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Vortex-assisted Liquid-liquid Microextraction for the Extraction and Preconcentration of Mercury Using Replacement of Zn(II) by Hg(II) in Zinc Dithizonate Complex and its Indirect Determination by Flame Atomic Absorption Spectrometry

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A simple, rapid, and efficient vortex-assisted liquid-liquid microextraction procedure was proposed for the extraction and preconcentration of Hg(II) ions at trace levels in aqueous samples prior to its indirect determination by flame atomic absorption spectrometry. In this study, at first, zinc ditizonate was formed in an aqueous solution and then extracted into carbon tetrachloride. Then it was added to the sample solution at µl-level and the obtained mixture was vortexed. In this step, Zn(II) in zinc ditizonate was replaced by Hg(II) in the aqueous phase and the concentration of Zn(II) in the organic phase was reduced. After centrifuging, carbon tetrachloride containing dithizonate complexes of Zn(II) and Hg(II) was sedimented. To determine the amount of Hg(II) in the sample solution, the sedimented phase was injected into the instrument and the concentration of the remained Zn(II) was determined. Finally, Hg(II) concentration was determined by the difference between the obtained absorbance and the absorbance of a blank (Hg(II)-free aqueous phase extracted by the above-mentioned procedure). Under the optimum experimental conditions, the linear range was obtained in the range of 0.25-15 µg l^{-1}. The relative standard deviations ($n = 6$) for the concentrations of 1 and 5 µg l^{-1} were obtained 5.2 and 3.3%, respectively. Moreover, the obtained detection and quantification limits were 0.04 and 0.10 µg l^{-1}, respectively. Finally, the suggested extraction method was successfully used for the extraction of Hg(II) ions in real water samples.

Keywords: Flame atomic absorption spectrometry, Indirect determination, Mercury, Vortex-assisted liquid liquid microextraction, Zinc ditizonate

INTRODUCTION

The entry of heavy metals into the environment and subsequently into the human food cycle in various ways has been reported and is one of the problems we face. Therefore, measuring of the level of these elements in foods and, more importantly, in water resources is of particular importance. Mercury and its derivatives are some of the most important members of heavy metals that are used at a relatively high level in heavy industries, electronics, manufacturing, and even in medicine and food industries. However symptoms of mercury poisoning depend upon the type, dose, method, and duration of exposure; but the most common symptoms include muscle weakness, poor coordination, numbness in the hands and feet, skin rashes, anxiety, memory problems, trouble speaking, trouble hearing or seeing, and long-term complications may include kidney problems and decreased intelligence [1].

Due to the high toxicity of mercury to living organisms, it is necessary to develop analytical methods with high sensitivity and low detection limit to control its amount in different samples. Therefore, different methods using

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several analytical instruments have been developed such as electrochemical methods [2-4], inductively coupled plasma-mass spectrometry [5-7], flame atomic absorption spectrometry (FAAS) [8,9], chromatographic techniques [10], graphite furnace atomic absorption spectrometry [11-13], and inductively coupled plasma-optical emission spectrometry [14-16]. In addition to the mentioned items, the cold vapor technique as a traditional method, is one of the most efficient methods for the determination of mercury [17-19]. Aside from all the advantages of this method including high sensitivity and accuracy, low detection limit, and high detection power, it is also associated with many problems such as unrepeatability, hard work, sample matrix effect, the need for high purity expensive solvents and chemicals, *etc*. [20-24]. Therefore, the need for an efficient and easy-to-use method for the determination of Hg is always sensing.

Liquid-liquid extraction (LLE) is one of the elementary sample preparation methods that is used in most laboratories and even industrial units with the least instrumentation and chemicals. LLE is a method to separate compounds based on their relative solubilities in two different immiscible liquids; usually water (a polar solvent) and an organic solvent (non-polar). Classical LLE despite all the advantages has a lot of environmental concerns due to the large amounts of organic solvents requirement and producing high waste. In addition to the difficulty and risk of working with a high volume of organic solvents for operators, the high cost of solvents, and time-consuming, led chemists to think about reducing the amount of organic solvents, which resulted in the emergence of microextraction methods. Liquid-liquid microextraction methods [25], in addition to covering the disadvantages of LLE method due to using a very small amount of the extraction solvents, achieving high enrichment factors (EFs) is also possible.

