

## Speciation of Cr(III)/Cr(VI) in Tannery Waste Waters by Using Ion-Exchange Resins

Ş. Kartal,\* Ş. Tokahoğlu, and B. Özkan

*Department of Chemistry, Faculty of Arts and Sciences, Erciyes University, TR-38039, Kayseri, Turkey*

*\*E-mail: kartal@erciyes.edu.tr*

*Received March 3, 2005*

A method has been described for the chemical speciation, preconcentration and determination of Cr(III) and Cr(VI) species in filtered tannery waste waters by flame atomic absorption spectrometry using ion-exchange resins. Amberlite IR-120(H<sup>+</sup>) strongly acidic cation exchanger and Amberlite IRA-410(Cl<sup>-</sup>) strongly basic anion exchanger resins were used for the separation and preconcentration of Cr(III) and Cr(VI) species, respectively. Optimum condition for preconcentration and speciation was obtained by testing pH of sample and eluent, flow rates of sample and eluent, amount of resins, volume of sample and eluents, and effect of foreign ions. The recommended method has been successfully applied for the preconcentration and determination of chromium species in the dissolved phase of waste water samples collected from a tannery waste water treatment plant in Kayseri, Turkey. The detection limits achieved were 0.73 µg/L for Cr(III) and 0.81 µg/L for Cr(VI). Recovery studies showed 99% for Cr(III) and 98% for Cr(VI), for samples spiked with single species.

**Key Words :** Speciation, Cr(III)/(VI), Tannery waste water, Ion-exchange resin

### Introduction

The need for reliable analytical methods for the determination of different species of a heavy and/or toxic metal in environmental samples has been rapidly increased because the different biological, nutritional and/or toxicological properties of metals depend extremely upon their chemical form or oxidation state,<sup>1</sup> so that this is an important feature which distinguishes metals from other pollutants. For almost all metals, the free hydrated form is most toxic for living organisms. With the exception of mercury, stable metal complexes or metals associated with macromolecules are less toxic.<sup>2</sup>

Chromium ions occur as chromate (CrO<sub>4</sub><sup>2-</sup>), cationic chromium(III) species such as Cr(OH)<sup>2+</sup> and Cr(OH)<sub>2</sub><sup>+</sup> etc., as being bound to organic matter, and Cr(III) species adsorbed as colloidal in natural and waste waters.<sup>3</sup> In addition, Cr(III) ions are inoffensive when present as large aquahydroxo complexes with the form [Cr(H<sub>2</sub>O)<sub>n</sub>(OH)<sub>6n</sub>]<sup>n-3</sup> that makes it almost impossible to penetrate cell membranes.<sup>1,4</sup> Hexavalent chromium compounds are considerably toxic and known to be carcinogenic species and mutagenic matter for humans, while trivalent chromium is virtually non-toxic and considered as an essential element in human diet at low concentrations,<sup>4</sup> owing to a vital role in metabolisms of protein, glucose and mainly lipids such as cholesterol.<sup>5</sup> As the toxicities of metal ions having different oxidation states could be as long as fairly different, all elements could be toxic at their high concentration levels. Due to high oxidation potential and easy diffusion through the cell walls, the compounds of Cr(VI) are more toxic about 100 folds than the Cr(III) compounds.<sup>2,3,6,7</sup> Additionally, chromium has been an important solid-waste pollutant parameter.<sup>8</sup> For that reason, the determination of Cr(VI) ions accompanied with Cr(III) ions via speciation is of a great importance

rather than the determination of total chromium content in the sample investigated, and it can give valuable information about its toxicity to the environment.

