Separation and preconcentration of inorganic and organomercury species in water samples using a selective reagent and an anion exchange resin and determination by flow injection-cold vapor atomic absorption spectrometry

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An on-line inorganic (InHg) and organomercury (OrHg) species separation, preconcentration and determination system consisting of cold vapor atomic absorption spectrometry (CV-AAS) coupled to a flow injection (FI) method was studied. The inorganic mercury species was retained on a column (id, 3 mm; length, 80 mm) charged with a Dowex 1X-8 resin (particle size 50–100 mesh) as the anionic complex formed with Methylthymol Blue (MTB), at pH 6.3. Previous oxidation of the organomercurial species permitted the determination of total mercury. Therefore, the separation of mercury species was obtained with the combined use of on-line selective formation of the InHg–MTB complex and the retention of this anionic compound on the anion exchange resin. The difference between total and inorganic mercury determined the organomercury content in the samples. The inorganic mercury was removed on-line from the micro-column with 3 M nitric acid. The mercury cold vapor generation was performed in an on-line system with 7.0% (w/v) $SnCl_2$ and 20% (v/v) HCl as reducing solution. A preconcentration factor of 180 was obtained for the preconcentration of 250 ml of aqueous solution. The detection limit for InHg and OrHg was 0.8 ng l^{-1}. The precision for ten replicate determinations at the 15 ng l^{-1} Hg level was 4.4% relative standard deviation (RSD), calculated from the peak heights obtained. The calibration graph using the separation and preconcentration system for mercury species was linear, with a correlation coefficient of 0.9994 at levels near the detection limit up to at least 100 μg l^{-1}. The accuracy of the method was evaluated by the analysis of a certified reference material QC Metal LL3 Mercury in Water. The method was successfully applied to the speciation of mercury in water samples.

Introduction

The potential consequences of mercury bioaccumulation in aquatic ecosystems have been of great concern since the Minamata incident. Mercury is a potential environmental toxicant because of the strong affinity of inorganic (InHg) and organomercurial (OrHg) compounds for thiol groups, its tendency to form covalent bonds with organic molecules, the high stability of the Hg–C bond due to a low affinity for oxygen, and its strong tendency to maximize bonding to two ligands in a linear stereochemical arrangement.[1,2] Mercury is a natural constituent of the ecosystem, although it is not essential for plant or animal life. The human population is exposed to mercury through its diet, the major source being methylmercury (MeHg) from fish. This organomercurial species (MeHg) is particularly interesting due to its toxicity (50–100 times more toxic than inorganic mercury) and its high proportion (95%) among organomercury species in the environment.[3,4] Moreover, it is the most significant form of mercury in both saline and fresh water due to its ready diffusion through biological membranes.[4]

Analytical methods used in the speciation of mercury generally involve a chromatographic separation technique, such as gas chromatography (GC),[5–8] high-performance liquid chromatography (HPLC)[9–12] combined with an atom-selective detection technique such as atomic emission spectrometry

(AES),[5,13–15] atomic absorption spectrometry (AAS),[7–9,11,16] atomic fluorescence spectrometry (AFS),[17–19] or inductively coupled plasma mass spectrometry (ICP-MS).[6,20,21] Although cold vapor atomic absorption spectrometry (CV-AAS) is the most common technique for trace level determination of inorganic and organic mercury, their low-level concentrations in natural water are not compatible with the detection limits of this technique.[13,22] Some of the proposed methods for mercury preconcentration in atomic spectrometry include, among others, amalgamation on Au,[23,24] liquid–liquid extraction,[5,23,25] and solid-phase extraction,[10,21] which presents some advantages over liquid–liquid procedures, such as higher preconcentration factors, better efficiency, greater reproducibility and greater simplicity in sample handling and transfer. In on-line preconcentration and/or speciation systems, many different types of solid sorbents[10,26–28] have been used with chelating reagents such as sodium diethyldithiocarbamate (DDC),[28] ammonium pyrrolidinedithiocarbamate (APDC),[16] 2-mercaptobenzothiazole (MBT),[26] thionalide (2-mercapto-N-2-naphthylacetamide),[29] and diphenylthiocarbazone (DZ).[10,28] However, these reagents are not selective chelating reagents for mercury species.

Methylthymol Blue (MTB) forms soluble chelates in aqueous medium with numerous metallic ions and it has been used as a reagent in the spectrophotometric determination of metallic ions,[30–35] including mercury. However, no

references in the literature have been found to its application to mercury speciation and preconcentration coupled with hydride generation and cold vapor systems.

