ORIGINAL PAPER

Salt-assisted liquid-liquid microextraction of Cr(VI) ion using an ionic liquid for preconcentration prior to its determination by flame atomic absorption spectrometry

Behrooz Majidi · Farzaneh Shemirani

Abstract We report on the salt-assisted liquid-liquid microextraction of cationic complexes of Cr(VI) ion using the hydrophilic ionic liquid (IL) 1-butyl-3-methylimidazolium tetrafluoraborate and potassium hydrogen phosphate. This is a novel, simple, non-toxic and effective technique for sample pretreatment technique that displays large extraction efficiency and represents a new platform where Cr(VI) is complexed with 1,5-diphenylcarbazide (DPC) in sulfuric acid medium. It was applied to the extraction of Cr(VI) in the form of the Cr(VI)-DPC complex prior to its determination by flame atomic absorption spectrometry. Cr(III) ion also can be determined by this procedure after oxidation to Cr(VI). Extraction is mainly affected by the amount of water-soluble IL, the kind and quantity of inorganic salts, by pH and the concentration of DPC. Calibration plots are linear in the range from 3 to 150 $\mu g\ L^{-1}$ of Cr(VI), and the limit of detection is 1.25 $\mu g\ L^{-1}$. The method was successfully applied to the speciation and determination of trace levels of Cr(III) and Cr(VI) in environmental water samples containing high levels of dissolved salts or food grade salts.

Keywords Salt-assisted liquid–liquid microextraction · Speciation of Cr · Ionic liquid · Flame atomic absorption spectrometry

Introduction

Most analytical instruments cannot directly handle the matrix. Moreover, sample preparation is used to perform a clean-up of dirty samples, as well as to enhance the concentration of analytes prior to their determination when their natural levels are below the dynamic linear range of the detection instrument.

Despite of wide use, liquid liquid extraction (LLE) poses several problems. Thus, the mode of operation in LLE gives rise to limited preconcentration factors as a consequence of the limited extractant to sample volume ratios employed. Moreover, coalescence and phase separation can be a slow step, especially when emulsions are formed. In addition, LLE involves the use of large sample volumes and toxic organic solvents and hence, the generation of large amounts of solvent waste makes LLE expensive, time-consuming and environmentally unfriendly, which are dangerous for human health [1].

The trend towards miniaturization has led to the development of a series of extraction modalities that minimize consumption of sample and solvent, and reduce analysis times, costs and risks. As miniaturized LLE technique, liquid phase microextraction (LPME) has attracted great attention due to its merits of being simple, rapid and utilizing microliter volumes of solvents. A drawback in the use of non-polar water-immiscible organic solvents in LPME is their low dielectric constant, they are relatively poor at the extraction of polar or charged solutes, and the extraction system is heterogeneous. More-polar solvents, that provide solubility for polar to non-polar compounds are frequently water-miscible and, thus cannot be used for conventional LPME [2]. In this promising research area, ILs have proved to be excellent tools that improve analytical performance.

Interest in ionic liquids (ILs) for their potential application in analytical chemistry continues to grow. As solvents, Room-temperature ionic liquids (RTILs) possess several advantages over conventional organic solvents such as

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negligible vapor pressure, non-flammability, good extractability for various organic compounds and metal ions as a neutral or charged complexes, as well as tunable viscosity and miscibility with water and organic solvents [3].

In recent years, RTILs have been developed as extraction solvents in classical LLE [4]. However, it requires a large amount of IL which is expensive. Several microextraction methods have been reported based on ionic liquids, such as ionic liquid-based headspace liquid phase microextraction [5], ionic liquid-based single-drop microextraction [6, 7], dispersive liquid-liquid microextraction based on ionic liquid [8, 9], cold induced aggregation microextraction (CIAME) [10, 11] and in situ solvent formation microextraction (ISFME) [12]. Main advantages of the mentioned techniques are their high speed and negligible volume of solvent used. However, in some of these methods due to slow mass transfer (the relatively high viscosity of ILs), increased wall effect (strongly tend to adhere on vessel wall), settlement or phase separation failure, variation of the extractant phase volume, two different ILs were used simultaneously and heating and cooling procedures performance significantly decreases [12]. In reported methods hydrophobic IL are used and to decrease the viscosity and facilitate sample handling dilution with organic solvent is necessary before injection. Thus by adding the volume of the diluting agent sensitivity and enrichment factor are decreased. At high concentration of salt, ILs are dissolved completely and the cloudy solution is not formed [9].

