

Determination of total chromium by flame atomic absorption spectrometry after coprecipitation by cerium (IV) hydroxide

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Received: 7 August 2006 / Accepted: 11 April 2007 / Published online: 12 June 2007
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Abstract A method for the preconcentration of the total chromium based on coprecipitation with cerium (IV) hydroxide is proposed for determination of chromium by flame atomic absorption spectrometry. Different factors including carrier element amount, pH, sample volume and matrix ion effects for the precipitation were examined. The detection limit of the total chromium ($k=3$, $N=15$) was $0.18 \mu\text{g l}^{-1}$. The presented method was applied for the determination of chromium in the wastewater samples from Kayseri and Nigde Organized Industrial Region-Turkey and in drinking water from our laboratory, Kayseri with satisfactory results (relative standard deviations below 8%, recoveries 95%). The analytical results obtained by the proposed method for certified copper sample was in good agreement with the certified value.

Keywords Cerium (IV) hydroxide · Coprecipitation · Flame atomic absorption spectrometry · Total chromium · Wastewater

Introduction

Chromium is widely used in various industries, such as steel, electroplating, tanning, paint and pigment production, and metallurgy, which possibly contaminate the environment. The contamination of chromium is mostly observed in wastewater. Chromium at trace levels may also enter in drinking water supply systems. Chromium exists in the contaminated water samples as chromium (III) and chromium (VI) oxidation states having different chemical and biological properties. Chromium (III) is essential for the organism, but chromium(VI) has toxic and carcinogenic effects (Berman 1980; Florence 1982; Zhitkovich 2005; Hosseini and Sarab 2007).

The allowable concentration of chromium by the United State Environmental Protection Agency (US-EPA) is limited to $100 \mu\text{g l}^{-1}$ in drinking water. In Japan, the maximum tolerable concentration of chromium in wastewater is $500 \mu\text{g l}^{-1}$ and $50 \mu\text{g l}^{-1}$ for total chromium and chromium(VI), respectively. The European Community Directive for drinking water standards has put the limit of total chromium not exceeding $50 \mu\text{g l}^{-1}$ (Narin et al. 2006). Therefore, the total chromium content is not an important criterion

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only for the control of industrial wastewaters, but also for the evaluating of pollution level of natural waters such as drinking, sea and river waters (Barrera et al. 1998; Boughriet et al. 1994; Marques et al. 2000; Gardner and Ravenscroft 1996; Wattoo et al. 2006). The low level of chromium given above is under the detection limit of flame atomic absorption spectrometry (FAAS). Thus, preconcentration-separation is frequently required in order to improve the detection capability of preconcentration technique.

The preconcentration and separation methods including solvent extraction, solid phase extraction, electrophoresis and coprecipitation have been used prior to instrumental determination of heavy metal ions (Efendioglu et al. 2007; Suleiman et al. 2007; Dogru et al. 2007; Li et al. 2007). Among these preconcentration methods, coprecipitation of chromium species with metal hydroxides such as gallium (Boughriet et al. 1994); ferric (Nakayama et al. 1981); hafnium (Ueda et al. 1997); indium (Hiraide et al. 1997); samarium (Saracoglu et al. 2003); cerium (Divrikli and Elci 2002) and erbium (Soylak et al. 2005) hydroxides is often chosen because of minimum contamination risk and relatively easy.

The aim of the present work is to show the performance of the cerium (IV) hydroxide coprecipitation procedure for preconcentration and separation of total chromium as chromium (III) plus chromium (VI) from natural water samples, without the use of any reduction or complexing reagent.

Experimental

Instruments

A Perkin Elmer Model 3110 atomic absorption spectrometer was used for the absorbance measurements. The instrument settings were shown in Table 1. The sample solutions as 100 μl were introduced into the nebulizer using an injection technique (Berndt and Jackwerth 1975). Nel 900 model pH-meter in combination with a glass-electrode was employed to adjust the pH of the model solution and the water samples.

