

## 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 sample preparation based on quantitative extraction of methylmercury from the sediment, avoiding interfering compounds and 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. For example, the sample digestion using an ultrasonic baths needs 45 min., and 3 hours in an oven. Recently, microwave irradiation and acid leaching has been successfully applied to methylmercury extraction from the sediment. This procedure has only been applied to gas chromatography linked to electron capture detection or to atomic absorption spectrophotometry, which implies a pH control of the solution before injection in the high performance liquid chromatography (HPLC) system. The sample preparation is in order of minutes and has higher extraction efficiency than classic procedures.

In order to avoid the pH control step, several experiments were performed combining the alkaline digestion (25% potassium hydroxide in methanol) with microwave irradiation. The procedure was tested with the reference certified material (BCR-580) using different experimental conditions and mass:volume ratios. The effect of exposure time and applied energy was studied in the range 30-210 seconds and 60-96 W, respectively. Subsequent to this microwave treatment, the suspension was stirred with dichloromethane and hydrochloric acid during 10 minutes, the organic phase separated and the organomercury species back-extracted into ultrapure water. Methylmercury determination in the aqueous phase was performed in a HPLC system, consisting in a reversed-phase C<sub>18</sub> column. The mobile phase used was a methanol-water mixture containing 2-mercaptoethanol and buffered at pH 5.5 with ammonium acetate and acetic acid. Methylmercury was oxidised to inorganic mercury by UV-irradiation followed by tin (II) chloride reduction to elemental mercury and detection of Hg (0) by atomic fluorescence spectrometry (AFS).

The best results were achieved employing a 2-min microwave treatment, the recovery being compared to values obtained by the classic methods. The methodology was subsequently validated by the analysis of two certified reference material of sediment, IAEA-356 and BCR 580, containing 5.46 and 75.5 ng (of methylmercury as Hg) g<sup>-1</sup>, respectively. The recovery achieved was higher than 95%. In conclusion, the proposed methodology offers adequate precision and accuracy for rapid determination of methylmercury in sediments.