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Silicate marine electrochemical sensor

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A R T I C L E I N F O

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A B S T R A C T

An autonomous electrochemical sensor suitable for *in situ* silicate detection and monitoring in marine environments, is presented without any use of liquid reagent. This paper shows silicate sensor characteristics and figures of merit using optimized chemical and electrochemical parameters. Under controlled laboratory conditions in a 40 L tank, good calibration between 1.63 and 132.8 μmol L^{-1} was obtained. The limit of detection and the limit of quantification obtained are respectively LOD = 0.32 μmol L^{-1} and LOQ = 1.08 μmol L^{-1}. No bias was found while analysing Certified Reference Material (CRM) solutions *i.e.* natural seawaters samples with different salinities and nutrients compositions. Repeatability test showed very good reproducibility of the measurement with low overall uncertainty, cumulating systematic error and reproducibility error, of 2.4 %. Accuracies obtained with the Silicate sensor are higher than 97.4 %, 95.3 % for the smallest concentration tested, under LOQ. Spike and recovery tests were conducted with two different CRM concentrations and showed 97.9–100.1 % recovery, indicating no matrix influence in the determination of silicate concentration using electrochemical sensor and its calibration process (realised with artificial seawater solutions). *In situ* deployment of silicate electrochemical sensor was realized in the Thau lagoon (Mediterranean Sea) at 1.6 m depth. A good agreement between the results obtained with the sensor compared to reference colorimetric measurements made at the Marine Station of Sète (France) validates sensor's performances.

1. Introduction

Silicate is one of essential nutrient used by certain types of phytoplankton to form their skeletal structure [1], such as diatoms who provide up to 45 % of the total oceanic primary production [2–7]. Lack of silicate in aquatic environments may limit biomass growth and affects the whole trophic levels. However, excessive silicate concentration can cause red tides due to phytoplankton bloom [8,9]. Silicate as the other nutrients *i.e.* phosphate and nitrate, are involved in carbon dioxide sequestration in the oceans [10–16] and their biogeochemical cycles are linked to the global carbon cycle and therefore contribute into climate regulation [17–19].

To efficiently monitor biogeochemical variables, to improve our understanding of their cycles and their impact on climate, and, considering the very high spatial and temporal variability found in Open Ocean, *in situ*, autonomous sensors are the only sustainable solution [20].

The common method to measure nutrients concentration is visible-spectrophotometry requiring liquid reagents [21–25]. Lab-on-chip *in situ* nutrient sensors based on colorimetric measurements have been successfully deployed in marine environments to detect nitrate and nitrite [26], phosphate [27,28]. The silicate *in situ* sensor developed by Cao et al. [29] shows satisfactory results with a detection limit of 45.1 nmol L^{-1} for a 300 s sensor response time. They deployed their sensor in routine and recorded high precision and robustness *in situ* data [29]. Although, the use of liquid reagents is an issue for long term monitoring, not to mention stability issues for some reagents, especially the ascorbic acid used for silicate determination [30]. Furthermore, colorimetric methods suffer from interferences and refractive index effects [31].

For these reasons, our group worked and proposed a reagentless method to monitor nutrients concentration in seawater using

Abbreviations: SD, standard deviation; RSD, relative standard deviation; CRM, certified reference material; LOD, limit of detection; LOQ, limit of quantification; PEEK, polyether ether ketone.

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Table 1
CRM composition, only silicate concentrations are indicated but samples contain phosphate, nitrate and nitrite. The complete composition is available at “http://www.kanso.co.jp/eng/production/available_lots.html”.

	Certified value ± SD (μmol kg^{-1})	Expanded uncertainty (μmol kg^{-1})	Salinity (psu)	Density	$[Si]_{CRM\_ref}$ (μmol L^{-1})
Lot. CK*	0.73 ± 0.006	0.08	35.211	1.0249	**0.75**
Lot. CL	13.8 ± 0.012	0.3	34.685	1.0245	**14.1**
Lot. CC	86.16 ± 0.052	0.48	34.338	1.0243	**88.25**
Lot. CB	109.2 ± 0.052	0.62	34.374	1.0243	**111.9**

* KANSO note: value for Silicate is below quantifiable detection limit, thus use this value as a guide.

Fig. 1. Silicate *in situ* sensor (left) and stainless steel cage implemented with the silicate sensor and its battery pack (right) ready for deployment.

electrochemistry [32–38]. Silicate is a non-electroactive specie and its determination is performed by measuring its corresponding silicomolybdic complex formed *in situ* at acidic pH after a simple oxidation of a molybdenum solid electrode while the counter electrode is isolated behind a Nafion® membrane [33,34]. Electrochemical detection of the silicomolybdic complex is selective, do not suffer from any interference and allows to considerably reduce the size of sensor. It is also compatible with long period of deployment as no liquid reagents bag is required, on the contrary of colorimetric methods.