Besides the use of a separation technique necessitated for the determination of Cr(III) and Cr(VI) species individually in the same sample, the application of a separation/preconcentration method is usually needed for making a reliable determination owing to the low concentrations of chromium species in environmental samples. By far a lot of methods have been given in the literature relevant to the determination and speciation of Cr(III) and Cr(VI) species. Mainly selective techniques for the speciation and determination of chromium are: coprecipitation,<sup>9,11</sup> separation with an ion exchanger and/or chelating resin,<sup>5,7,12,13</sup> solid phase extraction,<sup>3,14-18</sup> two-phase and H-point techniques,<sup>4,19</sup> solvent extraction,<sup>20</sup> catalytic cathodic stripping voltammetry<sup>21</sup> and spectrophotometric methods.<sup>6,22</sup> The on-line selective detection of the chromium species is successfully performed with chromatographic techniques hyphenated to atomic absorption spectrometry,<sup>1</sup> inductively coupled plasma-atomic emission spectrometry (ICP-AES)<sup>23</sup> and inductively coupled plasma-mass spectrometry (ICP-MS).<sup>5,24</sup> Moreover, some studies being performed for the speciative determination of Cr(III) and Cr(VI) species in various kind of wastewaters<sup>4,6,13,15,16,23,25</sup> and tannery waste waters<sup>1,2,11,16,26-30</sup> by using different separation/preconcentration techniques are reported in the literature. Several authors proposed the use of ion-exchange resins for the preconcentration, separation and speciative determination of chromium species in waters and/or tannery wastewaters.<sup>2,13,26,31</sup>

In this study, with the purpose of developing a separation, preconcentration and speciation procedure for determining the chromium species in the filtered tannery wastewater samples by FAAS, a cationic ion-exchange resin (Amberlite IR-120(H<sup>+</sup>)) and an anionic ion-exchange resin (Amberlite

IRA-410(Cl<sup>-</sup>)) were used aiming at the speciative separation and preconcentration of Cr(III) and Cr(VI), respectively. The method was successfully applied in the determination of Cr(III) and Cr(VI) species present in the dissolved phase of influents and effluents taken from the inlet and the outlet of a tannery wastewater treatment plant.

### Experimental Section

**Apparatus and Chemicals.** The determination of chromium species was performed by using an atomic absorption spectrometer (Model 3110, Perkin Elmer, USA) with an air/acetylene burner. Measurement of pH of aqueous solutions was performed by a pH-meter (Model 672, Jenco Instruments, Inc., USA). In the preconcentration process, glass columns and the resins as ion-exchanger, Amberlite IR-120(H<sup>+</sup>) strongly acidic cation exchanger with sulfonic acid functionality and Amberlite IRA 410(Cl<sup>-</sup>) strongly basic anion exchanger with quaternary ammonium functionality (Merck KGaA, Darmstadt, Germany), were used. A stock solution of 1000 mg/L Cr(VI) was prepared by dissolving 2.8316 g K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (Merck KGaA, Darmstadt, Germany) in about 200 mL doubly distilled deionized water and diluted to 1000 mL with dilute HNO<sub>3</sub> to be its final concentration of 1 mol/L. A stock solution of 1000 mg/L Cr(III) was prepared from 7.6967 g chromium(III) nitrate [Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O] (Merck KGaA, Darmstadt, Germany), by dissolving in about 200 mL doubly distilled deionized water and completed to 1000 mL with dilute HNO<sub>3</sub> to be its final concentration of 1 mol/L. The buffer solutions were prepared by mixing appropriate amounts of 1 mol/L solutions of each reagent (Merck KGaA, Darmstadt, Germany) interested as follows: pH 4.5 buffer solution made from 9.2 mL of concentrated acetic acid and 90 mL of 1 mol/L sodium acetate solution (for all buffer solutions with a final volume of 250 mL); pH 7.0 buffer solution made from 153 mL of 1 mol/L NaH<sub>2</sub>PO<sub>4</sub> and 97 mL of 1 mol/L Na<sub>2</sub>HPO<sub>4</sub> solutions, and pH 9.0 buffer solution made from concentrated NH<sub>3</sub> solution (~7 mL, 25% (w/w), 0.91 g/mL) and 160 mL of 1 mol/L NH<sub>4</sub>Cl solution.

In order to filter the wastewater samples, the membrane filters having 0.45 μm pore size and a 47 mm diameter (Advantec MFS, Inc., USA) were used with combining of a vacuum filter holder (Schleicher & Schuell, Dassel, Germany).

