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NOTE

Methylmercury Monitoring in Rainwater Samples using *in situ* Ethylation in Combination with GC–AFS and GC–ICP–MS Techniques

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In a monitoring study an analytical technique with atomic fluorescence (AFS) detection was used for methylmercury determination in atmospheric precipitation from the Baltic Sea at ultra-trace level. The methylmercury values in atmospheric precipitation obtained by the AFS system ranged from below the detection limit to 0.32 ng l^{-1}. The concentrations of methylmercury made up about 1–4% of the total mercury concentrations. Recently, when artifact formation of methylmercury had become an issue the analytical technique used was checked with a stable enriched mercury isotope for artifact formation of methylmercury during analysis. The analytical system, normally coupled with atomic fluorescence detection, was used with a mass spectroscopy, (ICP–MS) detector for isotope-specific mercury detection. The samples were spiked just before analysing with $^{200}Hg^{2+}$. A possible unintentional transformation into methylmercury during the analytical procedure could be detected with the isotope-specific methylmercury determination method. The results have shown that a direct ethylation of methylmercury in an atmospheric precipitation sample by sodium tetraethylborate produced no significant amount of artifactural methylmercury due to the spiked enriched $^{200}Hg^{2+}$. However when the water vapour distillation was applied for aqueous rain samples containing visible particles, an artifactural formation of methylmercury was observable. The particles were responsible for this formation. **Copyright © 1999 John Wiley & Sons, Ltd.**

Keywords: methylmercury; analysis; ethylation; rainwater; mercury isotope; artifact formation

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INTRODUCTION

In international monitoring programmes, ongoing measurement of heavy metals in wet deposition is becoming an increasingly central role in the production of basic data. The data are used for validation of transport models which estimate the atmospheric input of heavy metals to the environment. Methylmercury plays an important role in the balance of global mercury circulation, including transport and deposition processes at the atmosphere/aqueous and atmosphere/soil interface.[1–3] Methylmercury is a relatively stable compound and can be washed cut of the atmosphere by rain. Measurements of total and methyl-mercury are important for monitoring investigations. As part of the research projects of the German FEA (Federal Environmental Agency), measurements of mercury in wet deposition have been carried out by the

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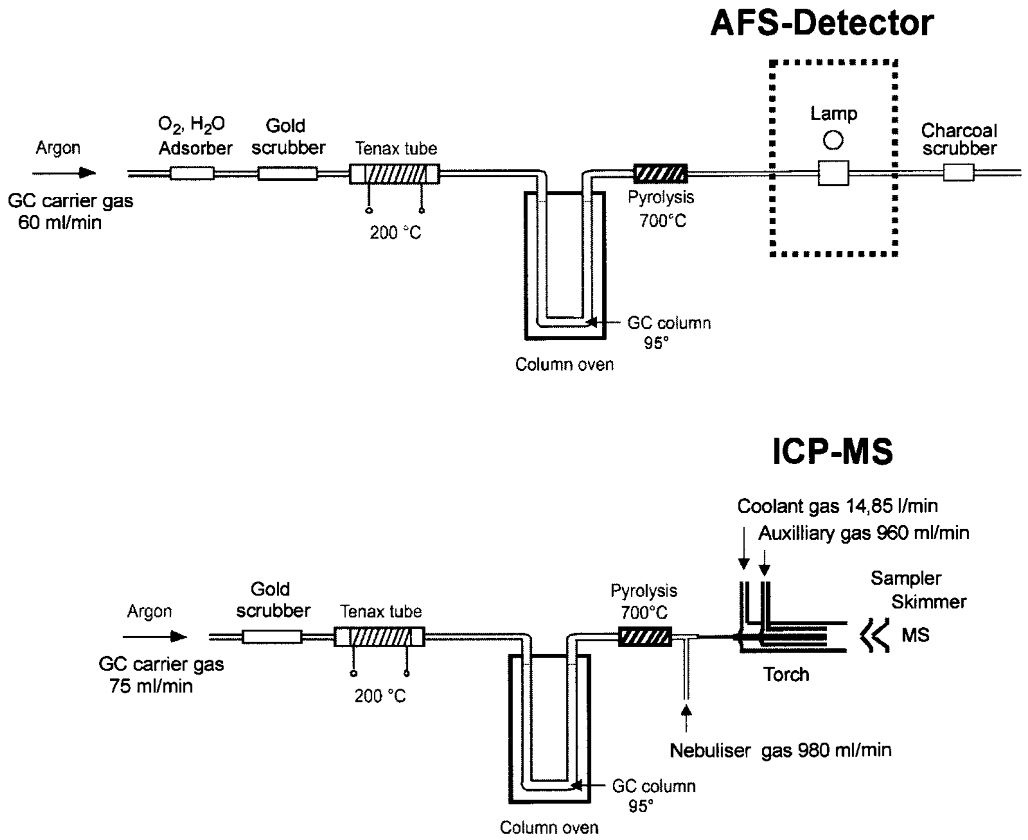

