

SOP 3

Determination of total alkalinity in sea water

1. Scope and field of application

This chapter 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 $\mu\text{mol}\cdot\text{kg}^{-1}$) and can be adapted easily to measure higher levels such as those that have been observed in the Black Sea (3200–4600 $\mu\text{mol}\cdot\text{kg}^{-1}$).

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 one kilogram of sample:

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

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 NH_3 and 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) or on a modified Gran approach (Note 1). 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 (Note 2).

4. Apparatus

4.1 Titration cell assembly

A closed, thermostated, titration cell with an internal volume of 100 cm³ or more is suitable. (Such a cell can be constructed from Lucite[®] incorporating an outer water jacket—see Figure 1.) 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:

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

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

¹ For more detail of the modified Gran approach see Hansson & Jagner (1973) or Bradshaw *et al.* (1981).

² 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).

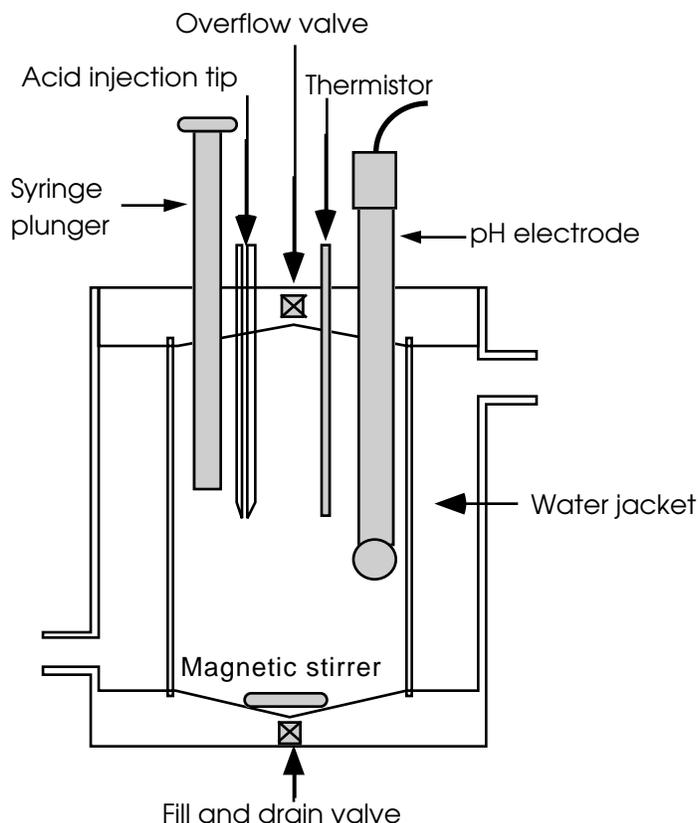


Figure 1. Closed titration cell for the determination of alkalinity.

This cell contains a combined glass / reference pH electrode (Note 3), 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 head-space. (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 § 8.5, can be used if this is not possible.

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

4.2 *pH meter*

A pH meter or a high input impedance digital voltmeter (Note 4) —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 motor-driven piston burette—reproducible to 0.001 cm³ 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 § 4.1 equation (2).

4.4 *Thermostat bath*

A thermostat bath capable of maintaining the cell at a known temperature to within ± 0.05 °C. This ensures that the E° of the pH cell and the Nernst factor do not vary significantly during the titration.

5. Reagents

- 5.1 Reagent grade hydrochloric acid
- 5.2 Reagent grade sodium chloride
- 5.3 Primary standard grade sodium carbonate, dried at 280 °C for >2 hours and cooled overnight in a desiccator (Note 5)
- 5.4 Deionized water

6. Sampling

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

7. Procedures

7.1 *Solution preparation*

- 7.1.1 *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⁻¹). (The HCl

⁴ 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.

⁵ A method for preparing suitable Na₂CO₃ is detailed in IUPAC (1969).

concentration is chosen to match the size of the burette and of the cell, see § 4.1, equation (2).)

7.1.2 *Background medium*: A solution of sodium chloride ($0.7 \text{ mol}\cdot\text{kg}^{-1}$).

7.1.3 *Calibration solutions* (Note 6): Three solutions (Note 7) of sodium carbonate in the background medium (~ 0.5 , 1.0 and $1.25 \text{ mmol}\cdot\text{kg}^{-1}$) made up carefully by weight; *i.e.* total alkalinities of ~ 1000 , 2000 and $2500 \text{ }\mu\text{mol}\cdot\text{kg}^{-1}$.

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 (Note 8) 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 few cm^3 ; 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^3) into the cell from the burette (Note 9). 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—(Note 10).

⁶ 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 US National Institute for Standards & 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).

⁷ A single calibration solution ($\sim 1.25 \text{ mmol}\cdot\text{kg}^{-1}$) 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 $C(\text{HCl})$ —§ 8.4.

⁸ This is to rinse the acid out, thus any sea water is suitable for this and it is unnecessary to use valuable sample.

⁹ Some investigators prefer to add acid so as to ensure approximately equal e.m.f. changes between titration points.

¹⁰ The hydrated CO_2 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.

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) 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 m g of acid of concentration C have been added to m_0 g of sample (Note 11),

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

This can be equated to the previous expression for C_H :

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

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 (Note 12):

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

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, 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 the Annexe 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.

¹¹ 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.

¹² A number of investigators make further use of the titration curve from the blank determination (see § 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° 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.

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 (Note 13). 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. Data from a titration of the background medium alone (*i.e.* NaCl without Na₂CO₃) 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 Na₂CO₃ in the background medium (see next section).

8.4 Calibration of the acid titrant (Note 14)

The total alkalinity of each calibration solution titrated (including a background solution with no added Na₂CO₃) is given by the sum

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

where $A_T(\text{blank})$ is the total alkalinity of the NaCl background solution, $m(\text{Na}_2\text{CO}_3)$ the mass of Na₂CO₃ 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 Na₂CO₃—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, 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 $a = 1$.

¹³ This is not strictly true as the residual alkalinity cannot be removed completely by acidifying and stripping with a CO₂ free gas. Nevertheless, the error from assuming this is small.

¹⁴ 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.

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

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

This calculation is iterated to obtain a consistent set of values (Note 15). 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 (Note 16). It is necessary to know the approximate salinity (± 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 the Annexe to this procedure).

¹⁵ 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.

¹⁶ This is not the best way to determine C_T ; far preferable is to use 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.

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 the Annexe 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 (Note 17):

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

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 CO₂ survey. The initial targets specified for this are: a within cruise precision (1 std. dev.) of 3 μmol·kg⁻¹ and an overall between cruise (and between laboratory) range of bias of less than 6 μmol·kg⁻¹.

