Anal Bioanal Chem (2004) 379: 1113–1119
DOI 10.1007/s00216-004-2677-z

ORIGINAL PAPER

Ricardo D. Riso · Matthieu Waeles
Sébastien Garbarino · Pierre Le Corre

Measurement of total selenium and selenium(IV) in seawater by stripping chronopotentiometry

Received: 8 March 2004 / Revised: 4 May 2004 / Accepted: 9 May 2004 / Published online: 13 July 2004

Abstract We developed a stripping chronopotentiometric method (constant current stripping analysis, CCSA) with a mercury film electrode for selenium quantification in seawater. A sensitivity and detection limit of 222 ms ng^{-1} l and 4 ng l^{-1} (50 pM), respectively, were accomplished for a 3-min electrolysis time. Compared to the other chronopotentiometric methods available for a single selenium measurement only in natural waters, our procedure exhibits a ten times better sensitivity. It, therefore, allows one to reach the current concentration thresholds found in coastal and oceanic waters (30–200 ng l^{-1}). Moreover, a simple change in operating conditions enables one to also quantify Se(IV), a toxic dissolved species. With respect to the other electrochemical methods of current use, our procedure is beneficial because of its ease-of-use: it needs neither degassing step, nor catalyser.

Keywords Stripping chronopotentiometry · Selenium · Selenium(IV) · Seawater

Introduction

The metalloid selenium is essential for the vital functions of marine organisms. The enzyme, glutathion peroxidase, requires it as a cofactor to catalyse reactions. Total selenium is found in seawater at low concentrations [1], i.e. within 30–200 ng l^{-1}; but, they can reach 400 ng l^{-1} in the estuaries submitted to high anthropogenic pressure [2, 3]. Anthropogenic selenium inputs to the marine environment come mainly from refining, fossil fuels combustion (coal, oil), mining and agriculture because of its use as pesticide and antifungal agent [4].

R. D. Riso (✉) · M. Waeles · S. Garbarino · P. Le Corre
Laboratoire de Chimie Marine,
Université de Bretagne Occidentale (IUEM),
UMR CNRS 7127 Roscoff, Place Nicolas Copernic,
Technopôle Brest-Iroise, 29280 Plouzané, France
E-mail: riso@univ-brest.fr

Though being useful, selenium is also known for its toxicity, which depends not only on its total concentration, but also on its speciation. In seawater, dissolved selenium is, indeed, found as inorganic compound at the following oxidation degrees +IV ($HSeO_3^-$, SeO_3^{2-}) and +VI (SeO_4^{2-}); among the selenium species, the latter, selenate, is the major one, whereas the former, selenite, shows the highest toxicity [5].

Selenium can be measured by various techniques such as hydride generation followed with electrothermal atomic absorption spectrometry [6, 7], atomic fluorescence spectrometry [8], high performance liquid chromatography [9], gas chromatography [10], inductively coupled plasma mass spectrometry [11] and electrochemical stripping methods. Among them, the electrochemical stripping ones seem a good choice for metal analysis because of their performances, especially their very high-sensitivity and high-selectivity associated with quite low detection thresholds. Moreover, the seawater matrix is an "ideal" electrolyte for such measurements. It is worth noting that the instruments required for these low-cost and quick measurements are compact and well-suited for field measurements on oceanographic vessels.

All electrochemical stripping procedures require two steps: over the first one, the metal of concern is preconcentrated at the surface of the working electrode, and the second step corresponds to the metal stripping. The current methods for selenium electrochemical analysis are based on voltammetry, i.e. cathodic stripping voltammetry (CSV) [12–22], catalytic CSV [5, 23] or anodic stripping voltammetry (ASV) [24]. Even though all of them reach detection limits sufficient for selenium quantification in the seawater, the existence of organic matter in the studied medium restricts their use. So, another possible solution would be chronopotentiometry, i.e., constant current stripping analysis (CCSA). With this technique, the pre-concentration step is like the one in voltammetry procedures, whereas stripping is performed through the application of a constant current instead of a potential sweeping. In CCSA, the potential change of the working electrode is measured as a func-

tion of time and the metal determination is therefore not based on current measurement. This eliminates measurement errors caused by the liquid resistance between the electrodes and the potential drop over the electrical double layer around the electrode. This technique is then much less affected by adsorbed organic matter than other technique such ASV [25, 26]. Moreover, it enables one to work with non-deoxigenated samples [27–29], which avoids perturbations in the medium induced by addition of a gas, e.g., variation of the chemical equilibrium, pH,... and saves about 10 min over the whole analysis time.

