

SOP 3b

Determination of total alkalinity in sea water using an open-cell titration

1. Scope

In this method, an open-cell, potentiometric titration procedure used to determine total alkalinity in sea water is described. The results are expressed as moles per kilogram of sea water. The method is suitable for assaying oceanic levels of total alkalinity (2000–2500 $\mu\text{mol kg}^{-1}$). Lower values may be encountered in coastal and surface polar waters. This method should be suitable for the lower range with a smaller initial acid addition.

2. Terms and definitions

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 $K \leq 10^{-4.5}$ 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, 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 when studying open ocean water; they may, however, be significant in anoxic environments.

3. Principle

A known amount of sea water is placed in an open cell where it is titrated with a solution of hydrochloric acid in a two-stage titration. The sample of sea water is first acidified to a pH between 3.5 and 4.0 with a single aliquot of titrant. The solution is then stirred for a period of time to allow for the escape of CO_2 that has evolved. The titration is continued until a pH of about 3.0 has been reached.

The acid is made up in a sodium chloride background to approximate the ionic strength of sea water so as to maintain approximately constant activity coefficients during the titration. The use of an open cell allows one to assume, in subsequent data processing, that the total dissolved inorganic carbon (and so the amount of residual bicarbonate ion) is approximately zero in the pH region of 3.0 to 3.5. The progress of the titration is monitored using a pH glass electrode/reference electrode cell, and the total alkalinity is computed from the titrant volume and e.m.f. measurements using a non-linear least-squares approach that corrects for the reactions with sulfate and fluoride ions.

4. Apparatus

4.1 Measurement of sample size

- Calibrated balance to weigh¹ 200 g to within 0.01 g,
- 125 cm³ plastic screw-cap bottle with cap.

4.2 Titration cell assembly

- 250 cm³ capacity jacketed beaker with 2¼ inch (~ 6 cm) internal diameter;
- Calibrated thermometer readable to 0.01°C. This is used to confirm that the solution temperature remains constant during the titration and to provide the value of solution temperature for use in subsequent calculations;
- Thermostat bath capable of maintaining temperature to better than ± 0.05°C;
- Magnetic stirrer with a 1½ inch × 5/16 inch (~ 4 cm × 0.8 cm) stir bar;
- Holder for burette tip, electrode, and thermometer.

4.3 E.M.F. measuring assembly

- Digital voltmeter readable to 0.00001 V;
- High-impedance voltage follower amplifier system. The system is used to buffer the e.m.f. of the combination pH glass electrode/reference electrode cell so that it can be measured accurately using a digital voltmeter²;
- Combination pH glass electrode/reference electrode cell^{3,4}.

¹ Because weighing on a balance can not be done aboard ship, volume-based methods can be used as a substitute, *e.g.*, a properly calibrated (see SOP 12), water-jacketed pipette.

² A custom made amplifier, based on an operational amplifier obtained from Burr-Brown (#9323), is satisfactory. A digital pH meter (± 0.1 mV) can be used instead of a digital voltmeter and voltage-follower amplifier, but there will be inferior measurement precision.

³ 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 even be necessary to replace a new electrode.

⁴ Radiometer Model PHC2402 (#945-505), together with a Type 7 to BNC adaptor (Radiometer #617-801), permits connection to a voltage-follower amplifier.

4.4 Burette assembly

- Metrohm Dosimat[®] Model 665 burette base with keypad;
- Metrohm Dosimat[®] 5 cm³ burette exchange unit;
- Metrohm Dosimat[®] anti-diffusion tip;
- Calibrated digital thermometer readable to 0.1°C (used to measure acid temperature).

A highly reproducible burette (± 0.001 cm³) is necessary to obtain the highest quality results. Unfortunately, although the burette specified is capable of the high reproducibility needed, its accuracy is typically not as good, and the burette system must be calibrated prior to use.

4.5 Air flow to purge carbon dioxide

- A pump whose flow rate can be controlled to provide *ca.* 100 ml min⁻¹;
- A flowmeter to indicate gas flow rate (*ca.* 100 ml min⁻¹);
- Tubing leading to a bubbler in the cell.

