



Determination of ultra-trace Sb(III) in seawater by stripping chronopotentiometry (SCP) with a mercury film electrode in the presence of copper

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ARTICLE INFO

Article history:

Received 21 September 2009

Received in revised form

18 December 2009

Accepted 24 December 2009

Available online 11 January 2010

Keywords:

Stripping chronopotentiometry

Antimony

Inorganic species

Seawater

Estuary

ABSTRACT

This work reports the determination of ultra-trace of Sb(III) in seawater by using a stripping chronopotentiometric (SCP) method with a mercury film electrode. A sensitivity and detection limit of $360 \text{ ms L } \mu\text{g}^{-1}$ and 8 ng L^{-1} (70 pM), respectively, were accomplished for a 15-min electrolysis time. Compared to the only two chronopotentiometric methods reported for Sb(III) determination in seawater, our method is more sensitive and does not need to use a medium exchange procedure before the stripping step. Moreover, the use of a double electrolysis potential (-450 mV and -250 mV) allows the analysis of Sb(III) independently from the Cu level in the sample. The method was successfully used to study the behaviour of dissolved Sb(III) in the Penzé estuary, NW France.

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1. Introduction

Non-biodegradable and potentially toxic elements are permanently supplied to seawater. Antimony and its compounds are one of the priority contaminants listed by the Environmental Protection Agency of the United States [1] and the Council of the European Communities [2]. Natural sources of Sb to seawater consist of rock weathering, soil runoff and atmospheric deposition. Anthropogenic sources are linked to glass, ceramic and painting manufacturing [3,4]. Sb compounds are also used in flame retardant mixtures for textiles, plastics or paper. Because of their uses in brake linings and tires [5], road traffic is also a major source of Sb to the environment.

Total dissolved antimony concentrations in coastal and oceanic waters varied between 1.5 and 8 nM [3,6–9]. As for most trace metals and metalloids, the potential toxicity of Sb highly depends on its chemical forms in solution. In seawater, inorganic Sb(V) is the major species whereas Sb(III), although in minor amounts, is considered to be the most toxic fraction [9]. The toxicity of Sb in seawater is not certain but some recent studies have shown oxidative DNA damage in workers exposed to Sb_2O_3 and SbCl_3 [10,11].

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The most used techniques for analysis of Sb species are based on hydride generation coupled with different spectrometric techniques, i.e. atomic absorption spectrometry (AAS), atomic emission spectrometry (AES), atomic fluorescence spectrometry (AFS) or mass spectrometry (MS) [12–18]. Because of their low-cost and compactness, electrochemical stripping analysis represents an interesting alternative to them. Moreover, the seawater matrix, which causes severe difficulties with spectrometric techniques, is a good electrolyte. Voltammetric methods, i.e. differential pulse anodic stripping voltammetry (DPASV) and differential pulse adsorptive stripping voltammetry (DPAdSV), are the most developed and have been associated with several different electrodes [7,19–25]. Another analytical possibility consists of stripping chronopotentiometry (SCP) [26–29]. In these techniques, the pre-concentration step is like the one used in voltammetric procedures, whereas stripping is performed through the application of a low constant current (constant current stripping chronopotentiometry) or by chemical oxidation instead of potential sweeping. SCP gave rise to low-detection methods for metals and metalloids determination in seawater [30–35]. These methods are poorly affected by organic matter and are relatively easy to implement. In the case of antimony, there are only two reported SCP methods for seawater analyses [26,36]. The method by Adeloju and Young [26] has a detection limit (7.5 nM) that is not sufficient for determining typical Sb concentrations in seawater. Despite a relatively good detection limit (0.3 nM for 10-min deposition time), the method by Huiliang

et al. [36], which uses a gold fibre electrode, is inconvenient in some respects: it is necessary to change the media before the stripping step and the stripping media are highly acidic (4 M HCl). These constraints can prevent the routine use of this procedure.

In this study, we evaluate the possibility of using a mercury film electrode in conjunction with constant current stripping chronopotentiometry for determining Sb(III) in seawater, keeping in mind that copper is the main problem to solve on a mercury electrode because its potential overlaps from the Sb stripping peak [7,19,36]. The objective is to develop a simple, sensitive and reliable method. Our aim was also to use the developed method to assess the distribution of Sb(III) species along the salinity gradient of the Penzé estuary (Morlaix Bay, NW France).

2. Experiments

2.1. Chemicals

All solutions were prepared with ultrapure water (>18 M Ω) from a Milli-Q Element system (Millipore[®], Billerica, MA, USA) and the HCl stock solution used was a 30% Suprapur from Merck. The 1000 ppm Sb(III) solution was made up by dissolving an appropriate amount of SbCl₃ in 20% HCl. From this stock solution, diluting standards (2.5 ppm and 50 ppb) were prepared in 20% HCl. All these Sb(III) solutions were stable for at least 3 weeks. The 0.5 M NaCl solution was created with SigmaUltra NaCl(s) from Sigma and then acidified to pH ~2. In order to stabilise the Sb(III) form and avoid its oxidation to Sb(V), a 2 M stock solution of hydrazine was daily made up by using N₂H₄·2HCl (s) from Fluka (puriss. p.a.). The Hg²⁺ solution used to perform mercury film plating was prepared by dissolving hexadistilled mercury in concentrated HNO₃ (Suprapur, Fluka) and was adjusted to a concentration of 0.01 M. All sample manipulations and reagent preparations were carried out in a class-100 laminar flow hood-equipped laboratory to avoid any risk of pollution.