In the present work, a non-chromatographic method for the separation, preconcentration, and determination of mercury species using a Dowex 1X-8 anion exchange resin is proposed. Inorganic mercury was retained in the form of an InHg–MTB complex. The selectivity of the MTB reagent in the formation of complexes with mercury species prevented the cationic organomercurial species from being retained on the resin with the consequent separation of the species (inorganic mercury from organomercury species). Previous oxidation of the organomercurial species to inorganic mercury allowed the determination of total mercury. The determination was performed using CV-AAS coupled with on-line separation and preconcentration methodology. All variables related to cold vapor generation and detection by AAS were studied.

Experimental

Instrumentation

The measurements were performed with a Shimadzu AA-6800 atomic absorption spectrometer (Tokyo, Japan) equipped with a 15 cm long (0.8 cm id) absorption cell. The AAS operating conditions were: lamp current, 6 mA; slit-width, 0.7 nm; quartz cell dimensions, 150 mm × 8 mm; analytical line of Hg, 253.7 nm. A Gilson Minipuls 3 peristaltic pump (Villiers-Le-Bel, France) was used. Sample injection was achieved using a Rheodyne (Cotati, CA, USA) Model 50 four-way rotary valve. The spectrophotometric determinations were effected with a Beckman DU 520 UV/VIS spectrophotometer. For sorption of the complex, a microbore glass column (80 mm length; 3 mm internal diameter) fitted with porous 25 µm glass frits was used as the resin holder. Tygon-type pump tubing (Ismatec, Cole-Parmer, Vernon Hills, IL, USA) was employed to propel the sample, reagent and eluent. A home-made gas–liquid separator was used for the separation of mercury vapor. The dimensions were as follows: 95 mm long, 15 mm id. Two inlets were present, one for the gas–liquid mixture and the other for nitrogen. Continuous waste extraction was accomplished with the use of a peristaltic pump and the whole device was connected to the quartz cell.

Reagents

A 10^{-2} M solution of MTB (Aldrich, Milwaukee, WI, USA) was prepared by dissolution in ultrapure water. Lower concentrations were prepared by serial dilution.

A stock inorganic mercury standard (1000 mg l^{-1}) was prepared from mercury(II) chloride (Merck, Darmstadt, Germany) in nitric acid and made up to 1000 ml with ultrapure water.

Stock methyl- (MeHg) and phenylmercury (PhHg) solutions (1000 mg l^{-1}) were prepared from methylmercury chloride and phenylmercury chloride (Merck) in ethanol and methanol (Merck), respectively. Working standard solutions were prepared daily. The organomercurial solutions were stored away from light at 4 °C to prevent decomposition.

The acetic acid–acetate buffer solution was prepared from a 2 M acetic acid solution adjusted to pH 6.3 by dissolution of sodium hydroxide.

A 7% (w/v) $SnCl_2$ solution in 20% (v/v) HCl (Merck) was used as the reducing agent.

Potassium persulfate oxidizing agent was prepared fresh daily by dissolving 25 g of analytical-reagent grade potassium persulfate (Merck) in 500 ml of ultrapure water and heating gently on a hot-plate until dissolution was complete.

Sub-boiling distilled concentrated hydrochloric, sulfuric, and nitric acid (Ultrex® II Mallinckrodt Baker, Phillipsburg, NJ,

USA) were used in the sample pre-treatment stage and mercury determinations.

Ultrapure water (18 MΩ cm^{-1}) was obtained from EASY-pure RF (Barnstead, IA, USA).

All reagents were of analytical-reagent grade and the presence of mercury was not detected in the working range.

Sample collection and preparation

A clean sample collection procedure was followed in order to reduce contamination of the natural water samples.[36] Since in this method the only target analyte was mercury, the water samples were collected in 1000 ml borosilicate glass bottles[37] and filtered through 0.45 µm pore size membrane filters (Millipore, Bedford, MA, USA). Immediately after sampling, the 1000 ml water aliquots were acidified with 5 ml of 12 M HCl[37,38] and stored at 4 °C. The manipulation and analysis was developed immediately after sampling in a clean laboratory environment. All the instruments used were previously washed with a 10% v/v HNO_3 solution and then with ultrapure water before drying in a clean air hood.

Preconcentration and determination of total mercury

In order to determine the concentration of total mercury as inorganic mercury the sample was treated as follows:[39,40] 250 ml of sample were transferred into a precipitation vessel and 10 ml of concentrated sulfuric acid and 5 ml of concentrated nitric acid were added and mixed. Then, 20 ml of 5% (w/v) potassium persulfate were also added and mixed. The mixture was subsequently heated for 2 h in a covered water-bath maintained at 95 °C. Finally, the solution pH was adjusted to 5 with NaOH, and the solution was made up to a final volume of 250 ml with ultrapure water.

