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Cold-Induced Aggregation Microextraction: A Novel Sample Preparation Technique Based on Ionic Liquids for Preconcentration of Cobalt Prior to Its Determination by Fiber Optic-Linear Array Detection Spectrophotometry in Real Water Samples

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1. Introduction

Despite good development in modern analytical instruments, direct determination of trace analytes at low concentrations is often a problem for analytical chemists and, as a result, a sample-preparation step is required. The sample preparation in analytical process typically consists of an extraction–separation step, which offers not only the ability to isolate target analytes from the matrix solution, thus reducing or even eliminating originally present interferences but also the opportunity for these analytes to be preconcentrated and determined at very low levels. Liquid–liquid extraction (LLE), based on the partitioning of an analyte from one liquid phase to another immiscible liquid phase, is a still widely used traditional sample preparation technique. However, this method is time-consuming and tedious. Also large amounts of high purity solvents, which are expensive and toxic, are inevitable to be used. The continuous quest for novel sample preparation procedures has led to a development of new methods, which have main advantages like rapidity and reduction of solvents consumption, such as cloud point extraction (CPE), solid-phase microextraction (SPME), single drop microextraction (SDME), hollow fiber-liquid phase microextraction (HF-LPME), dispersive liquid–liquid microextraction (DLLME) and others.

Cloud point extraction is considered to be a green extraction method because the extraction is performed while using surfactants, which may exhibit lower toxicity, volatility and flammability compared with organic solvents used in other extraction techniques. This technique is widely used in extraction of metals (Bezerra et al., 2005; Dallali et al., 2009), organic compounds (Carabias-Martinez et al., 2000) and proteins (Saitoh & Hinze, 1995). Despite many benefits when using CPE, in rather high content of salt, background is increased since the enrichment phase is composed of a little aqueous sample. Also in the presence of more than 3 % of water-miscible organic solvents such as acetone the phase separation does not occur and the extraction system is destroyed (Manzoori & Karim-

Nezhad, 2003). In addition, the application of this technique is limited by the influence of temperature, pressure, pH, and selection of specified surfactants (Paleologos et al., 2005).

Solid-phase microextraction (SPME), a widely used sample preparation technique, is a solventless, simple and convenient method, which combines extraction, preconcentration and sample introduction in one step (Risticevic et al., 2009). However, it is expensive; its fiber is fragile and has a limited lifetime. Unfortunately, large amounts of eluents are used in this method. In addition, the carryover between extractions is also problematic when determining some analytes at very low concentrations.

Single-drop microextraction is a type of solvent microextraction (SME) technique that is performed by exposing a single drop of solvent to the headspace or directly into the matrix of the sample (Genfa & Dasgupta, 2000; He & Lee, 1997; Jeannot & Cantwell, 1996; Liu & Dasgupta, 1995). It was developed as a solvent-minimized sample preparation procedure, which is inexpensive and advantageous. Since very little amount of the solvent is used, there is a minimal exposure to toxic organic solvents (Ahmadi et al., 2006; Jeannot & Cantwell, 1997). In comparison with solid phase microextraction, it has advantages like wide choice of extraction solvents, cheaper devices and simpler operation and no analyte carryover occurs. However, relatively small volumes of extractant drop lead to lower sensitivity. In addition, it is time-consuming and at fast stirring rates, the organic drop is broken up and air bubbles are formed.

Hollow-fiber liquid-phase microextraction is a sample preparation technique, in which the analytes are extracted into an organic layer filled in pores of a suspended hollow fiber or further extracted back into an aqueous phase inside the fiber, depending on whether a two-phase or three-phase system is applied (Pedersen-Bjergaard & Rasmussen, 1999; Rasmussen & Pedersen-Biergaard, 2004). Because of the larger contact area between the analyte aqueous solution and extraction phase, the extraction efficiency obtained with this method is higher than with SDME. However, the extraction procedure is tedious and in most cases, the extraction equilibrium is not attained during a short time. Moreover, carryover and contamination of the hollow fiber can be an outcome.

Dispersive liquid-liquid microextraction (DLLME), another type of SME which was developed in 2007, is simple, fast and inexpensive. However, the amount of used disperser solvent is relatively high, therefore it may lead to decrease of the extraction recovery of less hydrophobic species.

In recent years, room-temperature ionic liquids (RTILs) have attracted increasing interest and are applied more and more as the extraction solvent replacing the volatile solvent in sample preparation (Huddleston et al., 1998), due to their unique chemical and physical properties, such as negligible vapour 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. However, most of them were conducted in the liquid–liquid extraction and as a result a large volume of ionic liquid was required (Smirnova et al., 2004; Xia et al., 2006), which is tedious and costly. Then the microextraction based on ILs was developed by Liu et al. (Liu et al., 2003). Subsequently, due to a combination of the viscosity and the expense of ionic liquids, we used an ionic liquid (IL) at the microscale for the analytical extraction and the determination of mercury ions in water samples by using spectrophotometric detection (Gharehbaghi et al., 2009).

