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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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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 ms L μg^{-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.

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].

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 preconcentration 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

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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 MΩ) 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 $SbCl_3$ 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 $N_2H_4{\cdot}2HCl$ (s) from Fluka (puriss. p.a.). The Hg^{2+} solution used to perform mercury film plating was prepared by dissolving hexadistilled mercury in concentrated HNO_3 (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 KNO_3 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 μm) 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 Hg^{2+} ions added at a concentration of 50 μM 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-μm 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 ±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 $ngC\,L^{-1}$. Humic substances were determined by adsorptive cathodic voltammetry [38], using a μAutolab potentiostat (Ecochemie, Netherlands) connected to a hanging mercury drop electrode (HMDE, Metrohm model 663VA), with a 2.5 $\mu gC\,L^{-1}$ 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).

$$Sb^{3+} + 3e^- + Hg(s) \underset{2}{\overset{1}{\rightleftarrows}} Sb(Hg)$$

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-μm filter (Millipore®-HA 47 mm), spiked with a low amount of Sb(III) and degassed with nitrogen for 10 min.

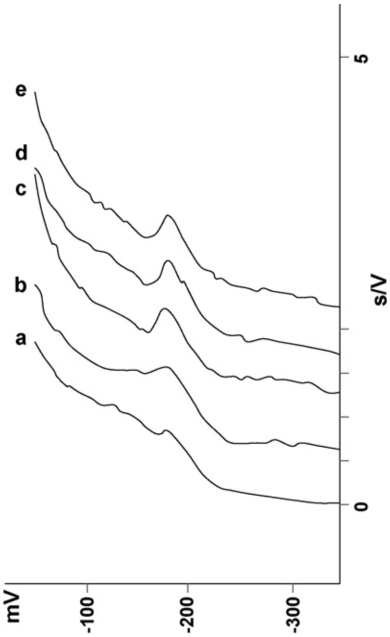

Fig. 1. Influence of N_2H_4 concentration on Sb(III) stripping signal. Seawater sample with [HCl] = 0.15 M, $[Hg^{2+}]$ = 50 μM, $[Sb^{3+}]$ = 85 ng L^{-1}, $E_e = -450$ mV, t_e = 600 s, i_s = 3.5 μA, $[N_2H_4]$= (a) 0.02 M, (b) 0.04 M, (c) 0.06 M, (d) 0.08 M and (e) 0.1 M.

3.1. Chemical parameters

Preliminary experiments have been carried out for testing the stability of Sb(III). In an acidified seawater sample (0.5 M HCl) spiked with 0.5 ppb, a rapid signal loss is observed (~30% after 10 min and ~80% after 1 h). In order to avoid oxidation of Sb(III) to Sb(V), the stabilisation of Sb(III) is thus required when sampling seawater. The most common used agents are ascorbic acid [7] and hydrazine [26,27]. Because a lack of linearity was always observed during preliminary tests with ascorbic acid, hydrazine was selected as the stabilising agent. The influence of hydrazine concentration on Sb(III) signal was thus explored (Fig. 1). From 0.02 to 0.06 M, the sensitivity increased (from 175 to 250 ms L μg^{-1}), then remained relatively constant at concentrations higher than 0.06 M. Consequently, a N_2H_4 concentration of 0.1 M was chosen for subsequent experiments. This concentration was sufficient to prevent the ill-defined signal on the anodic side as shown in Fig. 1a and b. As reported by Waller and Pickering [39], hydrazine at 0.1 M does not promote chemical reduction of Sb(V) to Sb(III); hydrazine probably acting as a depolarising agent, rather than a chemical reductant.

The choice of the electrolytic solution is essential, not only for obtaining well-defined signals, but also to control the Sb speciation. Acidic electrolytes are employed in order to avoid the hydrolysis of Sb(III) and Sb(V) into $Sb(OH)_3$ and $Sb(OH)_6{}^-$. Because chloride ions stabilise Sb via formation of chlorocomplexes, hydrochloric acid is usually preferred [26,40]. Moreover, Quentel and Fillela [7], using a DPASV technique and a mercury drop electrode, have shown that it is possible to determine either Sb(III) or total inorganic Sb(III + V) by adjusting the HCl concentration.

