



HAL
open science

Reagentless and silicate interference free electrochemical phosphate determination in seawater

Justyna Jońca, William Giraud, Carole Barus, Maurice Comtat, Nicolas Striebig, Danièle Thouron, Véronique Garçon

► To cite this version:

Justyna Jońca, William Giraud, Carole Barus, Maurice Comtat, Nicolas Striebig, et al.. Reagentless and silicate interference free electrochemical phosphate determination in seawater. *Electrochimica Acta*, 2013, vol. 88, pp. 165-169. 10.1016/j.electacta.2012.10.012 . hal-00877769

HAL Id: hal-00877769

<https://hal.science/hal-00877769>

Submitted on 29 Oct 2013

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Open Archive TOULOUSE Archive Ouverte (OATAO)

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible.

This is an author-deposited version published in : <http://oatao.univ-toulouse.fr/>
Eprints ID : 9929

To link to this article : DOI:10.1016/j.electacta.2012.10.012
URL : <http://dx.doi.org/10.1016/j.electacta.2012.10.012>

To cite this version : Jońca, Justyna and Giraud, William and Barus, Carole and Comtat, Maurice and Striebig, Nicolas and Thouron, Danièle and Garçon, Véronique. *Reagentless and silicate interference free electrochemical phosphate determination in seawater*. (2013) *Electrochimica Acta*, vol. 88 . pp. 165-169. ISSN 0013-4686

Any correspondence concerning this service should be sent to the repository administrator: staff-oatao@listes-diff.inp-toulouse.fr

Reagentless and silicate interference free electrochemical phosphate determination in seawater

Justyna Jońca^{a,*}, William Giraud^a, Carole Barus^a, Maurice Comtat^b, Nicolas Striebig^c, Danièle Thouron^a, Véronique Garçon^a

^a Laboratoire d'Etudes en Géophysique et Océanographie Spatiales, UMR 5566, 18 Avenue Edouard Belin, 31401 Toulouse Cedex 9, France

^b Laboratoire de Génie Chimique, UMR 5503, Université Paul Sabatier, 118 Route de Narbonne, 31062 Toulouse Cedex, France

^c Observatoire Midi-Pyrénées, UMS 831, Groupe d'Instrumentation Scientifique (GIS), 14 Avenue Edouard Belin, 31400 Toulouse, France

A B S T R A C T

An electrochemical method for phosphate determination in seawater was based on the oxidation of molybdenum in order to form molybdates and protons and subsequently, to create the phosphomolybdic complex electrochemically detectable by means of amperometry at a rotating gold disk electrode [J. Jońca et al., *Talanta* 87 (2011) 161]. To avoid silicate interferences, the method required an appropriate ratio of protons over molybdates equal to 70. Since the ratio of protons over molybdates created during molybdenum oxidation is only 8, the previous method still needed addition of sulfuric acid and thus was not free from addition of liquid reagents. In the present work, this aspect is solved by modification of the electrochemical cell construction. The method is now totally free from addition of any liquid reagents and gives a possibility to determine phosphate by amperometry in the concentrations range found in the open ocean with a detection limit of 0.11 μM . Having in mind the energy savings for future *in situ* sensor development, amperometry at rotating gold disk electrode was replaced by differential pulse voltammetry at static one. Phosphate can then be determined with a detection limit of 0.19 μM . Both methods are characterized by good reproducibility with an average measurements precision of 5.7% (amperometry) and 3.8% (differential pulse voltammetry). Results also show a good accuracy with an average deviation from theoretical values of phosphate concentration of 3.1% for amperometry and 3.7% for differential pulse voltammetry.

Keywords:

Phosphate
Amperometry
Differential pulse voltammetry
Silicate interference
Reagentless method

1. Introduction

Phosphorus, in the form of phosphate, plays a key role in photosynthesis (*i.e.*, primary productivity) and the availability of this macronutrient in marine systems can strongly influence the marine carbon cycle and the sequestration of atmospheric carbon dioxide [1]. Thus, the biogeochemical cycle of phosphorus is one of the main research topics in chemical and biological oceanography, and measuring accurately the concentration of phosphate is very important.

