁺ | 2000 | KCl | 98 ± 2 |
| Ca ²⁺ | 500 | CaCl ₂ | 97 ± 2 |
| Mg ²⁺ | 1000 | MgCl ₂ | 95 ± 1 |
| SO ₄ ²⁻ | 500 | (NH ₄) ₂ SO ₄ | 99 ± 5 |
| Cl ⁻ | 1000 | NH ₄ Cl | 98 ± 5 |
| Zn ²⁺ | 50 | ZnSO ₄ | 93 ± 1 |
| Cd ²⁺ | 50 | CdSO ₄ | 94 ± 1 |
| Mn ²⁺ | 50 | MnCl ₂ | 101 ± 6 |
| Pb ²⁺ | 50 | Pb(NO ₃) ₂ | 103 ± 3 |
| Co ²⁺ | 50 | Co(NO ₃) ₂ | 95 ± 2 |
| Cu ²⁺ | 50 | Cu(NO ₃) ₂ | 106 ± 4 |
| Ni ²⁺ | 50 | Ni(NO ₃) ₂ | 100 ± 2 |
| Al ³⁺ | 50 | Al(NO ₃) ₃ | 96 ± 3 |
| Fe ³⁺ | 15 | Fe ₂ (SO ₄) ₃ | 101 ± 2 |

Table 4
Chromium content of mineral and tap water samples without adding oxidizing reagent $K_2S_2O_8$ ($N=4$)

| Sample | Added chromium | Found chromium(VI) (μg) | Recovery (%) |
|------------------|--------------------------------------------------|--------------------------------------|--------------|
| Mineral water I | – | BDL | – |
| | 1 μg Cr(III) + 1 μg Cr(VI) | 1.04 \pm 0.04 | 104 \pm 4 |
| Mineral water II | – | BDL | – |
| | 1 μg Cr(III) + 1 μg Cr(VI) | 1.03 \pm 0.02 | 103 \pm 2 |
| Tap water III | – | BDL | – |
| | 1 μg Cr(III) + 1 μg Cr(VI) | 1.03 \pm 0.02 | 103 \pm 2 |
| Tap water IV | – | BDL | – |
| | 1 μg Cr(III) + 1 μg Cr(VI) | 1.00 \pm 0.04 | 100 \pm 4 |

BDL, below the detection limit.

Table 5
Chromium contents of mineral and tap water samples after oxidizing added Cr(III) to Cr(VI) ($N=4$)

| Sample | Added chromium (μg) | Total chromium (μg) | Found chromium (μg) | Recovery (%) |
|------------------|----------------------------------|----------------------------------|----------------------------------|--------------|
| Mineral water I | – | – | BDL | – |
| | 1.00 Cr(III) + 0.50 Cr(VI) | 1.50 | 1.46 \pm 0.03 | 97 \pm 2 |
| Mineral water II | – | – | BDL | – |
| | 1.00 Cr(III) + 0.50 Cr(VI) | 1.50 | 1.47 \pm 0.02 | 98 \pm 1 |
| Tap water I | – | – | BDL | – |
| | 1.00 Cr(III) + 0.50 Cr(VI) | 1.50 | 1.62 \pm 0.02 | 108 \pm 1 |
| Tap water II | – | – | BDL | – |
| | 1.00 Cr(III) + 0.50 Cr(VI) | 1.50 | 1.61 \pm 0.02 | 107 \pm 1 |

BDL, below the detection limit.

chromium species were investigated by adding known concentrations of each ion in a solution containing analytes. The results were summarized in Table 3. The tolerated amounts of each ion were the concentration values tested that caused less than 5% the absorbance alteration. Also no influence from the anions such as sulfate and chloride was observed. This results show that the proposed preconcentration/separation method could be applied to the highly saline samples and the samples that contains some transition metals at $\mu\text{g L}^{-1}$ levels.

3.7. Calibration curve

Using the optimized condition of preconcentration, calibration graph were prepared for Cr(VI) (0–0.25 $\mu\text{g mL}^{-1}$). Linear equations were as follows:

$$\text{Cr(VI)} \quad A = 0.994 C + 0.0324 \quad r = 0.998 \quad (N : 6)$$

where A is absorbance and C the concentration of chromium(VI) ($\mu\text{g mL}^{-1}$).

