



Rapid analysis of chromium (III, VI) in water and wastewater samples based on Task-specific ionic liquid by the ultra-assisted dispersive ionic liquid-liquid microextraction

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ABSTRACT

Exposure to hexavalent chromium (Cr VI) causes cancer in cells of the human body. So, the speciation and determination of the Cr (VI) and Cr (III) in water and human samples based on sensitive techniques are necessary. In this research, 2-mercapto-1-methylimidazole a novel Task-specific ionic liquid ($C_4H_6N_2S$; $HS-CH_3-IM$) was used with a new approach for speciation of Cr (III, VI) from water samples by ultra-assisted dispersive ionic liquid-liquid microextraction procedure (USA-D-ILLME). Due to the procedure, 100 mg of $HS-CH_3-IM$ and 0.2 mL of acetone were mixed and injected into 10 mL of water or standard Cr (III) and Cr (VI) solution in the conical tube. After stirring for 5 min, the Cr (VI) and Cr (III) were extracted with a positive and negative charge of the thiol group (HS^{2+} , HS^-) in pH 2 or 8 and pH 5, respectively. The mixture of the $HS-CH_3-IM$ was collected at the bottom of the conical tube by centrifuging. The upper liquid phase was vacuumed with a peristaltic pump and the Cr (III, VI) loaded on the $HS-CH_3-IM$ was back-extracted in a liquid solution. Finally, the concentration of the Cr (III, VI) ions in a remained solution were measured with ET-AAS after dilution up to 0.5 mL with DW. The total chromium was determined in water samples by summarizing the Cr (VI) and Cr (III) contents. All parameters such as the amount of $HS-CH_3-IM$, the sample volume, pH, and the shaking/centrifuging time were optimized. Under the optimal conditions, good linear range (LR), LOD, and enrichment factor (EF) were obtained 0.05–1.7 $\mu g L^{-1}$, 15 $ng L^{-1}$, and 19.82 respectively (RSD% < 1.45). The procedure was validated by spiking samples and good accuracy and precision results were achieved.

1. Introduction

Heavy metals have a toxic effect on environmental matrixes (air, soil, water). they can enter from waters, food, or vegetables and accumulate in brain, liver, or renal tissues. A trace amount of heavy

metals can cause cellular damage in the human body. Chromium(VI) is a major pollutant for the environment and enters from many sources such as chemical industries, steelworks, and electroplating. The chromium cause diseases such as gene mutations, carcinogen effect, and DNA lesions in human [1,2]. Two different oxidation forms of chromium exist in the environment (Cr III and Cr VI). Cr (III)

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compounds have an important role in the metabolism of glucose and protein in humans[3]. Moreover, the Cr (VI) has carcinogenic effects in cell tissues with a strong oxidation potential in the human body which enables to provide damage to DNA. Also, Cr (VI) is harmful to the lungs and kidneys [4,5]. Chromium values in drinking water are lower than $2 \mu\text{g L}^{-1}$ [6]. The World Health Organization (WHO) was reported that the genotoxicity of Cr (VI) in humans is $50 \mu\text{g L}^{-1}$. The ACGIH announced the normal range for chromium levels in human blood and urine were achieved at $1.8 \mu\text{g L}^{-1}$ and $2.0 \mu\text{g L}^{-1}$, respectively [7,8]. The Federal Committee on drinking water (FCDW) has reported new information on Cr(III, VI) and guideline technical documents on Cr(III, VI) in drinking water. The FCDW showed a maximum acceptable concentration (MAC) of $50 \mu\text{g L}^{-1}$ to Cr(VI). This document focuses on the health effects of Cr(VI) and total chromium considered about $100 \mu\text{g L}^{-1}$. Some of the analytical methods measure the total chromium Cr(III, VI) in drinking water at the lower limit of the reported MAC[9]. Many sample preparations based on adsorbents or ligands were used for extraction chromium from water samples. In addition, Cr(III) is likely to be converted to oxidized form [Cr(VI)] after sample preparation. Therefore, it is important to analyze chromium species and total chromium(TCr) in waters. In conventional studies, the best method for the treatment TCr is coagulation based on filtration and ion exchange [10]. Coagulation-based filtration and ion exchange are favorite methodologies for extracting Cr(VI) from drinking water. The drinking water treatment technologies able to be certified to international standards for reduction of TCr, Cr(VI), and Cr(III) individually, include adsorption, reverse osmosis, and distillation [11]. Recently, the different techniques, include, ion chromatography(IC), inductively coupled plasma mass spectrometry (ICP-MS) [12], stripping voltammetry (SV) [13], co-precipitation [14], flame atomic absorption spectrometry (F-AAS) [15], , inductively coupled plasma optical emission spectrometry (ICP-OES) [16], ion chromatography inductively coupled plasma-mass spectrometry (IC-ICP-MS) [17] and