Today's *in situ* monitoring of phosphate is based on a common method where the reaction of phosphate and molybdate in acidic medium is used in order to form the phosphomolybdate complex. This complex is then treated with ascorbic acid in the presence of antimony to yield the phosphomolybdenum blue as described

firstly by Murphy and Riley [2]. The reaction is followed by colorimetric detection at a wavelength of about 882 nm. ANAIS developed in our laboratory [3] is one of the *in situ* phosphate (and other nutrients) analyzers based on this method. These types of analyzers are characterized by good sensitivity and accuracy, but they are heavy and large. Additionally, they require addition of reagents and significant energy. To overcome these problems, progress toward miniaturization and decrease in energy consumption is crucial. Within a large number of analytical methods, electrochemistry provides promising reagentless approach to go further in miniaturization, decrease in response time and energy requirements. In aquatic systems, electrochemical methods are used routinely for monitoring pH by potentiometry, dissolved oxygen by amperometry [4], trace metals and speciation by voltammetry [5,6], conductivity and therefore salinity by impedimetry.

Electrochemistry also 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 detection exists nowadays. However, electrochemistry has been used

* Corresponding author at: Laboratoire d'Etudes en Géophysique et Océanographie Spatiales, 14, av Edouard Belin, 31400 Toulouse, France. Tel.: +33 0561332913; fax: +33 0561253205.

E-mail address: justyna.jonca@legos.obs-mip.fr (J. Jońca).

for determination of phosphate in laboratory conditions. The determination of phosphate has been performed by pulse voltammetry with a great sensitivity [7], cyclic voltammetry [8,9] and amperometry [10,11]. Recently, a totally new electrochemical method was developed in our group for determination of silicate [12,13] and phosphate [14]. The method was based on the anodic oxidation of molybdenum in seawater in order to form silico- or phosphomolybdate complex electrochemically detectable either by means of cyclic voltammetry or amperometry. These reactions took place in an electrochemical cell divided in two by a non-proton exchange membrane in order to avoid protons reduction on the platinum cathode. Thus, molybdenum, working and reference electrodes were in the first compartment of the cell whereas the platinum electrode was in the second one. This method had an obvious drawback of cross interference in the ocean samples which contain both silicate and phosphate. Three solutions were proposed to address the silicate interferences issue [14], either by detection of phosphates in presence of silicates by amperometry at a suitable potential of 0.5 V or in a very acidic medium (pH 0.5) or with an adequate ratio of protons over molybdates equal to 70. The latter method was used for phosphate detection in the oxygen minimum zone (OMZ) offshore Peru during the Pelagico 1011-12-BIC OLAYA cruise in November–December 2010. The results showed an excellent agreement when compared to classical colorimetric measurements, but the method still required extra addition of acid to achieve the appropriate ratio of protons over molybdates [14].

In this work we will present the continuation of the development of the phosphate sensor along two routes. One is designing a new electrochemical cell including membrane technology to avoid any addition of liquid reagents. The second is to decrease energy requirements by switching to differential pulse voltammetry.

2. Experimental

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 [15] with potassium dihydrogen phosphate (KH_2PO_4 , Merck) and sodium silicofluoride (Na_2SiF_6 , Merck).

Phosphate artificial samples determinations by colorimetry are performed using reagents:

- An ammonium heptamolybdate solution (15 g of ammonium heptamolybdate in 500 mL of Milli-Q water).
- An acidic solution (140 mL of sulfuric 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 sulfuric 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 was done with a UV–vis spectrophotometer (Varian Inc. Cary 50, Australia)

using 10 mm 100-QS quartz cuve (Hellma Analytics, Germany). The absorbance was registered at 882 nm following the method of Strickland and Parsons [16]. The baselines were done with artificial seawater. Reproducibility tests were performed and the precision of 2.25% was found.

