



Ionic liquid-based zinc oxide nanofluid for vortex assisted liquid liquid microextraction of inorganic mercury in environmental waters prior to cold vapor atomic fluorescence spectroscopic detection

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ABSTRACT

Zinc oxide nanofluid (ZnO-NF) based vortex assisted liquid liquid microextraction (ZnO-NF VA-LLME) was developed and employed in extraction of inorganic mercury (Hg^{2+}) in environmental water samples, followed by cold vapor atomic fluorescence spectrometry (CV-AFS). Unlike other dispersive liquid liquid microextraction techniques, ZnO-NF VA-LLME is free of volatile organic solvents and dispersive solvent consumption. Analytical signals were obtained without back-extraction from the ZnO-NF phase prior to CV-AFS determination. Some essential parameters of the ZnO-NF VA-LLME and cold vapor generation such as composition and volume of the nanofluid, vortexing time, pH of the sample solution, amount of the chelating agent, ionic strength and matrix interferences have been studied. Under optimal conditions, efficient extraction of 1 ng/mL of Hg^{2+} in 10 mL of sample solution was achieved using 50 μL of ZnO-NF. The enrichment factor before dilution, detection limits and limits of quantification of the method were about 190, 0.019 and 0.064 ng/mL, respectively. The intra and inter days relative standard deviations ($n=8$) were found to be 4.6% and 7.8%, respectively, at 1 ng/mL spiking level. The accuracy of the current method was also evaluated by the analysis of certified reference materials, and the measured Hg^{2+} concentration of GBW08603 (9.6 ng/mL) and GBW(E)080392 (8.9 ng/mL) agreed well with their certified value (10 ng/mL). The method was applied to the analysis of Hg^{2+} in effluent, influent, lake and river water samples, with recoveries in the range of 79.8–92.8% and 83.6–106.1% at 1 ng/mL and 5 ng/mL spiking levels, respectively. Overall, ZnO-NF VA-LLME is fast, simple, cost-effective and environmentally friendly and it can be employed for efficient enrichment of the analyte from various water samples.

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1. Introduction

Sample preparation, one of the stages in analytical procedure which results in the isolation and enrichment of target analytes, plays a vital role in analytical methods. It is the most challenging process, and can affect the quality as well as the precision of analytical data [1]. The most widely employed strategies in the pool of literature for the extraction of analytes from liquid samples are liquid liquid extraction [2] and solid-phase extraction [3]. The field of microextraction has gained wide attention from green analytical chemistry (GAC) perspective due to limited consumption of the extraction solvent (< 100 μL) [2]. There are various microextraction approaches like dispersive liquid liquid microextraction (DLLME) [4–7], solid phase

(micro)extraction [8–12], single drop microextraction [13] and hollow fiber supported liquid phase microextraction [14] which have been investigated for the isolation and enrichment of trace analytes from the complex samples prior to detection.

DLLME is cheap, simple and fast microextraction technique which presents high enrichment factor [15], even though difficulty to automation and the use of environmentally unfriendly solvents have been narrated as its limitations. One of the disadvantages of this technique is the use of dispersive solvent, which may cause environmental problem and decrease the value of distribution ratio. Therefore, addition of such solvents should be avoided from the extraction procedures as much as possible. To avoid the use of dispersive solvent in DLLME, emulsification techniques like ultrasonication and vortexing have been investigated [16]. In addition to replacing the dispersive solvent, these techniques also improve the analyte extraction, eliminate the coalescence effect and stirring-induced heating effect, and also help for ease phase separation in centrifugation [17]. Vortexing, the physical agitation method for the

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complete mixing of sample and extraction solvent, is more cost effective than ultrasonication and form thermodynamically unstable dispersion that facilitates the phase separation [16].

The use of aforementioned microextraction techniques reduce environmental impact and the exposure of personnel to solvent vapors [16]. This can be stated as one step advancement in greening the sample preparation strategies. However, avoiding the consumption of toxic solvents, using relatively green reagents, further reducing solvent consumption, minimizing waste generation, extraction time and labor are still of interesting from GAC point of view. Very recently, we reported the use of ionic liquid-based zinc oxide nanofluid (IL-ZnO-NF) as alternative environmentally benign solvent for single drop microextraction of selected fungicides from environmental waters [18]. Nanofluids, obtained from suspension of nanoparticles (size, < 100 nm) in base fluids [19], have got great attention in the field of analytical chemistry because of their ability to enhance the mass transfer coefficient in extraction processes [20–22].

Mercury (Hg) is a chemical element which exists in several forms (organic and inorganic) in the environment. Due to the high toxicity of Hg and its ability to bio-accumulate in organisms on one side, and the main incorporation route to human body is *via* drinking water on the other side, its level in waters should be monitored [23]. The permitted (threshold) level of Hg in drinking water was set to be 1 ng/mL [24] or 2 ng/mL [25]. However, the concentration of Hg is commonly in the range of low ng/L in environmental waters [23] which indicate that sample pretreatment and sensitive detection techniques are essential for its quantitative analysis. Moreover, appropriate sampling and storage conditions are also necessary to avoid any external contamination or analyte inter conversions [26,27].

