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Phosphate determination in seawater: Toward an autonomous electrochemical method

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ABSTRACT

Initial steps to create an autonomous *in situ* electrochemical sensor for orthophosphate determination in seawater are presented. First, the optimal conditions to form the molybdophosphate complex in artificial seawater medium were determined by addition of sulphuric acid and sodium molybdate to the solution containing orthophosphate. Secondly, the anodic oxidation of molybdenum to form molybdate ions and protons was used to create the molybdophosphate complex without addition of any liquid reagents. The molybdophosphate complex is detectable by amperometry with an average precision of 2.2% for the concentration range found in the open ocean and the detection limit is 0.12 μM.

Three solutions are proposed to address the silicate interferences issue and one of these methods is used for the natural samples collected in the coastal waters offshore Peru during the Pelagico 1011-12-BIC OLAYA cruise in November–December 2010. Results showed a good precision with an average of 2.5% and a reasonable deviation of the amperometric analysis as compared with colorimetric measurements (4.9%).

1. Introduction

Phosphorus is an essential nutrient element for organisms in the marine environment and may be sometimes a limiting factor for primary production [1]. The phosphorus cycle still remains one of the important research topics in biogeochemical oceanography [2]. Thus, rapid and selective methods for the determination of orthophosphate, the major form of phosphorus in the open ocean, constitute an important target. The common analytical method to measure phosphate in natural waters is spectrophotometry which is now frequently carried out in an automated continuous flow system [3,4]. The method requires the addition to the sample of an acidic molybdate solution to convert phosphate into the Keggin anion, $PMo_{12}O_{40}{}^{3-}$ which is intensely blue after reduction by ascorbic acid with a maximum of absorption at 810 nm. Alternate methods based on electrochemistry have also been proposed. Amperometric procedures have been reported for the determination of phosphate as molybdophosphate complex [5,6]. Phosphate has been also determined by using voltammetric methods with carbon paste electrode [7], gold microdisk electrode [8] and glassy carbon electrode [9]. The obtained voltammetric signals are based on the reduction of the molybdophosphate complex and the detection limit was a few micromoles per liter. Other electrochemical phosphate sensors include: liquid–membrane electrodes with organotin carriers [10], coated-wire electrode [11], heterogeneous membrane electrodes [12] and a large number of biosensors [13–15]. The latter usually require more than one enzyme and a rigorous control of the activity and stability of the used enzymes. Electrochemistry offers a wide range of possibilities for achieving an excellent phosphate determination in seawater with the following figures of merit: long lifetime, high precision, low detection limit, fast response time, good reproducibility but no autonomous electrochemical sensor for *in situ* phosphate determination exists nowadays.

Our team developed an electrochemical method for silicate determination in seawater based on anodic oxidation of molybdenum [16,17]. The aim of the present work is to adopt this method to phosphate detection in seawater and to create an electrochemical cell where molybdate ions and protons will be produced in order to create molybdophosphate complex electrochemically detected either by means of cyclic voltammetry or amperometry. The situation is more delicate because of cross interference in the natural seawater samples which contain both silicate and phosphate.

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This work is a first step to develop an autonomous *in situ* sensor for electrochemical detection of phosphate in seawater. First, the method with the addition of sodium molybdate and sulphuric acid solutions to the phosphate artificial samples is described. Then the electrochemical oxidation of molybdenum to form molybdate and protons is presented. The silicate interference problem is discussed and a comparison with classical phosphate detection (colorimetry) is provided. Finally, an application of our method to natural seawater samples collected during an oceanographic cruise off Peru is presented.

2. Methods

2.1. Reagents and calibration standards

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

Artificial sea water for standards calibration, phosphate and silicate samples is prepared at a salinity of 34.4.

Working calibration standards are prepared as described in the WOCE operation and method manual [4] with potassium dihydrogen phosphate (KH_2PO_4, Merck) and sodium silicofluoride (Na_2SiF_6, Merck).

The reagents used for electrochemical phosphate detection are sulphuric acid (H_2SO_4, 5 N, Merck) and sodium molybdate solution ($Na_2MoO_4{\cdot}2H_2O$, Merck).

