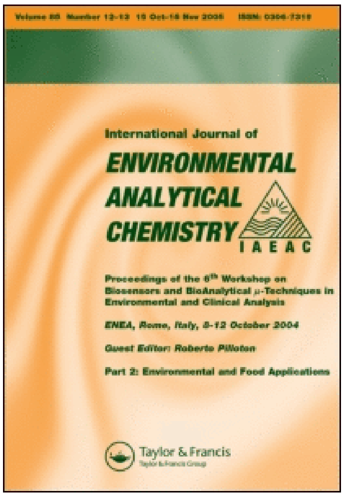

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Determination of chromium(III) and total chromium in natural waters using a surface ion-imprinted silica gel as selective adsorbent

Qun He[a]; Xijun Chang[a]; Hong Zheng[b]; Na Jiang[a]; Xiaoyan Wang[a]
[a] Department of Chemistry, Lanzhou University, Lanzhou, PR China [b] Qinghai Normal University, Xining, PR China

To cite this Article He, Qun , Chang, Xijun , Zheng, Hong , Jiang, Na and Wang, Xiaoyan(2008) 'Determination of chromium(III) and total chromium in natural waters using a surface ion-imprinted silica gel as selective adsorbent', International Journal of Environmental Analytical Chemistry, 88: 6, 373 — 384
To link to this Article: DOI: 10.1080/03067310701710870
URL: http://dx.doi.org/10.1080/03067310701710870

Intern. J. Environ. Anal. Chem.
Vol. 88, No. 6, 15 May 2008, 373–384

Taylor & Francis
Taylor & Francis Group

Determination of chromium(III) and total chromium in natural waters using a surface ion-imprinted silica gel as selective adsorbent

Qun He[a], Xijun Chang[a]*, Hong Zheng[b], Na Jiang[a] and Xiaoyan Wang[a]

[a]*Department of Chemistry, Lanzhou University, Lanzhou, PR China;* [b]*Qinghai Normal University, Xining, PR China*

(*Received 22 June 2007; final version received 5 September 2007*)

A sensitive and selective method has been developed to determine Cr(III) and total Cr in natural water samples by ICP-AES with a Cr(III)-imprinted aminopropyl-functionalised silica gel adsorbent. The Cr(III)-imprinted and non-imprinted adsorbent were prepared by an easy one-step reaction with a surface imprinting technique. Their maximum static adsorption capacities for Cr(III) were $11.12\,\mathrm{mg\,g^{-1}}$ and $3.81\,\mathrm{mg\,g^{-1}}$, respectively. The relative selectivity factors (α_r) for Cr(III)/Co(II), Cr(III)/Au(III), Cr(III)/Ni(II), Cr(III)/Cu(II), Cr(III)/Zn(II), and Cr(III)/Cr(VI), were 377, 21.4, 15.4, 27.7, 26.4, and 31.9, respectively. Under the optimal conditions, Cr(III) can be absorbed quantitatively, but Cr(VI) was not retained. Total chromium was obtained after reducing Cr(VI) to Cr(III) with hydroxyammonium chloride. The detection limit (3σ) for Cr(III) was $0.11\,\mathrm{ng\,mL^{-1}}$. The relative standard deviation was 1.2%. The proposed method has been validated by analysing two certified reference materials and successfully applied to the determination and speciation of chromium in natural water samples with satisfactory results.

Keywords: Cr(III); ICP-AES; speciation; surface ion-imprinted silica gel

1. Introduction

Metal speciation has become an important topic in biological and environmental science because their toxicological and biological properties depend on their chemical forms [1,2]. Chromium(III), for example, is one of the essential trace nutrient elements in human bodies, and plays an important role in the metabolism of glucose and certain lipids, whereas Cr(VI) is carcinogenic and toxic, and may cause death in humans if ingested in large doses [3]. Chromium is usually found in the environment in these two different oxidation states. It is therefore important to accurately define the individual quantity of both valence forms in environmental samples.

Many modern instrumental techniques such as inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma-mass spectrometry (ICP-MS), electro-thermal atomic absorption spectrometry (ETAAS), and flame atomic absorption spectrometry (FAAS) can only yield total chromium concentration, and as a result, preliminary species preconcentration and separation are normally

---

*Corresponding author. Fax: +86-931-8912582. Email: hequn03@lzu.cn

ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067310701710870
http://www.informaworld.com

carried out before detection. Nowadays, solid-phase extraction (SPE) is being widely utilised for preconcentration or separation of metal ions because of its flexibility, simplicity, high preconcentration factor, and safe and easy automation [4,5]. Numerous substances have been proposed and applied for speciation analysis of chromium as adsorbents, including modified silica [6], chelate resin [7], actived alumina [8], actived carbon [9], and nano-TiO_2 [10,11]. However, the selectivity associated with SPE using these solid adsorbents still needs to be improved for chromium.