Till now, selenium quantification by stripping chronopotentiometry had been carried out only in biological matrices and natural waters [30–32] where it has been found at concentrations higher (i.e., within 0.5–10 $\mu g\ l^{-1}$) than those observed in seawater; no chronopotentiometric method is available for selenium analysis in the seawater. This led us to develop a sensitive and reliable procedure for routine measurement of total selenium in this medium. In addition, our aim was also to use it to assess, among selenium species, the concentration of the most toxic of them, Se(IV).

Experimental

Instrumentation

A TraceLab PSU22 potentiometric stripping unit (RADIOMETER Copenhagen) with a potential sampling rate of 90 kHz during the stripping step [28], interfaced to a personal computer and controlled by the TAP2 Trace Talk program (RADIOMETER) was used to get the potentiograms. All instrumental settings (electrolysis-potential and -time, stirring, stripping current, evaluation of stripping signals, calculation of sample pre-concentrations and statistical treatment of data) were pre-programmed into the TAP2 program and automatically executed.

The system operates on a three-electrode basis: (1) a rotating glassy carbon electrode (EDI101T, 5 mm in diameter) coated with a mercury film and connected to a CTV101 unit that provides a constant rotating rate, (2) a laboratory-made Ag/AgCl (Saturated KCl, suprapur MERCK) reference electrode, and (3) a platinum auxiliary electrode (P136, RADIOMETER). The third one is isolated from the sample via a 0.1-M HNO_3 solution-filled saline bridge (suprapur MERCK). This prevents chlorine from forming at the auxiliary electrode during the stripping step in a chloride-rich matrix when relatively high currents are used. Indeed, the existence of chlorine near the working electrode may induce selenite oxidation into selenate, a non-electroactive species, and therefore would cause signal loss [33].

The mercury film is plated on the working electrode just before the first selenium measurement. It is deposited through the application of −900 mV for 10 min from Hg^{2+} ions added to the sample at the 50 μM concentration. Then, the electrode is conditioned for 30 s under a −500-mV potential prior to any electrolysis-stripping cycle.

During mercury film plating, electrode conditioning and pre-concentration step, the angular velocity of the working electrode was kept constant at 3,000 rpm. It was set to the lowest possible value (3 rpm) throughout the stripping step.

Pre-treatment of the working electrode

As the exchange of electrons occurs at the surface of the working electrode, physical conditioning of the glassy carbon is critical to obtain a high quality mercury film electrode. Before the beginning of the trials, the electrode was polished with a diamond paste of gradually decreasing grain size (6, 3, 1 and 0.25 μm) until a mirror like surface was obtained. A washing with ethanol and a ultrasonic cleaning was then conducted to remove residual particles.

Chemicals

All solutions were made with deionised water from a Milli-Q RG system. The $Hg(NO_3)_2$ solution (0.01 M) was prepared by dissolving Hg (hexadistilled) in concentrated HNO_3 (suprapur MERCK). The working standard solution of Se(IV) (10 ng L^{-1}) was prepared every day [33] by dilution from a $SeO_2$1,000 ppm stock (MERCK). The other reagents used, HCl (30%), NaOH (30%) and $CaCl_2$, $4H_2O$ (1.6 M), were of suprapur quality from MERCK. All handling and measurements were performed in a 100-class laminar flow chamber.

Sample collection and treatment

A coastal seawater was collected in the Bay of Brest (France) with a polypropylene-made bottle specifically designed for trace metal analysis (NOEX-modified by INSU, France). In the next 30 min, the seawater was passed through a 0.45-μm-MILLIPORE-HA filter, then fractionated into aliquots stored in Nalgene flasks and freezed. Among selenium species, Se(IV) is the only electroactive one. Total selenium measurement needs prior UV-digestion of the seawater to transform the various chemical species into Se(IV) under appropriate chemical conditions. Various procedures being available [5, 6, 20]; we selected the one described by Lange and van den Berg [5] because of its simplicity, which limits sample contamination. It consists in a 4-hour UV-digestion at pH > 8.3.

