Ultrasonic-assisted Supramolecular Solvent Liquid-liquid Microextraction for Inorganic Chromium Speciation in Water Samples and Determination by UV-Vis Spectrophotometry

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ABSTRACT: A simple and fast ultrasonic-assisted green supramolecular solvent liquid-liquid microextraction method (UA-SS-LLME) was developed for the determination of Cr(VI) and Cr(III). A Cr(VI) stock solution was complexed with 1,5-diphenylcarbazide (DPC) reagent to form a metal ligand reaction, followed by UV-Vis spectrophotometric analysis at 540 nm. Tetrahydrofuran (THF) and decanoic acids were also used for the microextraction of chromium speciation. Cr(III) was oxidized to Cr(VI) by using H₂SO₄ for the determination of total chromium. The Cr(III) concentration was calculated by subtracting the Cr(VI) concentration from total chromium. The parameters for sample volume, H₂SO₄ concentration, DPC concentration, and ultrasonic bath time were optimized at 20 mL, 0.002 mol L⁻¹, 1.25×10⁻⁴ mol L⁻¹, and 4 min, respectively. The interference effects of the matrix components were also examined. The limit of detection (LOD), limit of quantification (LOQ), enhancement factor, and the relative standard deviation were found at 0.79 µg L⁻¹, 2.64 µg L⁻¹, 50 and 2.40 %, respectively. The accuracy of the method was verified by analyzing two certified reference materials (TMDA-64.2 Fortified Lake Water and TMDA-53.3 Fortified Environmental Water). The proposed method was successfully used to the analysis of real environmental waters.

INTRODUCTION

Heavy trace elements are extensively used in industry and contribute to the pollution of soil and water, causing degradation of the food chain and toxicity to human beings.^{1,2} One of the trace elements widely studied in environmental or geochemical samples is chromium (Cr) because its toxicity depends on the

oxidation state. In the form of Cr(III) ions, it is an important nutrient for humans (recommended daily dose of 50–200 µg)³ and is involved in the regulation of insulin, determines the fat and protein metabolism, the storage of carbohydrates, and the level of glucose in the blood.^{4,5} At the same time, it also helps to lower the cholesterol levels of the blood, and contributes to the production of the serotonin hormone which to reduce the

risk of depression.^{6–8} However, Cr as Cr(VI) has a high redox potential, is a strong oxidant, extremely irritating to skin, and has a harmful effect on the lungs, liver, and kidneys. The World Health Organization (WHO) announced maximum permissible concentration of Cr(VI) in drinking water to be 0.05 mg L⁻¹.⁹ It also easily passes through the cell membrane and can trigger apoptosis (cell death).^{10–12} The hexavalent form of Cr was classified by the International Agency for Research on Cancer (IARC) as a Class I Carcinogen and by the U.S. Environmental Protection Agency (EPA) as highly toxic.^{12–14}

Different compounds of Cr can be formed depending on its oxidation state which may be essential or toxic. Therefore, the oxidation state of Cr needs to be analyzed separately, known as speciation.^{15–17} Speciation is the determination of the total concentration of Cr by analyzing its different physicochemical structures.¹⁸ The need for trace level determination of Cr in environmental and water samples has increased widely and is reported in environmental pollution and public health studies.^{7,9,15,17,19} Total Cr is analyzed using instrumental techniques such as inductively coupled plasma mass spectrometry (ICP-MS), flame atomic absorption spectrometry (FAAS), inductively coupled plasma atomic emission spectrometry (ICP-OES), electrothermal atomic absorption spectrometry (ETAAS), and UV-Vis spectrophotometry.

For this study, UV-Vis spectrophotometry analysis was used for Cr speciation because the method is low cost and provides fast and easy automation.^{13,14} A direct analysis approach for Cr would be difficult due to the low concentrations of the analyte and the high matrix interferences found in environmental samples.¹⁹

