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## Chromium speciation using task specific ionic liquid/aqueous phase biphasic system combined with flame atomic absorption spectrometry

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### ARTICLE INFO

### ABSTRACT

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Keywords: Chromium speciation IL/aqueous phase biphasic system Salicylate based ionic liquid Central composite design Flame atomic absorption spectrometry In this work, 1-alkyl-3-methylimidazolium based ionic liquids combined with salicylate or thiosalicylate anions as task specific ionic liquids were used to form a stable ionic liquids (IL)/aqueous biphasic systems for extraction of Cr(III) and Cr(VI) species prior to flame atomic absorption spectrometry (FAAS) determination. It was found that the 1-octyl-3-methylimidazolium salicylate was selective to extract Cr(III). The Cr(VI) content was calculated by subtracting Cr(III) from the total chromium with conversion of Cr(VI) to Cr(III) in the presence of ascorbic acid. Based on the preliminary experiments, the factors influencing phase behavior of the IL/aqueous biphasic system were investigated. The main factors affected the extraction of Cr(III) were modeled by using central composite design and optimized by using non-linear Nelder-Mead method. Under the defined optimum conditions, the calibration curves were linear over the concentration range of 40–470  $\mu$  L<sup>-1</sup> and 55–500  $\mu$  L<sup>-1</sup> for Cr(III) and total Cr, respectively. The limit of detection (3Sb/m) for Cr(III) was 7.7  $\mu$  L<sup>-1</sup>. The relative standard deviations for six replicate determinations of 250  $\mu$  L<sup>-1</sup> of Cr(III) and total Cr were 5.5% and 7.6%, respectively. Finally, the proposed system has been successfully applied to the extraction and speciation of Cr in real water and urine samples.

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### 1. Introduction

Chromium (Cr) is a metal found in small quantities associated with other metals, particularly iron. Due to extensive use of Cr in industrial processes, large quantities of Cr compounds are discharged into the environment [1–3]. Although Cr exists in all oxidation states from 0 to VI, but Cr(III) and Cr(VI) are the most prevalent [4]. Even though Cr(III) is an essential nutrient. Cr(VI) is a known mutagen and carcinogen, and it is more soluble and mobile than Cr(III) [5–7]. The toxicity of chromium largely depends on which of these two chemical species is prevalent. Therefore, the total amount of Cr does not always provide a right indication of the effects of the available Cr in a sample. A more accurate assessment of the real effects of Cr can be gained by discriminating the Cr(III) and Cr(VI) species. As a result, accurate determination of Cr species at trace levels is an important challenge, because the analytical techniques such as flame or electrothermal atomic absorption spectrometry, inductively coupled plasma-atomic emission spectrometry, and inductively coupled plasma-mass spectrometry, can only detect the total amount of Cr. Consequently, sample preparation methods are required for separation and preconcentration of Cr species before detection [8–15]. On the other hand, most of the reported pretreatment procedures are neither selective nor sensitive enough. Among the sample preparation methods, conventional liquid-liquid extraction (LLE) is used in routine separation of metal ions in comparison with other sample preparation techniques e.g. solid-phase extraction owing to its simplicity and easy operation [16–19]. However, the use of large sample volumes and toxic organic solvent as well not selective chelating agents make LLE as an expensive, time-consuming, laborious, and not eco-friendly sample pretreatment method [20]. To overcome these drawbacks, several liquid-liquid microextraction methods were developed such as single drop microextraction [21,22], cloud point extraction [23], hollow fiber liquid-liquid microextraction [24], and dispersive liquid-liquid microextraction methods are usually combined with the analytical techniques to minimize potential interferences from diverse components present in real samples and concentrate Cr species.