**Preparation of the Columns.** For the speciation of Cr(III) and Cr(VI) a glass column (10 mm i.d. and 20 cm length) was used. 1.5 g of Amberlite IR-120(H<sup>+</sup>) resin was put into the column and washed with 50 mL of 3 mol/L of HCl and then 30-35 mL of water for conditioning and cleaning the column. 1.5 g of Amberlite IRA 410(Cl<sup>-</sup>) resin was put into another column and 50 mL of NaCl solution (10%, w/v) was passed through the column and then washed with about 30-35 mL of water for conditioning and cleaning it. After this treatment, the columns were ready for separation, preconcentration and speciation studies for chromium(III) and (VI) species.

**Separation and Preconcentration Procedure for Cr(III) and Cr(VI) Ions.** In order to optimize the separation and

preconcentration technique, 100 mL of model solutions including 20 μg of Cr(III) were used. Then, pH of these solutions were adjusted to the optimum value (pH 4.5) at which the recovery for Cr(III) was the highest value. The resulting solution was passed through the column filled with Amberlite IR-120(H<sup>+</sup>) ion-exchange resin at a flow rate of 1-2 mL/min. The retained Cr(III) ions on the resin were eluted with 15 mL of 3 mol/L HCl acid at a flow rate of 1-2 mL/min. After evaporating the eluate to near dryness the residue was taken into 2.5 mL with 1 mol/L HNO<sub>3</sub> and Cr(III) content was determined by flame AAS.

For the Cr(VI), 100 mL of model solutions containing 20 μg Cr(VI) were prepared and their pHs were adjusted to pH 9.0 by using an NH<sub>3</sub>/NH<sub>4</sub>Cl buffer solution. The prepared solutions were passed through a column containing 1.5 g of Amberlite IRA 410(Cl<sup>-</sup>) resin at a flow rate of 1-2 mL/min. The retained Cr(VI) ions on the column were eluted with 10 mL of 0.5% (w/w) sodium sulfite solutions at a flow rate of 1-2 mL/min. After evaporating the eluate to near dryness the residue was taken into 2.5 mL with 1 mol/L HNO<sub>3</sub> and Cr(VI) content was determined by flame AAS.

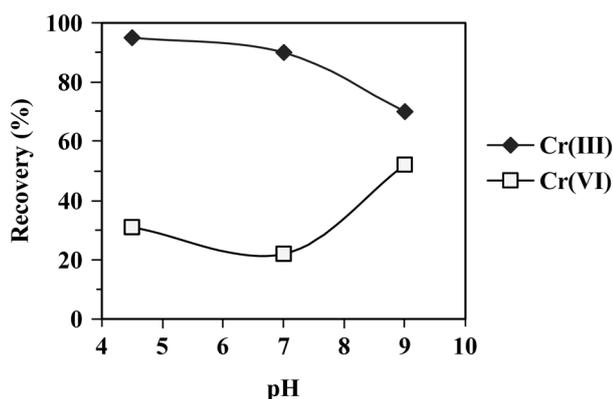
### Results and Discussion

In the determination of Cr(III) and Cr(VI) *via* speciation, the influences of some analytical parameters on the recovery were investigated. These parameters are pH of sample solution, eluent volume, eluent type and eluent concentration, sample volume, amount of resin, and flow rate of sample and eluent. To achieve the optimum experimental conditions for both chromium species, 100 mL of model working solutions containing 20 μg Cr(III) and/or 20 μg Cr(VI) ions were used throughout all the experiments and the final measurement volume was always 2.5 mL of 8 μg/mL of chromium.

**Effect of pH.** The sample's acidity is one of the critical variables for the retention of Cr(III) on the cation exchange resin. The effects of pH on the quantitative recovery of Cr(III) species were studied over the pH range from 4.5 to 9.0. The results acquired for Cr(III) are graphically depicted in Figure 1. The results indicate that the recovery decreases with increasing pH and is not quantitative beyond the pH 7.0. It is obvious that the optimum pH for the sorption of Cr(III) is about 4.5. Therefore, the pH 4.5 was chosen for Cr(III) in subsequent experiments.

