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Silicate determination in sea water: Toward a reagentless electrochemical method

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Abstract

Silicate has been determined in sea water by four different electrochemical methods based on the detection of the silicomolybdic complex formed in acidic media by the reaction between silicate and molybdenum salts. The first two methods are based on the addition of molybdate and protons in a seawater sample in an electrochemical cell. Cyclic voltammetry presents two reduction and two oxidation peaks giving four values of the concentration and therefore increasing the precision. Then chronoamperometry is performed on an electrode held at a constant potential. A semi-autonomous method has been developed based on the electrochemical anodic oxidation of molybdenum, the complexation of the oxidation product with silicate and the detection of the complex by cyclic voltammetry. This method is tested and compared with the classical colorimetric one during ANT XXIII/3 cruise across Drake Passage (January–February 2006). The detection limit is 1 μM and the deviation between both methods is less than 3% for concentrations higher than 10 μM . Finally a complete reagentless method with a precision of 2.6% is described based on the simultaneous formation of the molybdenum salt and protons in a divided electrochemical cell. This latter method should be very useful for developing a reagentless sensor suitable for long term *in situ* deployments on oceanic biogeochemical observatories.

Keywords: Silicate; Chronoamperometry; Voltammetry; Molybdenum; Reagentless method; Drake Passage

1. Introduction

Silicate is an essential nutrient element for organisms in aquatic environments and it is important to measure it

accurately. Quantitative analysis in seawater is based on its reaction with molybdenum salts in acidic medium to form a silicomolybdic complex. This technique based on spectrophotometry has received a wide acceptance because of its precision. Alternate methods based on the electrochemical determination of the silicomolybdic complex have recently been proposed. Silicate is a non electroactive ion but Er-Kang and Meng-Xia (1982)

have shown that its electrochemical determination through an amperometric detection in flow injection analysis was feasible. Fogg and Bsebsu (1983) showed that pulse voltammetry could improve the sensitivity. Carpenter et al. (1997) have described microelectrode procedures for the determination of silicate in water with the addition of molybdate. Then Hodgson and Pletcher (1998) improved this study for both silicate and phosphate determination using amperometric detection.

ANAIS (Thouren et al., 2003) is one of the few analyzers adapted for *in situ* silicate measurements and for profiling the water column to 1000 m depth. But submersible colorimetric analyzers need significant energy and reagents, and their main drawbacks are their lack of autonomy, weight and size. Progress toward miniaturization and decrease in energy consumption requires to investigate new methodological avenues. Electrochemistry provides some methods for achieving excellent 'figures of merit' (lifetime, high precision, low detection limit, fast response time, good reproducibility). For instance Luther et al. (2001) used voltammetry in extreme conditions such as hydrothermal vents with high pressure and temperature gradients.

We present here the development of an electrochemical reagentless method for silicate determination and its application in a field study in the southern ocean across Drake Passage. It is ideally suited for such application since across Drake Passage, silicate is present in the whole concentrations range found in the open ocean. This new method should be very useful for the development of a new generation sensor of a small size, with little power requirement and without reagent. It could be adapted on observatories for long term *in situ* measurements.

The paper is structured as follows. The Section 2 presents the different methods used to measure silicate and the data set collected within Drake Passage. The electrochemical methods with the addition of reagent are presented in Section 3. Then the development of the semi-autonomous detection, the on board comparison of this method with the classical silicate detection (colorimetry) and field study results are reported. Finally a complete reagentless method is described and we conclude by investigating potential routes of improvement of our electrochemical method.

2. Methods

2.1. Reagents and calibration standards

All solutions were prepared in Milli-Q water (Millipore Milli-Q water system) with reagent grade salts.

Artificial seawater for standards calibration, silicate and phosphate samples was prepared at a salinity of 34.7 g/L with 32.13 g of sodium chloride (NaCl), 7.13 g of magnesium-sulfate heptahydrate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) and 0.17 g of sodium carbonate (NaCO_3), by liter of Milli-Q water.

