

RESIDUES AND TRACE ELEMENTS

A Novel Method for Speciation of Chromium: Coprecipitation Without Carrier Element by Using a Triazole Derivative

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A coprecipitation method has been established for speciation of chromium(III) and chromium(VI) in real samples. The procedure is based on the coprecipitation of Cr(III), by using a new organic coprecipitant, 3-phenyl-4-*o*-hydroxybenzylidenamino-4,5-dihydro-1,2,4-triazole-5-one, without adding any carrier element. After reduction of Cr(VI) by concentrated H₂SO₄ and ethanol, the method was applied to the determination of total Cr. The level of Cr(VI) was calculated by the difference of total Cr and Cr(III) levels. For optimum recovery of Cr(III), different analytical factors such as pH, amount of coprecipitant, centrifugation rate and time, and effect of sample volume, were investigated. The influences of some anions, cations, and transition metals on the recoveries were also investigated, and no significant interferences were observed. The preconcentration factor was 100. The detection limit based on 3 times standard deviation (σ) of the blank ($n = 10$) for Cr(III) was 0.50 $\mu\text{g/L}$. In order to evaluate the accuracy of the method, certified reference materials (CRM-TMDW-500 Drinking Water and National Institute of Standards and Technology Standard Reference Material 1573a Tomato Leaves) were analyzed, and the results obtained were in good agreement with certified values. The presented procedure was applied for Cr speciation in various solid and liquid samples with successful results.

Some heavy metals generally present at trace concentration in environmental samples are very harmful to plants and animals. Most of them are well known risk factors for human health (1). Because of this, the monitoring of the levels of heavy metal ions in environmental samples is important (2). Due to extensive use of chromium in industrial processes, such as electroplating, metallurgy,

tanning factories, wood preservation, textile dyeing, etc., large quantities of this element are discharged into the environment and cause ecosystem contamination; thus, Cr is a major pollutant of the environment (3, 4). Chromium can exist in oxidation states from III to VI, but in aqueous solution the most stable and common forms of Cr are trivalent and hexavalent species (5, 6). These species have different properties, and oxidation state and concentration of species determine the toxicity of Cr (7, 8). Cr(III) combines with various enzyme systems, and, therefore, it is an essential trace element for living organisms to regulate functioning glucose, lipid, and protein metabolism (9, 10). On the other hand, water-soluble Cr(VI) can be toxic for biological systems because it can diffuse as CrO_4^{2-} and HCrO_4^- through cell membranes and oxidize biological molecules with toxic results (11). Cr(VI) is known to have carcinogenic and mutagenic properties, and the major toxic effects are chronic ulcers, dermatitis, hepatic and renal tubular necrosis, corrosive reaction in nasal septum, and local effects in lungs (12). Cr(VI), the most toxic form of Cr, is found as CrO_4^{2-} , HCrO_4^- , or $\text{Cr}_2\text{O}_7^{2-}$ depending on the pH of the medium.

The maximum permissible levels of Cr(VI) in drinking and industrial waste water are 50 and 200 $\mu\text{g/L}$, respectively (13). Toxicity of an element can be affected by the change of the oxidation state. Therefore, it is important to separate Cr(III) and Cr(VI) species in environmental samples and determine the concentration of 2 species separately rather than only the total Cr content.

Because the Cr concentration in real samples is at a low level (ng/mg), direct determinations of Cr species including Cr(III) and Cr(VI) are difficult by instrumental techniques, including atomic absorption spectrometry (AAS; 14), inductively coupled plasma-atomic emission spectrometry (15), and column high-performance liquid chromatography (16). Only total Cr could be determined by these techniques. Thus, speciation studies require both a separation/preconcentration process and selective removal of one of the species from the sample before the determination (17–19). For this purpose various analytical methods, such as coprecipitation (20, 21), liquid–liquid extraction (22), solid-phase extraction (23, 24), ion

Received April 9, 2008. Accepted by AK May 29, 2008.