electrothermal atomic absorption spectrometry (ETAAS) [18] were used for determination of chromium species in water samples. Due to difficulty matrixes and low detection for chromium in water samples, treatment process such as liquid-liquid extraction (LLE) [19], dispersive liquid-liquid microextraction (DLLME) [20], magnetic solid-phase extraction (SPE) [21], dithiocarbamate-modified magnetite nanoparticles (DC-MNPs) [22] and cloud point extraction (CPE) [23] are developed. Dispersive liquid-liquid microextraction (DLLME) is a conventional technique, where the extraction phase (a microliter of hydrophobic solvent) was dispersed in the water sample. Many organic solvents (ethanol, methanol, toluene) were used in the extraction phase. Recently, ionic liquids (IL) as green solvent, low vapor pressure, high stability, and large viscosity have been used in LLE [24,25].

The aim of this study is the speciation of Cr (III) and Cr (VI) in water samples based on HS-CH₃-IM by the USA-D-ILLME procedure. The important parameters for the extraction of chromium were optimized and the concentration of chromium was determined by ET-AAS.

2. Experimental

2.1. Instrumental

Chromium was determined with an atomic absorption spectrometer (AAS, GBC Plus 932, Australia) using a graphite furnace accessory (GF3000, ET-AAS). The main parameters such as temperature (ash, atomized, drying), auto-sampler into graphite tube, flowrate Ar gas, and temperature programming for the chromium were adjusted by the book manufacturer. A hollow cathode lamp of chromium (HCLcr) tuned at a current (6 mA) and a wavelength of 357.9 nm with a slit of 0.2 nm was used. The linear range ($1.5\text{--}33 \mu\text{g L}^{-1}$) and sample injection of $20 \mu\text{L}$ was used (Peak Area). The pH of samples was controlled by a digital pH meter (Metrohm 744). A centrifuge and shaker (Germany, Product N: SIAL311GZ2F) was used for dispersing and separating IL from samples. For validation results, ICP-MS (Perkin Elmer) was used for ultra-trace determination of chromium in standard and water samples.

2.2. Reagents and materials

Ultra-trace reagents with HPLC or AAS analytical grade purchased from Merck or Sigma Co. (Germany). The modifier for chromium $[\text{Mg}(\text{NO}_3)_2]$ for increasing ashing temperature, hexane, ethanol, acetone, HNO_3 , H_2SO_4 , and HCl were prepared from Merck, Germany. The standard solution of Cr (III) was prepared from an appropriate amount of $\text{Cr}(\text{NO}_3)_3$ in $0.01 \text{ mol L}^{-1} \text{ HNO}_3$ (1000 mg L^{-1} Cr III, 1.0 g L^{-1}). The standard solution of Cr (VI) was purchased from Merck which was prepared by 1.0 g of K_2CrO_4 in 1% HCl (1000 mg L^{-1} CrVI). The standard solutions for the calibration curve of chromium (0.1, 0.2, 0.4, 0.5, 1.0, $1.5 \mu\text{g L}^{-1}$) were prepared daily by dilution of the stock solution. The pH adjustments were made using appropriate buffer solutions including sodium phosphate for pH 2.0-2.5, ammonium acetate for pH 4.0-5.5 and ammonium chloride for pH 8-10 (Merck). 2-Mercapto-1-methylimidazole as Task-specific ionic liquid was purchased from Sigma, Germany ($\text{HS-CH}_3\text{-IM}$, CAS N: 60-56-0, 25 g). Ultra-pure water (DW) was obtained from a pure Water System (RIPI).

2.3. Water Sampling

The glass tubes were washed with HNO_3 solution (1 M) for two days and rinsed 10 times with DW. Due to low concentrations of chromium in water samples, even trace contamination, and sample storage caused to affect the accuracy of the results. The acidified water sample was put into the conical tube (10-20 mL) and kept at -20°C . After filtering, water samples were prepared from river water from Karaj, well water from Varamin city, drinking water

from Tehran city, industrial wastewater, Tehran, Iran prepared by ASTM procedure for waters.

