



Development of a coprecipitation system for the speciation/preconcentration of chromium in tap waters

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ABSTRACT

A method for the speciation of chromium(III), chromium(VI) and determination of total chromium based on coprecipitation of chromium(III) with dysprosium hydroxide has been investigated and applied to tap water samples. Chromium(III) was quantitatively recovered by the presented method, while the recovery values for chromium(VI) was below 10%. The influences of analytical parameters including amount of dysprosium(III), pH, centrifugation speed and sample volume for the quantitative precipitation were examined. No interferences were observed from alkali, earth alkali and some transition metals for the analyte ions. The detection limits ($k = 3$, $N = 15$) were $0.65 \mu\text{g/L}$ for chromium(III) and $0.78 \mu\text{g/L}$ for chromium(VI). The validation of the presented method was checked by the analysis of certified reference materials.

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1. Introduction

Chromium (Cr) is the seventh most abundant element on earth [1]. Chromium is widely used in a number of industrial processes, such as Cr plating, leather tanning, or wood preservation. Chromium can exist in different oxidation states (e.g. 0, +III, +VI). Chromium can be both beneficial and toxic to animals and humans depending on its oxidation state and concentration [2–4]. At low concentration, chromium(III) is essential for animal and human health. Chromium(VI) compounds are highly soluble, mobile and bioavailable compared with chromium(III) species. Chromium(VI) is dangerous for humans due to its toxicity and carcinogenic properties [2,5,6].

A lot of methods have been given in the literature relevant to the determination and speciation of chromium(III) and chromium(VI) species [3,7,8]. Mainly selective techniques for the speciation and determination of chromium are: coprecipitation, liquid–liquid extraction, electrodeposition or solid phase extraction followed by instrumental analysis. Low chromium levels are usually determined by separation of one specific form, the second form is then determined, after it has been reduced or oxidized, as the resid-

ual chromium content in the solution. In recent years, several methods of preconcentration and separation of chromium(III) and chromium(VI) have been developed [9–16]. Instrumental analysis methods including atomic absorption spectrometry and inductively coupled plasma mass spectrometry always request previous steps of several separation–preconcentration procedures including solid phase extraction, ion exchange, cloud point extraction have been performed as separation technique [17–21].

Coprecipitation has been also widely used for preconcentration – separation studies for heavy metals, due to its several advantages: simple, fast, high preconcentration factor, etc. Heavy metals are coprecipitated by inorganic or organic precipitants, environmentally and by a carrier element. As an inorganic precipitant, hydroxides are an important place in the enrichment–separation studies. Coprecipitation by hydroxide of various metal ions including magnesium [22–24], indium [25,26], terbium [27], europium [28], ytterbium [29,30], erbium [31], gallium [32], and hafnium [33] as carrier element has been reported for the preconcentration – separation of trace elements from various media.

Dysprosium hydroxide [34] was also used as coprecipitant for various metal ions at trace level in environmental samples by our working group. Solubility product of dysprosium hydroxide is $K_{sp} 1.4 \times 10^{-22}$ [35]. It is firstly used for the speciation of chromium species in the presented work prior to flame atomic absorption spectrometric determinations. The proposed method was validated by certified reference material and applied successfully on tap waters.

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2. Experimental

2.1. Instruments

The determination of chromium was performed by using a PerkinElmer, Model 3110 atomic absorption spectrometer (Norwalk, CT, USA) with an air/acetylene burner. Measurement of pH of aqueous solutions was performed by a pH-meter (Model 672, Jenco Instruments, Inc., USA).

2.2. Reagents and solution

All reagents and solvents were of analytical grade. The water used in all experiments was purified in a Human model RO 180, resulting water with a conductivity of $1 \mu\text{S cm}^{-1}$. A stock solution of 1000 mg/L chromium(VI) was prepared by dissolving 2.8316 g $\text{K}_2\text{Cr}_2\text{O}_7$ (Merck, Darmstadt, Germany) in about 200 mL distilled deionized water and diluted to 1000 mL with dilute HNO_3 to be its final concentration of 1 mol/L. A stock solution of 1000 mg/L chromium(III) was prepared from 7.6967 g chromium(III) nitrate [$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] (Merck), by dissolving in about 200 mL distilled deionized water and completed to 1000 mL with dilute HNO_3 to be its final concentration of 1 mol/L.