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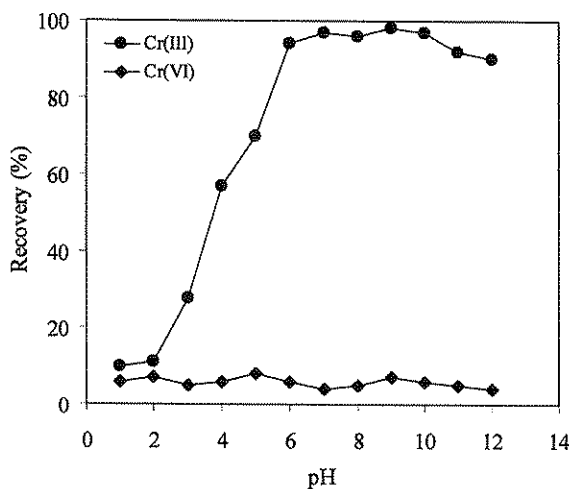


Figure 1. Effect of pH on the recovery of Cr species ($n = 3$).

chromatography (25), and cloud point extraction (26), have been used.

Coprecipitation is an efficient preconcentration technique for trace heavy metal ions. The method has several advantages including simplicity, short analysis time, high preconcentration factor, and low consumption of organic solvent, and several analyte ions can be separated from the matrix. Heavy metals are coprecipitated by organic or inorganic coprecipitants using a carrier element (27, 28).

The aim of the present work was to apply a coprecipitation method as a separation and preconcentration step combined with flame AAS (FAAS) for the speciation of Cr. For this purpose, we established a new coprecipitation method by using only an organic coprecipitant, 3-phenyl-4-*o*-hydroxybenzylideneamino-4,5-dihydro-1,2,4-triazole-5-one (POHBAT), without adding any carrier element.

Experimental

Apparatus

A Unicam model AA-929 (Solar System ATI Unicam Analytical Technology Inc., Cambridge, UK) flame atomic absorption spectrometer equipped with single-element hollow cathode lamps and N_2O /acetylene burner (5 cm) was used for the determination of Cr. The instrumental parameters were those recommended by the manufacturer. The wavelength selected for the determination of Cr was 357.9 nm. The pH measurements were made on HANNA pH-211 digital pH meter with glass electrode (HANNA Instruments, Cluj-Napoca, Romania). An MSE Mistral 2000 model centrifuge (Lab Extreme, Inc., Kent City, MI) was used for centrifugation of solutions. A Milestone Ethos D closed vessel microwave system (Milestone Inc., Sorisole (BG), Italy) with maximum pressure of 1450 psi and maximum temperature of 300°C was used for digestion of the solid samples.

Reagents and Solutions

All of the chemicals used in this work were analytical grade from Merck (Darmstadt, Germany) or Fluka (Buchs, Switzerland). Distilled/deionized water was used for all experiments. Stock solutions of Cr(III) and Cr(VI) were prepared from $Cr(NO_3)_3$ in 0.5 M HNO_3 and K_2CrO_4 in water with a concentration of 1000 mg/L. The model and standard solutions of the metals were prepared by diluting the stock solutions. HNO_3 and NaOH (Merck) were used for pH adjustments. POHBAT used as a coprecipitating agent was synthesized as reported elsewhere (29).

The glassware used was soaked in 10% (v/v) HNO_3 solution for 1 day before use and then rinsed repeatedly with distilled/deionized water. Water samples were stored in polypropylene bottles (5 L) prior to analysis.

Determination of Chromium

The coprecipitation method was tested prior to application for the speciation of Cr(III) and Cr(VI) in environmental samples. For that purpose, 0.75 mL coprecipitating agent solution prepared in ethanol (0.1%, w/v) was added to 50 mL aqueous solution containing 12.5 μg Cr(III) ions. The pH of the solution was adjusted to 7.0. After standing 10 min, the solution was centrifuged at 3000 rpm for 20 min. The supernatant was removed. The precipitate adhering to the tube was dissolved with 1 mL concentrated HNO_3 . The final volume was diluted to 5 mL with distilled/deionized water, and then the solution was analyzed by FAAS for the determination of the analyte ions.