Aqueous biphasic systems (ABSs) are a new promising liquid-liquid extraction method that usually composed of an aqueous phase and a hydrophobic phase such as polymers, a polymer and a salt, or surfactants which are used for separation and pretreatment of the target from complex matrices [26,27]. Such ABSs with the right properties of hydrophobic phase and proper salt can be used as an alternative extraction medium to conventional liquid-liquid or liquid–solid extraction. Compared with the latter systems, ABS is considered to be an environmentally friendly method, because the volatile organic solvents are not used in the whole process. For the first time, a new type of aqueous biphasic system consisting of an ionic liquid (IL) and salts were reported

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in 2003 by Rogers et al. [28]. Then, the IL-salt/aqueous biphasic systems have been applied to the separation and preconcentration of organic and inorganic compounds, and biomolecules in different matrices [29, 30]. Because, the unique combination of cations and anions influences the properties of ILs, they have been considered as the designer solvents for extraction of various targets from aqueous environments [31]. A biphasic system for extraction of metal cations should contain an extractant in the hydrophobic phase to ensure the complete and selective removal of the metal ions from the aqueous phase. The hydrated nature of most metal ions lowers their affinity for the hydrophobic phase, thus, it is necessary to use either an organic ligand to provide a hydrophobic complex with the metal ions or to find conditions under which the metal ion species can be selectively extracted from aqueous phase containing inorganic complexing ions.

Recently, the development of functionalized ionic liquids which is referred to task-specific ionic liquids (TSILs) have been received much attention due to specific chemical and/or physical properties of ILs in which a functional group is incorporated as a part of their cation or anion structures; enhancing their capacity for interaction with specific solute types. Most of TSILs for extracting applications described in the literature are based on imidazolium cations and fluorine containing anions, whereas diverse functional groups are generally appended to the cation [32]. An attractive alternative may be ILs, which contains complexing anions, in particular, tetraalkyl ammonium carboxylates. Recently, the newly ILs based on a hydrophobic, long chain tetraalkyl ammonium cation with aliphatic and aromatic carboxylate anions were synthesized [33]. The prepared ILs contain carboxylate, salicylate or thiosalicylate were evaluated as potential extracting agents for metal cations from different aqueous solutions [34–38].

In the present work, alkyl derivatives of the 3-methylimidazolium cation with salicylate or thiosalicylate anions as task specific ionic liquids were prepared and aimed to develop a feasible extraction approach to separate Cr species in an IL/aqueous biphasic system. Salicylate and thiosalicylate ions have been chosen as anions, because ILs with anions containing fluoride like PF<sub>6</sub> and BF<sub>4</sub> are poor chelating extractant for metal cations and decompose in contact with water to produce a very toxic by-product of HF. In addition, these ions have low solubility in water to form better ABS. The factors that influenced the phase formation and Cr extraction capacity of the proposed IL/aqueous system, e.g. sample pH, type and concentration of coexisting ions in aqueous phase, amount of added IL, and time, were discussed. These factors were investigated by using preliminary experiments, and then the significant factors were modeled by central composite design (CCD). The optimum condition was defined using non-linear Nelder-Mead optimization, and then the proposed method was successfully applied for speciation of Cr in water and urine samples.

### 2. Materials and methods

### 2.1. Apparatus

A Shimadzu Model AA-6300G flame atomic absorption spectrometer (Kyoto, Japan) was employed to determine the concentrations of Cr. A Cr hollow cathode lamp (Hama-Matsu Photonics, Japan) was used as a radiation source at current of 10 mA and wavelength of 357.9 nm with slit width of 0.7 nm. Deionized doubly distilled water was obtained from an AquaMax water purification system (Younglin, Anyang, Korea). The pH measurements were carried out using a SCHOTT pH meter (Mainz, Germany) equipped with a combined glass electrode.

### 2.2. Standard solutions and reagents

All chemicals used were of the analytical grade, and all solutions were prepared in deionized doubly distilled water (DDW; 18 M $\Omega$  cm<sup>-1</sup>). Sodium salicylate and sodium thiosalicylate were obtained from Sigma-Aldrich(St. Louis, MO, USA) and were used without further purification.

*N*-methylimidazole, 1-bromobutane,1-bromohexane, and 1bromooctane were obtained from Merck (Darmstadt, Germany), and were used for synthesis of salicylate and thiosalicylate based ILs. Stock solutions of Cr(III) and Cr(VI) at a concentration of 1000 mg L<sup>-1</sup> were freshly prepared by dissolving appropriate amounts of Cr(NO<sub>3</sub>)<sub>3</sub>· 6H<sub>2</sub>O and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in DDW, respectively. The working standard solutions were obtained by appropriate dilution of the stock standard solutions. Acetic acid and sodium acetate were used to prepare buffer and the pH adjustment was carried out with 1.0 mol L<sup>-1</sup> solutions of NaOH or HCl.