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 working electrode (Metrohm, diameter 3 mm). The working electrode is polished with lapping film sheet (3 M aluminum oxide, 1 μm) and electrochemically cleaned in 0.5 mol L⁻¹ sulfuric acid solution (5 scans, from 0.0 to 1.5 V, 200 mV s⁻¹) before each measurements.

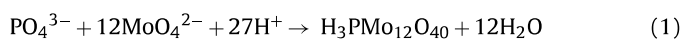
The molybdenum electrode has a surface of around 100 mm² (Goodfellow). Molybdate is produced by molybdenum anodic oxidation performed at a constant electrolysis current of 50 mA or at constant potential of 2 V.

The simultaneous production of molybdate and protons with the appropriate ratio is based on the use of a cell divided in three parts. In the first one (1 mL), a primary molybdenum electrode is oxidized and thanks to a very thin (30 μm) proton exchange membrane (FuMaTech, fumapem^R F-930) only protons can pass through to the second compartment and thus acidify the medium to pH 1. In the second compartment (5 mL), a secondary molybdenum electrode is oxidized during a short time and thus achieving a ratio of protons over molybdates of 70. To avoid the reduction of protons formed during the two previous oxidations of molybdenum, the platinum electrode is placed in the third compartment which is in contact with the former two parts of the cell by a non-proton exchange membrane with thickness of 180 μm (N117 Du PontTM Nafion^R PFSA Membranes). During molybdenum oxidation, the platinum electrode acts as a cathode, whereas during phosphate determination it acts as a counter electrode. The schematic of the cell is presented in Fig. 1.

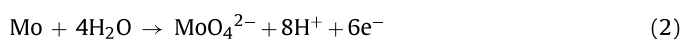
3. Results and discussion

3.1. In situ reagents formation in an electrochemical cell

Phosphate is not an electroactive species but the electrochemical detection is possible in acidic media (at pH 1) in presence of molybdate salts due to the following reaction (1) where the electroactive phosphomolybdate complex is formed [14].



In order to eliminate the addition of molybdate and protons, a method based on anodic oxidation of molybdenum was developed [12,13]. Due to this process (2), all reagents required for phosphomolybdate complex creation are formed:



Since the silicomolybdate complex is formed at these conditions, the method described above has an obvious problem of cross interference in the ocean samples which contain both silicate and phosphate. A few methods to avoid these interferences are tested before using differences in electrochemistry of the two complexes, influence of pH on complex formation and differences in kinetics of complex formation by choosing an appropriate ratio of protons over molybdates of 70 [14]. The latter one was chosen and improved in this work.

