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www.elsevier.com/locate/talanta

PII: S0039-9140(15)30528-2
DOI: http://dx.doi.org/10.1016/j.talanta.2015.12.004
Reference: TAL16173

To appear in: *Talanta*

Received date: 10 August 2015
Revised date: 24 November 2015
Accepted date: 1 December 2015

Cite this article as: Meseret Amde, Jing-Fu Liu, Zhi-Qiang Tan and Deribachew Bekana, Ionic liquid-based zinc oxide nanofluid for vortex assisted liquid liqui microextraction of inorganic mercury in environmental waters prior to cold vapo atomic fluorescence spectroscopic detection, *Talanta* http://dx.doi.org/10.1016/j.talanta.2015.12.004

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# 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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Key words: Nanofuid; LLME; Inorganic mercury; Environmental waters; CV-AFS

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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 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 complete

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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-

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assisted liquid liquid microextraction (ZnO-NF VA-LLME) for the extraction of $Hg^{2+}$ 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 $Hg^{2+}$. The 3% (m/v) $HNO_3$ and 1% (m/v) $KBH_4$ 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 $KBH_4$ solutions in hydride generation. The generated elemental mercury ($Hg^0$) was carried to the detection cell by argon stream. Hg hollow cathode lamp was employed as radiation source. Concentration of $Hg^{2+}$ 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.

Table 1 Suggested here

### 2.2. Chemicals and reagents

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Compressed argon (purity, ≥99.99%) was purchased from Beijing Haikeyuanchang Practical Gas Co., Ltd. (Beijing, China). Stock standard solution of $Hg^{2+}$ (1000 mg/L) was obtained from National 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). $KBH_4$ (purity, ≥98.5%) was obtained from Tianjin Institute of Fine Chemicals (Tianjin, China). Mineral acid, 65% $HNO_3$ was purchased from Merck KGaA (Darmstadt, Germany). Ionic liquid, 1-hexyl-3-methylimidazolium hexafluorophosphate ([HMIM][$PF_6$]) 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 $^{o}$C until analysis time.

2.4. Preparation of ZnO-NF

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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][$PF_6$], 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 $Hg^{2+}$ 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 CV-AFS. The schematic representation of ZnO-NF VA-LLME procedure is provided in Fig. 1.

Fig. 1 Suggested here

2.6. Quality control/quality assurance

The sample solution were pretreated with acid to avoid the possible contamination and loss of the target analytes. All the glassware employed in the current study were soaked in acid bath

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(10% $HNO_3$) for 24 hr., rinsed with Millipore water and dried before use. Blank samples were investigated passing through the whole extraction procedure in the same way to the sample solutions. The analyte were quantitatively determined using 10 calibration points. Linearity of the method was obtained by investigating water samples spiked with concentration range of the analyte from 0.1 to 10 ng/mL. The LOD and LOQ was calculated as 3*(s/m) and 10*(s/m), respectively (where s is the standard deviation of the y-intercepts and m is the slope of calibration curve after extraction, n=8) [28]. Intra-day and inter-day relative standard deviations (RSDs) at eight replicates (n=8) investigated with water samples containing 1 ng/mL of the analyte were used to evaluate the precision of the method. The robustness of the method in different waters was reflected by the recoveries determined for various water samples spiked at 1 and 5 ng/mL.

## 3. Results and Discussion

### 3.1. Study of the chemical vapor generation

Cold vapor generation of $Hg^0$ from the ZnO-NF in the dilution solvent was studied to figure out suitable vapor generation condition for the best analytical sensitivity. Since $KBH_4$ was employed as reductant, its appropriate concentration was optimized to avoid the side effects of the reaction in the closed CV system. The influence of $KBH_4$ and $HNO_3$ concentrations on CV-AFS analytical signals was studied in the range of 0.1 – 2% (m/v) (in 0.5% (m/v) KOH) and 0.5 – 5% (v/v), respectively. The analytical signal of $Hg^{2+}$ increased with increasing concentration of the $KBH_4$ and $HNO_3$ up to 1% (m/v) and 3% (v/v), respectively. It was verified that the best analytical signal was obtained at 1% (m/v) reductant concentration and 3% (v/v) $HNO_3$ and these concentrations were adopted as optimized compositions in the subsequent experiments.

