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Water quality — Determination of total alkalinity in sea water using high precision potentiometric titration

Qualité de l'eau — Détermination de l'alcalinité totale dans l'eau de mer en utilisant une titration potentiométrique de haute précision

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Foreword

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The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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ISO 22719 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

Introduction

The greenhouse effect, induced by anthropogenic carbon dioxide, CO_2, in the atmosphere is a serious global environmental issue. A key factor controlling the concentration of atmospheric CO_2 is its absorption into the ocean. Since the volume of ocean water is huge, the change in the oceanic carbonate system from year to year is slight, and it is necessary to measure its components continuously with great precision over a long period. Furthermore, the oceanic carbonate system is related to many components such as water temperature, salinity, dissolved oxygen, and nutrient elements.

The oceanic carbonate system can be depicted by measuring at least two parameters of four: total inorganic carbon; total alkalinity; fugacity of CO_2; and pH of sea water. At the time of publication, it is possible to determine the first two parameters more precisely for subsurface water. Analytical methods for sea water samples, however, require specific conditions and techniques essential to the precise and accurate determination. This International Standard describes a method for the determination of total alkalinity in sea water with an error of less than 0,1 %.

This method is designed to provide international compatibility of accurate data sets on total alkalinity in sea water, which are collected by various communities. Such compatibility is the basis for national and international operational observation and monitoring programs of the oceanic carbonate system, as well as individual research work.

Water quality — Determination of total alkalinity in sea water using high precision potentiometric titration

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

IMPORTANT — It is absolutely essential that tests conducted according to this International Standard be carried out by suitably trained staff.

1 Scope

This International Standard specifies an open-cell potentiometric titration determination of total alkalinity in sea water. The results are expressed in moles per kilogram of sea water. The method is suitable for assaying oceanic levels of total alkalinity (2 000 µmol kg^{-1} to 2 500 µmol kg^{-1}) for normal sea water of practical salinity ranging from 30 to 40.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 5667-1, *Water quality — Sampling — Part 1: Guidance on the design of sampling programmes and sampling techniques*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
total alkalinity
A_T
⟨sea water⟩ number of moles of hydrogen ion equivalent to the excess of proton acceptors (bases formed from weak acids with a dissociation constant, $K \leqslant 10^{-4,5}$ at 25 °C and zero ionic strength) over proton donors (acids with $K > 10^{-4,5}$) in 1 kg of sample

NOTE   This definition is taken from Reference [5].

3.2
practical salinity
S
⟨sea water⟩ the ratio K_{15} of the electrical conductivity of the sea water sample at the temperature of 15°C and the pressure of one standard atmosphere, to that of a potassium chloride (KCl) solution, in which the mass fraction of KCl is 32,435 6 × 10^{-3}, at the same temperature and pressure

NOTE   This definition is taken from Reference [6], p. 12, and was formulated and adopted by the UNESCO/ICES/SCOR/IAPSO Joint Panel on Oceanographic Tables and Standards, Sidney, B.C., Canada, September 1-5, 1980, and endorsed by those international bodies. As a ratio, the practical salinity has no unit.

4   Principle

A known amount of sea water is placed in an open cell where it is titrated in a two stage procedure with a solution of hydrochloric acid. The acid solution also contains sodium chloride to compensate for the sodium ion concentration of the sea water and to maintain approximately constant activity coefficients during the titration. An open cell is used so that, in subsequent data processing, it can be assumed that the total dissolved inorganic carbon (and hence the residual bicarbonate ion concentration) is approximately zero between pH 3,0 and pH 3,5. The progress of the titration is monitored using a pH glass-reference cell, and the total alkalinity is computed from the titrant volume and electromotive force (EMF) measurements using a non-linear least-squares approach allowing for the reactions of hydrogen ion with sulfate and fluoride ions.

5   Apparatus

The setup of apparatus specified in 5.2 and 5.4 is shown in Figure 1.

