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

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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 $\mu\text{mol kg}^{-1}$.

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 ($f\text{CO}_2$), 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 $\pm 2 \mu\text{mol kg}^{-1}$; Feely et al., 2008, Millero et al., 1993), are typically poorer than the corresponding uncertainties for C_T measurements (± 2 and $\pm 1 \mu\text{mol kg}^{-1}$; Millero, 2007). The recent inter-laboratory comparison of Bockmon and Dickson (2015) showed that few of the 60 labs in the study were within $2 \mu\text{mol kg}^{-1}$ of the assigned A_T values for test samples.

Spectrophotometry-based methods (Yao and Byrne, 1998, Li et al., 2013, Martz, 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 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 $\pm 1 \mu mol kg^{-1}$ 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. 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 $K \leq 10^{-4.5}$ at 25°C and zero ionic strength) over proton donors (acids with $K > 10^{-4.5}$) in 1 kg of sample (Dickson, 1981) :

$$A_T = [\text{HCO}_3^-]_T + 2[\text{CO}_3^{2-}]_T + [\text{B}(\text{OH})_4^-]_T + [\text{OH}^-]_T + 2[\text{PO}_4^{3-}]_T + [\text{HPO}_4^{2-}]_T + [\text{SiO}(\text{OH})_3^-]_T - [\text{H}^+]_f - [\text{HSO}_4^-]_T - [\text{HF}]_T + \dots \quad (1)$$

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):

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

where $[\text{HCl}]_A$ is the concentration of the added acid (mol kg^{-1} solution); M_A is the mass of acid added; $[\text{H}^+]_{\text{ASW}}$ 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 $M_{\text{SW}} + M_A$; $[\text{HI}]_{\text{total}}$ is the total concentration of a pH indicator in both its protonated and unprotonated forms (mol kg^{-1} (acidified seawater)); $\Delta(\text{HI})$ 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 ($< 0.2 \mu\text{mol kg}^{-1}$) and can be ignored (Yao and Byrne, 1998). A_T can then be calculated according to the equation

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

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

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:

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

where $[\text{HCl}]_{\text{AV}}$ 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} ($M_{\text{ASW}} = M_{\text{SW}} + M_{\text{A}}$) is determined by measuring the volume and density of the acid ($M_{\text{A}} = V_{\text{A}}\sigma_{\text{A}}$, where σ_{A} is the density of the acid). The acid concentration ($[\text{HCl}]_{\text{AV}}$), 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 $[\text{HCl}]_{\text{AV}}$).

$[\text{H}^+]_{\text{ASW}}$ 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):

$$\text{pH}_{\text{T}} = 5.8182 + 0.00129 (35 - S) + \log((R(25) - 0.00381) / (2.8729 - 0.05104 R(25))) \quad (3a)$$

where

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

and $R(t)$ is the absorbance ratio measured at temperature t for $29 \leq S \leq 37$ and $13^\circ\text{C} \leq t \leq 32^\circ\text{C}$ (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 ($[\text{HCl}]_{\text{AV}}$), 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 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.

To calibrate the A_T sample bottles, the volume (*V*) of each was determined based on the difference between the weight (*w*) of the empty bottle and the weight of the bottle completely filled with MilliQ water (SOP 13, Dickson et al., 2009):

$$w(\text{H}_2\text{O}) = w(\text{filled bottle}) - w(\text{empty bottle}). \quad (4)$$

The accuracy of the weight determinations was approximately ± 0.01 g. The water weight was typically ~ 300 g.

The mass (*m*) of water in the bottle was calculated by correcting for air buoyancy:

$$m(\text{H}_2\text{O}) = w(\text{H}_2\text{O}) \left(\frac{1 - \rho(\text{air}) / \rho(\text{weights})}{1 - \rho(\text{air}) / \rho(\text{sample})} \right) \quad (5)$$

where ρ is density.

The volume of water in the bottle at the calibration temperature t_c ($^{\circ}\text{C}$) was then calculated according to

$$V(t_c) = m(\text{H}_2\text{O}) / \rho(\text{H}_2\text{O}, t_c), \quad (6)$$

where the density of air-saturated water (kg m^{-3}) is given by (Jones and Harris, 1992):

$$\rho(\text{H}_2\text{O}, t) = 999.84847 + 6.337563 \times 10^{-2} (t) - 8.523829 \times 10^{-3} (t)^2 + 6.943248 \times 10^{-5} (t)^3 - 3.821216 \times 10^{-7} (t)^4 \quad (7)$$

for $5 \leq t \leq 40^{\circ}\text{C}$.

