Analusis, **1999**, *27*, 871-875

Microwave-assisted determination of total mercury and methylmercury in sediment and porewater

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Abstract. Existing methods for total mercury and methylmercury determination in sediment and porewaters were improved by applying open microwave heating for extraction of Hg species from the sample and decomposition of MeHg prior to detection as Hg(II) by CV AFS. It was shown that nitric acid can quantitatively leach Hg from sediment, already at a low microwave power (30 W, 5 min). Methylmercury can be quantitatively leached from sediment by dilute sulphuric acid (1 mol/L) at a power of 60 W during 5 minutes, without being decomposed. So obtained extract can be further distilled with a reduced possibility for artefactual MeHg formation, as it contains much lower levels of inorganic Hg, compared to the original sediment. Microwave-assisted BrCl oxidation was shown to be more effective for decomposition of MeHg and stable organomercury complexes in water solutions (sediment distillate and porewater), as compared with BrCl oxidation at room-temperature. Therefore, the application of low-power microwave digestion can significantly improve determination of Hg species in sediment and porewater, both in terms of time and efficiency.

Keywords. Mercury – methylmercury – sediment – microwave digestion.

Introduction

Microwave-assisted extraction methods for sample preparation have been evaluated in various environmental applications, as are total digestion for element analysis or extraction of selected organic compounds. This technique has been confirmed as a method of choice over conventional procedures for digestion of mineral and biological samples for total Hg determination [1,2,3], due to a shorter extraction time, a higher extraction efficiency and easier control of digestion parameters. Both closed and open microwave systems are used for the digestion of samples for the total Hg analyses. However, determination of the total Hg in environmental samples is not sufficient, as Hg is partly in the form of methylmercury (MeHg), which is considerably more toxic than the inorganic Hg. A particularly difficult task is the determination of MeHg in sediment, where it makes a very low percentage of the total Hg (< 2 %). Only recently, an open low-power focused microwave system has been verified as an appropriate tool for preparation of solid samples for organometallic speciation analysis [4]. It has been used for developing of the isolation procedure of MeHg in sediment based on the microwave-assisted leaching of MeHg with dilute acids [5].

In this work, the application of open microwave system for the total Hg and MeHg determination in sediment and porewater is described. Microwave-assisted leaching of the total Hg and MeHg from sediment with an acid extractant, provided a rapid way of separation of these species from the matrix prior to detection by CV AFS (cold vapour atomic fluorescence spectroscopy). Microwave-assisted BrCl oxidation was proved to be more effective for the decomposition of MeHg and stable organomercury complexes in solution (distillate or porewater), as compared with BrCl oxidation at room temperature.

Material and methods

Reagents

Acids used were of analytical quality (HNO_3, HCl) or suprapur grade (HCl, Merck). Hg standard was prepared from stock standard solution (1 g/L, Merck). A standard solution was prepared weekly in 10 % HNO_3 and 0.01 % of $K_2Cr_2O_7$, whereas reference standard solutions were prepared daily in 1 % HNO_3. A reductant solution (5 % $SnCl_2$ in 10 % HCl) was prepared by dissolving $SnCl_2$ in concentrated HCl and diluting with water. The certified reference sediments used for verification were PACS-1 (National Research Council of Canada - NRCC) and CRM 580 (Community Bureau of Reference of the European Communities - BCR).

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Received July 20, 1999, revised October 29, 1999, accepted November 5, 1999.

Instruments

Sample digestion was carried out in a single-mode reflux focused microwave system (Microdigest A-300, Prolabo, Paris, France) with a maximum power setting of 300 W. Specially designed glass vessels and the construction of the system allow digestion under atmospheric pressure without any microwave leakage. For Hg detection a CV AFS method was used, consisting of vapour generator (PSA 10.003), a gold platinum trap (PSA 10.501 Galahad) connected with an atomic fluorescence detector (PSA 10.023 Merlin) and is described in details elsewhere [6,7].