2.4. Extraction Procedure

A pre-concentration procedure based on $\text{HS-CH}_3\text{-IM}$ by the USA-D-ILLME was performed as follows: first, 100 mg of $\text{HS-CH}_3\text{-IM}$ as a TSIL, 0.2 mL of acetone were mixed and injected into 10 mL of water and chromium standard samples (Fig.1). After shaking for 5 min, the Cr VI and Cr III were extracted by thiol group of $\text{HS-CH}_3\text{-IM}$ at pH 2 and 5, respectively. For optimizing, 10 mL of $0.1 - 1.5 \mu\text{g L}^{-1}$ Cr (III) and Cr (VI) standard solutions as the lower and upper limit of quantification was used instead of water samples in a conical centrifuge tube. First, 100 mg of $\text{HS-CH}_3\text{-IM}$ dispersed in 0.2 mL of acetone in a 1 mL syringe and injected to 10 mL of chromium standard in a conical tube. The pH was adjusted at 2 and 5 by the buffer solutions, then the mixture solution was shaken for 5 min, and chromium extracted by TSIL at 25°C . To separation phase, the turbid solution was centrifuged for 5 min at 4000 rpm and the liquid phase was vacuumed with an autosampler. Then, Cr (III) and Cr (VI) were back-extracted from TSIL in acidic and basic by adding 0.25 mL of $1.2 \text{ mol L}^{-1} \text{ HNO}_3$ and 0.2 mL of $1.0 \text{ mol L}^{-1} \text{ NaOH}$, respectively. Finally, the remained aqueous phase was determined by ET-AAS after dilution with DW up to 0.5 mL. In the optimum pH conditions, total chromium was calculated by summarizing Cr (VI) to Cr (III) contents. The blank solutions proceeded in the same way and were used for the calibration ET-AAS. The extraction conditions based on the $\text{HS-CH}_3\text{-IM}$ (IL) for chromium speciation were shown in Table 1.



Fig.1. The extraction and speciation chromium based on $\text{HS-CH}_3\text{-IM}$ by the USA —D-ILLME procedure

Table 1. Extraction conditions for chromium (III, VI) based on *HS-CH₃-IM* by the USA –D-ILLME method

Parameters	Value
pH	4 for Cr(III) and 2 for Cr(VI)
Sample volume	10 mL
Volume of back-extraction reagents	0.2 mL for KOH/0.25 mL for HNO ₃
Volume of Buffer (0.1-0.2 mol L ⁻¹)	1 mL
Concentration of back-extraction	1.0 mol L ⁻¹ for KOH/1.2 mol L ⁻¹ for HNO ₃
Amount of IL	100 mg
Volume of Acetone	200 mL
Shaking time	5 min
Centrifugation time	5 min

3. Results and discussion

The TSIL (*HS-CH₃-IM*) with the USA-D-ILLME procedure was used for chromium speciation in the standard solution and water samples. The results showed us, the mean concentrations of Cr (III and VI) in wastewater samples were significantly higher than water samples [(5.13 ± 0.22 µg L⁻¹, 3.92 ± 0.18 µg L⁻¹) and (0.19 ± 0.02 µg L⁻¹, 0.12 ± 0.01 µg L⁻¹)], respectively.

The extraction recovery (Equation 1) was obtained as the percentage of the ratio of the extraction chromium (C_{ex}) into the IL phase vs total chromium in water (C_{total}).

$$\text{Extraction Recovery} = \left(\frac{C_{ex}}{C_{total}} \right) \times 100 = \left[\frac{C_{ex} V_{oil}}{C_t V_{aq}} \right] \times 100 \quad (\text{Eq. 1})$$

