



# Extraction of trace amounts of mercury with sodium dodecyl sulphate-coated magnetite nanoparticles and its determination by flow injection inductively coupled plasma-optical emission spectrometry

Mohammad Faraji, Yadollah Yamini\*, Mohammad Rezaee

Department of Chemistry, Tarbiat Modares University, P.O. Box 14115-175, Tehran, Iran

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## ABSTRACT

A new method for solid-phase extraction and preconcentration of trace amounts Hg(II) from environmental samples was developed by using sodium dodecyl sulphate-coated magnetite nanoparticles (SDS-coated Fe<sub>3</sub>O<sub>4</sub> NPs) as a new extractant. The procedure is based on the adsorption of the analyte, as mercury–Michler's thioiketone [Hg<sub>2</sub>(TMK)<sub>4</sub>]<sup>2+</sup> complex on the negatively charged surface of the SDS-coated Fe<sub>3</sub>O<sub>4</sub> NPs and then elution of the preconcentrated mercury from the surface of the SDS-coated Fe<sub>3</sub>O<sub>4</sub> NPs prior to its determination by flow injection inductively coupled plasma-optical emission spectrometry. The effects of pH, TMK concentration, SDS and Fe<sub>3</sub>O<sub>4</sub> NPs amounts, eluent type, sample volume and interfering ions on the recovery of the analyte were investigated. Under optimized conditions, the calibration curve was linear in the range of 0.2–100 ng mL<sup>-1</sup> with  $r^2 = 0.9994$  ( $n = 8$ ). The limit of detection for Hg(II) determination was 0.04 ng mL<sup>-1</sup>. Also, relative standard deviation (R.S.D.) for the determination of 2 and 50 ng mL<sup>-1</sup> of Hg(II) was 5.2 and 4.7% ( $n = 6$ ), respectively. Due to the quantitative extraction of Hg(II) from 1000 mL of the sample solution an enhancement factor as large as 1230-fold can be obtained. The proposed method has been validated using a certified reference materials, and also the method has been applied successfully for the determination of Hg(II) in aqueous samples.

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## 1. Introduction

It is well known that mercury is one of the most toxic heavy metals because of its accumulative and persistent character in the environment and living organisms. Although mercury is not an abundant chemical element in nature, it has become dangerously widespread as a result of many industrial and agricultural applications [1–4]. Therefore, the determination of mercury is very important in environmental and toxicological studies. One of the routes of incorporation of mercury into the human body is by drinking water [1–4]. Hence, its determination in water samples has become very important. Recent reports estimate a total mercury concentration in non-polluted waters ranging from 0.006 to 5 ng mL<sup>-1</sup> [5–14]. The Environmental Protection Agency (EPA) has set an enforceable standard called maximum contaminant level (MCL). The MCL for mercury has been set at 2 ng mL<sup>-1</sup> by EPA [15], since it is the lowest level to which water systems can be reasonably required to remove this contaminant, should it occur in drinking water. The World Health Organization (WHO) has set the guideline value for inorganic mercury in drinking water at 6 ng mL<sup>-1</sup>

[16]. Therefore, the routine monitoring and controlling of mercury have become increasingly important, especially for water systems. In recent years, continuous progress in the improvement of analytical instrumentations has been made; however still the direct determination of trace mercury in environmental samples is difficult, this is due, sometimes to various factors, particularly when present in low concentrations in non-polluted waters, as well as the matrix effects. Thus, highly sensitive and selective determination techniques are required.

In various literatures, different analytical methods have been reported for the determination of trace amounts of mercury, but the most commonly used ones are cold vapour atomic absorption spectrometry (CV-AAS) [8,9,12], spectrometry [7,17,18], atomic fluorescence spectrometry (AFS) [19,20], inductively coupled plasma-optical emission spectrometry (ICP-OES) [11,21,22], and inductively coupled plasma mass spectrometry (ICP-MS) [6,23]. Although ICP-OES and CV-AAS are the most often used techniques in the determination of trace amounts of mercury, the low concentration level of mercury in the water itself is not compatible with the detection limits of these techniques. Under these circumstances, a separation and enrichment step prior to its determination could be a good choice. Several methods have been proposed for separation and preconcentration of trace amounts of mercury such as cloud point extraction [9,11,23], liquid–liquid extraction

\* Corresponding author. Tel.: +98 21 82883417; fax: +98 21 88006544.  
E-mail address: [yyamini@modares.ac.ir](mailto:yyamini@modares.ac.ir) (Y. Yamini).

