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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.

2.3. Specimen collection

The exogenous contamination was avoided by cleaning all the plastic bottles used for specimen collection with HNO_3 10% v/v and then rinsed gently with ultra-pure water and dried at room temperature. The urine specimens were collected in clean plastic bottles and acidified with HCl for mercury species preservation as recommended by Leermakers et al. [14] (5 mL of HCl to ca. 250 mL of urine). Along the text the non-treated urine is referred to this one.

The optimization of parameters was performed with 24 h urine. This urine was taken daily from a male volunteer, healthy student (22 years old).

2.4. Pre-concentration procedure

2.4.1. Step 1: urine oxidation

In previously decontaminated polyethylene tubes (50 mL capacity), 60 mg of $KMnO_4$, 20 mL of urine sample and 1 mL of concentrated hydrochloric acid were introduced. In spiked samples, 0.240 mL of 1 μg mL^{-1} mercury standard solution was added to check recoveries. Then, each sample was irradiated with ultrasound using the 6-mm microtip during 3 min at a power setting of 40% (7–8 W delivered as digital LCD displayed). The urine oxidation was considered complete when a colourless solution was obtained. A complete description of the oxidation procedure is given in Fig. 1. A comprehensive guide for steps 2 and 3 is given in Fig. 2.

2.4.2. Step 2: liquid–solid mercury extraction

(a) Ultrasonic dynamic procedure

The columns used for the on-line mercury retention (52 mm × 2 mm i.d.) were made from acrylamide and were filled with 40 mg of Chelex 100 or 70 mg of Dowex. The treated or untreated spiked urine was passed throughout the columns with the aid of a peristaltic pump at 1 or 2 mL min^{-1} (i.e. different contact times, 10 or 5 min).

(b) Ultrasonic static procedure

The Chelex and the Dowex resins (70–1000 mg), were directly added to the urine sample (oxidized or not) after the first step without pH adjustment. Magnetic stirring was used for a certain time (5–60 min). Then, the samples were centrifuged at 4500 rpm for 2 min. The urine was carefully withdrawn and the resin allowed to stand.

2.4.3. Step 3: solid–liquid mercury back-extraction

(a) Ultrasonic dynamic procedure

Once the urine was passed throughout the column, 4.5 mL of different acid solutions were used to back-extract the mercury from the resins with a flow rate of 1 mL min^{-1}. The back-extraction was developed (1) without ultrasonication or (2) with an ultrasonic field provided by (i) an ultrasonic bath and (ii) high intensity focused ultrasound (6 mm probe tip and 40% sonication amplitude) in conjunction with an ultrasonic bath. Finally, the mercury was measured by FI-CV-AAS.

(b) Ultrasonic static procedure

Different acid solutions (2.5 mL each) were added to the resin and focused ultrasound was applied for 2 min with the 3 mm probe and 40% sonication amplitude to extract the mercury from the resins into solution. Then, the samples were centrifuged at 4500 rpm for 2 min. The extracting