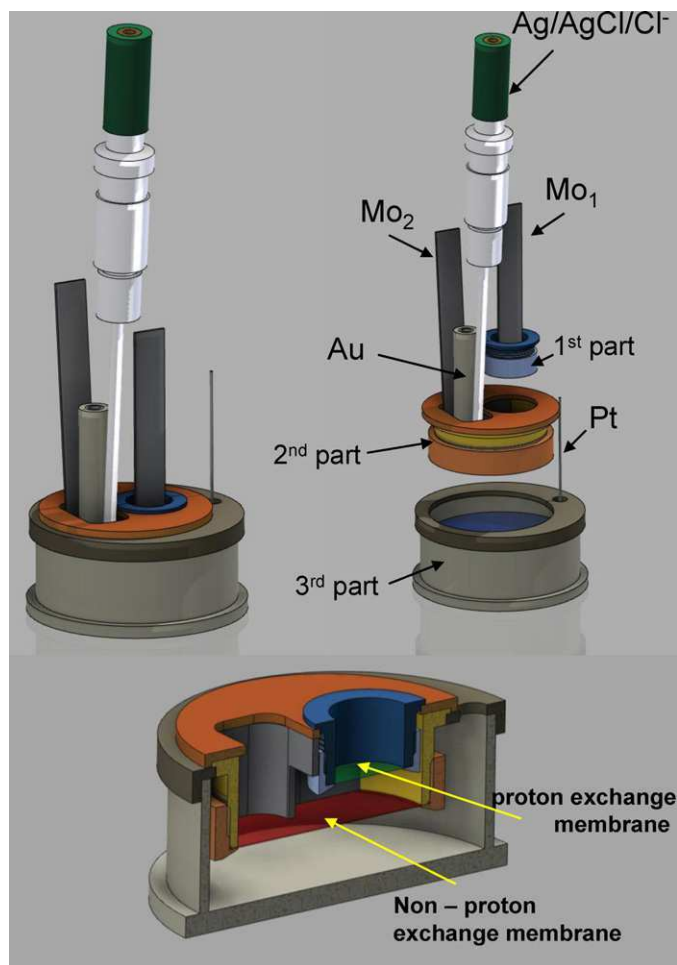


Fig. 1. Schematics of the electrochemical cell with application of membrane technology (Ag/AgCl/Cl⁻-reference electrode, Au-gold working electrode, Pt-platinum counter electrode, Mo₁-first molybdenum electrode, Mo₂-second molybdenum electrode, 1st part-first compartment of the cell with the proton exchange membrane, 2nd part-second compartment of the cell with the non proton exchange membrane, 3rd part-third compartment of the cell, simulating the open ocean).

Zhang et al. [17] indicated that when working with a ratio of protons over molybdates close to 70 at pH 1 (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 electrochemistry. According to reaction (2), the ratio of protons over molybdate is 8 during the oxidation of molybdenum. At the beginning, we achieved an appropriate ratio of 70 by addition of acid [14]. In this work, we present a method where the desired ratio of protons over molybdate is achieved without addition of any liquid reagents. This method is based on the application of membrane technology and a special design of the electrochemical cell described in details in Section 2.3 (Fig. 1). Oxidation of the first molybdenum electrode was performed at a stable potential of 2 V since such high potential will ensure fast molybdenum oxidation and effective acidification of the solution in the second compartment. To achieve a desired pH of 1 in the second compartment, the first molybdenum electrode has to be oxidized during about 1000 s. This time is long but this is due to a large volume of the cell (5 mL) used in this work. The *in situ* sensor which will be developed in the future years will have a volume of a few hundreds μL and thus the reaction time will be much shorter. Excellent reproducibility of pH was achieved, when measuring pH in the second compartment after oxidation of the first

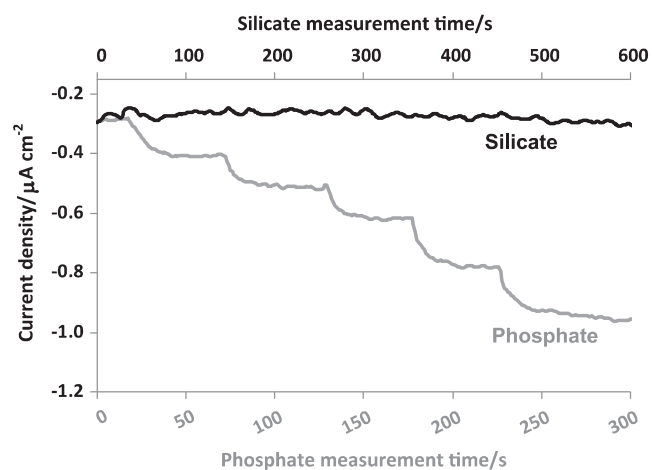


Fig. 2. Amperometric measurement made on a rotating gold disk electrode (0.29 V, 2000 rpm) for silicomolybdate (black) and phosphomolybdate (grey) complexes formed in artificial seawater during anodic oxidation of molybdenum. The signals were achieved by addition of standard solution of silicate (8.5–154.5 μM) and phosphate (0.59–3.49 μM), pH 1.0, ratio protons/molybdates 70.

molybdenum electrode—the precision calculated from 10 measurements is 2.0% with the average pH of 1.02. The second molybdenum electrode was oxidized in the second compartment at a stable current intensity of 50 mA during 80 s to ensure that concentration of formed molybdates is 1.5 mM as it is predicted by Faraday's law. The created phosphomolybdate complex was detected in the second compartment as described below.