9.2.1 Quality of individual titrations

For each titration, the quality can be assessed by examining the values of the residuals, Δ_{*i*}, and of the “goodness of fit”:

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

where *m* is the total number of titration points and *n* is the number of parameters fitted (*n*=4; see Annexe). *s* is typically around 2 μmol·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 quality control chart (see SOP 22).

¹⁷ The figure 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.

9.2.3 Analysis of a sea water reference material

A stable reference material (Note 18) should be analyzed regularly. Plot the results obtained on a property quality 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 quality control chart (see SOP 22).

References

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¹⁸ Available from Dr. Andrew G. Dickson, Marine Physical Laboratory, Scripps Institution of Oceanography, University of California, San Diego, 9500 Gilman Drive, La Jolla, CA 92093-0902, U.S.A. (telefax 1-619-456-9079).

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Annexe

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 & 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 (Note 19). If the titration is being performed on a solution in $0.7 \text{ mol}\cdot\text{kg}^{-1}$ 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.

¹⁹ 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.

Instead of adjusting E° directly in the least squares procedure it is convenient to define a multiplier:

$$f = [\text{H}^+]/[\text{H}'] \quad ; \quad (\text{A.1})$$

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

$$[\text{H}'] = \exp\left(\frac{E^{\circ'} - E}{RT/F}\right) . \quad (\text{A.2})$$

The program then adjusts f to minimize the sum-of-squares rather than adjusting the value of E° directly.

Equation (6) is rewritten as:

$$\begin{aligned} & A_T - C_T \left(\frac{K_1 f [\text{H}'] + 2K_1 K_2}{(f [\text{H}'])^2 + K_1 f [\text{H}'] + K_1 K_2} \right) - B_T \left(\frac{1}{1 + (f [\text{H}'])/K_B} \right) \\ & - P_T \left(\frac{K_{1P} K_{2P} (f [\text{H}']) + 2K_{1P} K_{2P} K_{3P} - (f [\text{H}'])^3}{(f [\text{H}'])^3 + K_{1P} (f [\text{H}'])^2 + K_{1P} K_{2P} (f [\text{H}']) + K_{1P} K_{2P} K_{3P}} \right) \\ & - Si_T \left(\frac{1}{1 + (f [\text{H}'])/K_{Si}} \right) - NH_{3T} \left(\frac{1}{1 + (f [\text{H}'])/K_{NH_3}} \right) \\ & - H_2S_T \left(\frac{1}{1 + (f [\text{H}'])/K_{H_2S}} \right) + S_T \left(\frac{1}{1 + K_S Z / (f [\text{H}'])} \right) \\ & + F_T \left(\frac{1}{1 + K_F / (f [\text{H}'])} \right) + \left(\frac{m_0 + m}{m_0} \right) \left(\frac{f [\text{H}']}{Z} - \frac{K_W}{f [\text{H}']} \right) - \frac{m}{m_0} C \\ & = 0 \end{aligned} \quad (\text{A.3})$$

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

Note in equation (A.3) how the free hydrogen ion concentration is calculated directly from the total hydrogen ion concentration when needed by using the expression:

$$[\text{H}^+]_F = [\text{H}^+]/Z \quad ; \quad (\text{A.4})$$

where Z is defined in Table 1 (overleaf). 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.

Table 1: Equations for the sea water acid–base system

Mass-conservation equations:

$$C_T = [\text{CO}_2^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (\text{A.5})$$

$$B_T = [\text{B}(\text{OH})_3] + [\text{B}(\text{OH})_4^-] \quad (\text{A.6})$$

$$S_T = [\text{HSO}_4^-] + [\text{SO}_4^{2-}] \quad (\text{A.7})$$

$$F_T = [\text{HF}] + [\text{F}^-] \quad (\text{A.8})$$

$$P_T = [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}] \quad (\text{A.9})$$

$$Si_T = [\text{Si}(\text{OH})_4] + [\text{SiO}(\text{OH})_3^-] \quad (\text{A.10})$$

$$NH_{3T} = [\text{NH}_4^+] + [\text{NH}_3] \quad (\text{A.11})$$

$$H_2S_T = [\text{H}_2\text{S}] + [\text{HS}^-] \quad (\text{A.12})$$

Equilibrium constants:^a

$$K_1 = [\text{H}^+][\text{HCO}_3^-]/[\text{CO}_2^*] \quad (\text{A.13})$$

$$K_2 = [\text{H}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-] \quad (\text{A.14})$$

$$K_W = [\text{H}^+][\text{OH}^-] \quad (\text{A.15})$$

$$K_B = [\text{H}^+][\text{B}(\text{OH})_4^-]/[\text{B}(\text{OH})_3] \quad (\text{A.16})$$

$$K_S = [\text{H}^+]_F [\text{SO}_4^{2-}]/[\text{HSO}_4^-] \quad (\text{A.17})$$

$$K_F = [\text{H}^+][\text{F}^-]/[\text{HF}] \quad (\text{A.18})$$

$$K_{1P} = [\text{H}^+][\text{H}_2\text{PO}_4^-]/[\text{H}_3\text{PO}_4] \quad (\text{A.19})$$

$$K_{2P} = [\text{H}^+][\text{HPO}_4^{2-}]/[\text{H}_2\text{PO}_4^-] \quad (\text{A.20})$$

$$K_{3P} = [\text{H}^+][\text{PO}_4^{3-}]/[\text{HPO}_4^{2-}] \quad (\text{A.21})$$

$$K_{Si} = [\text{H}^+][\text{SiO}(\text{OH})_3^-]/[\text{Si}(\text{OH})_4] \quad (\text{A.22})$$

$$K_{NH_3} = [\text{H}^+][\text{NH}_3]/[\text{NH}_4^+] \quad (\text{A.23})$$

$$K_{H_2S} = [\text{H}^+][\text{HS}^-]/[\text{H}_2\text{S}] \quad (\text{A.24})$$

Additional definitions:

$$Z = 1 + S_T/K_S \quad (\text{A.25})$$

- a. 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).