Phosphate artificial samples determinations by colorimetry are performed using:

- an acidified ammonium heptamolybdate solution (6 g of ammonium heptamolybdate, 0.15 g potassium antimonyl tartrate, 40 mL of sulphuric acid, H_2SO_4 0.051 M in 1000 mL of Milli-Q water),
- an ascorbic solution (7.58 g of L-ascorbic acid in 250 mL of Milli-Q water and 0.5 mL of Aerosol 22).

Phosphate natural samples determinations by colorimetry are performed using:

- an ammonium heptamolybdate solution (15 g of ammonium heptamolybdate in 500 mL of Milli-Q water),
- an acidic solution (140 mL of sulphuric acid, H_2SO_4 in 900 mL of Milli-Q water),
- an ascorbic acid solution (27 g of ascorbic acid in 500 mL of Milli-Q water),
- an antimonyl potassium tartrate solution (0.34 g of antimonyl potassium tartrate in 250 mL of Milli-Q water).

These solutions are mixed together (100 mL ammonium heptamolybdate, 250 mL sulphuric acid, 100 mL ascorbic acid and 50 mL antimonyl potassium tartrate) and the final solution is used for phosphate determination (10 mL for each 100 mL of the sample).

2.2. Colorimetric method

Colorimetric detection of phosphate artificial samples is done following Le Corre and Tréguer's method [18] and an Auto-Analyzer 3rd generation (AAIII Bran Luebbe) is used. Colorimetric detection of phosphate natural samples is developed following the method of Strickland and Parsons [19] and a spectrophotometer UV-VISIBLE LAMBDA 45 is used. The baselines are made with artificial seawater.

Reproducibility tests are performed for both spectrophotometers. The average precision obtained for artificial samples is 1.10%, whereas for natural samples this value is 2.37%.

2.3. Electrochemical method

Electrochemical measurements are carried out with a potentiostat μ-Autolab III (Metrohm). The reference electrode is an Ag/AgCl/KCl 3 M electrode (Metrohm). All the following potentials are given relative to this electrode. Measurements at a stationary or rotating disk electrode are recorded in a three electrode cell with a platinum counter electrode and gold or glassy carbon working electrode (Metrohm, diameter 3 mm). The working electrode is polished with lapping film sheet (3 M Aluminum Oxide, 1 μm) before the measurements.

The molybdenum electrode has a surface of 20 mm^2 (Goodfellow). Molybdate is produced by molybdenum anodic oxidation performed at a constant electrolysis current (50 mA) in a 5 mL cell.

The simultaneous production of molybdate and protons is based on the use of a cell divided in two parts by a Nafion membrane (N117 Du Pont^{TM} Nafion^R PFSA Membranes). The first half of the cell is filled with 3 mL of the solution and the second half with 17 mL of solution. The first half contains the molybdenum, reference and sensing electrodes. The counter electrode is placed in the second half. Molybdate and protons are produced by molybdenum anodic oxidation performed at a constant electrolysis current (50 mA) during 500 s.

2.4. Seawater collection

The collection of seawater samples from four east–west transect lines was made during the Pelagico 1011-12-BIC OLAYA cruise aboard R/V Jose Olaya Balandra off Peru during austral spring 2010 (November–December), when intense upwelling occurs. Samples for phosphate analysis by both colorimetric and amperometric methods were collected during the leg from Puerto Pizzaro (3.67°S) to Salaverry (8.13°S) from November 10th to November 29th, 2010. Among the 22 CTD profiles performed during this leg, 7 vertical profiles were analyzed by both methods for phosphate determination.

Seawater was collected using 12 L Niskin bottles mounted on a cable equipped with a CTD-O_2 Sea Bird 25.

Samples were collected, frozen immediately and stored in 250 mL Nalgene plastic flasks then transported to the laboratory of the Chemical Research Unit of the Instituto del Mar del Peru (UIOQ-IMARPE) for analysis.

3. Results and discussion

3.1. Voltammetric and amperometric methods

The electrochemical determination of the non electroactive phosphate is based on the formation of a complex with molybdate. The complex is formed by the reaction of Na_2MoO_4 in an acidic solution (pH 1.0) to form a Keggin anion according to reaction (1). Molybdate is in large excess (20 mM) and the pH is adjusted with sulphuric acid.

$$PO_4{}^{3-} + 12MoO_4{}^{2-} + 27H^+ \rightarrow H_3PMo_{12}O_{40} + 12H_2O \qquad (1)$$

Cyclic voltammetry of the formed Keggin anion shows two reduction peaks at 0.32 V and 0.46 V and two oxidation peaks at 0.40 V and 0.53 V. The complexation takes about 60 s and cyclic voltammetry gives 4 correlation curves for concentrations greater than 5.0 μM. Unfortunately the concentrations of phosphate found in the open ocean are smaller (less than 3.0 μM) and in this concentration range the voltammograms show only one reduction and one oxidation peak which are not well marked because of the large ratio between the capacitive and the faradic currents.