Figure 1 also represents the effect of pH on the uptake behaviour of Cr(VI) on the resin. As can be seen from Figure 1, the recoveries for Cr(VI) were not quantitative with elution using 10% (w/v) of NaCl solution, only about 50% at pH 9.0. The studies performed later showed that the quantitative recovery (> 95%) for Cr(VI) could be obtained by using 0.5% (w/v) sodium sulfite solution at pH 9.0 as can be seen from Table 1. All the experiments were run in triplicate analyses.

**Effect of Type and Concentration of Eluent.** For the determination of Cr(III) ion by using a column of Amberlite IR-120(H<sup>+</sup>) resin, the solutions of HCl acid at different



**Figure 1.** The influence of the sample pH on the recoveries of Cr(III) and Cr(VI) ions (20  $\mu\text{g}$  of each one, 100 mL of sample volume, 2.5 mL of final solution,  $N = 3$ ). Eluents: 3 mol/L HCl for Cr(III) and 0.5%  $\text{Na}_2\text{SO}_3$  for Cr(VI).

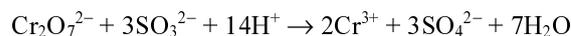
concentrations (ranging from 1 to 5 mol/L) were tested as eluent at optimum pH 4.5. For this purpose, 100 mL of model solutions containing 20  $\mu\text{g}$  Cr(III) were used at optimal experimental conditions, *i.e.*, 2-3 mL/min of sample or eluent flow rate and 10 mL of eluent volume. As can be seen from Table 1, satisfactory results for recovery of Cr(III) ions were obtained with 3 mol/L of HCl solution.

The effectiveness of different eluents for the elution of Cr(VI) ions from the resin, Amberlite IRA 410( $\text{Cl}^-$ ), was investigated using 10 mL of eluents at optimum pH 9. Each of 100 mL of working solutions contained an amount of 20  $\mu\text{g}$  Cr(VI) ion. As a means of elution, first, 3 mol/L HCl acid, 5% (w/v) of  $\text{Na}_2\text{SO}_3$ , 10% (w/v) of NaCl, 2 mol/L NaOH and 2% (w/v) of  $\text{H}_2\text{NOH}\cdot\text{HCl}$  solutions were tested. Of these eluents about 60% of recovery was obtained at best by using 5% (w/v) of  $\text{Na}_2\text{SO}_3$  solution acidified with 2 mol/L  $\text{H}_2\text{SO}_4$ . In order to find another proper concentration of  $\text{Na}_2\text{SO}_3$  eluent, then afterwards 1% and 0.5% (w/v) of  $\text{Na}_2\text{SO}_3$  solutions less than 5% were tested. As can be seen from Table 1, a good recovery yield (about 95%) was acquired using the 0.5% (w/v) of  $\text{Na}_2\text{SO}_3$  solution as an eluent. The reason for the choice of  $\text{Na}_2\text{SO}_3$  as an eluent is that it plays a role of reducing agent for Cr(VI) ions in acidic

**Table 1.** Effect of type and concentration of the eluents on the recovery for chromium species (20  $\mu\text{g}$  of each chromium species, volume of sample: 100 mL, volume of final solution: 2.5 mL, volume of eluent: 10 mL,  $N = 3$ )

Cr(III)		Cr(VI)	
Eluent : HCl (mol/L)	Recovery (%)	Eluent type	Recovery (%)
1	10 $\pm$ 1	3 mol/L HCl	40 $\pm$ 6
2	55 $\pm$ 1	10% (w/v) NaCl	52 $\pm$ 2
3	90 $\pm$ 2	2% (w/v) $\text{H}_2\text{NOH}\cdot\text{HCl}$	55 $\pm$ 4
4	66 $\pm$ 4	2 mol/L NaOH	15 $\pm$ 1
5	61 $\pm$ 6	5% (w/v) $\text{Na}_2\text{SO}_3$	60 $\pm$ 1
		1% (w/v) $\text{Na}_2\text{SO}_3$	75 $\pm$ 3
		0.5% (w/v) $\text{Na}_2\text{SO}_3$	95 $\pm$ 2

solutions according to the following reaction equation:



