Chem. Anal. (Warsaw), **47**, 429 (2002)

Analytical Performance of Solid Sorbents for Mercury Speciation**

by A. Krata, E. Kopyść, K. Pyrzyńska and E. Bulska*

Department of Chemistry, Warsaw University,
ul. Pasteura 1, 02–093 Warszawa, Poland

Key words: mercury speciation, solid sorbents, cold vapour AAS

Several solid sorbents (Dowex 50Wx4, Amberlyst A–27, C–16 and Chelex 100) were tested in respect to their efficiency of sorption and elution of inorganic and organic mercury compounds. It was found that both forms of mercury could be effectively trapped by all investigated sorbents. However the selective elution of organic and inorganic mercury compounds by 0.1% thiourea in 3% or 8% HCl was achieved with the use of Dowex 50Wx4. The detection limit for Hg^{2+} and $PhHg^{+}$ was 0.013 mg L^{-1} and 0.075 mg L^{-1} respectively. The precision of the determination was 5.2% at the level close to detection limit, and 0.8% at the level of 50 mg L^{-1}. The developed procedure, based on the retention of both mercury species and their sequential elution, was tested by analysis of the springly water spiked with known amount of Hg^{2+} and $PhHg^{+}$.

Zbadano możliwość zatężenia i rozdzielenia nieorganicznych i organicznych związków rtęci na wybranych złożach sorpcyjnych (Dowex 50Wx4, Amberlyst A–27, C–16 i Chelex 100). Stwierdzono, że obie formy rtęci efektywnie zatężają się na wszystkich badanych sorbentach. Selektywne wymycie zatężonych związków rtęci za pomocą roztworu 0.1% tiomocznika w 3% lub 8% kwasie solnym uzyskano przy stosowaniu złoża Dowex 50Wx4. Granica wykrywalności dla Hg^{2+} i $PhHg^{+}$ wyniosła odpowiednio 0.013 mg L^{-1} i 0.075 mg L^{-1}. Precyzja pomiarów na poziomie bliskim granicy wykrywalności wyniosła 5.2%, natomiast na poziomie stężenia 50 mg L^{-1} - 0.8%. Zaproponowana procedura wykorzystująca jednoczesne zatężenie, a następnie sekwencyjne wymycie obu związków rtęci 0.1% roztworem tiomocznika w 3% lub 8% HCl, została wykorzystana do badania specjacji rtęci w próbkach wody oligoceńskiej z dodatkiem znanej ilości Hg^{2+} i $PhHg^{+}$.

** Devoted to 100th Anniversary of Professor Wiktor Kemula birthday

* Corresponding author. E-mail: ebulska@chem.uw.edu.pl

Mercury is a toxic element of widespread environmental and clinical significance. It can be found in either inorganic or organic forms, which significantly differ in their toxicity. It is well known that organomercury compounds (*e.g.* methylmercury) are much more toxic than inorganic species. Therefore, it is essential to develop accurate and precise analytical method for the determination of trace amount of various mercury species.

Methods used for the trace detection of total mercury have been recently reviewed [1]. To determine different species of this element both gas and liquid chromatographic techniques are usually coupled to selective and sensitive detectors such as atomic absorption spectrometry (AAS) [2, 3], atomic fluorescence spectroscopy (AFS) [4,5], microwave induced plasma atomic emission spectrometry (MIP–AES) [6–9] or inductively coupled plasma mass spectrometry (ICP–MS) [10–12]. The simple alternative to the hyphenated techniques mentioned above is the application of preconcentration/separation procedure consists of solid-phase extraction followed by cold vapour atomic absorption spectrometry (CVAAS) determination of mercury. The CVAAS offers several advantages as high sensitivity, absence of spectral interferences, relatively low operation costs, speed and simplicity and is used for the determination of mercury in environmental and biological samples [1,13].

The efficiency of different solid sorbents have been studied mostly for preconcentration of mercury inorganic forms, *e.g.* Hg(II) [14–19]. The most effective sorbents for this purpose are chelating resins with sulfur containing ligands, such as dithizone [15,19], thiocarbazide [16,18], thiosalicylate [17] or thiocarbamate [20,21]. Few reports can be found in the literature regarding the speciation of mercury with the use of solid sorbents [21–26]. Chwastowska *et al.* have used for preconcentration of inorganic mercury and alkylmercury compounds, the chelating resin obtained by immobilization of thionalide [23] or 2-mercaptobenzatthiazole [24] on a macroporous acrylic ester polymer bed. Both mercury species were eluted with an acidic aqueous solution of thiourea and determined by CVAAS after their successive reduction by tin(II) chloride. Sorption of mercury species on a microcolumn of suphydryl cotton [25], C_{18} support modified with diethyldithiocarbamate [21] or baker's yeast immobilized on silica gel [26] was also reported.

