Sequential eluent injection technique as a new approach for the on-line enrichment and speciation of Cr(III) and Cr(VI) species on a single column with FAAS detection

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ABSTRACT

This paper introduces a sequential eluent injection (SEI) technique combined with an on-line preconcentration/separation system for a fast and sensitive FAAS determination of trace amounts of Cr(III) and Cr(VI) species. The method is based on the simultaneous retention of Cr(III) and Cr(VI) on a single mini-column packed with a chloromethylated polystyrene functionalized with N,N-bis(naphthylideneimino)diethylenetriamine (PS-NAPdien) at pH 6.7. The retained chromium species was eluted by sequential injection of HCl for desorption of Cr(III), and NH_3 and NH_4NO_3 buffer solutions for desorption of Cr(VI). All the chemical and flow injection variables were optimized for the quantitative preconcentration and speciation of Cr(III) and Cr(VI). Under the optimum conditions, the calibration graph obtained is linear over the concentration range of 2.0–60.0 $\mu g\,L^{-1}$ for Cr(III), and 8.0–180.0 $\mu g\,L^{-1}$ for Cr(VI). The preconcentration factors for Cr(III) and Cr(VI) were 70 and 30, respectively. The 3σ detection limits were 0.6 $\mu g\,L^{-1}$ and 2.5 $\mu g\,L^{-1}$ for Cr(III) and Cr(VI), respectively. The relative standard deviations were 2.55% and 0.8%, respectively, for 6 replicate determinations of Cr(III) and Cr(VI) at the 40.0 $\mu g\,L^{-1}$ level. The proposed method was applied for determination of Cr(III) and Cr(VI) in different water samples with satisfactory results.

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1. Introduction

Toxic heavy metal ions are major sources of pollution in environmental and water resources. Speciation study of heavy metal ions is very important since toxicity of some of them depends on their chemical properties, oxidation states, and bioavailabilities [1]. Chromium is one of the most abundant elements having the potential to contaminate groundwater, and so can be a major source of drinking water contamination [2]. In aqueous solution, chromium can usually be found in two different oxidation states including hydrated Cr(III) and Cr(VI) species with different physiological effects [2]. Cr(III) is a trace element essential for maintaining glucose, cholesterol, and fatty acid metabolisms in biological cells [3–5]. On the other hand, Cr(VI) with a high oxidation potential and relatively small size can easily permeate through biological cell membranes, and is known as a carcinogenic and mutagenic substance for humans [3]. Due to the high solubility of Cr(VI) in water, drinking water could be one of the routes to the incorporation of chromium into the human body. The United States Environmental Protection Agency (EPA) has set a limit of 0.1 mg L^{-1}

of total chromium for drinking water. The guideline value recommended by World Health Organization (WHO) is 50 $\mu g\,L^{-1}$ [3]. Only few analytical techniques such as graphite furnace atomic absorption spectrometry (GFAAS) and inductively coupled plasma mass spectrometry (ICP-MS) can show sufficient sensitivity for the direct determination of such $\mu g\,L^{-1}$ levels of total chromium in water samples [6]. According to these facts, development of simple, accurate, and sensitive analytical methodologies for separation and determination of chromium species in water samples takes an important role in analytical chemistry.

Flame atomic absorption spectrometry (FAAS) is the most well-known method for routine determination of metal species in a variety of samples. This technique, however, has some limitations such as its low sensitivity for determination of trace metals at $\mu g\,L^{-1}$ level, and only the total amount of metal species can be determined. Due to the low concentration levels of chromium species in complex water matrices, combinations of FAAS with high selectivity for speciation and low detection limit for determination are required. In this regard, many preconcentration procedures such as coprecipitation [7,8], solvent extraction [9–11], and ion exchange [12,13] have been developed for the determination of chromium species in different samples.

Solid phase extraction (SPE) has been used as a powerful preconcentration/separation procedure for preconcentration of trace

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metals and elimination of matrix interference. This technique has advantages such as high recovery, short analysis time, high enrichment factor, and low consumption of organic solvents. SPE can be combined with FAAS in the off-line (bath) and on-line (flow injection) modes. Flow injection (FI) on-line separation and preconcentration coupled with the FAAS technique, with mini-columns containing appropriate SPE sorbents, has been a much used method in the analytical determination of trace metals due to the low cost of equipment and its high analytical velocity [14,15]. Up to now, several on-line SPE methods have been reported for the simultaneous separation and preconcentration of Cr(III) and Cr(VI) and determination by FAAS [16–31]. These methods can be divided into several categories based on their sorbents or initial separation of the species. Some of these methods are based on the separation and determination of Cr(III) and the total chromium [16–21]. Other procedures enable separation and determination of Cr(VI), and Cr(III) concentration is calculated as the difference between the concentrations of total chromium and Cr(VI) [22–26]. Also some of these methods have sufficient sensitivity and selectivity, although all of them suffer from several drawbacks in the routine speciation of chromium species. General disadvantages of such procedures are: (i) concentrations of Cr(VI) and Cr(III) in waters are usually different about one order of magnitude, and their determination as a difference between two much higher values may generate large errors; (ii) chromium species must be oxidized or reduced to produce a retainable oxidation state, and this requires additional sample pretreatment using proper reagents; and (iii) this procedure is time consuming due to sequential preconcentration steps. A few methods have been reported for determination of the real concentration of each ion separately. These methods are based on the sequential retention of chromium species at different pH values [27–29] or simultaneous using of two different columns [30,31]. These methods are free from the drawbacks (i) and (ii), but are time consuming due to sequential preconcentration steps. Therefore, it is very important as a starting step to simultaneously preconcentrate these two species from their matrices, and determine the real concentration of each ion.

To overcome the above disadvantages, this paper reports the ability of a single mini-column packed with polystyrene functionalized with N,N-bis(naphthylideneimino) diethylenetriamine (NAPdien) (Fig. 1) for the simultaneous retention of Cr(III) and Cr(VI) from their matrices for precise and accurate speciation, and FAAS determination of the two ions individually using a sequential eluent injection strategy. To the best of our knowledge, this is the first report on the on-line simultaneous preconcentration, speciation, and FAAS determination of chromium species on a single column based on sequential eluent injection.

