

A nanomagnetic and 3-mercaptopropyl-functionalized silica powder for dispersive solid phase extraction of Hg(II) prior to its determination by continuous-flow cold vapor AAS

Hamid Reza Sobhi¹ · Mahnaz Ghambarian² · Ali Esrafil^{3,4} · Mohammad Behbahani⁵

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Abstract The authors describe a method for the trace determination of Hg(II) in human fluids using magnetic dispersive solid phase extraction. A silica powder magnetized with Fe₃O₄ nanoparticles was functionalized with 3-mercaptopropyl groups, and the resulting sorbent was characterized by scanning electron microscopy, energy dispersive X-ray, X-ray diffraction, vibrating sample magnetometry and FTIR. Following microwave-assisted digestion of the sorbent, mercury was quantified by continuous-flow CV-AAS. Factors affecting the sorption and desorption of Hg(II) were optimized. The calibration plot is linear in the 0.2–50.0 µg L⁻¹ Hg(II) concentration range. The accuracy in real sample analysis is in the range from 87 to 114%, and precision varies between 2.4 and 8.9%. The method was successfully applied to the determination of low levels of Hg(II) in plasma, urine and saliva.

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✉ Ali Esrafil
ali.esrafil@gmail.com

¹ Department of Chemistry, Payame Noor University, Tehran, Iran

² Iranian Research and Development Center for Chemical Industries, ACECR, Tehran, Iran

³ Research Center for Environmental Health Technology, Iran University of Medical Sciences, Tehran, Iran

⁴ Department of Environmental Health Engineering, School of Public Health, Iran University of Medical Sciences, Tehran, Iran

⁵ Research Center for Environmental Determinants of Health (RCEDH), Kermanshah University of Medical Sciences, Kermanshah, Iran

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Introduction

Mercury is widely distributed in nature, circulating among several media, and is found in different states and chemical forms, exhibiting various degrees of toxicity. Mercury has also been considered as a human health hazard because it may cause kidney toxicity, neurological damage, paralysis, chromosome breakage, and birth defects [1, 2]. Therefore, efficient assessment of suspected mercury intoxication through determination of mercury levels in various human fluid matrices, particularly blood, saliva and urine, is vitally important [3–6].

The most frequently used procedures for the extraction of mercury from biological samples are based on ultrasound or microwave assisted alkaline or acidic leaching. Ultrasound- and microwave assisted extractions have gained strength, since they offer enhanced sample throughput and require lower amounts of the reagents [6–14].

To date, several methods such as liquid extraction [15], column packed solid-phase extraction (SPE) [16] and magnetic solid-phase extraction (MSPE) [17] have been extensively applied for the separation of mercury from wide variety of media. Among these methods, MSPE appears to be one of the most effective selections owing to its ease of automation, high extraction efficiency and rapid phase separation [18–23].

Several analytical instruments have been used to detect concentration of mercury. These include: chromatographic methods such as gas chromatography (GC) [24] and liquid chromatography (LC) [15], and predominately non-chromatographic methods such as graphite furnace atomic absorption spectrometer (GF-AAS) [8], inductively coupled

plasma-mass spectrometry (ICP-MS) [3] and cold vapor atomic absorption spectrometry (CV-AAS) [24, 25]. CV-AAS is widely applied and preferred over the formers due to its high sensitivity, simplicity and relatively low cost determination [26]. It should be noted that electrochemical method can be used for detection of mercury ions [27].

Hg(II) has been determined in various human fluid samples [3, 16, 24]. We have applied a nanomagnetic silica-based thiol-functionalized sorbent for solid phase extraction for CV-AAS measurement of Hg(II) concentration in human fluid samples. The nano magnetic silica-based powder was functionalized with 3-mercaptopropyl and the resulting sorbent was characterized by scanning electron microscopy, energy dispersive X-ray, X-ray diffraction, vibrating sample magnetometer and Fourier transform Infra-red techniques. Finally, the introduced method was successfully applied for determination of low levels of Hg(II) in various human fluids such as plasma, urine and saliva samples.