Recently, ion-imprinted polymers (IIPs) have attracted widespread attention as highly selective adsorbents for SPE to concentrate and clean up samples prior to analysis [12,13]. For traditional ion imprinting, the template and functionality are totally embedded in the polymer matrices. Most of these materials have a poor site accessibility to the target ion. For that reason, the kinetics of the sorption/desorption process is unfavourable, and the mass transfer is relatively slow. Surface imprinting technique [14–16] has been made to deal with this problem. The essence of this technique is to coat the mesopore surface with complexes of the ligands and target metal ions instead of the free ligands. This technique has been shown to be successful in creating selective recognition sites on mesoporous sorbents and precise control of stereochemical arrangement of ligands on the adsorption sites. Surface-based imprinted polymer is simple and convenient to prepare; it not only has a high selectivity but also avoids problems with mass transfer and binding kinetics [17].

To the best of our knowledge, investigations on Cr(III)-imprinted polymers have been scarcely reported to date. The only work for Cr(III) imprinting was reported by Birlik *et al.* [18], who applied methacryloylhistidine as a functional monomer. In our paper, a novel chromium(III)-imprinted aminopropyl-functionalised silica gel adsorbent was prepared by a surface imprinting technique. The adsorption characteristics of this adsorbent for Cr(III) and Cr(VI) were studied in detail. Cr(III) and the total chromium content after reducing Cr(VI) to Cr(III) were determined. The Cr(VI) content was then calculated by subtracting the Cr(III) content from the total chromium content. This proposed method was applied to the determination and speciation of chromium in natural water samples with satisfactory results.

2. Experimental

2.1 *Instruments and apparatus*

An IRIS Advantage ER/S inductively coupled plasma emission spectrometer (TJA, USA) (RF power supply: 1.15 kW, Ar carrier-gas flow rate 0.6 L min^{-1}, Ar auxiliary-gas flow rate 1.0 L min^{-1}, Ar coolant-gas flow rate 14.0 L min^{-1}, viewing height 15 mm, wavelength of element: Cr 283.563 nm, Co 238.892 nm, Cu 327.396 nm, Ni 231.604 nm, Au 242.795 nm and Zn 213.856 nm) was used. A pHS-10C digital pH meter (Xiaoshan Instrument Factory, China) was used for the pH adjustments. The specific surface area and pore size of the adsorbent were measured using the Brunauer–Emmett–Teller (BET) model using an SSA-4200 system (Beijing, China). A UV-Cary100 spectrophotometer (Varian, Australia) was used for the colorimetric determination of Cr(VI) by diphenylcarbazide at 540 nm. Infrared spectra were recorded on a Nicolet NEXUS 670 FT-IR apparatus (Nicolet, USA). A YL-110 peristaltic pump (General Research Institute for Nonferrous Metals, Beijing, China) was used in the preconcentration process. A minimum-length polytetrafluoroethylene (PTFE) tube (0.5 mm i.d.) was used for flow-injection connections. A PTFE microcolumn (20 mm × 3 mm i.d.) was used in this study.

2.2 *Chemicals and reagents*

Unless otherwise stated, reagents of analytical and spectral purity were used for all experiments, and double-distilled water was used throughout. Silica gel (200–300 mesh, Qingdao Hailang Chemical Factory, Qingdao, China), tetraethylorthosilicate (TEOS) and 3-aminopropyltrimethoxysilane (Ocean University Chemical Company, Qingdao, China) were used. Stock solutions ($1.0\,\mathrm{mg\,mL^{-1}}$) of the Cr(III), Zn(II), Co(II), Cu(II), Ni(II), and Au(III) were purchased from National Research Center for Certified Reference Materials (Beijing, China). Standard stock solutions of Cr(VI) $100\,\mu\mathrm{g\,mL^{-1}}$ was prepared by dissolving spectral pure-grade $K_2Cr_2O_7$ (Shanghai First Reagent Factory, Shanghai, China). The standard working solution was diluted daily prior to use.

2.3 *Sample preparation*

The water certified reference materials (GBW 08608) and the river sediment certified reference materials (GBW 08301) were purchased from National Research Center for Certified Reference Materials (Beijing, China). The sediment reference material was treated according to the previous procedure [19].

Tannery effluent was collected from Lanzhou Leather Factory (Lanzhou, China). River water was collected from Yellow River (Lanzhou, China). Lake water was collected from South Lake (Lanzhou, China). The tap-water sample was taken from our research laboratory. The water sample was filtered through a 0.45-µm membrane filter (Tianjin Jinteng Instrument Factory, Tianjin, China) and stored at 4°C. The water sample must not be acidified before storage, the usual acidification might lead to changes in the relative proportions of Cr(III) and Cr(VI) [11].

