



# Immersed single-drop microextraction–electrothermal vaporization atomic absorption spectroscopy for the trace determination of mercury in water samples

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## ARTICLE INFO

### Article history:

Received 7 May 2008

Received in revised form 27 August 2008

Accepted 30 September 2008

Available online 15 October 2008

### Keywords:

Single-drop microextraction  
Electrothermal vaporization atomic  
absorption spectroscopy  
Mercury  
Environmental analysis  
Water analysis

## ABSTRACT

A new method based on single-drop microextraction (SDME) combined with electrothermal vaporization atomic absorption spectroscopy (ETV-AAS) was developed for the trace determination of mercury in water samples. A microdrop of *m*-xylene was applied as the extraction solvent. After extraction, the microdrop was introduced, directly, into a graphite furnace of AAS. Some important extraction parameters such as type of solvent, volume of solvent, sample stirring, ionic strength, sample pH, chelating agent concentration, sample temperature, and extraction time were investigated and optimized. The highest possible microdrop volume of 10  $\mu\text{L}$ , a sampling temperature of 27  $^{\circ}\text{C}$ , and use of *m*-xylene containing dithizone, as complexing agent, are major parameters led to achieve a high enrichment factor of 970. Under the optimized conditions, the detection limit of the method was 0.01  $\mu\text{g L}^{-1}$  and the relative standard deviation was 6.1% ( $n = 7$ ). The proposed method has been successfully applied to the determination of Hg in two river water samples. The effects of interfering species such as Pt, Pd, Cu, Au, and Bi, having the tendency to form complexes with dithizone, at two concentration levels of 100 and 1000  $\mu\text{g L}^{-1}$  were also studied.

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## 1. Introduction

A solvent-miniaturized sample pretreatment procedure, known as single-drop microextraction (SDME), has gained lots of attentions in the last decade [1–5]. This method provides a suitable strategy towards preconcentration and matrix separation prior to detection. This micro-solvent approach is rather inexpensive and needs common laboratory equipments. It does not suffer from carry-over between extractions that may be experienced using solid phase extraction and solid phase microextraction. Although, this method was originally developed for isolation of organic species from aquatic media, its applicability for preconcentration of metals and metallic species has been demonstrated [6,7].

Two modes of headspace (HS) and direct sampling can be performed. The HS-SDME mode is applied to volatile or semivolatile analytes while the direct mode is applicable to less volatile compounds [8]. Between these two modes, HS-SDME is often preferred to avoid extraction of potentially interfering nonvolatile species. An important additional feature of SDME is the integration of extraction and injection in a microsyringe, making it possi-

ble to employ this miniaturized medium for extraction as well as an introduction device for the appropriate analytical device [9–11].

Mercury is an environmentally and toxicologically important element and its neurotoxicity has been reported to result in hearing loss, mental deterioration, speech difficulty, impaired vision, vestibular dysfunction and autism [12]. The World Health Organization (WHO) sets the allowed level in drinking water at 1  $\mu\text{g L}^{-1}$  [13]. It is considered by the Environmental Protection Agency (EPA) as a highly dangerous element because of its accumulative and persistent character in the environment and biota. The development of reliable methods for the determination of mercury in environmental and biological materials is therefore quite important. The routine methods for low-level determination of mercury include thermolysis coupled with atomic absorption spectrometry, cold vapor atomic fluorescence spectrometry, gas chromatography, neutron activation analysis and isotope mass spectrometry. However, all of them need long analysis time and considerable sample volumes.

Various techniques and methods for trace determination of mercury, including spectrometric, electrochemical, radiometric as well as other common and novel techniques have been reviewed, extensively [14]. Mercury contamination has been detected in real samples by microwave digested-CV-AAS successfully [15].

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**Table 1**  
Thermal program for determination of mercury by ETV-AAS following single-drop microextraction.

Stage	Temperature (°C)	Hold time (s)	Gas flow rate (L min <sup>-1</sup> )
Drying	85	5.0	3.0
Ashing	95	40.0	3.0
	120	10.0	3.0
Atomization	1800	0.8	0.0
	1800	2.0	0.0
Cleaning	2000	2.0	3.0

Recently, the principle of SDME in combination with various of spectroscopic methods has been applied for preconcentration of different elemental species [7,16–18]. The method is usually based on the formation of hydrides derivatives, headspace sampling and trapping onto a Pd(II)-containing aqueous drop. Trapping of the hydrides onto the drop does not rely on their partitioning among the gas phase and the solvent phase, as typically developed for organic compounds, but on their catalytic decomposition onto the Pd(0) formed in the drop as a result of the hydrogen evolved during the derivatisation reaction. A faster mass transfer was observed for the methyl mercury hydride from the headspace to the drop in comparison with SPME, which allowed equilibrium to be reached in a significantly shorter time [19].