Our reagentless silicate sensor has been successfully deployed for the first time in the upwelling of the central-northern zone of Chile and data collected were in good agreement with physical data recorded as well with a reference sample analysed by colorimetry [39]. In this paper, a complete characterisation of silicate sensor is presented including validation using Certified Reference Materials (CRM KANSO CO., LTD., Osaka, Japan). A rigorous intercomparison between our silicate sensor and colorimetry has been performed for the first time during a deployment in the Thau lagoon (Mediterranean Sea) at Sète Marine Station (France), where two water samples per day were analysed.

2. Experimental

2.1. Chemicals and materials

All solutions were prepared in Milli-Q water (Millipore Milli-Q water system). One litre of artificial seawater was made with a mix of 32.74 g sodium chloride (NaCl, VWR), 7.26 g magnesium sulphate heptahydrate ($MgSO_4$, $7H_2O$, VWR) and 0.172 g sodium hydrogenocarbonate ($NaHCO_3$, VWR) (adapted from [40]). Polymethylpentene or polypropylene containers were used instead of glass to avoid silicon contamination. Silicate solutions were prepared with certified standard solution from Sigma-Aldrich at 1003 ± 5 mg L^{-1} as SiO_2, corresponding to 16693 ± 83 μmol L^{-1}, diluted into artificial seawater electrolyte at pH≈ 7 and salinity closed to 35 psu. Four different Certified Reference Material (CRM) supplied by KANSO CO., LTD, Japan were used to validate the sensor: Lot. CK (Issue no.: 2019-00170), Lot. CL (Issue no.: 2019-00171), Lot. CC (Issue no.: 2019-00169) and Lot. CB (Issue no.: 2019-00168). Respective silicate compositions as well as salinities are described in Table 1. Sulfuric acid at 98 % supplied by Merck has been used to activate electroactive surface of gold electrodes. Molybdenum plate, silver, gold and platinum rods and titanium grid used to build sensor electrodes were purchased from GoodFellow.

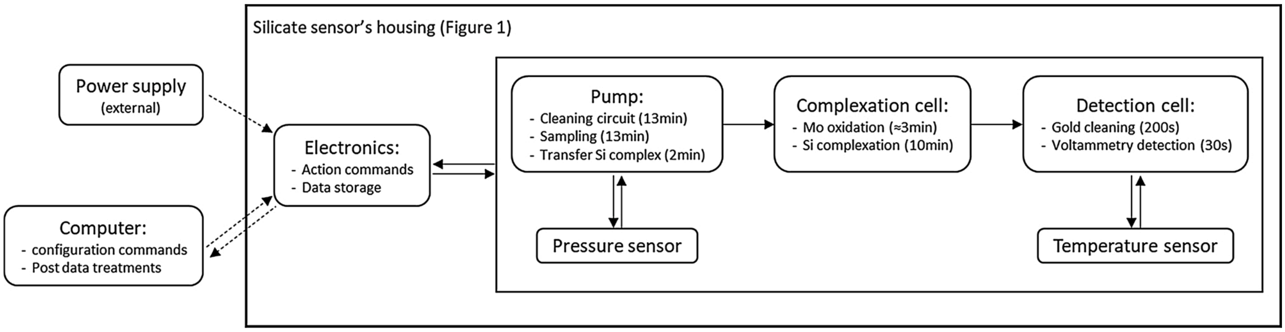

Fig. 2. Functioning procedure of the Silicate sensor.

2.2. Silicate sensor: description and process

In situ silicate sensor previously described in [39] and presented in left on Fig. 1 is an anodized aluminium cylinder of 9 cm diameter and 25 cm long with a weight of 2.2 kg in air without the battery pack (external, shown in right on Fig. 1). The housing has been validated up to 60 bars (600 m depth). A solenoid pump from Lee-Company, placed into dielectric oil filled reservoir equipped with a membrane (Fig. 1, left) avoiding pressure constraint, is used to sample and clean the whole circuit.

