

Direct sensing of total alkalinity profile in a stratified lake

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Abstract

We demonstrate the direct detection of a total alkalinity depth profile through the use of an integrated thin layer electrochemical modulation instrument which acts as an alkalinity sensor. The technique uses a chemically selective proton pump that alters the concentration of hydrogen ions in the thin layer sample. As the proton pump releases hydrogen ions the resulting pH is recorded at the pH probe placed directly opposite the thin sample gap. This results in an acid-base titration that takes place directly in the thin layer sample and therefore obviates the need for traditional sample manipulation. Collected samples from a stratified lake were assessed with this alkalinity probe to record a total alkalinity profile, indicating a substantial increase from 2.59 to 4.11 mM with depth. Results of the new method were in excellent agreement with titration alkalinity data, and offer the potential for autonomous on site measurements of this key parameter.

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Introduction

Calcium carbonate precipitation in hard water lakes is triggered by blooms of algae and cyanobacteria (Dittrich *et al.*, 2004). The heterotrophic conditions in the deep water (Gruber *et al.*, 2000), and at the sediment-water interface, lead to the accumulation of dissolved CO₂ and a decrease in pH accompanied by partial carbonate dissolution (Ramisch *et al.*, 1999; Müller *et al.*, 2003). As a consequence, the concentration gradients of Ca²⁺ and HCO₃⁻ with depth are often increasing and thereby strengthen the stratification of the water column in summer (Gruber

et al., 2000). In anoxic systems, sulphate reduction in the sediments and the release of reduced substances like NH₄⁺ further contribute to an increase of alkalinity with depth (Pasche *et al.*, 2009). Precise profiling of alkalinity (Stumm and Morgan, 1996) in stratified waters is therefore essential to quantify the dynamics of the carbon cycle, to constrain the pathways of organic carbon mineralisation, and to understand the burial of carbonates in the sedimentary record (Schrage *et al.*, 2013). Typically, alkalinity profiles are obtained from sub-sampling Niskin bottles followed by titration in the laboratory. This approach is cumbersome and offers only limited resolution in space and time and requires additional precautions for anoxic deep-waters where alkalinity changes can occur due to rapid oxidation of reduced components.

Today, techniques have become available to generate the titrant electrochemically and thus provide the possibility of titrations in volumes of a few microlitres without the need for traditional sample manipulation. Early examples include the electrogeneration of hydroxide at an antimony/antimony oxide electrode (Karlmark *et al.*, 1982), while recent efforts used the direct electrochemical transformation of water to produce strong acid or base (van der Schoot *et al.*, 2005). Once integrated into microfluidic devices, these reagent generation principles were combined with a pH probe to realise a so-called flash titrator. Side reactions involving other electroactive species may lower the coulometric conversion efficiency of direct water electrolysis, rendering its use in complex samples problematic.

Autonomous *in situ* detection of alkalinity in seawater samples has been demonstrated by Spaulding's group, based on bulk titration and indicator colour change (Spaulding *et al.*, 2014). Classical acid-base titration was also applied for alkalinity detection by Li's group, where the indicator colour change was monitored spectroscopically to predict the endpoint (Li *et al.*, 2013). In these reports, traditional volumetry was applied that requires reagents (indicator, acid and base) and complex instrumentation such as pumps, injection valves, and optical detectors.

An alternative approach less prone to interferences involves the electrochemically driven transport of ions across ion-selective membranes (Nagy *et al.*, 1977; Bhakthavatsalam *et al.*, 2006; Ghahraman Afshar *et al.*, 2014, 2015ab). They can be used for the direct detection of total alkalinity by applying a constant current across the membrane and measuring the time required for localised depletion of base to occur. This chronopotentiometric technique is limited by an influence of the diffusion coefficient of the base of interest on the signal (as does the flash titrator mentioned above) and so far exhibits a limited measuring range not suitable for environmental analysis (Crespo *et al.*, 2012; Ghahraman Afshar *et al.*, 2014).

Recently, our group used a selective proton pump membrane to inject hydrogen ions into a thin layer sample while measuring the resulting pH with a pH probe placed directly opposite to the proton pump (Ghahraman Afshar *et al.*, 2015a), thereby realising a direct alkalinity sensor. The thin sample layer

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(ca. 100 μm) ensures that the injected hydrogen ions are equilibrated after a short time (~2 min), thereby giving a sensor response directly analogous to a volumetric titration. This methodology was assessed here for the direct *on site* measurement of an alkalinity depth profile in Lake Greifen (Switzerland).