Usual laboratory equipment, and in particular the following.

5.1   Sampling equipment.

5.1.1   For laboratory use.

5.1.1.1   Calibrated balance, capable of weighing 200 g to within ± 0,01 g.

5.1.1.2   Plastic screw-cap bottle, of capacity 125 ml, with cap.

5.1.2   For use on board ship, preferably a **volumetric dispensing system**, containing a constant volumetric pipette made of glass with valves at each end, maintained at constant temperature by an air bath or a water jacket. The sample water — maintained at the same temperature — is flushed into the pipette using pressurised air. A constant volume of water is dispensed by switching the valve. The temperature of the sample water shall be known to within ± 0,4 °C.

A **manual pipette** may be used on condition that the temperature of sample water and room air is strictly controlled.

5.2   Titration cell assembly.

5.2.1   Jacketed beaker, of capacity 200 ml. A glass beaker enclosed by a water jacket (Figure 1), of internal diameter 57 mm.

5.2.2   Calibrated thermometer, readable to 0,01 °C, used to confirm that the solution temperature remains constant to within ± 0,05 °C during the titration and to provide the value of solution temperature for use in subsequent calculations.

5.2.3   Water bath, capable of being maintained at a constant temperature to within ± 0,05 °C.

5.2.4   Magnetic stirrer, of dimensions 38 mm × 8 mm.

5.2.5   Holder for burette tip, electrode, and thermometer

5.3   EMF-measuring assembly.

5.3.1   Digital voltmeter, readable to 0,01 mV.

5.3.2   High-impedance voltage follower amplifier system, used to buffer the EMF of the glass electrode-reference cell so that it can be measured accurately using the digital voltmeter.

NOTE   A digital pH meter (± 0,1 mV) can be used instead of a digital voltmeter and voltage-follower amplifier, but with a loss in precision.

5.3.3 pH glass-reference electrode

A very rapid response pH glass electrode system in sea water is essentially important. The 90 % response time during a pH change of 0,1 should be less than 10 s when sea water is titrated by acid titrant. To reduce the sample volume, the combination of a pH glass-reference electrode is more suitable.

The performance of the pH electrode is paramount for achieving high quality results. The performance of a new electrode can be assessed by measuring A_T on a sea water reference material. If the certified value is not obtained, it may be necessary to replace the electrode.

5.4 Burette assembly.

A highly reproducible burette ($\pm$ 0,001 ml) is necessary to obtain the highest quality results. Unfortunately, although the burette is capable of the high reproducibility needed, its accuracy is typically not as good, and the burette system shall be calibrated prior to use.

5.4.1 Automatic burette, of capacity 5 ml $\pm$ 0,002 ml, equipped with an anti-diffusion tip.

5.4.2 Calibrated thermometer, readable to 0,1 °C, used to measure acid temperature.

5.5 Miscellaneous.

5.5.1 Transfer device for samples by mass, designed to allow dispensation from a bottle with a greased ground-glass joint in a manner that ensures that grease is not transferred to the weighing bottle. Such a system may comprise a rubber stopper to which two rigid plastic tubes are skewered; the rubber stopper is secured to the sample bottle with a metal clamp. Connected tubes should be chemically inert and acid resistant. One of the tubes is long enough to make contact with the bottom of a 500 ml sample bottle, and the other tube protrudes about 6 mm below the stopper. The shorter tube is attached with about 500 mm of tubing to a rubber bulb, which is used to pressurise the system. The other tube is attached to a length of tubing (approx. 500 mm) and is closed with a pinch clamp. This tube is used to dispense the sample.

5.5.2 Basin for waste.

5.5.3 Wash bottle, containing water (6.2).

6 Reagents

6.1 Titrant, calibrated solution for normal sea water samples, containing hydrochloric acid, 0,1 mol/kg, and sodium chloride, 0,6 mol/kg.

