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Non-chromatographic screening method for the determination of mercury species. Application to the monitoring of mercury levels in Antarctic samples

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ABSTRACT

A simple non-chromatographic method for the determination of mercury (Hg^{2+}), methylmercury ($MeHg^+$), dimethylmercury (Me_2Hg), and phenylmercury ($PhHg^+$) employing atomic fluorescence spectrometry (AFS) as detection technique was developed. Mercury species showed a particular behavior in the presence of several reagents. In a first stage $SnCl_2$ was employed for Hg^{2+} determination; in a second step, [Hg^{2+} + $PhHg^+$] concentration was determined using $SnCl_2$ and UV radiation. $MeHg^+$ decomposition was prevented adding 2-mercaptoethanol. In a third stage, [Hg^{2+} + $PhHg^+$ + $MeHg^+$] concentration was determined using $K_2S_2O_8$. Finally, the four species were determined employing $NaBH_4$. Reagents concentration and flow rates were optimized. The extraction technique of mercury species involved the use of 2-mercaptoethanol as ion-pair reagent. The limits of detection for Hg^{2+}, $PhHg^+$, $MeHg^+$, and Me_2Hg were 1, 40, 68, and 99 ng L^{-1} with a relative standard deviation of 1.5, 3.1, 4.7 and 5.8%, respectively. Calibration curve was linear with a correlation factor equal to 0.9995. The method was successfully applied to the determination of the mercury species in two Antarctic materials: IRMM 813 (*Adamussium colbecki*) and MURST-ISS-A2 (*Antarctic Krill*).

1. Introduction

Public health reasons and the fact that mercury *is a highly toxic element that is found both naturally and as an introduced contaminant in the environment* have increased the interest on its speciation analysis in a variety of biological, industrial, and food samples. The toxicity of mercury depends on its concentration and chemical form [1,2]. Mercury occurs principally in three different chemical species: elemental, inorganic, and organic forms such as monomethylmercury (CH_3Hg, hereafter referred to as "$MeHg^+$") and dimethyl mercury [$(CH_3)_2Hg$, hereafter referred to as "Me_2Hg"] [3,4]. Within these above-named forms, organic mercury species are more toxic than the others [4,5]. Therefore, it is important to determine inorganic and organic species instead of total mercury.

Mercury species may induce alterations in the normal development of the brain of infants and may induce neurological changes in adults [6]. $MeHg^+$ is a known neurotoxin causing reproductive, immunosuppressive, neurobehavioral risks to biota [7] and the Minamata disease in humans [8]. It is produced mainly by microbial methylation of inorganic mercury (Hg) in the aquatic environment [9] and is one of the most common contaminants in fish and marine mammals due to its biomagnifications along the food chain [10].

Environmental monitoring in Antarctica plays a key role for assessing ongoing pollution phenomena on a planetary scale in order to preserve as much as possible the pristine conditions in this ecosystem [11–13]. Antarctic ecosystems have unique characteristics resulting from their distances from continents with high populations. Anthropogenic contamination is negligible because there is no human impact due to any significant human work activities. Mercury is emitted to the atmosphere mainly as vapor by natural or anthropogenic sources and it is the only metal that biomagnifies through food chains [14]. The relative long residence time in the atmosphere (circa 1 year) and consequent long-range transport, together with natural transformation into methylmercury, make exposure of target organisms to mercury, potentially serious, even in remote areas [15].

Antarctic Krill (Fig. 1) are a small planktonic crustaceans primarily present in the southern ocean, with a total biomass estimated

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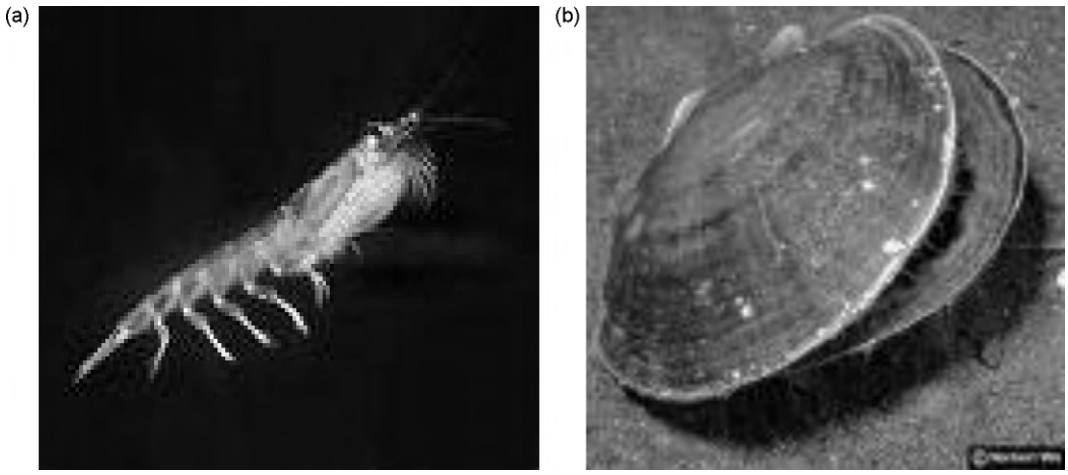