Experimental

Chemicals

3-Mercaptopropyltrimethoxysilane (3-MPTS) was purchased from Aldrich Company. Hg (NO₃)₂·H₂O, FeCl₂·4H₂O, FeCl₃·6H₂O, Sodium silicate (Na₂SiO₃), Sodium hydroxide (NaOH), Phosphoric acid, Nitric acid (HNO₃), Hydrogen peroxide (H₂O₂), Sodium borohydride (NaBH₄) and Hydrochloric acid (HCl) were all supplied from Merck (Darmstadt, Germany, www.merck.de). Double distilled water was used throughout for the preparation of all aqueous solutions. Other reagents used in this study were of analytical grade. Argon (99.99%) was used as the carrier gas. Working aqueous standards were prepared from a stock solution of 10 mg L⁻¹ Hg(II) prepared in 0.1 mol L⁻¹ HNO₃. Calibrators were prepared at Hg(II) concentrations of 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, 20.0 and 50.0 µg L⁻¹ by dilution with water (aqueous calibrators) or spiking into the pooled lot of blank plasma, saliva or urine (matrix matched calibrators) from the non-exposed volunteers. Of the calibrators, three concentrations (0.5, 2.0 and 5.0 µg L⁻¹) were used as quality controls (QC).

Instruments

A Perkin Elmer AAnalyst 700 (Norwalk, CT, USA) atomic absorption spectrometer equipped with MHS-15 mercury/hydride System was used in this study. A hollow cathode lamp operating at 6 mA was used and a spectral bandwidth of 0.7 nm was selected to isolate the 253.7 nm mercury line. A domestic microwave oven was also employed for total digestion of the fluid samples.

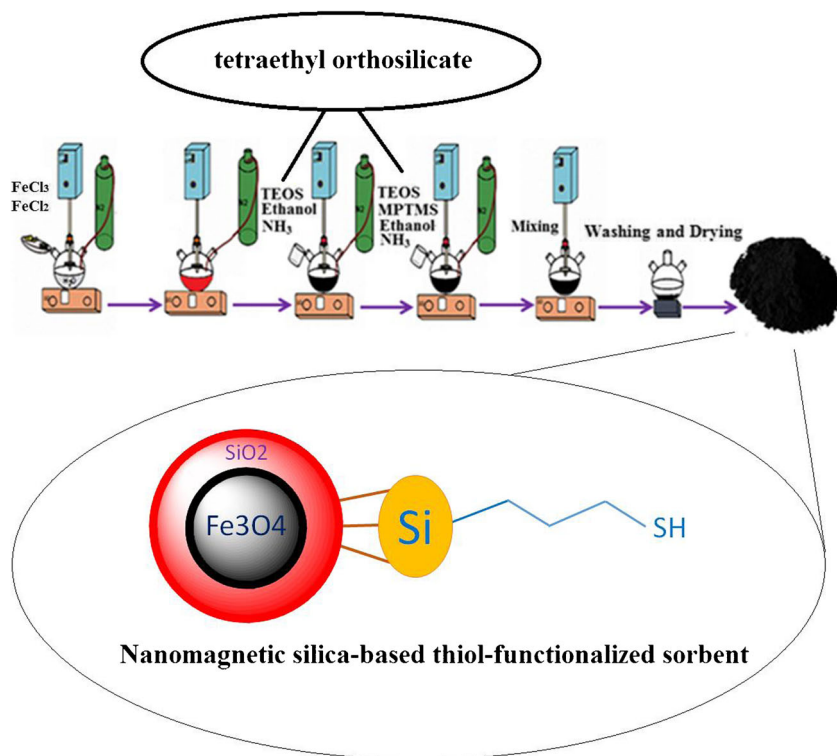
For characterization of the functional groups on the surface of the samples, fourier transform infrared spectroscopy (FT-IR) spectra were recorded using a Perkin-Elmer (Germany) spectrometer under dry air at room temperature by the KBr pellets method. The spectra were collected over the range from 400 to 4000 cm⁻¹. The X-ray diffraction (XRD) studies were performed with a Philips XRD instrument (Siemens D-5000, Germany) using Cu Kα radiation (λ = 1.5406 Å) at wide-angle range (2θ value 4–80°) at 40 kV of accelerating voltage and at 30 mA of emission current. The surface morphology of Fe₃O₄ and TF-SCMNPs nanoparticles was obtained studied by a field emission scanning electron microscopy (Mira3, Tescan, Czech Republic). The SEM images were further supported by energy dispersive X-ray (EDX) to provide direct evidence for the purity, existence and distribution of specific elements in a solid sample. The magnetic property of nanoparticles was characterized by vibrating Sample Magnetometer (VSM, MDKFD, Iran).