2. Experimental

2.1. Apparatus

The flow system (Fig. 2) comprising a variable speed 12 channels peristaltic pump (Hidolph, Model 5201) equipped with Tygon tubes, a home-made polyethylene column (2 mm i.d., 10.0 cm long), and two six-way rotary injection valve (Rheodyne, Model 5011) were used for chromium preconcentration and speciation. Other parts of the system were connected using PTFE tubing (1.3 mm i.d.), provided from Supelco. A Shimadzu Model AA-670 flame atomic absorption spectrometer with an air–acetylene flame was used for the chromium species determination. A chromium hollow cathode lamp was used under the manufacturer recommended conditions. The wavelength, slit width, and burner height had conventional values. The aspiration rate of the nebulizer was about 3.3 mL min^{-1}.
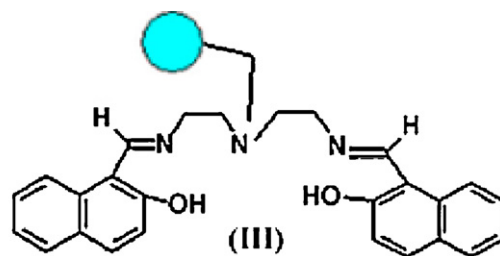

Fig. 1. Proposed structure of synthesized PS-NAPdien.

The IR spectra were recorded on a Shimadzu IR-470 spectrometer. The pH measurements and adjustments were carried out using a Metrohm 691 pH-meter equipped with a combined glass electrode.

2.2. Chemicals and solutions

All the chemicals were obtained from Merck or Riedel-de Haën, and were used without purification. The laboratory glassware was kept overnight in a 10% (v/v) nitric acid solution, and washed before use with deionized water. Doubly distilled water was used to wash the glassware, and to prepare all solutions.

A 1000 mg L^{-1} Cr(III) stock solution was prepared by dissolving CrCl$_3$·6H$_2$O (0.5283 g) in water in a 100-mL volumetric flask. A 1000 mg L^{-1} Cr(VI) stock solution was prepared by dissolving K$_2$Cr$_2$O$_7$·2H$_2$O (0.3175 g) in water in a 100-mL volumetric flask. Dilute working solutions were prepared daily by serial dilution with doubly distilled water.

Phosphate buffer solution was prepared by mixing appropriate volumes of 0.15 M Na$_2$HPO$_4$ and 0.15 M KH$_2$PO$_4$, and adjusting the pH to 6.7 using a pH-meter.

A 1.5 M HCl solution was used as eluent for Cr(III) ions, and a buffer solution of 2.5 M ammonium nitrate and 1.0 M ammonia solutions was used as eluent for Cr(VI) ions.

Chloromethylated polystyrene (cross-linked with 2% divinylbenzene, 4–5% Cl content, 1.14–1.40 mmol/g Cl) was used for preparation of the sorbent.

2.3. Preparation of the ligand NAPdien

The ligand NAPdien was prepared according to the following literature procedure [32,33]: 2-hydroxy-1-naphthaldehyde (12.2 g, 0.10 mol) was dissolved in 75 mL methanol, and to this was added a solution of diethylenetriamine (5.15 g, 0.050 mol) in 25 mL methanol. The reaction mixture was refluxed on a water bath for 1 h. After reducing the volume of the solvent to ca. 50 mL, the content was transferred into a beaker, and excess solvent was evaporated under a current of air until the viscous yellow-red oil was obtained. This was further dried in vacuum. Purity of the ligand was checked by IR and electronic absorption spectra. IR (KBr): 3450, 2950, 2885, 1635, 1583, 1460, 1280, 1215, 1145, 1045, 845, and 750 cm^{-1}. UV–vis, λ_{max} (nm): 400, 310, 285, 247, 220.

2.4. Preparation of PS-NAPdien

The immobilization of NAPdien on chloromethylated polystyrene was carried out according to our previously reported procedure [34,35]. Successful functionalization of the polymer was confirmed by IR spectra. IR (KBr): 3425, 3025, 2915, 1635, 1586, 1477, 1452, 1426, 1349, 1280, 1210, 1150, 1070, 1050, 985, 905, 865, 845, 750, 697, 563, and 490 cm^{-1}.
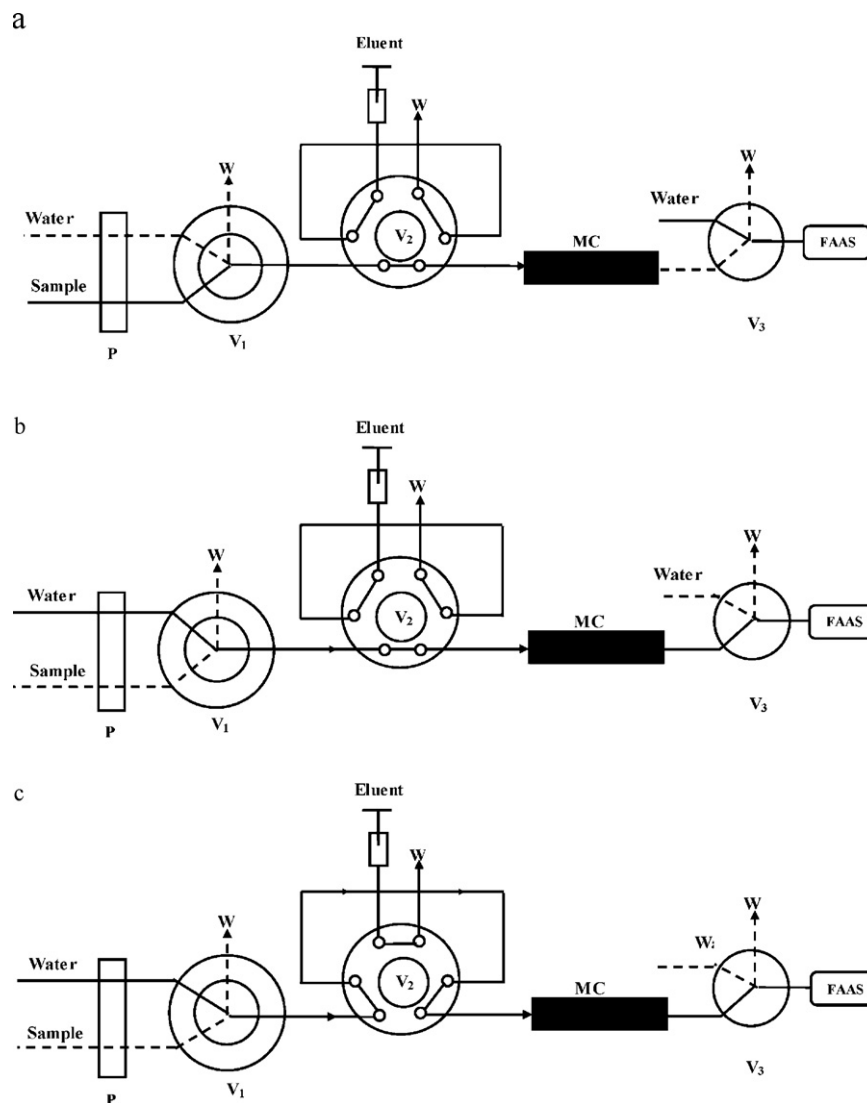
Fig. 2. Schematic diagram for FI-manifold: (a) preconcentration, (b) washing and (c) elution steps. P: peristaltic pump, V_1, V_2, V_3 selection valves and W: waste.