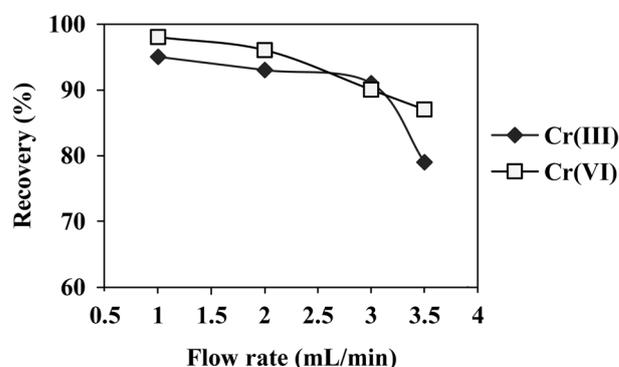
On the other hand, the  $\text{Na}_2\text{SO}_3$  solution was first used by us for eluting the Cr(VI) species from the column, to the best knowledge of our.

**Effect of Eluent Volume.** Under the optimum experimental conditions obtained in this study, the effects of eluent volume on the recovery for both Cr(III) and Cr(VI) species were studied with 5, 10 and 15 mL of 3 mol/L of HCl, and 0.5% (w/v) of  $\text{Na}_2\text{SO}_3$  solutions as the eluents, respectively. As can be seen from Figure 2, 97% for Cr(III) and 95% for Cr(VI) were recovered using 15 mL of 3 mol/L HCl and 10 mL of 0.5% (w/v)  $\text{Na}_2\text{SO}_3$ , respectively as the eluents.

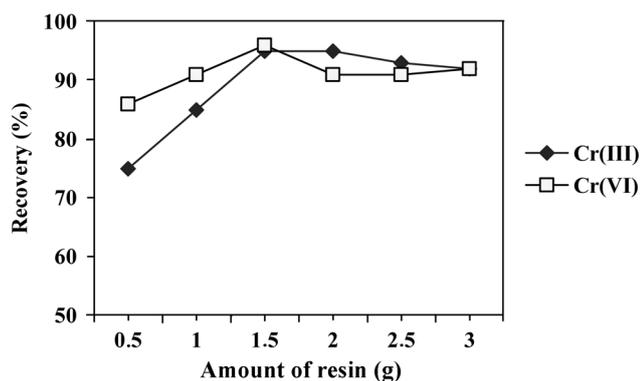
**Effect of Flow Rate of Eluent.** The effects of flow rates of the eluent for the recovery (%) of Cr(III) and Cr(VI) ions were investigated at the optimised experimental conditions. As can be seen from Figure 2, the recovery yields for both species decrease with increasing of flow rates. The recoveries were found lower than 90% at the flow rates higher than 3 mL/min for both Cr(III) and Cr(VI) ions. It was concluded that the flow rates of the eluent higher than 3 mL/min are not satisfactory for preconcentration and separation purposes for both chromium species. Therefore, the flow rates of 1-2 mL/min were chosen for the elution processes for the two chromium species.

**Effect of the Resin Amount.** To determine the influences of the resin amount on the recovery, the amounts of resins, Amberlite IR-120( $\text{H}^+$ ) resin for Cr(III) and Amberlite IRA-410( $\text{Cl}^-$ ) resin for Cr(VI), were studied between 0.5 and 3 g with changing intervals of 0.5 g. As can be seen from Figure 3, 1.5 g of resin was found to be sufficient for quantitative recoveries for both Cr(III) and Cr(VI) ions.