Reagents and solutions

Analytical reagent grade chemicals were employed for the preparation of all solutions. Freshly prepared

Table 1 FAAS analytical conditions for chromium

Absorption line (nm)	Lamp current (mA)	Slit (nm)	Burner height (mm)	Air (l min^{-1})	C_2H_2 (l min^{-1})
357.9	15	0.7	7.5	9.5	2.3

double distilled water was used in all experiments. A stock standard solution of 1,000 mg l^{-1} Cr (III) was prepared from 7.6960 g chromium nitrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$, Merck, Darmstadt, Germany) dissolved in double distilled water and diluted to a final volume of 1,000 ml. A stock standard solution of 1,000 mg l^{-1} Cr (VI) was prepared from 2.8290 g potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$, Merck, Darmstadt, Germany) dissolved in double distilled water and diluted to a final volume of 1,000 ml.

A cerium (IV) solution (1 mg ml^{-1}) was freshly prepared by dissolving the requisite amounts of $\text{Ce}(\text{SO}_4)_4 \cdot 4 \text{H}_2\text{O}$ (E.Merck, Darmstadt, No: T61454) in small amounts of nitric acid and diluting to 100 ml with double distilled water. Ammonia solution (6 mol l^{-1}) was prepared in water from ammonia (E.Merck, Darmstadt) and used for pH adjustment. The cellulose nitrate membrane filters were purchased from Sartorius ($0.45 \mu\text{m}$ pore size, 47 mm diameter). The standard reference materials used in experimental studies were certified copper sample (CRM Cu 1/3 alloy – China).

Sampling

The wastewater samples were collected in pre-washed-cleaned polyethylene bottles from Kayseri and Nigde Organized Industrial Regions-Turkey. The collected water samples were filtered through $0.45 \mu\text{m}$ pore size cellulose nitrate membrane filters immediately after sampling. The samples were stored in a polyethylene (PE) bottle at 4°C in a refrigerator, prior to use.

Preconcentration procedure

A 50 ml of model solution containing $10 \mu\text{g}$ Cr (III) and/or $10 \mu\text{g}$ Cr (VI) was prepared. 9 mg of cerium (IV) as cerium (IV) sulfate was added to this solution and the pH of solution was adjusted to desirable pH over the range of 2–11, using 6 mol l^{-1} ammonia

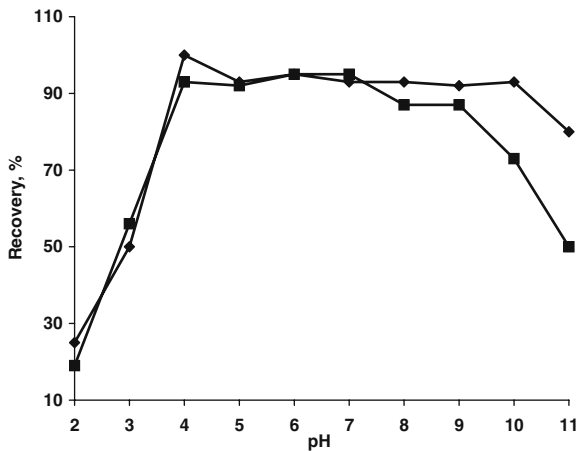


Fig. 1 Dependence of Cr(III) (—◆—) and Cr(VI) (—■—) coprecipitations on pH of solutions (Amount of cerium (IV) : 9 mg, N:3)

solution. The formed precipitate, $Ce(OH)_4$, was settled for 20 min then, it was filtered by suction using a cellulose nitrate membrane filter from Sartorius, 0.45 μm pore size, 47 mm diameter. The membrane loaded with the precipitate was dissolved with 1 ml of concentrated HNO_3 and the solution was diluted to 2 ml with 1 mol l^{-1} HNO_3 . Then, to determine the chromium in the concentrated solutions for the samples, an aliquot 100 μl of the solution was introduced to the nebulizer of the flame atomic absorption spectrometer by micro injection method.

Procedure for the certified copper CRM sample

For copper analysis, a portion (0.04 g) of the certified copper sample (CRM Cu 1/3 Cu alloy from China)

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Table 2 Tolerable levels of some ions on proposed coprecipitation procedure (Sample volume: 50 ml, total chromium: 10 μg , N=3)