4.6 Miscellaneous

4.6.1 Sample transfer device

This device was designed to allow a sample to be dispensed from a bottle with a greased, ground-glass joint in a manner that ensures that grease is not transferred to the weighing bottle. The system we use comprises a rubber stopper (#8–9) through which two rigid plastic tubes are skewered; the rubber stopper is secured to the sample bottle with a metal clamp. One of the tubes is long enough to make contact with the bottom of a 500 cm³ sample bottle, and the other tube protrudes about ¼ inch (~ 0.6 cm) below the stopper. The shorter tube is attached with about 20 inches (~ 50 cm) of Tygon[®] tubing to a rubber bulb, which is used to pressurize the system. The other tube is attached to a length of Tygon[®] tubing (*ca.* 18 inches (~ 45 cm)) and is closed with a pinch clamp. This tube is used to dispense the sample.

4.6.2 Basin for waste

5. Reagents/Supplies

- Calibrated titrant solution of concentration approximately 0.1 mol kg⁻¹ in hydrochloric acid and 0.6 mol kg⁻¹ in sodium chloride⁵,
- Wash bottle containing Milli-Q[®] deionized water,
- Kimwipes[®].

⁵ The hydrochloric acid titrant solution is calibrated with an accuracy of better than $\pm 0.02\%$ using a coulometric titration procedure. In addition, the density of this titrant solution must be known as a function of temperature with an accuracy of better than $\pm 0.02\%$.

6. Procedure

6.1 Apparatus set-up

Assemble the apparatus as shown in Figure 1.

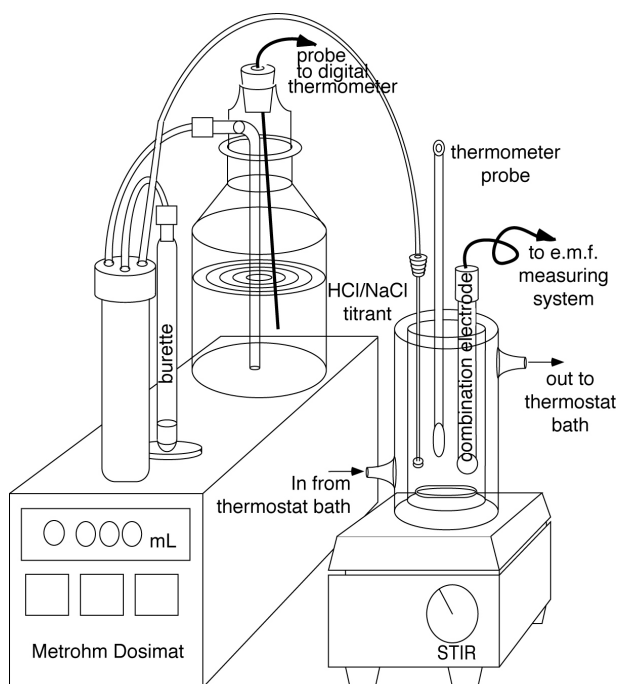


Fig. 1 Open-cell alkalinity measurement set-up.

- 6.1.1** Assemble the apparatus as shown in the diagram above. Use extra caution assembling the Dosimat[®] glass pieces and tubing. Make all connections finger tight, and do not over-tighten. The most common cause of leaks and bubbles is damaged threads and chipped glass.
- 6.1.2** Set the thermostat bath to 25°C.
- 6.1.3** Mix the hydrochloric acid titrant solution to ensure a consistent temperature and composition.
- 6.1.4** Ensure that the Dosimat[®] burette and tubing are thoroughly flushed with the titrant solution and that no air bubbles are present.

6.2 Titration set-up⁶

- 6.2.1** Thoroughly mix the contents of the sample bottle. Remove the stopper, and use a Kimwipe[®] to remove as much grease as possible. Dry the longer tube of the sample transfer device (section 4.6); insert it into the

⁶ If the system has not been used for some hours, it may be necessary to condition the pH glass-reference electrode system. Simply use it for one or more titrations where the result(s) will be discarded. (This first measurement is often a little lower than the correct value.)

sample bottle, securing it with the metal clamp. Pressurize the bottle, and flush the tubing with about 20 cm³ of sample (discard to waste).

