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Chromium speciation and preconcentration using zirconium(IV) and zirconium(IV) phosphate chemically immobilized onto silica gel surface using a flow system and F AAS

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Abstract

A procedure for chromium speciation by F AAS using a flow system has been proposed. In this system, Cr(III) and Cr(VI) ions were adsorbed sequentially onto a mini-column packed with silica gel modified with zirconium phosphate and a mini-column packed with silica gel modified with zirconium oxide, respectively. The elution of Cr(III) and Cr(VI) was made with, respectively, nitric acid solution and tris(hydroxymethyl)methylamine (THAM) solution in reverse mode and determination by flame atomic absorption spectrometry without interference of the matrix. Chemical and flow variables as well as concomitant ions were studied in the developed procedure. The enrichment factor for Cr(III) and Cr(VI) was 20.8 and 24.9, respectively, using a preconcentration time of 3.75 min. The limit of detection for Cr(III) and Cr(VI) was 1.9, and 2.3 $\mu g\,l^{-1}$, respectively. The precision of the method, evaluated as the relative standard deviation in solutions containing 100 $\mu g\,l^{-1}$ of chromium species, by analyzing a series of seven replicates, was lower than 3.0%. The accuracy was assessed through recovery experiments of water samples and using another methodology.

Keywords: F AAS; Flow injection analysis; SiO_2–Zr; SiO_2–ZrP; Chromium species

1. Introduction

The toxicity and reactivity of some elements depend on the chemical form or oxidation state in which the element is present [1]. Trace amounts of Cr(III) are essential to mammals for their maintenance of glucose, lipid and protein metabolism, and are therefore essential for human health [2]. On the other hand, Cr(VI) is extremely toxic to humans since it is a potentially carcinogenic agent [2]. Chromium species can enter the environment from industrial effluent or waste-disposal sources, such as wasted water from steel works, electroplating, and tanning industries [3]. So, traces of chromium also enter drinking water systems. The US EPA has set the concentration of 0.1 $mg\,l^{-1}$ of total chromium for drinking water as “maximum contaminant level goals”. WHO states that the guideline values of 50 $\mu g\,l^{-1}$ of Cr(VI), are thought to be too high compared with its high risk of carcinogenicity by the inhalation route and its genotoxicity. Consequently, chromium species must be monitored and require a sufficiently selective and highly sensitive method.

The most widely employed procedures for chromium speciation in waters by atomic spectrometry are based on the selective retention of Cr(IV) and Cr(III). In these procedures a redox reaction prior to retention by the same column is required. Chelating and/or ion exchange type sorbents showed a preferential affinity for a single oxidation state of chromium, normally Cr(III). So, Cr(VI) could be reduced and the method would enable the determination of total chromium. Cr(VI) in the original mixture may be calculated by difference [4–8]. Chromium speciation is also possible by adsorption of Cr(VI) using a strong basic anion exchange resin, followed by reduc-

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tive elution [9,10]. Cr(III) could be oxidized to Cr(VI) and its concentration calculated on the basis of the difference between the data found before and after oxidation.

Another option for chromium speciation is a simultaneous retention of Cr(III) and Cr(VI). These retentions can occur on the same sorbent [11,12] or on different sorbents [13–16]. When the same sorbent is used the determinations are based on the use of different conditions for retention and elution of both species, where pH is the most important parameter. The methods that achieve a physical separation between the species and, that directly quantify are better because they are relatively faster and require only minimal sample pretreatments [12].

Great numbers of sorbent materials are used for preconcentrated chromium species from water samples. Among them, silica gel is one of the most used solid materials due its well-established particle size, well-defined porosity, high surface area and high mechanical, chemical and thermal stability. Usually its surface is modified by a ligand or complexing reagent to improve its preconcentration efficiency [17,18]. On the other hand, few studies of metal preconcentration using inorganic functionalized silica have been described in the literature [19–22]. These materials can present advantages such as stability, adsorption of cations or anions depending on the solution pH, and high selectivity, giving rise to separation or even speciation.

The purpose of this work is to explore the potential of silica gel modified with zirconium for the development of a method for chromium speciation in atomic spectrometry. In this study a selective method is reported involving flow-injection separation and preconcentration of chromium species in a two-mini-column ion-exchange system. The sample is passed sequentially through silica gel modified with zirconium phosphate (SiO_2–ZrP) and silica gel modified with zirconium(IV) oxide (SiO_2–Zr). The chromium species retained by each mini-column are stripped and detected with F AAS. The SiO_2–ZrP retains positively charged Cr species and the SiO_2–Zr retains negatively charged Cr species.

