Enhanced spectrophotometric detection of Hg in water samples by surface plasmon resonance of Au nanoparticles after preconcentration with vortex-assisted liquid-liquid microextraction

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ABSTRACT

This article presents an efficient, simple, and cost-effective method for the determination of trace amounts of Hg by vortex-assisted liquid-liquid microextraction (VALLME) coupled to microvolume UV–Vis spectrophotometry. This method correlates changes in the intensity of localized surface plasmon resonance (LSPR) of tetraoctylammonium bromide (TOABr) coated Au nanoparticles (NPs) after interaction with Hg^{2+} ion. Spectroscopic measurements of the TOABr-coated Au NPs phase with particular absorption properties (strong and well-defined absorption bands) after analyte extraction by VALLME, provide an accurate and sensitive determination of Hg in water samples, comparable with measurements obtained by atomic absorption spectrometry (AAS). Different variables including sample volume, extraction time, and TOABr-coated Au NPs dispersion volume were carefully studied; final experimental conditions were 5 mL, 120 μL and 5 min respectively. The limit of detection (LOD) was 0.8 ng mL^{-1}. The calibration curve was linear at concentrations between the limit of quantification (LOQ) (4.9 ng mL^{-1}) and up to at least 120 ng mL^{-1} of Hg. The relative standard deviation for six replicate determinations of 20 ng mL^{-1} of Hg was 4.7%. This method exhibited an excellent analytical performance in terms of selectivity and sensitivity and it was finally applied for Hg determination in spiked tap and mineral water samples.

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1. Introduction

Mercury is identified as one of the most toxic elements because of its accumulative and persistent occurrence in the environment and living organisms [1]. Mercury has no beneficial biological function, and its presence in living organisms is associated to cancer, birth defects, and other undesirable outcomes [2]. The incorporation of Hg into the human body comes mainly from drinking water [3]. Therefore, the routine monitoring and controlling of this toxic element have become increasingly important, especially to assure drinking water quality. Accordingly, The World Health Organization (WHO) has set the guideline value for inorganic mercury in drinking water at 6 ng mL^{-1} [4]. Therefore, highly sensitive and selective analytical techniques are required for accurate determination of Hg in water samples. In past years, continuous progress in the improvement of analytical instrumentation including atomic absorption spectrometry (AAS), atomic

fluorescence spectrometry (AFS), inductively coupled plasma-optical emission spectrometry (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS) have been performed [5]; however, the operation cost and robustness of such instrumentation are still challenging to some routine analytical laboratories.

In recent years, nanoparticles (NPs) have attracted substantial interest in the analytical field because of their fascinating properties [6–9]. The high surface to volume ratio, the possibility of surface functionalization, and the optical properties of nanomaterials provide the required flexibility for a broad range of analytical applications [10–12]. Sensing approaches based on optical properties of metal NPs have received considerable attention due to their extreme simplicity and low cost since the method of detection does not require any expensive or complex instrumentation [13–15]. Particularly, the optical plasmon properties of Au NPs are one of the most remarkable features [13,16,17]. This phenomenon occurs when the frequency of collective oscillation of electrons, arising from metallic nanostructures (i.e.; metal NPs), matches that of the incident electromagnetic radiation. Consequently, a strong absorption band or increased scattering intensity of the radiation takes place at certain wavelengths for Au NPs [13,18]. As a result of the inherent optical properties, the spectrum in the visible