Examination of HCl concentration on our Sb stripping signal has been investigated (Fig. 2). As expected, HCl concentration has an important influence. An increase of the signal is observed from 0.01 to 0.2 M. At concentrations higher than 0.2 M, the sensitivity declined and the signals were no longer resolved for HCl concentrations over 1 M. A HCl concentration of 0.15 M was, therefore, selected for subsequent experiments. The look of the obtained curve was similar to the one reported by Adeloju and Young [26]. These authors also used a mercury film electrode and a chronopotentiometric technique that consisted of a chemical oxidation. However, their optimal HCl concentration was 1 M. This difference in optimal HCl concentration can be related to the way of plating the mercury film. Adeloju and Young used a concentrated Hg^{2+} solution (4×10^{-3} M) and a short electrolysis time (1 min). In our study, the Hg plating was realised by using a diluted Hg^{2+} concentration ($\sim 5 \times 10^{-5}$ M) and a long electrolysis time (10 min). According with previously experiments on film electrodes [30,31,41], this latter approach gives a better analytical efficiency. In the case of antimony, our way of plating probably prevents the use of highly acidic media whereas the former approach allows the use of HCl concentrations until 5 M [26,27].

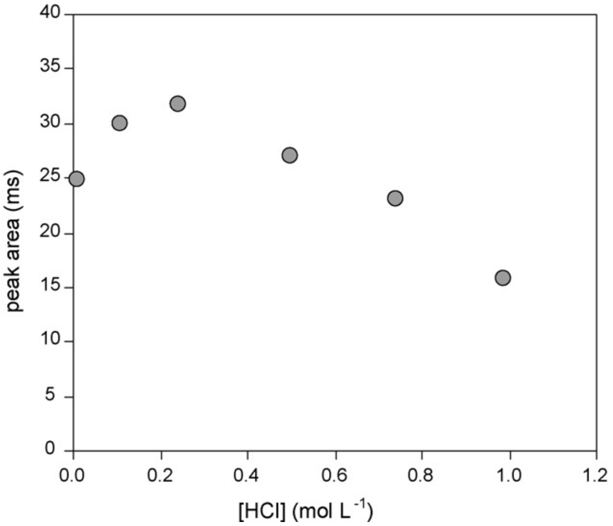

Fig. 2. Influence of HCl concentration on Sb(III) stripping signal. Seawater sample with $[N_2H_4]$ = 0.1 M, $[Hg^{2+}]$ = 50 μM, $[Sb^{3+}]$ = 175 ng L^{-1}, $E_e = -450$ mV, t_e = 300 s, i_s = 3.5 μA.

3.2. Electrochemical parameters

At a mercury electrode and under the chemical conditions retained (HCl 0.15 M), the Sb(III) peak is located at approximately −150 mV vs Ag/AgCl (KCl, 3 M) (Fig. 6). Thus, the electrolysis potential (E_e) should be sufficiently cathodic from −150 mV to reduce Sb(III) at the working electrode. As illustrated in Fig. 3, the peak area increased as the electrolysis potential was varied from −300 mV to −450 mV. At lower potentials the signal slowly decreased. Taking this evolution into account, an electrolysis potential of −450 mV was chosen for subsequent analysis.

The stripping current (i_s) is one of the most influent parameter on the method sensitivity. As described by Eq. (1), the stripping signal (t_s) that corresponds to the time needed to strip Sb from the electrode, should inversely vary with the stripping current.

$$t_s = k\frac{[\mathrm{Sb(III)}]}{i_s - i_0} \tag{1}$$

where k is a constant that incorporates D (the diffusion coefficient of the element, $cm^2\,s^{-1}$), δ_e (the thickness of the diffusion layer, cm), i_s the magnitude of the applied current and i_0 the amount of this current lost through side reactions due to the diffusion of oxidable species to the electrode and reactions at the electrode substrate surface. Assuming that the condition $i_s \gg i_0$ is fulfilled, small variations in the diffusion layer will not noticeably affect t_s in this respect [42].