### 2.3. Synthesis of salicylate and thiosalicylate based ILs

Fig. 1 illustrates the general synthesis of salicylate and thiosalicylate based ILs [39–41]. Firstly, 20 mmol of 1-bromobutane, 1-bromohexane, or 1-bromooctane was added to 20 mmol of *N*-methylimidazole, and the mixture was refluxed while being stirred at 140 °C for 30 min until a yellow liquid with high viscosity was obtained. The prepared ILs ([BMIM][Br], [HMIM][Br], or [OMIM][Br]) were extracted with 10 mL diethyl ether and washed with DDW, respectively, dried over anhydrous sodium sulfate and evaporated under vacuum. Secondly, because the halide salts underwent metathesis reaction to give the desired ionic liquid, 20 mmol of sodium salicylate was added to the obtained IL in water, and the mixture was stirred at room temperature for 72 h until the anion-exchange process was done. The water was removed with rotary evaporator and the by-product salt of NaBr was removed by filtration after addition of methanol. Finally, salicylate based IL as a yellow liquid was dried under vacuum.

The preparation of thiosalicylate based IL as a green viscous liquid was carried out with the same procedure except for the fact that sodium thiosalicylate was used instead of sodium salicylate in the second step.

### 2.4. Procedure for Cr speciation using proposed IL/aqueous system

An aliquot of 10 mL aqueous solution containing 250  $\mu$ g L<sup>-1</sup> of each Cr(III) and Cr(VI) species in acetate buffer ( $pH = 4.7, 0.3 \text{ mol } L^{-1}$ ) was transferred into a 15.0 mL conical bottom centrifuge tube. Then, 220 µL of salicylate based IL was added to the sample solution. To increase the extraction efficiency, Triton X-114 and sodium nitrate were added at concentrations of 0.05%(w/v) and 0.1%(w/v), respectively. Then, the solution was stirred for 8.5 min and the resulted biphasic mixture was centrifuged for 25 min at 4000 rpm, so that the IL phase containing salicylate complex of Cr(III) was separated from aqueous phase. About 220 µL of IL would be separated. The separated IL was diluted up to 500 µL with ethanol: water mixture (50:50), and its Cr content as Cr(III) was determined by FAAS. For the analysis of total Cr, the Cr(VI) was converted to Cr(III) by addition of 100 µL of 10% (w/v) ascorbic acid. In this step, the total Cr was determined according to the procedure described above for extraction of Cr(III). The Cr(VI) content was obtained by subtraction of Cr(III) from total Cr. The extraction efficiency (EE%) of Cr species was obtained as the following:

$$EE\% = \frac{C_{IL\times}V_f}{C_0 \times V_0} \times 100 \tag{1}$$

where  $C_{IL}$  and  $C_0$  are concentrations of Cr species in the IL and initial aqueous phases, and  $V_0$  and  $V_f$  are the volumes of initial phase and solvent added to the separated ionic liquid, respectively.

### 2.5. Experimental design

Experimental design methodology was used in this study to determine the main factors that influence the Cr(III) extraction by the proposed IL/aqueous biphasic system. On the basis of the preliminary experiments, the factors which had the greatest influence on EE% of Cr(III) were selected. The important factors were applied by using CCD in order to build a predictive model for the EE% of Cr(III) as the response.



Fig. 1. Schematic diagram for synthesis of salicylate and thiosalicylate anions based ILs.

Then, the response surface plots based on the defined models were chosen to find the best experimental conditions for obtaining the maximum extraction of Cr(III). The statistical computer package "Design-Expert 8.0.0 Trial" (State-Ease Inc., Minneapolis, USA) was used for experimental design.

### 3. Results and discussion

### 3.1. Preliminary experiments

Various factors affected the extraction and separation procedure that was performed by using proposed IL/aqueous biphasic systems. Some of these factors e.g. sample pH, type and concentration of anions and cations existing in aqueous phase, affected the formation of biphasic system. On the other hands, some of factors, e.g. sample pH, amount of added IL, and time, affected the EE% of Cr species. Since the investigation of all factors in a wide range is not possible, preliminary experiments have to be done to get useful information about proposed system. For this purpose, firstly, factors that can affect the formation of IL/aqueous biphasic system were investigated, and higher amounts of separated IL from the aqueous solution was considered as favorable. On the other hand, selectivity and high EE% of the system were also considered.

