

# SOP 3a

## Determination of total alkalinity in sea water using a closed-cell titration

### 1. Scope and field of application

This SOP describes an automated, closed-cell, potentiometric titration procedure used to determine total alkalinity in sea water. The results are expressed as moles per kilogram of sea water. The method is suitable for the assay of oceanic levels of total alkalinity (2000–2500  $\mu\text{mol kg}^{-1}$ ) and can be adapted easily to measure higher levels such as those that have been observed in the Black Sea (3200–4600  $\mu\text{mol kg}^{-1}$ ).

### 2. Definition

The total alkalinity of a sample of sea water 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 kilogram of sample:

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

Brackets represent total concentrations of these constituents in solution,  $[\text{H}^+]_F$  is the free concentration of hydrogen ion (see Chapter 2) and the ellipses stand for additional minor acid or base species that are either unidentified or present in such small amounts that they can be safely neglected. The concentrations of  $\text{NH}_3$  and  $\text{HS}^-$  are typically so low that they can be neglected in open ocean water; they may, however, be significant in anoxic environments.

### 3. Principle

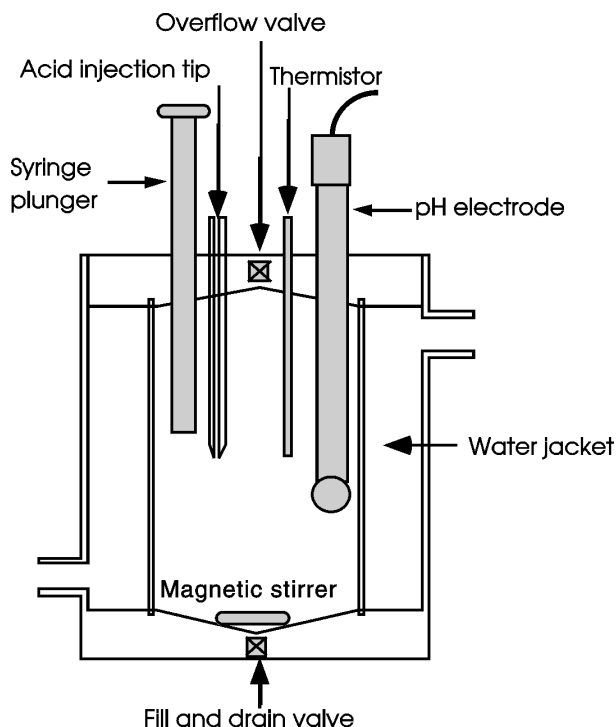
A known amount of sea water is placed in a closed cell where it is titrated with a solution of hydrochloric acid. The acid is made up in a sodium chloride background to approximate the ionic strength of sea water so as to maintain activity coefficients approximately constant during the titration. The use of a closed cell allows the subsequent data evaluation to assume that the total dissolved inorganic carbon remains constant throughout the titration—apart from the effect of dilution.

The progress of the titration is monitored using a glass electrode/reference electrode pH cell. Total alkalinity is computed from the titrant volume and e.m.f. data using either a least-squares procedure based on a non-linear curve fitting approach (see Annexe 1) or on a modified Gran approach<sup>1</sup>. Both total alkalinity and total dissolved inorganic carbon are computed from such titration data; however, the more direct extraction/coulometric method detailed in SOP 2 provides a more accurate procedure for the determination of total dissolved inorganic carbon<sup>2</sup>.

## 4. Apparatus

### 4.1 Titration cell assembly

A closed, thermostated, titration cell with an internal volume of 100 cm<sup>3</sup> or more is suitable. (Such a cell can be constructed from Lucite<sup>®</sup> incorporating an outer water jacket—see Figure 1.)



**Fig. 1** Closed titration cell for the determination of alkalinity.

<sup>1</sup> For more detail of the modified Gran approach, see Hansson and Jagner (1973) or Bradshaw *et al.* (1981).

<sup>2</sup> Typically,  $C_T$  is underestimated by a potentiometric titration, either because of omitting acid-base species, such as phosphate (see Bradshaw *et al.*, 1981), or because the actual Nernst factor for the electrode pair used is less than the theoretical value that is assumed to apply (see Millero *et al.*, 1993).

There is an optimal relationship between the size of the titration cell, the size of the piston burette and the strength of the acid used:

$$\frac{V(\text{burette})}{V(\text{cell})} \times C(\text{HCl}) = 3.5 \times 10^{-3} \text{ mol kg}^{-1}. \quad (2)$$

This equation is based on the assumption that a solution with a total alkalinity of  $2.5 \times 10^{-3} \text{ mol kg}^{-1}$  is titrated using a complete burette of acid to a final pH of 3, *i.e.*,  $[\text{H}^+] = 1.0 \times 10^{-3} \text{ mol kg}^{-1}$ .

This cell contains a combined glass/reference pH electrode<sup>3</sup>, a thermometer, a capillary tube that supplies acid from the burette and a plunger which is free to move, thus adjusting the volume of the cell as acid is added and allowing the titration to be carried out without a headspace. (The size of the plunger must therefore be matched to the size of the burette used.) A magnetic stirrer is used to stir the solution during the titration. It is desirable to know the internal volume,  $V_0$ , of this cell accurately (with the plunger fully depressed). Ideally,  $V_0$  should be measured using the technique outlined in SOP 13. However, an alternative calibration procedure, outlined in section 8.5, can be used if this is not possible.

