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# Ultra-trace determination of methylmercuy in seafood by atomic fluorescence spectrometry coupled with electrochemical cold vapor generation

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## HIGHLIGHTS

- Methylmercury detection by ECVG-AFS without pre-separation by HPLC is proposed.
- Methylmercury is atomized by direct electrochemical reduction with no reductant.
- Remarkably better sensitivity is obtained than the traditional HPLC-UV-AFS method.
- Glassy carbon is the best cathode material to generate Hg vapor from methylmercury.

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## ABSTRACT

A homemade electrochemical flow cell was adopted for the determination of methylmercury. The cold vapor of mercury atoms was generated from the surface of glassycarbon cathode through the method of electrolytic reduction and detected by atomic fluorescence spectroscopy subsequently. The operating conditions were optimized with 2 ng mL$^{-1}$ methylmercury standard solution. The caliberation curve was favorably linear when the concentrations of standard $HgCH_3^+$ solutions were in the range of 0.2–5 ng mL$^{-1}$(as Hg). Under the optimized conditions, the limit of detection (LOD) for methylmercury was $1.88 \times 10^{-3}$ ng mL$^{-1}$ and the precision evaluated by relative standard deviation was 2.0% for six times 2 ng mL$^{-1}$ standard solution replicates. The terminal analytical results of seafood samples, available from local market, showed that the methylmercury content ranged within 3.7–45.8 ng g$^{-1}$. The recoveries for methylmercury spiked samples were found to be in the range of 87.6–103.6% and the relative standard deviations below 5% ($n$ = 6)were acquired, which showed this method was feasible for real sample analysis.



## 1. Introduction

Mercury is toxic heavy metallic element, which can be accumulated in environment, foods and organism, etc [1,2]. The sources of mercury covers both agricultural and industrial scopes, mainly the large-scale production and use of mercury-containing chemicals, such as pesticides, batteries, etc [1,3]. The biochemical properties and toxicity of mercury vary greatly with its existing states. Methylmercury is the dominant form of organomercury, and it is also the most hazardous species of mercury for human health as it can concentrate in the blood, transfer the blood brain barrier easily, and do great harm to the central nervous system, especially to the brain [2,4]. Furthermore, it remains in organs for a long time due to its strong affinity to –SH of protein and lipid tissues [5,6]. The half-life of methylmercury in brains is up to 200 days and it can be converted from inorganic mercury by means of biomethylization process. Generally speaking, seafood samples are with high risk on accumulating methylmercury due to the strong bio-methylizing reaction and the sustainable increase of Hg loading on sea waters, although some works on mercury removal of sea waters were eye-catching, such as bio-sorption, chemical accumulation, etc [7–9]. As deep-water column is the main origin of methylmercury in marine biota, methylmercury accumulation in seafood may greatly increase with increasing forage depth, but not

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remarkably be influenced by the weight [10]. The FAO/WHO regulates the income amount of methylmercury for a person cannot exceed 0.0033 mg $kg^{-1}$ per week. High toxicity exhibited by low dose of methylmercury forces the development of methods for detecting trace or even ultral trace amount of methylmercury in seafood with high performance and sensitivity.

At the present time, the determination of mercury is usually carried out by cold vapor atomic absorption spectrometry (CV-AAS) [6,11–12], cold vapor atomic fluorescence spectrometry (CV–AFS) [13–15], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [16], inductively coupled plasma-mass spectrometry (ICP-MS) [17], etc. And the determination of methylmercury is based on hyphenated techniques, coupling a separation technique such as chromatograph method to the detectors above [18,19]. However, most of these means require reducing the $HgCH_3^+$ compound into Hg atoms by reducing agent, such as $NaBH_4$ and $SnCl_2$. However, the atomizing efficiency of $HgCH_3^+$ was significantly low, and the introduction of those reductants will bring interferences to the analytical results as the reductants are unstable. In some works, the applications of UV [20] and some electrochemical methods [21] were used to improve the atomizing efficiency, yet the process is too complicated and the analytic process is time-consuming and high-cost.

