Cr(III)/Cr(VI) speciation in water samples by extractive separation using Amberlite CG-50 and final determination by FAAS

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A simple and sensitive method has been developed for speciation and preconcentration of trace amounts of Cr(III) and Cr(VI) in water samples using Amberlite CG-50. The Cr(III) content of the sample solutions was sorbed on the resin at pH of 5.5, desorbed by 3% H_2O_2 at pH of 9.5 and then determined by FAAS. After reduction of Cr(VI) to Cr(III) by K_2SO_3 at pH of 3, the total chromium was determined, and the Cr(VI) was obtained by difference. The optimum conditions for reduction and sorption/desorption processes were investigated on several experimental parameters, such as pH of sample and eluent, contact time, the resin quantity, type of the reductant, eluent, and their concentrations. No considerable interferences have been observed due to the presence of a number of anions and cations, which may be found in the natural water samples. The dynamic range for the determination of both Cr(III) and Cr(VI) was found to be 2.0×10^{-7} to 2.0×10^{-6} M. By repeating the treatment (*n*: 7) with the solutions of 1.00×10^{-6} M Cr(III) and the blanks, the relative standard deviation (RSD) and detection limit (DL) were 2.56% and 8.00×10^{-8} M, respectively. This method has been successfully applied for the determination of the chromium species in various natural water samples. The recoveries for the spiked amounts of chromium species to the water samples were found to be more than 95% at the 95% confidence level, which satisfactorily confirmed the reliability of the method.

Keywords: Chromium speciation; Amberlite CG-50; FAAS; Sulfite ion

1. Introduction

Cr(III) and Cr(V1) species enter the environment as a result of effluent discharge from steel works, electroplating, tanning industries, oxidative dyeing, chemical industries, and cooling water towers. The metal may also enter the drinking-water supply systems from the corrosion inhibitors used in water pipes and containers or by contamination of the underground water from sanitary landfill leaching. Despite the fact that Cr(III) is considered as an essential trace element for mammals to be able to maintain glucose, lipid, and protein metabolisms, Cr(V1) is reported to be highly toxic because of its ability to oxidize other species and its adverse impact on lung, liver, and kidney [1, 2].

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Owing to these two contrary effects, the precise determination of both species is essential. The direct determination of chromium species in water samples may not be possible using valence-specific techniques, such as molecular absorption spectrophotometry [3, 4] and voltammetry [5, 6], due to insufficient sensitivity, low concentrations, and matrix interferences. On the other hand, valence-non-specific methods, such as flame or graphite furnace atomic absorption spectrometry (FAAS, GFAAS) [7, 8], inductively coupled plasma atomic emission spectrometry (ICP-AES) [9, 10], inductively coupled plasma atomic mass spectrometry (ICP-MS) [11, 12], and isotope dilution mass spectrometry (IDMS) [13], despite their feasibility to determine the trace or ultra-trace amounts, are not able to detect the chromium species. Thus, in encountering trace or smaller amounts of chromium, speciation studies require either a preliminary valence-specific separation/preconcentration process or selective removal of one of the species from the sample before the determinations. For this purpose, various analytical methods, such as coprecipitation [14–17], liquid–liquid extraction [18–20], solid-phase extraction [21–28], ion exchange [29–31], and chelating resins [32–34], have been developed. Among these methods, the use of conventional ion exchangers has been developed further. One of the important features of conventional ion exchangers is the high capacity factor. For example, a strong acid cation exchanger can be employed to remove heavy metal ions; however, it may also remove innocuous cations, such as sodium, calcium, and magnesium. In such cases, because of the lack of selectivity, the high capacity factor may not be used, effectively. This drawback can be moderately eliminated using weak acid cation-exchange resins, wherein carboxylate groups are linked to a styrenic or ethylenic backbone [35, 36].