Determination of Total Chromium

Total Cr was determined as Cr(III) by the method described above after reducing Cr(VI) to Cr(III) by the addition of 0.5 mL concentrated H_2SO_4 and 0.5 mL ethanol (30) into 50 mL aqueous solution containing 12.5 μg

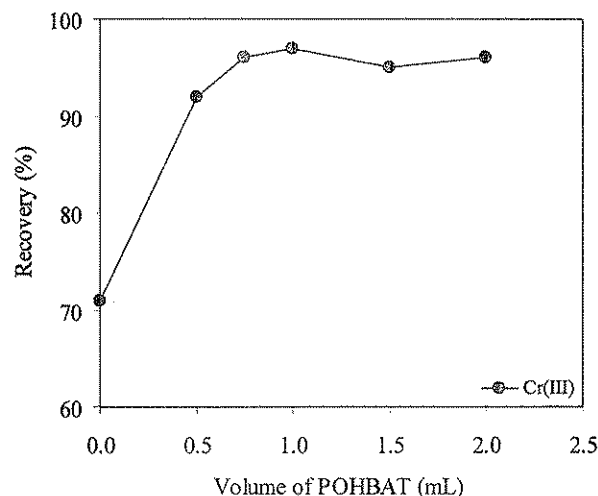


Figure 2. Effect of POHBAT amount on the recovery of Cr(III) ($n = 3$; sample volume = 50 mL).

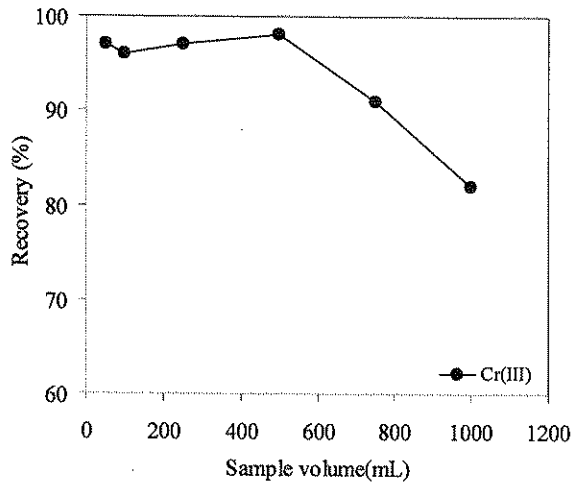


Figure 3. Influence of sample volume on Cr(III) recovery ($n = 3$).

Cr(III) and 12.5 μg Cr(VI) ions. After cooling at room temperature, the pH of the solution was adjusted to 7.0. Then the procedure described above was applied to this solution. After reduction of Cr(VI) to Cr(III) by using ethanol in acidic media, the method was applied to the determination of the total Cr. The concentration of Cr(VI) was calculated by subtracting the content of Cr(III) from total Cr content.

Analysis of Real Samples

The procedure was applied to the speciation of Cr in tap water and mineral spring water as real liquid samples, and gold ore and red pepper as real solid samples. The method was also applied to standard reference materials Certified Reference Materials (CRM)-Trace Metals in Drinking Water (TMDW)-500 Drinking Water (High-Purity Standards Inc., Charleston, SC) and National Institute of Standards and Technology Standard Reference Material (NIST SRM) 1573a Tomato Leaves (Gaithersburg, MD). Various amounts of Cr species were also spiked into real liquid samples.

The water samples analyzed were collected in prewashed (in turn with detergent, doubly distilled/deionized water, dilute HNO_3 , and doubly distilled/deionized water) 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, acidified with 1 mL 1% nitric acid, and subsequently stored at 4°C in a refrigerator.

Before the analysis, the pH of the liquid samples (500 mL for tap water and mineral spring water and 25 mL for CRM-TMDW-500 Drinking Water) were adjusted to 7.0. Then appropriate amounts of 0.1% POHBAT were added, and the procedure given above was applied. The final volume of the solutions was diluted to 5 mL with distilled/deionized water. The levels of the Cr in the samples were determined by FAAS. Total Cr in these liquid samples was determined as

Cr(III) after reduction of Cr(VI) to Cr(III) by the addition of concentrated H_2SO_4 and ethanol.

