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Determination of Mercury in indoor dust samples by ultrasonic probe microextraction and stripping voltammetry on gold nanoparticles-modified screen-printed electrodes

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ABSTRACT

A miniaturized, fast, and efficient ultrasonic probe assisted method for Hg(II) extraction from indoor dust samples, in hydrochloric acid medium, was developed. The combination of the extraction method with the electrochemical determination of mercury by square-wave anodic stripping voltammetry (SWASV) on gold nanoparticles-modified screen-printed carbon electrodes (AuNPs-SPCEs) resulted in a convenient method for rapid, sensitive, and reliable mercury monitoring. Parameters involved in the extraction such as acid concentration, sonication amplitude, and sonication time were optimized using a Face-centered cube Central Composite Design. ICP-MS was also used to contrast the methodology and good agreement with electrochemical results was verified. Optimization and validation of the procedure were carried out by using NIST Standard Reference Material® 2583 Trace Elements in Indoor Dust. Finally, the proposed methodology was successfully applied for Hg(II) determination in dust samples collected at different indoor ambients.

1. Introduction

Indoor dust is a heterogeneous and complex mixture including fibers from clothing and furnishings, mites, hair, chemical contaminants (e.g., pesticides, PAHs, heavy metals, plasticizers and flame retardants), combustion products (e.g., carbon monoxide, environmental tobacco smoke, nitrogen dioxide) and others. The composition of indoor dust samples is a function of numerous factors including environmental and seasonal factors, ventilation and air filtration, owner activities, and indoor and outdoor sources. These contaminants have the potential to persist and accumulate in indoor dust as they are not subjected to the same degradation processes that occur outdoors. Compounds associated with indoor dust particles are protected from sunlight, fluctuations in temperature and humidity and the overall effects of weathering [1].

Routes of human exposure to indoor dust consist mainly of inhalation, non-dietary ingestion, and dermal adsorption [2]. Allergenic and immune system effects, respiratory, cardiovascular, nervous effects, and irritating effects of the skin and mucous membrane or cancer, are described as possible adverse health impacts [1]. These facts support the interest of indoor dust as a matrix for environmental analysis aimed at estimate exposure of the general population (homes) and workers (labor places). Trace element profiles in indoor dust are valuable tools for risk assessment and source apportionment [3]. Within this pollutant class, mercury has been specifically tested as a relevant air pollutant in indoor dust samples at workplaces [4].

About sampling of indoor dust, the optimal collection method will depend on the surface to be sampled and the goal of study. Nevertheless, simple active sampling of passively deposited material like surface wiping or brushing, press sampling or sweeping can be used, thus avoiding the need of sophisticated active samplers [5].

About sample pre-treatment for analyte solubilization, ultrasonic irradiation has been explored as an alternative for solid–liquid extraction since ultrasound facilitates an auxiliary energy and it accelerates some steps [6]. As described by Capelo et al. [7], when an ultrasonic wave passes through a liquid sample, the wave's oscillating pressure can cause a cavitation phenomenon which involves the generation and implosions of gas bubbles. Extreme temperature and pressure are generated at the centered of each collapsed bubble as well as radicals during sonolysis of the solvent. Therefore, ultrasonic techniques can also overcome the disadvantages of conventional extraction procedures in terms of time, efficiency, and solvent consumption [8,9]. Optimization of the extraction methods involves the selection of several variables. If the optimization is carried out by monitoring the influence of one factor at a time on the analytical signal, the interactive effects

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of the variables on the response is ignored, and the number of experiments increase. Trying to solve these drawbacks, the more recent trend is performing the optimization of pre-treatments by using multivariate statistic techniques. Response Surface Methodology (RSM) is one of the most relevant multivariate technique used [10]. It allows generation of an adequately fitting second order polynomial equation that contains the significant factors affecting the responses as well as the interactions between the parameters to obtain the best system performance [11].