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187 3.2. Optimization of the ZnO-NF VA-LLME

188 Various experimental parameters affecting the extraction capability of ZnO-NF VA-
189 LLME (Section 2.5) like composition of the NF, volume of the NF, vortexing time, amount of
190 the chelating agent, pH of the sample solution, and ionic strength were optimized based on $Hg^{2+}$
191 recovery (%) under different experimental conditions and all experiments were performed in
192 replicate (n=3).

193

194 3.2.1. Composition of the ZnO-NF

195 Pure [HMIM][$PF_6$] and four ZnO-NFs obtained by dispersing various amounts of ZnO
196 NPs, 0.005, 0.01, 0.05 and 0.1% (m/m), in [HMIM][$PF_6$] [18] were applied as extraction solvent,
197 to investigate the effect of ZnO NPs composition on the extraction method. As can be seen in
198 Fig. 2, the highest recovery (%) was obtained with 0.005% (m/m) ZnO-NFs. Dispersing the NPs
199 in the IL enhanced the extraction efficiency which is in line with our recent report [18] and this
200 might be attributed to the higher coefficient of mass transfer due to Brownian motion
201 [20,21,29,30]. The high extraction efficiency at lower ZnO NPs composition may be attributed to
202 saturation of the ILs at higher composition [18,31] which may prevents the extraction of the Hg-
203 APDC complex. Therefore, 0.005% (m/m) ZnO-NF was selected as a proper solvent in the
204 subsequent experiments.

205

206 Fig. 2 Suggested here

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208 3.2.2. Effect of the volume of ZnO-NF

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To examine effect of the extraction solvent volume, 10 – 120 µL of 0.005% ZnO-NF were subjected to the ZnO-NF VA-LLME procedure by 10 µL interval. As shown in Fig. 3, the recovery (%) continuously increases with volume of the ZnO-NF in the range of 10 – 50 µL, and then exhibited similar recovery (%) with further increase in the solvent volume. Therefore, 50 µL of the solvent was considered as optimal volume in further experiments.

Fig. 3 Suggested here

3.2.3. Effect of the vortexing time

The extraction time was optimized using 50 µL of 0.005% ZnO-NF by increasing the extraction time from 0 to 3 min at 0.5 intervals. Until equilibrium point, the extraction efficiency of liquid liquid microextraction increases with time, and further longer extraction time could decrease the extraction efficiency due to the possible dissolution of the ZnO-NF. The effect of extraction time on the extraction efficiency shown in Fig. 4 depicts that the highest recovery (%) was obtained in 2 min, and further vortexing does not have significant effect on the extraction process. Therefore, 2 min was taken as the optimized extraction time.

Fig.4 Suggested here

3.2.4. Effect of the amount of the chelating agent

The effect of amount of APDC on the recovery (%) of ZnO-NF VA-LLME was investigated and the results are presented in Fig. 5. The volume of 0.3% (m/v) APDC was investigated in the range of 0 – 150 µL, and the extraction recovery (%) increases with the

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amount of APDC and attained its maximum value at 100 µL. Therefore, 100 µL was selected as optimized amount of the chelating agent solution.

Fig. 5 Suggested here

3.2.5. Effect of pH of the sample solution

The extraction of $Hg^{2+}$ with ZnO-NF VA-LLME involves prior complexation of the analyte for efficient extraction [32,33] and the complex formation is dependent on the pH of the sample solution [4]. In this study, the possible pH effect on the complex formation and extraction of $Hg^{2+}$ was investigated in the pH range of 2–10. The result showed that the pH of sample solution demonstrated significant effect, raised significantly up to pH 4 and exhibited declining tendency beyond pH 4 (Fig. 6). Similar optimum pH value has been also reported for the enrichment of $Hg^{2+}$ from waters [4,32]. On the basis of these results, pH 4 was selected in the subsequent experiments.

