

Determination of total mercury and monomethylmercury in water samples, estuarine sediments and biological samples

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Abstract: The purpose of the present work was to compare the independent analytical techniques used by two different laboratories for determination of total mercury (Hg-T), and monomethylmercury mercury (MeHg) in seawater samples from the Atlantic Ocean (Adour Estuary), in sediments and biological samples from the Mediterranean Sea and Atlantic Ocean.

Key words: intercomparison, environmental samples, mercury speciation

INTRODUCTION

In studies investigating the fate of mercury in the natural environment is of essential importance to obtain reliable and precise data, which can be achieved by implementing adequate QA/QC protocols. Therefore, in the initial phase of the EU project »MERCYMS - An Integrated Approach to Assess the Mercury Cycling in the Mediterranean Basin« an interlaboratory testing programme was performed to assure the validity and comparability of results among the research teams. In this presentation the results from the interlaboratory study carried out between the Jožef Stefan Institute (JSI), Ljubljana, Slovenia and the Laboratoire de Chimie

Analytique Bio-Inorganique et Environnement (LCABIE), Pau, France are presented. In this exercise different environmental samples were analysed for total mercury (Hg-T) and methylmercury (MeHg) including seawater, sediments and biological samples (zooplankton, oyster tissue, sea urchin, mussel tissue, golden grey mullet, anchovy) from the Mediterranean Sea and Atlantic Ocean. Analyses of the selected samples were performed using the various analytical techniques available in both laboratories (HORVAT ET AL., 1991, 1993A,B; LIANG ET AL., 1994; LOGAR ET AL., 2001; RODRIGUEZ MARTIN-DOIMEADIOS ET AL., 2002; STOICKEV ET AL., 2002, TSENG ET AL., 1999).

The accuracy of the results at JSI was checked by the use of the certified reference materials BCR 580 Polluted Marine Sediment; SRM 2976 Mussel tissue; SRM 1566b Oyster tissue and DOLT-1 Dogfish liver. At LCABIE IAEA 405 Estuarine Sediment; RM 278R Mussel Tissue; RM 710 Oyster Tissue were used.

RESULTS AND DISCUSSION

The results of the present study are summarized in Figure 1.

In spite of the fact that some deviations are observed on comparing results obtained by JSI and LCABIE in different samples, a good agreement is generally found on comparing all the results. It is evident from Figure 1 that all the data sets for both mercury species (Hg-T and MeHg) are well correlated. The results of this study confirmed that the methods used in the laboratories at LCABIE and IJS are suitable for determination of Hg-T and MeHg in biological samples using isotope dilution at LCABIE and simultaneous determination of inorganic Hg and MeHg at JSI.

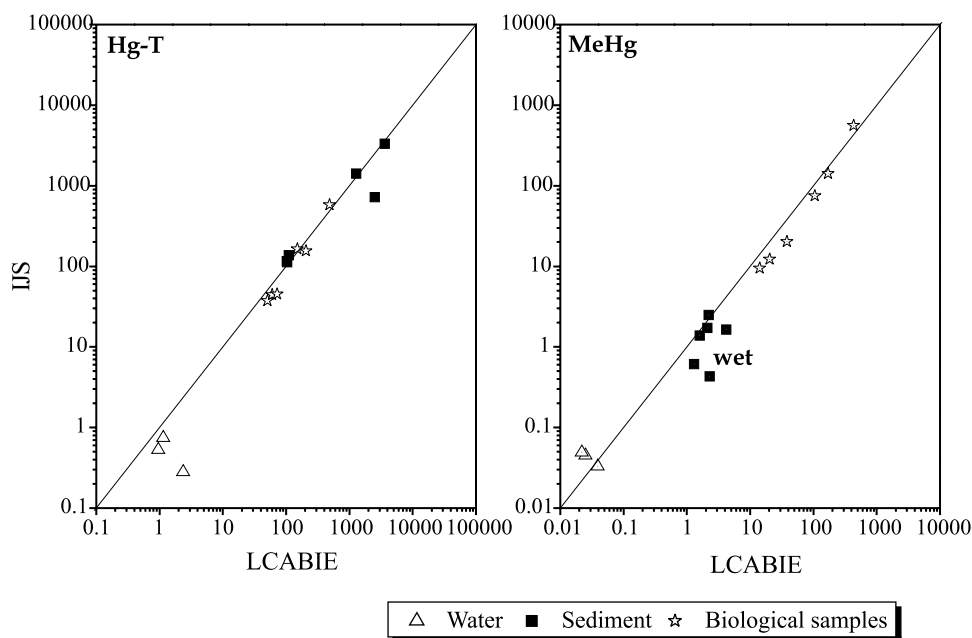


Figure 1. Comparison of the data for a) Hg-T and b) MeHg obtained by JSI and LCABIE in all investigated samples.