In order to overcome the problem a new salt-assisted liquid–liquid microextraction with ionic liquid abrivated [SALLME-IL] was designed and developed as novel medium for LPME in the study. A special apparatus, such as conical-bottom test tubes, syringe, tedious procedures of centrifugation and pure disperser solvent associated with similar techniques are not necessary in the new procedure.

This system avoids the dilution of the extract prior to measurement because each phase contains 70–90% water, which means that allows enhance the concentration of analytes prior to their determination, short preconcentration time and freedom from sample memory effects.

Quick phase separation, low viscosity, little emulsion formation, no need of using volatile organic solvents in the whole process, clear phase boundary and rapid partition equilibrium are the major advantages of this technique. Weak intermolecular forces, e.g., hydrogen bonds, between organic molecules or non-electrolytes and water are easily disrupted by the hydration of electrolytes.

A new type of aqueous two-phase systems, consisting of an IL and a salt solution, was first reported in 2003 by Rogers and co-workers [13]. In mixture with aqueous solutions of kosmotropic (water-structuring) salts and the hydrophilic ILs have been investigated as an alternative to hydrophilic polymers and surfactants [14]. Such an extraction system has been successfully used to extract of biomolecules, such as cells, organelles, membrane fractions and proteins [15]. With the use of ATPS, one can simultaneously carry out purification, extraction and enrichment from high ionic strength solutions.

The aim of the present work was to use microliter volume (typically 150 μL) of water-miscible ionic liquid and to optimize the experimental conditions of (SALLME-IL) and analysis by FAAS. To the best of our knowledge, no much information has been reported for the extraction of hydrophilic metal complex in IL-based SALLME. Such information is very useful for the design of green process of metal purification from high ionic strength solutions. The exploitation of aqueous two-phase systems for the preconcentration, separation and recovery of desired metal ions is gaining importance in the last years, not only for analytical applications, but also for industrial ones [16].

Normally, chromium complexes in different valent states coexist in the same product, both trivalent and hexavalent chromium in most cases, but the toxicity of these species differ significantly. Cr(III) is an essential material for humans and animals, and plays an important role as a glucose-tolerance factor (GTF) in insulin, lipin, and protein metabolism. On the other hand, Cr(VI) is very toxic for humans and living organisms [17, 18]. The determination of Cr(VI) especially in solid samples such as samples with high content of salt, food grade salts, etc., is regarded as one of the most challenging specification tasks due to interconversion between Cr(VI) and Cr(III) in the course of an analytical process [19].

Experimental

Instrumentation

A Varian model AA-400 atomic absorption spectrometer (Varian Australia Pty Ltd, Mulgrave, Australia; www.varianinc.com), equipped with a deuterium lamp background and with chromium hollow cathode lamp was used for the determination of chromium. The lamp was operated at 4 mA, using the wavelength at 357.9 nm, slit of 0.5 nm, burner height of 8 mm and acetylene gas flow rate of 1.5 L min^{-1}. All measurements were carried out in peak high mode (measurement time of 5 s). The digital pH-meter (model 692, Herisau, Switzerland http://www.metrohm-ag.com), equipped with a glass-combination electrode was used for pH adjustment. A home-made microsample introduction system was used for aspiration of the extractant phase in flame atomic absorption spectrometry [8, 9].

Reagents and solutions

All chemicals used in this work were of analytical grade of Merck (Darmstadt, Germany, www.merck.de) or Aldrich

(Chemical Co., Milwauke, WI, USA, www.sigmaaldrich.com). All standard solutions were prepared in double-distilled deionized water stock standard solution of Cr(VI) at a concentration of 1,000 μg mL^{-1} was prepared by dissolving amounts of $K_2Cr_2O_7$ in 100 mL of water. Working standard solutions were obtained by appropriate dilution of the stock standard solution. 1-butyl-3-methyl-imidazolium tetrafluoroborate $[C_4mim][BF_4]$ and all salts used were obtained from Merck (Darmstadt, Germany).

A solution of 1×10^{-3} mol L^{-1} 1,5-diphenylcarbazide (DPC) was prepared daily by dissolving appropriate amount of DPC Merck (Darmstadt, Germany) in acetone.

