Selective Determination of Cr(VI) by FAAS After Solid Phase Extraction on Bis(3-aminopropyl)amine-Bonded Silica Gel

Elif Akyuz, Mustafa Imamoglu*, and Huseyin Altundag
Department of Chemistry, Faculty of Arts and Sciences, Sakarya University
54187 Sakarya, Turkey

INTRODUCTION

Chromium (Cr) is classified as a heavy metal and used widely in various industrial activities such as leather tanning, steel production, plating, corrosion control, cellulose, and paper production. It is thus released into environmental water bodies by wastewater from these industries (1-3). Mainly, Cr can be found in environmental samples in two oxidation states of Cr(III) and Cr(VI) (1,4). It is well-known that Cr(III) is required for humans, especially for glucose metabolism. However, in contrast to Cr(III), Cr(VI) is highly toxic and carcinogenic to humans. The ingestion of Cr(VI) compounds at high dose may also cause death (3,5,6). For these reasons, wastewaters should be treated and the concentration of Cr(VI) should be reduced to acceptable levels (e.g., 0.5 mg L⁻¹ in Turkey) before being discharged into the environment.

In order to protect human health, the level of Cr(VI) in food, drinking water, etc., should also be monitored. Hence, the development of a methodology for its determination is a very important analytical task. Atomic spectroscopic techniques, widely used for the determination of metal ion levels in many laboratories, such as flame and electrothermal atomic absorption spectrometry (FAAS and ETAAS), inductively coupled plasma atomic emission or mass spectrometry (ICP-AES and ICP-MS),

ABSTRACT

In this study, a novel method was developed for the selective determination of Cr(VI) based on column solid phase extraction (SPE) using bis(3-aminopropyl)amine-bonded silica gel (BAPA-SG). To optimize the SPE procedure, the effects of various variables, including pH, sample volume, eluent type and volume, matrix ions and sample flow rate, were studied. The column SPE studies showed that BAPA-SG could selectively collect Cr(VI) ions at the pH of 2.0 from a sample volume up to 1000 mL in the presence of Cr(III).

The recovery of the Cr(VI) ions was not affected by anions and cations widely found in environmental water samples. Adsorbed Cr(VI) on the column could be easily eluted using 5.0 mL of a 2.0M HCl solution. Cr(VI) adsorption dynamics onto BAPA-SG were also studied batch-wise by investigating the effects of contact time, initial Cr(VI) concentration, and temperature. Increasing the temperature showed adverse effects on the adsorption of Cr(VI). A Langmuir model best fit the experimental data. The maximum adsorption capacity was 75.5 mg g⁻¹. The developed SPE procedure was successfully applied to the determination of Cr(VI) in spiked solutions by flame atomic absorption spectrometry. The pre-concentration factor of 200 permitted a detection limit of 0.11 ng/mL.

can be used for the determination of total Cr concentration (6-8). The determination of the oxidation state of Cr is not possible by these instruments without pre-treatment of the sample. Some of these methods, however, can fail due to matrix effects present in real samples and the low concentration of Cr (1,8). To overcome all these issues, several preconcentration and separation methods, including solid phase extraction (6,7), liquid-liquid extraction (3,9), cloud point extraction (10,11), ionic liquid-based dispersive liquid-liquid microextraction (12,13) and co-precipitation (14-16), have been investigated and proposed by different researchers. Some review papers about the preconcentration and/or speciation of Cr have been published (17-19).

Sorption can be considered among the widely used methods for both treatment of wastewater containing Cr(VI) ions and column solid phase extraction of trace Cr(VI) ions before the measurement step. Sorption is more effective than chemical precipitation and electrochemical methods for the treatment of wastewater including metal ions at low concentrations. Sorption methods as preconcentration techniques also have various advantages, such as providing high preconcentration factors, rapidity, low cost, and ease of combination with various instrumentation (20-24).