In 2008 Baghdadi and Shemirani developed a new method called cold-induced aggregation microextraction (CIAME), which was based on the use of ILs in homogeneous liquid–liquid microextraction (HLLME) (Baghdadi & Shemirani, 2008). In this method, a very small

amount of hydrophobic IL as an extractant solvent is dissolved in the sample solution containing Triton X-114. Triton X-114 prevents IL from sticking onto the surface of a centrifuge tube wall, therefore we have named it "anti-sticking agent". One should be aware that there is no interface between the water and the extractant phases; as a result mass transfer from aqueous phase into separated phase has no important effect on the extraction step. After dissolving, the solution is cooled in the ice bath, a cloudy solution is formed due to the solubility reduction of IL and fine droplets of it are formed. During the formation of fine droplets of the extractant phase, the hydrophobic species are collected by the extractant molecules and the extraction process is completed after the formation of the droplets. After centrifuging, the fine droplets of extractant phase settle to the bottom of the conical-bottom glass centrifuge tube.

This method is simple, rapid, safe and robust against high content of salt and water-miscible organic solvents. In comparison with CPE, background is too low in case of saline solutions, because of very low solubility of water in ILs. Also, owing to high viscosity of ILs, removal of bulk aqueous phase is easier. This method is more suitable for the extraction of heat-susceptible species in comparison with CPE. CIAME provides a high recovery and has a low toxicity since only very small amounts of IL as a "green extraction solvent" is used.

2. Importance

2.1 Cobalt; the occurrence, benefits and applications, exposure and toxicity and methods of determination

Cobalt is a natural element found throughout the environment, used in pigment manufacture and used to make superalloys (alloys that maintain their strength at high temperatures approaching their melting points). It can benefit or harm human health. Cobalt is an essential element in people's lives, as a constituent of vitamin B_{12}. It has also been used as a treatment for anemia, because it stimulates red blood cell production. The significance of cobalt as a transition metal in its wide spectrum of applications is covering many frontier areas of study, particularly in medicine. We can be exposed to low levels of cobalt by breathing air, eating food or drinking water. Food and drinking water are the largest sources of exposure to cobalt for general population.

Toxicological effects of large amounts of cobalt include vasodilatation, flushing and cardiomyopathy in men and animals (Yuzefovsky et al., 1994). Even though cobalt is not considered to be as toxic as most heavy metals, it is an equally harmful element. Hence owing to the importance of cobalt, its determination from associated elements by extractive spectrophotometry has been of a considerable importance.

A wide variety of chelating agents has been reported for the spectrophotometric determination of cobalt (Appadoo & Bhagwat, 1994; Carvalho et al., 1996; Chaudhari & Sawant, 1993; Dasilva & Martins, 1992; Kalika et al., 1993; Kamburova et al., 1994; Khambekar & Sawant, 1997; Lokhande et al., 1996; Maheshwari & Balasubramanian, 1995; More & Sawant, 1992; Pillai & Shinde, 1995; R.A. Chaudhari & A.D. Sawant, 1993; Reddy & Sarma, 1994; Sharma & Dave, 1997; Shen et al., 1995; Taher & Puri, 1995; Toral et al., 1993; Umebayashi & Ishiguro, 1996). However, these methods suffer from limitations such as critical pH (Dasilva et al., 1992; Maheshwari et al., 1995; Pillai et al., 1995), long color development time (Umebayashi et al., 1996) and interference with some ions (Chaudhari et al., 1993; Kalika et al., 1993; Lokhande et al., 1996; Maheshwari et al., 1995; More et al., 1992; Pillai et al., 1995; Reddy et al., 1994; Toral et al., 1993; Umebayashi et al., 1996).

In addition, the preconcentration and determination of cobalt (II) has been studied in various extraction methods such as: liquid-liquid extraction (LLE), flow injection extraction (FIE), cloud point extraction (CPE), solid phase extraction (SPE) and dispersive liquid-liquid microextraction (DLLME).

New LLE methods based on liquid membranes (Kakoi et al., 1998; Ribeiro et al., 2004) and hollow fiber contactors (Soldenhoff et al., 2005) were used for extraction and preconcentration of cobalt. However, it is time-consuming, tedious and uses large amounts of high purity solvents, which are expensive and toxic. The continuous quest for novel sample preparation procedures has led to a development of new methods, among which main advantages belong their speed and negligible volume of used solvents. Initial efforts to address the problem of large solvent consumption have led to a development of the FIE method. Some of these methods have been applied for cobalt extraction (Andac et al., 2001; Cao et al., 1999; Cassella et al., 2001; Dadfarnia & Jafarzadeh, 1999; Dzherayan et al., 2002; Fujimoto et al., 1999; Li et al., 2006a; Li et al., 2006b; Nogueira et al., 1998; Shabani et al., 2003; Song et al., 2006; Tsakovski et al., 2002). FIE has some advantages compared with LLE like low cost, high extraction speed and reduced solvent and sample consumption. However, the amount of used solvent is still in the order of several hundred micro liters per analysis.

Also preconcentration of cobalt in some CPE methods has been reported (Bezerra et al., 2007; Chen & Teo, 2001; Donati et al., 2006; Ghaedi et al., 2008; Gil et al., 2008; Nascentes & Arruda, 2003; Safavi et al., 2004; Shemirani & Shokoufi, 2006; Shokoufi et al., 2007b). Despite many benefits from the use of CPE, in high content of salt, background is increased since the enrichment phase is composed of a little aqueous sample and in very high content of salt, the density of the sample becomes equal or even higher than that of micelles, therefore they can not be settled. Also in the presence of more than 3 % of water-miscible organic solvents such as acetone phase separation does not occur.

Several SPE preconcentration procedures for cobalt have been reported using various sorbents (Blitz-Raith et al., 2007; Ghaedi et al., 2007; Praveen et al., 2005; Yang et al., 2002).