Ideally, the hydrochloric acid titrant solution is calibrated with an accuracy of better than $\pm$ 0,02 % using a coulometric titration procedure (see e.g. Reference [7]). In addition, the density of this titrant solution should be known as a function of temperature with an accuracy of better than $\pm$ 0,02 % experimentally by using a pyknometer (e.g. ISO 758). However, these procedures are complicated and require a great deal of skill. Furthermore, acid concentration and density may be changed by evaporation in several days. It is necessary to recalibrate the acid from time to time. Thus, the calibration of acid titrant using certified reference material (CRM) is recommended (see B.1.3).

6.2 Deionised ultrapure water, of resistivity about 18 MΩ cm.

7 Procedure

7.1 Sampling

Collect the sea water sample according to the standard method for water sampling of dissolved gases (see ISO 5667-1). It is strongly recommended that the sample is analysed within a few hours. When analysis is not

possible immediately after sampling, add mercury(II) chloride. Recommended minimum amount is about 0,02 % by volume of saturated aqueous solution. Store the samples in a cool, dark place (preferably refrigerated, but not frozen) until use.

WARNING — Dispose of samples containing mercury(II) chloride in accordance with local government regulations.

7.2 Equipment setup

Assemble the apparatus as shown in Figure 1.

Use extra caution when assembling the burette glass pieces and tubing. Make all connections finger tight, and do not overtighten. The most common cause of leaks and bubbles is damaged threads and chipped glass.

Set the water bath to a suitable temperature (close to room temperature).

Mix the hydrochloric acid titrant solution to ensure a consistent temperature and composition.
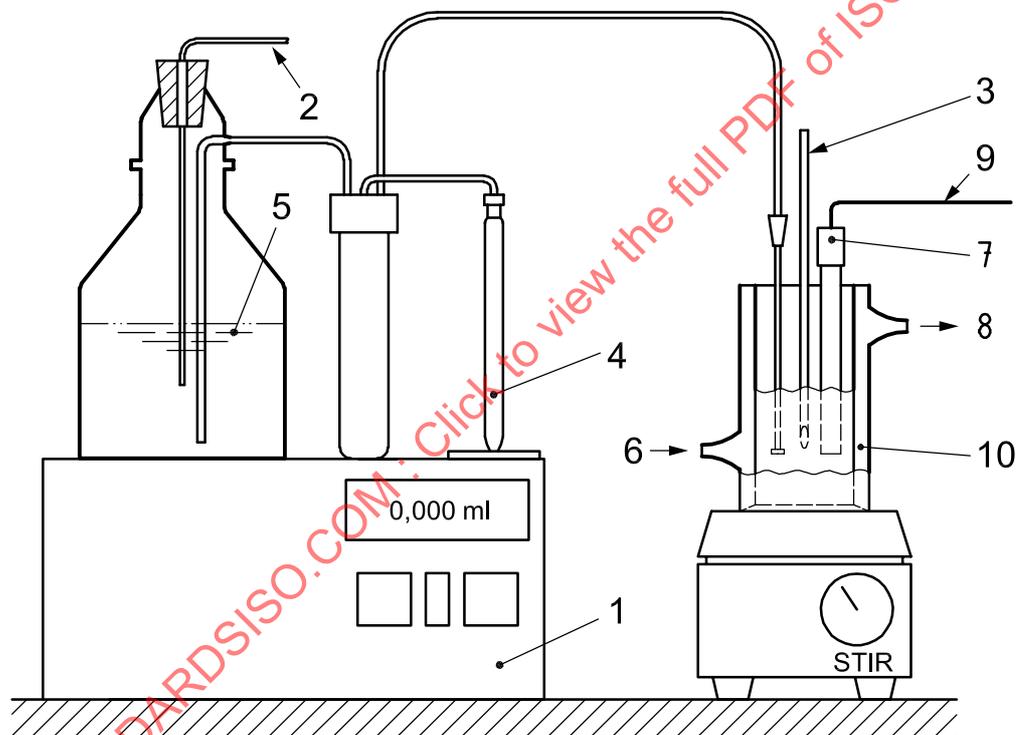
Key

1 automatic burette
2 sensor for thermometer
3 thermometer
4 burette reservoir
5 HCl/NaCl titrant
6 inlet from water bath
7 combination electrode
8 outlet to water bath
9 lead to EMF-measurement system
10 jacketed beaker

Figure 1 — Open-cell alkalinity measurement setup

Ensure that the automatic burette and tubing are thoroughly flushed with the titrant solution and that there are no air bubbles present.