Figure 1 Top: GC–AFS system for the determination of methylmercury. After desorption the ethylated mercury compounds were separated on the column and detected after pyrolysis by atomic fluorescence. Below: GC–ICP–MS system. With the same procedure the separated mercury compounds were detected by mass-specific ICP-MS. An isotope-specific determination of methylmercury is thus possible.

Nordum Institute at monitoring stations on the Baltic Sea and North Sea coasts since 1993; these have included methylmercury determinations during the last two years.[4]

In the last year researchers have reported on the artificial formation of methylmercury during the analytical process, and it has become is more important a issue.[5–8] Therefore it was necessary to investigate the analytical procedure which was applied to the determination of methylmercury in the large quantity of samples measured in the research framework. Examination of the method by coupling with an ICP–MS, and involving isotope experiments to observe unintentional species transformation processes during the determination of methylmercury,[9–11] is described in the following sections.

EXPERIMENTAL AND OPTIMIZED WORKING CONDITIONS

Reagents, standard solutions and derivatization procedure

A stock solution of methylmercury chloride was prepared in methanol–water (50:50 v/v) and stored in the dark at 4 °C. An enriched stable mercury isotope $^{200}Hg^{2+}$ standard was prepared by dissolving 10 mg of ^{200}HgO from Chemotrade Chemiehandels GmbH in 1 ml HCl and diluting to 10 ml with high-purity water. The enrichment of the ^{200}HgO was 96.41%; the natural abundance is 23.13%. The ethylation reagent, a 1% sodium tetraethylborate solution in water in an argon atmosphere, was subdivided into 1.5-ml portions

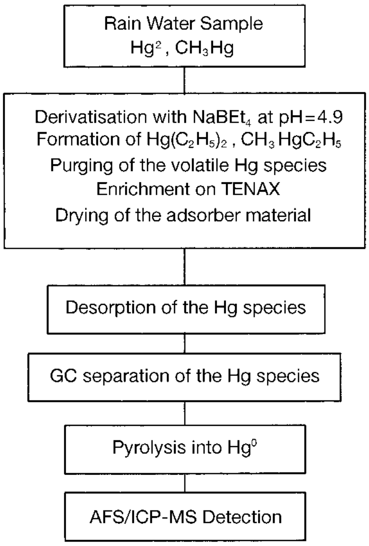

Figure 2 Scheme for the determination of methylmercury in rainwater by aqueous-phase ethylation by sodium tetraethylborate, Tenax trapping, thermal desorption, GC separation, pyrolysis and GC–AFS/ICP–MS.

and frozen; 20 μl of this solution was sufficient for complete ethylation of the mercury compounds in a 100-ml rainwater sample. For optimal ethylation of methylmercury a pH of 4.9 ± 0.1 was necessary. The pH in the sample was adjusted by adding 400 μl of the buffer solution, acetic acid–sodium acetate (50:50, v/v). For complete ethylation of methylmercury a reaction time of 10–15 min was necessary. A purging time of 20 min with a gas stream of 300 ml min^{-1} was sufficient for complete trapping of the methylethylmercury produced. For investigation of the particles, the rainwater samples (200–500 ml) were filtered (0.45 μm cellulose nitrate, NC 45, Schleicher and Schnell). The sample was sucked through the filter with the aid of a vacuum. Two blank distillations with the addition of enriched isotope were carried out to examine the self-methylation potential of the cellulose nitrate filters. No methylation due to the filter was observable. The filters with the particulate phase were put into a glass flask and distilled according to Horvat *et al.*[9] The distillate obtained was prepared for methylmercury determination with ICP–MS as described below for the rainwater samples.