Following our research activities on the trace determination of metallic species [20–22] in aquatic matrices and successful application of SDME using the direct [9,10] and headspace mode [11], a SDME-based technique for the trace determination of mercury in water samples was developed. An immersed microdrop of *m*-xylene solvent containing dithizone, as a complexing agent, was shown to be a suitable extraction medium, while the extraction temperature was kept at 27 °C. Influences of other important parameters on extraction and presence of possible interferences were also investigated.

## 2. Experimental

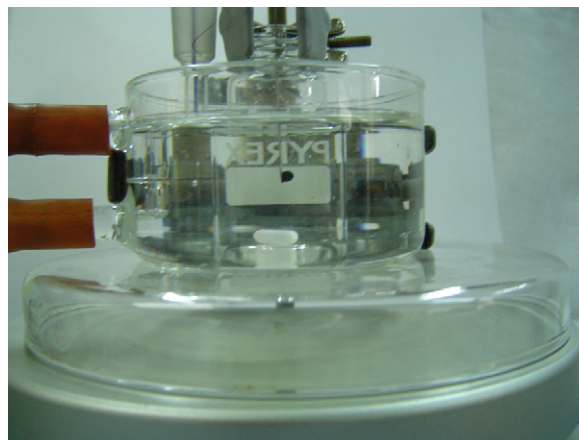
### 2.1. Instrumentation

A Varian (Australia) model AA-220 atomic absorption spectrometer equipped with a GTA-110 graphite furnace was used. A mercury hollow cathode lamp operated at 4.0 mA was employed as a radiation source. Atomic absorption measurements were carried out at 273.7 nm using a slit width of 0.5 nm. Pyrolytic graphite-coated graphite tubes and D<sub>2</sub>-background correction were employed throughout the analysis. The optimized thermal program for Hg is shown in Table 1.

UV digester (UV exposure time, 3 min), it is made as follows: a 400 W Hg vapor lamp (high pressure Hg, 220 V C, 50 Hz, OSRAM) that ignited with a suitable starter and chock, placed inside a quartz coil made of quality fused silica tubing approximately 100 cm long, 3 mm i.d., 0.6 mm wall thickness and a coil diameter of approximately 5 cm. (Note: a proper exhaust was used in conjunction with the UV digester to vent off the ozone produced during irradiation).

### 2.2. Reagents

High purity deionized water purified by a Milli-Q analytical reagent grade water purification system (Millipore, Milford, MA, USA). All water samples were filtrated through 0.45 μm cellulose Millipore filter and were used throughout this work.



**Fig. 1.** The set-up of SDME based on use of 10 μL of *m*-xylene.

All laboratory wares (glass and PTFE) thoroughly cleaned by soaking in nitric acid (1:1) for at least 24 h. All acid washed wares were rinsed with Milli-Q water and dried, immediately prior to use.

The stock solution of Hg (1000 mg L<sup>-1</sup>) was prepared from analytical reagent grade HgCl<sub>2</sub>·2H<sub>2</sub>O. To avoid adsorption effect of Hg on laboratory wares all solutions were stabilized with 1.0 M nitric acid and 0.01% w/v potassium dichromate [23]. Working standard solutions were prepared by appropriate dilution of the stock standard solution just before use. All reagents used were of analytical reagent grade (Merck, Darmstadt, Germany). Dithizone was purified according to the previous reports [24,25]. Stock solution of dithizone was prepared in a brown bottle containing 1 mL of 1 M H<sub>2</sub>SO<sub>4</sub> and stored at 4 °C. This stock solution was used to prepare the respective reagent solutions by dilution with *m*-xylene, immediately before being used.

### 2.3. Extraction apparatus and SDME procedure

The details of the developed device have been, already, explained in elsewhere [26–28]. After SDME of Hg in a certain time, the extract was finally introduced into the ETV-AAS system. The SDME set-up is shown in Fig. 1.

