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Methylmercury determination in marine sediment and organisms by Direct Mercury Analyser

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ABSTRACT

An analytical method for simple and rapid determination of methylmercury in sediment and organism samples is described. The proposed method employs the oxygen combustion-gold amalgamation using Direct Mercury Analyser (DMA-80) after complete removal of MeHg by organic extraction and back extraction to an aqueous medium. DMA-80 instrument is equally suitable for the analysis of solid and liquid materials and has a good detection limit. The analytical performance of this method was evaluated by analysis of certified reference materials (CRM-580, IAEA-405, DORM-2, DOLT-3, SRM-2976 and SRM-2977) assessing its quality in terms of accuracy, repeatability and quantification limit. Furthermore total mercury and methylmercury have been analysed in sediment and organism samples collected during the XXI Italian Antarctic Expedition in Terra Nova Bay (Ross Sea, Northern Victoria Land). The results obtained show the validity of the proposed method as ready-to-use analytical method to analyse real samples.

1. Introduction

The biogeochemistry of mercury (Hg) has received, in the last decades, considerable attention because of the extreme toxicity of methylmercury (MeHg) and its ability to bioaccumulate in biota and to biomagnificate in aquatic food web. In fact, Hg is the only metal which bioaccumulates through all levels of the aquatic food chain; accordingly, Hg contamination in fish has been a widespread health concern. [1,2]. Also MeHg becomes biomagnified in the food chain through passage from bacteria, plankton, macroinvertebrates, herbivorous fish, piscivorous fish and, finally to humans. Each step results in an increased concentration of MeHg, which may end being many times higher in the animal than the initial concentration in the water [3]. MeHg blocks the binding sites of enzymes, and interferes with the protein synthesis as well as thymidine incorporation into DNA. Fetus and neonates are known to be high-risk groups for MeHg: it can be transferred to the fetus through the placenta and to offspring through breast milk and can be caused severe effects on neurological development [4–6].

One of the most catastrophic example in modern history is mercury pollution in Minamata, Japan, where waste water containing inorganic mercury was released into the Shiranui Sea between 1932 and 1966 by the Chisso Factory. This inorganic mercury was transformed into MeHg through the aquatic ecosystem and ingested by a large number of people because of their traditional seafood-based diet. [3,7].

In several countries MeHg is frequently determinated in fish samples to control the contamination level prior market sales. Recently, monitoring of MeHg content in sediment has been started in research laboratories for the purpose of pollution monitoring and geochemical studies [8–11]

A large assortment of microorganisms is capable of converting inorganic Hg^{2+} into CH_3Hg^+. Rates of MeHg formation depend on the amount of Hg that is available for methylation reactions, rather than on T-Hg concentrations, and on various physical, chemical and biological factors [12,13]: the microbial activity, composition of sediment and the organic content [14], the sulphidic character of sediment [15], the oxygen concentration, pH and the presence of inorganic and organic complexing agents [16]. In general the methylation rates are favoured in anaerobic sediment. Methylation rates are usually highest in the upper 2 cm of sediments where the microbiological activity is highest [17].

The determination of MeHg in sediments is not easy: the very low concentrations, and the presence of interfering substances (such as sulphides, humic acids, aminoacids and protein able to strongly bind methylmercury) are the main analytical complications [18]. In fact the most critical compartments for speciation are still linked to solid phase. Extraction is a very subtle step because the whole species content may not be liberated, and artefacts can occur

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so that some organomercury species can be destroyed or formed (interspecies exchange) [19].

It is important to note that because of low MeHg concentrations in marine matrices the measurement protocol must be carefully designed; besides analytical procedures for each of mercurial species are quite different. Numerous analytical methods based on the home-made hyphenations between an appropriate separation technique and a sensitive and selective detector (gas or liquid chromatography and mass spectrometry, fluorescence spectrometry, electron capture) have proposed to measure MeHg in sediment and marine organisms. Beside separation and detection, these methods involve several crucial points, as extraction, derivatization, preconcentration and clean-up, that are potential source of errors and may lead to low precision and lack of repeatability [20–23].

Since Governmental Bodies and Environmental Protection Agencies starts to be sensitive towards Hg pollution problem, it is necessary to have ready-to-use analytical methods which are simple, low cost and fast sample treatment.

In this paper the analysis of MeHg in marine sediment and biota samples by separation of the MeHg from the sample matrix in order to avoid interference during the extraction reaction, then MeHg extraction with organic solvent has been carried out; after complete removal of MeHg by organic extraction, it has been transferred to an aqueous medium, than its analysis has been possible by AAS. The T-Hg concentration in all environmental samples has been also determined.