[7,8], stir bar sorptive extraction [10] and solid-phase extraction (SPE) [6,13,14,17,19]. Among these techniques, the SPE procedures, either off- or on-line, are considered superior to the other procedures for their simplicity, consumption of small volumes of organic solvents, and its ability to achieve a higher enrichment factor.

Recently, nanometer-sized materials have attracted substantial interest in the scientific community because of their special properties [24,25]. These materials have been used in various scientific fields such as; biotechnology, engineering, biomedical, environmental, and material science [26,27]. More recently, the use of NPs for sample extraction is gaining researchers interest [6,28–40]. Compared with micrometer-sized particles used in the SPE, the NPs offer a multitude of benefits that make it a better choice. They have a significantly higher surface area-to-volume ratio and a short diffusion route, resulting in a higher extraction capacity; rapid dynamics of extraction and its higher extraction efficiencies [41,42] are just some of their benefits. Also, NPs' surface functionality can be easily modified to achieve the selective sample extraction or cell collection [43,44]. Moreover, by using superparamagnetic NPs such as that of  $\text{Fe}_3\text{O}_4$  can achieve a shorter analysis time, due to the magnetically assisted separation of these particles from the sample solution. The NPs are attracted to a magnetic field but retain no magnetic charge after the field is removed. This property makes them particularly suitable for sample preparation because no centrifugation or filtration of the sample is needed after extraction in comparison with non-magnetic adsorbents.

The aim of the present study was to develop a NP-based method for the preconcentration and determination of trace amounts of Hg(II).  $\text{Fe}_3\text{O}_4$  NPs were coated with sodium dodecyl sulphate (SDS) and used as an SPE adsorbent for the extraction of Hg(II) as its complex with Michler's thioiketone ( $[\text{Hg}_2(\text{TMK})_4]^{2+}$ ) from water samples. The level of Hg(II) was then determined by flow injection (FI)-ICP-OES. To the best of our knowledge, this methodology has not been employed previously in the extraction and determination of trace amounts of Hg(II) from aqueous samples.

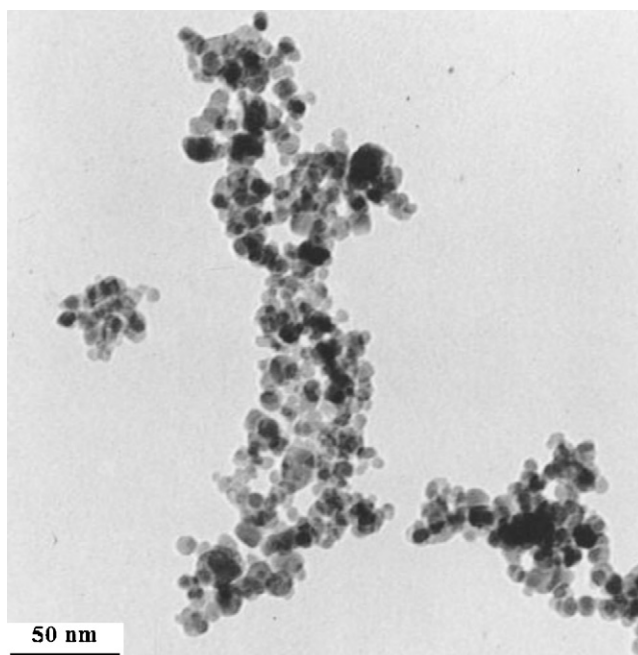
## 2. Experimental section

### 2.1. Instrumentation

A radial view Varian Vista-Pro simultaneous ICP-OES (Springvale, Australia) coupled to a V-groove nebulizer and equipped with a charge coupled device (CCD) was applied for the determination of the metal ions. Operational conditions and selected wavelength for Hg(II) were optimized and summarized in Table 1. A home-made sample loop (50 mm length  $\times$  2.5 mm i.d.), prepared from a silicon tube, was used for the FI introduction during the preconcentrated phase into the nebulizer of the ICP-OES. A six-way two-position injection valve (Tehran University, Iran) was used for the injection/elution process. The pHs of the solutions were measured with a WTW pH meter (Inolab, Germany) which was supplied with a combined electrode. TEM images were obtained with an H-800 transmission electron microscope (Hitachi, Japan).

