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Agnieszka Krata · Krystyna Pyrzyńska · Ewa Bulska

Use of solid-phase extraction to eliminate interferences in the determination of mercury by flow-injection CV AAS

Abstract Solid-phase extraction with two-step elution has been developed for effective elimination of copper and iron interference with mercury determination by flow-injection cold vapour atomic absorption spectrometry (CV AAS). Sodium tetrahydroborate(III) was used as reducing agent. Cation-exchanger Dowex 50Wx4 was applied for the sorption of mercury and both interfering ions. In the first step elution of Cu(II) and Fe(III) was performed using $0.5\,\mathrm{mol\,L^{-1}}$ KF solution. Then mercury was eluted with 0.1% thiourea in 8% HCl. The detection limit (3δ) for Hg(II) was $27\,\mathrm{ng\,L^{-1}}$. The expanded uncertainty estimated for the whole procedure was about 6%. The accuracy of the proposed method was evaluated by determination of the recovery of known amount of mercury added to mineral, spring, and tap waters, and by analysis of a certified reference material BCR-144R (sewage sludge).

Keywords Mercury · CV AAS · Interferences · Solid-phase extraction

Introduction

Determination of trace amounts of mercury in environmental samples is still of great importance due to its high toxicity and accumulative character. Mercury toxic potency is also increased by transformation into organic forms via biomethylation [1]. One of the most common analytical approaches for the determination of total mercury is cold vapour atomic absorption spectrometry (CV AAS). Sodium tetrahydroborate(III) is often preferred as the reducing agent because it offers effective and fast reduction of mercury into its elemental form also for organic compounds that are not reduced by $SnCl_2$ [2]. Moreover, tin(II) shows

strong adsorption on the walls of the reaction vessel [3]. Although other atomic spectrometric methods, e.g. inductively coupled plasma optical emission spectrometry (ICP–OES) [4], inductively coupled plasma mass spectrometry (ICP–MS) [5], and graphite furnace atomic absorption spectrometry (GFAAS) [6], can also be used, directly or after vapour generation, CV AAS is a very good compromise between sensitivity and operating cost.

The direct determination of mercury in real samples is, however, not free from various interferences and therefore precautions are required at all stages of the analytical procedure [7, 8]. Most pronounced are chemical interferences particularly those caused by elements that could simultaneously undergo reduction and form amalgams [9, 10]. A solution of 1,10-phenanthroline and thiosemicarbazide has been applied to suppress the effects of Cu, Pb, Ag, Au, Pt, Pd, and Se [9]. It was also found that the standard addition and successive dilution might be successfully used in the presence of Zn, Bi, Cd, and Pt [10]. Welz and Schubert-Jacobs [11] proposed the addition of Fe(III) in the presence of hydrochloric acid to eliminate the effects of copper, nickel, and silver.

The matrix interferences could be also avoided by applying a separation step before the reduction. Beside separation from matrix components, enrichment of an analyte could be achieved. In the case of mercury, various preconcentration/separation procedures include liquid–liquid extraction [12], amalgamation on a gold trap [7, 13], and the application of solid sorbents [14, 15, 16, 17, 18, 19, 20, 21]. Chelating resins containing sulfur atoms in the functional groups, such as dithiocarbamate and dithizone [14, 15], thiocarbahydrazide [16], thiosalicylate [17], and 6-mercaptopurine [18], have been mainly evaluated for this purpose. Other reported approaches include the formation of the diethyldithiophosphate complex and its retention on a C_{18} microcolumn [19] and 7(4-ethyl-1-methyl-octyl)-8-hydroxiquinoline adsorbed on Bondapack C18 (Kelex-100) [20]. Many of the proposed sorbents were synthesised in the laboratory and therefore are not commercially available [15, 16, 17, 18]. Some resins, particularly those based on poly(dithiocarbamate), are reluctant

A. Krata · K. Pyrzyńska · E. Bulska (✉)
Faculty of Chemistry, Warsaw University,
Pasteura 1, 02–093 Warsaw, Poland
e-mail: ebulska@chem.uw.edu.pl

to release retained analyte and the dissolution of the resin prior to analysis is necessary [21].