Performance and efficiency of the sorption method is dependent on the physical and chemical properties of sorbents. Selectivity of the sorbents is mainly determined by their surface functional groups. Carbon nanotubes (25), functional

* Corresponding author.
E-mail: imamoglu_m@yahoo.com
Tel: +90 264 295 60 53

polymers (26), activated carbons (27), modified silica gels (28), and chelating resins (29) have been widely used as sorbents. Chelating resins bearing functional groups are more selective than other sorbents due their complexing abilities with metal ions. These resins can be prepared by incorporating organic functional groups to organic or inorganic support materials such as silica (30). The structure of the functional groups should contain N, S, O, and P atoms for the chelation of metal ions (31). According to Pearson's acid base concept, HSAB (hard and soft acids and bases), hard metal ions (e.g., Cu and Ni) can coordinate with hard donor atoms (e.g., O); and soft metal ions (e.g., Pt and Ag) can coordinate with soft donor atoms (e.g., S). The nitrogen donor atom is classified in the borderline group and can coordinate with two groups (32). The main properties of N-bearing resins are their action as anion exchanger in acidic media and as chelator in near neutral pH or under basic conditions. In acidic conditions, the N atom will be charged positively as a result of protonation (33). Hence, N-containing resins are promising for the adsorption of negatively charged Cr(VI) ions. Some studies (34-36) reported on the adsorption of Cr(VI) ions onto N-containing resins. According to our literature survey, no studies have been performed on the adsorption and solid phase extraction of Cr(VI) ions onto bis(3-amino-propyl)amine bonded silica gel (BAPA-SG).

In this study, column solid phase extraction (SPE) and adsorption of Cr(VI) ions onto BAPA-SG were investigated. The influence of sample pH, flow rate, volume, and eluent type was studied. A batch procedure was used for the analysis of the Cr(VI) adsorption dynamics by investigating effective variables such as temperature, initial concentration, and contact time. Trace lev-

els of Cr(VI) ions were determined in spiked water samples by FAAS after column SPE of Cr(VI) under optimal conditions.

EXPERIMENTAL

Instrumentation

A Shimadzu Model AA-6701F flame atomic absorption spectrometer was used for the determination of Cr concentration. The measurement conditions used were as follows: fuel: air-acetylene, slit width: 0.5 nm, wavelength: 357.9 nm. The pH measurement was performed using a pH meter (Schott, CG840). A temperature-controlled orbital shaker (IKA KS 4000i) was employed for shaking the samples for batch studies.

Materials, Reagents, and Standard Solutions

The preparation and characterization of BAPA-SG has been described elsewhere (37). All glass equipment was cleaned by immersing in 10% of HNO₃ solution (w/v). Unless otherwise stated, all chemicals used throughout the study were of analytical grade. The distilled water was further purified using a Millipore Milli-Q™ system to obtain water at a resistivity of 18.2 MΩ cm. A stock solution of Cr(VI) was prepared from K₂Cr₂O₇ at 1000 mg L⁻¹ concentration. A spectroscopic grade Cr(III) solution was purchased from Merck KGaA (Darmstadt, Germany). Working solutions were prepared carefully by serial dilution. In order to adjust the pH of the working solutions, dilute solutions of HCl or NaOH (0.1 M) were used.

Column SPE Procedure

To optimize the column SPE procedure, several parameters, such as pH, flow rate, volume and matrix content of model solution, and type and volume of eluent solution, were investigated. A glass column (15 cm and 0.8 mm i.d.), fitted with

Teflon® stopcocks, was used in the column SPE experiments. The column was filled with 0.4 g of BAPA-SG. A dropping funnel was placed at the top of the column and a peristaltic pump was connected to the outlet in order to regulate the flow rate of the sample solution. The Cr(VI) model solution (50 mL) was prepared at 0.5 mg L⁻¹. After adjusting the pH of the sample solution to the value of 2.0, the solution was passed through the column at a flow rate of 5 mL min⁻¹. The Cr(VI) ions retained on the BAPA-SG-loaded column were stripped using 5 mL of 2.0 M HCl solution. The concentration of Cr(VI) in the eluates was determined by FAAS. The recovery of the Cr(VI) ions was calculated using the following equation:

$$\text{Recovery (\%)} = \frac{C_e \cdot V_e}{C_s \cdot V_s} \times 100 \quad (\text{Eq. 1})$$

where C_e and C_s = concentration of Cr(VI) ions in the eluate and model sample solution (mg L⁻¹), respectively, and V_e and V_s = volume of eluate and sample solution (L), respectively (38).