A solution of 0.1% Dy_2O_3 was prepared by dissolving 0.1 g of Dy_2O_3 (Merck) in distilled deionized water and diluted to 100 mL. A stock solution of 0.5% KI was prepared by dissolving 0.1 g of KI (Merck) in distilled deionized water and diluted to 100 mL. In order to filter the coprecipitated samples, the membrane filters having 0.45 μm pore size and a 47 mm diameter (Advantec MFS, Inc., USA) were used with combination of a vacuum filter holder (Schleicher & Schuell, Dassel, Germany).

2.3. Separation and preconcentration procedure for chromium(III) and total chromium

In order to optimize the separation and preconcentration technique, 25 mL of model solutions including 25 μg of chromium(III) and 1000 μL of 0.1% Dy_2O_3 were used. Then, pH of these solutions was adjusted to the optimum value (pH 12) by using 1 M NaOH solution. The solutions were centrifuged for 20 min at 3000 rpm. The precipitate was dissolved by 0.5 mL of 1 M HNO_3 and diluted to 10 mL by distilled deionized water and chromium(III) content was determined by flame AAS.

For total chromium 25 mL of model solutions containing 25 μg chromium(VI) were prepared and their pHs were adjusted to pH 1.0 using 2 M H_2SO_4 solution. 10 mL of 5% KI solution was added and heated for 30 min at 100 °C. After cooling the solution to the room temperature 1000 μL of 0.1% Dy_2O_3 was added and the pH is adjusted to pH 12 by using 1 M NaOH solution. The solutions were centrifuged for 20 min at 3000 rpm. The precipitate was dissolved by 0.5 mL of 1 M HNO_3 and diluted to 10 mL by distilled deionized water and chromium(III) content was determined by flame AAS.

2.4. Applications

Certified reference materials (GBW 07309 Stream Sediment, NIST 2710 Montana Soil, GBW 07402 Soil) weighed 100 mg directly in the Teflon beaker and treated with 10 mL of aqua regia to decompose the matrix. The digested solution heated at 120 °C to evaporate extra acid to nearly dryness. This process repeated twice and 5 mL of HF was added to the residue and heated again nearly dryness. 10 mL of distilled water was added to the residue and the suspension was filtered through a blue band filter paper, and the insoluble part was washed with distilled water. The preconcentration procedure given above was applied to the final

solutions after adjusting the pH to 12 by using 1 M NaOH solution.

The water samples analyzed were collected in pre-washed (with detergent, distilled deionized water, dilute HNO_3 and distilled deionized water, respectively) polyethylene bottles. The samples were filtered through a Millipore cellulose membrane of pore size 0.45 μm . The samples were stored in 1 l polyethylene bottles and acidified to 1% with nitric acid and were subsequently stored at 4 °C in a refrigerator. Before the analysis, the pHs of the samples were adjusted to 12 by using 1 M NaOH solution. The preconcentration procedure given above was applied to the final solutions.

3. Results and discussion

In the determination of chromium(III) and chromium(VI) via speciation by coprecipitation, the influences of some analytical parameters on the recovery were investigated. These parameters are pH of sample solution, dysprosium amount, sample volume, centrifuge speed and time, effect of matrix ions.

3.1. Effect of pH

The effect of pH on the quantitative recovery of chromium(III) and chromium(VI) species over the pH range of 8.0 to 12.0 have been investigated. The results acquired for chromium(III) and chromium(VI) are graphically depicted in Fig. 1. The chromium(III) was quantitatively recovered by the presented method at the pH range of 9.0–12.0, while the recovery of chromium(VI) was lower (10%) at pH range of 11.0–12.0. Therefore, the pH was adjusted to about 12.0 for the quantitative speciation of chromium(III) and chromium(VI) in subsequent experiments.

3.2. Effect of amount of dysprosium on the recoveries of chromium(III)

To find the required amount of dysprosium for the quantitative coprecipitation of chromium(III) in sample solutions, containing dysprosium in the range of 0–2.5 mg is studied. The results are shown in Fig. 2. The recovery of chromium(III) was 15% without using dysprosium. The recovery of chromium(III) was increased with the increasing amounts of dysprosium due to the formation of dysprosium hydroxide. The quantitative values were obtained between 1.0 and 2.5 mg of dysprosium. Two mg dysprosium was chosen for the recovery of chromium(III).