SALLME-IL procedure

For the SALLME-IL, standard solution containing Cr(VI) at concentrations in the linear range, 0.3 mL of a 1×10^{-3} mol L^{-1} DPC solution, 0.5 mL of H_2SO_4 (1 mol L^{-1}) and 150 μL $[C_4mim][BF_4]$ were added into a flask. Next, the mixture was shaken and a homogeneous phase was formed instantaneously, and then the mixture was diluted to 10 mL with water and mixed with 2.5 g of finely powdered K_2HPO_4, in 0.5 g portions under mechanical stirring of solutions, until the solution was saturated and a small amount of salt remained undissolved and then it was separated into two clear phases easily and rapidly. After that, the volumes of two phases were recorded and the upper layer was collected and 50 μL of the ionic liquid was aspirated into the flame atomic absorption spectrometer using a home-made microsample introduction system as described in the previous work [8, 9]. A diagrammatic sketch of SALLME–IL of cationic complex is shown in Fig. 1.
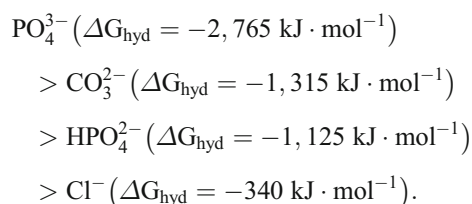
Oxidation Cr(III)

Total chromium was determined as Cr(VI) by the method described above after oxidizing Cr(III) to Cr(VI) by the addition of $KMnO_4$ in acid medium. For this purpose, 4 or 5 drops of $KMnO_4$ (0.02 mol L^{-1}) solution and 0.5 mL of concentrated H_2SO_4 were added into 250 mL beaker containing 100 mL of the spiked solution Cr(VI) and Cr(III). The beaker was covered with a watch glass and heated without boiling (45 °C) for about 15 min to complete oxidation. The solution was cooled and sodium azide solution [2.5% (w/v)] was added drop wise to reduce the excess of $KMnO_4$ (decolorize the pink solution), waiting a few seconds after the addition of each drop.

Results and discussion

As a process of ionic hydration, when a salt is dissolved in an aqueous solution, its ions are surrounded by a layer of water molecules. These water molecules are immobilized (hence the adjectives kosmotropic), and their role as solvents to other molecules or ions is reduced. In the present case, the formation of IL-salt may be considered to be a competition between the hydrophilic IL and the inorganic salt for the water molecules. The competition is won by the inorganic ions because of their stronger affinity for the water. In other words, there is a "migration" of water molecules away from the ions of the IL to those of the inorganic salt, which, in turn, decreases the hydration and hence the solubility of the ions of the IL. Consequently, a phase rich in the salted-out IL separates from the rest of the solution. This means that the salting-out effect must be directly correlated to the hydration strength of the different ions of the inorganic salt.

The ability of the salts studied for phase separation follows the order: $Na_2CO_3 > Na_2HPO_4 > Na_2SO_4 > NaH_2PO_4 >$ NaCl. The kosmotropic ions, CO_3^{2-}, HPO_4^{2-}, SO_4^{2-}, $H_2PO_4^-$ and Cl^-, which exhibit stronger interaction with water molecules, are beneficial to the ILATPS formation. This implies that anions with a higher valence are better salting out agents than those with a lower valence because the higher valence anion hydrates more water molecules than the lower valence anion, thus decreasing the amount of water available to hydrate the ILs [20]. The salting-out ability may also be related to the Gibbs energy of hydration of the ions. Considering the fact that these salts share a common cation but contain different anions, it is easy to see that the salting-out ability of the anions follows the order:

$$PO_4^{3-} \left(\Delta G_{hyd} = -2,765 \text{ kJ} \cdot \text{mol}^{-1}\right)$$
$$> CO_3^{2-} \left(\Delta G_{hyd} = -1,315 \text{ kJ} \cdot \text{mol}^{-1}\right)$$
$$> HPO_4^{2-} \left(\Delta G_{hyd} = -1,125 \text{ kJ} \cdot \text{mol}^{-1}\right)$$
$$> Cl^- \left(\Delta G_{hyd} = -340 \text{ kJ} \cdot \text{mol}^{-1}\right).$$

This order follows the Hofmeister series for the strength of the kosmotropic salts. The hydrophobic interactions between complex and the IL-rich top phase in ILATPS probably are the main driving force for their extraction.

