

Reference materials for oceanic CO₂ analysis: a method for the certification of total alkalinity

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Received 21 September 2002; received in revised form 30 October 2002; accepted 1 November 2002

Abstract

This paper describes a method used to certify reference materials based on seawater for total alkalinity. The technique employs a two-stage, potentiometric, open-cell titration using coulometrically analyzed hydrochloric acid. The equivalence point is evaluated from titration points in the pH region 3.0–3.5 using a least-squares procedure that corrects for the reactions with sulfate and fluoride ions. The reproducibility (one standard deviation) of this technique is less than 1 μmol kg⁻¹; the accuracy is within 2 μmol kg⁻¹.

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Keywords: Chemical analysis; Analytical techniques; Alkalinity; Titration

1. Introduction

The total alkalinity of a seawater sample 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):

$$\begin{aligned} A_T = & [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] \\ & + [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] + [\text{SiO}(\text{OH})_3^-] + [\text{NH}_3] \\ & + [\text{HS}^-] + \dots - [\text{H}^+]_F - [\text{HSO}_4^-] - [\text{HF}] \\ & - [\text{H}_3\text{PO}_4] - \dots \end{aligned} \quad (1)$$

The brackets represent total concentrations of these constituents in solution, $[\text{H}^+]_F$ represents the free hydrogen ion concentration, and the ellipses indicate additional minor acid or base species that are either unidentified or present in such small amounts that they need not be considered. The concentrations of NH₃ and HS⁻ are typically so low that they too are unimportant in open ocean water; they may, however, be significant in anoxic environments.

For over a hundred years, the alkalinity of seawater has been measured by some form of acidimetric titration (Dickson, 1992). Nevertheless, it was not until Dyrssen and Sillén advocated the Gran (1952) technique for locating the titration equivalence point (Dyrssen, 1965; Dyrssen and Sillén, 1967) that the general precision of the method improved significantly.

Additional development work by Edmond (1970) and by Arnold Bainbridge and the GEOSECS oper-

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ations group (Bradshaw et al., 1981) helped to refine Dyrssen's experimental technique into the closed-cell titration technique that has been in widespread use for over 20 years (e.g., Bradshaw et al., 1981; Brewer et al., 1986; Millero et al., 1993). Refinement of the algorithms used to calculate the equivalence point (Hansson and Jagner, 1973; Bradshaw et al., 1981; Dickson, 1981; Johansson and Wedborg, 1982; DOE, 1994) has further improved the precision of this technique.

Unfortunately, these improvements in precision have not always been accompanied by improvements in the accuracy of the procedure, as witnessed by a long history of adjusting alkalinity data from various oceanographic expeditions so as to place them on what was believed to be a common basis (e.g., Broecker and Takahashi, 1978; Gruber et al., 1996). Furthermore, in 1987, an intercomparison study of measurements of total alkalinity was carried out by a number of laboratories (Poisson et al., 1990a,b) with disappointing results; the range of variation found between measurements performed by different laboratories corresponded to nearly the entire oceanographic range for alkalinity (i.e., about $200 \mu\text{mol kg}^{-1}$).

We thus set out to develop an accurate method that could be used to assign total alkalinity values to the reference materials we had been producing since 1990 (Dickson, 1990; Dickson et al., submitted for publication; Unesco, 1991). Once one can be sure of cruise to cruise comparability of total alkalinity measurements, it becomes practical to use this data more effectively, for example, to demonstrate the regional patterns in the salinity–alkalinity relationship of the world's oceans (Millero et al., 1998). Such relationships are approximately linear and the residual variance corresponds to a standard deviation of about $10 \mu\text{mol kg}^{-1}$, i.e., meaningfully larger than the error of measurement ($2 \mu\text{mol kg}^{-1}$). As further high-quality alkalinity data is collected, we trust that a better understanding of the geochemical processes affecting alkalinity distributions in the ocean will result.

2. Open-cell titration procedure

2.1. Introduction

We titrated a weighed amount of seawater with hydrochloric acid, following the titration by meas-

uring the electromotive force (e.m.f.) generated using a combination glass-reference pH cell. The equivalence point was located using a curve-fitting technique that takes explicit account of the various acid-base equilibria believed to occur in the solution.

Although this approach is similar to that used previously to determine the total alkalinity of seawater, we incorporated a number of modifications that have reduced the uncertainty of this technique significantly:

- The titrant (hydrochloric acid in a sodium chloride medium) is standardized by coulometric titration, a highly accurate technique.
- The burette used to deliver titrant is calibrated ($\pm 0.0007 \text{ cm}^3$), and the density of the titrant used is determined as a function of temperature. This approach is used presently by some groups (e.g., Millero et al., 1993); it is *essential* for accurate measurements.
- The e.m.f. of the pH cell is measured to $\pm 0.00001 \text{ V}$.
- The pH electrodes used for these titrations are regularly tested by making a series of measurements on a well-characterized reference material. If the average of four or more measurements of a reference material (made in 1 day) is more than $2 \mu\text{mol kg}^{-1}$ different from the certified value, or if the standard deviation of these analyses is greater than $1 \mu\text{mol kg}^{-1}$, the electrode quality is questioned. If a new electrode improves the results, the old one is discarded.
- An open titration cell is used, in contrast to the closed cells developed by Edmond (1970) or Bradshaw and Brewer (1988), which makes it straightforward to weigh out a known quantity of seawater for analysis. This is a much simpler operation than calibrating the volume of a closed-cell system. The closed-cell approach has been pursued extensively despite this difficulty, because it appears to have the added benefit of allowing the estimation of the total dissolved inorganic carbon of the sample simultaneously with the estimation of the total alkalinity (Dyrssen and Sillèn, 1967). However, this has been problematic; see Bradshaw et al. (1981), Brewer et al. (1986), Bradshaw and Brewer (1988), and Millero

et al. (1993) to better understand the limitations inherent in this approach.