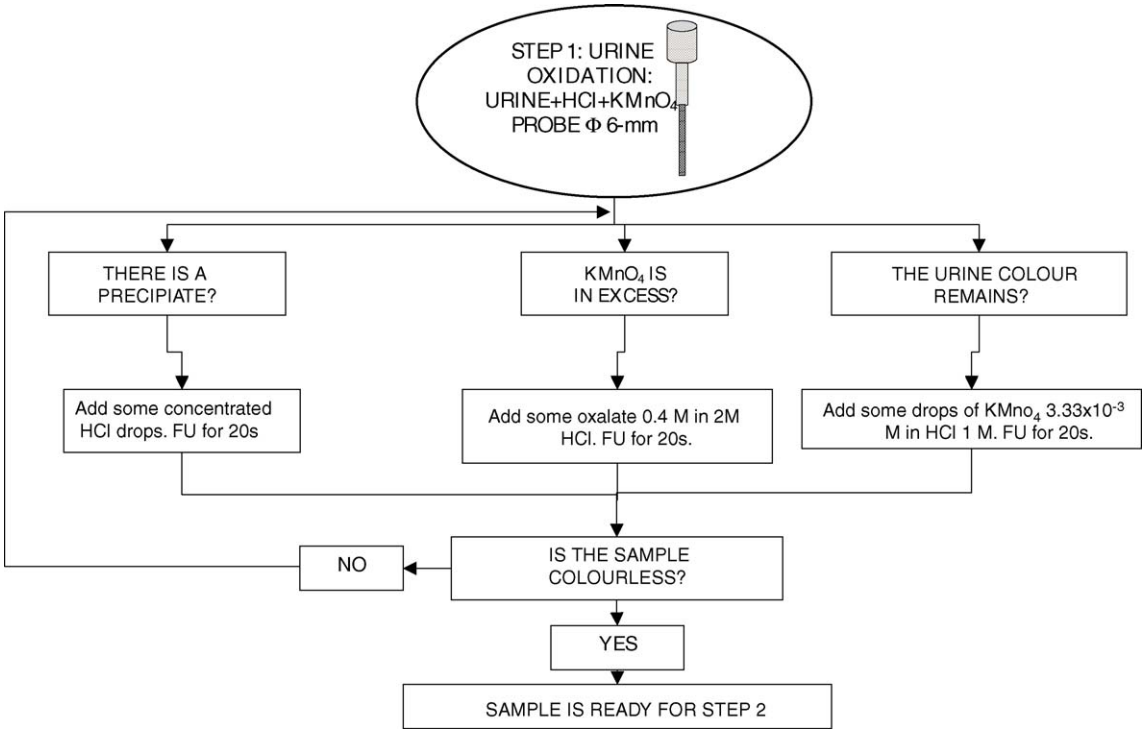

Fig. 1. Step 1: oxidation procedure: FU, focused ultrasound.

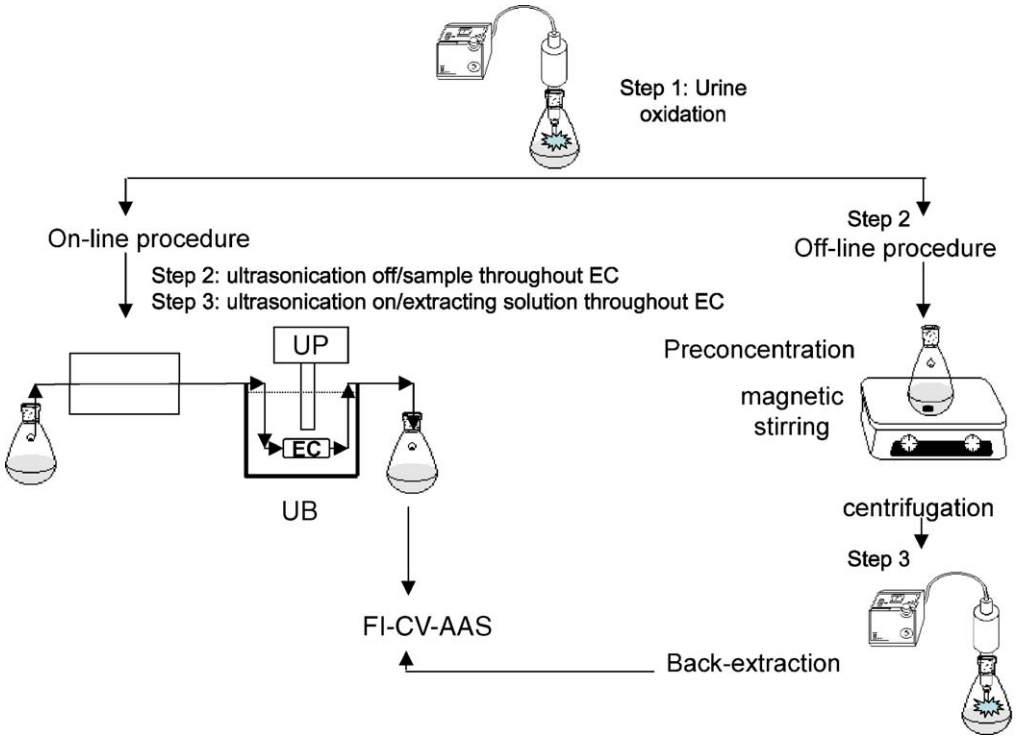

Fig. 2. Description of on-line and bath procedures: UP, ultrasonic probe; UB, ultrasonic bath; EC, extraction column.

solution was carefully withdrawn and the resin was allowed to stand. Then, the mercury was measured by FI-CV-AAS.

