



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



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ABSTRACT

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 $\mu\text{g L}^{-1}$ and 55–500 $\mu\text{g L}^{-1}$ for Cr(III) and total Cr, respectively. The limit of detection ($3S_b/m$) for Cr(III) was 7.7 $\mu\text{g L}^{-1}$. The relative standard deviations for six replicate determinations of 250 $\mu\text{g L}^{-1}$ 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 as 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 [25]. These preconcentration 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 PF₆ and BF₄ 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 MΩ cm⁻¹). 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 1-bromooctane 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⁻¹ were freshly prepared by dissolving appropriate amounts of Cr(NO₃)₃·6H₂O and K₂Cr₂O₇ 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⁻¹ 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 µg L⁻¹ of each Cr(III) and Cr(VI) species in acetate buffer (pH = 4.7, 0.3 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:

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

where C_{IL} and C₀ are concentrations of Cr species in the IL and initial aqueous phases, and V₀ 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.

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