#### 3.1.1. Selection of IL type

The crucial step for separation of Cr species into biphasic system was the control of phase forming behaviors and partitioning of the target species in this system. The preliminary assessment of the performance of the type of extractants of salicylate and thiosalicylate anions based ILs containing *N*-methylimidazolium cation with various alkyl chain lengths for speciation of Cr was performed by the procedure presented in Section 2.4. The effect of alkyl chain length on imidazolium ion on liquid-liquid equilibrium was investigated in terms of increasing their hydrophobicity and poorer affinity for water to extract Cr species. It can be observed from Table 1, the complexation of salicylate with Cr(VI) ions is poor, whilst thiosalicylate extract both species into the IL phase. In addition, the hydrophobicity of phase forming ILs exerts a crucial influence on the partitioning of Cr species into the IL rich phase. With increasing the carbon chain of IL, the hydrophobicity of the IL will increase; this may improve the stability of two phase system. It was found that 1-octyl-3-methylimidazolium salicylate ([OMIM][salicylate]) had a better ability to form ABS than butyl and hexyl chains of 1-alkyl-3-methylimidazolium salicylate ILs which promoted the selective extraction of Cr(III) into IL rich phase in ABS. In addition, the amount of formed IL rich phase was increased. Thereby, the [OMIM][salicylate] as an efficient extractant and complexing agent for separation of Cr(III) from Cr(VI) in aqueous solution was chosen for further investigations.

## 3.1.2. Effect of type and concentration of anions on IL/aqueous biphasic system

The effect of type of existing anion in aqueous phase on formation of IL based ABS and also on EE% of Cr(III) was investigated. By considering the fact that mono-valent and bivalent cations provide similar behaviors and have negligible effect on EE% of Cr(III) in such biphasic systems [42], examination of the type of cations is not necessary. Therefore, the ability of sodium salts of the anions Cl<sup>-</sup>, SO<sup>2</sup><sub>4</sub><sup>-</sup>, PO<sup>3</sup><sub>4</sub><sup>-</sup>, HPO<sup>2</sup><sub>4</sub><sup>-</sup>, H<sub>2</sub>PO<sup>4</sup><sub>4</sub>, HCO<sub>5</sub>, or CH<sub>3</sub>COO<sup>-</sup> to induce the formation of IL based ABS by means of evaluation of EE% of Cr (III) were evaluated. The results presented in Table 2 show that acetate anion was the best anion for formation of this biphasic system with an appropriate EE% of Cr (III). The tendency of salts to

### Table 1

Effect of *N*-methylimidazolium cations with salicylate and thiosalicylate anions on the amount of separated ionic liquid and extraction efficiencies of Cr(III) and Cr(VI) species. Extraction conditions: sample volume, 10 mL; Cr concentration, 250  $\mu$ g L<sup>-1</sup>; Triton X-114, 0.05% (w/v); acetate buffer, 0.2 mol L<sup>-1</sup>, pH = 5; volume of added IL, 500  $\mu$ L).a, b

Type of IL <sup>a</sup>	EE <sup>b</sup> (%) of Cr(VI)	EE(%) of Cr(III)	Amount of separated IL(µL)
[BMIM][salicylate]	48.6	85.5	110-115
[HMIM][salicylate]	27.5	78.8	390-395
[OMIM][salicylate]	11.1	92.5	465
[BMIM][thiosalicylate]	74.5	82.1	205-210
[HMIM][thiosalicylate]	80.3	85.0	450
[OMIM][thiosalicylate]	65.0	88.7	480

<sup>a</sup> Ionic liquid.

<sup>b</sup> Extraction efficiency.

form biphasic system in the mixtures with [OMIM][salicylate] is related to the pH values of the systems induced by adding salt, implying that the pH changes in the [OMIM][salicylate] IL-inorganic salt biphasic system affect the polar interactions in aqueous the phase. Therefore, the acetate buffer was selected for pH adjustment in further experiments. In order to investigate the effect of acetate anion on the formation of the biphasic system and phase separation capability, some experiments were performed by changing the acetate buffer concentration from 0.1 to 0.4 mol  $L^{-1}$  and the effect of concentration on the EE% of Cr(III) and the amount of separated IL phase was also assessed. The results in Table 3 are shown the volume of separated IL as well as the EE% of Cr(III) were increased with further increase in buffer concentrations until 0.3 mol L<sup>-1</sup>, and was constant thereafter. With an increase of the acetate amount and formation of their hydrated complexes, the phase separation was more completed, which further caused an increase in the volume of the IL phase.