For the speciation and preconcentration of Cr, liquid-liquid extraction (LLE), solid phase extraction (SPE), and cloud point extraction (CPE) are generally used. However, these methods are time-consuming and require a high volume of toxic solvents, thus produce

toxic waste. In recent years, liquid-liquid microextraction (LLME) and solid phase microextraction (SPME), called the green methods, have been used for extraction studies.^{17–25} The LLME method is commonly used as an extraction process for organic and inorganic analytes, is environmentally friendly, low cost, and a simple technique. Eco-friendly solvents such as supramolecular ionic liquids and deep eutectic solvents (DESSs) have become popular.¹⁷ Another method is the ultrasonic-assisted supramolecular liquid-liquid microextraction (UA-SS-LLME), which uses green solvents. The method is generally applied to the extraction of metals and hydrophobic organic compounds in environmental and biological liquid samples. Supramolecular solvents are water-immiscible and disperse in a continuous phase. These solvents are molecular and nano-structured liquids composed of amphiphilic groups by self-sequential coupling. They are generally obtained by mixing tetrahydrofuran (THF) with solvents having a long carbon chain with hydroxyl and carboxylic acid groups in their structures.²⁶ Supramolecular solvent formation takes place in two stages: (a) Amphiphilic groups form aqueous micelle, reverse micelle, and vesicle structures; (b) The micelles are then separated from the mass of the colloidal solution as the large liquid phase by optimizing the parameters (such as pH, electrolyte, and auxiliary organic solvents addition by phase separation known as coacervation) and form supramolecular clusters. Thus, they create a perfect reaction medium, interact more with the analyte, and provide high extraction efficiency.^{27–32}

1, 5-diphenylcarbazide (DPC) is commonly used as the complexing reagent for the determination of Cr(VI) because it is sensitive, specific, and selective. In this medium, Cr(VI) forms a soluble, dense purple-colored complex with DPC in the acidic medium. The colored complex occurs more slowly, but as the acid concentration increases, the solution reaches a purple color density in a very short time.^{33–36} According to a

literature survey; this is the first time that THF and decanoic acid are used in a supramolecular solvent system for the microextraction of Cr speciation with DPC as the complexing agent.

In this study, a new, simple, fast, sensitive, and selective UA-SS-LLME method is proposed for the separation, preconcentration, and speciation of Cr(III)/Cr(VI) in water samples by UV-Vis spectrophotometry. The critical analytical parameters, such as supramolecular solvent type and volume, amount of decanoic acid, H₂SO₄ concentration, and sample volume, were examined to establish the extraction efficiency of the proposed method.

EXPERIMENTAL

Instrumentation. Separation of Cr with the UA-SS-LLME method and determination of Cr(VI) as DPC complex was performed using a Hitachi UV-Vis spectrophotometer at 540 nm (Hitachi, Ltd., Japan). Ultra-pure water was obtained with a Millipore® Milli-Q® Direct 18 system (18 MΩ cm resistivity, Millipore Corporation, USA). The solution preparation and sonication studies were realized by using a DT-255 ultrasonic bath (Sonorex, Canada). The DPC volume was weighed with a Model Adventurer Pro precision scale (±0.1 mg) (Ohaus Europe GmbH, Switzerland).

Stock solutions and reagents. The Cr(III) and Cr(VI) stock solutions were prepared with analytical purity Cr(NO₃)₃·9H₂O and K₂Cr₂O₇ (Merck, Germany) and diluted to the appropriate concentrations. The DPC solution used to form a metal ligand complex with Cr(VI) was prepared daily in ethanol (Sigma-Aldrich, USA). Decanoic acid and THF acid were purchased from Sigma-Aldrich and the Merck, respectively.

UA-SS-LLME procedure. For optimization of the method, the preconcentration studies were carried out in an acidic solution medium containing 1.25×10^{-4} mol L⁻¹ DPC, 1 µg Cr(VI), and 0.002 mol L⁻¹ H₂SO₄. After the

purple-colored complex formed between Cr(VI) and DPC, 200 mg of decanoic acid and 700 µL THF were quickly added to the solution. The resulting sample solution was left standing in the ultrasonic bath for 4 minutes which then formed a cloudy solution. This solution was centrifuged at 4000 rpm for 10 minutes to accelerate the transition of the resulting complex from the extraction phase to the water phase. At the end of the centrifugation, the extraction phase was completely separated from the aqueous phase. The bottom water phase was removed with an injector and discarded. The extraction phase remaining in the tube was completed to 400 µL volume with ethanol. The absorbance measurements of the final solution were carried out with the UV-Vis spectrophotometer at 540 nm.

