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An automated procedure for laboratory and shipboard spectrophotometric measurements of seawater alkalinity: Continuously monitored single-step acid additions

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ARTICLE INFO

ABSTRACT

Building on the spectrophotometric procedure of Yao and Byrne (1998), an automated analysis system has been developed for laboratory and shipboard measurements of total alkalinity at a rate of 6 samples per hour. The system is based on single-point hydrochloric acid (HCl) titrations of seawater samples of a known volume with bromocresol purple as an indicator. The titration is continuously monitored using visible spectroscopy to guide the titration rate according to the real-time pH of the samples. Each titration is terminated just below the equivalence point to achieve a precision and accuracy near 1 µmol kg^{-1}.

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1. Introduction

Comprehensive surveys of inorganic carbon in the global ocean are essential for understanding oceanic uptake, transport, and storage of anthropogenic carbon dioxide (CO_2). Complete characterizations of the seawater CO_2 system require measurements of at least two of four key system parameters: total inorganic carbon (C_T), total alkalinity (A_T), carbon dioxide fugacity (fCO_2), and pH (Millero, 1995, 2007). A_T is unique among these four in that its value does not change when CO_2 is exchanged between the ocean and the atmosphere. This parameter is therefore generally considered to be one of the preferred parameters for field measurements and is a cornerstone of analytical assessments of oceanic CO_2 cycling and ocean acidification.

Determinations of total alkalinity are typically based on adding acid to a seawater sample and potentiometrically measuring the resulting pH (Bockmon and Dickson, 2015). The acid may be added in a single step with direct determination of the excess acid (Culberson et al., 1970) or it may be added stepwise with algorithmic determination of equivalence points on the titration curve as proposed by Dyrssen and Sillen (1967). The multi-step procedure (Bradshaw et al., 1981; Bradshaw and Brewer, 1988; Millero et al., 1993) has been adopted as a standard operating procedure (SOP 3, Dickson et al., 2007) for shipboard measurements. The accuracy and precision of such analyses

(± 4 and ± 2 µmol kg^{-1}; Feely et al, 2008; Millero et al., 1993), are typically poorer than the corresponding uncertainties for C_T measurements (± 2 and ± 1 µmol kg^{-1}; Millero, 2007). The recent inter-laboratory comparison of Bockmon and Dickson (2015) showed that few of the 60 labs in the study were within 2 µmol kg^{-1} of the assigned A_T values for test samples.

Spectrophotometry-based methods (Yao and Byrne, 1998; Li et al., 2013; Martz et al., 2006) offer an alternative to potentiometric methods in that they avoid some of the problems associated with the glass pH electrodes used to monitor the acid titrations (e.g., susceptibility to large systematic errors and unpredictable drift, Wanninkhof et al., 2003). Breland and Byrne (1993) updated the potentiometric single-step alkalinity procedure of Culberson et al. (1970) by combining the speed and conceptual simplicity of the original method with the precision of modern spectrophotometric pH determinations (The precision of spectrophotometric pH analyses is ± 0.0004 (Clayton and Byrne, 1993) whereby H$^+$ concentrations are precise to $\pm 0.1\%$). Yao and Byrne (1998) further developed the simplified procedure by using rapid-scan array spectrometers to continuously monitor the acid-addition process. This rapid titration procedure allows acid additions to be terminated when a seawater sample's hydrogen ion concentration just exceeds the residual bicarbonate concentration. As a result, subsequent to purging the CO_2 that is evolved from protonation of bicarbonate ions, the excess acid terms are very small. The analytical precision of the alkalinity measurement is then strongly dominated by the uncertainty of the gravimetric or volumetric determinations of the

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amounts of sample and added acid. Through the use of gravimetric measurements and carefully standardized acid, the procedures developed by Yao and Byrne (1998) yield a precision better than ± 1 µmol kg^{-1} for seawater alkalinity. The dependence on gravimetric procedures, however, makes this approach unsuitable for shipboard analyses and for automated measurements in any setting.

In view of the demand for accurate and precise seawater A_T measurements, we developed a low-cost, simple, and robust automated spectrophotometric system for laboratory and shipboard alkalinity analyses (Table 1). The procedures outlined in this work retain the advantages of single-point spectrophotometric alkalinity titrations (Yao and Byrne, 1998) and incorporate two modifications that make the method suitable for automated or at-sea analyses: use of (1) sample bottles of pre-certified volumes and (2) an automated titrator that is responsive to solution pH. The first modification eliminates the original reliance on gravimetric determinations of seawater, while the second not only eliminates the original reliance on acid weights but also improves analytical precision and sample throughput rates.

2. Theory

The total alkalinity of a sample of seawater is defined as the number of moles of hydrogen ion equivalent to the excess of proton acceptors (bases formed from weak acids with a dissociation constant $K \le 10^{-4.5}$ at 25 °C and zero ionic strength) over proton donors (acids with $K > 10^{-4.5}$) in 1 kg of sample (Dickson, 1981):

$$A_T = [HCO_3^-]_T + 2[CO_3^{-2}]_T + [B(OH)_4^-]_T + [OH^-]_T + 2[PO_4^{-3}]_T$$
$$+ [HPO_4^{-2}]_T + [SiO(OH)_3^-]_T - [H^+]_f - [HSO_4^-]_T - [HF]_T + \dots \quad (1)$$

The brackets indicate constituent concentrations, with the subscripts T and f indicating total or free ion concentrations. The ellipsis represents additional minor acid or base species that are either unidentified or are present in minor amounts (e.g., NH_3 and/or organic protolytes).