Instrumentation

The atomic fluorescence and ICP–MS detectors were each coupled with gas chromatographic (GC) separation for the determination of methylmercury after sodium tetraethylborate derivatization at program level in aqueous samples.[9] The set-up of both systems is shown in Fig. 1. The AFS system was used for the monitoring study of methylmercury in atmospheric precipitation. The ICP–MS system was suitable for the isotope experiments. The measurements were carried out with the following equipment: Tekran 2500 AFS, Perkin-Elmer Elan 5000 ICP–MS and column heating at 95 °C (HP 5890 GC oven and Shimadzu GC oven).

Procedure for sample detection

The volatile ethylated mercury compounds were purged on a Tenax TA [glass traps filled with 150 mg Tenax TA (20–35 mesh, 100 mm $\times$ 4 mm i.d.)] in a separate purging system. After the trapping procedure complete thermal desorption of the ethylated mercury compounds was reached at 200 °C within 30 s in the analysing system. The compounds were desorbed with a mobile argon gas stream of 60 ml min^{-1} (AFS). The argon used for the AFS system was cleaned with the aid of an oxygen–water adsorber and a gold scrubber. For cleaning of the nebulizer gas stream in the ICP–MS, only a gold scubber was necessary. The species mercury (0), methylethylmercury and diethylmercury were separated on a packed glass column obtained from Chrompack (0.6 m $\times$ 6 mm), packed with Chromosorb W, HP (80–100 mesh), stationary phase (15% silicone OV-3). The column was heated in a GC oven at a constant temperature of 95 °C. After the separation, the compounds were thermally transformed at 700 °C in a pyrolysis unit to mercury (0) (Hg^0). For atomic fluorescence detection the gas stream was transferred directly into the detector.

The scheme for the determination of methylmercury in the rainwater samples by aqueous-phase ethylation by sodium tetraethylborate is shown in Fig. 2. For ICP–MS detection the GC gas stream was added to the nebulizer gas stream and subsequently transported into the plasma of the ICP–MS for a mass-specific detection at m/z = 199, 200 and 202. The compounds were separated in the following order: Hg^0, $CH_3HgCH_2CH_3$, $CH_3CH_2HgCH_2CH_3$. The optimum separation of the three compounds was obtained by a column gas flow of 60 ml min^{-1} (AFS), a Tenax trap desorption temperature of 200 °C adjusted within 30 s and an isothermal column temperature of 95 °C. The detection was carried out with either AFS or ICP–MS detectors (Fig. 2).[8–10] The detection limit for the GC–AFS coupling was 0.05 ng l^{-1} ($A_b + 3S_b$).

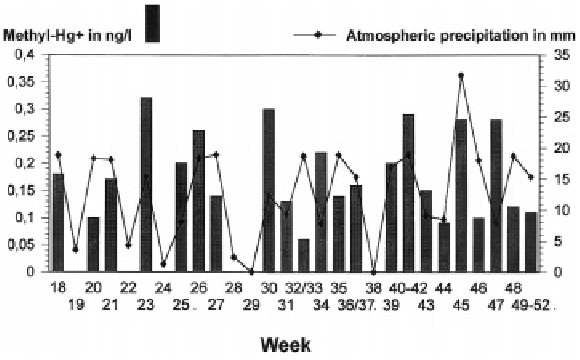

Figure 3 Weekly methylmercury values in rainwater samples with the respective amounts of precipitation at the Zingst station from May till December 1996.

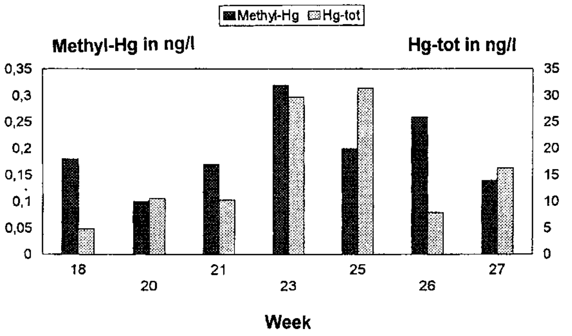

Figure 4 Methylmercury and total mercury measurement in rainwater samples obtained during seven different weeks in 1996.