3.2. Amperometric detection of phosphate in presence of silicate

The phosphomolybdate complex created as described above can be detected by electrochemical reduction at rotating gold electrode by amperometry at a potential of 0.29 V. Calibration curves for silicate and phosphate are presented in Fig. 2. It is clear that there is no amperometric signal for the silicomolybdate complex, whereas those for phosphomolybdate complex are well defined. The method gives a good linear response for phosphate in the concentration range found in the open ocean ($I = -0.1866C - 0.0066$, $R^2 = 0.9995$). The detection limit calculated as a signal measured between the highest and the lowest value of noise multiplied by three is 0.11 μM . The reproducibility tests reported in Table 1 exhibit quite good precision in the concentration range usually found in the open ocean. The average precision for the reproducibility test is 5.7%.

Amperometric method gives excellent possibility to detect phosphate in seawater but requires utilization of the rotating disk electrode which consumes energy and will complicate measurements in the future *in situ* sensor. Amperometry at static disk electrode shows no signals for phosphate in the concentration range found in the open ocean.

Classical cyclic voltammetry shows two reduction peaks at 0.32 V and 0.46 V and two oxidation peaks at 0.40 V and 0.53 V which give 4 correlation curves for concentrations greater than 5 μM [18]. Unfortunately the concentrations of phosphate found in

Table 1

Reproducibility test carried out for 10 measurements of amperometric or differential pulse voltammetric signal for adequate phosphate concentrations in artificial seawater.

	Phosphate concentration (μM)		
	0.65	1.60	3.01
Amperometry	5.5%	5.7%	5.8%
Differential pulse voltammetry	3.8%	4.0%	3.7%

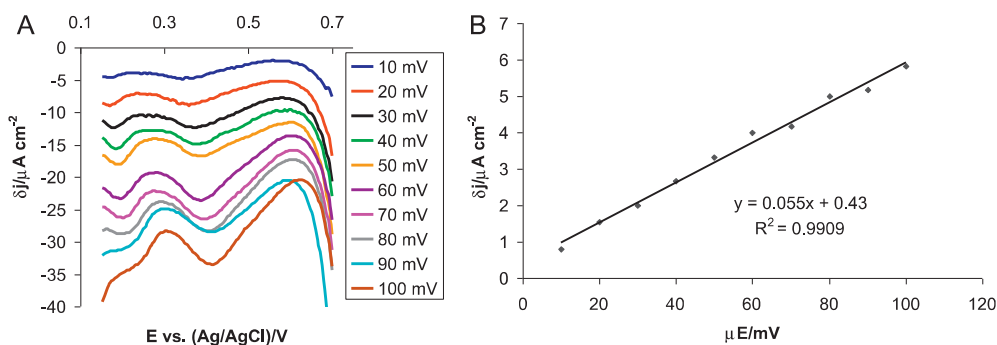


Fig. 3. (A) Differential pulse voltammetry for $3.49 \mu\text{mol L}^{-1}$ phosphomolybdate complex at different pulse amplitudes from 10 mV to 100 mV, (B) differential current density vs. pulse amplitude achieved from voltammograms presented in (A).

the open ocean are smaller (less than $3 \mu\text{M}$) and in this concentrations range the voltammograms show only one reduction and one oxidation peaks which are very weak due to the high capacitive current as compared to the faradic one. The problem is associated with complicated electrode reactions where the reduction of complex on the gold electrode is coupled with an homogenous chemical step, protonation, which prevent rapid detection of the phosphomolybdate complex. This problem was discussed before [14,18]. Having all this in mind, we start to work toward the differential pulse method.

3.3. Phosphate detection using differential pulse voltammetry

The pulse amplitude was varied in the range 10–100 mV in order to find the best conditions for the phosphomolybdate complex detection. Fig. 3A represents the achieved voltammograms and Fig. 3B a plot of the differential current density vs. pulse amplitude. The results show an increase of differential current density value with an increase of pulse amplitude. In the same time, the peak width increases with pulse amplitude as well, which is characteristic for this type of detection method [19]. Besides, the potential peak (at about 0.25–0.30 V) is shifted slightly to more positive values as pulse amplitude increases. The second peak at more positive potentials is not well distinguished and thus impossible to measure. The peak is too close to potentials where formation of gold chlorides occurs at gold electrode in seawater at greater positive potentials. For further analysis, a pulse amplitude of 50 mV was chosen.

