An autonomous sensor for in situ measurement of total alkalinity

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Overview

We present the first data from a new autonomous sensor for the measurement of total alkalinity (TA) in seawater, based on lab-on-chip technology. This sensor has been tested in the lab and used for field deployments.

System description

Total alkalinity represents the proton buffering capacity of a solution. Our sensor uses the single-point closed-cell acid titration method to measure TA [1], implemented on a modified version of a microfluidic platform developed for autonomous ocean biogeochemical analysis [2]. On-board pumps and valves collect a sample of seawater or reference material and mix it with a titrant containing acid and a pH-sensitive indicator dye inside microfluidic channels in a PMMA substrate. The CO_2 produced is removed from the solution in a gas-exchange tube. The solution's pH is then determined by on-board optical absorbance measurements at two wavelengths, from which the sample's TA is calculated.

Performance metrics in the laboratory

Two certified reference materials (CRMs) with TA of 2217.4 and 2403.7 µmol/kg were mixed in nine different ratios. The two pure CRMs were used as calibration points; the mixtures were each measured 5 times and the measurements averaged. The averaged measurements of the TA of the nine sample fluids were all within 5 µmol/kg of the expected value and the mean error was 1.9 µmol/kg.

Repeat measurements of the pure CRMs showed a slow drift over five days, with a standard deviation of <5 µmol/kg (n=58) without recalibration. In the field, the sensor can automatically recalibrate against CRMs as often as needed.

Field deployments

Preliminary field tests of the TA sensors have taken place in an estuary, where a high-alkalinity chalk river means that the TA is locally inversely related to salinity. The sensor has also been deployed on a ship's underway system and in the North Sea on a lander at 120 m depth. Several of these TA sensors will be deployed again during a field experiment in the North Sea in spring 2019 and data from these deployment and others will also be presented.

References

[1] Breland & Byrne (1993) *Deep Sea Res. I* 40, 629–641.

[2] Beaton et al (2012) *Environ. Sci. Technol.* 46, 9548-9556.