$$[\text{HCO}_3^-] = \frac{C_T K_1 [\text{H}^+]}{[\text{H}^+]^2 + K_1 [\text{H}^+] + K_1 K_2} \quad (\text{A.26})$$

$$[\text{CO}_3^{2-}] = \frac{C_T K_1 K_2}{[\text{H}^+]^2 + K_1 [\text{H}^+] + K_1 K_2} \quad (\text{A.27})$$

$$[\text{B}(\text{OH})_4^-] = B_T / (1 + [\text{H}^+] / K_B) \quad (\text{A.28})$$

$$[\text{OH}^-] = K_W / [\text{H}^+] \quad (\text{A.29})$$

$$[\text{H}_3\text{PO}_4] = \frac{P_T [\text{H}^+]^3}{[\text{H}^+]^3 + K_{1P} [\text{H}^+]^2 + K_{1P} K_{2P} [\text{H}^+] + K_{1P} K_{2P} K_{3P}} \quad (\text{A.30})$$

$$[\text{H}_2\text{PO}_4^-] = \frac{P_T K_{1P} [\text{H}^+]^2}{[\text{H}^+]^3 + K_{1P} [\text{H}^+]^2 + K_{1P} K_{2P} [\text{H}^+] + K_{1P} K_{2P} K_{3P}} \quad (\text{A.31})$$

$$[\text{HPO}_4^{2-}] = \frac{P_T K_{1P} K_{2P} [\text{H}^+]}{[\text{H}^+]^3 + K_{1P} [\text{H}^+]^2 + K_{1P} K_{2P} [\text{H}^+] + K_{1P} K_{2P} K_{3P}} \quad (\text{A.32})$$

$$[\text{PO}_4^{3-}] = \frac{P_T K_{1P} K_{2P} K_{3P}}{[\text{H}^+]^3 + K_{1P} [\text{H}^+]^2 + K_{1P} K_{2P} [\text{H}^+] + K_{1P} K_{2P} K_{3P}} \quad (\text{A.33})$$

$$[\text{SiO}(\text{OH})_3^-] = S_{iT} / (1 + [\text{H}^+] / K_{Si}) \quad (\text{A.34})$$

$$[\text{NH}_3] = N_{H_3 T} / (1 + [\text{H}^+] / K_{\text{NH}_3}) \quad (\text{A.35})$$

$$[\text{HS}^-] = H_2 S_T / (1 + [\text{H}^+] / K_{\text{H}_2\text{S}}) \quad (\text{A.36})$$

$$[\text{H}^+]_F = [\text{H}^+] / (1 + S_T / K_S) \quad (\text{A.37})$$

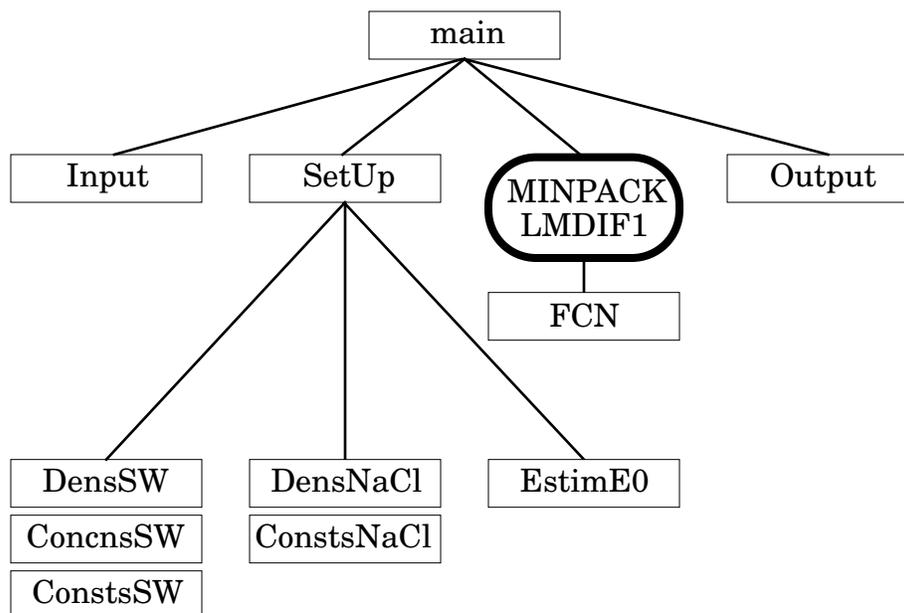
$$[\text{HSO}_4^-] = S_T / (1 + K_S / [\text{H}^+]_F) \quad (\text{A.38})$$

$$[\text{HF}] = F_T / (1 + K_F / [\text{H}^+]) \quad (\text{A.39})$$

The actual data fitting is performed using a general non-linear least-squares routine. Equation (A.3) 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 (Note 20) minimizes the sum-of-squares of these residuals by adjusting the four parameters: f , A_T , C_T and K_1 . LIMDIF1 uses a Marquardt procedure for this calculation, and computes the necessary 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 listed here.

The program listed on the following pages is written in FORTRAN 77. It has the following structure.



A machine readable version of this code is available from

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²⁰ J. J. Moré, B. S. Garbow, & K. E. Hillstom (1980) User guide for MINPACK-1. Report ANL-80-74 of the Argonne National Laboratory, Argonne, Illinois.

Test data set

SAMPLE CO2 TITRATION DATA

S = 34.80 salinity of sample
 PT = 0.0 $\mu\text{mol/kg}$ total phosphate
 SiT = 0.0 $\mu\text{mol/kg}$ total silicate

 T = 20.05 $^{\circ}\text{C}$ temperature of sample when titrated
 W0 = 165.391 cm^3 volume of sample titrated
 C = 0.20455 mol/kg concentration of acid titrant
 DACID = 1.02409 g/cm^3 density of acid titrant

V/cm3	E/V
0.000	-0.03249
0.100	-0.01320
0.200	0.00049
0.300	0.01055
0.400	0.01866
0.500	0.02559
0.600	0.03179
0.700	0.03753
0.800	0.04300
0.900	0.04831
1.000	0.05360
1.100	0.05900
1.200	0.06460
1.300	0.07060
1.400	0.07720
1.500	0.08476
1.600	0.09393
1.700	0.10601
1.720	0.10897
1.740	0.11218
1.760	0.11574
1.780	0.11959
1.800	0.12390
1.820	0.12868
1.840	0.13389
1.860	0.13951
1.880	0.14524
1.900	0.15097
2.000	0.17332
2.100	0.18664
2.200	0.19560
2.300	0.20227
2.400	0.20755

Output from test data set

Enter name of titration data file): testdata

SAMPLE CO2 TITRATION DATA

S = 34.800
 PT = 0.00 $\mu\text{mol/kg}$
 SiT = 0.00 $\mu\text{mol/kg}$

T = 20.05 deg C
 V0 = 165.391 cm3
 C = 0.20455 mol/kg
 DACID = 1.02409 g/cm3

LMDIF1 exit parameter 1
 Function calls 9
 Jacobian calls 28

E0 = 0.393609 V
 AT = 2320.21 $\mu\text{mol/kg}$
 CT = 2344.26 $\mu\text{mol/kg}$
 pK1 = 5.9090