2. Experimental

2.1. Instrumentation

The absorption measurements were made with a Hitachi Model Z-8230 flame atomic absorption spectrometer, equipped with Zeeman background correction and a chromium hollow cathode lamp from Hitachi (Mitorika, Ibaraki, Japan). The operational conditions used are described in Table 1.

Table 1
Operating parameters employed to determine Cr by F AAS

Wavelength (nm)	359.3
Flame	Air–C_2H_2
Burner height (mm)	7.5
Lamp current (mA)	5.0
Slit (mm)	0.7
Signal	Height
Aspiration flow (ml min^{-1})	6.0

A Spectronic 21D Milton Roy spectrophotometer (USA) was used for colorimetric chromium determinations (Standard method, 1998).

A 320 Mettler Toledo pH meter was used to adjust the pH of the solutions.

The components of the preconcentration system were a MS-Reglo Ismatec peristaltic pump with four channels (Glattbrugg, Switzerland) provided with Tygon® tubes, a four-way flow manual manifold, polyethylene tubing (0.8 mm i.d.) and two mini-columns (43 mm × 3 mm, each) containing, respectively, 100 mg of SiO_2–ZrP and 100 mg of SiO_2–Zr.

2.2. Reagents and solutions

Ultrapure water from a Milli-Q water purification system (Millipore) was used to prepare all solutions. All chemicals were of analytical grade and were used without previous purification. The laboratory glassware was kept overnight, respectively, in a 2% (v/v) Extran® solution (Merck, Darmstadt, Germany) and 10% (v/v) nitric acid solution (Vetec, Rio de Janeiro, Brazil). Before use, the glassware was washed with deionized water and dried in a dust free environment.

Chromium(VI) and chromium(III) working standard solutions were all freshly prepared by appropriate dilution of, respectively, 1000 mg l^{-1} $CrCl_3.6H_2O$ (Vetec, Rio de Janeiro, Brazil) and of 1000 mg l^{-1} $K_2Cr_2O_7$ (Merck, Darmstadt, Germany) stock solutions.

Hydrochloric, nitric, sulfuric and phosphoric acid solutions were prepared by appropriate dilution of their concentrated solutions from Merck (Darmstadt, Germany). Sodium and ammonium hydroxyl solutions were prepared by appropriate dilution of their concentrated solutions from Vetec (Rio de Janeiro, Brazil). Those solutions were used for separation and preconcentration procedures.

Solution of tris(hydroxymethyl)methylamine (THAM) 0.1 mol l^{-1} from Aldrich (Milwaukee, USA) was prepared by dissolving 1.2 g of the substance in 100 ml of deionized water. The pH of this solution was adjusted to 8.5 using 0.1 mol l^{-1} nitric acid.

In the colorimetric procedure for chromium speciation 1,5-diphenylcarbazide (DPC) from Riedel (Hannover, Germany), $KMnO_4$ from Carlo Erba (Milan, Italy) and NaN_3 from Strem Chemicals (Newburyport, MA, USA) were used. A Solution of 1.5-diphenylcarbazide was prepared by dissolving 0.25 g of DPC in 50 ml of acetone. A Solution of NaN_3 was prepared by dissolving 0.5 g of the substance in 100 ml of deionized water. A Solution of $KMnO_4$ was prepared by dissolving 4 g of the substance in 100 ml of deionized water.

2.3. Preparation of the solid sorbents

The silica gel (Fluka, average pore diameter of 60 Å, and particle size 0.2–0.7 mm) was chemically modified, as described by Peixoto et al. [23]. Firstly, 50 g of activated silica gel was added to 11.6 g (0.05 mol) of zirconium tetrachloride, previously dissolved in 300 ml of dry ethanol. The mixture was maintained at reflux for 8 h with stirring. The resulting material was washed by decantation, dried at 150 °C for 4 h and hydrolyzed by immersing the solid in deionized water. After removing all chloride ions with deionized water, the material (SiO_2–Zr) was dried at 120 °C for 5 h.

The phosphate group was introduced onto the SiO_2–Zr surface by adding 1.0 g of this material to 10 ml of 0.1 mol l^{-1} phosphoric acid. The mixture was stirred for 8 h, at room temperature. The product (SiO_2–ZrP) was then filtered, washed and dried in an oven at 100 °C.