Procedures

For the total Hg determination wet or dry sediment (0.05-0.1 g) was digested with 5 mL of concentrated HNO_3 in a glass vessel for microwave digestion at a chosen power setting (10-20 %) for 3-5 min. The sample was left to cool, transferred into Teflon tube and centrifuged for 10 min at 10 000 rpm. The supernatant was diluted according to the concentration range of the samples for Hg detection by CV AFS. The sediment porewater was isolated from the sediment under the nitrogen atmosphere by centrifugation and acidified with 1 % HNO_3. Reactive Hg was determined within few days of sampling after $SnCl_2$ reduction. The total Hg in porewater was measured after Hg oxidation by BrCl, overnight at room temperature [8], or within 3 min at a power of 30 W in the microwave oven. For comparison samples were also decomposed by UV irradiation (150 W UV lamp) within 12 hours [9]. MeHg was isolated from the sediment matrix by distillation of the entire sediment or the sediment leachate. For the sediment distillation 8.5 mL of water, 1 mL of 10 % NaCl and 1 mL of 8 mol/L H_2SO_4 [10] was added to 0.2-0.5 g of dry or wet sample. To obtain the sediment leachate dry sample (0.2-0.5 g) was digested with 10 mL of 1 mol/L H_2SO_4 in the glass vessel for microwave digestion at a power setting of 20 % (60 W) for 5 min. After cooling the sample solution was centrifuged for 10 min at 10 000 rpm. An aliquot of supernatant (8 mL) was transferred into distillation vessel, 1 mL of 10 % NaCl was added and volume was adjusted to 10 mL with 1 mol/L H_2SO_4. Distillation was performed in all-glass system at a temperature of 160 °C under a nitrogen flow-rate of 60 mL/min. The distillate (8-8.5 mL) was diluted to 20 mL with Hg-free water and an aliquot was checked for any inorganic Hg present. In the rest of the sample MeHg was decomposed by BrCl oxidation (0.25 mL of BrCl was added to 10 mL of sample and left overnight), or by microwave-assisted BrCl oxidation (0.05 mL of BrCl was added to 10 mL of sample and digested for 3 minutes at a power of 30 W) and detected by CV AFS as inorganic Hg.

Results and discussion

Applied microwave irradiation must be strong enough to achieve a quantitative Hg extraction from sediment, but in the same time sufficiently mild to avoid Hg losses by overheating and/or volatilisation. Experiments performed on the certified reference sediment PACS-1 (Tab. I) showed that digestion with concentrated HNO_3 for 3 min at 60 W (20 %) was insufficient for a quantitative Hg extraction from PACS-1, while digestion for 5 min at 90 W or 10 min at 60 W caused losses of Hg as a consequence of sample overheating. Microwave irradiation during 5 min at 30 W (10 %) was found to offer optimum conditions for leaching of the total Hg from PACS-1 with HNO_3. A mixture of different acids (HNO_3, HCl, H_2SO_4) is usually used for the total Hg extraction from mineral samples [1,2]. The results obtained demonstrate that, by applying an adequate microwave procedure, HNO_3 only is sufficient for a quantitative leaching of Hg, thus providing a very simple and rapid manner for Hg determination in sediments.

It has been recently demonstrated that distillation, one of the frequently used methods for MeHg isolation from solid matrices [10], was prone to artefact formation of MeHg during distillation (up to 0.1 % of the total Hg; [11,12]). The artefact may be significant in sediments where naturally occurring MeHg usually makes less than 2 % of the total Hg. In addition, clogging of the system due to formation of the precipitate during distillation can create difficulties during distillation of some types of sediments. Both disadvantages could be minimised by extracting MeHg from sediment particles before distillation and carrying out a distillation of the sediment leachate. This objective could be achieved by the microwave-assisted leaching of MeHg from sediment with dilute mineral acids [5]. As it was shown that the optimum conditions for MeHg distillation were obtained using dilute H_2SO_4 [13], a leaching of MeHg from sediments with dilute H_2SO_4 was investigated. A study on the stability of MeHg in 1 mol/L H_2SO_4 (Tab. II) showed that

Table I. Optimisation of microwave digestion of sediments with concentrated HNO_3 for the total Hg analysis in PACS-1.

Power (W)	*Time (min)*	*Hg (mg/kg d.w.)*
30	5	4.63 ± 0.12
60	3	4.13 ± 0.06
60	5	4.46 ± 0.12
60	10	3.80 ± 0.17
90	5	3.56 ± 0.12

- certified value for Hg in PACS-1: 4.57 ± 0.16 mg/kg

Table II. Influence of microwave parameters on the stability of MeHg in 1 mol/L H_2SO_4.