Effect of DPC concentration and effect of acidity on complex formation

The variation of the analytical signal as a function of the ligand concentration was evaluated for chromium complex formation during the procedure. Figure 2 shows the variation of absorbance over the DPC concentration when 10 mL of solution containing certain amount Cr(VI). Concentration of DPC was varied in the range of $(0.1–3) \times 10^{-5}$ mol L^{-1}. The absorbance increases up to a DPC concentration of 0.7×10^{-5} mol L^{-1}, then reach a plateau.
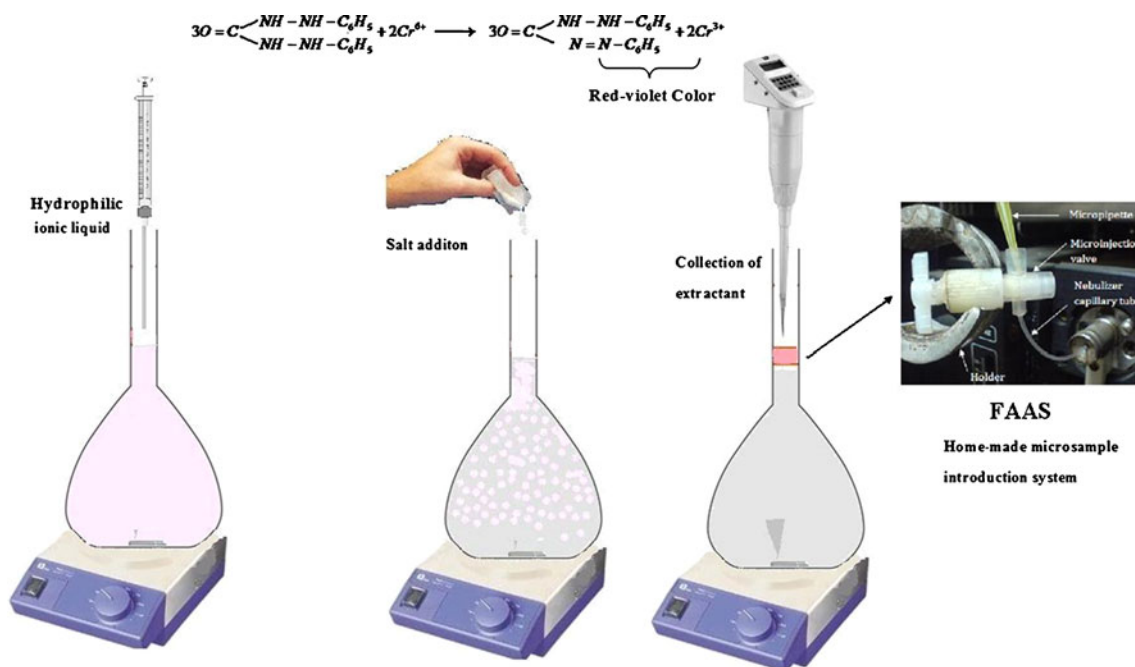
Fig. 1 Schematic representation SALLME-IL enrichment method

Because of some other ions that could be present in solution and probably react with DPC, we used a concentration of 3×10^{-5} mol L^{-1} DPC in our experiments.

In SALLME-IL method pH plays a unique role on formation and subsequent extraction. The effect of acidity of the aqueous solution on the formation of metal-chelate was studied in the range of 0.01–0.10 mol L^{-1} sulfuric acid. The results illustrated in Fig. 3 reveal that the quantitative recovery (>95%) was found as 0.05 mol L^{-1} sulfuric acid concentration and for the higher concentrations the recovery of Cr(VI) was quantitative while the recovery of Cr(III) is rather low (<5%). In further studies, the acidity of the model solutions was adjusted to 0.05 mol L^{-1} with sulfuric acid.
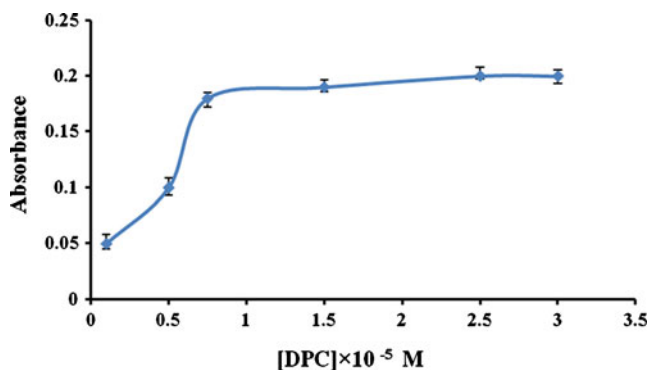
Effect of the type of inorganic salt