Sample preparation and analytical procedure

Plasma samples were taken from non-exposed volunteers and placed in 10 mL tubes containing citrate and immediately centrifuged (1850×g, 4 °C, 10 min) upon their arrivals. The resulting supernatants were transferred into polypropylene tubes and kept at -20 °C until the time of analysis. Saliva and urine samples were also collected from non-exposed volunteers and kept at -20 °C and 4 °C, respectively. All mentioned-above fluid samples were rapidly thawed in a water bath and immediately kept on ice and used as blank (later reconfirmed to be mercury free) or spiked with Hg(II) solution, unless mentioned otherwise. A microwave assisted acid digestion procedure was carried out to obtain Hg(II) which as follows:

An aliquot of 1.0 mL of each sample was transferred to a Teflon cup of acid digestion bomb. Nitric acid (65% w/v, 4.0 mL) and hydrogen peroxide (30% v/v, 1.0 mL) were added. The digestion bomb flask was closed and placed at room temperature for 10 min. The flasks were closed and submitted to the microwave for 3 min at 650 W. The digested samples were then transferred to a 50 ml of volumetric flask and volume was made up with 0.1 mol L⁻¹ HCl. Firstly, 80 mg of the nanomagnetic sorbent was dispersed into 50 mL of the fluid samples for 10 min at room temperature followed by the addition of the phosphate buffer (pH 6.0, 0.2 mol L⁻¹) to achieve pH 6.0. Secondly, the resulting mixture was vortexed vigorously for 5 min. Then, the nanomagnetic sorbent was separated from the solution by using a magnet and washed three times with double-distilled water. Finally, 3 mL of the eluent containing HCl 1 M and 5% (w/v) thiourea was added to the solution to remove Hg(II) from the nanomagnetic sorbent followed by its measurement by CVAAS. Sodium borohydride was used as the reducing agent in the determination of mercury. The solution was freshly prepared containing 0.3% NaBH₄ in 0.5%

Fig. 1 Schemes of TF-SCMNP preparation



NaOH. The hydrochloric acid solution (3 mol L^{-1}) was prepared by adequate dilution of the concentrated HCl. The analytical measurement was based on peak height. Reading time and argon flow rate were 10 s and 50 mL min^{-1} , respectively.

Synthesis of the nanomagnetic silica-based thiol-functionalized sorbent

The Fe_3O_4 nanoparticles were prepared using the coprecipitation method described in previous works. The appropriate amount of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were