DLLME is a type of solvent microextraction (SME), which has been developed in 2007. A combined method including fiber optic-linear array detection spectrophotometry (FO-LADS) and DLLME was developed for preconcentration and determination of cobalt (Shokoufi et al., 2007a). In this method 1,2-dichlorobenzene (a harmful solvent) was used as an extractant. Another DLLME method, which was applied to preconcentrate trace levels of cobalt as a prior step to its determination by spectrophotometric detection, was reported (Gharehbaghi et al., 2008). This method is simple, fast and inexpensive. However, the amount of used disperser solvent is relatively high, therefore it may happen that recoveries of relatively less hydrophobic species decrease.

Homogeneous liquid-liquid microextraction (HLLME) utilizes the phase separation phenomenon from a homogeneous solution and the target solutes are extracted into a separated phase. However, HLLME has some problems; for instance, sometimes it is not compatible with some instrumental analysis and it also requires an addition of a reagent such as acid, base, salt, etc. As a result, some interesting compounds are probably destroyed; moreover, the addition of the reagent causes a release of heat during the extraction.

2.2 Vantage points of cold-induced aggregation microextraction method

In this research the performance of CIAME was investigated with the determination of cobalt in water samples using FO-LADS. The effects of various experimental parameters on

the extraction were investigated. This method is simple, rapid and viscosity independent for extraction and preconcentration of metal ions and organic compounds from water samples, and is robust against high content of salt and water-miscible organic solvents. Additionally, in comparison with the organic solvent extraction, it is much safer since only small amounts of surfactant and IL are used which are being considered as "green solvents" for various separation processes and in comparison with IL-based DLLME, the extraction recoveries of CIAME are relatively high (Gharehbaghi et al., 2009).

Another important capability of this method is that it can be operated in a continuous mode. If the solution is cooled during centrifuging, fine droplets of extractant phase are continuously formed and analytes are extracted and transferred to the bottom of the centrifuge tube. In order to have a good recovery in case of microextraction in which the volume of the extractant solvent is very small, a large distribution coefficient is necessary, unless the recovery is low and continuous microextraction is required. This project is currently being performed in our laboratory.

3. Experimental

3.1 Instrumentation

A UV–vis light source, optical fiber and spectrograph model 2048 were prepared from Avantes (Eerbeek, Netherlands) for FOLADS. A 50 µL quartz cylindrical micro-cell (Hellma, Mullheim, Germany) was used as a determination cell. A Universal 320R refrigerated centrifuge equipped with an angle rotor (6-place, 9000 rpm, Cat. No.1620A) and a Jeio Tech BW-05G water bath were obtained from Hettich (Kirchlengern, Germany).

3.2 Reagents

All used reagents were of analytical grade. Triply distilled water was used throughout the experiment. 1-(2-pyridylazo)-2-naphthol (PAN), acetone, ethanol, acetic acid, 1-hexyl-3-methylimidazolium hexafluorophosphate [Hmim][PF_6] and 1- hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide [Hmim][Tf_2N] and all used salts were obtained from Merck (Darmstadt, Germany). Triton X-100 and Triton X-114 were purchased from Fluka (Buchs, Switzerland). A stock solution of cobalt (II) (1000 mg L^{-1}) was prepared by dissolving appropriate amount of $CoCl_2 \cdot 6H_2O$ and working standard solutions were obtained by appropriate stepwise dilution of the stock standard solutions. All stock and working standard solutions were stored in plastic (polypropylene) bottles with leak proof screw cap, which were cleaned before being used by soaking in 10% nitric acid solution for at least 24 h and then rinsed thoroughly with triply distilled water. A 10^{-3} mol L^{-1} PAN solution was prepared by dissolving the appropriate amount in absolute ethanol. The viscosity of ILs is high and their handling is difficult, therefore working solutions ([Hmim][PF_6], 0.8 mg μL^{-1} and [Hmim][Tf_2N], 0.5 mg μL^{-1}) were prepared in acetone.

3.3 Cold-induced aggregation microextraction procedure

The sample or standard solution containing Co(II) in the range of 1.5–65 ng mL^{-1}, PAN (2.5×10^{-5} mol L^{-1}), Triton X-114 (0.05 %, w/v), sodium nitrate (0.25 %, w/v), oxalate (4.0×10^{-3} mol L^{-1}) was poured in a 10 mL conical-bottom glass centrifuge tube. After 1 or 2 min, while greenish complex of cobalt was formed, pH of the solution was adjusted to 1 by concentrated HCl. [Hmim][PF_6] (64mg) and [Hmim][Tf_2N] (5 mg) were added and the volume of the solution was adjusted to 10.0 mL by triply distilled water. After that, tube was

kept in a thermostated bath at 35 ◦C for 4 min. After shaking, it was placed in an ice-water bath for 10 min and a cloudy solution was formed. Then, the mixture was centrifuged for 5 min at 5000 rpm. As a result, fine droplets of IL settled at the bottom of the centrifuge tube (about 8 μL). The bulk aqueous phase was removed simply by inverting the tubes. The extraction steps are illustrated in Fig. 1. Afterwards, IL-phase was dissolved in 50 μL of pure ethanol and transferred to quartz cylindrical micro-cell. The absorbance of the complex was measured at 578 nm.