Batch Adsorption Procedure

The adsorption dynamics of the Cr(VI) ions using BAPA-SG were studied using a batch adsorption model, and the influence of agitation time, initial Cr(VI) concentration, and temperature were examined. A 50-mL volume of Cr(VI) solution at known concentrations was mixed with specific amounts of BAPA-SG in Erlenmeyer flasks fitted with glass stoppers. After agitation on a temperature-controlled orbital shaker for a predetermined period of time, the suspension was filtered off using blue ribbon filter paper (Macherey-Nagel GmbH & Co. KG, Düren, Germany). The concentration of the Cr(VI) ions remaining in the solutions was measured by FAAS and the amount of Cr(VI) ions

adsorbed onto the BAPA-SG was calculated by the following equation:

$$q_e = (C_o - C_e) \frac{V}{m} \quad (\text{Eq. 2})$$

where q_e = adsorbed amount of Cr(VI) ions onto BAPA-SG (mg g^{-1}), C_o and C_e = concentration of Cr(VI) ions at initial and equilibrium conditions, respectively, (mg L^{-1}), V is the volume of Cr(VI) solutions (L), and m = amount of BAPA-SG (g) (39).

RESULTS AND DISCUSSION

Optimization of Cr(VI) SPE Procedure

Sample solution pH plays a significant role in the SPE procedure of heavy metal ions, using most of the sorbents such as porous polymer, activated carbon, modified silica gel, and functional group-bearing polymers (40,41).

The SPE of Cr(III) and Cr(VI) ions onto a BAPA-SG-loaded column was studied using their individual solutions at a concentration of 0.5 mg L^{-1} . The pH of the solutions was adjusted to values ranging from 1.0 to 7.0. Figure 1 shows that increasing the pH from 1.0 to 2.0 increases the Cr(VI) recoveries, and

quantitative recoveries ($\geq 95\%$) were obtained for Cr(VI) ions from this pH value to pH 6.0. At a pH higher than 6.0, a decrease in the recoveries occurred. At the same time, the recoveries of the Cr(III) ions were below 5% at pH 1.0 to 4.0. But, at pH 4.0 and higher, the Cr(III) recoveries increased sharply. These results revealed that a BAPA-SG-loaded column could be used for the selective extraction of Cr(VI) ions from aqueous solutions containing Cr(III) and Cr(VI) ions. From these findings it can be concluded that the optimum pH value is 2.0 for SPE of Cr(VI) ions. In order to understand the mechanism of Cr(VI) adsorption onto BAPA-SG, the charge of both Cr(VI) and the functional group should be considered. Cr(VI) ions are mainly in the form of HCrO_4^- at the pH of 2–6, whereas BAPA-SG is positively charged by the protonation of the N atoms at acidic pH values. Hence, it may be concluded that the Cr(VI) ions were mainly retained on BAPA-SG by electrostatic interactions.

The selection of a suitable eluent solution is considered to be one of the key factors affecting the recovery of analytes. To desorb Cr(VI) ions retained on the column,

hydrochloric and nitric acid solution at various volumes and concentrations were examined. The obtained results are presented in Table I. Quantitative recoveries were obtained using 10 mL of 2.0M HNO_3 and 0.5–2.0M HCl. However, only 1.0 and 2.0M HCl solutions provided quantitative recoveries when a volume of 5 mL was used.

