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On-line micro-volume introduction system developed for lower density than water extraction solvent and dispersive liquid–liquid microextraction coupled with flame atomic absorption spectrometry

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ABSTRACT

A simple and fast preconcentration/separation dispersive liquid–liquid micro extraction (DLLME) method for metal determination based on the use of extraction solvent with lower density than water has been developed. For this purpose a novel micro-volume introduction system was developed enabling the on-line injection of the organic solvent into flame atomic absorption spectrometry (FAAS). The effectiveness and efficiency of the proposed system were demonstrated for lead and copper preconcentration in environmental water samples using di-isobutyl ketone (DBIK) as extraction solvent. Under the optimum conditions the enhancement factor for lead and copper was 187 and 310 respectively. For a sample volume of 10 mL, the detection limit (3 s) and the relative standard deviation were 1.2 μg L^{-1} and 3.3% for lead and 0.12 μg L^{-1} and 2.9% for copper respectively. The developed method was evaluated by analyzing certified reference material and it was applied successfully to the analysis of environmental water samples.

1. Introduction

The drive toward greener extraction methods has led to remarkable reduction of the required organic solvent volume [1]. As a result various microextraction techniques have been developed, i.e., single-drop microextraction (SDME), hollow-fiber liquid phase microextraction (HF-LPME), dispersive liquid–liquid microextraction (DLLME) and solidified floating organic drop (SFO) microextraction with extreme reduction of extraction solvent volume [2,3].

DLLME was first introduced by Assadi and his co-workers [4] in 2006 based on ternary component solvent systems. In fact, DLLME is a modified solvent extraction method in which acceptor-to-donor phase ratio is greatly reduced compared with other preconcentration methods [5]. The strengths of this method include high performance such as high extraction efficiency, rapidity, low cost, and low consumption of organic reagents. DLLME has been applied for preconcentration and determination of organic compounds as well as for metals [6–17] mainly with electrothermal atomic absorption spectrometry (ETAAS) [9–11] and flame atomic absorption spectrometry (FAAS) [12–17]. The choice of a proper extractant is an important one. It should have high immiscibility with aqueous phase, high extraction efficiency, selectivity and hydrophobicity [18]. In order to facilitate the separation of the two phases (organic and aqueous) via centrifugation, the extraction solvent should have higher density than water such as chloroform [12], chlorobenzene [13] and carbon tetrachloride [15].

Compared to traditional solvent-based extraction protocols, the most important drawback of DLLME is that the selection of proper extraction solvents is usually limited to those that have higher density than water in terms of simpler handling and collection [18,19]. Such solvents are rather few and are generally toxic (e.g. halogenated hydrocarbons). On the other hand, despite some obvious advantages such as low toxicity and higher availability, low-density solvents have rather limited applicability on the basis of difficulties in practical handling e.g. withdrawal and introduction to the analytical technique in use after separation [20–22]. Some recently reported attempts to facilitate the use of low-density organic solvents were reviewed recently [19]. For example, Saleh et al. proposed a home-designed centrifuge glass vial that – according to the authors – enables the convenient collection of the floating organic solvent on the aqueous sample [20]. The common feature of all these attempts is that the collection and transfer of the organic phase involve manual handling.

The on-line transfer of the extractant to the analytical instrument offers obvious advantages in terms of rapidity, simplicity and precision. Recently, Naseri et al. reported a microsample introduction system that enabled the introduction of as little as 20 μL of

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extractant to FAAS [15]. As already mentioned in the previous paragraph, the drawback of the proposed setup was that the organic phase should still be collected and transferred manually. Additionally, there was no demonstration using low-density solvents.

In the present work an organic solvent like DIBK with lower density than water was used for the first time as the extractant in the conventional DLLME method combined with atomic spectrometry broadening the range of effective extraction solvents. Manual collection and transfer were eliminated by a novel introduction system that enables on-line injection of the micro-volume organic solvent into FAAS. The effectiveness and efficiency of the proposed system have been demonstrated by the determination of lead and copper in environmental water samples and certified reference material.

2. Experimental

2.1. Instrumentation

A Perkin-Elmer, Norwalk, CT, USA (http://las.perkinelmer.com) model 5100 PC flame atomic absorption spectrometer was utilized as the detection system. Lead electrodeless discharge lamp (EDL) and copper hollow cathode lamp (HCL) were used as the light source operated at 10 mA and 15 mA respectively. The monochromator spectral bandpass (slit) was set at 0.7 nm, while the wavelength was set at 283.3 nm and 324.7 nm resonance line for lead and copper respectively. A time-constant of 0.2 s was used for peak height evaluation. The air and acetylene flow rate were 10.0 L min^{-1} and 2.0 L min^{-1} respectively. The nebulizer's free uptake flow rate was 5.0 mL min^{-1}.