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region of Au NPs may suffer changes when they are aggregated [13]. Thus, chemical interaction between the analyte and the NPs surroundings may cause changes in the absorbance spectrum indicating the presence and concentration of the analyte. Moreover, surface modification with functional groups grafted on the NPs surface could provide extra selectivity when NPs are used as separation media [9]. For example, recent progress in DNAzymes/DNA molecules functionalized nanostructured biosensors for heavy metal detection was recently reviewed by Zhou et al. [19]. On the other hand, the search for alternatives to conventional extracting solvents in miniaturized techniques based on liquid-liquid microextraction (LLME) is a current topic. Conventional solvents in LLME could lead to low efficiency and time consuming extraction process [20]. Therefore, other extractant phases are subject of recent investigation [21]. The combination of LLME with NPs dispersed in organic solvents could result into a very attractive extraction phase for trace elements preconcentration [21]. Moreover, Au NPs dispersed in organic solvents used for LLME may result in an efficient approach for spectrophotometric determination of trace elements. Furthermore, the introduction of vortex agitation to enhance the efficiency of microextraction is a strategy with several advantages over other methods aimed to dispersion of an extraction phase, like ultrasound irradiation o the use of a dispersion agent [22,23]. The dispersion formed under vortex-mixing is thermodynamically unstable, thus, the extraction phase can be separated without difficulty [22].

Several works based on the implementation of magnetic NPs for microextraction procedures have been reported in the last years [24–29]. Magnetic nanomaterials have the additional advantage that their separation from the sample it is achieved by a magnetic field, thus eliminating centrifugation steps [24]. Magnetite (Fe_3O_4) NPs has received extensive attentions among other magnetic nanomaterials, due to the feasibility of preparation and excellent magnetic properties. However, a silica protection layer is required to ensure its chemical stability and improve their dispersability in microextraction sytems [30,31]. Additionally, magnetic NPs have been used in extraction methods mainly for organic analytes and not much for inorganic ones, most probably due to possible interference caused by Fe on trace metal determination. On the other hand, Au NPs have several advantages for metal determination such as well-defined structure, facile preparation, self-assembly capability for a wide range of functionalization procedures, as well as the suitable stability and reusability [28].

In this work, a novel analytical method for trace Hg determination based on the changes caused by this analyte on the localized surface plasmon resonance (LSPR) of organic coated Au NPs combined with vortex-assisted liquid-liquid microextraction (VALLME) was developed. The interaction of Hg^{2+} ion with tetraoctylammonium bromide (TOABr) coated Au NPs was the principle for Hg preconcentration. Plasmon changes were determined by UV–Vis spectrophotometry by means of a micro-volume quartz cell. Finally, the proposed methodology was applied for trace Hg determination in drinking water samples. To the best of our knowledge, Au NPs in combination with VALLME technique prior to spectrophotometry determination of Hg has not yet been proposed. Moreover, this methodology represents a simple, sensitive, and cost-effective alternative for Hg determination at trace levels in water samples.

2. Experimental

2.1. Instrumentation

UV–Vis measurements were acquired on a UV–Vis Perkin Elmer Lambda 35™ Spectrophotometer (Norwalk, CT, USA) in a wavelength range between 300 and 900 nm with a spectral band pass of 0.7 nm. The spectral scanning speed was 480 nm min^{-1}. An ultra-micro spectroscopy cell of Quartz SUPRASIL® with PTFE Lid (PerkinElmer) was used. The light path of the cell was: 10 mm. The filling and chamber volume of the cell were 50 μL and 30 μL, respectively.

A centrifuge (Luguimac, Buenos Aires, Argentina) model LC-15 was used to accelerate the phase separation process. A vortex model Bio Vortex V1 (Boeco, Hamburg, Germany) was used for VALLME.

2.2. Reagents

A 1000 μg mL^{-1} Hg stock solution was prepared from mercury(II) chloride (Merck, Darmstadt, Germany) in 0.1 mol L^{-1} HNO$_3$ (Ultrex® II Mallinckrodt Baker, Phillipsburg, NJ, USA). Lower concentrations were prepared by diluting the stock solution with 0.1 mol L^{-1} HNO$_3$. Acid concentration in the samples and standards was adjusted with HCl (Ultrex® II Mallinckrodt Baker, Phillipsburg, NJ, USA). Ultrapure water (18 MΩ cm) was obtained from a Millipore Continental Water System (Bedford, MA, USA). The reagents used for the synthesis of TOABr-coated Au NPs were as follows: HAuCl$_4$ (99%), Sodium borohydride NaBH$_4$ (99%), tetraoctylammonium bromide Oct$_4$NBr (99%), toluene (99.9%) Plus for HPLC, all purchased from Aldrich (Milwaukee, WI, USA). All reagents were of analytical grade and the presence of Hg was not detected within the working range.