- 6.2.2 Fill a 125 cm³ plastic bottle with sample, cap tightly, and weigh; record the weight to 0.01 g.
- 6.2.3 Carefully pour the sample into the clean 250 cm³ jacketed beaker containing a 1½ inch (~ 4 cm) stir bar.
- 6.2.4 Recap the plastic bottle, and record the empty weight. The sample weight is obtained by difference in the two.
- 6.2.5 Begin stirring.
- 6.2.6 Position the holder assembly over the beaker so the four parts are well into the sample without interfering with the stir bar.

6.3 Titration procedure

- 6.3.1 With slow stirring, dispense enough hydrochloric acid to bring the sample to a pH just above 3.5 (~ 3 cm³).⁷
- 6.3.2 Increase the stirring rate until it is vigorous but not splashing. Turn on air flow through the solution.
- 6.3.3 Leave the acidified sample stirring for at least 6 minutes to allow for CO₂ degassing.
- 6.3.4 Titrate the sample using 0.05 cm³ increments to a final pH of *ca.* 3.0 (~ 20 increments). After each addition, record the total dispensed volume to 0.001 cm³, the e.m.f. to 0.00001 V and the sample temperature to 0.01°C.

6.4 Cleanup after each titration

- 6.4.1 Once the titration is complete, remove the holder assembly from the beaker, and position it over the waste basin.
- 6.4.2 Purge the remaining acid in the burette (from the previous titration) into the waste basin, and refill the burette⁸. (To prevent bubbles from forming in the burette and tubing, vent the acid bottle during each filling of the burette.)
- 6.4.3 Record the hydrochloric acid solution temperature to 0.1°C.
- 6.4.4 Rinse the acid tip, electrode, and thermometer thoroughly with water from the wash bottle. Gently touch-dry with Kimwipes[®].
- 6.4.5 Pour the spent sample into the waste basin. Use the wash bottle to rinse the beaker and stir bar three times. Thoroughly dry the beaker and stir bar with Kimwipes[®], and return the stir bar to the beaker.

⁷ The amount of acid added will depend on the approximate alkalinity of the sample. Typically, this is known well enough to allow estimation of the initial acid addition.

⁸ Purging the burette is a precautionary measure that is not universally used. It is intended to prevent contamination of the acid in the burette tip.

6.5 Cleanup for system storage

If the apparatus will be left out overnight, leave the burette tip, thermometer, and electrode in the last solution titrated. If no more samples will be run for 2 days or longer, clean up the apparatus in the following manner:

- 6.5.1 Cover the clean, dry beaker and stir bar to protect them from dust.
- 6.5.2 Disconnect the acid bottle, and seal it with a lightly greased, ground glass stopper⁹.
- 6.5.3 Use Milli-Q[®] water to thoroughly rinse the glass piece from the acid bottle and the thermometers, then set it out to dry in a place protected from dust.
- 6.5.4 Refill the burette with air.
- 6.5.5 Remove the burette and plunger, and thoroughly rinse with Milli-Q[®] water.
- 6.5.6 Replace the burette, and dispense 5 cm³ to purge any acid remaining in the tubing.
- 6.5.7 As the burette refills, submerge the flexible tubing end (goes to the acid bottle) in a beaker of Milli-Q[®] water so that the burette is filled with Milli-Q[®] water.
- 6.5.8 Again, dispense 5 cm³ and fill the burette with Milli-Q[®] water to flush out all the acid.
- 6.5.9 Finally, refill the burette with air, and purge the tubing of all remaining liquid.
- 6.5.10 Disconnect the burette, and set it to dry protected from dust.
- 6.5.11 Rinse the outside of the acid tip, and place it in the test tube holder.
- 6.5.12 Cover the Dosimat[®] valve and all tubing with a plastic bag.
- 6.5.13 Rinse the electrode, cover the filling hole, and place it in a suitable storage solution in an airtight container.
- 6.5.14 Turn off all instruments.

7. Calculation and expression of results

7.1 Introduction

The titration data can be processed using an Excel[®] spreadsheet program. Points from the pH region 3.0 to 3.5 are treated using an approach in which the equivalence point is determined using a 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 sulfuric acid and hydrogen fluoride formation.