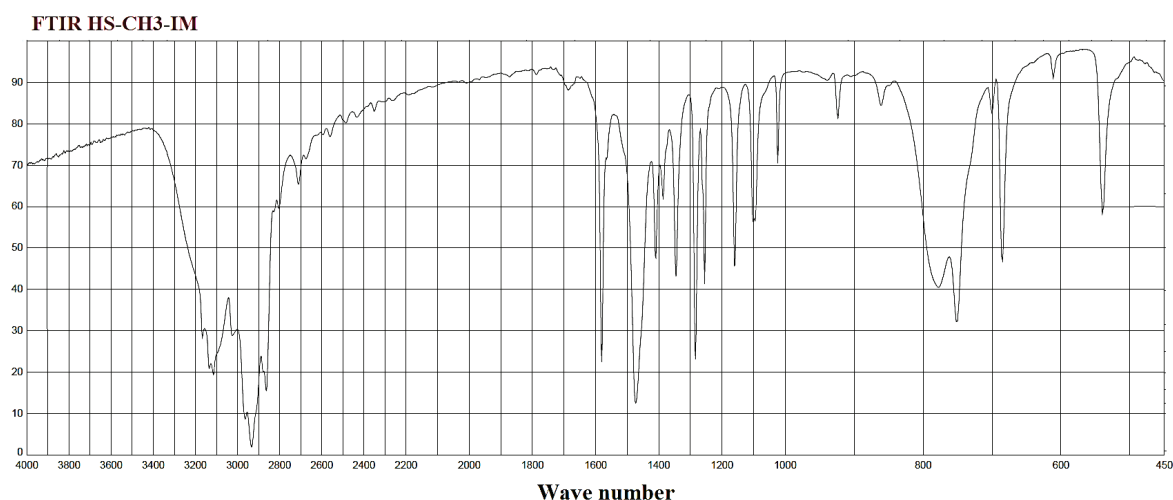
3.1. FTIR spectrum

The FT-IR spectra of *HS-CH₃-IM* are presented in Figure 2. The peak of FT-IR spectra at 1600 cm⁻¹

is related to C=O bond vibration of the carboxylic acid groups. The spectrum shows a band around 3100 cm⁻¹ which can be attributed to the hydroxyl groups. In addition, bands around 2900 cm⁻¹ are due to regular C-H stretching of the CH₂ groups of *HS-CH₃-IM*.

3.2. PH effect

The effect of pH on extraction of Cr (III) and Cr(VI) ions on the *HS-CH₃-IM* as a TSIL was investigated using different pH from 2 to 12 for 0.1 µg L⁻¹ Cr (III) and Cr(VI) ions as a lower LOQ and 1.5 µg L⁻¹ Cr (III) and Cr(VI) ions as upper LOQ. The extraction was strongly dependent on the pH of solutions and subsequently affected recovery. The results show that the highest extraction efficiency for Cr (III) was achieved at pH 4 to 6 by the thiol group of the *HS-CH₃-IM* and the Cr (VI) extracted at pH 2-3. Thus, the procedure was applied to speciation of two forms of chromium at pH 5 and 2 for the Cr (III)

**Fig.2.** FTIR spectra for *HS-CH₃-IM*

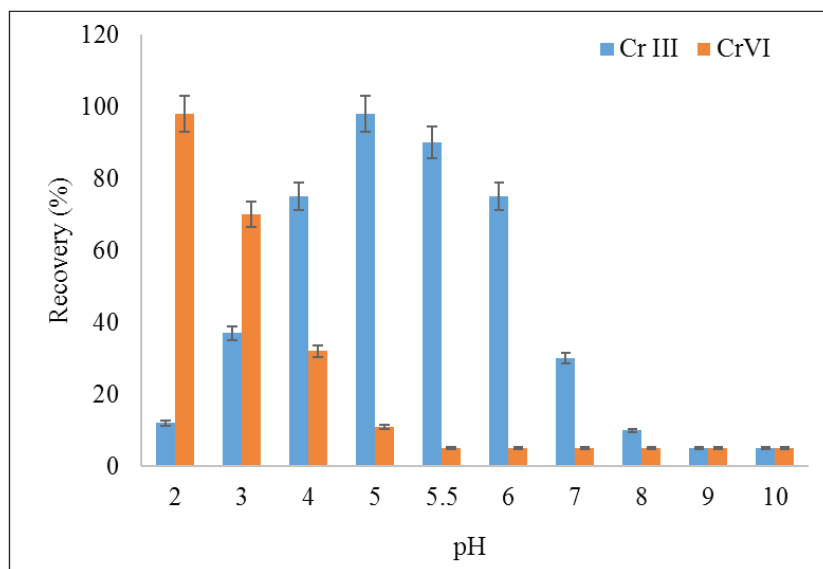


Fig.3. Effect of pH on extraction and speciation of Cr (III) and Cr(VI) ions based on *HS-CH₃-IM* by the USA –D-ILLME procedure

