Neodymium(III) Hydroxide Coprecipitation-FAAS System for the Speciation of Chromium in Natural Waters

Mustafa Soylak* and Nebiye Kizil
Erciyes University, Faculty of Sciences, Chemistry Department
38039 Kayseri, Turkey

INTRODUCTION

The speciation of metals in environmental samples is critical for assessing their potential environmental impact before disposal (1, 2). In particular, the accurate determination of different ionic species of elements at trace levels, such as Cr(III) and Cr(VI), Sb(III) and Sb(V), or As(III) and As(V), is very important because each ionic species has a different toxicology (3–6). Because of the different toxicology of Cr(III) and Cr(VI), the speciation study of chromium is very important (7–10). Cr(VI) is more toxic than Cr(III), and Cr(VI) is carcinogenic and mutagenic to humans, animals, and plants (11–13).

The direct determination of metal ions with two oxidation states in the same samples, such as Cr(III) or Cr(VI), is not possible in atomic absorption spectrometric analysis (14–16). Generally, the first step in sample preparation includes the separation of the species from each other prior to atomic absorption spectrometric detection of the analytes for speciation. In the second step, total chromium is determined after reduction of Cr(VI) or oxidation of Cr(III) (17–20). Solid phase extraction, solvent extraction, cloud point extraction, and membrane filtration are the most widely used sample preparation techniques for the speciation of chromium species in environmental samples (15–20). The speciation of

ABSTRACT

A new coprecipitation procedure is presented for the speciation of Cr(III) and Cr(VI) on neodymium(III) hydroxide precipitate. Chromium determination was performed by flame atomic absorption spectrometry. Total chromium was determined by application of the same procedure after reducing Cr(VI) to Cr(III). The concentration of Cr(VI) was calculated by the concentration difference between total Cr and Cr(III). The optimal parameters that affected the quantitative recoveries of Cr(III) were investigated. The influences of co-existing ions were controlled. The detection limit and preconcentration factor for Cr(III) were 2.1 µg/L and 100, respectively. The method was applied to the speciation and determination of chromium in natural water samples.

chromium can also be performed using coprecipitation procedures (21–23) which are simple, rapid, and efficient techniques with a high preconcentration factor. The use of various hydroxides of the metals is popular for this purpose.

In this study, we used Nd(III) hydroxide precipitate for the coprecipitation and speciation of Cr(III) and Cr(VI). Various analytical parameters such as pH, amount of Nd(III), sample volume, and matrix effects were optimized. The procedure was applied to the speciation of chromium in natural water samples.

EXPERIMENTAL

Instrumentation

The instrumental detection system used for this study was a PerkinElmer® Model 3110 flame atomic absorption spectrometer (PerkinElmer, Inc., Shelton, CT, USA), equipped with a chromium hollow cathode lamp operated at 25 mA. The wavelength and spectral band pass were set at 357.9 nm and 0.7 nm, respectively. A 10-cm single-slot burner head and an air-acetylene flame were used. The nebulizer uptake rate was adjusted to provide optimum response for conventional sample introduction resulting in 6.0 mL/min. An acetylene flow rate of 2.5 L/min was used with an air flow rate of 17.0 L/min.

A pH meter, model Nel pH-900 (Ankara, Turkey), equipped with a glass electrode, was employed for measuring the pH values in the aqueous phase. Distilled/deionized water (Millipore® Milli-Q™ system) was used for preparation of the sample solutions.

Reagents and Standard Solutions

Analytical reagent-grade chemicals were employed for the preparation of all solutions. All laboratory glassware was kept overnight in a 10% (v/v) HNO₃ solution and then rinsed with deionized doubly distilled water. The Cr(III) and Cr(VI) stock solutions were prepared from Cr(NO₃)₃ in 0.5 mol L⁻¹ HNO₃ and K₂CrO₄ in distilled water, respectively, with a concentration of 1000 mg L⁻¹. A 0.1% solution of Nd(III) was prepared fresh daily by

*Corresponding author.
E-mail: soylak@erciyes.edu.tr
Fax: +90 352 4374933

dissolving Nd(III) oxide (Suprapur® grade, E. Merck, Darmstadt, Germany) in small amounts of nitric acid and diluting to 50 mL with doubly distilled water (24). Diluted NaOH solutions (1 mol L⁻¹) were used for pH adjustments.

The certified reference materials (CRMs) used were TMDA-53.3 Fortified Water (National Water Research Institute of Canada, Burlington, ON, Canada) and SPS-WW2 Wastewater Level 2 (Spectrapure Standards AS, Oslo, Norway).