In this work several commercially available solid sorbents were examined for the preconcentration and separation of inorganic as well as organic mercury species. These sorbents can be used for *in situ* field sampling followed by the elution of mercury species from the microcolumn in the laboratory and their final determination.

EXPERIMENTAL

Apparatus

A FIMS flow-injection atomic absorption spectrometer (Perkin–Elmer, Germany) was used for all experiments. A sample loop of 200 µL was used. Measurements were performed in the peak-height modes.

Peristaltic pump (Zalimp, type PP2B–15. Poland) was used for transferring the analyzed solutions as well as eluent solution through the columns.

Reagents

Inorganic mercury standard solution was prepared by appropriate dilution of a 1 g L^{-1} mercury(II) nitrate stock solution (GUM, Poland) in 3% (v/v) hydrochloric acid. An organic mercury solution (0.1 g L^{-1}) was prepared by dissolving an appropriate mass of phenylmercury acetate (Merck, Germany) in 100 mL of water. The final concentration was achieved by dilution with 5% (v/v) HCl. Working solutions were prepared before use by dilutions of the stocks solutions with water.

Thiourea (Fluka, Sweden) solution was prepared by dissolution an adequate amount of thiourea in hydrochloric acid (Merck, Germany).

Sodium tetrahydroborate(III) solutions were prepared daily by dissolving the appropriate amount of $NaBH_4$ (Aldrich, England) in 0.008 mol L^{-1} of KOH.

The following solid sorbents were used: cation-exchanger Dowex 50 WX4 Heidenberg, 50–100 mesh (Serva, Germany), anion-exchange resin Amberlyst A–27, 16–50 mesh (BDH, England), reverse phase silica bonded with hexadecyl functional groups Diasorb 130–C–16T, 60–160 mesh (BioChemMack, Russia) and chelating resin with iminodiacetic acid exchange groups Chelex (100–200 mesh) from BioRad Laboratories, U.S.A. All sorbents were conditioned with 2 mol L^{-1} HCl solution, than washed with water until the pH was neutral. C_{16} was washed in ethanol, then in water.

Procedure

The microcolumns made from pipets tips of 5 mL, packed with 0.5 g of respective sorbent, with glass wool stoppers at the ends were used. In the preconcentration step 8.6 mL 100 µg L^{-1} mercury solutions were passed (at a flow-rate of 2.8 mL min^{-1}) through the microcolumns. Before elution columns were washed with doubly distilled water. For elution 5 mL of thiourea solution in HCl was passed at a flow-rate of 2.8 mL min^{-1}. The concentration of mercury was determined by CVAAS method using $NaBH_4$ as reducing agent [27].

RESULTS AND DISCUSSION

Sorption of mercury species

Dowex 50Wx4 — cation exchanger, Amberlite A–27 — anion exchange resin, silica support C_{16} — analogous to C_{18} and Chelex 100 — chelation exchange resin with iminodiacetate functional groups were tested in respect to their efficiency for sorption of inorganic (Hg(II)) as well as organic (PhHg) mercury species. In experiments defined volume of the solutions containing 100 mg L^{-1} of mercury were passed through the columns packed with appropriate sorbent as it was described in experimental section. Quantitative sorption of both mercury species was achieved for Dowex 50Wx4, Amberlite A–27 and Chelex 100 resin. In the case of columns packed with C_{16} silica nearly 100% of sorption efficiency was observed for PhHg and only 90% for Hg(II). The retention mechanism of mercury on the silica support seems to be a simple adsorption/desorption process [26]. The results obtained with Chelex 100 were predictable, because this chelating resin has been used extensively to enrichment of many transition metals [28].

The kinetics of sorption was studied by varying the flow-rate of the sample solution in the range of 0.5–3.5 mL min^{-1}. It was found that in all experiments, after 4 min of loading time the concentration of mercury in eluent solution was below the detection limit. Therefore, it could be concluded that the retention kinetics is satisfactory. For further work the flow-rate of 2.8 mL min^{-1} was chosen.

It was also found that the pH of the sample solution was not a critical factor. Both Hg(II) and PhHg species exhibit high affinity towards investigated sorbents in acidic media and could be preconcentrated in pH range of 2–8. These conditions are very suitable for the natural water samples, which should be acidified after on field sampling.

The detection limit for Hg^{2+} and $PhHg^{+}$ was 0.013 μg L^{-1} and 0.075 μg L^{-1} respectively. The precision of the determination was 5.2% at the concentration level close to detection limit and 0.8% at the level of 50 μg L^{-1}.