## 3. Results and discussion

Due to two different characteristics of mercury, volatility and biotransformation, this element has been considered as a unique environmental toxicant. According to EPA, mercury appears to bind to dissolved matter or fine particulates in aquatic systems, while the transport of mercury bound to dust particles in the atmosphere or bed sediment particles in rivers and lakes is generally less substantial. Due to the nature of SDME, which is based on the partition of analytes between two immiscible liquid phases, extracting such a pollutant are rather challenging as it mostly tend to remain in aqueous media. The feasibility of an immersed SDME method for extraction of mercury from aquatic media based on the use of a chelating agent was, therefore, considered.

### 3.1. Optimization

The performance and efficiency of SDME depends on many parameters including the type of solvent, microdrop size, stirring rate, sample pH, ionic strength of the sample solution, the concentration of chelating agent, temperature of sample solution and extraction time. A univariate approach was employed to optimize influential factors in this method.

**Table 2**  
Physical properties of different organic solvents used for extraction of Hg chelate.

Solvent	Physical properties			
	Density (g L <sup>-1</sup> )	Boiling point (°C)	Solubility in water	Drop stability
Octanol	0.826	195.0	Insoluble	Unstable
Chloroform	1.485	61.20	Slightly soluble	Unstable
Hexyl acetate	0.890	169.2	Insoluble	Unstable
<i>n</i> -Decane	0.723	174.0	Insoluble	Stable
Toluene	0.866	110.7	Insoluble	Stable
<i>m</i> -Xylene	0.878	138.8	Insoluble	Stable

Since SDME was originally developed for isolation of organic compounds based on the use of two immiscible phases, one possible way to transfer Hg from the aqueous phase to the organic phase is to convert mercury into an organometallic compound. To do so, a number of complexing agents had to be taken into consideration. Well-known reagents such as cupferron, *N*-benzoyl-*N*-phenylhydroxylamine (BPA), 1,5-diphenylcarbazon, 1,5-diphenylthiocarbazon (dithizone) which form highly-stable complexes with mercury were employed, although none of them are selective. Since the ratio of organic solvent volume to sample volume is rather low it is important to have a complexing agent with the least amount of solubility. Dithizone has a low solubility ( $5\text{--}7.2 \times 10^{-6}$  g/100 mL of H<sub>2</sub>O) and a high extraction constant ( $pK_{\text{ex}} = 26.85$  in CCl<sub>4</sub> at pH 1–1.5). Due to the high extraction capacity of dithizone and ability to work at low pH, it is possible to perform the extraction with some degree of selectivity if it prevents the possible co-extraction of most of other interfering species. The dispersion of dithizone in the aquatic media is expected to be quite limited during the extraction process, while working under the mild acidic condition imparts some degree of selectivity. Considering all these aspects, dithizone was found to be a remarkable solvent as the complexing agent.

Taking into account a well-known equation for enrichment factor,  $E_e$ :

$$E_e = \frac{1}{(V_{\text{org}}/V_{\text{aq}} + 1/K)} \quad (1)$$

high  $E_e$  can be achieved when  $V_{\text{org}}/V_{\text{aq}}$  ratio is low and distribution constant,  $K$ , is high. Considering our work, in which 10  $\mu\text{L}$  (optimized value) of organic solvent and 15 mL of sample are used (1:1500), high enrichment factors are expected to be obtained if  $K$  values are sufficiently high. This is especially true when the entrapment of Hg is achieved by the complexation with dithizone. In addition,  $K$  is another key player, which is highly dependent on the nature and type of organic solvent. Six water-immiscible solvents including octanol, chloroform, hexyl acetate, *n*-decane, toluene, and *m*-xylene were examined in order to find the most suitable solvent for SDME. Table 2 shows the physical properties of different organic solvents used for simultaneous extraction and complexation of Hg. Solvent selection was evaluated for the extraction of 15 mL of sample containing 10  $\mu\text{g L}^{-1}$  of mercury in deionized water. The stirred solution (300 rpm) was sampled at 27 °C for 15 min using 10  $\mu\text{L}$  of appropriate organic solvent containing dithizone.

Among these solvents octanol, chloroform and hexyl acetate were quite unstable and could be easily dislodged from the needle of syringe. Although *n*-decane was quite stable but the solubility of dithizone in this hydrocarbon is quite low. Both *m*-xylene and toluene were found to be quite applicable with high stability and sufficient solubility for dithizone. However, since toluene exhibited higher background in ETV-AAS measurements, *m*-xylene was selected as the extracting solvent. Other solvents were, therefore, excluded from further investigation.