and Cr(VI), respectively (Fig. 3). The mechanisms of Cr (III) and Cr(VI) ions on the *HS-CH₃-IM* were obtained by complex formation between Cr (III) and Cr(VI) ions and HS groups of the *HS-CH₃-IM* at optimized pH. The HS can be deprotonated (SH^-) at a wide range of pH from 4 to 9. The extraction efficiency of Cr (III) can be attributed to the affinities of HS of the *HS-CH₃-IM* as a TSIL for the Cr^{3+} cations existing at pH from 4 to 6. The different anionic species of Cr (VI) exist at low and high pH ($\text{pH}=2$ and $\text{pH} > 8$), namely HCrO_4^- , CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ and negatively charged of anionic species can be extracted by positive charges of SH^{2+} group.

3.3. Sample volume

Sample volume is the main parameter for the extraction of chromium in the water sample. So, the effect of sample volume was studied in a range of 2- 25 mL for $0.1 - 1.5 \mu\text{g L}^{-1}$ of Cr (III) and Cr(VI), respectively. High extraction was obtained between 2 mL and 12 mL of the water sample. At more volumes, the extraction efficiency was decreased. On the other hand, TSIL can be soluble partially in water at higher sample volumes and cause non-reproducible results. Therefore, a sample volume of 10 mL was used for this study with *HS-CH₃-IM* by the USA-D-ILLME method (Fig. 4).

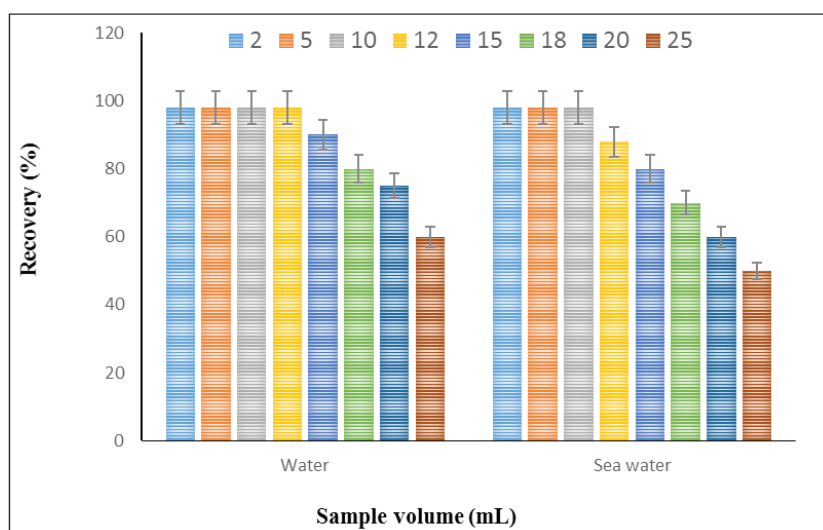


Fig. 4. Effect of sample volume on extraction and speciation of Cr (III) and Cr(VI) ions based on *HS-CH₃-IM* by the USA –D-ILLME procedure