The three reagents used for silicate spectrophotometric determinations are:

- an acidified ammonium heptamolybdate solution (10 g of ammonium heptamolybdate, 40 mL of sulphuric acid, H_2SO_4 5N in 1000 mL of Milli-Q water),
- an oxalic solution (7 g of oxalic acid and 50 mL H_2SO_4 in 1000 mL of Milli-Q water and 1 mL of Aerosol 22(Sigma)),
- an ascorbic solution (17.8 g of L-ascorbic acid and 25 mL of acetone in 1000 mL of Milli-Q water and 1 mL of Aerosol 22).

Working calibration standards were prepared as described in the WOCE operation and method manual (Gordon et al., 1993) with sodium silicofluoride (Na_2SiF_6 , Merck) and potassium dihydrogen phosphate (KH_2PO_4 , Merck).

2.2. Colorimetric method

Colorimetric detection was developed following Le Corre and Tréguer's (1976) method. Comparison of the colorimetric and voltammetric methods was made in the laboratory with an Auto-Analyzer Technicon II (AAII, Bran Luebbe). On board comparison of both methods was made with an Auto-Analyzer (Skalar). Baseline was made with artificial seawater. Standards solutions used on board were tested back in the laboratory with commercial standards (OSIL, 1000 μM) and no difference was observed.

Reproducibility tests were performed on board. The precision obtained for the concentration ranges of the samples is reported in Table 1, and ranged between 1.5 and 2.9%. For the purpose of this discussion, we consider a precision of 2.9%. This precision is obtained by a multiplication of the standard deviation by two (2σ).

2.3. Electrochemical methods

The reference electrode was an Ag/AgCl electrode (Metrohm). All the following potentials are given relative to this electrode.

Electrochemical measurements were carried out with a potentiostat μ -Autolab III (Metrohm).

Table 1

Precision of on board colorimetric method for various silicate concentration ranges

Sample concentrations (μM)	0–10	10–20	20–40	40–50	60–70	80	90	100	110–120	120–140
Precision (%)	1.9	2.9	1.8	2.8	2.2	1.5	2.0	2.1	2.6	1.9

Voltammograms at a stationary or rotating disk electrode were recorded in a three electrode cell with a carbon counter electrode. Working electrodes were in gold, platinum, or glassy carbon (Metrohm, area 0.07 cm^2). The glassy carbon disk was polished with lapping film sheet (3 M Aluminium Oxide, $1\ \mu\text{m}$) before each measurement. Chronoamperometry was made with a glassy carbon disc working electrode (Metrohm, area 0.07 cm^2) held at a constant potential of 200 mV.

The molybdenum electrode (Good Fellow Metals, purity: 99.9%) has an area of 1.2 cm^2 . For the semi-autonomous method, molybdate was produced by molybdenum anodic oxidation performed at a constant electrolysis current (50 mA) during 420 s, in a 5 mL cell. pH is adjusted to 1.5 by sulphuric acid H_2SO_4 5N addition.

The reagentless method is based on the use of a 6 mL cell divided in two by a porous polyethylene membrane thus each part of the cell was filled with 3 mL of the solution. Molybdenum, reference and sensing electrodes were in the anodic compartment while the counter electrode was in the cathodic compartment. Molybdate was produced by molybdenum anodic oxidation performed at a constant electrolysis current (50 mA) during 360 s.

For the voltammetric measurements, four calibration curves were made with the two oxidation peaks and the two reduction peaks.

2.4. Seawater collection

The collection of seawater samples and surface-to-bottom Conductivity Temperature Depth casts (CTD casts) were made during the ANT XXIII/3 cruise aboard the R/V Polarstern during the austral summer 2006. A poleward transect from Puntas Arenas (Chile) to the Antarctic Peninsula took place from January 14th to January 26th 2006, and the return (northward) transect from January 31st to February 8th. Among the 105 CTD casts performed, 22 profiles were analyzed both with the colorimetric and the voltammetric methods for silicate determination:

- 8 CTD stations during the outward journey with 22 levels at each station,
- 14 stations during the return transect with between 11 and 22 levels at each station.

Seawater was collected using 12 L Niskin bottles mounted on a Sea Bird SBE 32 Rosette equipped with a CTDO₂ Sea Bird SBE 11.

Samples were collected in Nalgene flasks following the sampling procedure by [Gordon et al. \(1993\)](#) and the analyses were performed either immediately after sampling or on samples stored at $4\text{ }^\circ\text{C}$ and analyzed within 8 h.