The sample for Cr(III) determination was directly adjusted to pH 6. The sample for total chromium determination was first through a step of reduction from Cr(VI) to Cr(III) with hydroxyammonium chloride [20], and then was adjusted to pH 6.

2.4 *Preparation of the Cr(III)-imprinted and non-imprinted aminopropyl-functionalised silica gel adsorbent*

Activation of silica gel surface was first accomplished by refluxing in concentrated hydrochloric acid for 4 h, then filtered off and washed repeatedly with doubly distilled water until neutral and dried in an oven at 80°C for 12 h.

To prepare the Cr(III)-imprinted aminopropyl-functionalised silica gel adsorbent, 2.154 g of $CrCl_3 \cdot 6H_2O$ was dissolved in 80 mL of methanol under stirring and heating, and then 4 mL of 3-aminopropyltrimethoxysilane was added into the mixture. The solution was stirred and refluxed for 1 h, the 2 mL of TEOS was added and stirred for 5 min, and then 6.0 g of activated silica gel was added. After 24 h of stirring and refluxing the mixture, the product was obtained by filtration, washed with ethanol to remove the remnant reactants, and treated with adequate $1\,\mathrm{mol\,L^{-1}}$ HCl to remove Cr(III) from the polymer. The final product was cleaned with double-distilled water and then dried under a vacuum at 80°C for 12 h. The non-imprinted adsorbent was also prepared using an identical procedure without adding $CrCl_3 \cdot 6H_2O$.

2.5 *Recommended procedure*

2.5.1 *Batch procedure*

Adsorbent (50 mg) was added to 10 mL of Cr(III) aqueous solution after adjusting to the desired pH value. Then, the mixture was shaken vigorously for 30 min to facilitate adsorption of the metal ions onto the Cr(III)-imprinted adsorbent. After the solution was centrifuged, the concentrations of the metal ions in the solution were directly determined by ICP-AES.

2.5.2 *Column procedure*

The PTFE microcolumn was packed with 50 mg of the Cr(III)-imprinted adsorbent. A small amount of glass wool was placed at both ends to prevent loss of the polymer particles during sample loading. Before use, 1.0 mol L^{-1} HCl solution and double-distilled water were successively passed through the microcolumn in order to clean, neutralise, and condition it. Then, each solution was passed through the column at a flow rate of 1.2 mL min^{-1} (controlled by a peristaltic pump) after adjusting to pH 6. The metal ions adsorbed on the column were eluted with 3 mL 1.0 mol L^{-1} HCl. The analytes in the eluate were determined by ICP-AES.

2.5.3 *Constants*

The adsorption capacity, the distribution ratio, the selectivity coefficient, and the relative selectivity coefficient were calculated from the following equations:

$$Q = \frac{(C_0 - C_e)V}{W}; \quad D = \frac{1000Q}{C_e}; \quad \alpha = \frac{D_{Cr}}{D_M}; \quad \alpha_r = \frac{\alpha_i}{\alpha_n}$$

where Q represents the adsorption capacity (mg g^{-1}), C_0 and C_e represent the initial and final concentration of Cr(III) (µg mL^{-1}), W is the mass of Cr(III)-imprinted adsorbent (mg), and V is the volume of metal ion solution (mL); D is the distribution ratio (mL g^{-1}); α is the selectivity coefficient, D_{Cr} and D_M represent the distribution ratios of Cr(III) and Au(III), Cu(II), Ni(II), Co(II), Zn(II), Cr(VI); α_r is the relative selectivity coefficient, α_i and α_n represent the selectivity factor of imprinted sorbent and non-imprinted sorbent.

3. Results and discussion

3.1 *Characteristics of the Cr(III)-imprinted and non-imprinted adsorbents*

The specific surface areas were found to be 264.6 $m^2 g^{-1}$ for Cr(III)-imprinted and 249.8 $m^2 g^{-1}$ for non-imprinted adsorbents. The pore diameter of Cr(III)-imprinted and non-imprinted adsorbent was 5.48 nm and 5.19 nm, respectively. To confirm the presence of aminopropyl- in the matrix, FT-IR spectra were obtained from activated silica gel, non-imprinted and Cr(III)-imprinted adsorbents. Figure 1(a) shows the bands of activated silica gel around 3436 and 1631 cm^{-1} assigned to O–H vibrations. The observed features around 1100 cm^{-1} and 951 cm^{-1} indicated Si–O–Si and Si–O–H