2.3. Synthesis and characterization of TOABr-coated Au NPs

The TOABr-coated Au NPs were synthesized according to the procedure described in previous works [18,32]. Briefly, 0.71 mL of 25 mM HAuCl$_4$ was dissolved in 25 mL of water and 0.012 g of TOABr was dissolved in 50 mL of toluene. The two solutions were combined and stirred until all of AuCl$_4^-$ was transferred into the toluene phase. The solution turned into a dark wine red color after a 10-fold excess of NaBH$_4$ was added to the toluene solution with stirring. All reactions were conducted at ambient conditions. The TOABr-coated Au NPs prepared by this procedure exhibited a size of 4.39 ± 1.25 nm according to transmission electron microscopy (TEM). Finally, the product was kept at low temperature (4 °C) for further uses.

2.4. Sample collection and conditioning

For tap water samples collection, domestic water was allowed to run for 20 min and approximately a volume of 1000 mL was collected in a beaker. Tap water samples were filtered through 0.45 μm pore size membrane filters (Millipore Corporation, Bedford, MA, USA) and were analyzed immediately after sampling. Mineral water was used as a commercial product. The manipulation and analysis of the samples were developed in a clean laboratory environment. All the material used in this work was previously washed with a 10% (v/v) HNO$_3$ solution followed by ultrapure water before drying in a clean air hood.

2.5. General VALLME procedure and Hg determination

The extraction procedure was performed as follows: 400 μL of concentrated HCl were added to 5 mL of water sample in a centrifuge tube. For optimizing the preconcentration technique, 5 mL of 50 μg L^{-1} Hg standard solution was used instead of the water sample. Thus, 120 μL of a TOABr-coated Au NPs dispersion prepared in toluene was added to the mix and the resulting system was shacked for 5 min with a vortex stirrer (3000 rpm). In order to separate the phases, the turbid solution was centrifuged during 7 min at 3500 rpm (2054.3 ×g) and 50 μL of the organic phase was withdrawn from the top of the centrifuge tube with a micropipette and it was transferred into the quartz micro cell. Finally, the UV–Vis absorption spectra were recorded. All experiments including the UV–Vis absorption spectra acquisition were performed at room temperature. Instrumental and other conditions were as depicted in Table 1. Calibration was performed against aqueous standard solutions submitted to the same extraction procedure. Blank solutions were analyzed in the same manner as standard and sample solutions.

Table 1
Instrumental and experimental conditions for Hg determination.

Instrumental conditions	
Spectral band width (nm)	1
Spectral scanning speed (nm min^{-1})	480
Light path of the cell (mm)	10
Wavelength range (nm)	300–900
VALLME conditions	
Sample volume (mL)	5
TOABr-coated Au NPs volume (μL)	120
HCl concentration (mol L^{-1})	1
Shacking time (min)	5

3. Results and discussion

3.1. Optimization of the proposed VALLME method

Gold nanometer-sized material presents a large number of advantages compared with micrometer-sized particles for analytical microextraction. Au NPs have a significantly high surface area-to-volume ratio and a short diffusion route [11], turning these NPs useful for extraction and detection of Hg, since a higher extraction efficiency and rapid dynamics of extraction can be obtained. The study of the VALLME-UV–Vis spectrophotometric method focused on the optimization of the extraction and detection conditions including, the amount of Au NPs, volume of sample solution, shacking and phase separation time and acid concentration. The investigation was performed by modifying one variable at time, while keeping the others constant. This procedure allowed the study of individual effect of each variable on the extraction and determination of the analyte by means of TOABr-coated Au NPs.

