Handbook of Methods for the Analysis of the Various Parameters of the Carbon Dioxide System in Sea Water.

Prepared for the U. S. Department of Energy,
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Global survey of carbon dioxide in the oceans.

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Acknowledgments

The procedures and advice contained in this handbook result from various meetings, conversations and written materials provided by the following persons; where a particular person contributed substantially to a particular procedure, the SOP number is identified after their name.

1

Introduction to the handbook

The collection of extensive, reliable, oceanic carbon data is a key component of the Joint Global Ocean Flux Study (JGOFS). A portion of the U. S. JGOFS oceanic carbon dioxide measurements will be made during the World Ocean Circulation Experiment (WOCE) Hydrographic Program with funding from the U. S. Department of Energy (DOE) Special Research Grant Program 89-7A: Global survey of carbon dioxide in the oceans. A science team has been formed from the investigators supported by the DOE to plan and co-ordinate the various activities needed to produce high quality oceanic carbon dioxide measurements under this program.

This handbook was prepared at the request of, and with the active participation of, that science team. The procedures detailed in the following pages have been agreed on by the members of the science team and describe well tested-methods. They are intended to provide standard operating procedures (SOPs), together with an appropriate quality control plan, for measurements made as part of this survey. These are not the only measurement techniques in use for the parameters of the oceanic carbon system; however, they do represent the current state-of-the-art for ship-board measurements.

In the end, we hope that this handbook can serve widely as a clear and unambiguous guide to other investigators who are setting up to analyze the various parameters of the carbon dioxide system in sea water. We envision it as an evolving document, updated where necessary, much in the fashion of a computer manual. The editors will welcome comments and suggestions for use in preparing future revisions.

The procedures described here are not simply descriptions of a particular method in current use in a single laboratory, but rather provide standard operating procedures which have been written in a fashion that will—we trust—allow any chemist to implement the method successfully. On occasion some lack of consensus

about the best approach still remains; these areas are identified in the footnotes to the various procedures amongst other hints and tips. We are in the process of conducting collaborative studies of the various methods described here to assess whether or not such differences are significant. The results of such studies will be cited in this handbook once they have been reported.

In addition to the written procedures, general information about the solution chemistry of the carbon dioxide system in sea water has been provided (Chapter 2) together with recommended values for the physical and thermodynamic data needed for certain computations (Chapter 5). This information is needed to understand certain aspects of the procedures and users of this handbook are advised to study Chapter 2 carefully. General advice about appropriate quality control measures has also been included (Chapter 3).

The SOPs (Chapter 4) are numbered. Numbers less than 10 are reserved for procedures describing sampling and analysis, numbers 11–20 for procedures for calibration, *etc.*, and numbers 21 and upward for procedures for computations, quality control, *etc.* This scheme allows for the addition of further SOPs in the future. Each of the procedures has been marked with a date of printing and a version number. When citing a particular SOP in a report or technical paper, we recommend stating the version number of the procedure used. We conceive of this handbook as being expanded and updated; thus the version number identifies unambiguously the exact procedure that is being referred to.

2

Solution chemistry of carbon dioxide in sea water

1. Introduction

This chapter outlines the chemistry of carbon dioxide in sea water so as to provide a coherent background for the rest of this Handbook. The following sections lay out the thermodynamic framework required for an understanding of the solution chemistry; the thermodynamic data needed to interpret field and laboratory results are presented in Chapter 5 of this handbook.

2. Reactions in solution

The reactions which take place when carbon dioxide dissolves in water can be represented by the following series of equilibria:

$$CO_2(g) = CO_2(aq) \quad , \tag{1}$$

$$CO_2(aq) + H_2O(l) = H_2CO_3(aq) \quad , \tag{2}$$

$$H_2CO_3(aq) = H^+(aq) + HCO_3^-(aq) \quad , \tag{3}$$

$$HCO_3^-(aq) = H^+(aq) + CO_3^{2-}(aq) \quad ; \tag{4}$$
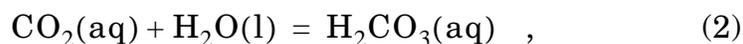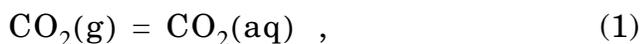
the notations (g), (l), (aq) refer to the state of the species, *i. e.* a gas, a liquid or in aqueous solution respectively. Unfortunately, it is difficult to distinguish between the species $CO_2(aq)$ and $H_2CO_3(aq)$ by analytical means. It is thus usual to lump the concentrations of $CO_2(aq)$ and $H_2CO_3(aq)$ together and to express this sum as the concentration of a hypothetical species, $CO_2^*(aq)$.

Reactions (1), (2) and (3) are redefined in terms of this species:

$$CO_2(g) = CO_2^*(aq) \quad , \tag{5}$$

$$CO_2^*(aq) + H_2O(l) = H^+(aq) + HCO_3^-(aq) \quad . \tag{6}$$
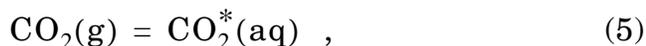
The equilibrium relationships between the concentrations of

these various species can then be written as:

$$K_0 = [CO_2^*] \big/ f(CO_2) \quad , \tag{7}$$

$$K_1 = [H^+][HCO_3^-] \big/ [CO_2^*] \quad , \tag{8}$$

$$K_2 = [H^+][CO_3^{2-}] \big/ [HCO_3^-] \quad . \tag{9}$$

In these equations, $f(CO_2)$ is the fugacity of carbon dioxide in the gas phase and brackets represent total stoichiometric concentrations[*] of the particular chemical species enclosed. These equilibrium constants are functions of the temperature, pressure and composition (salinity) of the solution (sea water) and have been measured on a variety of occasions (see Chapter 5).

3. Fugacity

The fugacity of carbon dioxide is not the same as its partial pressure—the product of mole fraction and total pressure, $x(CO_2)p$ —but rather takes account of the non-ideal nature of the gas phase. The fugacity of a gas such as CO_2 can be determined from a knowledge of its equation of state:

$$f(CO_2) = x(CO_2)p \, \exp\left(\int_0^p \frac{(V(CO_2) - RT/p')\mathrm{d}p'}{RT} \right) \quad . \tag{10}$$

The equation of state of a real gas such as CO_2, either alone or in a mixture, can be represented by a virial expression:

$$\frac{pV(CO_2)}{RT} = 1 + \frac{B(x, T)}{V(CO_2)} + \frac{C(x, T)}{V(CO_2)^2} + \dots \tag{11}$$

This equation, truncated after the second term, is usually adequate to represent p–V–T properties at pressures up to a few atmospheres (Dymond & Smith, 1980).

It is known from statistical mechanics that the virial coefficient $B(x, T)$ results from pair-wise interactions in the gas phase (Guggenheim, 1967); this property can be used to

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[*]　Strictly, equations (7) to (9) should be expressed in terms of activities rather than concentrations. However, as the activity coefficients are approximately constant for small amounts of reacting species in a background medium, these expressions are valid and correspond to "ionic medium" equilibrium constants based on a sea water medium.

estimate $B(x, T)$ for particular gas mixtures—such as CO_2 in air—from measurements on binary mixtures or from a model expression for the intermolecular potential energy function for the molecules concerned. The magnitude of the fugacity coefficient—the ratio between fugacity and partial pressure—is a function both of temperature and of gas phase composition (figure 1).
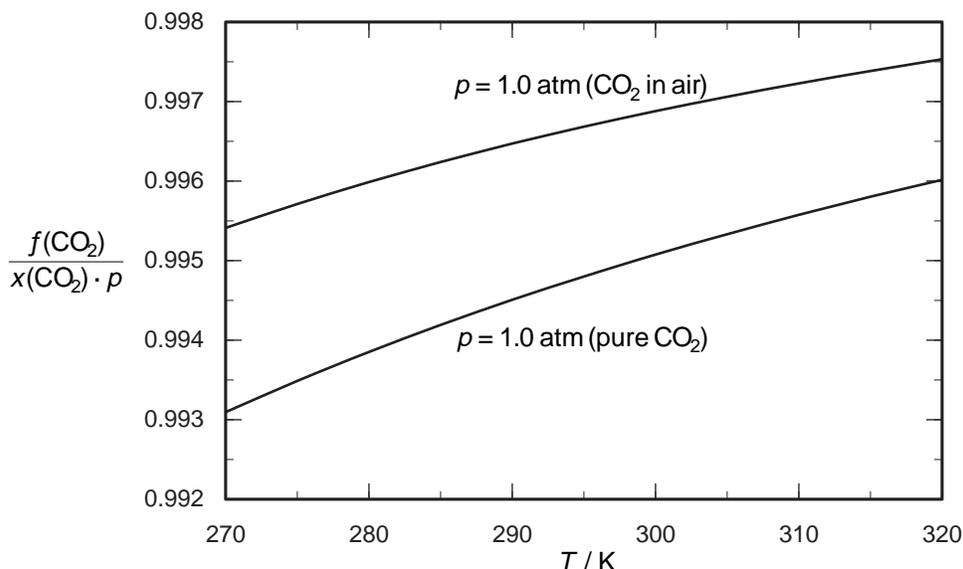
Figure 1. Variation of fugacity coefficient with temperature at 1 atm total pressure for pure CO_2 gas and for CO_2 in air: $x(CO_2) = 350 \times 10^{-6}$ (calculated using the procedure described in SOP 24 of this Handbook).

4. Analytical parameters of the CO_2 system

Unfortunately, the concentrations of the individual species of the carbon dioxide system in solution cannot be measured directly. There are, however, four parameters that can be measured. These are used together with ancillary information to obtain a complete description of the carbon dioxide system in sea water. Methods for determining each of these parameters are detailed in Chapter 4.

Total dissolved inorganic carbon. The total dissolved inorganic carbon in a sea water sample:

$$C_T = [CO_2^*] + [HCO_3^-] + [CO_3^{2-}] \quad , \qquad (12)$$

can be measured directly by acidifying the sample, extracting the CO_2 gas that is produced and measuring its amount.

Total alkalinity. The total alkalinity of a sample of sea water is a form of mass-conservation relationship for hydrogen ion. It is rigorously defined (Dickson, 1981) 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." Thus

$$A_T = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}]$$
$$+ 2[PO_4^{3-}] + [SiO(OH)_3^-] + [NH_3] + [HS^-] + \dots$$
$$- [H^+]_F - [HSO_4^-] - [HF] - [H_3PO_4] - \dots, \tag{13}$$

where 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. $[H^+]_F$ is the *free* concentration of hydrogen ion—see equation (14).

Fugacity of CO₂ in equilibrium with a sea water sample. This measurement typically requires a gas phase that is in equilibrium with a sea water sample at a known—measured—pressure and temperature. The concentration of CO_2 is then determined in that gas phase and the corresponding value of $f(CO_2)$—for that temperature—estimated from equation (10).

