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Determination of methyl mercury and inorganic mercury in natural waters at the pgL^{-1} level: Intercomparison between PT-GC-Pyr-AFS and GC-ICP-MS using Ethylation or Propylation derivatization

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Abstract. Mercury speciation analysis of both inorganic and methyl Hg in ultrapure and natural waters by purge-and-trap gas chromatography pyrolysis atomic fluorescence spectrometry (PT-GC-Pyr-AFS, MERX-M, Brooks Rand) was performed. This automated analytical setup was also compared with gas chromatography inductively coupled plasma mass spectrometry (GC-ICPMS, X Serie 2 ThermoFisher). In addition, a reagent cleaning step of the buffer solution and derivatizing reagents (NaBEt_4 and NaBPr_4) was evaluated to improve the detection limit of the method. PT-GC-Pyr-AFS experiments analyzing Milli-Q and Deionized water (Millipore) using cleaned reagents and quantifying by external calibration led to MeHg^+ and Hg^{2+} concentration values significantly lower than those obtained using uncleaned reagents. The limit of detections (LODs) after cleaning was found significantly low using both NaBEt_4 and NaBPr_4 . However, the lowest LODs were obtained when using cleaned NaBPr_4 (range: $1\text{--}2 \text{ pgL}^{-1}$ for MeHg^+ and $9\text{--}10 \text{ pgL}^{-1}$ for Hg^{2+}). Matrix effects have been finally investigated using both PT-GC-Pyr-AFS and GC-ICPMS to characterize and quantify potential interferences in natural water samples with different salinities and organic matter contents, including coastal water reference material (CRM) certified for total mercury concentration (IRMM BCR-579).

Key words: Speciation, Mercury, PT-GC-Pyr -AFS, GC-ICPMS

Introduction

For many years mercury has been one of the elements monitored at concentrations below 1 ngL^{-1} in environmental samples such as surface waters. Several methods for determining the concentration of mercury species have been developed; most of them are commonly achieved by the coupling of separation techniques with an element specific detector (Stoichev et al., 2006). In this study, two gas chromatographic systems coupled to different detectors (PT-GC-Pyro-AFS, GC-ICPMS) currently used for mercury speciation analysis were evaluated in terms of linearity, precision, accuracy and limits of detection.

Materials and Methods

Pure and ultrapure waters were obtained from three different water purification systems. Surface fresh and

coastal water samples were collected from the Adour River (South-West, France) in November 2011. Different salinities (0-33 ‰) of water samples were prepared by mixing coastal and fresh waters. Hg speciation analyses of the coastal and fresh water samples (40mL) were performed using ethylation or propylation previously described by Monperrus et al. (2008). All solvents and reagents used were of analytical grade, sodium tetraethylborate (NaBEt_4) and sodium tetra n-propylborate (NaBPr_4) were prepared daily and stored in the dark. Acetate buffer solution (pH 4) was used. A cleaning procedure was tested for both buffer solution and derivatizing reagents (NaBEt_4 and NaBPr_4) using liquid-liquid extraction with iso-octane. An experiment was set up to evaluate the matrix effect for natural fresh and coastal waters. Both species under study (MeHg^+ and Hg^{2+}) were analyzed simultaneously by two different methods, PT-GC-Pyr-AFS and GC-ICPMS. Quantification was performed by external calibration for

both methods, standard addition for PT-GC-Pyr-AFS and by isotopic dilution for GC-ICPMS. Certified reference water (BCR-579) was used to evaluate the accuracy of analytical procedures and to compare both techniques used.

Results and Discussion

Analytical performances of both techniques were evaluated with MeHg^+ and Hg^{2+} calibration solutions for both derivatizing reagents. Using PT-GC-Pyr-AFS system, good linear regression coefficients were obtained between peak area and concentrations in the range of 0-1000 pgL^{-1} . No significant differences were observed between the calibration slopes of MeHg^+ or Hg^{2+} when using NaBEt_4 or NaBPr_4 . The limit of detection (LOD) was calculated from three times the standard deviation of ten blank measurements. The reproducibility was achieved by the relative standard deviation obtained for ten standard solution (1000pgL^{-1}) determinations. The results showed that the RSD of the peak areas for MeHg^+ and Hg^{2+} were below 10% using both techniques. The MeHg^+ and Hg^{2+} concentrations in different ultrapure water samples before and after cleaning using the derivatizing reagents (NaBEt_4 and NaBPr_4) were determined by PT-GC-Pyr-AFS (Fig. 1). The clean-up of the buffer solution and derivatizing reagents allow decreasing systematically the MeHg^+ and Hg^{2+} levels and thus to decrease LODs of blank analysis ($n=10$). Better results for MeHg^+ were obtained using NaBPr_4 as derivatizing reagent. However, when using NaBEt_4 , the LODs obtained by PT-GC-Pyr-AFS (MeHg^+ 1.6pgL^{-1} , Hg^{2+} 9.2pgL^{-1}) are similar and sometimes lower than