Fig. 6 Suggested here

3.2.6. Effect of the ionic strength

The addition of salt increases the ionic strength of aqueous solution and decreases the solubility of the analyte in the sample solution which improve the extraction efficiency [34]. The influence of ionic strength on ZnO-NF VA-LLME performance was investigated by adding different amounts of NaCl (0–10%, w/v) to the sample solution. It was found that the salt concentration exhibited insignificant effect on the recovery (%) (Fig. 7). However, at higher

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concentration, there might be possible dissolution of the ZnO-NF due to high concentration of $Cl^-$ in the solution or displacement of the $PF_6^-$ of the IL could hence decrease the extraction efficiency, which was also observed in our previous work [18]. Therefore, no salt was added in the optimized experiments.

Fig. 7 Suggested here

3.3. Interference study

The effects of coexisting metal ions regularly found in water samples were studied by determining the analytical signals in the presence of constant $Hg^{2+}$ concentration and different amounts of the co-existing ions ([interference]/[$Hg^{2+}$] ratios of 100:1 and 1000:1, Table 2). The recoveries of $Hg^{2+}$ in the presence of foreign ions were in the range of 81.7 – 101.4% and 81.3 – 94.27% at 100 and 1000 [interference]/[$Hg^{2+}$] ratios, respectively, except for $Ni^{2+}$, $Cr^{3+}$ and $Al^{3+}$ which exhibited 56.2, 56.6 and 66.7% recovery values, respectively at 1000 [interference]/[$Hg^{2+}$] ratio. This investigation indicates that the effect of interferences from the foreign ions is not significant and can be ignored, suggesting the applicability of the proposed method for preconcentration and determination of the Hg species in environmental water samples with complex composition.

Table 2 Suggested here

3.3. Method Validation

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The analytical performance of the proposed method was evaluated based on the limits of detection (LOD) and quantification (LOQ), linear range, enrichment factor and precision. The LOD and LOQ were calculated to be 0.019 and 0.064 ng/mL, respectively. The calibration curve showed good linearity with a correlation coefficient ($R^2$) of 0.9951. High enrichment factor before dilution (190) was obtained as the ratio of the analyte concentration in the nanofluid before dilution to its concentration in the sample solution. The intra-day and inter-day relative standard deviations were obtained to be 4.6% and 7.8%, respectively, which showed good precision of the method.

Besides, the proposed method was validated by the analysis of two certified reference materials, GBW08603 and GBW(E)080392, with a certified value and the difference between the certified and obtained values was insignificant as confirmed using t-test (Table 3).

Table 3 Suggested here

3.4. Analysis of real samples

Applicability of the developed method was assessed using the ZnO-NF VA-LLME for the determination of $Hg^{2+}$ in four real water samples. Trace $Hg^{2+}$ in the samples were preconcentrated and determined using the procedure described in ZnO-NF VA-LLME. However, the analyte species was not detected according to the optimized procedure, indicating that its concentration was below the method LOD. In order to evaluate applicability of the proposed method, the water samples were spiked with 1 and 5 ng/mL of $Hg^{2+}$ and analyzed with the proposed technique. The obtained recovery values of the analyte in effluent, influent, lake and river water samples were in the ranges of 79.8 – 92.8% and 83.6 – 106.1% at 1 and 5 ng/mL

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spiking levels, respectively (Table 4). The recovery values were satisfactory, and it can be said that the matrix effect from the water samples on the ZnO-NF VA-LLME and CV-AFS for $Hg^{2+}$ determination was not significant.

Table 4 Suggested here

### 3.5. Comparison with other methods

Determination of $Hg^{2+}$ in different waters by ZnO-NF VA-LLME was compared with other DLLME methods and the results are presented in Table 5. As can be seen in the table, the ZnO-NF VA-LLME is simple and exhibited short extraction time, lower solvent and sample consumption and lower detection limits which are in line with the principles of GAC. Therefore, ZnO-NF VA-LLME can be used as a preconcentration technique in trace analysis of $Hg^{2+}$ in different aqueous solutions.