Dispersive liquid-liquid microextraction (DLLME) is one form of microextraction method developed in 2006 by Rezaei *et al.* [26]. In this method, a mixture of a water-immiscible solvent and a water-miscible solvent (as extraction solvent and disperser solvent, respectively) is rapidly injected into an aqueous sample. It results in the formation of a cloudy solution. In the end, the fine droplets of the extracting solvent are separated from the aqueous phase by centrifuging. This method, in addition to reducing the ratio of the extracting solvent to the initial sample volume, enhances the extraction efficiency; and reduces extraction time as a key factor in analytical work by increasing the interface between the two phases. This method, along with being environmentally friendly, is simple, low cost, fast, and has high extraction recovery (ER). However, using the relatively high volumes (at ml-level) of dispersive solvents in classical DLLME, increases the solubility of the analytes in the aqueous solution and leads to relatively low ERs [27-29]. To solve this problem, some developed methods such as ultrasound-assisted emulsification microextraction [30,31] and vortex-assisted liquid-liquid microextraction (VALLME) [32] were developed. In VALLME, as a disperser solvent-free technique, dispersion of the extraction solvent into an aqueous sample is performed with the assistance of a vortex along with a mild emulsification procedure.

In the present work, due to the difficulty of the cold vapor method, developing a simple, sensitive and efficient method based on VALLME for simple, safe, environment-friendly, and low cost extraction and preconcentration of trace amount of Hg(II) was aimed. Zinc dithizonate solution is stable but dithizone decomposes readily and cannot be stored for more than a few days. Therefore, zinc dithizonate is usually employed for overcoming the problem of the instability of the free dithizone [33]. In this study, because of the higher sensitivity of FAAS for zinc in comparison with mercury and the higher stability of zinc(II) dithizonate, its solution in carbon tetrachloride was used as the extraction solvent. It was dispersed in the sample solution with the assistance of a vortex (disperser). The greater tendency of Hg(II) ions to form a complex with dithizonate relative to Zn(II) ions causes them to replace Zn(II) with Hg(II) in zinc(II) dithizonate. Finally, the concentration of Hg(II) in the initial aqueous solution was determined according to decreasing concentration of Zn(II) in carbon tetrachloride.

EXPERIMENTAL

Reagents and Solutions

A stock solution of Hg(II), 100 mg l^{-1}, in deionized water (Ghazi company, Tabriz, Iran) was prepared by dissolving appropriate amount of $Hg(NO_3)_2$ (Merck, Darmstadt, Germany). It was diluted daily with deionized water till to 5 µg l^{-1}, and used as the working standard solution. A solution of Zn(II) with a concentration of 1 mg l^{-1} was prepared from analytical reagent-grade $ZnSO_4.7H_2O$ (Merck) in deionized water. A solution of dithizone with a concentration of 10^{-4} M was prepared from analytical reagent-grade dithizone (Merck) in carbon tetrachloride and kept in a refrigerator. 1,1,2,2-Tetrachloroethylene (1,1,2,2-TCE), 1,2-dibromoethane (1,2-DBE), chloroform, ammonia solution (25%, *w/w*), and sodium chloride were bought from Merck (with the highest purity).

Real Samples

Tap water was collected from our laboratory. Spring water and river water samples were collected from Hemejane (West Azerbaijan province, Miandoab, Iran) and Sufi Chay (Maragheh, East Azerbaijan, Iran), respectively. All of the samples were centrifuged for 8 min at 8000 rpm to remove possible solid particles. Then, they were kept at 4 °C in a refrigerator and were directly subjected to the extraction procedure without any pretreatment or dilution.

Apparatus

An atomic Absorption 6300 (Shimadzu, Kyoto, Japan) FAAS equipped with a 100-mm burner head, a deuterium background correction, and an air-acetylene flame was used. The used radiation source was zinc hollow cathode lamp (Hamamatsu Photonics, Shizuoka, Japan) and the operation conditions were: current 10 mA and wavelength 213.9 nm (resonance line of zinc). A Labinco L46 vortex mixer (Netherlands) and a Rotofix 32A Hettich centrifuge (Kirchlengern, Germany) were used for mixing and phase separation, respectively. A Metrohm pH meter equipped with a glass electrode (Herisau, Switzerland) and a laboratory stirrer (Gerhardt, Konigswinter, Germany) were used in pH measurements.

