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. Therefore, 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 (C4H6N2S; HS-CH3-IM) was used as a novel Task-specific ionic liquid for the speciation of Cr (III, VI) from water samples by ultrasound-assisted dispersive ionic liquid-liquid microextraction procedure (USA-D-ILLME). Due to the procedure, 100 mg of HS-CH3-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 a 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-CH3-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-CH3-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-CH3-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 μg 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.

Keywords: Chromium III, VI; Water samples; 2-Mercapto-1-methylimidazole; Dispersive ionic liquid-liquid microextraction, Electrothermal atomic absorption spectrometry

1. Introduction
Heavy metals have a toxic effect on environmental matrices (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)
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 µg L⁻¹ [6]. The World Health Organization (WHO) was reported that the genotoxicity of Cr (VI) in humans is 50 µg L⁻¹. The ACGIH announced the normal range for chromium levels in human blood and urine was achieved at 1.8 µg L⁻¹ and 2.0 µg 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 µg L⁻¹ to Cr(VI). This document focuses on the health effects of Cr(VI) and total chromium considered about 100 µg L⁻¹. Some of the analytical methods measure the total chromium Cr(III, VI) in drinking water. 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 water samples. 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 (1.5-33 µg L⁻¹) and sample injection of 20 μL 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 \([\text{Mg(NO}_3\text{)}_2]\) for increasing ashing temperature, hexane, ethanol, acetone, \(\text{HNO}_3\), \(\text{H}_2\text{SO}_4\), and \(\text{HCl}\) were prepared from Merck, Germany. The standard solution of Cr (III) was prepared from an appropriate amount of \(\text{Cr(NO}_3\text{)}_3\) in 0.01 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 \(\text{K}_2\text{CrO}_4\) in 1 % HCl (1000 mg L\(^{-1}\) CrVI). The standard solutions for 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 (HS-\(\text{CH}_3\text{-IM}\), 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 \(\text{HNO}_3\) 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 HS-\(\text{CH}_3\text{-IM}\) by the USA-D-ILLME was performed as follows: first, 100 mg of HS-\(\text{CH}_3\text{-IM}\) 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 HS-\(\text{CH}_3\text{-IM}\) 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 HS-\(\text{CH}_3\text{-IM}\) 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 mol L\(^{-1}\) \(\text{HNO}_3\) and 0.2 mL of 1.0 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 HS-\(\text{CH}_3\text{-IM}\) (IL) for chromium speciation were shown in Table 1.

![Fig.1. The extraction and speciation chromium based on HS-CH3-IM by the USA-D-ILLME procedure](image-url)
3. Results and discussion

The TSIL (HS-CH$_3$-IM) with the USA-D-ILLME procedure was used to determine the speciation of chromium in standard solutions and water samples. The results showed that the mean concentrations of Cr (III and VI) in wastewater samples were significantly higher than in 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 ($C_{total}$).

$$\text{Extraction Recovery} = \left( \frac{C_{ex}}{C_{total}} \right) \times 100 = \left( \frac{C_{ex} \cdot V_{eq}}{C_{t} \cdot V_{eq}} \right) \times 100$$

(Eq. 1)

3.1. FTIR spectrum

The FT-IR spectra of HS-CH$_3$-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 CH$_2$ groups of HS-CH$_3$-IM.

3.2. PH effect

The effect of pH on the extraction of Cr (III) and Cr(VI) ions on the HS-CH$_3$-IM as a TSIL was investigated using different pH values 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 an 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-CH$_3$-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).

Table 1. Extraction conditions for chromium (III, VI) based on HS-CH$_3$-IM by the USA ─D-ILLME method

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>4 for Cr(III) and 2 for Cr(VI)</td>
</tr>
<tr>
<td>Sample volume</td>
<td>10 mL</td>
</tr>
<tr>
<td>Volume of back-extraction reagents</td>
<td>0.2 mL for KOH/0.25 mL for HNO$_3$</td>
</tr>
<tr>
<td>Volume of Buffer (0.1-0.2 mol L$^{-1}$)</td>
<td>1 mL</td>
</tr>
<tr>
<td>Concentration of back-extraction</td>
<td>1.0 mol L$^{-1}$ for KOH/1.2 mol L$^{-1}$ for HNO$_3$</td>
</tr>
<tr>
<td>Amount of IL</td>
<td>100 mg</td>
</tr>
<tr>
<td>Volume of Acetone</td>
<td>200 mL</td>
</tr>
<tr>
<td>Shaking time</td>
<td>5 min</td>
</tr>
<tr>
<td>Centrifugation time</td>
<td>5 min</td>
</tr>
</tbody>
</table>

Fig. 2. FTIR spectra for HS-CH$_3$-IM
and Cr(VI), respectively (Fig. 3). The mechanisms of Cr (III) and Cr(VI) ions on the HS-CH$_3$-IM were obtained by complex formation between Cr (III) and Cr(VI) ions and HS groups of the HS-CH$_3$-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-CH$_3$-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 (pH=2 and pH > 8), namely HCrO$_4^-$, CrO$_4^{2-}$ and Cr$_2$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 μg 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-CH$_3$-IM by the USA-D-ILLME method (Fig. 4).
3.4. Amount of HS-CH$_3$-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-CH$_3$-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-CH$_3$-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-CH$_3$-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-CH$_3$-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, HNO$_3$, H$_2$SO$_4$, 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 HNO$_3$
(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 satisfactorily 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.