Usually, kosmotropic salts are small and highly charged, while chaotropic salts are large and low charged. It has been reported that the contribution of the anion for the formation of ATPS is generally more pronounced than that of the cation in determining the effectiveness of a particular salt. Additionally, multivalent anions are the most effective in inducing phase formation, and monovalent anions least effective. The inorganic salt mixture allows the adjustment of a physiological pH. After the studying of the four different salts (Na_2CO_3,
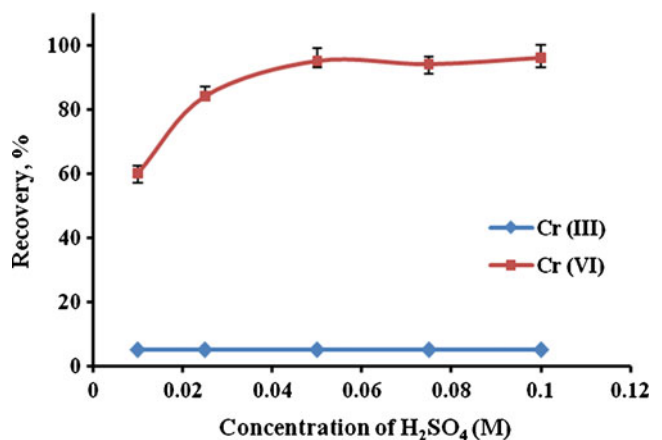

Fig. 2 Effect of DPC concentration on the absorbance of Cr(VI). Conditions: 50 μg L^{-1} Cr(VI), 0.5 mol L^{-1} of H_2SO_4, sample volume 10 mL, 150 μL of ionic liquid and 2.5 g of K_2HPO_4 was added for phase separation

Fig. 3 Effect of the H_2SO_4 concentration on the extraction recovery of Cr(VI) and Cr(III). Conditions: 50 μg L^{-1} Cr(VI) and Cr(III), 3×10^{-5} mol L^{-1} DPC, sample volume 10 mL, 150 μL of ionic liquid and 2.5 g of K_2HPO_4 was added for phase separation

NH_4SO_4, K_2HPO_4, K_3PO_4), cationic Cr(VI) complexes was directly extracted to the top phase of $[C_4mim][BF_4]$–salt. When Na_2CO_3 used as the salting-out agent, first the solution was adjusted to a certain pH value (~4) then the mixture was diluted to 10 mL with water. Figure 4 shows the changes in the extraction efficiency of metal chelate when adding different salts. The results indicated that KH_2PO_4 showed the highest extraction efficiency. When a certain amount of NH_4SO_4, K_2HPO_4, Na_2CO_3, K_3PO_4 were added into the system the pH of the system was about 5.5, 8.5, 11.5 and 13 respectively. The cationic complex was stable in pH 1.0~9.0, while in strong alkaline condition was unstable [21]. In our work, we choose $[C_4mim][BF_4]$–K_2HPO_4 to extract of metal-chelate and the pH of the $[C_4mim][BF_4]$–K_2HPO_4 was about 8.5, so we did not adjust the pH in the whole extraction process.

In order to the concentration of K_2HPO_4 on the ILATPS formation and phase separation ability, various quantities of salt were added to a 10 mL 2% $[C_4mim][BF_4]$ solution at room temperature. As illustrated in Fig. 5, the further adding of K_2HPO_4 could improve ILATPS formation and make phase separation easier. This was because of the fact that the fine IL droplets increased along with the addition of K_2HPO_4 and more chelate complex were transferred into the IL droplets, which leaded to the higher enrichment performance.

When the amount of K_2HPO_4 was up to 2.5 g, the top phase volume reached 100 μL and kept constant, this is because the salting-out ability of K_2HPO_4 has reached the maximum. So the amount of K_2HPO_4 used in the $[C_4mim]$ $[BF_4]$–K_2HPO_4 ILATPS was 2.5 g.