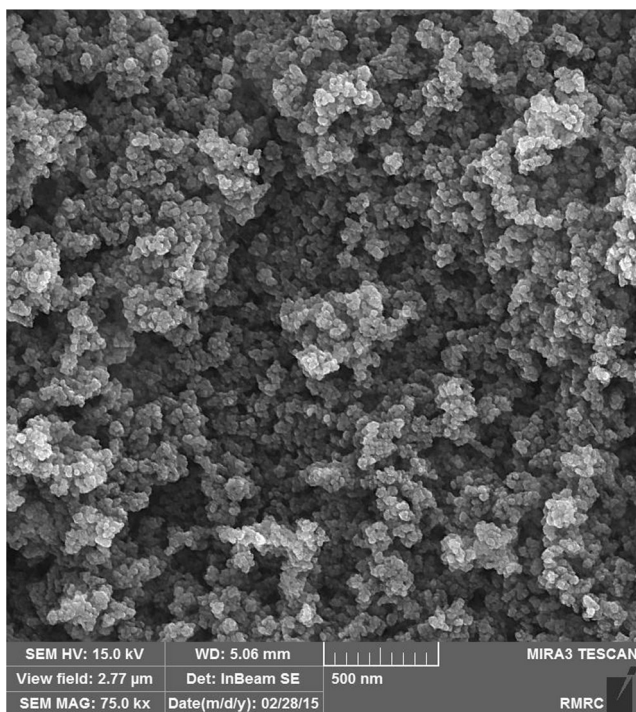


Fig. 2 SEM image of TF-SCMNP

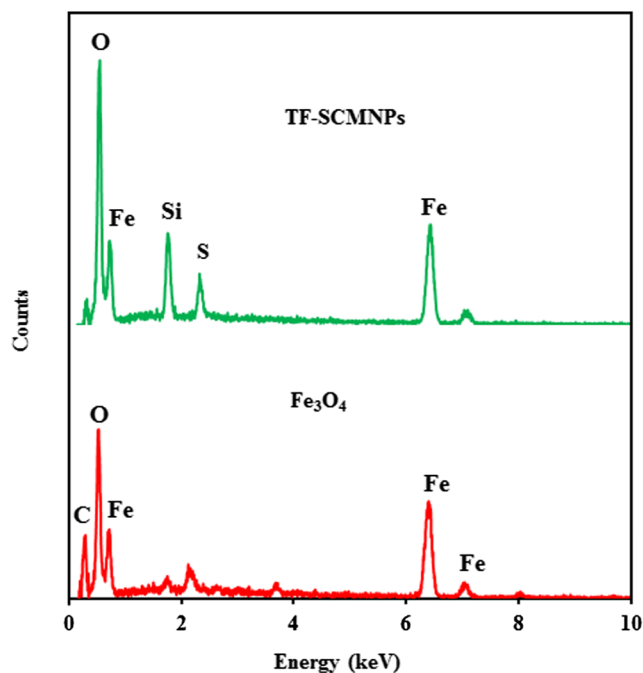


Fig. 3 EDX image of sorbent

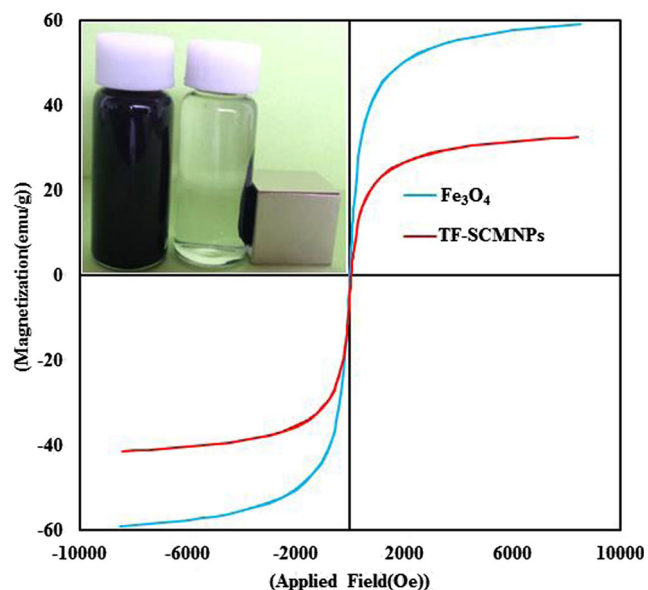


Fig. 4 VSM analysis of sorbent

dissolved in 200 mL deionized water. NH_4OH 25% (25 mL) was added drop-wise to the precursor solution to obtain an alkaline medium ($\text{pH} = 8$) producing a black and gelatinous precipitate of Fe_3O_4 nanoparticles under nitrogen gas. It was heated at 80°C for 2 h with continuous stirring. The desired Fe_3O_4 nanoparticles was collected by a permanent magnet and then washed with deionized water and ethanol for five times and dried at 80°C in vacuum for 5 h. Then, appropriate amount of the TEOS (Tetraethyl orthosilicate), ethanol and NH_3 were added to the previous stage to obtain $\text{Fe}_3\text{O}_4@\text{SiO}_2$ under nitrogen gas while agitating for 2 h. Meanwhile, According to the Pearson's hard soft acid–base theory (HSAB) mercury is classified as a soft acid, which tends to form very strong bonds with soft Lewis base groups, such as $-\text{CN}$, $-\text{RS}$, and $-\text{SH}$ [14]. Therefore, 3-MPTS as a common silanizing reagent was chosen to modify $\text{Fe}_3\text{O}_4@\text{SiO}_2$ to obtain a mercaptopropyl functionalized sorbents ($\text{Fe}_3\text{O}_4@\text{SiO}_2-\text{SH}$) for the extraction of mercury

Table 1 Effect of interfering ions on the recovery of Hg(II) in water sample

Ion	Ion/Hg ratio	Recovery \pm sd* ($n = 3$)
K^+	1000	97.2 ± 3.8
Na^+	1000	96.8 ± 4.2
Mg^{2+}	1000	104.1 ± 4.9
Ca^{2+}	1000	98.2 ± 3.3
Cl^-	1000	102.7 ± 3.5
F^-	1000	103.7 ± 4.4
CO_3^{2-}	1000	97.1 ± 4.1

*(standard deviation)

from human fluid solutions. Thiol-function nanoparticles were prepared by appropriate addition of the MPTMS, TEOS, ethanol and NH_3 to the latter stage under nitrogen gas and agitation for 24 h. The obtained thiol-functionalized nanoparticles was collected by a permanent magnet and then washed with deionized water and ethanol for five times. Then it was dried at 80°C in vacuum for 5 h. The procedure of synthesis of functionalized nanoparticles (TF-SCMNPs) is summarized in Fig. 1.