Power (W)	*Time (min)*	*MeHg added (ng/L)*	*Hg (II) found (ng/L)**
30	5	20 - 40	< 2
60	5	20 - 40	< 2
90	5	20 - 40	2 - 5

* a presence of Hg (II) in solution indicates MeHg decomposition during microwave irradiation (2 ng/L is detection limit of the method)

during irradiation for 5 min and power up to 60 W MeHg was not decomposed. The experiment on the leaching of sediment with 1 mol/L H_2SO_4 demonstrated that only a minimum amount of inorganic Hg (regularly less than 1 % of Hg_{tot}) was extracted from sediment under such conditions. It is important from the point of view of possible artefactual MeHg formation, as a very low amount of Hg in the solution which is subjected to distillation, will allow less formation of MeHg during distillation. If up to 0.1 % of the inorganic Hg could be methylated [11,12] it would represent maximum 0.001 % of the total Hg originally present in sediment. This amount will be minor compared with a percentage of MeHg naturally occurring in sediments (0.1-2 %). A comparison of MeHg determination by distillation of the entire sediment and H_2SO_4 extract was performed on the certified reference sediment CRM 580 and on the several sediments taken from the Seine estuary (Tab. III). A good agreement between different isolation methods indicated that under the microwave condition used, 1 mol/L H_2SO_4 extracted quantitatively MeHg from both CRM 580 and this type of natural sediments (Hg_{tot}: 200-700 ng/g, orgC: 2-5 %). Tseng *et al.* [5] obtained, using microwave leaching (60 W, 3 min) with 1 mol/L H_2SO_4, too low MeHg recovery from certified sediment samples. A longer irradiation time and thus more powerful extraction, could probably explain the greater efficiency of MeHg extraction from sediments obtained with our procedure. Similar MeHg concentrations obtained by distillation of the whole sediment and H_2SO_4 extract suggest that artefact formation of MeHg during distillation of the whole sediment is not significant, compared to the natural MeHg level in these samples. For CRM 580 it is in accordance with the results showing that distillation based techniques are in good agreement with techniques not involving distillation [14,15].

In the method used in this work MeHg in the sediment distillate is finally detected as inorganic mercury. Therefore, it should be completely transformed to Hg(II) before CV AFS detection. For such purpose a decomposition by UV light or a chemical oxidation by BrCl can be used. For a quantitative oxidation of MeHg by BrCl at room temperature, a rather high concentration of BrCl (2.5 %) during prolonged time (several hours) was required. It was suggested that digestion of MeHg by BrCl could be promoted at elevated temperature [16], or by microwave-assisted BrCl oxidation used in the on-line method for Hg determination in slurried samples [17]. Our results (Tab. IV) showed that microwave-assisted MeHg oxidation by BrCl was very efficient and that Hg demethylation can be accomplished within few minutes by using much lower (0.5 %) BrCl concentration. Three different methods of MeHg decomposition in distillate (BrCl, UV, BrCl+MW) tested on several sediment samples gave comparable results for MeHg level in different types of sediment (Tab. III).

Procedure for the total Hg determination in sediment porewaters usually include oxidation of the non-labile Hg fraction with 0.5 % BrCl prior to Hg(II) reduction with $SnCl_2$. Analysis of porewaters isolated from the sediment of

Table III. Comparison of MeHg determination by different isolation and decomposition methods in CRM 580 and in sediments from the Seine estuary.

Sediment sample	*MeHg concentration (µg/kg d.w.)* *Method A*	*Method B*	*Method C*	*% MeHg of HgT in sediment*
CRM 580	72.6 ± 6.2	–	73.8 ± 5.8	0.06
Coastal sediment 1	0.7 ± 0.1	0.9	0.8 ± 0.1	0.20
Coastal sediment 2	1.9 ± 0.2	2.0	1.8 ± 0.2	0.40
Estuarine sediment 1	3.3 ± 0.3	2.9	3.3 ± 0.4	1.24
Estuarine sediment 2	5.3 ± 0.4	5.0	5.7 ± 0.5	1.72
Estuarine sediment 3	0.1 ± 0.1	0.1	0.2 ± 0.1	0.05
Riverine sediment	1.4 ± 0.2	1.3	1.1 ± 0.2	0.82

A - distillation of sediment with a final MeHg decomposition by BrCl
B - distillation of sediment with a final MeHg decomposition by UV
C - distillation of H_2SO_4 extract with a final MeHg decomposition by BrCl or BrCl+MW
– certified value for MeHg in CRM 580: 75.5 ± 5.0 µg/kg
– detection limit of the method is 0.1 µg/kg

Table IV. Influence of microwave parameters on the oxidation of MeHg by BrCl solution in MQ water.