Before loading, the column was conditioned for the preconcentration at the correct pH with a diluted buffer solution (0.2 M), valve V being in the load position [Fig. 1(a)]. Then, 250 ml of the pre-treated aqueous sample solution containing the total mercury as inorganic mercury (at a flow rate of 20 ml min^{-1}) and 5.5×10^{-4} M MTB buffered to pH 6.3 with acetic acid–acetate buffer (at a flow rate of 2 ml min^{-1}) were previously mixed on-line in a knotted reactor (KR) to form the metal complex. After the loading time, the sample still present in the lines and the column was removed by further washing with buffer-diluted solution. Finally, valve V was switched to the injection position (b) and the retained metal complex was eluted in countercurrent mode (i.e., reversal of the flow direction through the column during elution with respect to sample loading) with 3 M HNO_3 at a flow rate of 1.5 ml min^{-1}. This solution was mixed with 7% (w/v) $SnCl_2$ in 20% (v/v) HCl (at a flow rate of 1 ml min^{-1}) and carried directly to the gas–liquid separator and AAS. The operating conditions were established, and the determination was carried out. FI system measurements were expressed as peak-height absorption, which was corrected against the reagent blank.

Determination of mercury species

For the determination of inorganic mercury, the procedure previously described was followed. However, in this case, the pre-treatment of the sample was not required. The difference between total mercury and inorganic mercury determined the organomercurial content in the sample.

Safety considerations

Inorganic mercury and organomercury species are highly toxic. Organomercurial species are easily absorbed through the skin. Thus, these compounds must be handled with maximum precaution and only in an adequately ventilated environment using appropriate personal protection equipment.
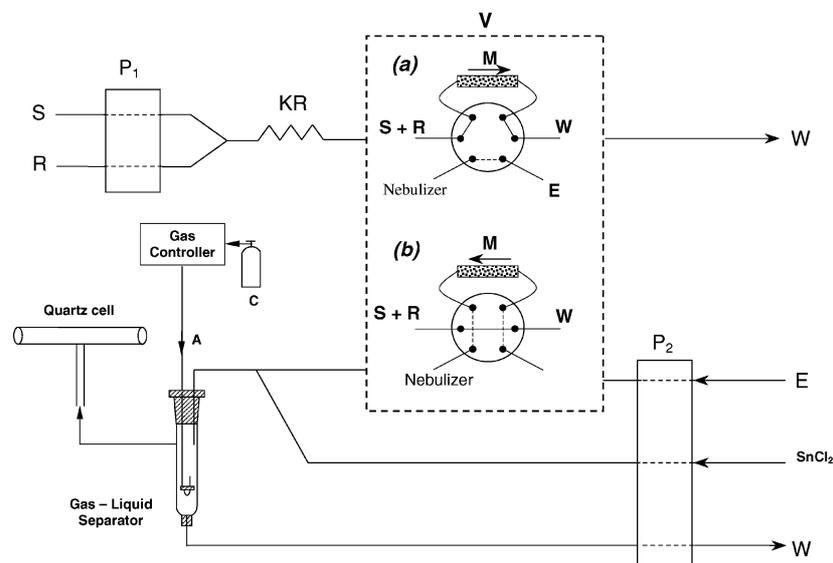
Fig. 1 Schematic diagram of instrumental set-up. R, 5.5×10^{-4} M MTB solution (2.0 ml min^{-1}); S, sample (flow rate: 20 ml min^{-1}); E, eluent (flow rate: 1.5 ml min^{-1}); C, N$_2$ (flow rate: 250 ml min^{-1}); CV, cold vapor generation; W, waste; P$_1$, P$_2$, peristaltic pumps; V, injection valve; KR, knotted reactor. Valve positions: (a) sample loading; (b) injection.

Results and discussion

To optimize the system, most efforts were focused on the conditions for sample loading and mercury elution from the column, as well as the flow system which was coupled on-line with the preconcentration and separation unit in order to obtain highly sensitive, accurate and reproducible results. The optimization study of complexing, preconcentration and separation variables was performed by modifying one variable at a time.

