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Voltammetric studies on the electrochemical determination of methylmercury in chloride medium at carbon microelectrodes

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Abstract

Electroanalytical techniques have been used to determine methylmercury at low levels in environmental matrices. The electrochemical behaviour of methylmercury at carbon microelectrodes in a hydrochloric acid medium using cyclic, square wave and fast-scan linear-sweep voltammetric techniques has been investigated. The analytical utility of the methylmercury reoxidation peak has been explored, but the recorded peak currents were found to be poorly reproducible. This is ascribed to two factors: the adsorption of insoluble chloromercury compounds on the electrode surface, which appears to be an important contribution to hinder the voltammetric signal of methylmercury; and the competition between the reoxidation of the methylmercury radical and its dimerization reaction, which limits the reproducibility of the methylmercury peak. These problems were successfully overcome by adopting the appropriate experimental conditions. Fast-scan rates were employed and an efficient electrochemical regeneration procedure of the electrode surface was achieved, under potentiostatic conditions in a mercury-free solution containing potassium thiocyanate—a strong complexing agent. The influence of chloride ion concentration was analysed. Interference by metals, such as lead and cadmium, was considered. Calibration plots were obtained in the micromolar and submicromolar concentration ranges, allowing the electrochemical determination of methylmercury in trace amounts. An estuarine water sample was analysed using the new method with a glassy carbon microelectrode.

Keywords: Methylmercury determination; Carbon microelectrodes; Square wave voltammetry; Fast-scan linear-sweep voltammetry; Water analysis

1. Introduction

Monitoring of toxic chemical species in environmental samples has become an important analytical problem, prompting much research globally. Electroanalytical approaches are in many cases the techniques of choice because of their great precision, accuracy and relatively cheap cost [1]. Detection and quantification at trace level of different species of a chemical by these techniques in aquatic media usually does not require pretreatment—a significant advantage for monitoring programmes. Methylmercury is an extremely toxic chemical species that is found in the environment [2,3]. It usually appears as a result of the conversion of inorganic mercury by microorganisms into much more toxic organomercury forms, particularly the water soluble monomethylmercury cation. Its solubility in lipids leads to elevated concentration in the biological tissues. The inclusion of methylmercury in the food chain is very harmful to humans because of its cumulative effects. Consequently the analytical determination of methylated forms of mercury in dilute samples is of primary importance for food safety.

Although non-electrochemical methods for quantifying organomercury species have been widely applied, they are somewhat complicated and time-consuming, and usually require expensive instrumentation [4–9]. High pressure liquid chromatography (HPLC) with electrochemical detection has also been employed [10]. Procedural and economic advantages make voltammetric techniques very attractive for analyses. However, there are very few reports in the literature describing the voltammetric determination of methylmercury [11–15], most probably because of the complexity of the particular electrochemical reduction process [11,16]. Several papers have reported mechanistic studies on the electrochemical reduction of methylmercury, some of them presenting controversial results [17–19], but over the last 30 years the mechanism proposed by Heaton

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and Laitinen [11] has become accepted. Two single-electron steps are involved in this mechanism: one being the reversible generation of the methylmercury radical, the other being an electron-transfer reaction associated with the irreversible reduction of the methylmercury radical to mercury and methane. A linear calibration plot for the determination of methylmercury at a mercury drop electrode was obtained over the concentration range from 10^{-4} to 10^{-7} M [11]. Other analytical studies using mercury film [10,14] or gold film [12] electrodes have been reported. Lower detection limits down to the nanomolar concentration range were achieved using polymer-coated carbon electrodes [13,15].

The voltammetric determination of methylmercury has been usually based on the reversible wave, where the reduction to methylmercury radical takes place. However, the subsequent reactions involving the production of elemental mercury and other reaction products need to be investigated and taken into account for the analysis, especially when solid electrodes are employed. The shape and size of the reversible wave, as well as its poor reproducibility, appear to be influenced significantly by the modification of the solid electrode surface, which is due to the deposition of reaction products derived in subsequent steps, including free mercury. Therefore, the hypothesis of formation of a mercury-modified electrode during the electrochemical process has to be considered. Complexing matrices will inevitably influence this process [16].