To increase the sensitivity of the detection, an amperometric method was chosen. The working gold electrode was held at a constant potential of 0.29 V. Fig. 1 shows an amperometric linear

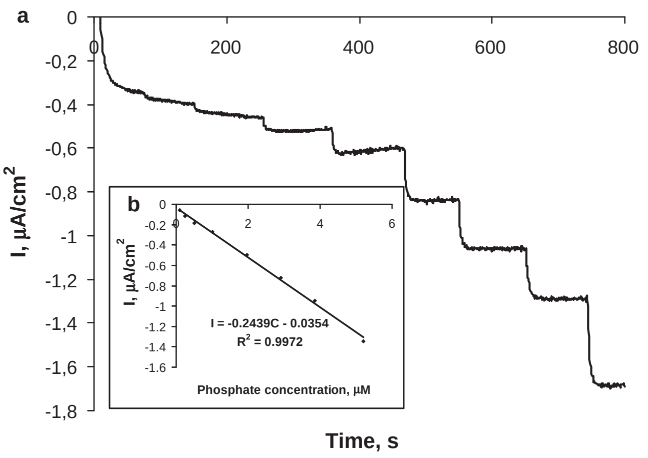

Fig. 1. Variation of current for the molybdophosphate complex measured by amperometry at a rotating gold electrode (0.29 V, 1000 rpm) as a function of time (a) and phosphate concentration (b). The calibration curve was achieved by addition of standard phosphate solution in the concentration range of 0.10–5.21 µM; molybdate concentration 20 mM, pH 1.0.

response in an experiment carried out in artificial seawater at pH 1.0 and with a concentration of molybdate of 20 mM. This calibration curve was obtained by addition of standard phosphate solution in the concentration range of 0.10–5.21 µM. The detection limit for this method is 0.05 µM. The detection limit was calculated as a signal measured between the highest and the lowest values of noise multiplied by three. The method is characterized by a good repeatability and the precision for each concentration is smaller than 3%. Amperometry is a very simple method, well adapted to the flow injection analysis, but the main drawback of this method for achieving an *in situ* long term sensor is that it requires the addition of molybdate and protons in the sample before measurements.

To optimize the method, influence of pH, electrode rotation rate and molybdate concentration were investigated. A pH range between 1.75 and 0.50 was examined by amperometry and we obtained the best results with a pH around 1.0. Fig. 2 shows the variation of current for a phosphate concentration of 1.0 µM in different pH conditions. The influence of the electrode rotation and molybdate concentration was studied by linear sweep voltammetry. Results show that the current increases with the angular frequency of the electrode rotation and with the concentration of molybdate. Fig. 3a shows the current versus potential curves for the molybdophosphate complex in different molybdate concentrations performed in artificial seawater containing phosphate at constant concentration. No significant influence of the concentration of molybdate on current for the molybdophosphate complex was detected for concentrations larger than 20 mM.

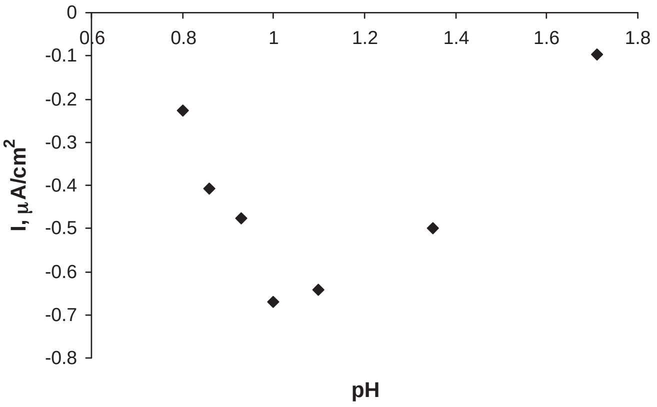

Fig. 2. Variation of current measured by amperometry at rotating gold electrode (0.29 V, 1000 rpm) as a function of pH for molybdophosphate complex performed in artificial seawater containing phosphate in concentration of 1.0 µM.

