



Thulium hydroxide: A new coprecipitant for speciation of chromium in natural water samples[☆]

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ABSTRACT

A coprecipitation procedure has been established for chromium speciation in natural water samples. The procedure is based on the coprecipitation of Cr(III) on thulium hydroxide precipitate. After reduction of Cr(VI) to Cr(III) by using potassium iodide, the presented method was applied to the determination of the total chromium. The level of Cr(VI) is calculated by difference of total chromium and Cr(III) levels. The procedure was optimized for some analytical parameters including pH, sample volume, matrix effects, etc. The detection limits based on 3σ criterion were $0.87 \mu\text{g L}^{-1}$ for Cr(III) and $1.18 \mu\text{g L}^{-1}$ for Cr(VI). The procedure presented was validated by the analysis of BCR-144R Sewage Sludge (domestic origin). The presented method was applied for the speciation of chromium in environmental sample with satisfactory results (recoveries > 95%, R.S.D.s < 10%).

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1. Introduction

Chromium is a naturally occurring metal, mainly found in natural samples including water, minerals, rocks, soil, plants, volcano dust and gases [1,2]. Although, chromium is known to exist in different oxidation states from Cr(0) to Cr(VI), chromium(III) and chromium(VI) species are the most widespread in the nature [1,3]. Environmental behavior of chromium depends on its oxidation states. These oxidation states have different physiological effects on human life [4,5]. Chromium(VI) compounds are known as toxic and carcinogenic owing to its oxidizing potential and easy permeation through biological membrane of human body [4]. Cr(III) is considered as an essential trace element, important in glucose, lipid, and protein metabolism [4,6–8]. The speciation of inorganic chromium in environmental samples is required for accurate assessment of pollution levels. Total chromium measurement cannot be used to determine environmental impact due to the considerable difference in toxicity of the two elemental forms [7–10]. Chromium species are major water pollutants, usually as a result of some industrial pollution including tanning factories, steel works, industrial electroplating, wood preservation, etc. and artificial fertilizers

[9–12]. Due to these importance of Cr(III) and Cr(VI), the accurate and sensitive determinations of these ions are the important part of the analytical chemistry. Except some techniques including electroanalytical methods, direct and simultaneous determination of Cr(VI) and Cr(III) is difficult by the instrumental techniques like flame and graphite furnace atomic absorption spectrometry, inductively coupled plasma-optical emission spectrometry [13–17].

The speciation procedures for chromium are generally based on the preconcentration and separation of one of the chromium species (Cr(III) or Cr(VI)). It was reported in literature that total chromium was determined after the reduction of Cr(VI) or by the oxidation of Cr(III) [18–23]. Most preconcentration methods for separating the two chromium oxidation states involve ion-exchange, solid-phase extraction, cloud point extraction and liquid–liquid extraction have also been used [20–26].

Coprecipitation is a separation–preconcentration technique based on phase separation. Analyte ions could be precipitated in the procedure with the combination of a carrier element and a suitable chelating agent [27–29]. Studies on chromium speciation by coprecipitation using various reagents have been suggested by the researchers [30–33]. According to our literature knowledge, thulium hydroxide precipitate is not used for the speciation of chromium.

In the presented coprecipitation work, speciation of chromium in environmental samples has been performed by using thulium hydroxide precipitate. The analytical parameters including pH,

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Table 1
FAAS operating conditions for chromium

Wavelength (nm)	357.9
Slit width (nm)	0.5
Lamp current (mA)	12
Flame type	Air/acetylene
Fuel flow rate (L s ⁻¹)	1.0

sample volume, matrix effects, etc. on the quantitative speciation of chromium were discussed.

2. Experimental

2.1. Apparatus

UNICAM 989 Model flame atomic absorption spectrometer (Unicam 989, Thermo Elemental Corp., Franklin, MA, USA) was used for the determination of chromium. The instrument was optimized daily before measurement and operated as recommended by the manufacturers as given in Table 1.