Electrochemical hydride generation (EcHG) has proved to be high efficient in generation of hydride forming elements like As, Bi, Ge, Sb, Se and Cd [22–26] for spectrometric determination. Besides, electrochemical generation of Hg [22] cold vapor was also involved in some works, whereas electrochemical reduction of methylmercury coupled with spectrometric determination was not mentioned. Our work determined ultra trace amount of methylmercury by electrochemical cold vapor generation (ECVG) coupled with AFS. ECVG is a novel technique to generate Hg vapor by means of electrolytic reduction. Compared with the traditional CV method using much unstable reductant which needs preparing daily and high purity, ECVG has a particular advantage that clean electron transfer is used to realize the atomizing process and the anode electrolyte could be recycled, by which reagent pollution and the blank can be eliminated to a large degree. Thus, more chemical reagents and time could be saved, and it is more environmental-friendly as well. On the meanwhile, the electrochemical cell can be coupled with AFS instrument conveniently. Despite a number of methods for methylmercury determination using AFS as final detector coupled with certain separation and online digestion technique have been proposed [27–31], they are all based on traditional chemical cold vapor generation. Methylmercury determination by AFS based on EcVG sampling was not reported before. Besides, an extremely excellent analytical performance were acquired in our study. While keeping the similar stability, remarkably better sensitivity was observed compared with the CV-AFS method in our study.

## 2. Experimental

### 2.1. Reagents

Methylmercury (II) chloride was reagent grade purity (Alfa Aesar). All the acids were of guarantee grade (G.R., from Beijing Fine Chemicals Ltd.), sodium chloride was of guarantee grade (G.R., from Tianjin Yingdaxigui Chemicals Ltd.) and other reagents were of analytical grade. Ultra pure water (>18.2 MΩ) was obtained from a Millipore ultra purewater system. $Hg^{2+}$ standard stock solution (GBW08617) was acquired from China measuring science institute. The Methylmercury standard stock solution of 1000 mg $L^{-1}$ was prepared by dissolving 0.1252 g $CH_3HgCl$ (0.1000 g Hg) in 100 mL ultra pure water, and this solution was kept at 4 °C. Calibration solutions (0.2–5 ng $mL^{-1}$) were daily prepared by appropriate dilution of the stock solution with 0.5 mol $L^{-1}$ sulfuric acid. Besides, all the glassy wares were immersed in the 10% nitrous acid for 24 h and washed clean with ultra pure water.

### 2.2. Sample preparation

Ortiz et al. [32] compared different sample pre-treatment methods for mercury species, and the results showed acid leaching was effective. Six seafood samples were purchased from the local market (Beijing, China). The fish tissue removed of skin and bone was cut up, added equal amount of sodium chloride, and pestled to homogenization. Meanwhile the kelp sample was smashed and

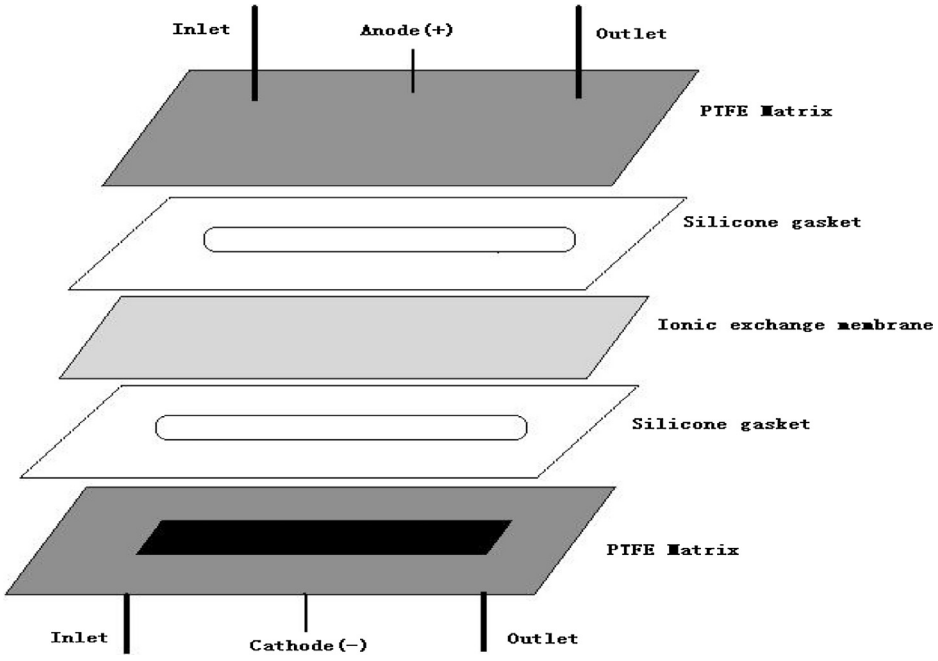


**Fig. 1.** The configuration of the electrochemical flow cell.