Many applications about the ultrasonic extraction of trace metals from biological and environmental matrixes have been reviewed [7,12]. The ultrasonic approach is especially attractive for mercury extraction by allowing a simple and cheap but highly effective room temperature and ambient pressure treatment, capable of preventing the well documented problem of mercury volatilization during sample treatment. In this sense, ultrasonic treatment can be an appropriate alternative compared with more sophisticated procedures based on high pressure and elevated temperature digestion in closed vessels to minimize volatilization, e.g. microwave assisted extraction. Specifically, for inorganic Hg methods based on bath ultrasonic extraction from urine [13] and tuna fish samples [12] have been published. Also, different research papers have been described the development of methods based on ultrasound probe assisted extraction of Hg from mussel tissues [8], soil and sediments [14], human urine [15], several kinds of fish [16], and street dust samples [17] employing different acid media for the ultrasonic extraction which several spectrometric techniques for Hg detection have been used (CV-AAS, AFS or ICP-MS). Also, a number of research works have been published on the electrochemical determination of Hg (usually, by Anodic Stripping Voltammetry, ASV) at different gold electrodes (micro, film, rotating disk) [18–22] and gold nanoparticles-modified carbon electrodes [23–24]. Moreover, the applicability of the recent technology based on gold screen-printed sensors [25–28] and gold nanoparticles-modified screen-printed carbon sensors [29–30] has been demonstrated successfully for this purpose. Surprisingly, a single reference which combines the ultrasonic extraction method with electrochemical determination of mercury was found in the literature. Munoz et al. [13] describe in that work an efficient, fast, and reliable bath ultrasonic-assisted treatment of urine samples for chronopotentiometric stripping determination of mercury at gold film electrodes. No reference has been found about the combination of ultrasonic probe for extraction and screen-printed electrodes for mercury determination by ASV.

In the present work, we have aimed at explore a simplified strategy for mercury determination in indoor dust samples, based on the development of miniaturized, fast, and efficient ultrasound probe assisted extraction method and electrochemical detection by a previously optimized Square-Wave Anodic Stripping Voltammetry (SWASV) methodology [29] on commercial gold nanoparticles-modified screen-printed carbon electrodes (AuNPs-SPCEs). A Face-Centered Central Composite Design (FCCD), which comes under RSM approach, was employed for the optimization of the parameters involved in the probe ultrasonic extraction of mercury, such as extraction media, sonication amplitude, and sonication time. Optimization and validation of the procedures were carried out by using standard reference material. The proposed combination of methods was applied to Hg(II) measurement in dust samples collected at different indoor ambients.

2. Experimental

2.1. Chemicals and solutions

All chemicals for the preparation of stock and standard solutions were used of analytical grade. 10 mg/L stock solution of Hg(II) (ICP quality) was supplied by Perkin Elmer (Spain). Dilute standards for calibration were prepared directly into the voltammetric cell. Hiperpur grade HCl purchased from Panreac (Spain) was used for the preparation of supporting electrolyte and also, for ultrasonic extraction of the samples. The ultrapure water (18.2 MΩ · cm at 25 °C) was obtained from an Ultramatic system (Wasserlab, Spain). Samples and dilute standard solutions were adjusted to desirable pH with sub boiled HNO_3 obtained from a quartz distiller (Kürner, Germany) before ICP-MS analysis. NaOH (Scharlau, Spain) was used to adjust the pH when needed for electrochemical determinations. Glassware and polyethylene containers were thoroughly conditioned for trace analysis i.e. soaked in hot nitric acid at 10% (v/v) for 48 h, rinsed with ultrapure water, dried in stove, and kept in hermetic plastic bags. The methacrylate voltammetric cell was similarly immersed in nitric acid at 10% (v/v) for 24 h, rinsed in ultrapure water, and air dried before use.

2.2. Reference material and real samples

NIST Standard Reference Material® 2583 Trace Elements in Indoor Dust was used for the optimization of the probe ultrasonic extraction procedure through the surface response methodology.

Dust samples were collected in indoor ambient, specifically, in a research laboratory and in a private garage by brush sweeping into polyethylene auto sealable bags. The samples presented a cottony aspect so they had to be manually homogenized (grinding with a stainless steel scraper and sieved trough 2 mm). They were kept in a fridge (4 °C) until analysis.

2.3. Instrumentation and software

Ultrasound probe assisted extraction experiments were carried out with a Hielscher (Teltow, Germany) UP200S stand mounted ultrasonic device, fitted with a 200 W, 24 kHz high-frequency generator and equipped with a S1 1 mm diameter titanium probe suitable for volumes from 0.1 to 5 mL. An Ortoalresa Digicen 21 (Madrid, Spain) centrifuge equipped with a hermetic closure rotor and a 24 microtubes sample holder was used for separation of solid residues after ultrasonic extractions.

Square wave voltammetric measurements were performed on a computerized hand-held, battery-powered PalmSens potentiostat/galvanostat (Palm Instruments BV, The Netherlands) interfaced with a laptop and controlled by the PSTrace 1.1 software. Gold nanoparticles-modified screen-printed electrode strips were purchased from DropSens (Oviedo, Spain). They were designed in three electrode configuration printed on the same platform. Working electrode (Ø 4 mm), counter electrode, and pseudo-reference electrode were made of gold nanoparticles-on-carbon, carbon, and silver, respectively. An insulating layer serves to delimit the working area and silver electric contacts. Ink formulation and production characteristics of commercial AuNPs-SPCEs are regarded by the manufacturers as proprietary information. A specific connector was used to connect the electrochemical strip to the potentiostat. A methacrylate voltammetric cell (DropSens, Spain) was used to perform the analysis. It was especially suitable for SPEs and it was designed to perform batch analysis with volume of solution between 5 to 10 mL allowing optional stirring by means of a magnetic stirrer. The screen-printed strip was immersed in the solution trough a cut on the top lid and was placed in parallel direction to the sides of the cell, leaving the electrical connections outside.