On the top of the sensor, opposite to the connector (Fig. 1, left), the electrochemical cells (with the electrodes) include a complexation cell of 376 μL and a detection cell of 94 μL. These technical parts of the sensor are designed in PEEK (polyether ether ketone). Silicates not being electroactive, there are firstly complexed with molybdates at acidic pH in the complexation cell using molybdenum electrode. After molybdenum oxidation (Eq. (1)) to form *in situ* the needed reagents and optimised complexation time around 10 min, the silicomolybdic complex ($Si(Mo_{12}O_{40})^{4-}$) formed (Eq. (2)) is transferred into the detection cell using the pump and detected by cyclic voltammetry in between 0.0 and 0.5 V/ref using a scan rate of 100 mV s^{-1}. Cyclic voltammograms show two reversible peaks corresponding to the reduction of the complex in two steps observed at 0.32 V and 0.25 V/ref respectively [39]. In this potential window (0.0 and 0.5 V/ref), at the pH ≃ 1.5 obtained, only silicomolybdate is detected, showing good selectivity of our silicate electrochemical sensor.

$$Mo + 4H_2O \rightarrow MoO_4^{2-} + 8H^+ + 6e^- \quad (1)$$

$$Si(OH)_4 + 12\ MoO_4^{2-} + 20\ H^+ \rightarrow \left[Si(Mo_{12}^{(VI)}O_{40})\right]^{4-} + 12\ H_2O \quad (2)$$

A conventional three-electrode system is used in both cells, where molybdenum plate (S =118 mm^2) and gold disc (φ =2 mm) are used as working electrodes in complexation cell and detection cell respectively. Before first use, gold electrode is polished with aluminium oxide (0.3 μm diameter, PRESI), then electrochemically cleaned in 0.5 mol L^{-1} sulphuric acid with classical cleaning protocol [39]. Silver wire (φ =1 mm, l =25 mm) and silver disc (φ =2 mm), used as reference electrodes, are covered with silver chloride layer using PGSTAT 128 N potentiostat supplied by Metrohm. All the potentials are expressed *versus* Ag/AgCl/Cl- (0.6 mol L^{-1}), written as V/ref. In the complexation cell, the counter electrode (*i.e.* titanium grid (φ =25 mm)) is isolated from the sample behind a 180 μm Nafion® membrane (N117 Du Pont™ Nafion® PFSA Membrane) in order to reach the acidic pH needed (pH ≃ 1.5) for Eq. (2), thus avoiding H^+ reduction at counter electrode's surface [33,39]. A platinum disc (φ =2 mm) is used as counter electrode in the detection cell.

The electronics, placed into a dry compartment, controls the whole analytical procedure schematized in the Fig. 2, including the pump action to clean the circuit (13 min), to sample (13 min) and transfer seawater (2 min), the electrochemical cleaning of the gold electrode (polarized at -0.2 V/ref during 200 s), the oxidation of Molybdenum (around 3 min) and the silicomolybdic complex detection by cyclic voltammetry (30 s) after a complexation time (10 min). The whole procedure takes around 45 min. The device is also equipped with pressure and temperature sensors. Pressure is measured at the beginning and the end of the water sampling while temperature is monitored during the silicomolybdic complex detection.

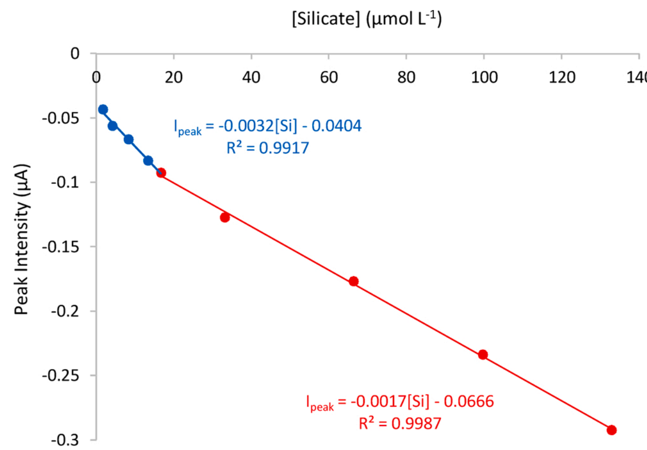

Fig. 3. Sensor calibration at room temperature between 1.63–132.8 μmol L^{-1} of silicate standards in artificial seawater.

2.3. In situ experiment

Silicate sensor has been deployed at 1.6 m depth in the Thau lagoon (Mediterranean Sea) at the Sète Marine Station (France), attached together with its battery pack, to an stainless steel cage (Fig. 1, right). The sensor recorded silicomolybdic signal every 45 min between the 8th and the 12th of July 2019.