- The titration itself is carried out in a two-stage procedure. An initial increment of acid is added to lower the pH of the solution to about 3.6; the solution is stirred for more than 10 min to allow carbon dioxide to degas; the titration is then continued to a pH of about 3. This allows us to evaluate the equivalence point for the titration without needing to take account of any contributions due to carbon dioxide species.

To estimate the accuracy of this procedure, we compared the results obtained from our technique with the alkalinity values assigned to simple synthetic solutions: from a knowledge of their composition (i.e., the individual alkalinity contributions of the components used to make up the solutions) and by direct measurements using a well-characterized coulometric back-titration procedure.

2.2. Apparatus

The basic equipment used for this titration is as follows:

- Calibrated balance used to weigh samples for analysis to within 0.01 g (A&D model FX-3000).
- A 250-cm³ capacity jacketed beaker with 2 1/4" internal diameter.
- Thermostat bath capable of maintaining temperature to within 0.02 °C (Fisher model 9110).
- Magnetic stirrer and stir bar.
- Calibrated thermometer readable to 0.01 °C (Guildline model 9540), which is used to confirm that the solution temperature remains constant during the titration and to provide the value of solution temperature for use in subsequent calculations.
- Digital voltmeter readable to 0.000 01 V (Keithley model 199).
- High-impedance voltage-follower amplifier (home-made) used to buffer the e.m.f. of the glass electrode assembly so it can be measured accurately using a digital voltmeter.
- Combination pH electrode (Orion model 8102).
- Calibrated digital thermometer readable to 0.1 °C (used to measure the acid temperature).

- Metrohm Dosimat® Model 665 burette, 5-cm³ exchange unit, and antidiffusion tip. The burette used is capable of the high reproducibility (± 0.001 cm³) needed to obtain the highest quality results. Regrettably, the nominal burette volumes are typically not this accurate, so it is essential to calibrate the burette system prior to use. We calibrate our burette by weighing water and have reconfirmed our calibration on a number of separate occasions.

2.3. Description of procedure

The acid titrant, prepared by weight from an approximate 1 M stock solution, has a concentration of 0.1 mol kg⁻¹ and is prepared in a 0.6 mol kg⁻¹ sodium chloride background to approximate the ionic strength of seawater (0.7 mol kg⁻¹). This ensures that activity coefficients remain approximately constant during the titration. The concentration of the acid titrant is determined coulometrically (Appendix A). The density of this titrant has been determined as a function of temperature to convert volumes dispensed to masses for the evaluation of the equivalence point (Section 2.4). The acid temperature is recorded to 0.1 °C at the beginning of each titration.

A sample of seawater (about 135 g) is weighed into the titration cell where it is titrated with hydrochloric acid in two stages. The seawater is first acidified to a pH of about 3.6 with a single aliquot of titrant (~ 3 cm³) then the solution is stirred vigorously for at least 10 min to allow the carbon dioxide that evolves to escape. Next, the titration is continued in a series of about 20 additions of 0.05 cm³ each until a final pH of about 3.0 is reached. After each addition, the total dispensed volume is recorded to 0.001 cm³; the e.m.f. of the combination pH electrode is recorded to ± 0.000 001 V (as the average of 10 readings, each measured to 0.000 01 V); and the sample temperature is recorded to 0.01 °C.

2.4. Calculation of the total alkalinity from the titration data

The defining equation for total alkalinity, Eq. (1) is used to write a proton condition corresponding to

this equivalence point (ignoring minor unidentified species):

$$\begin{aligned}
 & [\text{H}^+]_{\text{F}} + [\text{HSO}_4^-] + [\text{HF}] + [\text{H}_3\text{PO}_4] \\
 &= [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] \\
 &+ [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] + [\text{SiO}(\text{OH})_3^-] \\
 &+ [\text{NH}_3] + [\text{HS}^-].
 \end{aligned} \quad (2)$$

At each point in the titration, the analytical total concentration of hydrogen ion (relative to this proton condition) is

$$\begin{aligned}
 C_{\text{H}} &= [\text{H}^+]_{\text{F}} + [\text{HSO}_4^-] + [\text{HF}] + [\text{H}_3\text{PO}_4] - [\text{HCO}_3^-] \\
 &- 2[\text{CO}_3^{2-}] - [\text{B}(\text{OH})_4^-] - [\text{OH}^-] \\
 &- [\text{HPO}_4^{2-}] - 2[\text{PO}_4^{3-}] - [\text{SiO}(\text{OH})_3^-] \\
 &- [\text{NH}_3] - [\text{HS}^-].
 \end{aligned} \quad (3)$$

This initial analytical concentration of hydrogen ion in the solution is the negative of the total alkalinity. After a mass m of acid (concentration C mol kg⁻¹) has been added to a mass m_0 of sample,

$$C_{\text{H}} = \frac{-m_0 A_{\text{T}} + mC}{m_0 + m}, \quad (4)$$

which can be substituted in Eq. (3) to give

$$\begin{aligned}
 \frac{-m_0 A_{\text{T}} + mC}{m_0 + m} &= [\text{H}^+]_{\text{F}} + [\text{HSO}_4^-] + [\text{HF}] + [\text{H}_3\text{PO}_4] \\
 &- [\text{HCO}_3^-] - 2[\text{CO}_3^{2-}] - [\text{B}(\text{OH})_4^-] \\
 &- [\text{OH}^-] - [\text{HPO}_4^{2-}] - 2[\text{PO}_4^{3-}] \\
 &- [\text{SiO}(\text{OH})_3^-] - [\text{NH}_3] - [\text{HS}^-].
 \end{aligned} \quad (5)$$