Total hydrogen ion concentration. Although the concept of a total hydrogen ion concentration is somewhat confusing—see Dickson (1984; 1993) for a detailed discussion of the various pH scales that have been used in sea water—it is needed to define acid dissociation constants accurately in sea water media (Dickson, 1990). Total hydrogen ion concentration is defined as

$$[H^+] = [H^+]_F (1 + S_T/K_S) \; ; \tag{14}$$

$[H^+]_F$ is the *free* concentration of hydrogen ion in sea water, S_T is the total sulfate concentration ($[HSO_4^-] + [SO_4^{2-}]$) and K_S is the acid dissociation constant for HSO_4^-. The approximation

$$[H^+] \approx [H^+]_F + [HSO_4^-] \tag{15}$$

only holds well at pH values above 4. (Note: pH = $-\log [H^+]$.)

Typically, the various equilibrium constants required to describe acid–base chemistry in sea water are measured in the laboratory (see Chapter 5 of this handbook for recommended values). In

addition, the total amounts of the various other (non-CO_2) acid/base systems in the sample of interest are usually known; either from the salinity—for conservative constituents such as borate, sulfate and fluoride—or from measurements—for constituents such as phosphate, silicate, ammonia or hydrogen sulfide. As a result, it is only necessary to know two parameters from the four above to have a complete description of the system—see Park(1969), Skirrow (1975) and the annexe to this chapter.

This practice assumes that our present knowledge about the nature, total concentrations and thermodynamic properties of all the possible acid-base species in sea water is complete. It is probably better at this stage to over-determine the system whenever possible, *i.e.* to measure more than two of these parameters on any given sample and to use the redundancy to confirm that the measurements fit with our understanding of the thermodynamics of acid–base processes in sea water.

5. References

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Annexe

Equations that describe the CO_2 system in sea water

The rank of the system of equilibrium equations that describes the acid–base chemistry of sea water—*i.e.* the number of linearly independent variables—is equal to the number of independent mass-conservation relationships plus the number of acid-base pairs considered (the number of dissociation constants). It is therefore possible to obtain a *complete* description of the carbon dioxide system in a sample of sea water at a particular temperature and pressure provided that the following information is known:

- the solubility constant for CO_2 in sea water, K_0,
- the equilibrium constants for each of the acid/base pairs that are assumed to exist in the solution,
- the total concentrations of all the non-CO_2 acid/base pairs,
- the values for at least two of the CO_2 related parameters: C_T, A_T, $f(CO_2)$, $[H^+]$.

Although the rank is determined by the chemical description of the system, the optimal choice of experimental variables is dictated by the nature of the problem being studied and remains at the discretion of the investigator.

Note that although each of the CO_2 related parameters are linearly independent, they are not orthogonal. For certain combinations there are limitations to the accuracy with which the other parameters can be predicted from the measured data. This results from error propagation through the equations presented here. Such errors result from all the experimentally derived information—including the various equilibrium constants. As a consequence it is usually better to *measure* a particular parameter directly using one of the methods detailed in Chapter 4 rather than to calculate it from other measurements, particularly if accurate value is needed for geochemical purposes.

When more than two of the CO_2 related parameters have been measured on a single sea water sample, it is possible to use the various possible pairs of parameters to compute the other redundant parameters and thus to assess the internal consistency of our knowledge of the system. Again, it is necessary to take all the sources of error into account when doing this. Alternately, one can describe the system independently of one or more of the dissociation constants for carbonic acid. Equations that allow each of these possibilities to be realized are derived here.

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

Mass-conservation equations:

$$C_T = [CO_2^*] + [HCO_3^-] + [CO_3^{2-}] \tag{A.1}$$

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

$$B_T = [B(OH)_3] + [B(OH)_4^-] \tag{A.3}$$

$$S_T = [HSO_4^-] + [SO_4^{2-}] \tag{A.4}$$

$$F_T = [HF] + [F^-] \tag{A.5}$$

$$P_T = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] \tag{A.6}$$

$$Si_T = [Si(OH)_4] + [SiO(OH)_3^-] \tag{A.7}$$

$$NH_{3\,T} = [NH_4^+] + [NH_3] \tag{A.8}$$

$$H_2S_T = [H_2S] + [HS^-] \tag{A.9}$$

Equilibrium constants:

$$K_0 = [CO_2^*]/f(CO_2) \tag{A.10}$$

$$K_1 = [H^+][HCO_3^-]/[CO_2^*] \tag{A.11}$$

$$K_2 = [H^+][CO_3^{2-}]/[HCO_3^-] \tag{A.12}$$

$$K_W = [H^+][OH^-] \tag{A.13}$$

$$K_B = [H^+][B(OH)_4^-]/[B(OH)_3] \tag{A.14}$$

$$K_S = [H^+]_F [SO_4^{2-}]/[HSO_4^-] \tag{A.15}$$

$$K_F = [H^+][F^-]/[HF] \tag{A.16}$$

$$K_{1P} = [H^+][H_2PO_4^-]/[H_3PO_4] \tag{A.17}$$

$$K_{2P} = [H^+][HPO_4^{2-}]/[H_2PO_4^-] \tag{A.18}$$

$$K_{3P} = [H^+][PO_4^{3-}]/[HPO_4^{2-}] \tag{A.19}$$

$$K_{Si} = [H^+][SiO(OH)_3^-]/[Si(OH)_4] \tag{A.20}$$

$$K_{NH3} = [H^+][NH_3]/[NH_4^+] \tag{A.21}$$

$$K_{H2S} = [H^+][HS^-]/[H_2S] \tag{A.22}$$

Table 2: Expression for the concentrations of the various
species in equation (A.2).

$$[HCO_3^-] = \frac{C_T K_1 [H^+]}{[H^+]^2 + K_1 [H^+] + K_1 K_2} \tag{A.23}$$

$$[CO_3^{2-}] = \frac{C_T K_1 K_2}{[H^+]^2 + K_1 [H^+] + K_1 K_2} \tag{A.24}$$

$$[B(OH)_4^-] = B_T / (1 + [H^+]/K_B) \tag{A.25}$$

$$[OH^-] = K_W / [H^+] \tag{A.26}$$

$$[H_3PO_4] = \frac{P_T [H^+]^3}{[H^+]^3 + K_{1P}[H^+]^2 + K_{1P}K_{2P}[H^+] + K_{1P}K_{2P}K_{3P}} \tag{A.27}$$

$$[H_2PO_4^-] = \frac{P_T K_{1P}[H^+]^2}{[H^+]^3 + K_{1P}[H^+]^2 + K_{1P}K_{2P}[H^+] + K_{1P}K_{2P}K_{3P}} \tag{A.28}$$

$$[HPO_4^{2-}] = \frac{P_T K_{1P}K_{2P}[H^+]}{[H^+]^3 + K_{1P}[H^+]^2 + K_{1P}K_{2P}[H^+] + K_{1P}K_{2P}K_{3P}} \tag{A.29}$$

$$[PO_4^{3-}] = \frac{P_T K_{1P}K_{2P}K_{3P}}{[H^+]^3 + K_{1P}[H^+]^2 + K_{1P}K_{2P}[H^+] + K_{1P}K_{2P}K_{3P}} \tag{A.30}$$

$$[SiO(OH)_3^-] = Si_T / (1 + [H^+]/K_{Si}) \tag{A.31}$$

$$[NH_3] = NH_{3\,T} / (1 + [H^+]/K_{NH3}) \tag{A.32}$$

$$[HS^-] = H_2S_T / (1 + [H^+]/K_{H2S}) \tag{A.33}$$

$$[H^+]_F = [H^+] / (1 + S_T/K_S) \tag{A.34}$$

$$[HSO_4^-] = S_T / (1 + K_S/[H^+]_F) \tag{A.35}$$

$$[HF] = F_T / (1 + K_F/[H^+]) \tag{A.36}$$

[H⁺] and A_T

The carbonate alkalinity (*i.e.* the contribution of carbonate species to the total alkalinity) is defined as

$$A_\text{C} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \quad . \tag{A.37}$$

The concentrations of the non-CO_2 species that contribute to A_T are calculated using the expressions given in table 2, thus

$$
\begin{aligned}
A_\text{C} = \ & A_\text{T} - [\text{B(OH)}_4^-] - [\text{OH}^-] - [\text{HPO}_4^{2-}] \\
& -2[\text{PO}_4^{3-}] - [\text{SiO(OH)}_3^-] - [\text{NH}_3] - [\text{HS}^-] \\
& + [\text{H}^+]_\text{F} + [\text{HSO}_4^-] + [\text{HF}] + [\text{H}_3\text{PO}_4] \, .
\end{aligned} \tag{A.38}
$$

Then from (A.11),

$$[\text{HCO}_3^-] = \frac{[\text{CO}_2^*]K_1}{[\text{H}^+]} \quad , \tag{A.39}$$

and from (A.12)

$$[\text{CO}_3^{2-}] = \left(\frac{[\text{CO}_2^*]K_1}{[\text{H}^+]}\right)\frac{K_2}{[\text{H}^+]} \quad . \tag{A.40}$$

Substituting into (A.37) and rearranging

$$[\text{CO}_2^*] = \frac{A_\text{C}[\text{H}^+]^2}{K_1([\text{H}^+]+2K_2)} \quad , \tag{A.41}$$

and hence

$$[\text{HCO}_3^-] = \frac{A_\text{C}[\text{H}^+]}{[\text{H}^+]+2K_2} \quad , \tag{A.42}$$

$$[\text{CO}_3^{2-}] = \frac{A_\text{C}K_2}{[\text{H}^+]+2K_2} \quad . \tag{A.43}$$

C_T is calculated from (A.1) and $f(\text{CO}_2)$ from (A.10):

$$f(CO_2) = [CO_2^*]/K_0 .$$
(A.44)

[H$^+$] and f(CO$_2$)

$[CO_2^*]$ is calculated from (A.10):

$$[CO_2^*] = K_0 f(CO_2) .$$
(A.45)

Thus, from (A.11) and (A.12),

$$[HCO_3^-] = \frac{K_0 K_1 f(CO_2)}{[H^+]} ,$$
(A.46)

$$[CO_3^{2-}] = \frac{K_0 K_1 K_2 f(CO_2)}{[H^+]^2} .$$
(A.47)

C_T is calculated from (A.1) and A_T from (A.2); $[HCO_3^-]$ and $[CO_3^{2-}]$ are given by (A.46) and (A.47), the remaining terms are calculated from the expressions given in table 2.

[H$^+$] and C_T

Equations (A.11) and (A.12) are rearranged and substituted into (A.1) to give

$$C_T = [CO_2^*]\left(1 + \frac{K_1}{[H^+]} + \frac{K_1 K_2}{[H^+]^2}\right) .$$
(A.48)

Thus

$$[CO_2^*] = \frac{C_T [H^+]^2}{[H^+]^2 + K_1 [H^+] + K_1 K_2} ,$$
(A.49)

$$[HCO_3^-] = \frac{C_T K_1 [H^+]}{[H^+]^2 + K_1 [H^+] + K_1 K_2} ,$$
(A.50)

$$[CO_3^{2-}] = \frac{C_T K_1 K_2}{[H^+]^2 + K_1 [H^+] + K_1 K_2} .$$
(A.51)

$f(CO_2)$ is calculated from (A.44) and A_T from (A.2); the various terms needed are calculated from the expressions given in table 2.