those usually found by other published techniques and by GC-ICPMS (Stoichev et al. 2006, Monperrus et al., 2005, Vivien et al., 2011). Potential matrix interferences were evaluated for CRM, natural fresh and coastal waters while MeHg^+ and Hg^{2+} concentrations were determined simultaneously by PT-GC-Pyr-AFS and GC-ICPMS using (NaBEt_4 and NaBPr_4). To evaluate this matrix effect standard addition, isotope dilution and external calibration have been compared (Fig.2 A,B). High salt content in the CRM and coastal water samples produced strong matrix effects during the derivatization reaction leading to lower concentration levels than those obtained by isotope dilution or standard addition quantification. This significant decrease is due to the lower derivatization efficiency using both NaBEt_4 and NaBPr_4 reagents in the presence of salts. It should be emphasized that the use of isotope dilution GC-ICPMS provides similar results for MeHg^+ and Hg^{2+} levels in fresh and coastal waters, and generally both techniques are accurate regarding to the CRM results. For validation of accuracy, MeHg^+ and Hg^{2+} in certified reference water (BCR-579) were determined using both techniques mentioned previously. The concentration values are always found in full agreement with the certified value ($1900\pm 500\text{pgL}^{-1}$).

Conclusion

The results of this study have shown the possible determination of MeHg^+ and Hg^{2+} in natural waters using PT-GC-Pyr-AFS and GC-ICPMS systems at the pgL^{-1} level.

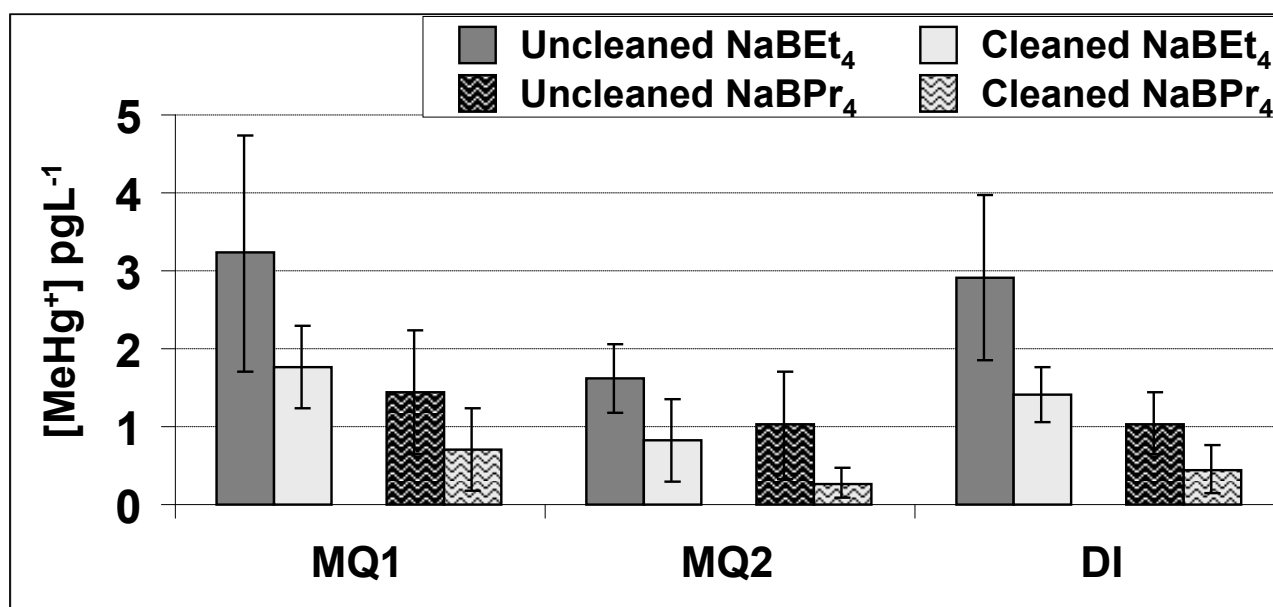


Fig. 1. MeHg^+ concentrations in different ultrapure waters (MQ1: Elix 30 (9 M Ω cm) + Millipore (18.2M Ω cm), MQ2: Elix Advantage (15M Ω cm) + Millipore (18.2M Ω cm), DI: Elix 30 (9 M Ω cm) electrodeionization) obtained by PT-GC-Pyr-AFS using cleaned and uncleaned reagents.