Eq. (5) is the basis of the computations involved in this procedure. However, as only pH data in the range 3.0–3.5 are used, and as the carbon dioxide generated by the reaction with the acid titrant is lost into the atmosphere, the majority of these terms can be safely omitted. Hence, Eq. (5) can be reduced to

$$\frac{-m_0 A_{\text{T}} + mC}{m_0 + m} = [\text{H}^+]_{\text{F}} + [\text{HSO}_4^-] + [\text{HF}]. \quad (6)$$

This equation is the basis of our method.

Eq. (6) is almost identical to the expression

$$\frac{-m_0 A_{\text{T}} + mC}{m_0 + m} = [\text{H}^+]_{\text{F}} + [\text{HSO}_4^-] + [\text{HF}] - [\text{HCO}_3^-] \quad (7)$$

proposed by Hansson and Jagner (1973) as the basis of their *modified Gran plot*. Whereas they use information about the total dissolved inorganic carbon concentration (calculated from the same closed-cell titration) to compute $[\text{HCO}_3^-]$, we neglect this term as we have shown that more than 95% of the inorganic carbon is lost during the degassing step of our procedure. We then use a nonlinear least-squares procedure to estimate A_{T} (and also the electrode calibration factor E°), rather than the iterative linear approach they employed.

To use a nonlinear procedure for this, it is necessary to start with reasonable estimates for A_{T} and E° so as to ensure convergence. We achieve this by using a simple Gran (1952) approach as follows.

Eq. (6) is first approximated by

$$\begin{aligned}
 \frac{-m_0 A_{\text{T}} + mC}{m_0 + m} &\approx [\text{H}^+] = \exp\left(\frac{E - E^\circ}{RT/F}\right) \\
 &= k \exp\left(\frac{E}{RT/F}\right),
 \end{aligned} \quad (8)$$

where $[\text{H}^+]$ is the total hydrogen ion concentration, defined as

$$[\text{H}^+] = [\text{H}^+]_{\text{F}}(1 + S_{\text{T}}/K_{\text{S}}) \approx [\text{H}^+]_{\text{F}} + [\text{HSO}_4^-]; \quad (9)$$

in this expression, S_{T} is the total sulfate concentration, and K_{S} is the acid dissociation constant of HSO_4^- —the values used are from DOE (1994). Thus, this assumes that $[\text{HF}]$ is negligible, and that $[\text{HSO}_4^-] \ll [\text{SO}_4^{2-}]$. (Neither of these are very good assumptions, yet they are adequate for the purpose of estimating initial values for A_{T} and E° for our least-squares procedure.)

Eq. (8) is rearranged to give the Gran function

$$F_1 = (m_0 + m) \exp\left(\frac{E}{RT/F}\right); \quad (10)$$

this function is linear in m and has a zero at $A_{\text{T}} = mC/m_0$, which is estimated from a linear least-squares fit

of F_1 against m . Once this estimate of A_T has been calculated, Eq. (8) is rearranged to calculate an estimate of E° at each titration point:

$$E^\circ = E - (RT/F) \ln \left(\frac{-m_0 A_T + mC}{m_0 + m} \right); \quad (11)$$

these values are averaged to obtain the initial estimate of E° .

A nonlinear least-squares calculation is then used to refine these values of A_T and E° . However, rather than adjusting E° directly, it is convenient to define a multiplier:

$$f = [\text{H}^+]/[\text{H}']; \quad (12)$$

where estimates of $[\text{H}^+]$ are computed from the initial estimate of E° ($E^{\circ'}$):

$$[\text{H}'] = \exp \left(\frac{E^{\circ'} - E}{RT/F} \right), \quad (13)$$

i.e., the error in E° (the difference between this initial estimate and the *true* value) appears as a multiplicative factor in the hydrogen ion concentration (f) that can then be adjusted in the least-squares procedure (rather than adjusting the value of E° directly).

Eq. (6) is thus rewritten as

$$A_T + \left(\frac{S_T}{1 + K_S Z / (f[\text{H}'])} \right) + \left(\frac{F_T}{1 + K_F / (f[\text{H}'])} \right) + \left(\frac{m_0 + m}{m_0} \right) \frac{f[\text{H}']}{Z} - \frac{m}{m_0} C = 0, \quad (14)$$

where F_T is the total fluoride concentration and K_F is the acid dissociation constant of (the values used are from DOE, 1994). In this equation, the total hydrogen ion concentration is represented by the product $f[\text{H}']$, and the free hydrogen concentration by $f[\text{H}']/Z$, where $Z = (1 + S_T/K_S)$, and thus

$$[\text{H}^+]_F = [\text{H}^+]/Z = [\text{H}^+]/(1 + S_T/K_S). \quad (15)$$

This approach (though seemingly cumbersome) renders the calculation essentially independent of errors in K_S .

The actual data fitting is performed using a Levenberg–Marquardt nonlinear least-squares routine. Eq. (14) is used to define a vector of residuals (i.e., the extent to which the left-hand side differs

from 0), and the software then minimizes the sum-of-squares of these residuals by adjusting the parameters f and A_T . During this procedure, care is taken to ensure that the initial and final titration points of the data set processed are those for which the calculated $\text{pH}(-\log[\text{H}^+])$ lies the closest to the values 3.5 and 3.0, respectively. Points that lie outside this region are excluded from the calculation.