## 4.2 pH meter

A pH meter or a high input impedance digital voltmeter<sup>4</sup>—readable to at least 0.1 mV—is connected to the pH cell and also interfaced to the computer which controls the titration.

## 4.3 Piston burette

A calibrated (see Annexe 2) motor-driven piston burette—reproducible to  $0.001 \text{ cm}^3$  in the delivered volumes—is interfaced to the computer which controls the titration. The appropriate burette size depends on the cell size and on the concentration of acid used; see section 4.1 equation (2).

## 4.4 Thermostat bath

A thermostat bath capable of maintaining the cell at a known temperature to within  $\pm 0.05^\circ\text{C}$ . This ensures that the  $E^\circ$  of the pH cell and the Nernst factor do not vary significantly during the titration.

## 5. Reagents

- Reagent grade hydrochloric acid,
- Reagent grade sodium chloride,

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<sup>3</sup> Using a separate glass electrode/reference electrode pair can often improve the stability of the e.m.f. readings obtained.

<sup>4</sup> An external circuit based on a high input impedance operational amplifier (*e.g.*, an FET electrometer amplifier) configured as a voltage follower (unity gain amplifier) can be used to achieve this.

- Primary standard grade sodium carbonate, dried at 280°C for > 2 hours and cooled overnight in a desiccator<sup>5</sup>,
- Deionized water.

## 6. Sampling

Samples should be collected, poisoned and stored in accordance with the procedures detailed in SOP 1.

## 7. Procedure

### 7.1 Solution preparation

*Titrant* — A solution of hydrochloric acid containing enough sodium chloride to adjust the total ionic strength to approximate that of sea water (0.7 mol kg<sup>-1</sup>). (The HCl concentration is chosen to match the size of the burette and of the cell; see equation (2).)

*Background medium* — A solution of sodium chloride (0.7 mol kg<sup>-1</sup>).

*Calibration solutions*<sup>6,7</sup> — Three solutions<sup>8</sup> of sodium carbonate in the background medium (~ 0.5, 1.0 and 1.25 mmol kg<sup>-1</sup>) made up carefully by weight, *i.e.*, total alkalinities of ~ 1000, 2000 and 2500 μmol kg<sup>-1</sup>.

### 7.2 Titration procedure

**7.2.1** Bring the solution to be titrated to the approximate temperature that the titration will be carried out at before filling the cell. It is often convenient to place the sample bottle in the thermostat bath for a time to ensure this.

**7.2.2** Rinse the titration cell thoroughly with sea water<sup>9</sup> and then with the solution to be analyzed (background medium, or calibration solution). Fill the cell with the solution to be analyzed, overflowing the cell by a

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<sup>5</sup> A method for preparing suitable Na<sub>2</sub>CO<sub>3</sub> is detailed in IUPAC (1969).

<sup>6</sup> The procedure here assumes that the acid is calibrated against weighed amounts of a solid acidimetric standard. Of course, a simpler approach is to use a certified sea water reference material (see Footnote 19) as a source of a solution of known alkalinity. However, doing so limits the ability to use the reference material as an independent quality control sample.

<sup>7</sup> An alternate solid that is well suited as an acidimetric standard is TRIS (2-amino-2-hydroxy-1,3-propanediol). It is available for this purpose from the U.S. National Institute for Standards and Technology (NIST). In many ways, TRIS is more convenient to use than sodium carbonate: it has a higher formula weight per mole of alkalinity and is easier to weigh. However, a different approach is needed to treat the resulting data (*e.g.*, a Gran treatment of data from past the equivalence point).

<sup>8</sup> A single calibration solution (~ 1.25 mmol kg<sup>-1</sup>) can be used. However, using a series of solutions will improve the estimate of the “blank” attributable to the NaCl background and thus the estimate of *C*(HCl)—section 8.4.

<sup>9</sup> This is to rinse the acid out, thus any sea water is suitable for this and it is unnecessary to use a valuable sample.

few cm<sup>3</sup>; finally, close the cell ensuring that the piston is in its “down” position and that no air bubbles are present.

- 7.2.3** Add the acid solution in about 20–30 small increments (0.1–0.2 cm<sup>3</sup>) into the cell from the burette<sup>10</sup>. After each acid addition, record the total volume of acid added and the e.m.f. of the pH cell—using the computer to check that the e.m.f. is stable<sup>11</sup>.
- 7.2.4** Once sufficient acid has been added to the sample to reach a pH of about 3, the titration is ended and the resulting data are used to compute the total alkalinity of the sample.

## 8. Calculation and expression of results

### 8.1 Introduction

There are two alternate approaches to estimating total alkalinity and total dissolved inorganic carbon from titration data: the use of a non-linear least-squares approach (see Annexe 1) or the use of modified Gran functions (where the equations are rearranged to a linear form and then fitted iteratively by the method of least-squares). Both approaches are based on the same mass-balance and equilibrium relationships; they differ only in how the experimental data are weighted in the least-squares fitting.