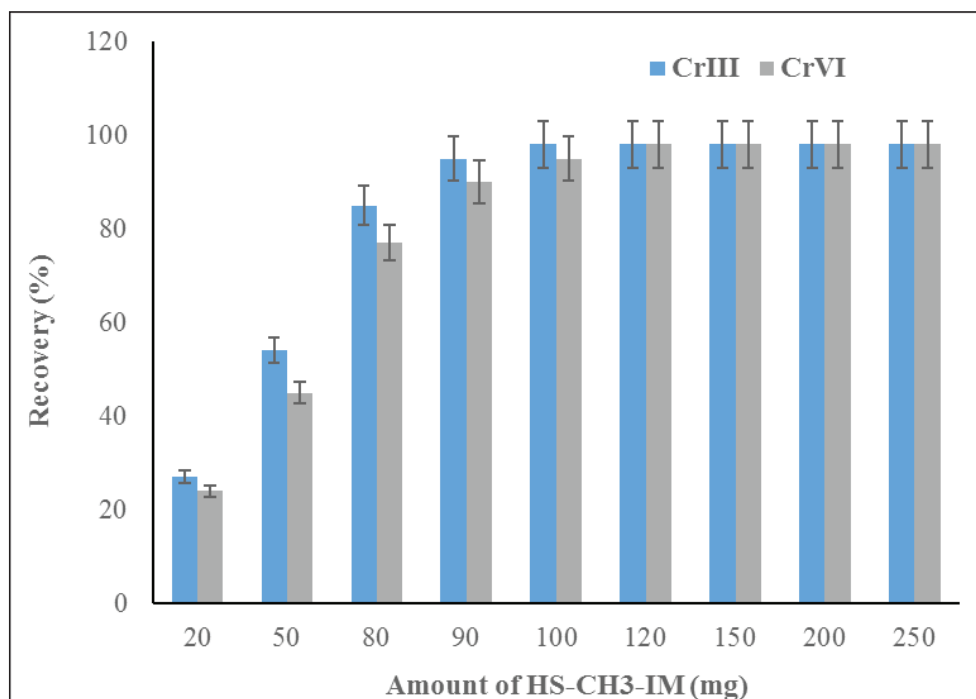


Fig. 5. Effect of *HS-CH₃-IM* on extraction and speciation of Cr (III) and Cr(VI) ions by the USA –D-ILLME procedure

3.4. Amount of *HS-CH₃-IM*

The results showed us that the extraction efficiency of Cr (III) and Cr(VI) ions was remarkably affected by the amount of TSIL. Therefore, the amount of TSIL was evaluated within the range of 50–250 mg. The extraction recovery was observed at more than 80 mg TSIL. So, 100 mg of TSIL (*HS-CH₃-IM*) was chosen as optimum IL for extraction of Cr (III) and Cr(VI) ions in water samples at pH 2 and 5 by the HS group (Fig. 5). For salty water such as seawater, 120 mg of TSIL for 10 mL of seawater must be used at optimized pH.

3.5. Centrifuge and sonication time

The sonication and centrifuge time are crucial to achieving an efficient extraction based on *HS-CH₃-IM* by the USA-D-ILLME procedure. In this research, the various sonication and centrifuge times between 1-10 min was evaluated for chromium extraction in water samples. The result showed us, by increasing the sonication time the relative response for extraction of chromium

increased and reached the maximum value at 4.5 seconds for *HS-CH₃-IM*, and then remained constant. Therefore, the ultrasonic times of 5.0 minutes for the Cr (III) and Cr(VI) extraction was used. Also, the centrifuge time of 5.0 minutes was selected for Cr (III) and Cr(VI) extraction in water.

3.6. Effect of reagents on back-extraction

Due to the viscosity and organic structure of ionic liquids, injection of IL into the graphite tube of the furnace of ETAAS was not possible. So, based on the USA-D-ILLME procedure, Cr (III) and Cr(VI) were back-extracted from the *HS-CH₃-IM* with acid and base reagents. Due to previous research, decreasing pH leads to dissociation and releasing of chromium ions released into the aqueous phase by decreasing or increasing pH. So, the different concentrations of reagents such as HCl, HNO₃, H₂SO₄, KOH (0.5 -2.0 mol L⁻¹) were used for chromium back-extraction from the TSIL (Fig. 9). The research showed that 1.2 mol L⁻¹ of HNO₃