The organic coatings allow further manipulation and solubility control of NPs in different solvents [33,34]. In this work, toluene was used due to the high solubility of TOABr-coated Au NPs in this solvent, while led to form a biphasic extraction system with the water samples. The concentration of TOABr-coated Au NPs in toluene was the same for all experiments. This was set by adding toluene to the dispersed NPs until a maximum SP intensity of 0.36 a.u. was obtained at 520 nm. Furthermore, the possibility of suspending TOABr-coated Au NPs in a wide variety of solvents, without causing aggregation [35,36], permitted to investigate the effect of Hg on the surface plasmon absorption of Au NPs working with water samples in a LLME methodology. After TOABr-coated Au NPs suspended in toluene got in contact with the sample containing Hg, the UV–Vis spectrum of TOABr-coated Au NPs undertook a significant decrease in the surface plasmon (SP) band intensity of TOABr-coated Au NPs (Fig. 1). The increase in Hg concentration was proportional to the decrease of SP band intensity of Au NPs, allowing spectral changes correlation with the analyte concentration. As Fig. 1 shows, TOABr-coated Au NPs offer excellent LSPR properties exhibiting a strong and well-defined absorption band around 520 nm. LSPR strongly depends on particle size, shape, geometry, refractive index of the medium, interparticle distance and aggregation state in solution. Any alteration in these parameters might modify the plasmon-resonance frequency, affecting the color and the strength of the plasmonic intensity [13]. Other mechanisms that contribute to the damping of the plasmons are subject of recent investigations [37]. In this work we hypothesize that the plasmon energy of the Au NP may be degenerate by the absorption energy of the nearby molecules formed between Hg and TOABr, thus, the interaction becomes resonant. The strong and confined electromagnetic field induced by the metal nanoparticle polarizes the molecule. This consecutively modifies the electron oscillations in the metal nanostructures. As a result, the optical response of the plasmonic nanostructure is changed by the interaction of the molecule and the plasmon. In this regard, more experiments are in progress in order to better elucidate this phenomenon.
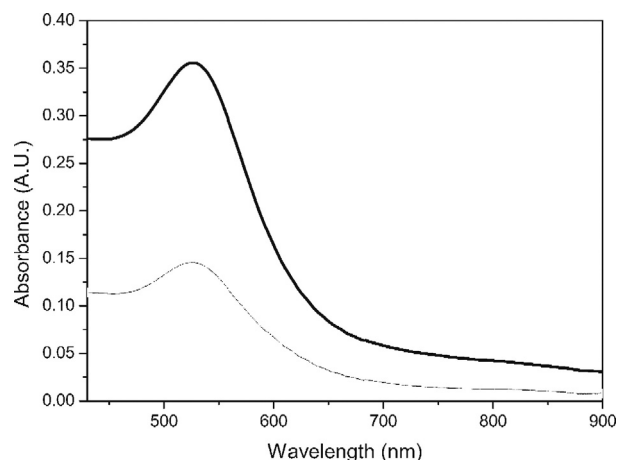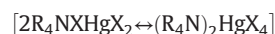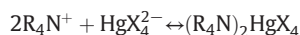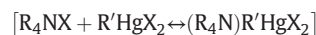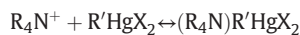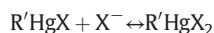

Fig. 1. UV–Vis plot showing absorbance peaks for TOABr-coated Au NPs before (—) and after Hg extraction (initial Hg concentration: 90 μg L^{-1} (⋯)). Experimental conditions are listed in Table 1.

