

Poster Presentations: Session 1

[PP 1.1]

Speciation of Organotin and Methylmercury Compounds by GC-MIP-AED in Water, Soils, Sediments and Biological Materials: The Application for Routine Controls

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Speciation of an element, that is to say the determination of its different physico-chemical forms present in a given medium, is necessary when speaking of the toxicological risk represented by the presence of this element. The identification and quantification of the organometallic compounds is particularly important as they are generally more toxic than their inorganic analogs. It is particularly necessary when actually considering elements such as tin and mercury, as their organic forms have been and continue to be used in various industrial applications. Organotin compounds have been used as stabilizing agents in polymers, and as pesticides and antifouling agents in paints, causing a disastrous impact on oyster production in France, for example. Methylmercury halides were used as agricultural seed dressings and fungicides before the 1960s and their presence is frequently observed in sites contaminated by inorganic mercury through natural biosynthetic reactions and in their bioaccumulation throughout the food chain.

There is an increasing demand from industrials and control agencies for routine analysis of these compounds in various matrices such as waters, sediments, soils and biomaterials, for specific studies or regular quality controls. In a laboratory of control such as the European Institute of Environment of Bordeaux (IEEB), it was then necessary to develop a routine method for the speciation of tin and mercury that could be used on large series of samples, with a cost and duration lowered to their minimum. The method developed was based on an acidic extraction (eventually assisted with ultrasounds or microwaves), followed by an ethylation with NaEt₄ and an analysis by GC-MIP-AED. The method was tested on several certified materials from the BCR: sediments (PACS-2, IAEA-356) or biological materials (DORM-2), and then applied on various natural samples: waters, sediments, soils and biological materials. The aim of IEEB is to obtain the COFRAC recognition of this method by 2001 and to propose it as a standardized procedure for this kind of analysis in laboratories of control.

[PP 1.2]

A Microwave-Assisted Extraction Method for Methylmercury Determination in Sediments

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Methylmercury is the most toxic of the mercurial species. Several works have reported its formation in sediments, in spite of difficulties in determining methylmercury due to analytical problems related to the matrix nature and its time-consuming procedure. Analytical methods are usually based on the combination of efficient separation techniques associated to specific detectors. Several methods have been used for the sample preparation based on the quantitative extraction of methylmercury from the sediment, avoiding interfering compounds and the conversion of mercury species during the extraction. The Westoo method is widely employed for different matrices, but alkaline digestion, distillation and supercritical fluid extractions are also considered as adequate alternatives. However, all these extractions are very time-consuming. Recently, microwave irradiation and acid leaching has been successfully applied to methylmercury extraction from the sediment, with a shorter sample preparation period and higher extraction efficiency than classic procedures. This work reports a new methodology for determining methylmercury in sediments by coupling a 2-minute microwave irradiation

technique and an alkaline digestion with 25% potassium hydroxide in methanol. Subsequent to this treatment, the suspension is stirred with dichloromethane and hydrochloric acid for 10 min, the organic phase is separated and the organomercury species back-extracted into ultrapure water. Methylmercury determination in the aqueous phase is performed in an high performance liquid chromatography (HPLC) system. Methylmercury is oxidised to inorganic mercury by UV-irradiation followed by reduction to elemental mercury and detection of Hg (0) by atomic fluorescence spectrometry (AFS). The effect of exposure time and applied energy was studied in the range 30-210 s and 60-96 W, respectively. The methodology was validated by the analysis of two certified reference materials of sediment, IAEA-356 and BCR 580, containing 5.46 and 75.5 ng (of methylmercury as Hg) g⁻¹, respectively. The recovery achieved was higher than 95%. The proposed methodology therefore offers adequate precision and accuracy for the rapid determination of methylmercury in sediments.