For this study, the influence of i_s was examined between 6 and 2 μA (0.17 and 0.50 μA^{-1}). As described in Fig. 4, the linear relationship between $i_s{}^{-1}$ and the stripping signal was verified. Although

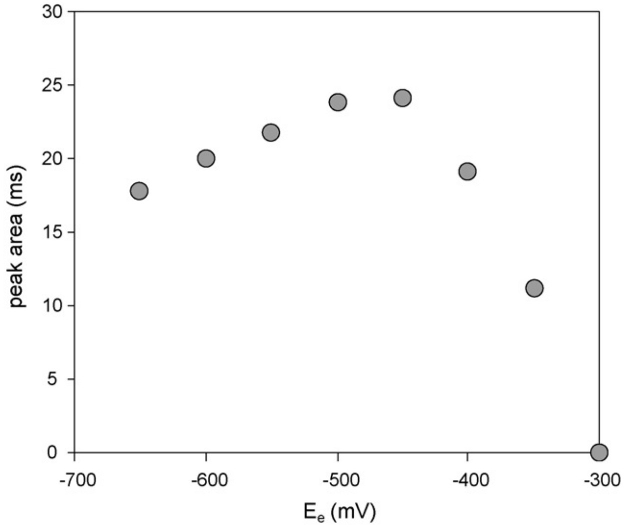

Fig. 3. Influence of electrolysis potential on Sb(III) stripping signal. Seawater sample with $[N_2H_4] = 0.1$ M, $[HCl] = 0.15$ M, $[Hg^{2+}] = 50$ μM, $[Sb^{3+}] = 175$ ng L^{-1}, $t_e = 300$ s, $i_s = 3.5$ μA.

the response was most prominent for stripping currents of less than 2.5 μA (0.40 μA^{-1}), high residual currents rendered the analytical signal noisy and irreproducible. An oxidation current of 3.5 μA was therefore selected for Sb(III) quantification.

The influence of electrolysis time (or deposition time) on the signal area was also studied. In accordance with theory, Fig. 5 shows a linear between 30 s and 20 min. The electrolysis time to be chosen would, therefore, be a function of the quantity of antimony present in the sample.

3.3. Validation of the method

Validation of the method was carried out under the optimum conditions retained: $[HCl] = 0.15$ M; $[N_2H_4] = 0.1$ M; $E_e = -450$ mV and $i_s = +3.5$ μA. Reproducibility was tested through five repetitive analysis of a coastal seawater sample. This sample was filtered on a 0.45-μm filter and spiked with Sb(III) at 170 ng L^{-1}. The obtained mean ± s.d. value was 176 ± 18 ng L^{-1} (1.4 ± 0.2 nM) that gives a 6% reproducibility. Repeatability, estimated over six repeated electrolysis-stripping cycles conducted on the same sample, was 8%. The method sensitivity was given by the slope of the standard addition calibration plot. It was evaluated on a coastal sweater sample containing approximately 17 ng L^{-1} Sb(III). The obtained sensitivity was 360 ms L μg^{-1} using an electrolysis time of 15 min (Fig. 6). Assessment of the detection limit at the 3σ level was conducted from six consecutive electrolysis-stripping cycles [43], for a seawater sample containing about 17 ng L^{-1}. Using the method sensitivity (360 ms L μg^{-1}), the achieved detection limit was 8 ng L^{-1} (70 pM) for a 15-min electrolysis time.

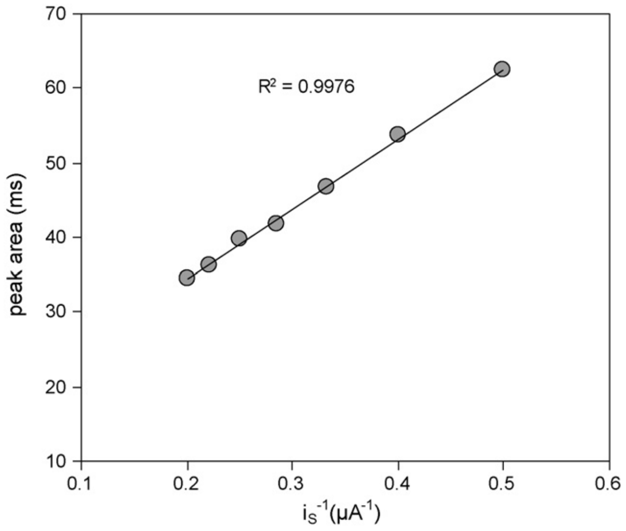

Fig. 4. Influence of stripping current on Sb(III) stripping signal. Seawater sample with $[N_2H_4] = 0.1$ M, $[HCl] = 0.15$ M, $[Hg^{2+}] = 50$ μM, $[Sb^{3+}] = 175$ ng L^{-1}, $E_e = -450$ mV, $t_e = 300$ s.