Two bottles were closed at the same depth at station DRA 075, and reproducibility tests of both methods were made at different stations.

3. Results and discussion

3.1. Voltammetric and chronoamperometric methods

The electrochemical determination of the non electroactive silicate is based on the formation of a complex with molybdate according to the reaction (1):



The molybdosilicate complex is formed by the reaction of hexafluorosilicate in an acidic solution (pH ~ 1.5) to form a Keggin anion. Molybdate is in large excess (10 mM) and the pH is adjusted with sulphuric acid.

Voltammetry of the Keggin anion formed shows two reduction and two oxidation waves ([Carpenter et al., 1997](#); [Hodgson and Pletcher, 1998](#)).

[Fig. 1](#) shows cyclic voltammograms recorded with a gold, a platinum and a glassy carbon disk electrode in artificial seawater containing $145\ \mu\text{M}$ of Si(OH)_4 , which is nearly the maximum of concentration found in the open ocean. These voltammograms show two reduction peaks at $+357\text{ mV}$ and $+238\text{ mV}$ and two oxidation peaks at $+300\text{ mV}$ and $+405\text{ mV}$ on glassy carbon electrode.

The complexation with an addition of sodium molybdate in large excess (10 mM) takes about 6 min (at $24\text{ }^\circ\text{C}$) and gives 4 good correlation curves for concentrations between 0.3 and $160\ \mu\text{M}$ and for each oxidation and reduction. The detection limit obtained is lower than in previous studies ($0.3\ \mu\text{M}$ versus $1\ \mu\text{M}$ for [Carpenter et al., 1997](#)) for voltammetric detection, while for chronoamperometric analysis [Hodgson and Pletcher](#)

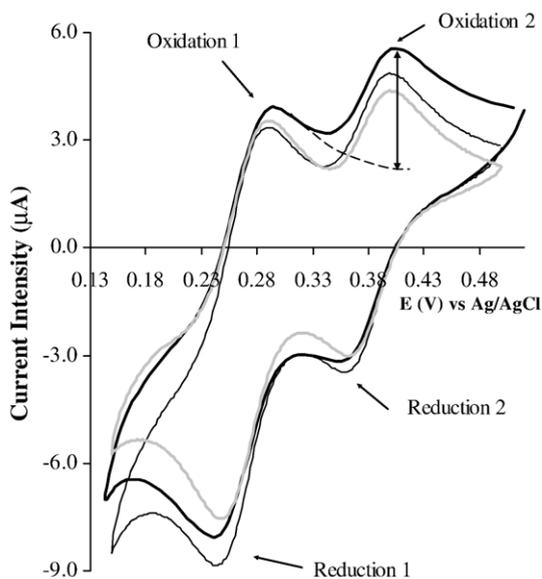


Fig. 1. Voltammograms ($\text{Si}(\text{OH})_4=145 \mu\text{M}$, molybdate=10 mM and $\text{pH}=1.5$) at a gold electrode (bold black line), a platinum electrode (thin black line) and a glassy carbon electrode; scan rate=200 mV/s. Extrapolation is represented by the dotted curve, according to Cottrell's law.

(1998) found a detection limit lower than $1 \mu\text{M}$ with microdisk array electrodes made of carbon.

Fig. 2 shows a chronoamperometric linear response in an experiment carried out in artificial seawater at $\text{pH} 1.5$ and a concentration of molybdate at 10 mM. The working glassy carbon electrode was held at a constant potential of +200 mV. Such a potential prevents the reduction of Mo (VI) in Mo (0) and thus the deterioration of the electrode. The response of the different increases in silicate concentration is linear, similar to previous studies.