Results and discussion

Characterization of the sorbent

The information regarding the FT-IR and XRD of the synthesized sorbent was presented in the [electronic supplementary materials](#).

SEM images of TF-SCMNPs nanoparticles are shown in Fig. 2. As can be seen, the average size of TF-SCMNPs from SEM image was around 10 nm. EDX microanalysis was used to characterize the elemental composition of the Fe_3O_4 and TF-SCMNPs nanoparticles. EDX pattern of the Fe_3O_4 and TF-SCMNPs nanoparticles are depicted in Fig. 3. According to the EDX analysis, the major elements were Fe (57.63%), O (29.18%), Si (5.88%), and S (3.15%) indicating good hybridization thiol-functionalized silica-coated magnetite nanoparticles. VSM was used to measure magnetite property of Fe_3O_4 and TF-SCMNPs. The VSM magnetization curve of the Fe_3O_4 and TF-SCMNPs nanoparticles at room temperature is depicted in Fig. 4. The saturated magnetization value of Fe_3O_4 and TF-SCMNPs nanoparticles were determined 58.97 and 32.43 $\text{emu}\cdot\text{g}^{-1}$, respectively. These results also indicates that the TF-SCMNPs nanoparticles showed an excellent magnetic response to a magnetic field. Therefore, it can be separated rapidly due to this high magnetic sensitivity.

Optimization of extraction parameters

It is evident that the extraction of Hg(II) ions using the nanomagnetic sorbent is strongly affected by some conditions such as pH of sample solution, the type of eluent and its concentration, amounts of sorbent, and the selectivity of method. Therefore, these parameters should be optimized before using the sorbent for measurement of Hg(II) in real fluid samples. It is noted that the aqueous calibrator of $1.0\ \mu\text{g}\ \text{L}^{-1}$ was used for all experiments regarding the optimization process. The interaction can be described by the following chemical reactions long known from alkyl thiols:

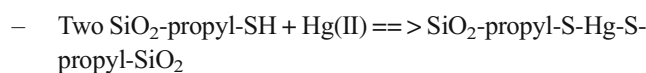


Table 2 A comparison between the method and previously published articles

Applied sorbent	Applied method	LOD ($\mu\text{g L}^{-1}$)	RSD (%)	Reference
$\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{AMPTs}$	CV-AAS	0.017	2.4	23
$\text{Fe}_3\text{O}_4@\text{SnO}_2$ yolk-shell	CV-AAS	0.03	---	28
rGO-SEP	ASV	0.14	3.4	29
DPC-doping magnetic nanoparticles	CV-AAS	0.16	2.2	30
AC-ATSC	ICP-OES	0.12	4	31
Nanomagnetic silica-based thiol-functionalized sorbent	CV-AAS	0.06	2.4	This work

The following parameters were optimized: (a) Sample pH value; (b) Eluent; and (c) Sorbent amount. Respective data and Figures are given in the [Electronic Supporting Material](#) [section 3.2.1; 3.2.2 and 3.2.3]. It was found that the following experimental conditions yielded the best results: (a) A sample pH value of 6.0; (b) 5 mL of 1.0 M HCl containing 5 w/w % thiourea as the elution solvent; and (c) 80 mg of the sorbent.

The effect of potentially interfering ions

To evaluate the selectivity of the method, the influence of several ions - predominantly present in human fluids - such as K^+ , Na^+ , Mg^{2+} , Ca^{2+} , Cl^- , F^- and CO_3^{2-} on the extraction and measurement of Hg(II) was studied. The aqueous solutions containing Hg(II) at $1.0 \mu\text{g L}^{-1}$ and the above-mentioned ions at various concentrations were monitored. By definition, the effect of an ion is considered significant when its presence causes a variation greater than 5% in the value of the analytical response. Accordingly, no significant interference was observed due to the presence of the above-mentioned ions (Table 1).

Method validation

For validation of the method, the following parameters were determined: linearity range, intra- and inter assay precision, accuracy, recovery and limit of quantification (LOQ). It is

noted that in all validation tests to come the calibrators (as described in section 2.3.1.) were used.