The phosphomolybdate complex was detected by differential pulse voltammetry at stationary gold electrode using pulse amplitude optimized above. The signals measured for phosphate in the concentration range found in the open ocean is presented in Fig. 4A. The calibration curve is described by equation $\delta j = 0.8082C + 0.9614$, $R^2 = 0.9897$ and the detection limit is $0.19 \mu\text{M}$. Great care must be taken to measure properly the peak height. Here, we measure peak height as presented in Fig. 4B. The reproducibility tests reported in Table 1 exhibit a good precision. The average precision for the reproducibility test is 3.8%. For clarity and comparison, the reproducibility test for amperometry and differential pulse voltammetry were gathered in the same table. The results show that differential pulse voltammetry offers a better reproducibility.

3.4. Accuracy estimation for electrochemical and colorimetric methods

An estimation of the deviation from theoretical values of phosphate concentration is provided for the classical colorimetric method, amperometry and differential pulse voltammetry methods. The same phosphate standards were used for all methods

to perform calibration curves and then 3 samples containing low ($0.65 \mu\text{M}$ phosphate, $8.59 \mu\text{M}$ silicate), medium ($1.60 \mu\text{M}$ phosphate, $57.1 \mu\text{M}$ silicate), and high ($3.01 \mu\text{M}$ phosphate, $140.9 \mu\text{M}$ silicate) silicate and phosphate concentrations were

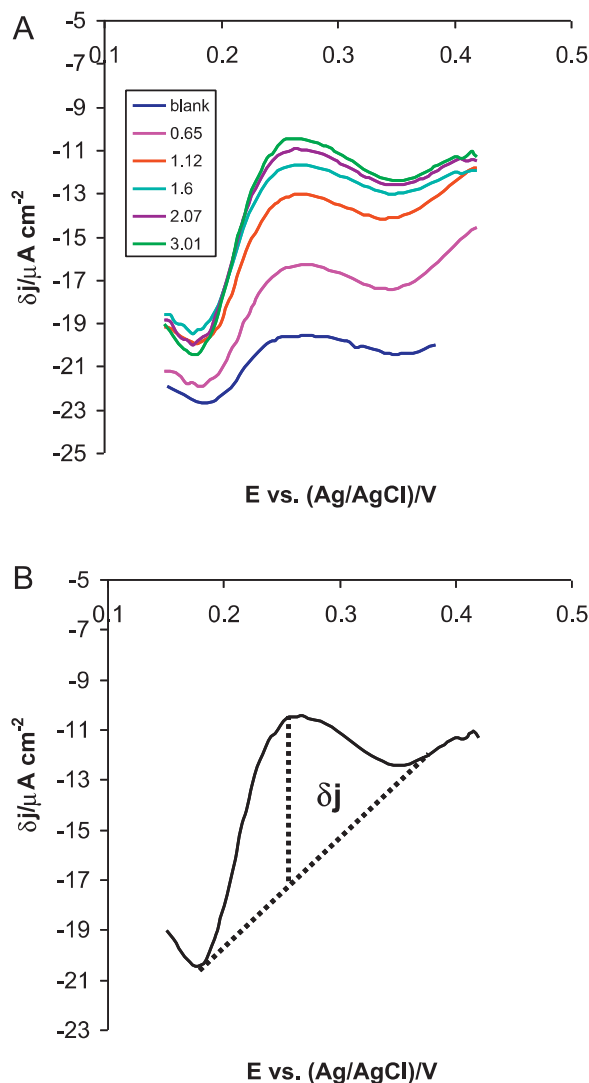


Fig. 4. (A) Differential pulse voltammetry measurement made on a gold disk electrode (at pulse amplitude of 50 mV) for phosphomolybdate complex formed in artificial seawater during anodic oxidation of molybdenum. The signals were achieved for different phosphate concentrations ($0.65\text{--}3.01 \mu\text{M}$); pH 1.0, ratio protons/molybdates 70, (B) method used in this work for determination of peak height.