Table 5 Suggested here

## 4. Conclusions

In this study, we developed a simple, fast, cost-effective and reliable ZnO-NF VA-LLME technique for preconcentration of $Hg^{2+}$ in water samples for CV-AFS analysis. Ionic liquid based ZnO-NF is proposed as dispersive and extraction solvent in the microextraction approach. The proposed method exhibited efficient extraction of $Hg^{2+}$ in various real water samples with reasonable linearity, high precisions, and satisfactory relative recoveries. The merits of the current method include the use of ZnO-NF as extraction solvent instead of volatile organic

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solvents, which is relatively safe and environmentally compatible, low LOD, precise, and acceptable recovery values. In addition to these qualities, the short extraction time and the absence of additional dispersive solvent indicate its high potential. In conclusion, ZnO-NF based VA-LLME presents a simple, effective, fast and relatively environmentally benign technique with low sample consumption that can be used for the preconcentration of $Hg^{2+}$ in various water samples.

Acknowledgments

This work was supported by the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB14020101). Meseret Amde and Deribachew Bekana acknowledge the support of CAS-TWAS President's Fellowship for their PhD study.

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352 References


353 [1] S. Armenta, S. Garrigues, M. de la Guardia, Trends Anal. Chem., DOI: 10.1016/j.trac.2014.12.011
354 (2015).
355 [2] J.M. Kokosa, Trends Anal. Chem., 43 (2013) 2-13.
356 [3] A. Spietelun, L. Marcinkowski, M. de la Guardia, J. Namiesnik, J. Chromatogr. A, 1321 (2013) 1-13.
357 [4] E. Stanisz, J. Werner, H. Matusiewicz, Microchem. J., 110 (2013) 28-35.
358 [5] M. Hossien-poor-Zaryabi, M. Chamsaz, T. Heidari, M.H.A. Zavar, M. Behbahani, M. Salarian, Food
359 Anal. Method., 7 (2014) 352-359.
360 [6] F. Yang, J. Li, W. Lu, Y. Wen, X. Cai, J. You, J. Ma, Y. Ding, L. Chen, Electrophoresis, 35 (2014) 474-481.
361 [7] P. Liang, J. Yu, E. Yang, Y. Mo, Food Anal. Method., 8 (2015) 236-242.
362 [8] L.O. dos Santos, V.A. Lemos, Water Air Soil Pollut., 225 (2014) 2086-2087.
363 [9] L. Adlnasab, H. Ebrahimzadeh, A.A. Asgharinezhad, M.N. Aghdam, A. Dehghani, S. Esmaeilpour, Food
364 Anal. Method., 7 (2014) 616-628.
365 [10] B. Parodi, A. Londonio, G. Polla, M. Savio, P. Smichowski, J. Anal. At. Spectrom., 29 (2014) 880-885.
366 [11] N. Thakur, S.A. Kumar, A.K. Pandey, S.D. Kumar, A.V.R. Reddy, Anal. Methods, 6 (2014) 7823–7830.
367 [12] M. Ali Karimi, A. Hatefi-Mehrjardi, A.A. Kabir, Croat. Chem. Acta, 87 (2014) 129-136.
368 [13] C. Mitani, A. Kotzamanidou, A.N. Anthemidis, J. Anal. At. Spectrom., 29 (2014) 1491-1498.
369 [14] Z. Wang, Q. Xu, S. Li, L. Luan, J. Li, S. Zhang, H. Dong, Anal. Methods, 7 (2015) 1140-1146.
370 [15] M. Rezaee, Y. Assadi, M.R. Milani Hosseini, E. Aghaee, F. Ahmadi, S. Berijani, J. Chromatogr. A, 1116
371 (2006) 1-9.
372 [16] A. Spietelun, L. Marcinkowski, M. de la Guardia, J. Namiesnik, Talanta, 119 (2014) 34-45.
373 [17] V. Andruch, M. Burdel, L. Kocúrová, J. Šandrejová, I.S. Balogh, Trends Anal. Chem., 49 (2013) 1-19.
374 [18] M. Amde, Z.Q. Tan, R. Liu, J.F. Liu, J. Chromatogr. A, 1395 (2015) 7-15.
375 [19] S.U.S. Choi, in: ASME International Mechanical Engineering Congress & Exposition, San Francisco,
376 USA, 1995, pp. 99-105.
377 [20] J. Saien, H. Bamdadi, Ind. Eng. Chem. Res., 51 (2012) 5157-5166.
378 [21] A. Bahmanyar, N. Khoobi, M.R. Mozdianfard, H. Bahmanyar, Chem. Eng. Process., 50 (2011) 1198-
379 1206.
380 [22] A. Bahmanyar, N. Khoobi, M.M.A. Moharrer, H. Bahmanyar, Chem. Eng. Res. Des., 92 (2014) 2313-
381 2323.
382 [23] K. Leopold, M. Foulkes, P.J. Worsfold, Trends Anal. Chem., 28 (2009) 426-435.
383 [24] Guidelines for Drinking-water Quality 3 ed., World Health Organization, 2008.
384 [25] National Primary Drinking Water Regulations, 2009.
385 [26] K. Leopold, M. Foulkes, P. Worsfold, Anal. Chim. Acta, 663 (2010) 127-138.