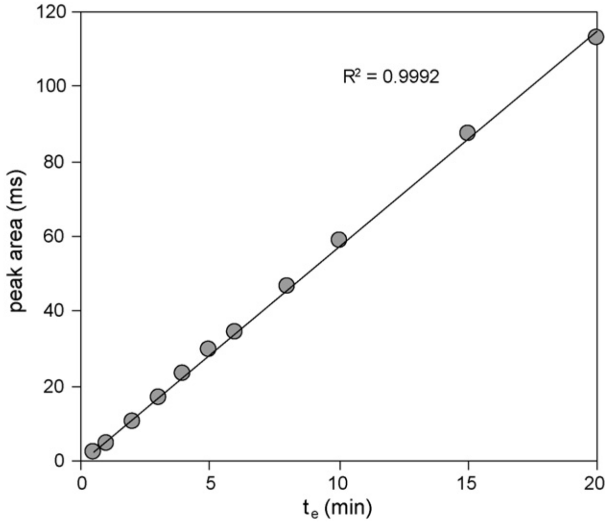

Fig. 5. Influence of electrolysis time on Sb(III) stripping signal. Seawater sample with $[N_2H_4] = 0.1$ M, $[HCl] = 0.15$ M, $[Hg^{2+}] = 50$ μM, $[Sb^{3+}] = 175$ ng L^{-1}, $E_e = -450$ mV, $i_s = 3.5$ μA.

3.4. Analysis in the presence of copper

A problem in determining antimony with mercury electrodes is the potential overlap from the copper stripping peak [19,36]. This interference is particularly serious for coastal seawater samples because copper levels are 20- to 50-fold higher than that of Sb. In order to solve this problem, a double electrolysis potential (−450 mV and −250 mV) has been tested. It consists of several 21-s cycles so that Sb and Cu are both concentrated at the working electrode during electrolysis at −450 mV (20-s duration), then, at −250 mV (1-s duration) Sb is still concentrated whereas Cu is oxidised and leaves the mercury film electrode. According to our experience on double electrolysis potentials [31], a frequent removal (short cycles) of the interferent is necessary. Otherwise, a rapid saturation of the electrodes would occur. For a 15-min deposition step, 43 cycles of 21 s are programmed. Fig. 7 illustrates the analysis of an estuarine sample with (i) the application of a classic single electrolysis potential and (ii) the use of a double electrolysis potential. Under the second option, the copper signal is clearly removed and the antimony signal is better defined. This solution allows determining antimony independently from the Cu level in the sample.

3.5. A comparative study with other electrochemical methods for Sb measurement in seawater

Table 1 summarizes the characteristics and performances of the electrochemical methods for Sb(III) determination in seawater. Five voltammetric techniques and one chronopotentiometric technique have been previously reported. In some of them (e.g. [19,25]), detection limits are too high to measure with precision the concen-

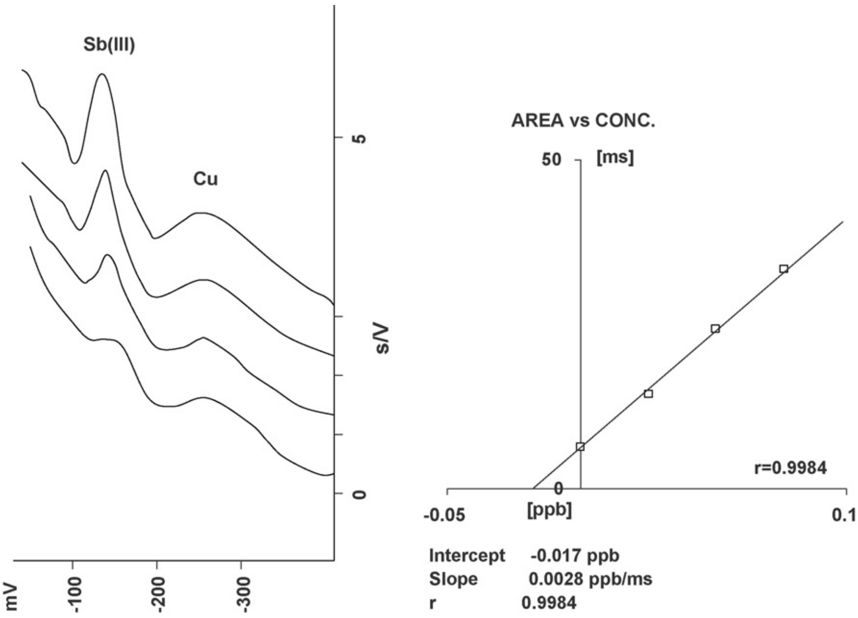

Fig. 6. Sb(III) measurement in a coastal seawater sample ($[N_2H_4] = 0.1$ M, $[HCl] = 0.15$ M, $[Hg^{2+}] = 50$ μM, $t_e = 15$ min, $E_e = -450$ mV, $i_s = 3.5$ μA).