Experimental Section

Reagents, materials and equipment. Potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (KTFPB), tetrakis(4-chlorophenyl)borate tetradodecylammonium salt (ETH 500), chromoionophore I, 2-nitrophenyloxy-lether (o-NPOE), tris(hydroxymethyl)aminomethane (Tris), acetic acid, sodium acetate, sodium chloride, sodium hydroxide (1 M), hydrochloric acid (1 M), high molecular weight poly(vinyl chloride) (PVC) and tetrahydrofuran (THF) were purchased from Sigma-Aldrich (analytical grade). Porous polypropylene (PP) membranes (Celgard, 0.237 cm^2 surface area, 25 μm thickness) were kindly provided by Membrana in Wuppertal, Germany.

Electrochemical equipment. A double-junction Ag/AgCl/3 M KCl/1 M LiOAc reference electrode was used in potentiometric and voltammetric measurements (6.0726.100 model, Metrohm, Switzerland). Electrode bodies (Oesch Sensor Technology, Sargans, Switzerland) were used to mount both the Celgard and PVC polymeric membranes. A platinum-working rod (3.2 cm^2 surface area) was used as a counter electrode. Potentiometric measurements were performed using a high impedance input 16-channel EMF monitor (Lawson Laboratories, Inc., Malvern, PA). Voltammetric measurements were carried out with an Autolab PGSTAT101. Portable pH meter model 826 pH was applied for pH detection (Metrohm AG, Switzerland). A commercial submersible multiparameter CTD probe OCEAN SEVEN 305Plus (Idronaut, Brugherio, Italy) equipped with pH electrode (a combination of pH and reference electrodes in contact with electrolyte solution behind a gas permeable membrane) and appropriate software provided by the manufacturer (ITERM, REDAS) was used for *in situ* pH profiling. All the calibration solutions were prepared in 10 mM of NaCl as background electrolyte.

Membrane preparation. Proton pump membranes were fashioned from porous polypropylene (PP) membranes (Celgard, 0.237 cm^2 surface area, 25 μm thickness) as supporting material. The membranes were washed with THF for 2–3 min to remove contaminants. An excess volume of 4 μL of the THF-free cocktail solution was deposited on the membrane when it was found to be completely dry (see cocktail preparation below). The impregnation of the cocktail was found to be instantaneous. The pore filling solution composition was assumed to remain identical to the initial THF-free cocktail. The membrane was conditioned in 0.01 M HCl for 40 min and mounted in the electrode body. The inner compartment was filled with 0.01 M HCl. The chemical composition of the proton pump membrane was 120 mmol kg^{-1} of Chromoionophore I (mmol per kg of cocktail), 60 mmol kg^{-1} of KTFPB, 90 mmol kg^{-1} of ETH 500, 150 mg of o-NPOE, total mass of 200

mg and 1 mL of THF. The THF was only used to solubilise the solid compounds into the plasticiser and was removed by evaporation before membrane casting membranes. The potentiometric pH probe membrane was based on a solvent cast PVC membrane, composed of 15 mmol kg^{-1} of Chromoionophore I, 5 mmol kg^{-1} of KTFPB, 135 mg of o-NPOE and 62 mg PVC, total mass of 200 mg, which was dissolved in 2 mL of THF and poured into a glass ring (10 mm ID) affixed onto a glass slide. The solution was allowed to evaporate overnight, giving membranes of ca. 0.15 mm thickness. This parent membrane was cut with a hole-puncher into disks of 8 mm diameter and mounted into Ostec electrode bodies. The inner compartment consisted of 0.01 M HCl.

Electrochemical cell setup. The cell consisted of a five electrode system in an acrylic container: a proton pump, a pH indicator electrode, a counter and two reference electrodes. A two-electrode arrangement (see Fig. S-1) with the reference and counter electrodes immersed in the outer contacting solution was used. The distance between indicator electrode and proton pump was defined by a 100 μm thick piece of paper tightly placed between them that was removed before filling the vessel with sample.

Electrochemical protocol. Coulometric pulses were applied at the proton pump while the potentiometric readout was recorded at the pH sensor. An automated method (NOVA, Autolab) consisted of i) open circuit potential determinations for 5 s at a sampling rate of 10 Hz (no current flow), ii) anodic potential pulses of varying duration (from 30 s to 210 s) at 500 Hz. Immediately afterwards, the pH was recorded potentiometrically at the pH probe.

The proton pump is an ion-selective electrode based on a hydrogen ion-selective membrane made from doped porous polypropylene instead of PVC owing to its faster mass transport properties (Malon *et al.*, 2007). An inner solution of 0.01 M HCl was used as a high concentration of acid is required to release hydrogen ions. The released proton concentration in the thin layer sample was calculated from the total released charge (current integration) and the thin layer volume. A volume of 40 μL is typically predicted for the thin layer sample, the value of which is determined by calibration using Faraday's law.