The linear sweep voltammetry presented in Fig. 3b shows two reduction waves. In agreement with previous studies [8] the first reaction involves two electrons and the second three. Thus, the first reaction is the reduction of molybdate (VI) to molybdate (IV) and the second reaction is the reduction of molybdate (IV) to molybdate (I).

The voltammetry for the reduction of the phosphomolybdate species differs from that of the silicomolybdate complex [17] in several ways. The waves are not as well formed, they are less steep and they overlap to a greater extent. The limiting currents for the phosphomolybdate complex are lower than for the silicomolybdate one and they are not proportional to the radii of the microdisks, with the currents being less than expected. This characteristic is typical for electrode reactions where the electron transfer is preceded by a homogeneous chemical step which limits the rate of a protonation step or the rate of an isomerization which prevents rapid reduction of all the phosphomolybdate species in solution. This problem was already discussed by Carpenter et al. [8].

3.2. *Oxidation of molybdenum*

To avoid the addition of sodium molybdate in the sample we worked toward an electrochemical way to produce this ion in seawater medium. Molybdate is formed directly in the acidic medium by anodic oxidation of molybdenum at constant current of 50 mA in a 5 mL cell, according to reaction (2).

$$\mathrm{Mo} + 4\mathrm{H_2O} \rightarrow \mathrm{MoO_4}^{2-} + 8\mathrm{H}^+ + 6\mathrm{e}^- \qquad (2)$$

Electrochemical oxidation of molybdenum has been performed in several solutions [20,21] and in sea water [16,17]. However, our knowledge about the different forms of molybdates produced during this process is limited. Numerous works on molybdate solutions were done. The nature of the formed molybdate species depends strongly on the molybdate concentration and pH [22]. At very low concentrations ($<10^{-4}$ M) mononuclear species predominate. At higher concentrations numerous teams have shown the existence of the polynuclear species [23]. A longer oxidation time of molybdenum leads to higher molybdate concentration in the solution and the percentage of polynuclear species increases with oxidation time. Besides, the formation of polymolybdates consumes some protons and more and more complex polymolybdates are created with growing acidification. Having all this in mind, we assume that reaction (2) will change with time during the molybdenum oxidation.

3.3. *Electrochemical production of molybdate and protons*

In order to avoid the addition of both sodium molybdate and sulphuric acid, a method based on an electrochemical cell divided in two by a membrane was developed. Separation of the molybdenum anode from the cathode by a Nafion diaphragm eliminates the consumption of the protons on the platinum cathode. Thus, the protons formed according to reaction (2) accumulate in the anodic part of the cell. The optimal pH for the molybdophosphate complex formation was determined to be close to 1.0 (Section 3.1). To obtain this pH, it is necessary to oxidize the molybdenum electrode during 500 s at a stable current of 0.05 A in seawater starting with an average initial pH of 7.8. Reproducibility tests show a precision of 1.7% for this time of oxidation and the average value of pH is 1.02. During the oxidation we observed the evolution of molybdate and pH with time. Fig. 4 shows the evolution of the molybdate peaks in the reaction cell as a function of the molybdenum oxidation time