**Table 1**  
The optimum instrumental conditions of ICP-OES.

Plasma gas	Argon
Plasma gas flow rate	15 L min <sup>-1</sup>
Auxiliary gas flow rate	1.5 L mm <sup>1</sup>
Frequency of RF generator	40 MHz
RF generator power	1.65 kW
Observation height	6 mm
Nebulizer pressure	170 kPa
Eluent	25% (v/v) 1-propanol in water
Elution rate	1.2 mL min <sup>-1</sup>
Wavelength	253.652 nm



**Fig. 1.** TEM image of prepared  $\text{Fe}_3\text{O}_4$  NPs.

### 2.2. Reagents

All reagents used were of analytical grade. Ferric chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), ferrous chloride ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ), sodium hydroxide, Michler's thioiketone (TMK), mercury chloride ( $\text{HgCl}_2$ ), sodium acetate, sodium dodecyl sulphate (SDS), methanol, acetone, and 1-propanol, hydrochloric acid were all purchased from Merck (Darmstadt, Germany). The stock solution of Hg(II) ( $1000 \mu\text{g mL}^{-1}$ ) was prepared by dissolving the appropriate amounts of  $\text{HgCl}_2$  in doubly distilled water. A solution of  $1 \times 10^{-3} \text{ mol L}^{-1}$  TMK was prepared by dissolving the appropriate amount of this reagent in 1-propanol and was then kept away from the light. A buffer solution (pH 3) was prepared by mixing a sodium acetate solution ( $0.1 \text{ mol L}^{-1}$ ) with a concentrated nitric acid ( $14 \text{ mol L}^{-1}$ ) solution.

### 2.3. Synthesis of $\text{Fe}_3\text{O}_4$ NPs

The chemical co-precipitation method was used in the preparation of the  $\text{Fe}_3\text{O}_4$  NPs [32]. First, for preparing a stock solution, 10.4 g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , with 4.0 g of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and 1.7 mL of HCl ( $12 \text{ mol L}^{-1}$ ) were mixed and dissolved in 50 mL of deionized water in a beaker which was then degassed using nitrogen gas for 20 min before use. Simultaneously, 500 mL of  $1.5 \text{ mol L}^{-1}$  NaOH solution was degassed (for 15 min) and heated to  $80^\circ\text{C}$  in a reactor. The stock solution was then added dropwise using a dropping funnel for 30 min under nitrogen gas protection and vigorously stirring (1000 rpm) using a glassware stirrer. During the whole process, the solution temperature was maintained at  $80^\circ\text{C}$  and nitrogen gas was used to prevent the intrusion of oxygen. After the reaction, the obtained  $\text{Fe}_3\text{O}_4$  NPs precipitate was separated from the reaction medium by using a magnetic field, and then washed four times with 500 mL of deionized water. Finally, the obtained NPs were resuspended in 500 mL of degassed deionized water. The pH of the suspension after the washings was 11.0 and the concentration of the generated NPs in the suspension was estimated to be about  $10 \text{ mg mL}^{-1}$ . The obtained NPs were stable under these conditions for up to about one month. The obtained NPs were characterized by using a transition electron microscope (TEM) and the obtained image is shown in Fig. 1.

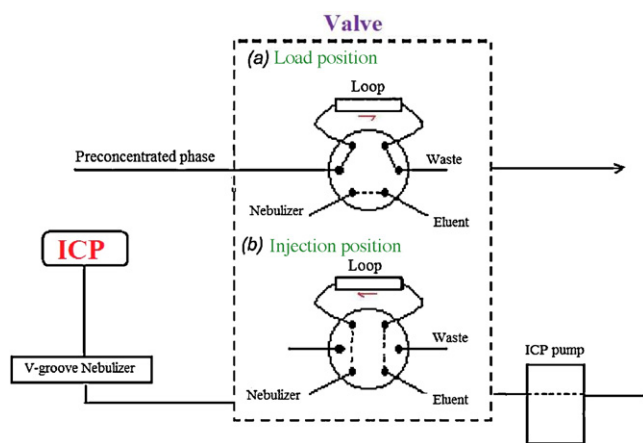


Fig. 2. Schematic representation of the injection system.