Sample collection and *in situ* pH measurement. The samples from different depths were collected using a Niskin Water Sampler (Model 1010: General Oceanic, Miami, USA) and stored in polyethylene containers, used here because transition metals were assessed in the same field study. The containers were completely filled to minimise loss of CO_2 and the containers were kept closed until measurement. All measurements were performed within a few hours after sampling. One lake-water profile consisted of seven depths: 1, 2.5, 4, 5.5, 7, 8.5 and 12.5 m. pH was detected *in situ* using an OCEAN SEVEN 305Plus multiparameter CTD probe. The calibration of the pH sensor was performed as requested by the manufacturer using one-point calibration (pH 7, non-stirring conditions).



Theoretical fit. Equilibrium theory was used to fit the titration curve of the lake water samples by considering carbonate and bicarbonate as major alkaline species using pK_{a1} of 6.30 for bicarbonate, pK_{a2} of 10.32 for carbonate and the initial pH value obtained by the *in situ* sensor.

Results and Discussion

Alkalinity depth profiles were investigated by the thin layer coulometric approach described recently (Ghahraman Afshar *et al.*, 2015a), marking the first time that this technique is applied for an environmental application. The electrochemical cell consisted of a membrane-based proton pump and pH probe (see Fig. S-2 for potentiometric response of the latter) separated by a thin layer sample (see Fig. 1 for scheme). The lower detection limit (DL) of the methodology is about 0.1 mM, obtained by monitoring the minimum detectable pH change in the absence of buffer. The upper DL is found to be at least 100 mM, predicted by the titration of the highest possible concentration of strong base (sodium hydroxide) solution. This makes the methodology applicable to environmental systems including highly buffered carbonate lakes (Müller *et al.*, 2016). The thin sample layer remained in physical contact with the bulk lake sample at all times (100 mL) and was therefore allowed to re-equilibrate after each perturbation step by convective stirring of the bulk

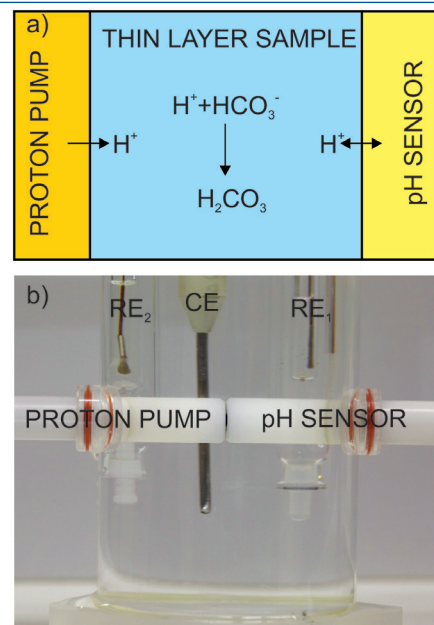


Figure 1 (a) Schematic illustration of the alkalinity probe. (b) Electrochemical cell composed of a proton pump and a pH probe placed directly opposite. The two reference electrodes (RE1 and RE2) and counter electrode (CE) are inserted in the bulk sample solution. The carbonate species are titrated with the hydrogen ions released from the proton pump. The resulting change of pH is subsequently assessed potentiometrically at the pH probe.

sample. Alkalinity in the unfiltered lake water samples from depths of 1 to 12.5 m were determined from the inflection point of the titration curves using the thin layer electrochemical instrument (Figs. 2a, S-9b to S-15b). pH was monitored at the pH indicator electrode as a function of charge, and hence of the released proton concentration, at the proton pump for 11 consecutive excitation pulses of 300 mV (*vs.* OCP) of 10 to 110 s duration with 10 s increment (see Fig. S-3).

The potentiometric response of the pH electrode after each imposed pulse allowed the determination of the time required to reach equilibration of pH between the two opposite electrodes and re-equilibration of the thin layer with the natural sample. These values are similar to those determined previously from thin-layer electrochemical titrations in synthetic solutions (Ghahraman Afshar *et al.*, 2015a), suggesting the absence of matrix effects and/or fouling problems. This hypothesis was supported by the comparative alkalinity levels for the same samples obtained from traditional volumetry (reference method ISO 9963:1994, volumetric acid-base titration), which is in quantitative agreement with the values obtained with the alkalinity sensor. Figure 2b shows the correlation between the proposed and reference methods: solid line indicates ideality with unity slope and zero intercept. The two methods are in excellent agreement as the least squares fit gives a slope of almost unity and an intercept close to zero ($y = 1.018x - 0.062$, $r^2 = 0.997$), giving an average relative error of 1 % (see Fig. S-4).