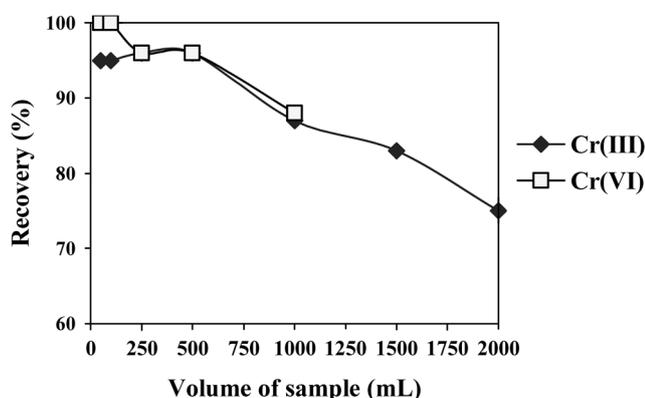
**Effect of the Sample Volume.** In order to study with tannery samples, it is important to know the maximum applicable sample volume. For this objective, 50, 100, 250, 500, 1000, 1500 and 2000 mL of model solutions including together 20  $\mu\text{g}$  Cr(III) and 20  $\mu\text{g}$  Cr(VI) ions were separately passed through the columns under the optimum conditions described before for the two chromium species. For the both



**Figure 2.** Effect of the eluent flow rate on the recoveries (20  $\mu\text{g}$  of each chromium species, 100 mL of sample volume, 2.5 mL of final solution,  $N = 3$ ). Eluents: 3 mol/L HCl for Cr(III) and 0.5%  $\text{Na}_2\text{SO}_3$  for Cr(VI).



**Figure 3.** Effect of the resin amount on the recoveries of Cr(III) and Cr(VI) ions (20  $\mu\text{g}$  of each chromium species, 100 mL of sample volume, 2.5 mL of final solution,  $N = 3$ ). Eluents: 3 mol/L HCl for Cr(III) and 0.5%  $\text{Na}_2\text{SO}_3$  for Cr(VI).



**Figure 4.** Effect of sample volume on the retention of Cr(III) and Cr(VI) ions (20  $\mu\text{g}$  of each chromium species, 2.5 mL of final solution,  $N = 3$ ). Eluents: 3 mol/L HCl for Cr(III) and 0.5%  $\text{Na}_2\text{SO}_3$  for Cr(VI).

chromium species, the quantitative recoveries more than 96% were obtained up to 500 mL of sample solution. As from this point, the recoveries decreased slowly with increasing volume of the sample solutions; for example, 87 and 88% for 1000 mL of sample volumes for Cr(III) and Cr(VI) ions, respectively, and 75% for 2000 mL of sample volume for Cr(III) only. This is originated from the dilution effect that is not significant for the sample volumes up to 500 mL for the both chromium species.<sup>32</sup> The results for the both species are given together in Figure 4. Consequently, it is possible to obtain a preconcentration factor of 200 using the proposed method for the both chromium species with a sample solution of 500 mL when it is concentrated to a 2.5-mL of final measurement solution.

**Effect of Matrix Ions.** The influences of diverse foreign ions such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ , which present in water samples as main component, on the determination of chromium species were investigated. The main purpose of this separation study was to apply to waste water samples taken from a tannery treatment plant. The results are illustrated in Table 2. The relevant experiments were performed using 100 mL of model solutions including

**Table 2.** Effect of the foreign ions on recovery of Cr(III) and Cr(VI) ions (20  $\mu\text{g}$  of each chromium species, volume of sample: 100 mL, volume of final solution: 2.5 mL,  $N = 3$ ). Eluents: 3 mol/L HCl for Cr(III) and 0.5%  $\text{Na}_2\text{SO}_3$  for Cr(VI)

Ion	Cr(III)		Cr(VI)	
	Conc. <sup>a</sup> (mg/L)	R <sup>b</sup> (%)	Conc. (mg/L)	R (%)
$\text{Na}^+ : \text{NaCl}$	5000	95 $\pm$ 2	2500	93 $\pm$ 4
$\text{K}^+ : \text{KCl}$	500	93 $\pm$ 2	500	93 $\pm$ 2
$\text{Mg}^{2+} : \text{MgCl}_2$	2500	65 $\pm$ 4	2500	78 $\pm$ 1
$\text{Ca}^{2+} : \text{CaCl}_2$	500	96 $\pm$ 5	500	83 $\pm$ 1
$\text{Cl}^- : \text{NaCl}$	5000	93 $\pm$ 2	2500	94 $\pm$ 3
$\text{SO}_4^{2-} : \text{Na}_2\text{SO}_4$	5000	102 $\pm$ 8	1000	89 $\pm$ 8
$\text{NO}_3^- : \text{Ca}(\text{NO}_3)_2$	5000	98 $\pm$ 6	1000	90 $\pm$ 6
$\text{NO}_3^- : \text{NaNO}_3$	5000	100 $\pm$ 6	1000	90 $\pm$ 6

<sup>a</sup>Concentration. <sup>b</sup>Recovery.