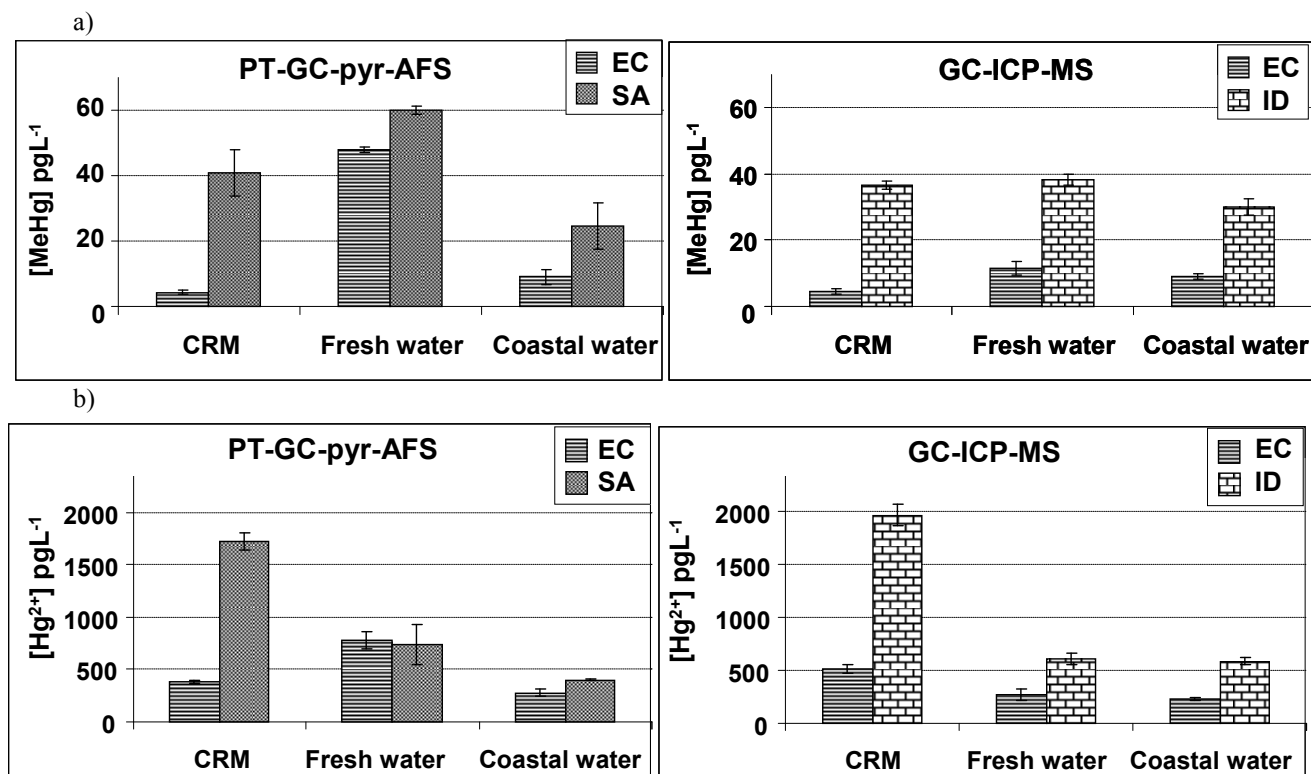


Fig. 2. Concentrations of A) MeHg⁺ and B) Hg²⁺ in CRM, fresh and coastal waters determined by PT-GC-Pyr-AFS (EC: quantified by external calibration; SA: quantified by standard addition) and GC-ICPMS (ID: quantified by isotope dilution) using NaBet₄.

Conclusion

The results of this study have shown the possible determination of MeHg⁺ and Hg²⁺ in natural waters using PT-GC-Pyr-AFS and GC-ICPMS systems at the pgL⁻¹ level. Although both ethylation and propylation could be used, standard addition and/or isotope dilution quantification is required due to strong matrix effect when using natural water samples containing significant amounts of salts and/or organic matter.

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