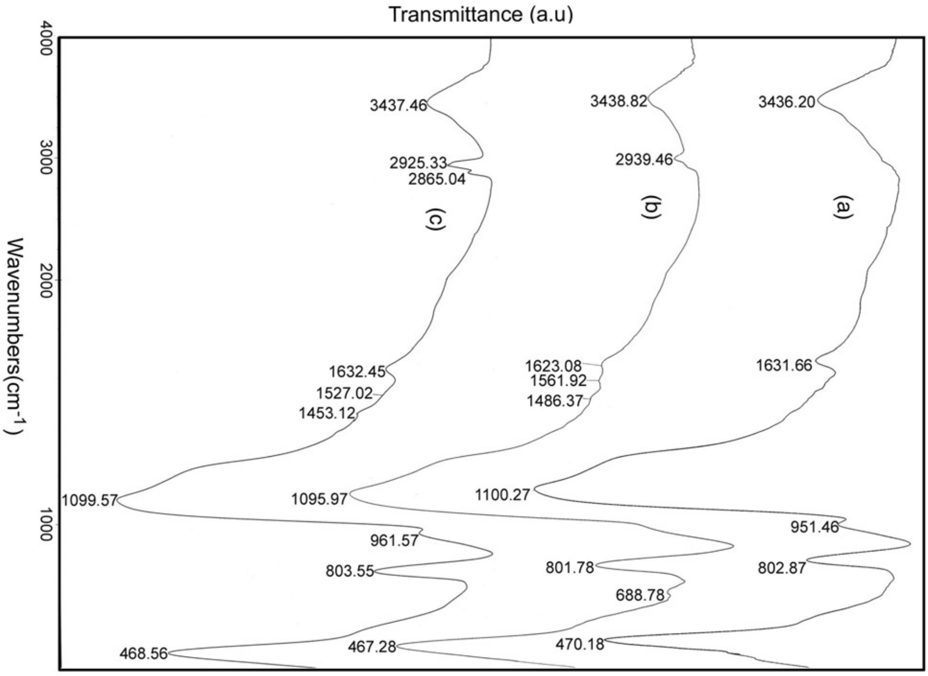

Figure 1. FT-IR spectra of the activated silica gel(a), non-imprinted(b) and Cr(III)-imprinted(c) adsorbent.

stretching vibrations, respectively. The bands around 802 and 470 cm^{-1} resulted from Si–O vibrations. These results show that the main absorption peaks of activated silica gel are in agreement with the standard spectrum of SiO_2 [21]. The characteristic features of the imprinted adsorbent (Figure 1(c)) compared with activated silica gel are the N–H bond around 1527 cm^{-1} and the C–H bond around 2925 cm^{-1}, 2865 cm^{-1}, and 1453 cm^{-1} [16,22]. The imprinted and non-imprinted adsorbents showed a very similar location and appearance of the major bands. These show that aminopropyl- was grafted onto the surface of the activated silica gel after modification.

3.2 *Effect of pH on adsorption of Cr(III) and Cr(VI)*

According to the recommended procedure (batch procedure), the effect of pH on adsorption of Cr(III) and Cr(VI) was investigated in the pH range of 1–8 and then analysed by ICP-AES.

From Figure 2(a), we can see that the Cr(III)-imprinted sorbent exhibited a low affinity for Cr(III) in acidic conditions, and no Cr(III) was retained on ion-imprinted adsorbent below pH 3. This is mainly because of the protonation of the amine moiety, which diminished the ability of the amino group to be involved in chelate formation with the Cr(III) in aqueous solution [23]. The adsorption percentage of Cr(III) increased as the pH of the aqueous solution increased from 3 to 6 and then remained constant with further increases in pH 6–8.

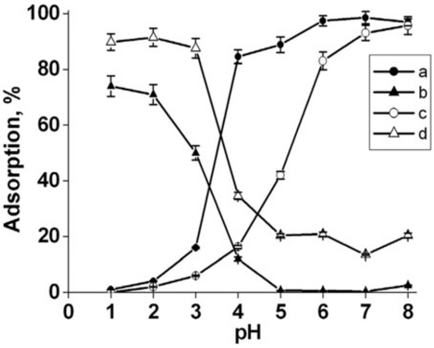

Figure 2. Effect of pH on the adsorption of Cr(III) (a) and Cr(VI) (b) on Cr(III)-imprinted adsorbent, Cr(III) (c) and Cr(VI) (d) on non-imprinted adsorbent. Cr(III) and Cr(VI): 1 μg mL^{-1}.

Figure 2(b) and (d) shows that a part of Cr(VI) was adsorbed on imprinted and non-imprinted adsorbent at lower pH values, mainly because the Cr(VI) ion in aqueous solution exists as a negative ion, and this charged species may be retained on imprinted adsorbent by the ion-exchange process [24]. A quick decrease in retention of Cr(VI) was observed with increasing pH value, because of the deprotonation of the adsorbent. The adsorption percentage of Cr(VI) on imprinted adsorbent was lower than that on non-imprinted adsorbent under the same pH values, which was due to the function of imprinting process.