Effect of pH on preconcentration performance

Since the solution pH affects the extent of complexing, which in turn determines the percentage of metal retained by the resin, the preconcentration of inorganic mercury from solutions buffered at different pH was studied. The influence of the pH on the degree of preconcentration was studied in the pH interval between 2 and 10. The mercury signal was monitored by measuring it with CV-AAS as solutions of different pH were passed through the sorption micro-column. It can be seen from Fig. 2(a) that the optimum pH range for preconcentration is 5.5–7. Therefore, a pH of 6.3 was selected.

Effect of concentration and flow rate of MTB

In order to achieve total on-line complexing and retention of inorganic mercury, the concentration and loading flow rate of the MTB solution were optimized. As regards the variation of response with the concentration of MTB, the signal remained constant between 4.0×10^{-7} M and at least 5.0×10^{-4} M. In order to avoid the rapid saturation of the resin and since at the working pH MTB is also in its anionic form, a minimum concentration that guaranteed complete complexing of inorganic mercury was employed. An MTB concentration of 5.0×10^{-5} M was found to be compatible with the performance of the preconcentration. The loading rate of the MTB solution that gave the best results with regard to the efficiency of the on-line preconcentration process was 2.0 ml min^{-1}.

Sample solution flow rate

The flow rate of the sample through the micro-column is a very important parameter, since this is one of the steps that controls the time of analysis. It could be verified that sample flow rates up to 20 ml min^{-1} did not significantly affect analyte recovery,
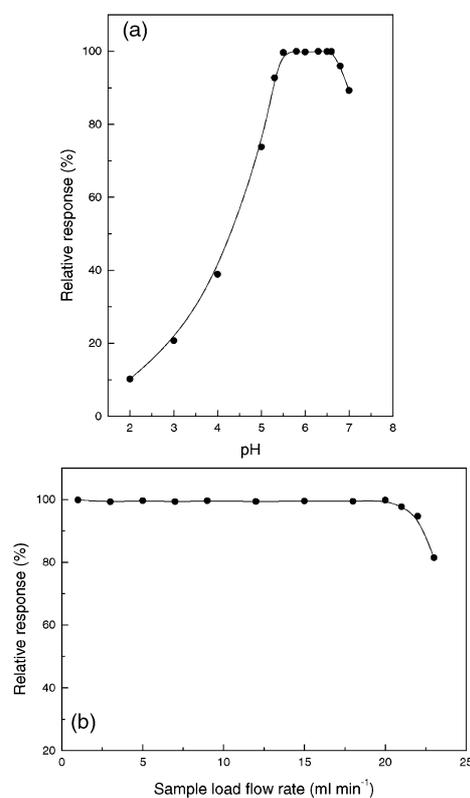
Fig. 2 (a) Dependence of Hg preconcentration on pH of loading solution. Sample load flow rate, 20 ml min^{-1}; InHg concentration, 5 μg l^{-1}; MTB concentration, 5.5×10^{-4} M. (b) Influence of sample load flow rate on the recovery. InHg concentration, 5 μg l^{-1}; MTB concentration, 5.5×10^{-4} M; pH, 6.3.

which under optimum conditions was 100%. Fig. 2(b) shows that recovery decreases at higher flow rates. Therefore, an important advantage of the present methodology is the possibility of using elevated rates of the sample solution load flow while keeping a maximum retention of the analyte on the resin, which permits the time of each determination to be reduced. Furthermore, this technique reduces the retention of other anionic species that may require longer times for the process of interchange on the resin,[41] with a potential increase of the selectivity.

Selective complexing and preconcentration of mercury species

By means of a spectrophotometric study of the complexing of mercury species with the reagent MTB, it could be determined that this chelating reagent exhibits a selective behavior as regards the formation of Hg–MTB complexes at the working pH value (pH = 6.3). Thus, for inorganic mercury, an absorption band with a peak at 630 nm was observed against the reagent blank, which indicates the formation of its respective complex with the reagent MTB. On the other hand, no bands were exhibited by the absorption spectra when the same experiment was performed with the organomercurial species (methyl and phenyl), suggesting that there was no formation of the respective complexes with the MTB reagent.

In order to evaluate the separation of the mercury species using the Dowex 1X-8 anion exchange resin, the proposed method was separately applied to the determination of inorganic mercury and organomercurial species in synthetic samples at two different concentration levels, viz., 50 ng l^{-1} and 10 μg l^{-1}. A 100% recovery was obtained for inorganic mercury, while no retention of the organomercurial species on the resin was observed, indicating the total separation of the mercury species. The separation of the mercury species is due to the formation of the InHg–MTB anionic complex, which is retained on the Dowex 1X-8 resin, whereas, since organomercurial species do not form complexes with the reagent MTB, they remain as cations in solution and are not retained by the resin. Thus, the present methodology appears suitable for distinguishing between inorganic and organic mercury species.