Preparation of Zinc(II) Dithizonate Solution

10 ml of Zn(II) solution with a concentration of 1 mg l^{-1}, and 10 ml of dithizone solution (10^{-4} M in carbon tetrachloride) were mixed in a 50-ml separatory funnel, and then 1 ml ammonia solution (0.1 M) was added. It was shacked for 2 min to form zinc(II) dithizonate complex. In this step color of organic phase changed to purple (from green), that's a sign for transfer of Zn(II) from aqueous solution into the organic phase by formation of zinc(II) dithizonate complex. Then the aqueous phase was discarded, and to wash off the excess dithizone, the organic phase was washed with 10 ml ammonia solution (0.1 M) for two min for three times. Finally, the organic phase was stored in a sealed container.

Procedure

A 5 ml standard solution of Hg(II) (5 µg l^{-1}) or real sample was transferred into a 10-ml conical glass test tube and 10% (*w/v*) sodium chloride salt was dissolved in it. Then 100 µl of the synthesized zinc(II) dithizonate solution (section 2.4) was added. It was vortexed for one min to disperse the zinc(II) dithizonate solution into the sample solution. In this step, Hg(II) was partially substituted instead of zinc(II) in the dithizonate complex, and Hg(II)-dithizonate was extracted into the carbon tetrachloride. Following this process, the mixture was centrifuged (10 min, 5000 rpm). Finally carbon tetrachloride (containing zinc(II) dithizonate and Hg(II) dithizonate) sedimented at the bottom of the tube. In the following, the organic phase was removed by a microsyringe and injected into FAAS by a home-made microsample introduction system [34] to reading the absorbance of Zn. In all experiments, one blank was used. In this case, instead of Hg(II) solution, extraction procedure was done on 5 ml deionized water, and final organic phase was injected into FAAS. Concentration of mercury was determined by the difference between the absorption of organic phases obtained using standard solution of Hg(II) and blank (Hg-free).

RESULTS AND DISCUSSION

Selection of Extraction Solvent

The extraction solvent in the proposed VALLME method should have properties such as different density of water, ability to extract zinc and mercury dithizonates, and low solubility in water. To study the effect of the type of extraction solvent, different solvents such as carbon tetrachloride, 1,2-DBE, 1,1,2,2-TCE, and chloroform were studied by keeping the other parameters constant. According

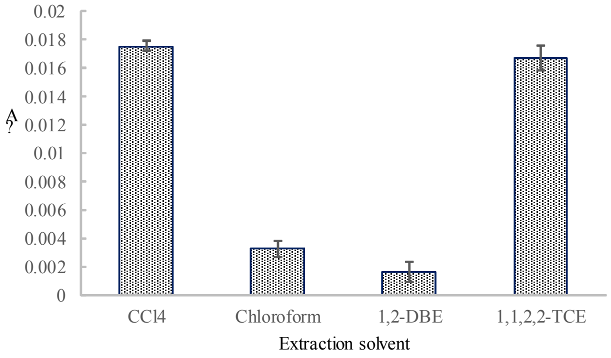

Fig. 1. Selection extraction solvent. Extraction conditions: Zn(II), 10 ml with a concentration of 1 mg l^{-1}; dithizone, 10 ml with a concentration of 1 M in each selected solvent; sample volume, 5 ml; Hg(II); 5 µg l^{-1}, pH 7; injection volume of dithizone solution, 100 µl; centrifuging rate, 7000 rpm; centrifuging time, 7 min. The error bars represent standard deviations (n = 3).

to the comparison results in Fig. 1, carbon tetrachloride was selected as the optimum extraction solvent.

Optimization of Aqueous Phase Volume

To investigate the effect of aqueous phase volume on extraction efficiency, solutions containing Hg(II) with a constant concentration (5 µg l^{-1}) in various volumes (3, 5, and 8 ml) were studied. As shown in Fig. 2, in volumes more than 5 ml, the extraction efficiency remains constant, so it was selected as the optimal volume and used in the continuation of studies.