4. Results and discussion

It is necessary to investigate the effect of all parameters that can probably influence the extraction performance. In this methodology these parameters are the kind and amount of IL and anti-sticking agent, ligand concentration, pH, salt concentration, temperature and centrifuge conditions, which were investigated and optimized in order to achieve a high recovery and enrichment factor. In all optimization steps concentration of cobalt was 30 ng mL^{-1}.

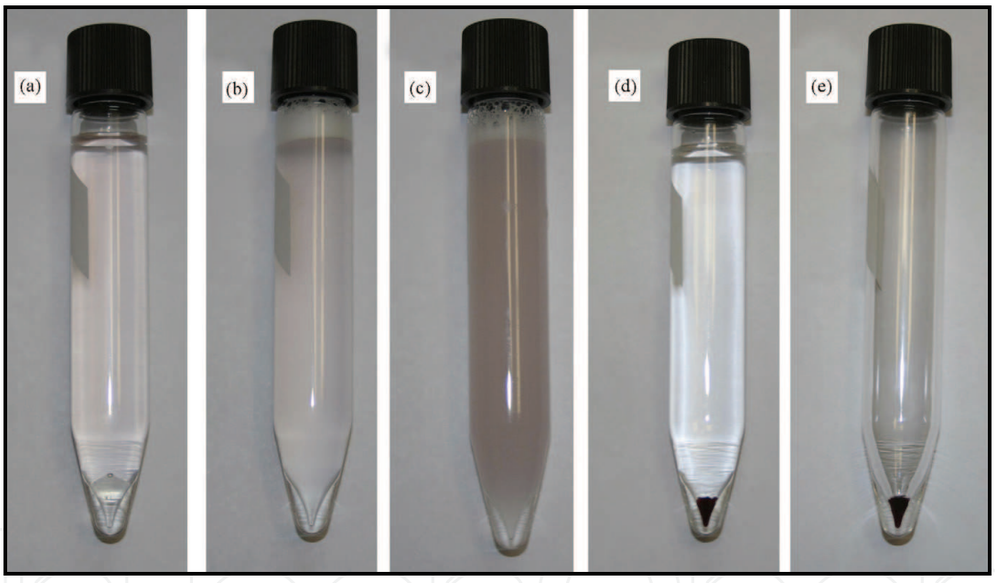

Fig. 1. Photography of different steps in CIAME: (a) after adding IL in the sample solution, (b) after shaking and dissolving the IL, (c) after cooling and phase separation, (d) after centrifuging and (e) after removing the bulk aqueous phase.

4.1 Selection of ionic liquid

For the selection of a suitable IL some considerations were recommended, which were mentioned in the previous work (Baghdadi et al., 2008). In this work, we focused on ILs containing imidazolium cation. Imidazolium-ILs containing PF_6^- as an anion are hydrophobe, relatively inexpensive and liquid in experimental conditions, therefore they are suitable for LLE. From [Bmim][PF_6], [Hmim][PF_6] and [Omim][PF_6] according to some physicochemical properties like density, viscosity and water solubility (Liu et al., 2005) and with regard to the point that the sample volume was 10 mL, [Hmim][PF_6] was chosen as an extractant. Thus, about 75 mg of this IL was solved in the aqueous sample solution.

4.2 Selection of anti-sticking agent

Like in the previous work, after centrifugation, it was observed that some of the IL-phase stick on the wall of the centrifuge tube. In order to overcome this problem, a non-ionic surfactant was added to the sample solution (Baghdadi et al., 2008). In the presence of non-ionic surfactant and during the phase separation, molecules of the surfactant surround the fine droplets of IL. Hence, interactions of IL with the wall of the centrifuge tube decrease and consequently, IL-phase does not stick on the wall of the centrifuge tube. The effects of two non-ionic surfactants (Triton X-114 and Triton X-100) were investigated and compared. In the presence of Triton X-100 absorbance decreased, while in the case of using Triton X-114 absorbance increased. Therefore, the Triton X-114 was chosen as the anti-sticking agent at the optimum concentration of 0.05 % (w/v).

4.3 Effect of pH and PAN concentration

In CIAME method pH plays a unique role in the metal-chelate formation and the subsequent extraction. The effect of pH on the extraction of cobalt from water samples was studied in the range of 0.5–6 after Co–PAN complex formation. Results reveal that the absorbance is slightly reduced by increasing pH. As well as at low pH, cations are less likely to precipitate; pH 1 seems a proper choice for extraction.

The effect of PAN concentration on the absorption is shown in Fig. 2. As it is well expected, in accordance with ML_2 stoichiometry of the complex the absorption is higher when increasing the PAN concentration. We investigated PAN concentration in the range of 1.5×10^{-7} to 4×10^{-5} mol L^{-1}. The maximum absorbance was obtained at a concentration of 2.5×10^{-5} mol L^{-1} of the ligand and after that, the absorbance stays approximately constant.