The pH values were measured using WTW inoLab Level 3 with terminal Level 3 (Weilheim, Germany). Rotina 38 Hettich model centrifuge (Buckinghamshire, UK) was used to centrifuge of solutions. The water that used all the experiments was purified in Millipore Synergy 185 (Billerica, MA, USA).

2.2. Reagents and solutions

High purity reagents from Sigma (St. Louis, MO, USA) and Merck (Darmstadt, Germany) were used for all preparations of the standard and sample solution. Stock solutions of analyte ions, 1000 mg L⁻¹, was diluted daily for obtaining reference and working solutions. 0.2% (w/v) thulium(III) solution was prepared freshly by dissolving Tm₂O₃ (Fluka) in small amounts of 1 M HNO₃ and diluting to 100 mL with double distilled water. Cr(VI) and Cr(III) stock solutions (1000 mg L⁻¹) were prepared from K₂CrO₄ and Cr(NO₃)₃·9H₂O. Stock solutions of diverse elements were prepared from the high purity compounds (99.9%) (St. Louis, MO, USA).

2.3. Test procedure

2.0 mg of thulium(III) was added to 10 mL of solution containing 25 µg of Cr(III) ions. Then the pH of the solution was adjusted to related pH by the addition of 1 M NaOH. After 10 min, the precipitate was collected through a cellulose nitrate membrane filter of 0.45 µm size and 47 mm diameter. The precipitates together with the membrane were dissolved in 0.5 mL of concentrate nitric acid, and then the solution was diluted to 5 or 10 mL with water. The metal contents of the final solution were determined by flame AAS. The number of replicates for the test workings was 3.

Reduction of Cr(VI) to Cr(III) has been performed by using the procedure given in literature [34,35]. After adjustment of the pH of the solution 1 by 1.0 M H₂SO₄, 10 mL of 5% KI was added. The solution was boiled for 30 min. The solution was cooled to room temperature. Then test procedure given above was applied to this solution. Chromium was determined by FAAS. After reduction of Cr(VI) to Cr(III), the method was applied to the determination of the total chromium. The level of Cr(VI) is calculated by difference of total chromium and Cr(III) concentrations.

2.4. Analysis of real samples

The application of the presented procedure was performed by BCR-144R Sewage Sludge (domestic origin) certified reference. 0.1 g of certified reference material was digested with 15 mL of aqua regia

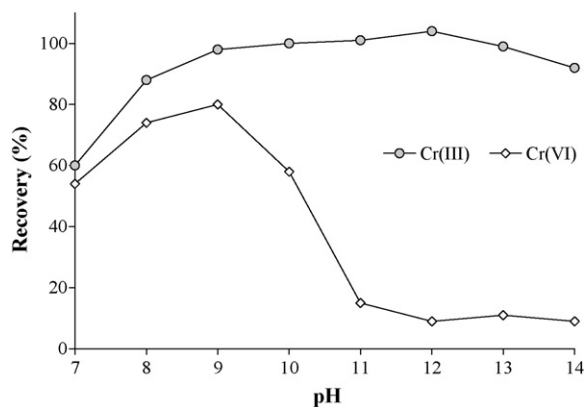


Fig. 1. Influences of pH on the recoveries of Cr(III) and Cr(VI) ($N=3$).

at room temperature then it was heated to 95 °C. After the evolution of NO₂ fumes had ceased, the mixture was evaporated almost to dryness on a sand-bath and mixed with 8 mL of aqua regia. Then the mixture was again evaporated to dryness. After evaporation 8–9 mL of distilled water was added and the sample was mixed. The resulting mixture was filtered through a blue band filter paper. The filtrate was diluted to 25 mL with distilled water. pH of this solution was adjusted to 12.0 by the addition of 1 M NaOH. Then the coprecipitation procedure given in Section 2.3 was applied.

Water samples analyzed were filtered through a cellulose membrane filter (Millipore) of 0.45 µm pore size. The pH of the samples was adjusted to 12 by the addition of 1 M NaOH. Then the procedure given above was applied. The levels of chromium in the samples were determined by flame atomic absorption spectrometry. Total chromium in natural water samples was determined as chromium(III) after the reduction of chromium(VI) to chromium(III) in the natural waters. The reduction of Cr(VI) to Cr(III) was performed by the procedure given in literature [34,35].