Since the solubility and mobility of Cr(VI) are higher than that of Cr(III) species [37], the separation and preconcentration studies have been frequently emphasized on Cr(VI) and conversion of Cr(III) species to Cr(VI) before the determination process. Consequently, in such cases, anion exchangers should be employed. These procedures benefit from appropriate fast kinetic future and precise results; however, the disadvantage of such treatments is conversion of non-toxic Cr(III) to Cr(VI) species, which is in contrast to the environmentally friendly chemistry. In connection with this viewpoint, it is essential to identify redox reactions capable of affecting the oxidation state of chromium in environmental water samples. In particular, the reduction of Cr(VI) to Cr(III), which results in the conversion of a toxic and mobile element into a less toxic and immobile one, is an important step in remediating chromium-contaminated sites. One of the most common methods for this purpose is bioremediation, in which chromate can be reduced under both aerobic [38] and anaerobic conditions [39]. Frequently, natural detoxification via bacterial reduction is unable to fully convert Cr(VI) into non-toxic Cr(III) species, which may be due to the presence of some chromate-resistant bacteria (CRB) in the environmental waters [40]. Thus, much attention should be focused on controlling the loads and concentrations of Cr(VI) discharged into the environment *via* chemical reduction. Recently, it was reported that the sulfite ion is one of the most operative reagents for this purpose [41]. This feasibility is attributed to the high compatibility of reaction products with the environments and rapid completion of the reaction.

The purpose of the current work was to develop a simple environmentally friendly and cost-effective method for chromium speciation studies through the reduction of Cr(VI) to Cr(III) non-toxic species using S(IV). We combined this effective operative procedure with the batch method of separation and preconcentration of Cr(III) species

using Amberlite CG-50 as a well-known weak cation-exchange resin, and a widely used FAAS method of determination in which total chromium has been determined. The concentration of Cr(III) was directly determined without the reduction process, and the Cr(VI) content was obtained by difference. After obtaining the optimum conditions, the procedure developed has been successfully employed for monitoring the Cr(III) and Cr(VI) species in natural water samples.

2. Experimental

2.1 *Instrumentation*

A Shimadzu AA 6300 flame atomic absorption spectrometer equipped with a deuterium arc was used for chromium determination. The operating conditions were as follows: wavelength 357.9 nm, lamp current 8 mA, bandpass 0.5 nm, and fuel flow rate 1.4 L min^{-1}. Deuterium lamp background correction was used. An Istek 915PDC pH meter with a combined glass and Calomel electrode was employed for measuring the pH values.

2.2 *Materials and solutions*

All solutions were prepared by dissolving the required amounts of the reagents in fresh double-distilled water and diluting to the mark. The applied reagents were of analytical reagent grade or better. All chemical reagents together with Amberlite CG-50 (wet mesh size 100–200) were obtained from Merck (Darmstadt, Germany).

The stock solutions of Cr(VI) and Cr(III) were prepared at a concentration of 1.0×10^{-3} M using appropriate amounts of K_2CrO_4 and $Cr(NO_3)_3$, $9H_2O$, respectively. These were used for preparing the working solutions. A series of 1 M buffered solutions were prepared separately and used to adjust the pH of the working solutions. These buffers consist of the solutions: hydrochloric acid–glycine (pH 1–3), acetic acid–sodium acetate (pH 3–6), ammonium acetate–ammonia (pH 6–8), and ammonium nitrate–ammonia (pH 8–9). An eluent-buffered solution containing 3% H_2O_2 was also prepared using the stock solution of H_2O_2 and the ammonium nitrate–ammonia solution. All of the solutions were stored in PTFE bottles and kept in the dark. As a reductant, a solution of 0.1 M of potassium sulfite was daily prepared and kept in stoppered glassware. Amberlite CG-50 resin was used after washing with methanol, 1 M HCl solution, and water, respectively, then dried for 2 h at 60°C.

2.3 *General separation, preconcentration, and determination procedure*

To an aliquot of 500 mL of a solution containing up to 52 µg of chromium, 0.5 g of Amberlite CG-50 resins was added and placed on a magnetic stirrer. By stepwise addition of acetic/acetate solutions, its pH was adjusted to 5.5. To complete the sorption of the Cr(III) contents on the resins, it was stirred for 12 h. The solution was then separated from the resins using a sintered glass filter, and the resins were treated with 10 mL of ammonium/ammonia-buffered solution of pH of 9.5 containing 3% H_2O_2.

After shaking vigorously for 10 min, the eluted solution was filtered and subjected to the atomic absorption burner for measuring the desorbed Cr(III) content. By treating the resins with 10 mL of 0.1 M HCl, it was totally regenerated and could be reused.

To determine the total chromium contents, after adjusting the pH of the solution to 3.0 by dropwise adding 0.5 M nitric acid, 5 mL of the reductant was added, and the mixture stirred for 5 min. The procedure was then followed according to the details in the previous paragraph. The Cr(VI) was calculated by subtracting Cr(III) from the total.