Selection of the resin

In the present work a bead size of 50–100 mesh for the Dowex 1X-8 resin was considered adequate for the preconcentration procedure in the micro-column. Smaller resin particles would have increased the back-pressure of the micro-column and therefore the flow rate ought to have been reduced, with a subsequent increase in preconcentration time. Our choice of the Dowex 1X-8 anion exchange resin was motivated by the fact that InHg–MTB is an anionic complex.[30] In addition, this resin is highly stable in both acidic and basic solution, which allows the use of the micro-column for a large number of samples without degradation of performance, after using 3 M HNO_3 as eluent. Moreover, many researchers have studied the behavior of Dowex 1X-8 resins as adsorbents of anionic substances and as supports for chelating agent-impregnated resins.[14,41]

Optimization of the column dimensions

The micro-column dimensions were carefully optimized. As can be seen from Table 1, very little retention is achieved with a short column (less than 10 mm), maximum efficiency being achieved with an 80 mm column. Considering the high breakthrough capacity of the column, lengths greater than 100 mm are not necessary for the proposed system. An increase in resin volume led to an appreciable enlargement of the elution peaks with a consequent decrease in the detection limit. A very small volume of resin could result in saturation of the

Table 1 Retention efficiencies observed for the InHg–MTB complex at pH 6.3 with Dowex 1X-8 resin in micro-columns of different lengths and 3 mm id. Sample flow rate: 20 ml min^{-1}

Column length/mm	Retention efficiency (%)
10	35
20	53
40	79
60	92
80	100
100	100

absorption sites with a decrease in recovery. The effect of the column internal diameter on the elution profile dispersion is widely known,[42] 3.0 mm being considered as an acceptable column id.

In our work, the column used has an id of 3 mm and is 80 mm in length, although it can be increased to 100 mm without changes being observed in the magnitude of the signal and the measurement precision.

Optimization of the elution conditions

In order to elute inorganic mercury adsorbed on the resin, different eluents at different concentrations were tested. Phosphate, potassium hydroxide, ammonia solution, acetic acid, hydrochloric acid, sulfuric acid, and nitric acid were evaluated as eluents. Nitric acid was the eluent which offered the best mercury signal at a concentration of 3 M. The mercury analytical signal observed with hydrochloric and sulfuric acid was lower (53% in a concentration range of 2–5 M) than that obtained with nitric acid [Fig. 3(a)]. Use of the remaining above-mentioned eluents led to transitory signals with elevated dispersion and unacceptably long elution times, which did not permit high sensitivity conditions to be obtained. According to these results, 3 M HNO_3 was selected as the eluent.

Countercurrent elution substantially improves the elution profiles as compared with uni-directional flow. Inorganic mercury was completely eluted from the resin with 2.2 ml of 3 M HNO_3. As can be observed in Fig. 3(b), the optimum flow rate of the eluent was 1.5 ml min^{-1}.