3. Results and discussion

3.1. Effects of pH

Quantitative recoveries for the analytes have been generally obtained for the analytes in the recent hydroxide coprecipitation works at the basic pH values [28,32,36]. Because of these points, the influences of the pH of the model solutions on the quantitative recoveries of chromium species on the thulium(III) hydroxide coprecipitation system were investigated in the pH range of 7.0–14.0. The results were depicted in Fig. 1. Quantitative recovery values were obtained for Cr(III) in the pH range of 9.0–13.0. The recoveries of chromium(VI) were not quantitative at the all working pH. Especially, the recoveries for Cr(VI) were lower than 10% at the pH range of 12.0–14.0. These results show that quantitative and selective separation of Cr(III) and Cr(VI) is possible at the pH range of 12.0–14.0. All subsequent works were performed at pH 12 for speciation of chromium species.

3.2. Effects of amounts of thulium(III)

The effects of amount of thulium(III) on the recoveries of Cr(III) on the presented coprecipitation system were also investigated in the range of 0–4.0 mg. The results are depicted in Fig. 2. The recovery of chromium(III) was below 20% without thulium(III). The recovery values increased with the increasing amounts of thulium(III). After 1 mg of thulium(III), the recovery values were quantitative. Further studies were carried out with 2 mg of thulium(III).

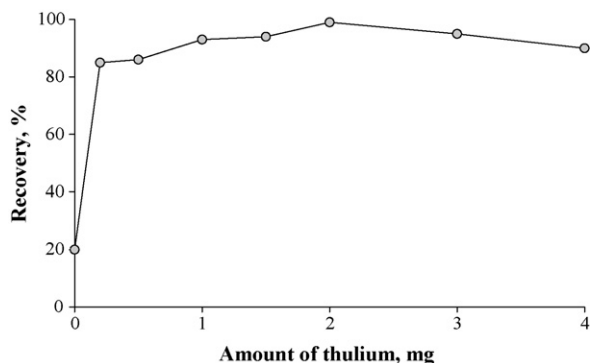


Fig. 2. Effects of amount of thulium(III) on the recoveries of Cr(II) on the presented coprecipitation system, $N = 3$.

Table 2
Effects of duration time on the recoveries of Cr(III) ($N = 3$)

Duration time (min)	Recovery (%)
0	85
5	93
10	95
15	96
20	97
30	99
45	101
60	100

3.3. Effects of duration time for coprecipitation

The influences of duration time for the coprecipitation on the recoveries of analytes were also studied in the time range of 0–60 min. The results are given in Table 2. Quantitative recoveries for all the analytes were obtained after 10 min of duration time. The studies were performed at 10 min of duration time.

3.4. Sample volume

Because sample volume is an important factor to obtain high preconcentration factor [36,37,24,38–41], the influences of sample volume of the samples on the recoveries of Cr(III) were investigated on the sample volume range of 25–1000 mL by using model solutions prepared at the optimal conditions. The results for this study are depicted in Fig. 3. Cr(III) was quantitatively recovered in the sample volume range of 25–1000 mL. The final volume of the coprecipitation work was 5.0 mL. A preconcentration factor of 200 can be achieved when the final volume was 5.0 mL.

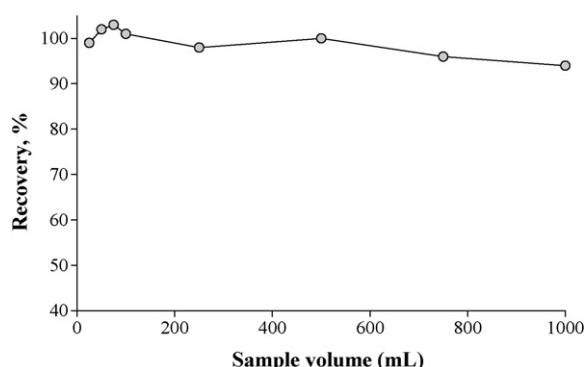


Fig. 3. Influences of sample volume on the recoveries of Cr(VI), $N = 3$.