A Perkin Elmer ELAN 9000 (Massachusetts, USA) quadrupole ICP-MS equipped with a cross flow nebulizer, a demountable quartz torch, a niquel skimmer and sampler cones, and a ryton scott spray chamber was used for mercury determination. It was also used for accuracy check of the electrochemical results.

The images of the dust samples were obtained by scanning electron microscopy (SEM) using a Hitachi FE-SEM S-4800II instrument (Tokyo, Japan) which was also used for registering EDX spectra.

The software package The Unscrambler® v9.7 CAMO Software AS (Trondheim, Norway) was used for the application of chemometrics.

2.4. *Procedures*

2.4.1. *Ultrasonic probe-assisted extraction method*

Ultrasound probe assisted extractions was carried out for the extraction of Hg(II) from the dust samples and reference materials, before determination of mercury by ASV and ICP-MS.

An appropriate amount of sample was weighed in a 1.5 mL conical bottom Eppendorf micro centrifuge tube with snap cap. 1 mL of extraction reagent (HCl) was added and the titanium ultrasonic probe was immersed. Then, the sonication of the samples was started at room temperature. Optimal conditions of the extraction with ultrasonic probe were achieved through the surface response methodology derived of the application of a face-centered cube central composite design of experiments (FCCD). After application of the extraction method, the samples were centrifuged for 15 min at 5000 rpm. For the determination of Hg(II) on AuNPs-SPCEs by SWASV, the appropriate volume of supernatant was transferred to 10 mL flask and the pH was adjusted to 1 with concentrated NaOH as previously described [29]. Although for the analysis of Hg(II) by ICP-MS, the desired amount of supernatant liquid was transferred to a flask and the final volume was made up to 10 mL with 5% HNO_3 and 5 ng/mL In(III) as internal standard. Blanks were treated in the same ways.

2.4.2. *Determination of Mercury by ICP-MS*

The sample extracts were analyzed by a standard ICP-MS protocol for the determination of total mercury as follows: RF power 1000 W, Ar plasma flow rate 1 L/min, washing time 35 s and 3 replicates per sample. The most abundant mercury isotope ^{202}Hg was used for data evaluation. Quantification was performed by internal standard method using In(III).

2.4.3. *Determination of Mercury by anodic stripping voltammetry on AuNPs-SPCEs*

The sample extracts were placed in the voltammetric cell (10 mL) and the SWASV determination was started. No electrochemical activation procedure and no deaireation before voltammetric determination were needed. The applied voltammetric parameters were as described previously [29]: conditioning potential +0.7 V for 15 s, deposition potential +0.2 V for 120 s (without stirring), equilibration time 5 s, amplitude 40 mV, step potential 6 mV, and frequency 25 Hz. Initial and final potentials were +0.15 V and +0.7 V. Bulk stripping voltammetric signals were used for peak current measurement. Hg(II) quantification in the real samples and standard reference material was performed by the standard additions method. All experiments were performed in duplicate.

3. Results and discussion

3.1. *Optimization of ultrasonic probe-assisted extraction by the response surface methodology*

The optimization of the probe ultrasonic extraction procedure of Hg was performed by analyzing the NIST Standard Reference Material® 2583 Trace Elements in Indoor Dust by ICP-MS. Different acid media have been reported in the literature for the ultrasonic extraction of mercury. Río-Segade and Bendicho [8] and López et al. [16] demonstrated the efficiency of HCl, in concentration of 5 and 7 M respectively, for the extraction of Hg (II) from mussel tissue samples, swordfish, and zebra fish using an ultrasonic probe. Reyes et al. [12] established a comparison of methods including an ultrasonic bath assisted extraction of Hg from tuna fish using 5 M HCl as acid medium. About solid environmental samples, Collasiol et al. [14] used the mixture 30% (v/v) HNO_3–0.15% KCl for the extraction of Hg from soil and sediment by ultrasonic bath treatment. Recently, Marín et al. [17] reported an ultrasonic probe assisted leaching of Hg, among other elements from street dust samples using concentrated aqua regia (HNO_3–HCl 1:3, v/v). In the present work, the previous experiments of probe ultrasonic extraction were performed in HNO_3 and HCl media. In both cases, quantitative recoveries of Hg(II) were obtained, but HCl was finally selected because the determination of Hg by anodic stripping voltammetry on AuNPs-SPCE was optimal in this medium [28,29].Anyway, several authors have investigated which parameters are involved directly in the extraction of heavy metals from several kinds of matrices with a microtip ultrasonic probe [8,14,16,17]. Taking these in account the variables included in the experimental design carried out in the present work were the acid concentration, the sonication time, and the sonication amplitude.

