Analytical Methods

Magnetic stirrer induced dispersive ionic-liquid microextraction for the determination of vanadium in water and food samples prior to graphite furnace atomic absorption spectrometry

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ABSTRACT

A new dispersive liquid–liquid microextraction, magnetic stirrer induced dispersive ionic-liquid microextraction (MS-IL-DLLME) was developed to quantify the trace level of vanadium in real water and food samples by graphite furnace atomic absorption spectrometry (GFAAS). In this extraction method magnetic stirrer was applied to obtained a dispersive medium of 1-butyl-3-methylimidazolium hexafluorophosphate [C4MIM][PF6] in aqueous solution of (real water samples and digested food samples) to increase phase transfer ratio, which significantly enhance the recovery of vanadium – 4-(2-pyridylazo) resorcinol (PAR) chelate. Variables having vital role on desired microextraction methods were optimised to obtain the maximum recovery of study analyte. Under the optimised experimental variables, enhancement factor (EF) and limit of detection (LOD) were achieved to be 125 and 18 ng L^{-1}, respectively. Validity and accuracy of the desired method was checked by analysis of certified reference materials (SLRS-4 Riverine water and NIST SRM 1515 Apple leaves). The relative standard deviation (RSD) for 10 replicate determinations at 0.5 µg L^{-1} of vanadium level was found to be <5.0%. This method was successfully applied to real water and acid digested food samples.

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1. Introduction

The exposure of trace elements to the environment has triggered the science community to develop new analytical techniques and instrumentation, capable of measuring concentrations at trace level (Arain et al., 2008). The compounds of V are released in atmosphere by burning of fossil fuels and from various industrial processes, which creates environmental exposure to life (Steenland & Boffetfa, 2000). Concentrations of vanadium in drinking water may range from about 0.2 to >100 µg L^{-1}, while permissible level of vanadium in natural water is 50 µg L^{-1}, according to the Environmental Protection Agency (EPA) (da Silva, Campos, & Miekeley, 1998). Various instrumental techniques have been used for the determination of vanadium (Al-Swaidan, 1993; Amorim et al., 2007; Pyrzynska, 2005). The concentration of vanadium in water samples is lower than detection limit of atomic absorption spectrometry. Prior to assess the trace level of vanadium in complex matrixes, separation and preconcentration techniques are necessary to eliminate or minimise matrix effects and to achieve high extraction efficiencies and

preconcentration factors. A number of preconcentration techniques have been developed for the separation of different metal ions but most of them are tedious and created environmental contamination due to used of organic solvents (Fan, Hu, & Jiang, 2005; Ghaedi, Mokhtari, Montazerozohori, Asghari, & Soylak, 2014; Ghaedi et al., 2013; Pekiner, Naeemullah, & Tuzen, 2014; Paleologos, Koupparis, Karayannis, & Veltsistas, 2001). Liquid–liquid microextraction is one of the most reliable and convenient separation tools, which can effectively decrease the detection limit and eliminating the matrix interferences (Cantwell & Losier, 2002; Ma & Cantwell, 1999). Recently new microextraction technique based on dispersive liquid–liquid microextraction (DLLME) has been introduced, but it still has some drawbacks, including the difficulty to automate and required a third component (dispersing solvent) that usually decreases the partition coefficient of the analytes into the extracting solvent. Furthermore, the extractant and dispersive solvent used in DLLME are often volatile organic compounds (Farahani, Norouzi, Dinarvand, & Ganjah, 2007; Farajzadeh, Bahram, & Jonsson, 2007; Garcia-Lopez, Rodriguez, & Cela, 2007; Nagaraju & Huang, 2007; Rezaee et al., 2006; Zhao, Zhao, Han, Jiang, & Zhou, 2007).

Recently room temperature ionic liquids (RTILs) have attracted considerable attention due to their unique chemical and thermal

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properties (Aguilera-Herrador, Lucena, Cárdenas, & Valcárcel, 2010; Ghaedi, Elhamifar, Roosta, & Moshkelgosha, 2014). RTILs are highly viscous and water immiscible than common organic solvent and are considered as a potential alternatives of conventional organic solvents (Ghaedi, Elhamifar, Negintaji, & Banakar, 2013; Shah, Yilmaz, Kazi, Afridi, & Soylak, 2012). Since one of the most remarkable properties of RTILs is reduced or non-detected volatility, these solvents have been proposed as alternatives to classical organic solvents, therefore diminishing environmental and safety concerns related with high solvent consumption during classical LLE (Bai, Zhou, Xie, & Xiao, 2010; Li, Cai, Hu, Chen, & Liu, 2009; Naeemullah et al., 2013).

In this work, we used magnetic stirrer induced ionic liquid dispersive microextraction (MS-IL-DLLME) method coupled to graphite furnace atomic absorption spectrometry (GFAAS). It was first time applied for preconcentration and determination of trace levels of vanadium. Vanadium preconcentration was mediated by chelation with the 4-(2-pyridylazo) resorcinol reagent (Fernández-de Córdova, Molina-Díaz, Pascual-Reguera, & Capitán-Vallvey, 1995; Vachirapatama, Dicinoski, Townsend, & Haddad, 2002), followed by extraction with the 1-butyl-3-methylimidazolium hexafluorophosphate [C4MIM][PF6]. The aim of this work is to introduce a novel and simple microextraction approach for the trace determination of vanadium in various food and water samples.