A_T and C_T

The easiest approach to using this pair of parameters is to rewrite (A.2)—the expression for A_T—in terms of total concentrations and $[H^+]$ (see table 2). The resulting equation is solved for $[H^+]$ using either a Newton-Raphson technique or a simple iterative approach; a suitable initial estimate for calculations involving ocean water is $[H^+] = 10^{-8}$.

Once $[H^+]$ has been calculated,

$$[HCO_3^-] = \frac{C_T K_1 [H^+]}{[H^+]^2 + K_1[H^+] + K_1 K_2} \quad , \tag{A.52}$$

$$[CO_3^{2-}] = \frac{C_T K_1 K_2}{[H^+]^2 + K_1[H^+] + K_1 K_2} \quad . \tag{A.53}$$

Hence

$$[CO_2^*] = [H^+][HCO_3^-]/K_1 \quad ; \tag{A.54}$$

$f(CO_2)$ is calculated from (A.44).

A_T and $f(CO_2)$

$[CO_2^*]$ is calculated from (A.10):

$$[CO_2^*] = K_0 f(CO_2) \quad . \tag{A.55}$$

Equations (A.11) and (A.12) are then rewritten as:

$$[HCO_3^-] = \frac{K_0 K_1 f(CO_2)}{[H^+]} \quad , \tag{A.56}$$

$$[CO_3^{2-}] = \frac{K_0 K_1 K_2 f(CO_2)}{[H^+]^2} \quad . \tag{A.57}$$

These terms are substituted into (A.2) together with the remaining terms from table 2. The resulting expression is solved for $[H^+]$ using either a Newton-Raphson technique or a simple iterative approach; a suitable initial estimate for ocean water is $[H^+] = 10^{-8}$. Once $[H^+]$ has been calculated, C_T is calculated from (A.1) using the final values obtained for $[HCO_3^-]$ and $[CO_3^{2-}]$.

C_T and $f(CO_2)$

For this calculation, it is convenient to define the constant

$$K = K_1/K_2 = \frac{[HCO_3^-]^2}{[CO_2^*][CO_3^{2-}]} \quad . \tag{A.58}$$

for the equilibrium process

$$CO_2^*(aq) + CO_3^{2-}(aq) + H_2O(l) = 2HCO_3^-(aq) \quad . \tag{A.59}$$
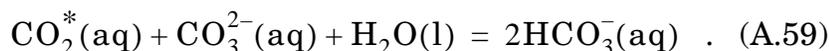
$[CO_2^*]$ is calculated from (A.10):

$$[CO_2^*] = K_0 f(CO_2) , \tag{A.60}$$

(A.45) is then combined with (A.58) and (A.1) to give

$$C_T = K_0 f(CO_2) + [HCO_3^-] + \frac{[HCO_3^-]^2}{KK_0 f(CO_2)} \quad . \tag{A.61}$$

Rearranging,

$$[HCO_3^-]^2 + KK_0 f(CO_2)[HCO_3^-]$$
$$+ KK_0 f(CO_2)(K_0 f(CO_2) - C_T) = 0 . \tag{A.62}$$

The solution is[*]

$$[HCO_3^-] = \frac{-KK_0 f(CO_2)}{2}$$
$$+ \frac{\sqrt{(KK_0 f(CO_2))^2 - 4(KK_0 f(CO_2))(K_0 f(CO_2) - C_T)}}{2} \tag{A.63}$$

and

$$[CO_3^{2-}] = C_T - [CO_2^*] - [HCO_3^-] \quad . \tag{A.64}$$

$[H^+]$ is calculated from (A.11)

$$[H^+] = \frac{K_1[CO_2^*]}{[HCO_3^-]} ; \tag{A.65}$$

A_T from (A.2): the various terms needed are calculated from the expressions given in table 2.

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[*] The alternate solution implies that $[HCO_3^-] < 0$.

[H⁺], A_T and C_T

The concentrations of the non-CO_2 species that contribute to A_T are calculated using the expressions given in table 2. The carbonate alkalinity, A_C, is then calculated from (A.38). Equations (A.1), (A.11) and (A.37) can then be combined to give

$$2C_T - A_C = [CO_2^*]\left(2 + \frac{K_1}{[H^+]}\right) \quad . \tag{A.66}$$

Hence

$$[CO_2^*] = \frac{[H^+](2C_T - A_C)}{2[H^+] + K_1} \quad , \tag{A.67}$$

$$[HCO_3^-] = \frac{K_1(2C_T - A_C)}{2[H^+] + K_1} \quad , \tag{A.68}$$

$$[CO_3^{2-}] = A_C - C_T + [CO_2^*]$$

$$= \frac{[H^+]A_C + K_1(A_C - C_T)}{2[H^+] + K_1} \quad . \tag{A.69}$$

An expression for $[CO_2^*]$ can also be derived in terms of K_2:

$$[CO_2^*] = C_T - [HCO_3^-] - [CO_3^{2-}] \quad . \tag{A.70}$$

$[HCO_3^-]$ and $[CO_3^{2-}]$ are given by (A.42) and (A.43), thus

$$[CO_2^*] = C_T - \frac{A_C([H^+] + K_2)}{[H^+] + 2K_2} \quad . \tag{A.71}$$

In both of these cases $f(CO_2)$ is calculated from (A.10).

[H⁺], A_T and $f(CO_2)$

The concentrations of the contributions of the various non-CO_2 species to A_T are calculated using the expressions given in table 2. A_C is calculated from (A.38). Then, from (A.10)

$$[CO_2^*] = K_0 f(CO_2) \quad . \tag{A.72}$$

and from (A.11)

$$[HCO_3^-] = \frac{K_0 K_1 f(CO_2)}{[H^+]} \quad . \tag{A.73}$$

Then, from (A.12) and (A.37),

$$[CO_3^{2-}] = \frac{A_C[H^+] - K_0 K_1 f(CO_2)}{2[H^+]} \quad . \tag{A.74}$$

There are no equations that can be used to calculate these independently of K_1. C_T is calculated from (A.1).

[H⁺], C_T and f(CO₂)

From (A.10)

$$[CO_2^*] = K_0 f(CO_2) \quad . \tag{A.75}$$

$[HCO_3^-]$ is given either by

$$[HCO_3^-] = \frac{K_0 K_1 f(CO_2)}{[H^+]} \quad , \tag{A.76}$$

or can be obtained from (A.1) and (A.12):

$$[HCO_3^-] = C_T - [CO_2^*] - \frac{[HCO_3^-]K_2}{[H^+]}$$

$$= \frac{[H^+](C_T - K_0 f(CO_2))}{[H^+] + K_2} \quad . \tag{A.77}$$

$[CO_3^{2-}]$ can be obtained either from [H⁺] and f(CO₂):

$$[CO_3^{2-}] = C_T - [CO_2^*] - [HCO_3^-]$$

$$= C_T - K_0 f(CO_2)(1 + K_1/[H^+]) \quad , \tag{A.78}$$

or from the equation for $[HCO_3^-]$ above, (A.77),

$$[CO_3^{2-}] = \frac{(C_T - K_0 f(CO_2))K_2}{[H^+] + K_2} \quad . \tag{A.79}$$

A_T is then calculated from (A.2), the terms for $[HCO_3^-]$ and $[CO_3^{2-}]$ are given by either (A.76) and (A.78)—in terms of K_1—

or (A.77) and (A.79)—in terms of K_2. The remaining terms are calculated from the expressions given in table 2.

[H⁺], A_T, C_T and $f(CO_2)$

The following set of equations have the property that they do not embody directly either of the ionization functions K_1 or K_2. The carbonate alkalinity, A_C, is first calculated from A_T and [H⁺] using (A.38) and the expressions in Table 2.

$[CO_2^*]$ is calculated from

$$[CO_2^*] = K_0 f(CO_2) \quad , \tag{A.80}$$

and then

$$[HCO_3^-] = 2C_T - A_C - 2K_0 f(CO_2) \quad , \tag{A.81}$$

$$[CO_3^{2-}] = A_C - C_T + K_0 f(CO_2) \quad . \tag{A.82}$$

The ionization constants for carbonic acid can then be calculated from (A.11) and (A.12).

3

Quality assurance

1. Introduction

This chapter is intended to indicate some general principles of analytical quality assurance appropriate to the measurement of oceanic CO_2 parameters for a global survey of CO_2 in the oceans. Specific applications of analytical quality control are detailed as part of the individual standard operating procedures (Chapter 4).

Quality assurance constitutes the system by which an analytical laboratory can assure outside users that the analytical results they produce are of proven and known quality (Dux, 1990). In the past, the quality of much oceanic carbon data has depended on the skill and dedication of individual analysts and typically a formal quality assurance program has been lacking. Clearly the collection of a global data set for oceanic carbon, depending as it will on the consistency between measurements made by a variety of laboratories over an extended period of time, demands more attention to such matters.[*]

A quality assurance program consists of two separate related activities, quality control and quality assessment (Taylor, 1987):

Quality control — The overall system of activities whose purpose is to control the quality of a measurement so that it meets the needs of users. The aim is to ensure that data generated are of known accuracy to some stated, quantitative, degree of probability, and thus to provide quality that is satisfactory, dependable and economic.

Quality assessment — The overall system of activities whose purpose is to provide assurance that the overall quality control job is being done effectively. It provides a continuing evaluation of the quality of the analyses and of the performance of the analytical system.

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[*] An outline of how to go about establishing a formal quality assurance program for an analytical laboratory has been described by Dux (1990), additional useful information can be found in the book by Taylor (1987).

2. Quality control

The aim of quality control is to provide a stable measurement system whose properties can be treated statistically, *i.e.* the measurement is "in control". Anything that can influence the measurement process must be optimized and stabilized to the extent necessary and possible if reproducible measurements are to be obtained. Measurement quality can be influenced by a variety of factors that are classified into three main categories (Taylor & Oppermann, 1986): management practices, personnel training and technical operations.

Although emphasis on quality by laboratory management, together with competence and training of individual analysts, is essential to the production of data of high quality (see Taylor & Oppermann, 1986; Taylor, 1987; Vijverberg & Cofino, 1987; Dux, 1990), these aspects are not discussed further here. The emphasis in this Handbook is on documenting various standard procedures so that all technical operations are carried out in a reliable and consistent manner.

The first requirement of quality control is for the use of suitable and properly maintained equipment and facilities. These are complemented by the use of documented Good Laboratory Practices (GLPs), Good Measurement Practices (GMPs) and Standard Operating Procedures (SOPs).

GLPs refer to general practices that relate to many of the measurements in a laboratory such as maintenance of equipment and facilities, records, sample management and handling, reagent control, and cleaning of laboratory glassware. GMPs are essentially technique specific. Both GLPs and GMPs should be developed and documented by each participating laboratory in such a fashion as to identify those critical operations which can be identified as assignable causes of variance or bias.

SOPs describe the way specific operations or analytical methods are to be carried out. They comprise written instructions which define completely the procedure to be adopted by an analyst to obtain the required result. Well written SOPs include tolerances for all critical parameters that must be observed to obtain results of a specified accuracy. This Handbook contains a number of such SOPs which are in use by members of the DOE CO_2 survey science team.