This choice of pH range is appropriate for the following reasons. If there is some bicarbonate present, it will be a negligible amount ($< 0.5 \mu\text{mol kg}^{-1}$) even at the highest pH used (3.5) and will be still less at the lower pHs. Furthermore, at pHs lower than 3.0, the simple Nernst Eq. (8) no longer holds true, as the liquid junction potential for a pH cell is a function of hydrogen ion concentration ($\sim 30 \text{ mV/mol-H}^+ \text{ kg}^{-1}$; see Dickson and Riley, 1979); in addition, the effect of uncertainties in K_S become more problematic at low pHs.

3. Data quality

3.1. A focus on accuracy

A cornerstone of high-quality measurements is carefully calibrated instrumentation. Therefore, we use high-quality, certified equipment in this procedure and also regularly reconfirm the calibration of various items including balances, thermometers, voltmeters, timer, and the burette.

To obtain an accurate value for the total alkalinity of a sample, it is essential to ensure that the following are accurate: the amount of sample being titrated, the amount of acid added at each titration step, and the method used to locate the alkalinity equivalence point.

- The sample was weighed directly into the titration cell.
- Tests on the precision and accuracy of the coulometric method used to calibrate our titrant are detailed in Section 3.2. Because the titrant concentration is expressed in mol kg^{-1} , it would be preferable to dispense the acid gravimetrically; but this is not practical for regular work. However, we achieved a high accuracy by using a carefully calibrated piston burette to dispense the acid titrant

volumetrically, together with a knowledge (determined experimentally) of the titrant density as a function of temperature to estimate the mass of titrant dispensed. The acid temperature is measured immediately prior to each titration.

- Locating the equivalence point is more problematic. We based our approach on a well-established equilibrium model for acid-base processes in seawater (Section 2.4); the two-step titration approach minimizes the amount of carbon dioxide present, making the model independent of uncertainties in the thermodynamic representation of carbon dioxide equilibria in seawater. The pH range chosen for the data (3.5–3.0) also makes the equations used independent of likely uncertainties in the other thermodynamic information used (i.e., K_S , K_F , S_T , F_T). Additionally, we assume that there are no unidentified acids or bases present that need to be considered in the equation for locating the equivalence point (cf. Bradshaw and Brewer, 1988). Restricting the pH range makes this a plausible assumption, as only acids with a pK in the range 2.5–4.0 will have any effect, and such acid groups are rare.

To estimate the accuracy of the overall procedure, we titrated a variety of synthetic solutions made up from ingredients whose contribution to the total solution alkalinity could be characterized accurately (Section 3.3). It is the degree of agreement between the measured and calculated stoichiometric alkalinities of these solutions that provides the basis for our overall accuracy estimate.

3.2. Coulometric calibration of the hydrochloric acid used as titrant

An essential part of our method for measuring the total alkalinity of seawater is the use of a precise and accurate method for determining the concentration of the acid titrant used. We chose to use a coulometric titration technique similar to that developed at the US National Bureau of Standards (now the National Institute for Standards and Technology) (Smith and Taylor, 1959; Taylor and Smith, 1959), which is used to certify their acid-base Standard Reference Materials.

The precision of this technique is extremely high, with a relative standard deviation typically between

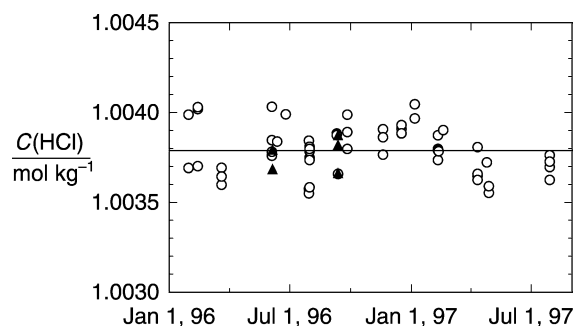


Fig. 1. Coulometric analyses (open circles) of the concentration of stock acid solution (Batch E). The triangles represent analyses made against Tris (NIST SRM 723)—see Table 1.

0.01% and 0.02% (Fig. 1; Table 1). The accuracy of the value assigned to various stock solutions of hydrochloric acid can be assessed by direct comparison with values obtained by a number of alternate techniques (Table 1). Based on these results, we conclude that (with the possible exception of Batch D) the overall uncertainty of our analyses of hydrochloric acid (~ 1 M) is comparable to the standard deviation.

This coulometric titration approach can also be used to assay dilute solutions of hydrochloric acid in a sodium chloride background, the titrant used for the alkalinity determinations, and we do so regularly. We confirmed the accuracy of our normal method for analyzing such solutions by analyzing solutions that had been diluted by mass from the original stock solution (Table 2). The agreement was excellent, confirming that there was no significant error in the calibration of the dilute acid solutions used as titrants.

3.3. Measurement of the alkalinity of synthetic solutions

To estimate the accuracy of this procedure, we compared the results obtained from our technique with the alkalinity values assigned to simple synthetic solutions from a knowledge of their composition. To achieve this, we needed to be able to assign an alkalinity to the sodium chloride-based ionic medium used to prepare such solutions (the background alkalinity) and the purity of the bases used to make up our synthetic solutions.