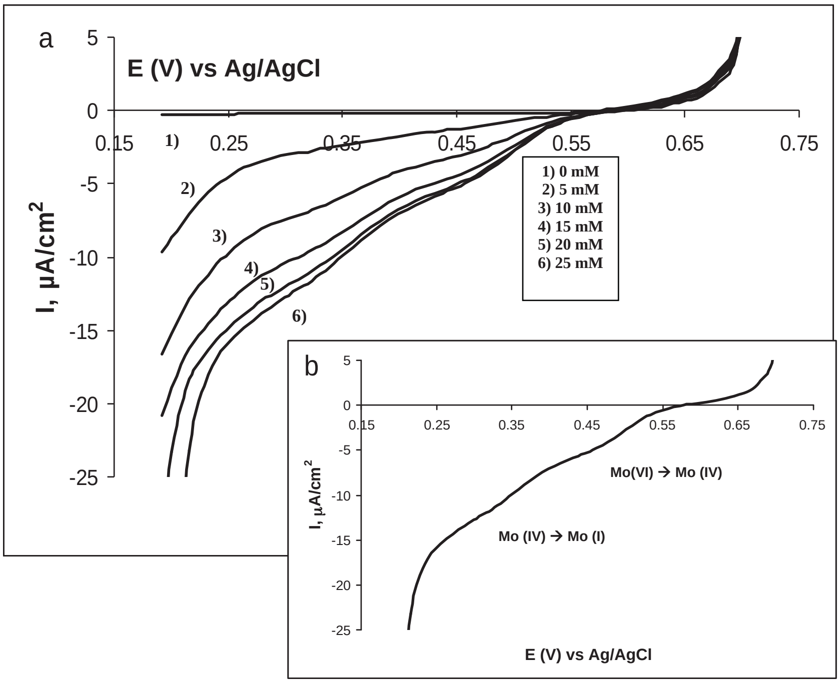

Fig. 3. Linear sweep voltammetry (5 mV/s) at a gold rotating disk electrode (1000 rpm) for molybdophosphate complex at pH 1.0 and different concentrations of molybdate (0, 5, 10, 15, 20, 25 mM), phosphate concentration 100 µM. (a) Optimization of molybdate concentration and (b) two steps of reduction of the molybdophosphate complex.

and pH. Molybdate reduction peak occurs at about −0.60 V. Moreover, the position of the peaks is shifted to more negative potentials for reduction peak and to more positive ones for oxidation peak as molybdenum oxidation goes along. Based on the influence of the rates of complex formation, difference in the electrochemical behavior is due to the formation of more and more complex polymolybdate species which are difficult to reduce and then to oxidize.

The molybdophosphate complex formed as described above can be detected in the electro-reduction process on the gold electrode at a potential of 0.29 V. This method gives a good linear response for phosphate in the concentration range of 0.33–3.20 µM and the detection limit is 0.12 µM ($I = -0.266C + 0.038$; $R^2 = 0.9973$; I in µA/cm^2). However, we also noticed a good linear correlation for smaller concentrations (0.10–1.0 µM) but with a lower sensitivity ($I = -0.216C + 0.007$; $R^2 = 0.9992$; I in µA/cm^2). The detection limit was calculated as a signal measured between the highest and the lowest values of noise multiplied by three. The reproducibility tests reported in Table 1 exhibit a good precision in the concentration range usually found in the open ocean.

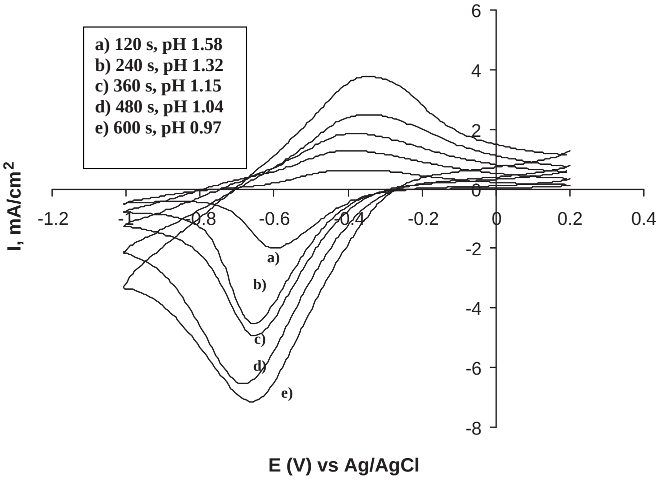

Fig. 4. Monitoring of pH and molybdate formation versus time: voltammograms obtained on stationary carbon glass electrode (200 mV/s) after several electrode time intervals of molybdenum oxidation in artificial seawater.

3.4. Silicate interferences

There is an obvious problem of cross interference in the ocean samples which contain both silicate and phosphate. Thus methods described above have to be adapted to overcome this challenge. A few approaches to avoid silicate interferences are proposed using differences in kinetics of complex formation [24], differences in electrochemistry of the two complexes and influence of pH on complex formation [8,25].