s = 1.209 $\mu\text{mol/kg}$

V/cm3	E/V	$-\log[\text{H}]$	$\Delta\text{H}/(\mu\text{mol/kg})$
0.000	-0.03249	7.3241	-3.575
0.100	-0.01320	6.9925	-0.183
0.200	0.00049	6.7572	1.914
0.300	0.01055	6.5843	2.035
0.400	0.01866	6.4449	1.786
0.500	0.02559	6.3258	1.101
0.600	0.03179	6.2192	0.359
0.700	0.03753	6.1206	-0.265
0.800	0.04300	6.0265	-0.519
0.900	0.04831	5.9353	-1.031
1.000	0.05360	5.8443	-1.311
1.100	0.05900	5.7515	-1.035
1.200	0.06460	5.6553	-1.082
1.300	0.07060	5.5521	-0.604
1.400	0.07720	5.4387	-0.182
1.500	0.08476	5.3087	0.262
1.600	0.09393	5.1511	0.890
1.700	0.10601	4.9435	1.351
1.720	0.10897	4.8926	1.196
1.740	0.11218	4.8374	0.921
1.760	0.11574	4.7762	0.912
1.780	0.11959	4.7100	0.420
1.800	0.12390	4.6360	0.207
1.820	0.12868	4.5538	0.049
1.840	0.13389	4.4642	-0.249
1.860	0.13951	4.3676	-0.398
1.880	0.14524	4.2692	-0.872
1.900	0.15097	4.1707	-1.016
2.000	0.17332	3.7865	-1.273
2.100	0.18664	3.5575	-0.933
2.200	0.19560	3.4035	-0.193
2.300	0.20227	3.2889	0.530
2.400	0.20755	3.1981	0.788

Program listing

```

* Driver routine for the evaluation of the total alkalinity (AT) and
* total dissolved inorganic carbon (CT) from potentiometric titration
* data. This routine calls LMDIF1 from MINPACK to adjust the values
* of F (E0), AT, CT, and K1 so as to minimize the sum-of-squares of
* residuals in the concentration of total hydrogen (defined relative
* to the alkalinity equivalence point).
*
* Written by Andrew G. Dickson (last modified February 1994)

      IMPLICIT NONE

* Parameter:
*   MaxPts - maximum number of titration data points
*           (In routines MAIN, SetUP and FCN)

      INTEGER MaxPts
      PARAMETER (MaxPts = 100)

* Common block /TITN/:
*   C - concentration of titrant acid (mol/kg)
*   W0 - mass of sample titrated (g)
*   W - array containing titrant amounts (g)
*   H - array containing [H'] = 10**((E0 - E)/K)
*       based on the initial E0 estimate
*   BT - total boron (mol/kg-soln)
*   ST - total sulfate (mol/kg-soln)
*   FT - total fluoride (mol/kg-soln)
*   PT - total phosphate (mol/kg-soln)
*   SiT - total silicate (mol/kg-soln)
*
*   K1 - [H][HCO3]/[H2CO3]
*   K2 - [H][CO3]/[HCO3]
*   KB - [H][BO2]/[HBO2]
*   K1P - [H][H2PO4]/[H3PO4]
*   K2P - [H][HPO4]/[H2PO4]
*   K3P - [H][PO4]/[HPO4]
*   KSI - [H][SiO(OH)3]/[Si(OH)4]
*   KS - [h][SO4]/[HSO4]
*   KF - [H][F]/[HF]
*   KW - [H][OH]
*   Z - pH scale conversion factor [H] = [h](1 + ST/KS)

      DOUBLE PRECISION C, W0, W(MaxPts), H(MaxPts),
+     BT, ST, FT, PT, SIT,
+     K1, K2, KB, K1P, K2P, K3P, KSi, KW, KS, KF, Z

      COMMON /TITN/ C, W0, W, H,
+     BT, ST, FT, PT, SIT,
+     K1, K2, KB, K1P, K2P, K3P, KSi, KW, KS, KF, Z

* Common block /EVAL/:
*   ICOUNT(1) - total number of function evaluations
*   ICOUNT(2) - total number of Jacobian calculations

      INTEGER ICOUNT(2)
      COMMON / EVAL/ ICOUNT

* Additional variables used by subroutine Input

      CHARACTER Fname*32, Header*80
      DOUBLE PRECISION S, T, V0, DAcid, V(MaxPts), E(MaxPts)

* Additional variables used by subroutine SetUp

      DOUBLE PRECISION KNernst, E0

```

```

*   MINPACK function
      DOUBLE PRECISION DPMPAR

*   Additional variables used by subroutine LMDIF1 of MINPACK
      INTEGER NPar, LWA
      PARAMETER (NPar = 4, LWA = MaxPts*NPar + 5*NPar + MaxPts)
      INTEGER NPts, INFO, IWA(NPar)
      DOUBLE PRECISION X(NPar), FVEC(MaxPts), TOL, WA(LWA)

*   External function called by MINPACK
      EXTERNAL FCN

*   Prompt user for the file name of the input data file
      WRITE (*, '( / ' Enter name of titration data file: ' $)')
      READ *, FName

*   Read titration data from file
*   FName   - name of file containing the titration data
*   Header  - sample identifier
*   S       - salinity of titrated sample
*   PT      - total phosphate in sample (mol/kg-soln)
*   SiT     - total silicate in sample (mol/kg-soln)
*   T       - titration temperature (deg C)
*   V0      - volume of titration cell (cm3)
*   C       - concentration of acid titrant (mol/kg-soln)
*   DAcid   - density of acid titrant (g/cm3)
*   NPts    - number of titration points
*   V       - array of volumes of titrant used (cm3)
*   E       - array of corresponding e.m.f.s (V)

      CALL Input (MaxPts, FName,
+      Header, S, PT, SiT, T, V0, C, DAcid, NPts, V, E)

*   Set up the titration calculation. The data needed for the
*   calculation is passed to FCN in common block /TITN/.
*   KNernst - Nernst parameter (appropriate to titration)
*   E0      - estimate of E0 for pH cell used

      CALL SetUp (S, T, V0, DAcid, NPts, V, E, KNernst, E0)

*   Initialize solution vector, X, and ICOUNT
      x(1) = 1.0
      x(2) = 2.0
      x(3) = 2.0
      x(4) = 1.0

      ICOUNT(1) = 0
      ICOUNT(2) = 0

*   Set the desired convergence parameter to sqrt(machine precision)
*   DPMPAR  - MINPACK function to get machine dependent info.

      TOL = SQRT(DPMPAR(1))

*   Use MINPACK routine LMDIF1 to adjust X so as to minimize RSS.
*   FCN     - name of routine used to calculate residuals
*   NPts    - number of functions (data points)
*   Npar    - number of parameters adjusted by LMDIF1
*   X       - array containing solution vector
*   X(1)    - F = [H]/[H']      )
*   X(2)    - AT * 1E3         ) scaled to make components
*   X(3)    - CT * 1E3         ) of X approx. equal to 1
*   X(4)    - K1 * 1E6         )
*   FVEC    - array containing residuals (calculated by FCN)

```

```

*      TOL      - tolerance for fitting
*      INFO     - flag indicating if minimization was successful
*      IWA      - )
*      WA       - ) working areas used by LMDIF1
*      LWA      - )