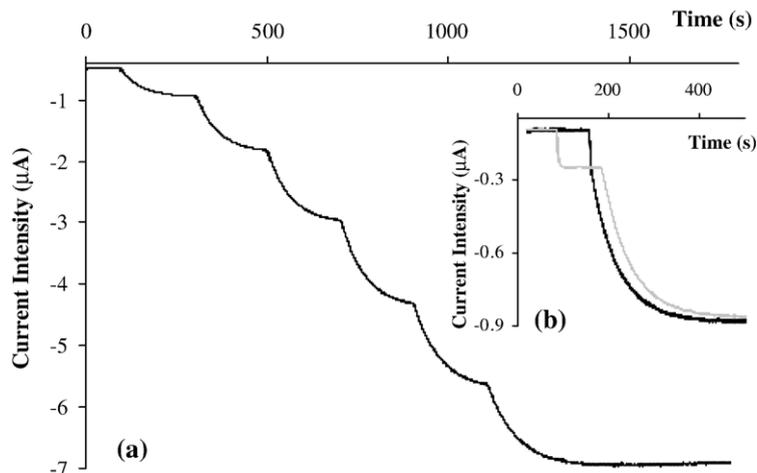


Fig. 2. (a) Chronoamperometric measurements at a glassy carbon electrode for different silicate concentrations (10 μM , 30 μM , 56 μM , 90 μM , 122 μM and 155 μM). (b) Difference of phosphate and silicate kinetics for an addition of phosphate to 9.4 μM first then an addition of silicate to 10.0 μM (grey line) and for an addition of phosphate to 9.4 μM and silicate to 10 μM at the same time (black line).

Methods have been suggested to study the interferences with phosphate based on the differences of kinetics (Hodgson and Pletcher, 1998). Fig. 2 shows this difference with first the very fast response of phosphate and secondly the response of silicate. The steady state value gives the concentration of silicate + phosphate while the first step appears to be the measurement of phosphate. This difference of kinetics can be exploited to eliminate the interference of phosphate. However this interference is not significant for concentration ranges found in the ocean. Experiments were made to study this interference at two different relevant concentration ratios (silicate/phosphate: 56 and 6). No significant difference was found for both amperometric and voltammetric methods.

The amperometry is the simplest method and takes less than 6 min but voltammetry provides four values of the concentration and therefore increases the precision. These methods are well adapted to the flow injection analysis. The main drawback of both methods for achieving an *in situ* long term sensor is that they require the addition of molybdate and protons in the sample before measurements.

3.2. Semi-autonomous method

In order to eliminate the need for molybdenum reagents, we developed a semi-autonomous method that produces molybdenum salts as the product of molybdenum metal oxidation in the reaction cell. Electrochemical oxidation of molybdenum has been performed in several solutions (Wang et al., 1998; De Rosa et al., 2004) but to our knowledge never in sea water.

Fig. 3 shows the intensity curve for the oxidation of the molybdenum in artificial sea water. The Tafel plot of

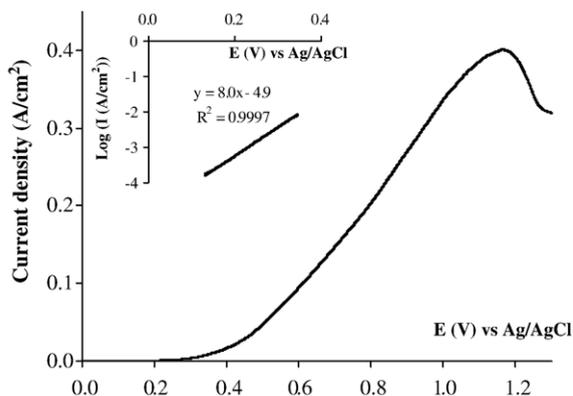


Fig. 3. Voltammogram (1 mV/s) of the oxidation of molybdenum in artificial sea water. Tafel plot is also represented at the top left corner.

this oxidation is also represented at the top left corner. According to Wang et al. (1998), the anodic wave for potential higher than 0.3 V corresponds to the formation of Mo (VI) oxide. In the present work, molybdate is formed directly in the medium by electro-oxidation of molybdenum in a 5 mL cell, according to reaction (2):



The Tafel plot is a useful device for evaluating kinetic parameters. The anodic branch of this plot can be described by the Eq. (3):

$$\text{Ln } j = \text{Ln } j_0 + \alpha \cdot n \cdot F \cdot R^{-1} \cdot T^{-1} \cdot \eta \quad (3)$$

Where j is the current density (A cm^{-2}), j_0 the exchange current density (A cm^{-2}), α the transfer

coefficient, η the overpotential (V), F the Faraday constant (C), n the number of electrons and R the molar gas constant ($\text{J mol}^{-1} \text{K}^{-1}$).