Table 1
Analyses of various batches of 1 M hydrochloric acid

Assay	By coulometry ^a	Against Tris ^b	Against Na ₂ CO ₃ ^c	Against pure silver ^d	By gravimetry ^e
Batch A (Oct. 1989)	1.02905 ± 0.00050 (22)	1.02896 ± 0.00015 (18)	–	1.02913 ± 0.00022 (3)	–
Batch B (Nov. 1992)	1.02746 ± 0.00026 (35)	1.02682 ± 0.00017 (9)	–	–	–
Batch C (Apr. 1994)	1.02959 ± 0.00016 (17)	–	–	–	–
Batch D (Sep. 1995)	1.01352 ± 0.00022 (21)	1.01298 ± 0.00005 (7)	–	–	1.01291 ± 0.00007 (3)
Batch E (Jan. 1996)	1.00379 ± 0.00013 (55)	1.00377 ± 0.00009 (5)	1.00401 ± 0.00004 (6)	–	–
Batch F (Jul. 1997)	0.99675 ± 0.00009 (11)	–	–	–	–

Results expressed in mol kg⁻¹ as mean ± standard deviation (number of analyses).

^a Using the technique described in Appendix A to this paper.

^b By reaction with Tris (NIST SRM 723) and coulometric titration of excess acid (Appendix A).

^c By reaction with sodium carbonate (NIST SRM 413) and coulometric titration of excess acid (Appendix A).

^d By the method described by the Analytical Chemists' Committee I.C.I. (1950) (also Woodward and Redman, 1973).

^e By gravimetric analysis as silver chloride using the method detailed by Little (1971).

Since the background alkalinity of commercially available sodium chloride can be significant, contributing 10–30 μmol kg⁻¹ of alkalinity to the solution, we developed a purification technique to reduce this background. This involved recrystallizing sodium chloride from a saturated solution that had been bubbled with chlorine gas. The sodium chloride obtained was then dried in a furnace at a temperature of 550 °C. The background alkalinity of the purified sodium chloride was estimated by a coulometric back-titration technique. This purification procedure allowed us to reduce the amount of basic impurity in such solutions from an initial level of about 15 μmol kg⁻¹ (using unpurified bulk sodium chloride) to a final level that was essentially independent of the amount of sodium chloride and was thus believed to be zero (Dickson and Anderson, in preparation).

Table 2
Assay of diluted solutions of 1 M hydrochloric acid used as titrants

Batch of hydrochloric acid	Calculated concentration	Assayed concentration
Batch C + H ₂ O + NaCl	0.100499	0.100493 ± 0.000017 (25)
Batch E + H ₂ O + NaCl	0.100358	0.100386 ± 0.000012 (42)
Batch E + H ₂ O + NaCl	0.100433	0.100450 ± 0.000029 (43)

Results expressed in mol kg⁻¹ as mean ± standard deviation (number of analyses).

Three bases were used for these tests: 2-amino-2-hydroxymethyl-1,3-propanediol (Tris), sodium carbonate, and borax. The purity of these bases was assayed coulometrically; the Tris and the sodium carbonate are available from the National Institute for Standards and Technology (NIST) with certified purities as SRM 723 and SRM 413, respectively. The borax was purified using the method described in Vogel (1961) and was stored at constant humidity in a hygrostat containing a solution saturated with both sodium chloride and sucrose. Its measured purity, estimated using our coulometric titration technique, was 99.998 ± 0.016% (4).

Solutions were prepared using weighed amounts of our purified sodium chloride together with weighed amounts of the desired base (borax was used straight from the hygrostat; Tris and sodium carbonate were dried in accordance with the instructions from NIST) and weighed amounts of water. The stoichiometric alkalinity was then calculated assuming that the sodium chloride background did not contribute any alkalinity. Aliquots of these solutions were titrated using both our open-cell titration technique and a coulometric back-titration technique. The Gran (1952) technique was used to locate the equivalence point in both cases, though the pH range used for the data points was somewhat different: 3.0–3.5 for the open-cell system, 3.5–4.0 for the

Table 3

Results from measurements on synthetic solutions and natural sea water

	Coulometric back-titration ^a	Open-cell titration	Calculated alkalinity ^b
NIST SRM 723 (Tris)	2191.00 ± 0.57 (4)	2190.25 ± 0.81 (4)	2189.5
NIST SRM 413 (Na ₂ CO ₃)	2172.48 ± 0.88 (4)	2172.21 ± 0.51 (4)	2172.0
Borax	2001.01 ± 0.22 (3)	1998.58 ± 0.44 (3)	2000.5
Natural seawater ^c	2278.52 ± 0.85 (3)	2279.15 ± 0.37 (9)	–

Results expressed in $\mu\text{mol kg}^{-1}$ as mean ± standard deviation (number of analyses).

^a See Appendix A for a description of this procedure.

^b The calculated alkalinities assume a zero background alkalinity due to the NaCl.

^c The seawater was sterilized by filtration through a 0.1- μm filter. The presence of mercuric ion prevents accurate coulometric analysis as it is preferentially reduced at the electrode.

coulometric back-titration. Results from such analyses showed an agreement that was always within 2 $\mu\text{mol kg}^{-1}$, both for the synthetic solutions and also for measurements on natural seawater (Table 3). This then is an estimate of our accuracy.

4. Results on seawater reference materials

The open-cell titration described here has been used to certify our reference materials for total alkalinity. We started certifying reference materials with Batch 33 (certified July 30, 1996) and continue to do so. In addition, we certified an additional 22 earlier batches from archived samples (for the certified values, see Dickson et al., submitted for publication). Hence, only four of the batches that have been certified for total dissolved carbon have not also been certified for total alkalinity because samples from these batches were no longer available.

We can establish the reproducibility (both short- and long-term) for this method from extensive sets of replicate measurements. The short-term reproducibility is estimated by pooling the standard deviations of replicate measurements made on individual bottles of reference material. Such analyses are typically carried out by a single operator on a single day using one electrode and one batch of acid. The resultant standard

deviation calculated from all our analyses on 60 bottles of Batch 35 was 0.58 $\mu\text{mol kg}^{-1}$ (estimated with 107 degrees of freedom).