Effects of the mount of $[C_4mim][BF_4]$ on extraction efficiency and enrichment factor

BF_4^- is more chaotropic (water-destructuring) than Cl^-. Following considerations can ease to select desired IL selection:
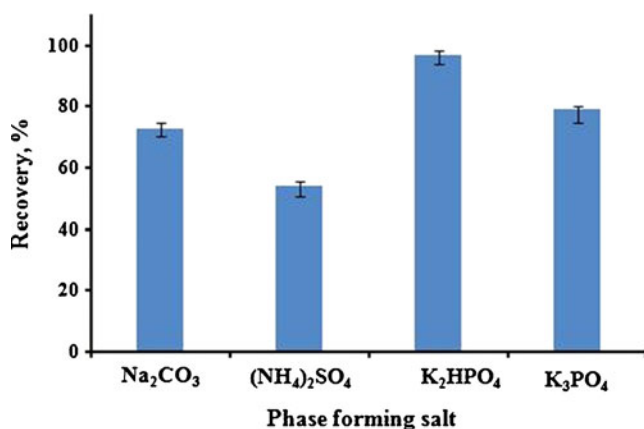

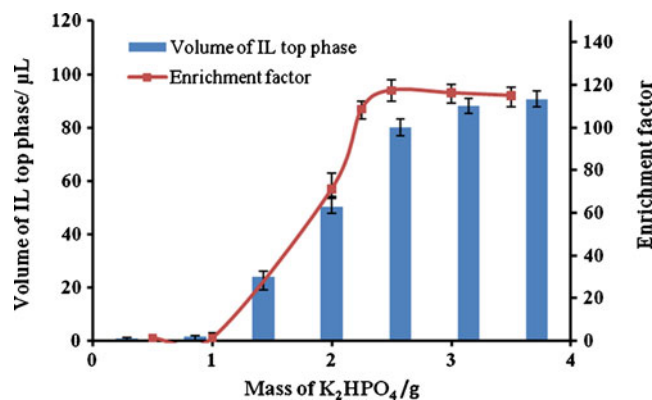Fig. 4 Effect of adding salt species for phase separation on the recovery% of Cr(VI)

Fig. 5 Effect of amount of K_2HPO_4, 0.5–3.5 g, used in the SALLME-IL of Cr(VI). Conditions: 50 μg L^{-1}Cr(VI), 0.5 mol L^{-1} of H_2SO_4, 3×10^{-5} mol L^{-1} DPC, sample volume 10 mL and 150 μL of ionic liquid

1. With increasing the carbon chain of IL, the hydrophobicity of the nonpolar end of IL will increase. This may enhance the facility for phase separation.

2. Longer alkyl chains lead to a decrease in the coulombic and polar interactions and to an increase in dispersive-type interactions between the IL ions. Increasing the size of the alkyl side chain increases the IL-free volume, while decreasing the surface tension of the system, and thus decreasing the energy of cavity formation to accommodate a metal complex [22].

3. The viscosities of the IL-rich phase decrease in the order:

$$[C_8mim][BF_4] > [C_6mim][BF_4] > [C_4mim][BF_4]$$
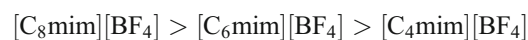
The low-viscosity systems favor the mass transfer of the solute between the two phases, as well as in improving the phase's handling.

4. Many of the current hydrophobic ILs have fluorine-containing anions that are expensive to produce and/or difficult to dispose of.

Consequently, according to the above-mentioned considerations, it seems reasonable to consider $[C_4mim]$ $[BF_4]$ as a chaotropic IL in this work.