```

```
CALL LMDIF1(FCN, NPts, NPar, X, FVEC, TOL, INFO, IWA, WA, LWA)
```

```
* Output a table of results on channel 6 (the screen)
```

```
CALL Output (6,
+  INFO, ICOUNT, NPar, X,
+  Header, S, PT, SiT, T, V0, C, DAcid,
+  NPts, V, E, H, FVEC, KNernst, E0)
```

```
END
```

```
*****
```

```
SUBROUTINE Input (MaxPts, FName,
+  Header, S, PT, SiT, T, V0, C, DAcid, NPts, V, E)
```

```
IMPLICIT NONE
INTEGER MaxPts, NPts
CHARACTER FName*32, Header*80
DOUBLE PRECISION S, PT, SiT, T, V0, C, DAcid, V(MaxPts), E(MaxPts)
```

```
* Subroutine to read in the titration data file
```

```
*
```

```
* Written by Andrew G. Dickson (last modified February 1994)
```

```
*
```

```
* Called with:
```

```
*   MaxPts - maximum number of titration points
*   FName  - name of file containing data to be processed
```

```
*
```

```
* Returns:
```

```
*   Header - character string identifying sample
*   S      - salinity of titrated sample
*   PT     - total phosphate in sample (mol/kg-soln)
*   SiT    - total silicate in sample (mol/kg-soln)
*   T      - titration temperature (deg C)
*   V0     - volume of sample titrated (cm3)
*   C      - concentration of acid titrant (mol/kg-soln)
*   DAcid  - density of the acid titrant (g/cm3)
*   V      - array of volumes of titrant used (cm3)
*   E      - array of corresponding e.m.f.s (V)
```

```
INTEGER I
```

```
OPEN (1, FILE = FName)
```

```
* Read in sample information and adjust PT and SiT to mol/kg
```

```
READ (1, '(A80)') Header
READ (1, *)
READ (1, '(8X, F8.0)') S
READ (1, '(8X, F8.0)') PT
  PT = 1D-6 * PT
READ (1, '(8X, F8.0)') SiT
  SiT = 1D-6 * SiT
```

```
* Read in titration information
```

```
READ (1, *)
READ (1, '(8X, F8.0)') T
READ (1, '(8X, F8.0)') V0
READ (1, '(8X, F8.0)') C
READ (1, '(8X, F8.0)') DAcid
```

```

*   Read in volume and e.m.f. data
      READ (1, '(//)')
      DO 200 I = 1, MaxPts
        READ (1, '(F6.0, F12.0)', END=300) V(I), E(I)
200  CONTINUE

      WRITE (6, '(1X, 'More than MaxPts (100) data points in file!')')
      CLOSE (1)
      STOP

300  NPts = I - 1
      CLOSE (1)

*   Convert mV to V

      IF (ABS(E(NPts) - E(1)) .GT. 1) THEN
        DO 400 I = 1, NPts
          E(I) = E(I)/1000
400  CONTINUE
      ENDIF
      RETURN

      END

*****

      SUBROUTINE SetUp(S, T, V0, DAcid, NPts, V, E, KNernst, E0)
      IMPLICIT NONE

      INTEGER NPts
      DOUBLE PRECISION S, T, V0, DAcid, V(NPts), E(NPts), KNernst, E0

*   Subroutine to set up calculation ready for MINPACK processing
*
*   Written by Andrew G. Dickson (last modified August 1994)
*
*   Called with:
*   S           - salinity of titrated sample
*   T           - titration temperature (deg C)
*   V0          - volume of sample titrated (cm3)
*   DAcid       - density of the acid titrant (g/cm3)
*   NPts        - number of titration points
*   V           - array of volumes of titrant used (cm3)
*   E           - Array of corresponding e.m.f.s (V)
*
*   Returns:
*   KNernst    - Nernst parameter (appropriate to titration)
*   E0         - Estimate of E0 of pH cell
*
*   Parameter:
*   MaxPts     - maximum number of titration data points
*                (In routines MAIN, SetUP and FCN)

      INTEGER MaxPts
      PARAMETER (MaxPts = 100)

*   Common block /TITN/:
*   C           - concentration of titrant acid (mol/kg)
*   W0          - mass of sample titrated (g)
*   W           - array containing titrant amounts (g)
*   H           - array containing [H'] = 10*((E0 - E)/K)
*                based on the initial E0 estimate
*   BT         - total boron (mol/kg-soln)
*   ST         - total sulfate (mol/kg-soln)
*   FT         - total fluoride (mol/kg-soln)
*   PT         - total phosphate (mol/kg-soln)
*   SiT        - total silicate (mol/kg-soln)
*

```

```

*      K1      -  [H][HCO3]/[H2CO3]
*      K2      -  [H][CO3]/[HCO3]
*      KB      -  [H][BO2]/[HBO2]
*      K1P     -  [H][H2PO4]/[H3PO4]
*      K2P     -  [H][HPO4]/[H2PO4]
*      K3P     -  [H][PO4]/[HPO4]
*      KSI     -  [H][SiO(OH)3]/[Si(OH)4]
*      KS      -  [h][SO4]/[HSO4]
*      KF      -  [H][F]/[HF]
*      KW      -  [H][OH]
*      Z      -  pH scale conversion factor [H] = [h](1 + ST/KS)

      DOUBLE PRECISION C, W0, W(MaxPts), H(MaxPts),
+      BT, ST, FT, PT, SIT,
+      K1, K2, KB, K1P, K2P, K3P, KSi, KW, KS, KF, Z

      COMMON /TITN/ C, W0, W, H,
+      BT, ST, FT, PT, SIT,
+      K1, K2, KB, K1P, K2P, K3P, KSi, KW, KS, KF, Z

      INTEGER I
      DOUBLE PRECISION DensNaCl, DensSW

      IF (S .GE. 5) THEN
*      It is a sea water sample with salinity, S:
*      Calculate mass of sample titrated (g)

          W0 = V0 * DensSW (S, T)

*      Calculate values for the total concentrations

          CALL ConcnsSW (S, BT, ST, FT)

*      Calculate values for the equilibrium constants

          CALL ConstsSW (S, T, K1, K2, KB, K1P, K2P, K3P, KSi,
+          KS, KF, KW)

*      Calculate pH conversion factor from "free" to "total" scale

          Z = 1 + ST/KS

      ELSE
*      It is a NaCl solution with concentration S (mol/kg-soln):

          W0 = V0 * DensNaCl (S, T)
          BT = 0
          ST = 0
          FT = 0
          CALL ConstsNaCl (S, T, K1, K2, KW)
          Z = 1
      ENDIF

*      Calculate mass of acid titrant at each titration point (g)

      DO 100 I = 1, NPts
          W(I) = V(I) * DACID
100    CONTINUE

*      Calculate appropriate Nernst Factor: E = E0 +/- (RT/F)ln[H]

          KNernst = 8.31451 * (273.15 + T) / 96485.309
          IF (E(1) .GT. E(NPts)) KNernst = -KNernst

*      Estimate E0 using last two titration points (at low pH)

          CALL EstimE0 (W0, W(NPts-1), W(NPts), E(NPts-1), E(NPts),
+          C, KNernst, E0)