#### 2.4. NP-based SPE procedure

An aliquot of 1000 mL of water samples (pH 3.0) was transferred to 1000 mL glassware beakers. Then, 3.0 mL of  $1 \times 10^{-3} \text{ mol L}^{-1}$  TMK, 8.0 mL of the suspension of  $\text{Fe}_3\text{O}_4$  NPs and 6.5 mL of the SDS solution ( $5 \text{ mg mL}^{-1}$ ) were sequentially added together and completely mixed with the sample solutions. The mixtures were shaken and allowed to complete the extraction process for 1 min. Subsequently, an Nd-Fe-B strong magnet ( $10 \text{ cm} \times 5 \text{ cm} \times 4 \text{ cm}$ , 1.4 T) was placed at the bottom of the beakers, and the SDS-coated  $\text{Fe}_3\text{O}_4$  NPs were isolated from the solutions. After about 10 min, the solutions became limpid and supernatant solutions were decanted. Finally, the pre-concentrated Hg(II) complex was eluted from the isolated particles with 1.0 mL of 1-propanol and 200  $\mu\text{L}$  of this solution was injected into the nebulizer of the ICP-OES using the six-way two-position injection valve. The injection system is schematically shown in Fig. 2.

#### 2.5. Wet digestion procedure

Wet digestion of a CRM sample (IAEA-436, Fish Homogenate) was performed using an oxi-acidic mixture. Twelve milliliters of freshly prepared mixture of the concentrated  $\text{HNO}_3\text{-H}_2\text{O}_2$  (2:1, v/v) was added to 1.0 g of the sample in a beaker that was kept for 10 min at room temperature, the content of the beaker was then heated on an electric hot plate to about  $60\text{--}70^\circ\text{C}$  for around 2–3 h until a clear, transparent digest was obtained. Finally, the solution was diluted to 950 mL using double distilled water. The solution was collected into a polyethylene flask and kept at  $-4^\circ\text{C}$  till the final analysis was performed. Blank digestion was also carried out in the same way [45].

### 3. Result and discussion

#### 3.1. Effect of pH

The pH of the sample solution plays a key role in the SPE procedure. An appropriate pH value can improve the adsorption efficiency, and also reduce interference from the matrix. The degree of the amount of adsorption that mercury as a complex collects on the adsorbent's surface is primarily influenced by the surface's electrical charge, which is influenced by the solution's pH. The effect of pH on the extraction efficiency for mercury was studied between the pH ranges of 2–7, the results are shown in Fig. 3. Based on the obtained results, the extraction efficiency of Hg, increased as the pH in the aqueous solution was increased from 2 to 3, then it decreased when the pH increased from 4 to 7. Therefore, the optimum pH was

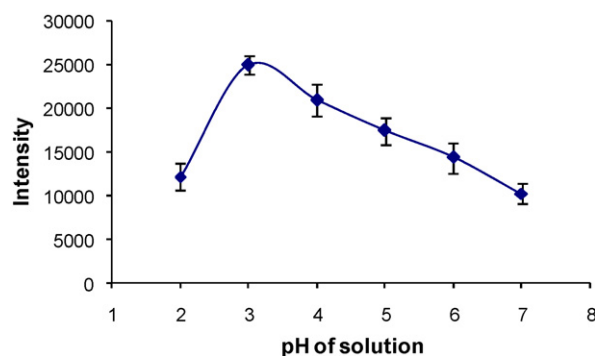


Fig. 3. Effect of sample pH on extraction efficiency. Sample volume = 500 (mL); sample's pH 3.5; concentration of mercury =  $100 \text{ ng mL}^{-1}$ ; 0.2 (mL) of  $0.001 \text{ mol L}^{-1}$  TMK solution ( $L/M=10$ ); 60 (mg)  $\text{Fe}_3\text{O}_4$  NPs; 12.5 (mg) SDS; extraction time = 10 (min); 1.0 (mL) eluent and desorption time = 5 (min).

3 for extraction of Hg(II) from the aqueous solution. Similar results were reported for extraction of Hg(II) by using TMK [7]. It is worthy to note that no precipitation of the mercury hydroxide is expected in the pH range of 4–7 [6,35].

The surface charge of bare  $\text{Fe}_3\text{O}_4$  NPs is neutral at the  $\text{pH} \approx 7.0$  ( $\text{pH}_{\text{pzc}}$ ) [33]. Below the  $\text{pH}_{\text{pzc}}$ , surface of  $\text{Fe}_3\text{O}_4$  NPs are positively charged. Under this circumstance, by increasing of the pH from 4 to 7 the positive charge density on the surface of the  $\text{Fe}_3\text{O}_4$  NPs is decreased. As a result, the physically adsorption of SDS on the surface is decreased; therefore, extraction efficiency is decreased. Thus a pH of 3 was chosen for all subsequent experiments and an acetate/acetic acid buffer was chosen for the pH adjustment.