The solid samples were digested with a closed microwave digestion system to obtain clear solutions prior to application of the speciation procedure for Cr(III) and Cr(VI) based on coprecipitation. For that purpose, 0.50 g gold ore, 1.00 g red pepper, and 0.25 g NIST SRM 1573a Tomato Leaves were weighed into separate Teflon vessels, and 4.5 mL HCl, 1.5 mL HNO_3 , and 2.0 mL hydrofluoric acid for gold ore and 6.0 mL HNO_3 and 2.0 mL H_2O_2 for Tomato Leaves standard and red pepper were added into the vessels. Digestion conditions for the microwave system for the samples were (35 bar) 6 min at 250 W, 6 min at 400 W, 6 min at 650 W, 6 min at 250 W, vent 3 min, respectively. Then the volume of the solution was completed to 50 mL with distilled/deionized water. The blank solutions were prepared in the same way as the real samples, but omitting the sample. The preconcentration procedure given above was applied to the samples. The level of the Cr ions in the samples, was determined by FAAS after the final volume of the solutions was made up to 5 mL with distilled/deionized water.

Results and Discussion

Effect of pH

Because the pH of the aqueous solution was an important factor affecting the speciation studies based on the coprecipitation method, the influence of pH on the recoveries of Cr(III) and Cr(VI) was investigated in the range of 1–12. The pH of the solutions was adjusted in this range by using HNO_3 and NaOH, and the present method was applied to the solutions. The results are given in Figure 1. The recoveries for Cr(III) in the pH range 6–10 were quantitative (>95%), while the recovery of Cr(VI) was lower at all investigated pHs. The

Table 1. Influence of some ions on the recovery of Cr(III)^a

Ions	Concn, mg/L	Recovery, %
Na^+	10000	94 \pm 3
K^+	1000	97 \pm 5
Ca^{2+}	1000	95 \pm 5
Mg^{2+}	1000	96 \pm 6
Cl^-	15000	101 \pm 4
PO_4^{3-}	1000	95 \pm 4
SO_4^{2-}	1000	93 \pm 2
NO_3^-	5000	98 \pm 7
Al^{3+} , Cd^{2+} , Cu^{2+} , V^{5+} , Mn^{2+} , Ni^{2+} , Co^{2+}	50	103 \pm 5
Mixed ^b		94 \pm 4

^a Sample volume = 50 mL; $n = 3$.

^b The solution contains 10 000 mg/L Na^+ , 15 000 mg/L Cl^- , 500 mg/L Ca^{2+} , Mg^{2+} , K^+ , SO_4^{2-} , and PO_4^{3-} , 1000 mg/L NO_3^- , and 10 mg/L Al^{3+} , Cd^{2+} , Cu^{2+} , V^{5+} , Mn^{2+} , Ni^{2+} , and Co^{2+} .

Table 2. Determination of total Cr in spiked test solutions^a

Cr(III)	Added, μg		Found, μg	
	Cr(VI)	Total Cr	Total Cr	Recovery, %
0	20	20	20.2 \pm 1.2	101
5	15	20	18.9 \pm 0.7	95
10	10	20	19.2 \pm 1.1	96
15	5	20	20.4 \pm 0.8	102
20	0	20	19.3 \pm 1.2	97

^a Sample volume = 50 mL; $n = 3$.

recovery values for Cr(VI) were below 5% at all the investigated pHs. The results show that the separation and speciation of Cr(III) and Cr(VI) are possible by the present procedure in the pH range 6–10. All subsequent work was performed at pH 7.0.

Effect of POHBAT Amount

The speciation procedure is based on the coprecipitation of Cr(III) with POHBAT organic reagent. The effect of the amount of POHBAT on the recoveries of Cr was investigated in the range of 0–2 mL of a 0.1%, w/v, POHBAT solution in ethanol with the other parameters constant. The results are shown in Figure 2. When the experiments were performed without POHBAT, the recovery of Cr was not quantitative. The recovery of Cr(III) increased with increasing amounts of POHBAT. The results show that quantitative recoveries of Cr(III) were obtained after addition of 0.75 mL POHBAT, and this amount was used in all subsequent work.

