

[PP 1.5]

Determination of Methyltin Species by Cathodic Stripping VoltammetryHelena M.V.M. Soares¹ and Sónia M.O. Teixeira²¹ CEQUP, Department of Chemical Engineering, Faculty of Engineering, University of Oporto, Rua dos Bragas, 4050-123 Porto Codex, Portugal; e-mail: hsoares@fe.up.pt² Department of Chemical Engineering, Faculty of Engineering, University of Oporto, Rua dos Bragas, 4050-123 Porto Codex, Portugal

Methyltin compounds have been found in rain, in a variety of natural waters and in sediments [1-3]. Methylated species are generally thought to be derived from natural origins via a wide range of alkylation and dealkylation, chemically or biologically mediated. Tin metal and most inorganic tin compounds are relatively non-toxic. However, the formation of one or more tin-carbon bonds has a profound effect on its biological behaviour and organotin compounds exert very powerful biocidal activity with varying degrees of toxicity. The phytotoxicity of methyltin compounds prevents their use in agriculture [4] and, although trimethyltin derivatives possess a high insecticidal activity, their use in the field has also been precluded by their mammalian toxicity [5].

Therefore, evaluation of the environmental risk of these compounds cannot be achieved by the conventional chemical determination of the total tin, but speciation analysis must be employed.

In the present contribution, the application of cathodic stripping voltammetry (CSV) to the determination of monomethyltin (MMT), dimethyltin (DMT) and trimethyltin (TMT) compounds in 20% (v/v) methanol/water acetate buffer (0.08 mol/L, pH 4.5) solution containing 3.0×10^{-4} mol/L tropolone

is described. Peak potentials, detection limits and linear response limits were: -0.32 V, 2.2×10^{-8} mol/L, 5.1×10^{-7} mol/L for MMT, -0.84 V, 1.3×10^{-8} mol/L, 1.7×10^{-7} mol/L for DMT and -0.83 V, 1.6×10^{-7} mol/L, 1.7×10^{-6} mol/L for TMT. The coefficients of variation of 6.7×10^{-8} mol/L for MMT (n=6), 4.2×10^{-8} mol/L for DMT (n=7) and 6.7×10^{-7} mol/L for TMT (n=7) were 2.0%, 3.3% and 5.5%, respectively. These results show that MMT and DMT, and MMT and TMT can be determined simultaneously at trace levels by CSV, but DMT and TMT cannot.

In order to make the accurate determination of the three methyltin compounds in a mixture, a previous separation technique for coupling with this methodology is under study.

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[PP 1.6]

Inorganic Speciation of Arsenic in Natural Waters by Square Wave Cathodic Stripping VoltammetryM. M. Correia dos Santos¹, Cristina Maria Barra²¹ Centro de Química Estrutural, Instituto Superior Técnico, Avenida Rovisco Pais, 1049-001 Lisboa, Portugal; e-mail: mcsantos@alfa.ist.utl.pt² Departamento de Química, Instituto de Ciências Exatas, Universidade Federal do Rio de Janeiro, Antiga Rio S. Paulo, km 47, CEP 23851-970, Seropédica, Rio de Janeiro, Brasil

Inorganic speciation of arsenic in many natural water systems is mandatory in the assessment of the contamination risk. Among the variety of methods that have been used to obtain speciation data, voltammetric techniques present several advantages and provide a simple and sensitive way to directly speciate As(V) and As(III) since they exhibit different electrochemical behavior: Arsenate is not electroactive so that arsenite can be reduced to the elemental state in most cases and is used for electrochemical studies.

In this work we present a fast and sensitive method for the determination of As(III) and As(III)+As(V) in natural waters using Cathodic Stripping Voltammetry based on the peak of cathodic reduction of pre concentrated arsenic on a Hanging Mercury Drop Electrode in the presence of copper(II) and 1M HCl. In an attempt to shorten the time of analysis, a Square Wave pulse was used in the stripping step. In this way all determinations could be done in the presence of dissolved oxygen. Also, chemically less aggressive conditions were tested for the reduction process. A solution of potassium iodide and ascorbic acid, which is often

used in Atomic Absorption Spectroscopy determinations with the hydride generation technique, was chosen as a reducing agent. Factors that may influence the analytical determination were investigated, in particular whether the presence of the reductants and the products of their oxidation disturbed the voltammetric signal. Potential interferences of some organic substances were examined. Working conditions like deposition potential and deposition time were optimized.

Just varying the composition of the supporting electrolyte discrimination between As(III) and InorgAs (As(V)+As(III)) was achieved. For an accumulation time of 60 s the detection limits were 0.7 ppb for As(III) and 0.6 ppb for InorgAs. The relative standard deviation was calculated as 11% (n=10) at 2 ppb standard. Speciation measurements may be hampered in solutions containing high amounts (>1 ppm) of dissolved organic matter. The method was then applied in the determination of As(V) and As(III) in real and synthetic natural water samples.

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