```

```

*   Calculate [H] using this initial estimate of E0
      DO 300 I = 1, NPts
        H(I) = EXP((E(I) - E0)/KNernst)
300  CONTINUE

      RETURN
      END

*****

      SUBROUTINE Output (NOUT,
+   INFO, ICOUNT, NPar, X,
+   Header, S, PT, SiT, T, V0, C, DAcid,
+   NPts, V, E, H, FVEC, KNernst, E0)

      IMPLICIT NONE
      INTEGER NOUT, INFO, ICOUNT(2), NPar, NPts
      CHARACTER Header*80
      DOUBLE PRECISION X(NPar), S, PT, SiT, T, V0, C, DAcid,
+   V(NPts), E(NPts), H(NPts), FVEC(NPts), KNernst, E0

*   Subroutine to print out results as a table
*
*   Written by Andrew G. Dickson (last modified February 1994)
*
*   Called with:
*   NOUT   - channel number for printing
*   INFO   - flag from LMDIF1 indicating if minimization was successful
*   NPar   - number of parameters being adjusted (4)
*   X      - array containing final values of adjusted parameters
*   Header - sample identifier
*   S      - salinity of titrated sample
*   PT     - total phosphate in sample (mol/kg-soln)
*   SiT    - total silicate in sample (mol/kg-soln)
*   T      - titration temperature (deg C)
*   V0     - volume of sample titrated (cm3)
*   C      - concentration of acid titrant (mol/kg-soln)
*   DAcid  - density of acid titrant (g/cm3)
*   NPts   - number of titration points
*   V      - array of volumes of titrant used (cm3)
*   E      - array of corresponding e.m.f.s (V)
*   FVEC   - residuals in total hydrogen ion (mol/kg-soln)
*   KNernst - appropriate Nernst factor  $E = E0 +/- K \cdot \ln[H]$  (V)
*   E0     - estimate of E0 (V)

      INTEGER I
      DOUBLE PRECISION ENORM

      WRITE (NOUT, *)
      WRITE (NOUT, '(1X, A80 /)') Header

      WRITE (NOUT, '(1X, 'S      = ', F7.3)') S
      WRITE (NOUT, '(1X, 'PT     = ', F6.2, '   μmol/kg')') 1D6*PT
      WRITE (NOUT, '(1X, 'SiT    = ', F6.2, '   μmol/kg')') 1D6*SiT

      WRITE (NOUT, *)
      WRITE (NOUT, '(1X, 'T      = ', F6.2, '   deg C')') T
      WRITE (NOUT, '(1X, 'V0     = ', F7.3, '   cm3')') V0
      WRITE (NOUT, '(1X, 'C      = ', F7.5, '   mol/kg')') C
      WRITE (NOUT, '(1X, 'DACID = ', F7.5, '   g/cm3')') DACID

      WRITE (NOUT, '(' LMDIF1 exit parameter ', I3)') INFO
      WRITE (NOUT, '(' Function calls      ', I5)') ICOUNT(1)
      WRITE (NOUT, '(' Jacobian calls      ', I5,/)') ICOUNT(2)

      IF (INFO .GT. 3) WRITE (NOUT, '(' ***LMDIF1 DID NOT CONVERGE!***')')

      WRITE (NOUT, '(1X, 'E0     = ', F8.6, '   V')') E0 - KNernst*LOG(X(1))
      WRITE (NOUT, '(1X, 'AT     = ', F7.2, '   μmol/kg')') 1D3*X(2)

```

```

WRITE (NOUT, '(1X, 'CT = ', F7.2, ' μmol/kg')) 1D3*X(3)
WRITE (NOUT, '(1X, 'pK1 = ', F6.4 /)') -LOG10(1D-6*X(4))

* Use MINPACK function ENORM to calculate Euclidean Norm

WRITE (NOUT, '(1X, 's = ', F5.3, ' μmol/kg'))
+ 1D6*SQRT(ENORM(NPts,FVEC)**2/(NPts-NPar))

WRITE (NOUT,
+ '( / 4X, 'V/cm3', 6X, 'E/V', 6X, '-log[H]', 3X, 'ΔH/(μmol/kg)' /)')

WRITE (NOUT, '(3X, F6.3, F11.5, F11.4, F12.3)')
+ (V(I), E(I), -LOG10(H(I)*X(1)), 1D6*FVEC(I), I = 1, NPts)

RETURN
END

*****

SUBROUTINE FCN (M, N, X, FVEC, IFLAG)
IMPLICIT NONE
INTEGER M, N, IFLAG
DOUBLE PRECISION X(N), FVEC(M)

*
* Subroutine to calculate the vector of residuals, FVEC,
* corresponding to the current values of X
*
* Written by Andrew G. Dickson (last modified February 1994)
*
* Called with:
* NPts - number of titration points
* Npar - number of parameters being adjusted (4)
* X - current estimate of the solution
* IFLAG - set by MINPACK to identify if called for function
* or Jacobian evaluation.
*
* Returns:
* FVEC - array of residuals in HTOT (mol/kg)
*
* Parameter:
* MaxPts - maximum number of titration data points
* (In routines MAIN, SetUP and FCN)

INTEGER MaxPts
PARAMETER (MaxPts = 100)

* Common block /TITN/:
* C - concentration of titrant acid (mol/kg)
* W0 - mass of sample titrated (g)
* W - array containing titrant amounts (g)
* H - array containing [H'] = 10*((E0 - E)/K)
* based on the initial E0 estimate
* BT - total boron (mol/kg-soln)
* ST - total sulfate (mol/kg-soln)
* FT - total fluoride (mol/kg-soln)
* PT - total phosphate (mol/kg-soln)
* SiT - total silicate (mol/kg-soln)
*
* K1 - [H][HCO3]/[H2CO3]
* K2 - [H][CO3]/[HCO3]
* KB - [H][BO2]/[HBO2]
* K1P - [H][H2PO4]/[H3PO4]
* K2P - [H][HPO4]/[H2PO4]
* K3P - [H][PO4]/[HPO4]
* KSI - [H][SiO(OH)3]/[Si(OH)4]
* KS - [h][SO4]/[HSO4]
* KF - [H][F]/[HF]
* KW - [H][OH]
* Z - pH scale conversion factor [H] = [h](1 + ST/KS)