Table 2

Comparison of colorimetric, amperometric and differential pulse voltammetric measurements for different phosphate concentration. Deviation between each method and theoretical value of phosphate concentration is given in brackets.

[PO ₄ ³⁻] μM theoretical	[Si(OH) ₄] μM theoretical	[PO ₄ ³⁻] μM by colorimetry	[PO ₄ ³⁻] μM by amperometry	[PO ₄ ³⁻] μM by differential pulse voltammetry
0.65	8.59	0.68 (4.6%)	0.63 (3.1%)	0.62 (4.6%)
1.60	57.1	1.61 (0.6%)	1.57 (1.9%)	1.56 (2.5%)
3.01	141	2.97 (1.3%)	2.88 (4.3%)	2.89 (4.0%)

tested. A good agreement between all methods confirms no interference from silicate. Accuracy comparison for all methods is presented in Table 2. The average deviation from theoretical values of phosphate concentration is 3.1% for amperometry, 3.7% for differential pulse voltammetry and 1.3% for colorimetry.

4. Conclusions

We described a thorough documentation necessary to set up an electrochemical detection of phosphate. Thanks to a special construction of an electrochemical cell and utilization of membrane technology coupled with molybdenum oxidation, the method is free from addition of any liquid reagents and free from silicate interferences. During molybdenum oxidation in a sample containing phosphate, the phosphomolybdic complex is formed. The complex is then detected by amperometry or differential pulse voltammetry on a gold electrode. The method allows detecting phosphate in the concentration range found in the open ocean with good detection limit, reproducibility and accuracy. The method will be tested for natural seawater samples as soon as it will be possible.

The further steps will be miniaturization and adaptation of the cell described above to the marine harsh environment (protection against corrosion, biofouling and high pressure) in order to achieve the first electrochemical *in situ* sensor for detection of phosphate in seawater. This sensor will be characterized by low energy consumption and quite fast response time due to the decrease of volume combined with application of large surface of membrane surfaces. We will be working simultaneously on calibrationless method as it was done for silicate in our team [20]. Additionally, long term behavior of gold electrode in seawater will be investigated and potential *in situ* cleaning procedure will be found.

Acknowledgments

We would like to thank Marcel Belot from the OMP-GIS (Observatoire Midi-Pyrénées-Groupe d'Instrumentation Scientifique, Toulouse, France) for the mechanical manufacturing of the electrochemical cell. We are grateful to the GET (Géoscience Environment Toulouse) Laboratory (Toulouse, France) for access to a spectrophotometer. Justyna Jońca is supported by a Marie Curie PhD grant within SENSEnet ITN (EC Framework Programme 7, grant agreement No. 237868). William Giraud is supported by the Foundation STAE (Sciences and Technologies for Space and Aeronautics) within the project "MAISOE" (Microlaboratories of *in situ* Analyses for Environmental Observatories).