The aim of the present work was to investigate the effect of several metal ions as potential interferents in trace mercury determination in natural water samples and to develop the procedure for on-line separation of mercury, mainly from Cu and Fe, using Dowex 50Wx4 cation-exchange resin.

Experimental

Reagents

Mercury standard solution was prepared by appropriate dilution of a 1000 mg L^{-1} $Hg(NO_3)_2$ stock solution (GUM, Poland). The solutions of sodium, potassium, calcium, magnesium, nickel, zinc, iron, cadmium, copper, selenium(IV), selenium(VI), antimony(III), antimony(V), arsenic(III), and lead were prepared by dilution of 1 g L^{-1} respective standard solutions, all from Merck, Germany. Thiourea (Fluka) solution was prepared by dissolving appropriate amounts of reagent in suprapure 37% (v/v) hydrochloric acid (Merck). Sodium tetrahydroborate(III) solutions were prepared daily by dissolving the appropriate amount of NaBH$_4$ (Aldrich, The Netherlands) in 0.008 mol L^{-1} KOH solution.

Certified reference material BCR-144R (sewage sludge of domestic origin) was obtained from the Institute for Reference Materials and Measurements (Geel, Belgium). For digestion the mixture of acids used was: 2 mL 65% (m/m) HNO$_3$, 1 mL 37% (m/m) HCl, and 200 µL of 40% (m/m) HF.

Cation-exchanger Dowex 50Wx4, 50–100 mesh (Serva, Germany), was applied in the separation step. This resin was conditioned with 2 mol L^{-1} HCl solution, then washed with water until the pH was neutral.

Apparatus

An FIMS (Perkin–Elmer, Germany) atomic absorption spectrometer with flow-injection unit was used for determination of mercury. Samples were introduced by means of a 200-µL loop and reduction was performed by freshly prepared 0.025% w/v NaBH$_4$ solution. Measurements were performed in the peak-height mode. An Analyst 300 (Perkin–Elmer) flame atomic absorption spectrometer was used for the determination of Cu, Fe, and Se. A peristaltic pump (Zalimp, Poland) was used for controlling the flow rates of analyte solutions and eluent through the microcolumns. A Multiwave (Perkin–Elmer) closed microwave sample-preparation system was employed for decomposition of the samples.

Procedure

The microcolumns were made from the tips of pipettes and packed with 0.5 g ion exchanger Dowex 50Wx4. In the first step 6 mL of a solution containing mercury and other interferent metal ions was passed at a flow rate of 1 mL min^{-1} through the microcolumn, which was then washed with 1 mL double-deionised water. Elution of Cu and Fe was performed using 10 mL 0.5 mol L^{-1} KF solution. For elution of mercury, 15 mL of 0.1% w/v thiourea in 8% w/v HCl was passed through the microcolumn (1 mL min^{-1} flow rate). The concentration of mercury was determined by CV AAS.

Reference material (0.1 g) was accurately weighed into digestion vessels and digestion acids were added. The digestion vessels were then inserted into the microwave unit and the power/temperature program was run. The digestion was performed according to the recommendation of the BCR-144R producer [22]. After the digestion vessels had cooled their contents were transferred into 25 mL calibrated flasks. Next 5 mg L^{-1} copper and 5 mg L^{-1} iron were added to each flask and the solutions were diluted to volume.

Results and discussion

Effects of interference on Hg determination

The presence of matrix components often has an influence on the signal of mercury determination by CV AAS, because other elements can interfere by either solution- or gaseous-phase reactions. Taking into account the elemental composition of natural water three groups were chosen for the preliminary investigation:

1. alkali and alkaline earth elements, which are present in natural water in large amounts and no data on their potential interferences were found in the literature – Na, K, Mg, and Ca;
2. elements which, in the applied conditions, undergo reduction and form amalgams – Ni, Fe, Zn, Cd, and Cu; and
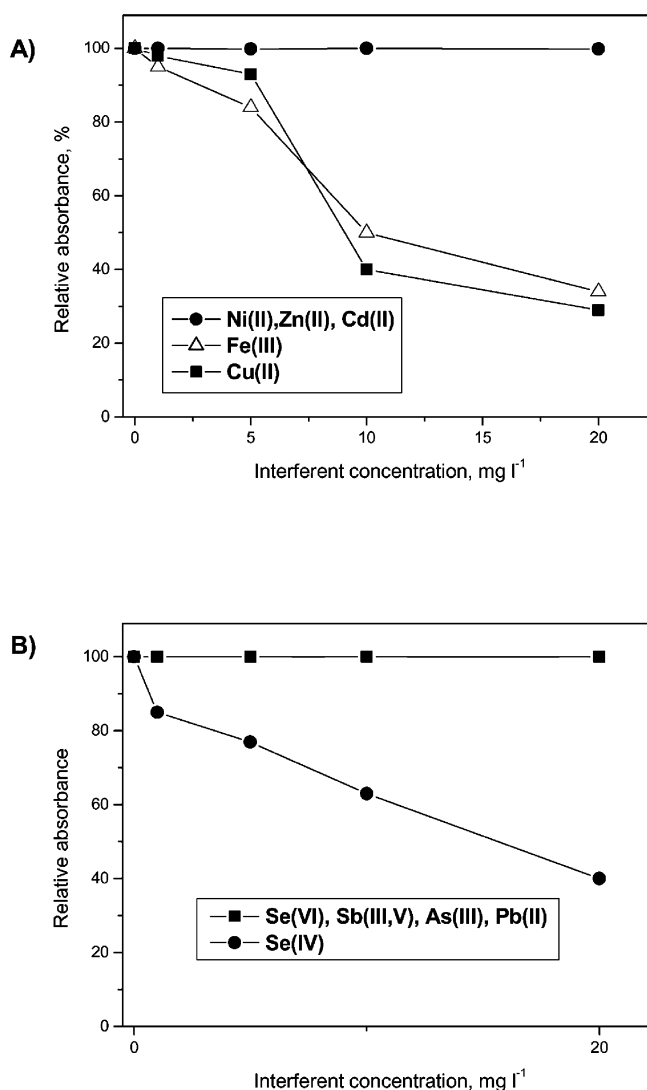

Fig. 1 Effect of the presence of interferents on the signal for 10 µg L^{-1} Hg: (**A**) metals which undergo reduction and form amalgamates; (**B**) metals which form volatile hydrides

3. elements which, in the applied conditions, form volatile hydrides – Se, Sb, Sb, As, and Pb

In all experiments the influence of increasing concentrations of the investigated elements on the signal of mercury ($10\,\mu g\,L^{-1}$) was evaluated. The blank value was taken into consideration in all measurements.

No interferences were observed in the presence of alkali and alkaline earth metals at concentrations up to $50\,mg\,L^{-1}$. It was also found that Ni, Zn, and Cd at concentrations up to $50\,mg\,L^{-1}$ do not affect the mercury signal. On the other hand, the presence of $10\,mg\,L^{-1}$ of Cu and Fe decreases the absorption signal of Hg by almost 50% and 40%, respectively (Fig. 1A). This is in agreement with the results reported by other groups [9, 10, 23], although Pszonicki et al. [10] did not observe interference from iron up to $100\,mg\,L^{-1}$.

The third group of elements was chosen because they can be simultaneously reduced to volatile species and thus influence the reduction of mercury into its elemental form (Fig. 1B). It was found, however, that the presence of up to $50\,mg\,L^{-1}$ Se(VI), Sb(V), Sb(III), As(III), and Pb(II) had no influence on the mercury signal. Only Se(IV) at a concentration of $5\,mg\,L^{-1}$ causes significant suppression of the mercury signal, which could be explained by the reduction of selenium to its elemental form and simultaneous adsorption of Hg on the resulting colloidal selenium [24]. The content of selenium in natural waters is usually well bellow this concentration thus the interferences are not expected to occur. Thus, further work was concentrated on elimination of interferences from Cu(II) and Fe(III), the concentrations of which in the natural water samples are much higher.