If, however, we track Batch 35 over a period of about 3 years (Fig. 2), including the additional variance due to changes of such parameters as electrodes, operator, and acids, we obtain a standard deviation of 0.70 $\mu\text{mol kg}^{-1}$. This estimate compares well with that obtained from pooling standard deviations of the certified measurements for Batches 33–53 (excluding Batch 39, which was not certified): 0.74 $\mu\text{mol kg}^{-1}$ (553 degrees of freedom). Analyses for each of these certifications were typically performed within 3 months of bottling. A slightly larger estimate of the reproducibility was obtained by pooling the standard deviations from *all* the batches of reference material analyzed (Table 2 of Dickson et al., submitted for publication) to obtain an estimate of the standard deviation of 0.83 $\mu\text{mol kg}^{-1}$ (835 degrees of freedom). This almost certainly included some additional bottle-to-bottle variability that existed in some of our archived sets of reference materials, which acted to increase the overall standard deviation.

A careful examination of Fig. 2 indicates that our measurement results over these 3 years were independent of the batch of acid titrant (4 batches), the electrode (10 different pH electrodes), and the operator (2 individuals) involved in the titrations.

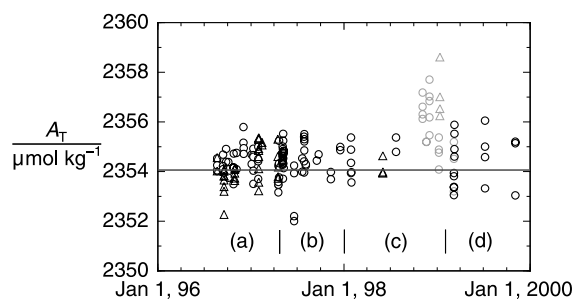


Fig. 2. Results obtained for the total alkalinity of Batch 35. The line corresponds to the certified value [$A_T = 2354.05 \pm 0.50$ (34) $\mu\text{mol kg}^{-1}$] based on measurements made on or before November 5, 1996. The mean and standard deviation of all the measurements was 2354.35 ± 0.70 (143) $\mu\text{mol kg}^{-1}$. (Pale grey symbols denote results from a period where we were having electrode problems and so were omitted from these statistics; see Section 4.) The different symbols (circles, triangles) indicate titrations performed by two different analysts; the date ranges—(a), (b), (c), (d)—indicate the use of different batches of acid titrant.

However, this figure also shows the existence of some problems. During a period of about 3 months, our analysis was not “in control”; results obtained during this period were (on average) about $1.6 \mu\text{mol kg}^{-1}$ higher than the mean of the other 143 measurements, and the scatter was higher than we were used to.

As was mentioned in Section 2.1, we typically associate such discrepancies with an electrode problem, and our first action was to exchange the electrode for a new one. Such an action typically resolves such discrepancies; however, not on this occasion, despite trying a number of electrodes. Measurements on other batches of reference material, however, also indicated a problem, so we chose to overhaul our entire titration apparatus. The calibration of the voltmeter (and associated voltage follower circuitry) was checked, the thermometers used were recalibrated, the acid titrant was reanalyzed, and the burette calibration was re-confirmed. No obvious problem came to light. Eventually, use of a further new electrode resolved the discrepancy, and no further unidentifiable problems have occurred in the ensuing years.

So what happened? We are inclined to believe that we had a series of “problem” electrodes. The discrepancy was quite small, was not immediately obvious, and would have been almost impossible to detect without access to a large supply of well-characterized seawater (our batches of reference material). Since we started making regular analyses in 1996, we have had a number of discrepancies that were immediately resolved by replacing the electrodes, but only two that were not electrode related. These were ultimately traced to small leaks in the burette system.

The accuracy of these total alkalinity analyses (as stated earlier) is believed to be within $2 \mu\text{mol kg}^{-1}$. A possible concern is whether the open-cell titration provides alkalinity values that are in any way systematically different from the more commonly used closed-cell approach. Although we have confirmed in our laboratory (for a limited number of samples) that this is not the case, additional weight is given to this assertion by the data shown in Fig. 3. Here, we compare our certified values (measured on archived samples) with those determined earlier using a closed-cell titration technique in Dr. F.J. Millero’s laboratory at the University of Miami in

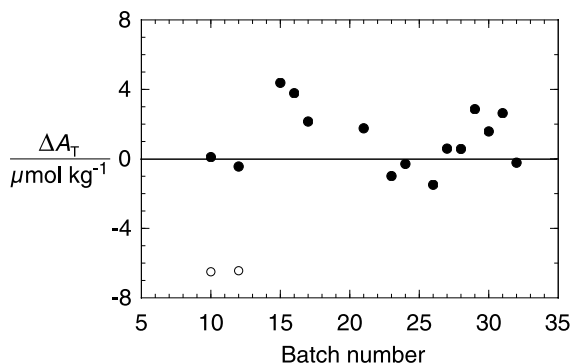


Fig. 3. Comparison of certified values measured on archived samples of reference materials with measurements made previously in the laboratory of Dr. F.J. Millero at the University of Miami. The data represented by the filled circles are reported in Millero et al. (1998) [note; the total alkalinity value for Batch 10 in Table 1 of that paper is wrong, the one used here was obtained directly from Dr. Millero]. The data represented by open circles are from Lee and Millero (1995)—see discussion in Section 5.