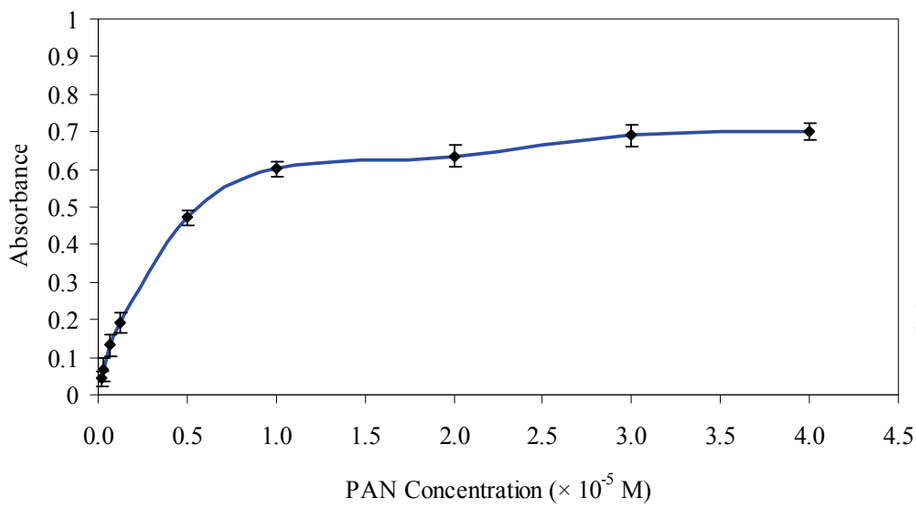

Fig. 2. Effect of PAN concentration on the absorbance of complex. Utilized conditions: Cobalt 30 ng mL^{-1}, pH = 1, $NaNO_3$ 0.2 % (w/v), Triton X-114 0.05 % (w/v), [Hmim][PF_6] 60 mg, [Hmim][Tf_2N] 5 mg, diluting agent 50 µL.

4.4 Effect of IL amount

In the presence of high content of salt, the solubility of [Hmim][PF_6] increases and phase separation does not occur. But according to the common ion effect, solubility decreases in

the presence of IL with a common ion (such as [Hmim][Tf_2N]). This is one of the interesting properties of ILs. The effect of [Hmim][PF_6] in the presence and absence of [Hmim][Tf_2N] is shown in Fig. 3. In the presence of [Hmim][Tf_2N], lower amount of [Hmim][PF_6] was required for the phase separation. The optimum amount of [Hmim][PF_6] for the complete extraction was 70 and 60 mg in the absence and presence of [Hmim][Tf_2N], respectively.

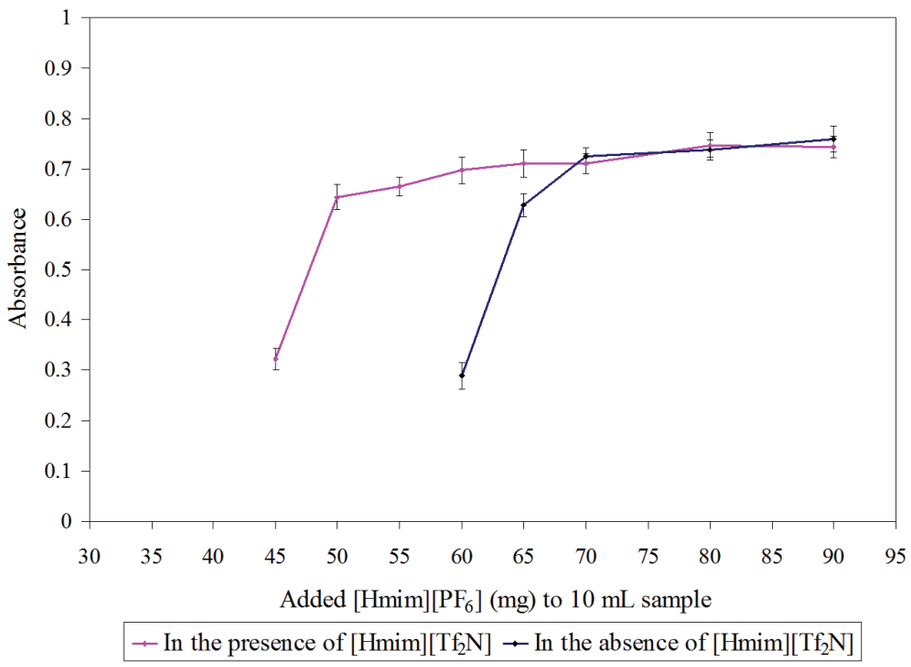

Fig. 3. Effect of the amount of [Hmim][PF_6] on the absorbance of Co-PAN complex. Utilized conditions: Cobalt 30 ng mL^{-1}, PAN 2.5×10^{-5} mol L^{-1}, pH = 1, $NaNO_3$ 0.2 % (w/v), Triton X-114 0.05 % (w/v), [Hmim][Tf_2N] 5 mg, diluting agent 50 µL.

4.5 Effect of salt concentration and water-miscible organic solvents

$NaNO_3$ was chosen in order to study the salt effect in the range of 0–1 % (w/v). The absorbance slightly increased as a result of the salting out effect. A concentration of 0.2% (w/v) $NaNO_3$ was selected for subsequent experiments in order to increase recovery. Also to investigate the robustness of the method against salty solutions, various solutions with the concentration up to 10% were examined. As shown in Fig. 4, in the absence of [Hmim][Tf_2N], absorbance decreased by increasing the salt concentration as a result of increasing in solubility of [Hmim][PF_6], but in the presence of [Hmim][Tf_2N] phase separation occurred up to 10% $NaNO_3$.

Since acetone and ethanol were selected as the solvents for the IL and ligand, their effects were investigated, too. In the presence of acetone, the absorbance was nearly constant up to 10 % and afterwards, it decreased and in the presence of ethanol, the absorbance was almost constant up to 12 %. This is one of the advantages of CIAME compared to CPE. In case of CPE, the extraction system is destroyed in the presence of over 3% water-miscible organic solvents (Manzoori et al., 2003). Even in case of DLLME based on common organic solvents like chloroform, carbon tetrachloride, etc., the extraction efficiency was clearly reduced for solutions containing water-miscible organic solvents.

