



# Mercury species determination by task specific ionic liquid-based ultrasound-assisted dispersive liquid–liquid microextraction combined with cold vapour generation atomic absorption spectrometry

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## ABSTRACT

Task specific ionic liquid-based ultrasound-assisted dispersive liquid–liquid microextraction (TSIL USA DLLME) combined with cold vapour atomic absorption spectrometry (CV AAS) for determination of mercury species in water and biological samples was developed. The proposed procedure was free of volatile organic solvents, and there was no need to use any dispersive solvents and complexing agents, in contrast to standard DLLME. Analytical signals were obtained without the back-extraction of the mercury species from the TSIL phase into an aqueous phase prior to their determination by CV AAS. The reducing agent  $\text{Sn}^{2+}$  could reduce  $\text{Hg}^{2+}$  and  $\text{CH}_3\text{Hg}^+$  for determination of total mercury. Some essential parameters of the microextraction and cold vapour generation, such as the pH of sample solution, volume of the ionic liquid, ultrasonication time, cooling time, centrifugation time, matrix interferences and salt effect have been studied. Under optimal conditions, high extraction efficiency was achieved for the extraction of  $1.0 \text{ ng mL}^{-1}$  of  $\text{Hg}^{2+}$  and  $5 \text{ ng mL}^{-1}$   $\text{CH}_3\text{Hg}^+$  in  $10.0 \text{ mL}$  of water solution employing  $30 \mu\text{L}$  of methyltriethylammonium thiosalicylate as the extraction solvent. The enrichment factor for the method was 310 for  $\text{Hg}^{2+}$  and 200 for  $\text{CH}_3\text{Hg}^+$ . The detection limits were  $0.03 \text{ ng mL}^{-1}$  for  $\text{Hg}^{2+}$  and  $0.4 \text{ ng mL}^{-1}$  for  $\text{CH}_3\text{Hg}^+$  respectively. The accuracy of the proposed method was evaluated by analysis of the Certified Reference Materials (NRCC DOLT-2, NIST 1643e). The method was applied to analysis of the tap, river, lake and sea water samples. The recoveries for reference materials and spiked samples were in the range of 95–103%.

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## 1. Introduction

Mercury (Hg) is one of the most toxic trace elements and exists in the environment in several forms: mercuric ion ( $\text{Hg}^{2+}$ ), mercurous ion ( $\text{Hg}^+$ ), mercury sulfide ( $\text{HgS}$ ), methylmercury ( $\text{CH}_3\text{Hg}^+$ ), ethylmercury ( $\text{C}_2\text{H}_5\text{Hg}^+$ ), phenylmercury ( $\text{C}_6\text{H}_5\text{Hg}^+$ ) and dimethylmercury ( $(\text{CH}_3)_2\text{Hg}$ ). The study of methylmercury and dimethylmercury is particularly important due to their high toxicity and abundance among organomercury species in the environment. Organomercury forms are more toxic than inorganic, because of their high affinity to sulphanyl groups of biological molecules, lead to an accumulation in the human bodies causing carcinogenic effect. As a result, more sensitive, accurate and rapid analytical techniques are required to monitor mercury species in different environmental and biological samples [1–3]. For that reason the cold vapour atomic absorption spectrometry (CV AAS) has been used for the determination of mercury species in analytical samples. In order to improve the limits of detection, several different approaches including noble metal

amalgamation, solvent extraction and ion exchange have been proposed for the preconcentration of mercury species from the samples [4–6].

Modern trends in analytical chemistry tend to the miniaturization and simplification of a sample preparation step. The application of liquid-liquid extraction (LLE) technique has been limited by using toxic solvents, large volume of wastes and long-time procedures. The liquid-liquid microextraction (LLME) was developed to overcome these disadvantages. In the recent years a lot of new sample preparation techniques based on the microextraction have been proposed, such as single-drop microextraction (SDME) [7], cold-induced aggregation microextraction (CIAME) [8], hollow fiber-based liquid-phase microextraction (HF-LPME) [9] and dispersive liquid-liquid microextraction (DLLME) [10–13].

