



Semi-automatic system for methylmercury determination in biological samples

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ABSTRACT

For living creatures the presence of methylmercury is the most dangerous result of anthropogenic mercury emission. In order to improve and facilitate the determination of methylmercury (MeHg) with the manual Headspace Tenax Gas Chromatography - Atomic Fluorescence (HS-Tenax-GC-AFS) method, a low cost, semi-automatic measurement system (SA-GC-AFS) was designed and constructed. The developed MeHg determination method was optimized and validated according to the Eurachem recommendations. The validation parameters of the developed method were as follows: linearity: 0.9997, method detection limit: 1.4 ng/g; repeatability: 5.6%; recovery: 99–102%. The estimated combined uncertainty of the method was $U = 11.2\%$. Comparing with the manual method the repeatability was improved and the reduction of analyst effort was obtained. The SA-GC-AFS method was successfully applied to MeHg determination in 76 racoon (*Procyon lotor*) samples (muscle, liver, kidney, brain). The SA-GC-AFS system is the good, low cost alternative to the expensive commercial automated MeHg determination systems.

1. Introduction

Methylmercury (MeHg) is a global toxicant of concern and nearly 100% of all cases of human exposure involve seafood consumption [1]. Systematic studies enable us to evaluate the level of environmental contamination by organic mercury compounds [2–4]. In connection with the tendency of organomercury compounds to bioaccumulate, special attention should be devoted to the level of these compounds in the upper food chain such as predatory fish or birds [5–7]. As the fish is the major source of mercury for humans, many governments and health organizations developed legislation regulating maximum concentration of total methylmercury in fish. The EU Commission [8] established a 0.5 mg/kg limit for organic mercury, US FDA [9] – 1 mg/kg, China [10] and Japan [11] – 0.5–1 mg/kg (depending on fish species).

Currently for the determination of methylmercury in biological samples a number of different analytical methods are used. In the most cases mercury speciation is achieved by the coupling one of the separation techniques with a mercury selective detector. For the MeHg determination the most commonly used detectors are inductively coupled plasma mass spectrometers (ICP-MS) [12–20] and atomic fluorescence spectrometers (AFS) [4,20–26]. Both ICP-MS and AFS are very sensitive and selective techniques and are used at the research level as

much as in the laboratories devoted to routine analysis. The difference between them lies in their capabilities and costs. ICP-MS can be used to determine more than 70 elements, AFS is dedicated only to mercury. The choice of one of these two techniques depends on the needs and capabilities of the laboratory. Compared to AFS, the cost of maintaining the ICP-MS system is rather high; therefore, for research purposes or in case of small sample quantities, the system equipped with the AFS detector seems to be a more reasonable solution. Literature data indicates a slightly lower detection limit of the method (MDL) of ICP-MS systems, but in case of biological samples (which are most frequently of maritime origin) it is not a very significant parameter because the MeHg concentration in such samples are quite high. Only a few works describe methods using another detectors like Electron Capture Detectors (ECD) [27,28] or Atomic Absorption Spectrometers (AAS) [29] which also could be used for MeHg determination. At the mercury compounds separation step, mainly gas chromatography (GC) [4,12–14,18–20,24,25,27,28,30] and, less frequently, high-performance liquid chromatography (HPLC) [15–17] are used. The advantage of gas chromatography (GC) over liquid chromatography (LC/HPLC) lies in no need to use the sample nebulisation, which makes the GC systems less complicated. An important drawback of the GC is the need of derivatization step which is necessary to obtain volatile forms of

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mercury, but, taking into account the number of laboratories using this method, it is not a significant impediment. A very small amount of articles describe methods in which one of the steps is the selective extraction of organic mercury compounds [29]. As far as preconcentration methods are concerned, the Solid Phase Micro Extraction (SPME) [21,22] or Tenax, Carbotrap trap methods [30,31] are used during the determination of MeHg.

In order to determine MeHg using the GC-AFS method, the conversion of mercury to volatile derivatives is required [32]. The most common derivatisation methods are ethylation of MeHg^+ to MeHgEt and Hg^{2+} to HgEt_2 form in the water phase by sodium tetraethylborate (NaBEt_4) [33], phenylation with NaBPh_4 [34] and propylation with NaBPr_4 [35].

In the HS-Trap-GC-AFS method using NaBEt_4 as derivatising fluid, MeHgEt is decomposed by means of a pyrolyzer at 800–1000 °C and is determined with an AFS detector. The disadvantage of the manual Head Space-Tenax-Gas Chromatography-Atomic Fluorescence Spectroscopy method (HS-Tenax-GC-AFS) of MeHg determination (like EPA 1630 method with an adaptation to solid samples) is the large number of operations that should be performed during measurement. On the other hand, automated systems like Tekran 2700 [36] or MERX 4400 [37] are expensive and in the case of small amounts of analyzed samples their purchase may be unprofitable.