Method principle

Constant current stripping analysis consists of two steps. Over the first one (electrolysis) Se(IV) is reduced into

Se(-II) in acidic medium through the application of judiciously chosen potential. According to Kolthoff and Lingane [34] hydrogen selenide is the first produced compound:

$$H_2SeO_3 + 6H^+ + 6e^- \rightarrow H_2Se + 3H_2O \quad (1)$$

Then, in presence of mercury, it makes a poorly-soluble salt, HgSe, as follows:

$$H_2Se + Hg \rightarrow HgSe + 2H^+ + 2e^- \quad (2)$$

The overall reaction can be written as follows:

$$H_2SeO_3 + Hg + 4H^+ + 4e^- \rightarrow HgSe + 3H_2O \quad (3)$$

Over the second step (stripping), the Hg(II), previously deposited at the electrode surface as HgSe, is reduced into Hg(0) by application of a constant current:

$$HgSe + 2e^- + 2H^+ \rightarrow Hg + H_2Se \quad (4)$$

Selenium amount is, therefore, indirectly determined from the measured signal corresponding to the reduction of HgSe to metal mercury. During the stripping step, the potentiometric stripping unit measures the potential up to 90,000 times per second and counts how many times the measured potential is within a certain potential interval of 2 mV. The number of counts versus potential is registered as the scan curve. The signal is given by the area of the peak corresponding to the time, t_s used to strip HgSe from the electrode and expressed in millisecond (ms) as follows [30]:

$$t_S \propto \frac{[Se(IV)]t_eAK}{i} \quad (5)$$

where t_e is the electrolysis time, [Se(IV)] is the bulk concentration of the electroactive selenium, K is a constant that incorporates the diffusion coefficient of selenium and the thickness of the diffusion layer during electrolysis, i is the stripping current and A is the electrode surface area.

Results and discussion

Optimum chemical conditions for total selenium measurement

H_3O^+ and Cl^- concentration

Selenium is deposited as HgSe at the electrode surface further to the formation of an intermediate species, H_2Se, in acidic medium (1). Hydrochloric and sulphuric acids are the most used to get the H_3O^+ desired concentration in the medium [21]. In the specific case of chronopotentiometry, among these two acids the former is better because it allows a very good peak resolution together with a higher sensitivity [35]. Moreover, chloride is known to stabilise the formation of certain intermetallic complexes at the electrode surface [5]. We investigated the way selenium signal was affected by H_3O^+ and Cl^- through addition of HCl and $CaCl_2$ to seawater. Figure 1 shows a signal increase concomitant with elevation in H_3O^+ and Cl^- concentration. However, a H_3O^+ concentration more than 0.6 M, or a Cl^- one higher than 1 M (Fig. 1g–i) made sometimes appear a new peak that overlapped the selenium one and prevented us from conducting analyses. This new peak may correspond to a UV-digestion-released species, e.g., Cu liable to form an intermetallic complex with selenium during the deposition step [21]. By using 0.4 M H_3O^+ and 0.7 M Cl^- this interference was no longer observed. This led us to recommend these acid and chloride concentrations for total selenium measurements. It is worth noting that seawater initially contained 0.545 M Cl^-, which are not taken into account in the proposed concentration of 0.7 M.

Hg^{2+} concentration

The use of a mercury film electrode as working electrode requires to keep the concentration of Hg^{2+} in solution