In order to reach the optimum values for the three factors mentioned before, a face-centered cube central composite design, 2^3, with three central points was used [11,28]. This design included 17 experiments performed in random order and it was used with the aim of calculating simultaneously the effect of the change in each one of the variables and also their possible interactions. The assayed levels for each one of the variables were: 1, 5 and 10 M for [HCl]; 1, 3 and 5 min for sonication time; and 20, 50 and 80% for sonication amplitude. Table 1 shows the regression coefficients (also named, B-coefficients) of the proposed accuracy model and their *p*-values, which are used to determine the significant parameters (p-value < 0.05). An empirical relationship between the selected variables and the response function (percentage of recovery) was obtained that can be represented by the following regression equation:

$$\%\,\text{Recovery} = 87.11 + 0.179\,A + 7.427\,C - 3.719\,BC - 17.74\,C^2$$

The correlation's plot between experimental and predicted data obtained from the application of the model equation is represented in Fig. 1. In the corresponding analysis of variance (ANOVA) a second-grade quadratic model is assumed (p-value of model (95%) = 0.000). A multiple correlation value (R) of 0.992 and coefficient of determination (R^2) of 0.984 is obtained. They is closer to +1 which is in accordance with good predictive ability of the model; specifically, the value of R^2 indicates that the model could explain 98.4% of the variability in the response. Furthermore, the p-value (95%) calculated

Table 1
Estimate regression coefficients and their significance (*p*-values) obtained of the proposed method.

Coefficients	Estimated values	*P*-values
A (Sonication amplitude)	0.179	0.028
B (Sonication time)	2.170	0.061
C ([HCl])	7.427	0.000
AB	2.047	0.176
AC	−1.359	0.350
BC	−3.719	0.029
A^2	0.352	0.885
B^2	−2.305	0.359
C^2	−17.74	0.000

for lack of fit is 0.179 which means that the model described the true shape of the response surface.

Fig. 2, shows the response surfaces (contour plots) estimated by the model for each pair of variables. The information extracted of these plots indicates that the optimum values of the variables correspond to 55% sonication amplitude, 3.2 min sonication time, and 8.13 M hydrochloric acid concentration. It is noticeable that the saddle point observed in the contour plot of time vs. sonication amplitude indicates that the optimal value of the variable is not in the chosen range and also it does not correspond to the maximum value. In spite of this, the selection of the sonication amplitude optimal value is not affected because very good recoveries are observed when the variable is different to the maximum selected in the established range. Moderate amplitude is beneficial for long term protection of the titanium tip of the US probe also Fig. 3.

To evaluate the accuracy of the response surface model, four experiments were carried out using the optimal conditions. Two blank samples and four sub-samples (15 mg) of the Trace Elements in Indoor Dust standard reference material were extracted consecutively by the ultrasound probe treatment and analyzed by a standardized ICP-MS methodology. A very good agreement between certified concentration of Hg (1.56 ± 0.19 μg/g) and measured concentration (1.47 ± 0.67 μg/g) was found. In terms of percentage of recovery, the values obtained were in the range of 90 to 99%.

3.2. SWASV determination of Hg(II) in the ultrasonic extracts. Indoor dust standard reference material

In order to achieve a reliable, fast, reproducible, and miniaturized methodology for the analysis of Hg(II) in the indoor dust samples, the optimized ultrasonic probe microextraction was coupled to square wave anodic stripping voltammetric determination on AuNPs-SPCE [29]. This way, a sample (15 mg) of the indoor dust standard reference material was extracted and Hg(II) was sub sequentially analyzed by SWASV on AuNPs-SPCE. A set of voltammetric curves for the extraction protocol are represented in Fig. 4. The experimental value obtained by SWASV (1.68 ± 1.03 μg/g) was in good agreement with the certified value (1.56 ± 0.19 μg/g). The relatively high confidence interval measured by the proposed method can be assigned to proximity to the detection limit.