The volume at 20°C , for each batch of calibrated sample bottles, is calculated as (SOP 12, Dickson et al., 2007):

$$V(20) = V(t_c) (1 + 9.75 \times 10^{-6} (20 - t_c)). \quad (8)$$

Each calibrated bottle and its paired cap were individually numbered. Care was taken to ensure that the bottles and caps were not subsequently chipped or otherwise damaged, as any change in bottle shape (volume) would have degraded the quality of the A_T analyses.

3.4. Instrumentation

The automated spectrophotometric alkalinity system (Fig. 1) consists of a Metrohm Dosimat 665 that is controlled with custom software through serial communication (*Note: the newest model of Metrohm Dosimat could not be programmed with variable titration rate at the present time per conversation with Metrohm support and thus will not work well with applications that require variable titration rate*); a stir plate with an anchoring bottle holder; an Ocean Optics LS-1 tungsten halogen light source with a blue filter; and an Ocean Optics USB4000 spectrophotometer. The Dosimat is equipped with a 5-mL exchange unit thermostated at 18°C (slightly lower than room temperature to prevent bubble formation in the acid line). A portable computer controls acid delivery from the titrator and records BCP absorbances, which are used to guide subsequent acid additions.

The configuration of the sample bottle in the sample bottle holder is depicted in Fig 1b. The sample holder was designed as a rectangular polyvinyl chloride (PVC) box slightly taller than the sample bottle; grey PVC plastic was used to block ambient light. Two collimating lenses with SMA connectors that were interfaced to the spectrophotometer and light source were placed about 2 cm above the base. A 2 mm×20 mm stir bar was inserted into the sample bottle. The stir rate was adjusted to provide stable stirring at a very rapid rate of mixing. The acid tubing from the Dosimat 665 titrator was inserted just below the sample surface, while the N₂ gas purging tubing was inserted above the collimating lens level so that gas flow (bubbles) would not interfere with absorbance readings. Note that if the acid tubing is inserted too low in the bottle, the relatively dense acid can penetrate the solution into the light path, whereupon the titration may be terminated prematurely. A circular plastic foam secured each sample bottle in a fixed position during the shipboard spectrophotometric measurements. The optical fibers

of the titration system were similarly rigidly attached to the architecture of the sample cell to prevent the ship's vibration affecting spectrophotometric signals.

3.5. Sampling and determination of sample mass

Two types of samples were used to assess the shipboard precision, accuracy, and throughput rate of the automated A_T procedure: (a) certified reference materials (CRMs) obtained from Dr. Andrew Dickson at the Scripps Institution of Oceanography, and (b) seawater collected from a range of depths in the Arctic Ocean in October 2011. All analyses were conducted on board the U.S. Coast Guard Cutter *Healy* (Cruise HLY1103). For comparison with our prompt shipboard measurements, the A_T of poisoned and stored Arctic seawater samples was later measured potentiometrically using the Marianda VINDTA 3C in a laboratory at the University of Alaska Fairbanks. These measurements also followed recommended best practices (Dickson et al., 2007).

Because the quality of the spectrophotometric A_T analyses depends on accurate knowledge of the initial volume of each seawater sample, a rigorous protocol was followed for sample collection and handling. Each sample bottle was first rinsed three times with seawater flowing freely from a 10 L Niskin bottle through silicone tubing; each rinse volume was approximately one-third the sample-bottle volume. The tubing was then inserted to the bottom of the sample bottle, which was filled to overflowing; the overflow volume was approximately equal to the bottle volume. The sample temperature t_s (required to ascertain bottle volume and to convert sample volume to sample mass) was measured to better than 0.1°C using a digital thermometer and recorded. The tubing was then jostled with an up-and-down motion in the seawater sample to ensure that no air bubbles were trapped in the bottle. Once all bubbles were cleared, the bottle cap was rinsed with seawater and the bottle was sealed. Seawater in the flange area was eliminated and the bottleneck area was dried with a Kimwipe (with a wiping action identical to that used when the bottle volume, $V(t_c)$, was certified in the laboratory).

In the ship's laboratory, the outside of each bottle was carefully rinsed with tap water to remove any salt and the bottle surface was wiped clean with Kimwipes. If the sample temperature changed subsequent to collection, care was taken to ensure that no

alkalinity (seawater) was gained or lost. When the samples warmed and seawater was forced into the flanged bottle neck, care was taken to ensure no loss of sample (the bottle was maintained upright, and water within the flanged neck was not wiped away as the sample warmed).

