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Speciation of chromium by the combination of dispersive liquid–liquid microextraction and microsample injection flame atomic absorption spectrometry

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Abstract: A microextraction procedure was established for the speciation of total Cr, Cr(III), and Cr(VI). Sudan blue II was used as a ligand for speciation works. Some factors affecting the recoveries of chromium species, including type of extraction and dispersive solvents, pH, ligand amount, extraction time, and matrix ions, were examined. Optimum values for the dispersive liquid–liquid microextraction method were pH 6, LOD $0.34 \mu\text{g L}^{-1}$, and preconcentration factor 400. Chromium(III) was quantitatively recovered under optimal conditions, while the recovery of chromium(VI) was below 10%. The relative standard deviation for Cr(III) determinations for the 10-replicate measurement of $0.3 \mu\text{g mL}^{-1}$ Cr(III) was 6.2%. The accuracy was verified using BCR-144R Sewage Sludge, IAEA 336 Lichen, and TMDA 25.3 certified water for trace elements. The procedure was applied to speciation of chromium in water samples. Total chromium was determined in various wheat, bread, and hair samples.

Key words: Microextraction, chromium, Sudan blue II, speciation, preconcentration, microsample injection, atomic absorption spectrometry

1. Introduction

Chromium(III) and chromium(VI) are the main and important oxidation states of chromium.¹ They play different and important roles in the human body. Chromium(III) has a considerable effect on the normal glucose tolerance factor and metabolism in humans.^{2,3} The daily recommended intake of chromium(III) is 50–200 $\mu\text{g/day}$ for an adult.^{2,3} Chromium(VI) is known to be toxic and carcinogenic. Chromium(VI) can be an important source of cancer.^{4–6} Chromium is used in various industries such as tanning, paint, pigment, plating, and metal.^{7–9} Therefore, speciation of these 2 main species of chromium is very important in analytical chemistry.

Separation and enrichment procedures are frequently needed prior to the detection of ultratrace level chromium species.^{10–12} A high performance, rapid, economical, low chemical consumption microextraction technique explained as dispersive liquid–liquid microextraction (DLLME) has been established by Assadi and co-workers.¹³ DLLME has been efficiently used in the determination of inorganic cadmium,^{14,15} lead,^{16–18} and cobalt^{19–21} in environmental or biological samples. In recent years, DLLME has also been employed for the speciation of Cr(III) and Cr(VI) in environmental samples under different conditions.^{22,23} The proposed DLLME method also has different and novel conditions for chromium speciation.

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Sudan blue II (Solvent Blue 35 or Oil Blue 35) is derived from anthraquinone (Figure 1). It is used as a dye for various purposes and has complexes with metal ions.²⁴ According to our literature survey, Sudan blue II has not been used as a ligand for the speciation of Cr(III) and Cr(VI) using DLLME.

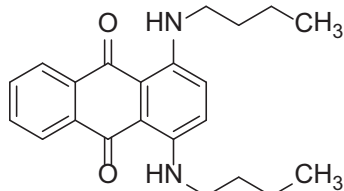


Figure 1. Sudan Blue II.

In the present work, a speciation procedure for Cr(III), Cr(VI), and total Cr based on microextraction was established. The effects of analytical parameters including pH, amounts of ligand, and matrix effects were investigated.

2. Experimental

2.1. Instrument

A PerkinElmer Model 3110 (Norwalk, CT, USA) model flame atomic absorption spectrometer was used for the determination of chromium. A chromium hollow cathode lamp and an air/acetylene flame atomizer were used for all measurements. The operating conditions were as follows: wavelength 357.9 nm, slit width 0.2 nm, lamp current 5.4 mA, and fuel flow rate 2.5 mL/min. Next, 50 μ L of the samples were injected into the nebulizer of the FAAS using the microinjection system.¹⁴ pH values were measured with a PHS-3C pH meter (model Nel pH-900 Nel Company, Ankara, Turkey) supplied with a combined glass electrode. Ultrapure water was prepared using a water purification system (Model RO 180, HUMAN Corp., Seoul, Korea) with a conductivity of 1 μ S cm^{-1} . An ALC PK 120 model centrifuge (Buckinghamshire, UK) was used.

2.2. Standard solutions and reagents

Stock solutions of 1000 mg L^{-1} Cr(VI) and Cr(III) were prepared by dissolving $\text{K}_2\text{Cr}_2\text{O}_7$ and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Merck, Darmstadt, Germany) in 1% nitric acid solution and were diluted daily for obtaining reference and working solutions. Solution of Sudan blue II (0.1%, m/v) was prepared in an ethanol/water (50/50, v/v) mixture.