The amount of Zr on the SiO_2 surface and the $PO_4{}^{3-}$ on the SiO_2–Zr surface were determined by X-ray fluorescence. The mean values were 2.8% for Zr (0.30 mol l^{-1}) and 2.5% for $PO_4{}^{3-}$ (0.27 mol l^{-1}).

2.4. On-line preconcentration system

The simple manual flow system, using two mini-columns sequentially, an injector–commutator and a peristaltic pump, is shown in Fig. 1. Working solutions and blanks were submitted to the same preconcentration procedure. In the first step with the injector–commutator in the loading position, the column containing SiO_2–ZrP, which retains Cr(III), and after the column containing SiO_2–Zr, which retains Cr(VI), were loaded with the working or blank solutions, pushed by the peristaltic pump. Between the two columns the sample pH was adjusted to 3 by adding a drop of 0.1 mol l^{-1} nitric acid solution. The remaining solution was discharged. The injector was then changed manually to its second position and a continuous volume of 0.1 mol l^{-1} nitric acid solution and 0.1 mol l^{-1} THAM solution were passed, respectively, through the SiO_2–ZrP mini-column and SiO_2–Zr mini-column, in the reverse direction, eluting the analytes. A discrete volume of eluates was collected simultaneously in Teflon cups of 2.0 ml capacity and introduced into the nebulizer. Finally, the mini-columns were reconditioned by passing 1 ml of 0.1 mol l^{-1} nitric acid solution. The same mini-columns were used during all experiments without loss of signal, indicating long life of these adsorbent materials. All solutions were placed manually in the proper line of the pump, intercalated by a minimum volume of air entering the tubing.

2.5. Colorimetric procedure for chromium speciation

In the diphenylcarbazide method, the Cr(VI) concentration is first measured colorimetrically at 540 nm as a complex with 1.5-diphenylcarbazide. For this purpose, 2 ml DPC solution, 0.25 ml of $H_3PO_4{}^{3-}$ solution and an adequate volume of Cr(III) and Cr(VI) stock solution were added to the 100 ml volumetric flask and the volume was adjusted to 100 ml with water. The pH of the spiked sample solution was adjusted to 1 using sulfuric acid solution. After 5 min the colorimetric measurement was achieved.

After oxidizing Cr(III) to Cr(VI) with suitable oxidants, total chromium was determined as Cr(VI) by the method described above. For oxidizing Cr(III) to Cr(VI), three drops of $KMnO_4$ solution and 1 ml of concentrated H_2SO_4 were added to a 250 ml beaker containing an adequate volume of the spiked sample. The volume of the beaker was adjusted to 40 ml and covered with a watch glass and heated until boiling for about 1 min to complete oxidation. The solution was cooled and 1 ml of sodium azide solution was added dropwise to reduce the excess of $KMnO_4$.

Then, the Cr(III) concentration was estimated indirectly by subtracting the Cr(VI) concentration before oxidation from the total chromium concentration.

3. Results and discussion

3.1. Optimization of chemical and flow parameters

The flow system was optimized by varying the chemical and flow conditions by using the univariate method, searching for the best sensitivity to Cr(III) and Cr(VI). For bet-

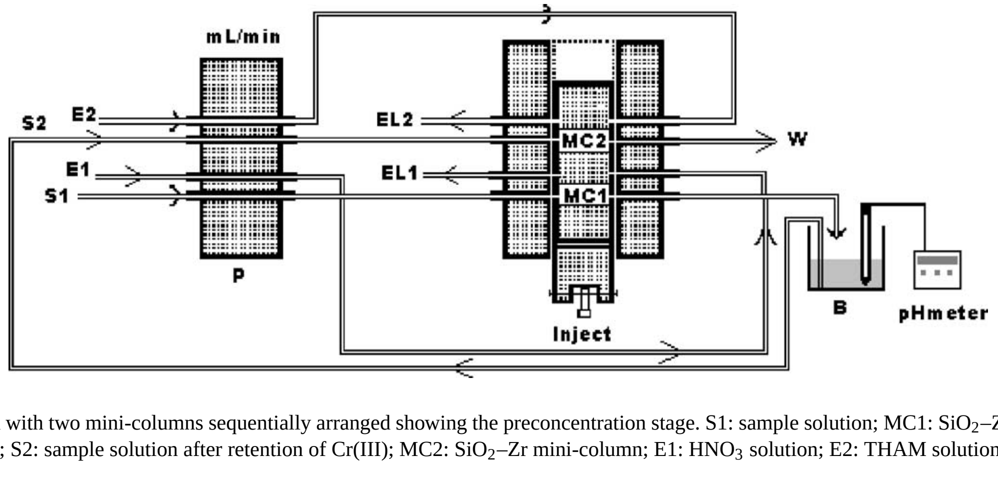

Fig. 1. Flow system with two mini-columns sequentially arranged showing the preconcentration stage. S1: sample solution; MC1: SiO_2–ZrP mini-column; B: collector flask to S2; S2: sample solution after retention of Cr(III); MC2: SiO_2–Zr mini-column; E1: HNO_3 solution; E2: THAM solution, and W: waste.