### 8.2 Derivation of basic equations

The defining equation for total alkalinity (1) is used to define a proton condition corresponding to the equivalence point:

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

(Note that the existence of minor unidentified species has been ignored in this expression.) At any point in the titration, the analytical total concentration of hydrogen ion (relative to this proton condition) is given by the expression

$$\begin{aligned}
 C_{\text{H}} = & [\text{H}^+]_{\text{F}} + [\text{HSO}_4^-] + [\text{HF}] + [\text{H}_3\text{PO}_4] - [\text{HCO}_3^-] \\
 & - 2[\text{CO}_3^{2-}] - [\text{B}(\text{OH})_4^-] - [\text{OH}^-] - [\text{HPO}_4^{2-}] \\
 & - 2[\text{PO}_4^{3-}] - [\text{SiO}(\text{OH})_3^-] - [\text{NH}_3] - [\text{HS}^-]. \quad (4)
 \end{aligned}$$

The initial analytical concentration of hydrogen ion in the solution is thus the negative of the total alkalinity. At any point in the titration, after a mass  $m$  of acid

<sup>10</sup> Some investigators prefer to add acid so as to ensure approximately equal e.m.f. changes between titration points.

<sup>11</sup> The hydrated CO<sub>2</sub> formed in the vicinity of the burette tip takes a finite time to dehydrate again. With proper stirring it is the rate of this reaction that controls the overall time to reach a stable reading, rather than the mixing.

with concentration  $C$  (mol kg-soln<sup>-1</sup>) has been added to a mass  $m_0$  of sample<sup>12</sup>,

$$C_H = \frac{mC - m_0 A_T}{m_0 + m}. \quad (5)$$

This can be equated to the previous expression for  $C_H$ :

$$\begin{aligned} \frac{mC - m_0 A_T}{m_0 + m} = & [\text{H}^+]_F + [\text{HSO}_4^-] + [\text{HF}] + [\text{H}_3\text{PO}_4] - [\text{HCO}_3^-] \\ & - 2[\text{CO}_3^{2-}] - [\text{B}(\text{OH})_4^-] - [\text{OH}^-] - [\text{HPO}_4^{2-}] \\ & - 2[\text{PO}_4^{3-}] - [\text{SiO}(\text{OH})_3^-] - [\text{NH}_3] - [\text{HS}^-]. \end{aligned} \quad (6)$$

This equation is the basis of all computations involved in this procedure, although for titrations in NaCl media most of the terms will be equal to zero. Equation (6) is used together with the ideal Nernst equation<sup>13</sup>

$$E = E^\circ - (RT/F) \ln[\text{H}^+] \quad (7)$$

that relates the e.m.f. of the pH cell to the total concentration of hydrogen ion (*i.e.*, including the effect of sulfate ion) and together with relationships that express the individual species concentrations in terms of the total concentrations and the appropriate equilibrium constants (see Annexe 1 Table 1).

A computer program for computing the total alkalinity of a sea water sample—or of a sample containing only sodium carbonate in a sodium chloride background—from titration data is presented in Annexe 1 to this procedure. This program uses a non-linear least-squares approach and has been provided to show in detail how the calculations outlined above can be implemented.

### 8.3 Determination of the “blank” in the background medium

This “blank” reflects the presence of small quantities of alkaline impurities in the NaCl solution used to fortify the sodium carbonate standards. In treating such titration data, the total concentrations of sulfate, fluoride, phosphate, borate, silicate, *etc.* are set to zero and it is assumed that the alkalinity “blank” is due solely to carbonate species<sup>14</sup>. Also, it is essential, both in this section and in the next, to use equilibrium constants and densities that are appropriate to the background NaCl medium.

<sup>12</sup> Strictly, only masses are additive in the manner described here; however, to a good approximation, volumes can be used in these various expressions provided that they are used together with equilibrium constants expressed on a volumetric basis.

<sup>13</sup> A number of investigators make further use of the titration curve from the blank determination (see section 8.3) to confirm that the electrode pair has a Nernst response ( $RT/F$ ). However, the value of the slope and the value of  $E^\circ$  obtained by fitting experimental results in this fashion are highly correlated and thus not particularly reliable. It is usually better to verify the response of the electrode pair used with suitable buffers (SOP 6). If the response is not theoretical within the experimental uncertainty, the electrodes should be rejected.

<sup>14</sup> This is not strictly true as the residual alkalinity cannot be removed completely by acidifying and stripping with a CO<sub>2</sub>-free gas. Nevertheless, the error from assuming this is small.

Data from a titration of the background medium alone (*i.e.*, NaCl without Na<sub>2</sub>CO<sub>3</sub>) can be used to calculate the total alkalinity of the background medium. However, it is better to combine this result with the results from titrations of different levels of Na<sub>2</sub>CO<sub>3</sub> in the background medium (see next section).

#### 8.4 Calibration of the acid titrant<sup>6,15</sup>

The total alkalinity of each calibration solution titrated (including a background solution with no added Na<sub>2</sub>CO<sub>3</sub>) is given by the sum

$$A_T = A_T(\text{blank}) + \frac{2m(\text{Na}_2\text{CO}_3)}{105.988} \times \frac{1}{m(\text{Na}_2\text{CO}_3 - \text{soln})} \quad (8)$$

where  $A_T(\text{blank})$  is the total alkalinity of the NaCl background solution,  $m(\text{Na}_2\text{CO}_3)$  the mass of Na<sub>2</sub>CO<sub>3</sub> used to prepare the solution and  $m(\text{Na}_2\text{CO}_3 - \text{soln})$  the total mass of solution prepared (there are two moles of alkalinity per mole of sodium carbonate).