The pH of the solutions was adjusted using buffer solutions. Phosphate buffer solutions at pH 2 and 3 were prepared by mixing appropriate volumes of 1 mol L^{-1} sodium dihydrogen phosphate and phosphoric acid solutions. Acetate buffer solutions at pH 4–6 were prepared by mixing appropriate volumes of 1 mol L^{-1} acetic acid and 1 mol L^{-1} sodium acetate solutions. For pH 6 and 7, phosphate buffer solutions were prepared by mixing appropriate volumes of 1 mol L^{-1} sodium dihydrogen phosphate and 1 mol L^{-1} sodium hydrogen phosphate. Ammonium buffer solutions at pH 8–9 were prepared by mixing appropriate amounts of 1 mol L^{-1} ammonia and 1 mol L^{-1} ammonium chloride solutions.

2.3. Analytical procedure

First, 25 mL of sample solution containing 0.3 $\mu\text{g mL}^{-1}$ Cr(III) at pH 6 was placed in a 50-mL conical tube and 100 μg of Sudan blue II solution was added. The pH of the model solution was adjusted to 6.0 by using 1

mol L⁻¹ acetate buffer solutions. After that, 125 μ L of carbon tetrachloride and 1 mL of ethanol were added to the model solution. A cloudy solution formed in the tube. The mixture was centrifuged at 3000 rpm for 8 min. Then 50 μ L of sediment phase was removed using a 100- μ L microsyringe and injected directly into the nebulizer of the FAAS.

2.4. Procedure for total chromium

First, 25 mL of sample solution containing 0.3 μ g mL⁻¹ Cr(III) and 0.3 μ g mL⁻¹ Cr(III) was placed a 100-mL beaker. The pH of the solution was adjusted to 1.0 by 1 M H₂SO₄ and 10 mL of 0.5% KI was included in the solution for reduction of Cr(VI) to Cr(III).²⁵⁻²⁷ The solution was heated for 30 min and then was cooled to 25 °C. Next, the procedure given in Section 2.3 was performed for the determination of total Cr. The amount of Cr(VI) was estimated by the difference in total Cr and Cr(III) levels.

2.5. Applications

First, 250 mg of BCR-144R Sewage Sludge, IAEA 336 Lichen certified reference materials, and sediment samples were digested with 10 mL of aqua regia at 95 °C. The mixture was evaporated almost to dryness on a plate and mixed with 10 mL of aqua regia and the mixture was again evaporated to dryness. Then 10 mL of distilled water was added. The mixture was filtered through Whatman blue band filter paper.

In addition, 1.0-g food and hair samples were digested with 10 mL of concentrated HNO₃ (65%) and 3 mL of H₂O₂ (30%) at 95 °C and evaporated to dryness. A 10-mL aliquot of water was added. The resulting mixture was filtered through Whatman blue band filter paper. Then the procedure given above was applied to the final solution.

The procedure was applied for different water samples including Certified Reference Water for Trace Elements (TMDA 25.3) and some water samples from various locations in Turkey. The waters were filtered through a membrane filter of 0.45-mm pore size. Next, 25-mL water samples were taken and the procedure given in Section 2.3 was applied to the final solution.

3. Results and discussion

3.1. Effect of pH

pH is a key factor for quantitative extraction and complex formation of analytes with ligands in microextraction studies.²⁸⁻³¹ Sudan Blue II has complexes with chromium(III).²⁴ The influences of pH values on recoveries of chromium species were investigated at the pH range 2.0–9.0 (Figure 2). The recovery values of Cr(III) were found quantitative at the pH range 6.0–9.0. The recovery values of Cr(VI) were lower than 10% in the pH range 2.0–7.0. Therefore, pH 6.0 was selected as the optimum value for Cr(III) and Cr(VI) speciation.

3.2. Influences of amounts of Sudan blue II

The effects of the amounts of Sudan blue II on the recovery values of Cr(III) were studied in the range 20–150 μ g of Sudan blue II. The results are illustrated in Figure 3. The recovery of Cr(III) was lower than 10% without Sudan blue II. The recovery values reached quantitative values after 80 μ g of Sudan blue II. All subsequent studies were done using 100 μ g of Sudan blue II.