Vapor generation from the eluent medium

The cold vapor generation from the eluent solution of the retained complex was carefully studied in order to reach the conditions of maximum sensitivity. The $SnCl_2$ concentration was an important parameter to be optimized so that it permitted cold vapor generation even in the eluent medium. It was verified that the best signal-to-noise ratio was obtained
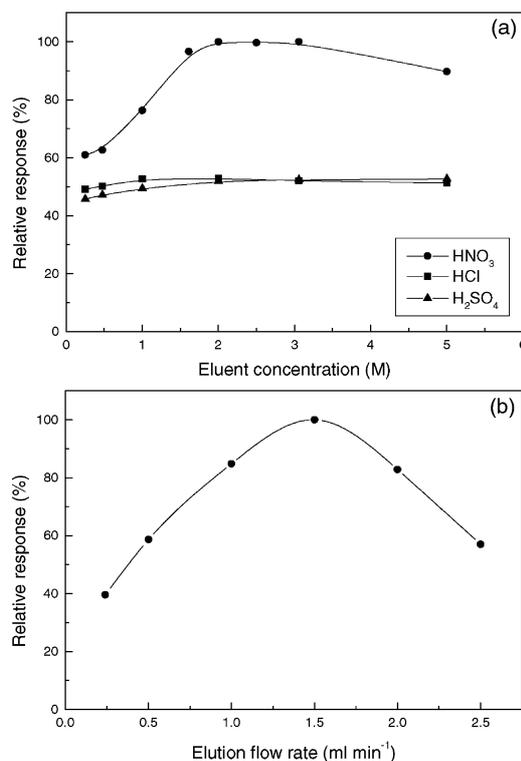
Fig. 3 (a) Influence of different types of eluents at different concentrations on the elution. (b) Influence of elution load flow rate. InHg concentration, 50 μg l^{-1}; MTB concentration, 5.5×10^{-4} M; pH, 6.3.
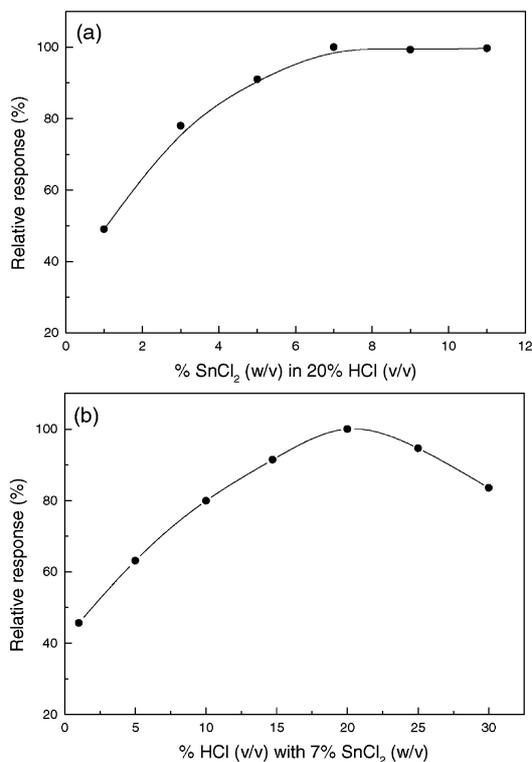
Fig. 4 (a) Effect of SnCl$_2$ concentration on the cold vapor generation. (b) Effect of HCl concentration on the cold vapor generation. InHg concentration, 50 μg l^{-1}; MTB concentration, 5.5×10^{-4} M; pH, 6.3.

with a concentration of 7.0% (w/v). It can be seen in Fig. 4(a) that higher concentrations of the reducing agent did not lead to significant signal changes. Hence, the above-mentioned SnCl$_2$ concentration was adopted as the working concentration.

The HCl concentration in the reducing solution that was most suitable and compatible with cold vapor generation was also studied. The results obtained showed [Fig. 4(b)] that the maximum response for the system was obtained at concentrations above 20% (v/v) HCl. Hence, 20% (v/v) HCl was adopted as the working concentration.

The reducing solution flow rate leading to the best results with regard to the efficiency of the on-line reduction process was 1.0 ml min^{-1}.

The effect of nitrogen carrier flow rate on absorption signals was also examined. The results obtained showed that the peak height increased with increasing nitrogen flow rates up to 250 ml min^{-1}; at values >250 ml min^{-1} the peak decreased. Therefore, a nitrogen flow rate of 250 ml min^{-1} was chosen.

Improvements in sensitivity and lower memory effects were attained with the home-made gas–liquid separator used for the separation of mercury vapor compared with the classical commercial model. These could be ascribed to the lower dead volume of the proposed model.

Interferences

The effects of representative potential interfering species (at the concentration levels at which they may occur in the samples studied) were tested. Thus, Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+} and Fe^{3+} could be tolerated up to at least 2000 μg l^{-1}. Ag$^+$ and Au$^+$ do not form complexes with the MTB reagent under the experimental conditions of this method; therefore, these elements did not lead to interfering effects. Commonly encountered matrix components such as alkali elements generally do not form stable complexes and are not retained on the resin. Alkaline earth elements such as Ca^{2+} and Mg^{2+} were not retained on the column either, because their complexing pH values (pH = 11.4 and 10.8, respectively)[30] are far from the working pH (pH = 6.3). On the other hand, anions such as S^{2-}, CO$_3$$^{2-}$, F$^-$, SO$_4$$^{2-}$, Cl$^-$, and PO$_4$$^{3-}$ could be tolerated at concentrations up to at least 500 mg l^{-1}. Organic acids commonly present in natural waters such as humic and fulvic acid did not cause any interference at concentration levels normally found in natural water samples.

Performance of the separation and preconcentration system

The overall time required for preconcentration of 250 ml of sample (12.5 min, at a flow rate of 20 ml min^{-1}), washing (0.1 min), elution and conditioning (1.4 min) was about 14 min. A preconcentration factor of 180 was obtained.