In this work, TOABr was selected as an organic coating for Au NPs to enhance the selectivity of the extraction process. According to previous articles [38–40], quaternary ammonium halide salts are effective extractants for Hg halides anionic complexes. Thus, the extraction mechanism proposed by Tajima et al. [40] to analyze Hg(II) halides in the presence of counterions such as tetra-n-alkylammonium halides might explain Hg interaction with TOABr-coated Au NPs. The following equations summarize the reactions involved during Hg anionic complexes formation with halides (X) and further interaction with quaternary ammonium salts [38,39]:

$$Hg^{2+} + 4X^- \leftrightarrow HgX_4^{2-}$$

$$2R_4N^+ + HgX_4^{2-} \leftrightarrow (R_4N)_2HgX_4$$

$$[2R_4NXHgX_2 \leftrightarrow (R_4N)_2HgX_4]$$

or:

$$R'HgX + X^- \leftrightarrow R'HgX_2$$

$$R_4N^+ + R'HgX_2 \leftrightarrow (R_4N)R'HgX_2$$

$$[R_4NX + R'HgX_2 \leftrightarrow (R_4N)R'HgX_2]$$

Therefore, these mechanisms demonstrate that both inorganic Hg and organo-Hg species are able to form extractable compounds in the

Table 2
Determination of Hg in water samples and analyte recovery study (95% confidence interval; n = 6).

Sample	Amount of Hg added (μg mL^{-1})	Amount of Hg found (μg mL^{-1})	Recovery (%)[a]
Mineral water 1	–	<LOD	–
	0.050	0.049 ± 0.002	98
	0.100	0.105 ± 0.005	105
Mineral water 2	–	<LOD	–
	0.050	0.048 ± 0.002	96
	0.100	0.095 ± 0.004	95
Tap water 1	–	<LOD	–
	0.050	0.048 ± 0.002	96
	0.100	0.104 ± 0.005	104
Tap water 2	–	<LOD	–
	0.050	0.049 ± 0.002	98
	0.100	0.098 ± 0.004	98

[a] $100 \times$ [(Found-Base)/Added].

Table 3
Characteristic performance data obtained by using the proposed method and others reported for Hg determination based on Au NPs.

Method	LOD ($\mu g\ L^{-1}$)	RSD (%)	Sample	Calibration range ($\mu g\ L^{-1}$)	Detection technique	Ref.
PDDA coated Au NPs[a]	5.0	n.r.[b]	Drinking and rain water, water extracted air samples	10.0–2005.9	UV–Vis	[43]
BSA-AuNCs[c]	6.0	n.r.[b]	River water	40–12,035.4	UV–Vis	[44]
MPA-HCys-AuNPs[d]-Cloud point	2	6%	Drinking water	2–100	UV–Vis	[45]
TOABr-coated Au NPs-VALLME	0.8	4.7	Tap and mineral water	4.9–120	UV–Vis	This work

[a] PDDA coated Au NPs: poly(diallyldimethylammonium) coated gold nanoparticles.
[b] n.r.: non reported.
[c] BSA-AuNCs: bovine serum albumin-capped gold nanoclusters.
[d] MPA-HCys-AuNPs: mercaptopropionic acid (MPA) and homocystine (HCys) gold nanoparticles.

presence of halide ions [38,39]. With the aim of ensuring the formation of Hg halides anionic complexes, HCl was added to samples and standard solutions. The effect of HCl concentration on the samples was studied in the range of 0.5 to 3 mol L^{-1} adding concentrated HCl. Quantitative extraction was observed for an HCl concentration of 1 mol L^{-1}. At this concentration of HCl the principal species present in the sample is $[HgCl_4]^{2-}$ [41,42]. The effect of the volume of TOABr-coated Au NPs on Hg extraction and preconcentration by VALLME was investigated in the range: 100–200 μL. It was observed that volumes smaller than 100 μL led to a significant reduction of analytical reproducibility due to the operational difficulty to separate the supernatant. Furthermore, the extraction efficiency increased for volumes up to 120 μL of the NPs solution. Therefore, 120 μL of the NPs solution was used in the proposed method.