During deployment period, 8 water samples have been taken and analysed by colorimetric method at the Sète Marine Station laboratory. Each sample has been analysed twice, the corresponding average and standard deviation are showed on the following results section. To determine silicate concentrations, two 13 mL aliquots were filtered on 3 times pre-washed PP 0.45 μm filters (25 mm, Agilent Technologies), stored at −20 °C until analysis and then analysed using a Continuous Flow Analyzer (SAN++, SKALAR) following the standard photometric analysis method [41]. This method is based on the following reaction: the sample is acidified and mixed with an ammonium heptamolybdate solution forming molybdosilicic acid. This acid is reduced with L(+) ascorbic acid to a blue dye, which is measured at 810 nm.

3. Results and discussion

3.1. Silicate sensor characterisation

3.1.1. Calibration and standards analyses

Calibration curve of the sensor (Fig. 3) corresponds to the concentration of silicate standards dissolved in artificial seawater plotted *versus* the peak intensity measured at E = 0.32 V/ref on cyclic voltammograms recorded at room temperature by the sensor after Molybdenum oxidation and silicomolybdic complex formation.

The range of silicate concentration in the open ocean goes between few nanomolar in surface waters up to 140 μmol L^{-1} at depths with very high regional and seasonal variability [42–44]. The targeted range chosen is 1.63–132.8 μmol L^{-1} and shows two linear behaviours with silicate concentration on Fig. 3.

Calibration's slope changings have also been observed in the literature, as well as saturation of the signal at higher silicate or phosphate concentrations, using electroanalytical [37,45–48] or colorimetric detections [29,49].

The formation of heteropolyoxomolybates and also its reduction are strongly dependent with experimental conditions especially the proton concentrations, molybdates forms and concentrations and also silicate (or phosphate) concentrations [37,50–56]. Several types of complexes can be formed as well as polymeric structures at high concentrations [32,33,48].

B. Wang and S. Dong showed that central atom (silicium) in the Keggin structure has non-negligible influence on electrode reactions of the silicomolybdic complex [57]. They reported a diffusion-controlled process at high silicate concentrations whereas the signals obtained with low silicate concentrations are mainly due to the adsorbed monolayer. Carpenter et al., also demonstrated that the electron transfer is not completely mass transport controlled and a probable protonation reaction occurs before the heteropolyoxomolybdate reduction that slows down the electron transfer [58].

The mechanism of its reduction is therefore very complicated and not all the authors agreed on the number of electrons exchanged. Carpenter et al. [58], Lacombe et al. [32,33], claimed that 2 then 3 electrons are exchanged whereas [57,59–62] agreed on 2 electrons processes.

We can conclude that at higher silicate concentrations, both diffusion and electron transfer rates are probably affected and slowed down due to the formation of higher valence structures or higher steric hindrance heteropolyoxomolybdates explaining the decrease in the calibration slope observed. In any cases, depending on the electrochemical signal measured by the sensor, the appropriate calibration will be used in order to determine the corresponding *in situ* silicate concentration.

In order to determine the limit of detection (LOD) and the limit of quantification (LOQ), a low silicate concentration was analysed 26 times. One value has been discarded by Dixon test [63]. The sample mean ($\bar{x}$) of silicate concentration obtained and its corresponding standard deviation (SD) are: $\overline{[Si]}_{low} = 1.93 \pm 0.11$ μmol L^{-1}.

From this result, the limit of detection defined as 3 times the SD and the limit of quantification as 10 times the SD, are deducted:

LOD = 0.32 μmol L^{-1}.

LOQ = 1.08 μmol L^{-1}.

If the silicate concentration analysed was appropriated to estimate the LOD, the compliance ratio R should be between 4 and 10.

In our case, we obtained a ratio: $R = \frac{\overline{[Si]}_{low}}{3 \times SD} = 6$, validating the method used.

3.1.2. Certified reference material analyses

In order to evaluate the accuracy and the precision of the sensor, 4 Certified Reference Material (CRM) supplied by KANSO were analysed. CRM are produced using treated natural seawater on the basis of quality control system under ISO 17034 (JIS Q 17034) [64,65]. The certified values represent the average of 30 bottles analysed by colorimetric method. Following ISO Guide 35 (JIS Q 0035) guideline, standard deviations are calculated based in the results of 180 bottles measured in duplicate. Reference concentrations ($[Si]_{CRM\_ref}$), expanded uncertainty, salinity and density gave by the supplier KANSO are indicated in the Table 1.

Table 2
Certified Reference Material (CRM) analysis using silicate sensor.