The relative standard deviation (RSD) for ten replicates containing 15 ng l^{-1} of inorganic mercury was 4.4%. The calibration graph was linear with a correlation coefficient of 0.9994 at levels near the detection limit up to at least 100 μg l^{-1}. The detection limit (DL), defined as the analyte concentration giving a signal equal to the mean of the blank analysis signal plus three times the standard deviation, was 0.8 ng l^{-1}.

Method validation

The recovery of the method was tested on spiked water samples of different nature containing known additions of inorganic mercury, MeHg and PhHg. The results are shown in Table 2. Additionally, the accuracy of the proposed method was tested by its application to a certified reference material (CRM), QC Metal LL3 Mercury in Water, with a mercury content of 6.48 ± 0.51 μg l^{-1}. The content of mercury determined in this CRM by the proposed method was 6.5097 ± 0.0018 μg l^{-1}.

Analytical applications

The method was applied to the determination of mercury in natural water samples from La Florida Lake and Rio Grande River (San Luis, Argentina). The results are shown in Table 2.

Table 2 Determination and recovery study of InHg and OrHg in spiked natural water samples (95% confidence interval; $n = 6$)

Sample	Spiked Hg (ng l^{-1}) as		InHg		OrHg	
	InHg	OrHg	Found/ng l^{-1}	Recovery (%)	Found/ng l^{-1}	Recovery (%)
Tap water	—	—	30.1 ± 1.2	—	<DL	—
	15	—	43.9 ± 1.7	97.5	<DL	—
	—	15	29.4 ± 1.2	—	14.6 ± 0.7	97.4
	15	15	43.7 ± 1.5	98.4	14.8 ± 0.6	98.9
River water	—	—	41.4 ± 1.6	—	8.8 ± 0.4	—
	15	—	55.4 ± 2.0	98.2	8.2 ± 0.4	—
	—	15	40.0 ± 1.5	—	23.4 ± 0.9	98.6
	15	15	54.9 ± 1.8	99.8	23.1 ± 0.9	99.4
Lake water	—	—	50.3 ± 1.8	—	9.9 ± 0.5	—
	15	—	65.1 ± 2.4	99.7	10.0 ± 0.5	—
	—	15	51.1 ± 1.8	—	25.2 ± 1.0	101.0
	15	15	66.1 ± 2.1	100.0	24.9 ± 1.1	99.8

Conclusion

The on-line formation of an inorganic mercury complex with the reagent MTB and the use of Dowex 1X-8 resin allowed the separation and determination of inorganic mercury and organomercury. The on-line coupling of a FI separation and preconcentration system with CV-AAS increases the speed of the preconcentration and analysis process, in addition to reducing sample consumption and contamination risks that are generally present in batch procedures. The preconcentration–speciation method shows the analytical selectivity and sensitivity requirements for reliable speciation analysis of mercury in natural water samples.

Fast and quantitative generation of cold vapor from the elution solution was obtained even in the presence of a large excess of the complexing reagent. Coupling of the preconcentration column to the cold vapor generation system was possible without major modifications as compared with conventional systems.