Florida. The mean difference is $1.13 \mu\text{mol kg}^{-1}$ with a standard deviation of $1.8 \mu\text{mol kg}^{-1}$. The apparent systematic nature of the deviation is not due to variability in our laboratory: the analyses of these archived samples (with the exception of Batch 22) were overlapped in time over a period of only 4 months so as to ensure that they could be compared directly with each other.

5. Discussion

To analyze alkalinity accurately, it is essential to know exactly how much hydrogen ion is delivered at each titration step. This requires accurate titrant calibration, combined with knowledge of burette calibration and titrant density as a function of temperature.

The high degree of agreement between our analyses and those in Fig. 3 is due to the acid calibration performed coulometrically in both laboratories (we also analyzed Dr. Millero’s acids on a number of occasions during the period of these analyses). In addition, both laboratories calibrate the burette used to deliver the acid and determine the density of the acid as a function of temperature. [Note that the initial alkalinity values for Batches 10 and 12 reported by Lee and Millero (1995), depicted by open circles in

Fig. 3, were not based on coulometric titrant calibrations.]

If one lacks a coulometric system to analyze the titrant, alkalinity standards are typically prepared using sodium carbonate in a sodium chloride background, and a titration procedure is used to assign a concentration to the acid (e.g., DOE, 1994). This approach is fraught with difficulties. First, it is important to characterize the background alkalinity due to the sodium chloride medium as it can contribute up to $30 \mu\text{mol kg}^{-1}$, which represents a potential error of up to 1.25%! Second, we have found on occasion the purity of so-called high-quality sodium carbonate to be as low as 99.8% (i.e., a potential error of up to $5 \mu\text{mol kg}^{-1}$); consequently, we recommend employing the NIST Standard Reference Material SRM 413.

Our use of an open-cell titration offers two principal advantages over the closed-cell approach: (1) ease of measuring the amount of sample being analyzed and (2) ease of removal of carbon dioxide, making the equivalence point determination more reliable. Finally, we have found that to ensure the highest accuracy, the electrodes must be selected and treated carefully. This is perhaps the weakest link in this method, and we are presently examining the possibility of using a spectrophotometric pH determination for equivalence point detection (Breland and Byrne, 1993; Yao and Byrne, 1998) so as to avoid this reliance on pH electrodes.

In conclusion, we have developed a suitable reference method for the measurement of total alkalinity in seawater, viz “a method which has been specified as capable, by virtue of recognized accuracy, of providing primary reference data” (Taylor, 1987).

Acknowledgements

This work was supported by the US National Science Foundation as part of the Joint Global Ocean Flux Study through grants OCE-8800474, OCE-9207265, OCE-9521976, and OCE-9819007 and by the US Department of Energy through Pacific Northwest National Laboratory subcontract No.121945 and grant DE-FG03-92-ER61410. We were encouraged early on in this work by Dr. Neil Andersen (then at NSF). We thank Dr. F.J. Millero for the results

presented in Fig. 3 and Mr. T.J. Leuker for some measurements performed using his closed-cell system. We also thank Judith Garfield of Biotext for assistance in preparing this manuscript for publication. US JGOFS Contribution Number 663.

Appendix A. A coulometric titration procedure for hydrochloric acid

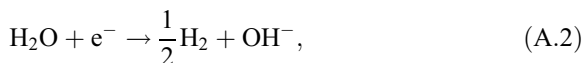
A.1. Experimental procedure

Samples of hydrochloric acid for assay are added to a 0.7 M sodium chloride solution that has been previously titrated to a neutral pH. Although it is almost impossible to achieve exact neutrality, the residual acidity (or alkalinity) of this background solution is determined from these initial titration data and is corrected for in processing the subsequent titration. If a solid base (Tris, Na_2CO_3 , borax) is being assayed, it is added to the cell together with an excess of a previously characterized hydrochloric acid sample. The excess acid is then assayed coulometrically. To measure the total alkalinity of a seawater sample, it is weighed into the cell in place of the sodium chloride background solution. An excess of a previously characterized hydrochloric acid sample is then added, and again the amount of excess acid is determined coulometrically making allowance for the side reactions with sulfate and fluoride (Section 2.4).

The excess hydrochloric acid is titrated with hydroxide ions:



These are generated coulometrically by electrolyzing water at a platinum cathode,



while silver is dissolved at the anode:



Hence, the amount of charge (in moles) required to titrate the hydrochloric acid is equivalent to the amount of acid present.

A special coulometric titration vessel (Fig. 4) based on the design of Taylor and Smith (1959) is

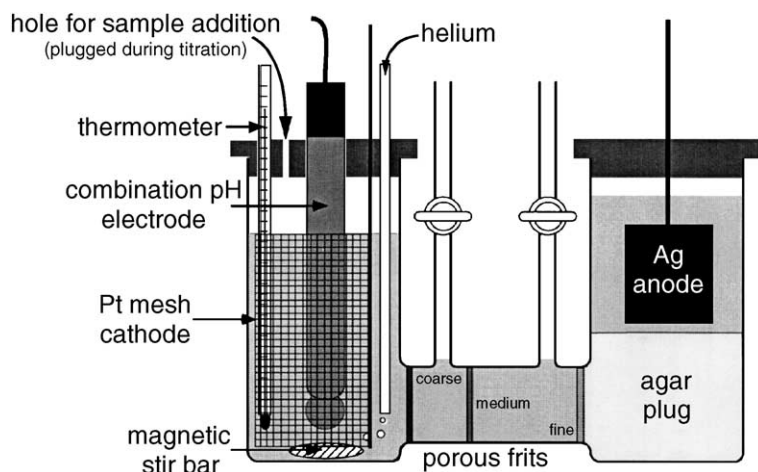


Fig. 4. Cell used for coulometric titrations.

used for these titrations to ensure 100% efficiency of the coulometric reactions. An agar plug is used in the anode compartment to prevent the silver ions that formed from migrating to the cathode. Furthermore, the electrode compartments are separated by a bridge (two small compartments separated by frits). Solutions in this bridge are manipulated during the titration in such a way as to minimize the transfer of hydrogen ions from the cathode compartment towards the anode and to ensure that the e.m.f. measured using the pH cell is representative of the solution composition at the time of measurement.

