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Ionic liquid-based dispersive liquid–liquid microextraction and enhanced spectrophotometric determination of molybdenum (VI) in water and plant leaves samples by FO-LADS

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ABSTRACT

A new simple and rapid ionic liquid-based dispersive liquid–liquid microextraction (IL-DLLME) has been applied to preconcentrate trace levels of molybdenum (VI) as a prior step to its enhanced determination by fiber optic-linear array detection spectrophotometry (FO-LADS). In this method, a small amount of [Hmim][Tf_2N] (1-hexyl-3-methylimmidazolium bis (trifluormethylsulfonyl) imid) as an extraction solvent was applied to extract molybdenum – pyrogallol red complex, which was formed in an aqueous solution in the presence of *N*-cetyl-*N*-*N*-*N*-trimethyl ammonium chloride as a sensitizing agent. Under optimum conditions, enhancement factor, detection limit and relative standard deviation ($n = 5$, for 30 μg L^{-1} of molybdenum (VI)) in 10 mL water sample were 72.6, 1.43 μg L^{-1} and 2.8%, respectively.

1. Introduction

Molybdenum does not naturally occur in the native state but is obtained from the ores molybdenite, wulfenite, ferrimolybdate and jordicite and is an essential element for humans and a vital factor in plant and animal nutrition for several metalloenzymes, including xanthine oxidase, aldehyde oxydase and sulphite oxydase to function correctly. In addition, it is widely used in a variety of industrial processes, being an important constituent of metal alloys, pigments, lubricants and chemical catalysis, among others. Relatively high concentrations are present in particulate matters emitted during fossil fuel combustion. Molybdenum can be released into the environment by weathering, use of molybdenum compounds in agriculture and industrial processes. Molybdenum occurs in soil, water, plants and animals to the extent of a few parts per million (Nordberg et al., 1986).

For the general population, the diet is the most important source of molybdenum, its concentration in water and air is usually negligible. Compared with some metals used in industry (antimony, arsenic, beryllium, cadmium, chromium, lead and mercury), molybdenum is of a low toxicity, however, if presented in higher concentrations, it can be toxic (Bagur et al., 1995; Reilly, 1980). Moreover, the assay of molybdenum in seawater is very important, since this metal is a part of biochemical phenomena in most marine flora and fauna (Filik et al., 2009).

There are many analytical techniques available for the determination of molybdenum, such as neutron activation analysis (NAA), inductively coupled plasma-mass spectrometry (ICP-MS) (Koplik et al., 2006; Simpkins et al., 2000), inductively coupled plasma-atomic emission spectrometry (ICP-AES), flame atomic absorption spectrometry (FAAS), etc. Giving the fact that most of these methods require rather sophisticated and relatively high cost instruments and being aware of the essentiality of molybdenum monitoring, its determination by extractive spectrophotometry as a simple and low cost method has been considered of importance.

However, due to the presence of molybdenum in environmental and biological samples at low levels, not only its separation from associated elements is necessary but also the use of a preconcentration method is usually inevitable.

A variety of procedures for preconcentration of metals, such as solid phase extraction (SPE) (Duran et al., 2007; Soylak et al., 2006; Tuzen and Soylak, 2009a), liquid–liquid extraction (LLE) (BermejoBarrera et al., 1996), coprecipitation (Divrikli et al., 2008; Tuzen et al., 2009; Tuzen and Soylak, 2009b) and cloud point extraction (CPE) (Baig et al., 2009; Citak and Tuzen, 2010) have been developed. Besides, the preconcentration and determination of molybdenum has been studied when using LLE, CPE, SPE and homogeneous liquid–liquid microextraction (HLLME).

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New LLE methods based on liquid membranes and hollow fiber contactors were used for extraction and preconcentration of Mo (Valdes et al., 2009). But this process presents some disadvantages like large volumes of solvents, which are expensive and toxic, high operation costs, possible formation of emulsions, large equipments and high residence time.

Besides, preconcentration of molybdenum in some CPE methods has been reported (Filik et al., 2009; Madrakian and Ghazizadeh, 2008). Despite many benefits when using CPE, in rather high content of salt, the 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 phase, separation does not occur and the extraction system is destroyed (Manzoori and Karim-Nezhad, 2003).

Several SPE preconcentration procedures for molybdenum have been reported using various sorbents (Escudero et al., 2008; Okutani et al., 1998; Tunceli and Turker, 2004). SPE is a solventless, simple and convenient method, which combines extraction, preconcentration and sample introduction in one step. Unfortunately, large amounts of eluents are used in these methods. Other shortcomings are usually long extraction time, poor repeatability and neediness of an enormous volume of sample.

Also molybdenum preconcentration by HLLME method has been reported (Ghiasvand et al., 2005). This method is simple and rapid, but the addition of one acid, base or salt for the conversion to biphasic system and preconcentration is inevitable. It is not a desirable subject because some analytes may be affected or decomposed by changing conditions.