3. Quality assessment

A key part of any quality assurance program is the monitoring of the effectiveness of the quality control program and the statistical evaluation of the quality of the data output (see SOPs 22 and 23). There are both internal and external techniques for quality assessment (table 1), most of these are self evident, some are discussed in more detail below.

Table 1. Quality assessment techniques (after Taylor, 1987)

Internal techniques
>   Repetitive measurements
>   Internal test samples
>   Control charts
>   Interchange of operators
>   Interchange of equipment
>   Independent measurements
>   Measurements using a definitive method
>   Audits

External techniques
>   Collaborative tests
>   Exchange of samples
>   External reference materials
>   Certified reference materials
>   Audits

Internal techniques

Duplicate measurement of an appropriate number of test samples provides much of the evaluation of precision that is needed while minimizing the work involved and eliminates all question of the appropriateness of the samples. At least 12 pairs are needed to estimate a standard deviation with reasonable confidence, such as is needed to establish control chart limits (the recommended way to use such data).

An internal test sample of reasonable stability—*e.g.* the use of deep ocean water to monitor the stability of measurements of total alkalinity—can also be used to monitor precision (and bias, if its value is known with sufficient accuracy). Historical data on a laboratory's own test sample can be used to develop a control chart and thus monitor and assess measurement precision.[*]

A laboratory should also conduct regular audits to ensure that its quality assurance program is indeed being carried out appropriately and that the necessary documentation is being maintained.

External techniques

External evidence for the quality of the measurement process is important for several reasons. First, it is the easiest approach in that it can minimize much of the effort required for internal evaluation. Second, it minimizes the danger of error due to introspection. It must however be emphasized that the attainment of acceptable precision, based on a laboratory's internal quality assessment program, is a prerequisite for participation in any external quality assessment activity.

Collaborative test exercises provide the opportunity to compare an individual laboratory's performance with that of others. If the results for the test samples are known with accuracy, bias can be evaluated. Such exercises are being organized as part of the DOE CO_2 survey in collaboration with other JGOFS scientists and the results will be reported as they become available. Exchange of samples, or of internal calibration standards, with other laboratories can provide similar evidence of agreement or disagreement, and this can be used to make inferences about bias or the lack thereof.

The use of reference materials to evaluate measurement capability is the procedure of choice whenever suitable reference materials are available. Reference materials are stable substances for which one or more properties are established sufficiently well to calibrate a chemical analyzer, or to validate a measurement process (Taylor, 1987). Ideally such materials are based on a matrix similar to that of the samples of interest, in this

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*   Considerable confusion exists between the terms *precision* and *accuracy*. Precision is a measure of how *reproducible* a particular experimental procedure is. It can refer either to a particular stage of the procedure, *e.g.* the final analysis, or to the entire procedure including sampling and sample handling. It is estimated by performing replicate experiments and estimating a mean and standard deviation from the results obtained. Accuracy, however, is a measure of the degree of agreement of a measured value with the "true" value. An accurate method is one capable of providing precise and unbiased results. It is a much more difficult quantity to estimate and can only be inferred by careful attention to possible sources of systematic error.

case sea water. The most useful reference materials are those for which one or more properties have been *certified* on the basis of their accuracy, preferably by the use of a definitive method in the hands of two or more analysts. Reference materials have the advantage of the ability to test the whole measurement process

The U. S. National Science Foundation has funded the development of reference materials for the measurement of oceanic CO_2 parameters; the U. S. Department of Energy has agreed to provide for the distribution of such reference materials to participants (both from the U. S. and from other nations) in the CO_2 survey being conducted as part of the WOCE Hydrographic Program; as well as to the JGOFS time-series stations at Hawaii and Bermuda. We recommend their use in the individual SOPs where appropriate (see Table 2 for their availability).

Table 2. Present status (1994) of reference materials for the quality control of oceanic carbon dioxide measurements.

analytical measurement	desired accuracy [a]	availability[b]
total dissolved inorganic carbon	$\pm$ 1 µmol·kg^{-1}	since May 1991[c]
total alkalinity	$\pm$ 1 µmol·kg^{-1}	projected for September 1994
pH ($-\log$ [H$^+$])	$\pm$ 0.002	since January 1994
$f(CO_2)$	$\pm$ 0.05 Pa (0.5 µatm)	—[d]

a. Based on considerations outlined in the report of SCOR Working Group 75 (SCOR, 1985). They reflect the desire to measure changes in the CO_2 content of sea water that will allow the increases due to the burning of fossil fuels to be observed.
b. 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).
c. Work is also currently in progress at the Institute of Ocean Sciences, Canada to develop such a reference material.
d. CO_2 in air reference materials are presently available through a variety of sources. However it is desirable to use a sterilized sea water sample as a reference material for a discrete $f(CO_2)$ measurement. The feasibility of doing this is currently being examined at the Scripps Institution of Oceanography in collaboration with Dr. Chipman of the Lamont-Doherty Earth Observatory of Columbia University.

4. Documentation

One aspect of quality assurance that merits emphasis is that of documentation. All data must be technically sound and supported by evidence of unquestionable reliability. While the correct use of tested and reliable procedures such as those described in Chapter 4 is, without doubt, the most important part of quality control, inadequate documentation can cast doubt on the technical merits and defensibility of the results produced. Accordingly, adequate and accurate records must be kept of:

- What is measured
- Who measured it
- How measurements are made
    - *i.e.* Equipment, Calibration, Methodology
- Data obtained
- Calculations
- Quality assurance support
- Reports

Although good analysts have historically kept such documentation, typically in bound laboratory notebooks, a quality assurance program should address in detail the way that such documentation is to be maintained.

5. References

Dux, J. P. (1990) *Handbook of quality assurance for the analytical chemistry laboratory.* 2nd edn. Van Nostrand Reinhold, New York, 203 pp.

SCOR (1985) *Oceanic CO_2 measurements.* Report of the third meeting of the Working Group 75, Les Houches, France, October 1985.

Taylor, J. K. (1987) *Quality assurance of chemical measurements.* Lewis Publishers, Chelsea, 328 pp.

Taylor J. K. & H. V. Oppermann (1986) *Handbook for the quality assurance of metrological measurements.* National Bureau of Standards Handbook 145.

Unesco (1991) Reference materials for oceanic carbon dioxide measurements. *Unesco Technical Papers in Marine Science No. 60.*

Vijverberg F. A. J. M. & W. P. Cofino (1987) *Control procedures: good laboratory practice and quality assurance.* ICES Techniques in Marine Science No. 6.

4

Recommended standard operating procedures

The procedures detailed in the following pages have been prepared by the members of the DOE CO_2 survey science team. They are intended to provide standard procedures for measurements of CO_2 parameters made as part of the DOE sponsored survey.

1. Procedures for sampling and analysis

SOP 1   Water sampling for the parameters of the oceanic carbon dioxide system

SOP 2   Determination of total dissolved inorganic carbon in sea water

SOP 3   Determination of total alkalinity in sea water

SOP 4   Determination of $p(CO_2)$ in air that is in equilibrium with a discrete sample of sea water

SOP 5   Determination of $p(CO_2)$ in air that is in equilibrium with a continuous stream of sea water

SOP 6   Determination of the pH of sea water using a glass / reference electrode cell

SOP 7   Determination of the pH of sea water using the indicator dye *m*-cresol purple

2. Procedures for calibrations, *etc.*

SOP 11   Gravimetric calibration of the volume of a gas loop using mercury

SOP 12   Gravimetric calibration of volume delivered using water

SOP 13   Gravimetric calibration of volume contained using water

SOP 14   Electronic calibration of the UIC Model 5011 coulometer

3. Procedures for computations, quality control, *etc.*

SOP 1

Water sampling for the parameters of the oceanic carbon dioxide system

1. Scope and field of application

This chapter describes how to collect samples—from a Niskin bottle or other water sampler—that are suitable for the analysis of the various parameters of the oceanic carbon dioxide system: total dissolved inorganic carbon, total alkalinity, pH and fugacity of CO_2 in equilibrium with a water sample.

2. Principle

The sample of sea water is collected in a clean borosilicate glass container in a manner designed to minimize gas exchange with the atmosphere (however, exchange of CO_2 gas does not affect alkalinity measurements). The sample is then treated with mercuric chloride to poison it thus preventing further biological activity and the container is closed to prevent any further exchange of carbon dioxide or water vapor with the atmosphere.

3. Apparatus

3.1 Flexible plastic drawing tube (Note 1), long enough to reach from the drain on the water sampler to the bottom of the sample bottle

3.2 Clean glass sample bottles with stoppers (Note 2)

3.3 Pipette to dispense the mercuric chloride solution

3.4 Sampling log book

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[1] Tygon® tubing is normally used for this purpose. However, if samples are being taken for measurement of dissolved organic carbon, they will be contaminated by the use of Tygon tubing and silicone rubber tubing should be used instead. The drawing tube can be pre-treated by soaking in clean sea water for at least one day. This minimizes the amount of bubble formation in the tube when drawing a sample.

4. Reagents

4.1 Solution of mercuric chloride (Note 3)

4.2 Apiezon® L grease (if using ground glass stoppers) (Note 4)

5. Procedures

5.1 Introduction

Collection of water at sea from the Niskin bottle or other sampler, must be done soon after opening the sampler and before much other water has been removed from it. This is necessary to minimize exchange of CO_2 with the head space in the sampler which typically results in a loss of CO_2. Samples for the various carbon dioxide parameters are not the first priority on the WOCE Hydrographic Program as samples to be analyzed for other gases are even more susceptible to contamination from gas exchange; it is however desirable that samples for all parameters, with the exception of total alkalinity (for which gas exchange is not a problem), be drawn before half of the Niskin bottle has been drained and within ten minutes of it being first opened.

5.2 Filling procedure

Rinse the sample bottle—If the bottle is not already clean, rinse it twice with 30 to 50 cm^3 of sample so as to remove any traces of a previous sample.

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2 *Bottle type* — High quality glass bottles, preferably made from borosilicate glass such as Schott Duran (l.c.e. 32×10^{-7}), are recommended for both temporary and longer term storage. The bottles should be sealed using greased ground glass stoppers held in place with some form of positive closure, or in some alternate gas-tight fashion.

   Bottle preparation — Bottles should be cleaned carefully before use. An established method is "ashing" at ~550 °C, followed by rinsing with deionized water. Chemical cleaning using a detergent has also been successful, when combined with careful rinsing. Bottles used for the temporary storage of samples before analysis at sea can be reused after adequate rinsing with the new sea water.

3 Saturated solutions of mercuric chloride are commonly used but have been found to clog certain repeating pipettes. Equivalent amounts of more dilute solutions (*e.g.* 50% saturated) can also be used successfully.

4 Although this grease has been found by experience to be suitable for this use, other greases may well be equivalent. However, the use of grease to provide an air-tight seal is inconvenient and further investigation of alternate closure systems is needed.