IMPORTANT — If the system has not been used for some time, it may be necessary to condition the pH glass-reference cell. This can be achieved by carrying out a titration whose result is discarded. (This first measurement is often a little lower than the correct value.)

7.3 Sample transfer

7.3.1 Preparation of sample

Bring the sample to the required testing temperature; thoroughly mix the content of the sample bottle.

Remove the stopper of the bottle and use tissue paper to remove as much grease as possible.

7.3.2 Sampling by mass in the laboratory

Dry the longer tube of the sample transfer device (5.5.1); insert it into the sample bottle, securing it with the metal clamp.

Pressurise the bottle, and flush the tubing with about 20 ml of sample (discard to waste).

Fill a plastic bottle (5.1.1.2) with sample, cap tightly, and weigh (5.1.1.1); record the mass to the nearest 0,01 g.

Carefully pour the sample into the clean 250 ml jacketed beaker containing a 38 mm stir bar.

Recap the plastic bottle, and record the empty mass. The sample mass is obtained by difference.

7.3.3 Sampling by volume on board ship

Maintain the sample water and pipette at the same temperature and record it to the nearest 0,1 °C.

Draw up a known volume of sample water using the exactly calibrated automatic volumetric dispensing system or manual pipette (5.1.2). Record the volume, for later conversion to mass using an expression for the density of sea water at a known salinity and temperature.

Dispense the sample water into a clean 250 ml jacketed beaker containing a 38 mm stir bar.

7.4 Titration procedure

Purge the remaining acid in the burette (from the previous titration) into the waste basin, and refill the burette. To prevent the forming of bubbles in the burette and tubing, vent the acid bottle during each filling of the burette.

Record the hydrochloric acid solution temperature to the nearest 0,1 °C.

Rinse the acid tip, electrode, and thermometer thoroughly with water from the wash bottle. Gently touch dry with tissue paper.

Position the holder assembly over the beaker such that three parts dip into the sample without interfering with the stir bar.

With slow stirring, dispense enough hydrochloric acid to bring the sample to just above pH 3,5.

NOTE   The volume dispensed depends on the alkalinity of the sample and the sample size.

Increase the stirring rate until it is quite vigorous, but not splashing.

Stir the acidified sample for at least 10 min to allow for CO_2 degassing.

Titrate the sample using 0,05 ml increments to a final value of approx. pH 3,0 (~20 increments). After each addition, record the total dispensed volume to the nearest 0,001 ml, the EMF to the nearest 0,01 mV, and the sample temperature to the nearest 0,01 °C.

7.5   Clean up after each titration

Once the titration is complete, remove the holder assembly from the beaker, and position it over the waste basin.

Pour the spent sample into the waste basin. Use the wash bottle to rinse the beaker and the bar three times. Thoroughly dry the beaker and the bar with tissue paper, and return the bar to the beaker.

7.6   Clean up for system storage

If the apparatus is left overnight, the burette tip, thermometer, and electrode may be left in the last solution titrated. If no more samples will be run for 2 d or longer, clean the apparatus as follows.

Cover the clean, dry beaker and stir bar to protect from dust.

Disconnect the acid bottle and seal it with a lightly greased ground-glass stopper.

Use water (6.2) to thoroughly rinse the acid bottle and the thermometers, then leave them to dry in a place protected from dust.

Refill the burette with air.

Remove the burette and plunger, and thoroughly rinse with water (6.2).