Our Tafel plot slope is 8.0 and the exchange current density is $10^{-4.9} \text{ A cm}^{-2}$ (Fig. 3), of the same order than those obtained for molybdenum oxidation in several media (Wang et al., 1998; De Rosa et al., 2004). Using Eq. (3) we can determine the factor $\alpha \cdot n$, equal to 0.63, to describe the oxidation of the molybdenum.

A constant current intensity of 50 mA is chosen for the oxidation in order to control the quantity of molybdate formed. The theoretical electricity quantity necessary to form molybdate in large excess is given by Faraday Law (4):

$$Q = n \cdot F \cdot V \cdot C = I \cdot t \quad (4)$$

where Q is the electricity quantity (Coulombs), V the volume (cm^3), C the molybdate concentration (mol cm^{-3}), I the intensity (A) and t the time (s).

This equation predicts the time to form molybdate at a concentration of 7 mM to be 400 s. Different oxidation times (around this theoretical time) were studied with an intensity of 50 mA, and for a 5 mL volume of reaction measuring the first oxidation peak intensity as a function of time (Fig. 4). The molybdenum oxidation of 420 s (corresponding to a concentration of 7.3 mM) presents a higher intensity limit ($2.5 \mu\text{A}$) than the molybdenum oxidation of 360 s. In addition the equilibrium is obtained faster. As a result the rate constant has a higher value for the longer oxidation ($8.2 \times 10^{-3} \text{ s}^{-1}$ for 360 s and $9.7 \times 10^{-3} \text{ s}^{-1}$ for 420 s of molybdenum oxidation).

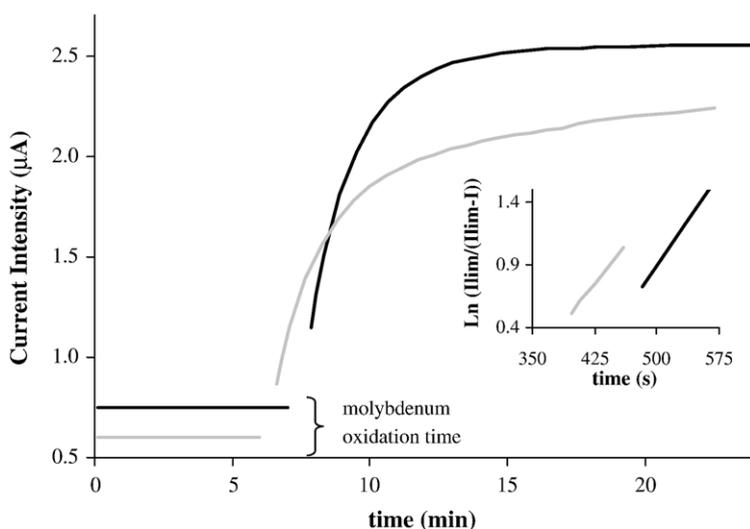


Fig. 4. Kinetics of molybdosilicate complexation after different molybdenum oxidation times (360 in grey and 420 s in black) obtained (at 22 °C, Silicate=200 μM) by the intensity current of the first oxidation peak as a function of time (after the addition of sulphuric acid to pH 1.5). The inset shows the data replotted as $\text{Ln } I_{\text{lim}}/(I_{\text{lim}}-I)$ vs. time.

Table 2

Laboratory reproducibility tests for the voltammetric method: concentrations obtained with the four peak calibrations and with the average of concentrations derived with the four calibrations

Sample concentrations (μM)	Precision (%)				
	Oxidation 1	Oxidation 2	Reduction 1	Reduction 2	Average
36.6	4.2	3.0	11.7	3.4	3.3
154.1	3.2	7.1	5.0	1.3	2.3

These constants are in agreement with [Carpenter et al. \(1997\)](#). The global reaction (oxidation and complexation) takes about 15 min at pH 1.5 (addition of 30 μL of sulfuric acid 5N). The detection limit is 1 μM .

The silicate concentrations are calculated using the 4 calibration curves for each oxidation and reduction. A good correlation is obtained between 5 μM and 170 μM for the four peaks.