The influence of shacking and centrifugation times on the Hg extraction efficiency achieved by the proposed VALLME method was studied in this work. A 5 min shacking time and a 7 min centrifugation time at 3500 rpm (2054.3 $\times g$) were chosen since complete separation was observed for these conditions and no appreciable improvements on analyte extraction were obtained for longer times. Likewise, optimal sample volume was determined in this study. Quantitative extraction was observed for a sample volume range of 1 to 6 mL. Therefore, a 5 mL sample volume was selected in order to obtain the higher analytical response.

3.2. Effect of concomitant ions

The effect of concomitant ions regularly found in tap and mineral water samples was also evaluated. The study was performed by analyzing 5 mL of a 50 μg L^{-1} Hg solution containing different concomitant ions at known concentrations and following the recommended extraction procedure. A concomitant ion was considered to interfere if it resulted in an analytical signal variation of ±5%. Thus, Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+} and Fe^{3+} could be tolerated up to at least 500 μg L^{-1}. Concentrations of anions usually present in water samples (Cl^-, SO_4^{2-}, CO_3^{2-}) did not produce an interference effect on the analytical signal. Furthermore, analytical signal of the blank was not modified in presence of the concomitant ions assayed.

3.3. Analytical performance and determination of Hg in water samples

Quantitative extraction and the highest analytical response were observed for a sample volume of 5 mL. This Au NPs based method was stable. The surface plasmon intensity of the solution could perdure for approximately 4 h. The relative standard deviation (RSD) resulting from the analysis of 10 replicates of 5 mL solution containing 20 μg L^{-1} of Hg was 4.7%. The calibration graph obtained with the proposed method was linear between the limit of quantification (LOQ) (4.9 ng mL^{-1}) and up to at least 120 ng mL^{-1} of Hg, with a correlation coefficient of 0.9992. The limit of detection (LOD) was calculated based on the signal at intercept and three times the standard deviation about regression of the calibration curve. A LOD of 0.8 ng mL^{-1} Hg was obtained for the proposed methodology.

The accuracy of the proposed method was evaluated by analysis of a certified reference material (CRM), QC Metal LL3 Mercury in Water (VKI Reference Materials), with a Hg concentration of 6.48 ± 0.51 μg L^{-1}. Concentration of Hg found in this CRM by the proposed method was 6.56 ± 0.85 μg L^{-1} (95% confidence interval; n = 6). Finally, the method was applied for Hg determination in different water samples. Hg concentrations in water samples were below the LOD. Furthermore, a recovery study was developed for the samples containing known additions of Hg. The results are shown in Table 2. Recoveries of Hg varied between 96 and 105%.

3.4. Comparison with other methods reported in the literature

A comparison of the proposed method with others reported in the literature using Au NPs for Hg determination is given in Table 3. The proposed method shows lower LOD and RSD than other works already reported based on LSPR. Although this method requires more stages than others, LLME previous UV–vis detection allows separation of a large number of interferents. In addition, the method requires a low volume of reagents, significantly diminishing waste generation in the analytical laboratory.

4. Conclusion

A novel microextraction methodology based on the use of TOABr-coated Au NPs was developed for the determination of Hg in drinking water samples. The use of Au NPs in biphasic systems offers several advantages over conventional liquid-liquid extraction methods, such as high capacity to extract Hg without the use of external or additional complexing reagents. This analytical methodology shows substantial improvements on various aspects as compared to earlier works, for instance, by making feasible analyte separation from water samples (i.e.; tap and mineral water samples) with a minimal amount of solvent required for the analysis. The novel VALLME method associated with UV–Vis detection can be proposed as a low organic solvent consuming extraction technique, which turns it into a low cost and environmentally friendly tool for elemental studies. Therefore, a green, simple, sensitive, and cost-effective method is proposed for determination of Hg at trace levels.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.saa.2016.05.028.

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