Accepted manuscript

ACCEPTED MANUSCRIPT

[27] H.F.V. Braaten, H.A. de Wit, C. Harman, U. Hageström, T. Larssen, Int. J. Environ. Anal. Chem., 94 (2014) 381-384.
[28] A. Shrivastava, V. Gupta, Chron. Young Sci., 2 (2011) 21-25.
[29] S. Krishnamurthy, P. Bhattacharya, P.E. Phelan, Nano Lett., 6 (2006) 419-423.
[30] X. Fang, Y. Xuan, Q. Li, Appl. Phys. Lett., 95 (2009) 203108.
[31] C. Ruiz-Palomero, M.L. Soriano, M. Valcarcel, Talanta, 125 (2014) 72-77.
[32] Z. Gao, X. Ma, Anal. Chim. Acta, 702 (2011) 50-55.
[33] X. Jia, Y. Han, C. Wei, T. Duan, H. Chen, J. Anal. At. Spectrom., 26 (2011) 1380-1386.
[34] Y. Wen, J. Li, F. Yang, W. Zhang, W. Li, C. Liao, L. Chen, Talanta, 106 (2013) 119-126.
[35] G. Leng, H. Yin, S. Li, Y. Chen, D. Dan, Talanta, 99 (2012) 631-636.
[36] E. Fernandez, L. Vidal, D. Martin-Yerga, C. Blanco Mdel, A. Canals, A. Costa-Garcia, Talanta, 135 (2015) 34-40.

Figure Captions

Fig. 1. Schematic illustration of ZnO-NF VA-LLME procedure.

Fig. 2. Effect of ZnO NPs composition on the recovery (%) of ZnO-NF VA-LLME. Error bars, standard deviation (n = 3); Extraction conditions: vortexing time, 2 min; vortexing rate, 3000 rpm; pH, 4; chelating agent, 100 µL 0.3% (m/v) APDC; volume of the extraction solvents, 50 µL; salt addition, no salt addition.

Fig. 3. Effect of the volume of 0.005% (m/m) ZnO-NF on the recovery (%) of $Hg^{2+}$ in ZnO-NF VA-LLME. Error bars, standard deviation (n = 3); Extraction conditions: vortexing time, 2 min; vortexing rate, 3000 rpm; pH, 4; chelating agent, 100 µL 0.3% (m/v) APDC; salt addition, no salt addition.

Fig. 4. Effect of the vortexing time on the recovery (%) of $Hg^{2+}$ in ZnO-NF VA-LLME. Error bars, standard deviation (n = 3); Extraction conditions: vortexing rate, 3000 rpm; pH, 4; chelating agent, 100 µL 0.3% (m/v) APDC; volume of the 0.005% (m/v) ZnO-NF, 50 µL; salt addition, no salt addition.

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Fig. 5. Effect of the amount of APDC on the recovery (%) of $Hg^{2+}$ in ZnO-NF VA-LLME. Error bars, standard deviation (n = 3); Extraction conditions: vortexing time, 2 min; vortexing rate, 3000 rpm; pH, 4; volume of the 0.005% (m/v) ZnO-NF, 50 µL; salt addition, no salt addition.

Fig. 6. Effect of the pH of the sample solution on the recovery (%) of $Hg^{2+}$ in ZnO-NF VA-LLME. Error bars, standard deviation (n = 3); Extraction conditions: vortexing time, 2 min; vortexing rate, 3000 rpm; 100 µL 0.3% (m/v) APDC; volume of the 0.005% (m/v) ZnO-NF, 50 µL; salt addition, no salt addition.