20  $\mu\text{g}$  Cr(III) and/or 20  $\mu\text{g}$  Cr(VI) ions in each case (8  $\mu\text{g}$ /mL in final solution of 2.5 mL). Additionally, in the analysis of Cr(III) and Cr(VI) ions, the effect of each chromium ion on the recovery of the other species was examined and no interference effect was observed as matrix ion.  $\text{Ca}^{2+}$  for Cr(VI) and  $\text{Mg}^{2+}$  for both Cr(III) and Cr(VI) ions were the most effective matrix components having suppression effects on the chromium signals in AAS.

**Validation of the Method.** In the studies being done for the recovery purpose, by spiking 1.7  $\mu\text{g}$  Cr(III) and 2.5  $\mu\text{g}$  Cr(VI) to the waste water samples taken from outlet of the treatment plant, the recoveries were obtained to be 99 and 98% for Cr(III) and Cr(VI), respectively.

**Application of the Method.** The proposed method was applied to the untreated and treated wastewater samples taken from a tannery plant in Develi far from 80 km to Kayseri for the speciation of Cr(III) and Cr(VI) species. The waste water samples were percolated through a cellulose nitrate membrane filter. The concentrations of Cr(III) and Cr(VI) ions in the tannery waste waters at inlet of the treatment plant taking 25 mL of waste water sample were found as being  $0.60 \pm 0.03$  and  $2.30 \pm 0.09$  mg/L ( $N = 7$ ), while at outlet of the plant taking 350 mL of sample their levels were found to be  $5.02 \pm 0.07$  and  $14.85 \pm 0.11$   $\mu\text{g}/\text{L}$  ( $p = 0.95$ ,  $N = 5$ ), respectively. The results indicate that the treatment efficiency of the plant is very high, about 99% for both chromium species as well.

## Conclusions

In this study, a new approach was described based upon the use of ion-exchangers for the preconcentration, separation, and separately determination of Cr(III) and Cr(VI) ions. The suggested method has been successfully applied to the tannery waste water samples with the satisfactory precision and accuracy. It can be concluded that reliable results can be acquired by the proposed method for the speciation of Cr(III) and Cr(VI) species by using Amberlite IR 120( $\text{H}^+$ ) and Amberlite IRA 410( $\text{Cl}^-$ ) ion-exchange resins and their

determinations can be made reliably by FAAS in waste waters and/or in any similar media, *i.e.*, lake and river waters etc. Both resins can be used repeatedly without deforming and the technique does not require the excess reagent consumption except for buffering solutions and not contain the oxidation and/or reduction steps which need extra analyzing time and procedures. Also, sodium sulfite solution (0.5%, w/v) was observed as a new and effective eluent in order to elute chromium(VI) species from the resin. Because of all these reasons, the proposed method are applicable almost in every laboratory, due to its enough rapidity, cheapness, economical, having some novelty, not requesting expensive and complicated systems such as ICP-MS etc.

**Acknowledgement.** This research was financed by the Research Foundation of Erciyes University with Contract No. 01-012-8.