Acknowledgement

References

1 T. Barkay, *Encyclopedia of Microbiology*, Academic Press, London, 1986, vol. 3.
2 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley-Interscience, New York, 4th edn., 1988.
3 T. Pérez-Corona, Y. Madrid-Albarrán, C. Cámara and E. Beceiro, *Spectrochim. Acta, Part B*, 1998, **53**, 321.
4 T. Suzuki, N. Imura and T. Clarkson, *Advances in Mercury Toxicology*, Plenum Press, New York, 1991.
5 C. Gerbersmann, M. Heisterkamp, F. C. Adams and J. A. C. Broekaert, *Anal. Chim. Acta*, 1997, **350**, 273.
6 S. Slaets, F. Adams, I. Rodriguez Pereiro and R. Lobinski, *J. Anal. At. Spectrom.*, 1999, **14**, 851.
7 B. He and G. B. Jiang, *Fresenius' J. Anal. Chem.*, 1999, **365**, 615.
8 B. Salih, R. Say, A. Denizli, Ö. Genç and E. Piskin, *Anal. Chim. Acta*, 1998, **371**, 177.
9 S. Río-Segade and C. Bendicho, *Talanta*, 1999, **48**, 477.
10 D. M. Sánchez, R. Martín, R. Morante, J. Marín and M. L. Munuera, *Talanta*, 2000, **52**, 671.
11 X. Yin, W. Frech, E. Hoffmann, C. Lüdke and J. Skole, *Fresenius' J. Anal. Chem.*, 1998, **361**, 761.
12 C. F. Harrington, *Trends Anal. Chem.*, 2000, **19**, 167.
13 M. Ceulemans and F. C. Adams, *J. Anal. At. Spectrom.*, 1996, **11**, 201.
14 P. Cañada Rudner, A. Garcia de Torres, J. M. Cano Pavón and F. Sanchez Rojas, *Talanta*, 1998, **46**, 1095.
15 M. R. Madson and R. D. Thompson, *J. AOAC Int.*, 1998, **81**, 808.
16 J. Qvarnström, Q. Tu, W. Frech and C. Ludke, *Analyst*, 2000, **125**, 1193.
17 K. C. Bowles and S. C. Apte, *Anal. Chem.*, 1998, **70**, 395.
18 K. C. Bowles and S. C. Apte, *Anal. Chim. Acta*, 2000, **419**, 145.
19 Y. Cai, R. Jaffé, A. Alli and R. D. Jones, *Anal. Chim. Acta*, 1996, **334**, 251.
20 C. F. Harrington and T. Catterick, *J. Anal. At. Spectrom.*, 1997, **12**, 1053.
21 Z. Mester, J. Lam, R. Sturgeon and J. Pawliszyn, *J. Anal. At. Spectrom.*, 2000, **15**, 837.
22 J. E. Sánchez Uría and A. Sanz-Medel, *Talanta*, 1998, **47**, 509.
23 S. McIntosh, *At. Spectrosc.*, 1993, **14**, 47.
24 R. C. Campos, C. L. Porto da Silveira and R. Lima, *At. Spectrosc.*, 1997, **18**, 55.
25 I. Rodriguez Pereiro, A. Wasik and R. Lobinski, *J. Anal. At. Spectrom.*, 1998, **13**, 743.
26 J. Chwastowska, A. Rogowska, E. Sterlinska and J. Dudek, *Talanta*, 1999, **49**, 837.
27 J. A. Gomez Neto, L. F. Zara, J. C. Rocha, A. Santos, C. S. Dakuzaku and J. A. Nóbrega, *Talanta*, 2000, **51**, 587.
28 M. F. García, R. Pereiro García, N. Bordel Gracía and A. Sanz-Medel, *Talanta*, 1994, **41**, 1833.
29 J. Chwastowska, W. Skwara, E. Sterlinska, J. Dudek and L. Pszonicki, *Chem. Anal. (Warsaw)*, 1998, **43**, 995.
30 K. L. Cheng, K. Ueno and T. Imamura, *Handbook of Organic Analytical Reagents*, CRC Press, Boca Raton, FL, 1982.
31 C. Bremer, H. Ruf and E. Grell, *J. Phys. Chem. A*, 1998, **102**, 146.
32 R. J. Cassella, R. E. Santelli, A. G. Branco, V. A. Lemos, S. L. C. Ferreira and M. S. de Carvalho, *Analyst*, 1999, **124**, 805.
33 D. G. Themelis, P. D. Tzanavaras, A. N. Anthemidis and J. A. Stratis, *Anal. Chim. Acta*, 1999, **402**, 259.
34 D. G. Themelis, P. D. Tzanavaras, A. N. Anthemidis and J. A. Stratis, *Anal. Chim. Acta*, 2000, **410**, 215.
35 D. G. Themelis, P. D. Tzanavaras and J. K. Papadimitriou, *Analyst*, 2001, **126**, 247.
36 EPA Method 1669, *Method for Sampling Ambient Water for Determination of Metals at EPA Ambient Criteria Levels*, EPA, Washington, DC, 1996.
37 EPA Method 1631, *Revision B: Mercury in Water by Oxidation, Purge and Trap and Cold Vapor Atomic Fluorescence Spectrometry*, EPA, Washington, DC, 1999.
38 F. Burriel Martí, F. Lucena Conde, S. Arribas Jimeno and J. Hernández Méndez, *Química Analítica Cualitativa*, Paraninfo, Spain, 17th edn., 2000.
39 C. P. Hanna and J. F. Tyson, *Anal. Chem.*, 1993, **65**, 653.
40 J. L. Burguera, I. A. Quintana, J. L. Salager, M. Burguera, C. Condón, P. Carrero, A. A. de Salager and Y. Petit de Peña, *Analyst*, 1999, **124**, 593.
41 J. Korkisch, *Handbook of Ion Exchange Resins: Their Application to Inorganic Analytical Chemistry*, CRC Press, Boca Raton, FL, 1989, vol. I.
42 Z.-L. Fang, *Flow Injection Separation and Preconcentration*, VCH, Weinheim, 1993.