Replace the burette and dispense 5 ml to purge any acid remaining in the tubing.

As the burette refills, submerge the flexible tubing end (that goes to the acid bottle) in a beaker of water (6.2) so that the burette is filled with water (6.2).

Again dispense 5 ml and fill the burette with water (6.2) to flush out all the acid.

Finally, refill the burette with air, and purge the tubing of all remaining liquid.

Disconnect the burette and leave to dry protected from dust.

Rinse the outside of the acid tip, and place it in the test tube holder.

Cover the burette valve and all tubing with a plastic bag.

Clean the electrode according to the manufacturer's instructions. Generally, rinse the electrode, cover the filling hole, and place it in a suitable storage solution in an airtight container.

Turn off all instruments.

8   Calculation and expression of results

8.1   General

Process the titration data using a computer program. Points from the range pH 3,0 to pH 3,5 are used to compute the total alkalinity using an non-linear least-squares fit of the results. To process sea water samples,

the total dissolved inorganic carbon is assumed to be zero, and corrections are made for HSO_4^- and HF formation. Details of calculation procedures are described in A.2.4.

8.2   Example calculation

8.2.1   Test data set

8.2.1.1   Sample and titration data

S	=	33,923	salinity of sample
T	=	24,25 °C	mean temperature of sample when titrated
m_0	=	140,32 g	mass of sample titrated
C	=	0,100 46 mol kg^{-1}	concentration of acid titrant
ρ_{acid}	=	1,023 9 g/ml	density of acid titrant

The volume of titrant, EMF and temperature of sample at each titration point are listed in Table 1.

Table 1 — Sample titration data – readings

Titrant volume V ml	EMF E V	Sample temperature T °C
3,500	0,186 07	24,25
3,550	0,188 93	24,26
3,600	0,191 50	24,27
3,650	0,193 85	24,25
3,700	0,196 01	24,25
3,750	0,198 00	24,24
3,800	0,199 87	24,23
3,850	0,201 60	24,25
3,900	0,203 22	24,25
3,950	0,204 74	24,24
4,000	0,206 18	24,22
4,050	0,207 53	24,23
4,100	0,208 80	24,25
4,150	0,210 02	24,26
4,200	0,211 21	24,27
4,250	0,212 33	24,26
4,300	0,213 41	24,26
4,350	0,214 46	24,26
4,400	0,215 46	24,25
4,450	0,216 41	24,25
4,500	0,217 33	24,25
4,550	0,218 21	24,25

8.2.2   Estimate of initial parameters for a non-linear least-squares calculation from test data set

A'_T =   2 263,54 µmol kg^{-1}

$E^{\circ\prime}$ =   0,394 28 V

These values are estimated from the simple approach of Reference [8], and used as initial values for a non-linear least-squares calculation (A.2.4).

8.2.3   Output from test data set as a result of a non-linear least-squares calculation

A_T =   2 260,10 µmol kg^{-1} alkalinity of sample (final result)

E° =   0,394 401 V

Table 2 — Non-linear least-squares calculation — values

Volume V ml	EMF E V	pH
3,500	0,186 07	3,530 4
3,550	0,188 93	3,481 9
3,600	0,191 50	3,438 4
3,650	0,193 84	3,398 5
3,700	0,196 01	3,361 9
3,750	0,198 00	3,328 2
3,800	0,199 86	3,296 5
3,850	0,201 59	3,267 2
3,900	0,203 21	3,239 8
3,950	0,204 73	3,214 0
4,000	0,206 17	3,189 6
4,050	0,207 53	3,166 7
4,100	0,208 80	3,145 2
4,150	0,210 02	3,124 5
4,200	0,211 20	3,104 4
4,250	0,212 33	3,085 4
4,300	0,213 41	3,067 1
4,350	0,214 46	3,049 3
4,400	0,215 45	3,032 3
4,450	0,216 41	3,016 2
4,500	0,217 32	3,000 6
4,550	0,218 20	2,985 7