Fill the sample bottle—Fill the bottle smoothly from the bottom using a drawing tube which extends from the Niskin drain to the bottom of the glass sample bottle. Overflow the water by at least a half, and preferably by a full, bottle volume (Note 5).

Adjust the head-space—A head-space of 1% of the bottle volume is left to allow for water expansion (see Annexe to this procedure), *i.e.* 2.5 cm^3 for a 250 cm^3 bottle. This can be achieved by removing excess water using a plastic pipette with a bulb.

Add mercuric chloride—Mercuric chloride is added to poison the sample; the recommended minimum amount is about 0.02% by volume of a saturated aqueous solution. Thus to poison a 250 cm^3 sample requires 0.05 cm^3 (50 µL) of saturated mercuric chloride (or 0.10 cm^3 of a 50% saturated solution).

Close the bottle—Seal the bottle carefully to ensure that it remains gas-tight. If it is to be sealed using a greased ground glass stopper (Note 6), first wipe the excess water from the ground glass in the bottle neck, then insert the stopper completely, and finally twist the stopper to squeeze the air out of the grease to make a good seal. Finally, secure the clip—or other positive closure—and shake the bottle to disperse the mercuric chloride solution thoroughly.

5.3 Sample storage

The samples should be stored in a cool, dark, location (preferably refrigerated but not frozen) until use.

5.4 Sample documentation

The following information must be recorded in the sampling log book at the time of sampling.

- Time and date when taken
- Full name of person who took sample
- Location: an unambiguous designation of the station, cast, and bottle number from which the sample was taken

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[5] The amount of overflow water can be estimated by measuring how long it takes to fill a sample bottle, and allowing the water to flow for a period of 1.5 times that.

[6] The recommended procedure for re-greasing (or greasing) a stopper is as follows: (a) wipe the stopper with a tissue to remove as much grease as possible, (b) grease the stopper with 4 strips of grease, each strip extending ^{2}/$_3$ of the way from the top towards the bottom of the ground portion of the stopper. This provides a path for air to escape when the stopper is inserted into the neck of the bottle.

- Container designation: a number or alphanumeric symbol unique to the sample container
- Comments: additional information such as conditions when sampling, problems with sample collection, *etc.*

6. Quality assurance

Some duplicate sampling is recommended, both from the same sampler (*e.g.* Niskin bottle) and, if possible, from two samplers tripped together at the same depth, to assess the quality of the sampling procedures.

Annexe

How large a head-space should be left in a sample bottle?

The volume of the head-space is chosen so as to leave room for expansion of the sea water on warming, while being sufficiently small to minimize the amount of gas exchange between the head space and the bulk of the sample. The closure system must be adequate to retain the pressure exerted by the expansion.

The apparent change in the volume of a fixed mass of sea water can be calculated by allowing for the change in the density of the sea water and the expansion of the glass container. The total change over the temperature range 0–40 °C is about 1%. (The effect of expansion on the volume of the borosilicate glass bottle is only 0.04% over this range.) One third of this expansion occurs on heating the sea water from 0 to 20 °C, the remaining two thirds on heating it from 20 to 40 °C.

The pressure in the head-space of a container heated from a temperature t_1 to t_2 can be estimated allowing for the following:

- the expansion of the sea water in the bottle,
- the change in solubility of gases such as N_2, O_2, Ar,
- the thermal expansion of the gas phase,
- the change in the vapor pressure of H_2O above the sea water contained

Defining the initial head-space ratio

$$r = \frac{V(\text{head-space})}{V(\text{sea water})} \quad , \tag{A.1}$$
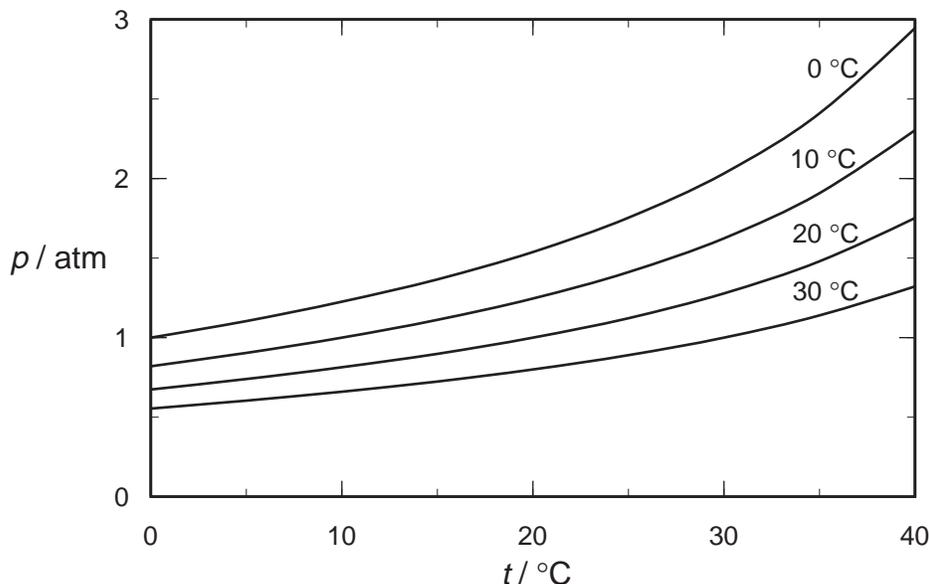
Figure 1. Pressure in head-space, with $r = 0.01$, as a function of temperature for various initial temperatures. In calculating this, it was assumed that the gases—N_2, O_2, Ar, H_2O—were initially at solubility equilibrium with sea water at the starting temperature, that they behaved ideally and that the initial pressure in the bottle at the indicated temperature was 1 atm.

allows the calculation of the approximate pressure in the head-space of a closed container as a function of temperature (Figure 1).

Clearly, if cold samples (< 10 °C) are likely to be heated above 30 °C, there is a risk of them leaking if the head-space ratio is significantly less than 1%.

There is, however, an additional factor to be taken into account when determining the optimal head-space size: gas exchange with the head-space. The change in total dissolved inorganic carbon (ΔC_T) resulting from this gas exchange can be derived from mass balance considerations:

$$\Delta C_T = \frac{\left(\dfrac{p(CO_2)V}{T}\right)_{inital} - \left(\dfrac{p(CO_2)V}{T}\right)_{final}}{R \cdot m(\text{sample})} \quad ; \qquad (A.2)$$

where $p(CO_2)$ is the partial pressure of CO_2 in a head-space of volume V and at a temperature T corresponding to the inital condition (when the bottle is closed) and the final condition (when the bottle is analyzed), R is the gas constant and $m(\text{sample})$ is the mass of the sample.

The volume of the head-space decreases as the contents heat up (due to the expansion of the sea water) partially compensating for

the decrease in the solubility of the various gases, thus the greatest loss of CO_2 will occur if the sea water has a high $p(CO_2)$ but does not warm up significantly in the container. Even then, provided that the head-space ratio is less than 0.01, ΔC_T will be less than 0.5 $\mu mol \cdot kg^{-1}$.

Gain or loss of CO_2 gas is not significant when collecting discrete samples for alkalinity measurement; however, if $p(CO_2)$ is to be measured the so-called "buffer factor" comes into play and the resultant relative error in $p(CO_2)$ is approximately 10 times that in C_T, *i.e.* for an change of -0.5 $\mu mol \cdot kg^{-1}$ in C_T the change in $p(CO_2)$ is about -0.25%. This corresponds to a change in pH of about $+0.001$.

A head-space of 1% is thus optimal for the collection of CO_2 samples provided one can be sure that they will not be exposed to temperature changes of 30 °C or more. If this cannot be assured, it might be preferable to allow a larger head-space and to estimate the appropriate correction.

SOP 2

Determination of total dissolved inorganic carbon in sea water

1. Scope and field of application

This procedure describes a method for the determination of total dissolved inorganic carbon in sea water, expressed as moles of carbon per kilogram of sea water. The method is suitable for the assay of oceanic levels of total dissolved inorganic carbon (1800–2300 μmol·kg^{-1}) and also for higher levels such as are found in the Black Sea (3800–4300 μmol·kg^{-1}).

2. Definition

The total dissolved inorganic carbon content of seawater is defined as:

$$C_{\mathrm{T}} \;=\; [CO_2^*] + [HCO_3^-] + [CO_3^{2-}] \quad . \tag{1}$$

where brackets represent total concentrations of these constituents in solution (in mol·kg^{-1}) and $[CO_2^*]$ represents the total concentration of all unionized carbon dioxide, whether present as H_2CO_3 or as CO_2.

3. Principle

A known amount of seawater is dispensed into a stripping chamber where it is acidified and purged with an inert gas. The presence of solid carbonates, such as $CaCO_3$, thus constitutes an interference in the method. The amount of CO_2 in the resulting gas stream is determined by absorbing the CO_2 in an absorbent containing ethanolamine and titrating coulometrically the hydroxyethylcarbamic acid that is formed. The pH of the solution is monitored by measuring the transmittance of thymolphthalein indicator at approximately 610 nm. Hydroxide ions are generated by the coulometer circuitry so as to maintain the transmittance of

the solution at a constant value. The relevant chemical reactions occurring in the solution are:

$$CO_2 + HO(CH_2)_2NH_2 \rightarrow HO(CH_2)_2NHCOO^- + H^+ \qquad (2)$$

and

$$H^+ + OH^- \rightarrow H_2O \ . \qquad (3)$$

The hydroxide ions used are generated at the cathode by electrolyzing water:

$$H_2O + e^- \rightarrow \tfrac{1}{2}H_2(g) + OH^- \quad , \qquad (4)$$

while silver is dissolved at the anode:

$$Ag(s) \rightarrow Ag^+ + e^- \ . \qquad (5)$$

The overall efficiency of the coulometric procedure is calibrated using known amounts of CO_2 gas, either from gas loops or from Na_2CO_3 solutions.

4. Apparatus (Note 1)

4.1 Sea water dispensing system

This is used to dispense an accurately known amount of sea water from the sample bottle into the extraction system without allowing any significant exchange of CO_2 with the atmosphere (Note 2). If a controlled volume of water is dispensed, its temperature must be known to within $\pm\ 0.4\ °C$.

4.2 CO₂ extraction system

The sea water is reacted with phosphoric acid in a borosilicate glass stripping chamber equipped with a drain for removing spent sample. The solution is stripped of CO_2 by bubbling the carrier gas through a fine frit submerged in the acidified sample. Carrier

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[1]   A computer operated instrument: the SOMMA system, is available commercially from the University of Rhode Island, Graduate School of Oceanography, Equipment Development Laboratory, P. O. Box 60, Narragansett, RI 02882-1197, U.S.A. (telefax 1-401-834-6755).

[2]   There are two principal means of effecting this: (a) using a syringe modified to deliver a controlled volume through a septum port into the extraction vessel (on land the amount of water dispensed can be determined by weighing the syringe before and after dispensing the sample); (b) using a calibrated pipette closed with valves at each end—this approach is taken on the SOMMA sytem.

gas leaving the stripping chamber is treated to prevent acid droplets from reaching the coulometer cell (Note 3).

