

A general strategy for monomethylmercury analysis: from low to highly polluted sediments

J.J. Berzas Nevado¹, R.C. Rodríguez Martín-Doimeadios², F.J. Guzmán Bernardo²
and M. Jiménez Moreno²

¹Regional Institute for Applied Scientific Research, University of Castilla-La Mancha, 13071 Ciudad Real/Spain

²Department of Analytical Chemistry and Food Technology, Faculty of Environmental Sciences, University of Castilla-La Mancha, E-45071 Toledo/Spain

The ecological and human health effects of mercury are generally related to the environmental transformations of inorganic mercury to the toxic and biomagnification-prone compound monomethyl mercury (MMHg). The methylation and demethylation processes preferably seem to occur in sediments. Therefore, the accurate and precise determination of MMHg in sediments is the key point to better understanding the biogeochemical cycling of this contaminant and to estimate the associated exposures.

The most critical compartments for speciation are still linked to the solid phase-biota and soil and/or sediments. There are traditional problems related to the extraction; basically, an adequate recovery should be obtained while the species distribution is kept. In soil and sediments the most critical is the very low concentration of organomercury species which are in presence of very high concentrations of inorganic mercury; in general, MMHg does not exceed 1.5 % of the total mercury content in sediments. Furthermore, there are problems in the chromatographic separation and also artificial MMHg generation is nowadays a matter of serious concern.

Thus, the aim of this work has been to develop a general strategy for real sediment analysis. Experiments have been carried out by using spiked natural sediments and certified reference materials. Preconcentration and cleaning procedures have been developed for both low and high polluted sediments specifically to detect low concentrations and to control artefact generation. Mercury species have been acid-extracted with 6M nitric acid by using closed vessel microwave-assisted extraction at the maximum extraction yield. In spite of significant benefits on offer in terms of time, efficiency, solvent consumption and minimum risk of losing volatile compounds, only a few applications have been done using this extraction technique.

The determination has been carried out by using the advantageous and underexploited coupling of capillary gas chromatography and atomic fluorescence spectrometry detection (CGC-pyro-AFS). The separation has been performed after conversion of MMHg into a peralkylated volatile compound. The stability of mercury species under different conditions has been checked. In presence of high inorganic mercury levels, spurious generation of MMHg (below 1%) has been found. Therefore, a cleaning procedure before derivatization (organic solvent extraction with methylene chloride in hydrochloric acid medium) is necessary in order to reduce inorganic mercury from the extract when inorganic mercury concentration is up to 500 ng g⁻¹. Meanwhile, a preconcentration step by nitrogen stream, which makes possible to achieve limits of detection of 2.6 ng g⁻¹ for MMHg (as Hg), is generally required because the analytical concentrations of MMHg in most sediments are very low. The final conditions have been validated by the analysis of two certified reference materials displaying very different mercury species concentration levels, IAEA-405 and ERM-CC-580, with satisfactory results.