Fig. 7. Effect of the ionic strength on the recovery (%) of $Hg^{2+}$ in ZnO-NF VA-LLME. Error bars, standard deviation (n = 3); Extraction conditions: vortexing time, 2 min; vortexing rate, 3000 rpm; pH, 4; chelating agent, 100 µL 0.3% (m/v) APDC; volume of the 0.005% (m/v) ZnO-NF, 50 µL.

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Table 1. CV-AFS conditions for $Hg^{2+}$ 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 |
| $KBH_4$ concentration | 1% (m/v) in 0.5% KOH (m/v) |
| $HNO_3$ concentration | 3% (v/v) in water |
| Sampling time | 5s |
| Injection time | 15s |
| Signal collection time | 5 s |

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Table 2. Effects of co-existing ions on the extraction efficiency of ZnO-NF VA-LLME (mean±SD, n=3).

| Metal | Recovery (%) | |
|---|---|---|
| | $[M]/[Hg^{2+}]$, 100 | $[M]/[Hg^{2+}]$, 1000 |
| $Ca^{2+}$ | 91.4±5.72 | 94.27±7.19 |
| $Fe^{3+}$ | 89.97±4.61 | 84.19±5.98 |
| $Cu^{2+}$ | 99.65±6.83 | 83.63±4.40 |
| $Mg^{2+}$ | 99.24±2.39 | 82.64±3.89 |
| $Zn^{2+}$ | 86.51±4.36 | 80.84±3.83 |
| $Ni^{2+}$ | 81.69±4.10 | 56.15±4.91 |
| $Al^{3+}$ | 101.43±9.32 | 66.69±3.76 |
| $Cr^{3+}$ | 89.41±3.07 | 56.38±6.09 |
| $Pb^{2+}$ | 81.71±6.52 | 81.27±3.73 |

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Table 3. Analytical results of the application of ZnO-NF VA-LLME on certified reference materials (mean±SD, n=4).

| Sample | $Hg^{2+}$ concentration (ng/mL) | | $t_{ex}$ | $t_{0.05,3}$ |
|---|---|---|---|---|
| | Certified | Determined | | |
| GBW08603 | 10 | 9.6±0.5 | 1.6 | 3.18 |
| GBW(E)080392 | 10 | 8.9±0.8 | 2.75 | 3.18 |

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Table 4. Analytical results of the application of ZnO-NF VA-LLME on the real samples (mean±SD, n=3).

| Sample | Recovery (%) | |
|---|---|---|
| | 1 ng/mL spiking level | 5 ng/mL spiking level |
| Effluent | 89.4±4.4 | 91.4±2.2 |
| Influent | 92.8±3.8 | 106.1±4.5 |
| Lake | 88.8±3.0 | 85.9±2.6 |
| River | 79.8±3.2 | 83.6±2.1 |

Table 5. Comparison of ZnO-NF VA-LLME with similar microextraction techniques for the preconcentration of $Hg^{2+}$ in environmental samples.

| Extraction technique | Detection method | Extraction solvent (ES), Dispersive solvent (DS) | LOD (ng/mL) | Extraction time (min) | Reference |
|---|---|---|---|---|---|

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| | | | | | |
|---|---|---|---|---|---|
| | | and volume (µL) | | | |
| VA-LLME | HPLC-CV-AFS | 1% (m/v) L-Cysteine (100 µL) | 0.029 | 3 | [35] |
| TSIL USA DLLME | CV-AAS | TSIL (30 µL) | 0.03 | 7 | [4] |
| DLLME | UV–vis | ES: Chloroform (70 µL)<br>DS: Ethanol (750 µL) | 0.15 | 1 | [5] |
| DLLME | CE-UV | ES: Benzyl bromide (50 µL)<br>DS: Ethanol (600 µL) | 1.5 | 1 | [6] |
| D-DLLME | GF-AAS | ES: Carbon tetrachloride (48 µL)<br>DS: Methanol (500 µL) | 0.019 | 2 | [7] |
| LIS-HS-SDME | ET-AAS | Dispersed $Pd^0$ (25 µL) | 0.48 | 5 | [13] |
| In-situ IL-DLLME | SPCnAuEs | [HMIM][$NTf_2$] 20 µL and 10 µL 4 M HCl aqueous solution | 0.2 | 14 | [36] |
| ZnO-NF VA-LLME | CV-AFS | IL-ZnO-NF (50 µL) | 0.019 | 2 | Current study |