### References

1. Marqués, M. J.; Morales-Rubio, A.; Salvador, A.; Guardia, M. de la. *Talanta* **2001**, 53, 1229.
2. Stein, K.; Schwedt, G. *Fresenius J. Anal. Chem.* **1994**, 350, 38.
3. Bağ, H.; Türker, A. R.; Lale, M.; Tunçeli, A. *Talanta* **2000**, 51, 895.
4. Akama, Y.; Sali, A. *Talanta* **2002**, 57, 681.
5. Donais, M. K.; Henry, R.; Rettberg, T. *Talanta* **1999**, 49, 1045.
6. Mohamed, A. A.; Ahmed, S. A.; El-Shahat, M. F. *J. Trace Microprobe T.* **2001**, 19(2), 297.
7. Wen, B.; Shan, X.-Q.; Lian, J. *Talanta* **2002**, 56, 681.
8. Borai, E. H.; El-Sofany, E. A.; Abdel-Halim, A. S.; Soliman, A. A. *Trends Anal. Chem.* **2002**, 21(11), 741.
9. Zhang, Q.; Minami, H.; Inoue, S.; Atsuya, I. *Anal. Chim. Acta* **1999**, 401, 277.
10. Hiraide, M.; Chen, Z.-S.; Kawaguchi, H. *Anal. Sci.* **1991**, 7(1), 65.
11. Gopi, K. P.; Mary, G. J.; Rambabu, U.; Rao, P. T.; Naidu, G. R. K. *Talanta* **2004**, 63(3), 541.
12. Abou-El-Sherbini, K. S.; Kenawy, I. M. M.; Hamed, M. A.; Issa, R. M.; Elmorsi, R. *Talanta* **2002**, 58, 289.
13. Kenawy, I. M. M.; Hafez, M. A. H.; Akl, M. A.; Lashein, R. R. *Anal. Sci.* **2000**, 16, 493.
14. Demirata, B.; Tor, I.; Filik, H.; Afşar, H. *Fresenius J. Anal. Chem.* **1996**, 356, 375.
15. Llobat-Estellés, M.; Mauri-Aucejo, A. R.; López-Catalán, M. D. *Fresenius J. Anal. Chem.* **2001**, 371, 358.
16. Adriá-Cerezo, D. M.; Llobat-Estellés, M.; Mauri-Aucejo, A. R. *Talanta* **2000**, 51, 531.
17. Tokaloğlu, Ş.; Kartal, Ş.; Elçi, L. *Bull. Korean Chem. Soc.* **2002**, 23(5), 693.
18. Rao, T. P.; Karthikeyan, S.; Vijayalekshmy, B.; Iyer, C. S. P. *Anal. Chim. Acta* **1998**, 369(1), 69.
19. Abdollahi, H. *Anal. Chim. Acta* **2001**, 442, 327.
20. Li, Y.; Pradhan, N. K.; Foley, R.; Low, G. K. C. *Talanta* **2002**, 57, 1143.
21. Wang, J.; Lu, J. *Analyst* **1992**, 117, 1913.
22. Mulaudzi, L. V.; van Staden, J. F.; Stefan, R. I. *Anal. Chim. Acta* **2002**, 467, 51.
23. Luo, S.-K.; Berndt, H. *Fresenius J. Anal. Chem.* **1998**, 360, 545.
24. Hirata, S.; Honda, K.; Shikino, O.; Maekawa, N.; Aihara, M. *Spectrochim. Acta B* **2000**, 55, 1089.
25. Doğutan, M.; Filik, H.; Tor, I. *Talanta* **2003**, 59(5), 1053.
26. Kocaoba, S.; Akçin, G. *Talanta* **2002**, 57(1), 23.
27. Kim, Y.-S.; Park, S.-J.; Choi, J.-M. *Bull. Korean Chem. Soc.* **1993**, 14(3), 330.
28. Balasubramanian, S.; Pugalenti, V. *Talanta* **1999**, 50, 457.
29. He, Y.; Cervera, M. L.; Garrido-Ecija, M. I.; de la Guardia, M. *Anal. Chim. Acta* **2000**, 421, 57.
30. Noroozifar, M.; Khorasani-Motlagh, M. *Anal. Sci.* **2003**, 19, 705.
31. Stasinakis, A. S.; Thomaidis, N. S.; Lekkas, T. D. *Anal. Chim. Acta* **2003**, 478(1), 119.
32. Baytak, S.; Türker, A. R. *J. Hazardous Mater.* **2006**, B129, 130.