The measured values of  $A_T$  (calculated by assuming an approximate value for the acid concentration,  $C$ ) should be a linear function of the alkalinity component contributed by the Na<sub>2</sub>CO<sub>3</sub>—the second term in equation (8). This line is fitted by the method of least squares (SOP 23). The slope should be unity; the intercept should be the alkalinity of the NaCl background medium. If the measured slope ( $a$ ) is not equal to one, the acid concentration should be adjusted:

$$C_{i+1} = C_i / a \quad (9)$$

and the whole set of calculations repeated until  $a = 1$ .

#### 8.5 Recalibration of the cell volume

Maintenance of the titration cell may require replacing the electrode(s), magnetic stirrer bar or plunger. As a result, the volume of the cell can change and will need to be measured again. Ideally, this is done gravimetrically (see SOP 13); however, when this is not practical (*e.g.*, at sea) it is computed using the following assumptions:

- the volume of the cell,  $V_0$ , is known approximately,
- the concentration of the acid is known accurately,
- the total alkalinity of a calibration solution is known accurately.

The following strategy is adopted. The cell is filled with a calibration solution of known total alkalinity and this is titrated with the calibrated acid. The e.m.f. and volume data are then used to compute a new value of  $V_0$  as follows: first assume an approximate value of the volume  $V_0'$ ; the computed total alkalinity is then related to the “true” volume,  $V_0$ , and to the “true” total alkalinity,  $A_T$ , by the expression

$$V_0 \approx V_0' A' / A_T. \quad (10)$$

<sup>15</sup> It is necessary to exclude e.m.f. data measured at pHs higher than 8 so as to minimize the errors due to sodium ion at the glass electrode.

This calculation is iterated to obtain a consistent set of values<sup>16</sup>. It is desirable to repeat this measurement at least four times and to use the mean value in subsequent computations. This will reduce the uncertainty associated with  $V_0$ .

## 8.6 Treatment of sea water data

Once the volume of the cell ( $V_0$ ) and the concentration of the acid titrant ( $C$ ) are known, volume and e.m.f. data from a titration of a sea water sample can be used to compute both the total alkalinity and an estimate of the total dissolved inorganic carbon in the sample<sup>17</sup>. It is necessary to know the approximate salinity ( $\pm 0.1$ ) of the sea water sample so as to compute both its density and the appropriate equilibrium constants for use in the data treatment (see Annexe 1 to this procedure).

## 8.7 Example calculation

An example of a complete titration curve of sea water and calculated values for the various parameters are given together with the computer code in Annexe 1 to this procedure.

For the most accurate work, a further minor correction needs to be made to compute the total alkalinity in the original sea water sample for the dilution by mercuric chloride when the sample was collected<sup>18</sup>:

$$A_T = 1.0002 \times A'_T. \quad (11)$$

## 9. Quality assurance

### 9.1 For general principles of analytical quality control see Chapter 3

### 9.2 Specific applications of analytical quality control

The various control limits outlined below are necessary to ensure that the accuracy and precision of the data are adequate for the purposes of a world-wide CO<sub>2</sub> survey. The initial targets specified for this are: a within cruise precision (1 SD) of 3  $\mu\text{mol kg}^{-1}$  and an overall between cruise (and between laboratory) range of bias of less than 6  $\mu\text{mol kg}^{-1}$ .

#### 9.2.1 Quality of individual titrations

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<sup>16</sup> Although this approach will not determine the physical volume of the cell as accurately as can be achieved gravimetrically, it does have the advantage of absorbing errors both in the concentration of the acid and in the burette calibration.

<sup>17</sup> This is not the best way to determine  $C_T$ . Far preferable is the use of a direct approach such as that detailed in SOP 2. Nevertheless, if the model of sea water acid–base chemistry is correct and if the pH cell behavior is Nernstian, both estimates should agree with each other.

<sup>18</sup> The value 1.0002 assumes that saturated mercuric chloride was used (0.02 % by volume—see SOP 1). If a 50% saturated solution was used to preserve the sample, the appropriate correction factor is 1.0004.



For each titration, the quality can be assessed by examining the values of the residuals,  $\Delta_i$ , and of the “goodness of fit”:

$$s = \left( \sum_i \frac{\Delta_i}{m-n} \right)^{1/2} \quad (12)$$

where  $m$  is the total number of titration points and  $n$  is the number of parameters fitted ( $n = 4$ ; see Annexe 1);  $s$  is typically around  $2 \mu\text{mol kg}^{-1}$  for the program used here.

### 9.2.2 Stability of computed volume and/or titrant concentration

The mean value should remain stable to within 0.1% throughout a cruise (except if the cell configuration is changed, thus changing its volume). Plot the volumes and/or acid concentrations obtained on a property control chart (see SOP 22).

### 9.2.3 Analysis of a sea water reference material

A stable reference material<sup>19</sup> should be analyzed regularly. Plot the results obtained on a property control chart (see SOP 22).

### 9.2.4 Duplicate analyses

A duplicate analysis should be made on every tenth sample. Plot the difference between each pair of analyses on a range control chart (see SOP 22).