Recently dispersive liquid-liquid microextraction (DLLME) based on dispersion of droplets of the extraction solvent within the aqueous sample solution has become very popular. The technique is characterized by the simplicity, rapidity, low sample volume, high recovery and high enrichment factors. Although, the high consumption of disperser solvents in DLLME has led to decrease in partition coefficients of analytes into the extracting solvent and increase the cost of analysis. In addition, the dispersive and extraction solvents used in DLLME are often toxic, flammable and environment damaging [10–13].

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Some of the ionic liquids (ILs) have been recently considered as replacement for the traditional organic solvents for the extraction procedures in samples preparation. This is due to their physicochemical properties such as lower toxicity and volatility, good solubility in organic solvents, higher thermal stability compared to conventional solvents as well as good extractability for various organic compounds and metal ions [14–17]. The recent interest in ionic liquids is connected with the principles of Green Chemistry and new approaches involve steps to decrease or eliminate the waste and hazards from the analytical procedures.

DLLME based on ionic liquids has been widely used for the extraction of organic compounds such as polycyclic aromatic hydrocarbons (PAHs) [18], pesticides [19] and metal ions such as nickel [20], cobalt [21–23], cadmium [24–26], lead [27,28] and mercury [29,30].

Ionic liquids usually have hydrophobic character (specially ILs with hexafluorophosphate or bis[(trifluoromethyl)sulfonyl]imide anions) that enables them to extract hydrophobic compounds in biphasic separations. Metal ions tend to stay in the aqueous phase because they are hydrated. Therefore, in order to remove metal ions from the aqueous phase into hydrophobic ionic liquid, analytes are usually needed to form complexes thereby increasing the metal's hydrophobicity [14–17].

The hydrophobic ionic liquids such as 1-butyl-3-trimethylsilylimidazolium hexafluorophosphate [29], tetradecyl (trihexyl)phosphonium chloride (CYPHOS IL 101) [31], 1-butyl-3-methylimidazolium hexafluorophosphate ([C<sub>4</sub>MIM][PF<sub>6</sub>]) [32], 1-hexyl-3-methylimidazolium hexafluorophosphate ([C<sub>6</sub>MIM][PF<sub>6</sub>]) [7] and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [30] as well as so-called Task Specific Ionic Liquids (TSILs, ionic liquids modified with thiol or urea groups) [9,33–36] were generally used as the extraction solvents for the mercury determination. For this purpose the complexing agents, such as dithizone (DTZ) [37,38], 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) [32], carboxyphenyldiazoamino-p-azobenzene (CDAA) [29] and 4,4'-bis(dimethylamino)thiobenzophenone (TMK) [30] can be used in the IL DLLME procedures.

The aim of the presented work was to combine the advantages of ionic liquids, ultrasounds and DLLME technique in order to develop a task specific ionic liquid-based ultrasound-assisted dispersive liquid-liquid microextraction (TSIL USA DLLME) for the preconcentration mercury species from aqueous samples. Task specific ionic liquid, methyltriethylammonium thiosalicylate (TOMAS) [36] was used as a dispersive and extraction solvent. Procedure was carried out without any chelating agents. To our knowledge, preconcentration of mercury species with TSIL USA DLLME and their subsequent determination by CV AAS in organic phase without back-extraction has not been reported yet. After ultrasonication, cooling, salting and centrifugation, mercury species were determined directly by CV AAS in the sedimented organic phase. The effect of various experimental parameters on the extraction efficiency was investigated and the method was applied to mercury determination in the certified reference material DOLT-2, spiked reference material NIST 1643e and the real water samples.

## 2. Experimental

### 2.1. Instrumentation

The analyses were carried out with a mercury analyser (Model Aula-254, Mercury Instruments, GmbH, Karlsfeld, Germany). The instrumentation for CV AAS was detailed in previous work [39] and is therefore briefly summarized here. A mercury electrodeless low pressure discharge lamp was used as the radiation source. Peak absorbance of the transient signal was chosen for quantification. Instrumental parameters were set up as follows: lamp intensity, 4–20 mA; wavelength, 253.7 nm; spectral bandpass, 0.4 nm; quartz cell temperature, 50 °C; measurement mode, peak height. A thermoelectric

gas dehumidifier and heating of the optical cell eliminated the moisture and prevented interferences from water vapour.