ter performance of the adsorbent materials, optimizations of some important flow and chemical variables were carried out for each adsorbent individually. The sample pH was studied first and it defined what adsorbent material would be used for each chromium species. A standard solution containing 100 μg l^{-1} of Cr(III) or Cr(VI) was continuously introduced into the flow system shown in Fig. 1. A sample flow rate of 3.0 ml min^{-1} and a pumping time of 5 min were initially chosen. The elution was done with 400 μl of 0.1 mol l^{-1} HNO_3 solution or 0.1 mol l^{-1} THAM solution for stripping, respectively, Cr(III) and Cr(VI). The flow rate for elution was 0.53 ml min^{-1} for both metals. All analyses were done in triplicate.

The effect of the sample pH on retention of each chromium species was determined for each adsorbent individually. The retention of Cr(III) and Cr(VI) on SiO_2–Zr was investigated within the pH range of 1–9. The sample pH was adjusted using 0.1 mol l^{-1} HNO_3 solution or 0.1 mol l^{-1} NaOH solution. Buffer solutions were avoided because a reduction in analytical sensitivity was observed. According to the results shown in Fig. 2, the maximum retention for Cr(VI) occurred in pH 3 and for Cr(III) it occurred above pH 4. The effect of the pH sample on retention of the Cr(III) and Cr(VI) on SiO_2–ZrP was also investigated within the pH range of 1–9. The results of this study are shown in Fig. 3. Because of its cationic exchange characteristic, the adsorption of Cr(VI) species in SiO_2–ZrP did not occur and Cr(III) was effectively adsorbed in pH 4–9. From this study, it was concluded that a chromium speciation would be carried out using SiO_2–ZrP mini-column and pH range of 5–9 for Cr(III) retention, and the SiO_2–Zr mini-column and pH of 3 for Cr(VI) retention.

The effect of the sample flow rate on the retention of Cr(III) on SiO_2–ZrP and Cr(VI) on SiO_2–Zr in the proposed system was also studied individually. The flow rate varied from 1.0 to 5.6 ml min^{-1}. The results of this study have shown that the analytical signals did not vary significantly with the sample flow rate for both metals. A flow rate of 4.0 ml min^{-1} was chosen, since larger flow rates allow the use of high volumes, improving the preconcentration factor.

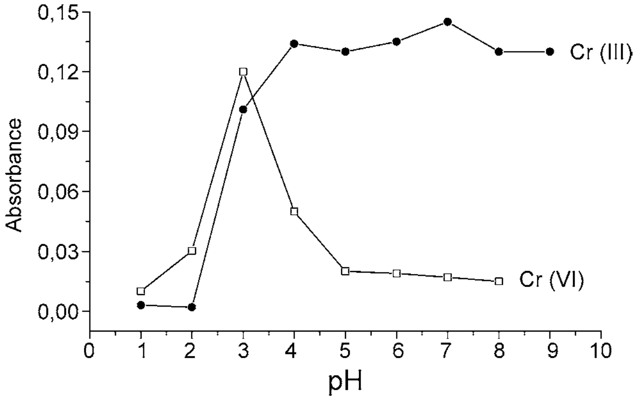

Fig. 2. Effect of sample pH on the peak height absorbance of 100 μg l^{-1} Cr(III) and Cr(VI) using SiO_2–Zr mini-column.

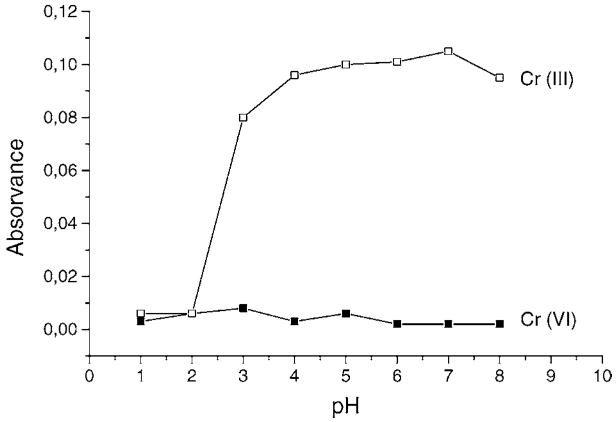

Fig. 3. Effect of sample pH on the peak height absorbance of 100 μg l^{-1} Cr(III) and Cr(VI) using SiO_2–ZrP mini-column.