The quantitative adsorption ($>95\%$) of Cr(III) on imprinted adsorbent was found within the pH range of 6–8, while the sorption quantity for Cr(VI) was negligible. This could allow Cr(III) to be separated from Cr(VI) with Cr(III)-imprinted adsorbent. However, parts of Cr(III) and Cr(VI) were adsorbed on non-imprinted adsorbent (Figure 2(c) and (d)) at these pH values. In order to avoid hydrolysing at higher pH values, pH 6 was selected as the enrichment acidity for subsequent work.

3.3 *Uptake kinetics of Cr(III) by the imprinted adsorbent*

In this work, different shaking times (ranging from 2 to 40 min) were studied at room temperature. The results revealed that the 95% uptake of Cr(III) was achieved within 10 min. It is clear that the solid-phase extraction process of the present adsorbent is faster than most of the traditional ion-imprinted adsorbents [25,26]. This indicates that the surface imprinting greatly facilitates diffusion of Cr(III) to the binding site.

3.4 *Adsorption capacity of Cr(III)-imprinted and non-imprinted adsorbents for Cr(III)*

The adsorption capacity was tested following the recommended procedure (batch procedure) described above. As can be seen in Figure 3, the amount of Cr(III) adsorbed per unit mass of imprinted adsorbent increased with the initial concentration of Cr(III) until the plateau values (adsorption capacity values) were obtained. The static adsorption capacity of the imprinted aminopropyl-functionalised silica gel sorbent for Cr(III) was calculated to be 11.12 mg g^{-1}, about three times higher than that of the non-imprinted sorbent (3.81 mg g^{-1}) for three replicate measurements. This difference

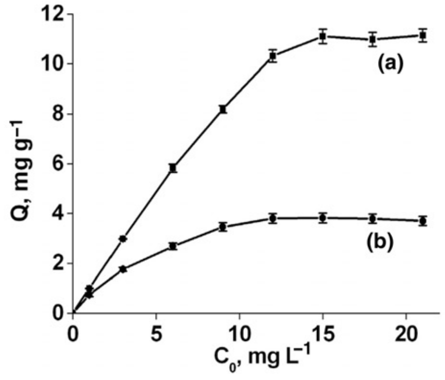

Figure 3. The effect of Cr(III) initial concentration(C_0) on the adsorption quantity(Q) of Cr(III)-imprinted(a) and non-imprinted(b) adsorbent. pH: 6; Sample volume: 50 mL.

indicates that imprinting plays an important role in the adsorption behaviour. During the preparation of the imprinted sorbent, the presence of Cr(III) made the ligands arrangement ordered. After the removal of Cr(III), the imprinted cavity and specific binding sites of functional groups in a predetermined orientation were formed, whereas there was no such specificity in non-imprinted adsorbent. Comparing this with traditional ion imprinting [18], a disadvantage of surface imprinting was that the maximum sorption capacity was slightly low. However, the capacity in the present work was enough for trace analysis [10,11,27].

3.5 *Elution condition and stability tests*

Since the adsorption of Cr(III) at pH <3 is negligible, we can expect elution to be favoured in acidic solution. Thus, various concentrations and volumes of HCl were studied for the desorption of retained Cr(III) following the general procedure (column procedure). The results reveal that quantitative recoveries ($>95\%$) of Cr(III) can be obtained using 3 mL of 1 mol L^{-1} HCl as eluent. Therefore, 3 mL of 1 mol L^{-1} HCl was used as eluent in subsequent experiments.

The repeated use of a commercial adsorbent is likely to be a key factor. To test the stability, it was subjected to several adsorption and elution batch operations under the above experimental conditions. The results from both tests agreed within $<5\%$ error up to 20 cycles of repeated experiments. The adsorbent shows better reusability and stability. Therefore, the surface-imprinted adsorbent is suitable for repeated use without decreasing their adsorption capacities significantly.

3.6 *Effect of flow rate*

Since the time of analysis and the sorption of elements on adsorbent depend upon the flow rate of the sample solution, the influence of the Cr(III) solution's flow rate was studied under the optimum conditions (pH, eluent, etc.) by passing 10 mL of sample solution through the column with a peristaltic pump. The flow rates were adjusted in the range of

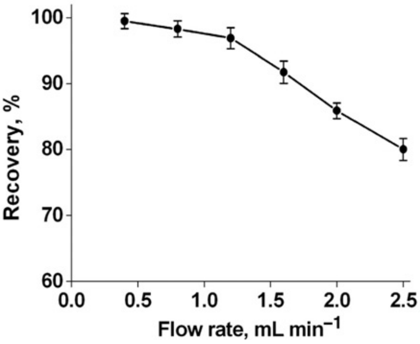

Figure 4. Effect of flow rate on analyte recovery. Sample volume 10 mL; pH 6; Cr(III): 1 μg mL^{-1}.