The singularity of proposed method is the possibility to estimate MeHg content in solid matrices (sediment and biota) using the same instrument for T-Hg determination [24]. This method allows to perform routine analysis of methylmercury in sediment and marine organisms by Direct Mercury Analyser (DMA-80) [25]. DMA-80 instrument does not require any pre-treatment of the samples, is equally suitable for the analysis of solid and liquid materials and has a good detection limit (LOD); moreover it offers the possibility of changing operational conditions as a function of the materials and quantity of samples [26,27]. The quality of the proposed method has been checked by analysis of certified reference materials (CRM) and its applicability to real samples has been proved by processing several organisms and sediment samples collected from the coastal sites during the austral summer from the XXI Italian Antarctic Expedition at Terra Nova Bay (Ross Sea, Northern Victoria Land).

2. Experimental

2.1. Materials and decontamination

All material (vessels, centrifuge tubes, etc.) used was decontaminated with the following procedure: washing with a common detergent rinsing with Milli Q quality water (three times) and soaking into a clean diluted HNO_3 20% (v/v) bath for 24 h at 25 °C. Each soaking was followed by an intensive rising with ultra-pure water (Milli-Q). Finally, all material was dried in clean environment.

2.2. Reagents and standards

All reagents used were of analytical-reagent grade unless otherwise stated. The solutions were prepared using ultra-pure water Milli-Q.

The calibration standard was prepared by making two appropriate dilutions in stock water solution (1000 mg L^{-1}) of CH_3Hg^+ in 2% HNO_3 and of Hg^+ in 2% HNO_3. A blank calibration solution was also used for a zero calibration.

Solutions employed for hydrolysis and back extraction were HCl (J.T. Baker), toluene (J.T. Baker) and L-cysteine solution (1%, v/w) that was prepared dissolving 1% L-cysteinium chloride in 12.5% anhydrous sodium sulfate and 0.775% sodium acetate.

2.3. Instrumentation

The analyses were carried out with a Direct Mercury Analyser (DMA-80, Milestone srl, Italy). The sample (liquid material for MeHg analysis and solid material for T-Hg determination) is dried and then thermally decomposed by controlled heating. Decomposition products are carried to a catalyst by an oxygen flow, then sample oxidation is completed and halogens and nitrogen/sulphur oxides are trapped. The final decomposition products pass through a mercury amalgamator which collects Hg^0. The Hg amalgamator is heated to 700 °C and the Hg^0 is released and quantified.

2.4. Sample preparation for MeHg determination

2.4.1. Sediment sample pre-treatment (i)

Approximately 1.0–2.0 g of a dry sediment (oven dried at 35 °C for 48 h) was weighed out in triplicate; each sample was placed in 100 mL screw-capped polypropylene tube and hydrolyzed with 6 M HCl (10 mL). The sample was shaken for 5 min using a mechanical vertical shaker, centrifuged at 2400 rpm for 10 min and the liquid phase was discarded (no significant MeHg concentration, <LOQ, was detected) (Fig. 1).

2.4.2. Organisms sample pre-treatment (ii)

ca. 1.5 g of soft tissue (oven dried at 35 °C for 48 h) was weighed out in triplicate; each sample was transferred in 50 mL polypropylene tube with screw caps and hydrolyzed with 10 mL of HBr (47–49%). After 5 min of shaking using a mechanical vertical shaker, 20 mL toluene was added (Fig. 1).

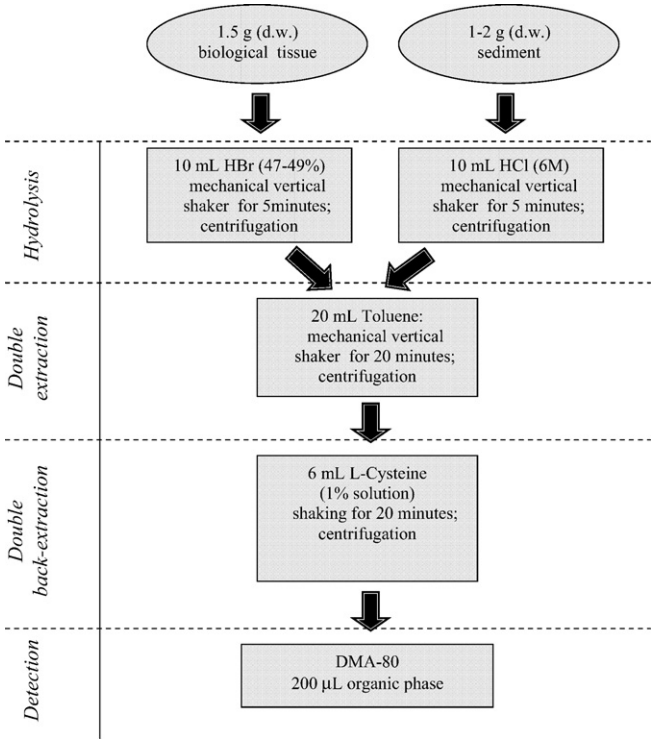

Fig. 1. Scheme of the proposed method for MeHg analysis in sediment and biological tissues.