Annex A
(informative)

Theoretical background and calculation of alkalinity in sea water

A.1 Practical definition of total alkalinity of a sea water sample

The total alkalinity of a sea water sample is defined as the number of moles of hydrogen ion equivalent to the excess of proton acceptors (bases formed from weak acids with a dissociation constant, $K \leqslant 10^{-4,5}$ at 25 °C and zero ionic strength) over proton donors (acids with $K > 10^{-4,5}$) in 1 kg of sample (Reference [5]):

$$A_T = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{2-}] + [SiO(OH)_3^-] + [NH_3] + [HS^-] + ...$$
$$- [H^+]_F - [HSO_4^-] - [HF] - [H_3PO_4] - ... \qquad (A.1)$$

Brackets represent total concentrations of these constituents in solution, $[H^+]_F$ is the free concentration of hydrogen ion, and the ellipses represent additional minor acid or base species that are either unidentified or present in such small amounts that they can be ignored. The concentrations of ammonia and hydrogen sulfide are typically so low that they can be neglected in open ocean water; they may, however, be significant in anoxic environments.

A.2 Calculation and expression of results

A.2.1 Values for fundamental constants

The values of the gas constant, R, and Faraday constant, F, are:

$R = 8,314\ 510(70)$ J K^{-1} mol^{-1}

$F = 96\ 485,309(29)$ C mol^{-1}

For each constant, the standard deviation uncertainty in the least significant digits is given in parentheses.

A.2.2 Symbols

A.2.2.1 Experimental data

T mean temperature, in degrees celsius, of sample when titrated

S salinity of sample (practical salinity scale)

V volume, in millilitres, of titrant

m_0 mass, in grams, of sample titrated

C concentration, in moles per kilogram, of acid titrant

ρ_{acid} density, in grams per millilitre, of acid titrant

E EMF, in volts, of each titration point

A.2.2.2 Various parameters for calculation

m	mass, in grams, of titrant acid
K_S	dissociation constant of hydrogensulfate ion;
K_F	dissociation constant of hydrogen fluoride
S_T	total concentration, in moles per kilogram, of sulfate
F_T	total concentration, in moles per kilogram, of fluoride
A_T	total alkalinity, in moles per kilogram
$E°$	standard electrode potential, in volts
$A'_T, E°'$	initial values of A_T and $E°$ for non-linear least-squares calculation

A.2.3 Derivation of basic equations

The defining Equation (A.2) for total alkalinity is used to define a proton condition corresponding to this equivalence point:

$$[H^+]_F + [HSO_4^-] + [HF] + [H_3PO_4] =$$
$$[HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{2-}] + [SiO(OH)_3^-] + [NH_3] + [HS^-] \qquad (A.2)$$

NOTE   The existence of minor unidentified species has been ignored in this expression.

At each point in the titration, the analytical total concentration of hydrogen ion (relative to this proton condition) is given by Equation (A.3):

$$C_H = [H^+]_F + [HSO_4^-] + [HF] + [H_3PO_4] -$$
$$[HCO_3^-] - 2[CO_3^{2-}] - [B(OH)_4^-] - [OH^-] - [HPO_4^{2-}] - 2[PO_4^{2-}] - [SiO(OH)_3^-] - [NH_3] - [HS^-] \qquad (A.3)$$

The initial analytical concentration of hydrogen ion in the solution is thus the negative of the total alkalinity. After a mass, m, of acid — at a concentration, C, in moles per kilogram of solution — has been added to a mass, m_0, of sample,

$$C_H = \frac{-m_0 A_T + mC}{m_0 + m} \qquad (A.4)$$

NOTE   Typically acid is added by volume and its density is known accurately. In the procedure described here, the acid temperature is monitored carefully and the appropriate density estimated from laboratory measurements of the acid density as a function of temperature.