Before applying this method on board, an intercomparison with the classical method on land was made and the reproducibility of the method was tested. For the highest concentrations (154 μM) a precision of 2.3% (for the average of the 4 concentrations obtained with the four calibration curves) was found while for each calibration the precision was between 1.3 and 7.0%. For lower concentrations (36 μM), the precision was 3.3% for the average of the 4 calibrations while for each calibration the precision is between 3.0 and 11.7%. In conclusion, the concentration average of these 4 concentrations seems the best way to have a good accuracy. The precision of analysis is lower than 2.5% for samples containing 154 μM (Table 2). The intercomparison with the laboratory classical method showed a good correlation between both methods with a deviation of about 3%.

3.3. On board intercomparison with the semi autonomous method

Reproducibility tests were made at four different stations (Table 3): three measurements on the same sample were made at three stations and ten measurements on the same sample were made for one depth at one station. Table 3 shows that the precision obtained is between 0.4 and 6.1% for the first oxidation, between 1.2 and 6.1% for the second oxidation, between 2.9 and 4.4% for the first reduction, and between 1.8 and 4% for the second reduction. Finally the average of the four concentrations gives a precision between 1.2 and 3%. These results confirm our first results obtained in the laboratory, showing that the average of the four concentrations obtained with the four calibration curves of reduction and oxidation peaks, yields the best precision.

The typical vertical profiles of silicate concentrations obtained in Drake Passage at stations DRA101, DRA020 and DRA046 demonstrate that our electrochemical method is in good agreement with the colorimetric flux analysis conventionally used for seawater silicate analysis (Fig. 5).

Samples from the two Niskin bottles closed at the same depth (400 m at Station DRA 075) provide the same silicate concentration (84 μM).

Table 3

Reproducibility tests performed on board for voltammetry with samples from DRA 035, 046, 050 and 063 (n =number of measurements and σ =standard deviation, precision= 2σ)

Station	Depth (m)	n		Oxidation 1	Oxidation 2	Reduction 1	Reduction 2	Average
DRA 035	2100	3	Average (μM)	130.8	138.1	133.9	139.7	135.6
			σ	0.2	4.2	1.9	2.8	0.8
			Precision %	0.4	6.1	2.9	4.0	1.2
DRA 046	1900	3	Average (μM)	125.0	134.4	126.9	134.0	130.0
			σ	4.0	2.2	2.2	1.5	1.5
			Precision %	6.5	3.3	3.5	2.2	2.4
DRA 050	900	3	Average (μM)	117.4	122.1	115.8	123.5	119.7
			σ	1.2	0.7	2.2	1.1	0.8
			Precision %	2.1	1.2	3.7	1.8	1.4
DRA 063	570	10	Average (μM)	92.0	97.0	92.5	94.5	94.0
			σ	2.7	1.9	2.1	1.7	1.4
			Precision %	5.8	4.0	4.4	3.5	3.0