2.5. Preparation of mini-column

A mini-column was prepared for solid phase preconcentration of chromium by packing 140 mg of the synthesized PS-NAPdien sorbent in a home-made polyethylene column (10.0-cm length and 2.0 mm internal diameter). The two ends of the column were sealed with glass wool. The column prepared was washed with HCl (2.0 M), then with NH_3 (2.0 M), and finally with water before use. Lifetime of the sorbent was very long, and the column had a constant performance during all experiments, and there was no need for any regeneration or repacking.

2.6. Preconcentration/speciation and determination procedure

The preconcentration/speciation and determination of Cr(III) and Cr(VI) were made using two line FI-manifold (Fig. 2) and a three step procedure. At the preconcentration step (Fig. 2a), the stream of the sample was selected by rotation of valve V_1 and an aliquot of 10.0 mL of sample or standard solution containing both Cr(III) and Cr(VI) was passed through a 10.0 cm mini-column packed with PS-NAPdien at flow rate of 4.0 mL min^{-1} for 150 s, and chromium ions were quantitatively adsorbed on the sorbent. In the washing step (Fig. 2b), the selection valve V_1 was rotated to another position,

while the injection valve V_2 was kept at load position and doubly distilled water was directed to the mini-column at the flow rate of 1.5 mL min^{-1} for 30 s for removal of contaminant that was weakly adsorbed on the sorbent. At this time, the loop of the injection valve V_2 was filled with 320 μL of 1.5 M hydrochloric acid solution. In the third step (Fig. 2c), the injection valve V_2 was rotated to injection position, and doubly distilled water was directed to the loop line to wash and transfer hydrochloric acid into the mini-column for quantitative elution of adsorbed Cr(III). The eluted Cr(III) ions were continuously transported to the FAAS, and the transient signal was recorded. Peak height (absorbance) of the recorded peak was used for quantification of Cr(III). To ensure complete washing of HCl from the mini-column, tubing and sample loop, the passing of water was continued for about 20 s. For elution of adsorbed Cr(VI), the injection valve V_2 was rotated to load position (as shown in Fig. 2b), and the loop was filled with 320 μL of the 2.5 M ammonium nitrate and 1.0 M ammonia buffer solution. By rotating the injection valve V_2 to the injection position (as shown in Fig. 2c), doubly distilled water was directed to the loop for transferring the loaded buffer solution into mini-column for quantitative elution of Cr(VI). For quantitative elution of Cr(VI), a repeated elution of Cr(VI) was carried out like the first one. The eluted Cr(VI) species were continuously transported to the FAAS, and two transient signals were recorded. Sum
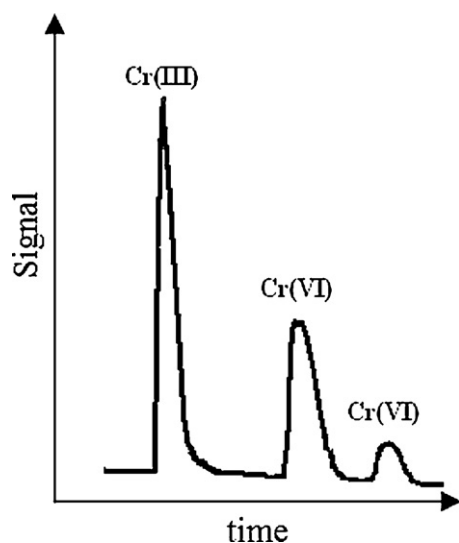
Fig. 3. Typical transient signals for preconcentration 10.0 mL of solution containing 40.0 μg L^{-1} of Cr(III) and Cr(VI).

Fig. 4. Effect of pH on the sensitivity. Conditions: preconcentration 10.0 mL of a solution containing 40.0 μg L^{-1} of Cr(III) and Cr(VI) at flow rate of 4.0 mL min^{-1} on a mini-column with length of 7.5 cm and sequential elution with 500 μL (loop volume) of HCl 2.0 M and NH$_4$NO$_3$ 2.0 M + NH$_3$ 0.5 M at flow rate of 4.0 mL min^{-1}.

of the heights (absorbances) of the two recorded peaks was used as analytical signal in Cr(VI) determination.

2.7. Recovery studies

For recovery test, 10.0 mL of a 40.0 μg L^{-1} solution containing both Cr(III) and Cr(VI) species was enriched under the optimum conditions. The first elution was performed by injection of 1.5 M HCl, output of the column was directed to a 1.0 mL sample vial, and exactly 1.0 mL of column output was collected. The collected solution contained 320 μL of eluted Cr(III) and 680 μL of carrier (water). The second elution was carried out by twice injection of 2.5 M ammonium nitrate, and 1.0 M ammonia buffer solution and exactly 1.0 mL of column output was collected in a sample vial (the collected solution contained 640 μL of eluted Cr(VI) and 360 μL of carrier (water)). The chromium content (in μg) of collected solutions was then determined by direct aspiration to FAAS. The recovery was defined as the ratio between the chromium mass (in μg) in the original sample solution and that in the collected solutions.