	$\overline{[Si]}_{CRM\_anal} \pm$ SD* (μmol L^{-1}) (RSD %)	Bias Assessment $t_{(95\%)}.SD/\sqrt{N}$ / $\lvert \overline{[Si]}_{CRM\_anal}$ - $[Si]_{CRM\_ref} \rvert$	Overall uncertainty	Accuracy
Lot. CK	0.78 ± 0.01 (1.7 %)	0.12 > 0.04	8.3%	95.3 %
Lot. CL	14.05 ± 0.13 (0.9 %)	0.05 < 0.09	2.4 %	99.4 %
Lot. CC	86.00 ± 0.67 (0.8 %)	5.98 > 2.25	4.1%	97.4 %
Lot. CB	111.95 ± 0.24 (0.2 %)	2.17 > 0.09	0.5%	99.9 %

* SD: 2 measurements were used to determine the standard deviations except for the lot. CL where 31 measurements were analysed.

Each lot has been analysed by the silicate sensor in duplicate, except the lot. CL where 31 measurements have been realised to evaluate the repeatability of the sensor. The silicate concentrations were determined using the appropriate calibration above. The average of the silicate concentration obtained using the sensor ($\overline{[Si]}_{CRM\_anal}$), their respective standard deviations (SD) and relative standard deviations (RSD) are indicated in the Table 2, together with bias assessment, overall uncertainty and accuracy.

The overall uncertainty (Eq. 3) cumulates systematic error (bias) and reproducibility error (SD).

$$\text{Overall uncertainty} = \frac{\left|\overline{[Si]}_{CRM\_anal} - [Si]_{CRM\_ref}\right| + 2.SD}{[Si]_{CRM\_ref}} (\%) \quad (3)$$

where $\overline{[Si]}_{CRM\_anal}$ and $[Si]_{CRM\_ref}$ represent respectively the mean of silicate concentration analysed by the sensor and the reference value of the CRM gave by the supplier KANSO found in Table 1.

The accuracy (Eq. 4) is defined by [100 - Relative error (%)]:

$$\text{Accuracy} = 100 - \frac{\left|\overline{[Si]}_{CRM\_anal} - [Si]_{CRM\_ref}\right|}{[Si]_{CRM\_ref}} (\%) \quad (4)$$

No bias exists between the mean of Silicate concentration measured by the sensor ($\overline{[Si]}_{CRM\_anal}$) and the reference value of the CRM ($[Si]_{CRM\_ref}$) if the term ($t_{(95\ \%)}.SD/\sqrt{N}$) is higher than ($\lvert \overline{[Si]}_{CRM\_anal}$ - $[Si]_{CRM\_ref} \rvert$) value. $t_{(95\ \%)}$ corresponds to the Student's t-distribution value for a 95 % confidence internal and N the number of measurements. As shown on Table 2, there is no bias for CK, CC and CB. A bias is detected for CL due to high number of measurements, however SD, RSD, as well as the overall uncertainty for CL are very low.

Very good overall uncertainties and accuracies have been obtained for the 4 CRM tested with our sensor. Higher overall uncertainty is observed for the lot. CK but considering the quite low silicate concentration measured, even under limit of quantification, this result is acceptable.

The repeatability test conducted with CL allows to determine the population mean (μ) (or true mean) for this CRM. Considering a t-Student distribution, the 95 % and 99 % confidence intervals of the true mean are:

Confidence interval (95 %): 14.00 μmol L^{-1} < $[Si]_{CRM\_CL\_true\ mean\_}95\ \%$ <14.10 μmol L^{-1},

Table 3
Recovery results.

	$[Si]_{added}$ (µmol L^{-1})	$\overline{[Si]}_{Total}$ ± SD* (µmol L^{-1}) (RSD%)	% Recovery
Lot. CK	6.68	7.47 ± 0.24 (3 %)	100.1 %
	13.35	14.10 ± 0.31 (2 %)	99.7 %
Lot. CC	20.70	104.37 ± 0.81 (1 %)	97.9 %
	41.40	126.15 ± 0.88 (1 %)	99.2 %

Confidence interval (99 %): 13.99 µmol L^{-1} < $[Si]_{CRM\_CL\_true\ mean\_99\ \%}$ <14.11 µmol L^{-1},

in good agreement with the reference value $[Si]_{CRM\_CL\_ref}$ = 14.1 ± 0.3 (expanded uncertainty) µmol L^{-1} (Table 1).

3.1.3. Recovery tests

To evaluate the degree of influence from the matrix (composition of seawater), recovery tests have been performed with CK and CC CRM solutions. From the CRM solution, a known quantity ($[Si]_{added}$) of the commercial SiO_2 standard solution (at 16693 µmol L^{-1}) is added. Each CRM and each spiked sample ($\overline{[Si]}_{Total}$) were analysed by the sensor twice. The corresponding silicate concentrations were determined using the previous calibration. Results obtained are shown in Table 3.