For a single-point titration, the alkalinity of a seawater sample that has been acidified and purged of CO_2 can be written as follows (Yao and Byrne, 1998):

$$A_T = \left\{ [HCl]_A M_A - [H^+]_{ASW} M_{ASW} - [HI]_{total} \Delta(HI) M_{ASW} \right\} / M_{SW} \quad (2a)$$

where $[HCl]_A$ is the concentration of the added acid (mol kg^{-1} solution); M_A is the mass of acid added; $[H^+]_{ASW}$ is the excess hydrogen ion concentration in the acidified CO_2-free seawater (mol kg^{-1} (seawater)); M_{ASW} is the mass of the acidified seawater, calculated as $M_{SW} + M_A$; $[HI]_{total}$ is the total concentration of a pH indicator in both its protonated and unprotonated forms (mol kg^{-1} (acidified seawater)); $\Delta(HI)$ is a dimensionless term that accounts for the H^+ gained or lost by the indicator in the final acidified seawater relative to the stock solution from which it was added; and M_{SW} is the mass of the seawater sample (kg). The indicator term is very small (<0.2 µmol kg^{-1})

Table 1
Summary of the automated spectrophotometric alkalinity procedure.

1. Samples are collected with 300 cm^3 BOD bottles. Surface samples are run first and samples are not poisoned with $HgCl_2$.
2. Put sample in the bottle holder. Take the cap out and briefly rinse the cap with MilliQ water.
3. Take a reference spectrum of the sample.
4. Add 0.1 mL of BCP indicator.
5. Titrate the sample using Dosimat titrator guided by monitoring the R ratio of the BCP. Terminate the titration at R ratio 0.070 for normal seawater.
6. Purge CO_2 using high purity N_2 gas.
7. Record sample information including sample temperature, purge ending temperature, volume of acid used, final R ratio.

and can be ignored (Yao and Byrne, 1998). A_T can then be calculated according to the equation

$$A_T = \left\{ [HCl]_A M_A - [H^+]_{ASW} M_{ASW} \right\} / M_{sw}. \quad (2b)$$

The $[H^+]_{ASW}$ term in Eq. (2b) provides proton concentrations directly in terms of moles per kg of seawater ($pH_T = -\log[H^+]_{ASW}$).

Because the gravimetric terms in Eq. (2b) are not directly suitable for shipboard operations, A_T in the present work is calculated using the following equation:

$$A_T = \left\{ [HCl]_{AV} V_A - [H^+]_{ASW} M_{ASW} \right\} / M_{SW} \quad (2c)$$

where $[HCl]_{AV}$ is the HCl concentration of the acid titrant in volumetric units, V_A is the volume of the added acid titrant, sample mass (M_{SW}) is obtained from volumetric measurements and solution densities (see Section 3.2), and the gravimetric M_A term in M_{ASW} ($M_{ASW} = M_{SW} + M_A$) is determined by measuring the volume and density of the acid ($M_A = V_A \sigma_A$, where σ_A is the density of the acid). The acid concentration ($[HCl]_{AV}$), in volumetric units, is determined by titrating a seawater certified reference material (a CRM with known A_T) with the acid used in the titrations (as the A_T of the CRM is known, Eq. (2c) is solved for $[HCl]_{AV}$).

$[H^+]_{ASW}$ in Eq. (2c) is measured spectrophotometrically through observations of bromocresol purple (BCP) absorbance ratios, $R = {}_{\lambda_2}A/{}_{\lambda_1}A$, where ${}_{\lambda_2}A$ is absorbance at 589 nm and ${}_{\lambda_1}A$ is absorbance at 432 nm. Solution pH_T is given as (Breland and Byrne, 1992; Yao and Byrne, 1998):

$$pH_T = 5.8182 + 0.00129(35 - S)$$
$$+ \log((R(25) - 0.00381)/(2.8729 - 0.05104R(25))) \quad (3a)$$

where

$$R(25) = R(t)\{1 + 0.01869(25 - t)\} \quad (3b)$$

and $R(t)$ is the absorbance ratio measured at temperature t for $29 \le S \le 37$ and 13 °C $\le t \le$ 32 °C (Yao and Byrne, 1998).

3. Materials and methods

3.1. Reagents

The titrant acid (0.2 N) was prepared from concentrated HCl (Fisher Scientific). The total ionic strength was adjusted with NaCl to 0.7 M. The concentration ($[HCl]_{AV}$), determined using certified reference materials (CRMs; Batch 109) from Dr. Andrew Dickson of the Scripps Institution of Oceanography, was 0.1970 N at 18 °C. The pH indicator, bromocresol purple sodium salt, was obtained from Sigma (Sigma B-4263 Lot 104H3625) without purification. A 0.01 M BCP solution was prepared in MilliQ water. The R ratio of this indicator stock solution was adjusted using HCl or NaOH solution to be about 0.3 (the targeted final R ratio observed after purging with N_2), and was measured with a 0.02 cm cylindrical cell in an Agilent 8453 spectrophotometer.

3.2. Sample bottles and certification of bottle volumes

M_{SW} in Eq. (2c) was obtained by collecting seawater samples in bottles whose volumes were known, through previous calibrations as a function of temperature. Particular attention was paid to the selection, calibration, and care of the sample bottles. Clear BOD (Biochemical Oxygen Demand) borosilicate bottles (Fisher Scientific) were chosen because of their optical clarity, flanged tops, and tapered caps that facilitated spectrophotometric monitoring and elimination of bubbles and also precluded sample-loss as seawater samples warmed after collection.