Table 1
Data on electrochemical stripping-based methods that provide Sb(III) measurements in seawater.

Reference	Stripping technique/working electrode	Chemical media	Electrolysis time (s)	Detection Limit (nM)
Gilbert and Hume [44]	DPASV/MFE	4 M HCl	600	0.1
Gillain et al. [19]	DPASV/HMDE	0.1 M HCl, 2 M NaCl	900	0.4
Capodoglio et al. [20]	AdCSV/HMDE	2 mM cathecol, pH 6	180	0.2
Quentel and Fillela [7]	DPASV/HMDE	0.5 M HCl, 0.5 M NaCl	600	0.09
Dominguez et al. [25]	DPASV/SPMFE	3 M HCl	720	12
Zong and Nagaosa [45]	SWCSV/BFE	0.1 M HCl, 10 g L^{-1} KCl	30	0.02
Adeloju and Young [26]	SCP/MFE	1 M HCl	600	7.5
Huiliang et al. [36]	SCP/GFE	Electrolysis: 0.1 M HCl, 0.01 M Fe(II), stripping: 4 M HCl	600	0.3
This study	SCP/MFE	0.15 M HCl, 0.1 M N_2H_4	900	0.07

DPASV: differential pulse anodic stripping voltammetry, AdCSV: adsorptive cathodic stripping voltammetry, SWCSV: square wave cathodic stripping voltammetry, SCP: stripping chronopotentiometry, MFE: mercury film electrode, HMDE: hanging mercury drop electrode, BFE: bismuth film electrode, GFE: gold film electrode, SPMFE: screen printed mercury film electrode.

trations encountered in marine ecosystems whereas in others (e.g. [44]), the HCl concentration used is particularly high which can prevent the routine use of these techniques. The most performing voltammetric methods are the ones developed by Capodoglio et al. [20] and Quentel and Fillela [7]. Recently, Zong and Nagaosa [45] developed a very sensitive method with a bismuth film electrode. This latter method is of particular interest in the context of the problematic use of mercury.

By comparison with Adeloju and Young [26] and Huilang et al. [36] procedures, which are the only chronopotentiometric methods reported for Sb determination in seawater, our method is preferable in some respects: it is more sensitive and does not need to use a medium exchange procedure before the stripping step.

3.6. Application study

The developed method was applied in order to study the distribution of Sb(III) in the Penzé estuary (Morlaix Bay, NW France). Sb(III) varied from 0.07 to 0.99 nM in the salinity range 13–35 and was not detected at lower salinities (Table 2). Thus, Sb(III) exhibits a non-conservative behaviour with a strong positive deviation from linearity indicative of an important enrichment that occurred in the downstream part of the estuary.

Sb(III) levels in the Penzé estuary are close to those previously found for various marine systems. As examples, Sb(III) was measured at values in the range 0.04–0.32 nM for the North Sea [46], 0.03–0.18 nM for the Atlantic Ocean [47] and 0.8–1.6 nM for the Kua Bay [48]. By comparison with the pristine Ochlockonee estuary [49,50], which is, to our knowledge, the only estuarine system

Table 2
Sb(III), DOC and refractory organic carbon concentrations in the Penzé estuary.

Salinity	Sb(III) (nM)	DOC (mg L^{-1})	Refractory organic carbon (mg L^{-1})
0.0	nd	2.4	2.07
1.1	nd		1.03
2.3	nd	2.4	1.24
2.9	nd		1.14
5.3	nd	1.7	0.95
7.5	nd		1.05
10.5	nd	1.6	1.61
12.9	0.65		0.81
17.6	0.70	1.4	0.84
20.5	0.77		0.67
27.0	0.99	1.3	0.43
34.6	0.07	0.9	0.17