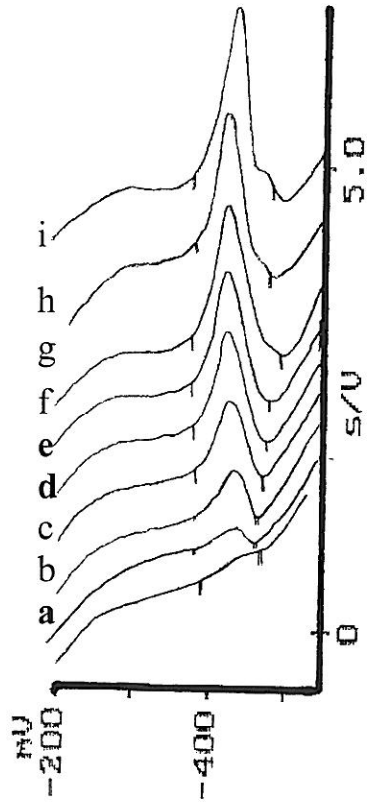

Fig. 1a–i Influence of H_3O^+ and Cl^- concentration on selenium measurement (UV-digested seawater + 2.5 nM Se(IV); $[Hg^{2+}]$ = 50 μM; E_e = −140 mV; i = −14 μA; t_e = 3 min): **a** $[H_3O^+]$ = 0.16 M, $[Cl^-]$ = 0.29 M; **b** $[H_3O^+]$ = 0.24 M, $[Cl^-]$ = 0.43 M; **c** $[H_3O^+]$ = 0.34 M, $[Cl^-]$ = 0.61 M; **d** $[H_3O^+]$ = 0.41 M, $[Cl^-]$ = 0.73 M; **e** $[H_3O^+]$ = 0.48 M, $[Cl^-]$ = 0.86 M; **f** $[H_3O^+]$ = 0.54 M, $[Cl^-]$ = 0.97 M; **g** $[H_3O^+]$ = 0.60 M, $[Cl^-]$ = 1.09 M; **h** $[H_3O^+]$ = 0.66 M, $[Cl^-]$ = 1.19 M; **i** $[H_3O^+]$ = 0.72 M, $[Cl^-]$ = 1.30 M

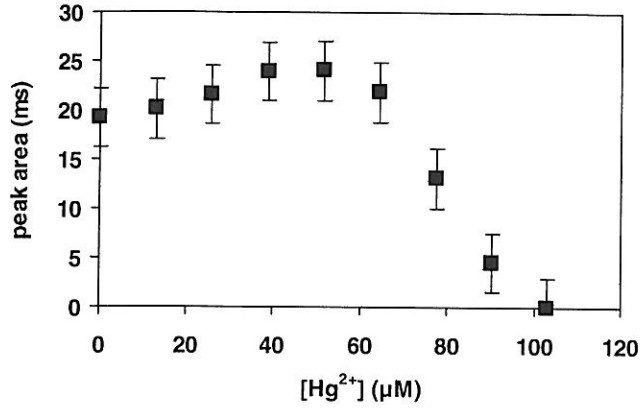

Fig. 2 Influence of Hg^{2+} concentration on selenium measurement (UV-digested seawater + 2.5 nM Se(IV); $[H_3O^+]$ = 0.4 M; $[Cl^-]$ = 0.7 M; E_e = −140 mV; i = −14 µA; t_e = 3 min)

and the amount of electrode-plated Hg(0) in equilibrium. Further to our experiments, Fig. 2 clearly evidences that the best selenium signal was produced for Hg^{2+} concentration in the solution within 40 and 60 µM. This observation led us to later use a 50 µM concentration.

Optimum electrochemical conditions for total selenium measurement

Electrolysis potential (E_e)

During the deposition step, Se(IV) is reduced to Se(-II) in acidic medium according to (1). This reaction occurs at a potential of −50 mV vs. Ag/AgCl [36]. We followed selenium signal evolution versus varying potential applied potential (between −100 and −240 mV) (Fig. 3).

One should note a first increase of the signal from −100 mV to a maximum at −140 mV, then a reduction of its intensity between −140 and −240 mV. The reduction of the selenium signal at potentials more negative than −140 mV could be due to the adsorption of Cu_2Se at the working electrode [37]. The maximum value, −140 mV, was therefore chosen for the next experiments.

Stripping current (i)

The current applied over stripping is likely the most influencing factors on the method sensitivity. Figure 4 plots selenium peak area versus $i^{-1}(t_s = -327i^{-1} + 2)$. It highlights enhancement of the response when the applied current was varied from −30 to −13 µA and shows agreement with the theory [relation (5)]. It is worth noting that application of the lowest currents in absolute values results in the highest intensities. However, the presence of strong residual currents brings noise and causes poor reproducibility. By taking all these considerations into account, a −14-µA stripping current was applied in further experiments.

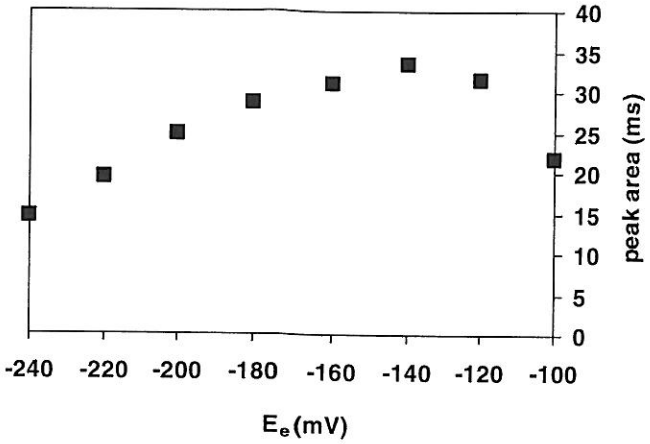

Fig. 3 Influence of electrolysis potential on selenium measurement (UV-digested seawater + 2.5 nM Se(IV); $[H_3O^+]$ = 0.4 M; $[Cl^-]$ = 0.7 M; $[Hg^{2+}]$ = 50 µM; i = −14 µA; t_e = 3 min)