### 3.1.3. Effect of pH on IL/aqueous biphasic system

Sample pH has an important role in formation of biphasic system and selective extraction of Cr(III). According to the experimental results, aqueous solutions with different pH values from 2.0 to 7.0 were prepared and applied for investigation of EE% of Cr(III) and Cr(VI). As shown in Table 4, the amount of separated IL was drastically decreased with decrease in pH, so that the amount of separated IL was zero at pH value of 2. This might be attributed to protonation of salicylate anion of [OMIM][salicylate] at low pH values [36]. The EE% of Cr(III) was considerably decreased at pH values lower than 4, whilst it showed a slight increase for Cr(VI). Also, the EE% of Cr(III) decreased at higher pH values than 6, most probably due to formation of CrL(OH) and CrL(HL)(OH) type hydroxo complexes, insoluble Cr(OH)<sub>3</sub> species and anionic Cr(OH)<sub>4</sub>- form. Finally, the best range pH for this study was 4–6 that were consistent with deprotonation of salicylate to complex with Cr species.

### 3.2. Response surface methodology (RSM)

Several classes of RSM such as central composite design (CCD), Box– Behnken design and three-level factorial design have different properties and characteristics, but CCD is a more popular rotatable and orthogonal technique applicable for modeling of the main factors and interaction factors with the response. The polynomial regression equation is most prominent relationship for analysis of correlation between factors and response.

Based on the preliminary experiments (Section 3.1), the best biphasic system with maximum separated IL and high EE% of Cr(III) was obtained with acetate buffer (0.3 mol  $L^{-1}$ ) in pH range of 4–6. It should be noted that other parameters such as the amount of [OMIM][salicylate] IL and time must be investigated to obtain the quantitative EE% of Cr(III). Also, the effect of anti-sticking agent (triton X-114) was investigated and the results showed that presence of antisticking agent had no influence on the formation of biphasic system and EE% of Cr(III), but small amount of anti-sticking agent could prevent

# Table 2 Effect of salt anion type on the amount of separated ionic liquid and extraction - efficiency of Cr(III) species (Extraction conditions are the same as Table 1 except for the volume of

	*		
of Cr(III) species (Extraction of	conditions are the san	ne as Table 1	except for the volume of
added IL that was 200 $\mu$ L).			

Type of anion	EE <sup>a</sup> (%) of Cr(III)	Amount of separated IL ( $\mu$ L)
$H_2PO_4^-$	7.3	200
CH <sub>3</sub> COO <sup>−</sup>	71.1	165
$SO_4^{2-}$	85.9	75
$HPO_4^{2-}$	8.0	85
HCO <sub>3</sub>	59.5	80
$PO_4^{3-}$	6.5	40
Cl <sup>-</sup>	_	0

<sup>a</sup> Extraction efficiency.

### Table 3

Effect of buffer concentration on the amount of separated ionic liquid and extraction efficiency of Cr(III) species. Extraction conditions are the same as Table 2.

Buffer concentration (mol $L^{-1}$ )	EE <sup>a</sup> (%) of Cr(III)	Amount of separated IL ( $\mu L)$
0.10	47.9	80
0.15	58.0	105–110
0.20	73.1	165–170
0.25	83.2	190–195
0.30	81.8	200
0.35	84.2	200
0.40	83.3	200

<sup>a</sup> Extraction efficiency.

