

Field sampling, preconcentration and determination of mercury species in river waters

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Abstract

A simple field sampling strategy for determination and speciation of inorganic mercury and methylmercury in river waters is described. River water samples are collected in situ by passing them with a pump through a minicolumn packed with C₁₈ modified with sodium diethyldithiocarbamate. This packing is able to isolate and retain the desired mercury species. Minicolumns loaded with the analytes are then returned to the laboratory where mercury species are eluted with 500 µl of 5% thiourea in 0.5% HCl. A detailed study of the construction of these minicolumns and the stability of the mercury species retained in the packing is presented. The separation of the two mercury species was carried out by liquid chromatography using a cysteine solution as mobile phase and final detection was accomplished by inductively coupled plasma mass spectrometry. Between-column relative standard deviations of 12% at the 200 ng l⁻¹ Hg level and limits of detection of 5.2 ng l⁻¹ for inorganic mercury and 5.6 ng l⁻¹ for methylmercury are obtained. The method has been applied to mercury speciation in clean river waters of the Asturias region of Spain. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

It is widely recognised that the toxicity of an element (e.g. Hg) is determined by the particular species of that element. In general terms, the organic forms of metals (more hydrophobic) can cross biological membranes more easily than the corresponding inorganic forms. Thus, organomercury compounds (e.g. methylmercury) should be much more toxic than inorganic mercury. Owing to this importance of speciation information we are witnessing a growing interest

in analytical measurements of mercury species in our environment [1].

The ideal analytical strategy for determining the speciation of toxic elements in the environment should be their direct in situ determination in the desired sample with minimal manipulation. In this way, one of the most stringent challenge of speciation determination, preservation of the original nature of each of the sought species, could be guaranteed. So far, in situ direct species-specific techniques are not sufficiently developed to solve speciation problems in real-life situations, usually due to lack of sensitivity or selectivity [2]. On the other hand, methods for in situ field sampling of several elements, allowing the final determination in the laboratory of different species in

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environmental samples, have already been published [3,4].

For mercury in natural waters, the main species to be identified and determined are inorganic mercury (Hg^{2+}) and methylmercury (CH_3Hg^+). It is important to note also that in natural waters methylmercury levels are usually much lower than those of inorganic mercury. Recent reports [5] estimate a total mercury concentration in natural waters ranging from 0.2 to 100 ng l^{-1} , while methylmercury levels are much lower (ca. 0.05 ng l^{-1} [6]). However, the possibility of artificial formation of methylmercury during sample preparation steps which could produce errors in its determination it is well known. The extent of accidental methylation varies with the kind of matrix and the technique applied [7], is caused by different agents and has been observed in a wide variety of matrices (sediments, soils, leaves, spruce needles, moss, algae, tea and grass samples). The highest values of methylmercury artefacts have been observed in sediment samples, with magnitudes of 50% and more in comparison to the ambient value [8]. For this reason, it is the responsibility of the analyst to verify and assess the quality of the results by means of alternative techniques and, if possible, standard reference materials.

Most toxic elements in the environment occur at extremely low levels in real samples. Thus, several sample preparation steps are usually required to develop an efficient speciation strategy [9]. The main steps are sampling, preconcentration, separation and final determination of the separated species using a hybrid technique (a powerful separation coupled to an atomic specific detector).

For mercury species, liquid–solid extraction is well suited for preconcentration. Several groups have investigated the use of immobilised dithiocarbamates, packed in microcolumns, to achieve methylmercury preconcentration [10–12]. The retained Hg species are eluted afterwards from the column (e.g. using an acidic thiourea solution) and finally extracted into toluene. There the extracted organomercury is derivatised (e.g. using a Grignard reagent) before its final separation and determination. Several techniques are possible, gas chromatography–microwave induced plasma–atomic emission spectrometer (GC–MIP–AES) being the most popular [10–16]. The type of preconcentration operation based on solid–liquid preconcentration can be also used as an alternative for in situ

sampling of water. In this way, a large volume of water can be passed through the minicolumn, retaining the desired species. Thus, the use of big flasks to store such water samples and perhaps the use of preservatives to minimise species changes can be eliminated.