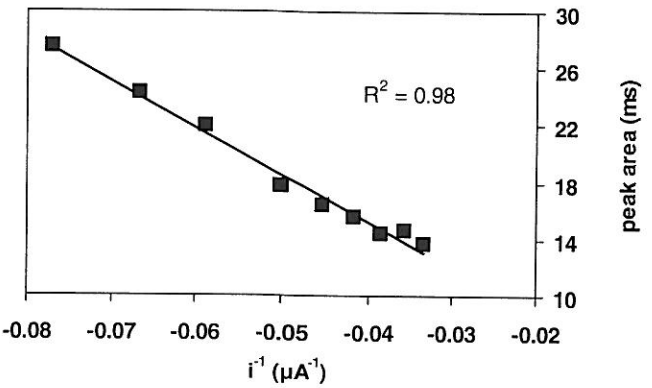

Fig. 4 Influence of stripping current on selenium measurement (UV-digested seawater + 2.5 nM Se(IV); $[H_3O^+]$ = 0.4 M; $[Cl^-]$ = 0.7 M; $[Hg^{2+}]$ = 50 µM; E_e = −140 mV; t_e = 3 min)

Electrolysis time (t_e)

Relation (5) sets that the peak area is proportional to the electrolysis time. Figure 5 shows a linear increase between one and about 4 min. For longer electrolysis times, selenium deposition at the electrode surface is less beneficial: under the analytical conditions used, the amount of deposited selenium can be limited by the saturation of the electrode surface [32]. Consequently, this parameter was fixed to 3 min. Table 1 lists all the chemical and electrochemical parameters selected for the analysis of total selenium in seawater.

Validation of the method

Repeatability was estimated over seven repetitive electrolysis-stripping cycles conducted on the same seawater sample under the conditions listed in Table 1. With a

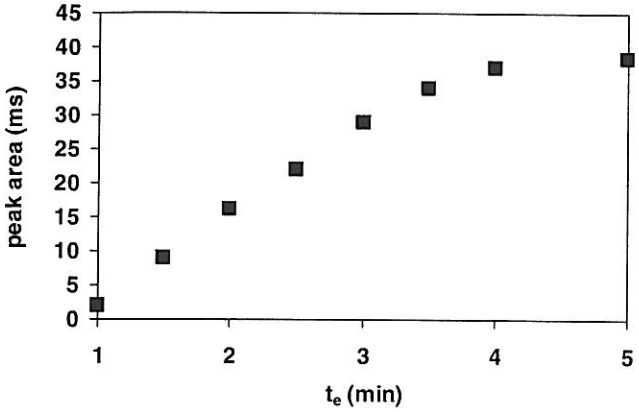

Fig. 5 Influence of electrolysis time on selenium measurement (UV-digested + 2.5 nM Se(IV); $[H_3O^+]$ = 0.4 M; $[Cl^-]$ = 0.7 M; $[Hg^{2+}]$ = 50 μM; E_e = −140 mV; i = −14 μA)

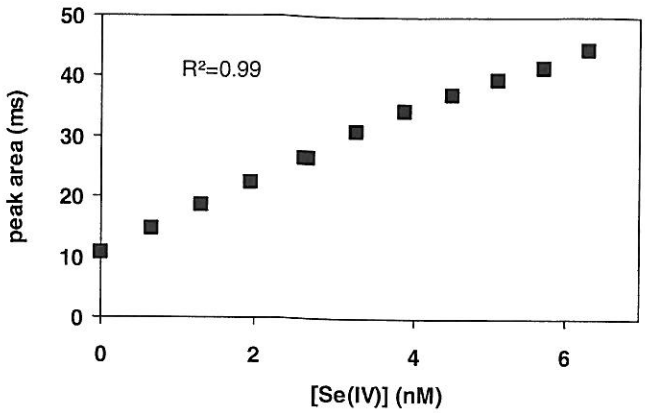

Fig. 6 Influence of selenium concentration on selenium measurement (UV-digested; $[H_3O^+]$ = 0.4 M; $[Cl^-]$ = 0.7 M; $[Hg^{2+}]$ = 50 μM; E_e = −140 mV; i = −14 μA; t_e = 3 min)

Table 1 Parameters selected for total selenium and selenium(IV) measurements

	Total Se	Se(IV)
$[H_3O^+]$ (M)	0.4	1.5
$[Hg^{2+}]$ (μM)	50	300
$[Cl^-]$ (M)	0.7	2.7
Electrolysis potential (E_e, mV)	−140	−180
Electrolysis time (t_e, min)	3	10
Stripping current (i, μA)	−14	−14

3-min electrolysis time, repeatability was 3% at a concentration level of 50 ng l^{-1}.