Linear range and determination of LOQ

The calibration curves (eight calibrators in duplicate) were fairly linear over the concentration ranges listed in Table 1S (ESM) for each fluid sample. The correlation coefficients were found to be greater than 0.98 within the mentioned concentration ranges.

The LOQ was measured based on the following definition: the lowest concentration at which the accuracy fell between 85% and 115% and the precision had a value of $\leq 10\%$ under five measurements. Accordingly, the LOQs were determined to be 0.2, 0.3, $0.4 \mu\text{g L}^{-1}$ for urine, saliva and plasma samples, respectively.

The analytical figure of merits for the method and previously published articles is presented in the Table 2 [23, 28–31].

Precision and accuracy

Accuracy (measured value/nominal value $\times 100$) and precision (coefficient of variation, C.V.: standard deviation of measured values/mean measured values $\times 100$) were determined for the QC samples (Table 3). Intra-day precision (%) and accuracy (%) were evaluated by extracting

Table 3 Values determined of mean recovery, accuracy and precision of the method

	concentration	Recovery (%) ($n = 5$)	Intra-day Precision ($n = 5$) (%)	Inter-day Precision ($n = 3 \times 3$) (%)	Intra-day Accuracy ($n = 5$) (%)
Urine	0.5	90	6.3	7.2	105
	2	93	5	9.1	103
	5	97	2.4	5.2	98
saliva	0.5	84	7.8	8.1	90
	2	89	5.8	6.9	94
	5	91	4.5	4.1	106
plasma	0.5	78	8.9	12.8	87
	2	85	7.4	8.3	114
	5	87	6.8	5.9	109

Table 4 Results for the analysis of the fluid samples ($n = 5$)

	Hg(II) added *	found*
urine	0.00	N.D.*
	1.00	1.12 ± 0.05
	2.00	1.92 ± 0.06
saliva 1	0.00	N.D.
	1.00	0.92 ± 0.05
	2.00	1.94 ± 0.05
saliva 2	0.00	N.D.
	1.00	0.90 ± 0.08
	2.00	1.87 ± 0.08
plasma	0.00	N.D.
	1.00	1.13 ± 0.09
	2.00	2.22 ± 0.07

*($\mu\text{g L}^{-1}$)

nd not detected

saliva 1: no dental feeling

saliva 2: with dental feeling

and analyzing the fluid samples at three QC levels (0.5, 2.0 and $5.0 \mu\text{g L}^{-1}$) five times each. Inter-day precision was evaluated by analyzing the QC levels 3 times each over three consecutive days. As can be seen in Table 3, the precision and accuracy of the method is relatively good for all fluid samples except for the plasma due to its highly complicated matrix.

Recovery

Mean recoveries were evaluated by spiking Hg(II) into the blank fluid samples to the QC levels five times each and by measuring the Hg(II) concentrations before and after the spiking. The results shown in Table 3 indicate that the more the fluid's medium is complicated, the less the extraction recovery will be.

Application to real sample analysis

In order to investigate the accuracy and applicability of the optimized method in real analysis, the concentration of Hg(II) was measured in human fluid samples such as plasma, urine and saliva. The plasma and urine samples were taken from our lab's colleagues. Various saliva samples were taken from both individual volunteers who have/not had mercury amalgam dental fillings. All above-mentioned samples underwent the same optimized sample preparation as discussed earlier in section "Sample preparation and analytical procedure". As can be deduced from the analytical results shown in Table 4., the method fulfills the necessary criteria for the measurement of Hg(II) in selected human fluids.

Conclusion

A simple dispersive solid-phase extraction method was successfully employed for validation and measurement of Hg(II) in human fluids by using a nanomagnetic silica-based thiol-functionalized sorbent. The sorbent was characterized and proved to be highly efficient for adsorption of mercury. Having been undergone the microwave digestion treatment, the fluid samples were introduced to a continuous-flow cold vapor atomic absorption spectrometer for final measurement of Hg(II). Once the method of analysis was optimized, it was validated by investigating various analytical parameters such as accuracy, precision, extraction recovery and limits of quantification. Finally, the method was successfully applied for determination of low levels of Hg(II) in various human fluids such as plasma, urine and saliva. Other heavy metals such as silver, lead, Bi and Cd also to be bound by the sorbent. It should be noted that, the mentioned metal ions will not interfere here because CVAAS and borohydride reduction are applied.

Compliance with ethical standards The author(s) declare that they have no competing interests.

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