the extraction of Cr(VI). Finally, the appropriate ranges for these three factors were defined based on previous experiments (Table 5). Due to the small number of factors, there is no need for screening by factorial design, so CCD was used directly. This design is performed using a combination of factorial points ( $N_f = 2^f$ ), axial points ( $N_\alpha = 2f$ ), and a set of center points  $(N_0)$ , so that 23 experiments containing 8 factorial points, 8 axial points, and 9 replications of the center point were carried out (Table 6). In all of these runs, the aqueous solutions containing 250  $\mu$ g L<sup>-1</sup>Cr(III), 0.05% (w/v) triton X-114, and 0.3 mol L<sup>-1</sup> acetate buffer were used, and the extraction efficiencies of Cr(III) as a response of the proposed system under the defined conditions were analyzed by Design Expert 8. It was found that the best fitted model was quadratic. The value of regression coefficient was calculated using backward mode of multiple linear regression (MLR) model to exclude non-significant effects from the model to avoid over-fitting. According to the overall predictive model, the EE% of Cr(III) as a response was related to the sample pH(A), amount of IL(B), and time (C) which is shown in terms of coded factors as Eq.(2).

$$\begin{array}{l} \text{EE\% of } Cr(\text{III}) = +97.46 - 2.12\text{A} + 10.63\text{B} \\ + 6.91\text{C} - 7.77\text{A}^2 - 5.06\text{B}^2 - 3.05\text{C}^2 \end{array} \tag{2}$$

The ANOVA for EE% of Cr(III) is shown in Table 7. The model revealed that linear terms of A, B, and C, and quadratic terms of  $A^2$ ,  $B^2$ , and  $C^2$  had significant effects on extraction of Cr(III) with *p*-values lower than 0.05. The adequacy of the second-order response surface model was tested by the lack of fit (LOF) F-value, in which the residual error was compared with the pure error, and it demonstrated that the LOF was not significant. It means that the LOF was not important relative to the pure error. The model F-value of 36.89 showed that the presented model was acceptable and significant. Based on the R<sup>2</sup> value, the variability in the data for EE% of Cr(III) was 95.08%. The predicted R<sup>2</sup> value of 0.9417, so it implied that there was no chance for indicating the not significant terms in the model. As illustrated in Fig. 2, the normal probability plot of studentized residuals shows that the errors are constant and normally distributed with the mean zero.

The response surface graphs were plotted based on the proposed model to study the factor effects and their interactions on EE% of Cr(III). The response surface plots visually showed the effects and

Table 4

Effect of sample pH on the amount of separated ionic liquid and extraction efficiency of Cr species. Extraction conditions are the same as Table 1 except for the acetate buffer concentartion that was 0.3 mol  $L^{-1}$ .

pН	EE <sup>a</sup> (%) of Cr(III)	EE <sup>a</sup> (%) of Cr(VI)	Amount of separated IL ( $\mu L)$
2	-	_	0
3	55.9	18.7	100–105
4	87.1	4.9	200
5	85.5	0	200
6	88.0	3.2	200
7	78.8	0	200

<sup>a</sup> Extraction efficiency.

### Table 5

Factors, their notations, and their levels in central composite design.

Factors	Factor Levels					
	notations	$-\alpha$	-1	0	+1	$+\alpha^a$
Sample pH	А	3.3	4.0	5.0	6.0	6.7
Amount of [OMIM][salicylate] (µL)	В	33	100	200	300	370
Time (min)	С	3.3	5.0	7.5	10.0	11.7

<sup>a</sup> For this rotatable CCD, the axial distance is 1.68.

interactions of the two experimental factors on the responses, while the other factors were kept constant at the center point. As mentioned in Section 3.1.2, the pH has an important role in complex formation between Cr(III) and salicylate anion of IL; since the maximum separated IL from aqueous solution was obtained at the pH range of 4–6, the formation of complex between Cr(III) and salicylate anion of IL was investigated in this pH range. Fig. 3 (a, b) shows that the best pH to reach the maximum EE% of Cr(III) was at 4.7. As illustrated in Fig. 3 (a, c), with increasing of [OMIM][salicylate] IL amount up to 220 µL, the EE% of Cr(III) was increased. Meanwhile, the IL amount of higher than 220 µL had a little effect on EE% of Cr(III). Although the excess salicylate anions promote complete formation of complex with Cr(III) at higher amount of IL, but the EE% of Cr(III) was approximately constant above 220 µL of IL. As can be seen from Fig. 3 (b, c), the EE% of Cr(III) was increased with increasing of time up to 8.5 min, however at higher times than 8.5 min, no considerable effect on Cr(III) extraction was observed. Finally, the non-linear Nelder-Mead optimization was carried out by using Design-Expert 8 trial version software, and the defined optimum condition for maximum extraction of Cr(III) using the proposed biphasic system was as follows: [OMIM][salicylate] amount of 220 µL, sample pH of 4.7, and time of 8.5 min. Other investigated factors in preliminary experiments were acetate buffer concentration of 0.3 mol L<sup>-1</sup>, and triton X-114 amount of 0.05% (w/v). Under the optimal condition, the optimum predicted EE% of Cr(III) was 102.8  $\pm$  2.7%. The validation of the predicted EE% was achieved by performing experiments under the optimal conditions. The experimental EE% of Cr(III) was found to be 97.6  $\pm$ 5.9%, and it was in close agreement with the CCD model prediction.