⁹ A screw cap with a Teflon[®] liner, as is provided with Dosimat[®] bottles, may also be used.

7.2 Derivation of basic equations

The defining equation for total alkalinity is used to specify a proton condition corresponding to this equivalence point:

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

(Note that 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

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

The initial analytical concentration of hydrogen ion in the solution is thus the negative of the total alkalinity. After a mass m of acid¹⁰ with concentration C (mol kg-soln⁻¹) has been added to a mass m_0 of sample,

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

This expression can be equated to the previous expression for C_{H} :

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

Equation (5) is the basis of the computations involved in this procedure; however, as only pH data in the range 3.0–3.5 are used, and as the CO₂ generated by the reaction with the acid titrant is lost to the atmosphere, the majority of these terms can be ignored (Dickson *et al.*, 2003). Hence, (5) can be reduced to

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

7.3 Computational procedures¹¹

Equation (6) is used to estimate A_{T} from titration data by means of a non-linear least-squares procedure. First, it is necessary to start with reasonable estimates

¹⁰ Typically, acid is added by volume, and its density is known accurately. In this procedure, the acid temperature is monitored carefully, and the appropriate density is estimated from laboratory measurements of the acid density as a function of temperature.

¹¹ The values used for R and F , the functions used for the acid dissociation constants, K_{S} and K_{F} , and the expressions for the total concentrations, S_{T} and F_{T} , are given in Chapters 2 and 5.

for A_T and E° so as to ensure convergence. A simple Gran approach is used for this. Equation (6) is approximated by

$$\frac{-m_0 A_T + m C}{m_0 + m} \approx [\text{H}^+] = \exp\left(\frac{E - E^\circ}{RT/F}\right) = k \exp\left(\frac{E}{RT/F}\right) \quad (7)$$

where $[\text{H}^+]$ is the “total” hydrogen ion concentration defined as¹²

$$[\text{H}^+] = [\text{H}^+]_F (1 + S_T / K_S) \approx [\text{H}^+]_F + [\text{HSO}_4^-]. \quad (8)$$

In this expression, S_T is the total sulfate concentration, and K_S is the acid dissociation constant of $[\text{HSO}_4^-]$. Equation (7) is rearranged to give the Gran function

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

This function is linear in m and has a zero at $A_T = mC/m_0$ that can be estimated from a linear least-squares fit of F_1 against m .

Once the A_T estimate has been obtained, (7) is rearranged to calculate an estimate of E° at each titration point:

$$E^\circ = E - \left(\frac{RT}{F}\right) \ln\left(\frac{-m_0 A_T + m C}{m_0 + m}\right). \quad (10)$$

These values are averaged to obtain an 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

$$f = [\text{H}^+]/[\text{H}'] \quad (11)$$

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

$$[\text{H}'] = \exp\left(\frac{E - E^\circ}{RT/F}\right), \quad (12)$$

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

Equation (6) is thus rewritten as

$$A_T + \left(\frac{S_T}{1 + K_S Z / (f [\text{H}'])}\right) + \left(\frac{F_T}{1 + K_F / (f [\text{H}'])}\right) + \left(\frac{m_0 + m}{m_0}\right) \left(\frac{f [\text{H}']}{Z}\right) - \left(\frac{m}{m_0}\right) C = 0 \quad (13)$$

¹² A comparison of (7) and (8) with (6) shows that the term $[\text{HF}]$ has been neglected for this initial stage of the calculation. It is, however, included in the non-linear least-squares evaluation.

where F_T is the total fluoride concentration, and K_F is the acid dissociation constant of [HF]. In this equation, the product, $f [H']$, represents the total hydrogen ion concentration and $f [H']/Z$ the free hydrogen ion concentration, where $Z = (1 + S_T / K_S)$, and thus

$$[H^+]_F = [H^+]/Z = [H^+]/(1 + S_T / K_S). \quad (14)$$

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

The actual data fitting is performed using a non-linear least-squares routine. Equation (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 minimizes the sum-of-squares of these residuals by adjusting the parameters, f and A_T . During this procedure, care is taken to ensure that the initial and final titration points of the data set processed are those for which the calculated pH lies the closest to the values 3.5 and 3.0, respectively. Points that lie outside this region are excluded from the calculation.