## 10. Bibliography

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<sup>19</sup> Available from Dr. Andrew G. Dickson, Marine Physical Laboratory, Scripps Institution of Oceanography, University of California, San Diego, 9500 Gilman Drive, La Jolla, CA 92093-0244, U.S.A. (fax: 1-858-822-2919; e-mail: co2crms@ucsd.edu).

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## Annexe 1

### A non-linear least squares procedure for evaluating $A_T$ from titration data

In the following pages a computer program is presented which allows the computation of total alkalinity from titration data for a closed-cell titration of sea water. This program is based on a non-linear least-squares evaluation of the data similar to that used by Dickson (1981) and by Johansson and Wedborg (1982). The assumption is made in defining the model that the errors on the e.m.f. measurements are negligible in comparison to the uncertainties in the titrant amounts.

The computer program is based on equations (6) and (7) and requires that the salinity of the sea water sample and the total concentrations of species such as phosphate, silicate, *etc.* are known before evaluating the titration data<sup>20</sup>. If the titration is being performed on a solution in  $0.7 \text{ mol kg}^{-1}$  NaCl, then the program will select the appropriate dissociation constants and set the total concentrations of species such as sulfate, fluoride, phosphate, silicate, *etc.* to zero. Note, this code does not contain expressions for incorporating ammonia and hydrogen sulfide; for open ocean use the total concentrations of these are essentially equal to zero.

Instead of adjusting  $E^\circ$  directly in the least-squares procedure, it is convenient to define a multiplier,

$$f = [\text{H}^+]/[\text{H}'] \quad (13)$$

where values of  $[\text{H}']$  are computed from an initial estimate of  $E^\circ$  ( $E^\circ'$ ):

$$[\text{H}'] = \exp\left(\frac{E^\circ' - E}{RT/F}\right) \quad (14)$$

The program then adjusts  $f$  to minimize the sum-of-squares rather than adjusting the value of  $E^\circ$  directly.

Equation (6) is rewritten as

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<sup>20</sup> This is rarely the case for the immediate evaluation of shipboard titrations of sea water samples; however, if sample salinity is known to within 0.1 and if species such as phosphate, silicate, *etc.* are neglected—assumed to have a zero concentration—the value of total alkalinity obtained will not be affected substantially. Nevertheless, the other adjusted parameters, such as  $C_T$  and  $K_1$ , will be in error and the quality of fit (sum-of-squares) will be degraded.

$$\begin{aligned}
& A_T - C_T \left( \frac{K_1 f [H'] + 2K_1 K_2}{(f [H'])^2 + K_1 f [H'] + K_1 K_2} \right) - B_T \left( \frac{1}{1 + (f [H'])/K_B} \right) \\
& - P_T \left( \frac{K_{1P} K_{2P} f [H'] + 2K_{1P} K_{2P} K_{3P} - (f [H'])^3}{(f [H'])^3 + K_{1P} (f [H'])^2 + K_{1P} K_{2P} (f [H']) + K_{1P} K_{2P} K_{3P}} \right) \\
& - Si_T \left( \frac{1}{1 + (f [H'])/K_{Si}} \right) - NH3_T \left( \frac{1}{1 + (f [H'])/K_{NH3}} \right) \\
& - H2S_T \left( \frac{1}{1 + (f [H'])/K_{H2S}} \right) + S_T \left( \frac{1}{1 + K_S Z / (f [H'])} \right) \\
& + F_T \left( \frac{1}{1 + K_F / (f [H'])} \right) + \left( \frac{m_0 + m}{m_0} \right) \left( \frac{f [H']}{Z} - \frac{K_W}{f [H']} \right) - \frac{m}{m_0} C = 0. \quad (15)
\end{aligned}$$

The various terms are defined in Table 1; correspondence with the terms in equation (6) can be seen in Table 2.

Note in equation (15) how the free hydrogen ion concentration is calculated directly from the total hydrogen ion concentration when needed by using the expression

$$[H^+]_F = [H^+] / Z \quad (16)$$

where  $Z$  is defined in Table 1. This allows the direct use of equilibrium constants defined on the total scale in the various computations and renders the calculation substantially independent of likely errors in  $K_S$ .

Note also that the amounts of titrant ( $m$ ) and of titrand ( $m_0$ ) are expressed as masses rather than volumes. Volumes are converted to masses using a knowledge of the densities of these solutions appropriate to the temperature of the titration.

The actual data fitting is performed using a general non-linear least-squares routine. Equation (15) is used to define a vector of residuals (*i.e.*, the extent to which the left hand side  $\neq 0$ ) that are calculated in the subroutine FCN; the MINPACK-1 software package<sup>21</sup> minimizes the sum-of-squares of these residuals by adjusting the four parameters:  $f$ ,  $A_T$ ,  $C_T$ , and  $K_1$ . LIMDIFI uses a Marquardt procedure for this calculation, and computes the Jacobian by a finite-difference approximation. Any similar non-linear least-squares fitting package could be used in place of MINPACK, requiring only minor alterations to the code.

<sup>21</sup> Moré, J.J., Garbow, B.S. and Hillstom, K.E. 1980. User guide for MINPACK-1. Report ANL-80-74 of the Argonne National Laboratory, Argonne, IL, U.S.A.