Table 3
Effects of concomitant ions on the recoveries of Cr(III) on the presented coprecipitation system ($N = 3$)

Added as		Concentration (mg L ⁻¹)	Recovery % for Cr(III)
Na ⁺	NaCl	10,000	93 ± 2
K ⁺	KCl	2,500	95 ± 4
Ca ²⁺	CaCl ₂	2,500	98 ± 4
Mg ²⁺	MgCl ₂	100	94 ± 1
SO ₄ ²⁻	Na ₂ SO ₄	2,500	98 ± 4
HPO ₄ ²⁻	Na ₂ HPO ₄ ·7H ₂ O	2,500	95 ± 2
CO ₃ ²⁻	Na ₂ CO ₃	2,500	93 ± 1
NO ₃ ⁻	KNO ₃	2,500	94 ± 2
I ⁻	KI	50,000	102 ± 4
Fe	Fe(NO ₃) ₃ ·9H ₂ O	10	100 ± 2
Al	Al ₂ (SO ₄) ₃ ·18H ₂ O	20	97 ± 2
Pb	PbCl ₂	20	95 ± 1
Ni	NiCl ₂ ·6H ₂ O	10	99 ± 2
Zn	ZnI ₂	10	101 ± 1
Cd	CdCl ₂	20	95 ± 2
Co	CoCl ₂ ·6H ₂ O	10	94 ± 1
Cu	Cu(NO ₃) ₂ ·3H ₂ O	10	95 ± 2
Cr ⁶⁺	K ₂ Cr ₂ O ₇	5	101 ± 2

3.5. Matrix effects

The influences of matrix components of the samples analyzed are also a main problem in the flame atomic absorption spectrometric determination of chromium and other metal ions [42–45]. In order to assess the possible analytical applications of the recommended procedure, the effect of some foreign ions which interfere with the determination of metal ions by the presented method or/and often accompany analyte ions in various real samples was examined with the optimized conditions mentioned above. Tolerable limit was defined as the highest amount of foreign ions that produced an error not exceeding 5% in the determination of investigated analyte ions. The results are summarized in Table 3. Chromium(III) ions were generally quantitatively recovered by the investigated matrix ions. This results show that the presented procedure could be applied to separation and preconcentration of chromium(III).

3.6. Determination of total chromium

In order to determine the total chromium, firstly model solutions that contain different amounts of Cr(VI) and Cr(III) were prepared. Then Cr(VI) ions in the model solutions were reduced to Cr(III) by using KI in acidic media [34,35]. Because of the quantitative recoveries for Cr(III) were obtained at pH 12.0, the pH of the solution was adjusted to pH 12.0 by the addition of 1 M NaOH. Then the procedure given in Section 2 was applied to these solutions. The results are given in Table 4. The results show that the proposed method could be applied for the determination of total chromium.

3.7. Figure of merits

The detection limit (LOD) of the present work was calculated under optimal experimental conditions after application of the preconcentration procedure to blank solutions. The detection limits ($k = 3$, $N = 15$) were 0.87 μg L⁻¹ for Cr(III) and 1.18 μg L⁻¹ for Cr(VI).

The precision of the determination of chromium(III) was evaluated under the optimum conditions mentioned above for the presented procedure ($n = 8$). The procedure was repeated 10 times for chromium(III). It was found that the recovery of Cr(III) was 96 ± 4 at 95% confidence level.