The choice of pH range is appropriate for the following reasons. If there is some bicarbonate present, it will be a negligible amount ($< 0.5 \mu\text{mol kg}^{-1}$) even at the highest pH used (3.5) and will be still less at the lower pH. Furthermore, at 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 ($\sim 30 \text{ mV/mol-H}^+ \text{ kg}^{-1}$); in addition, the effect of uncertainties in K_S becomes more problematic at low pHs.

7.4 Example calculation

An example of a complete set of titration data for a sea water sample, together with the resulting calculated values for A_T and E° , is given.

Sample information

Mass of sea water 140.32 g
Salinity 33.923

Hydrochloric acid titrant information

Concentration 0.10046 mol kg-soln⁻¹
Density 1.02393 g cm⁻³

Titration temperature

24.25°C

Titration values

V / cm^{-3}	E / V
3.500	0.18607
3.550	0.18893
3.600	0.19150
3.650	0.19384
3.700	0.19601
3.750	0.19800
3.800	0.19986
3.850	0.20159
3.900	0.20321
3.950	0.20473
4.000	0.20617
4.050	0.20753
4.100	0.20880
4.150	0.21002
4.200	0.21120
4.250	0.21233
4.300	0.21341
4.350	0.21446
4.400	0.21545
4.450	0.21641
4.500	0.21732
4.550	0.21820*

Titration results

$$A_T = 2260.06 \mu\text{mol kg-soln}^{-1}$$

$$E^\circ = 0.394401 \text{ V}$$

The point marked with an asterisk was excluded from the final processing as the calculated pH is outside the range 3.0–3.5.

For the most accurate work, a further minor correction may need to be made to compute the total alkalinity in the original sea water sample: for the dilution by mercuric chloride when the sample was collected¹³,

$$A_T = 1.0002 \times A_T' \quad (15)$$

8. Quality assurance

For general principles of analytical quality control, see Chapter 3.

8.1 Target control limits

8.1.1 Introduction

The various control limits outlined below are necessary to ensure that the accuracy and precision of the results are adequate for the purpose of certifying

¹³ The value 1.0002 assumes that saturated mercuric chloride was used (0.02% by volume—SOP 1. If a 50% saturated solution was used to preserve the sample, the appropriate correction factor is 1.0004.

reference materials. The targets specified to meet these requirements are a precision (1 SD) of better than $1 \mu\text{mol kg}^{-1}$ and an overall bias of less than $2 \mu\text{mol kg}^{-1}$.

8.1.2 Quality of individual titrations

For each titration, quality can be assessed by examining the standard deviation of the final E° value ($s(E^\circ)$). This is typically less than 0.04 mV for the apparatus used here (*i.e.*, measuring E to within 0.01 mV).

8.1.3 Analysis of a sea water reference material

A certified reference material should be analyzed regularly¹⁴. Plot the results obtained on a property control chart (see SOP 22). Expect a standard deviation on the order of $1 \mu\text{mol kg-soln}^{-1}$ or less¹⁵.

8.1.4 Duplicate analyses

A duplicate analysis should be made on each sample (including the certified reference material). Plot the difference between each pair of analyses on a range control chart (see SOP 22). Expect a standard deviation on the order of $0.5 \mu\text{mol kg-soln}^{-1}$.

8.2 Instrument calibration

Ensure that the calibrations of the various instruments used in this procedure are confirmed at least once a year, though the effects of sudden changes should show up on the control charts described above.

9. Bibliography

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- Gran, G. 1952. Determination of the equivalence point in potentiometric titrations. Part II. *Analyst* **77**: 661–670.
- Jones, F.E. and Harris, G.L. 1992. ITS-90 density of water formulation for volumetric standards calibration. *J. Res. Natl. Inst. Stand. Technol.* **97**: 335–340.

¹⁴ Suitable reference materials are 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).

¹⁵ If the analyses on a particular day are problematic, the electrode behavior is the usual suspect.