3. Results and discussion

3.1 *Analytical methodology*

To develop a methodology for chromium-speciation studies in aqueous media, the behaviour of Cr(VI) and Cr(III) and the significant differences need to be considered. It was seen that the stability of chromium valences is related to the pH of the solution. The standard reduction potential for the Cr(VI)/Cr(III) redox couple at high pHs is negative [22], which indicates that an alkaline medium favours stabilization of Cr(VI). In acidic media, the standard reduction potential for the Cr(VI)/Cr(III) redox couple is positive [42], which favours Cr(III) stabilization. pH is a very important factor that influences the relative stability of Cr(VI) and Cr(III) species, and any speciation study in acidic media should be essentially directed to Cr(III) species.

The initial experiments showed that the pH of the solutions slightly decreased for the duration of the sorption process. This phenomenon is due to the exchange of acidic protons of carboxylic acidic groups of the resins with the Cr(III) ions. To avoid such a pH decrease, the solutions were initially buffered using the acetic/acetate solutions.

For the treatment with cationic resins, generally the sorption efficiency is enhanced by increasing the pH of the solution containing the metal ions. However, in encountering the Cr(III) species, the sorption process might be hampered at high pHs because of either hydrolysis or conversion of Cr(III) ions to other species. Thus, the sorption process was investigated only at pHs up to 5.50 using aliquots of the solutions (500 mL) containing 1.00×10^{-6} M Cr(III), which was subjected to 0.5 g of the resins. After adjusting the pH of the solution, it was stirred for 12 h and then the amounts of Cr(III) sorbed on the resins were measured by FAAS. As indicated in figure 1, the sorption efficiency was improved by increasing the pH and reached a maximum when the pH was above 4.80. To ensure complete quantitative sorption of the Cr(III) contents, the pHs of the solutions were adjusted to 5.00 before the sorption process in subsequent examinations.

Usually, desorption of the metal ions from the cationic resins can be carried out using acidic reagents with adequate concentrations, such as hydrochloric acid, nitric acid, and so on. However, the total desorption of Cr(III) ions could not be carried out quantitatively, even using various concentrated acidic solutions. For example, the desorption efficiency using 10 mL of 0.1 M nitric acid solution was up to 60%, even after having stirred the resin/eluent for a long time (almost 12 h). This behaviour is attributed to the immobility of Cr(III) ions.
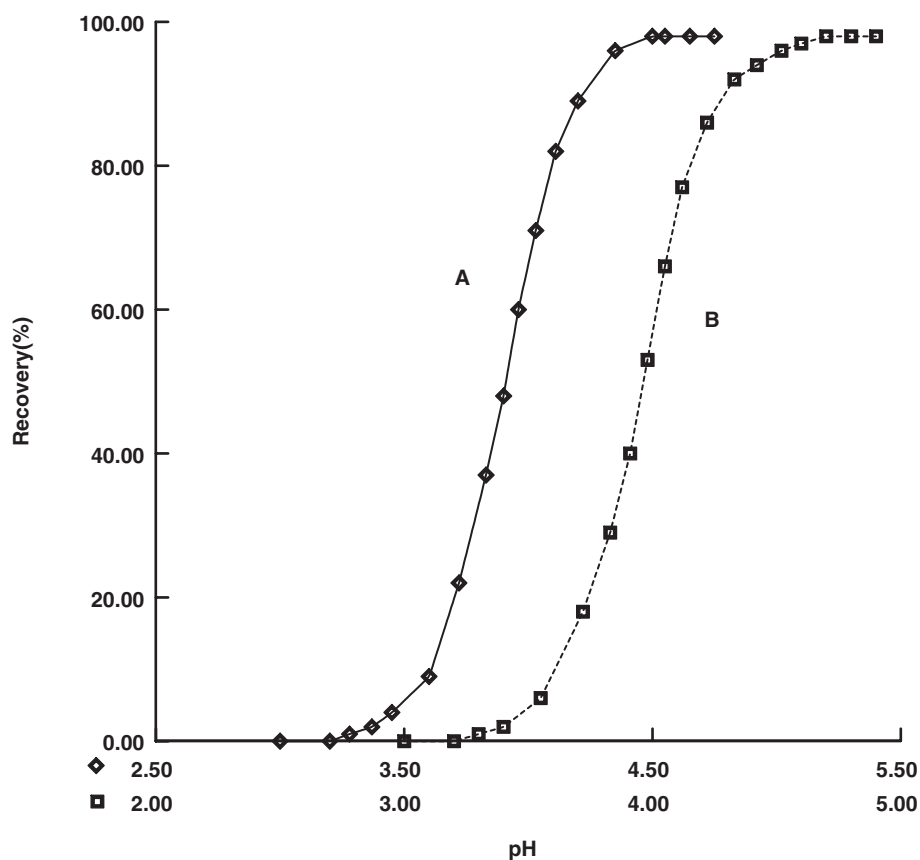
Figure 1. Effect of pH on sorption of Cr(III) species with a concentration of 1.00×10^{-6} M for resins in the absence (a) and presence (b) of Cr(VI) species equal concentrations.