In order to investigate the effect of sample solution flow rate on the recovery of Cr(VI) ions, 50 mL of Cr(VI) solution at 0.5 mg L^{-1} was percolated through the column at various flow rates ranging from 1 to 5 mL min^{-1} . Quantitative recoveries were obtained at all flow rates. Hence, the highest flow rate of 5 mL min^{-1} was used in the subsequent experiments.

Sample solution volume is another important factor that limits the use of SPE procedures when a large sample volume is needed. The effect of sample solution volume on the recoveries of Cr(VI) is illustrated in Figure 2, which shows that a BAPA-SG-loaded column can collect Cr(VI) ions from a volume of sample solution as large as 1000 mL. This is ultimately dependent on the capacity of the material, which was determined to

Fig. 1. Effect of pH on the recoveries of Cr(VI) and Cr(III) ions (sample volume=50 mL, amount of Cr(III) and Cr(VI)=0.025 mg, eluent=5 mL of 2.0M HCl solution, flow rate of sample solution=5 mL min^{-1} ($n=3$)).

TABLE I
Effect of Eluent Solution on Cr(VI) Recovery
Sample volume: 50 mL; amount of metal: 0.025 mg;
pH 2.0; flow rate of sample solution: 5 mL min^{-1} , ($n=3$)

Eluent	Eluent Volume (mL)	Recovery (%)
0.5M HNO_3	5	3 ± 2
	10	35 ± 4
1.0M HNO_3	5	25 ± 3
	10	86 ± 3
2.0M HNO_3	5	48 ± 1
	10	99 ± 2
0.5M HCl	5	54 ± 1
	10	99 ± 3
1.0M HCl	5	98 ± 2
	10	100 ± 2
2.0M HCl	5	98 ± 3
	10	100 ± 3

be 77.5 mg/g sorbent. The preconcentration factor, defined as the ratio of the sample volume (1000) to the eluent volume (5 mL), was found to be 200.

Matrix ions can widely restrict the use of the SPE procedures due to their adverse effect on the recovery of the analytes. Hence, the influence of some cations and anions widely found in aqueous solutions on the recoveries of Cr(VI) were examined. As seen from the results listed in Table II, all recoveries are quantitative up to the studied concentrations of the interferences. Therefore, it was concluded that the proposed method could be used for recovering Cr(VI) ions from real aqueous samples.

Analytical Performance of Proposed SPE Procedure

The performance of the developed method was evaluated under the following optimum conditions: (a) sample solution pH of 2.0, (b) eluent of 5 mL 2.0 M HCl, (c) flow rate of 5 mL min⁻¹, and (d) maximum applicable sample solution of 1000 mL.

Precision of the method was studied using 50 mL of Cr(VI) solutions at 0.5 mg L⁻¹ (n=10); the recovery (%) and RSD (%) were found to be 98 and 3, respectively.

Useful life is also an important parameter for the usage of the sorbents. BAPA-SG could be used 35–40 times without loss in performance.

The detection limit (LOD) of Cr(VI) ions by FAAS based on three times the standard deviation of a blank solution (3σ) was calculated as 22.8 ng mL⁻¹. The LOD of the proposed method was found to be 0.11 ng mL⁻¹ by dividing the LOD by the preconcentration factor of 200.

Influence of Contact Time

The effect of time on the adsorption of Cr(VI) was investigated batch-wise using two initial concentrations, namely 50 and 100 mg L⁻¹, at a temperature of 25±1°C. The results, presented in Figure 3, show that an increase in contact time increases the adsorption of Cr(VI) ions until equilibrium conditions are reached after 60 minutes. It

should also be noted that 94% of the adsorption of Cr(VI) ions occurred in the first five minutes for both initial concentrations. Hence, it can be stated that Cr(VI) adsorption is a rapid process.