The detection limit for the GC–ICP–MS coupling was 0.02 ng l^{-1} ($A_b + 3S_b$) (A_b = standard deviation of the base noise; S_b = standard deviation of the blank reading). The total mercury concentrations were determined by digestion of 100 ml of atmospheric precipitation by BrCl for 1 h. After addition of $NH_2OH{\cdot}HCl$ the samples were reduced by $SnCl_2$ in 1 M HCl. The measurements were carried out in the gold-trap AFS system. The detection limits based on ($A_b + 3S_b$) were 0.5 ng l^{-1}.

RESULTS

The methylmercury values in the atmospheric precipitation obtained by the AFS system normally range from below the detection limit to 0.32 ng l^{-1} (Fig. 3). Figure 4 illustrates the measured methylmercury and total mercury concentrations in the rainwater samples obtained over seven different weeks. The concentrations of methylmercury are about 1–4% of the total mercury concentrations.

The rain samples were collected at the Zingst FEA station (southwest of the island of Rügen on the Baltic Sea coast) from May to December 1996 and analysed weekly. The 100-ml samples were ethylated directly in a reaction flask without membrane filtration using a defrosted sodium tetraethylborate solution at a pH of 4.9 as described in Fig. 2. The measurements were checked with the standard addition method. Figure 5 shows a comparison of the results of methylmercury measurement without and with the aid of the standard addition method respectively for the same samples. The standard deviations are 10% and less than 10%. The standards showed a good linearity (r = 0.996). Beside methylmercury, elemental mercury and inorganic mercury were always present and detectable with the system. The methylmercury peaks showed a good resolution for determination of the values of methylmercury in the samples. After equipping the ICP–MS system with the same purge-and trap GC system used with AFS detection, it was possible to carry out isotope experiments to observe mercury species transformation processes. To 100-ml aqueous samples 1000 ng (absolute) enriched mercury isotope $^{200}Hg^{2+}$ was added. The total mercury value in the sample was therefore increased by a factor of about 100. After an equilibration time of 10 min the buffer and the

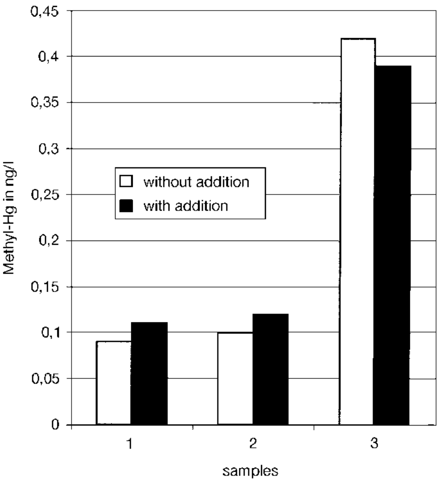

Figure 5 Determination of methylmercury by GC–AFS with and without the standard addition method.

ethylation solution were added to the reaction flask and shaken for 10 s. After a reaction time of 20 min the ethylated compounds were purged on the Tenax trap with argon and analysed by the GC–ICP–MS system. In a second experiment the particles obtained after filtration of rainwater samples (10–25 mg) were distilled according to Horvat *et al.*[9] Just prior to the distillation, 1000 ng (absolute) enriched mercury isotope was added to the sample. The distillate was subsequently ethylated as described above. The results of the experiments are shown in Fig. 6. In the first chromatogram a standard chromatogram of 75 pg methylmercury (Chrom. 1) is shown. In the second chromatogram (Chrom. 2) the isotope experiment with direct ethylation of the rainwater samples is shown. The mass trace 200 did not surmount or exceed the mass trace 202 in the methylmercury peak. This showed that no artificial formation of methylmercury was observable by applying direct ethylation to the rainwater sample. After distillation of the particles obtained by filtration of a rainwater sample spiked with enriched isotope $^{200}Hg^{2+}$, the third chromatogram (Chrom. 3) was obtained. In this chromatogram artificial formation of methylmercury during the sample preparation procedures was observable; the mass trace 200 slightly exceeded the mass trace 202 in the methylmercury peak. This indicates that formation of methylmercury occurred during the analysis, but was registered only qualitatively. In the fourth chromatogram a blank determination with double-distilled water (Chrom. 4) is shown.