3.8. Figure of merits

In order to estimate the accuracy of the speciation procedure, different amount of chromium(III) and chromium(VI) were added to 50 mL of the mineral and tap water samples. The procedure described above was applied to the mineral and tap water samples without adding oxidizing reagent $K_2S_2O_8$. The results are show in Table 4. A good agreement was obtained between the added chromium(VI) and measured chromium(VI)

amount. The recoveries of chromium(VI) were between 100% and 104%.

The accuracy studies were also performed with the mixture of chromium species after oxidizing with $K_2S_2O_8$. The results for these works were given in Table 5. Quantitative recoveries were also obtained for this study.

The limit of detection (LOD) of the proposed method for the determination of chromium(VI) was studied under optimal experimental conditions by applying the procedure for blank solutions. The detection limit of chromium(VI) based on three times the standard deviations of the blank ($N=21$, $X_L = X_b + 3 s$, X_L : limit of detection, X_b : blank value) was 3.4 $\mu\text{g L}^{-1}$.

3.9. Application to the real samples

The proposed preconcentration method was applied to determination of chromium in a tannery wastewater sample from the

Table 6
The level of chromium species in the real samples ($N=4$)

| Sample | Concentration ($\mu\text{g L}^{-1}$) | |
|-----------------------------------------------------------|----------------------------------------|--------------|
| | Chromium(III) | Chromium(VI) |
| Waste water from Organised Industrial Region of Bor-Nigde | 524 \pm 32 | BDL |
| Total chromium ($\mu\text{g g}^{-1}$) | | |
| Sediment from Tabakhane stream | 63.2 \pm 1.6 | |
| Soil from Nigde University | 9.4 \pm 1.0 | |

BDL, below the detection limit. Uncertainty at 95% confidence limit.

Table 7
Comparative data from some recent studies on Cr(III) and Cr(VI) speciation

| Technique | System | Media | Detection system | PF | DL ($\mu\text{g L}^{-1}$) | R.S.D. (%) | Reference |
|--------------------|---------------------------------------------------------------------------------------------------|-----------------------------------------------|-------------------|-----|-----------------------------|------------|--------------|
| CPE | Cr(III)—1-phenyl-3-methyl-4-benzoylpyrazol-5-one and reduction of Cr(VI) | Triton X-100 | ICP-AES | 20 | 0.81 | 3.2 | [23] |
| CPE | Cr(III)— <i>N,N'</i> -bis-(alpha-methyl salicylidene) propane-1,3-diimine and reduction of Cr(VI) | Triton X-100 | FAAS | – | 0.1 | 2.3 | [24] |
| CPE | Cr(III)—bis(2-methoxybenzaldehyde) ethylene diimine and reduction of Cr(VI) | Triton X-114 | FAAS | 57 | 0.17 | 2.1 | [25] |
| Coprecipitation | Cr(VI)—ethyl xanthate complex and oxidation of Cr(III) | – | FAAS | 100 | 0.5 | 3.1 | [26] |
| Solvent extraction | Cr(VI)—DPC and oxidation of Cr(III) | MIBK | Spectrophotometry | 20 | 2.22 | <1 | [27] |
| SPE | Cr(III)—1,1,1-trifluoroacetyl-acetone and reduction of Cr(VI) | Polyimide-coated silica fiber | GC | – | 2 | <7 | [28] |
| SPE | Cr(VI)—cetyltrimethyl ammonium bromide and oxidation of Cr(III) | C-18 bonded phase silica SPE disks | FAAS | 45 | 15–20 | <5 | [29] |
| SPE | Cr(VI)—ADPC and GFAAS | Diaion HP-2MG | GFAAS | – | 0.3 | <9 | [30] |
| SPE | Cr(III) and Cr(VI)—APDC | LiChrospher 100 RP-8 and LiChrospher 60 RP-18 | HPLC-UV detection | – | 0.2 | 2 | [31] |
| SPE | Cr(VI)—DPC and oxidation of Cr(III) | Ambersorb 563 | Spectrophotometry | 30 | 3.4 | <6 | Present work |

CPE, cloud point extraction; GC, gas chromatography; SPE, solid phase extraction; PF, preconcentration factor; DL, detection limit.

Organized Industrial Region of Bor-Nigde, a sediment sample from Tabakhane Stream-Nigde and a soil sample from Nigde University. The results were given in Table 6.

4. Conclusion

The procedure presented is simple, facile and economic for the speciation and preconcentration of chromium. The resin can be used all throughout the works without any loss in recovery values. Comparative data from some recent studies on Cr(III) and Cr(VI) speciation are given Table 7. The procedure presented is comparable for the procedure in the literature [30–34] with quantitative recovery values and lower detection limit for chromium speciation.