The influence of the amount of $[C_4mim][BF_4]$ on the extraction efficiencies of analytes and enrichment factor was also investigated. As shown in Fig. 6, with the increase of the amount of $[C_4mim][BF_4]$ used, the extraction efficiency of Cr(VI) obviously increased, while the enrichment factor decreased greatly. Generally, both high extraction efficiency and suitable enrichment factor are all crucial for the concentration of trace component. Considering these two respects, 150 μL $[C_4mim][BF_4]$ was really appropriate with an enrichment factor of 100 and extraction efficiency of 96% for Cr(VI).
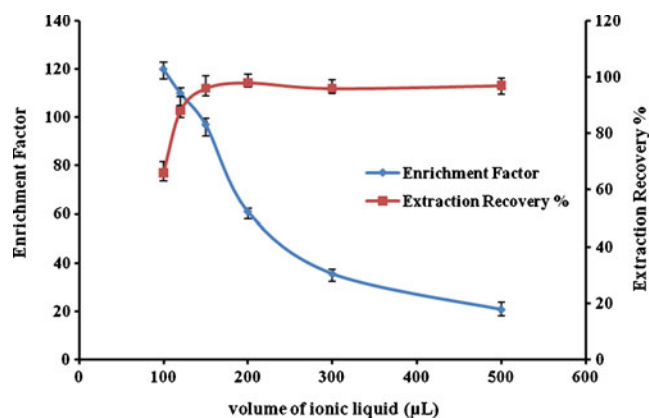
Fig. 6 Effect of volume of ionic liquid on the enrichment factor and extraction recovery% of Cr(VI). Conditions: 50 μg L^{-1}Cr(VI), 0.5 mol L^{-1} of H_2SO_4, 3×10^{-5} mol L^{-1} DPC, sample volume 10 mL and 2.5 g of K_2HPO_4 was added for phase separation

Interference studies

In order to evaluate the performance of this procedure, the highest tolerability of various common potentially interfering ions was studied. Interferences may occur due to the competition of other metal ions with DPC. Therefore, the tolerable limits of various potentially interfering ions were studied in sample solution, spiked with 50 μg L^{-1} of Cr(VI) by keeping the relative error between ±5% under optimum conditions. Table 1 shows tolerance limits of potentially interfering ions. In addition,

Table 1 Effects of the foreign ions on the recovery of 50 μgL^{-1} of Cr (VI) from the aqueous solutions

Ions	Concentration/mg L^{-1}	Recovery (%)
Li^+	3×10^4	100.1
Na^+	3×10^4	99.8
Ca(II)	1000	97.4
Mg(II)	1000	102.2
Ba(II)	1000	98.3
Ag^+	100	101.5
Mn(II)	100	103.6
Zn(II)	100	101.1
Co(II)	100	98.2
Cu(II)	100	97.6
Ni(II)	100	103.2
Cd(II)	10	98.6
Bi(III)	10	103.5
Al(III)	10	96.8
Pb(II)	10	98.7
Fe(III)	10	98.2
Hg(II)	10	102.6

a number of common anions like Cl^-, SO_4^{2-}, $NO_3,^-$ Br^- and I^- were tested. The results showed that they did not have significant effect on the separation and determination of Cr(VI) at the concentrations up to 100 mg L^{-1}. It can be seen that the presence of major cations and anions has no obvious influence on the adsorption of Cr (VI) under the selected conditions.

Analytical performance

Under the optimum conditions, a calibration graph was obtained for both species by preconcentrating several solutions according to the procedure. The limit of detection, calculated as three times the standard deviation of the blank signal ($k=3$, $N=10$), was 1.25 μg L^{-1} for the preconcentration of a 10 mL of sample solution. The enrichment factor defined as the ratio of the analyte concentration after extraction in the extractant phase and that before extraction in the aqueous sample was 100. The calibration graph was linear over a dynamic range from 3 to 150 μg L^{-1}, with a correlation coefficient of 0.9994. The regression equation of the calibration graph was $A = 3.81 \times 10^{-3} C + 0.03$, where A is the absorbance and C is the concentration of Cr (VI) in μg L^{-1}. The relative standard deviation (R.S.D.) resulting from the analysis of solution containing 40 μg L^{-1} Cr(VI) was 1.51% ($n=7$).

The presented method was compared with the other preconcentration methods used for the speciation and determination of trace levels of Cr(III), Cr(VI) and the results are shown in Table 2. As it can be seen, generally, the results obtained by the present method are comparable to those reported method in literatures. In addition, the SALLME-IL is free of volatile organic solvent by using the ionic liquid as the green extraction solvent and this method is robust against a very high content of salt in comparison with other methods. These characteristics are of key interest for laboratories doing routine trace metal ion analyses.