Procedure for total Cr. After oxidation of Cr(III) to Cr(VI) by addition of 1% (w/v) (NH₄)₂S₂O₈ to the acidic solution, the supramolecular solvent liquid-liquid microextraction method was applied. For the realization of oxidation, 0.5 mL of (NH₄)₂S₂O₈ (1%, w/v) solution and 0.5 mL of H₂SO₄ (0.1 mol L⁻¹) solution were added to the sample solution containing Cr(VI) and Cr(III). It was heated at 65 °C for about 30 min to complete the oxidation and to remove excess (NH₄)₂S₂O₈ from the solution medium.³⁷ The extraction phases were analyzed for Cr(VI) and Cr(III) by UV-Vis spectrophotometry.

Applications. The liquid phase microextraction procedure was applied to sea, lake, and tap water samples for method validation. Addition and recovery studies were carried out by adding Cr(III) and Cr(VI) to these samples at varying concentrations. In order to test the accuracy of the method, environmental water certified reference materials (CRMs) such as TMDA-64.2 Fortified Water and TMDA-53.3 Fortified Water (National Water Research Institute, Canada) were utilized for the determination of total Cr. All water samples analyzed were filtered through a 0.45 µm cellulose membrane filter assembly for the following UA-SS-LLME and Cr speciation studies.

RESULTS AND DISCUSSION

Effect of acid concentration. The effect of H_2SO_4 concentration on the recovery value is one of the most important parameters for complex formation between Cr(VI) and DPC in acidic medium. For this purpose, a series of optimization experiments were performed by using $0.0005\text{--}0.01\text{ mol L}^{-1}$ H_2SO_4 to investigate the effect of acid concentration on the recovery of Cr(III) and Cr(VI). As shown in Fig. 1a, recovery values up to 0.005 mol L^{-1} were obtained. When the acid concentration is higher than 0.005 mol L^{-1} , the phase separation may not be fully realized, and the extraction efficiency decreases as the analyte will be discarded with the water phase. While over 95% recoveries were obtained for Cr(VI) using H_2SO_4 concentration (Fig. 1a), less than 5% was calculated for the recovery of Cr(III). These results show that this method can be considered a valuable tool for the determination of Cr(VI). Even though this method only allowed for the determination of Cr(VI), both Cr forms [Cr(III) and Cr(VI)] can be analyzed separately by utilizing speciation. Therefore, the H_2SO_4 concentration of 0.002 mol L^{-1} was found to be optimum for the recovery of Cr(VI).

Effect of supramolecular solvent and amount of decanoic acid. The selection and amount of extraction and dispersing solvents are very important for extraction efficiency. For this purpose, THF was used as the dispersing solvent and the extraction efficiencies of 1-decanol and decanoic acid were investigated as an extraction solvent. This is an organic solvent which has the best extraction efficiency for Cr(VI). However, Cr(VI) could not be extracted once increasing volumes of 1-decanol (300–700 μL) was added, for recovers in the range of 5–30 %. Therefore, 1-decanol is not a suitable extraction solvent for this UA-SS-LLME method. Quantitative recovers for Cr(VI) were obtained by using decanoic acid (> 90%) (Fig. 1b), ($\%R = (Q_A/Q_A^0) \times 100$; Q_A^0 =Amount of analyte in sample, Q_A =Amount of analyte in preconcentrated medium). Subsequent studies were carried out using decanoic acid as the extraction solvent because of the high recoveries obtained (Fig 1b).

Due to the fact that decanoic acid has a lower density compared to water, lower volatility and lower melting point, this organic solvent was selected.³⁰ One of the most important factors affecting the transition of the

Fig. 1 Optimization of the separation parameters on the recovery of Cr(VI). H_2SO_4 concentration (a), decanoic acid amount (b), THF volume (c), DPC concentration (d), sample volume (e), and ultrasonic time (f).

ion-pair complex formed between the cationic chelate complex and the extracting decanoic acid from the coeservate phase to the water phase is the amount of decanoic acid. In order to examine the effect of decanoic acid on the recovery values, decanoic acid in the range of 50–250 mg was added to the solutions containing Cr(VI). Quantitative values were obtained for the recovery of Cr(VI) when 200 mg decanoic acid was used (Fig. 1b).