Acknowledgment

The authors would like to thank the Scientific and Technical Research Council of Turkey (TUBITAK) for financial helps (Project No: 104T330).

References

- [1] P. Bermejo-Barrera, M.C. Barciela-Alonso, B. Perez-Fernandez, A. Bermejo-Barrera, Direct speciation analysis of Cr(VI) by electrothermal atomic absorption spectrometry, based on the volatilization of Cr(III)-thenoyltrifluoroacetate from the graphite furnace, *Spectrochim. Acta* 58B (2003) 167.
- [2] J. Kotas, Z. Stasicka, Chromium occurrence in the environment and methods of its speciation, *Environ. Pollut.* 107 (2000) 263.
- [3] P. Pazos-Capeans, M.C. Barciela-Alonso, A. Bermejo-Barrera, P. Bermejo-Barrera, Chromium available fractions in aroous sediments using a modified microwave BCR protocol based on microwave assisted extraction, *Talanta* 65 (2005) 678.
- [4] M. de la Guardia, A. Morales-Rubiol, Sample preparation for chromium speciation, in: D. Barceló (Ed.), *In Comprehensive Analytical Chemistry XLI*, Elsevier Science, Amsterdam, Netherlands, 2003, pp. 1115–1171.
- [5] G. Tranter, J. Holmes, J. Lindon (Eds.), *Encyclopedia of Spectroscopy and Spectrometry, Three-Volume Set*, J.C. Lindon, Geology and Mineralogy, Applications of Atomic Spectroscopy, Academic Press, 1999, pp. 667–668.
- [6] S. Balasubramanian, V. Pugalenth, Determination of total chromium in tannery waste water by inductively coupled plasma-atomic emission spectrometry, flame atomic absorption spectrometry and UV–vis spectrophotometric methods, *Talanta* 50 (1999) 457.
- [7] M.I.C. Monteiro, I.C.S. Fraga, A.V. Yallouz, N.M.M. de Oliveira, S.H. Ribeiro, Determination of total chromium traces in tannery effluents by electrothermal atomic absorption spectrometry, flame atomic absorption spectrometry and UV–vis spectrophotometric methods, *Talanta* 58 (2002) 629.
- [8] S. Osaki, T. Osaki, Y. Takashima, Determination of chromium(vi) in natural waters by the sorption of chromium–diphenylcarbazone with xad-2 resin, *Talanta* 30 (1983) 683.
- [9] S. Balasubramanian, V. Pugalenth, Determination of total chromium in tannery waste water by inductively coupled plasma-atomic emission spectrometry, flame atomic absorption spectrometry and UV–vis spectrophotometric methods, *Talanta* 50 (1999) 457.
- [10] R.A. Gil, S. Cerutti, J.A. Gasques, R.A. Olsina, L.D. Martinez, On-line preconcentration and determination of chromium in parenteral solutions by inductively coupled plasma optical emission spectrometry, *Spectrochim. Acta* 60B (2005) 531.
- [11] A. Imran, Y.A. Hassan, Speciation of arsenic and chromium metal ions by reversed phase high performance liquid chromatography, *Chemosphere* 48 (2002) 275.
- [12] E.B. Sandel, H. Onishi, *Photometric Determination of Traces of Metals General Aspects*, Wiley Interscience, New York, 1978.
- [13] I. Narin, M. Soyak, K. Kayakirilmaz, L. Elci, M. Dogan, Speciation of Cr(III) and Cr(VI) in tannery wastewater and sediment samples on Ambersorb 563 resin, *Anal. Lett.* 35 (2002) 1437.