Because the seawater samples were collected at a temperature other than the calibration temperature (i.e., $t_s \neq t_c$), thermal expansion or contraction of the sample bottle must be accounted for. For borosilicate bottles (SOP 12, Dickson et al., 2007),

$$V(t_s) = V(20) (1 + 9.75 \times 10^{-6}(t_s - 20)). \quad (9)$$

The mass of seawater sample collected in the bottle at temperature t_s was then obtained from

$$M_{sw}(t_s) = V(t_s) \rho_{sw}(t_s) \quad (10)$$

where seawater density $\rho_{sw}(t_s)$ as function of salinity and temperature was calculated according to Millero and Poisson (1981):

$$\begin{aligned} \rho_{sw}(t) = & \rho(H_2O, t) + (8.24493 \times 10^{-1} - 4.0899 \times 10^{-3}(t) + 7.6438 \times 10^{-5}(t)^2 - \\ & 8.2467 \times 10^{-7}(t)^3 + 5.3875 \times 10^{-9}(t)^4)S + (-5.72466 \times 10^{-3} + 1.0227 \times 10^{-4}(t) - 1.6546 \times 10^{-6}(t)^2) \\ & S^{1.5} + 4.8314 \times 10^{-4}S^2. \end{aligned} \quad (11)$$

3.6. Spectrophotometrically guided sample titrations

For the titration procedure, the sample bottle was anchored with a bottle holder on a stir plate with a light source on one side and a spectrometer on the other (Fig. 1a). The bottle cap was removed and excess seawater was rinsed into the sample bottle with a small amount (1-2 mL) of MilliQ water. A small stir bar was inserted into the bottle, and stirring commenced. A stable stir-bar spinning at a high rate produced visible vertical mixing. The acid tube from the Dosimat titrator inserted just below the surface of the sample liquid ensures that the HCl is well mixed with the seawater before reaching the light path at the lower part of the bottle (Fig 1b). After a reference absorbance was recorded, 0.1 mL of the BCP stock solution was added. Acid was then delivered to the sample bottle, with the rate of acid addition being guided by continuous spectrophotometric monitoring of the seawater pH (Eq. 3). The initial rate of acid

addition was 5 mL per min. At an R value of 0.5 (pH $\sim$ 5.2), the rate was slowed, eventually dropping to 0.1 mL per min. A 3 sec delay after each rate change ensured adequate mixing of acid and sample before the next step. The titrations were terminated at $R = 0.070$ (pH $\sim$ 4.2). The time to complete each titration was $\sim$ 1 min. A fritted glass purging tube was then placed into the bottle above the light path and the solution was vigorously purged with N_2 until R was constant (0.002 unit in one minute ($\sim$ 5 min)). Finally, the temperature (0.01 °C precision) of the solution (t in Eq. (3b)) was measured with a digital thermometer and the final R ratio obtained at this temperature was used to obtain the final pH_T (Eq. 3a) used for calculation of seawater A_T according to Eq. 2c. The time from the start of a titration to the completion of purging was typically $\sim$ 6 min.

4. Results and Assessment

Precision and accuracy of the shipboard spectrophotometric alkalinity procedure were evaluated in two ways: (1) by comparison to the A_T value of a certified reference material (CRM) and (2) by comparison to A_T values measured by conventional shore-based methods (SOP 3, Dickson 2007) for Arctic Ocean seawater samples.

Table 2 shows the results of the CRM A_T measurements made at sea over the course of 20 days with six different volume-calibrated sample bottles. As an example, consider sample bottle No. 4. The volume of this bottle had been previously determined in the laboratory as $V(t_c) = 306.20$ mL at 20°C. At sea, the bottle was filled with a CRM solution at $t_s = 19.80$ °C. The volume of sample solution was therefore 306.20 mL, and the sample mass contained in the bottle (M_{sw}) was 313.41 g (Eq. 9). Over the course of the acid titration, 3.487 mL (V_A) of 0.1970 N HCl was delivered to achieve an R ratio of 0.070. After purging, the final $R(t)$ ratio was 0.230 and the temperature t was 20.31 °C. From Eqs. 3a and 3b, the pH of the final purged solution was 4.759 (i.e., $[H^+]_{ASW} = 17.42 \times 10^{-6}$ mol kg $^{-1}$). Note that, even with a 1% error in this measurement – very large for a spectrophotometric pH measurement - the error in the excess acid term would be less than 0.2 μ moles kg $^{-1}$. The spectrophotometric A_T of the CRM for this particular analysis, calculated using Eq. 2c, was therefore 2224.49 μ mol kg $^{-1}$.