3.3. Effect of sample volume on the recovery of chromium(III)

It is important to know the maximum applicable sample volume for an analytical method [34,36–41]. The influences of the sample volume on the recoveries of chromium(III) were also investigated.

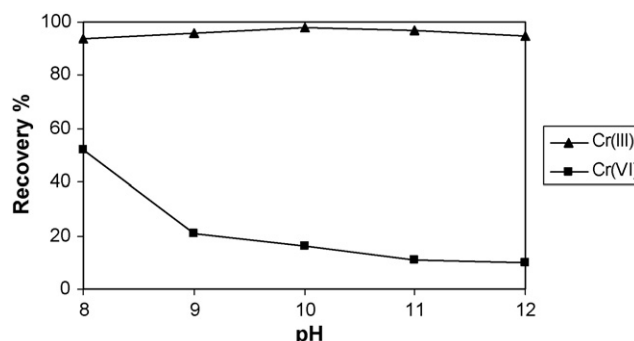


Fig. 1. Effect of pH on the recovery of chromium(III) and chromium(VI) ($N=3$).

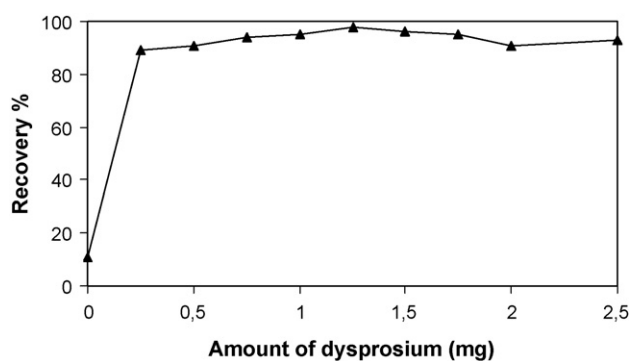


Fig. 2. Effect of amount of dysprosium on the recovery of chromium(III) ($N=3$).

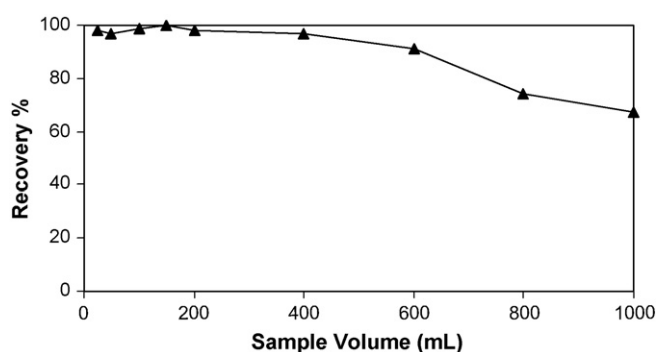


Fig. 3. Effect of sample volume on the recovery of chromium(III) ($N=3$).

Table 1
The effect of matrix ions on the recovery of chromium(III).

Ion	Salt added as	Concentration (mg L^{-1})	Recovery, % for Cr(III)
Na^+	NaCl	5000	96
K^+	KCl	1250	95
Ca^{2+}	CaCl_2	500	97
Mg^{2+}	MgCl_2	500	95
SO_4^{2-}	Na_2SO_4	1250	97
Fe^{3+}	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	5	95
Pb^{2+}	$\text{Pb}(\text{NO}_3)_2$	5	97
Ni^{2+}	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	5	94
Co^{2+}	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	5	97
Cu^{2+}	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	5	96

Model solutions including 20 μg chromium(III) ions in the sample volume range of 25, 50, 100, 250, 500 and 1000 mL were separately coprecipitated under the optimum conditions described before. The recoveries decreased slowly with increasing volume of the sample solution. The quantitative recoveries <95% were obtained up to 500 mL of sample solution. The results are shown in Fig. 3.

Table 2
Recoveries of chromium(III) and chromium(VI) from spiked tap water samples ($V_{\text{sample}} = 250 \text{ mL}$, $N=4$).