#### 3.2. Effect of TMK amount

Chemical structure of TMK is shown in Fig. 4. TMK can form Hg–TMK complexes with stoichiometries of 2:4 [46] and 1:2 (Hg:TMK) [47]. The advantages of using TMK can be summarized as follows: (a) TMK forms selective complex with Hg(II). Also, Hg(II) gives a color complex with TMK, it is especially suitable when the detection system used is a spectrophotometer; (b) reaction between Hg(II) and TMK is extremely fast and (c) Hg(II) complex with TMK is cationic, which can easily interact with the negatively charged surfaces of the SDS-coated  $\text{Fe}_3\text{O}_4$  NPs adsorbent.

The extraction recovery as a function of TMK to Hg(II) molar ratio ( $L/M$ ) is shown in Fig. 5. As it can be seen, the recovery increases up to an  $L/M=10$  and reaches near a quantitative extraction at this molar ratio. At higher  $L/M$  ratios ( $>20$ ), the extraction recovery decreased, perhaps due to the competition of TMK and Hg(II) in their ion-pairing with SDS. So an  $L/M=20$  was chosen for subsequent experiments.

#### 3.3. Effect of SDS amount

The adsorption of surfactants on the surface of mineral oxides is a favourable process and based on the added surfactants, they can form various aggregation on the surface (hemimicelles,

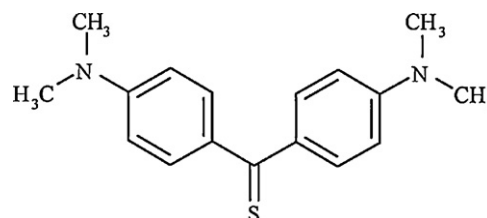


Fig. 4. Chemical structure of the Michler's thioketone.

mixed hemimicelles, and admicelles) [32,33,36]. The effect of SDS amounts on the extraction efficiency was considered in the ranges of 0–100 mg for the surfactants. Based on the obtained results, increasing the amount of SDS of up to 50 mg will cause an increase of the extraction recovery; after that, it remained constant. So 50 mg of SDS was the chosen optimum amount in order to achieve the highest possible extraction efficiency.

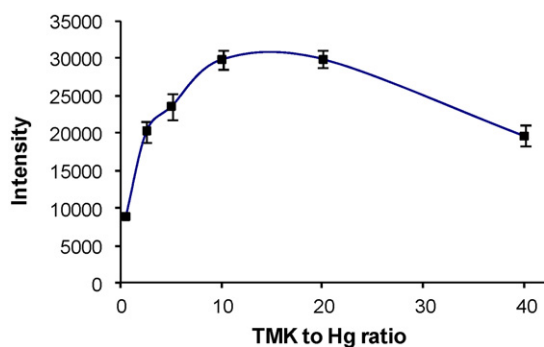
#### 3.4. Effect of the sorbent amount and extraction time

In comparison with the traditional sorbents (microsized sorbents), NPs offer a significantly higher surface area-to-volume ratio. Therefore, satisfactory results can be achieved with fewer amounts of NPs. In order to study the effect of the adsorbent, 25–125 mg of the  $\text{Fe}_3\text{O}_4$  NPs was added to 500 mL of the sample solution. The obtained results showed that by increasing the sorbent amounts from 25 up to 100 mg; due to the increasing of accessible sites, extraction recovery slowly increased than after, remained constant. So a 100 mg of the  $\text{Fe}_3\text{O}_4$  NPs was selected for all subsequent experiments.