Cr(VI) Adsorption Isotherms

To investigate adsorption isotherms of Cr(VI) ions, experiments were performed in batch mode at a temperature of 25±1°C. For this purpose, the pH of the Cr(VI) solutions (50 mL) at various concentrations ranging from 25 and 250 mg L⁻¹ was adjusted to 2.0; and the solutions were suspended with 50 or 100 mg of BAPA-SG and agitated for 60 minutes. At the end of this operation, the remaining Cr(VI) concentration was determined by FAAS and the amount of Cr(VI) ions adsorbed was calculated.

The Langmuir and Freundlich equations were used to investigate the Cr(VI) equilibrium data due to their simplicity, familiarity, reliability, and usability.

Fig. 2. Effect of sample volume on recovery of Cr(VI) ions. Flow rate of sample solution: 5 mL min⁻¹; amount of Cr(VI): 0.025 mg; pH, 2.0; eluent: 5 mL of 2.0M HCl solution, (n=3).

TABLE II
Effect of Matrix Ions on Recovery of Cr(VI) Ions
Flow rate of sample solution: 5 mL min⁻¹;
amount of Cr(VI): 0.025 mg; pH 2.0;
eluent: 5 mL of 2.0M HCl solution, (n=3)

Matrix Ions	Compound	Concentration (mg L ⁻¹)	Recovery (%)
Na ⁺	NaCl	1000	99 ± 1
K ⁺	KCl	500	98 ± 2
Ca ²⁺	CaCl ₂	500	95 ± 2
Mg ²⁺	MgCl ₂	100	98 ± 1
NH ₄ ⁺	NH ₄ Cl	250	97 ± 1
Cl ⁻	NaCl	1000	99 ± 1
NO ₃ ⁻	Na(NO ₃)	500	97 ± 3
SO ₄ ²⁻	Na ₂ SO ₄	250	98 ± 2
CH ₃ COO ⁻	CH ₃ COONa	500	98 ± 2
Cr ³⁺	Cr(NO ₃) ₃	10	103 ± 2
Ni ²⁺	Ni(NO ₃) ₂	10	102 ± 2
Cu ²⁺	Cu(NO ₃) ₂	10	98 ± 3
Fe ³⁺	Fe(NO ₃) ₃	10	101 ± 1

The Langmuir isotherm (42) is represented in non-linear form by:

$$q_e = \frac{K_L q_{\max} C_e}{1 + K_L C_e} \quad (\text{Eq. 3})$$

where q_e (mg g^{-1}) and C_e (mg L^{-1}) are the amount of Cr(VI) adsorbed per gram of BAPA-SG and the Cr(VI) concentration in the aqueous solution at equilibrium, respectively. $q_{\max}$ and K_L are constants related to the maximum adsorption capacity (mg g^{-1}) and a constant which accounts for the affinity of the binding sites (L mg^{-1}), respectively (43).

Freundlich's equation (44) is given by:

$$q_e = K_F C_e^{1/n} \quad (\text{Eq. 4})$$

where K_F = constant related to relative adsorption capacity, and n = empiric parameter related to intensity of adsorption; n also indicates the strength of the relationship between adsorbate and adsorbent (45).

Experimental Langmuir and Freundlich isotherms are presented in Figures 4 (a and b). Calculated coefficients of both isotherms and correlation coefficients are given in Table III. From both the magnitude of r^2 and the shape of the plots, it

was concluded that the adsorption of the Cr(VI) ions followed the Langmuir equation. The Cr(VI) adsorption capacity of BAPA-SG, based on the Langmuir isotherms, was 77.5 mg g^{-1} .

Influence of Temperature

The determination of adsorption thermodynamics is very important in order to decide whether the process is spontaneous or not. The effect of temperature on the adsorption of Cr(VI) ions was carried out batch-wise and the results are depicted in Figure 5. It can be inferred from this figure that the adsorption of Cr(VI) decreased with an increase in temperature which shows that the adsorption of Cr(VI) ions onto BAPA-SG is an exothermic process.

From the Cr(VI) adsorption data at various temperatures, thermodynamic parameters, such as ΔG , ΔH , and ΔS , were calculated as described in the literature (45).