The percentage of recovery is defined by Eq. (5):

$$\% \ recovery = \frac{\overline{[Si]}_{Total}}{\overline{[Si]}_{CRM\_anal} * + [Si]_{added}} \tag{5}$$

where $\overline{[Si]}_{Total}$ is the mean of silicate concentrations measured by the sensor on the spiked samples. $\overline{[Si]}_{CRM\_anal}$* corresponds to the mean of

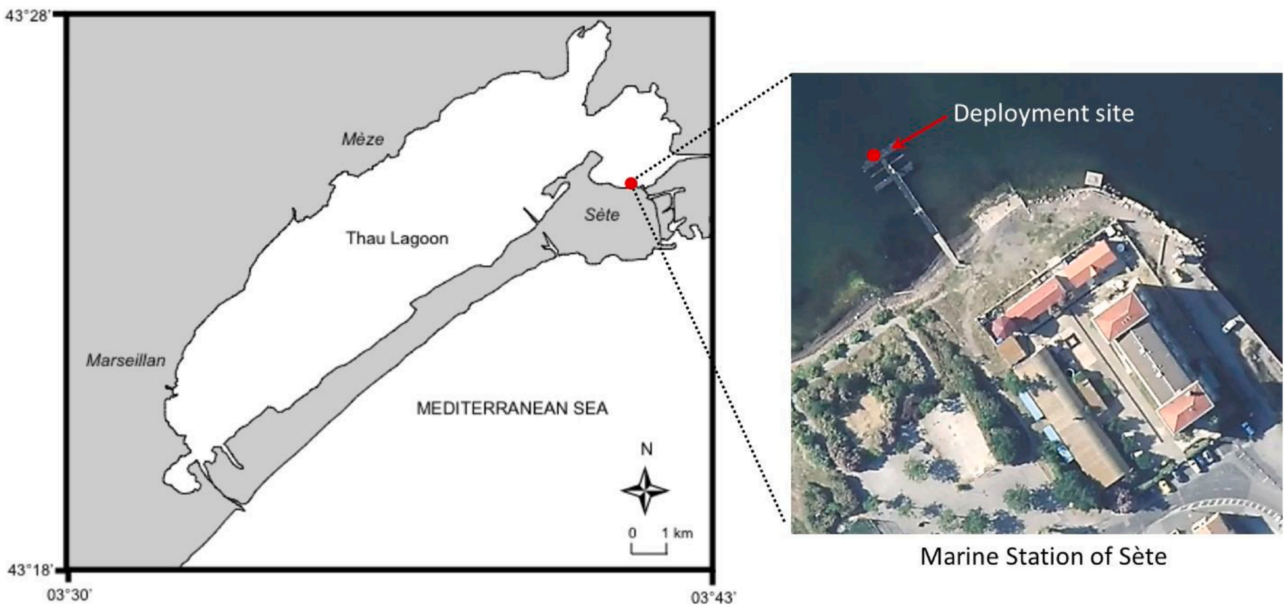

Fig. 4. Locations of Sète Marine Station and the deployment area of silicate sensor (at the end of Station pontoon, ●).