Elution of organic and inorganic mercury

Based on the results presented in literature [16,17,21,23] thiourea was chosen as the eluent. For preliminary experiments the solution of 5% thiourea in 3% HCl was applied. By using 15 mL of eluent the desorption efficiency of 80–100% for both mercury species from Chelex 100, C_{16} silica and Amberlite A–27 resin was achieved. In contrary, only 5% of Hg(II) and 15% of phenylmercury was eluted from microcolumn packed with Dowex 50Wx4.

Since the selective retention of both mercury species was not possible, the differentiation of inorganic and organic mercury species through their selective elution was evaluated. Therefore, it was of interest to investigate the influence of the thiourea as well as HCl concentration on the elution efficiency from Dowex 50Wx4. Various concentrations of thiourea (5%, 2.5%, 1%, 0.5%, 0.1%) and hydrochloric acid (3%, 5%, 6%, 8%, 10%) were tested. The results are presented in Figure 1 and Figure 2 respectively. When 3% HCl was used, elution of PhHg increased significantly with decreasing concentration of thiourea while elution of inorganic mercury is not affected. The most promising results were obtained for the solution of 0.1% thiourea in 3% HCl. The blank level for 0.1% thiourea in HCl was 0.6 mg L^{-1} and 0.4 mg L^{-1} for organic and inorganic mercury respectively. In these conditions nearly 100% of organic mercury and only 8% of inorganic mercury respectively were eluted. It was found that increasing the concentration of HCl caused the increase in efficiency of elution of both forms. Finally the 8% HCl was found to be sufficient to elute Hg(II).

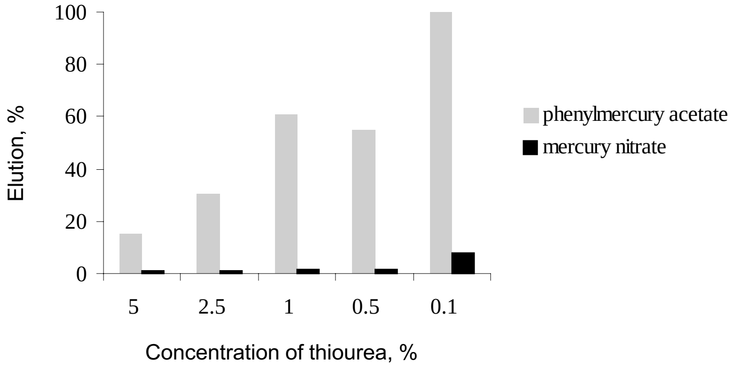

Figure 1. Effective elution of mercury species with various concentration of thiourea in 3% HCl from Dowex 50Wx4 resin

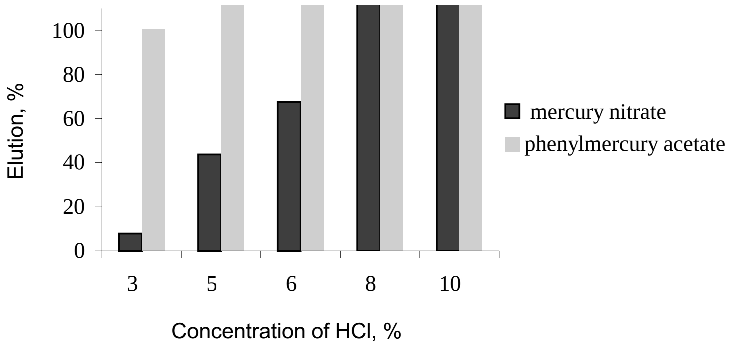

Figure 2. Effective elution of mercury species with 0.1% thiourea in various concentration of HCl from Dowex 50Wx4 resin

When efficiency of elution was investigated it was essential to use matrix matching standard solution for calibration. For this purpose phenylmercury acetate standard solution containing 10 µg L^{-1} of mercury (0.1% or 0.5% thiourea in 5% HCl) and mercury nitrate standard solution containing 10 μg L^{-1} of mercury (0.1% thiourea in 3% HCl) were prepared. It was found that the sensitivity is much lower for organic mercury when compared with inorganic mercury standard solution. However, it was observed, that the absorbance increases slowly during a few hours. Measurements of absorbance were performed every 6 min during first 30 min then every 30 min during 180 min. Results are presented in Figure 3.