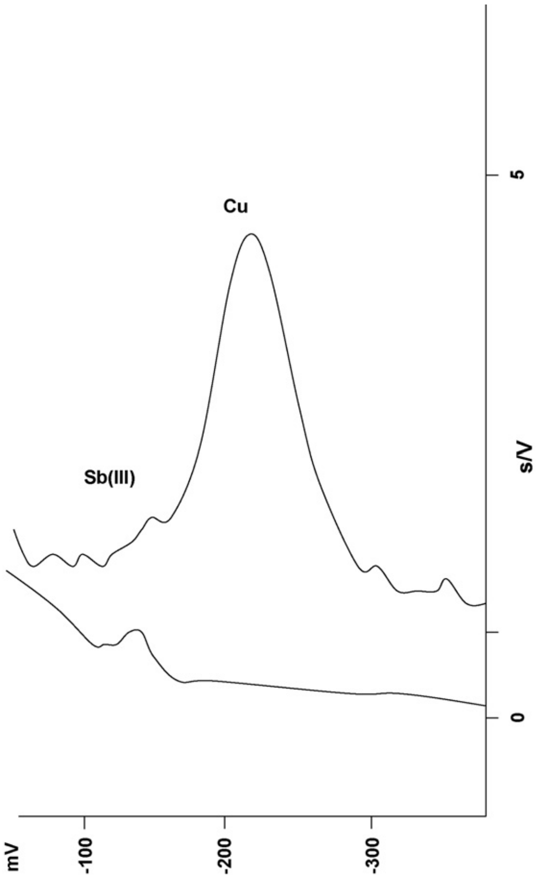

Fig. 7. Sb(III) measurement under application of (i) a single electrolysis potential (−450 mV) and (ii) a double electrolysis potential (−450 mV and −250 mV). Other parameters are the same as for Fig. 6.

where Sb(III) was previously measured (concentrations in the range 0.02–0.09 nM and a conservative behaviour), our system exhibited higher values.

Apart from the Andreae study [50] on the Ochlockonee estuary, the few studies that have dealt with Sb behaviour in estuaries [21,51–54] only reported total dissolved Sb concentrations. Sb behaviours in these estuaries were either conservative (e.g. St. Mary's and Satilla systems [53]) or non-conservative with Sb inputs to the water column. In the Tejo [51] and Tama [53] estuaries, anthropogenic inputs were at the origin of the positive deviation observed. In others systems (e. g. Geum, Savannah [53], Bravona [54]), inputs from sediment were responsible for Sb deviations. Because mineralisation of Sb in sediments can lead to a large release of Sb(III) in interstitial waters [50,55], this process and the remobilisation of this species to the water column should explain the Sb(III) deviation in the Penzé estuary.

The non-detection of Sb(III) in low-salinity estuarine samples should ensue from the complexation of Sb with organics. Organics could be present at levels sufficiently high to complex all Sb(III). The shape of the curves obtained in the standard addition of Sb(III) in these samples (e.g. at $S = 7$, Fig. 8) could support this hypothesis. These organic compounds could correspond to species that are not affected by acidification at pH 1 (i.e. fulvic substances). As a matter of fact, refractory organic carbon in these samples was above 1.0 mgC L^{-1} and represented more than 50% of the DOC (Table 2). Sb-organic complexes are assumed to be present in natural waters but have never been detected before because of the lack of sensitivity of the current techniques [9].

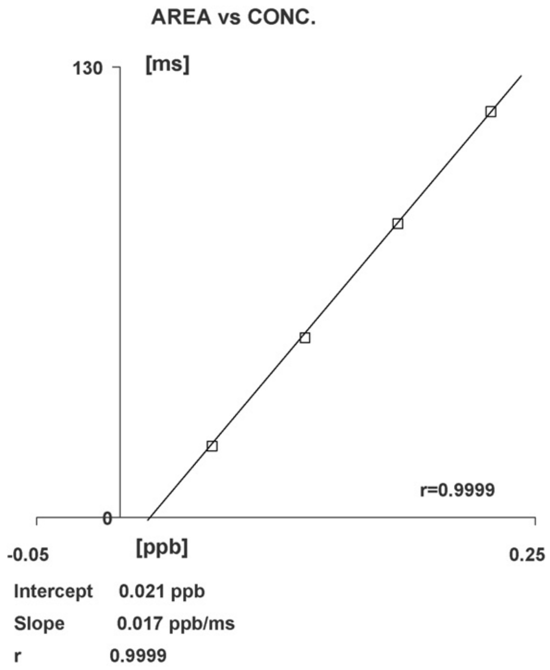

Fig. 8. Sb(III) standard additions in a sample from the Penzé estuary (Salinity = 7, [N_2H_4] = 0.1 M, [HCl] = 0.15 M, [Hg^{2+}] = 50 μM, t_e = 20 min, E_e = −450 mV and −250 mV, i_s = 3.5 μA).