Previously, it was found that the total desorption of Cr(III) ions from resins can be carried out quantitatively using a dilute H_2O_2 solution [43]. This observation is appreciable in view of the selective desorption of Cr(III) ions, so it was established that 10 mL of the 3% H_2O_2 solution is sufficient for eluting the total amount of Cr(III) ions from the resin. Although, desorption was carried out more rapidly by increasing the concentration of H_2O_2, the resin structure was damaged by such treatments.

The interference effect of Cr(VI) on the sorption process was also examined by repeating the sorption process in the presence of Cr(VI) ions with equal concentrations for the Cr(III) species. As shown in curve B in figure 1, the presence of Cr(VI) ions does not so much influence on the sorption process.

3.2 *Effect of contact time on the sorption process*

Figure 2 shows the recoveries obtained due to the sorption of Cr(III) ions on the resin with the initial concentration of 1×10^{-6} M *versus* the contact time. It was found that the sorption is a time-consuming process, having been completed after 12 h.
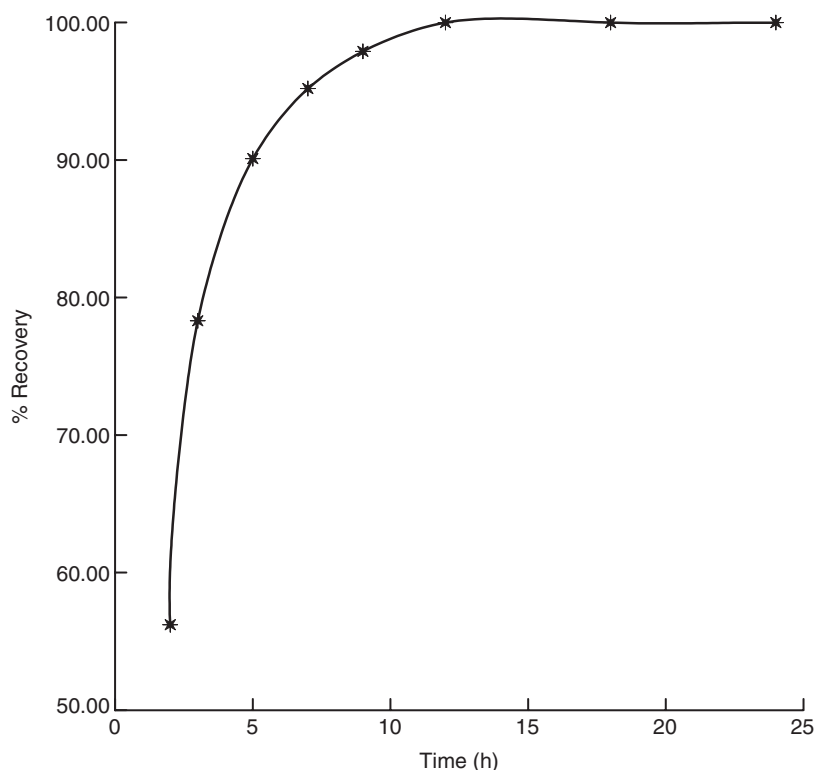
Figure 2. Effect of contact time on the sorption process under conditions in which the initial concentration of Cr(III) species was 1×10^{-6} M, the pH of the solution was adjusted to 5 by the buffering solutions, and the amount of the resins was 0.5 g.

This behaviour arises from the immobility of the Cr(III) ions. The experiments showed that in treatment with concentrations of Cr(III) ions less than the reported lower limit of the dynamic range, the sorption process develops more slowly until completion (typically, 24 h). This kinetic future of the sorption process is one of the important restrictions to decrease the lower limit of the dynamic range.