Analytical applications

In order to evaluate the capability of the presented method, the developed procedure was applied to the determination of chromium species in several samples, including water samples (seawater, mineral water and river water) and saline samples, including food additives (table salt, sodium nitrate and sodium acetate). Salt samples were dissolved in double-distilled deionized water (20%, w/v). All aqueous samples were filtered using a 0.45 μm pore size membrane filter to remove suspended particular matter. 10 mL of each of the samples was analyzed according to the presented method at optimum conditions. Analytical results on the original sample solutions and on the spiked sample

Table 2 Comparison of the published preconcentration methods with the proposed method in this work

Method	LOD (μg L^{-1})	Enrichment factor	RSD%	Matrix	Reference
LLE-spectrophotometer	7.5	5	75	Natural water	[23]
SPE-FAAS	45	25	–	Natural water	[24]
SPE-FAAS	2.3	24.9	3	Natural water	[25]
CPE-FAAS	0.65	75	–	sea water	[26]
CPE-FAAS	0.7	48	5.5	river water	[27]
CPE-HPLC	5.2	19	0.6	seawater and wastewater	[28]
DLLME-GFAAS	0.07	300	9.2	lake and tap water	[29]
DLLME-FAAS	0.07	275	2	Natural water	[30]
HLLE- FAAS[a]	1	100[b]	2.8	Natural water	[31]
SALLME-IL-FAAS	1.25	100	1	Environmental water and food grade salts	[This work]

[a] Homogeneous Liquid-Liquid Extraction

[b] Concentration factor is the volume ratio (V_a/V_s) of the aqueous phase (V_a) and final volume of sedimented phase (V_s)

solutions, to which known amounts of chromium species were added, were presented in Table 3. For spiking study, samples were split into two portions, and a known amount of a standard solution of chromium species was added to one portion. The accuracy of the method was evaluated by analysis in electrothermal atomic absorption spectrometry (ETAAS).The analytical results of total chromium in samples under study agreed well with those ETAAS. The results indicate that the presented method can be reliably used for determination of Cr(VI) in saline matrices.

Conclusion

The experimental results demonstrated that this new extraction technique coupled with FAAS for the pre-concentration and determination of hydrophilic metal complex. Quick phase separation, low viscosity, little emulsion formation, no need of using volatile organic solvents in the whole process, clear phase boundary, rapid partition equilibrium was the major advantages of the technique. Such information is very useful for the design

Table 3 Determination of Chromium species in various samples by the proposed FAAS method and ETAAS

Sample	Added(μg L^{-1})		Found (μg L^{-1})[a]		Recovery(%)		ETAAS (total Cr)
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	
Mineral water[b]	0	0	nd	nd	–	–	nd
	10	10	10.09±0.04	9.76±0.07	100.9	97.6	20±0.17
Sea water[c]	0	0	3.91±0.32	nd	–	–	4.14±0.16
	10	10	14.06±0.08	9.80±0.13	101.1	98	24.11±0.24
River water[d]	0	0	4.12±0.14	3.32±0.19	–	–	7.50±0.07
	10	10	14.17±0.08	13.24±0.32	100.5	99.2	27.51±0.13
Sodium nitrate[e]	0	0	3.72±0.03	3.03±0.03	–	–	6.86±0.12
	10	10	14.19±0.04	12.82±0.06	104.7	98.2	26.75±0.07
Sodium acetate[e]	0	0	3.77±0.02	4.22±0.13	–	–	8.12±0.16
	10	10	13.31±0.05	14.29±0.05	95.4	100.7	28.25±0.05
Table salt	0	0	nd	nd	–	–	nd
	10	10	10.13±0.04	10.24±0.06	101.3	102.4	21.11±0.05

[a] Mean of three experiments ± standard deviation

[b] From mineral water system of damavand Iran

[c] Caspian sea water, Iran

[d] Tehran river water

[e] From food grade

of green process of metal purification from high ionic strength solutions. Since only very small amounts of an IL as a' green extraction solvent' is used instead of environment damaging organic solvents. In this way, the separation of ionic liquid phase from the aqueous bulk was achieved without using extra-time consuming-centrifugation time consuming. The presented method offers the advantages of simplicity of the operation, rapidity, good extraction efficiency and enrichment factor. This presented method was a well alternative for the speciation and determination of trace levels of Cr (III) and Cr (VI) in environmental water samples containing high levels of dissolved salts and food grade salts

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