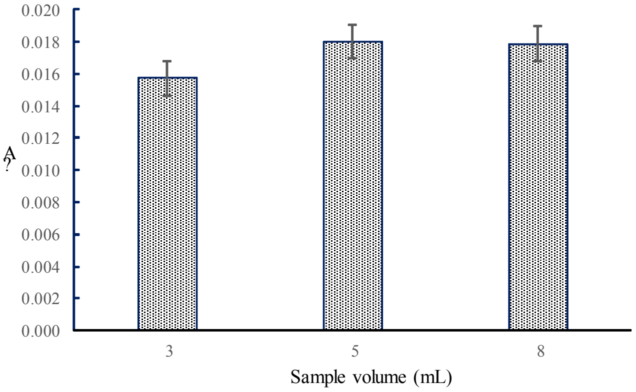

Fig. 2. Effect of sample volume. Extraction conditions: extraction solvent, carbon tetrachloride; the other conditions are the same as those used in Fig. 1.

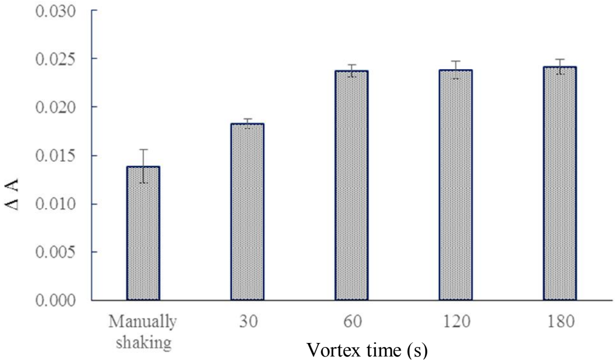

Fig. 3. Effect of vortex time on the extraction efficiency of the method. Extraction conditions: sample volume, 5 ml; the other conditions are the same as those used in Fig. 2.

Optimization of Vortex Time

In this study, dispersion of the extraction solvent (carbon tetrachloride) into the aqueous phase was done with the aid of vortexing. The vortex time actually refers to the amount of time that the extraction solvent is dispersed as tiny droplets inside the aqueous phase. By increasing vortex time, mass transfer between the phases and contact of the extraction solvent with the analytes, and naturally, the extraction efficiency of the method can be increased. Therefore, the effect of vortex time on the amount of the obtained signals was investigated at different times (30-180 s). As shown in Fig. 3, the use of vortex has a significant advantage over manually shaking due to more uniform distribution, producing finer droplets, and more contact surface between the extraction solvent and the aqueous phase; also there is no significant change in the analytical signals after 60 s. Therefore, it was selected as the optimum vortex time in the following experiments.

Optimization of Aqueous Phase pH

In this study, the determination of the amount of Hg(II) in the sample solution requires the replacement of Zn(II) with Hg(II) in zinc-dithizonate complex, and extraction of the formed hydrophobic complexes into tiny droplets of carbon tetrachloride. Therefore, the aqueous phase pH can be one of the most important parameters in the formation and extraction of the complexes. The amount of the obtained signal was studied by adjusting pH between 1 and 12 with NaOH and HCl. As shown in Fig. 4, the highest extraction efficiency is obtained in the pH range of 6-8. At low pH values, hydrogen ions interfere with the substitution reaction and complex formation; and result in a decreasing analytical signal. Also at high pH values, there is the possibility of hydrolysis of the cations. The pH of working and real sample solutions used in this study was in the range of 6-8, therefore, there is no need for pH adjustment.

Study of Salting out Effect

Adding salt to the aqueous phase can be used as one of the approaches for increasing the extraction efficiency of the method. Of course, salt addition can have a multi-effect in the extraction of different analytes from various samples. On one side, by adding the salt and increasing the ionic strength of the aqueous solution, the solubility of the extraction solvent in the aqueous phase decreases, and therefore volume of the accumulated phase increases. This allows using a small volume of the extraction solvent. Also, with increasing ionic strength, the solubility of the analyte in the aqueous medium may decrease and more amounts of the analyte may be transferred into the extraction solvent. This is due to the different tendencies of the analyte and the ions resulting from dissolving salt which is hydrated by water molecules. On the other hand, the addition of salt to the sample solution increases the viscosity of the aqueous solution and can reduce the analyte diffusion coefficient and extraction efficiency of the method. The dominance of each of the mentioned effects can cause a change in the extraction amount of the analyte. Therefore, investigating the amount of salt seems necessary. For this purpose, the amount of the obtained signal was studied in the presence of various sodium chloride amounts. The results are shown in Fig. 5. The results show that the analytical signal increases by increasing NaCl concentration up to 10% (*w/v*), and then decreases. Therefore, in the following steps, NaCl in the amount of 10% (*w/v*) was added to all the solutions.