Room-temperature ionic liquids (RTILs) have attracted increasing interest in analytical chemistry and are applied more and more as the extraction solvent, replacing the volatile solvent in the 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 neutral or charged complexes, as well as tunable viscosity and miscibility with water and organic solvents. Classical liquid–liquid extraction (LLE) based on ionic liquids (ILs) has been reported previously (Li et al., 2007; Papaiconomou et al., 2008). However, this method is monotonous and requires large amounts of IL, which is expensive. Subsequently, microextraction based on ILs was developed by Liu et al. (2003). Ionic liquids have been used in some novel microextraction techniques, such as liquid-phase microextraction (LPME), hollow fiber supported liquid-phase microextraction (HF-LPME), solid phase microextraction (SPME), single drop microextraction (SDME), ultrasound-assisted dispersive liquid-phase microextraction (USA-DLPME), cold-induced aggregation microextraction (CIAME) (Baghdadi and Shemirani, 2008; Gharehbaghi et al., 2009b) and in situ solvent formation microextraction based on ionic liquids (ISFME) (Baghdadi and Shemirani, 2009). Use of ILs in dispersive liquid–liquid microextraction (DLLME) has been suggested for the first time by our group in 2008 and it resulted into development of a new, simple and rapid method for preconcentration of trace levels of mercury as a prior step to its determination by spectrophotometric detection (Gharehbaghi et al., 2009a). Along with the other mentioned methods, advantages of ionic liquid-based dispersive liquid–liquid microextraction (IL-DLLME) are simplicity of operation, rapidity, high recovery, high enrichment factor and environmental benignity, with wide application prospects in trace analysis. Besides, it seems to be a more low-priced method.

The performance of IL-DLLME was investigated with an enhanced spectrophotometric determination of molybdenum in water and plant leaves samples using fiber optic-linear array detection spectrophotometry (FO-LADS). It is noticeable that at $\lambda_{max} = 612.0$ nm an improvement of the absorbance signal of molybdenum complex in the presence of an appropriate sensitizing agent *N*-cetyl-*N*-*N*-*N*-trimethyl ammonium chloride (CTAC) is accessible (about twice the value). Moreover, the absorbance of the extracted ternary complex is stable and time independent. This method is simple, rapid for the extraction and preconcentration of Mo(VI) from various samples and is superior against a rather high content of salt (up to 20%) and water-miscible organic solvents, such as acetone, compared with CPE. Further, in comparison with organic solvent extraction, it is much safer since only small amounts of IL are used, which is considered to be a 'green solvent' for various separation processes. Another important capability of this method is that it can be operated in a continuous mode, which our group is presently investigating.

2. Materials and methods

2.1. Apparatus

A UV–Vis light source, optical fiber and spectrograph model 2048 were purchased from Avantes (Eerbeek, Netherlands) for FO-LADS. 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) was obtained from Hettich (Kirchlengern, Germany).

2.2. Reagents

All used reagents were of analytical reagent grade. Triply distilled water was used throughout the experiment. Pyrogallol red (PR), acetone, ethanol, ascorbic acid, acetic acid, hydrochloric acid, [Hmim][Tf_2N] (1-hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl)imide) and all used salts were obtained from Merck (Darmstadt, Germany).

A stock solution of Mo(VI) (1000 mg L^{-1}) was prepared by dissolving the appropriate amount of ammonium molybdate tetrahydrate. Working standard solutions were prepared freshly by proper dilutions of the standard stock solution. A 4.8×10^{-3} mol L^{-1} solution of PR was prepared by dissolving the required amount in 25 mL of ethanol and then diluting it to 250 mL with triply distilled water and a 1% (w/v) solution of *N*-cetyl-*N*-*N*-*N*-trimethyl ammonium chloride (CTAC) obtained from Sigma (St. Louis, MO, USA) were prepared by dissolving the appropriate amounts in triply distilled water. Buffer solution (pH 4.0, 4 mol L^{-1}) was prepared by mixing 82.0 mL of acetic acid (4 mol L^{-1}) and 18.0 mL of sodium acetate (4 mol L^{-1}).

2.3. Instrumentation setup

The spectrograph accepts light beam transmitted through the single-stand optical fiber (200 μm diameter) by SMA (Sub Miniature version A) connection and disperses it via a fixed grating across the 2048 element CCD-linear array detector, that responses in the range of 200–1100 nm. The output data from CCD-linear array detector are transferred to PC by USB connection to obtain spectra.

2.4. IL-DLLME general procedure

A total of 200 μL of buffer (pH 4.0, 4 mol L^{-1}), 200 μL of $NaNO_3$ 10% (w/v) and 600 μL of CTAC 1% (w/v) were added into a 15 mL conical-bottom glass centrifuge tube containing molybdenum in the range of 5–100 ng mL^{-1}. Then 1.25 mL of pyrogallol red (PR) (4.8×10^{-3} mol L^{-1}) was added to the solution and the final volume was adjusted to 10.00 mL with triply distilled water. The violet-bluish ternary complex of Mo–PR–*N*-cetyl-*N*-*N*-*N*-trimethyl ammonium ions (CTA) was formed. Afterwards, 500 μL of the binary solution containing 60 mg of [Hmim][Tf_2N] (extraction solvent) and acetone (disperser solvent) was rapidly injected into the sample solution using a syringe. Thus, a stable cloudy solution was obtained and the ternary complex of Mo was extracted into the fine droplets of IL. The mixture was then centrifuged for 4 min at 4000 rpm. Consequently, the fine droplets of IL settled at the bottom of the centrifuge tube. After removing the whole aqueous solution, the extraction phase was diluted with 125 μL of pure ethanol, transferred to a 50 μL quartz cylindrical micro-cell and the absorbance was measured at 612.0 nm against a blank as a reference.

2.5. Sampling

The leaves of plants (mint, pepper black and fenugreek) were collected from growing lands in a vicinity of city of Tehran, Iran. The samples were placed in plastic bags. In the laboratory, the leaves of plants were washed thoroughly using tap water to remove soil or debris and then washed with distilled water. The samples were dried at room temperature on a sheet of paper to eliminate the excess