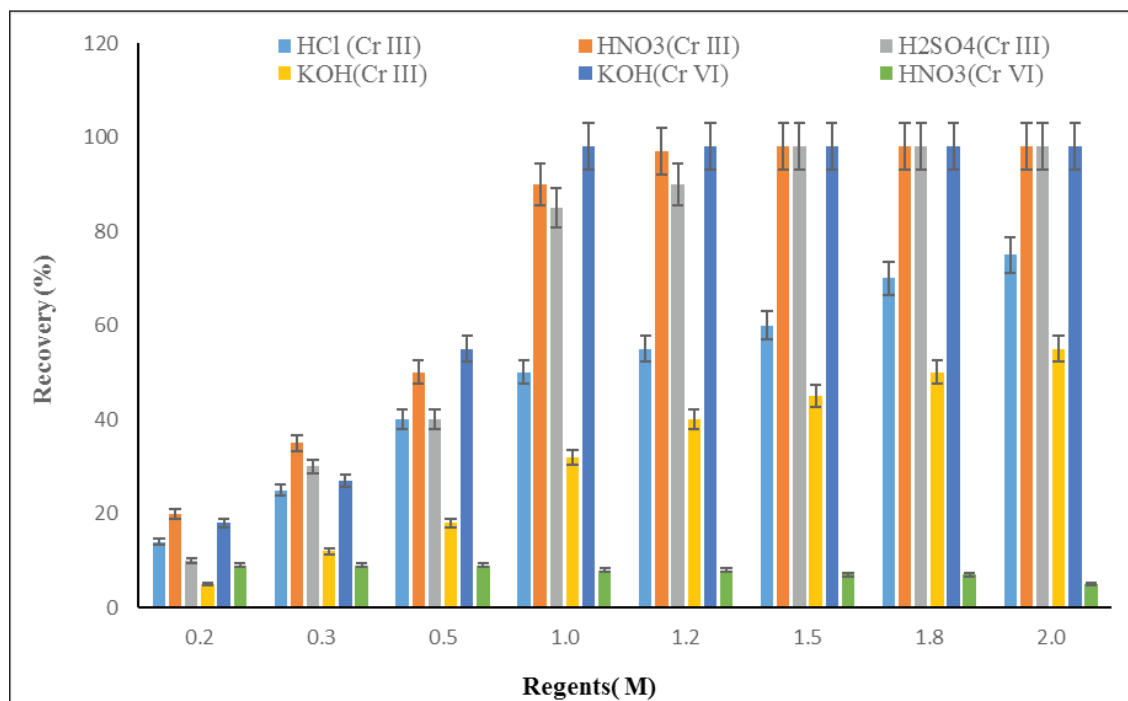


Fig. 6. Effect of reagents (acid and base) on back-extraction of Cr (III) and Cr(VI) ions by the USA –D-ILLME procedure

(0.25 mL) can be back-extracted Cr (III) from the HS-CH₃-IM to the liquid phase. Also, 1.0 mol L⁻¹ of KOH (0.2 mL) can be back-extracted Cr (VI) from the HS-CH₃-IM phase. After back-extraction, the resultant solution was adjusted to 0.5 mL with DW in a centrifuge conical tube before determining by ET-AAS (Fig. 6).

3.7. Validation of methodology

The USA –D-ILLME method was applied to determine Cr (VI) and Cr (III) found in 10 mL of water samples. The Cr (VI) and Cr (III) in wastewater and water samples were evaluated (20 n). The mean concentration of Cr (VI) and Cr (III) in wastewater was higher than in water samples. Also, the mean concentration of Cr (VI) in well water was lower than Cr (III) concentration. The coloration analysis was achieved between Cr (III) and Cr (VI) in industrial water and drinking waters and there was a high correlation ($r > 0.66$). In addition, in drinking waters, no correlation and regression were shown between Cr (III) and Cr

(VI) ($r > 0.12$). The spiked water and wastewater samples were used to demonstrate the reliability and validation of the method for speciation and determination of Cr (III) and Cr (VI) (Table 2). By back-extraction process, the remaining solution was spiked with standard solutions of Cr (VI) and Cr (III) and analyzed with ET-AAS after extraction based on the HS-CH₃-IM by the USA-D-ILLME method (Table 3). The recovery of spiked samples is satisfactory results, which shows the ability of the procedure for determination and speciation of the Cr (VI) and Cr (III) in water samples. For validation of the proposed method, certified reference materials in waters (CRM) were obtained by ICP-MS. The spiking CRM with the chromium standard solution showed us the validation of methodology for speciation and determination of Cr (VI) and Cr (III) in water samples (Table 4). Due to results, high efficiency and accuracy were achieved for the determination and speciation of Cr (VI) and Cr (III) in water samples.

Table 2. The coloration analysis for chromium determination of wastewater and water samples in different cities, Iran (n=20, $\mu\text{g L}^{-1}$)

City	*Wastewater (n=20)		water (n=20)		Wastewater	
	Cr ^{III}	Cr ^{VI}	Cr ^{III}	Cr ^{VI}	r	P-value
Tehran	1.07 \pm 0.77	4.28 \pm 0.04	0.09 \pm 0.22	0.11 \pm 0.02	0.098	<0.002
Karaj	2.51 \pm 0.03	2.03 \pm 0.69	0.14 \pm 0.02	0.07 \pm 0.04	0.331	<0.001
Kerman	0.75 \pm 0.13	1.94 \pm 0.81	0.10 \pm 0.11	0.06 \pm 0.05	0.113	<0.005

*Wastewater diluted with DW up to 50 mL (1:5)

Table 3. Validation of chromium speciation based on the HS-CH₃-IM with spiking water samples by the USA-D-ILLME method