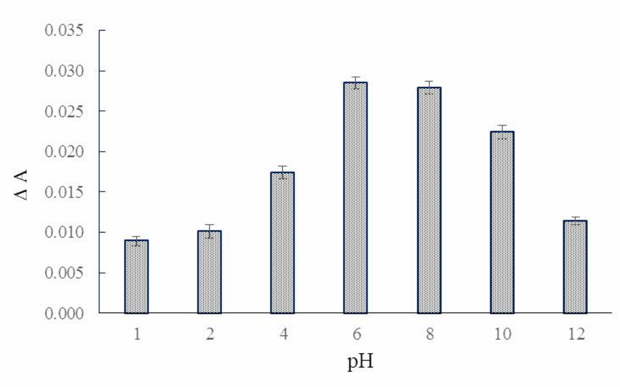

Fig. 4. Study of sample pH. Extraction conditions: vortex time, 60 s; the other conditions are the same as those used in Fig. 3.

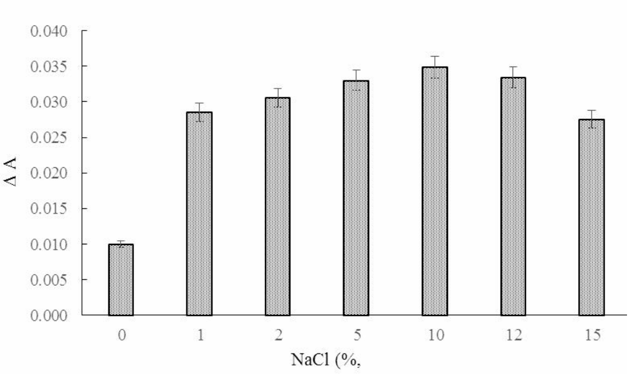

Fig. 5. Effect of salt addition on extraction efficiency of the method. Extraction conditions are the same as those used in Fig. 4, without pH adjustment.

Study Effect of Extraction Solvent Volume

Extraction solvent volume may be considered one of the important parameters in improving extraction efficiency. It is clear that by increasing the volume of the extraction solvent, the amount of the extracted analyte increases, but, on the other hand, it causes to increase in the collected organic phase volume resulting in EF decreasing due to dilution. To study the effect of this parameter, volumes between 50 and 200 µl of the extraction solvent were tested. According to the results in Fig. 6, a decrease in analytical signal is observed in volumes less than or more than 100 µl. The results show that the volume of less than 100 µl (50 µl)

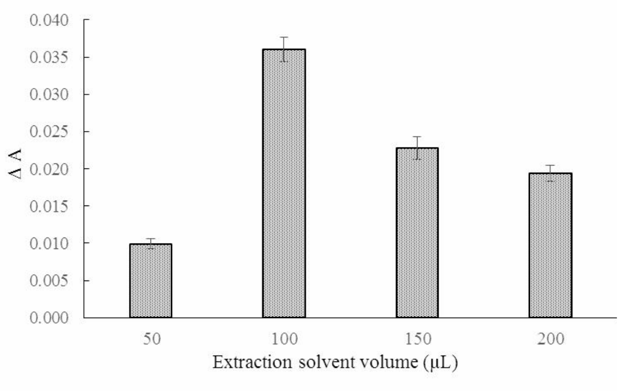

Fig. 6. Study of extraction solvent volume. Extraction conditions: NaCl, 10% (*w/v*); the other conditions are the same as those used in Fig. 5.