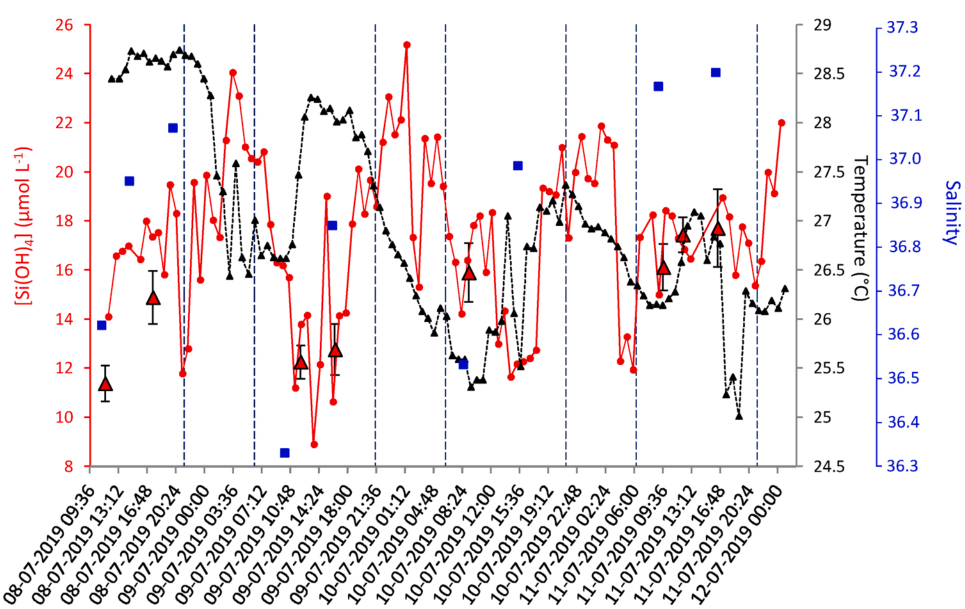

Fig. 5. Time (UTC + 2) evolution of silicate concentration (●) and temperature (▲) measured by the *in situ* sensor at 1.6 m depth in Thau lagoon (Mediterranean Sea) and of reference colorimetric measurements (▲) and (■) salinity measured on discrete samples.

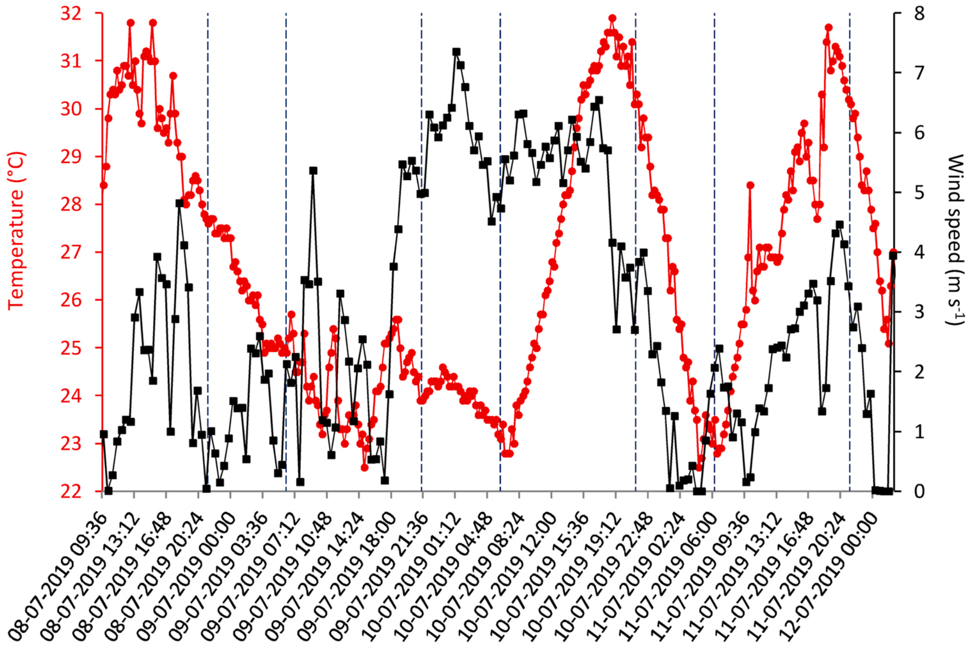

Fig. 6. Time (UTC + 2) evolution of air temperature (●) and half-hourly mean value of surface wind speed (■) measure on the pontoon of Marine Station during deployment period.

silicate concentrations measured by the sensor in CRM solutions ($\overline{[Si]}_{CRM\_anal}$ found on Table 2) corrected with dilution factor due to the standard additions of SiO_2. The volume added is however considered small enough to neglect matrix's dilution.

Very good recovery values, from 97.9 to 100.1%, have been obtained (Table 3) at both low (CK: 0.75 μmol L^{-1}) and high (CC: 88.25 μmol L^{-1}) concentrations, indicating no matrix influence in the determination of silicate concentration with our electrochemical sensor and its calibration process.

3.2. *In situ validation*

The silicate sensor has been deployed in Thau lagoon (Mediterranean Sea) from a pontoon of the Marine Station of Sète (France) between the 8th and the 12th of July 2019 at 1.6 m depth (Fig. 4). The Thau lagoon is located in the south of France, connected to the sea by the canal of Sète. The Thau lagoon is a shallow coastal lagoon (4 m average depth) located in the North Western Mediterranean shore (43°24'00" N, 3°36'00" E) and connected to the Mediterranean Sea through three narrow channels. The study site is characterized by a large water temperature and salinity seasonal fluctuation (from about 4–29 °C and 28.5–40 psu respectively, [66]) and strongly affected by meteorological conditions bringing high nutrients variability [67]. Nutrients discharges and significant increases of primary production are observed during river flood events [68]. Tidal range is lower than 1 m, therefore the wind, playing an important role in the hydrodynamics [69], and temperature represent the main vectors of vertical mixing in the lagoon. During summer (July, August), high water temperature (around 30 °C), high salinity (above 38 psu) and low wind velocity (under 5 m s^{-1}) are observed that lead to oxygen depletion in bottom waters (anoxia). In anoxic conditions, silicate concentration range varies from few micromolar to around 50 μmol L^{-1} [70,71].