Effect of THF volume. According to the literature, the most suitable supramolecular solvent system for reverse micelle formation and occurrence of coacervation was obtained when using THF. It is a dispersing solvent which is most capable of dissolving alkyl carboxylic acids.^{32,38,39} In the present study, THF was used as the dispersing solvent for the recovery of Cr(VI). Due to the fact that THF provides the transfer of Cr(VI) to the extraction phase, the effect of THF volume is one of the most important parameters. For this purpose, 200 mg of decanoic acid and increasing volumes of THF were added to the model solutions containing Cr(VI). When THF was used in the range of 200–800 μL , the highest recoveries were found at 700 μL of THF (Fig. 1c).

Effect of DPC concentration. DPC, which is the specific reagent for Cr(VI) speciation, was prepared daily in ethanol and utilized for the microextraction method in acidic medium. The effect of DPC on the microextraction efficiency was investigated in the concentration range of 0.5×10^{-4} to $1.5 \times 10^{-4} \text{ mol L}^{-1}$. When 1×10^{-4} and $1.25 \times 10^{-4} \text{ mol L}^{-1}$ DPC were used, recoveries of 95% were obtained (Fig. 1d). Therefore, all optimization steps were performed using the optimal ligand concentration of $1.25 \times 10^{-4} \text{ mol L}^{-1}$ DPC.

Effect of sample volume. Determining the highest sample volume without reducing the recovery value is important in the calculation of the analytical parameters such as preconcentration factor (PF) and limit of detection (LOD). The effects of sample volume on the recovery of Cr(VI) under optimum conditions were

studied for model solutions in the range of 10–25 mL. The results indicate (Fig. 1e) that the recovery of Cr(VI) was quantitative below 20 mL (>95%). However, it began to decrease above 20 mL sample volume. Thus, the maximum sample volume of 20 mL was used for further studies.

Effect of ultrasonic bath time. In this study, phase separation, called coacervation, and nano-molecular size micelles were formed in the ultrasonic bath. The mixing time in the ultrasonic bath is important for the extraction efficiency. For this purpose, the solutions containing Cr(VI) were prepared under optimum conditions and left in the ultrasonic bath from 2 to 8 min. Highest recovery value was obtained at the 4th min (Fig. 1f).

Effect of matrix ions. The tolerance concentrations of each of the foreign ions, such as alkali metals, alkaline earth metals and anions, were studied to evaluate their matrix effects while applying the UA-SS-LLME method to real samples. For this purpose, common coexisting ions in natural water samples in different concentrations were added to 20 mL sample solutions and the method was performed. The results show that the method was applied successfully at the specified concentrations (Table 1). Since the common foreign ions have no interference effect on the determination of Cr(VI) using the proposed method.

Analytical performance. The analytical performance of the proposed UA-SS-LLME method for the determination of Cr(VI) was examined by calculating the limit of detection (LOD), limit of quantification (LOQ),

Table 1. Effect of some foreign ions on Cr(VI) recovery (n=3)

Foreign ions	Added as	Concentration (mg L^{-1})	Recovery (%)
SO_4^{2-}	Na_2SO_4	1000	98 $\pm$ 2
CO_3^{2-}	Na_2CO_3	250	95 $\pm$ 4
Cd^{2+}	$\text{Cd}(\text{NO}_3)_2$	1	98 $\pm$ 7
Mn^{2+}	$\text{Mn}(\text{NO}_3)_2$	10	98 $\pm$ 4
Pb^{2+}	$\text{Pb}(\text{NO}_3)_2$	5	96 $\pm$ 3
Zn^{2+}	$\text{Zn}(\text{NO}_3)_2$	5	97 $\pm$ 6
Al^{3+}	$\text{Al}(\text{NO}_3)_3$	10	96 $\pm$ 1

Table 2. Spiking recovery of Cr species in waters (n=3)

Samples	Added, $\mu\text{g L}^{-1}$		Found, $\mu\text{g L}^{-1}$		Recovery, %	
	Cr (III)	Cr (VI)	Cr(VI)	Total Cr	Cr (III)	Cr (VI)
Tap water (1)	0.00	0.00	N.D. ^a	N.D.	--	--
	0.50	0.25	0.24±0.01	0.73±0.13	98	96
	0.50	0.50	0.50±0.05	1.01±0.12	102	98
Tap water (2)	0.00	0.00	N.D.	N.D.	--	--
	0.50	0.25	0.25±0.01	0.71±0.05	92	100
	0.50	0.50	0.50±0.07	0.98±0.03	96	100
Sea water	0.00	0.00	N.D.	0.24±0.01	--	--
	0.50	0.25	0.24±0.01	0.94±0.01	94	96
	0.50	0.50	0.49±0.01	1.24±0.07	101	98
Lake water	0.00	0.00	N.D.	N.D.	--	--
	0.50	0.25	0.24±0.03	0.70±0.10	92	96
	0.25	0.75	0.71±0.04	0.96±0.04	100	95