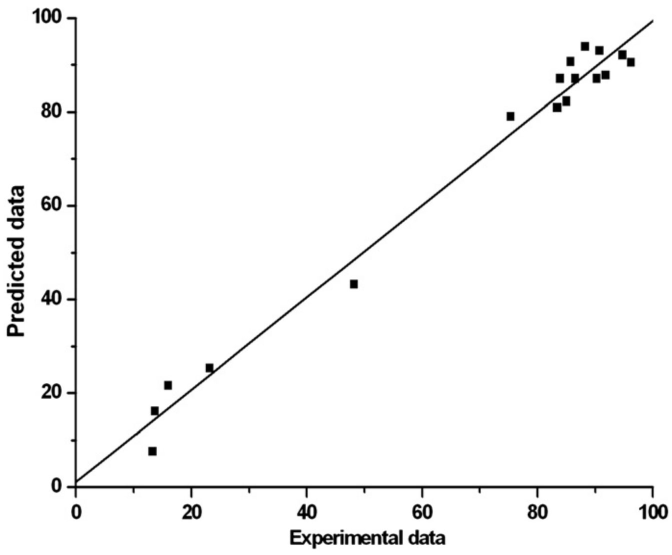

Fig. 1. Correlation of experimental and predicted values of Hg peak intensity.

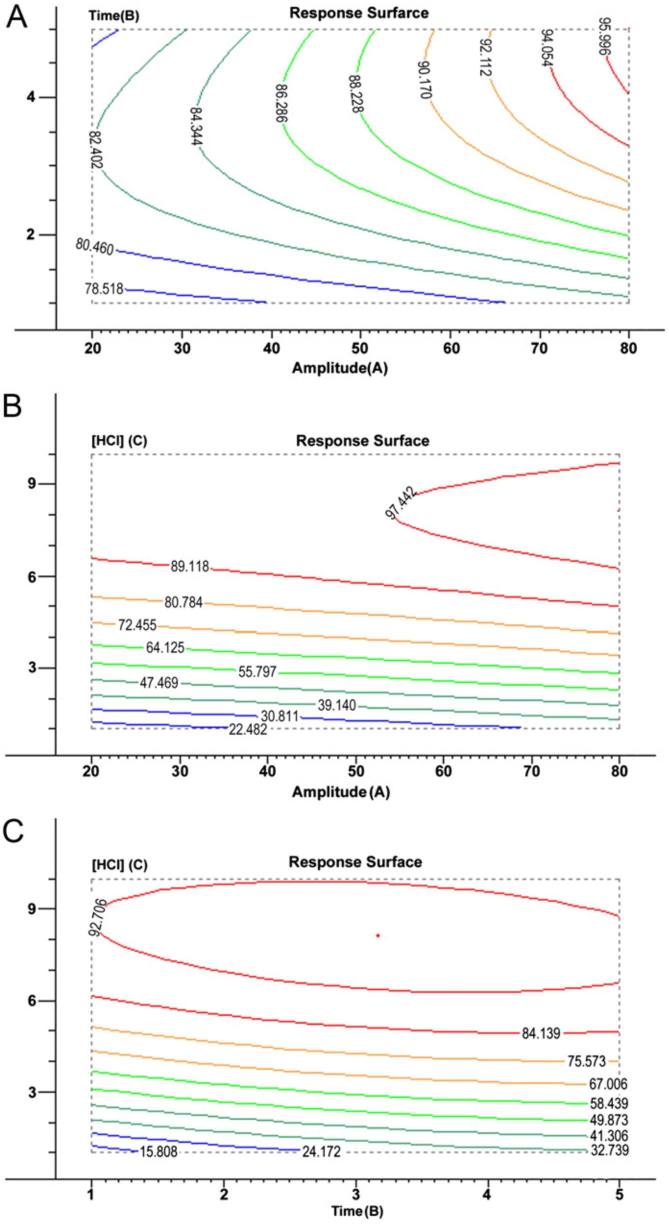

Fig. 2. Contour plots estimated for each pair of variables after model fit (A: Time vs. Amplitude; B: [HCl] vs. Amplitude; C: Time vs. [HCl]).

3.3. SWASV determination of Hg(II) in real indoor dust samples

Indoor dust samples collected in a private garage and a research laboratory were previously characterized using SEM and EDX techniques (Fig. 4). After drying, reduction of particle size and sieving, an appropriate portion of each dust sample was placed on an adhesive tape for surface analysis. The SEM images showed in both cases random distribution of microparticles but significantly different morphological structures. The physical appearance of lab dust (Fig. 4a) was like cotton, so, the SEM analysis highlighted the most elongated aspect of the particles. On the other hand, finer particles, spherical, and fibrous structures predominate in the SEM image of the garage dust (Fig. 4b). EDX analysis showed several metal and metalloid peaks. Cu, Pb, and Zn were observed only in the EDX spectrum of the garage dust probably, derived from vehicle exhaust. Sensitivity of x-ray spectroscopy was not enough to detect mercury on the dust samples.

