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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