**Table 1** Equations for the sea water acid–base system.**Mass-conservation equations**

$$C_T = [\text{CO}_2^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (17)$$

$$B_T = [\text{B}(\text{OH})_3] + [\text{B}(\text{OH})_4^-] \quad (18)$$

$$S_T = [\text{HSO}_4^-] + [\text{SO}_4^{2-}] \quad (19)$$

$$F_T = [\text{HF}] + [\text{F}^-] \quad (20)$$

$$P_T = [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}] \quad (21)$$

$$Si_T = [\text{Si}(\text{OH})_4] + [\text{SiO}(\text{OH})_3^-] \quad (22)$$

$$NH_{3T} = [\text{NH}_4^+] + [\text{NH}_3] \quad (23)$$

$$H_2S_T = [\text{H}_2\text{S}] + [\text{HS}^-] \quad (24)$$

**Equilibrium constants<sup>22</sup>**

$$K_1 = [\text{H}^+][\text{HCO}_3^-]/[\text{CO}_2^*] \quad (25)$$

$$K_2 = [\text{H}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-] \quad (26)$$

$$K_B = [\text{H}^+][\text{B}(\text{OH})_4^-]/[\text{B}(\text{OH})_3] \quad (27)$$

$$K_W = [\text{H}^+][\text{OH}^-] \quad (28)$$

$$K_S = [\text{H}^+]_F[\text{SO}_4^{2-}]/[\text{HSO}_4^-] \quad (29)$$

$$K_F = [\text{H}^+][\text{F}^-]/[\text{HF}] \quad (30)$$

$$K_{1P} = [\text{H}^+][\text{H}_2\text{PO}_4^-]/[\text{H}_3\text{PO}_4] \quad (31)$$

$$K_{2P} = [\text{H}^+][\text{HPO}_4^{2-}]/[\text{H}_2\text{PO}_4^-] \quad (32)$$

$$K_{3P} = [\text{H}^+][\text{PO}_4^{3-}]/[\text{HPO}_4^{2-}] \quad (33)$$

$$K_{Si} = [\text{H}^+][\text{SiO}(\text{OH})_3^-]/[\text{Si}(\text{OH})_4] \quad (34)$$

$$K_{NH_3} = [\text{H}^+][\text{NH}_3]/[\text{NH}_4^+] \quad (35)$$

$$K_{H_2S} = [\text{H}^+][\text{HS}^-]/[\text{H}_2\text{S}] \quad (36)$$

**Additional definitions**

$$Z = 1 + S_T / K_S \quad (37)$$

<sup>22</sup> All these equilibrium constants—except  $K_S$  (which is on the free hydrogen ion scale)—are based on the total hydrogen ion pH scale, *i.e.*, incorporating the effect of sulfate (but not of fluoride).

**Table 2** Expression for the concentrations of the various species in equation (6).

$$[\text{HCO}_3^-] = \frac{C_T K_1 [\text{H}^+]}{[\text{H}^+]^2 + K_1 [\text{H}^+] + K_1 K_2} \quad (38)$$

$$[\text{CO}_3^{2-}] = \frac{C_T K_1 K_2}{[\text{H}^+]^2 + K_1 [\text{H}^+] + K_1 K_2} \quad (39)$$

$$[\text{B(OH)}_4^-] = B_T / (1 + [\text{H}^+] / K_B) \quad (40)$$

$$[\text{OH}^-] = K_w / [\text{H}^+] \quad (41)$$

$$[\text{H}_3\text{PO}_4] = \frac{P_T [\text{H}^+]^3}{[\text{H}^+]^3 + K_{1P} [\text{H}^+]^2 + K_{1P} K_{2P} [\text{H}^+] + K_{1P} K_{2P} K_{3P}} \quad (42)$$

$$[\text{H}_2\text{PO}_4^-] = \frac{P_T K_{1P} [\text{H}^+]^2}{[\text{H}^+]^3 + K_{1P} [\text{H}^+]^2 + K_{1P} K_{2P} [\text{H}^+] + K_{1P} K_{2P} K_{3P}} \quad (43)$$

$$[\text{HPO}_4^{2-}] = \frac{P_T K_{1P} K_{2P} [\text{H}^+]}{[\text{H}^+]^3 + K_{1P} [\text{H}^+]^2 + K_{1P} K_{2P} [\text{H}^+] + K_{1P} K_{2P} K_{3P}} \quad (44)$$

$$[\text{PO}_4^{3-}] = \frac{P_T K_{1P} K_{2P} K_{3P}}{[\text{H}^+]^3 + K_{1P} [\text{H}^+]^2 + K_{1P} K_{2P} [\text{H}^+] + K_{1P} K_{2P} K_{3P}} \quad (45)$$