We observed by linear sweep voltammetry that the reduction of the molybdophosphate complex starts at a potential close to 0.55 V while the reduction for the molybdosilicate complex starts at 0.45 V. Fig. 5 shows the linear sweep voltammetry for both complexes in the potential range 0.20–0.70 V. Two reduction waves for each species clearly indicate that if we choose one of the potentials in the range at 0.45–0.55 V we would eliminate the interference from silicate. We found that for a potential of 0.50 V we do not obtain an amperometric signal for silicate while the signal for phosphate was exhibiting a linear correlation with concentration. However, this potential corresponds only to the first reduction wave and we lose some sensitivity. Besides, for the conditions where molybdate and protons were produced during anodic

Table 1
Reproducibility tests for molybdophosphate amperometric detection obtained for different phosphate concentrations in artificial sea water samples. Each sample was measured 10 times.

Concentration (µM)	0.33	0.83	1.48	2.28	3.22
Standard deviation	0.11	0.33	0.42	0.92	1.19
Precision (%)	2.3	2.6	1.7	2.3	2.0

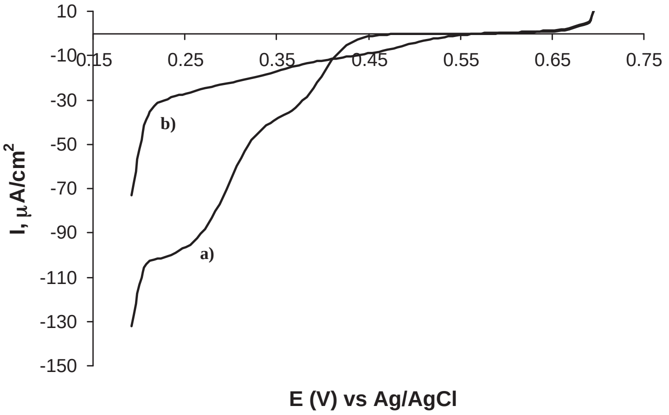

Fig. 5. Steady state voltammograms (5 mV/s) for molybdophosphate and molybdosilicate complexes on a gold rotating disk electrode (1000 rpm) in artificial seawater containing 100 μM of silicate (a) and 100 μM phosphate (b); molybdate concentration 20 mM, pH 1.0.

oxidation of molybdenum in seawater containing both silicate and phosphate species, we observe on the amperogram at a stable potential of 0.50 V not only the reduction of the molybdophosphate complex but also oxidation of other molybdate species formed during oxidation of molybdenum, which makes it impossible to detect phosphate.

Carpenter et al. [8] and Hodgson and Pletcher [25] indicated that at pH smaller than 0.50 there was no formation of the molybdosilicate complex. For this pH we did not obtain any signal for silicate in the concentration range found in the open ocean, while the signal for phosphate was well formed. Fig. 6 shows the amperometric response for silicate and phosphate under different pH conditions. We lose some sensitivity because a pH of 0.50 is not the optimized one. In addition, when molybdenum is oxidized in a sample containing both species, the molybdosilicate complex is formed at the beginning of this process and further acidification does not destroy it.

Zhang et al. [24] indicated that when working with a ratio of protons/molybdates close to 70 at pH 1.0 (meaning the molybdate concentration has to be close to 1.5 mM), the interference from silicate can be avoided. Although the method was used for colorimetric detection of phosphate in presence of silicate, we confirmed that it was also adequate using amperometry. According to reaction (2), the ratio of protons/molybdate is 8 during the oxidation of molybdenum. We achieved an appropriate ratio of 70 by an extra addition of sulphuric acid. The last method seems to be the most promising one. Indeed, it does not require any modification of potential applied to the gold electrode during reduction of the molybdophosphate complex. Fortunately, the pH required for this method is 1.0 which happens to be the optimized value of pH we found. It will be thus easier to find a method for the protons production equivalent to this pH, than for example to go down to pH 0.50. Finally, with the molybdate concentration required for this method, the oxidation time is much shorter, 50 s in a 3 mL cell, than before (Section 3.3). Since the time of formation of the complex is about 60 s, the total reaction time is 110 s. Fig. 7 presents a calibration curve made in the mentioned conditions. It is clear that there is no signal for silicate, whereas the signal for phosphate exhibits a linear correlation in a concentration range 0.49–3.33 μM and with a detection limit of 0.22 μM. This latter method was used for the natural samples collected off Peru during the Pelagico 1011-12 cruise aboard the R/V OLAYA.