It is undeniable that the most popular and powerful instrumental approach to real-life species determination consists of coupling a chromatographic separation with a sensitive atomic detector. In fact, determination of the speciation of mercury in environmental samples is mainly carried out by resorting to chromatographic separation techniques, particularly GC with MIP–AES detection [10–16]. In an attempt to overcome the several drawbacks associated with the GC determination of organomercury compounds [17], different authors have resorted to alternative separation procedures. Particularly, liquid chromatography (LC) techniques [18–20] have been also tried with the final aim of establishing a reliable procedure for the determination of mercury species in environmental samples. Of course, LC techniques are better suited for polar species separation (in principle manipulations to obtain a volatile derivative could be avoided). Therefore, LC could be advantageous for determining organomercury and inorganic mercury speciation in natural waters. In fact, the most effective detection incorporates an atomic specific detector for mercury vapour. Interfaces to couple LC columns with the atomiser are simple, via the direct connection of the exit of the column with the nebuliser of the atomic detector (e.g. using simple PTFE tubing). However, LC methods are significantly less sensitive than GC procedures and this is a great limitation for real samples [9]. A general way-out to this lack of sensitivity of LC hybrid techniques is on-line derivatisation to form a cold vapour of mercury at the exit of the column. Till date, SnCl_2 and NaBH_4 are the most popular reductants for this purpose [12,21].

Analytical plasmas, both at atmospheric and reduced pressures [22], offer great analytical potential in element-specific detection; particularly ICP–mass spectrometry (MS) offers most of the main desirable features of an ‘ideal’ detector for hybrid chromatographic techniques. Thus, the number of papers devoted to the use of ICP–MS detection for mercury speciation is not surprising [23–27].

In this paper, the analytical potential of C_{18} minicolumns modified with sodium diethyldithiocarba-

mate for extraction/preconcentration and in situ field sampling of inorganic mercury and methylmercury is investigated. The method involves final elution of mercury species from the minicolumn in the laboratory, separation of methylmercury and inorganic mercury on a C₁₈ stationary phase using a cysteine solution [28] as mobile phase and final detection of the corresponding mercury species using ICP-MS.

2. Experimental

2.1. Reagents

All reagents were of analytical-reagent grade and all aqueous solutions were prepared in high-purity water (Millipore Corp., Milford, MA).

A 1000 mg l⁻¹ stock solution of inorganic mercury was obtained from Merck (Darmstadt, Germany). Methylmercury stock solutions (1000 mg l⁻¹) were prepared by dissolving the appropriate amount of methylmercury chloride (Merck) in 10 ml of acetone and diluting to 100 ml with water. All stock solutions were stored in dark glass bottles at 4°C. Working standard solutions were freshly prepared by dilution of the corresponding stock solution with water.

Sodium diethyldithiocarbamate (DDTC) solutions (Merck) were prepared by dissolving the appropriate amount of the salt in an ammonium acetate buffer (pH 9.2).

Amberlite XAD-7 (Sigma, Poole, Dorset, UK) and C₁₈ (Waters, Milford, MA) were used while the 0.45 µm filters were obtained from Millipore. All other reagents used were of analytical reagent grade.

2.2. Instrumentation

The experimental setup for LC-ICP-MS experiments consisted of an LC pump (Model 6400, Knauer, Berlin, Germany) with an attached sample injection valve (Rheodyne, Berkeley, CA) equipped with a 100 µl loop. The separation column was Spherisorb ODS 2 (250 mm × 4.6 mm i.d.) packed with a C₁₈ bonded silica stationary phase. The mobile phase A consisted of 0.06 mol l⁻¹ ammonium acetate, 1.0% (v/v) acetonitrile in water and 0.005% (v/v) 2-mercaptoethanol in water; mobile phase B consisted of 0.06 mol l⁻¹ ammonium acetate (pH 4) containing 0.5% cysteine.