Reproducibility was evaluated through seven repetitive analyses of a seawater sample. The final concentration found for total selenium was 51 ± 3 ng l^{-1}, which corresponds to a 6% reproducibility.

The method sensitivity is given by the slope of the standard-addition calibration plot; it was, here, 222 ms ng^{-1} l. This value is about ten times higher than the one determined by Adeloju and Young [32] with a similar electrolysis time.

Assessment of the detection limit at the 3σ level, after a 3-min electrolysis time, from seven consecutive electrolysis-stripping cycles [38] on a seawater sample containing about 50 ng l^{-1} of total selenium gave 4 ng l^{-1}. Table 2 introduces the final results obtained for the statistical validation of the total selenium measurement. Selenium response linearity was tested by spiking a sample with known amounts of standard. Figure 6 highlights the linearity of the response in the range 0–4 nM (0–320 ng l^{-1}).

Table 2 Analytical performances for total selenium and selenium(IV) measurements

	Total Se	Se(IV)
Repeatability (%)	3	8
Reproducibility (%)	6	14
Sensitivity (ms ng^{-1} l)	222	92
Detection limit (ng l^{-1})	4	7

Performance comparison with other CCSA methods

Table 3 sums up the CCSA-produced detection limits reported in the literature about total selenium analysis. The detection limit reported by Adeloju and Young [32] is 10 ng l^{-1} under a 60-min electrolysis time. Such a detection threshold would theoretically allow selenium measurement in the seawater, but the time needed for analysis is too long for routine procedure. By using another type of electrode, Adeloju et al. [33] obtained a detection limit of 100 ng l^{-1} for a 2-min electrolysis; this elevated value prevents one from applying the described method to the determination of selenium in the marine ecosystems (current concentrations in the range 30–200 ng l^{-1}). The method proposed here is easily implemented, and its low detection limit makes it a valuable and reliable tool for total selenium quantification in the seawater.

Se(IV) measurement

As previously recalled, Se(IV) is the only electroactive species among selenium ones. To reach it the electrochemical measurement must be conducted on a non-UV-

Table 3 CCSA methods used for the measurements of total selenium

References	t_e (min)	Sensitivity (ms ng^{-1} l)	Detection limit (ng l^{-1})
Adeloju and Young [32]	2.5	16	700
	60	249	10
Adeloju et al. [33]	2	2.2	100
This study	3	222	4

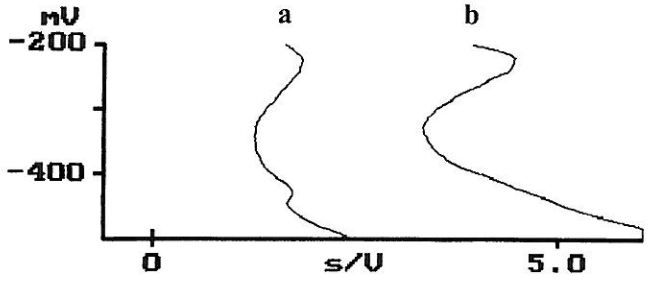

Fig. 7a, b Selenium measurement under conditions retained for total selenium measurement (Table 1) **a** with UV-digestion and **b** without UV-digestion

digested sample in order to not affect the selenium speciation. In such a way, the organic substances contained in the seawater can be deposited at the electrode surface, and thus reduce analyte deposition or even prevent it. Even though CCSA technique is less affected than the current voltammetric methods by the organic matter, our experimental data depicted in Fig. 7 show that the analysis of non-UV-digested seawater sample with our method is no longer possible: indeed, the stripping curve displays a significant elevation of the residual current accompanied with the loss of selenium signal. The latter likely results from the quantification of only the Se(IV) because of the missing UV-digestion, whereas the former is due to the adsorbed organic matter.