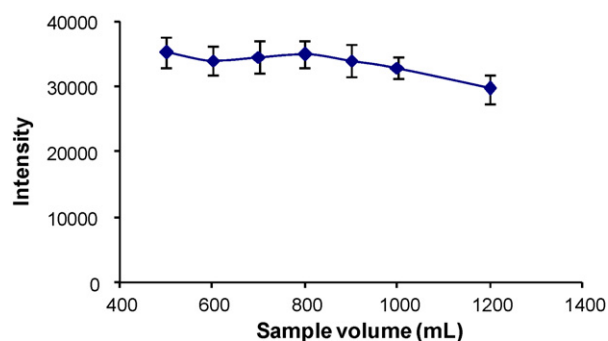
Also, the effect of the extraction time on the extraction recovery of Hg(II) was investigated. Due to the shorter diffusion route for NPs plus the magnetically assisted separation of the MNPs from the sample solutions, extraction of Hg(II) can be achieved in less time even for larger volumes of samples. The effect of the extraction time has upon extraction recovery was investigated, the findings ranged from 1 to 15 min. Results proved that extraction time has no significant effect on the extraction recovery of Hg(II) ions. Therefore, a time of 1 min was chosen as optimum value in order to obtain a shorter analysis time.

#### 3.5. Effect of eluent type

According to the reported results [32,33], adsorbed analytes on the surface of mineral oxides in the presence of a surfactant can be quantitatively eluted using organic solvents. Therefore, to find the best eluent, different organic solvents were tested. Also, the effect of eluent's pH on its desorption efficiency was investigated. Obtained results showed that as expected, the alkaline pH had a negative effect on the elution of mercury. Among the tested organic solvents propanol was found to be the superior solvent in comparison with other solvents for desorption of mercury from the surface of the SDS-coated- $\text{Fe}_3\text{O}_4$  NPs. To achieve the highest recovery of the adsorbed mercury ions, the effect of the volume of the eluent was also tested. The minimum volume of propanol required for a quantitative elution of the retained analyte complexes was 1.0 mL.



**Fig. 5.** Effect of TMK amount on extraction efficiency. Sample volume = 500 mL; sample's pH 3.0; concentration of mercury = 100 (ng mL<sup>-1</sup>); 60 (mg)  $\text{Fe}_3\text{O}_4$  NPs; 12.5 (mg) SDS; extraction time = 10 (min); 1.0 (mL) eluent and desorption time = 5 (min).



**Fig. 6.** Effect of sample volume on extraction efficiency. Sample's pH 3.0; concentration of mercury = 100 (ng mL<sup>-1</sup>); 0.4 (mL) of 0.001 (mol L<sup>-1</sup>) TMK solution ( $L/M = 20$ ); 100 (mg)  $\text{Fe}_3\text{O}_4$  NPs; 30 (mg) SDS; extraction time = 1 (min); 1.0 (mL) eluent and desorption time = 1 (min).

#### 3.6. Effect of sample volume

In order to obtain a higher enrichment factor, a larger volume of sample solution is required. Fortunately, due to the magnetically assisted separation of the adsorbent ( $\text{Fe}_3\text{O}_4$  NPs), it is possible to collect the adsorbent from larger volumes of the sample solution. Thus the extraction of 50  $\mu\text{g}$  of Hg(II) ions from different volumes of the water samples ranging from 500 to 1200 mL was investigated (Fig. 6). It was found that the best quantitative recovery (>90%) was obtained when the sample volumes were less than 1000 mL. However, the extraction efficiency would slightly decrease when the sample volumes were more than 1000 mL. Hence, a sample volume of 1000 mL was selected as the ideal volume for trace analysis of Hg(II) ions in water samples.

#### 3.7. Interference studies

To study the effect of foreign ions on the extraction efficiency of Hg(II) ions, the extraction of 100  $\mu\text{g}$  of Hg(II) ions from a 1000 mL of the sample solutions containing different concentrations of foreign ions was studied. The tolerance limits of different cations are shown in Table 2. Results showed that  $\text{Cu}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Au}^{3+}$  and  $\text{Pd}^{2+}$  can interfere in the extraction and determination of Hg(II) ions at a higher concentration levels. However, by using higher amounts of TMK ( $L/M = 20$ ) the interference effect of them on the extraction of Hg(II) was decreased. The results indicated that the complexes of  $\text{Cu}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Au}^{3+}$  and  $\text{Pd}^{2+}$  with TMK can be extracted, the findings showed that a 20-fold of  $\text{Cu}^{2+}$  and 5-fold of  $\text{Ag}^+$ ,  $\text{Au}^{3+}$  and  $\text{Pd}^{2+}$  do not reduce the extraction efficiency of Hg(II) obviously when  $L/M = 20$ .