The *m*-xylene dropsize was another important parameter, which was investigated. The speed of extraction is influenced by observed

rate constant ( $\text{s}^{-1}$ ) given by:

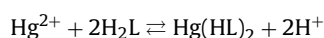
$$k = A_i \beta_{\text{org}} \left( \frac{K}{V_{\text{aq}}} + \frac{1}{V_{\text{org}}} \right) \quad (2)$$

where  $A_i$  is the interfacial area,  $\beta_{\text{org}}$  is the overall mass transfer coefficient with respect to the organic phase, and  $V_{\text{org}}$  and  $V_{\text{aq}}$  are the volume of organic solvent and aqueous sample, respectively [26–28]. By increasing the drop volume both  $A_i$ , and  $V_{\text{org}}$  are also enhanced. The influence of dropsize, therefore, originates from the integrated influence of two factors, justifying why the AAS response enhances with increasing dropsize up to 10  $\mu\text{L}$ . However, one has to note that having higher volume of organic solvent is rather critical in here. This is due to the fact that dithizone complexing agent should be included in the *m*-xylene microdrop. This has to be carried out in a way that saturation of microdrop is prevented.

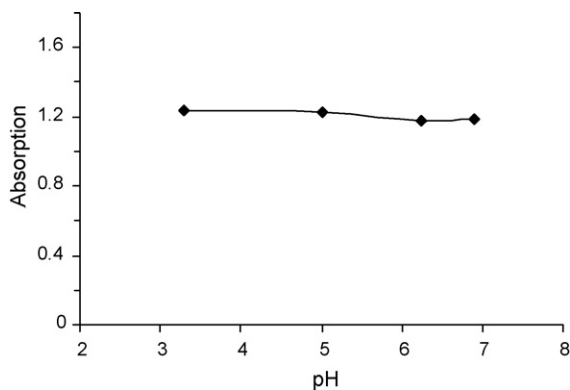
Sample agitation is another important parameter having a great role for enhancing extraction efficiency and reducing extraction time. According to the film theory convective–diffusive mass transfer [5,4] at higher stirring rate the thickness of static solution layer around the drop will be reduced and this leads to a better mass transfer between the sample solution and the extracting microdrop. In this study, a 10  $\mu\text{L}$  *m*-xylene drop was exposed at 27 °C for 15 min to a 15 mL water sample spiked with 20  $\mu\text{g L}^{-1}$  of Hg. Although high stirring rates increase the enrichment factors considerably, the stability of a microdrop at the tip of the needle could be dramatically affected. This is especially true when prolonged sampling times and a microdrop volume of 10  $\mu\text{L}$  are applied. Thus, for all further experiments a stirring rate of 300 rpm was used. Using an appropriate magnet with consistent stirring rate and avoiding any temperature convection was quite essential for achieving an acceptable precision.

The influence of salt addition on the efficiency of SDME was also investigated. Usually, the presence of salt increases the extraction efficiency. This can be explained by the engagement of water molecules in the hydration spheres around the ionic salt. These hydration spheres reduce the concentration of water available to dissolve solute molecules. This should, then, drive additional solutes into a non-polar sorbent or extractant. The presence of high concentration of salt, in this work, led to the instability of the microdrop. Our results showed a four times increase in extraction efficiency of mercury when 80  $\text{g L}^{-1}$  of NaCl was used.

Effect of pH was another parameter which considered for optimization. The reaction of mercury with dithizone can be written as follow:



The complex,  $\text{Hg}(\text{HL})_2$ , is clearly more stable at higher values of pH. However, due to the high complex formation constant the complexation reaction between mercury and dithizone can occur under acidic condition. The number of ions, capable of forming complexes with dithizone, would be expected to be much less if extraction is performed under acidic condition. No wonder in spectrophotometric determination of Hg, in order to prevent the interference of other

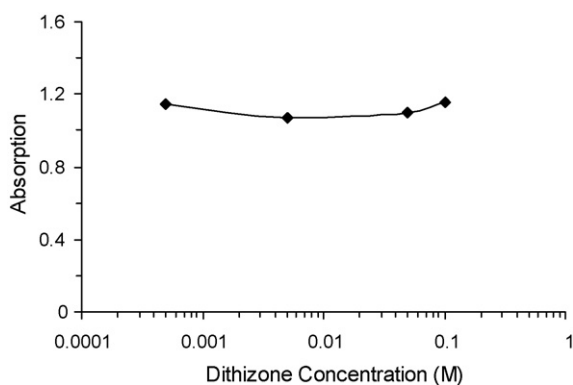


**Fig. 2.** Effect of sample pH on the extraction efficiency. Experimental condition as follows: extraction of 15 mL sample solution spiked at  $10 \mu\text{g L}^{-1}$  Hg at  $27^\circ\text{C}$  with 300 rpm agitation and  $0.08 \text{ g mL}^{-1}$  salt, using  $10 \mu\text{L}$  of *m*-xylene containing  $0.05 \text{ M}$  dithizone after 15 min extraction time.