4.3 Coulometer system

4.3.1 Model 5011 CO_2 coulometer
(UIC Inc., P. O. Box 863, Joliet, IL 60434)

4.3.2 Coulometer cell (Note 4)

4.3.3 Electrodes: platinum spiral cathode and silver rod anode.

4.4 Gas loop calibration system (Note 5)

4.4.1 Eight port chromatography valve at controlled temperature (Note 6, Note 7)

4.4.2 Two loops of stainless steel tubing of known volume (within ± 0.02 %—Note 8)

4.4.3 Thermometer accurate to ± 0.05 °C

4.4.4 Barometer accurate to ± 20 Pa (± 0.2 mbar)

4.5 Computer control

Although computer control is not essential for this procedure, it simplifies the operation of the instrument significantly and allows experimental results to be available immediately for quality assessment. If a computer is used, it should be interfaced so as to acquire the data from the coulometer. It is also possible to

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[3]   Several methods are in use for this. The SOMMA employs a water-jacketed condenser, a tube of drying agent and an activated silica gel trap in series; other investigators prefer to remove ærosols from the gas stream by impacting them either on pyrex wool or on a teflon filter, rather than removing them by chemical means.

[4]   It is desirable to control the temperature of this cell to within ±0.2 °C. The pK of the indicator used to sense pH in the solution is temperature sensitive; a substantial change in temperature between the beginning and end of an analysis will cause an error. The magnitude of this error is about 200 counts per degree Centigrade per 100 mL of cathode solution. Although this is rarely significant for a sea water sample, it complicates accurate measurement of the background titration rate.

[5]   This is not essential to the operation of the coulometer, as the instrument can be calibrated successfully using carefully prepared solutions of sodium carbonate. It is however strongly recommended.

[6]   The SOMMA has the loops and the associated valve assembly in an enclosure where the air is well stirred.

[7]   A plumbing diagram for the Valco 8 port valve (W type) is shown in Annexe A to this procedure.

[8]   The loops can be calibrated with water while mounted on the valve (see Wilke *et al.,* 1993) or off the valve using mercury (SOP 11).

automate the sample dispensing and stripping system, as well as to operate the gas loop calibration system (if present), and to acquire the related temperature and pressure information.

5. Reagents

5.1 Compressed gases

5.1.1 CO_2 free carrier gas: *e.g.* nitrogen >99.995% pure or CO_2 free air

5.1.2 Calibration gas: carbon dioxide >99.99% pure (needed only if gas loop calibration is being used)

5.2 Removal of CO_2 from the carrier gas (if needed)

5.2.1 Ascarite (II)® or Malcosorb® can be used

5.3 Acidification of sample

5.3.1 Reagent grade phosphoric acid diluted with deionized water by a factor of 10:1 (~8.5%)

5.4 Sample gas stream purification (see Note 3)

5.4.1 Removal of water vapor: Dehydrite® (magnesium perchlorate)

5.4.2 Removal of other acidic and reactive gases: activated silica gel trap, ORBO-53® from Supelco, Inc.

5.4.3 For samples which contain H_2S, a further chemical scrubber is used: a solution of Ag_2SO_4 in 5% sulfuric acid, with 3–4 drops of 10% H_2O_2 added

5.5 Coulometer cell solutions (Note 9)

5.5.1 Cathode solution (from UIC, Inc.)
A proprietary mixture which contains water, ethanolamine, tetra-ethyl-ammonium bromide, and thymolphthalein in solution in dimethyl sulfoxide (DMSO).

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[9] DMSO and ethanolamine are potentially hazardous chemicals and should be handled and disposed of appropriately. The vapor leaving the coulometer cell contains significant amounts of these chemicals; they can be removed from the gas stream using an activated charcoal trap; however, care must be taken to avoid restricting flow through this trap, thus pressurizing the cell and causing flow through the frit separating the anode and cathode compartments.

5.5.2   Anode solution (from UIC, Inc.)
    A solution containing saturated potassium iodide (crystals present) in water and DMSO.

5.5.3   Potassium iodide crystals, reagent grade
    Added to the anode solution in the cell to ensure that it remains saturated with potassium iodide.

6.   Sampling

It is essential that the samples analyzed are collected, poisoned and stored according to the procedure detailed in SOP 1. Care must be taken to avoid the exchange of CO_2 with the atmosphere both during sampling and during subsequent manipulation.

7.   Procedures

7.1   Introduction

An analysis session, starting with fresh solutions in the coulometer (Note 10), consists of the sequence of activities outlined in Table 1 (overleaf). At each stage of this procedure, compare the results obtained with the system's previous history to ensure that the method is performing according to prescribed specifications (see §9). Once the initial tests are complete, water samples can be analyzed. The calibration factor is verified, both during the course of the sequence of analyses and again at the end before the cell solutions are discarded (Note 11).

7.2   Check of calibration of sea water dispensing system

Deliver an aliquot of deionized water into a pre-weighed serum bottle using the dispensing system. Seal the bottle and save it to be reweighed later (on return to shore). Comparison of the results from replicate analyses using alternate dispensers can be used to detect discrepancies on board ship. Analyses of a reference material will also indicate if problems exist.

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[10]   Ideally, the coulometer should be left on at all times to avoid problems with drift and temperature stability of the electronics. For optimal stability, the maximum current of the system is adjusted to 50 mA (see coulometer instruction manual p. 22).

[11]   The cell solutions should be replaced: either after 12 hours of use, after a cumulative total of 2 mmol CO_2 have been titrated, or after the change in calibration factor is considered excessive (see §9). The cell solutions should be disposed of safely (Note 9).

Table 1. Recommended sequence of activities in an analysis session.

Activity	Section
• check calibration of sea water dispensing system	§7.2
• fill cell with fresh anode and cathode solutions	
• two "junk" sea water samples (to condition system)	§7.5
• background level determination	§7.3
• full calibration	§7.4
• analyze sea water reference material	§7.5
• analyze samples	§7.5
• confirm calibration	§7.4
• analyze further samples	§7.5
• confirm calibration	§7.4
• discard cell solutions	Note 11
• clean cell and electrodes	§7.6

7.3   *Determination of the background level*

Run CO_2 free carrier gas through the extraction system and into the cell of the coulometer. Once the background titration rate is stable, determine the background level by summing over a 10 minute period. If the background level is within the specified tolerance (see §9), note its value and begin the various analyses.

7.4   *Determination of the calibration factor for the coulometer*

The electrical calibration of the coulometer is not perfectly accurate (see SOP 14) and the current efficiency of the electrode processes occurring in the coulometer cell has been shown to vary from 100%; it is therefore preferable to calibrate the coulometer for each set of samples (*i.e.* for each fresh set of cell solutions) and to confirm the calibration regularly (after every 10 to 12 water samples or every 4 hours, whichever is the sooner). There are two principal means of achieving this: using a known amount of pure CO_2 gas dispensed from a calibrated gas loop at a known temperature and pressure, or using aqueous solutions of sodium carbonate which are treated as if they were samples. Both approaches are described here (Note 12).

*Calibration using gas loop*s—Such loops are incorporated into a chromatography valve which can be controlled from a computer. Fill the loop with pure CO_2 gas and allow the temperature and

pressure to equilibrate. Measure temperature and pressure and turn the valve to allow the contents of the loop to be flushed with carrier gas into the coulometer cell. Record the final coulometer reading when the coulometer titration rate returns to the background level.

The mean calibration factor—calculated as in §8.2—obtained from a pair of loops which bracket the range of CO_2 present in the samples, is used for calibration purposes. The value of the calibration factor can be confirmed using a single loop. Compare the results obtained with those obtained previously to ensure that the system remains in control (see §9).

Calibration using sodium carbonate solutions—Sodium carbonate solutions (see Annexe B for preparation procedure) are treated like sea water samples (see §7.5). It is desirable to use a suite of solutions to measure the calibration factor (Note 13) although a single solution can be used to confirm the constancy of the calibration factor during a run. Compare the results—calculated as in §8.2—with those obtained previously to ensure that the system remains in control (see §9).

7.5 *Analysis of a sea water sample*

Once the background level and calibration factor have been determined satisfactorily, use the system to analyze sea water samples. Handle the water samples so as to minimize CO_2 exchange between the water sample and any head-space.

Dispense the sample ($\sim$30 cm^3) into the stripping chamber and acidify it with phosphoric acid ($\sim$1.5 cm^3). Ensure that the sample delivery system is rinsed adequately with fresh sample. The

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[12] The relative merits of these two approaches are still debated. Gas loops are difficult to calibrate initially (see Wilke *et al.*, 1993 or SOP 11) and their use requires accurate measurement of temperature and pressure (§ 4.4), but once in place they are particularly convenient as a means to calibrate the coulometer response alone (*i.e.* not the volume delivery or extraction efficiency). Sodium carbonate solutions need to be prepared frequently and it is desirable to use a series of them for each calibration. However, the apparatus required is inexpensive and using such solutions calibrates the entire system response: delivery volume, extraction efficiency and coulometer response.

[13] Because of the experimental problems inherent in weighing and transferring small amounts of Na_2CO_3 crystals and because of the ubiquitous CO_2 background in deionized water, it is typically not possible to make up a single solution with an uncertainty of less than 1 μmol$\cdot$kg^{-1}. By using a series of such solutions, the resultant error in the calibration factor is minimized.

phosphoric acid must either be CO_2 free (Note 14) or an acid blank correction must be determined. Record the final coulometer reading when the coulometer titration rate returns to the background level.

The temperature of the sample on delivery ($\pm$ 0.4 °C) and its salinity ($\pm$ 0.1) are needed to compute the sample density.

7.6 *Cleaning the apparatus*

Clean the sea water dispensing and stripping systems by rinsing thoroughly with deionized water. Clean the coulometer cell by rinsing first with acetone and then with deionized water, taking care to force these solvents through the frit. If the frit is particularly dirty, it may be necessary to clean the cell with *aqua regia* and then to rinse it thoroughly with deionized water. Dry the cell before use (Note 15).

The platinum cathode should be rinsed in nitric acid occasionally to remove any deposits of silver and the silver anode should be abraded with glass wool to remove any deposits of silver iodide.

8.   Calculation and expression of results

8.1 *Calculation of background titration rate*

Compute the background titration rate—expressed in counts / min (Note 16):

$$b = \frac{N_b}{10} , \qquad (6)$$

where

N_b = the coulometer reading for a 10 minute period (counts).

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[14] If the acid is dispensed into the stripping cell prior to the addition of sea water, it can be purged of CO_2 *in situ*.

[15] If a black rubber stopper—as was originally supplied by UIC—is being used to hold the electrodes, this should also be rinsed with deionized water and baked in an oven at 50 °C for 12 hours.

[16] The unit counts (mode 0) corresponds to the most sensitive setting of the coulometer. The results obtained using other settings such as μg C (*e.g.* mode 2) can also be interpreted as arbitrary units for use in these equations.