Recently, the application of microelectrodes to electroanalysis has received considerable attention, as these offer many advantages over macroelectrodes [20–22]. High mass transport with low ohmic drop and charging currents make them very convenient for direct speciation measurements in resistive solutions in the presence of dissolved oxygen, when fast electrochemical techniques are employed. On the other hand, the goal is now to develop environmental friendly sensors as alternatives to the highly toxic mercury electrodes, which clearly are prone to unavoidable contamination of the environment. The trend is to avoid mercury as an electrode material thereby protecting the environment. We demonstrated in an earlier paper that carbon microelectrodes are promising tools for *in situ* determination of methylmercury in natural waters [16]. Firstly, they allow direct measurements in environmental samples taking advantage of the microelectrodes features, and secondly they support a clean methodology by using environmentally friendly electrodes.

A method for the experimental determination of methylmercury in aqueous matrices is developed and applied to the analysis of a natural water sample. In the present work, the application of voltammetric techniques for monitoring low levels of methylmercury in natural aquatic systems using carbon microelectrodes is explored and investigated. The implications of the presence of chloride ions and the deposition of mercury compounds on the electrode surface are considered. The influence of metal ions, such as lead and cadmium, is also studied.

2. Experimental

Supporting electrolyte solutions, hydrochloric acid and potassium thiocyanate, were prepared from reagents of Suprapur quality (Merck) in Millipore Milli-Q ultrapure water (conductivity < 0.1 μS cm^{-1}). Pb(II) and Cd(II) solutions were prepared from lead acetate and cadmium chloride (Merck) of analytical grade without further purification. The solutions were stored in Pyrex glass flasks for a few days. Transfer of methylmercury(II) chloride (Aldrich) require special Viton gloves (Sigma-Aldrich) and masks. Milimolar stock solutions of methylmercury(II) chloride were prepared by introducing weighed amounts of the salt into Pyrex volumetric flasks and then filling them to the marks with Milli-Q water. The working solutions were obtained by adding the stock solution to the appropriate supporting electrolyte. The disposable pipette tips employed were rinsed with a 1% HNO_3 aqueous solution before being discarded.

The experiments were performed in a homemade glass cell (25 mL) equipped with a platinum wire counter electrode, an Ag | AgCl | 3 M NaCl reference electrode, from Bioanalytical Systems, Inc. (BAS) and a carbon microelectrode as the working electrode. Carbon fiber microelectrodes (Ø11 ± 2 μm), from BAS, and glassy carbon microelectrodes (Ø10 ± 2 μm), from Princeton Applied Research (PAR), were employed. A platinum microelectrode (Ø10 ± 2 μm) and a glassy carbon rotating disc electrode (area: 0.385 cm^2) were also used.

Electrodes were hand-polished with 0.05 μm alumina slurry (Buehler), rinsed thoroughly with Milli-Q water and allowed to dry. After running experiments, the microelectrodes were immersed in nitric acid in an ultrasound bath. Whenever found necessary they were also electrochemically cleaned to ensure a more efficient removal of the deposited mercury.

A computer-controlled Autolab PGSTAT12 potentiostat (Eco Chemie, Utrecht, The Netherlands) equipped with a low current amplifier module (ECD) and a dual channel fast analogue-to-digital converter (ADC750) with the GPES software (Version 4.9) was used for running the electrochemical experiments. A Bacharach Coleman Model 50B atomic absorption spectrometer equipped with a peristaltic pump for cold vapour analysis was employed for the photometric determination of mercury.

Voltammograms were recorded keeping the cell in a Faraday cage, in order to eliminate electronic noise. All experiments were conducted at temperatures of (25 ± 1) °C.

3. Results and discussion

3.1. Voltammetric behaviour of methylmercury at carbon microelectrodes

The study of the electrochemical reduction of the methylmercury cation at a carbon electrode is an interesting but not a straightforward task. The experimental results are poorly reproducible and denote unusual electrochemical behaviour.

Cyclic voltammetry of methylmercury in HCl was carried out at carbon microelectrodes. Similar cyclic voltammograms (CVs) were obtained using either carbon fiber or glassy carbon as electrode materials. Typical voltammograms run over different potential ranges are shown in Figs. 1 and 2. Fig. 1 illustrates the reduction of methylmercury, starting at −0.3 V, and the corresponding oxidation peak, A_1(E_p = −0.33 V). In progressing to more positive potentials, the presence of elemental mercury as