To quantify mercury in the indoor dust samples, probe ultrasound-assisted extraction was carried out using the optimal experimental conditions described in the previous sections and the extracts were analyzed by SWASV on AuNPs-SPCE. Standard addition method of 3, 6, and 9 ng/mL Hg(II) was used for calibration. Sample regressions are shown in Figs. 5 and 6 for the lab dust and the garage dust, respectively. Measured concentrations of Hg(II) in the real dust samples are summarized in Table 2, which shows also the results of ICP-MS assay of the extracts. As seen in Table 2, the proposed method gave results in good agreement with ICP-MS

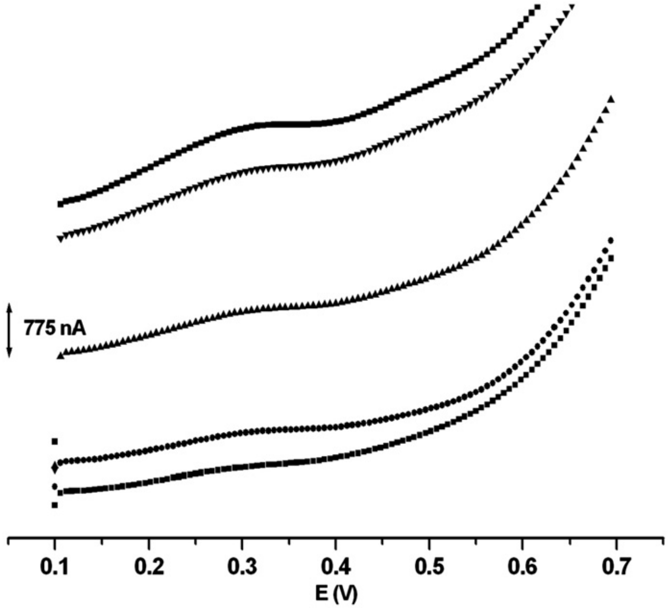

Fig. 3. Voltammetric curves obtained by the standard addition method for the determination of Hg(II) in indoor dust standard reference material using an ultrasonic probe on AuNPs-SPCE. Square-wave voltammetric stripping measurements performed in 0.1 M HCl and in a convective cell with a frequency of 25 Hz, step potential 6 mV, amplitude 40 mV, deposition potential +0.1 V and deposition time 120 s.

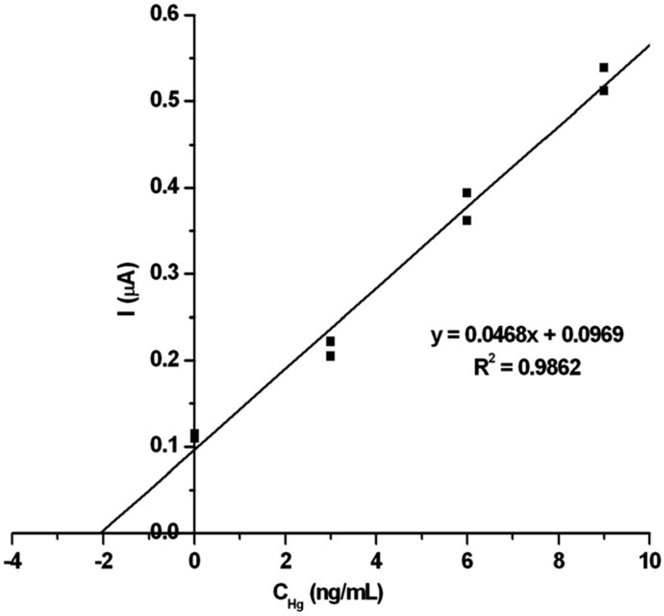

Fig. 5. Regression curve obtained for standard addition determination of Hg(II) in lab dust samples extracted using an ultrasonic probe and analyzed by SWASV on AuNPs-SPCE.