Ions	Added as	Tolerable concentration, mg l^{-1}	Concentration in the effluent, mg l^{-1}
Na^+	NaCl	50,000	118
Cl^-	NaCl	50,000	BDL
K^+	KCl	2,500	919
Ca^{2+}	$CaCl_2$	1,000	95
Mg^{2+}	$MgCl_2$	2,500	342
SO_4^{2-}	Na_2SO_4	320	BDL
Cu^{2+}	$Cu(NO_3)_2$	800	50
Ni^{2+}	$Ni(NO_3)_2$	250	24
Co^{2+}	$Co(NO_3)_2$	250	44
Pb^{2+}	$Pb(NO_3)_2$	250	17
Zn^{2+}	$Zn(NO_3)_2$	250	44
Fe^{3+}	$Fe(NO_3)_3$	200	169
Fe^{2+}	$FeSO_4$	250	98

BDL Below the detection limit

as accurately weighed into a 50 ml beaker and 0.5 ml of concentrated nitric acid was added to the sample. The beaker was covered with a watch-glass and the mixture was evaporated on a hot plate about 95°C almost to dryness. Then the solution was cooled and diluted to 10 ml with distilled water. Finally, the preconcentration procedure given above was applied to the final diluted solution. The same procedure was applied to the blank solution.

Analysis of water samples

To apply the examined method, 9 mg of Ce (IV) carrier element was added to 400 ml portion of wastewater or drinking water samples and pH of the solution was adjusted to about 6 for coprecipitation of Cr (III) and Cr (VI). Then the procedure given above was followed. The total chromium in the final solutions was determined by flame atomic absorption spectrometry.

Results and discussion

Effect of pH

The most important parameter is pH to obtain the quantitative recoveries in the preconcentration with coprecipitation. Because, the chemical forms of analyte and the quality of coprecipitation depend on pH of sample solution. Therefore, pH was firstly optimized. The coprecipitation of chromium (III) and chromium (VI) with cerium (IV) hydroxide was

Table 3 Analysis of drinking water samples spiked total chromium (Sample volume: 50 ml, Final volume: 2 ml, *N*:3)

Sample	Added (μg)	Found (μg)	Recovery (%)
Drinking water	0	BDL	–
	3	2.85	95 \pm 2
	6	5.89	98 \pm 2
	12	11.60	97 \pm 1
Waste water	0	0.24	–
	3	3.39	105 \pm 3
	6	5.96	95 \pm 2
	12	12.00	98 \pm 1

BDL Below the detection limit

investigated in the pH range of 2–11. Figure 1 shows that chromium (III) and chromium (VI) were coprecipitated quantitatively in the pH range of 4–10 and in the range pH 4–7, respectively. Considering these results, the selected pH was 6.0 for the total chromium in all further experiments.

Adsorption mechanism

In the pH range that chromium (VI) is quantitatively coprecipitated; pH 4–7, there is equilibrium between H_2CrO_4 and HCrO_4^- as dominant species in aqueous solutions (Kotas and Stasicka 2000). For this reason, probably, Cr (VI) as H_2CrO_4 and/or HCrO_4^- forms may be coprecipitated by cerium (IV) hydroxide. Cr (III) in the presence of Ce (IV) can be oxidized to Cr (VI) as depending on their redox potentials (Skoog et al. 1996). However, Cr (III) ions are strongly hydrated and most stable in range of pH 4–9 (Kotas and Stasicka 2000). Moreover, aqua/hydroxo Cr (III) complexes have a strong tendency to be adsorbed by solids. On the other hand, it is known that both Cr (III) and Cr(VI) can strongly sorb to iron hydroxide solids from water samples (Parks et al. 2004). On basing these knowledges, it may be concluded that Cr (III) as Cr (VI) and/or hydrated Cr (III) species may be also coprecipitated by cerium (IV) hydroxide under the experimental conditions. Yet, these ideas have been not investigated as experimental in detail.

Effect of cerium (IV) amounts on recovery of chromium

The amount of cerium (IV) as sulfate was examined for the quantitative coprecipitation of the chromium ions with cerium (IV) hydroxide in the range of 0–12 mg cerium (IV). Without any cerium (III), the recovery of chromium was 43% under the working conditions.

Until 9 mg of Ce (IV), the recoveries were under 95%. The quantitative recoveries, $\geq 95\%$ for Cr (III) and Cr (VI) ions were obtained in the range of 9–12 mg cerium. Therefore, in the following works, 9 mg of cerium was used for the coprecipitation.