0.4–2.5 mL min^{-1}. As shown in Figure 4, quantitative recoveries of the metal ions will decrease with further increases in the flow rate over 1.2 mL min^{-1}. Thus, a flow rate of 1.2 mL min^{-1} was selected in this work.

3.7 *Maximum sample volume and enrichment factor*

The enrichment factor was studied by increasing the volume of Cr(III) solution and keeping the total amount of loaded Cr(III) constant to 1.0 μg. For this purpose, 10, 50, 100, 150, 200, 250, and 300 mL of sample solutions containing 1.0 μg of Cr(III) were passed through the column at the optimum flow rate. The results showed that the maximum sample volume can be up to 150 mL with a recovery $>95\%$. Therefore, 150 mL of sample solution was adopted for the preconcentration of analytes from sample solutions, and an enrichment factor of 50 was obtained when 3 mL of 1 mol L^{-1} HCl was used as eluent in these experiments.

3.8 *Interfering effect of other ions—selectivity*

Different foreign ions were added to equal quantities of the diluted mixed standard solutions and adsorbed and desorbed according to the general procedure. The results showed that up to 2000 μg mL^{-1} of K(I), Na(I), NO_3^-, and Cl^-, 500 μg mL^{-1} of SO_4^{2-}, 400 μg mL^{-1} of Ca(II), Mg(II), Ba(II), and $H_2PO_4^-$, 100 μg mL^{-1} of Mn(II) and Au(III), 50 μg mL^{-1} of Ni(II), Co(II), Cu(II), Cd(II), and Zn(II) showed no significant interference with the determination of 1 μg mL^{-1} of Cr(III).

In order to further evaluate the selectivity of the imprinted adsorbent, competitive enrichment of Cr(III)/Co(II), Cr(III)/Au(III), Cr(III)/Ni(II), Cr(III)/Cu(II), Cr(III)/Zn(II), and Cr(III)/Cr(VI) from their binary mixture was also investigated in the batch procedure because these ions hold the same charge or similar ionic radius. The results are listed in the Table 1. The relative selectivity factors (α_r) of Cr(III)/Co(II), Cr(III)/Au(III), Cr(III)/Ni(II), Cr(III)/Cu(II), Cr(III)/Zn(II), and Cr(III)/Cr(VI), were 377, 21.4, 15.4, 27.7, 26.4, and 31.9, respectively. It can be seen that the distribution factor values of Cr(III) are much greater than those of other metals. There are three possible reasons for this. First is the amino-functionalised group inherent affinity selectivity. The cavity-size selectivity is also an important factor. In this work, the size of Cr(III) exactly

Table 1. Selectivity of the Cr(III)-imprinted silica gel adsorbents for Cr(III).

	D_i		D_n				
Metal ions[a]	Cr	M	Cr	M	α_i	α_n	α_r
Cr(III)	15 160		1877				
Co(II)	9252	77.8	1029	3267	118.9	0.315	377
Au(III)	8789	180	907	397	48.8	2.285	21.4
Ni(II)	10 973	191	1258	336	57.5	3.74	15.4
Cu(II)	13 089	1877	1142	4533	6.97	0.252	27.7
Zn(II)	8186	1204	1738	3624	6.80	0.48	26.4
Cr(VI)	10 449	17.6	1405	75.5	593.7	18.6	31.9

[a] Initial concentration: 10 μg mL^{-1}.

Table 2. Analysis of total chromium in standard reference material ($n = 5$)[a].

		Certified value		Measured by proposed method	
Samples	Element	(μg L^{-1})	(μg g^{-1})	(μg L^{-1})	(μg g^{-1})
GBW 08608	Cr	30 ± 7		27 ± 3	
GBW 08301	Cr		90 ± 4		88 ± 1.2

[a] The value following "±" is the standard deviation.

fits the cavity of the Cr(III)-imprinted sorbent. The third factor is the coordination-geometry selectivity because the Cr(III)-imprinted silica gel sorbent can provide the ligand groups arranged in a suitable way required for coordination of Cr(III) ion [14]. Although some ions have a similar size to the Cr(III) ion, and some ions have a high affinity with the amino ligand, the Cr(III)-imprinted sorbent still exhibits a high selectivity for extraction of Cr(III) in the presence of other metal ions.