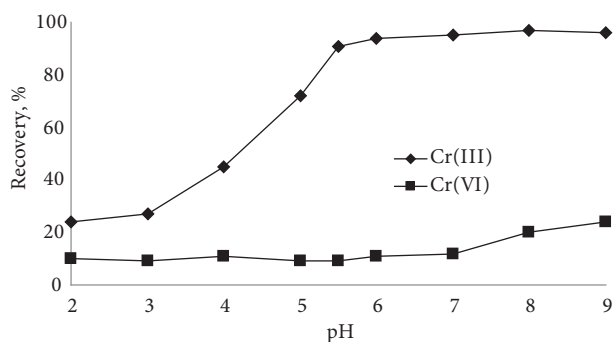


Figure 2. Influences of pH on the speciation of chromium (n = 3).

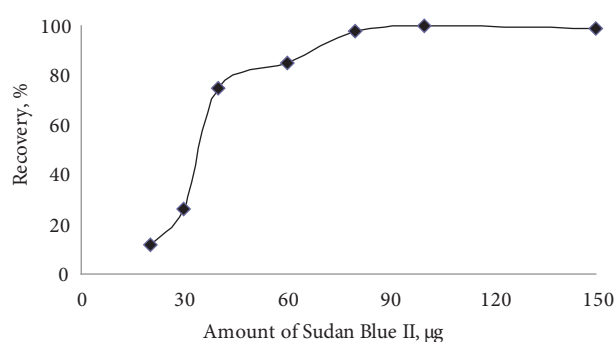


Figure 3. Effects of amount of Sudan blue II on recovery values of Cr(III).

3.3. Extraction solvent

Carbon tetrachloride, chloroform, carbon disulfide, and dichloromethane were used as extraction solvents using 1000 μL of ethanol. The recovery values were 98 %, 94%, 91%, and 91% for CCl_4 , CHCl_3 , CS_2 , and CH_2Cl_2 , respectively. CCl_4 was selected as the extraction solvent for all further work.

The volume of carbon tetrachloride was tested in the range 25–250 μL . The results are given in Figure 4. The recovery values were found quantitative after using 125 μL of CCl_4 . Therefore, 125 μL of carbon tetrachloride was chosen as optimal for all further work.

3.4. Disperser solvent

Acetonitrile, acetone, isopropanol, methanol, and ethanol were tested as disperser solvent. The recovery values were 75%, 92%, 82%, 85%, and 98% for acetonitrile, acetone, isopropanol, methanol, and ethanol, respectively. The recoveries were quantitative using ethanol. Therefore, ethanol was chosen for further work.

The influence of the volume of ethanol on the recoveries was also studied in the range 0.10–2 mL. The results are shown in Figure 5. Quantitative recoveries were obtained after 1 mL of ethanol.

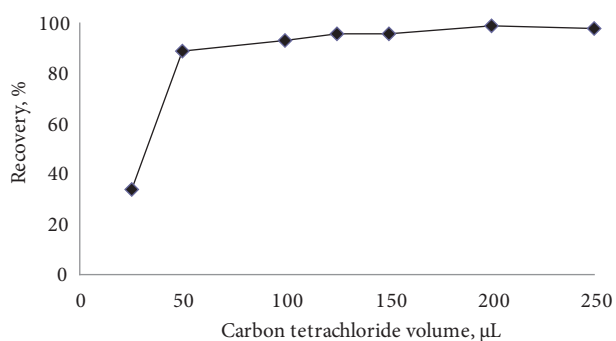


Figure 4. Effects of carbon tetrachloride volume on recovery values of Cr(III).

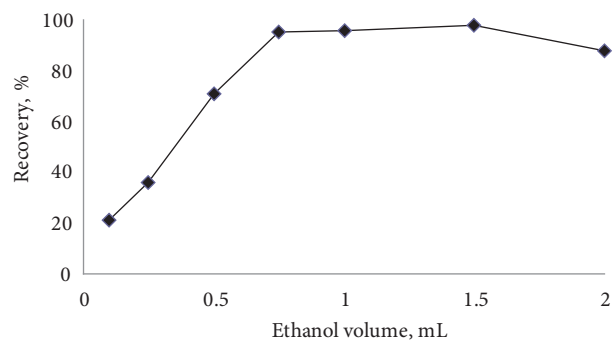


Figure 5. Effects of ethanol volume on recoveries of Cr(III).

3.5. Effects of centrifugation speed and time

The influences of centrifugation speed were studied in the speed range 500–4500 rpm. The recoveries for chromium(III) were higher than 95% in the range 1500–4500 rpm. The effects of centrifugation time were also studied in the range 4–15 min. The recovery values of chromium(III) of the presented method of DLLME were

higher than 95% in the range 8–15 min. Centrifugation speed and time of 1500 rpm and 8 min were chosen for further work.