ΔG was calculated from the following equation:

$$\Delta G = -RT \ln K_d \quad (\text{Eq. 5})$$

where R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the temperature (K), and K_d is the distribution coefficient. The adsorp-

Fig. 3. Effect of contact time on the adsorption of Cr(VI) onto BAPA-SG.

Fig. 4. Cr(VI) adsorption isotherms at different dosage of BAPA-SG: (a) 50 mg and (b) 100 mg.

tion equilibrium constant (K_d) value was calculated using the following equation (6):

$$K_d = \frac{C_a}{C_e} \quad (\text{Eq. 6})$$

where C_a is the Cr(VI) concentration adsorbed on unit mass of BAPA-SG (mg L^{-1}) and C_e are the equilibrium concentration of Cr(VI) in the solution (mg L^{-1}) (45).

The relation between ΔG , ΔH , and ΔS is given by the following equations (Eq. 7 and 8) (46,47):

$$\Delta G = \Delta H - T\Delta S \quad (\text{Eq. 7})$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (\text{Eq. 8})$$

The values of ΔH and ΔS were calculated from a plot of $\ln K_d$ versus $1/T$ (see Figure 5) and given in Table IV.

The negative value of ΔG indicates that the adsorption of Cr(VI) onto BAPA-SG is spontaneous and feasible. The negative ΔH value indicates that Cr(VI) adsorption onto BAPA-SG is an exothermic process, since the sorption capacity decreases with temperature. The negative ΔS value indicates a decrease in randomness at the solid/solution interface during the adsorption of Cr(VI) adsorption onto BAPA-SG (48,49).

Analytical Application of Proposed SPE Procedure

Since commercial aqueous certified reference material, including both Cr(III) and Cr(VI) ions, are unavailable, synthetic solutions containing Cr(III) and Cr(VI) were analyzed by spectrophotometry and by the proposed SPE method. The spectrophotometric method

is based on the formation of a colored complex between Cr(VI) and 1,5-diphenylcarbazide (DPC) as given elsewhere in detail (50). This same approach was carried out in other studies (51). The results presented in Table V show that the developed method can be successfully employed for the selective determination of Cr(VI) in solutions containing both species of Cr. It should also be noted that the LOD of the SPE method was found to be 0.11 ng mL^{-1} and the detection limits of the DPC method were reported to be 8 ng mL^{-1} in the literature (46). Thus, a lower level of Cr(VI) could be determined using the SPE technique.

The SPE procedure was also applied to solutions, including various amounts of Cr(III) and Cr(VI), for the selective determination of Cr(VI) ions using FAAS. The results

TABLE III
Langmuir and Freundlich Constants for Cr(VI) Adsorption onto BAPA-SG

Amount of BAPA-SG (mg)	Langmuir Constants			Freundlich Constants		
	$q_{\max}$ (mg g^{-1})	K_L (L mg^{-1})	r^2	K_F (mg g^{-1})	n	r^2
50	77.5	0.28	0.9989	26.0	3.9	0.6937
100	76.9	0.15	0.9988	14.8	2.6	0.8244

TABLE IV
Thermodynamic Parameters for Cr(VI) Adsorption Onto BAPA-SG

T (K)	ΔG ($\text{J mol}^{-1}\text{K}$)	ΔS ($\text{J mol}^{-1}\text{K}^a$)	ΔH ($\text{J mol}^{-1}\text{K}^a$)
298	-4.5		
308	-4.0	-61.8	-23.1
318	-3.4		
328	-2.8		

^a Measured between 298 and 338 K.

Fig. 5. Effect of temperature on the adsorption Cr(VI)
Sample volume: 50 mL; amount of Cr(VI): 3.5 mg; BAPA-SG dosage: 50 mg ($n=3$).