Amount added (μg)		Found and calculated (μg)			Recovery (%)		
Cr(III)	Cr(VI)	Cr(III) + Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III) + Cr(VI)
0	0	0.76 ± 0.06	0.61 ± 0.06	0.14 ± 0.04	–	–	–
0	25	25.2 ± 0.3	–	23.9 ± 0.3	–	95 ± 1	98 ± 1
5	20	25.5 ± 0.4	5.7 ± 0.2	19.8 ± 0.2	101 ± 2	98 ± 1	98 ± 2
12.5	12.5	25.1 ± 0.3	12.4 ± 0.2	12.7 ± 0.1	94 ± 1	100 ± 2	97 ± 1
20	5	25.2 ± 0.2	20.3 ± 0.2	5.0 ± 0.3	98 ± 1	97 ± 5	97 ± 1
25	0	25.5 ± 0.1	24.6 ± 0.2	–	96 ± 1	–	99 ± 2

$\bar{X} \pm s$ Cr(III) + Cr(VI):(found), Cr(III):(found), Cr(VI) (calculated).

3.4. Effect of matrix ions on the recovery of chromium(III)

Interference of the matrix ions on the recovery of the analytes is a problem for the determinations by flame or graphite furnace atomic absorption spectrometry [42–46]. The influences of diverse foreign ions such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- and SO_4^{2-} on the recovery of chromium(III) species were investigated. The results are shown in Table 1. Tolerance limits for the foreign ions was taken as a value which did not cause an error more than $\pm 5\%$ in the absorbance.

3.5. Centrifugation time and speed

The effect of the centrifugation time and speed on the recoveries of chromium(III) were investigated in the time range of 5–20 min, and centrifuge speed range of 1500–4000 rpm. The quantitative recoveries were obtained in the range of 10–20 min, and 2000–4000 rpm. 20 min and 3000 rpm were chosen for the further works.

3.6. Reduction of chromium(VI) to chromium(III)

Chromium(III) is coprecipitated and recovered quantitatively by the method using Dy_2O_3 to form dysprosium hydroxide. Therefore the conditions to reduce chromium(VI) to chromium(III) were investigated. Ascorbic acid and KI solutions were used for reduction of chromium(VI) to chromium(III). The recoveries were 99 ± 1.5 for KI and 14 ± 1.0 for ascorbic acid, respectively.

3.7. Detection limits

The limits of detection (LOD) of the coprecipitation method for the determination of chromium(III) and chromium(VI) was studied under optimal experimental conditions by applying the procedure for blank solutions. The detection limits ($k=3$, $N=15$) were 0.65 $\mu\text{g/L}$ for chromium(III) and 0.78 $\mu\text{g/L}$ for chromium(VI).

3.8. Validation of the method

For the validation of the proposed coprecipitation method tests of addition/recovery in the experiments for chromium(III) and chromium(VI) determinations were performed on tap water sample taken from the laboratory. Total chromium was 25 μg in the spiked samples. The results are shown in Table 2. As seen from the results recoveries were quantitative.

3.9. Applications

The proposed method was applied to CRM samples and three tap water samples taken from different parts of Kayseri. The results of CRM samples are shown in Table 3 and the results of the tap water samples are shown in Table 4.

Table 3
Total chromium in CRM samples ($N=5$).

CRM sample	Total Cr (certified), (mg/kg)	Total Cr found (mg/kg)	RSD (%)
GBW 07309 stream sediment	85 ± 7	82 ± 4	-3.5
NIST 2710 montana soil	39	38 ± 3	-2.6
GBW 07402 soil	47 ± 4	45 ± 3	-4.3

$P: 0.95; \bar{X} \pm ts/\sqrt{N}$.

Table 4
Chromium(III) and chromium(VI) in tap water samples ($V_{\text{sample}} = 400 \text{ ml}$, $N=4$).

	Concentration ($\mu\text{g/L}$)	
	Cr(III)	Cr(VI)
Sample 1	0.96 ± 0.11	BDL
Sample 2	1.03 ± 0.14	BDL
Sample 3	0.80 ± 0.07	BDL

$P: 0.95; \bar{X} \pm ts/\sqrt{N}$; BDL: below detection limit.

4. Conclusions

The presented method of coprecipitation with $\text{Dy}(\text{OH})_3$ in this study is most promising for chromium(III) and chromium(VI) ions as the preconcentration factor is 100. The method is relatively rapid as compared with previously reported procedures. Chromium(III) and chromium(VI) ions can be sensitively determined by atomic absorption spectrometry without any influence of dysprosium hydroxide. The amount of Dy(III) used in the experiments is approximately 2.0 g. In this study, a new approach was described based upon the use of coprecipitation for the preconcentration, separation, and separately determination of chromium(III) and chromium(VI) ions. The suggested method has been successfully applied to the CRM and tap water samples.

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