References

- [1] A. Paytan, K. McLaughlin, The oceanic phosphorus cycle, *Chemical Reviews* 107 (2007) 563.
- [2] J. Murphy, J.P. Riley, A modified simple solution method for the determination of phosphate in natural waters, *Analytica Chimica Acta* 27 (1962) 31.
- [3] D. Thouron, R. Vuillemin, X. Philippon, A. Lourenço, C. Provost, A. Cruzado, V. Garçon, An autonomous nutrient analyzer for oceanic long-term *in situ* biogeochemical monitoring, *Analytical Chemistry* 75 (2003) 2601.
- [4] N.P. Revsbech, L.H. Larsen, J. Gundersen, T. Dalsgaard, O. Ulloa, B. Thamdrup, Determination of ultra-low oxygen concentrations in oxygen minimum zones by the STOX sensor, *Limnology and Oceanography* 7 (2009) 371.
- [5] G.W. Luther III, B. Glazer, L. Hohmann, J. Popp, M. Talleferf, T. Rozan, P. Brendel, S. Theverge, D. Nuzzio, Sulfur speciation monitored *in situ* with solid state gold amalgam voltammetric microelectrodes: polysulfides as a special case in sediments, microbial mats and hydrothermal vent waters, *Journal of Environmental Monitoring* 3 (2001) 66.
- [6] M.L. Tercier-Waerber, F. Confalonieri, G. Riccardi, A. Sina, S. Nöel, J. Buffle, F. Graziottin, Multi physical-chemical profiler for real-time *in situ* monitoring of trace metal speciation and master variables: development, validation and field applications, *Marine Chemistry* 97 (2005) 216.
- [7] A.G. Fogg, N.K. Bsebsu, Differential pulse voltammetric determination of phosphate as molybdovanadophosphate at a glassy carbon electrode and assessment of eluents for the flow injection voltammetric determination of phosphate, silicate, arsenate and germanate, *Analyst* 106 (1981) 1288.
- [8] N.G. Carpenter, A.W.E. Hodgson, D. Pletcher, Microelectrode procedures for the determination of silicate and phosphate in waters-fundamental studies, *Electroanalysis* 9 (1997) 1311.
- [9] L. Guanghan, W. Xiaogang, L. Yanhua, Y. Shenkai, Studies on 1:12 phosphomolybdic heteropoly anion film modified carbon paste electrode, *Talanta* 49 (1995) 511.
- [10] S.M. Harden, W.K. Nonidez, Determination of orthophosphate by flow injection analysis with amperometric detection, *Analytical Chemistry* 56 (1984) 2218.
- [11] J.C. Quintana, L. Idrissi, G. Palleschi, P. Albertano, A. Amine, M. El Rhazi, D. Moscone, Investigation of amperometric detection of phosphate. Application in seawater and cyanobacterial biofilm samples, *Talanta* 63 (2004) 567.
- [12] M. Lacombe, V. Garçon, D. Thouron, N. Le Bris, M. Comtat, Silicate electrochemical measurements in seawater: chemical and analytical aspects towards a reagentless sensor, *Talanta* 77 (2008) 744.
- [13] M. Lacombe, V. Garçon, M. Comtat, L. Oriol, J. Sudre, D. Thouron, N. Le Bris, C. Provost, Silicate determination in sea water: toward a reagentless electrochemical method, *Marine Chemistry* 106 (2007) 489.
- [14] J. Jońca, V. Leon-Fernandez, D. Thouron, A. Paulmier, M. Graco, V. Garçon, Phosphate determination in seawater: toward a reagentless electrochemical method, *Talanta* 87 (2011) 161.
- [15] L.I. Gordon, J.C. Jennings, A.A. Ross, J.M. Krest, WOCE, Method Manual, W. H. P. Office Report, 1993, p. 68.
- [16] J. Strickland, T. Parsons, Practical Handbook of Seawater Analysis, vol. 167, Fisheries Board of Canada, Bulletin, Ottawa, 1972, p. 49.
- [17] J.-Z. Zhang, C.J. Fischer, P.B. Ortner, Optimization of performance and minimization of silicate interference in continuous flow phosphate analysis, *Talanta* 49 (1999) 293.
- [18] J. Jońca, C. Barus, W. Giraud, D. Thouron, V. Garçon, M. Comtat, Electrochemical behaviour of isopoly- and heteropolyoxomolybdates formed during anodic oxidation of molybdenum in seawater, *International Journal of Electrochemical Science* 7 (2012) 7325.
- [19] A. Bard, L.R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2nd ed., John Wiley and Sons, Inc., Hoboken, NJ, 2001.
- [20] W. Giraud, L. Lesven, J. Jońca, C. Barus, M. Gourdal, D. Thouron, V. Garçon, M. Comtat, Reagentless and calibrationless silicates measurement in oceanic water, *Talanta* 97 (2012) 157.