Journal of Molecular Liquids 216 (2016) 666–670

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Development of ionic liquid-based in situ solvent formation microextraction for iron speciation and determination in water and food samples

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ARTICLE INFO

Article history:
Received 4 January 2016
Received in revised form 29 January 2016
Accepted 2 February 2016
Available online xxxx

Keywords:
In situ solvent formation microextraction
Iron
Speciation
Ionic liquid
Spectrophotometric analysis

ABSTRACT

In the present work, a novel, simple, and efficient method for the iron (Fe) speciation and determination in different water and food samples was developed using in situ solvent formation microextraction (ISFME) technique followed by spectrophotometric analysis. The procedure is based on the complexation of Fe (II) with 1, 10-phenanthroline. A hydrophilic ionic liquid (IL), 1-Hexyl-3-methylimidazolium tetrafluoroborate ([Hmim][BF_4]), was added to the aqueous media and then ion-pairing agent, sodium hexafluorophosphate ($NaPF_6$), was added in order to obtain a hydrophobic IL ([Hmim][PF_6]) as the extraction solvent. The hydrophobic extraction solvent formed under these conditions was completely dispersed into the sample solution. After centrifugation, the fine droplets of the extractant phase settled to the bottom of the conical-bottom glass centrifuge tube. The absorbance of the enriched analyte in the final solution was determined by UV–Vis spectrophotometer against a reagent blank. Total iron was determined after the reduction of Fe (III) to Fe (II) by using ascorbic acid as reducing agent. To obtain the best extraction results, some experimental parameters affecting the extraction efficiency were optimized. Under optimum conditions, the calibration curve was linear in the concentration range of 1.0–60.0 μg L^{-1}, with the square correlation coefficient (r) equal to 0.998. The limit of detection and the enrichment factor were 0.3 μg L^{-1} and 80, respectively. The method was successfully applied to the analysis of iron in water and food samples.

1. Introduction

Iron has an essential role in many metabolic functions and is one of the most important elements in environmental and biological systems. In fresh waters, iron is also an important nutrient for phytoplankton and other organisms. It is known that the biological activity in certain oceanic regions is affected by iron [1]. Iron is not normally considered a toxic element, but it becomes toxic when accumulated, especially when present as a free ion [2–4]. Excessive concentration of iron is potentially toxic to human due to its pro-oxidant activity. Iron has two readily interconverted oxidation states [5,6]. Determination of the oxidation state of iron in aquatic systems is very important for environmental and biological studies due to the influence of the chemical forms on the bioavailability of iron and physicochemical and toxicological properties of other trace elements and organic substrates [7–9].

Various methods for quantitative analysis of iron have been developed: inductively coupled plasma-optical emission spectrometry/mass spectrometry (ICP-OES/MS) [10,11], atomic absorption spectrometry (AAS) [12,13], electrochemistry [14], and ion chromatography (IC) [15]. Though all of these methods are highly sensitive, their main disadvantages are the necessity of expensive and sophisticated instrumentation [16]. Spectrophotometric methods are less expensive and easily operated but they suffer from a high limit of detection. Separation and preconcentration procedures are of great importance in the elemental analysis as they eliminate or minimize matrix effects and concomitants, lowering the detection limit and enhancing the sensitivity of detection techniques toward metals and their species.

Several procedures such as liquid–liquid extraction (LLE) [17–19], co-precipitation [20], solid phase extraction (SPE) [21–23], and dispersive liquid–liquid microextraction [24–28] have been developed for the separation and preconcentration of contaminants from environmental matrices. Recently, Baghdadi and Shemirani proposed an extraction procedure similar to ionic liquid based dispersive liquid–liquid microextraction (IL-DLLME), which they termed "in situ solvent formation microextraction" (ISFME) [29]. The method is based on the dissolution of a hydrophilic ionic liquid (IL) in an aqueous solution containing the analytes of interest, followed by the addition of an ion-exchange reagent which undergoes an in situ metathesis reaction forming an insoluble IL. Thus, analytes are extracted and preconcentrated once the IL is insolubilized. There is no interface between the aqueous media and the extraction phase. Thus, mass transfer from aqueous media into IL has no significant effect on the performance of the extraction method. ISFME is a simple and efficient method for the separation and

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http://dx.doi.org/10.1016/j.molliq.2016.02.003
0167-7322/

preconcentration of metal ions from aqueous solutions with high ionic strength [29,30].

In this work, an ISFME methodology has been developed and optimized for the extraction and determination of iron. The method is based on chemical complexation of Fe (II) by 1, 10-phenanthroline and ion-association formation with hexafluorophosphate anion. ISFME technique was used to extract ion-association and the spectrophotometry was used to analyze the extracted product. Potential parameters affecting the ISFME and analytical performance are studied and optimized in detail.

2. Experimental

2.1. Instrumentation

Spectrophotometric measurements were made using a Perkin Elmer spectrophotometer (Lambda 35, USA) and using 1.00 cm quartz cells. A Hettich centrifuge (Universal 320R, Germany) was used for centrifugation. The pH values were measured with a Metrohm pH- meter (Model: 827, Switzerland) supplied with a glass-combination electrode.

