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Dynamic versus static ultrasonic sample treatment for the solid–liquid pre-concentration of mercury from human urine

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Abstract

Dynamic and static ultrasonic procedures involving ultrasonic bath and tandem focused ultrasound (i.e. two probes were used in the same sample treatment) have been assessed in order to implement a reliable solid–liquid back extraction of mercury from commercial resins (dowex and chelex-100), previously used to concentrate Hg(II) from treated urine. The urine had been previously treated with an advanced oxidation process provided by the conjunction of potassium permanganate, hydrochloric acid and high intensity focused ultrasound, which allowed that organic matter degradation was achieved in less than 3 min. 95 ± 10% of mercury in the certified urine and 97 ± 6% of the spiked methyl-mercury was recovered with the dowex resin plus the static ultrasonic procedure, whilst 96 ± 11% of the spiked mercury was recovered with the dowex resin plus the dynamic procedure, for which ultrasonication was not necessary. The Hg pre-concentration factor used in this work was 8 (20 mL of urine to 2.5 mL of acid), but different volume ratios can be used in order to increase this factor.

Keywords: Dynamic ultrasound; Static ultrasound; ET-AAS; Dowex; Chelex-100; Mercury; Urine

1. Introduction

The determination of mercury in urine can provide important information concerning human exposure to this metal [1,2]. Total mercury determination in human urine has been done mainly by flow-injection cold vapour atomic absorption spectrometry (FI-CV-AAS), and requires: (i) the total or partial organic matter degradation of the sample [2,3] and (ii) the mercury release from the organomercurials present in the urine prior to total mercury determination. To achieve the aforementioned items different methodologies have been cited in literature based on off-line or on-line procedures with a plethora of reagent combinations [2–6]. In many instances, potassium permanganate is used as strong oxidant for organic matter and organomercurials degradation. Nevertheless, some mercury compounds, namely phenyl-mercury(II) acetate and methyl-mercury chloride, are only partially oxidised by this reagent [5]. Furthermore, some problems are found when the potassium permanganate is used: (i) in on-line procedures the interaction of potassium permanganate with other reagents is critical in order to oxidize mercury organocompounds [5], and a careful choice of the concentration of the reagents is necessary in order to achieve accurate results [5], (ii) in off-line procedures, the most serious problem cited in the literature is due to the hydrated manganese(IV) oxide, which is formed when the potassium permanganate is used at pH values of 4–5. The hydrated manganese(IV) oxide forms a film on the surfaces of sample vessels, tubing and other manifold components where mercury may be adsorbed [7]. Tandem Focused Ultrasound in conjunction with potassium permanganate and hydrochloric acid has been recently cited as a fast methodology for mercury determination in urine by electrothermal atomic absorption spectrometry, ET-AAS [6]. Briefly, the methodology entails the liquid–liquid mercury preconcentration in three steps along with the use of two sonication probes of different diameters in order: (i) to degrade the organic matter/organomercurials present in solution (step 1, probe 1), (ii) to extract the mercury into an organic solution (step 2, dithizone in cyclohexane) and (iii) to back-extract

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the mercury into an aqueous solution for mercury determination by ETAAS (step 3, probe 2). The whole procedure allowed to pre-concentrate the mercury by a minimum factor of 14.

The pre-concentration of mercury from aqueous solutions, such as urine, can be done by liquid–liquid extraction, as it was done in the previous work [6], or by liquid–solid extraction. The liquid–solid extraction procedure does not use organic reagents, being more environmental friendly than the liquid–liquid pre-concentration approach. In addition, it also has some further advantages, as the following: (1) can be used in situ, avoiding flasks to store the sample or the use of preservatives; (2) high pre-concentration factors can be obtained; (3) simplicity in sample's handling and transfer; (4) the separation and pre-concentration can be performed on-line. The liquid–solid mercury pre-concentration is a well established technique in Analytical Chemistry and commercially available resins have been used for the pre-concentration of mercury from environmental matrices for decades. As some examples, Amberlite XAD7 and C_{18} were used for the field sampling, pre-concentration and determination of mercury species in river waters [8], Cherlite was used for the pre-concentration of mercury from agroindustrial samples [9], and Chelex-100 was used in a flow injection system for the pre-concentration of mercury from sea water [10].