Sorption of mercury in the presence of interfering ions

In our recent work [25] cation-exchanger resin Dowex 50Wx4 was found very useful for sorption of inorganic mercury as well as its organic species. It was also found that the presence of Na, K, Ca, and Mg at concentrations typical of natural water does not influence the sorption efficiency. This was also confirmed by the results presented in Table 1, as the efficiency of sorption of mercury in spring water was close to 100%. The content of those elements in spring water is as follows: $30\,mg\,L^{-1}$ Na; $3\,mg\,L^{-1}$ K; $20\,mg\,L^{-1}$ Ca; and $3.5\,mg\,L^{-1}$ Mg. In this work the efficiency of Hg(II) sorption in the presence of Cu and Fe

Table 1 Efficiency of sorption/desorption of mercury from natural water samples[a] (amount added $10\,\mu g\,L^{-1}$)

Water	Sorption (%)	Desorption (%) (recovery)
Distilled	100±1	100±0.8
Spring	100±1.5	98±2.2
Mineral	100±1	98.4±1.8
Tap	86.2±3.6	79±2.5
Tap (boiling 30 min)	94.5±2.4	88.6±3

[a]mean±s, n=6

were examined. For this purpose 6 mL of a solution containing $10\,\mu g\,L^{-1}$ of mercury in the presence of Cu and Fe ($5\,mg\,L^{-1}$ of each) was passed through the microcolumn packed with Dowex 50Wx4. The advantage of the proposed approaches is that quantitative sorption for Hg(II) was achieved even with the use of only 0.5 g of the sorbent, which means that excess Cu and Fe does not influence sorption efficiency. The efficiency of sorption of mercury on an anion-exchange resin loaded with thiocarbonohydrazide [16] and 8-hydroxyquinoline immobilised on vinyl copolymer Toyopearl gel [20] was strongly reduced in the presence of other metal ions which were chelated by the column packing.

It was also found that the pH of the sample solution was not a critical factor, thus mercury could be preconcentrated on Dowex 50Wx4 over a broad pH range. These conditions are very suitable for natural water samples, which have to be acidified after sampling.

The influence of the flow rate of the sample in the range of 1–$6\,mL\,min^{-1}$ was investigated. Up to $2\,mL\,min^{-1}$ the recovery of mercury was stable, then a decrease was observed owing to the short residence time of the sample, which results in incomplete retention of mercury. It should be noted that a resin functionalised with 6-mercaptopurine is suitable for column operation only at low ($0.5\,mL\,min^{-1}$) flow rates [16].

Preconcentration of larger sample volumes at a defined sample flow rate usually leads to increased sensitivity. However, it does not offer unlimited possibilities to lower detection limit, because with the larger volume of the sample, an increase of the blank signal was noted [7]. With the proposed approach a volume up to $100\,mL$ of a sample containing $10\,\mu g\,L^{-1}$ mercury could be used. It was found out that under such conditions mercury ions are completely retained on the microcolumn.

The detection limit for Hg(II) was calculated on the basis of the standard deviation of the blank. The value of $27\,ng\,L^{-1}$ was obtained, which means that the determination could be done in the sub-ppb range, even using such inexpensive detection as AAS.