Procedure for Speciation

A solution of 20–30 mL, containing 20 µg of Cr(III) and 1.0 mg of Nd(III), was used. The pH was adjusted to the desired value by addition of 1 mol L⁻¹ NaOH solution. The solution was centrifuged at 2500 rpm for 10 minutes and the supernatant removed. The Nd(III) hydroxide precipitate adhering to the tube was dissolved with 1 mL of 1 mol L⁻¹ HNO₃ and its final volume was completed to 10.0 mL with distilled water.

The reduction for Cr(VI) to Cr(III) was performed by using the procedure given in the literature (25, 26). An amount of 0.5 mL con-

centrated sulphuric acid and 0.5 mL ethanol was added to the model solution. After reduction of Cr(VI) to Cr(III), the method described above was applied to the determination of total Cr. The level of Cr(VI) was calculated by the difference between the total chromium and Cr(III) concentrations.

Application to Real Samples

TMDA-53.3 Fortified Water or SPS-WW2 Wastewater Level 2 certified reference material was used directly and the coprecipitation procedure given above applied after adjusting the pH to 10.0 with 1 mol L⁻¹ NaOH solution.

The proposed method was applied to natural water samples including a tap water from Erciyes University and water from a well at Kayseri. The water samples analyzed were collected in pre-washed polyethylene bottles. Before analysis, the pH of the water samples was adjusted to 10.0 with 1 mol L⁻¹ NaOH solution. The coprecipitation procedure discussed above was applied and the chromium levels were determined using the flame atomic absorption spectrometer.

RESULTS AND DISCUSSION

Optimization

In the coprecipitation of metal ions with hydroxide precipitates, the pH of the working media is generally basic (27–29). The effect of pH on the precipitation-separation efficiency of both chromium species was examined separately in the range of 7.0–12.0 by adjustment with 1 mol L⁻¹ NaOH (Figure 1). The recoveries of Cr(III) were quantitative (> 95%) in the working pH range, while the recovery of Cr(VI) was lower than 7%. In light of these results, it is possible to separate Cr(III) from Cr(VI) in the pH range of 7.0–12.0. Thus, pH 10 was selected for further studies.

The influence of amount of neodymium on the recovery values of Cr(III) was investigated in the range of 0.5–3.0 mg at pH 10.0 (Figure 2). The recovery values increased and reached quantitative values in the range of 1.0–3.0 mg Nd(III). Thus, the use of Nd(III) hydroxide makes quantitative separation of Cr(III) feasible. The optimum amount of 1.0 mg of Nd(III) was selected for all further studies.

Fig. 1. The relation of recovery of chromium species and pH (N=3).

Fig. 2. Effect of Nd(III) amount on the recovery of Cr(III) (N=3).

The standing time was examined in the range of 0–30 minutes due to the formation of a precipitate (Table I). Quantitative recovery values were obtained after 5 minutes of standing time and were selected for this study.

TABLE I
Influences of Standing Time on the Recoveries of Cr(III) (N=3)

Standing Time (min.)	Recovery (%)
0	92±2 ^a
5	97±2
10	98±1
20	98±1
30	97±2

^a Mean ± standard deviation.

TABLE II
Relationship Between Centrifugation Speed and Recovery of Cr(III)

Centrifugation Speed (rpm)	Recovery (%)
1000	79±3 ^a
1500	89±2
2000	93±2
2500	95±1
3000	97±3
3500	98±1
4000	98±2

^a Mean ± standard deviation.

TABLE III
Influence of Centrifugation Time on the Recoveries of Cr(III)

Centrifugation Time (min)	Recovery (%)
2	88±3 ^a
5	95±2
10	95±1
20	97±1
30	99±1

^a Mean ± standard deviation.

The effects of centrifugation speed on the recoveries of Cr(III) were studied in the range of 1000–4000 rpm (Table II). Quantitative values were obtained in the range of 2500–4000 rpm. Thus, the centrifugation speed of 2500 rpm was used for all further work.

The influence of centrifugation time on the present neodymium hydroxide coprecipitation system for Cr(III) was studied in the range of 2–30 minutes (Table III). The recovery values were quantitative in the time range of 5–30 minutes. The optimum value of 10 minutes was selected for this study.

To improve the preconcentration factor, the sample volume of the working media is a key factor in preconcentration studies for metal ions (30–35). The effects of sample volume on the recoveries of Cr(III) in the neodymium hydroxide coprecipitation system were investigated in the 20–1000 mL range. The results in Figure 3 show that Cr(III) was quantitatively recovered at all working ranges of the sample volume and a preconcentration factor of 100 was obtained (sample volume: 1000 mL, final volume: 10 mL).