Table 1
ICP-MS HP 4500 operating conditions

Operating parameters	
Power RF	1300 W
Carrier gas flow rate	1 l min ⁻¹
Cones	
Sampler	Ni (1 mm)
Skimmer	Ni (0.4 mm)
Data acquisition parameters	
Mode	Resolved time
Points per peak	1
Integration time	0.25 s
Isotopes	²⁰⁰ Hg, ²⁰² Hg

Detection was carried out using a Hewlett-Packard ICP-MS Model HP 4500 instrument. The ICP-MS operating conditions used throughout this study are given in Table 1. Conventional nebulisation was employed for mobile phase B while a cold vapour generation system was used with mobile phase A. A four-channel peristaltic pump (Minipuls 2, Gilson, Villiers-le-Bel, France) and a laboratory-made gas-liquid separator [29] were employed for the continuous cold vapour Hg generation system.

For non-chromatographic experiments, a flow injection-cold vapour-atomic absorption spectrometry (FI-CV-AAS) system was assembled by using a six-way injection valve (Omnifit, Cambridge, UK) with a 250 µl sample loop. A Philips AAS PU 9400 instrument equipped with a mercury hollow cathode lamp and quartz cell (12 cm × 1 cm i.d.) was used for detection. The AAS measurements were carried out at 253.7 nm, slit 0.5 nm, lamp intensity 6 mA and with deuterium background correction.

2.3. Procedures

The field sampling and preconcentration procedure was developed using laboratory made minicolumns of PTFE (40 mm × 3 mm i.d.) packed with 30 mg of C₁₈ bonded silica. In order to prepare the column, a slurry of C₁₈ in methanol was pumped at a flow rate of 2 ml min⁻¹ into the empty mini-column, using a peristaltic pump. Once packed, the column was washed with methanol (5 ml) and water (5 ml) and then modified, in the same way, by pumping a 0.05% (m/v) sodium DDTC solution (5 ml). Before use the microcolumns were decontaminated of mercury by

Table 2

Percent retention of Hg species with the preconcentration systems tested^a

	pH 3.0		pH 4.0		pH 5.0		pH 6.0		pH 7.0		pH 8.0	
	Hg(II)	CH ₃ Hg ⁺	Hg(II)	CH ₃ Hg ⁺	Hg(II)	CH ₃ Hg ⁺	Hg(II)	CH ₃ Hg ⁺	Hg(II)	CH ₃ Hg ⁺	Hg(II)	CH ₃ Hg ⁺
C ₁₈ with DDTC	100±5	100±4	100±6	100±5	100±5	100±5	100±6	100±5	100±7	100±6	100±6	100±4
C ₁₈ with mercaptoethanol	100±6	91±8	100±4	95±7	100±6	100±7	100±5	100±4	100±8	100±5	100±7	100±5
XAD-7 with DDTC	100±7	100±6	100±6	100±5	100±6	93±6	100±4	85±6	100±4	80±6	100±5	70±8
XAD-7 with mercaptoethanol	80±5	65±4	92±6	70±4	100±5	70±4	83±4	85±4	80±3	60±5	75±4	55±7

^a All results are mean±S.D. (n=3).

passing 1 ml of the eluent (thiourea solution) through them.

The field sampling and preconcentration step were performed off-line by pumping the water sample at 2 ml min⁻¹ after on-line filtration with a 0.45 µm filter. The minicolumns, containing the possible mercury species, were carried to the laboratory and there eluted with 0.5 ml of 5% (m/v) thiourea in 0.5% (v/v) HCl solution (at a flow rate of 0.5 ml min⁻¹). Finally, 100 µl of the eluted mercury-thiourea complexes were injected into the analytical LC column, directly connected to the ICP-MS instrument.

3. Results and discussion

3.1. Field sampling and preconcentration conditions

3.1.1. Column preparation

In order to establish which was the more adequate column, two resins and two chelating reagents were tested. XAD-7 resin and C-18 packing were investigated as supports and two organic reagents, DDTC and mercaptoethanol, able to react with the mercury species, were tested. Table 2 shows the retention of inorganic mercury and methylmercury obtained for all systems. The best solid support/reagent combination for the sorbent-extraction of mercury species over the whole pH range studied was C₁₈-diethyldithiocarbamate.