8.2   Calculation of calibration factor

8.2.1   Based on a single loop

Compute the calibration factor (c)—expressed in counts / mol—from the coulometer reading for the analysis of $n(CO_2)$ moles of CO_2 dispensed from a gas loop of known volume, at a known temperature and pressure:

$$c = \frac{N_c - b \cdot t}{n(CO_2)} \, , \tag{7}$$

where

N_c = the coulometer reading for the gas sample (counts),

b = the background level of the system (counts / min),

t = the time required to measure that sample (min),

$n(CO_2)$= the amount of CO_2 dispensed from the loop (mol),

$$n(CO_2) = \frac{V(T)}{V(CO_2)} \, . \tag{8}$$

$V(T)$ is the volume of the loop at the calibration temperature T (see SOP 11 §6.3*)*; $V(CO_2)$ is the molar volume of pure CO_2 at the temperature T and pressure p of the calibration and is calculated from the expression

$$V(CO_2) = \frac{RT}{p}\left(1 + \frac{B(CO_2, T)}{V(CO_2)}\right) \, . \tag{9}$$

Values of the virial coefficient $B(CO_2, T)$ are given by the expression

$$\frac{B(CO_2, T)}{cm^3 \cdot mol^{-1}} = -1636.75 + 12.0408\left(\frac{T}{K}\right)$$

$$- 3.27957 \times 10^{-2}\left(\frac{T}{K}\right)^2 + 3.16528 \times 10^{-5}\left(\frac{T}{K}\right)^3 \, . \tag{10}$$

where $265 < (T/K) < 320$.

If the calibration factors from the two loops agree well (see §9), they should be averaged to give a mean calibration factor for use in further computations.

8.2.2 Based on a series of sodium carbonate solutions (SOP 14)

The calibration factor c is computed from the results obtained for a series of sodium carbonate solutions:

$$\frac{N_s - b \cdot t - a}{V_s} = (c \cdot dw) + c \cdot M \; ; \tag{11}$$

where

N_s = the coulometer reading for the Na_2CO_3 sample (counts),

a = the acid blank (counts) (Note 17)

b = the background level of the system (counts / min),

t = the time required to measure the Na_2CO_3 sample (min),

V_s = the volume of the Na_2CO_3 sample (dm^3)—(Note 18),

dw = the background level of CO_2 in the deionized water used to prepare the samples ($mol \cdot dm^{-3}$),

M = the nominal concentration of the Na_2CO_3 sample ($mol \cdot dm^{-3}$) computed from the mass of Na_2CO_3 used (see Annexe B).

The calibration factor c is computed as the slope of the straight line (11); its associated uncertainty is given by the standard error of the slope (see SOP 23). The intercept gives the deionized water "blank": dw. A prior knowledge of the value for dw thus does not play a role in the determination of the calibration factor; its uncertainty is averaged over all the standard solutions (including a solution where $M = 0$ $mol \cdot dm^{-3}$).

8.3 Calculation for a sea water sample

Calculate the total dissolved inorganic carbon in a sea water sample:

$$C_T' = \frac{N_s - b \cdot t - a}{c} \times \frac{1}{V_s \cdot \rho} \; . \tag{12}$$

---

[17] If a SOMMA system is used, the acid is added to the extraction cell and then stripped of CO_2 before commencing an analysis, *i.e.* $a = 0$ counts.

[18] A comparison of equation (11) with equation (12) shows that if V_s is assumed to be the same in both equations, errors in the calibration of pipette volume cancel out. Note, this assumes that the Na_2CO_3 solution and the sea water are delivered at the same temperature.

The various terms are

$C_T{}'$ = the total dissolved inorganic carbon in the sample ($mol \cdot kg^{-1}$),

N_s = the coulometer reading for the sea water sample (counts),

a = the acid blank (counts) (Note 17),

b = the background level of the system (counts / min),

c = the coulometer calibration factor (counts / mol),

t = the time required to measure the water sample (min),

V_s = the volume of the sea water sample at the temperature of use (dm^3) (SOP 12). (If Na_2CO_3 solutions were used for calibration, see Note 18.)

ρ = the density of the sea water sample ($g \cdot cm^{-3}$) (see Chapter 5 of this Handbook).

For the most accurate work, two further minor corrections may need to be made to compute the total dissolved inorganic carbon in the original sea water sample: for the dilution by mercuric chloride when the sample was collected (Note 19) and for the exchange of CO_2 with the head-space in the sampling bottle (Note 20):

$$C_T = 1.0002 \times (C_T{}' - \Delta C_T) \qquad (13)$$

where ΔC_T is the change in C_T resulting from exchange with the head-space of the bottle. Provided that r is less than 1%, this correction will always be less than 0.5 $\mu mol \cdot kg^{-1}$.

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[19] 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.

[20] See Annexe to SOP 1, equation (A.2):

$$\Delta C_T = \frac{\left(\dfrac{p(CO_2)V}{T}\right)_{inital} - \left(\dfrac{p(CO_2)V}{T}\right)_{final}}{R \cdot m(sample)} \quad ;$$

$p(CO_2)$ is the partial pressure of CO_2 in a head-space of volume V and at a temperature T corresponding to the inital condition (when the bottle is closed) and the final condition (when the bottle is analyzed); R is the gas constant; $m(sample)$ is the mass of the sample.

8.4   An example calculation (Note 21)

8.4.1   Calculation of the blank

N_b = 100 counts in 10 minutes

b = 100 / 10

= 10 counts / min .

8.4.2   Calculation of the calibration factor for a single loop:

T = 298.15 K ;
p = 101.325 kPa ;
$V(298.15\ \text{K})$ = 1.5000 cm^3 ;
$B(CO_2, 298.15\ \text{K})$ = −123.2 $\text{cm}^3 \cdot \text{mol}^{-1}$;
N_c = 294033 counts in 15 minutes ;

Thus

$$V(CO_2) \ = \ 24341.7 \ \ \text{cm}^3 \cdot \text{mol}^{-1} .$$

and

$$n(CO_2) \ = \ 1.5 / 24341.7 \ \ \text{mol}$$

$$= \ 61.6226 \ \mu\text{mol} .$$

Hence

$$c \ = \ \frac{294033 - 10 \times 15}{61.6226 \times 10^{-6}}$$

$$= \ 4.76908 \times 10^9 \ \ \text{counts / mol} .$$

8.4.3   Calculation of the calibration factor using 6 Na₂CO₃ solutions

b = 10 counts / min ; a = 40 counts ; V_s = 27.0000 cm^3 ;

M_1 =   0.0 $\mu\text{mol} \cdot \text{dm}^{-3}$; N_s =   1892 counts in 15 min
M_2 =   498.8 $\mu\text{mol} \cdot \text{dm}^{-3}$; N_s =   66537 counts in 15 min
M_3 = 1001.9 $\mu\text{mol} \cdot \text{dm}^{-3}$; N_s = 130818 counts in 15 min
M_4 = 1500.8 $\mu\text{mol} \cdot \text{dm}^{-3}$; N_s = 195216 counts in 15 min
M_5 = 2002.5 $\mu\text{mol} \cdot \text{dm}^{-3}$; N_s = 260068 counts in 15 min
M_6 = 2497.1 $\mu\text{mol} \cdot \text{dm}^{-3}$; N_s = 323456 counts in 15 min

Linear regression (SOP 23) gives:

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[21]   The apparent excess of significant figures is provided to aid in checking computer implementations of these computations.

$$\text{slope} \quad = 4.76908 \times 10^9 \quad \text{counts / mol}$$
$$\text{intercept} = 67695.1 \quad \text{counts / dm}^3.$$

Thus

$$c = 4.76908 \times 10^9 \quad \text{counts / mol} ,$$

and hence

$$dw = 14.195 \ \mu\text{mol·dm}^{-3} .$$

8.4.4 Calculation for a sea water sample:

$$S = 35.00 ; \quad t = 25.0 \ °\text{C} ; \ \rho(S, t) = 1.02334 \ \text{g·cm}^3 ;$$
$$V_\text{s} = 27.0000 \ \text{cm}^3 ;$$
$$a = 40 \ \text{counts} ; \ b = 10 \ \text{counts / min} ;$$
$$N_\text{s} = 289\,874 \ \text{counts in 15 minutes} .$$

Then

$$C_\text{T}{}' = \frac{289874 - 10 \times 15 - 40}{4.76908 \times 10^9} \times \frac{10^3}{27 \times 1.02334}$$

$$= 2\,198.40 \ \mu\text{mol·kg}^{-1} .$$

Correcting for the addition of mercuric chloride (0.02% of a saturated solution),

$$C_\text{T} = 2198.84 \ \mu\text{mol·kg}^{-1}.$$

9. Quality assurance

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

9.2 Specific applications of analytical quality control

The various control limits outlined below are necessary to ensure that the accuracy and precision of the data are adequate for the purposes of a world-wide CO_2 survey. The targets that have been specified for this are: a maximum within cruise precision (1 std. dev.) of 1.5 μmol·kg^{-1} and an overall between cruise (and between laboratory) range of bias of less than 4 μmol·kg^{-1}. Results from a collaborative study of this method indicate that these targets are attainable.

Calculate preliminary results immediately and update the control charts outlined below as soon as possible. Maintain a logbook detailing all the analyses carried out and describing any adjustments made to the analytical system.

The following goals are recommended for various parameters:

9.2.1   Stability and magnitude of the background level
The background should be less than 25 counts / min (0.05 µg C / min) and should remain stable to within ± 10 counts / min. Plot the values obtained for the background level on a property control chart (SOP 22).

9.2.2   Agreement between gas loops of two different sizes
The amounts of CO_2 dispensed by the gas loops should be chosen to bracket the expected values obtained from samples. The two loops should provide the same calibration factor to within 0.05%.

9.2.3   Quality of sodium carbonate calibration
The computed relative standard error of the slope should be less than or equal to 0.05%.

9.2.4   Stability of calibration factor
The mean value from the pair of loops, or the slope of the line when using Na_2CO_3 should remain stable within 0.1%. Plot the results obtained on a property control chart (SOP 22).

9.2.5   Analysis of a sea water reference material
A stable reference material (Note 22) should be analyzed regularly (at least once per filling of coulometer solution). Plot the results on a property control chart (SOP 22).

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

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Annexe A

Plumbing of gas loop calibration valve

This figure illustrates the correct way to plumb an 8 port valve (*e.g* W type valves from Valco Instruments Co., P. O. Box 55803, Houston, Texas 77255, U.S.A.) to provide two gas loops where the volume of the valve rotor channels is not part of the loop volume. It is taken from Valco Instruments Co. Inc. Product Bulletin 101 "GC Applications for in-line rotary valves" (1992).
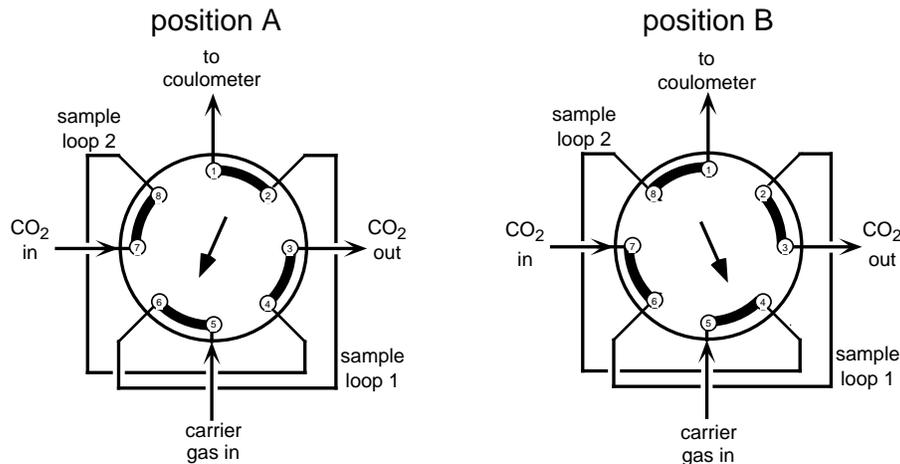
Annexe B

Procedure for preparing sodium carbonate solutions for the calibration of coulometric C_T measurements

1.   Scope and field of application

This procedure describes the preparation of a set of aqueous sodium carbonate solutions which are to be used for the calibration of the determination of total dissolved inorganic carbon by extraction / coulometry. Such solutions provide an alternative to the use of gas loops for the calibration of this apparatus.