Table 1. Tolerance Limit of Interferent/Hg(II) Ratio in Determination of Hg(II) Using the Proposed Method

Species	Tolerance limit of interferent/Hg(II) ratio
Mg^{2+}	4000
Ca^{2+}	4000
K^{+}	700
Co^{2+}	200
Ni^{2+}	500
Cl^{-}	12000
NO_3^{-}	12000
SO_4^{2-}	6000

was not enough to extract the analyte, and also, in the volumes, more than 100 µl (the collected organic phase volume increased from 104 ± 2 to 210 ± 3 µl) dilution of the analyte in the collected organic phase is a dominant effect, and it can result in decreasing of the analytical signal. Therefore, 100 µl was utilized in the following experiments.

Optimization of Centrifugation Time and Speed

Centrifugation was used to completely separate the organic phase from the aqueous phase. For this purpose, the speed and time of the centrifugation were investigated in the ranges of 3000-7000 rpm and 3-12 min, respectively. Thus, two types of experiments were performed: in the first part of the experiments, 5 min was selected as a constant centrifugation time, while its speed examined at different rates (3000-7000 rpm); in the other part of the experiments, different centrifugation times (3-12 min) was examined at the optimized centrifugation speed (5000 rpm). According to the results, 5000 rpm and 10 min, were selected as the optimal rate and time of centrifugation, respectively.

Study of Interferences

One of the factors that shows the efficiency of a method is low interference of other materials and elements and even the absence of interference. For this purpose, the effect of common ions coexisting in real samples on the extraction efficiency of Hg(II) was studied. In these experiments, 5 ml of an aqueous solution containing 5 µg l^{-1} of Hg(II) and different concentrations of the studied ions was treated according to the proposed extraction procedure. A studied ion was considered as an interfere if it resulted in a ±5% increase or decrease the analytical signal. The results are shown in Table 1.

Analytical Characteristics

After achieving the optimal conditions, some quantitative characteristics of the proposed method such as the limit of detection (LOD), the limit of quantification (LOQ), linear range (LR), and precision were calculated and collected in Table 2. Good linearity in the range of 0.25-15 µg l^{-1} with a coefficient of determination of 0.9973 was obtained. The LOD using the definition of $3S_B/m$ (S_B is the standard deviation of the blank and m is the slope of the calibration graph) was obtained as 0.04 µg l^{-1}. The LOQ as $10S_B/m$ was also obtained as 0.10 µg l^{-1}. Repeatability or precision (as a measure of data uniformity and reliability of the method) expressed as relative standard deviation was investigated in the concentrations of 1 and 5 µg l^{-1} in the day and within different days. It was obtained ≤ 7.7% for intra- (n = 6) and inter-day (n = 5).

Real Samples Analysis

The efficiency of the proposed method in measuring mercury was evaluated by analyzing real samples including water samples from different sources. Also, to investigate the effect of the matrix in the real samples, they were spiked

Table 2. Quantitative Characteristics of the Proposed Method for the Analysis of Hg(II) in Aqueous 6amples

					RSD (%)[e]			
LR	calibration curve equation	r^2 [b]	LOD	LOQ	Intra-day		Inter-day	
(μg l^{-1})[a]			(μg l^{-1})[c]	(μg l^{-1})[d]	1 μg l^{-1}	5 μg l^{-1}	1 μg l^{-1}	5 μg l^{-1}
0.25-15	Y = 0.004X + 0.0002[f]	0.9973	0.04	0.10	5.2	3.3	7.7	5.1

[a]Linear range. [b]Coefficient of determination. [c]Limit of detection. [d]Limit of quantification. [e]Relative standard deviation intera- (n = 6) and inter- day (n = 5) precision. [f]Y and X are absorbance and concentration (μg l^{-1}), respectively.

Table 3. Determination of Hg(II) in Real Samples and Study of Matrix Effect

Spiked concentration (μg l^{-1})	Tap water		Spring water		River water (Sufi Chay)	
	Found concentration (μg l^{-1}) ± S.D.[a] (n = 3)	Relative recovery ± S.D. (n = 3)	Found concentration (μg l^{-1}) ± S.D. (n = 3)	Relative recovery ± S.D. (n = 3)	Found concentration (μg l^{-1}) ± S.D. (n = 3)	Relative recovery ± S.D. (n = 3)
0.0	N.D.[b]	-	N.D.	-	0.8 ± 0.1	-
2.5	2.3 ± 0.1	92.0 ± 2.3	2.5 ± 0.3	100.0 ± 2.5	3.0 ± 0.2	89.2 ± 3.2
5.0	5.1 ± 0.3	102.0 ± 2.9	4.8 ± 0.2	96.0 ± 3.3	6.0 ± 0.4	104.2 ± 2.8