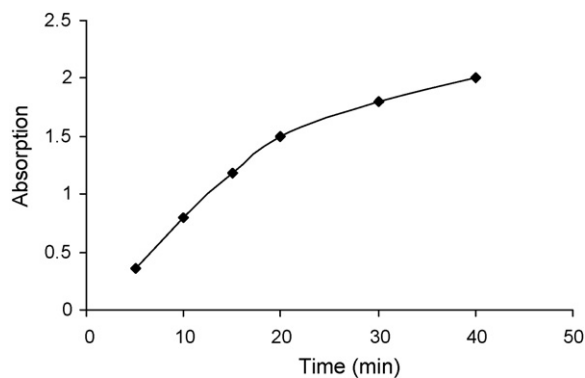
cations, the liquid liquid extraction of mercury usually occurred at pH 1–1.5 [29,30]. Our results revealed that using a pH range of 3.3–7.0 has no pronounced effect on extraction efficiency (Fig. 2). It was not possible to use the pH values below 3.3 as the microdrop was unstable.

The concentration of dithizone in the organic drop has a great role in this work. It is quite clear that by increasing the concentration of dithizone the capacity of organic solvent to extract the cations will be enhanced. In the mean time, the microdrop density will be increased at higher concentration of dithizone and this could lead to the instability of microdrop. Moreover, this caused higher background in the absorption determination. Concentrations of 0.1000, 0.0500, 0.0050 and  $0.0005 \text{ M}$  of dithizone in *m*-xylene were made and added to the *m*-xylene microdrop. Our results revealed no significant difference on the extraction efficiency of a solution spiked at  $10 \mu\text{g L}^{-1}$  of mercury (Fig. 3). The color of free dithizone solution in *m*-xylene is green while it becomes yellow when it is in the complexing form. When a concentration of  $0.0005 \text{ M}$  of dithizone for extraction of a solution of  $10 \mu\text{g L}^{-1}$  of Hg was used, the pale green could be observed at the end of extraction. On the other hand using a concentration of  $0.1 \text{ M}$  led to high background. A concentration of  $0.05 \text{ M}$  of dithizone was, therefore, employed to ensure complete complexation.

Temperature is a major parameter affecting extraction efficiency. In almost all SDME works, rising temperature has led to higher enrichment factors. In previously reported works, when up



**Fig. 3.** Effect of complexing agent concentration on the extraction efficiency of mercury from aquatic medium. Experimental condition as follows: extraction of 15 mL sample solution spiked at  $10 \mu\text{g L}^{-1}$  Hg at  $27^\circ\text{C}$  with 300 rpm agitation and  $0.08 \text{ g mL}^{-1}$  salt, adjusted at pH 3.3, using  $10 \mu\text{L}$  of *m*-xylene after 15 min extraction time.



**Fig. 4.** SDME time profile obtained for the mercury content in aqueous sample. Experimental condition as follows: extraction of 15 mL sample solution spiked at  $10 \mu\text{g L}^{-1}$  Hg at  $27^\circ\text{C}$  with 300 rpm agitation and  $0.08 \text{ g mL}^{-1}$  salt, adjusted at pH 3.3, using  $10 \mu\text{L}$  of *m*-xylene containing  $0.05 \text{ M}$  dithizone, after 15 min extraction time.

to  $3 \mu\text{L}$  microdrop was employed, the microdrop became unstable at temperatures higher than  $40^\circ\text{C}$ . This part of work was carried out using two temperatures of 27 and  $35^\circ\text{C}$  employing a laboratory-made device. The average analytical signal obtained after three replicate analyses were 0.585 and 0.581 at 27 and  $35^\circ\text{C}$ , respectively. No significant difference was observed between these two and the temperature of  $27^\circ\text{C}$  was therefore selected as the temperature of choice.