4. Conclusion

We have established a stripping chronopotentiometric (SCP) method with a rotating mercury film electrode for the determination of antimony(III) in seawater. The accomplished detection limit is 0.07 nM (8 ng L^{-1}) for a 15-min deposition time. These characteristics are better than those obtained with the other chronopotentiometric methods available for natural waters; they are similar to those obtained by the most sensitive voltammetric methods. Moreover, the described procedure involves a supporting electrolyte less rich/acidic than most of the electrochemical methods reported for Sb measurement in seawater. By using a double electrolysis potential, low amounts of Sb(III) can be determined independently from sample Cu levels. This method had been successfully applied to the study of dissolved Sb(III) in an macrotidal estuary.

References

[1] United States Environmental Protection Agency, Water Related Fate of the 129 Priority Pollutants, vol. 1, USEPA, Washington, DC, USA, EP-440/4-79-029A, 1979.
[2] Council of the European Union, Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption, Off. J. L330, 321 (1998) 32.
[3] M. Fillela, N. Belzile, Y.-W. Chen, Earth-Sci. Rev. 59 (2002) 265.
[4] O. Dominguez-Renedo, M.J. Gomez Gonzalez, M.J. Arcos Martinez, Sensors 9 (2009) 219.
[5] D.S.T. Hjortenkrans, B.G. Bergbäck, A.V. Häggerud, Environ. Sci. Technol. 41 (2007) 5224.
[6] M.J. Ellwood, W.A. Maher, Deep Sea Res. I: Oceanogr. Res. Pap. 49 (2002) 1971.
[7] F. Quentel, M. Fillela, Anal. Chim. Acta 452 (2002) 237.
[8] F.-Y. Zheng, S.-H. Qian, S.-X. Li, X.-Q. Huang, L.-X. Lin, Anal. Sci. 22 (2006) 1319.
[9] M. Fillella, P.A. Williams, N. Belzile, Environ. Chem. 6 (2009) 95.
[10] H. Huang, S.C. Shu, J.H. Shih, C.J. Kuo, I.D. Chiu, Toxicology 129 (1998) 113.
[11] D. Cavallo, I. Iavicoli, A. Setini, A. Marinaccio, B. Perniconi, G. Carelli, S. Iavicoli, Environ. Mol. Mutagen. 40 (2002) 184.
[12] M.J. Nash, J.E. Maskall, S.J. Hill, J. Environ. Monit. 2 (2000) 97.
[13] T.-L. Deng, Y.-W. Chen, N. Belzile, Anal. Chim. Acta 432 (2001) 293.
[14] L. Abranko, Z. Stefanka, P. Fodor, Anal. Chim. Acta 493 (2003) 13.
[15] J.-Y. Cabon, C.L. Madec, Anal. Chim. Acta 504 (2004) 209.
[16] T. Zoltan, Z. Benzo, M.M.E. Marcano, C. Gomez, J. Salas, M. Quintal, Anal. Bioanal. Chem. 382 (2005) 1419.