3. Results and discussion

PS-NAPdien (Fig. 1) was prepared by incorporation of a nitrogen/oxygen donor (N$_3$O$_2$-type) Schiff base ligand namely NAPdien on the polystyrene (PS) polymeric support. The immobilization reaction of NAPdien on the chloromethylated polystyrene polymer and its characterization details have been reported in our previous papers [34,35]. In these papers, we have also reported the capability of PS-NAPdien in the on-line solid phase preconcentration and determination of Co(II) [34] and Cd(II) [35] in different water samples. The presence of multi-active chelating sites gives the ability to PS-NApdien to sorb more chromium; Cr(III) is retained by forming a stable complex, and chromate is adsorbed by forming the ion pair molecule [H$_2$PS-NAPdien]$^{2+}$[CrO$_4$]$^{2-}$, where [H$_2$PS-NAPdien]$^{2+}$ is the protonated form of PS-NApdien in acidic media. Therefore we decided to examine the capability of PS-NAPdien as a new sorbent for the on line preconcentration and speciation of chromium ions on a single column packed with PS-NApdien using a sequential eluent injection flow system.
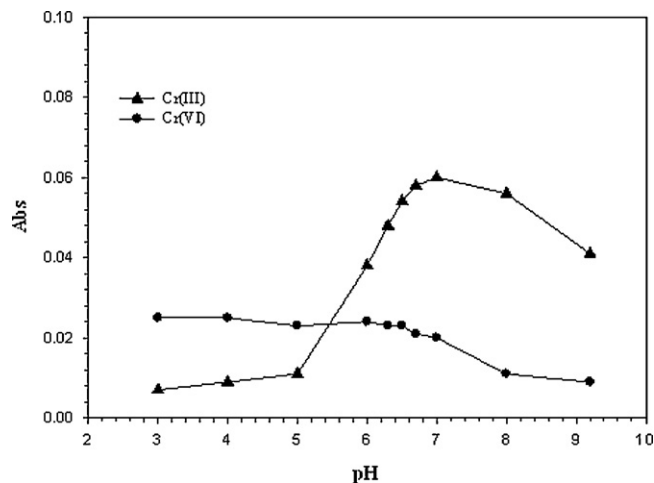
3.1. Sequence for selective elution of Cr(III) and Cr(VI)

Some studies were carried out to determine the best sequence for selective elution of the retained Cr(III) and Cr(VI). The results obtained show that when a mini-column containing retained Cr(III) and Cr(VI) is first eluted with hydrochloric acid and subsequently with a buffer of ammonium nitrate and ammonia solutions, Cr(III) is completely eluted at first, while desorption of Cr(VI) is not observed. This is due to the fact that in acidic media, Cr(III) complex is completely destroyed, whereas phenolic groups remain in their protonated forms and the [H$_2$PS-NAPdien]$^{2+}$[Cr$_2$O$_7$]$^{2-}$ ion pair remains stable. In the second elution with an alkaline solution (buffer of ammonium nitrate and ammonia), the phenolic groups are deprotonated and Cr(VI) is desorbed. Further studies showed that complete desorption of Cr(VI) did not occur with a single elution, and for complete desorption of Cr(VI), it is essential to elute the mini-column twice with the buffer solution of ammonium nitrate and ammonia. Therefore, for a selective and quantitative elution of Cr(III) and Cr(VI), first the column must be eluted using the HCl solution and then twice with the NH$_4$NO$_3$ and NH$_3$ buffer solution. Fig. 3 shows the typical transient absorbance signals for preconcentration of a solution containing 40.0 μg L^{-1} Cr(III) and Cr(VI), and then sequential elution by injection of two different eluents. In this figure, the first sharp peak corresponds to Cr(III), and the other two peaks are related to Cr(VI). Further investigations were carried out on the solutions containing Cr(III) or Cr(VI) and both Cr(III) and Cr(VI) with different concentrations buffered at different pH values. Measurement and comparison of the analytical signals (peak heights) obtained from preconcentration and sequential elution of Cr(III) and Cr(VI) in different solutions show that behaviors of the Cr(III) and Cr(VI) species in individual solutions are exactly the same as their behavior when they are present together in a solution. Therefore, preconcentration and sequential elution and determination of Cr(III) and Cr(VI) in a solution is practical.

3.2. Optimization of variables

In order to get the best performance for the flow system, various chemicals and instrumental variables for preconcentration/speciation and determination of Cr(III) and Cr(VI) were optimized using the one-at-a-time optimization method. The corresponding absorbences (peak heights) for the two chromium
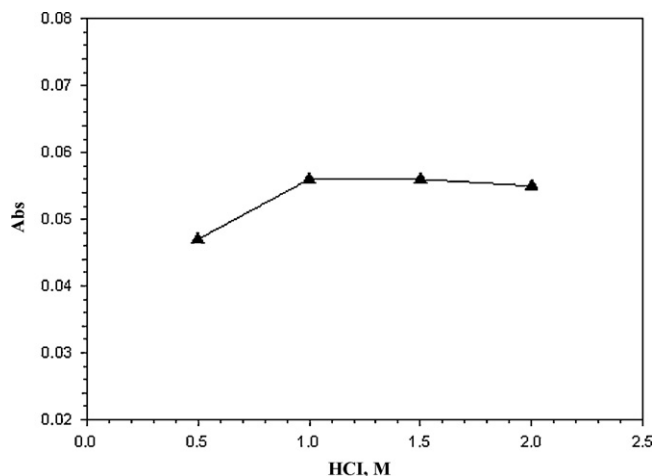
Fig. 5. Effect of HCl concentration on absorbance of Cr(III). Conditions: preconcentration 10.0 mL of a solution containing 40.0 μg L^{-1} of Cr(III) and Cr(VI) buffered at pH 6.7 with flow rate of 4.0 mL min^{-1} on a mini-column with length of 7.5 cm and elution with 500 μL (loop volume) HCl at flow rate of 4.0 mL min^{-1}.

species were used as the analytical signals in the optimization procedure.

3.2.1. Effect of pH

Since the sorption of Cr(III) ions is a complex formation reaction, and Cr(VI) retention occurs by electrostatic attraction between positive charge of protonated hydroxyl groups and negative charge of $C_rO_4{}^{2-}$, pH of the sample solution is one of the most important variables controlling the retention of chromium species. The effect of pH was investigated in the range of 3.0–9.2 using solutions containing 40.0 μg L^{-1} of each species. In this study, pH values for sample solutions were adjusted to the desired pH value by adding 5 mL of appropriate buffers to 50-mL volumetric flasks. Then 10.0 mL of sample solutions were passed through a 7.5 cm mini-column packed with PS-NAPdien resins (105 mg) with a flow rate of 4.0 mL min^{-1}. The column was first eluted by 500 μL stream of 2.0 M HCl solution to desorbs Cr(III), and subsequently the adsorbed Cr(VI) was eluted by two sequential elution with the buffer solution of 2.0 M NH$_4$NO$_3$ and 0.50 M NH$_3$ at flow rate of 4.0 mL min^{-1}. Fig. 4 shows that sorption of Cr(III) increases with increase in pH, reaching a maximum value at a pH value between 6.5 and 7.0, whereas retention of Cr(VI) is high up to pH 6.5 and then decreases

sharply. This is due to this fact that in acidic media, phenolic groups are protanated, and formation of ion pair is preferred over the formation of Cr(III) complex. With increase in pH (to 6.7), the probability of ion pair formation decreases, and the retention of Cr(VI) decreases. This observation indicates the possibility of simultaneous retention of these two species of chromium by adjusting the pH of the solution to 6.7. Thus all sample and standard solutions were buffered at pH 6.7 by phosphate buffer solution with final concentration of 0.015 M.