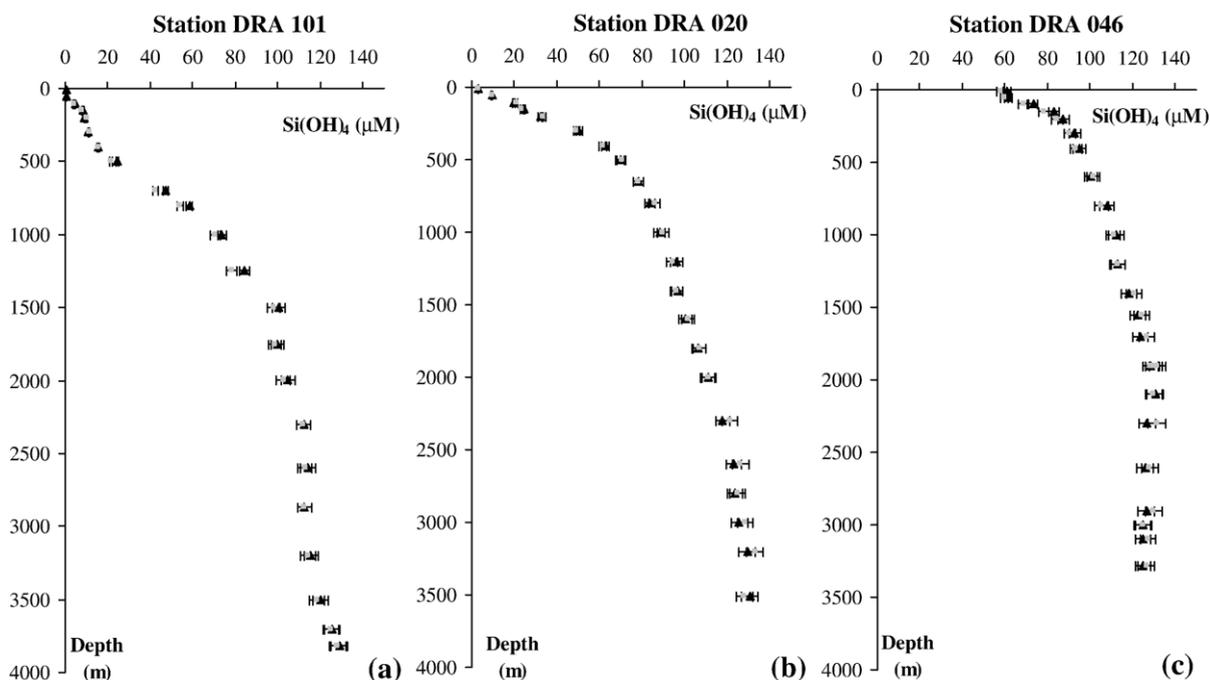


Fig. 5. Comparison of the two methods, voltammetry in black and colorimetry in grey at stations DRA 101 (a), DRA 020 (b) and DRA 046 (c).

The deviation obtained by the comparison of voltammetric analysis and colorimetric analysis is shown on Fig. 6. For the highest concentrations (60–140 μM), 90% of the concentrations have a deviation lower than 5%, with an average of 2.4%. For the concentrations between 10 and 60 μM , all concentrations have a deviation lower than 10%, with an average of 5.1%. For the lower concentrations (<10 μM), the deviation is about 20% and the method does not seem efficient. The average thus obtained for the concentrations larger than 10 μM is 3.0%. Moreover the good agreement between both methods confirms the little interference from phosphate.

3.4. Reagentless method

Acidification of the sample is performed by means of the protons released during the molybdenum oxidation in reaction (2). This was confirmed by the experiment we did separating the anode from the cathode by a polyethylene diaphragm. The pH obtained in the anode cell (1.5) after 360 s of oxidation was close to the theoretical pH (1.1) calculated using reaction (2) and Eq. (4). Fig. 7 (a) shows the calibration for concentrations from 2 μM to 152 μM obtained by the two oxidation and two reduction peaks for the reagentless method. A very good linearity is observed. Kinetics of molybdosilicate complexation after a molybdenum oxidation of 360 s

show that the complex is completely formed after 15 min at 19 °C. Reproducibility tests were performed showing precision of 2.6% for a concentration of 100 μM .

The precision of the electrochemical method could be increased changing the voltammogram post-treatment procedure, doing an extrapolation of the current of the

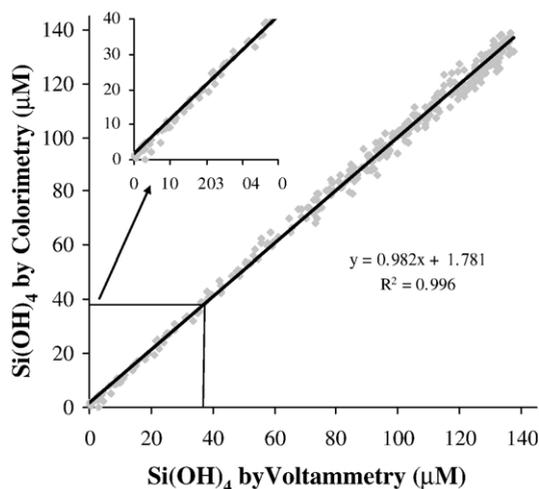


Fig. 6. Deviation of voltammetric analysis compared to colorimetric measurements over all samples.