The main aim of this article was to present a unique, low cost semi-automatic measurement system that automates a manual HS-Trap-GC-AFS method (based on EPA 1630 method with an adaptation to solid samples). The developed method has been successfully validated. The automation of the manual HS-Trap-GC-AFS procedure improved the reproducibility of MeHg determinations from $\text{RSD} = 9.6\%$ to 1.2% . The independent semi-automated Head Space - Trap module, could be used in other analytical systems. The low costs of HS-Tenax-GC-AFS system automation (about \$2.000) makes the developed MeHg determination method more accessible to researchers who, for various reasons, do not want or cannot afford an expensive automated MeHg determination systems.

2. Experimental

2.1. Apparatus

2.1.1. Apparatus developed for the determination of MeHg in biota samples

In order to determine MeHg in biota samples an semi-automatic HS-Tenax-GC-AFS system (SA-GC-AFS) was designed and constructed. SA-GC-AFS system enabled us to automate ten stages (20 min) of manual MeHg determination by means of the HS-Tenax-GC-AFS method. The SA-GC-AFS system, presented in Fig. 1, consists of the following main elements: a Tekran 2500 detector, a Gas Chromatograph (Hewlett Packard 5890), a pyrolysis unit, a Tenax trap with a heater (H7), a flow section with six electromagnetic brass valves (EV1-EV6), an Electronic Control Unit and a PC with Peak Simple software. Operations of electromagnetic valves and the Tenax trap heater are controlled by means of the Electronic Control Unit specifically designed and constructed for this application. All connections in the SA-GC-AFS system are made of (3mm OD) PTFE tubing or an untreated capillary column (0.5 mm OD). In the SA-GC-AFS system, cheap electromagnetic brass valves were applied. It was possible thanks to such a design of the system where the sample does not flow through the electromagnetic valves (the risk of analyte loss). The pyrolysis unit is a 20 cm-long electric furnace. The temperature of 950 °C is maintained by means of a temperature controller. An inexpensive Hot Air Soldering Iron has been successfully used as the Tenax trap heater for several years. Activated carbon traps protect two outlets of the system.

The unique sample chamber, shown in Fig. 2, was designed specifically for the SA-GC-AFS system. The vial cup construction enables repeatable flow through the vial. It is a very important issue as far as reproducibility is concerned. The cap is equipped with two needles slots so that the exact placement of the needles in the vial may be reiterated. The argon flow is directed to the walls of the vial. The ID of the outlet needle is larger than the inlet needle.

2.1.2. The operation of the semi-automatic system

At the beginning of the experimental day the following preliminary operations were performed.

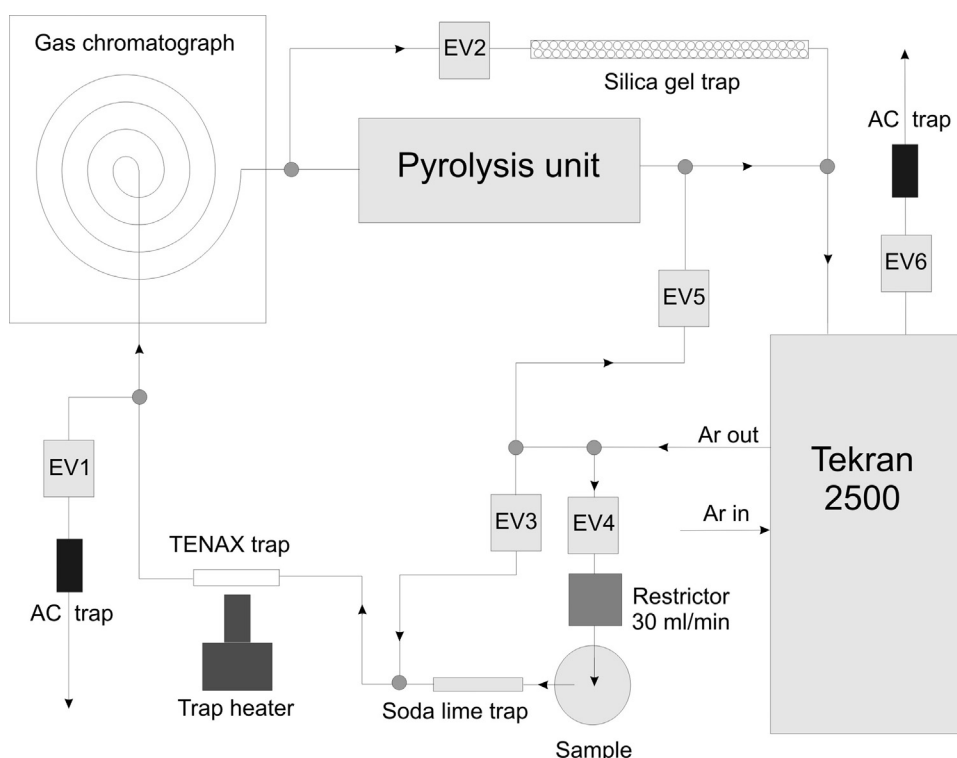


Fig. 1. The design of the Automatic System for MeHg determination (ASMeHg).

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