3.2.2. Type and concentration of Cr(III) eluent

As mentioned earlier, the desorption of adsorbed Cr(III) could occur only in acidic media. Thus some efforts were made to choose the best type of acid for elution of Cr(III). Hydrochloric acid and nitric acid with the same concentration of 2.0 M were used as Cr(III) eluent. The results show that nitric acid is not suitable for elution of Cr(III), because it partially desorbs Cr(VI) and causes error in the correct determination of Cr(VI) ions, while hydrochloric acid has a high elution ability for Cr(III) without desorption of Cr(VI). Thus hydrochloric acid was selected as the best eluent for elution of retained Cr(III). The effect of hydrochloric acid concentration was studied in the range of 0.50–2.0 M with a constant injection volume of 500 μL. The results (Fig. 5) show that absorbance increases with increase in hydrochloric acid concentration up to 1.0 M, and then it remains constant at higher concentrations. Thus a HCl concentration of 1.5 M was chosen for subsequent studies.

3.2.3. Type and concentration of Cr(VI) eluent

In order to select the best eluent for desorption of Cr(VI), different solutions including 2.0 M HNO$_3$, 2.0 M NH$_3$, 2.0 M NH$_4$NO$_3$, and 1.5 M NH$_4$NO$_3$ and 0.50 M NH$_3$ buffer solution were injected as eluent. The results show that the of NH$_4$NO$_3$ and NH$_3$ buffer solutions has the best potential for elution of Cr(VI). Thus this solution was selected as the best eluent for the Cr(VI) species. The effect of NH$_4$NO$_3$ and NH$_3$ concentrations on the sensitivity was studied using a constant injection volume of 500 μL. In the first study, the concentration of NH$_3$ in the buffer solution was fixed at 0.50 M and that for NH$_4$NO$_3$ was varied in the range of 1.5–3.0 M. According to the results (Fig. 6a), it is clear that absorbance increases with increase in NH$_4$NO$_3$ concentration up to 2.0 M, and then it remains constant at higher concentrations. In another study, the concentration of NH$_4$NO$_3$ in the buffer solution was fixed at 2.5 M and that for NH$_3$ was changed in the range of 0.50–1.3 M. The results (Fig. 6b) show that with increase in the NH$_3$ concentration up to

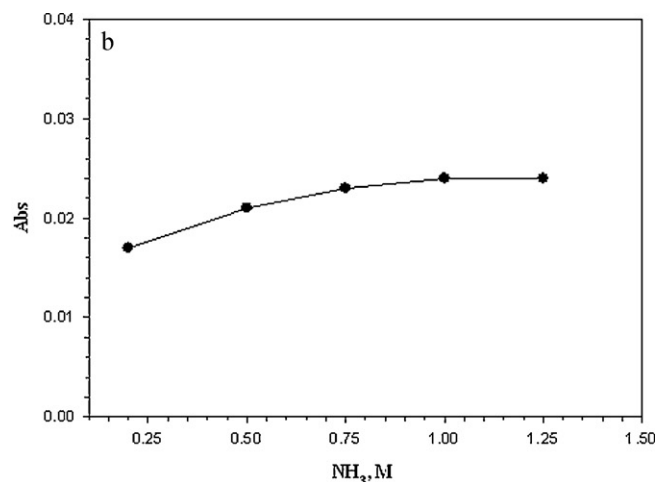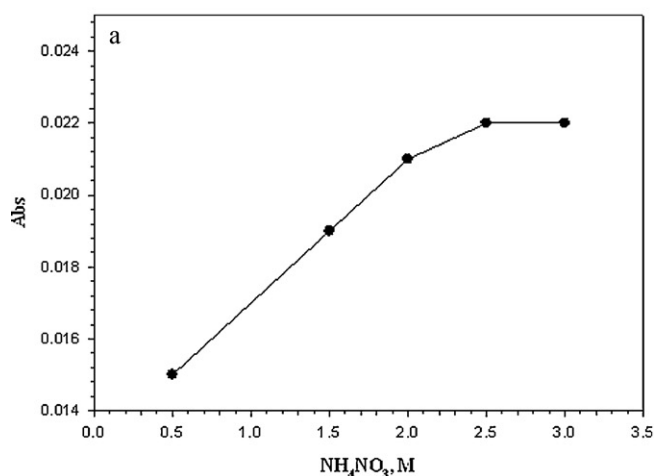**Fig. 6.** Effect of (a) NH$_4$NO$_3$ and (b) NH$_3$ concentrations on the absorbance of Cr(VI). Conditions: preconcentration 10.0 mL of a solution containing 40.0 μg L^{-1} of Cr(III) and Cr(VI) buffered at pH 6.7 with flow rate of 4.0 mL min^{-1} on a mini-column with length of 7.5 cm and sequential elution with 500 μL (loop volume) of HCl 2.0 M and a buffer of NH$_4$NO$_3$ and NH$_3$ at flow rate of 4.0 mL min^{-1}.
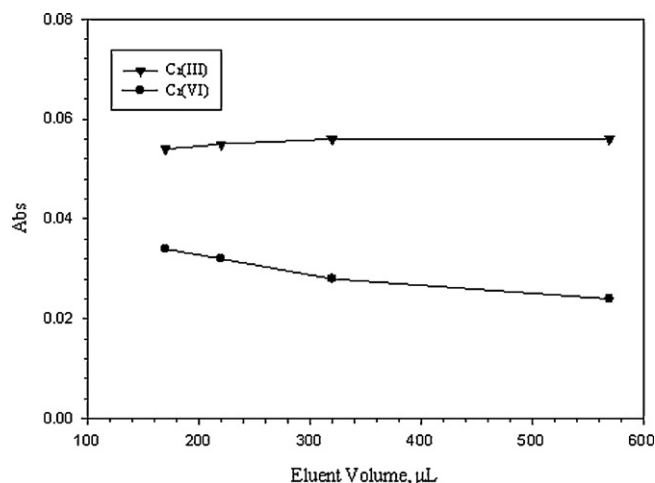
Fig. 7. Effect of eluent volume on the absorbance. Conditions: preconcentration 10.0 mL of a solution containing $40.0 \mu g L^{-1}$ of Cr(III) and Cr(VI) buffered at pH 6.7 with flow rate of $4.0 \, mL \, min^{-1}$ on a mini-column with length of 7.5 cm and sequential elution with HCl 2.0 M and a buffer of NH_4NO_3 2.5 M and NH_3 1.0 M at flow rate of $4.0 \, mL \, min^{-1}$.