- [14] A. Tunceli, A.R. Turker, Speciation of Cr(III) and Cr(VI) in water after preconcentration of its 1,5-diphenylcarbazone complex on amberlite XAD-16 resin and determination by FAAS, *Talanta* 57 (2002) 1199.
- [15] H. Bag, A.R. Turker, M. Lale, A. Tunceli, Separation and speciation of Cr(III) and Cr(VI) with *Saccharomyces cerevisiae* immobilized on sepiolite and determination of both species in water by FAAS, *Talanta* 51 (2002) 895.
- [16] V. Camel, Solid-phase extraction, in: D. Barceló (Ed.), In *Comprehensive Analytical Chemistry XLI*, Elsevier Science, Amsterdam, Netherlands, 2003, pp. 393–457.
- [17] K. Ueno, T. Imamura, K.L. Cheng, *Handbook of Organic Analytical Reagents*, CRC, Florida, 2000.
- [18] J.A. Lebo, J.N. Huckins, J.D. Petty, K.T. Ho, Removal of organic contaminant toxicity from sediments—early work toward development of a toxicity identification evaluation (TIE) method, *Chemosphere* 39 (1999) 389.
- [19] S. Saracoglu, M. Soylak, L. Elci, The enrichment/separation of Fe, Co, Pb, Cd, and Cr on Ambersorb 563 prior to their flame atomic absorption spectrometric determinations, *J. Anal. Chem.* 58 (2003) 1127.
- [20] I. Narin, M. Soylak, The uses of 1-(2-pyridylazo) 2-naphthol (PAN) impregnated Ambersorb 563 resin on the solid phase extraction of traces heavy metal ions and their determinations by atomic absorption spectrometry, *Talanta* 60 (2003) 215.
- [21] S. Saracoglu, M. Soylak, L. Elci, Determination of trace amounts of copper in natural water samples by flame atomic absorption spectrometry coupled with flow injection on-line solid phase extraction on Ambersorb 563 adsorption resin, *Chem. Anal.* 48 (2003) 77.
- [22] M. Hoenig, Preparation steps in environmental trace element analysis-facts and traps, *Talanta* 54 (2001) 1021.
- [23] P. Liang, J. Li, Speciation of chromium with cloud point extraction separation and determination by ICP-OES, *At. Spectrosc.* 26 (2005) 89.
- [24] F. Shemirani, S.D. Abkenar, R.R. Kozani, M.S. Niasari, A.A. Mirroshandel, The application of cloud point extraction for the preconcentration and speciation of chromium by Flame Atomic Absorption Spectrometry, *Can. J. Anal. Sci. Spectrosc.* 49 (2004) 31.
- [25] F. Shemirani, S.D. Abkenar, A.A. Mirroshandel, M.S. Niasari, R.R. Kozani, Preconcentration and speciation of chromium in water samples by atomic absorption spectrometry after cloud-point extraction, *Anal. Sci.* 19 (2003) 1453.
- [26] P. Gopi Krishna, J. Mary Gladis, U. Rambabu, T. Prasada Rao, G.R.K. Naidu, Preconcentrative separation of chromium(VI) species from chromium(III) by coprecipitation of its ethyl xanthate complex onto naphthalene, *Talanta* 63 (2004) 541.
- [27] M. Noroozifar, M. Khorasani-Motlagh, Specific extraction of chromium as tetra-butylammonium-chromate and spectrophotometric determination by diphenylcarbazide: Speciation of chromium in effluent streams, *Anal. Sci.* 19 (2003) 705.
- [28] T.H. Ding, H.H. Lin, C.W. Whang, Determination of chromium(III) in water by solid-phase microextraction with a polyimide-coated fiber and gas chromatography-flame photometric detection, *J. Chromatogr.* 1062 A (2005) 49.
- [29] M.S. Tehrani, A.A. Ebrahimi, F. Rastegar, Chromium speciation by surfactant assisted solid-phase extraction and flame atomic absorption spectrometric detection, *Ann. Chim.* 94 (2004) 429.
- [30] J. Chwastowska, W. Skwara, E. Sterlinska, L. Pszonicki, Speciation of chromium in mineral waters and salinas by solid-phase extraction and graphite furnace atomic absorption spectrometry, *Talanta* 66 (2005) 1345.
- [31] M. Bittner, J.A.C. Broekaert, Speciation of chromium by solid-phase extraction coupled to reversed-phase liquid chromatography with UV detection, *Anal. Chim. Acta* 364 (1998) 31.
- [32] H.F. Maltez, E. Carasek, Chromium speciation and preconcentration using zirconium(IV) and zirconium(IV) phosphate chemically immobilized onto silica gel surface using a flow system and F AAS, *Talanta* 65 (2005) 537.
- [33] R.A. Gil, S. Cerutti, J.A. Gásquez, R.A. Olsina, L.D. Martinez, Preconcentration and speciation of chromium in drinking water samples by coupling of on-line sorption on activated carbon to ETAAS determination. *Talanta*, in press.
- [34] S.Q. Memon, M.I. Bhangar, M.Y. Khuhawar, Preconcentration and separation of Cr(III) and Cr(VI) using sawdust as a sorbent, *Anal. Bioanal. Chem.* 383 (2005) 619.