The aim of the present work was to combine the advantages of IL-ZnO-NF, vortex emulsification and LLME technique in order to develop zinc oxide nanofluid based vortex-assisted liquid liquid microextraction (ZnO-NF VA-LLME) for the extraction of Hg²⁺ in aqueous samples. In the method, ZnO-NF was used as a dispersive and extraction solvent. The extraction procedure was carried out using ammonium pyrrolidine dithiocarbamate (APDC) as a chelating agent and without any additional dispersive solvent. After vortex emulsification, centrifugation and diluting in ethanol, the Hg species was determined directly by cold vapor atomic fluorescence spectrometry (CV-AFS).

2. Experimental

2.1. Instrumentation

An AFS-8130 atomic fluorescence spectrometer (Titan Instruments Co., Ltd, Beijing, China) equipped with a flow injection system was used for the determination of Hg²⁺. The 3% (m/v) HNO₃ and 1% (m/v) KBH₄ in 0.5% (m/v) KOH were used as a carrier solution and reducing agent, respectively. Fully-automatic intermittent pump is adopted for delivering sample and KBH₄ solutions in hydride generation. The generated elemental mercury (Hg⁰) was carried to the detection cell by argon stream. Hg hollow cathode lamp was employed as radiation source. Concentration of Hg²⁺ in the samples was determined using calibration curve. AFS-830 software (AFS-8x) was used for data acquisition. The experiment conditions of CV-AFS are given in Table 1.

2.2. Chemicals and reagents

Compressed argon (purity, ≥ 99.99%) was purchased from Beijing Haikeyuanchang Practical Gas Co., Ltd. (Beijing, China). Stock standard solution of Hg²⁺ (1000 mg/L) was obtained from National

Table 1
CV-AFS conditions for Hg²⁺ determination.

Parameters	Optimized values
Lamp	Mercury HCL 253.7 nm
Lamp current	30 mA
PMT voltage	– 300 V
Argon flow rate	300 mL/min
Atomization temperature	Room temperature
KBH₄ concentration	1% (m/v) in 0.5% KOH (m/v)
HNO₃ concentration	3% (v/v) in water
Sampling time	5 s
Injection time	15 s
Signal collection time	5 s

Center of Analysis and Testing for Nonferrous Metals and Electronic Materials (Beijing, China). APDC (purity, 98%) was purchased from Alfa Aesar China (Tianjin) Co., Ltd. (Tianjin, China). NaCl and KOH (both GR Grade), and NaOH (purity, ≥ 96%) were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). KBH₄ (purity, ≥ 98.5%) was obtained from Tianjin Institute of Fine Chemicals (Tianjin, China). Mineral acid, 65% HNO₃ was purchased from Merck KGaA (Darmstadt, Germany). Ionic liquid, 1-hexyl-3-methylimidazolium hexafluorophosphate ([HMIM][PF₆]) was obtained from Aladdin Industrial Corporation (Shanghai, China). Ethanol (AR, 99.7%) was purchased from Beijing Chemical Works (Beijing, China). High-purity water (Millipore water) obtained by MilliQ water purification system (Millipore, Billerica, MA, USA) was used throughout the experiments. The interference study was performed using 1000 mg/L stock solutions of each metals.

2.3. Sample collection and preservation

Environmental water samples, effluent, influent, lake and river waters, were collected and employed to investigate the applicability of the current method. The effluent and influent water samples were collected from Qinghe wastewater treatment plant (Beijing, China), the lake water sample was collected from Weiming Lake located in Peking University (Beijing, China) and the river water was collected from Chaobai River (Beijing, China). The samples were filtered with 0.22 μm pore size filter membrane and stored at 4 °C until analysis time.

2.4. Preparation of ZnO-NF

The two-step method, preparation of the nanoparticles and then dispersion in base fluid, was used in preparation of the nanofluid [18]. In brief, known amount of ZnO NPs, prepared and characterized in our recent report [18] (data not shown here) was dispersed in [HMIM][PF₆], base fluid, and homogeneously distributed and then sonicated for about 90 min to break up any potential clusters of the NPs. Nanofluids with various ZnO NPs compositions were prepared and employed as extraction solvent.

2.5. ZnO-NF VA-LLME procedure

A 10 mL of sample solution (pH 4) spiked with 1 ng/mL Hg²⁺ were placed in 15 mL centrifuge tube with a conic bottom, and 100 μL of 0.3% (m/v) APDC was added as a chelating agent followed by addition of 50 μL of ZnO-NF as extraction solvent. Then, the sample mixture was continuously agitated (vortexing rate, 3000 rpm) for 2 min to allow efficient extraction of the chelated Hg to the ZnO-NF droplets. After that, the mixture was centrifuged for 10 min at 5000 rpm so that the dispersed ZnO-NF droplets were joined together and sedimented at the bottom of the centrifuge tube. After careful removal of the aqueous phase, the nanofluid phase was diluted to 2 mL with ethanol and then investigated by

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