Sample*	Added ($\mu\text{g L}^{-1}$)		*Found ($\mu\text{g L}^{-1}$)		Total	Recovery (%)	
	Cr (III)	Cr (VI)	Cr (III)	Cr (VI)		Cr (III)	Cr (V)
Water 1	---	---	1.235 \pm 0.034	1.028 \pm 0.037	2.263 \pm 0.088	---	---
	1.0	---	2.205 \pm 0.104	1.055 \pm 0.032	3.260 \pm 0.126	97.0	---
	---	1.0	1.229 \pm 0.029	1.996 \pm 0.097	3.225 \pm 0.127	---	96.8
Water 2	---	---	0.224 \pm 0.012	0.188 \pm 0.013	0.412 \pm 0.022	---	---
	0.2	---	0.419 \pm 0.019	0.191 \pm 0.012	0.610 \pm 0.028	97.5	---
	---	0.2	0.226 \pm 0.011	0.393 \pm 0.021	0.619 \pm 0.031	---	102.5
**Wastewater 1	---	---	4.213 \pm 0.186	2.450 \pm 0.105	6.663 \pm 0.298	---	---
	2.0	---	6.197 \pm 0.304	2.447 \pm 0.094	8.644 \pm 0.386	99.2	---
	---	2.0	4.198 \pm 0.191	4.406 \pm 0.178	8.604 \pm 0.411	---	97.8
**Wastewater 2	---	---	2.155 \pm 0.086	3.175 \pm 0.128	5.330 \pm 0.237	---	---
	2.0	---	4.163 \pm 0.204	3.179 \pm 0.132	7.342 \pm 0.335	100.4	---
	---	3.0	2.162 \pm 0.094	6.104 \pm 0.275	8.266 \pm 0.403	---	97.6
Water 5	---	---	0.532 \pm 0.025	0.082 \pm 0.004	0.614 \pm 0.031	---	---
	0.5	---	1.026 \pm 0.045	0.079 \pm 0.003	1.105 \pm 0.048	98.8	---
	---	0.1	0.528 \pm 0.024	0.177 \pm 0.005	0.705 \pm 0.032	--	95.0

*Mean of three determinations \pm confidence interval (P = 0.95, n = 5)**wastewater diluted with DW (1:5), so the result calculated after dilution factor (DF \times 5)

Water 1: River water from Karaj

Water 2: Drinking water from Tehran city

Water 5: Well water from Varamin city

Table 4. Comparing chromium speciation and determination based on the HS-CH₃-IM/ET-AAS with CRM analysis by ICP-MS

CRM	ICP-MS (µg L ⁻¹)			HS-CH ₃ -IM (µg L ⁻¹)		
	Cr ^{III}	Cr ^{VI}	Total	Cr ^{III} Found	Cr ^{VI} Found	Total
SS ^a	0.205 ± 0.012	0.198 ± 0.010	0.403 ± 0.019	0.195 ± 0.013	0.211 ± 0.014	0.406 ± 0.021
	0.714 ± 0.031	0.508 ± 0.024	1.222 ± 0.048	0.698 ± 0.034	0.494 ± 0.026	1.192 ± 0.055
Water	---	---	1.321 ± 0.054	1.005 ± 0.054	0.318 ± 0.014	1.323 ± 0.068
	0.50	---	1.804 ± 0.086	1.493 ± 0.069	0.305 ± 0.018	1.798 ± 0.087
	---	0.50	1.818 ± 0.081	1.012 ± 0.051	0.811 ± 0.042	1.823 ± 0.093

*Mean of three determinations ± confidence interval (P = 0.95, n = 5)

^aSS: Standard Solution

4. Conclusions

In this study, a novel method based on HS-CH₃-IM as TSIL was used for the speciation and determination of the Cr (III) and Cr (VI) in water samples by the USA-D-ILLME procedure. The important factors for high extraction were optimized. By procedure, a sensitive, efficient, low cost, and simple method for speciation and preconcentration of the Cr (III) and Cr (VI) in water samples were achieved. Under optimized conditions, the working range (WR), LOQ, and RSD% were obtained 0.05–3.6 µg L⁻¹, 50 ng L⁻¹, and 1.45, respectively. The performance of the method for quantification analysis of chromium in water samples was obtained. The analytical performances of detection of Cr (III) and Cr (VI) in water samples are comparable to previously reported methods. Finally, the speciation chromium based on HS-CH₃-IM was revealed that most of Cr (VI) and Cr (III) exist in industrial wastewaters.

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