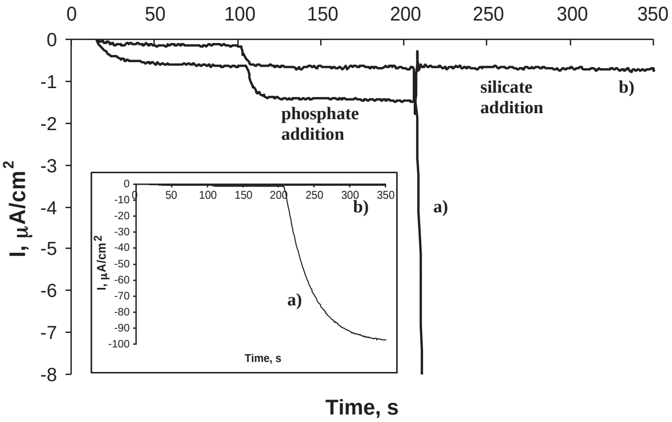

Fig. 6. Amperometric response for molybdosilicate and molybdophosphate complexes on a gold rotating disk electrode (0.29 V, 1000 rpm) in artificial seawater. The signals were achieved by addition of standard phosphate solution in concentration of 3.0 μM and standard silicate solution in concentration of 150 μM; sodium molybdate 20 mM, pH 1.0 (a) and 0.50 (b). Inset presents the full signal for silicate when pH is 1.0.

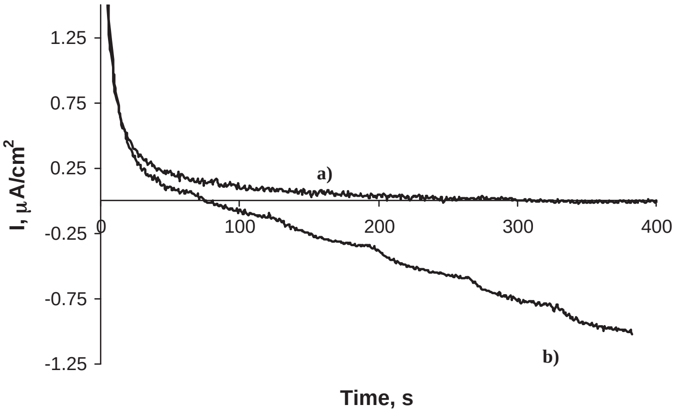

Fig. 7. Amperometric measurements made on a rotating gold electrode (0.29 V, 2000 rpm) for molybdosilicate and molybdophosphate complexes performed in artificial seawater. The signals were achieved by addition of standard solutions of: (a) silicate (5.0–140 μM) and (b) phosphate (0.49–3.30 μM); pH 1.0, ratio protons/molybdate = 70.

3.5. *Comparison for sea water samples*

Before applying this method to the natural samples, reproducibility of the method was tested for different phosphate concentrations representative of the seawater gradient reported in the Oxygen Minimum Zone off Peru and an intercomparison with the classical method was made. The reproducibility test performed on artificial sea water samples shows a precision of 2.1% for the highest phosphate concentration of 3.4 μM, 2.8% and 6.1% for intermediate concentrations of 2.2 μM and 1.2 μM, respectively and 6.3% for the lowest concentration of 0.5 μM. The reproducibility test was made with ten measurements for each sample. The intercomparison of the electrochemical method for artificial sea water samples with the laboratory classical method showed a good correlation with an average deviation of about 5.1%.

For the natural samples, the reproducibility tests were made at different CTD stations covering different *in situ* configurations (e.g. near the coast/off-shore, lower/higher latitude stations of the cruise, shallower/deeper depths) with a triplicate measurement on the same sample at each depth. Table 2 provides the obtained precision between 1.1 and 3.9% with an average value of 2.5%.

The typical vertical profiles of phosphate concentrations obtained offshore Peru in the coastal waters demonstrate that the electrochemical method is in excellent agreement with the colorimetric analysis conventionally used for seawater analysis (Fig. 8).