Prior to Se(IV) concentration measurement in the seawater, the chemical and electrochemical parameters of the analysis had to be modified. The whole test procedure was, therefore, redone on non-UV-digested seawater.

Optimum chemical and electrochemical conditions for Se(IV) measurement

Table 1 reports the most suitable conditions for Se(IV) analysis. Compared to the condition retained for total selenium measurement, Se(IV) quantification requires a medium about five times more concentrated in H_3O^+, Hg^{2+} and Cl^-. Moreover, analysis needs to be carried out with another value for electrolysis-potential (−180 mV) and a longer electrolysis time (10 min).

The results of statistical validation of the Se(IV) measurement parameters are listed in Table 2. Accuracy of this procedure was evaluated by five repetitive analyses of a certified reference seawater sample (CASS-3 from the National Research Council of Canada) The concentration we measured (25 ± 4 ng l^{-1}) felt within the certified limits (20 ± 5 ng l^{-1}), and thus highlighted the good accuracy of the technique.

Analytical application

Figure 8a and b depict the total selenium and Se(IV) concentrations measured in a coastal seawater sample

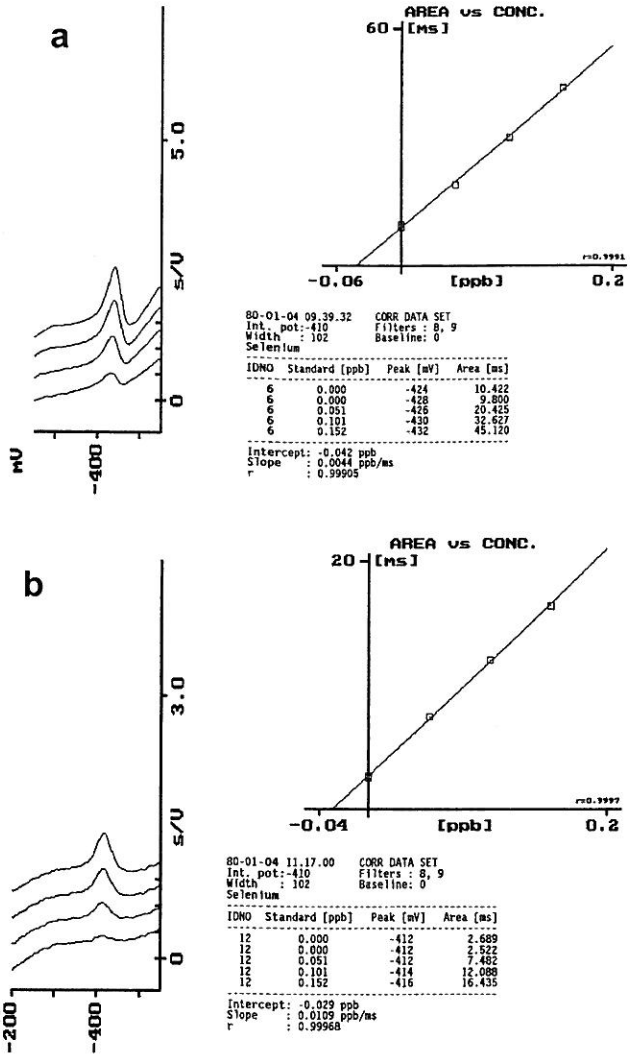

Fig. 8a, b Measurement of **a** total selenium in an UV-digested seawater sample under the optimum conditions (Table 1) and **b** Se(IV) in a non-UV-digested seawater sample under the optimum conditions (Table 1)

under the optimal conditions (Table 1). These two analyses were made by spiking the seawater samples with known selenium concentrations. The average concentrations found were 42 ± 3 ng l^{-1} for total selenium and 29 ± 5 ng l^{-1} for Se(IV).

Conclusion

A chronopotentiometric method (CCSA) with a TraceLab PSU22 (RADIOMETER Copenhagen) and a mercury film electrode (5 mm) for measurement of total selenium in seawater was developed. The accomplished sensitivity and detection limit for a 3-min electrolysis time were 222 ms ng^{-1} l and 4 ng l^{-1} (50 pM), respectively. These characteristics allow one to measure total selenium concentrations alike those currently found in

coastal and oceanic waters. Change in the operating conditions permitted us to also quantify Se(IV), the selenium species with the highest toxicity: sensitivity and detection limit were, then, 92 ms ng^{-1} l and 7 ng l^{-1} (90 pM), respectively for a 10-min electrolysis time.