```

```

      DOUBLE PRECISION C, W0, W(MaxPts), H(MaxPts),
+      BT, ST, FT, PT, SIT,
+      K1, K2, KB, K1P, K2P, K3P, KSi, KW, KS, KF, Z

      COMMON /TITN/ C, W0, W, H,
+      BT, ST, FT, PT, SIT,
+      K1, K2, KB, K1P, K2P, K3P, KSi, KW, KS, KF, Z

*      Common block /EVAL/:
*      ICOUNT(1) - total number of function evaluations
*      ICOUNT(2) - total number of Jacobian calculations

      INTEGER ICOUNT(2)
      COMMON / EVAL/ ICOUNT

      INTEGER I
      DOUBLE PRECISION F, AT, CT

*      Count number of times FCN is called:

      ICOUNT(IFLAG) = ICOUNT(IFLAG) + 1

*      Parameters being adjusted:
*      F      - correction factor for E0
*      AT     - total alkalinity
*      CT     - total dissolved inorganic carbon
*      K1     - first dissociation constant of carbonic acid

      F = X(1)
      AT = X(2)*1D-3
      CT = X(3)*1D-3
      K1 = X(4)*1D-6

*      Calculate the residuals at X (mol/kg-soln)

      DO 100 I = 1, M
        FVEC(I) = AT
+        - CT*((K1*F*H(I) + 2*K1*K2) /
+          ((F*H(I))**2 + K1*F*H(I) + K1*K2))
+        - BT/(1 + F*H(I)/KB)
+        - PT*((K1P*K2P*F*H(I) + 2*K1P*K2P*K3P - (F*H(I))**3) /
+          ((F*H(I))**3 + K1P*(F*H(I))**2 +
+            K1P*K2P*F*H(I) + K1P*K2P*K3P))
+        - SiT/(1 + F*H(I)/KSi)
+        + ST/(1 + KS*Z/(F*H(I)))
+        + FT/(1 + KF/(F*H(I)))
+        + (W0 + W(I))/W0 * (F*H(I)/Z - KW/(F*H(I)))
+        - (W(I)/W0)*C
100    CONTINUE

      RETURN
      END

*****

      DOUBLE PRECISION FUNCTION DensSW (S, T)
      IMPLICIT NONE
      DOUBLE PRECISION T, S

*
*      Function to calculate the density of sea water.
*      Based on Millero & Poisson (1981) Deep-Sea Res. 28, 625.
*
*      Written by Andrew G. Dickson (last modified February 1994)
*
*      Called with:
*      S      - salinity of sample
*      T      - titration temperature (Centigrade)

      DOUBLE PRECISION DH2O, A, B, C

```

```

* Density of SMOW (kg/m3)
  DH2O = 999.842594 + 6.793952D-2 * T - 9.095290D-3 * T**2 +
+ 1.001685D-4 * T**3 - 1.120083D-6 * T**4 + 6.536332D-9 * T**5

* Density of sea water
  A = 8.24493D-1 - 4.0899D-3 * T + 7.6438D-5 * T**2 -
+ 8.2467D-7 * T**3 + 5.3875D-9 * T**4
  B = -5.72466D-3 + 1.0227D-4 * T - 1.6546D-6 * T**2
  C = 4.8314D-4

  DensSW = (DH2O + A*S + B*S**1.5 + C*S**2)/1000

  RETURN
  END

*****

  SUBROUTINE ConcnsSW (S, BT, ST, FT)
  DOUBLE PRECISION S, BT, ST, FT
*
* Subroutine to calculate appropriate total concentrations,
* for sea water of salinity, S.
*
* Written by Andrew G. Dickson (last modified August 1994)
*
* Called with:
*   S - salinity of sample
*
* Returns:
*   BT - total boron (mol/kg-soln)
*   ST - total sulfate (mol/kg-soln)
*   FT - total fluoride (mol/kg-soln)
*
* Upstrom (1974) Deep-Sea Res. 21, 161.
  BT = (0.000232/10.811) * (S/1.80655)
*
* Morris & Riley (1966) Deep-Sea Res. 13, 699
  ST = (0.1400/96.062) * (S/1.80655)
*
* Riley (1965) Deep-Sea Res. 12, 219.
  FT = (0.000067/18.998) * (S/1.80655)

  RETURN
  END

*****

  SUBROUTINE ConstsSW (S, T,
+ K1, K2, KB, K1P, K2P, K3P, KSi, KS, KF, KW)

  IMPLICIT NONE
  DOUBLE PRECISION T, S,
+ K1, K2, KB, K1P, K2P, K3P, KSi, KS, KF, KW

* Subroutine to calculate values of dissociation constants,
* appropriate to sea water of salinity, S, and temperature, T.
*
* Written by Andrew G. Dickson (last modified August 1994)
*
* Called with:
*   S - salinity of sample
*   T - titration temperature (deg C)
*
* Returns:
*   K1 - [H][HCO3]/[H2CO3]
*   K2 - [H][CO3]/[HCO3]
*   KB - [H][BO2]/[HBO2]
*   K1P - [H][H2PO4]/[H3PO4]
*   K2P - [H][HPO4]/[H2PO4]
*   K3P - [H][PO4]/[HPO4]

```

```

*      KSI      -  [H][SiO(OH)3]/[Si(OH)4]
*      KS       -  [h][SO4]/[HSO4]
*      KF       -  [H][F]/[HF]
*      KW       -  [H][OH]
*
DOUBLE PRECISION TK, IS

TK = 273.15 + T
IS = 19.924*S/(1000 - 1.005*S)

* Roy et al. (1993) Mar. Chem. 44, 249
  K1 = exp (
+     -2307.1266/TK + 2.83655 - 1.5529413*LOG(TK) +
+     (-4.0484/TK - 0.20760841)*SQRT(S) + 0.08468345*S -
+     0.00654208*S**1.5 + log(1 - 0.001005*S)
+   )

  K2 = exp (
+     -3351.6106/TK - 9.226508 - 0.2005743*LOG(TK) +
+     (-23.9722/TK - 0.106901773)*SQRT(S) + 0.1130822*S -
+     0.00846934*S**1.5 + log(1 - 0.001005*S)
+   )

* Dickson (1990) Deep-Sea Res. 37, 755
  KB = exp (
+     (-8966.90 - 2890.53*SQRT(S) - 77.942*S + 1.728*S**1.5 -
+     0.0996*S**2)/TK + (148.0248 + 137.1942*SQRT(S) + 1.62142*S) +
+     (-24.4344 - 25.085*SQRT(S) - 0.2474*S)*LOG(TK) + 0.053105*SQRT(S)*TK
+   )

* Millero (1995) -- composite data (Geochim. Cosmochim Acta 59, 661)
  K1P = exp (
+     -4576.752/TK + 115.525 - 18.453*LOG(TK) +
+     (-106.736/TK + 0.69171)*SQRT(S) + (-0.65643/TK - 0.01844)*S
+   )

  K2P = exp (
+     -8814.715/TK + 172.0883 - 27.927*LOG(TK) +
+     (-160.340/TK + 1.3566)*SQRT(S) + (0.37335/TK - 0.05778)*S
+   )

  K3P = exp (
+     -3070.75/TK - 18.141 +
+     (17.27039/TK + 2.81197)*SQRT(S) + (-44.99486/TK - 0.09984)*S
+   )

* Millero (1995) -- composite data (Geochim. Cosmochim Acta 59, 661)
  KSi = exp (
+     -8904.2/TK + 117.385 - 19.334*LOG(TK) +
+     (-458.79/TK + 3.5913)*SQRT(IS) +
+     (188.74/TK - 1.5998)*IS + (-12.1652/TK + 0.07871)*(IS)**2 +
+     log(1 - 0.001005*S)
+   )

* Millero (1995) -- composite data (Geochim. Cosmochim Acta 59, 661)
  KW = exp (
+     -13847.26/TK + 148.9652 - 23.6521*LOG(TK) +
+     (118.67/TK - 5.977 + 1.0495*LOG(TK))*SQRT(S) - 0.01615*S
+   )

* Dickson (1990) -- free hydrogen ion scale (J. Chem. Thermodynamics 22, 113)
  KS = exp (
+     -4276.1/TK + 141.328 - 23.093*log(TK) +
+     (-13856/TK + 324.57 - 47.986*log(TK)) * sqrt(IS) +
+     (35474/TK - 771.54 + 114.723*log(TK)) * IS -
+     2698*IS**1.5/TK + 1776*IS**2/TK + log(1 - 0.001005*S)
+   )