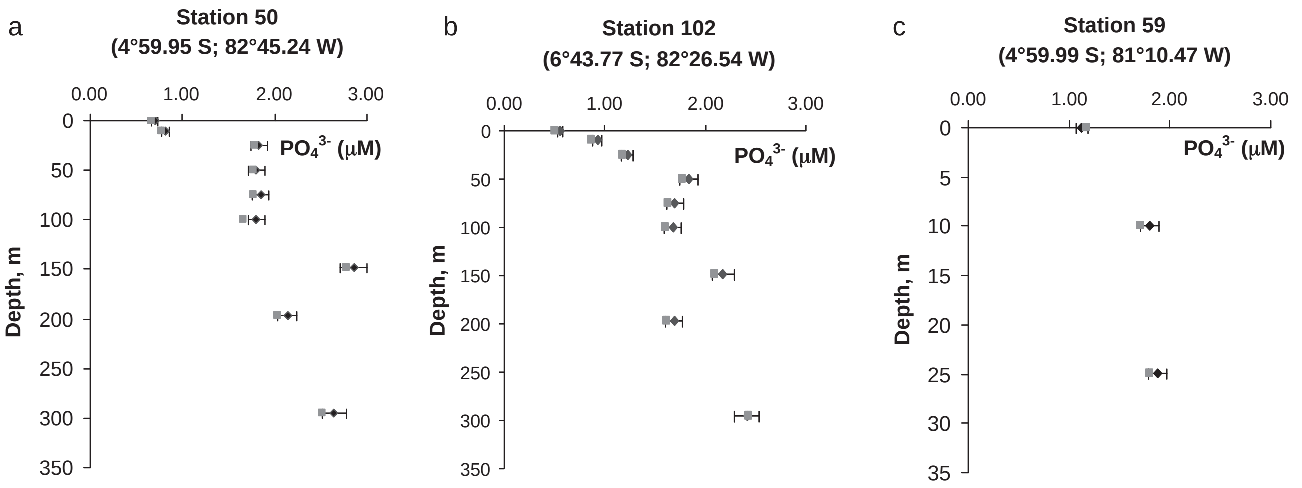

Fig. 8. Comparison of both methods, amperometry (black) and colorimetry (grey) at CTD stations 50 (a), 102 (b), 59 (c). Station 59 is situated very close to the coast and stations 50 and 102 more off-shore.

Table 2
Reproducibility tests made for natural phosphate samples (σ = standard deviation). Test made for the samples collected during the Pelagico 1011-12-BIC OLAYA cruise aboard R/V Jose Olaya Balandra.

Station	Depth (m)	Average (μM)	σ	Precision (%)
1	25	0.91	0.18	1.7
11	2	0.88	0.3	3.0
11	70	1.93	0.25	1.1
11	440	1.77	0.71	3.3
50	25	1.83	0.38	1.7
50	100	1.8	0.78	3.5
59	2	1.12	0.42	3.2
95	50	1.99	0.3	1.1
102	2	0.56	0.21	2.6
102	100	1.68	0.46	2.0
174	2	1.19	0.66	3.9

The average deviation obtained for all phosphate concentrations is 4.9%.

4. Conclusion

We have shown a thorough documentation necessary to set up an electrochemical method for phosphate detection in seawater. With molybdate and sulphuric acid addition to the seawater sample containing phosphate, we optimize the best conditions to produce the phosphomolybdate complex. We then created an electrochemical cell where molybdate ions and protons are produced by anodic oxidation of molybdenum in order to form phosphomolybdate complex without addition of liquid reagents. The created complex is detected electrochemically by means of amperometry with a detection limit of 0.12 μM.

We presented here a discussion about silicate interferences and we proposed three methods to solve this problem: detection of phosphate in presence of silicate by amperometry at a potential of 0.50 V, at pH 0.50 or at an appropriate ratio of protons/molybdate (70). The latter method was used during the “Pelagico 1011-12” cruise aboard the R/V OLAYA offshore Peru and showed that the amperometric approach is reliable for the analysis of phosphate in the water column. Thus, the method is very promising but presently appropriate ratio of protons/molybdate is achieved by an extra addition of sulphuric acid. We are currently working on introducing proton exchange membranes in order to avoid the acid addition in the cell. Identification of the molybdate species obtained during anodic oxidation of molybdenum in seawater is also under investigation. This recognition is being performed by both electrochemical and spectroscopic methods. This study is crucial to entirely solve the problem with silicate interferences and to elucidate the complex chemistry of isopoly- and heteropoly-molybdates.

It is worth noticing that the investigated method can be used for analysis of phosphates in other aqueous environments such as lakes or rivers where silicate concentrations are negligible as compared to phosphate concentrations so that the analysis can be performed without interferences.

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