Electrochemical Determination of Methyltin Compounds

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Abstract. The electrochemical behaviour of monomethyltin, dimethyltin and trimethyltin compounds in 20% (V/V) methanol/water solution, 0.05 mol/L in tetraethylammonium perchlorate at pH 2.5, has been investigated by differential pulse polarography and differential pulse anodic stripping voltammetry. In differential pulse polarography, dimethyltin and trimethyltin gave one reversible wave with peak potentials at −0.70 V and −1.07 V, respectively. Detection limits were 6.6 × 10⁻⁷ mol/L for dimethyltin and 4.1 × 10⁻⁶ mol/L for trimethyltin. The electrochemistry of monomethyltin was found to be more complex. By differential pulse anodic stripping voltammetry, monomethyltin, dimethyltin and trimethyltin produced distinct stripping peaks (−0.39 V, −0.75 V and −1.14 V, respectively), which allow to determine these compounds at trace levels. Using this new method, detection limits were: 1.2 × 10⁻⁷ mol/L for monomethyltin, 1.7 × 10⁻⁷ mol/L for dimethyltin and 1.4 × 10⁻⁶ mol/L for trimethyltin. For monomethyltin, a second peak ($E_p = −0.60$ V), less sensitive (detection limit of 2.5 × 10⁻⁶ mol/L), was also observed at concentrations above 4.2 × 10⁻⁷ mol/L.

Recoveries of methyltin compounds added separately to tap water samples at the 0.42–16.9 μmol per litre level ranged from 84.5 to 99.8% depending upon the methyltin species.

Key words: Methyltin compounds; differential pulse polarography; differential pulse anodic stripping voltammetry.

Methyltin compounds have been found in rain, in a variety of natural and estuarine waters and in sediments [1–5]. Methylated species are generally thought to be derived from natural origins via a wide range of alkylation and dealkylation, chemically or biologically mediated. Methylation is environmentally important because this process increases the volatility, the lipophilicity, the adsorptivity and the toxicity of tin, and probably its mobility in the environment [6].

Tin metal and most inorganic tin compounds are relatively non-toxic. However, formation of one or more tin-carbon bonds has a profound effect on its biological behavior and organotin compounds exert very powerful biocidal activity with varying degrees of toxicity. The phytotoxicity of methyltin compounds prevents their use in agriculture [7] and, although trimethyltin derivatives possess a high insecticidal activity, their use in the field has also been precluded by their mammalian toxicity [8]. In addition, literature describes the intoxication of humans [9, 10] by methyltin compounds. The evaluation of the environmental risk of these compounds cannot be achieved by conventional chemical determination of total tin but speciation analysis must be employed.

In Portugal, cassiterite beds are very common and its exploration has been widely performed. Cassiterite ore mainly consists of dioxide of tin (IV) with traces of ferric and tantalum oxides. Because we are interested in studying the assessment of metal contamination in natural waters due to cassiterite mining activities, analytical methods for speciation of methyltin compounds were needed.

Many papers have recorded the analysis of methyltin in waters [11–14], soils and sediments [11, 15–17] and biological samples [10, 18, 19]. These
analytical approaches include the hybridization of separation techniques [capillary electrophoresis, gas chromatography (GC) or high-performance liquid chromatography (HPLC)] coupled to a wide variety of detectors. Even though HPLC and capillary electrophoresis have been used, GC has been the most applied. Prior to GC analysis, it is necessary to convert the organotin compounds to more volatile and thermostable derivatives. Derivatization yields should be carefully evaluated but the absence of commercially available derivatized compounds of proven purity makes it a difficult task. The use of radiolabelled compounds and/or synthesized derivatized standards in one’s own laboratory should be considered.

Electrochemical techniques can be an attractive alternative since they are independent of any derivatisation procedure and the reliability and compactness of modern electronic and mechanical components allows electrochemical equipment to be designed for field studies, e.g., in mobile laboratories. The success of applying these techniques depends on the availability of trained staff.

An analysis of the literature showed that, while the electrochemical behavior of butyl and phenyltin compounds have been widely studied [20–32], the application of electrochemical methods for quantitative determination of methyltin compounds, as far as we know, has never been performed.