Fig. 6. Effect of reagents (acid and base) on back-extraction of Cr (III) and Cr(VI) ions by the USA ─D-ILLME procedure
**Table 2.** The coloration analysis for chromium determination of wastewater and water samples in different cities, Iran (n=20, μg L\(^{-1}\))

<table>
<thead>
<tr>
<th>City</th>
<th>Wastewater (n=20)</th>
<th>Water (n=20)</th>
<th>Wastewater</th>
<th>Cr III</th>
<th>Cr VI</th>
<th>r</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tehran</td>
<td>1.07 ± 0.77</td>
<td>4.28 ± 0.04</td>
<td>0.09 ± 0.22</td>
<td>0.11 ± 0.02</td>
<td>0.098</td>
<td>&lt;0.002</td>
<td></td>
</tr>
<tr>
<td>Karaj</td>
<td>2.51 ± 0.03</td>
<td>2.03 ± 0.69</td>
<td>0.14 ± 0.02</td>
<td>0.07 ± 0.04</td>
<td>0.331</td>
<td>&lt;0.001</td>
<td></td>
</tr>
<tr>
<td>Kerman</td>
<td>0.75 ± 0.13</td>
<td>1.94 ± 0.81</td>
<td>0.10 ± 0.11</td>
<td>0.06 ± 0.05</td>
<td>0.113</td>
<td>&lt;0.005</td>
<td></td>
</tr>
</tbody>
</table>

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

**Table 3.** Validation of chromium speciation based on the HS-CH\(_3\)-IM with spiking water samples by the USA-D-ILLME method

<table>
<thead>
<tr>
<th>Sample*</th>
<th>Added (μg L(^{-1}))</th>
<th>Found (μg L(^{-1}))</th>
<th>Total</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cr (III)</td>
<td>Cr (VI)</td>
<td>Cr (III)</td>
<td>Cr (VI)</td>
</tr>
<tr>
<td>Water 1</td>
<td>---</td>
<td>---</td>
<td>1.235 ± 0.034</td>
<td>1.028 ± 0.037</td>
</tr>
<tr>
<td></td>
<td>---</td>
<td>1.0</td>
<td>2.205 ± 0.104</td>
<td>1.055 ± 0.032</td>
</tr>
<tr>
<td>Water 2</td>
<td>---</td>
<td>---</td>
<td>0.224 ± 0.012</td>
<td>0.188 ± 0.013</td>
</tr>
<tr>
<td></td>
<td>---</td>
<td>0.2</td>
<td>0.419 ± 0.019</td>
<td>0.191 ± 0.012</td>
</tr>
<tr>
<td><strong>Wastewater 1</strong></td>
<td>2.0</td>
<td>---</td>
<td>6.197 ± 0.304</td>
<td>2.447 ± 0.094</td>
</tr>
<tr>
<td></td>
<td>---</td>
<td>2.0</td>
<td>4.198 ± 0.191</td>
<td>3.406 ± 0.012</td>
</tr>
<tr>
<td><strong>Wastewater 2</strong></td>
<td>2.0</td>
<td>---</td>
<td>4.163 ± 0.204</td>
<td>3.179 ± 0.132</td>
</tr>
<tr>
<td></td>
<td>---</td>
<td>3.0</td>
<td>2.162 ± 0.094</td>
<td>6.104 ± 0.275</td>
</tr>
<tr>
<td>Water 5</td>
<td>---</td>
<td>---</td>
<td>0.532 ± 0.025</td>
<td>0.082 ± 0.004</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>---</td>
<td>1.026 ± 0.045</td>
<td>0.079 ± 0.003</td>
</tr>
<tr>
<td></td>
<td>---</td>
<td>0.1</td>
<td>0.528 ± 0.024</td>
<td>0.177 ± 0.005</td>
</tr>
</tbody>
</table>

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

**Wastewater diluted with DW (1:5), so the result calculated after dilution factor (DF× 5)**

*Water 1: River water from Karaj
*Water 2: Drinking water from Tehran city
*Water 5: Well water from Varamin city
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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