Separation of interfering ions and elution of inorganic mercury

As Cu and Fe ions are sorbed on the column packed with Dowex 50Wx4 together with mercury, the next step in our study was to find the optimal conditions for sequential elution of an interfering ions and analyte. It is known [3, 14, 17, 18, 25] that thiourea solution effectively elutes mercury from solid sorbents. Unfortunately under the reported conditions Cu(II) and Fe(III) were also eluted simultaneously from the microcolumn. Therefore, the possibility of using as a first step a solution containing fluorides was evaluated for elution of interfering metals. A solution containing $10\,\mu g\,L^{-1}$ mercury, $5\,mg\,L^{-1}$ copper, and $5\,mg\,L^{-1}$ iron ions was passed through the microcolumn at a flow rate of $1\,mL\,min^{-1}$. Then 10 mL of KF solution was pumped through the column for Cu(II) and Fe(III) elution.
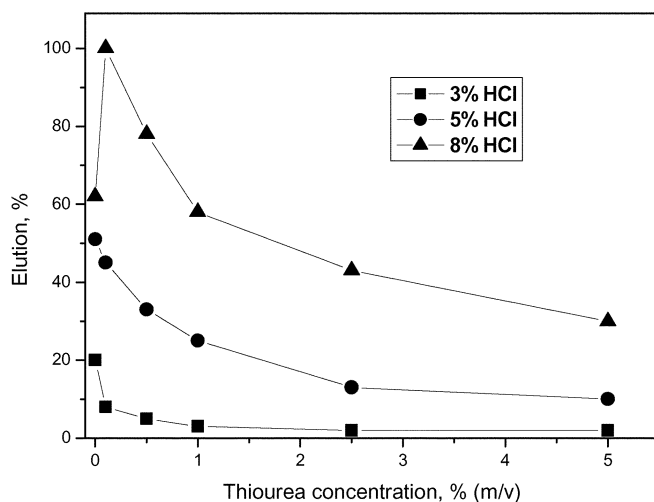
Fig. 2 Effect of the composition of the solution used for elution of 0.86 μg Hg(II) from the Dowex 50Wx4 microcolumn

Table 2 Mercury content (μg g^{-1}), with expanded uncertainties, of certified reference material BCR-144 (sewage sludge of domestic origin)

Certified value	3.11±0.18 μg g^{-1}
Direct determination[a]	2.96±0.05 μg g^{-1}
Direct determination after spiking with Cu and Fe (5 mg L^{-1} each)[a]	1.89±0.08 μg g^{-1}
Determination after separation of matrix components[a]	2.89±0.13 μg g^{-1}

[a]mean±U, n=4

was determined without or after separation of interfering ions on Dowex 50Wx4. It was found that in the presence of excess Cu(II) and Fe(III) significantly lower results were obtained by the direct determination. When the developed approach with sequential elution was applied for separation of interfering ions the results were again in a good agreement with the certified value.

Effective elution of both ions, which are retained together with Hg(II) on Dowex 50Wx4 column, was achieved by using 10 mL 0.5 mol L^{-1} KF. It should be stressed that in such conditions mercury remains completely on the column. Decreasing the eluent volume to 5 mL and using a higher concentration (1 mol L^{-1}) results in loss of analyte (about 15%).

The next step was to determine the conditions for quantitative elution of mercury ions. Both thiourea and hydrochloric acid alone were found to be inefficient, therefore mixtures of thiourea and hydrochloric acid at different concentrations were tested (Fig. 2). The best results were obtained using 15 mL 0.1% (w/v) thiourea in 8% (v/v) HCl.

These results encouraged us to apply the developed procedure with two-step sequential elution for determination of mercury in various natural waters. For this purpose commercially available mineral water, spring water from an underground source in Warsaw, and tap waters were analysed. The proposed procedure was tested by recovery of known amounts of Hg(II) added to the water samples (Table 1). Good recovery was obtained in the case of mineral and spring waters. The lower recovery (79%) obtained in the case of a tap water could, to some extent, be explained by the presence of chlorine, which is added as a disinfecting agent to municipal drinking water. According to previous experience [26, 27] boiling of the tap water for 30 min before spiking results in the increased recovery.

The accuracy of the proposed procedure was evaluated with the use of certified reference material BCR-144R (Table 2). In the first approach mercury was determined directly by CV AAS after microwave-assisted digestion and results were in good agreement with the certified value within the uncertainty range. This was according our expectation as this material does not contain Cu(II) and Fe(III) ions. In order to investigated the effect of interferences, the digest sample was spiked with Cu(II) and Fe(III) (5 mg L^{-1} each metal). Then the content of mercury

Conclusions

It was demonstrated that the direct determination of mercury by CV AAS could be strongly influenced by the presence of Se(IV), Cu(II), and Fe(III). The cation-exchanger Dowex 50 Wx4 was effectively applied for sorption of mercury and for separation of interfering components. It is expected the developed procedure could be applied for the determination of mercury in natural waters.

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