2.2. Reagents and solutions

All reagents used were of analytical reagent grade. Deionized water was used throughout the experiments. Stock standard solutions of iron (II) and iron (III) at a concentration of 1000 mg L^{-1} were prepared by dissolving analytical grade $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ in 1.0 mol L^{-1} HCl (Merck, Darmstadt, Germany), respectively. Working solutions were prepared daily from the stock solutions by stepwise dilution. A 0.010 mol L^{-1} solution of 1, 10-phenanthroline (Merck, Darmstadt, Germany) was prepared in pure ethanol. Ascorbic acid (Merck, Darmstadt, Germany) 1.0% (*w*/*v*) stock solution was prepared by dissolving 1.0 g of ascorbic acid in 100 mL of distilled water. A fresh solution was prepared every day and kept in a cool and dark place to minimize oxidation. 1-Hexyl-3-methylimidazolium tetrafluoroborate ([Hmim][BF_4]), ethanol, and sodium chloride were purchased from Merck (Darmstadt, Germany). Sodium hexafluorophosphate ($NaPF_6$) was purchased from ACROS (Geel, Belgium).

All glass vessels used for trace analysis were stored in 10% nitric acid for at least 24 h and washed four times with doubly distilled water before use.

2.3. Preparation of the real samples

Spinach sample bought at the local market was washed with deionized water, cut, and oven-dried at 90 °C for 24 h. Next, it was ground in a household grinder. 1.00 g of the sample was placed in a 100 mL beaker, and 10 mL of concentrated HNO_3 (65% *w*/w) was added to it. The mixture was evaporated to near dryness on a hot plate at about 130 °C for 30 min. After cooling to room temperature, 5 mL of concentrated hydrogen peroxide (30%, *w*/w) was added. The mixture was again evaporated to near dryness. The resulting solution was diluted to 25 mL with deionized water. The result was filtered and the solution was diluted to 50 mL with deionized water.

All of the collected water samples (tap, mineral, river, and sea water) were filtered through a cellulose membrane filter (Millipore) of pore size 0.45 μm, and after acidification to 1% with concentrated HCl, were stored in polyethylene bottles in the dark at 4 °C.

2.4. In situ solvent formation microextraction procedure

Aliquot of 80 ml Fe (II) sample (or standard solution) was transferred to a 100 mL centrifuge tube; 0.5 mL of 1.0×10^{-2} mol L^{-1} 1, 10-phenanthroline solution, 2.0 mL acetate buffer solution (pH 6.0), and 150 μL of [Hmim][BF_4] were added into the sample solution were added into the sample solution and the tube was manually stirred to ensure complete homogenization of the IL in the aqueous sample. Then, 4.0 mL of $NaPF_6$ solution (1.0 mol L^{-1}) was quickly added, following which a turbid solution was formed. In order to accelerate phase separation, the cloudy solution was centrifuged for 5 min at 5000 rpm. As a result, the IL-phase settled at the bottom of the centrifuge tube. The aqueous phase was then separated completely by a syringe. In order to reduce the viscosity of the IL-phase, the extract in the tube was made up to 1.0 mL by adding ethanol. The absorbance was measured at the wavelength of maximum absorbance of the complex, 508 nm, for Fe (II)-phen complex against a reagent blank.

Total iron was determined after the reduction of Fe (III) to Fe (II) by using ascorbic acid as reducing reagent (1 mL of 1.0% ascorbic acid solution). Then, the concentration of Fe (III) was calculated by subtracting the concentration of Fe (II) from the total iron concentration.

3. Results and discussion

To obtain high sensitivity, it is necessary to investigate the effects of all parameters that could influence the chemical reactions and the performance of ISFME.

3.1. Selection of ionic liquid

Selecting IL with appropriate water miscibility is essential for establishing the ISFME procedure. It is preferable for the IL to have specific properties such as, low solubility in water, good extraction ability, and higher density than water [29]. In this study, according to the above considerations, 1-Hexyl-3-methylimidazolium tetrafluoroborate [Hmim][BF_4] and sodium hexafluorophosphate ($NaPF_6$) were selected as the hydrophilic IL and ion-pairing agent, respectively.

3.2. Effect of pH

Separation of metal ions by ISFME involves prior complex formation with sufficient hydrophobicity to be extracted into the small volume of the IL-phase. The pH of the sample solution is one of the important factors affecting the formation of complexes and the subsequent extraction. The effect of pH on the ISFME efficiency of Fe (II) was studied in the pH range of 2.0–10.0 and the results are shown in Fig. 1. As can be seen, maximum absorbance was obtained in the pH range of 5.0–7.0 (the optimum range for Fe (II)-phen complex formation). The raising of pH above this optimum range caused a gradual decrease in absorbance intensity probably due to the hydrolysis of Fe (II). Competition between protons and Fe (II) ions could explain the weak extraction in acid medium. Thus, pH 6.0 was used for the extraction of Fe (II) in the following work. In order to control the pH during the analytical procedure, it was adjusted to 6.0 with sodium acetate/acetic acid buffer solution.

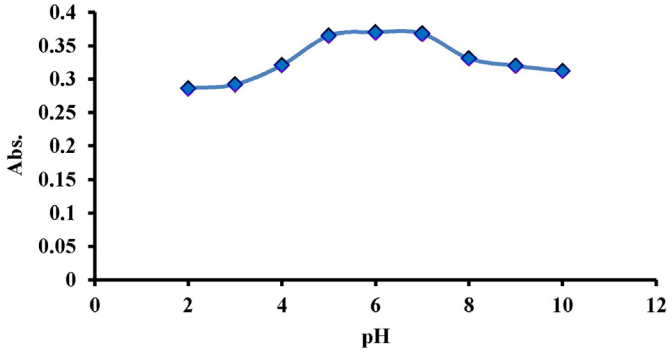

Fig. 1. Effect of pH on the analytical signals. Conditions: Sample volume 80 mL, Fe (II) concentration: 20.0 μg L^{-1}, 1, 10-phenanthroline concentration 1.0×10^{-4} mol L^{-1}, [Hmim][BF_4] volume: 150 μL, $NaPF_6$ concentration: 0.05 mol L^{-1}, centrifugation: 4000 rpm, 4 min.