The certified A_T value was $2224.26 \mu\text{mol kg}^{-1}$ (CRM batch 109, salinity 33.5). The overall average of the spectrophotometric A_T measurements (Table 2) was $2224.14 \mu\text{mol kg}^{-1}$ ($n = 6$, over 20 days) with a standard error of $0.76 \mu\text{mol kg}^{-1}$. The difference between the average measured A_T and the certified A_T was $< 0.2 \mu\text{mol kg}^{-1}$.

To further test the precision of the procedure, samples from the ship's underway system were collected in a large container to ensure homogeneity and distributed to a group of eight bottles. The sample temperature was about 3°C . Results from eight measurements had a standard deviation of $0.7 \mu\text{mol kg}^{-1}$, similar to the CRM result obtained during the cruise.

Fig. 2 shows a comparison of the spectrophotometric (shipboard) and potentiometric (laboratory) A_T measurements for the Arctic seawater samples ($n = 274$). Over the entire range of observations, $A_T \sim 1900$ to $2500 \mu\text{mol kg}^{-1}$ and salinity from 26 to 35, the two methods showed good agreement with no observable bias. Fig. 3 shows the differences (residuals) for the two sets of measurements. The average difference (1σ) was $1.2 \mu\text{mol kg}^{-1}$.

A small amount of water (1 to 2 mL) used to rinse off the cap changed the salinity and final mass of the samples. The effect was evaluated at different R ratios and salinities by adding water stepwise to the purged acidified seawater. The data obtained in this assessment are summarized in Table 3. At a low terminating R ratio after purging (< 0.2), there is a small decrease in A_T (a 5 mL of water addition decreases A_T by about $0.2 \mu\text{mol kg}^{-1}$). When the R ratio was high enough (> 0.3), the residual H^+ is less than $10 \mu\text{mol kg}^{-1}$, whereupon changes in A_T for a 5 mL addition of water are $< 0.1 \mu\text{mol kg}^{-1}$. Most of our measurements were terminated at R about 0.3. With 2 mL water additions, the change in A_T due to this rinsing is smaller than $0.1 \mu\text{mol/kg}$, which is not observable using this method.

5. Discussion

The spectrophotometric A_T procedures evaluated in this work are inherently accurate and precise. The sample A_T is proportional to the volume of acid used in the titration compared to the CRM. The mass of sample can generally be calculated to

approximately $\pm 0.01\%$ (0.02 g in 300 g). The acid delivery is precise to about $\pm 0.03\%$ (0.001 ml in 3 ml). The overall A_T precision of the procedure is about 0.05%. Our data for samples collected in the Arctic Ocean show that duplicate samples routinely agree within $1 \mu\text{mol kg}^{-1}$. The result of CRM measurements throughout the month long cruise indicates that the measurement system does not require frequent calibration as long as the acid concentration is stable.

The automated spectrophotometric A_T system requires relatively small sample volumes and offers procedural simplicity—advantages that can be especially important for work at sea. The 300 ml BOD bottles with the tapered cap and flanged neck, allow accounting for thermal-expansion and full-bottle solution titrations. Conducting the titration directly in the sample bottle at near-ambient temperature (as opposed to using a separate titration cell for a thermo-equilibrated sample) also eliminates some procedural steps, thus speeding the analyses and minimizing the likelihood of sample contamination. Samples should always be measured in non-condensing conditions. Condensation on optical surfaces at very low temperatures can affect absorbance readings. Low temperature samples should be allowed about a half hour warm up time before analysis.

For the current spectrophotometric method, ~ 1 minute is required for each sample to be titrated to $R \sim 0.07$ (and ~ 5 minutes is required to purge the sample of CO_2 and complete the measurement). This can be compared to about 20 minutes per sample for potentiometric-based methods (such as the Marianda VINDTA 3C). Sample rates could be further improved by integrating multiple titrators and processing multiple samples simultaneously. With four such units, the spectrophotometric A_T system could process samples at a speed matching that of shipboard manual spectrophotometric pH measurements (i.e., 20 samples hr^{-1}). For samples that differ significantly in salinity compared to a normal seawater range, a slight adjustment in the initial titration R ratio is needed. For lower salinity (S about 20) and for fresh water, the desired R ratio prior to purging should be about 0.08 to 0.09 so that the final R ratio after purging will be stable within the range of 0.2 to 1.