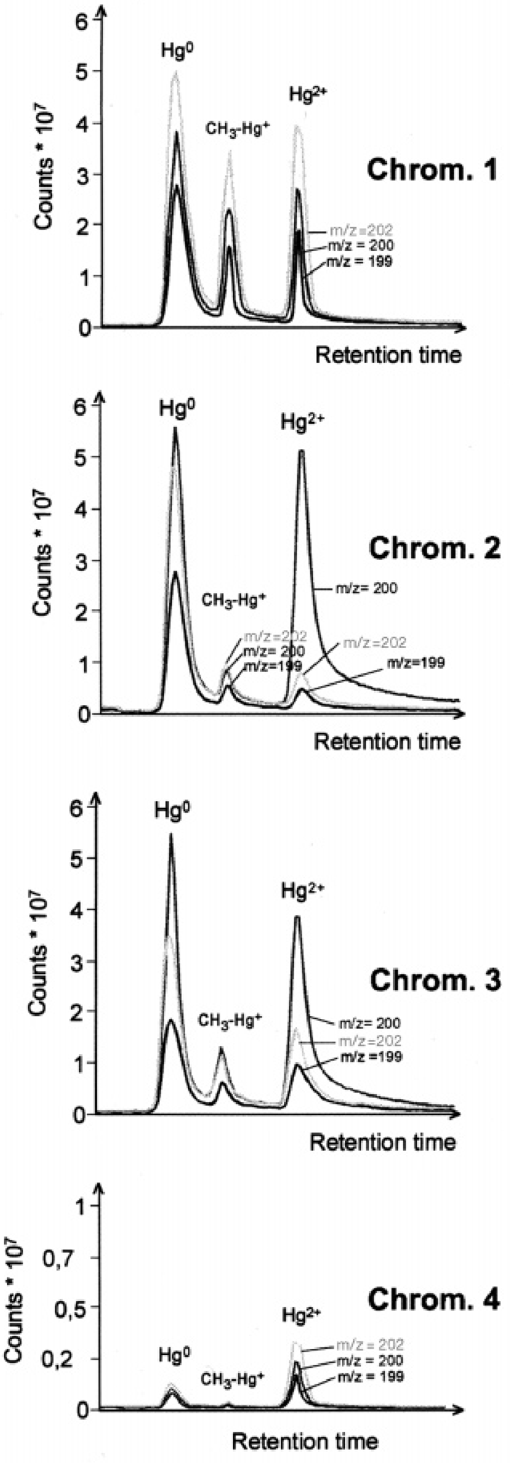

Figure 6 Chrom 1: a standard chromatogram with isotope-specific determination of methylmercury by the GC–ICP–MS system. The mercury mass traces show the natural abundance ratio of mercury isotopes. Chrom 2: chromatogram obtained after spiking of a rainwater sample with 1000 ng of enriched stable mercury isotope $^{200}Hg^{2+}$ and direct ethylation of the sample. Chrom 3: determination of methylmercury on particles obtained after filtration of the rainwater samples. The samples were distilled according to Horvat *et al.* (Ref. 9). In the methylmercury peak, artificial formation of methylmercury due to the spiked enriched stable isotope is observable. The mass trace 200 exceeds the mass trace 202. Chrom 4: blank determination of methylmercury in the reaction flask.

CONCLUSION

The results have shown that, beside[3] artificial formation of methylmercury in different matrices such as sediment and soil, particles from rainwater samples were also prone to artifact formation during water vapour distillation. A direct ethylation of methylmercury in the rainwater samples showed no artificial formation due to a high spike of enriched stable inorganic mercury isotope $^{200}Hg^{2+}$. When the water vapour distillation is applied the increase in the recoveries is possibly due to an artificial formation of methylmercury during the distillation. We are not able to distinguish at present between complete ethylation and an additional production during the distillation of a DOC-rich water sample. This can be carried out by isotope experiments but we have no evidence that the methylation behaviour of the ambient inorganic mercury is the same as that of the spiked inorganic mercury or enriched stable isotope. The added isotope could be better or more poorely methylated. Therefore a calculation of the amount of artifact formation of methylmercury during the distillation would be speculative. The comparability of the isotope spikes has to be proved. We have to accept that our standard addition method represents the methylmercury that we have just spiked and that is free in solution. Matrix-bonded methylmercury is probably not ethylated during this process. Therefore an unknown error will always be present and at the moment this is not determinable. With the aid of the developments we have made, we now have the basics for future research. For statistical certainty, more experiments have to be carried out.

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