The effect of the kind and concentration of the eluent for elution of the Cr(VI) from the SiO_2–Zr mini-column and Cr(III) from the SiO_2–ZrP mini-column was studied. The elution of Cr(VI) using 0.1 mol l^{-1} NaOH was not satisfactory because reduction of sensitivity was observed after a few cycles. An attack on the surface was observed by the strong alkali used. This problem was resolved using 0.1 mol l^{-1} (pH 8–9) THAM solution that allowed a quantitative elution of Cr(VI). The elution of Cr(III) was tested using a nitric acid solution with a concentration range of 0.01–2.0 mol l^{-1}. Nitric acid solution with a concentration of 0.1 mol l^{-1} was chosen because it was sufficient for the quantitative recovery of Cr(III) and also the efficiency of the column wash. Under such conditions, the sorption and desorption operations for both chromium species could be repeated many times without any change in the exchange properties of the materials. The influence of the eluent flow rate on the Cr(VI) and Cr(III) desorption from the mini-columns was also studied. This study showed a maximum analytical signal for both metals at a flow rate of 0.53 ml min^{-1}.

The effect of the eluent volume on the Cr(VI) and Cr(III) desorption from the mini-columns was also studied using optimized conditions of extraction for each mini-column. In this study seven eluent fractions of 100 μl were collected separately and injected into the F AAS. For the functioning of this investigation, it was decided to collect 400 μl of eluent corresponding to the fractions 2–5 that represent the richest fraction of eluent. A discrete eluent volume of 100 μl was injected into the F AAS.

The capacity of the SiO_2–Zr and SiO_2–ZrP mini-columns to retain, respectively, Cr(VI) and Cr(III) was also evaluated considering both the aqueous phase volume, which passes through the mini-columns and the amount of the metals that are retained in this process. The effect of the sample volume on the Cr(VI) and Cr(III) extraction was studied by passing various sample volumes (15–200 ml) with the same analyte mass through the mini-columns. The dilution effect was not significant until there was 200 ml for Cr(VI) retention and 100 ml for Cr(III) retention. The maximum amounts of the elements retained in the mini-column were determined by passing growing concentrations of chromium species through the mini-columns. The capacity of retention for both mini-columns was 8.7 μmol g^{-1} for each metal.

3.2. *Influence of foreign ions on the preconcentration of the analytes*

The influence of foreign ions that might be adsorbed in SiO_2–Zr and SiO_2–ZrP was investigated in order to identify potential interferences. This study was carried out individually for each mini-column. Optimized parameters for the preconcentration system and water samples containing 100 μg l^{-1} of chromium were used. The proposed procedure was applied using a sample volume of 15.0 ml, and the maximum concentration of the foreign ions studied was 100 mg l^{-1}. Levels of tolerated concentration (defined as the maximum concentration found to cause a change in signal by less than 10% compared with the signal for analyte alone) of ions were studied. The interferents studied were: Cu(II), Fe(III), Cd(II), Pb(II), Hg(II), Mn(II), Co(II), Ni(II), Zn(II), chloride, nitrate, sulphate, phosphate and permanganate. The results showed that extraction of Cr(VI) using SiO_2–Zr and pH 3 was affected only by the presence of the anion phosphate at a proportion above 1:25 (metal:anion). The high affinity between this anion and the hydrated zirconium(IV) oxide was expected and was described by Boichenova and Tsaihou [24]. The cations used in this study did not interfere with the retention of Cr(VI), except Cr(III) in accordance with Fig. 2. The alkaline and alkaline earth metal ions did not interfere with the extraction of Cr(VI) as described by Vassilera and Furuta [22]. The presence of cations in the proportion above 1:5 decreased the analytical signal for retention of Cr(III) on SiO_2–ZrP. The retention of Cr(III) was not affected by the presence of anions. Therefore, the use of anions to eliminate metal interference could be used, considering either their capacity for complex formation with the interferent species or their precipitation with the foreign metal. Good results were obtained by Matoso et al [19] to reduce the interferent species like Fe(II), Co(II), Ni(II), Zn(II) and Mn(II) ions on the extraction of Cu(II) and Pb(II) when a 0.1 mol l^{-1} NaF solution was used.