Currently there is increased interest in understanding the alkalinity contributions of unknown bases, such as those attributable to organics in coastal environments and

oceans, such as the Arctic, that receive especially high river input. The method presented in this work is being further developed to measure alkalinity contributions from natural organics at low concentrations. Spectrophotometric titrations are particularly useful for this purpose because spectrophotometric indicators equilibrate on millisecond time scales.

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Fig. 1. The Automated Spectrophotometric Alkalinity System, ASAS. (a) A general schematic of the ASAS system. (b) Configuration of sample bottle and lightpath.

Fig. 2. Comparison of spectrophotometric A_T and potentiometric A_T measured in seawater samples from the Arctic Ocean over an A_T range from 1900 to 2500 $\mu\text{mol kg}^{-1}$ and salinity from 26 to 35. The spectrophotometric analyses were conducted shipboard and the potentiometric analyses were conducted post-cruise in the laboratory.

Fig. 3. Differences between spectrophotometric (shipboard) ($A_T(\text{spec.})$) and potentiometric (laboratory) ($A_T(\text{pot.})$) measurements of A_T in Arctic Ocean seawater samples.

Table 1 Summary of Automated Spectrophotometric Alkalinity Procedures

1. Samples are collected with 300 cm³ BOD bottles. Surface samples are run first and samples are not poisoned with HgCl₂.
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 CO₂ using high purity N₂ gas.
7. Record sample information including sample temperature, purge ending temperature, volume of acid used, final R ratio.

Table 2. Automated spectrophotometric measurements of CRM A_T.

Bottle ID	t _s	t	R(t)	V _A	V ₂₀	V _{ts}	ρ _{sw}	M _{sw}	pH	A _T
20	22.2	22.80	0.197	3.493	306.32	306.33	1022.894	313.34	4.667	2223.80
2	19.3	19.89	0.214	3.518	308.64	308.64	1023.673	315.95	4.726	2225.01
2	19.8	20.65	0.205	3.516	308.64	308.64	1023.54	315.91	4.701	2222.89
4	19.8	20.31	0.230	3.487	306.20	306.20	1023.54	313.41	4.756	2224.49
7	23.0	22.70	0.299	3.504	308.40	308.41	1022.668	315.40	4.852	2224.72
4	20.4	21.30	0.231	3.486	306.20	306.20	1023.383	313.36	4.750	2223.93
average										2224.14
std error										0.76

V₂₀ is the sample-bottle calibration volume at 20 °C. The temperature of the solution at the time of sample collection is given by t_s; t is the temperature at the conclusion of the titration. R(t) is the final measured absorbance ratio. V_A is the volume of 0.1970 N HCl delivered over the course of the titration. V_{ts} is the volume contained at the sample filling temperature. ρ_{sw} is density of seawater. M_{sw} is mass of seawater contained in sample bottle. The certified A_T value (CRM batch 109) was 2224.26 μmol kg⁻¹.

Table 3. Evaluation of effect of water rinse on alkalinity measurements

t	Water added (mL)	S	R(t)	pH	H ⁺	A _T
21.1	0	36.206	0.1686	4.6079	2.47E-05	2276.64
21.1	1	36.082	0.169	4.6091	2.46E-05	2276.62
21.1	2	35.94971	0.1693	4.6101	2.45E-05	2276.59
21.1	3	35.81802	0.1694	4.6105	2.45E-05	2276.52
21.1	4	35.6873	0.1693	4.6104	2.45E-05	2276.42
21.05	0	35.55753	0.5272	5.1135	7.7E-06	2203.37
21.05	1	35.4287	0.5275	5.1139	7.69E-06	2203.35
21.05	2	35.30079	0.5274	5.1140	7.69E-06	2203.33
21.05	3	35.17381	0.5282	5.1149	7.68E-06	2203.31
21.05	4	34.92257	0.5287	5.1156	7.66E-06	2203.30
21.05	5	35.04774	0.5294	5.1160	7.66E-06	2203.28
20.9	0	22.80267	0.4735	5.0837	8.25E-06	1461.57
20.9	1	22.71852	0.474	5.0843	8.24E-06	1461.55
20.9	2	22.635	0.4743	5.0847	8.23E-06	1461.53
20.9	3	22.55209	0.475	5.0854	8.21E-06	1461.51
20.9	4	22.46978	0.4764	5.0868	8.19E-06	1461.51
20.9	5	22.38807	0.4778	5.0882	8.16E-06	1461.51