### 3.3. Interference studies

The effect of co-existing cations and anions on extraction of Cr(III) by the proposed biphasic system was examined under the defined

Table 6

Design matrix and responses for CCD.

Run	Block	А	В	С	EE (%) of Cr(III)
1	1	0	0	0	99.4
2	1	+1	-1	+1	76.4
3	1	-1	+1	+1	102.5
4	1	+1	+1	-1	84.1
5	1	-1	-1	-1	65.1
6	1	0	0	0	98.3
7	1	0	0	0	94.3
8	2	+1	-1	-1	64.4
9	2	0	0	0	96.0
10	2	+1	+1	+1	90.6
11	2	-1	-1	+1	87.1
12	2	0	0	0	97.4
13	2	-1	+1	-1	91.3
14	2	-1.68	0	0	101.6
15	3	0	0	0	73.0
16	3	0	+1.68	0	98.0
17	3	0	0	+1.68	101.8
18	3	+1.68	0	0	99.5
19	3	0	0	0	73.9
20	3	0	0	0	96.8
21	3	0	0	0	95.5
22	3	0	0	-1.68	74.1
23	3	0	-1.68	0	60.4

Table 7	
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Analysis of variance (ANOVA) for CCD.

Factor	SS <sup>a</sup>	df <sup>b</sup>	MS <sup>c</sup>	F-Value	p-Value <sup>d</sup>
Block	64.21	2	32.10	2.79	
Model	3817.11	9	424.12	36.89	<0.0001
А	65.52	1	65.52	5.35	0.0411
В	1542.20	1	1542.20	134.13	<0.0001
С	652.76	1	652.76	56.77	<0.0001
AB	7.41	1	7.41	0.64	0.4391
AC	27.01	1	27.01	2.35	0.1536
BC	33.21	1	33.21	2.89	0.1173
A <sup>2</sup>	958.03	1	958.03	83.32	<0.0001
$B^2$	407.11	1	407.11	35.41	<0.0001
$C^2$	147.59	1	147.59	12.84	0.0042
Residual	126.48	11	11.50	_	
LOF	91.96	5	18.40	3.20	0.0967
Pure error	34.52	6	5.75	_	
Cor total	4007.80	22	-	-	_

<sup>a</sup> Sum of square.

<sup>b</sup> Degree of freedom.

<sup>c</sup> Mean square.

<sup>d</sup> The bold items indicate to significant effects.

optimum conditions. In this investigation, different amounts of possible cations or anions were added to aqueous solutions containing 250  $\mu$ g L<sup>-1</sup> of each Cr species, and the proposed extraction procedure was performed on these binary solutions. A concentration of the added ions that imposes more than  $\pm$  5% change in response was defined as tolerance limit. The alkaline and alkaline earth cations up to 1000 fold excess had no interference for extraction of Cr(III), although a minor effect on the amount of separated IL phase was observed. Among the other studied cations, Sn<sup>2+</sup>, Cd<sup>2+</sup>, Al<sup>3+</sup>, and Pb<sup>2+</sup> up to 300 fold excess, and Mn<sup>2+</sup> and Ni<sup>2+</sup> up to 150 fold excess had no significant effect on extraction of Cr(III). Also, Co<sup>2+</sup>, Zn<sup>2+</sup>, and Cu<sup>2+</sup> cations up to 50 fold excess had no interference in extraction of Cr(III), while the tolerance limit for Fe(III) was 25 fold excess. The interferences of halides were also investigated, and they had no interference up to 1000 fold excess in Cr(III) extraction procedure.