3.6. Influence of sample volume

The influence of sample volume on the recoveries of chromium(III) was studied in the range 10–50 mL. The recovery values of Cr(III) were quantitative (95%) with 50 mL. A preconcentration factor of 400 can be obtained when using 50 mL of the sample volume and 125 μL of final volume.

3.7. Effects of coexisting ions

Matrix effects are a very problematic point in the instrumental detection of trace metallic species.^{32–38} The influences of some anions and cations on the recovery values of Cr(III) were investigated separately. The results obtained are given in Table 1. The tolerance limit is described as some heavy metals, cations, and anions ion concentrations causing a relative error smaller than 5%. The results obtained defined good tolerance of coexisting ions studied in water and food samples.

Table 1. Matrix effect for recovery of chromium(III) (n = 3).

Concomitant	Concentration ($\mu\text{g mL}^{-1}$)	Added as	Recovery % (Cr(III))
Na^+	9000	NaCl	96 ± 2
K^+	1500	KCl	97 ± 1
Mg^{2+}	750	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	100 ± 1
Ca^{2+}	1750	CaCl_2	99 ± 1
NO_3^-	1000	KNO_3	98 ± 2
SO_4^{2-}	1500	Na_2SO_4	95 ± 2
Cl^-	15,000	NH_4Cl	95 ± 3
Al^{3+}	30	$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	99 ± 1
Cu^{2+}	20	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	97 ± 2
Co^{2+}	15	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	94 ± 3
Mn^{2+}	15	$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	95 ± 2
Ni^{2+}	15	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	95 ± 1
Pb^{2+}	20	$\text{Pb}(\text{NO}_3)_2$	96 ± 2
Cd^{2+}	20	$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	96 ± 2
Fe^{3+}	10	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	94 ± 2

3.8. Total chromium

A reduction procedure for Cr(IV) to Cr(III)^{25–27} was performed. After reduction, the procedure given in Section 2.3 was applied. The results are listed in Table 2. Quantitative results were obtained. These results show that the proposed method could be applied to the determination of total chromium in environmental samples.

3.9. Analytical figures of merit

The calibration graph was linear in the range 0.5–4.0 $\mu\text{g mL}^{-1}$ with a correlation coefficient (r^2) of 0.9991. The regression equation was $A = 0.016C + 0.0001$ (A: absorbance, C: concentration). The limit of detection (LOD) of the DLLME method was calculated under optimal experimental conditions by applying the procedure

for blank solutions. The detection limit of Cr(III) based on 3 times the standard deviations of the blank (n = 10) divided by preconcentration factor was $0.34 \mu\text{g L}^{-1}$.

Table 2. Speciation of chromium in spiked model solutions (Sample volume 25 mL, n = 3).

Added (μg)		Found (μg)			Recovery, %		
Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Total Cr	Cr(III)	Cr(VI)	Total Cr
0	20	-	19.6 ± 0.3	19.6 ± 0.3	-	98 ± 1	98 ± 1
5	15	4.8 ± 0.1	14.7 ± 0.2	19.5 ± 0.2	96 ± 2	98 ± 2	97 ± 2
15	5	14.9 ± 0.2	4.7 ± 0.1	19.6 ± 0.2	99 ± 1	94 ± 2	98 ± 1
20	0	19.5 ± 0.4	-	19.5 ± 0.3	97 ± 1	-	96 ± 2

The relative standard deviation (RSD) of $0.3 \mu\text{g mL}^{-1}$ chromium(III) determinations for 10-replicate measurement was 6.2%. It was found that the recovery of Cr(III) was 97 ± 3 at 95% confidence level.

3.10. Applications

We investigated the applicability of the developed speciation method for the determination of chromium(III), chromium(VI), and total chromium in water samples. The proposed preconcentration–speciation method was carried out for the determination of chromium species. The results are given in Table 3. The recoveries of chromium(III), chromium(VI), and total chromium for spiked samples were in the range 94%–100%. The proposed procedure was carried out with BCR-144R Sewage Sludge, IAEA 336 Lichen, and certified reference water for trace elements (TMDA 25.3) materials and street sediment, water, wheat, bread, and hair samples. The results are given in Table 4 for SRM and in Table 5 for street sediment, water, wheat, bread, and hair samples. The values obtained are in agreement with the certified values. The results showed that the development procedure was suitable for the determination of Cr(III), Cr(VI), and total chromium in real samples.

Table 3. Speciation of chromium in spiked real samples (volume of river water: 25 mL, amount of wheat: 1 g, n = 3).