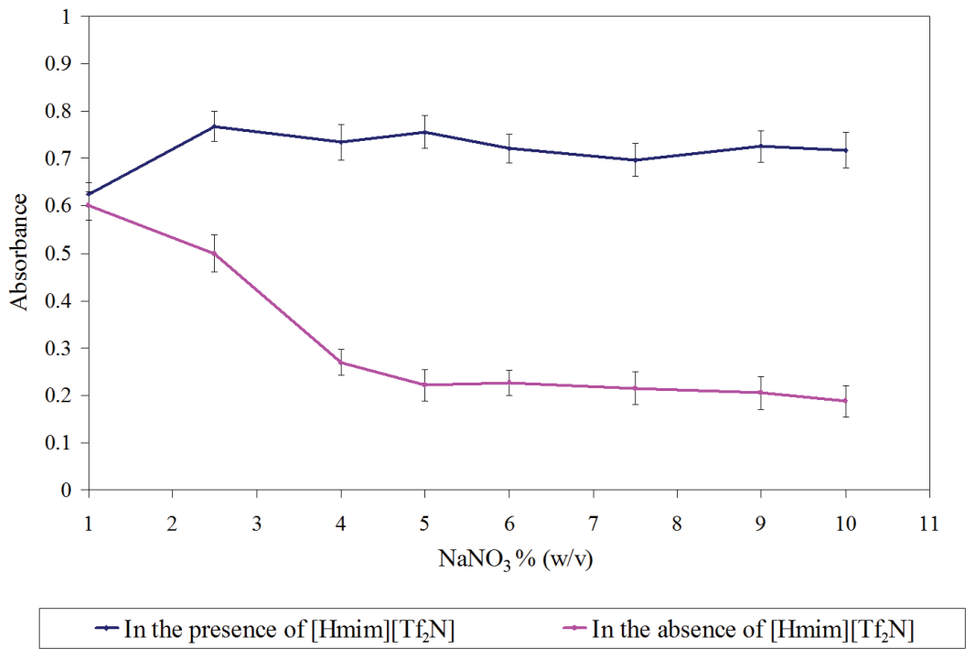

Fig. 4. Effect of $NaNO_3$ on the absorbance of Co-PAN complex in the range of 1-10 % (w/v). Utilized conditions: Cobalt 30 ng mL^{-1}, PAN 2.5×10^{-5} mol L^{-1}, pH = 1, Triton X-114 0.05 % (w/v), [Hmim][PF_6] 64 mg, [Hmim][Tf_2N] 5 mg, diluting agent 50 µL.

4.6 Effect of temperature

Before shaking the solutions containing IL, they were heated in the range of 20-60 °C. In this range the absorbance was constant; warming of the solution had no effect on the extraction process. This is another advantage of CIAME in comparison with CPE, especially if the species are heat-sensitive. Since ILs are dissolved more easily at the temperatures above 30 °C, a temperature of 35 °C was chosen for the heating step.

After dissolving of IL, samples were cooled in the temperature range of 0-25 °C. As the temperature decreased, the absorbance increased, as a result of decreasing IL solubility. Hence, a temperature of 0 °C was applied in all experiments by placing the centrifuge tubes in an ice bath for 10 min.

4.7 Effect of centrifuge conditions

The effect of centrifugation rate on the absorbance was studied in the range of 1000 - 7000 rpm. It was found, that over 4000 rpm IL-phase completely settled, therefore a rate of 5000 rpm was selected as the optimum point.

At the optimum rate, the absorbance was investigated as a function of the centrifugation time. Over 2 min, absorbance was constant, indicating complete transfer of IL-phase to the bottom of centrifuge tube. Therefore, the optimum centrifugation time was chosen as 3 min.

4.8 Effect of coexisting ions

The effects of coexisting ions in real water samples on the recovery of cobalt were also studied. In these experiments, 10mL solutions containing 30 ng mL^{-1} of cobalt and various

amounts of interfering ions were treated. A given species was considered to interfere if it resulted in a ± 5% variation of the absorbance. The obtained results are given in Table 1.
Most of the examined cations and anions did not interfere with the extraction and determination of Co^{2+}. However, some of the tried species, such as Fe^{3+}, Cu^{2+} and Pd^{2+} interfered with the determination of Co^{2+} ion. These interferences were eliminated in the presence of proper masking agents, such as 1.5×10^{-4} mol L^{-1} acetylacetone for Pd^{2+}, 4.0×10^{-3} mol L^{-1} oxalate for Fe^{3+} (and Ca^{2+}) and 2.5×10^{-3} mol L^{-1} ascorbic acid and 4.0×10^{-3} mol L^{-1} iodide for Cu^{2+}. In the presence of the masking agents, no interference was observed for Ca^{2+} up to 1000, Fe^{3+} and Cu^{2+} up to 100 and Pd^{2+} up to 10 times relative to Co^{2+} concentration. Thus, a quantitative extraction of Co^{2+} was possible.