The ultrasonic–acid extraction of metals from solid matrices has been reported in literature in off-line (static) [11] and on-line (dynamic) procedures [12,13]. In on-line procedures, there are two different approaches [12]: the open and closed systems. In the open system fresh extractant flows continuously through the sample, in the closed system a pre-set volume of extractant is continuously circulating through the solid sample. To the best of our knowledge, the coupling of high intensity focused ultrasound to solid–liquid extraction of metals from a column filled with a resin has not been attempted yet despite of its easy implementation.

The aims of the present work are (i) to assess the sample treatment developed in this work, based on liquid–solid pre-concentration of mercury from human urine, and compare it with the liquid–liquid pre-concentration described by Capelo et al. [6]; (ii) to implement a procedure using high intensity focused ultrasound to transfer the analyte mass equilibrium into the liquid phase, diminishing in this way the time and acid concentration used to perform the back-extraction; (iii) to develop and to compare dynamic versus static procedures based on ultrasonication.

2. Experimental

2.1. Apparatus

The flow injection system used for cold vapour generation consisted of a four channel Gilson (Villiers le Bel, France) Minipuls 2 peristaltic pump, a Perkin-Elmer (Überlingen, Germany) membrane gas–liquid separator, a four-way Rheodyne (Supelco, Bellefonte, PA) injection valve with a 500-mL loop, and a Fisher and Porter (Warminster, PA) flow meter (0–100% N_2). Tygon tubing of different internal diameters was used for carrying the reducing agent, carrier solution, carrier gas and waste solution. The initial conditions for cold vapour generation using $NaBH_4$ as a reducing agent were established in previous works [3,6] in which a similar FI system was used and were: 0.3% mass/v $NaBH_4$ solution stabilized in 1% mass/v NaOH; 3 mL min^{-1}; 3%, v/v HCl solution used as carrier, 10 mL min^{-1}; carrier gas (N_2), 200 mL min^{-1}. A WIFUG (London, Great Britain) centrifuge model Labor-50M, was used. A Branson Sonifier 150 ultrasonic cell disruptor-homogenizer (100 W, 22.5 kHz, Branson Ultrasonics Corporation, USA) equipped with a 3- and 6-mm diameter titanium micro tip was used. The ultrasonic energy irradiation was fixed at any desired level using a power setting in the 10–50% range. The Sonifier 150 has a digital LCD display which provides a continuous read-out of the watts delivered to the end of the probe (range 5–12 W for the 6-mm probe and 2–5 W for the 3-mm probe). A Shimadzu UV-2501 spectrophotometer was used when necessary to assess the degradation of the urine organic matter. Mercury absorbance was measured with a Varian (Cambridge, UK) atomic absorption spectrometer model SpectrAA 20 plus equipped with a home-made quartz tube. The quartz tube was kept at room temperature during operation. A mercury hollow-cathode lamp operated at 4 mA was used as a radiation source. The mercury line at 253.7 nm and a slit width of 0.5 nm were selected for measurements.

2.2. Reagents

Since a pre-concentration procedure was developed special care was taken in order to choose the highest pure reagents available on the market. Milli-Q ultrapure water was used throughout. $KMnO_4$ pro analyse (max. 0.000005% Hg, N 105084), sodium oxalate pro analyse (N 106557), hydrochloric acid (N 113386) and nitric acid (N 317.1000) were purchased from Merck (Darmstadt, Germany). Sodium hypochlorite solution was purchased from Aldrich (Wisconsin, USA). Sodium tetrahydroborate(III) (N 1.06371.0100, Merck) was prepared fresh daily by dissolving the solid in sodium hydroxide solution (N 106371 Merck). An inorganic mercury stock standard solution (N 35443, 1 g dm^{-3}, Merk) was used. A methyl-mercury stock standard solution (0.1 g dm^{-3}) was prepared from methyl-mercury chloride (N 33368, Riedel-de Häen, Seelze, Germany) by dissolving the appropriate amount of the solid and making up the volume with a 5% v/v solution of ethanol (N 100983 Merck). All stock standard solutions were stored in a refrigerator at 4 °C and protected from light. Working standard solutions were prepared every day just before use by appropriate dilution of the stock standard solution. Certified Urine, H-02-04, from the INSPQ, Institut National de Santé Publique du Québec, Canada (http://www.inspq.qc.ca/), with 24 nmol/L certified total mercury concentration, was used for validation purposes. Chelex 100 (Biorad, USA, part N 143-3832, 100–200 μm mesh) sodium form resin and Dowex 50 W X 8 (Fluka, USA, N 44504) were dried up at 60 °C for 24 h before use. No additional modifications were made to the resins.