Effect of sample volume on recovery of chromium

The influences of the sample volume were examined to obtain high preconcentration factor, as a function of the volume of sample solution containing chromium species at constant amount such as 5 μg for each of Cr (III) and Cr (VI) in the range of 50–800 ml. The results indicated that recoveries of chromium were quantitative up to 400 ml of sample volume. After 400 ml, the coprecipitation for chromium was not quantitative. Highest preconcentration factor was 200, when the final volume was 2 mL.

Effect of amount of chromium on recovery of chromium

The influence of the amounts of the chromium species for the quantitative recoveries was also investigated. For this purpose, the proposed procedure was applied to 50 ml solution containing equal amounts of the

Table 4 Concentrations of total chromium in water samples (Sample volume: 400 ml, Final volume: 2 ml, *N*: 5)

Samples	Chromium concentration ($\mu\text{g l}^{-1}$)
Drinking water (Erciyes Uni.)	BDL
Waste water (Kayseri)	4.90 \pm 0.49
Waste water (Nigde)	3.53 \pm 0.07

Mean expressed as 95% tolerance limit

both chromium species at various levels. Quantitative recoveries were obtained from 2 to 400 µg of total chromium, with equal amounts of Cr (III) and Cr (VI). After 400 µg of total chromium, the coprecipitation efficiency was not quantitative.

Effect of matrix ions

To assess the possible analytical applications of the proposed procedure, the effect of some foreign ions which interfere with the determination of metal ions by flame atomic absorption spectrometry or/and often accompany analyte ions in various water real samples was examined. The results were given in Table 2. The tolerance limit of foreign ions was considered as the ion concentration causing a relative error smaller than ±5% related to the preconcentration and determination of the chromium ion. As it is seen, large numbers of ions used have no considerable effect on the determination of total chromium. The concentrations of these ions in the analysed water samples were found lower than that of their tolerance limits on the recovery of chromium.

Figure of merits

The limit of detection (LOD) of the proposed method was studied by applying the procedure for blank solutions. The detection limit based on three times the standard deviations of the blank for flame atomic absorption spectrometric measurements for total chromium was found as 0.18 µg l⁻¹.

The analytical performance of coprecipitation with cerium (IV) hydroxide-flame atomic absorption spectrometry system was also considered. To validate the present method, the recovery of chromium spiked into analyzing wastewater and drinking water from Kayseri was studied, satisfactory results were obtained as shown in Table 3. The quantitative recovery values

confirm the accuracy of the procedure and the absence of matrix effects. The preconcentration factor was 200.

The precision of the coprecipitation procedure was evaluated as the relative standard deviation (RSD) obtained after replicate analyses of wastewater samples. The relative standard deviation was between 1.6 and 8.0% (Table 4). The analytical figures given above for the proposed coprecipitation of chromium are better or comparable with the data from some recent studies on determination of chromium species given in the literature (Narin et al. 2006).

Application to the real samples

The method with the characteristic performance data given above was successfully applied to the determination of total chromium in two industrial wastewater samples from the metal plants in the industrial organized region of Kayseri and Nigde-Turkey. The presented method was also applied to a drinking water samples taken from Erciyes University. The results are given in Table 4.

The accuracy of the proposed cerium (IV) hydroxide with coprecipitation method was examined by determination of total chromium in certified copper sample from China. The results are given in Table 5. The relative error for the recommended procedure is -7.7%. The relative standard deviation was 2.8% for the analysis of the certified sample. These analytical parameters are satisfactory for many purposes.

Conclusion

The combination of coprecipitation with cerium (IV) hydroxide and FAAS has been evaluated and demonstrated to be a promising for determination of total chromium at low levels in wastewater, drinking water and certified samples. The procedure is easy and fast. The proposed coprecipitation has shown adequate accuracy and precision, besides being simple and economical for preconcentration of total chromium without to use a complexing reagent.

Acknowledgements The authors wish to express thanks to the Unit of the Scientific Research Project of Erciyes University (Kayseri-Turkey) for the financial support for this study. Also, the authors would like to thank the Scientific and Technological Research Council of Turkey (TUBITAK) for providing Perkin-Elmer 3110 atomic absorption spectrometer used in the present study.

Table 5 Results of the analysis of standard reference materials (CRM Cu I/III), (N: 7)

Element	Concentration (w/w) %	
	Certified value	Observed value
Cr	2.20×10^{-2}	$(2.03 \pm 0.01) \times 10^{-2}$

Mean expressed as 95% tolerance limit

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