3. Results and discussion

The choice of the resins used for pre-concentration bases itself upon literature. Chelex-100 is a well known resin that has been reported by other authors in on-line procedures for the pre-concentration of mercury from sea-water [10,15]. Chelex-100 possesses a high selectivity for polyvalent ions, without any retention of alkali and alkaline earth elements. The Dowex resin has also been successfully used for pre-concentration of mercury from fresh water and sea water [16,17]. The mini-columns used for pre-concentration were filled with chelex-100, and dowex resins, 40 and 70 mg, respectively. These were the maxima quantities of resin introduced into the columns without clogging. Higher resin masses were tried but after the passage of a small quantity of urine (5 mL) the system clogged and the analytical procedure have to be stopped. First attempts were oriented to study the mercury recoveries from spiked untreated urine versus urine dilution. Results (data not shown) revealed that the urine dilution increased the mercury retention in the column for both resins studied. The higher the organic matter contents in the sample the poorer the performance in the liquid–solid extraction. Concerning extraction efficiencies, the best results in our conditions were obtained with the dowex resin for all studied cases, the mercury retained being ca. 35% with the dilution factor of 3. As consequence of the low yields obtained we tried the liquid–solid extraction after different sample treatments based on advanced oxidation processes, namely on ultrasonication.

3.1. Urine oxidation

A complete guide of the experimental involving this procedure is found in the works developed by Capelo et al. [2,3,6]. A flow chart is provided in Fig. 1.

3.2. Ultrasonic dynamic procedure (on-line)

3.2.1. Liquid–solid mercury extraction

The on-line procedure is depicted in Fig. 2. During the liquid–solid extraction the ultrasonic probe and the ultrasonic bath were off. The recovery of mercury was calculated by subtracting the mercury content from non-spiked samples to the spiked ones (0.240 mL of Hg 1 μg mL^{-1}). By varying the pump speed we tried to apply a different urine-resin contact time, from 10 to 20 min. The urine obtained after circulation through the column was checked for non-retained mercury. Results showed that all inorganic spiked mercury was retained in the columns either filled in with dowex (ca. 70 mg) or chelex (ca. 40 mg), using a pump speed of 1 mL min^{-1}.

3.2.2. Solid–liquid mercury back-extraction

The on-line mercury back extraction from the resin into an acid solution (4.5 mL) was done firstly without the aid of an ultrasonic field. Surprisingly, we were not able to extract all mercury from the resins. We tried the following solutions: HCl 2 mol dm^{-3}, HCl 4 mol dm^{-3} and a combination of HCl and HNO_3 (2 and 1 mol dm^{-3} respectively) as given by Bravo-Sanchez et al. [10]. Although the contact time was 4.5 min the recoveries were below 55% for all the aforementioned solutions. Similar problems with the elution of mercury from resins packed

in mini-columns after the passage of sea water were reported by Bravo-Sanchez et al. [10], but they were able to recover 100% of spiked mercury using the above mentioned mixture of HCl and HNO_3. Instead of trying an increment in the acid concentration or a time consuming screening of different acids or reagent combinations to achieve the total mercury back-extraction, we decided to improve the process using an ultrasonic field. In a first approach (see Fig. 2) an open dynamic system with an ultrasonic bath was tried. These procedures have been reported in literature and have also been recommended by recognised authors [12,13,18]. Nevertheless, from a theoretical point of view, ultrasonication through containers walls should be avoided, since the effectiveness of ultrasonic wave decreases rapidly, and less cavitation efficiency is expected as a function of thickness of the container's walls. For a detailed description of the advantages and disadvantages of ultrasonication through vessels containers see ref. [19], pp. 52–53. The results obtained with the dynamic system were surprisingly low: only ca. 55% of the mercury was recovered. In order to enhance the solid–liquid extraction, the dynamic system was improved increasing the ultrasonic field adding an ultrasonic probe (6 mm diameter) 2 cm above the mini-column, as it is depicted in Fig. 2. Despite that both ultrasonic systems were on at the same time, and that total resin-solution contact time was as high as 5 min, it was not observed an increment in the extraction yields. In order to check whether the wall thickness of the micro-columns was the cause of the poor sonication efficiency or not, tygon tubes with thickness as short as 0.86 mm were used as mini-columns, and the whole sonication procedure (i.e. UB plus FU) was used to perform the solid–liquid extraction. Nevertheless, the recoveries were of the same order as the ones obtained with the initial mini-column. Perez-Corona et al. [20] have reported adsorption of mercury on the column walls when they studied the stability of inorganic mercury and methyl-mercury on yeast-silica gel micro-columns. So we performed an experience in which a sample was passed through non filled columns in the same range time than if they were filled with resin. The mercury recovery was $95 \pm 7\%$ ($n = 3$), concluding that the column did not retained mercury. In order to quantify the mercury retained in resin, the whole procedure was developed and the dowex resin was withdrawn from the column, introduced in an eppendorf type vessel with 4.5 mL of HNO_3 5.8 mol dm^{-3} and subjected to ultrasonication with probe (2 min, 6 mm diameter, 40% amplitude, 7–8 W). At this time, the mercury recovered was $97 \pm 6\%$ ($n = 3$). Hence, it was demonstrated that the mercury was fully retained in the resin, but was not eluted, even with the aid of the ultrasonic field. Finally, a solution of HNO_3 7.2 mol dm^{-3} was passed throughout the columns filled with dowex resin pumped at 1 mL min^{-1}. The mercury recoveries were of $105 \pm 7\%$ and $104 \pm 5\%$ with and without ultrasound, respectively.