**Table 2**  
Tolerance limit of interfering ions.

Coexisting ion	Ratio [coexisting ions]/[Hg]	Relative recovery (%)
$\text{Na}^+$	10,000	107
$\text{K}^+$	1000	108
$\text{Mg}^{2+}$	1000	109
$\text{Ca}^{2+}$	1000	92
$\text{Ba}^{2+}$	1000	103
$\text{Co}^{2+}$	1000	96
$\text{Mn}^{2+}$	1000	93
$\text{Zn}^{2+}$	1000	107
$\text{Pb}^{2+}$	1000	96
$\text{Al}^{3+}$	1000	107
$\text{Ni}^{2+}$	1000	93
$\text{Cd}^{2+}$	100	108
$\text{Cr}^{3+}$	100	98
$\text{Cu}^{2+}$	20	95
$\text{Ag}^+$	5	97
$\text{Pd}^{2+}$	5	95
$\text{Au}^{3+}$	5	94

**Table 3**

Figures of merit of the proposed method for the extraction and determination of the mercury.

Enhancement factor	Limit of detection ( $\mu\text{g L}^{-1}$ )	RSD% ( $n=6$ )		Linear range ( $\mu\text{g L}^{-1}$ )	Calibration equation	$R^2$	% Extraction
		2 ( $\mu\text{g L}^{-1}$ )	50 ( $\mu\text{g L}^{-1}$ )				
1230	0.04	5.2	4.7	0.2–100	$I = 516C + 761$	0.9996	100

On the other hand, the concentrations of the studied metal ions found in natural water samples are usually lower than the tolerance limits reported for them.

Also, some complementary experiments were done on co-extraction of organic mercury (phenyl mercury). The results showed that phenyl mercury forms a complex with TMK and can be extracted by the proposed procedure quantitatively. Therefore, the method can be used for determination of total mercury in natural and biological samples.

### 3.8. Analytical performance

The method showed a good linearity over the calibration range (0.2–100  $\text{ng mL}^{-1}$ ) and the correlation of determination ( $r^2$ ) was higher than 0.999. The limit of detection (LOD = 0.04  $\text{ng mL}^{-1}$ ) was calculated as  $3S_b/m$  ( $S_b$ , standard deviation of the blank signals and  $m$ , slope of calibration curve after preconcentration). The results are summarized in Table 3. An enhancement factor of 1230 was calculated as the ratio between the slopes of the calibration curve submitted by the SPE procedure (for  $V = 1000$  mL) and the direct calibration curve (without preconcentration). The relative standard deviation (R.S.D.) for the determination of 2 and 50  $\text{ng mL}^{-1}$  of Hg(II) was 5.2 and 4.7% ( $n=6$ ), respectively. Also, the extraction recovery was complete. The overall time required for the extraction and determination of Hg(II) ions in a 1000 mL of the solution was approximately 13.5 min (1 min, for extraction; 10 min for the magnetic separation of the adsorbent; 1.0 min for the eluting of Hg(II) ions from the adsorbent; 1.0 min for the magnetic separation of the adsorbent from the eluent then another 0.5 min for the injection of the preconcentrated phase into ICP-OES). Thus, under these conditions the proposed method has an output of approximately 4 samples per hour.

### 3.9. Analysis of mercury content in real sample

The proposed method was applied for the determination of Hg(II) ions in tap, well and mineral water samples. The standard addition method was applied to 1000 mL of each sample. Hg(II) was not detected in the samples. Therefore, known amounts of Hg(II) (2 and 10  $\text{ng mL}^{-1}$ ) were added to each sample for testing the accuracy of the method. Table 4 shows that obtained relative recoveries of Hg(II) ions from the water samples for the spiked levels of 2 and

**Table 4**

Determination of mercury in different water samples by applying the proposed method.

Sample <sup>a</sup>	Added ( $\text{ng mL}^{-1}$ )	Found ( $\text{ng mL}^{-1}$ ) <sup>b</sup>	Relative recovery (%)
Tap water	2.00	$1.93 \pm 0.09$	95
	10.00	$9.78 \pm 0.35$	97
Well water	2.00	$1.86 \pm 0.05$	95
	10.00	$10.34 \pm 0.45$	103
Mineral water 1	2.00	$2.13 \pm 0.21$	105
	10.00	$9.92 \pm 0.15$	99
Mineral water 2	2.00	$1.82 \pm 0.35$	90
	10.00	$9.67 \pm 0.62$	96

<sup>a</sup> Determination of copper in seawater was performed using standard addition method.