^a Not detected.

enhancement factor, and relative standard deviation (%). For this purpose, the UA-SS-LLME method was applied to 11 parallel blank solutions under optimum conditions. The detection limit (LOD) and the quantification limit (LOQ) of the method were calculated as $0.79 \mu\text{g L}^{-1}$ and $2.64 \mu\text{g L}^{-1}$ using the Equations $3s/B$ and $10s/B$ (S =standard deviation of blank solution, B =slope of the calibration graph), respectively. The enhancement factor was found as 50 from the slope ratio of the calibration graph with and without preconcentration. The linear calibration curve was obtained using Equation $A = 9.62 \times C + 0.0061$, $R^2 = 0.9997$ (A , Absorbance; C , Concentration). The linear range was calculated as $4.5\text{--}135 \mu\text{g L}^{-1}$ and the relative standard deviation (RSD) was found as 2.40% ($C=20 \mu\text{g L}^{-1}$, $n = 5$).

Analysis of water CRMs and real samples. The speciation analysis of Cr were performed for real environmental samples using the proposed UA-SS-LLME method. Addition and recovery studies for the analyte in tap, sea, and lake waters were carried out to assess the correctness of the proposed method. As listed in Table 2, the recoveries were between 92 and 102%. Thus, it can be stated that this method was successfully applied to the real samples for Cr speciation. As listed in Table 3, the accuracy of developed method was verified by two water CRMs.

Table 3. Results of water CRMs ($\mu\text{g L}^{-1}$, n=3)

Water CRMs	Found	Certified value	Recovery (%)
TMDA-53.3	342± 8	344±26	99
TMDA-64.2	271±14	290±20	93

Table 4. Comparison between the developed UA-SS-LLME method and the reported methods

Methods	Detection system	LOD, $\mu\text{g L}^{-1}$	RSD, %	EF ^a	Reference
Ultrasonification assisted supramolecular solvent LLME	UV-Vis spectrophotometer	0.79	2.40	50	This work
Supramolecular dispersive LLME-based solidification of floating organic drops	Electrothermal atomic absorption spectrometry	0.0018	4.2	127	20
Solidified floating organic drop dispersive LLME	UV-Vis spectrophotometer	0.23	3.8	50	29
Sequential injection analysis	SI-RST optic-fiber sensor spectrophotometer	2.4	1.3	/	33
Solid phase extraction	UV-Vis spectrophotometer	3.4	<6	30	37
Liquid phase microextraction	UV-Vis spectrophotometer	2.22	1.6	20	40
Solid phase extraction	Flame Atomic absorption spectrometry	15	<5	-	41
Solid phase extraction	Flame Atomic absorption spectrometry	45	<1	25	42

^a EF: Enhancement factor.

Comparison of UA-SS-LLME method with other reported methods. The results of some studies in the literatures for Cr speciation are listed in Table 4. The developed UA-SS-LLME method is compared with other procedures in terms of limit of detection, enhancement factor, and relative standard deviation. Compared to other LLME methods, the present study can be applied using higher sample volumes and quantitative recoveries can be obtained.^{20,29,40} The accuracy of the study was calculated from repeated measurements and was found to be better than that of other methods.^{20,29,37,41} The developed method also achieves lower LOD and higher enhancement factor than those of the most reported methods (Table 4).

CONCLUSIONS

An UA-SS-LLME was developed for the determination and speciation of Cr(VI) and Cr(III) ions. The complex with Cr(VI) and DPC was formed in acidic medium and spectrophotometric analysis was performed with UV-Vis spectrophotometry at 540 nm without matrix effects for samples such as tap, sea, and lake water. The matrix ion concentrations were highly tolerable for speciation of Cr. The spiking recovery studies for trace level determination of Cr in environmental samples were high and found between 92 and 102 %. The advantages of UA-SS-LLME method include low detection limit, high enhancement factor, and low organic solvent consumption, can be used with different analytical instruments for the speciation of inorganic Cr.

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Notes

The authors declare no competing financial interest.

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