A Gilson Minipuls3® peristaltic pump (http://www.gilson.com/en/) was used as the propulsion system equipped with Tygon type tubes. The connecting tubing between the introduction system and the FAAS nebulizer was made of PTFE (15 cm/0.5 mm i.d.). In order to balance the nebulizer's free uptake flow rate (5.0 mL min^{-1}) and the flow rate of the injected extraction solvent (3.0 mL min^{-1}), a flow compensation (FC) unit was used between the FAAS nebulizer and the on-line introduction system (Fig. 1) [23]. The FC unit was a VICI® (Valco Instruments Co. Inc. and VICI AG, http://www.vici.com/cfit/c_tees.php) three-section "Tee" type confluence connector made of PEEK with 0.5 mm i.d. bore size.

2.2. Reagents and samples

All chemicals were of analytical reagent grade and were provided by Merck (Darmstadt, Germany, http://www.merck.de). Ultra-pure quality water (resistivity > 18 Ω cm) was used throughout which was produced by a Milli-Q system (Millipore, Bedford, USA, http://www.millipore.com). All standard solutions were prepared immediately before use, by stepwise dilution with water of Pb(II) and Cu(II) stock standard solutions (1000 mg L^{-1} in 0.5 mol L^{-1} HNO_3, Merck Titrisol) to the required sub μg L^{-1} levels. The solution of the chelating agent, 0.3% (m/v) ammonium pyrrolidine dithiocarbamate (APDC) solution was prepared daily by dissolving the appropriate amount of APDC (Aldrich) in methanol (disperser solution) without any further purification. Di-isobutyl ketone (DIBK) was previously saturated with ultra-pure water. All environmental water samples were filtered through 0.45 μm membrane filters, acidified to 0.02 mol L^{-1} HNO_3 (pH ~ 2.0) and stored at 4 °C in acid-cleaned polyethylene bottles until analyzed (<48 h).

2.3. Dispersive liquid–liquid microextraction procedure

A volume of 10 mL of sample or standard solution was transferred to a 15 mL centrifuge screw-cap glass tube. 1500 μL of methanol solution (disperser solution) containing 0.3% m/v APDC and 75 μL of DBIK were injected rapidly into the sample solution (aqueous phase) by using a micropipette. As a result, a stable cloudy solution was produced consisted of fine droplets of DIBK dispersed into the entire aqueous phase. In this way, the analyte (lead or copper ions) reacts with APDC forming a chelating complex extractable into the fine droplets of DIBK. Subsequently, in order to separate the organic phase, the liquid mixture was centrifuged for 3 min at 5000 rpm. The DIBK droplets were joined together and settled at the upper level of the aqueous phase at the top of the glass tube. Finally, the extractant was injected into the flame atomizer of FAAS by using the proposed micro-volume introduction system. Five replicate measurements were made in all instances.

3. Results and discussion

3.1. On-line micro-volume introduction system

When using an extraction solvent with lower density than water the micro-volume of the organic phase is accumulated at the top of the aqueous phase. At this level the internal diameter of the centrifuge tube is quite large. For this reason the aspiration of a precise volume is a very difficult and risky task. In order to solve this, an on-line micro-volume introduction system was developed based on the idea of displacement bottle. This means that an organic solvent (immiscible with water) may be displaced and delivered from the glass tube by pumping water into the tube as shown schematically in Fig. 1. The proposed device consists of a centrifuge glass tube, sealed with a modified screw-cap and a restriction-cap made of hydrophobic and solvent resistant plastic such as polytetrafluoroethylene (PTFE) as it is shown in Fig. S1 (Supplementary material). The restriction-cap has engraved a conical cavity of ca. 30 μL and an inlet and an outlet through which PTFE tubes are fixed. After the phase separation (centrifugation) each glass tube is capped with the restriction-cap and water is pumped through the inlet by means of a peristaltic pump, while the inlet tube is extended to the bottom of the glass tube. As a result the extraction solvent can be delivered toward the analytical instrument through the outlet tube at flow rates equal with that of water pumped into the glass-tube. The micro-volume introduction system offers the possibility to collect/deliver precisely any volume of the extraction solvent into the analytical instrument by means of an on-line mode.

Typically, the uptake rate of a FAAS nebulizer ranged between 4.0 and 8.0 mL min^{-1} depending on the manufacturer guidelines. In the case of coupling a flow system with FAAS the nebulizer flow rate and the introduction flow rate should be taking into consideration. The effect of the flow rate of the extractant introduction into the FAAS by the proposed micro-volume introduction system was studied in the range of 2.0–5.0 mL min^{-1}, using 80 μL of DIBK containing a fixed amount of 100 μg L^{-1} Pb(II) and 10 μg L^{-1} Cu(II). The peak height absorbance was increased by increasing the flow rate up to 2.8 mL min^{-1} while for higher flow rates the signal was leveled off (Fig. S2, Supplementary material). In addition, the shape of the recorded signal was sharper by increasing the introduction flow rate. A feed flow rate of 3.0 mL min^{-1} was adopted for the subsequent studies.

3.2. Study of extraction variables

For high sensitivity, the effect of the main extraction parameters, like sample acidity, chelating agent concentration into disperser solvent, type and volume of extraction and disperser organic solvent, volume of sample, ionic strength and extraction time, were