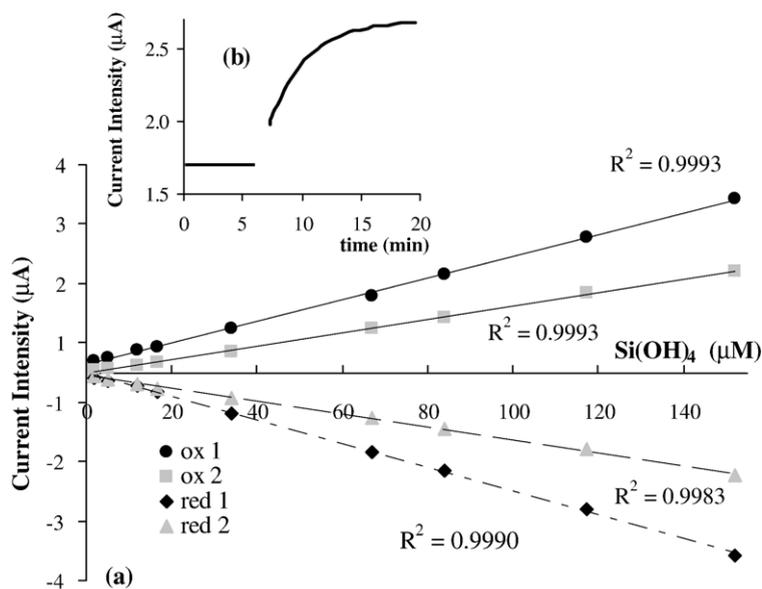


Fig. 7. (a) Calibration for concentrations from 1 μM to 152 μM , obtained by the two oxidation and two reduction peaks for the reagentless method. (b) Kinetics of molybdosilicate complexation after a molybdenum oxidation of 360 s obtained (at 19 $^{\circ}\text{C}$, $\text{Si} = 100 \mu\text{M}$) by the intensity current of the first oxidation peak as a function of time for the reagentless method.

first silicomolybdate oxidized and the first silicomolybdate reduced (Fig. 2). As the electrode reaction is limited by diffusion, it is possible to extrapolate the intensity for a potential after the peak according to the Cottrell equation. After the potential of the first oxidation or reduction peak, the absolute current intensity decreases with time according to Eq. (5) (Bard and Faulkner, 2001):

$$I = n \cdot F \cdot A \cdot C \cdot D^{1/2} \cdot \pi^{-1/2} \cdot t^{-1/2} \quad (5)$$

Where A is the electrode area (cm^2) and D the diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$).

This method improves the data precision from Oxidation 2 and Reduction 1 (Fig. 2) of about 0.9%.

One way to increase the speed of sample analysis would be the increase of the molybdenum surface electrode and/or the current oxidation and/or a decrease of the reaction volume in order to increase the concentration of molybdate in the reaction volume.

To develop a long term autonomous sensor will require the adaptation of an *in situ* cleaning of the electrode holding it at very low potential or with several scanning of the potential. Phosphate interferences might be avoided with the amperometric method (Hodgson and Pletcher, 1998) based on the kinetics differences. In addition phosphate concentrations in the open ocean are very low ($<3 \mu\text{M}$) and as the factor between the two elements is high, orthophosphate would not interfere

with silicate (Liang et al., 2007). Furthermore the temperature effect has to be studied and modelled because it will have an important effect on the kinetics of the complexation. Sampling of a small volume should be achieved to decrease as much as possible the time measurement.

These results show that this voltammetric method is suitable for environmental applications and especially for long term oceanic monitoring. It is a reagentless method, with little power requirement and the sensor size is very small as compared to other existing sensors. It is also very well adapted at extreme conditions such as high pressure gradient.

4. Conclusions

This study shows the first electrochemical molybdenum oxidation and manual addition of H^+ leading to a semi-autonomous method for silicate determination using cyclic voltammetry as a detection method. Electrochemical determination of silicate in seawater was performed in the overall concentration range found in the open ocean. Results obtained during the ANT XXIII/3 cruise across Drake Passage (Jan–Feb 2006) showed that the voltammetric semi-autonomous method is reliable for the analysis of silicate in the water column. The comparison with classical colorimetric measurements is excellent. Finally a complete reagentless method is proposed for the first time. In that case, it is possible to prepare an

electrochemical cell of small volume full of seawater in which both molybdate and protons are produced. It provides a small size sensor using little energy. In the future, cleaning of the electrode will be possible on gold or platinum working electrode.

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