$$[\text{SiO(OH)}_3^-] = S_{iT} / (1 + [\text{H}^+] / K_{Si}) \quad (46)$$

$$[\text{NH}_3] = N_{H_{3T}} / (1 + [\text{H}^+] / K_{\text{NH}_3}) \quad (47)$$

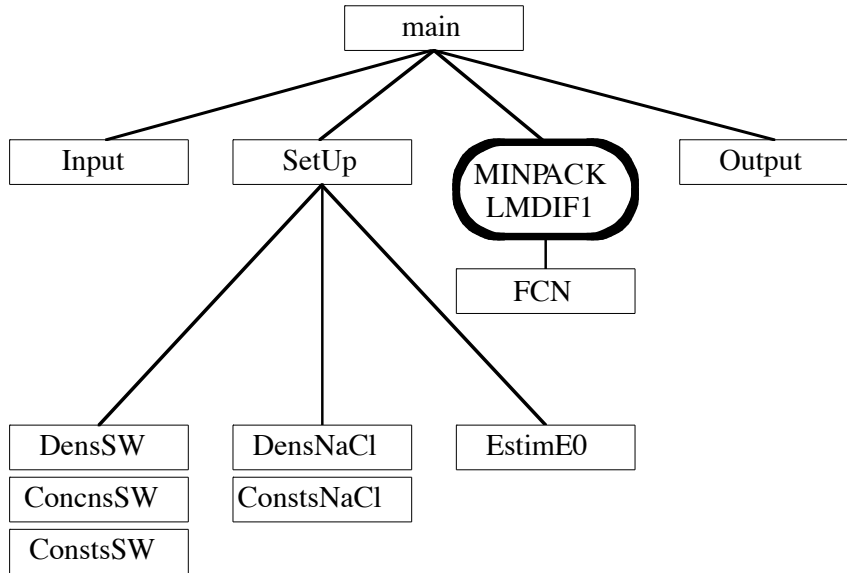
$$[\text{HS}^-] = H_{2S_T} / (1 + [\text{H}^+] / K_{\text{H}_2\text{S}}) \quad (48)$$

$$[\text{H}^+]_F = [\text{H}^+] / (1 + S_T / K_S) \quad (49)$$

$$[\text{HSO}_4^-] = S_T / (1 + K_S / [\text{H}^+]_F) \quad (50)$$

$$[\text{HF}] = F_T / (1 + K_F / [\text{H}^+]) \quad (51)$$

A FORTRAN 77 program is available to do these calculations. It has the following structure.



The source code is available from:

Dr. Andrew G. Dickson  
Marine Physical Laboratory – 0244  
University of California, San Diego  
9500 Gilman Drive  
La Jolla, CA 92093-0244, U.S.A.  
Fax: 1-858-822-2919  
E-mail: [adickson@ucsd.edu](mailto:adickson@ucsd.edu)

## Annexe 2

### Dosimat<sup>®</sup> burette calibration procedure

#### 1. Scope and field of application

The goal of this procedure is to calibrate a Metrohm Dosimat<sup>®</sup> burette accurately so that it can be used in the open-cell, alkalinity titration procedure (see procedure).

#### 2. Principle

The burette is filled with deionized water whose temperature is equilibrated to that of the surrounding room and measured accurately. Aliquots of the water are dispensed into pre-weighed vials that are capped and re-weighed. The true volumes dispensed are then calculated from a knowledge of the density of the deionized water and a “calibration function” is prepared for the burette under consideration.

#### 3. Apparatus

- Metrohm Dosimat<sup>®</sup> burette base unit,
- Metrohm Dosimat<sup>®</sup> exchangeable burette (5 cm<sup>3</sup> capacity),
- 15 × 5 cm<sup>3</sup> capacity screw-capped glass bottles<sup>23</sup>,
- Analytical balance readable to 0.0001 g,
- Calibrated thermometer readable to 0.1°C,
- Waste container.

#### 4. Reagents

- Deionized water (Milli-Q<sup>®</sup> quality).

#### 5. Procedure

- 5.1** Fill the Dosimat<sup>®</sup> reservoir with deionized water and allow to equilibrate to room temperature.

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<sup>23</sup> Although glass containers are superior, excellent results can be obtained with plastic containers provided that appropriate anti-static precautions are taken when weighing.



- 5.2** Assemble the Dosimat<sup>®</sup> as usual except remove the anti-diffusion portion of the dispensing tip.
- 5.3** Submerge the thermometer in a reservoir bottle.
- 5.4** Fill and empty the Dosimat<sup>®</sup> burette several times; check to be sure that there are no bubbles in the burette and delivery tubing.
- 5.5** Weigh a dry, screw-capped glass bottle.
- 5.6** Dispense the water in the burette into a waste container. Make sure that the delivery tip is below the surface of the water. After dispensing, slowly withdraw the tip from the water.
- 5.7** Record the temperature as burette refills.
- 5.8** Dispense between 0.05 and 5.00 cm<sup>3</sup> of water into a weighed glass bottle<sup>24</sup>. Ensure that the delivery tip is immersed in dispensed solution.
- 5.9** Withdraw the tip slowly, cap the bottle and reweigh.
- 5.10** Repeat, varying the amount of water dispensed; repeat the measurement at least twice for each volume dispensed.