2. Experimental

2.1. Chemicals and reagents

The chemicals were analytical grade and prepared in ultrapure water. A stock solution ($1000\ \mu g\ mL^{-1}$) of vanadium(V) was prepared by dissolving desired amount of NH_4VO_3 Merck (E. Merck, Darmstadt, Germany). The 4-(2-pyridylazo) resorcinol was obtained from Sigma (St. Louis, MO, USA) and prepared a solution of $5 \times 10^{-3}\ mol\ L^{-1}$ in ultrapure water. $1000\ mg\ L^{-1}$ of palladium nitrate solution was prepared by dissolving required amount of $Pd(NO_3)_2$ (Merck) in 0.1% (v/v) HNO_3. A $1.0\ mol\ L^{-1}$ solution of $Mg(NO_3)_2$ Merck (E. Merck, Darmstadt, Germany) was prepared by dissolving required amount of $Mg(NO_3)_2$ in 100 mL of deionized water. 1-Butyl-3-methylimidazolium hexafluorophosphate [C4MIM][PF6] was purchased from Sigma (St. Louis, MO, USA). The $0.1\ mol\ L^{-1}$ phosphate buffer for pH 2 and 3, $0.1\ mol\ L^{-1}$ acetate buffer for pH 4 and 6, $0.1\ mol\ L^{-1}$ borate buffer for pH 7 and $0.1\ mol\ L^{-1}$ of ammonia buffer for pH 8 were used.

2.2. Instrumentation

A Perkin Elmer Model 700 (Norwalk, CT, USA) atomic absorption spectrometer equipped with a deuterium background correction system and electrothermal atomizer, HGA-800 was used for vanadium determination. Operating conditions of instrument for vanadium are reported in previous work (Naeemullah et al., 2013; Wadhwa, Tuzen, Kazi, & Soylak, 2013). Nuve NF 800 (Turkey) model centrifuge was used for centrifugation. Milestone Ethos D (Sorisole-Bg Italy) model microwave digestion system (maximum pressure 1450 psi, maximum temperature 300 °C was used for acid digestion of solid samples.

2.3. Plan of (MS-IL-DLLME) for vanadium

We design the following procedure for (MS-IL-DLLME), 10 mL of each standard and real sample were taken into vials with PTFE septum and magnetic bar. Then $100\ \mu L$ of $0.1\ mol\ L^{-1}$ acetate/borate buffers were used to adjust a pH range of (2.0–8.0), then added $100\ \mu L$ of PAR in the concentration range

1.0×10^{-4}–5.0×10^{-4}) $mol\ L^{-1}$ and (20–80 μL) of IL as a extractive solvent were added. The vial was placed on a magnetic hot plate, stirrer with different stirring rate of (100–800 rpm). Separation of the phases was achieved by centrifugation for 5–12 min at 1000–4000 rpm. The contents of the tubers were cooled in an ice bath to increase the viscosity of the enriched phase and the bulk aqueous phase was decanted carefully by inverting the tube. The ionic liquid enrich phase was treated with 200 μL of $0.1\ mol\ L^{-1}$ HNO_3 in ethanol (1:1, v/v) in order to reduce its viscosity and facilitate sample handling. Blank solution was submitted to same procedure and measured in parallel to the standards and real samples.

3. Result and discussion

3.1. Effect of pH

pH has a key role in the metal complexes formation and extraction efficiency of the desired method. The PAR is very stable and selective hydrophobic complexing reagent which reacts with most of the cations at different pH. In present study the pH range of 2.0–8.0, was selected to investigate the effect of pH on extraction efficiency of analyte. The results illustrated that the recovery is nearly constant at pH range of 5.5–7.0 (Fig. 1). The progressive decrease in extraction of studied metal ions at lower pH is due to the competition of hydrogen ion with analyte for reaction with PAR. A quantitative recovery was observed ($\geqslant 95\%$) in the pH range of 5.5–7.0. So, pH 6 was selected as a working value for subsequent experimental work.

3.2. Effect of magnetic stirring

Dispersing of ionic liquid by magnetic stirrer in aqueous medium was used to achieve high extraction efficiency and reduces the time reaction mechanism. Previously a number of procedures have been applied to disperse ionic liquid to obtained high extraction efficiency (Li, Cai, Hu, Chen, & Liu, 2009; Shah et al., 2012; Naeemullah et al., 2013). The proposed method is very simple and easy, to obtain high analytical response of the desired methods. Experiment was carried out to investigate the effect of stirring rates in the range of 100–800 rpm. The results have shown that the integrated absorbance increases with increasing stirring at >500 rpm (Fig. 2). As we increased stirring rate, gradually increase in recovery was observed might be due more dispersion, could lead to more contact with aqueous medium. So, 600 rpm was selected as a desired stirring rate to maximum dispersion of ionic liquid and get reliable result.
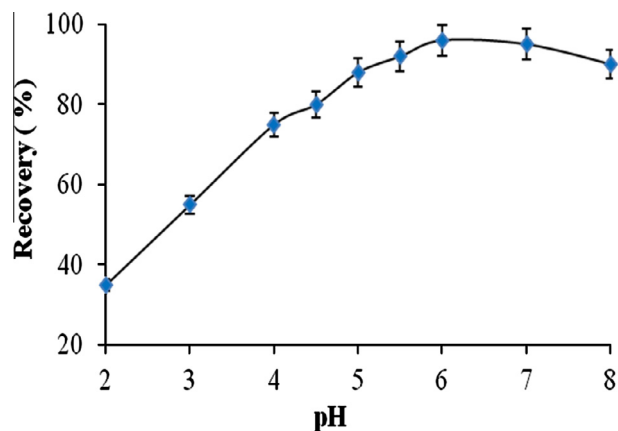

Fig. 1. Effect of pH on the recovery (%) of (MS-IL-DLLME): 0.5 $\mu g\ L^{-1}$ vanadium, PAR $2.5 \times 10^{-4}\ mol\ L^{-1}$, 55 μL IL, magnetic stirrer rate (600 rpm), centrifugation time and rate 10 min (3000 rpm).