The electrolysis is performed using the circuit and instrumentation shown in Fig. 5. It is carried out using computer control to switch the current from the dummy cell to the coulometric cell. This allows us to control the magnitude of the charge added and to be able to measure it accurately. The current (I) is measured approximately every 0.1 s during the flow of charge using a standard resistor (R_S) and a calibrated voltmeter (V_i). The time interval (Δt) is measured using a high precision counter that is started when the current is switched from the dummy cell to the coulometric cell and halted when it is switched back. The charge added is calculated from Δt and the mean current ($\langle I \rangle$):

$$Q = \Delta t \cdot \langle I \rangle = \Delta t \cdot \left(\frac{1}{n} \right) \sum_{i=1}^n (V_i / R_S). \quad (\text{A.4})$$

Approximately, 95% of the hydrochloric acid is titrated in a single initial electrolysis carried out at a current of ~ 100 mA. The remaining acid is then titrated with 10 or more approximately equal additions of charge (at a current of ~ 10 mA). After each of these, the solution in the cell—including that in the bridge compartments—is mixed thoroughly.

After each addition, the total charge added and the e.m.f. reading of the pH cell are recorded. The density of the acid solution is also needed to correct the weight of the acid solution to mass. This is measured using a calibrated pycnometer.

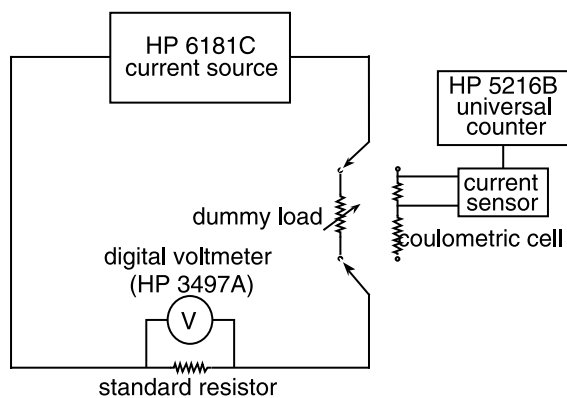


Fig. 5. Circuit used to provide and time the charge additions for constant-current coulometric titrations. The current is determined by measuring the average voltage across a standard resistor (Electro Scientific Industries) and the counter-timer is switched by amplifying the voltage across a sensing resistor.

A.2. Calculation procedure

The defining equation for the equivalence point in this titration is the proton condition:

$$[\text{H}^+] = [\text{OH}^-]. \quad (\text{A.5})$$

At each point in the titration, the total concentration of hydrogen ion (relative to this proton condition) is given by

$$C_{\text{H}} = \frac{m(\text{HCl}) \cdot C(\text{HCl}) - (\Sigma Q)/F}{m_0} \\ = [\text{H}^+] - [\text{OH}^-], \quad (\text{A.6})$$

where m (HCl) is the mass of HCl being titrated, C (HCl) is its concentration (mol kg^{-1}), is the total amount of charge added up to that point, F is the Faraday constant ($96485.309 \text{ C mol}^{-1}$), and m_0 is the total mass of solution being titrated (background medium plus added hydrochloric acid).

The approach taken to using Eq. (A.6) to estimate C (HCl) is the Gran (1952) approach. Eq. (A.6) is approximated (in acid solutions) by

$$[\text{H}^+] \approx \frac{m(\text{HCl}) \cdot C(\text{HCl}) - (\Sigma Q)/F}{m_0}; \quad (\text{A.7})$$

in addition, the ideal Nernst equation can be written as

$$[\text{H}^+] = \exp\left(\frac{E - E^\circ}{RT/F}\right) = k \exp\left(\frac{E}{RT/F}\right), \quad (\text{A.8})$$

where R is the gas constant ($8.314510 \text{ J mol}^{-1} \text{ K}^{-1}$).

Eqs. (A.7) and (A.8) are combined and rearranged to give the Gran function

$$F_1 = \exp\left(\frac{E}{RT/F}\right); \quad (\text{A.9})$$

this function is linear in ΣQ and has a zero at

$$(\Sigma Q)/F = m(\text{HCl}) \cdot C(\text{HCl}), \quad (\text{A.10})$$

which can be estimated from a linear least-squares fit of F_1 against. Points from the pH region 3.6–4.2 are treated using a Gran function (Gran, 1952) in which the equivalence point is determined using a linear least-squares fit of the results. The titration points are selected so as to improve the linearity. In this way,

points are sometimes rejected at the beginning and/or end of a data set. (They are never rejected in the middle.)

Once this estimate of $C(\text{HCl})$ has been calculated, Eq. (A.8) is rearranged to calculate an estimate of E° at each titration point:

$$E^\circ = E - (RT/F) \ln \left(\frac{m(\text{HCl}) \cdot C(\text{HCl}) - (\Sigma Q)/F}{m_0} \right). \quad (\text{A.11})$$

These values are averaged to obtain an overall estimate of E° .

Associate editor: Prof. C.T. Arthur Chen

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