3.3. Ultrasonic static procedure (bath procedure)

3.3.1. Liquid–solid mercury extraction

The bath procedure is depicted in Fig. 2. As far as liquid–solid extraction is concerned, the contact time ranged from 5 to 60 min (see Fig. 3a), and magnetic stirring was used to ensure maximum contact. A 70 mg of dowex and 70 mg of chelex-100 were used. The best results were obtained with the dowex resin. After 40 min of contact the mercury recovered from the treated urine was $95 \pm 3\%$ ($n = 2$) for dowex versus $83 \pm 3\%$ ($n = 2$) for chelex. These results are attained for treated urine (step 1), otherwise Hg recovery is below 40%. A longer contact time (60 min) did not improve the extraction efficiency for the chelex resin ($84 \pm 2\%$, $n = 2$). In order to reduce the time needed in this step, the amount of resin was increased in the range 70–1000 mg and the selected contact time was 20 min. As can be seen in Fig. 3b, with 20 min of contact time, total recovery was only achieved with 500 mg of the dowex resin, whilst the maximum amount of mercury recovered with chelex was $79 \pm 5\%$, even with an amount of resin of 1000 mg.

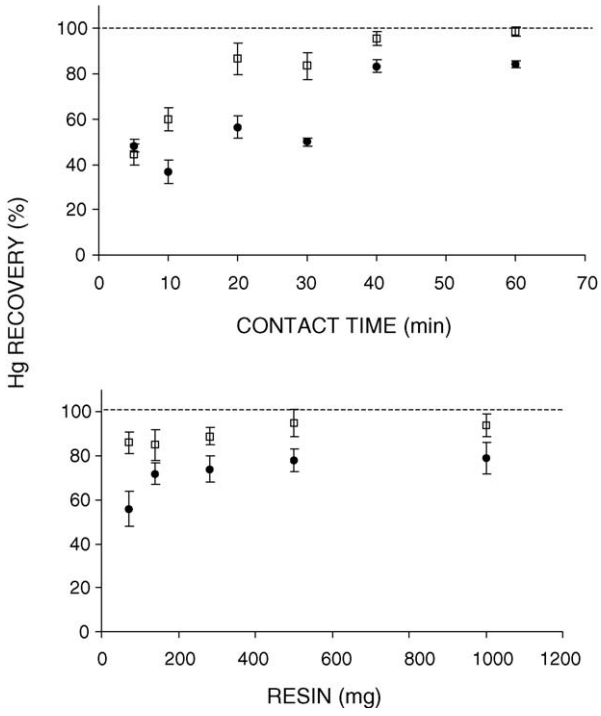

Fig. 3. (a) Mercury recovery as function of the resin-urine contact time (step 2) in static experiments: (□) 70 mg dowex resin; (●) 70 mg chelex resin. Conditions for back-extraction (step 3): 3 mm sonication probe; 2 min sonication time; 40% sonication amplitude; HNO_3 7.2 mol dm^{-3} as extracting solution. (b) Mercury recovery as function of the resin mass in static experiments. Resin-urine contact time of 20 min with magnetic stirring. Conditions for back-extraction (step 3): 3 mm sonication probe; 2 min sonication time; 40% sonication amplitude; HNO_3 7.2 mol dm^{-3} as extracting solution.