3.3 Reduction feasibility

According to the following reaction, the reduction of chromate to Cr(III) is affected by both the acidity and the sulfite concentration of the solution:

$$2CrO_4^{2-} + 3SO_3^{2-} + 10H^+ \rightarrow 2Cr^{3+} + 3SO_4^{2-} + 5H_2O.$$
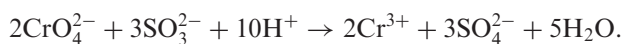
To determine the optimum conditions for quantitative reduction of Cr(VI) species, triplicate examinations were carried out in which the concentrations of chromate were 2.0×10^{-6} M, the initial concentrations of sulfite in each series were fixed to 1.0×10^{-5}, 5.0×10^{-5}, and 1.0×10^{-4} M, respectively, while the pHs of each series of the solutions were adjusted arbitrarily in the range of 2.00–8.50 using the appropriate buffer solutions. After 30 min, the reduced fraction of the Cr(VI) species was measured by following the procedure in the first paragraph of section 2.3, and the residual percentage
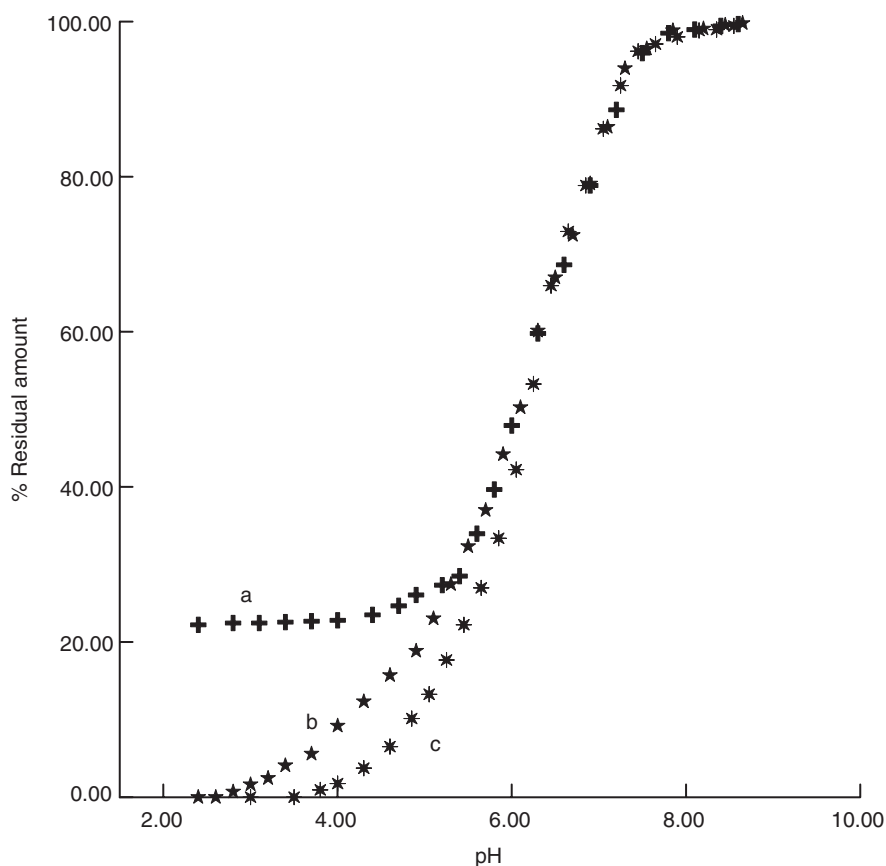
Figure 3.   Effect of sulfite concentration on reduction of Cr(VI) species at different pH values. The sorption process was carried out under optimal conditions in which the initial concentration of sulfite was (a) 1.0×10^{-5}, (b) 5.0×10^{-5}, and (c) 1.0×10^{-4} M.

of Cr(VI) species was determined in each of the solutions by subtracting the measured amount from the initial contents. As shown in figure 3, the reduction process is controlled by either the pH or sulfite concentration as the reduction process is completed at pHs below 4 and in the presence of excess sulfite ions. Hence, the solution was buffered at pH 3 using acetic/acetate solutions, and the initial concentration of sulfite was 1.0×10^{-4} M.

3.4 *Effect of resin dosage on sorption*

The dependence of Cr(III) sorption on the resin dosage was studied using aliquots of 500 mL of 2×10^{-6} M Cr(III) solution at a pH of 4 and temperature of 25°C by varying the amount of Amberlite CG-50 over the range of 0.05–0.5 g. It was found that the sorption of Cr(III) approached 100% when the amount of wet resin was above 0.5 g. Thus, this amount was subsequently used in the future experiments.