Interferent	Interferent/Co(II) (weight ratio)	Recovery (%)	Interferent	Interferent/Co(II) (weight ratio)	Recovery (%)
Ba^{2+}	1000	98	Cu^{2+}	100	-[c]
Mg^{2+}	1000	100		100	105[d]
Mn^{2+}	1000	99	Hg^{2+}	100	92
Cr^{3+}	1000	104		50	99
Cd^{2+}	1000	100	Pd^{2+}	10	188
Zn^{2+}	1000	103		10	95[e]
Ca^{2+}	1000	98[a]	I^-	1000	100
Ag^+	500	97	SO_4^{2-}	1000	101
Pb^{2+}	500	101	NO_3^-	1000	98
Al^{3+}	500	102	PO_4^{3-}	1000	98
Fe^{3+}	100	165	CH_3COO^-	1000	100
	100	98[b]	NO_2^-	1000	98

Table 1. Effect of interferents on the recovery of 30 µg L^{-1} Co(II) in water sample using CIAME
[a]Ca^{2+} masked with 4.0×10^{-3} mol L^{-1} oxalate .
[b]Fe^{3+} masked with 4.0×10^{-3} mol L^{-1} oxalate.
[c]In the presence of this interferent the shape of spectrum is changed completely.
[d]Cu^{2+} masked with 2.8×10^{-3} mol L^{-1} ascorbic acid and 3.9×10^{-3} mol L^{-1} iodide.
[e]Pd^{2+} masked with 1.9×10^{-4} mol L^{-1} acetylacetone.

4.9 Figures of merit

Table 2 summarizes analytical characteristics of the optimized method, including limit of detection, reproducibility and enhancement factor. The limit of detection (LOD = 0.14 ng mL^{-1}) was calculated as 3 S_b/m (S_b: standard deviation of the blank signals; m: slope of calibration curve after the preconcentration). A good correlation coefficient (r = 0.9997) was obtained and only small deviations between sequential determinations (RSD = 2.32 %) were found. The calibration curve was investigated up to 65 ng mL^{-1} which was linear. Enhancement factor (EF = 165) was obtained from the slope ratio of calibration curve after and before the preconcentration.

Parameter	Analytical Feature
Linear range (ng mL^{-1})	1.5-65
r^2	0.9995
Limit of detection (ng mL^{-1}) (3σ, n = 5)	0.14
Repeatability (RSD[a], %) (n = 5)	2.32
Enhancement factor[b] (EF)	165
Sample volume (mL)	10
Extraction time (min)	<20

Table 2. Analytical characteristics of CIAME for determination of Co(II)
[a]RSD was obtained for 30 µg L^{-1} concentration of Co(II) .
[b]Enhancement factor is the slope ratio of calibration graph after and before extraction.

The equation of the calibration curve after the preconcentration procedure is given in Eq. (1). Also the equation of the calibration curve before the preconcentration procedure is given at below in Eq. (2). (These standard samples of cobalt were chosen up to 200 ng mL^{-1} with execs PAN to measure their absorbance and obtain the equation of the calibration curve accurately).

$$A = 2.30 \times 10^{-2} C_{(Co)} + 0.0094 \quad (r^2 = 0.9995, r = 0.9997) \tag{1}$$

$$A = 1.39 \times 10^{-4} C_{(Co)} + 0.0323 \quad (r^2 = 0.9983, r = 0.9991) \tag{2}$$

4.10 Accuracy

For evaluating the accuracy of the method, a certified reference material (CRM) was analyzed. The Reference Standard "SCP-ES-L-1" (SCP SCIENCE Canada, ground water (Low level)) is a ground water that has been spiked with metals. The certified value and analytical results are presented in Table 3. The result indicates effectiveness and accuracy of the proposed method.

Certified reference material	Certified[a] (ng mL^{-1})	Found[b] (ng mL^{-1})	Found[c] (ng mL^{-1})	Recovery (%)
SCP-ES-L-1	51 ± 8	48.6 ± 0.2 [d]	49.5 ± 0.6 [d]	101.8

Table 3. Determination of cobalt in a standard reference material using DLLME
[a]Results after dilution 1 : 500.
[b]Determined by GFAAS.
[c]Determined by CIAME/FO-LADS.
[d]Mean value ± standard deviation based on five replicate measurements.

4.11 Analysis of natural water

The proposed methodology was applied for the determination of cobalt in different water samples. Damavand mineral water, Tajan river water and Caspian Sea water samples were collected from the north of Iran and analyzed by CIAME as a prior step to its determination by FO-LADS. No concentration of cobalt in the tap and mineral water samples was detected. Moreover, the robustness of the proposed method was checked by performing recovery tests on a saline serum and a synthetic sample (containing Mn^{2+}, Zn^{2+}, Mg^{2+}, Cd^{2+}, Cr^{3+} of 1000 ng mL^{-1} and Na^{+}, K^{+} of 3000 ng mL^{-1}). Each type of water was spiked with variable

amounts of Co(II) to assess matrix effects. The results are shown in Table 4. The relative recoveries of cobalt from mentioned water samples at various spiking levels were between 96.0 and 103.0 %. These results demonstrated that matrices of these water samples, under presented conditions, had little effect on CIAME of cobalt.