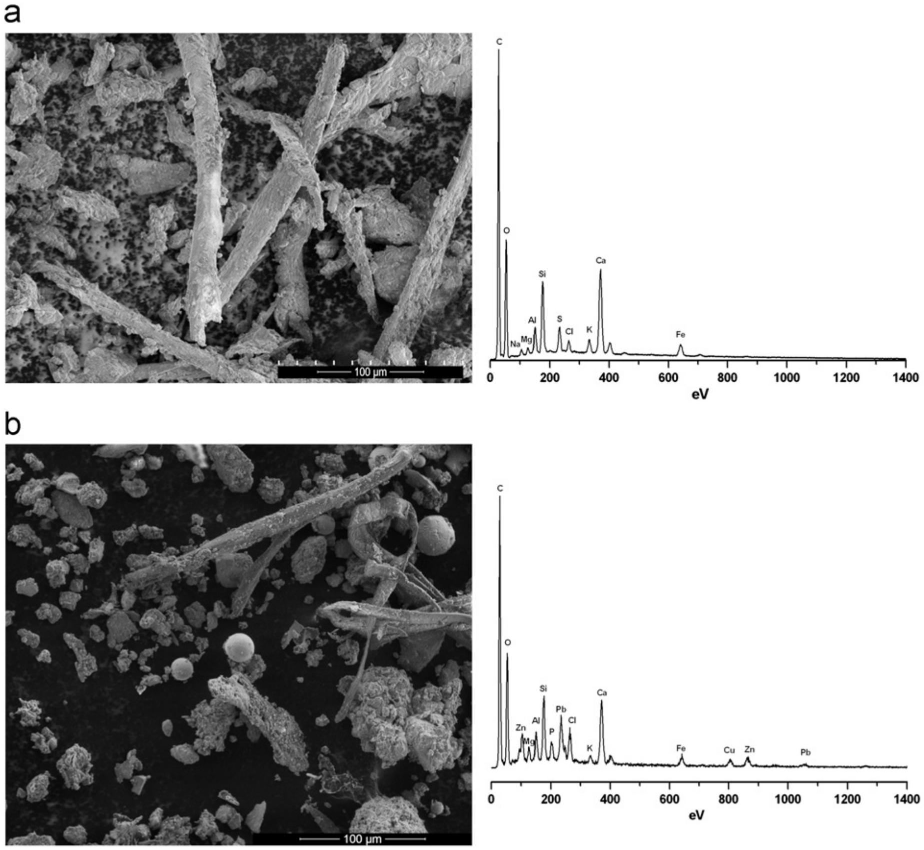

Fig. 4. SEM and EDX analysis of indoor dusts in samples taken from a research laboratory (a) and a private garage (b).

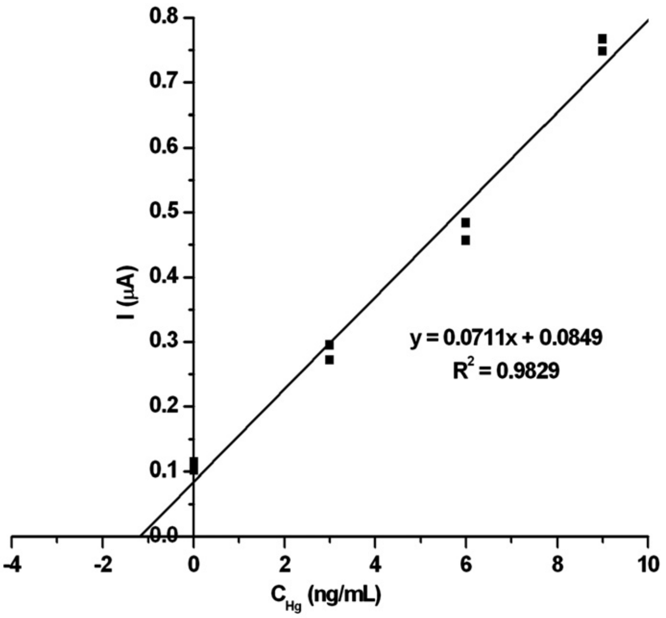

Fig. 6. Regression curve obtained for standard addition determination of Hg(II) in garage dust samples extracted using an ultrasonic probe and analyzed by SWASV on AuNPs-SPCE.

Table 2
Hg(II) concentration in real indoor dust samples extracted using ultrasonic probe.

Sample	Conc. Hg SWASV (µg/g)	Conc. Hg ICP-MS (µg/g)
Lab dust	131 ± 55	134 ± 32
Garage dust	0.78 ± 0.50	0.69 ± 0.15

determinations. Concentrations of dust mercury taken from the laboratory and the garage were considerably different, and also the measured confidence intervals. The somewhat high value determined in the laboratory dust sample was probably related to the long term use for polarography research. Concentration of dust mercury found in the garage is in the range of previously reported data for similar samples [17]. Both values are lower than others reported by Y. Liu et al. [4] in indoor dust collected at incineration plants from the district of Taiyuan city (China). These authors measured concentrations of dust mercury from 547 to 866 µg/g in the municipal solid waste incineration plant and over 1100 µg/g in the workplace of the hospital waste incineration plant, respectively.

These results demonstrate the potential applicability of the proposed ultrasonic methodology combined with stripping voltammetry for the determination of Hg(II) in complex dust samples from different environments.