3.3. *Analytical features*

The performance of the preconcentration system using the two mini-columns sequentially is shown in Table 2. Calibration curves for each metal were obtained using solutions containing a mixture of Cr(VI) in a concentration range of 0–250 μg l^{-1} and Cr(III) in a concentration range of 250–0 μg l^{-1}. The precision of the proposed method is evaluated as the relative standard deviation for a sample solution containing 100 μg l^{-1} of each metal, when 15.0 ml of sample was preconcentrated (3.75 min of preconcentration time). The limit of detection (LOD) is defined as the concentration of analyte that gives an equivalent response to three times the standard deviation (S.D.) of the blank ($n = 11$) using 3.75 min of preconcentration. The enrichment factor (EF) was calculated as the ratio of the slopes of the calibration curves obtained with and without preconcentration.

3.4. *Application of the proposed procedure to water samples*

The proposed method was applied to the analysis of water collected from a tap, well and lake in the city of Florianópolis, Brazil. The concentration of the analytes in water samples was below the detection limit of the method, as there was no spiking in the samples, the metallic ions could not be detected. In order to evaluate the accuracy of the preconcentration procedure, recovery experiments were carried out with spiked water samples and also by submitting the samples to spectrophotometric method [25] because of certified reference materials for Cr(III) and/or Cr(VI), the species are not available. The water samples were filtered before analysis through a cellulose membrane (Millipore) of 0.45 μm pore size and analyzed as soon as possible after sampling because water samples collected in the field usually are near redox equilibrium with their immediate surroundings. This condition may change significantly after the samples are collected. The water samples were not acidified before storage because this also would change the chemical species. The results of the preconcentration and recovery of the metal ions in water samples using the proposed method and the colorimetric method are shown in Table 3. Each sample was analyzed in

Table 2
Performance data for chromium speciation by sorption on SiO_2–Zr mini-column and SiO_2–ZrP sequentially arranged

Parameter	Cr(VI)/SiO_2–Zr	Cr(III)/SiO_2–ZrP
Working range (μg l^{-1})	25–250	25–250
Calibration curve with preconcentration (μg l^{-1})	−0.00269 + 0.00412[Cr(VI)]	0.0127 + 0.0003922[Cr(III)]
Correlation coefficient	0.9965	0.9944
Calibration curve without preconcentration (mg l^{-1})	0.01277 + 0.1655[Cr(VI)]	0.01036 + 0.01884[Cr(III)]
Correlation coefficient	0.9960	0.9983
Sensitivity (α) (l μg^{-1})	0.00412	3.922×10^{-4}
Enrichment factor	24.9	20.8
Recovery factor	0.98	0.97
Precision ($n = 7$) (%)	2.1	3.0
Detection limit (μg l^{-1}) (3 s)	2.3	1.9

Table 3
Recovery of Cr(III) and Cr(VI) added to water samples using the proposed method and colorimetric method

Sample		Spiked (μg l^{-1})	Recovery (%)	
			Proposed method	Standard method, 1998
Peri lake	Cr(III)	100	97.2 ± 2.0	87.3 ± 1.7
		200	97.0 ± 3.6	84.5 ± 2.0
	Cr(VI)	100	99.0 ± 3.0	90.1 ± 1.5
		200	99.0 ± 1.3	86.0 ± 1.3
Well water	Cr(III)	50	104.0 ± 4.9	84.0 ± 1.2
		100	102.0 ± 1.3	85.9 ± 2.0
	Cr(VI)	50	98.0 ± 2.0	85.6 ± 1.3
		100	98.1 ± 3.0	92.0 ± 1.9
Tap water	Cr(III)	100	104.8 ± 4.0	83.5 ± 1.5
		200	98.8 ± 2.9	92.2 ± 2.0
	Cr(VI)	100	101.0 ± 3.0	69.1 ± 1.2
		200	98.4 ± 2.9	103.3 ± 1.9

triplicate. The results shown in Table 3 demonstrate that the procedure has good accuracy for determination of Cr(VI) and Cr(III).

4. Conclusion

The use of SiO_2–ZrP and SiO_2–Zr mini-columns arranged in sequence can readily be used to determine chromium species from an aqueous solution using a flow preconcentration system. The quickness, with which metals ions are adsorbed, makes these materials potentially useful for analytical purposes. The sorbent packed mini-columns used in the proposed procedure did not show any over-pressuring or swelling. The proposed method presented good sensitivity, precision and accuracy for all analytes analyzed.

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