Sample	Spiked (ng mL^{-1})	Found (ng mL^{-1})[a]	Recovery (%)
Mineral water	–	N.D[b]	–
	10	10.1 ± 0.15	101.0
	20	20.3 ± 0.32	101.5
Tap water[c]	–	N.D[b]	–
	10	10.2 ± 0.22	102.0
	15	14.7 ± 0.35	98.0
River water	–	4.3 ± 0.39	–
	10	13.9 ± 0.23	96.0
	25	28.5 ± 0.33	96.8
Sea water	–	1.7 ± 0.27	–
	10	12.0 ± 0.32	103.0
	25	27.1 ± 0.55	101.6
Saline Serum[d]	25	25.6 ± 0.2	102.4
	45	43.9 ± 0.4	97.6
Synthetic sample	10	10.1 ± 0.18	101.0
	15.0	14.9 ± 0.23	99.3

Table 4. Determination of cobalt in real and synthetic samples
[a]Mean ± S.D. (n = 5).
[b]Not detected.
[c]From drinking water system of Tehran, Iran.
[d]Produced by Daru Paksh Company for injection.

4.12 Comparison of CIAME with other methods

A comparison of the represented method with other reported preconcentration methods is given in Table 5. In comparison with other reported methods, CIAME has low LOD (0.14 ng mL^{-1}), high enrichment factor (165) and relative short extraction procedure (less than 20 min). All these results indicate that CIAME is a reproducible, simple and low cost technique that can be used for the preconcentration of metal ions like cobalt from water samples.

5. Conclusions and future work

In this study, a new mode of HLLME based on IL, named cold-induced aggregation microextraction (CIAME), was developed for preconcentration of cobalt from water samples as a prior step to its determination by FO-LADS. Cobalt was employed as a test analyte and 1-(2-pyridylazo)-2-naphthol (PAN) as a complexing agent to assess the extraction procedure.

Method	LOD[a] (ng mL^{-1})	RSD.[b] (%)	Enhance-ment factor	Sample consumpt-ion (mL)	Calibration range (ng mL^{-1})	References
CPE/Spectrophot ometry	7.5	2.2	10[c]	10	20–200	(Safavi et al., 2004)
CPE/FAAS	1.06	5.41	28.5	12.5	25-200	(Nascentes et al., 2003)
CPE/FAAS	0.24	2.1	57[d]	50	0-120	(Chen et al., 2001)
SPE/Spectrophot ometry	10	2.23	100[e]	250	10-400	(Yang et al., 2002)
DLLME/FO-LADS	0.2	<4	165	10	1-70	(Shokoufi et al., 2007a)
DLLME/Spectrop hotometry	0.5	2.5	125	50	2-60	(Gharehbaghi et al., 2008)
CPE/FAAS	5	1.71	20[f]	10	0-200	(Giokas et al., 2001)
SPE/ETAAS	0.004	4.5	87	11.5	0.01–0.25	(Sant'Ana et al., 2002)
CIAME/FO-LADS	0.14	2.32	165	10	1.5-65	This work

Table 5. Characteristic performance data obtained by using CIAME and other techniques for determination of cobalt

[a]Limit of detection.

[b]Relative standard deviation.

[c]Ratio of the aqueous phase to final volume of surfactant-rich phase.

[d]The enhancement factor, as the ratio of absorbance of preconcentrated sample to that obtained without preconcentration.

[e]Ratio of the aqueous phase to final volume of eluent phase.

[f]Preconcentration factor.

This method is simple, rapid, safe and robust against high content of salt and water-miscible organic solvents. In comparison with CPE, background is too little in case of saline solutions, because of very low solubility of water in ILs. Also owing to high viscosity of ILs removing the bulk aqueous phase is easier. This method is more suitable for extraction of heat-susceptible species in comparison with CPE. CIAME provides high recovery and has low toxicity since only very small amounts of an IL as a "green extraction solvent" is used.
In addition, the proposed method offers good sensitivity in comparison with other combination methods, which were used, FAAS or conventional UV–vis spectrophotometer as the detection technique.

Our research group is currently working on CIAME in a continuous mode and as a future work would like to develop a microextraction technique in which the volume of the extractant solvent is very small. In order to have a good recovery, in this case a large distribution coefficient is necessary unless a continuous microextraction, in which fine droplets of extractant phase are continuously formed and analytes are extracted and transferred to the bottom of the centrifuge tube, is applied.

Financial support from University of Tehran, as well as proofreading by Barbora Ehrlichová is gratefully acknowledged.

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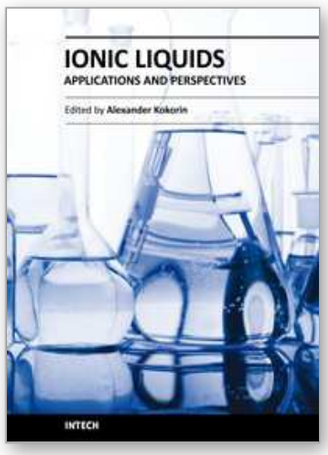

Ionic Liquids: Applications and Perspectives

Edited by Prof. Alexander Kokorin

ISBN 978-953-307-248-7
Hard cover, 674 pages
Publisher InTech
Published online 21, February, 2011
Published in print edition February, 2011

This book is the second in the series of publications in this field by this publisher, and contains a number of latest research developments on ionic liquids (ILs). This promising new area has received a lot of attention during the last 20 years. Readers will find 30 chapters collected in 6 sections on recent applications of ILs in polymer sciences, material chemistry, catalysis, nanotechnology, biotechnology and electrochemical applications. The authors of each chapter are scientists and technologists from different countries with strong expertise in their respective fields. You will be able to perceive a trend analysis and examine recent developments in different areas of ILs chemistry and technologies. The book should help in systematization of knowledges in ILs science, creation of new approaches in this field and further promotion of ILs technologies for the future.

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