4. Conclusions

Ultrasonic probe assisted extraction optimized by response surface methodology offers a fast, easy, efficient, and miniaturized sample preparation for the determination of Hg(II) in dust samples. The combination of the probe ultrasonic extraction with SWASV determination of Hg(II) on Au nanoparticles modified screen-printed electrodes results in a reliable, simple, inexpensive, reproducible, and selective methodology for Hg(II) analysis in complex dust samples. The effectiveness of the proposed methodology has been demonstrated by assaying a certified indoor dust standard reference material and real dust samples collected in different indoor ambients.

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References

[1] R.M. Maertens, J. Bailey, P.A. White, Mutat. Res. 567 (2004) 401–425.
[2] Y. Kang, K.Ch. Cheung, M.H. Wong, Environ. Int. 37 (2011) 637–643.
[3] S. Charlesworth, E. de Miguel, A. Ordoñez, Environ. Geochem. Health 33 (2011) 103–123.
[4] Y. Liu, Z. Zhan, F. Du, S. Kong, Y. Liu, Chemosphere 75 (2009) 266–271.
[5] P.J. Lioy, N.C. Freeman, J.R. Millete, Environ. Health Perspect. 110 (2002) 969–983.
[6] A. Elik, Talanta 66 (2005) 882–888.
[7] J.L. Capelo, C. Maduro, C. Vilhena, Ultrason. Sonochem. 12 (2005) 225–232.
[8] S. Río-Segade, C. Bendicho, J. Anal. At. Spectrom. 14 (1999) 263–268.
[9] C. Bendicho, I. de la Calle, F. Pena, M. Costas, N. Cabaleiro, I. Lavilla, Trends. Anal. Chem. 31 (2012) 50–59.
[10] M.A. Bezerra, R.E. Santelli, E.P. Oliveira, L.S. Villar, L.A. Escaleira, Talanta 76 (2008) 965–977.
[11] M Balachandran, S. Devanathan, R. Muraleekrishnan, S.S. Bhagawan, J. Mater. Design (2011) http://dx.doi.org/10.1016/j.matdes.2011.03.077.
[12] L.H. Reyes, G.M. Mizanur Rahman, T. Fahrenholz, H.M.Skip Kingston, Anal. Bioanal. Chem. 390 (2008) 2123–2132.
[13] R.A.A. Munoz, F.S. Felix, M.A. Augelli, T. Pavesi, L. Angnes, Anal. Chim. Acta 571 (2006) 93–98.
[14] A. Collaisol, D. Pozebon, S.M. Maia, Anal. Chim. Acta 518 (2004) 157–164.
[15] J.L. Capelo, C. Maduro, A.M. Mota, Ultrason. Sonochem. 13 (2006) 98–106.
[16] I. López, S. Cuello, C. Cámara, Y. Madrid, Talanta 82 (2010) 594–599.
[17] M.R. Palomo Marín, E. Pinilla Gil, L. Calvo Blázquez, J.L. Capelo-Martínez, Talanta 84 (2011) 840–845.
[18] Y. Bonfil, M. Brand, E. Kirowa-Eisner, Anal. Chim. Acta 424 (2000) 65–76.
[19] O. Ordeig, C.E. Banks, J. del Campo, F.X. Muñoz, R.G. Compton, Electroanalysis 18 (2006) 573–578.
[20] M.A. Augelli, R.A.A. Munoz, E.M. Richter, M.I. Cantagallo, L. Angnes, Food Chem. 101 (2007) 579–584.
[21] A. Giacomino, O. Abollino, M. Malandrino, E. Mentasti, Talanta 75 (2008) 266–273.
[22] B.K. Jena, C.R. Raj, Anal. Chem. 80 (2008) 4836–4844.
[23] O. Abollino, A. Giacomino, M. Malandrino, G. Piscioneri, E. Mentasti, Electroanalysis 20 (2008) 75–83.
[24] J. Gong, T. Zhou, D. Song, L. Zhang, X. Hu, Anal. Chem. 82 (2010) 567–573.
[25] S. Laschi, I. Palchetti, M. Mascini, Sens. Actuators B 114 (2006) 460–465.
[26] V. Meucci, S. Laschi, M. Minunni, C. Pretti, L. Intorre, G. Soldani, M. Mascini, Talanta 77 (2009) 1143–1148.
[27] A. Mandil, L. Idrissi, A. Amine, Microchim. Acta 170 (2010) 299–305.
[28] E. Bernalte, C. Marín Sánchez, E.Pinilla Gil, Anal. Chim. Acta 689 (2011) 60–64.
[29] E. Bernalte, C. Marín Sánchez, E.Pinilla Gil, Sens. Actuators B 161 (2012) 669–674.
[30] G. Aragay, J. Pons, A. Merkoçi, Chem. Rev. 111 (2011) 3433–3458.