3.3.2. Solid–liquid mercury back-extraction

The conditions used in step 3 during the optimization of the step 2 were 2.5 mL of HNO_3 7.2 mol dm^{-3}, a sonication probe of 3 mm, a sonication amplitude of 40% and a sonication time of 2 min (5–12 W delivered). Those conditions were chosen to ensure a rapid and total mercury back-extraction from resins. In order to minimize the acid concentration used, a study was developed with different acid concentrations, ranging 0–7.2 mol dm^{-3}%, v/v. The results are shown in Fig. 4 and revealed that the minimum acid concentration to recover all the mercury from the dowex resin was HNO_3 5.8 mol dm^{-3} whereas

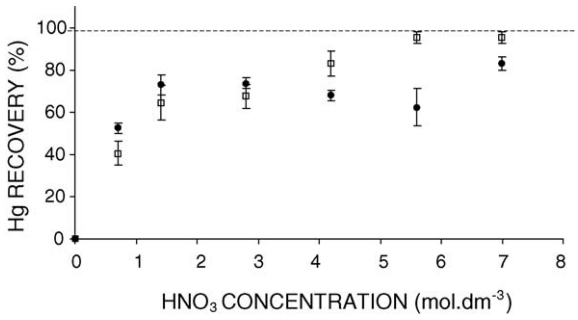

Fig. 4. Mercury recovery as function of the acid concentration (step 3) in static experiments. Experimental conditions of (i) step 2: 140 mg of resin, contact time 40 min with magnetic stirring; (ii) step 3: 3 mm sonication probe; 2 min sonication time; 40% sonicatio amplitude.

even with an acid nitric concentration as high as 7.2 mol dm^{-3} the yield obtained for the chelex resin was only ca. 80%. For dowex resin plus the highest nitric acid concentration tested, 7.2 mol dm^{-3} as extracting solution, the mercury recovery was 59 ± 9% without the aid of an ultrasonic field. We also tried with dowex resin the following combinations as extracting solutions: (i) HCl 2 mol dm^{-3} + HNO_3, 1 mol dm^{-3}, and HCl 1 mol dm^{-3} + NaClO, and 3%, v/v, respectively. Mercury recoveries were 49% for the first combination and 5% for the second one.

3.4. Validation of the methodology

The new analytical methodology was validated for the static procedure by using the reference material for mercury in urine (24 nmol dm^{-3}), H-02-04, from the INSPQ. The procedure developed in this work was applied to four replicates as follows: 5 mL of the reference material was diluted to 20 mL. Then steps 1–3 were done as described in sample treatment: the amount of dowex resin used was 140 mg and the contact time for step 2 was 40 min. In step 3, the nitric acid concentration and volume used were, 5.8 mol dm^{-3} v/v and 2.5 mL, respectively; the following sonication conditions were applied: 40% sonication amplitude, 2 min sonication time and a diameter tip of 3 mm. The mercury recovered was 95 ± 10%.

The conditions mentioned above for steps 1–3 were used with 20 mL of non-certified urine spiked with 0.24 mL of methylmercury 1 μg mL^{-1}. Following the procedure, steps 2 and 3 were done and the mercury recovery was 97 ± 6%.

3.5. Analytical figures of merit

The limit of quantification in urine, 0.25 ng mL^{-1} of Hg, was calculated from the measurement of 10 blanks with the criterion of 10σ and taking into account the pre-concentration factor of 8. The equation of the calibration graph was: absorbance (peak height) = $[0.0026 \pm 0.0002][Hg] + [0.001 \pm 0.0003]$ ($r = 0.999$; calibration range = 2–100 ng mL^{-1})

4. Conclusions

Researchers should carefully work with ultrasonic dynamic procedures in solid–liquid metal ion back extraction (step 3), since (i) it is actually far from be a reliable approach at the analytical laboratory, and (ii) it deserves more research to elucidate in which solid–liquid extractions is a realistic approach. It should be carefully consider if the achievements found in ultrasonic dynamic procedures for solid–liquid extraction of metals ions are caused by real or false ultrasonic effects as defined by Mason [21]. As an example, in a system like the one depicted in Fig. 2 for dynamic procedure, for sonication times longer than the ones here reported but commonly used by other authors, the ultrasonication induces heating of the water, and this temperature increment is transmitted to the extracting liquid that is in contact with the solid. Thus, the enhancement in extraction efficiency may be due to an increment in the mass transfer caused by heating rather than by real ultrasonic effects. As aforementioned, when the ultrasonic wave needs to cross the wall of the column, the ultrasonic efficiency is greatly decreased (for solid–metal extraction the efficiency includes not only cavitation but also mechanical impact and bubble collapse). In the experimental conditions used in this work, the ultrasonic dynamic approach was useless.