Fig. 1. (a) *Antarctic Krill* and (b) *Adamussium colbecki*.

to be around 600 billion individuals migrating in large groups over long distances [16]. *Adamussium colbecki* (Fig. 1) is an endemic Antarctic scallop, abundant in near shore waters, with the ability to accumulate contaminants [11]. These organisms take up and accumulate metals in great quantities in soft tissues, offering some advantages in the analysis of abiotic matrices. As a consequence, these organisms can be employed for the evaluation and assessment of pollution in marine coastal environments. In addition, they only accumulate the biologically available form of the pollutant [17]. Therefore, the determination of Hg species in biota collected in Antarctica is of prime importance to gain knowledge on levels of pollutants in pristine areas.

Quantification of mercury species normally requires the use of hyphenated techniques, involving a more complex instrumentation in comparison with that needed for single element measurements [18]. These systems are based on the use of highly efficient separation techniques such as gas chromatography (GC), high performance liquid chromatography (HPLC) or capillary electrophoresis (CE) coupled to sensitive and selective atomic spectrometric detectors, such as atomic absorption spectrometry (AAS) [19], atomic fluorescence spectrometry (AFS) [20], inductively coupled plasma mass spectrometry (ICP-MS) [21], inductively coupled plasma optical emission spectrometry (ICP-OES) [22], and microwave-induced plasma optical emission spectrometry (MIP-OES) [23]. Although these hyphenated methods are attractive for mercury speciation due to their excellent detection limits and selectivity, high instrumental and operational costs make them difficult to use in routine analysis or in laboratories with limited instrumentation.

Cold vapor atomic fluorescence spectrometry (CV-AFS) is a well known and widely used technique for mercury determination. Generation of a cold vapor from organo mercury species requires a step to achieve their conversion to Hg(II). Mercury speciation analysis was done by CV-AFS without chromatographic separations. The discrimination between inorganic mercury and total mercury was based on the differential behavior of mercury species with several reducing agents [24,25]. This conversion has been usually performed online and has been facilitated using a number of different approaches such as oxidation with potassium persulfate [23,26,27]. Although the chemical oxidation can be achieved at room temperature, the reaction time for an efficient conversion can be long. The use of UV irradiation is a valid alternative to facilitate the decomposition of mercury species [28–30].

In this study, a non-chromatographic method for the determination of Hg^{2+}, $MeHg^{+}$, Me_2Hg, and $PhHg^{+}$ is presented. The determination is based on the singular behavior of mercury species *versus* the different reagents/approaches involved in the cold vapor generation such as sodium borohydride, stannous chloride, potassium persulfate, and UV radiation. The proposed method was applied to the determination of mercury species in the candidate certified reference material IRMM 813 *A. colbecki*, and compared to the mercury content in CRM MURST-ISS-A2 *Antarctic Krill*. In order to extract the mercury species, 2-mercaptoethanol in acidic media was employed. The extraction efficiency was compared with a microwave-assisted digestion technique and the certified value (MURST-ISS-A2) reported for total Hg. To the best of our knowledge, this is the first time that four mercury species are determined employing a non-chromatographic methodology.

2. Experimental

2.1. Instrumentation

Mercury fluorescence measurements were carried out with an atomic fluorescence spectrometer, AI 3300, Aurora Instruments (Vancouver, British Columbia, Canada). The apparatus was equipped with a two-channel peristaltic pump for the continuous fluorescence measurements. A mercury hollow cathode lamp from Aurora Instruments (Vancouver, British Columbia, Canada) was employed as Hg fluorescence excitation source. The flow injection (FI) system used is shown in Fig. 2. Samples and solvents were delivered by a Minipulse 3 peristaltic pump Gilson (Villiers-Le-Bell, France). UV decomposition was achieved with a 400 W Hg vapor lamp (15 W G15T8 UV-C LONG LIFE high pressure Hg, PHILIPS) that ignited with a suitable starter and chock and surrounded by a 3-m PTFE tubing.

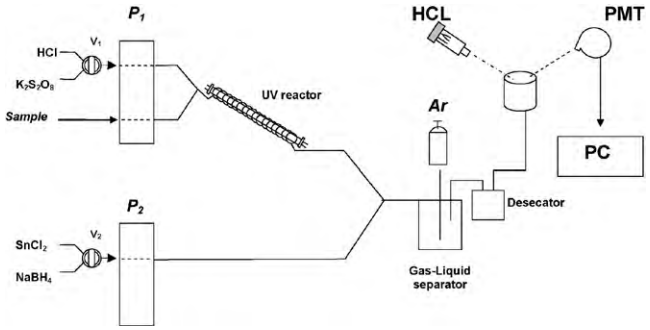

Fig. 2. Schematic diagram of the instrumental set-up. V_1, valve 1; V_2, valve 2; P_1, pump 1; P_2, pump 2; HCL, hollow cathode lamp; PMT, photomultiplier tube.