Effects of Concomitants

It is known that concomitant ions present at the µg/mL level in natural waters influence the determination of metal ions by atomic absorption spectrometry (36–44). The effects of some alkaline, alkaline earth, transition metals, and some anions on the recovery of Cr(III) were investigated and the results are summarized in Table IV. Since the recovery values for Cr(III) are generally quantitative in the presence of the investigated concomitant ions, it was found that the coprecipitation method can be applied to the analysis of natural water samples.

Total Cr

For the determination of total Cr, model solutions containing different amounts of Cr(VI) and Cr(III) were prepared (Table V). The reduction of Cr(VI) ions to Cr(III) was performed (25, 26) and the procedure proposed was applied to these solutions. The results in Table V show that the coprecipitation method can also be applied for the determination of total chromium in aqueous samples.

Fig. 3. The influence of sample volume (N=3).

TABLE IV
Influences of Concomitant Ions
on the Recoveries of Cr(III)

Concomitant	Concentration (μg/mL)	Recovery (%)
Mg ²⁺	3000	100±2 ^a
K ⁺	5000	95±3
Ca ²⁺	3000	95±2
Na ⁺	7000	97±1
SO ₄ ²⁻	2000	97±1
Cl ⁻	5000	100±1
Fe ³⁺	20	98±2
Al ³⁺	20	100±1
Cu ²⁺	20	98±2
Ni ²⁺	20	98±3
Co ²⁺	10	95±2
Cd ²⁺	10	100±1

^a Mean ± standard deviation.

Performance of the Method

The detection limit, defined as the concentration equivalent to three times the standard deviation (N = 20) of the reagent blank, was 2.1 μg/L. The precision of the present enrichment method, calculated as the relative standard deviation of the measurements carried out with the sample solutions (N=10), was below 5.0%.

Analysis of Real Samples

The proposed coprecipitation method was applied to two certified water reference materials (TMDA-53.3 Fortified Water and SPS-WW2 Wastewater Level 2). The results given in Table VI show good agreement with the certified values for chromium.

The coprecipitation method was also applied to the speciation of Cr(III) and Cr(VI) in natural water samples: well water and tap water. Chromium species were also spiked to these samples. The results listed in Table VII show that there is good agreement between the added and measured analyte amounts.

TABLE V
Determination of Total Chromium in Spiked Test Solutions (N=3)

Added (μg)		Found (μg)		Calculated (μg)
Cr (III)	Cr (VI)	Cr (III)	Total Cr	Cr (VI)
0	25	-	24.5±0.5	-
5	20	4.8±0.5 ^a	24.5±0.5	19.7±1
12.5	12.5	11.7±1.0	24.5±0.5	12.8±1
20	5	19.0±1.0	24.5±0.5	5.5±0.5
25	0	24.5±1.0	24.5±0.5	-

^a Mean ± standard deviation.

TABLE VI
Application of Proposed Method for Chromium Determination
in Certified Reference Materials (N=3)

	Certified value (μg/L)	Found by present method (μg/L)	Recovery (%)
TMDA-53.3 Fortified Water	340	337±1 ^a	99
SPS-WW2, Wastewater Level 2	1000	1050±32	105

^a Mean ± standard deviation.

TABLE VII
Application of the Presented Method to Water Samples (N=3)

Well Water				
Added (μg)		Found (μg)		Calculated (μg)
Cr(III)	Cr(VI)	Cr(III)	Total Cr	Cr(VI)
0	0	BDL ^a	-	-
15	15	14.1±1.0	28.2±1.0	14.1±0.5
30	0	28.9±1.0	28.9±1.0	-
Tap Water				
Added (μg)		Found (μg)		Calculated (μg)
Cr(III)	Cr(VI)	Cr(III)	Total Cr	Cr(VI)
0	0	BDL ^a	-	-
0	25	-	24.3±1.0	-
5	20	4.8±0.5	24.4±1.1	19.4±0.5
12.5	12.5	12.1±1.0	24.3±1.0	12.2±1
20	5	19.4±1.0	24.2±1.0	4.8±0.5
25	0	24±2.0	24.3±1.0	-

^a BDL = Below detection limit.

CONCLUSION

A new coprecipitation procedure has been presented by speciation of Cr(III) and Cr(VI) on neodymium(III) hydroxide precipitate. The optimum parameters that affected the quantitative recoveries of Cr(III) were investigated. The influences of co-existing ions were controlled and the detection limit for Cr(III) was found at 2.1 µg/L. The advantages of the present method include high salt tolerance, high preconcentration factor for Cr species, and applicability of the method to both oxidation states of Cr. The precision and accuracy of the method was satisfactory. The developed method is especially suitable for the determination of chromium species in natural water samples.

ACKNOWLEDGMENT

The authors are grateful for the financial support of the Unit of the Scientific Research Project of Erciyes University, Turkey.

Received June 10, 2013.

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