3.2. Optimum pH for sorbent-extraction of mercury

The reaction of inorganic mercury and methylmercury with complexing agents is highly dependent on the sample pH. In order to select the optimum pH value, 10 ml of aqueous solutions containing 5 µg of both inorganic mercury and methylmercury were

pumped through the minicolumn at pH value varying from 3 to 8. The solutions were collected at the exit at the minicolumn and analysed by FI-CV-AAS. The results of the influence of the pH of the water sample solution on the solid-phase extraction preconcentration are presented in Table 2. As can be seen, in the case of the C₁₈ systems, there is little effect of pH on the mercury recovery.

3.3. Elution

For inorganic mercury elution (strongly bound to the column) from the minicolumn, several reagents were tested. Table 3 summarises the results obtained for 1 ml of the studied eluents. The best elution system was a 5% (m/v) thiourea–0.5% (v/v) HCl solution, in

Table 3

Percent recoveries obtained for inorganic mercury with 1 ml of eluents

Eluent	Percent recovery
Acetonitrile	<20
Ethanol	<20
Methanol	<20
Methanol+5% mercaptoethanol	62±2
Methanol+10% mercaptoethanol	75±5
Methanol+20% mercaptoethanol	77±6
Methanol+30% mercaptoethanol	72±3
Methanol+0.05% SDDTC ^a	36±4
Methanol+2.5% APDC ^b	<20
Methanol+5% APDC	51±11
HNO ₃ (5%)	<20
HNO ₃ (10%)	<20
HNO ₃ (15%)	<20
HNO ₃ (20%)	<20
Thiourea (5%) in 0.5% HCl	97±3

^a Sodium diethyldithiocarbamate.^b Ammonium pyrrolidine dithiocarbamate.

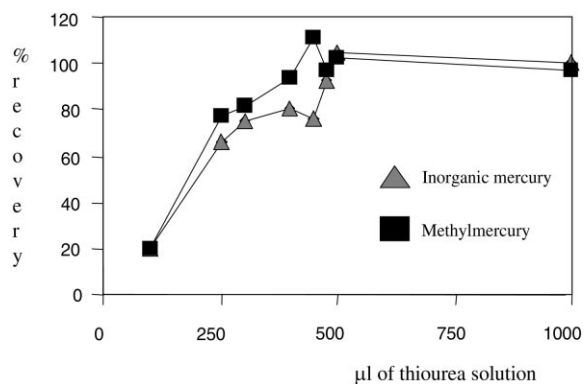


Fig. 1. Effect of the volume of eluent.

agreement with other authors [11–13]. Similar tests were carried out for elution of methylmercury using smaller volumes of eluent under the same experimental conditions. It was demonstrated that 0.5 ml of the eluent, as shown in Fig. 1 is able to elute the species. Hence, enrichment factors for the proposed sorbent preconcentration are of the order of 10^2 .

3.4. Breakthrough volume

The breakthrough volume of the column is a significant parameter for evaluating the application of sorbent extraction to real samples. Breakthrough measurements for both mercury species in ultrapure (Milli-Q) and river water were performed. Different sample volumes containing the same amount (30 ngHg) of both analytes were passed through the minicolumns and then eluted with 0.5 ml of the

Table 4
Stability experiments results

Storage	Percent recovery inorganic mercury	Percent recovery methylmercury
In the light at 15°C	102 ^a 40 ^b	98 ^a 35 ^b
In the darkness at 4°C	104 ^a 70 ^b	95 ^a 65 ^b

^a 7 days storage.

^b 14 days storage.

eluent. The eluates were analysed by FI-CV-AAS and the results appear in Fig. 2. As expected, the sample matrix may greatly affect the actual breakthrough volume of the conditioned minicolumn.

3.5. Stability of the minicolumns

The stability of the minicolumn after modification with DDTC was investigated for a 2-week period under different storage conditions. Experimental results, shown in Table 4, indicate that these minicolumns should be used during the first week after modification.

The stability of the two mercury species loaded on this minicolumn was also investigated. Different minicolumns were loaded with 200 ng l^{-1} each of Hg^{2+} or CH_3Hg^+ and their elution was carried out 6, 13, 19 and 30 days after storage in different conditions. The results observed are given in Fig. 3 and show that mercury species should be preferably eluted from the minicolumns for their determination during the first week after field sampling.