### 3.4. Analytical performance

Under the optimum conditions, the dynamic ranges of the proposed procedure were 40–470  $\mu$ g L<sup>-1</sup> and 55–500  $\mu$ g L<sup>-1</sup>for Cr(III) and total Cr, respectively. The limit of detection (LOD) as three times of the standard deviation of the blank signal over the slope of the calibration graph was calculated 7.7  $\mu$ g L<sup>-1</sup> for Cr(III). The repeatability (intra-day



Fig. 2. The normal probability plot of studentized residuals for the defined quadratic model.



**Fig. 3.** Response surface graphical representation of the EE% of Cr(III) versus: (a) sample pH-amount of IL ( $\mu$ L); (b) sample pH-time (min); (c) amount of IL ( $\mu$ L)-time (min).

precision) of the proposed procedure were 5.5 and 7.6% for Cr(III) and total Cr, respectively.

### 3.5. Analysis of real samples

To further demonstrate the applicability of the proposed system for monitoring of Cr(III) and total Cr, tap water (Shokat Abad, Birjand, South Khorasan), underground water (Bajestan, Ferdows, South Khorasan), and urine samples were analyzed by the proposed procedure under the optimum conditions. Firstly, pH of real samples was adjusted to 4.7 and after five fold dilution, the real samples were analyzed according to the proposed procedure in Section 2–4. The contents of Cr species were below of detection limit and no Cr species detected in the real samples. Thus, the real samples were spiked at three levels of concentrations, and the obtained recoveries were in the range of 96.6– 103.5%, 94.8–95.7%, and 93.9–99.5% at spiked levels of 50, 100, and 200 µg L<sup>-1</sup>, respectively (Table 8) with the RSD% ranged from 5.5 to 12.5%. The results suggested that the matrix of real samples had no

 Table 8

 Analysis of Cr(III) and total Cr in real samples using the propose

Analysis of Cr(III)	and total Cr III rea	ii sampies using the	proposed method.

Sample	Added ( $\mu g L^{-1}$ )		Recovery <sup>a</sup> (%)	
	Cr(III)	Cr(VI)	Cr(III)	Total Cr
Tap water	0	0	_	_
	50	50	$100.8\pm7.0$	$103.5\pm7.3$
	100	100	$97.1 \pm 7.6$	$95.5 \pm 5.2$
	200	200	$99.4\pm6.5$	$96.3\pm6.9$
Underground water	0	0	_	_
	50	50	$101.3 \pm 9.0$	$97.1 \pm 7.3$
	100	100	$97.6 \pm 10.3$	$94.8\pm8.6$
	200	200	$94.3\pm6.6$	$98.7\pm6.3$
Urine (non-diabetic human)	0	0	_	_
	50	50	$100.3\pm11.4$	$95.8\pm5.6$
	100	100	$94.9\pm7.0$	$96.1\pm4.1$
	200	200	$99.5\pm6.9$	$98.1\pm5.0$
Urine (non-diabetic human)	0	0	_	_
	50	50	$94.0\pm6.9$	$96.6 \pm 11.5$
	100	100	$91.7\pm8.4$	$95.3 \pm 10.0$
	200	200	$92.1 \pm 4.1$	$939 \pm 117$

<sup>a</sup> Mean value  $\pm$  SD (n = 3).

important effect on extraction and determination of Cr(III) and total Cr by the proposed procedure.

### 4. Conclusion

In this work, the salicylate or thiosalicylate anion based ILs containing N-methylimidazolium cation with different alkyl chain lengths were synthesized. Then, their applicability for formation of an IL/aqueous biphasic system for selective extractions of Cr species were investigated. Among the synthesized ILs, [OMIM][salicylate] was successfully applied for selective extraction of Cr(III). An aqueous/[OMIM][salicylate] biphasic system was successfully applied for analysis of Cr content in water and urine samples with good precision and low detection limits. Furthermore, robustness of the method against high salt concentration is the important advantage of the proposed procedure. Simplicity, ease of operation, and being free from organic solvent in extraction are other advantages of this method. The effect of important factors on EE% of Cr(III) was modeled by CCD and then the response surface plots were applied to investigate the behaviors of factors on EE% of Cr(III) to find the optimum values of these factors. Under the defined optimum condition, the co-existing ions had slight interference on Cr(III) extraction. The proposed method showed that salicylate based ILs could be useful for introduction of simple extraction methods for other metal ions.

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