Scientific rationale

- Nutrients limit oceanic primary production and serve as water mass tracers
- Long term monitoring and real time transmission of nutrients data will allow us to better understand biogeochemical cycles
- Monitoring of chemicals in the ocean requires an in situ miniaturized autonomous instrumentation
- Electrochemistry provides: miniaturisation, reagentless and calibrationless methods, reduction of energy requirement

Silicate

As silicate is not electroactive species a complexation at acidic medium (pH ≤ 1.5) with molybdates is required [1].

\[
\text{Si(OH)}_4 + 12 \text{MoO}_4^{2-} + 24 \text{H}^+ \rightarrow \text{H}_2\text{Si(Mo}_2\text{O}_6\text{)}_{10} + 12 \text{H}_2\text{O}
\]

The reagents needed are formed in situ by a simple oxidation of molybdenum. The acidic pH is reached through a non-proton exchanged membrane which avoids the reduction of protons on the counter-electrode.

\[
\text{Mo} + 4 \text{H}_2\text{O} \rightarrow \text{MoO}_4^{2-} + 8 \text{H}^+ + 6 \text{e}^-
\]

1st sensor prototype:

- Molybdenum cell
- Detection cell
- Non proton exchange membrane
- Working electrode (Au)
- Counter-electrode

Pump 50 µL

Cyclic voltammograms of silicate (140 µM) obtained with this prototype (± flow rates) compared with agitated solution

Calibrationless method

The use of 2 working electrodes with different sizes allows to determine silicate concentration directly, without any calibration step [2].

Macro Electrode (ME) (Ø=2 mm): \( I_{\text{ME}} = 2.69 \times 10^5 \pi^{1/2} \text{F} \pi^{1/2} \text{D}^{1/2} \text{C} \mu \text{A} \text{cm}^{-2} \text{ V}^{-1} \)

Ultra-Micro Electrode (UME) (Ø=15 µm): \( I_{\text{UME}} = 4 \pi \text{F} \text{D} \text{C} \mu \text{A} \text{cm}^{-2} \text{ V}^{-1} \)

\( \rightarrow 2 \text{ equations, 2 unknowns: simultaneous determination of } C \text{ and } D \)

I: intensity (A), n: electron number, S: surface (cm²), C: concentration (mol.cm⁻³), F: Faraday constant, D: diffusion coefficient (cm².s⁻¹), r: radius (cm), v: scan rate (V.s⁻¹)

Phosphate

Electrochemical detection of phosphate is possible in acidic medium (pH = 1) in the presence of molybdates [3].

\[
\text{PO}_4^{3-} + 12 \text{MoO}_4^{2-} + 27 \text{H}^+ \rightarrow \text{H}_3\text{PMO}_12\text{O}_{40} + 12 \text{H}_2\text{O}
\]

\[
\text{Mo} + 4 \text{H}_2\text{O} \rightarrow \text{MoO}_4^{2-} + 8 \text{H}^+ + 6 \text{e}^-
\]

Silicate interference issue: Use of an appropriate ratio H²⁺/MoO₄²⁻ of 70 and an electrochemical cell with a specialised membrane technology adaptation [5].

Silicate concentration by electrochemistry: in excellent agreement with the colorimetric analysis. The average deviation obtained for all phosphate concentrations is 4.9 % (natural seawater samples off Peru).

Nitrates

The detection of nitrate occurs on gold working electrode covered by silver nanoparticles. Two simultaneous catalytic processes are observed increasing the obtained electrochemical signal [6].

\[
\text{NO}_3^- + 2\text{H}^+ + 1\text{e}^- = \text{NO}_2^- + \text{H}_2\text{O}
\]

Conclusions and perspectives

- Electrochemical detection of nutrients without any addition of liquid reagents and no interferences
- Methods validated with natural samples
- Calibrationless method in progress for low concentration of silicate
- Development of electronic cards for silicate
- Fabrication of first in situ phosphate prototype
- Adaptation of silicate and phosphate sensors for in situ measurements in the ocean
- Decrease the detection limit of nitrate

References

[1] Lacombe et al., 'Silicate electrochemical measurements in seawater: Chemical and analytical aspects towards a reagentless sensor', Talanta 77 (2008) 744-750

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