<sup>b</sup> Mean  $\pm$  SD ( $n=3$ )

10  $\text{ng mL}^{-1}$  are in the acceptable ranges (95–103%).

Also, the proposed method was validated by analyzing a certified reference material IAEA-436 (Tuna fish flesh homogenate, AQC) after digestion by the method mentioned. Concentration of inorganic mercury in IAEA-436 was found to be  $4.0 \pm 0.3 \mu\text{g g}^{-1}$  which is commensurate with the certified value of  $4.19 \pm 0.36 \mu\text{g g}^{-1}$  for total mercury.

### 3.10. Comparison of the proposed method with other methods

The proposed method was compared with a variety of methods reported recently in the literature for the preconcentration and determination of Hg(II) ions. The distinct features of the proposed method are summarized in Table 5. As can be seen from Table 5, it is evident that the preconcentration factor obtained with the SDS-coated  $\text{Fe}_3\text{O}_4$  NPs is very high in comparison with other methods. Large dynamic linear range, and low LOD and RSD are the other significant features of the method which are comparable to or even better than some of them which use very sensitive detection method such as ICP-MS or CV-AAS. Also, there are several disadvantages associated with the use of AAS as a detection method; these arise from the limited dynamic linear range and spectral interference from non-specific background absorption of volatile organic species [21]. On the other hand, ICP-MS can be used

**Table 5**

Comparison of the proposed method with some of the methods reported in the literature for extraction and determination of mercury.

System	Analytical technique	EF	DLR <sup>a</sup>	LOD <sup>b</sup>	R.S.D.%	Ref.
Modified silica-coated magnetic nanoparticles	SPE-ICP-MS	427	c	$1.1 \times 10^{-3}$	8.3	[6]
Hg-TMK complex and ionic liquid	CIAME-UV-Vis <sup>d</sup>	35	Up to 150	0.3	1.3	[7]
Hg-CDA complex and ionic liquid	LLE-CV-AAS	c	10–120	0.01	1.2	[8]
Agar powder modified with 2-mercaptobenzimidazole	SPE-CV-AAS	c	0.04–2.4	0.02	<2.6	[9]
In situ alkylation with sodium tetraethyl borate	SBSE-TD-GC-MS <sup>e</sup>	50	0.5–10	0.2	<8.8	[10]
[Hg(II)-(5-Br-PADAP)] complex	CPE-FI-CV-ICP-OES	200	Up to 50	0.004	3.4	[11]
Diphenylcarbazone-functionalized silica gel	SPE-FI-UV-vis	500	1–1500	0.9	3.0	[14]
Hg-TMK complex	CPE-UV-vis	33	5.0–80	0.8	0.3	[15]
Hg-TMK complex	SPE-ICP-OES	1230	0.2–100	0.04	<5.0	This work

<sup>a</sup> Dynamic linear range ( $\text{ng mL}^{-1}$ ).

<sup>b</sup> Limit of detection ( $\text{ng mL}^{-1}$ ).

<sup>c</sup> Data not available.

<sup>d</sup> Cold-induced aggregation microextraction.

<sup>e</sup> Stir bar sorptive extraction

for the determination of mercury due to its high sensitivity, selectivity, and also because of the high sample throughput. But, the cost of instrumentation may be prohibitive to many laboratories, besides it is not free from interferences effects, specifically spectroscopic interferences and matrix effects [6]. The results indicate that SPE procedures based on SDS or other surfactants coated Fe<sub>3</sub>O<sub>4</sub> NPs adsorbents can be used as an efficient, simple and fast technique for the preconcentration of Hg(II) ions and/or other metal ions by same procedure.

#### 4. Conclusions

A new magnetic adsorbent of the SDS-coated Fe<sub>3</sub>O<sub>4</sub> NPs was prepared and applied for preconcentration and determination of Hg(II) ions from water samples by using an SPE-FI-ICP-OES setup. The proposed method offers a simple, sensitive, and inexpensive method for extraction and determination of Hg(II). Furthermore, Hg(II) was quantitatively extracted and an enhancement factor of 1230-fold was obtained. The results demonstrated that the method is very suitable for the rapid extraction of Hg(II) ions from large volumes of water samples at ppb levels besides having both good accuracy and precision. Also, sensitivity of the method is enough for the determination of Hg(II) in variety of environmental samples. The proposed method can be a guideline for the extraction of other metal ions from large volumes of environmental samples.

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