```

```

*   Dickson & Riley (1979) -- change pH scale to total (Mar. Chem. 7, 89)
      KF = 1590.2/TK - 12.641 + 1.525 * SQRT(IS) + log(1 - 0.001005*S)
      KF = KF + log(1 + (0.1400/96.062)*(S/1.80655)/KS)
      KF = exp(KF)

      RETURN
      END

*****

      DOUBLE PRECISION FUNCTION DensNaCl (CNaCl, T)
      IMPLICIT NONE
      DOUBLE PRECISION T, CNaCl
*
*   Function to calculate the density of a sodium chloride solution.
*   Based on equation by Lo Surdo et al.
*   J. Chem. Thermodynamics 14, 649 (1982).
*
*   Written by Andrew G. Dickson (last modified March 1994)
*
*   Called with:
*   CNaCl - concentration of sodium chloride (mol/kg-soln)
*   T     - titration temperature (Centigrade)

      DOUBLE PRECISION MNaCl, DH2O, DNaCl
*
*   Calculate the molality of NaCl

      mNaCl = CNaCl/(1 - 0.058443*CNaCl)
*
*   Density of SMOW (kg/m3)

      DH2O = 999.842594 + 6.793952D-2 * T - 9.095290D-3 * T**2 +
      + 1.001685D-4 * T**3 - 1.120083D-6 * T**4 - 6.536332D-9 * T**5
*
*   Density of NaCl (kg/m3)

      DNaCl = DH2O + mNaCl*(46.5655 - 0.2341*t + 3.4128D-3 * T**2
      + - 2.7030D-5 * T**3 + 1.4037D-7 * T**4) +
      + mNaCl**1.5 * (-1.8527 + 5.3956D-2 * T - 6.2635D-4 * T**2) +
      + mNaCl**2 * (-1.6368 - 9.5653D-4 * T + 5.2829D-5 * T**2) +
      + 0.2274 * mNaCl**2.5

      DensNaCl = 1D-3 * DNaCl

      RETURN
      END

*****

      SUBROUTINE ConstsNaCl (CNaCl, T, K1, K2, KW)

      IMPLICIT NONE
      DOUBLE PRECISION T, CNaCl, K1, K2, KW
*
*   Subroutine to calculate values of dissociation constants,
*   appropriate to a sodium chloride solution of concentration,
*   CNaCl, and temperature, T.
*
*   Written by Andrew G. Dickson (last modified August 1994)
*
*   Called with:
*   CNaCl- concentration of NaCl (mol/kg-soln)
*   T     - titration temperature (deg C)
*
*   Returns:
*   K1    - [H][HCO3]/[H2CO3]
*   K2    - [H][CO3]/[HCO3]
*   KW    - [H][OH]

```

```

DOUBLE PRECISION TK

TK = 273.15 + T

* At present this only provides constants for
* C(NaCl) = 0.7 mol/kg-soln and t = 25 °C.

IF (ABS(CNaCl - 0.7) .gt. 0.05) THEN
  WRITE (6, '(' ConstsNaCl: C(NaCl) .ne. 0.7"')
ENDIF
IF (ABS(T - 25) .gt. 0.1) THEN
  WRITE (6, '(' ConstsNaCl: T .ne. 25 "')
ENDIF

IF ((ABS(CNaCl - 0.7) .gt. 0.05) .or. (ABS(T - 25) .gt. 0.1)) STOP

* Dyrssen & Hansson (1973) Mar. Chem. 1, 137
K1 = exp(-13.82)
K2 = exp(-21.97)
KW = exp(-31.71)

RETURN
END

*****

SUBROUTINE EstimE0 (W0, WA, WB, EA, EB, C, KNernst, E0)
IMPLICIT NONE
DOUBLE PRECISION W0, WA, WB, EA, EB, C, KNernst, E0

* This subroutine estimates an initial value of E0 using a Gran
* function and the last two titration points to estimate AT.
* [H] is calculated at those 2 points and an average E0 estimated.
*
* Written by Andrew G. Dickson (last modified Feb 1994)
*
* Called with:
*   W0 - mass of sea water sample (g)
*   WA - mass of titrant at point (Npts-1) (g)
*   WB - mass of titrant at point (Npts) (g)
*   EA - e.m.f. at point (Npts-1) (V)
*   EB - e.m.f. at point (Npts) (V)
*   C - concentration of acid (mol/kg)
*   KNernst - appropriate Nernst factor (V)
*
* Returns:
*   E0 - estimate of standard potential for pH cell (V)

DOUBLE PRECISION A0, A1, AT, HA, HB

* Calculate Gran function (W0+W)exp(E/K) and fit to y = a0 + a1*x
*   A1 = (yB - yA) / (xB - xA)
*   A0 = yA - A1*xA

A1 = ((W0 + WB) * EXP(EB/KNernst) - (W0 + WA) * EXP(EA/KNernst))/
+ (WB - WA)
A0 = (W0 + WA) * EXP(EA/KNernst) - A1 * WA

* Calculate estimate of AT

AT = (-A1/A0) * C / W0

* Calculate [H] at those 2 points and hence an average E0.

HA = (WA * C - W0 * AT) / (W0 + WA)
HB = (WB * C - W0 * AT) / (W0 + WB)
E0 = (EA - KNernst * LOG(HA) + EB - KNernst * LOG(HB)) / 2

RETURN
END

```