[17] Z. Fan, Microchim. Acta 152 (2005) 29.
[18] A. Erdem, A.-E. Eroglu, Talanta 68 (2005) 86.
[19] G. Gillain, G. Duyckaerts, A. Disteche, Anal. Chim. Acta 106 (1979) 23.
[20] G. Capodoglio, C.M.G. van den Berg, G. Scarponi, J. Electroanal. Chem. 235 (1987) 275.
[21] C.M.G. van den Berg, S.H. Khan, P.J. Day, J.P. Riley, D.R. Turner, Estuar. Coast. Shelf Sci. 33 (1991) 309.
[22] A.M. Bond, S. Kratsis, O. Michael, G. Newman, Anal. Chim. Acta 372 (1998) 307.
[23] H. Guo, Y. Li, X. Chen, L. Nie, N. He, Sensors 5 (2005) 284.
[24] O. Dominguez Renedo, M.J. Arcos Martinez, Anal. Chim. Acta 589 (2007) 255.
[25] O. Dominguez Renedo, M.J. Gomez Gonzalez, M.J. Arcos Martinez, Sensors 9 (2009) 219.
[26] S.B. Adeloju, T.M. Young, Anal. Chim. Acta 302 (1995) 225.
[27] S.B. Adelojou, T.M. Young, D. Jagner, G.E. Batley, Analyst 123 (1998) 1971.
[28] N. Serrano, J.M. Diaz Cruz, C. Ariño, M. Esteban, Electroanalysis 19 (2007) 2039.
[29] V. Silva Santos, W. Rodrigues Santos, L.T. Kubota, C.R. Teixeira Tarley, J. Pharm. Biomed. Anal. 50 (2009) 151.
[30] R.D. Riso, M. Waeles, S. Garbarino, P. Le Corre, Anal. Bioanal. Chem. 379 (2004) 1113.
[31] R.D. Riso, M. Waeles, B. Pernet-Coudrier, P. Le Corre, Anal. Bioanal. Chem. 385 (2006) 76.
[32] J. Vandenhecke, M. Waeles, R.D. Riso, P. Le Corre, Anal. Bioanal. Chem. 388 (2007) 929.
[33] H. Eskilsson, C. Haraldsson, D. Jagner, Anal. Chim. Acta 175 (1985) 79.
[34] P. Salaun, B. Planer-Friedrich, C.M.G. van den Berg, Anal. Chim. Acta 585 (2007) 312.
[35] J. Wang, N. Foster, S. Armalis, D. Larson, A. Zirino, K. Olsen, Anal. Chim. Acta 310 (1995) 223.
[36] H. Huiliang, D. Jagner, L. Renman, Anal. Chim. Acta 202 (1987) 123.
[37] M.D. MacKinnon, Mar. Chem. 7 (1978) 17.
[38] F. Quentel, C. Madec, A. Lebihan, J. Courtot-Coupez, Anal. Lett. 19 (1986) 325.
[39] P.A. Waller, W.F. Pickering, Talanta 42 (1995) 197.
[40] M.M. Ghoneim, A.M. Hassaneim, E. Hammam, A.M. Beltagi, Fresenius J. Anal. Chem. 367 (2000) 378.
[41] R.D. Riso, M. Waeles, P. Monbet, C.J. Chaumery, Anal. Chim. Acta 410 (2000) 97.
[42] C. Hua, D. Jagner, L. Renman, Anal. Chim. Acta 197 (1987) 257.
[43] L. Anderson, D. Jagner, M. Josefson, Anal. Chem. 54 (1982) 1371.
[44] T.R. Gilbert, D.N. Hume, Anal. Chim. Acta 65 (1973) 451.
[45] P. Zong, Y. Nagaosa, Microchim. Acta 166 (2009) 139.
[46] G. Gillain, C. Brihaye, A routine speciation method for a pollution survey of coastal sea water, Oceanol. Acta 8 (1985) 231–235.
[47] J.J. Middelburg, D. Hoede, H.A. Van Der Sloot, C.H. Van Der Weijden, J. Wijkstra, Arsenic, antimony and vanadium in the North Atlantic Ocean, Geochim. Cosmochim. Acta 52 (1988) 2871–2878.
[48] C.H. Van der Weijden, G.J. de Lange, J.J. Middelburg, H.A. van der Sloot, D. Hoede, S. Shofiyah, Geochemical characteristics of Kau Bay water, Neth. J. Sea Res. 24 (1989) 583–589.
[49] M.O. Andreae, J.F. Asmode, P. Foster, L. Van't dack, Anal. Chem. 53 (1981) 1766.
[50] M.O. Andreae, in: C.S. Wong, E. Boyle, K.W. Bruland, J.D. Burton, E.D. Goldberg (Eds.), Trace Metals in Sea Water, Plenum, New York, 1983, pp. 1–19.
[51] M.O. Andreae, J.T. Byrd, P.N. Froehlich Jr., Environ. Sci. Technol. 17 (1983) 731.
[52] H.A. van der Sloot, D. Hoede, J. Wijkstra, J.C. Duinker, R.F. Nolting, Estuar. Coast. Shelf Sci. 21 (1985) 633.
[53] J.T. Byrd, Sci. Total Environ. 97 (1990) 301.
[54] C. Migon, C. Mori, Hydrobiology 392 (1999) 81.
[55] K.K. Bertine, D.S. Lee, in: C.S. Wong, E. Boyle, K.W. Bruland, J.D. Burton, E.D. Goldberg (Eds.), Trace Metals in Sea Water, Plenum, New York, 1983, pp. 21–38.