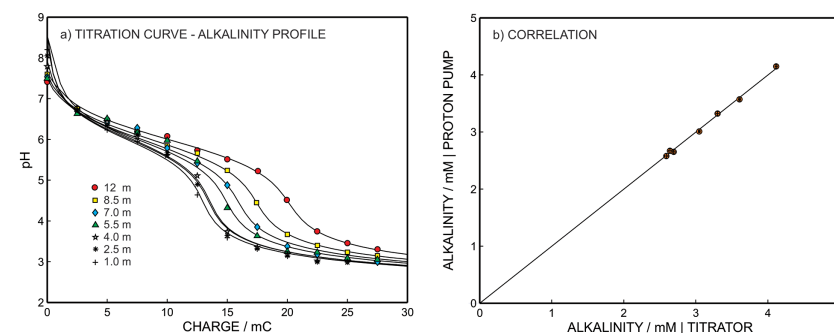


Figure 2 (a) The titration curve for various depths in the range of 1 to 12.5 m using the thin layer instrument. Solid line is theoretical. (b) Correlation between the thin layer chemical modulation method and volumetric acid-base titration reference method (ISO 9963-1:1994). Solid line shows ideality with unity slope and zero intercept.

The long-term stability of the pH sensor and proton pump were investigated, and a drift of 0.5 mV/h was obtained (Fig. S-5). The reproducibility of the proton pump was examined by applying repeated potential pulses of 300 mV for 30 s, finding an RSD of less than 1 % ($n = 5$), indicating a reproducible release system (Fig. S-6). The influence of temperature on the released charge was examined within the range of 20 to 30 °C. According to Figure S-7, the variation was negligible (RSD ≤ 2 %). Various sodium chloride concentrations between



10^{-5} to 0.1 M were examined as background (Fig. S-8), and the released charge was found to increase with higher background concentration. However, this should not affect the precision and accuracy of the technique as it is performed by stopping the potential pulse after reaching a predetermined charge value.

Figure 3b shows the alkalinity depth profiles together with the corresponding pH values (Fig. 3a) obtained *in situ* from the multiparameter CTD probe at the same depth. An alkalinity level in the range of 4 mM was observed below the bioactive surface layer, in agreement with earlier work (Müller *et al.*, 2016). As observed in Figure 3b, alkalinity increases with depth while Figure 3a shows that this is accompanied by decreasing pH.

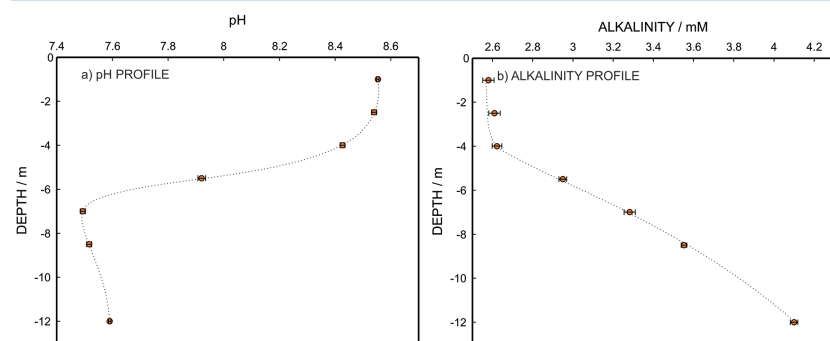


Figure 3 (a) Total alkalinity depth profile and (b) pH depth profile obtaining during field monitoring on the Lake Greifen (31 August 2015).

In surface waters and during the day, algae and other photosynthetic microorganisms consume CO_2 by photosynthesis, which results in an increase of pH. In hard water systems, this promotes the precipitation of CaCO_3 onto microorganisms and other microenvironments, which is eventually transported to greater depths by sedimentation, thereby reducing alkalinity at the surface (Gruber *et al.*, 2000). On the other hand, the sediments of hard water lakes act as a source of alkalinity due to anaerobic mineralisation processes and partial calcite dissolution (Dittrich *et al.*, 2009).

We demonstrated that a thin layer proton pump may work efficiently as an alkalinity sensing tool for profiling lake water. As a case study, the alkalinity level of Lake Greifen at various depths was successfully determined. These results were obtained after sampling lake water and performing the analysis at an on-shore location, thus significantly reducing the time from sampling to analysis, which is a critical factor for anoxic waters. It is conceivable that the methodology may be applied as a single-point titration system by means of a theoretical fit from the initial pH value, acidity constant and a single titration point, thereby drastically increasing measurement frequency. Future development will focus on the realisation of an alkalinity sensor that is deployable *in situ*, in analogy to a CTD probe.

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Additional Information

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