Table 4
Determination of total chromium in spiked test solutions ($N=3$)

Added (μg)		Found (μg)		Cr(VI)	Recovery (%)		
Cr(III)	Cr(VI)	Cr(III)	Total Cr		Cr(III)	Cr(VI)	Total Cr
0	25	–	$24.3 \pm 0.6^*$	24.3 ± 0.8	–	97 ± 3	97 ± 4
5	20	4.8 ± 0.2	24.3 ± 0.4	19.5 ± 0.3	96 ± 2	97 ± 1	97 ± 3
12.5	12.5	12.2 ± 0.1	24.0 ± 0.2	11.8 ± 0.2	97 ± 1	94 ± 2	96 ± 2
20	5	19.9 ± 0.3	24.8 ± 0.3	4.9 ± 0.1	99 ± 2	98 ± 2	99 ± 3
25	0	24.2 ± 0.5	24.2 ± 0.6	–	97 ± 3	–	97 ± 3

* Mean \pm standard deviation.**Table 5**
Total chromium determinations in spiked tap water solutions from Ankara ($V_{\text{sample}}: 250 \text{ mL}$, $V_{\text{final}}: 5 \text{ mL}$, $N=4$)

Added (μg)		Found (μg)		Cr(VI)	Recovery (%)		
Cr(III)	Cr(VI)	Total Cr	Cr(III)		Cr(III)	Cr(VI)	Total Cr
0	0	$1.04 \pm 0.13^*$	0.94 ± 0.16	0.10 ± 0.02	–	–	–
0	25	25.4 ± 0.5	–	24.1 ± 0.5	–	96 ± 2	95 ± 3
5	20	25.9 ± 0.2	5.6 ± 0.3	19.4 ± 0.4	94 ± 2	96 ± 1	98 ± 4
12.5	12.5	25.6 ± 0.2	12.9 ± 0.2	11.8 ± 0.2	96 ± 2	94 ± 2	97 ± 3
20	5	25.8 ± 0.3	20.0 ± 0.3	4.9 ± 0.4	95 ± 4	96 ± 2	99 ± 3
25	0	26.3 ± 0.4	25.3 ± 0.4	–	96 ± 3	–	99 ± 2

* Mean \pm standard deviation.**Table 6**
Application of presented procedure for the determination of total chromium in BCR-144R Sewage Sludge (domestic origin) certified reference material ($N=5$)

Certified value ($\mu\text{g g}^{-1}$)	90 \pm 6
Our value ($\mu\text{g g}^{-1}$)	87 \pm 4

* Uncertainty at 95% confidence limit.

3.8. Applications

We have explored feasibility of presented speciation procedure for the determination of Cr(III), Cr(VI) and total chromium in tap water from Ankara City. The preconcentration–speciation procedure was applied to the determination of chromium species by standard addition method. The reliability was checked by spiking experiments. The results were presented in Table 5. The recovery of spiked samples was satisfactory reasonable and was confirmed using addition method, which indicate the capability of coprecipitation system in the speciation of chromium in natural water samples.

The method was applied to BCR-144R Sewage Sludge (domestic origin) certified reference materials for the separation and preconcentration of chromium at trace level. The results in Table 6 are based on the average of five replicates. The results are in good agreement with the certified values for chromium. Also the application of the proposed procedure for total chromium was performed to the microwave digested samples given in Table 7.

Table 7
Application of presented coprecipitation procedure for the speciation of Cr(III) and Cr(VI) in various natural water samples ($V_{\text{sample}}: 500 \text{ mL}$, $V_{\text{final}}: 5 \text{ mL}$, $N=5$)

	Cr(III) ($\mu\text{g L}^{-1}$)	Cr(VI) ($\mu\text{g L}^{-1}$)
Izmir Tap Water	1.35 ± 0.12	BDL
Ankara Cubuk Tap Water	1.54 ± 0.18	BDL
Duzce Uğurlu Village Büyük Melen River	2.20 ± 0.14	3.06 ± 0.27
Kızılırmak Kesikköprü Dam	2.58 ± 0.22	1.88 ± 0.46
Isparta Değirmendere Chromium Mine Waste water	25.7 ± 2.7	2.6 ± 1.3
Yozgat Killiközü Chromium Mine Waste water	20.0 ± 2.2	6.5 ± 3.6

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

4. Conclusion

Thulium hydroxide precipitate is firstly used in the presented work for the coprecipitation of chromium species in natural water samples. The coprecipitation procedure presented for Cr(III) and Cr(VI) is simple, facile and economic for their speciation and preconcentration. No interferences of various matrix components of the natural water samples were observed.

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