Effect of Standing Time, and Centrifugation Rate and Time

The standing time and centrifugation rate and time were also examined because these parameters are the important factors influencing the quality of the precipitate that forms in the aqueous solution. For that purpose, 0.75 mL POHBAT was added into a series of solutions (50 mL) containing Cr(III). Then the solutions were kept standing from 0 to 20 min. After 10 min, quantitative recoveries were obtained. As a result, the optimum standing time was determined as 10 min for all subsequent work.

The effect of the centrifugation rate was examined in the range of 1500–3500 rpm, and the optimum rate was determined to be 3000 rpm. The influence of the centrifugation time on the recoveries of Cr(III) was investigated in the range of 5–30 min at 3000 rpm. After 20 min quantitative recoveries were obtained, so all other work was performed at 3000 rpm for 20 min.

Effect of Sample Volume

The influence of the sample volume on the recovery of Cr(III) was also investigated in order to obtain a high

preconcentration factor for real samples. In this study the sample volume was varied in the range of 50–1000 mL containing 12.5 μg Cr(III). For 50 mL sample volumes, the precipitates formed in a polyethylene tube and solutions were separated from each other by centrifugation. For sample volumes above 50 mL, the precipitates were filtered through a 0.45 μm cellulose nitrate membrane. The results given in Figure 3 show that Cr(III) recoveries were quantitative up to 500 mL of sample volume. Above 500 mL, the recovery value of Cr(III) decreased with increasing sample volume. The preconcentration factor, calculated as the ratio of the highest sample volume for Cr(III) and lowest final volume, was found 100 for Cr(III) when the final volume was 5 mL.

Effect of Diverse Ions

In order to evaluate possible analytical applications of the present speciation/preconcentration procedure, the effect of some foreign ions was examined under optimal conditions. For these studies, different amounts of each foreign ion were added to model solutions containing a fixed amount of Cr(III). Then the present procedure was applied. The recoveries of Cr(III) were higher than 93%. The results show that the presence of interfering anions and cations had no obvious influence on the present separation/preconcentration procedure under optimal conditions. The levels of some heavy metal ions examined in the present study (transition metals) were lower than their interference level. As a result, it is considered that the proposed separation/preconcentration method could be applied to highly saline samples. The tolerable levels of interferences are shown in Table 1.

Determination of Total Chromium

In order to determination total Cr by the presented method, model solutions that contained different amount of Cr(III) and Cr(VI) were first prepared. Then Cr(VI) in the model solutions was reduced to Cr(III) by using 0.5 mL concentrated H_2SO_4 and 0.5 mL ethanol. Because quantitative recoveries for Cr(III) were obtained at pH 7.0, the pH of the aqueous solution was adjusted to 7.0 by using HNO_3 and NaOH. Then the presented procedure was applied to these solutions. The results are given in Table 2. Quantitative recovery values were

Table 3. Level of Cr in the standard reference materials after application of the developed procedure^a

Sample	Certified value	Found value	Recovery, %
CRM-TMDW-500, $\mu\text{g/L}^b$	20.0 \pm 0.1	20.6 \pm 1.1	103
Tomato leaves 1573a, $\mu\text{g/g}^c$	1.99 \pm 0.06	1.90 \pm 0.07	96

^a $n = 3$.

^b Sample volume = 25 mL.

^c Quantity of tomato leaves standard was 0.25 g.

Table 4. Statistical evaluation of the result obtained in the accuracy study (Table 3) using the Student's *t*-test

Element	CRM-TMDW-500 Drinking Water						Tomato Leaves 1573a					
	SD ^a	X _R ^b	\bar{X} ^c	X _R - \bar{X}	tSD/√n ^d	Comparison	SD	X _R	\bar{X}	X _R - \bar{X}	tSD/√n	Comparison
Cr	1.1	20.0	20.6	0.6	2.7	0.6 < 2.7 (same)	0.07	1.99	1.90	0.09	0.17	0.09 < 0.17 (same)

^a SD = Standard deviation.

^b X_R = Value of the standard material.

^c \bar{X} = Mean value.