3.5 *Effect of sample volume on sorption*

For treatment with real samples, the maximum applicable sample volume must be determined. For this purpose, 50, 100, 150, 250, 500, 750, and 1000 mL of solutions containing 1.8×10^{-6} mol of Cr(III) and 1.2×10^{-6} mol of Cr(VI) were examined by replicating the experiments under the optimal conditions. It was established that the recovery is satisfactory and does not depend on the sample volume up to 500 mL. However, by increasing the volume above 500 mL, the recovery was decreased rapidly (55% for 750 mL and 42% for 1000 mL). Furthermore, the reproducibility was improved by increasing the volumes up to 500 mL and diminished afterwards. In such a manner, the highest preconcentration factor should be 50 as the eluate volume was 10 mL.

3.6 *Analytical figures of merit*

Under optimal conditions, the procedure was performed successively (six different concentrations), and Cr(III) was determined in the eluate by FAAS. A linear calibration curve was constructed as: $A = 2.00 \times 10^5 C - 0.0011$, where A is the absorbance; C is the concentration of Cr(III); M is the correlation coefficient (r^2): 0.9984; and the dynamic range is 2.00×10^{-7} to 2.00×10^{-6} M. The slopes of the calibration graph prepared by the standard curve method were found to be almost identical to those of the standard addition plot using the water samples. Hence, the standard curve method was used in the determination of various samples. For the treatment with solutions of 1.00×10^{-6} M of Cr(III), the mean recovery for seven determinations was $99.7 \pm 0.7\%$ at the 95% confidence level. The RSD obtained from these treatments was 2.56%. The detection limit was 8.00×10^{-8} M, which was determined as the concentration corresponding to three times the standard deviation of the blank signal (n:7) using 500 mL aliquots for the blank. The linear range, RSD, and detection limit for both Cr(III) and Cr(VI) were identical.

A linear calibration curve was also obtained as: $A = 4.127 \times 10^3 C + 0.005$, for the direct determination of Cr(III) over the range of 1.00×10^{-5} to 1.20×10^{-4} M, with the correlation coefficient of 0.9995. Generally, the experimental preconcentration factor is defined as the ratio of the slopes of the calibration graphs obtained with and without the preconcentration process [44], while the theoretical value is considered as the ratio of sample and eluate volumes. These values were found to be 48.46 and 50, respectively. A Student t-test at the 95% confidence limit showed that the difference was not statistically significant. Thus, the overall method recovery, which is defined as the experimental/theoretical ratio of the preconcentration factor was found to be 96.9%.

3.7 *Effect of foreign ions*

The effect of various ions that may be found in the environmental water samples was investigated in the determination of Cr(III) species. For this purpose, various metal ions with different concentrations were added individually to spiked solution (500 mL, both Cr(III) and Cr(VI) with a concentration of 1.0×10^{-6} M), and the general procedure was applied. Each of these ions was considered as an interfering agent, when the

Table 1. Tolerance ratio of foreign ions on the determination of Cr(III) and Cr(VI) with equal concentrations of 1.0×10^{-6} M in 500-mL aliquots of solutions.

Foreign ion	Tolerance ratio	Recovery[a] (%) $R \pm s$	
		Cr(III)	Cr(VI)
Al^{3+}	2000	96.0 ± 1.6	95.8 ± 1.8
Ca^{2+}	2000	98.2 ± 1.4	97.4 ± 1.5
Cd^{2+}	2000	97.3 ± 1.6	98.2 ± 1.8
Co^{2+}	2000	96.3 ± 1.7	95.7 ± 1.9
Mg^{2+}	2000	98.7 ± 1.3	96.8 ± 1.8
Mn^{2+}	2000	95.4 ± 2.1	97.2 ± 1.1
Ni^{2+}	2000	96.8 ± 1.4	95.9 ± 1.9
Pb^{2+}	2000	97.5 ± 2.1	98.2 ± 2.7
Zn^{2+}	2000	98.1 ± 1.8	96.5 ± 1.4
Cu^{2+}	1000	95.8 ± 1.2	98.1 ± 1.8
Fe^{3+}	100[b]	98.2 ± 1.7	96.3 ± 2.7
Fe^{2+}	2000[c]	97.8 ± 1.9	–
Fe^{2+}	10	98.2 ± 1.8	95.7 ± 1.8
Cl^-	2000	97.3 ± 2.1	98.4 ± 2.5
NO_3^-	2000	97.7 ± 1.8	96.9 ± 1.2
HCO_3^-	2000	95.8 ± 1.5	97.5 ± 1.8
SO_4^{2-}	2000	96.1 ± 2.2	98.3 ± 1.9