0.75 M, absorbance increases slightly and then remains constant. Thus a buffer solution of 2.5 M NH_4NO_3 and 1.0 M NH_3 was chosen as the best eluent for elution of Cr(VI).

3.2.4. Effect of eluent injection volume

The volume of eluents required for complete elution of Cr(III) and Cr(VI) from the column was studied in the range of 170–500 μL. In this study, some aliquots of the solutions containing $40.0 \mu g L^{-1}$ of Cr(III) and Cr(VI) were passed through the mini-column. After preconcentration, Cr(III) and Cr(VI) were sequentially desorbed from mini-column by injecting different volumes of 1.5 M HCl and then the buffer solution of 2.5 M NH_4NO_3 and 1.0 M NH_3, and the corresponding analytical signals were recorded. The results obtained are shown in Fig. 7. The recovery values for Cr(III) and Cr(VI) at different injected volumes of eluents (Table 1) were also determined according to the recovery study procedure (Section 2.7). The results (Fig. 7 and Table 2) show that the recovery values for Cr(III) and Cr(VI) reach their maximum values at 320 μL, while the analytical signals are nearly constant over the range studied. Therefore, for quantitative elution of retained species with high recovery, an eluent injection volume of 320 μL was selected. To ensure quantitative elution of adsorbed Cr(III), a second elution of the column was performed by another injection of 1.5 M HCl. No signal was observed in the second elution, which indicates that single elution of column with 320 μL of 1.5 M HCl is sufficient for quantitative desorption of the adsorbed Cr(III). The same procedure was carried out for Cr(VI) to ensure quantitative elution of adsorbed Cr(VI). The results obtained showed that a third elution of the column using 320 μL of 2.5 M NH_4NO_3 and 1.0 M NH_3 buffer solution gives no analytical signal. This means that elution of the column with twice injection of 320 μL of 2.5 M NH_4NO_3 and 1.0 M NH_3 buffer solution is sufficient for quantitative desorption of Cr(VI).

Table 1
Recoveries of Cr(III) and Cr(VI) at different injection volumes of eluent.

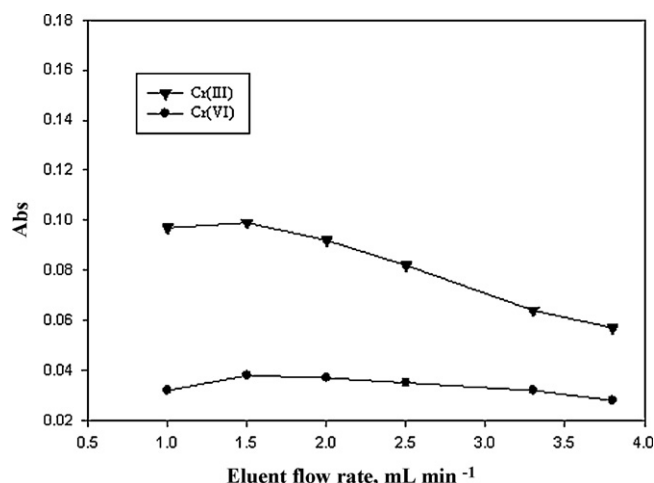| Eluent volume (μL)	Recovery (%)	
	Cr(III)	Cr(VI)
170	90.4	76.7
220	93.1	82.0
320	95.1	93.2
500	95.1	93.2

Fig. 8. Effect of eluent flow rate on the sensitivity. Conditions: preconcentration 10.0 mL of a solution containing $40.0 \mu g L^{-1}$ of Cr(III) and Cr(VI) buffered at pH 6.7 with flow rate of $4.0 \, mL \, min^{-1}$ on a mini-column with length of 7.5 cm and sequential elution with 320 μL of HCl 2.0 M and buffer of NH_4NO_3 2.5 M and NH_3 1.0 M.

3.2.5. Effect of sample loading flow rate

The performance of the on-line time-based preconcentration systems is influenced by the loading (sample) flow rate, because it regulates the maximum mass transfer from liquid to solid phase. At the carrier (eluent) flow rate of $4.0 \, mL \, min^{-1}$, the effects of sample flow rate on the preconcentration of 10.0 mL solution containing $40.0 \mu g L^{-1}$ Cr(III) and Cr(VI) were investigated in the range of $1.0–4.0 \, mL \, min^{-1}$. The results show that the absorbance is independent from sample flow rate over the whole range examined. This means that the kinetic of the complex formation of Cr(III) and electrostatic retention of Cr(VI) is fast, and these contact times are sufficient for complete sorption of chromium species. Hence, the flow rate of $4.0 \, mL \, min^{-1}$ was selected to achieve higher sample frequency.

3.2.6. Effect of carrier (eluent) flow rate

The eluent flow rate is an important parameter because the elution efficiency and analytical throughput could be influenced by this parameter. The effect of eluent flow rate was studied by varying the carrier flow rate within the range of $1.0–3.8 \, mL \, min^{-1}$. The results (Fig. 8) show that the maximum absorbance (peak height) is achieved at the flow rate of $1.5 \, mL \, min^{-1}$ for both Cr(III) and Cr(VI), while at higher flow rate values, the absorbance decreases. Thus a carrier flow rate of $1.5 \, mL \, min^{-1}$ was used for further experiments.

3.2.7. Effect of mini-column length (amount of sorbent)

The effect of length of the mini-column (amount of sorbent) on the sensitivity was investigated in the range of 2.5–11.0 cm using 10 mL of the sample solutions containing 0.40 μg of both Cr(III) and Cr(VI). This study was carried out under the optimized conditions for other variables. The results show that absorbance increases with increase in the column length up to 7.5 cm for Cr(III), and up to 9.0 cm for Cr(VI), and then remains constant. Since the preconcentration and speciation of both chromium species were done using a single column, a mini-column of 10.0 cm length (containing 140 mg of sorbent) was selected for sufficient sorption of different amounts of chromium species from 10 mL sample solution.