Combining Equations (A.3) and (A.4) gives Equation (A.5)

$$\frac{-m_0 A_T + mC}{m_0 + m} = [H^+]_F + [HSO_4^-] + [HF] + [H_3PO_4] -$$
$$[HCO_3^-] - 2[CO_3^{2-}] - [B(OH)_4^-] - [OH^-] - [HPO_4^{2-}] - 2[PO_4^{2-}] - [SiO(OH)_3^-] - [NH_3] - [HS^-] \qquad (A.5)$$

Equation (A.5) is the basis of the computations involved in this procedure; however, as only data in the range pH 3,0 to pH 3,5 are used, and as the CO_2 generated by the reaction with the acid titrant is lost into the

atmosphere, the majority of these terms can be safely neglected, and Equation (A.5) reduces to Equation (A.6):

$$\frac{-m_0 A_T + mC}{m_0 + m} \approx [H^+]_F + [HSO_4^-] + [HF]$$ (A.6)

A.2.4 Computational procedures

The values used in these calculations for the acid dissociation constants: K_S and K_F, and for the total concentrations: S_T and F_T, expressed as a function of salinity, S, and temperature, T, are given in Reference [9], Chapter 5.

If sample water is dispensed by a volumetric system, m_0 can be calculated from its volume and density. The density of sample water can be calculated from temperature and salinity using the equation given in Reference [9], Chapter 5.

The mass, m, of titrated acid at each titration point is calculated from the volume, V, and density, ρ_{acid}, of acid.

The mean temperature, $\overline{T}$, of sample when titrated is calculated by averaging the temperature during the titration.

Equation (A.6) is used to estimate A_T from titration data by means of a non-linear least-squares procedure. It is necessary to start with reasonable estimates for A_T and $E°$ so as to ensure convergence. A simple approach based on Reference [8] is used for this. Equation (A.6) is approximated by Equation (A.7):

$$\frac{-m_0 A_T + mC}{m_0 + m} \approx [H^+] = \exp\left(\frac{E - E°}{RT/F}\right) = k \exp\left(\frac{E}{RT/F}\right)$$ (A.7)

where [H⁺] is the total hydrogen ion concentration, defined by Equation (A.8):

$$[H^+] = [H^+]_F \left(1 + S_T/K_S\right) \approx [H^+]_F + [HSO_4^-]$$ (A.8)

The S_T and K_S values used are from Reference [9].

This approximation assumes that [HF] is negligible, and that $[HSO_4^-] \ll [SO_4^{2-}]$. (Neither of these are very good assumptions, but they are adequate for the purpose of estimating initial values for A_T and $E°$ for this least-squares procedure.)

Equation (A.7) is rearranged to give the Gran function of Reference [8]:

$$F_1 = (m_0 + m)\exp\left(\frac{E}{RT/F}\right)$$ (A.9)

This function is linear in m and equals zero at $A_T = mC/m_0$, which is estimated from a linear least-squares fit of F_1 against m. Once this estimate of A_T has been calculated, Equation (A.7) can be rearranged to calculate an estimate of $E°$ at each titration point by Equation (A.10):

$$E° = E - \left(\frac{RT}{F}\right)\ln\left(\frac{-m_0 A_T + mC}{m_0 + m}\right)$$ (A.10)

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

A non-linear least-squares calculation is then used to refine these values of A_T and $E°$. However, rather than adjusting $E°$ directly, it is convenient to define a multiplier by Equation (A.11):

$$f = \frac{[\text{H}^+]}{[\text{H}']}$$

(A.11)

where estimates of [H$^+$] ([H$'$]) are computed from the initial estimate of $E°$ $\left(E°'\right)$ by Equation (A.12):

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

(A.12)

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

Equation (A.6) is thus rewritten as

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

(A.13)

The values of F_T and K_F used are from Reference [9]. In Equation (A.13), the product, $f[\text{H}']$, represents the total hydrogen ion concentration, and $f[\text{H}']/Z$ the free hydrogen concentration, where $Z = (1 + S_T/K_S)$, and thus

$$[\text{H}^+]_F = \frac{[\text{H}^+]}{Z} = \frac{[\text{H}^+]}{\left(1 + S_T/K_S\right)}$$