TABLE V
Determination Cr(VI) in Spiked Solutions (50 mL) Containing Cr(III) and Cr(VI) Ions Using Spectrophotometric Procedure and SPE Method (Conditions for SPE; pH 2.0; Eluent: 5 mL 2.0 M HCl; $n=3$)

Added (μg)		Found value (μg) By developed SPE		By DPC Method (μg)	
Cr (III)	Cr (IV)	Total Cr	Cr(VI)	Cr(III)	Cr(VI)
5	5	10.1 ± 0.3	5.1 ± 0.3	5.0 ± 0.1	$5.0 \pm 0.$
10	10	19.8 ± 0.3	10.1 ± 0.2	9.7 ± 0.1	10.1 ± 0.2

are listed in Table VI and provide good agreement between the added and found amounts of Cr(VI) ions. These results clearly confirm that the found concentration of Cr(VI) was not affected by the presence of Cr(III) ions. Hence, it can be concluded that the developed method could be used successfully for the determination of Cr(VI) ions in solutions containing Cr(III) and Cr(VI) ions. Another approach was proposed by Willie and Sturgeon (52) for the selective determination of Cr(VI) based on the selective concentration of Cr(III) from natural waters with rejection of Cr(VI) using a column SPE technique which was loaded with immobilized diphenylcarbazide.

The developed preconcentration technique was also applied to environmental water samples collected around Sakarya city, Turkey, for the determination of Cr(VI) ions. The level of Cr(VI) in the Çark stream, Sakarya river, and tap water was determined by the SPE procedure using FAAS detection. The results presented in Table VII show the usefulness of the proposed SPE method for real water samples for the selective determination of Cr(VI) ions.

CONCLUSION

In this study, a novel column solid phase extraction (SPE) procedure was developed for the selective determination of trace levels of Cr(VI) ions in environmental aqueous samples based on the selective retention of Cr(VI) ions on bis(3-aminopropyl)amine-bonded silica gel (BAPA-SG). The Cr(VI) ions can be retained onto BAPA-SG at pH 2.0 and quantitative elution of adsorbed Cr(VI) ions achieved using 5 mL of 2.0M HCl solution. The method could be used for the collection of trace Cr(VI) ions from 1000 mL of the analyte solution. The proposed method provides a high preconcentration factor of 200

TABLE VI
Selective Determination Cr(VI) in Solutions
Containing Various Amounts of Cr(III) and Cr(VI) Ions
Sample volume: 50 mL; pH 2.0; eluent: 5 mL 2.0 M HCl (n=3)

Added (µg)		Found Cr(VI) (µg)	Recovery of Cr(VI) (%)
Cr(III)	Cr(VI)		
10	10	9.9 ± 0.1	98 ± 1
10	50	49.0 ± 1.4	98 ± 3
50	10	9.8 ± 0.4	98 ± 4
2	10	9.8 ± 0.1	99 ± 2
10	2	2.0 ± 0.1	98 ± 4

TABLE VII
Determination Cr(VI) in Some Natural Water Samples
Sample volume: 100 mL; pH 2.0; eluent: 5 mL 2.0 M HCl; (n=3)

Samples	Added(µg) Cr(VI)	Found (µg)	Recovery (%)	RSD (%)
Tap Water	-	< LOD ^a	-	-
	1.0	0.97 ± 0.02	97 ± 2	2.1
	2.0	1.93 ± 0.06	97 ± 3	3.1
Çark Stream Water	-	< LOD	-	-
	1.0	1.01 ± 0.03	101 ± 3	2.9
	2.0	1.93 ± 0.03	97 ± 1	1.5
Sakarya River Water	-	< LOD	-	-
	1.0	1.00 ± 0.05	100 ± 5	5.0
	2.0	2.00 ± 0.05	100 ± 3	2.5

^a Below limit of detection.

and is also not affected by anions and cations widely present in environmental water samples. If the level of total Cr is higher than the detection limits by FAAS, the developed SPE method could be used for Cr speciation in environmental water samples.

Thus, a novel, rapid, and effective method was developed for the selective determination of Cr(VI) by FAAS after solid phase extraction on bis(3-aminopropyl)amine bonded silica gel.

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