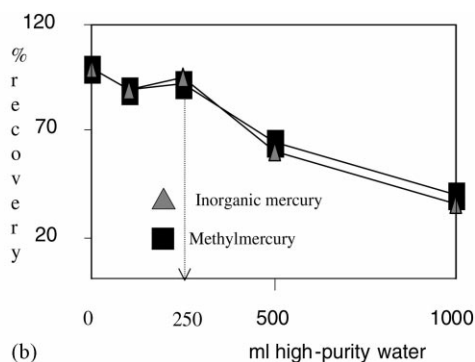
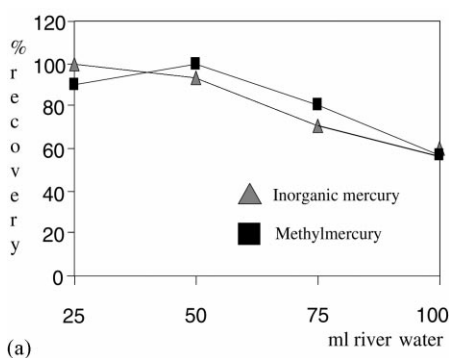


Fig. 2. Breakthrough volume with (a) river water and (b) high-purity water.

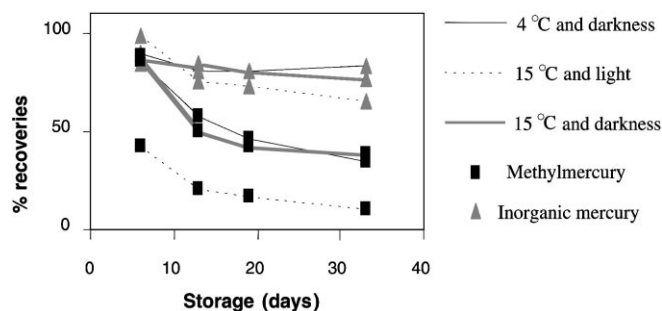


Fig. 3. Recoveries obtained for both species after storage in different conditions.

3.6. Chromatographic separation

For the separation of Hg^{2+} and CH_3Hg^+ , a C_{18} column was employed and two mobile phases A and B were tested. Using a mercaptoethanol solution as mobile phase, the chromatogram is similar to that reported by Bloxham et al. [24], for the separation of inorganic mercury and methylmercury with 2-mercaptoethanol. This behaviour indicates formation of the expected mercury complexes with the reagent.

The retention times observed for mobile phase A (using 1, 2, 3 and 5% acetonitrile) and B are given in Table 5. As can be seen, the best resolution and the fastest separation is achieved using the mobile phase B which is directly nebulised into the ICP. However, for mobile phase A, a cold vapour continuous system was necessary to avoid introducing acetonitrile into the plasma and so reducing the analyte sensitivity while increasing polyatomic ion formation and rapid deposition of solid carbon on the sampling orifices [30] of the ICP-MS instrument.

Table 5
Retention times of both species with the mobile phases tested

	Inorganic mercury ^a (min)	Methylmercury ^a (min)
Mobile phase A		
Mercaptoethanol with 1% acetonitrile	20.5	17.0
Mercaptoethanol with 2% acetonitrile	17.0	14.0
Mercaptoethanol with 3% acetonitrile	13.5	11.6
Mercaptoethanol with 5% acetonitrile	9.3	9.2
Mobile phase B		
Cysteine solution	2.8	4.3

^a % R.S.D. within 2%.

3.7. Analytical characteristics of the method

In order to evaluate the precision of the hybrid method proposed, three minicolumns were loaded with 50 ml of river water (spiked with 10 ng of each Hg species). The R.S.D. obtained was 10% for inorganic mercury and 12% for methylmercury (at 200 ng l^{-1} Hg). The observed limits of detection (LODs) calculated for a signal-to-noise ratio of 3, by injecting a sample volume of $100 \mu\text{l}$ were 5.2 and 5.6 ng l^{-1} Hg for inorganic mercury and methylmercury, respectively.