Highlights

- ZnO nanofluid based vortex assisted liquid liquid microextraction was developed



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- $Hg^{2+}$ in waters was extracted prior to CV-AFS detection
- Free from dispersive solvent and no requirement of back extraction
- The method is simple, fast, inexpensive and environmental friendly

Fig. 1.

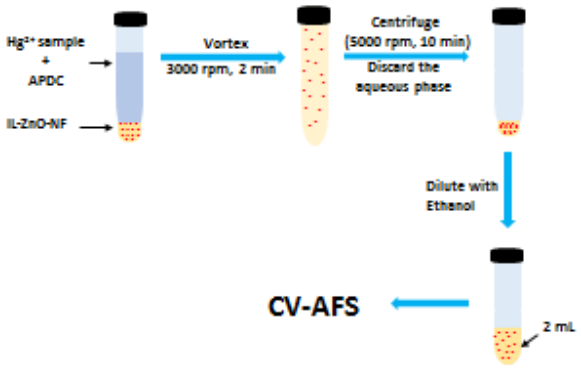



Fig. 2.

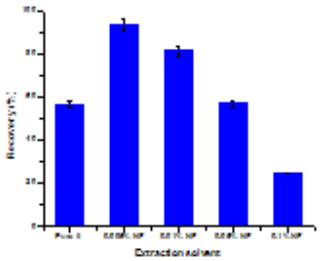
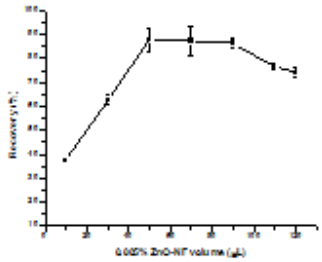
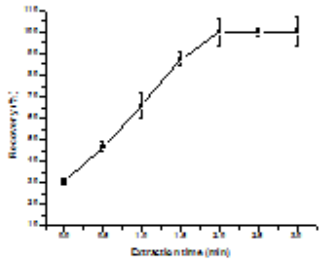


Fig. 3.



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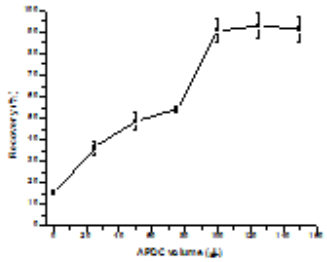
Fig. 4.



516

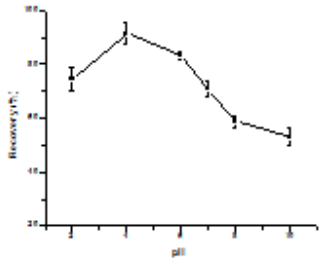
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Fig. 5.



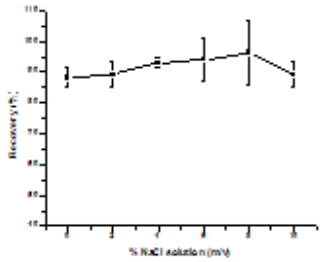
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Fig. 6.



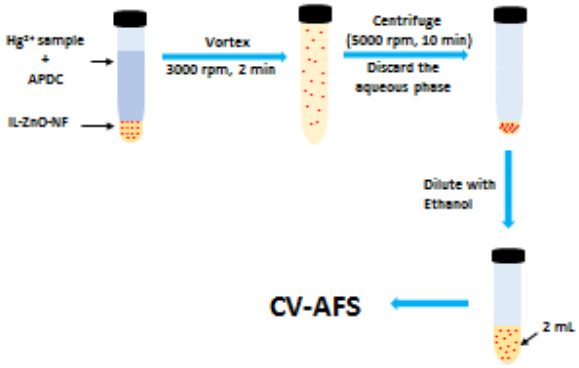
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Fig. 7.



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Graphical Abstract




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