Extraction time is a major parameter affecting the extraction efficiency. This effect was studied in the range of 5–40 min at room temperature keeping the stirring rate constant at 300 rpm. A series of spiked-water samples ( $20 \mu\text{g L}^{-1}$ ) were prepared and the variation of the analytical signal for the analyte was studied as a function of exposure time. Fig. 4 shows that the intensity increases with sampling time. It was quite difficult to work at longer times as microdrop could be dislodged from the needle. An extraction time of 20 min was found to be a reasonable compromise between enrichment factor and analysis time while sufficient sensitivity could be achieved.

### 3.2. Quantitative evaluation and real samples

To obtain the highest possible sensitivity, the ETV-AAS system was operated according to the optimized condition, listed in Table 1.

The optimized condition was examined for the extraction and determination of Hg in different real water samples. The enrichment factor and linearity was studied by preconcentration of 15 mL of Milli-Q water, spiked with a standard solution of Hg. An enrichment factor of 970 was obtained after microextraction of Milli-Q water, spiked at  $2 \mu\text{g L}^{-1}$  level of mercury. It should be noted that the usual values of enrichment factors obtained for organic compounds are 50–250 [31–33]. The superiority of this method in achieving such a great enrichment factor might be due to (i) the high complex formation constant between Hg and dithizone in comparison with lower distribution constants of organic compounds between water and organic solvent and (ii) the large phase ratio between these two immiscible phases.

A linear dynamic range of  $0.1\text{--}50 \mu\text{g L}^{-1}$  ( $r^2 = 0.998$ ) along with a relative standard deviation of 6.1% ( $n = 7$ ) and a detection limit of  $0.01 \mu\text{g L}^{-1}$  was obtained.

The proposed method was applied to Zayandeh-rood (Isfahan, Iran) and Karoon (Ahvaz, Iran) river water samples after UV radiation. The amount of mercury was found to be  $0.36$  and  $0.21 \mu\text{g L}^{-1}$  for these two river water samples, respectively. The results, conveniently, meet the limits required by the EPA and EU legislation.

**Table 3**

Comparison of analytical performance data of proposed method and other techniques in determination of mercury.

Method	LOD (ng L <sup>-1</sup> )	RSD (%)	Enrichment factor	Reference
HS-SDME-ETAAS	4000	7	40	[7]
Cloud point-ETAAS	10	4	22	[34]
SPE-CV-AAS	10	1.6	300	[35]
Micro column-ICP-OES	390	4.8	150	[36]
HS-SPME-ICP-MS	200	2.3	70	[37]
SDME-ETAAS	10	6.7	970	This work

Table 3 compares the performance of developed method with other works.

### 3.3. Matrix effect evaluation

The effect of matrix on extraction efficiency was taken into consideration. The effects of interfering species such as Pt, Pd, Cu, Au, and Bi, having the tendency to form complexes with dithizone, at two concentration levels of 100 and 1000 µg L<sup>-1</sup> were also evaluated. Since there is a relatively great amount of salt in the extraction medium presence of other cations such as Cu, could easily lead to the formation of precipitates. Our study revealed that even when these cations with a concentration of 1000 µg L<sup>-1</sup> are present there will be no precipitates. Since, the concentration of dithizone in comparison with mercury is much higher, the saturation of dithizone is therefore quite unlikely. Due to the fact that this study was performed using standard addition followed by highly selective AAS, the possible interfering species show no overlapping signals with mercury.

## 4. Conclusions

In this work, a microdrop of *m*-xylene containing dithizone was shown to be an efficient medium for SDME of mercury from aquatic samples. The method was based upon direct contact of the extracting microdrop with the sample solution. Influential parameters such as type of solvent, solvent droplet size, extraction time, stirring rate, temperature, and ionic strength were optimized. A volume of 15 mL of Milli-Q water, river water, spiked with standard solutions at ppb and sub-ppb levels, was sufficient to establish the method and obtain high enrichment factor. The developed method is rather rapid, simple, linear, and reproducible. It is applicable to be used for the qualitative and quantitative analysis of Hg while small volumes of sample and µ-scale size of *m*-xylene are needed. Taking into consideration the conventional difficulties in the determination of mercury, the proposed method conveniently overcome these problems. The high enrichment factor along with the ease of operation could be considered as other advantages for this work.

## Acknowledgments

We appreciate Dr. M. Saraji's (Isfahan University of Technology) great scientific and technical consultation. The Research Council of Sharif University of Technology (SUT) is acknowledged for supporting this project. Also, we would like to acknowledge the IDB for granting the loan in 1993 for purchasing the AAS instrument used in this work.

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