The differences found for MeHg concentrations in wet sediments compared to freeze dried sediments suggest that special care should be taken in the preparation procedure for MeHg determination in sediments. There-

fore, further investigation is needed to establish a suitable protocol for the sampling procedure for determination of MeHg in sediment samples in both laboratories. The reason for the discrepancies observed for Hg-

T and MeHg in water samples is sample instability and/or contamination of Hg-T and MeHg in water samples. The intercomparison of water samples should be done on board ship during the sampling cruise immediately after sample collection.

Intercomparison on board ship: In this exercise the concentrations of two Hg species dissolved gaseous mercury (DGM) and Hg-T in water samples were determined immediately after sample collection during the sampling cruise performed in March, 2004: Additionally, an intercomparison of different samplers was performed.

For Hg-T in water samples a good agreement was obtained between both groups involved (JSI and Institut Français de Recherches pour l'Exploitation de la Mer - IFREMER). It was found that the concentrations in the acid cleaned teflon coated sampler (IFREMER) were systematically lower compared to the Urania samplers. Also, Hg-T concentrations measured by JSI were systematically lower than those of IFREMER, but not statistically different.

For DGM, a problem arose in the first intercomparison with a large discrepancy between the results obtained by LCABIE and those by Göteborg University (UGOT) and JSI. We could not explain it even after controlling and crosschecking the calibration

procedures. Thus, a second and a third intercomparison were performed. In the second one we still found some discrepancies between groups, but to a lesser extent. In the third one, with a crosschecked purge and trap system and analysis system we obtained ideal results between the different groups. Therefore, a question concerning the two first intercomparisons still remains.

CONCLUSIONS

Good agreement of the results for Hg analysis and speciation was demonstrated in most of the samples, except those where mercury species are unstable (wet sediments and waters). Sample preparation and storage seem to be the most significant source of errors in mercury analysis in environmental samples. Therefore, it is recommended that water samples be analyzed as soon as possible after sampling. The same applies for sediments in which sampling and sample preparation may significantly influence the presence of mercury species.

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REFERENCES

- HORVAT, M., LUPŠINA, V. & PIHLAR, B. (1991): Determination of total mercury in coal fly ash by gold amalgamation cold vapour atomic absorption spectrometry; *Anal. Chim. Acta* 243, 71-79.
- HORVAT, M., LIANG, L. & BLOOM, N. S. (1993a): Comparison of distillation with other current isolation methods for the determination of methyl mercury compounds in low level environmental samples. Part 1: Sediments; *Anal. Chim. Acta* 281(1), 135-152.
- HORVAT, M., LIANG, L. & BLOOM, N. S. (1993b): Comparison of distillation with other current isolation methods for the determination of methyl mercury compounds in low level environmental samples. Part 2: Water; *Anal. Chim. Acta* 282(1) 153-168.
- LIANG, L., HORVAT, M. & BLOOM, N. S. (1994): An improved method for speciation of mercury by aqueous phase ethylation, room temperature precollection, GC separation and CV AFS detection; *Talanta* 41, 371-379.
- LOGAR, M., HORVAT, M., AKAGI, H., ANDO, T., TOMIYASU, T. & FAJON, V. (2001): Determination of total mercury and monomethylmercury compounds in water samples from Minamata Bay, Japan: an interlaboratory comparative study of different analytical techniques; *Appl. Organomet. Chem.* 15, 515-526.
- RODRIGUEZ MARTIN-DOIMEADIOS, R. C., KRUPP, E., AMOUROUX, D. & DONARD, O. F. X. (2002): Application of isotopically labeled methylmercury for isotope dilution analysis of biological samples using gas chromatography/ICPMS; *Anal. Chem.* 74, 2505-2512.
- STOICKEY, T., RODRIGUEZ MARTIN-DOIMEADIOS, R. C., AMOUROUX, D., MOLENAT & N., DONARD, O. F. X. (2002): Application of cryofocussing hydride generation and atomic fluorescence detection for dissolved mercury species determination in natural water samples; *J. Environ. Monitor.* 4, 517-521.
- TSENG, C. M., DE DIEGO, A., WASSERMAN, J. C., AMOUROUX & D., DONARD, O. F. X. (1999): Potential interferences generated during mercury species determination using acid leaching, aqueous ethylation, cryogenic gas chromatography and atomic spectrometry detection techniques; *Chemosphere* 39, 1119-1136.