The oxidation procedure developed in step 1 allows mercury pre-concentration in dowex resin without pH adjustment or previous resin treatment, and leads to a Hg recovery of ca. 100%, for the ultrasonic static approach and for the dynamic approach (the latter without ultrasounds). Chelex resin, in the conditions described in this work for the ultrasonic static approach, has a limited success, the mercury recovery being ca. 80%. The time needed for complete liquid–solid extraction with the ultrasonic static procedure with dowex resin was 40 min, for 70 mg or 20 min for 500 mg (step 2), whilst 20 min was the required time in the dynamic procedure for columns filled with 70 mg of dowex resin. The total amount of reagents was 1 mL of HCl conc. plus 60 mg of $KMnO_4$ (step 1) and 2.5 mL of HNO_3 5.8 mol dm^{-1} (step 3), matching the analytical minimalism concepts, that is, low reagents quantities. The higher concentration factor tried was 8 (20–2.5 mL). However, other factors can be achieved by varying the volume of urine, the volume of extracting agent and the amount of resin.

As far as comparison with liquid–liquid pre-concentration of Hg using high intensity focused ultrasound concerns, as demonstrated in previous work [6], the solid–liquid extraction using resins only offers the benefit of avoid organic solvents, since the whole time for the sample treatment in the liquid–liquid approach was 5 min, clearly shorter than the whole time needed in the solid–liquid approach.

This work open new approaches for ultrasonication at the analytical laboratory, since both ultrasonic procedures, static and dynamic, need of further research to elucidate their analytical robustness, i.e., for the same schemes presented in Fig. 2, different resins, samples and elements than the ones here presented must be assessed.

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References

[1] T. Tsubaki, K. Irukayama (Eds.), Minamata Disease, Methymercury Poisoning, Kodensha, Tokyo, 1977.
[2] J.L. Capelo, C. Maduro, A.M. Mota, Ultrason. Sonochem. 13 (2006) 98.
[3] J.L. Capelo, C. Maduro, A.M. Mota, J. Anal. At. Spectrom. 19 (2004) 1.
[4] C.J. Horng, S.R. Lin, Talanta 45 (1997) 75.
[5] T. Guo, J. Baasner, Anal. Chim. Acta 278 (1993) 189.
[6] J.L. Capelo, C.D. Dos Reis, C. Maduro, A. Mota, Talanta 64 (2004) 217.
[7] B. Welz, D.L. Tsalev, M. Sperling, Anal. Chim. Acta 261 (1992) 91.
[8] R.M. Blanco, M.T. Villanueva, J.E. Sanchez-Uría, A. Sanz-Medel, Anal. Chim. Acta 419 (2000) 137.
[9] J.A.G. Neto, L.F. Zara, J.C. Rocha, A. Santos, C.S. Dakuzaku, J.A. Nobrega, Talanta 51 (2000) 587.
[10] L.R. Bravo-Sanchez, B.S.V. de la Riva, J.M. Costa-Fernández, R. Pereiro, A. Sanz-Medel, Talanta 55 (2001) 1071.
[11] J.L. Capelo, P. Ximenez-Embun, Y. Madrid-Albarran, C. Camara, Trac-Trends Anal. Chem. 23 (2004) 331.
[12] J.L. Luque-García, M.D. Luque de Castro, Trac-Trends Anal. Chem. 22 (2003) 41.
[13] J. Ruiz-Jiménez, J.L. Luque-García, M.D. Luque de Castro, Anal. Chim. Acta 480 (2003) 231.
[14] M. Leermakers, W. Baeyens, P. Quevauviller, M. Horvat, Trac-Trends Anal. Chem. 24 (2005) 383.
[15] C. Guéguen, C. Belin, B.A. Thomas, F. Monna, P.Y. Favarger, J. Dominik, Anal. Chim. Acta 386 (1999) 155.
[16] J. Sanz, J.C. Raposo, J. Larreta, I. Martinez-Arkarazo, A. de Diego, J.M. Madariaga, J. Sep. Sci. 27 (2004) 1202.
[17] J.C.A. de Wuilloud, R.G. Wuilloud, R.A. Olsina, L.D. Martinez, J. Anal. At. Spectrom. 17 (2002) 389.
[18] M.C. Yebra-Biurrum, A. Moreno-Cid, S. Cancela-Perez, Talanta 66 (2005) 691.
[19] T.J. Mason, Sonochemistry, Oxford University Press, 1999.
[20] M.T. Perez-Corona, Y. Madrid-Albarran, C. Camara, Fresenius J. Anal. Chem. 368 (2000) 471.
[21] T.J. Mason, Ultrason. Sonochem. 10 (2003) 175.