Annexe

Dosimat[®] burette calibration procedure

1. Scope and field of application

The goal of this procedure is to calibrate a Metrohm Dosimat[®] 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 reweighed. 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[®] burette base unit,
- Metrohm Dosimat[®] exchangeable burette (5 cm³ capacity),
- 15 × 5 cm³ capacity screw-capped glass bottles¹⁶,
- Analytical balance readable to 0.0001 g,
- Calibrated thermometer readable to 0.1°C,
- Waste container.

4. Reagents

- Deionized water (Milli-Q[®] quality).

5. Procedure

- 5.1** Fill the Dosimat[®] reservoir with deionized water and allow to equilibrate to room temperature.

¹⁶ 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[®] 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[®] 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 cm³ of water into a weighed glass bottle¹⁷. 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:

$$w(\text{H}_2\text{O}) = w(\text{filled container}) - w(\text{empty container}). \quad (16)$$

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

$$m(\text{H}_2\text{O}) = w(\text{H}_2\text{O}) \left[1 + 0.0012 \left(\frac{1}{\rho(\text{H}_2\text{O}, t)} - \frac{1}{\rho(\text{weights})} \right) \right]. \quad (17)$$

The volume dispensed at the temperature noted (t) is

$$V(t) = m(\text{H}_2\text{O}) / \rho(\text{H}_2\text{O}, t). \quad (18)$$

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

$$\begin{aligned} \rho_w / (\text{kg m}^{-3}) = & 999.84847 + 6.337563 \times 10^{-2} (t / ^\circ\text{C}) \\ & - 8.523829 \times 10^{-3} (t / ^\circ\text{C})^2 + 6.943248 \times 10^{-5} (t / ^\circ\text{C})^3 \\ & - 3.821216 \times 10^{-7} (t / ^\circ\text{C})^4 \end{aligned} \quad (19)$$

where t is the temperature on ITS 90¹⁸. To achieve an accuracy of 1 part in 10⁴, t must be known to within 0.5°C.

¹⁷ This procedure is designed to provide a series of calibration points corresponding to dispensing from 0.000 cm³ on the burette.

¹⁸ 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[®] system used in our laboratory.

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

Nominal volume, V^* / cm^3	Dispensing temperature, $t / ^\circ\text{C}$	Weight dispensed, w / g	Volume dispensed, V / 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 ΔV obtained are plotted against the nominal volume (see Figure 2), *and* are fitted to provide a “calibration” function—typically a polynomial in $V(\text{nominal})$:

$$V = V^* [1 + aV^* + b(V^*)^2]. \quad (20)$$

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

$$V = V^*, \quad (21)$$

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).

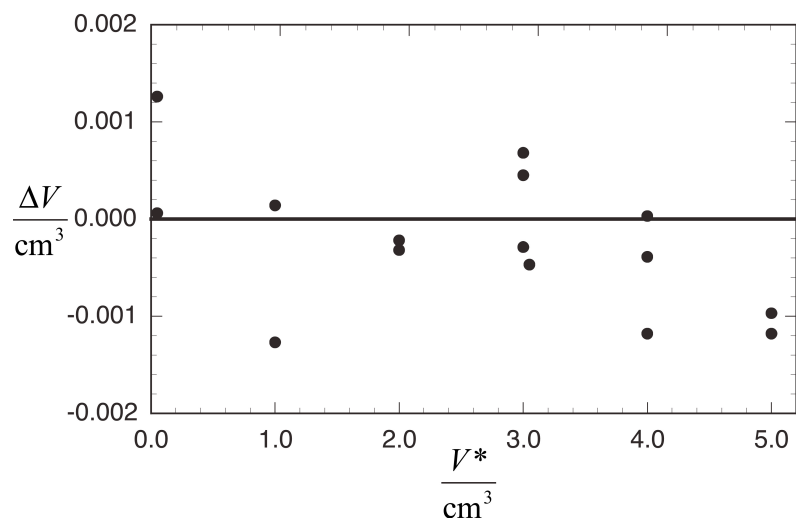


Fig. 2 Plot of $\Delta V = V - V^*$ against V^* for the calibration results for titration system 1 (December 12, 1996).

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).