3.2.8. Sample volume effect

The influence of loading time (sample volume) was studied by passing different volumes (2.0–60.0 mL) of sample solution with concentration of $40 \mu g L^{-1}$ for Cr(III) and Cr(VI). With the loading flow rate of $4.0 \, mL \, min^{-1}$, the corresponding loading times fall in

Table 2
Results for accuracy and precision studies.

Number	Added (μg L^{-1})		Found (μg L^{-1})		Recovery (%)		RSD (%)	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
1	10.0	100.0	10.3	100.4	103	100.4	3.9	4.1
2	20.0	20.0	20.4	19.0	102	96.5	2.5	2.2
3	40.0	40.0	39.2	40.9	98.0	102.2	2.6	0.80

the range of 0.5–15.0 min. The results obtained show that the analytical signal increases linearly with increase in the loading time up to 15 min (maximum tested). This means that the retention efficiency was constant within this time interval. However, a loading time of 2.5 min in flow rate of 4.0 mL min^{-1} (10 mL sample volume) was chosen for further studies as a compromise between sample consumption, sufficient sensitivity, and higher sampling frequency.

3.2.9. Salt effect

The influence of the ionic strength (salt effect) on the analytical signals for Cr(III) and Cr(VI) was also studied. For this study, 10 mL portions of 40.0 μg L^{-1} Cr(III)/Cr(VI) solution with different amounts of 0.0–0.50 M KCl were passed through the column at the optimum conditions. After preconcentration, chromium species were eluted by sequential injection of the specific eluents, and the corresponding analytical signals were recorded. The results obtained show that the KCl concentrations up to 0.40 M and 0.070 M do not have a significant effect on the analytical signals for Cr(III) and Cr(VI), respectively.

3.3. Analytical performance of flow system

Some analytical parameters were studied for the proposed eluent injection on-line preconcentration and speciation of Cr(III) and Cr(VI) under the optimum conditions (pH value of 6.7, sample flow rate of 4.0 mL min^{-1}, and sequential elution of mini-column with 320 μL of 1.5 M HCl and then with 2.5 M NH$_4$NO$_3$ and 1.0 M NH$_3$ buffer solution with flow rate of 1.5 mL min^{-1}.).

Using a manifold presented in Fig. 1, under the optimum conditions, linear calibration graphs were found in the range of 2.0–60.0 μg L^{-1} for Cr(III) and 8.0–180.0 μg L^{-1} for Cr(VI). The linear regression equations for calibration graphs were $A = 2.51 \times 10^{-3} C_{Cr(III)} + 0.001$ ($r = 9999$, $n = 9$), and $A = 1.00 \times 10^{-3} C_{Cr(VI)} - 0.001$ ($r = 9998$, $n = 11$) for Cr(III) and Cr(VI), respectively, where A is absorbance, and $C_{Cr(III)}$ and $C_{Cr(VI)}$ are concentrations in μg L^{-1} for Cr(III) and Cr(VI), respectively.

The limit of detection is given by LOD = KS_b/m, where K is a numerical factor chosen according to the confidence level desired, S_b is the standard deviation of the blank measurements, and m is the slope of calibration curve. With ten replicate measurements of blank (10 mL distilled water containing 0.015 M phosphate buffer with pH 6.7) and $K = 3$, the detection limits for Cr(III) and Cr(VI) were 0.60 μg L^{-1} and 2.5 μg L^{-1}, respectively.

In order to determine the precision of the proposed method, it was used for the analysis of the standard model solutions containing various amounts of Cr(III) and Cr(VI) under the optimum conditions. The relative standard deviations for six replicate determinations of Cr(III) and Cr(VI) in their mixtures are given in Table 2.

The enrichment factors for the preconcentration of 10.0 mL of sample solution, calculated as the ratio of the slopes of the calibration graphs with and without preconcentration ($A = 3.4 \times 10^{-5} C_{Cr} + 0.007$, where C_{Cr} is chromium concentration in μg L^{-1}), were 74 and 30 for Cr(III) and Cr(VI), respectively. The consumptive index is defined as the consumed sample volume in milliliters per unit of preconcentration factor [36]. The calculated consumptive indices were 0.14 and 0.33 mL for Cr(III) and Cr(VI), respectively.

The recovery is defined as the ratio between the chromium mass in the original sample solution and that in the concentrate after elution. Recovery studies were carried out under the optimum conditions (Section 2.7). The results showed recoveries of 95.0% and 93.0% for Cr(III) and Cr(VI), respectively.

With total analysis time of 225 s (150 s for preconcentration, 30 s for washing with doubly distilled water, and 45 s for elutions), a sampling frequency of 16 h^{-1} was obtained for 10 mL of sample solution.

The maximum capacity of the sorbent was determined by batch method. 100 mL of two aqueous solutions (pH 6.7), one containing 100 μg of Cr(III) and the other one containing 100 μg of Cr(VI), were stirred in contact with 100 mg of resin for 0.5 h. The remaining Cr(III) and Cr(VI) in the solutions were determined by direct aspiration to FAAS. The maximum capacity of the sorbent (PS-NAPdien) retention of Cr(III) and Cr(VI) was evaluated from the difference between the initial and remaining amount of chromium. The capacities of 207 μg of Cr(III) and 310 μg of Cr(VI) per gram of resin were found. The lifetime of the mini-column packed with PS-NAPdien was also studied. From the 200 (maximum tested) retention and elution cycle, it was found that the resin was usable with the same efficiency and capacity, indicating no appreciable loss of multi-active chelating sites and thus the high stability and long lifetime of sorbent. Because of the unlimited lifetime of the packing material, the column did not need any regeneration or repacking, and its performance was stable during all experiments.

3.4. Effect of diverse ions

The effects of various ions present in real samples on the preconcentration/speciation and determination of Cr(III) and Cr(VI) were investigated. Synthetic mixtures of solutions containing

Table 3
Interferences on the determination of Cr(III) and Cr(III) in a mixture with same concentration of 40.0 μg L^{-1}.