The sensor worked continuously and analysed a sample every 45 min. Electrochemical signals recorded by the sensor have been translated into concentrations using the calibration made with standards diluted in artificial seawater prior deployment. The time series obtained with the sensor are showed in red on the Fig. 5, together with the *in situ* temperature measured by the sensor in black on Fig. 5. Red triangles represent the silicate concentrations of the 8 discrete samples, taken at the same depth of the sensor, measured by colorimetric detection at the Marine Station, using the molybdenum blue method. The salinity of the discrete samples is measured by conductivity/salinity sensor (EC300 Model, VWR) and indicated in blue. The air temperature and wind speed during the period of deployment are determined with temperature probe (HMP45C Model, Campbell Scientific) and wind monitor (05103-L Model, Campbell Scientific) respectively, fixed on pontoon of Marine Station. These data are indicated on the Fig. 6. Vertical dotted lines indicate sunsets and sunrises delimiting days and nights.

During the four days of deployment, 102 data have been recorded by the sensor. The silicate concentration ranged from 8.90 to 25.19 μmol L^{-1} and *in situ* temperature at 1.6 m depth varied from 25.01 to 28.74 °C. The sensor needed 13 min to sample seawater. Therefore, the data for silicate concentration on Fig. 5 are plotted against the mean of the local sampling time (UTC + 2). However, the time for colorimetric measurements is the actual, instant time of the seawater sampling.

Through the deployment period, a good correlation was obtained between the sensor data and the reference colorimetric measurements realised at the Marine Station of Sète, indicating the sensor has not drifted after these four days of measurement. Only the first value recorded by the sensor seems far from the colorimetric analysis of the first discrete sample (Fig. 5), however, there are 30 min differences between the discrete sampling and the beginning of the sensor sampling. Also, the silicate concentration as well as the salinity were increasing, so the result obtained is rather consistent.

Nights and days insights show higher silicate concentrations during the night than during the daytime that has been previously observed by Throuzeau et al. [72]. During day light, within the upper of euphotic zone, silicate is consumed by phytoplankton for their growth explaining the decrease of silicate concentration observed in surface waters.

During night, the increase of silicate concentration can be explained by vertical mixing inducing silicate release in suspension from the sediment due to the wind (night of 9th-10th July) and also to the stratification linked to the decrease of both sea surface temperature and air temperature at nights (night of 8th-9th and night of 10th-11th July to a lesser extent) (Figs. 5 and 6). The maxima of silicate concentration at 25.19 μmol L^{-1} (Fig. 5) in the night between the 9th and the 10th of July was indeed correlated to a stronger wind (wind speed increased) recorded by Campbell Scientific wind monitor as shown on the Fig. 6.

Remineralisation or regeneration of silicate in the water column can also participate to the increase of silicate concentration in dark conditions.

4. Conclusion

An electrochemical *in situ*, reagentless, sensor has been designed to detect silicate concentration in marine environments. Silicate calibration between 1.63 and 132.8 μmol L^{-1} of SiO_2 standard solutions has been performed in artificial seawater. Limit of detection of 0.32 μmol L^{-1} and limit of quantification of 1.08 μmol L^{-1} were determined. The sensor showed no bias while analyzing Certified Reference Material solutions and good reproducibility and recovery have been obtained. *In situ* deployment in the Mediterranean Sea (Thau lagoon) gave accurate results in comparison with reference colorimetric measurements. Our sensor proved it is ready to be used in routine for *in situ* silicate concentration monitoring in the global ocean.

In order to decrease the response time of our sensor and drastically improve the performances in terms of measurement frequency, a new sampling system is currently under study and should be used in the next sensor generation.

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CRediT authorship contribution statement

Dr. Dancheng Chen Legrand as part of the OCEANSensor project, carried out the investigation, formal analysis and validation. She wrote the original draft.

Dr. Sébastien Mas was involved in investigation and resources (laboratory samples and analyses). He participated in the writing-review of this article.

Benoit Jugeau developed and provided instrumentation resources.

Dr. Arnaud David provided and supervised instrumentation and electronic resources. He participated in reviewing the article.

Dr. Carole Barus, project administrator of this work, was in charge of supervision, investigation and participated to formal analysis and data validation. She managed the writing-review & editing of the published work.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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