Calibration graphs for each of the mercury species were linear from the observed LOD to 600 ng l^{-1} (maximum concentration assayed).

3.8. Analysis of real samples

In order to ascertain the analytical possibilities of the proposed method and validate the results attainable for the speciation of inorganic mercury and methylmercury in real samples, unpolluted river waters were spiked with different amounts of each mercury species and analysed following the proposed method. Observed recoveries are given in the upper part of Table 6 and show good recoveries at the three levels of concentration tested. Results showed good agreement with those obtained by GC-glow discharge-atomic emission spectrometry [31]. The derivatisation step was carried out with STEB and a preconcentration by solid phase microextraction was necessary to achieve lower detection limits. The results are shown in Table 6. Moreover, total mercury was determined by double focusing-ICP-MS

Table 6
Analysis of mercury species in Asturian rivers

Inorganic mercury added (ng l^{-1})	Methylmercury added (ng l^{-1})	Inorganic mercury found (ng l^{-1})	Methylmercury found (ng l^{-1})
Unpolluted river (Nora River)			
51	52	41 ± 11	42 ± 10
102	99	95 ± 12	92 ± 13
145	147	139 ± 15	136 ± 16
Polluted river (Pigüña River)			
—	—	120 ± 20^a	$< 5^a$
—	—	130 ± 9^b	$< 2^b$

^a Total Hg was analysed by DF-ICP-MS and the result was $140 \pm 10 \text{ ng l}^{-1}$.

^b Results obtained by SPME-GC-GD-OES.

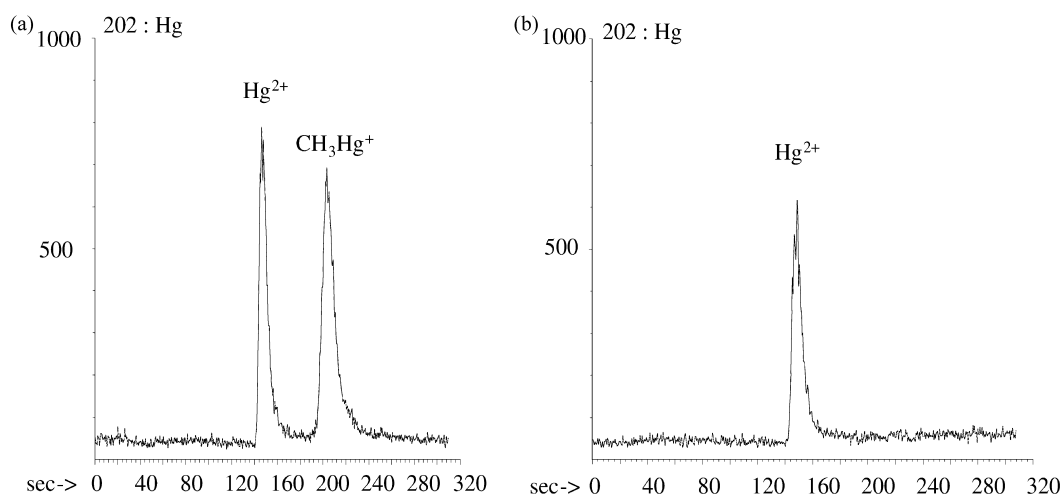


Fig. 4. Chromatogram of (a) a 20 ng ml^{-1} standard solution and (b) a sample from an Asturian river.

(Finnigan MAT, Bremen, Germany). Chromatograms of this sample and a standard solution are shown in Fig. 4.

4. Conclusions

A fully portable, field sampling method, based on the isolation and preconcentration of inorganic mercury and methylmercury by using modified mini-columns of C_{18} with subsequent element specific detection by LC-ICP-MS has been developed. The results have been compared with those given by an alternative method for an unpolluted river sample. The agreement between the two procedures shows that the proposed method can be applied for the determination of mercury species in river waters. Although artificial

methylmercury formation has been widely reported in the literature, in the present work it has not been observed probably due to the low levels of inorganic mercury, and moreover, because of it is complexed during the proposed method with different reagents (SDDTC, thiourea and cysteine).

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