3.9 *Analytical precision and detection limits*

Under optimal experimental conditions, 11 portions of 10 ng mL^{-1} Cr(III) were enriched and analysed simultaneously following the recommended procedure. The results showed that the relative standard deviation (RSD) was less than 1.2%. According to the IUPAC definition, the detection limit of the method was calculated based on three times the standard deviation of 11 runs of the blank solution. The detection limit of the proposed method for Cr(III) was 0.11 ng mL^{-1}.

3.10 *Application of the method*

In order to ascertain the validity of the proposed procedure, the method has been applied to the determination of total chromium in two certified reference materials (GBW 08608, water certified reference materials and GBW 08301, river sediment). The analytical results for the standard material (listed in Table 2) were in good agreement with the certified values.

Table 3. Analytical results of natural water samples ($n=5$)[a].

	Added ($\mu g\,L^{-1}$)		Found ($\mu g\,L^{-1}$)			Recovery (%)	
Sample	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Total Cr	Cr(III)	Cr(VI)
Tap water	0	0	2.10 ± 0.03	1.15 ± 0.08	3.25 ± 0.09	–	–
	2.0	2.0	4.14 ± 0.05	3.08 ± 0.09	7.22 ± 0.07	102	96.5
	4.0	4.0	6.07 ± 0.04	5.22 ± 0.11	11.29 ± 0.10	99.3	101.8
River water	0	0	3.96 ± 0.05	0.52 ± 0.06	4.48 ± 0.08	–	–
	2.0	2.0	6.01 ± 0.06	2.47 ± 0.09	8.48 ± 0.07	102.5	97.5
	4.0	4.0	7.87 ± 0.06	4.41 ± 0.11	12.28 ± 0.05	97.8	97.3
Lake water	0	0	0.69 ± 0.07	0.36 ± 0.07	1.05 ± 0.08	–	
	2.0	2.0	2.65 ± 0.05	2.28 ± 0.09	4.93 ± 0.09	98	96
	4.0	4.0	4.73 ± 0.08	4.32 ± 0.10	9.05 ± 0.11	101	99
Tannery effluent	–	–	14.95 ± 0.15	38.61 ± 0.19	53.56 ± 0.21	–	–

[a] The value following "±" is the standard deviation.

Table 4. Comparative date from some recent studies for chromium speciation by determination of Cr(III) and total Cr.

Methods	pH	Cr(III) capacity	Detection system	LOD ($ng\,mL^{-1}$)	PF	RSD (%)	Reference
5-Palmitoyl oxine-functionalized XAD-2 resin	4.5	1.22	Spectrophotometry	–	60	2.5–3.0	27
Saccharomyces cerevisiae immobilized on sepiolite	2–6	–	FAAS	94	75	5	29
Poly(aminophosphonic acid) chelating resin	5	–	FAAS	0.2	35	–	30
Activated carbon	5.0	–	ETAAS	0.003	35	4.0	9
Bacillus sphaericus loaded Diaion SP-850	5	6.95	AAS	0.50	50	5	31
Chromosorb 108	8.0	4.50	FAAS	0.75	71	9	32
Nanometre TiO_2	6.0	7.6	ICP-AES	0.32	50	2.4	11
Immobilized nanometre TiO_2	7.0	7.04	ICP-AES	0.22	50	3.5	10
Cr(III)-imprinted silica gel	6	11.12	ICP-AES	0.11	50	1.2	Present work

LOD: limit of detection; PF: preconcentration factor; AAS: atomic absorption spectrometry.

The results obtained have been evaluated using the *t*-test [28], proving that there is no significant difference at the 95% confidence level. The proposed method was applied to the speciation of Cr(III) and Cr(VI) in water samples. The standard addition method was used, and the results listed in Table 3 showed that the recoveries were reasonable for trace analysis in the range of 96.5–102.5%. The content of Cr(VI) in tap water is higher than that in river and lake water, which is due to the oxidation effect of the decolorant in the tap water.

4. Conclusions

In this paper, a novel method for the speciation of chromium was developed using Cr(III)-imprinted aminopropyl-functionalised silica gel as a solid-phase extractant.

The obtained surface imprinting exhibited rapid kinetics process for Cr(III). The maximum adsorption capacity of Cr(III)-imprinting for Cr(III) was 11.12 mg g^{-1}, which was larger than that of the non-imprinted adsorbent (3.81 mg g^{-1}). Competitive sorption studies showed that the selectivity of imprinted adsorbent for Cr(III) is higher than that of the non-imprinted adsorbent, even in the presence of Co(II), Au(III), Ni(II), Cu(II), Zn(II), and Cr(VI). The column packed with present IIPs was good enough for Cr(III) separation from Cr(VI) and was proposed for the determination and speciation of trace chromium in water samples with satisfactory results. A comparison of the presented method and some recent speciation procedures by determination of Cr(III) and total chromium in the literature are given in Table 4. The detection limits and preconcentration factors are superior to those of some preconcentration/separation techniques for analyses [10,11,27,29–32].