^d t = 4.30 (95% confidence intervals); n = 3.

obtained for these solutions, and a good agreement was found between the added Cr(III) and measured Cr(III) amount. The recoveries of Cr(III) were higher than 95%. The results show that the proposed method could be applied for the determination of total Cr.

Analytical Performance of the Method

The detection limit was calculated under optimal experimental conditions after application of the preconcentration procedure to blank solutions. The limit of detection for Cr(III) based on 3 times the standard deviation of the blank (n = 10) was 0.50 µg/L for a 50 mL of sample volume and 5 mL final volume.

The precision of the method was evaluated as the relative standard deviation obtained after replicated sample analysis. For this purpose, the procedure was repeated 10 times for Cr(III) under the optimum conditions mentioned above. It was found that the recovery of Cr(III) was 97 ± 4% at the 95% confidence level.

Application to Real Samples

The accuracy of the proposed separation/preconcentration method was examined by determination of total Cr in liquid CRM-TMDW-500 Drinking Water and solid certified reference material NIST SRM 1573a Tomato Leaves. The results are given in Table 3. The analytical values were in

good agreement with the certified values. Statistical evaluation was also applied to the results obtained from the accuracy study (Table 3) using the Student's *t*-test (Table 4; 31). The results revealed good agreement between the observed values and certified values.

The developed method was applied to the speciation of Cr(III) and Cr(VI) in tap water from Trabzon and mineral spring water from Yomra/Trabzon. Various amounts of Cr species were also spiked into these samples. The results are given in Table 5. Good agreement was obtained between the added and measured analyte amounts. These results confirm that the proposed method could be applied successfully for the separation, preconcentration, and speciation of trace amounts of Cr in tap water and mineral spring water samples. The accuracy of the results was quite satisfactory: relative error was lower than 6% for Cr(III), Cr(VI), and total Cr. The proposed method was applied to solid and liquid environmental samples for the separation and preconcentration of Cr at trace levels. The results are given in Table 6.

Conclusions

The developed speciation procedure for Cr(III) and Cr(VI) based on coprecipitation is simple, fast, and economical. The time required for the coprecipitation and determination was

Table 5. Determination of Cr(III), Cr(VI), and total Cr in tap water and mineral spring water^a

Sample	Added, µg		Found, µg			Recovery, %		
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Total Cr	Cr(III)	Cr(VI)	Total Cr
Tap water	—	—	1.6 ± 0.1	BDL ^b	1.6 ± 0.1	—	—	—
	5	10	6.5 ± 0.3	9.8 ± 0.5	16.3 ± 0.6	98	98	98
	10	5	11.8 ± 0.6	4.8 ± 0.1	16.6 ± 0.6	102	96	100
Mineral spring water	—	—	0.9 ± 0.05	BDL	0.9 ± 0.05	—	—	—
	5	10	6.1 ± 0.3	9.4 ± 0.4	15.5 ± 0.5	103	94	97
	10	5	11.2 ± 0.4	5.2 ± 0.2	16.4 ± 0.4	103	104	103

^a Sample volume = 500 mL; POHBAT volume = 0.75 mL (0.1%, w/v, in ethanol); n = 3.

^b BDL = Below detection limit.

Table 6. Level of Cr species in environmental samples after application of the developed procedure^a

Sample	Concn, µg/L		Total Cr, µg/g
	Cr(III)	Cr(VI)	
Tap water	3.2 ± 0.2	BDL ^b	
Mineral spring water	1.8 ± 0.1	BDL	
Powdered red pepper			0.73 ± 0.03
Gold ore			6.92 ± 0.4

^a Uncertainty at the 95% confidence limit; $n = 3$.

^b BDL = Below detection limit.

only 30 min. In this study, we used a new organic coprecipitant without the need for a carrier element. This is a great advantage because there is no risk of contamination of Cr from a carrier element. The present procedure was successfully applied to speciation of Cr species in various solid and liquid environmental samples. The preconcentration factor was 100 for 500 mL of sample volume.

Acknowledgments

We thank the Unit of the Scientific Research Projects of Karadeniz Technical University for financial support. We also thank Nuri Yildirim for his contributions.

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