In the present work, the electrochemistry of mono-methyltin (MMT), dimethyltin (DMT) and trimethyltin (TMT) compounds was initially examined in 20% (V/V) methanol/water solution, 0.05 mol/L in tetraethylammonium perchlorate (TEAP) at pH 2.5 by differential pulse polarography (DPP). Additionally, the feasibility of differential pulse anodic stripping voltammetry (DPASV) for the determination of methyltin compounds in the same background solution was investigated.

Experimental

Analytical-reagent grade chemicals were used unless indicated otherwise. All solutions were prepared from distilled and deionized water with a resistivity > 14 MΩcm. All glassware and polyethylene material was soaked in 20% nitric acid (HNO₃) for at least one day and then rinsed several times with distilled and deionized water. The methyltin compounds, methyltin trichloride (97%) and dimethyltin dichloride (97%) were purchased from Aldrich and trimethyltin chloride (> 98%) was purchased from Merck. Organotin stock solutions containing 8.4 x 10⁻³ mol/L of each compound were prepared by dissolving the respective substances in absolute methanol and stored at -10°C in the dark. Dilute working standard organotin solutions of 8.4 x 10⁻⁵ mol/L were prepared weekly from the stock standard solution by dilution with methanol. A stock solution of tetraethylammonium perchlorate (TEAP) 0.05 mol/L in 20% (V/V) methanol/water solution at pH 2.5 was prepared from the commercial product (Fluka). Volumes of 20 ml of the TEAP stock solution were placed in the glass voltammetric cell. The required amount of each dilute working standard organotin solution was also transferred into the cell. The solution was deaerated for 10 min and after that a nitrogen flow was maintained over the solution throughout the measurement.

Differential pulse polarograms and differential pulse anodic stripping voltammograms were recorded with a microAutolab voltammetry (Eco Chemie) connected to a multimode mercury electrode (Metrohm 663 VA stand). This working electrode was able to work as a dropping mercury electrode (DME) in DPP and as static mercury drop electrode (SMDE) in DPASV experiments. Potentials are given with respect to an Ag/AgCl(s), 3 mol/L KCl reference electrode and with a graphite rod as counter electrode. The precision of the peak potential is 0.01 V. The system was controlled by a personal computer using GPES 4.5 program (Eco Chemie).

Pulse duration of 60 ms, pulse height of 50 mV and a scan rate of 5 mV/s were used for DPP and DPASV measurements. DPP experiments were performed with a drop time of 1 s and initial and final potentials of −0.2 and −1.2 V, respectively. DPASV measurements were carried out with a deposition time of 120 s (90 s with stirring and 30 s for equilibration). Optimized experiments were performed using a deposition potential of −1.4 V for the three methyltin species. An initial potential of −1.2 V, for MMT and DMT, and of −1.4 V for TMT were also used.

Results and Discussion

DPP Experiments

It is well described in the literature that other organotin (butyl and phenyltin) compounds are directly reduced at the dropping mercury electrode [20, 22–24, 26–32]. In a first attempt, differential pulse (DP) polarograms of a blank solution, TEAP (0.05 mol/L) in 20% (V/V) methanol/water solution at pH 2.5, were recorded between 0 and −1.9 V; a peak with a current (iₚ) ≈ 2 x 10⁻⁶ A at a peak potential (Eₚ) ≈ −1.6 V was recorded due to the reduction of hydrogen from water. Preliminary DP polarograms, recorded for each one of the methyltin compounds between 0 V and −1.4 V, evidenced that for potentials more positive than −0.2 V and more negative than −1.2 V no additional peaks were obtained. Therefore, further polarograms were recorded between −0.2 and −1.2 V.

DP polarograms were recorded for the following range of methyltin concentrations: from 1.7 x 10⁻⁷ to 2.5 x 10⁻⁵ mol/L for MMT, from 1.7 x 10⁻⁷ to 3.8 x 10⁻⁵ mol/L for DMT and from 3.4 x 10⁻⁶ to 6.8 x 10⁻⁵ mol/L for TMT. No polarographic responses were observed up to 1.7 x 10⁻⁶ mol/L MMT and 7.6 x 10⁻⁶ mol/L TMT.