References

[1] R. Cornelis, H. Crews, O.F.X. Donard, L. Ebdon, and Ph. Quevauviller, Fresenius J. Anal. Chem. **370**, 120 (2001).
[2] P. Apostoli, Fresenius J. Anal. Chem. **363**, 499 (1999).
[3] A.M. Zayed and N. Terry, Plant Soil **249**, 139 (2003).
[4] Y. Guo, B.J. Din, Y.W. Liu, X.J. Chang, S.M. Meng, and J. Liu, Talanta **62**, 209 (2004).
[5] V. Camel, Spectrochim. Acta B **58**, 1177 (2003).
[6] H.F. Maltez and E. Carasek, Talanta **65**, 537 (2005).
[7] B.C. Mondal, D. Das, and A.K. Das, Talanta **56**, 145 (2002).
[8] A.C. Sahayam, Anal. Bioanal. Chem. **372**, 840 (2002).
[9] R.A. Gil, S. Cerutti, J.A. Gásquez, R.A. Olsina, and L.D. Martinez, Talanta **68**, 1065 (2006).
[10] P. Liang, Q. Ding, and Y. Liu, J. Sep. Sci. **29**, 242 (2006).
[11] P. Liang, T. Shi, H. Lu, Z. Jiang, and B. Hu, Spectrochim. Acta B **58**, 1709 (2003).
[12] X. Chang, N. Jiang, H. Zheng, Q. He, Z. Hu, Y. Zhai, and Y. Cui, Talanta **71**, 38 (2007).
[13] J. Pan, S. Wang, and R. Zhang, Int. J. Environ. Anal. Chem. **86**, 855 (2006).
[14] G.Z. Fang, J. Tan, and X.P. Yan, Anal. Chem. **77**, 1734 (2005).
[15] Q. He, X. Chang, H. Zheng, N. Jiang, Z. Hu, and Y. Zhai, Chem. Anal. (Warsaw) **51**, 715 (2006).
[16] D.M. Han, G.Z. Fang, and X.P. Yan, J. Chromatogr. A **1100**, 131 (2005).
[17] H.H. Yang, S.Q. Zhang, F. Tan, Z.X. Zhuang, and X.R. Wang, J. Am. Chem. Soc. **127**, 1378 (2005).
[18] E. Birlik, A. Ersöz, E. Açikkalp, A. Denizli, and R. Say, J. Hazard. Mater. **140**, 110 (2007).
[19] Y. Guo, B.J. Din, Y.W. Liu, X.J. Chang, S.M. Meng, and S.M. Tian, Anal. Chim. Acta **504**, 319 (2004).
[20] T. Sumida, T. Ikenoue, K. Hamada, A. Sabarudin, M. Oshima, and S. Motomizu, Talanta **68**, 388 (2005).
[21] R.A. Nyquist and R.O. Kagel, *Infrared Spectra of Inorganic Compounds* (Academic Press, New York, 1971), p. 94.
[22] N. Jiang, X. Chang, H. Zheng, Q. He, and Z. Hu, Anal. Chim. Acta **577**, 225 (2006).
[23] Y.K. Lu and X.P. Yan, Anal. Chem. **76**, 453 (2004).
[24] J.L. Manzoori, M.H. Sorouraddin, and F. Shemirani, Talanta **42**, 1151 (1995).
[25] Y.W. Liu, X.J. Chang, D. Yang, Y. Guo, and S.M. Meng, Anal. Chim. Acta **538**, 85 (2005).
[26] Y.W. Liu, X.J. Chang, S. Wang, Y. Guo, B.J. Din, and S.M. Meng, Anal. Chim. Acta **519**, 173 (2004).
[27] H. Filik, M. Doğutan, and R. Apak, Anal. Bioanal. Chem. **376**, 928 (2003).

[28] J.C. Miller and J.N. Miller, *Statistics for Analytical Chemistry* (Ellis Horwood, New York, 1988), p. 53.

[29] H. Bağ, A.R. Türker, M. Lale, and A. Tunçeli, Talanta **51**, 895 (2000).

[30] R.M. Cespón-Romero, M.C. Yebra-Biurrun, and M.P. Bermejo-Barrera, Anal. Chim. Acta **327**, 37 (1996).

[31] M. Tuzen, O.D. Uluozlu, and M. Soylak, J. Hazard. Mater. **144**, 549 (2007).

[32] M. Tuzen and M. Soylak, J. Hazard. Mater. **129**, 266 (2006).