## 6. Calculation and expression of results

### 6.1 Principle

Compute the weight of the water delivered from the difference between the filled and empty container volumes:

$$w(\text{H}_2\text{O}) = w(\text{filled container}) - w(\text{empty container}) . \quad (52)$$

Compute the mass of water contained, correcting for air buoyancy (see SOP 21):

$$m(\text{H}_2\text{O}) = w(\text{H}_2\text{O}) \left[ 1 + 0.0012 \left( \frac{1}{\rho(\text{H}_2\text{O}, t)} - \frac{1}{\rho(\text{weights})} \right) \right] . \quad (53)$$

The volume dispensed at the temperature noted ( $t$ ) is

$$V(t) = m(\text{H}_2\text{O}) / \rho(\text{H}_2\text{O}, t) . \quad (54)$$

The density of air-saturated water in the temperature range 5 to 40°C is given by the expression (Jones and Harris, 1992)

$$\begin{aligned} \rho_w / (\text{kg m}^{-3}) = & 999.84847 + 6.337563 \times 10^{-2} (t / ^\circ\text{C}) \\ & - 8.523829 \times 10^{-3} (t / ^\circ\text{C})^2 + 6.943248 \times 10^{-5} (t / ^\circ\text{C})^3 \\ & - 3.821216 \times 10^{-7} (t / ^\circ\text{C})^4 \end{aligned} \quad (55)$$

where  $t$  is the temperature on ITS 90<sup>25</sup>. To achieve an accuracy of 1 part in 10<sup>4</sup>,  $t$  must be known to within 0.5°C.

<sup>24</sup> This procedure is designed to provide a series of calibration points corresponding to dispensing from 0.000 cm<sup>3</sup> on the burette.

<sup>25</sup> The distinction between the temperature scales ITS90 and IPTS68 is not important for this procedure.

The volumes measured are then compared to the nominal volumes indicated by the burette display so as to develop a “calibration function” for the particular burette system being calibrated.

## 6.2 Sample calculation

The following table contains a set of calibration results for a Metrohm Dosimat<sup>®</sup> system used in our laboratory.

**Table 1** Calibration results for titration system 1 (December 12, 1996).

Nominal volume, $V^* / \text{cm}^3$	Dispensing temperature, $t / ^\circ\text{C}$	Weight dispensed, $w / \text{g}$	Volume dispensed, $V / \text{cm}^3$	Volume correction, $\Delta V / \text{cm}^3$
1.000	20.9	0.9971	1.0001	0.0001
1.000	20.9	0.9957	0.9987	-0.0013
1.000	20.9	0.9971	1.0001	0.0001
2.000	20.9	1.9936	1.9997	-0.0003
2.000	20.9	1.9937	1.9998	-0.0002
3.000	20.9	2.9906	2.9997	-0.0003
3.000	21.0	2.9915	3.0007	0.0007
3.000	21.1	2.9912	3.0004	0.0004
4.000	21.1	3.9865	3.9988	-0.0012
4.000	21.1	3.9877	4.0000	0.0000
4.000	21.1	3.9877	4.0000	0.0000
4.000	21.2	3.9872	3.9996	-0.0004
5.000	21.2	4.9833	4.9988	-0.0012
5.000	21.3	4.9834	4.9990	-0.0010
3.050	21.3	3.0400	3.0495	-0.0005
0.050	21.3	0.0511	0.0513	0.0013
0.050	21.4	0.0499	0.0501	0.0001

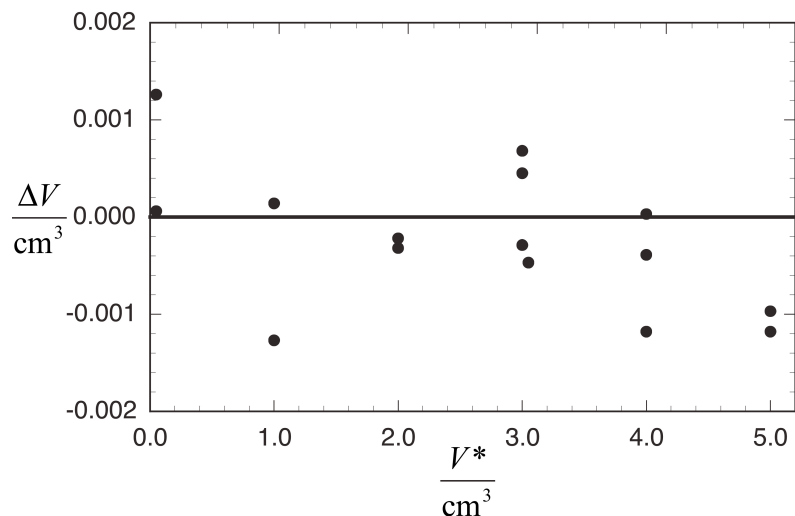
The measured values of  $\Delta V$  obtained are plotted against the nominal volume (see Figure 2), and are fitted to provide a “calibration” function—typically a polynomial in  $V(\text{nominal})$ :

$$V = V^* [1 + aV^* + b(V^*)^2]. \quad (56)$$

For the measurements given in Table 1, and shown in Figure 2, the calibration function is not significantly different from

$$V = V^*, \quad (57)$$

which is the function that is used for this burette. The volume uncertainty at any point in this calibration is  $\pm 0.0007 \text{ cm}^3$  (r.m.s. deviation).



**Fig. 2** Plot of  $\Delta V (= V - V^*)$  against  $V^*$  for the calibration results for titration system 1 (December 12, 1996).

## 7. Quality Assurance

It is essential to identify a complete burette system as a coherent unit for the purpose of calibration and subsequent use. If it is necessary to change any of the parts (particularly the burette assembly or the base unit), it is essential to recalibrate the burette.

A new burette system should be calibrated a number of times initially to ensure that the calibration is stable. After that, it should be recalibrated yearly (or if a possible problem is identified).