The reported method proved its suitability for seawater analysis. Among its assets, one should cite its low-cost and apparatus reduced-bulk which facilitates its implementation on-board oceanographic vessels. Compared to the other available electrochemical techniques, its use is simpler because it requires neither degasing, nor catalyser. Its only need is the mercury film plating.

Acknowledgements We sincerely thank Jean-Pierre Oldra for pretreating the glassy carbon electrode surface with great skill and Dr Marie-Paule Friocourt for revising English.

References

1. Cutter GA, Cutter LS (1998) Mar Chem 61:25–36
2. van der Sloot HA, Hoede D, Wijkstra J, Duinker JC, Nolting RF (1985) Est Coastal Shelf Sci 21:633–651
3. Cutter GA (1989) Est Coastal Shelf Sci 28:13–34
4. Munoz Olivas R, Donnart OFX, Camara C, Quevauviller P (1994) Anal Chim Acta 286:357–370
5. Lange B, van den Berg CMG (2000) Anal Chim Acta 418:33–42
6. Cabon J-Y, Erler W (1998) Analyst 123:1565–1569
7. Lespes G, Séby F, Sarradin P-M, Potin Gautier M (1994) J Anal Atom Spectrom 9:1433–1439
8. Rodriguez Rodriguez EM, Sanz Alaejos M, Diaz Romero C (1996) Anal Chim Acta 334:161–166
9. Guerin T, Astruc A, Astruc M, Batel A, Borsi M (1997) J Chromatogr Sci 35:213–220
10. Measures CI, Burton JD (1980) Anal Chim Acta 120:177–186
11. Buckley WT, Budac JJ, Godfrey DV, Koenig KM (1992) Anal Chem 64:724–729
12. Henze G, Monks P, Tolg G, Umland E, WeBling E (1969) Fresenius Z Anal Chem 295:1–6
13. Ferri T, Sangiorgio P (1999) Anal Chim Acta 385:337–343
14. Quentel F, Elleouet C (1999) Electroanalysis 11:47–51
15. Baltensperger U, Hertz J (1985) Anal Chim Acta 172:49–56
16. Rurikova D, Kunakova I (1999) Chem Pap 53:246–251
17. van den Berg CMG, Khan SH (1990) Anal Chim Acta 231:221–229
18. Elleouet C, Quentel F, Madec C (1996) Water Res 30:909–914
19. Zelic M, Branica M (1990) Electroanalysis 2:455–462
20. de Carvalho LM, Schwedt G, Henze G, Sander S (1999) Analyst 124:1803–1809
21. Adeloju SB, Bond AM, Briggs MH, Hugues HC (1983) Anal Chem 55:2076–2082
22. Ochsenkühn-Petropoulou M, Tsopelas F (2002) Anal Chim Acta 467:167–178
23. Wang J, Lu J (1993) Anal Chim Acta 274:219–224
24. Bryce DW, Izquierdo A, de Castro MDL (1995) Anal Chim Acta 308:96–101
25. Estela JM, Tomas C, Cladera A, Cerda V (1995) CRC Crit Rev Anal Chem 25:91–141
26. Soares HMVM, Vasconcelos MTSD (1995) Anal Chim Acta 303:255–263
27. Jagner D (1979) Anal Chem 51:342–345
28. Riso RD, Le Corre P, Chaumery CJ (1997) Anal Chim Acta 351:83–89
29. Riso RD, Monbet P, Le Corre P (1997) Analyst 122:1593–1596
30. Hua C, Jagner D, Renman L (1987) Anal Chim Acta 197:257–264
31. Lambert DF, Turoczy NJ (2000) Anal Chim Acta 408:97–102
32. Adeloju SB, Young TM (1994) Anal Chim Acta 296:69–76
33. Adeloju SB, Jagner D, Renman L (1997) Anal Chim Acta 338:199–207
34. Kolthoff IM, Lingane JJ (eds) (1952) Polarography, 2nd edn. Wiley, New York
35. Adeloju SB (1989) Analyst 114:455–461
36. Christian GD, Knoblock EC, Purdy WC (1963) Anal Chem 35:1128–1132
37. van den Berg CMG, Khan SH (1990) Anal Chim Acta 231:221–229
38. Anderson L, Jagner D, Josefson M (1982) Anal Chem 54:1371–1376
39. Cutter GA (1978) Anal Chim Acta 98:59–66