Interferences for Cr(VI)	Interferences for Cr(III)	Tolerance limit (w/w)
K$^+$, Na$^+$, Ca^{2+}, pb^{2+}, Li^{2+},Co^{2+}, S$_2$O$_5$$^{2-}$, SO$_4$$^{2-}$, NH$_4$$^+$, F$^-$, Cl$^-$, Br$^-$, I$^-$, Hg^{2+},Cu^{2+}, Mn^{2+},Cd^{2+},Mg^{2+},Zn^{2+}, EDTA, Sn^{2+}, C$_2$O$_4$$^{2-}$, NO$_2$$^-$, citrate	K$^+$, Na$^+$, Ca^{2+}, Li$^+$, Co^{2+}, SO$_4$$^{2-}$, NH$_4$$^+$, F$^-$, Cl$^-$, Br$^-$, I$^-$, C$_2O_4$$^{2-}$, NO$_2$$^-$, EDTA, Sn^{2+}, citrate	1000
CO$_3$$^{2-}$	Pb^{2+}, S$_2$O$_5$$^{2-}$, CO$_3$$^{2-}$, Mg^{2+}	800
CN$^-$	Cd^{2+}, Hg^{2+}, Mo^{2+}, CN$^-$	600
	Mn^{2+}	50

Table 4
Determination of Cr(III) and Cr(VI) in water samples.

Sample	Added ($\mu g\,L^{-1}$)		Found ($\mu g\,L^{-1}$)		Recovery (%)	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
Tap water(I)	–	–	ND	ND	–	–
	5.0	10.0	4.7 ± 0.2	10.6 ± 0.6	94.1	106.0
	10.0	30.0	10.3 ± 0.2	30.3 ± 0.6	103.0	101.0
	30.0	70.0	29.9 ± 0.1	69.7 ± 0.5	99.8	99.6
Tap water(II)	–	–	ND	43.0 ± 0.8	–	–
	10.0	20.0	10.1 ± 0.3	62.5 ± 0.4	101.0	99.2
	20.0	30.0	19.1 ± 0.2	75.2 ± 0.4	95.5	103.0
	–	10.0	ND	52.3 ± 0.3	–	93.0
	25.0	–	25.4 ± 0.4	43.40 ± 0.6	101.6	–
Mineral water	–	–	ND	ND	–	–
	28.0	40.0	27.7 ± 0.3	38.5 ± 0.4	98.9	96.2
	5.0	70.0	4.8 ± 0.3	68.6 ± 0.5	96.0	98.0

Table 5
Some recently reported methods for SPE-FAAS determination of Cr(III) and Cr(VI).

Sorbent	LOD ($\mu g\,L^{-1}$)		EF (sample volume, mL)		%RSD		Ref.
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	
Amberlite XAD-1180	–	7.7	–	75	–	–	[16]
Multiwalled carbon nanotubes	–	0.90	–	100(5)	–	9	[17]
Fiber	0.3	0.3	–	32(25)	–	4.8	[18]
Dowex M 4195	–	1.94	–	31(8)	4	3.6	[19]
Melamine	4.2	5.3	–	–	2–3	2–3	[20]
Amberlite XAD-2010	–	1.28	–	25(50)	–	–	[21]
Chromosorb 108	0.75	–	71(50)	–	–	9	[22]
BrPMAAm/AMPS/DVB	1.58	–	100(50)	–	–	–	[23]
SP-850 resin	0.50	–	–	–	1–5	–	[24]
silica gel	0.34	–	23(13.2)	–	4.6	–	[25]
XAD-16	20	14	100	140	2	2	[29]
silica gel	1.9	2.3	20.8(15)	24.9(15)	3	2.1	[30]
Ion exchange resins	0.442	0.532	–	–	3.27	3.66	[31]
Alumina	81	42	–	–	10	10	[37]
Duolite C_{20}	13.3	10	150	200	4	4	[38]
Polystyrene	0.6	2.5	70	30	2.5	2.2	This work

$40.0\,\mu g\,L^{-1}$ of both Cr(III) and Cr(VI) and various amounts of diverse ions were used as sample. The tolerance limit is defined as the concentration of the added ions causing a change in the absorbance more than ±5%. The results obtained in these experiments (Table 3) demonstrate that the presence of large amounts (1000-fold) of alkali, alkaline earth, and transition metal ions in the sample have no significant effect on the analytical signals for Cr(III) and Cr(VI). Also other ions up to 600-fold and 50-fold did not interfere with Cr(III) and Cr(VI), respectively.

3.5. Analysis of water samples

The proposed method was applied to the determination of Cr(III) and Cr(VI) ions in tap and mineral water samples. Tap waters were collected from local pipes at 10 different locations in the city of Shahrood (Tapwater(I)) and Sabzevar (Tapwater(II)), Iran. Bottled natural mineral water samples were prepared from Damavand Co., Iran. Since concentrations of the analytes in the water samples may be below the detection limit of the method, spiking of the samples was performed. In order to evaluate the accuracy of the preconcentration procedure, recovery experiments were carried out with spiked water samples. Each spiked sample was analyzed using the standard addition method by applying the proposed procedure (Section 2.6). The results are given in Table 4. It can be seen that the method gives good recoveries for added Cr(III) and Cr(VI) ions, and at the 95% confidence level, there is an agreement between the results and true spiked values.

4. Conclusion

The proposed method introduces a sequential eluent injection technique combined with an on-line preconcentration/separation system for fast determination of trace levels of Cr(III) and Cr(VI) species. The features of the synthesized PSNAPdien resin as a new solid phase sorbent and designed flow manifold allowed fast separation and determination of Cr(III) and Cr(VI) species in one step using only a single mini-column without the need for any excess oxidation or reduction reactants. The proposed procedure increases the speed of the analysis process and thus reduces analysis time, sample consumption, and contamination risks. The detection limits were $0.6\,\mu g\,L^{-1}$ and $2.5\,\mu g\,L^{-1}$ for Cr(III) and Cr(VI), respectively. The presented manifold provided an enrichment factor of 74 for Cr(III) and 30 for Cr(VI) as a consequence of good retention (95.0% and 93.0% for Cr(III) and Cr(VI), respectively). The proposed sorbent possesses high stability and lifetime (it can remain stable in strongly acidic and alkaline media), and thus there is no need for loading of any chelating agent onto the sorbent during the preconcentration procedure to obtain quantitative recovery of chromium ions. This feature also allows repeated use of sorbent. The figures of merit for the proposed method and some recently reported methods on the FAAS on-line solid phase preconcentration and speciation of the chromium species are given in Table 5. According to Table 1, it is clear that some of the reported methods have higher detection limits [16,19,20,22,23,29,30,37,38] and/or poorer precision [18,19,22,25,31,37,38] in comparison with the proposed method. Although some of these methods have better detection

limits [17,18,21,24,25], they are time consuming, and suffer from high consumption of reagents and sample due to the use of excess amounts of oxidizing or reducing agents and/or use of two separate preconcentration steps.

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