	Added Cr(III), $\mu\text{g L}^{-1}$	Added Cr(VI), $\mu\text{g L}^{-1}$	Found Cr(III), $\mu\text{g L}^{-1}$	Found Cr(VI), $\mu\text{g L}^{-1}$	Found Total Cr, $\mu\text{g L}^{-1}$	Recovery (%) for Cr(III)	Recovery (%) for Cr(VI)	Recovery (%) for Total Cr
River water	--	--	84 ± 4	60 ± 4	144 ± 8	-	-	-
	200	200	276 ± 12	256 ± 12	532 ± 16	96 ± 2	98 ± 2	97 ± 2
	200	200	460 ± 36	456 ± 28	916 ± 44	94 ± 1	99 ± 14	96 ± 2
	Added Cr(III), $\mu\text{g g}^{-1}$	Added Cr(VI), $\mu\text{g g}^{-1}$	Found Cr(III), $\mu\text{g g}^{-1}$	Found Cr(VI), $\mu\text{g g}^{-1}$	Found Total Cr, $\mu\text{g g}^{-1}$	Recovery (%) for Cr(III)	Recovery (%) for Cr(VI)	Recovery (%) for Total Cr
Wheat	--	--	1.1 ± 0.1	-	1.1 ± 0.1	-	-	-
	5	5	6.0 ± 0.2	4.9 ± 0.1	10.9 ± 0.6	98 ± 2	98 ± 2	98 ± 2
	10	10	10.7 ± 0.5	9.9 ± 0.2	20.6 ± 1.1	96 ± 1	99 ± 2	98 ± 1

3.11. Comparison with literature studies

A comparison of results with those of some other methods in the literature for chromium speciation, enrichment, and separation is given in Table 6. The optimal values are comparable for the studies in the literature. The detection limit and preconcentration factor of DLLME are superior to the literature values with some exceptions.

Table 4. Chromium levels in some certified reference materials (n = 3).

Samples	Certified value	Our value ^b	Recovery, %
TM-25.3 water	24.5 $\mu\text{g L}^{-1}$	24.7 \pm 0.6 $\mu\text{g L}^{-1}$	101 \pm 1
BCR-144R Sewage Sludge	90 \pm 6 $\mu\text{g g}^{-1}$	89 \pm 1 $\mu\text{g g}^{-1}$	99 \pm 2
Lichen (IAEA-336)	(1.06 $\mu\text{g g}^{-1}$) ^a	1.02 \pm 0.02 $\mu\text{g g}^{-1}$	96 \pm 2

^aNot certified.

^bMean \pm standard deviation

Table 5. Levels of chromium in water, food, and biological samples as an application of the presented method (n = 3).

	Cr(III) ($\mu\text{g L}^{-1}$)	Cr(VI) ($\mu\text{g L}^{-1}$)
Waste water	102 \pm 7 ^a	182 \pm 12
River water	2.1 \pm 0.1	1.5 \pm 0.1
Spring water	7.8 \pm 0.6	2.1 \pm 0.2
Well water	BDL	BDL
	Total chromium ($\mu\text{g g}^{-1}$)	
Hair 1	4.3 \pm 0.4	
Hair 2	3.4 \pm 0.3	
Wheat	1.1 \pm 0.1	
Street sediment	3.3 \pm 0.2	
Bread	BDL	

BDL: Below detection limit

^aMean \pm standard deviation

Table 6. Comparison of the presented procedure and some works in the literature for chromium speciation.

Method	Instrument	Preconcentration factor	LOD ($\mu\text{g L}^{-1}$)	References
Dispersive liquid–liquid microextraction	FAAS	262	0.08	13
Ultrasonic probe-assisted ionic liquid dispersive liquid–liquid micro extraction	ETAAS	300	0.07	22
Solid phase extraction	FAAS	71	0.7	31
Cloud point extraction	ICP-AES	20	0.81	39
Coprecipitation	FAAS	100	0.5	40
Solid phase extraction	FAAS	31	1.94	41
Dispersive liquid–liquid microextraction	EAAS	171	0.059	42
Dispersive liquid–liquid microextraction	FAAS	400	0.34	Present method

4. Conclusions

The presented method of dispersive liquid–liquid microextraction for trace amounts of chromium for its speciation is new, simple, and accurate prior to its flame atomic absorption spectrometric detection. Cr(III) is easily and quantitatively separated from Cr(VI) at pH 6.0 under optimal conditions. The use of organic solvent in this procedure is very low. The effects of concomitant ions are tolerable.

Acknowledgments

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