[a]Standard deviation. Not detected.

at two concentrations of mercury cation (2.5 and 5 μg l^{-1}), and then the extraction procedure was performed under the optimal conditions mentioned above. Finally, the obtained analytical signals were compared with those of deionized water spiked at the same concentrations. The results are summarized in Table 3. The obtained relative recoveries between 89.2 and 104.2% indicate that the real samples matrices have little effect on the efficiency of the current method.

Comparison of the Proposed Method with other Approaches

Table 4 compares the analytical characteristics of this method with the others published in the literature for measuring mercury. Most of the previous methods required the preparation or synthesis of expensive adsorbents with long and time-consuming extraction steps. On the other hand, the devices and accessories used in the previously published methods are not comparable to FAAS in the terms of availability, price, cost, and usability. The developed method has some advantages such as having a short extraction time, comparable LODs and LOQs, and waste reduction over the previously reported methods. Due to the fact that in the other methods more sensitive devices were used, it can be said that using this method, the results can be obtained with the same sensitivity and precision achieved by expensive analytical devices.

CONCLUSIONS

In this study, a VALLME procedure was used for the extraction and preconcentration of mercury using the replacement of Zn(II) by Hg(II) in zinc dithizonate complex and indirect determination of mercury by FAAS. Zinc(II) dithizonate solution in carbon tetrachloride and vortex was used as the extraction solvent and disperser, respectively.

Table 4. Comparison of the Proposed Method with other Methods Used in Preconcentration and Determination of Hg(II)

Sample preparation method/detection	Sample	LR (μg l^{-1})[a]	LOD (μg l^{-1})[b]	LOQ (μg l^{-1})[c]	RSD (%)[d]	Ref.
EME[e]/GFAAS[f]	Water samples	0.5-10	0.5		6.2-7.1	[13]
SPE[g]/ICP-OES[h]	Food samples	0.625-25	0.071	0.24	5.0	[15]
MSPE[i]/ICP-OES	Natural water samples	0.25-12.5	0.06	0.19	4.1	[16]
MOF[j]/CVAAS[k]	Sea food samples	0.05-50	0.01	-	5.5	[19]
SPE/HG-AAS[l]	Fish	0.12-16.5	0.018	-	2.8	[35]
SPE/ICP-AES[m]	Environmental and biological samples	-	0.04	-	3	[36]
CPE[n]/GFAAS	-	4-240	0.53	1.38	1.9	[37]
LPME-SFO[o]/GFAAS	Bottled and tap water samples	0.2-3	0.07		2.1-3.5	[38]
VALLME[p]/FAAS[q]	Environmental water samples	0.25-15	0.04	0.10	3.3	This study

[a] Linear range. [b] Limit of detection. [c] Limit of quantification. [d] Relative standard deviation. [e] Electromembrane extraction. [f] Graphite furnace atomic absorption spectrophotometry. [g] Solid phase extraction. [h] Inductively coupled plasma-optical emission spectrometry. [i] Magnetic solid phase extraction. [j] Metal-organic framework. [k] Cold vapor atomic absorption spectrophotometry. [l] Hydride generation-atomic absorption spectrometry. [m] Inductively coupled plasma-atomic emission spectrometry. [n] Cloud point extraction. [o] Liquid phase microextraction based on solidification of floating organic droplet. [p] Vortex-assisted liquid-liquid microextraction. [q] Flame atomic absorption spectrophotometry.

The obtained results indicated high sensitivity and selectivity of the proposed method. In addition, the obtained results showed that the suggested method has some advantages such as good repeatability, low LODs and LOQs, and simplicity of operation. The obtained results indicated that the developed method can be used as an applicable and routine analytical method for the determination of Hg(II) ions at μg l^{-1} in different water samples.

ABBREVIATIONS

ER: Extraction recovery, FAAS: Flame atomic absorption spectrometry, LOD: Limit of detection, LOQ: Limit of quantification, RSD: Relative standard deviation, VALLME: Vortex-assisted liquid-liquid microextraction.

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