BrCl added (mL/mL or %)	*Power (W)*	*Time (min)*	*MeHg added (ng/L)*	*MeHg found (%) as Hg(II)*
0.5/20 or 2.5 %	30	5	10 - 30	98 - 105
0.25/20 or 1.25 %	30	5	10 - 30	95 - 100
0.1/20 or 0.5 %	30	5	10 - 30	95 - 105
0.05/10 or 0.5 %	30	3	20 - 40	95 - 108

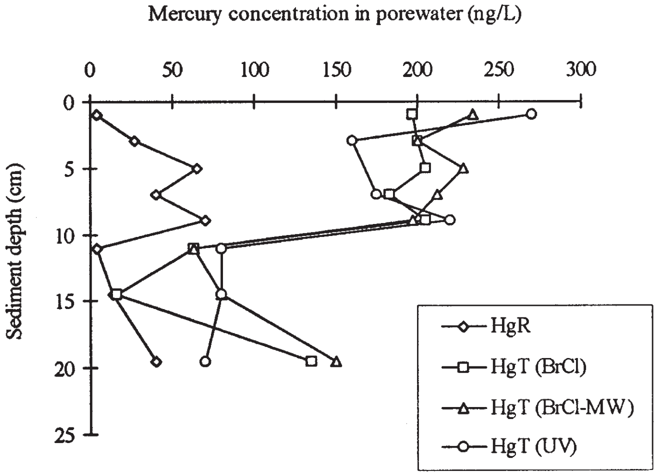

Fig. 1. Porewater mercury profile in sediment core of the Seine estuary sampled in September 1996 (HgR - reactive mercury, HgT - total mercury).

the Seine estuary demonstrated that oxidation with BrCl is not always sufficient. While in sediment collected in September 1996 the comparable total Hg levels in porewater were found after UV, BrCl and microwave-assisted BrCl oxidation (Fig. 1), in samples collected in March 1997 significantly lower concentrations were obtained after BrCl oxidation only (Fig. 2), indicating an incomplete Hg oxidation by BrCl in these samples. Therefore, microwave-assisted BrCl oxidation proved to be more efficient than BrCl oxidation at room temperature. These results also indicate that for some porewaters oxidation with BrCl may not be sufficient for the total Hg determination.

Presented results demonstrate that an open focused microwave system can be successfully applied in different stages of the procedure for the total Hg and MeHg determination in sediment and porewater, resulting in an improvement of the method in terms of time and efficiency.

Acknowledgements

N.M. thanks for a grant from the “Région Nord-Pas-de-Calais”. Z. Kwokal is thanked for technical assistance. This work was supported by the Ministry of Science and Technology of Croatia and the Seine-Aval Scientific Program.

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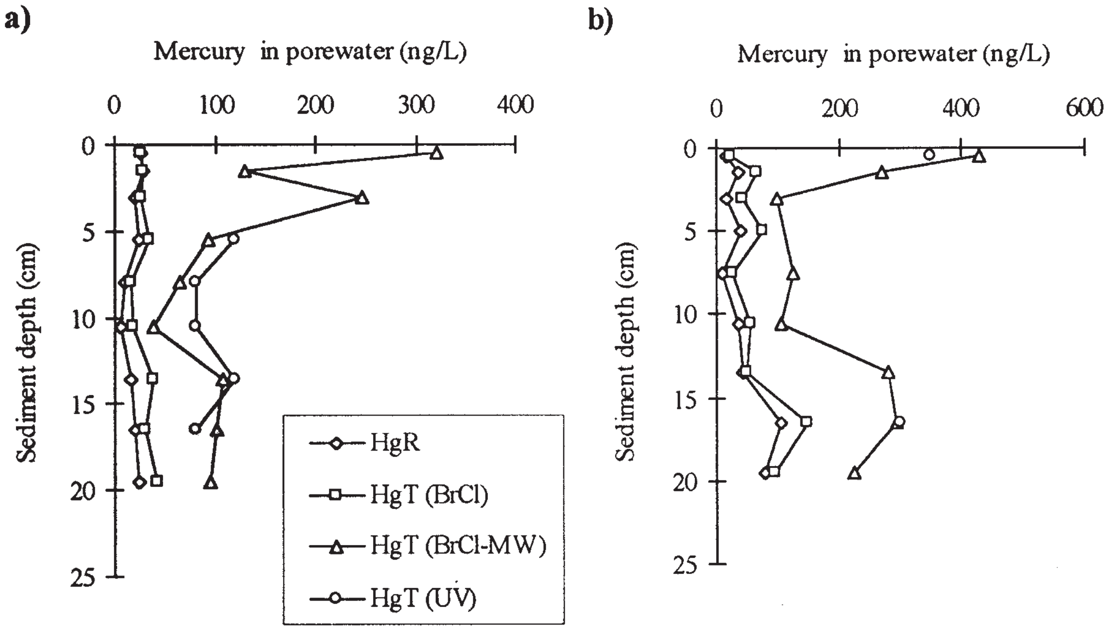

Fig. 2. Porewater mercury profiles in sediment cores of the Seine estuary (a - coastal, b - riverine) sample in Mars 1997 (HgR - reactive mercury, HgT - total mercury).

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