[a]Average and standard deviation of three determinations.
[b]Precipitated at a concentration higher than this value.
[c]Analysis carried out in the absence of Cr(VI) species.

recovery exhibited a deviation above $\pm 5\%$. It was found that alkali and alkaline earth elements are not interfered with, even at moderately large concentrations. Table 1 lists the foreign ions and the concentration ratio at which they were tolerated. As is shown, almost all of the cations and anions were not interfered with, even at high, considerably foreign ion/Cr(III) ratios. Only ferrous ions were found to interfere on Cr(VI) determination, which is attributed to reduction of Cr(IV) to Cr(III) by Fe^{2+} ions so that no Cr(VI) could be detected. Fortunately, in encountering the real samples, the concentrations of both Fe^{2+} and Fe^{3+} species are far too low for these to be considered a serious interfering agent.

3.8 *Application to real samples*

The proposed method was applied to speciation monitoring of Cr(VI) and Cr(III) in tap water and well water samples collected from Birjand and its water sources. The water samples were filtered through a membrane filter with a pore size of 0.45 μm before determination. The accuracy of the determinations was investigated by spiking water samples with Cr(III) and Cr(VI) ions at various concentrations. The results obtained are summarized in table 2. As can be seen from the results, the recoveries for the spiked amounts of chromium species were found to be 97.0–104.4%, which confirmed the accuracy at the 95% confidence level. The validity of the method was checked using a synthetic seawater sample, which was prepared according to the literature [45] as shown in table 3. The recoveries of Cr(III) and Cr(VI) spiked to the sample ranged from 95.2% to 104.6% and were in very good agreement.

Table 2. Determination of Cr(III) and Cr(VI) in 500-mL aliquots of samples.

Sample	Spiked (µg)		Found[a] (µg) $F \pm s$		Recovery (%) $R \pm s$	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
Drinking water	50	50	49.2 ± 0.8	47.5 ± 2.4	98.4 ± 1.6	97.0 ± 2.4
	100	100	98.3 ± 1.4	97.5 ± 1.7	98.3 ± 1.4	97.5 ± 1.7
Tap water	–	–	75.0 ± 0.4	24.2 ± 0.6	–	–
	50	50	123.2 ± 0.6	72.0 ± 0.7	98.6 ± 1.2	97.0 ± 0.4
Well water	–	–	110.8 ± 0.5	–	–	–
	50	50	156.7 ± 0.6	52.3 ± 0.5	97.4 ± 0.5	104.6 ± 1.2
Syn. seawater	50	50	47.8 ± 0.9	52.5 ± 1.5	95.6 ± 1.8	105.0 ± 3.0
	100	100	102.3 ± 0.5	97.8 ± 0.7	102.3 ± 0.5	97.8 ± 0.7

[a]Average and standard deviation of three determinations.

Table 3. Composition of the synthetic seawater sample containing major inorganic chemical constituents [45].

Component	Concentration (mg kg^{-1})
Sodium	10,760
Magnesium	1294
Calcium	413
Potasium	387
Strontium	8
Chloride	19,353
Sulfate	2712
Hydrogen carbonate	142
Bromide	67
Boron	4
Fluoride	1

4. Conclusion

In this work, a new approach has been described for chromium speciation in which a reducing agent such as the sulfite ion has been used to convert Cr(VI) to non-toxic species of Cr(III) in moderately weak acidic media. The procedure has been demonstrated as a selective method for sorption/desorption of Cr(III) species using a well known weak cation-exchange resin, such as Amberlite CG-50 with a high efficiency and combined with the widely used FAAS method of determination. The proposed method has been successfully applied to real water samples with adequate precision and accuracy. Although the procedure is time-consuming in comparison with conventional extraction methods, it has several environmentally friendly advantages; for example no pollutant reagents are needed, and the resin can be regenerated without the need for any toxic agents. Hence, in view of the green chemistry approach, it is environmentally friendly and does not create any severe environmental problems.

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