A Sonopuls HD 70 ultrasonic homogenizer (70 W, 20 kHz, Bandelin, Germany) equipped with 2 mm and 3 mm titanium probes was used for the mercury microextraction processes and for sample solubilization in formic acid. Additionally, a centrifuge (Hettich EBA 20, Tuttlingen, Germany), generates a speed in the range from 500 to 6000 rpm, was employed for phase separation after extraction procedure.

A UniClever focused microwave sample preparation system (Plazmatronika, Wrocław, Poland) operating at 2450 MHz and 300 W maximum output was used for samples digestion. The computer-controlled system with continuous temperature, pressure and microwave power monitoring was equipped with high-pressure TFM-PTFE vessel and water cooling system. The vessel capacity was 110 mL and the maximum pressure and maximum temperature were 100 atm and 300 °C, respectively.

### 2.2. Reagents, solutions and gases

Compressed argon of UHP 5.5 purity obtained from Air Products (Warsaw, Poland) was employed as a carrier gas without further purification.

Standard solutions of inorganic mercury – Hg<sup>2+</sup> were prepared from 1000 mg L<sup>-1</sup> mercury standard solution traceable to SRM from NIST (Certipur, Merck) stabilizing with potassium dichromate (5% m/v, GR, Merck). Standard solutions of methylmercury – CH<sub>3</sub>Hg<sup>+</sup> were prepared from 1000 mg L<sup>-1</sup> methylmercury(II) chloride, AA standard solution in H<sub>2</sub>O (Alfa Aesar, Germany). The stock solutions were stored at 4 °C prior to use. All working standard solutions were prepared daily to prevent any possible species change, the appropriate stock solution were diluted with high-purity water.

Methyltriethylammonium thiosalicylate (TOMAS, C<sub>32</sub>H<sub>59</sub>NO<sub>2</sub>S, ≥95%) was purchased from Sigma-Aldrich. Ethanol (absolute, min. 99.5%) from J.T. Baker (The Netherlands) was used as solvent for ionic liquid phase contains mercury before CV AAS procedure. In order to establish the effect of ionic strength on the efficiency of TSIL USA DLLME NaCl (Suprapur, Merck Darmstadt, Germany) was used.

For cold vapour generation stannous chloride (10% m/v) (max. 0.000001% Hg, GR, Merck) was used as a reducing agent. It was prepared by dissolving the appropriate mass of tin(II) chloride dihydrate (max. 0.000001% Hg, Emsure, Merck) in 2 mol L<sup>-1</sup> hydrochloric acid (32% v/v extra pure, Merck) in high-purity water. Additionally, a rinsing solution NH<sub>4</sub>OCl (0.1% (m/v)) was used.

The pH of the sample solutions was adjusted with 65% HNO<sub>3</sub> and 30% NaOH (Suprapur, Merck Darmstadt, Germany). All mineral acids (65% HNO<sub>3</sub>, 32% HCl) and hydrogen peroxide 30% (v/v) of the highest quality (Suprapur, Merck) were used. High-purity water: deionized and doubly distilled water (quartz apparatus, Bi18, Heraeus, Germany) were used throughout the experiments.

The interference study was performed with AAS standard solutions of the appropriate metals (1000 mg L<sup>-1</sup>, Certipur, Merck) and humic acid from Sigma-Aldrich.

### 2.3. Certified reference materials and real samples

Accuracy of the analytical procedure described in this work was verified using certified reference materials: DOLT-2 (Dogfish Liver) supplied by the National Research Council of Canada (NRCC) and Standard Reference Material (SRM) 1643e (Trace elements in water) supplied by the National Institute of Standards and Technology (NIST). In DOLT-2 the certified reference values were available for mercury, inorganic mercury and methylmercury, NIST 1643e was spiked with inorganic mercury and methylmercury before analyses.

During real sample collection procedure all glass bottles were washed before using with a 5% (v/v) HNO<sub>3</sub> solution and then with high-purity water. Samples of tap water, lake water and sea water

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