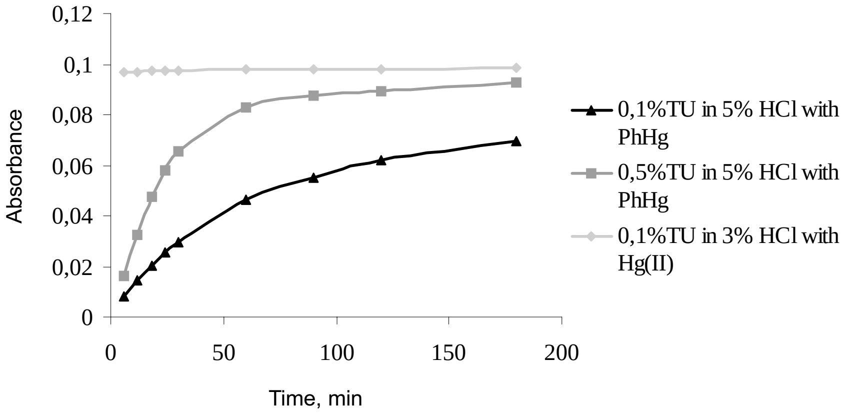

Figure 3. The effect of time on absorbance signal of 10 mg L^{-1} mercury compounds in thiourea/HCl solution

Sensitivity for standard solutions of phenylmercury acetate in the presence of 0.1% thiourea reached *plateau* after 3 h, thus allowing to get maximal sensitivity. This depen-dence is not observed for standard solution of inorganic mercury. In our work all measu-rements were performed immediately after elution, which made the experimental proce-dure much shorter. However the above described phenomena should be taken into account and always time of measurement should be controlled.

Separation of various mercury species from their mixture

Optimized conditions for the standard solutions containing individual compounds were verified by analyzing of model solutions composed of the mixture of organic and inorganic mercury. For this purpose the solution containing 100 μg L^{-1} of phenylmercury acetate and 100 μg L^{-1} of mercury nitrate was used. It was found that the sorption efficiency of both species in mixed solution on the Dowex 50Wx4 was close to 100%. Then, the sequential elution, described above was performed. In the first fraction phenylmercury acetate was eluted by 0.1% thiourea in 3% HCl. In the second fraction mercury nitrate was eluted by 0.1% thiourea in 8% HCl. This sequential elution was tested either with the use of one column (for the mixture of both species) either with two parallel columns (for the solutions containing individual species). The aim of this experiment was to evaluate whether any interaction between mercury species could occur during elution. Results for organic and inorganic mercury mixed solution eluted from one column are comparable with efficiency of elution of individual species from separate columns. That means that no interaction occurs during the elution.

This encouraged us to apply the developed procedure with sequential elution for natural samples. For this purpose the springly water from underground source in Warsaw was used, because of its well-defined and stable composition [29]. As the mercury content was found to be below detection limit the accuracy of the proposed procedure was tested by recovery of known amounts of Hg(II) and phenylmercury added to the samples. The obtained results are presented in Table 1.

Table 1. Recovery of 100 μg L^{-1} mercury species (%) from different sample matrix

Sample	PhHg	Hg(II)
Distilled water	100.4 ± 2.82	106.7 ± 0.86
Springly water	122.1 ± 4.45	78.1 ± 0.71

Higher results of recovery for organic mercury, when 0.1% thiourea in 3% HCl was used, arise probably from partial elution of inorganic mercury in these conditions. In fact, effective elution of Hg(II) with 0.1% thiourea solution in 8% HCl was lower. This means that sorption/desorption behaviour of Hg(II) is affected by the composition of the natural water. Perez–Corona *et al.* [30] reported that inorganic mercury solution seems to be less stable than methylmercury species since it remained unaltered for a maximum period of one week even when was stored at –20°C. A possible explanation for this observation could be the transformation into other mercury species. Also the recoveries for inorganic mercury from aged (1 month storage) columns packed with baker's yeast immobilized on silica gel were lower (only 70%) in comparison with those freshly prepared [30]. Moreover, in freshwater and sediment slurries samples part of inorganic mercury was converted into alkylmercury species probably *via* the activities of sulfate-reducing bacteria [31]. The investigation of sorption/desorption behaviour of inorganic mercury in different matrices will be undertaken in the future.

CONCLUSIONS

The examined solid sorbents Dowex 50Wx4, Amberlyst A–27, C_{16} silica and Chelex 100 were found to be sufficient for effective sorption of both forms of mercury compounds. However, the possibility to differentiate the mercury species by sequential elution was found only for Dowex 50Wx4. It was found that 0.1% of thiourea solution in 3% hydrochloric acid could be effective for the elution of phenylmercury and 0.1% thiourea solution in 8% HCl is effective for the elution of residual inorganic mercury. Therefore this sequence could be used for selective separation of mercury species. This procedure was verified by analysis of the springly water from underground source in Warsaw with additions of organic and inorganic mercury. The proposed method is very simple, can be adopted for routine analysis and it competes with sophisticated hyphenated techniques as a means of differentiating mercury species of different toxi-city. This method could be applied for on-field sample preparation and preconcentration followed by determination of mercury in the laboratory.

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Received September 2001
Accepted January 2001