2.2. Instrumentation

The chronopotentiograms were obtained with a TraceLab PSU 22 potentiometric stripping unit (Radiometer, Copenhagen, Denmark) interfaced with a personal computer and controlled by the TAP2 Trace Talk program (Radiometer). The system operates on a three-electrode basis. The working electrode was a rotating glassy carbon electrode (EDI101T, 2.5 mm in diameter) coated with a thin mercury film and connected to a CTV101 unit that provides a constant rotation rate. A lab-made Ag/AgCl (KCl 3 M, Suprapur) electrode and a platinum electrode were used as the reference and the auxiliary electrodes, respectively. The Pt auxiliary electrode was isolated from the sample with a 0.5 M KNO₃ solution-filled saline bridge. This prevents chlorine formation at the auxiliary electrode when working in a chloride-rich matrix. Indeed, the existence of chlorine near the working electrode can induce the oxidation of Sb(III) into electroinactive Sb(V), causing speciation changes and signal loss.

2.3. Mercury film electrode

Because exchange of electrons occurs at the surface of the working electrode, physical conditioning of the glassy carbon is critically important for obtaining a high-quality mercury film electrode. Before the beginning of the experiments the electrode was polished with diamond paste of gradually decreasing grain size (6, 3, 1, and 0.25 μ m) until a mirror-like surface was obtained. Ethanol wash and an ultrasonic cleaning were then conducted to remove residual particles. Such an electrode can be used for several years without additional polishing. The mercury film was plated by applying a

–1200 mV potential for 10 min from Hg²⁺ ions added at a concentration of 50 μ M in a 0.5 M NaCl solution acidified to pH ~2 with HCl. The film thus prepared is stable for approximately 6 h. Before any adsorption-stripping cycle the electrode was conditioned for 20 s at a potential of –50 mV vs Ag/AgCl (KCl 3 M). During the plating of the mercury film, the electrode conditioning and the pre-concentration step, the angular velocity of the rotating working electrode was kept constant at 3000 rpm. It was set to the lowest possible value (9 rpm) throughout the stripping step.

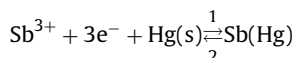
2.4. Sampling

Twelve samples were collected along the Penzé estuary (Brittany, NW France) in December 2008. The sampling locations were selected with the aim to cover the whole freshwater–seawater mixing area. Sampling was performed from a Zodiac inflatable boat with HDPE-Nalgene[®] bottles. Water was sampled by hand at ca. 0.5 m below the surface with the arm fully covered with a plastic glove (92 cm, Polysem[®]). 125-mL aliquots, intended for Sb(III) analysis, were immediately filtered on 0.45- μ m membrane filters (Millex-HA, Millipore[®]), spiked with 0.1 M of hydrazine dihydrochloride to avoid the oxidation of Sb(III) into Sb(V) species [26,27], acidified to pH ~2 and stored at 4 °C until analysis. Salinity (S) was measured with a WTW (Weilheim, Germany) ProfiLine LF197 probe (precision \pm 0.1).

Other aliquots were dedicated to the measurement of total dissolved organic carbon (DOC) and refractory organic matter (often referred to as humic substances). DOC was analysed by the dry oxidation method [37]. Precision on quantification was ca. 10% and blanks filters concentrations were lower than 1 ngCL⁻¹. Humic substances were determined by adsorptive cathodic voltammetry [38], using a μ Autolab potentiostat (Ecochemie, Netherlands) connected to a hanging mercury drop electrode (HMDE, Metrohm model 663VA), with a 2.5 μ gCL⁻¹ precision.

2.5. Method principle

Constant current stripping chronopotentiometry consists of 2 steps: electrolysis and stripping. During electrolysis, Sb(III) – the only electroactive species of antimony at the mercury film electrode – is reduced to Sb(0) as an amalgam with Hg (way 1). This first step is carried out by applying under mixing a sufficient reducing potential. After a short rest period without mixing, Sb is stripped through the application of an oxidative constant current (way 2).



The amount of Sb(III) is measured from the signal corresponding to the oxidation of Sb(0) to Sb(III) by recording the variation of the potential (E) of the working electrode as a function of time (t), at the maximum rate of 90 kHz. From this chronopotentiogram, data analysis establishes a derivative curve (i.e. dt/dE vs E) and the amount of stripped material can be determined from the peak size or peak area. The metal concentrations were evaluated by repeating the analysis three times, with each replicate being spiked with increasing amount of standard antimony.

3. Results and discussion

Chemical and electrochemical parameters have been optimized by studying their influence on the method sensitivity. The various tests were performed on a coastal seawater sample collected in the Bay of Brest, filtered on a 0.45- μ m filter (Millipore[®]-HA 47 mm), spiked with a low amount of Sb(III) and degassed with nitrogen for 10 min.

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