(A.14)

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

The actual data fitting is performed using a non-linear least-squares routine. Equation (A.13) is used to define a vector of residuals (i.e. the extent to which the left hand side differs from 0), and the software then minimises the sum-of-squares of these residuals by adjusting the parameters, f and A_T. During this procedure, care is taken to ensure that the initial and final titration points of the data set processed are those for which the calculated pH ($-\lg[\text{H}^+]$) lies the closest to the values 3,5 and 3,0, respectively. Points that lie outside this region are excluded from the calculation.

This choice of pH range is appropriate for the following reasons. If there is some bicarbonate present, it will be a negligible amount ($< 0,5$ μmol kg^{-1}) even at the highest pH used (3,5) and will be still less at the lower values of pH. Furthermore, at values of pH lower than 3,0, the simple Nernst equation no longer holds true, as the liquid junction potential for a pH cell is a function of hydrogen ion concentration (~30 mV/mol-H$^+$ kg^{-1}; see Reference [10]); in addition, the effect of uncertainties in K_S become more problematic at low pHs.

A.2.5 Example of calculation

A.2.5.1 Test data set

A.2.5.1.1 Sample titration data

See 8.2.1.1 and Table 1.

A.2.5.1.2 Calculation process

K_S, K_F, S_T and F_T, are calculated as a function of salinity, S, and temperature, T, given in Reference [9].

$$K_S \quad = \quad 0{,}101\ 0$$

$$K_F \quad = \quad 2{,}987 \times 10^{-3}$$

$$S_T \quad = \quad 2{,}736 \times 10^{-2}\ \text{mol kg}^{-1}$$

$$F_T \quad = \quad 6{,}6 \times 10^{-5}\ \text{mol kg}^{-1}$$

The mass of titrant acid, m, is calculated from V and ρ_{acid} at each titration point.

For example, at $V = 4{,}000$ ml, $m = 4{,}096$ g.

Function (A.9) can be calculated from m_0, m, E, R, T, and F at each titration point.

For example, at $V = 4{,}000$ ml, $F_1 = 4{,}503 \times 10^5$.

From a linear least-squares fit of F_1 against m, an intercept of m can be estimated at $F_1 = 0$.

At $F_1 = 0$, $m = 3{,}1618$ g.

The function has a zero at $A_T = mC/m_0$, then $A_T^{'}$ can be estimated from m at $F_1 = 0$.

$$A_T^{'} = 2\ 263{,}54\ \mu\text{mol kg}^{-1}.$$

At each titration point, E° can be calculated from $A_T^{'}$ using Equation (A.10). These values are averaged to obtain the initial estimate of E° $\left(E^{\circ\prime}\right)$.

$$E^{\circ\prime} = 0{,}394\ 28\ \text{V}$$

From Equation (A.12), [H'] is estimated at each titration point.

For example, at $V = 4{,}000$ ml, [H'] = $6{,}493 \times 10^{-4}$ mol kg^{-1}.

Then, the left hand side of Equation (A.13) can be calculated at each titration point substituting initial values $A_T = A_T^{'}$ and $f = 1{,}0$.

For example, at $V = 4{,}000$ ml, the left hand side of Equation (A.13) is equal to $6{,}692 \times 10^{-6}$ mol kg^{-1}.

The computational software minimises the sum of squares of these residuals (i.e. the extent to which the left hand side differs from 0) by adjusting the parameters f and A_T. Then, the following results are obtained.

$$f \quad = \quad 0{,}995\ 32, \text{ then } E^\circ = 0{,}394\ 401\ \text{V}$$

$$A_T \quad = \quad 2\ 260{,}10\ \mu\text{mol kg}^{-1} \quad \text{alkalinity of sample (final result)}$$