2.   Principle

Six different standard solutions are prepared which contain carefully weighed amounts of pure sodium carbonate, such that the concentrations are at approximately 500 µmol·dm^{-3} intervals from 0–2500 µmol·dm^{-3}. Care is taken during the preparation and use of these solutions to minimize contamination by atmospheric carbon dioxide.

3.   Apparatus

3.1 6×1 dm^3 calibrated volumetric flasks (SOP 13)

3.2   Balance capable of weighing the sodium carbonate to ± 1 µg

4.   Reagents

4.1   High purity sodium carbonate, > 99.95%
      (If you wish to prepare high purity sodium carbonate yourself, follow the procedure given in IUPAC, 1969).

4.2   Deionized water
      (If desired, carbon dioxide can be removed by boiling and allowing to cool in a stream of nitrogen.)

4.3   Cylinder of nitrogen gas

5.   Procedure

5.1 Preparation of solutions

Dry the sodium carbonate to constant weight in an oven at 280 °C for >2 hours, store it in a desiccator over phosphorus pentoxide until it is used.

The following procedure is carried out for each solution prepared:

5.1.1 Weigh out the necessary amount of salt in a small container, such as a plastic vial, which has been treated to reduce static charge (e.g. with an anti-static strip).

5.1.2 Flush the clean dry flask with nitrogen for 5 minutes.

5.1.3 Fill the flask $\frac{3}{4}$ full with deionized water, filling from the bottom of the flask through a piece of tubing.

5.1.4 Using a funnel, transfer the sodium carbonate from the vial to the flask. Rinse the vial and the funnel into the flask to ensure quantitative transfer of the sodium carbonate into the flask.

5.1.5 Adjust the volume of solution contained in the flask to the calibration mark.

5.1.6 Make sure that the head-space is filled with nitrogen gas, then close the flask with a lightly greased stopper. Once it is closed, shake it gently to dissolve all the sodium carbonate and to mix the solution.

These solutions will last for at least 1 week, provided that the head-space is kept filled with nitrogen and that the flasks are resealed after each use.

5.2 Calculation of concentrations of solutions

First correct the weight of Na_2CO_3 for air buoyancy effects (SOP 21):

$$m(Na_2CO_3) = w(Na_2CO_3)\left(\frac{1 - \rho(air)/\rho(weights)}{1 - \rho(air)/\rho(Na_2CO_3)}\right) \quad , \ (A.1)$$

Then combine this with information on the calibrated volume of the flask, V(flask) (SOP 13) and on the purity of the sodium carbonate (if known):

$$\frac{c(Na_2CO_3)}{mol \cdot dm^{-3}} = \frac{m(Na_2CO_3)/g}{105.988} \times \frac{1}{V(flask)/dm^3} \times purity \quad . \ (A.2)$$

5.3   Sample calculation

$$w(\text{Na}_2\text{CO}_3) = 0.21230 \text{ g} ;$$
$$V(\text{flask}) = 1.0001 \text{ dm}^3 ;$$
$$\rho(\text{weights}) = 8.0 \text{ g·cm}^{-3} ;$$
$$\rho(\text{Na}_2\text{CO}_3) = 2.532 \text{ g·cm}^{-3} ;$$
$$\text{purity of Na}_2\text{CO}_3 = 99.95\% .$$

Thus

$$m(\text{Na}_2\text{CO}_3) = 0.21230\left(\frac{1 - 0.0012/8.0}{1 - 0.0012/2.532}\right)$$

$$= 0.21237 \text{ g}$$

and

$$c(\text{Na}_2\text{CO}_3) = \frac{0.21237}{105.988} \times \frac{1}{1.0001} \times 0.9995$$

$$= 2002.5 \text{ µmol·dm}^{-3} .$$

6.   Quality assurance

The set of six calibration standards are used in a linear regression procedure (SOP 23 §3.6) to calibrate the extraction / coulometric system for measurement of total dissolved inorganic carbon. If the relative standard error of the slope obtained is too high ($> 0.15\%$), the data should be examined to ascertain the source of error. If necessary, additional standard solutions should be prepared. Furthermore, if the value of the intercept—the background level of carbon dioxide in the deionized water—is too high (>15 µmol·dm^{-3}), the solutions should be rejected and made again with freshly boiled deionized water.

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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 μmol·kg^{-1}) and can be adapted easily to measure higher levels such as those that have been observed in the Black Sea (3200–4600 μmol·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:

$$A_T = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}]$$
$$+ 2[PO_4^{3-}] + [SiO(OH)_3^-] + [NH_3] + [HS^-] + \ldots$$
$$- [H^+]_F - [HSO_4^-] - [HF] - [H_3PO_4] - \ldots; \qquad (1)$$

brackets represent total concentrations of these constituents in solution, $[H^+]_F$ 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 cm^3 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:

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

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

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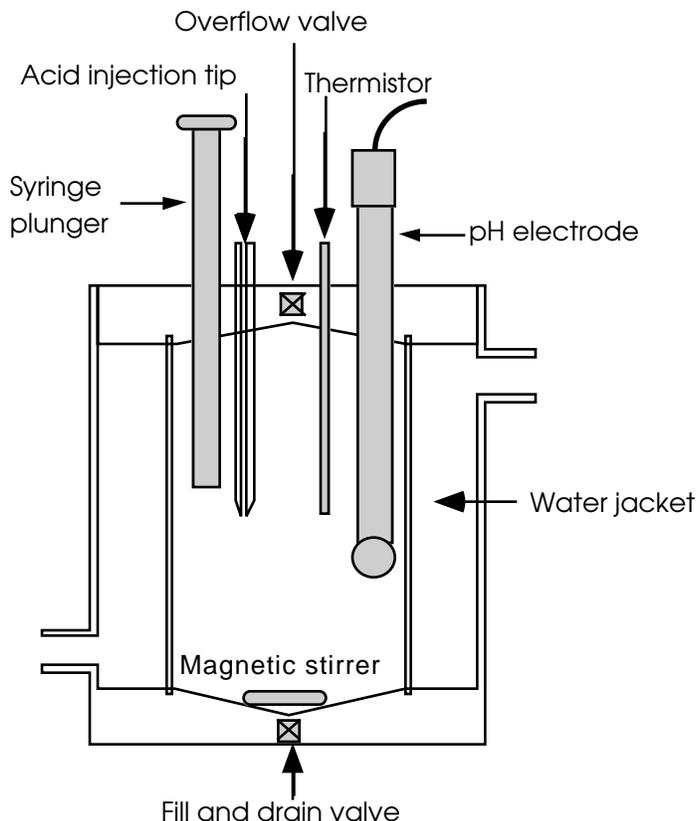
Figure 1. Closed titration cell for the determination of alkalinity.

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.

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[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 cm^3 in the delivered volumes—is interfaced to the computer which controls the titration. The appropriate burette size depends on the cell size and on the concentration of acid used, see § 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

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[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 Na_2CO_3 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 $(0.7\ \text{mol·kg}^{-1})$.

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

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 $(0.1\text{–}0.2\ \text{cm}^3)$ 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).

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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 (~1.25 mmol·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:

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

(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:

$$C_H = [H^+]_F + [HSO_4^-] + [HF] + [H_3PO_4]$$
$$-[HCO_3^-] - 2[CO_3^{2-}] - [B(OH)_4^-] - [OH^-]$$
$$-[HPO_4^{2-}] - 2[PO_4^{3-}] - [SiO(OH)_3^-] - [NH_3] - [HS^-] .$$
$$(4)$$

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),

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

This can be equated to the previous expression for C_H:

$$\frac{m\,C - m_0 A_T}{m_0 + m} = [H^+]_F + [HSO_4^-] + [\,HF\,] + [H_3PO_4]$$

$$-[HCO_3^-] - 2[CO_3^{2-}] - [B(OH)_4^-] - [OH^-]$$

$$-[HPO_4^{2-}] - 2[PO_4^{3-}] - [SiO(OH)_3^-] - [NH_3] - [HS^-] \quad . \tag{6}$$

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):

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

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.

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[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 Na_2CO_3) can be used to calculate the total alkalinity of the background medium. However it is better to combine this result with the results from titrations of different levels of Na_2CO_3 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 Na_2CO_3) is given by the sum

$$A_T = A_T(\text{blank}) + \frac{2\ m(Na_2CO_3)}{105.988} \times \frac{1}{m(Na_2CO_3\text{-soln})}\ ; \quad (8)$$

where $A_T(\text{blank})$ is the total alkalinity of the NaCl background solution, $m(Na_2CO_3)$ the mass of Na_2CO_3 used to prepare the solution, and $m(Na_2CO_3\text{-soln})$ the total mass of solution prepared (there are two moles of alkalinity per mole of sodium carbonate).

The measured values of A_T (calculated by assuming an approximate value for the acid concentration, C) should be a linear function of the alkalinity component contributed by the Na_2CO_3—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 $a = 1$.

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[13]   This is not strictly true as the residual alkalinity cannot be removed completely by acidifying and stripping with a CO_2 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

$$V_0 \approx V_0' \, A_T' / A_T. \tag{10}$$

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 ($\pm\ 0.1$) of the sea water sample so as to compute both its density and the appropriate equilibrium constants for use in the data treatment (see the Annexe to this procedure).

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[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):

$$A_T = 1.0002 \times A_T'. \tag{11}$$

9. Quality assurance

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

9.2 Specific applications of analytical quality control

The various control limits outlined below are necessary to ensure that the accuracy and precision of the data are adequate for the purposes of a world-wide CO_2 survey. The initial targets specifiedfor this are: a within cruise precision (1 std. dev.) of 3 $\mu mol \cdot kg^{-1}$ and an overall between cruise (and between laboratory) range of bias of less than 6 $\mu mol \cdot kg^{-1}$.

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":

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

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 $\mu mol \cdot kg^{-1}$ 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).

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[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).

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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 mol·kg^{-1} NaCl, then the program will select the appropriate dissociation constants and set the total concentrations of species such as sulfate, fluoride, phosphate, silicate, *etc.* to zero. Note, this code does not contain expressions for incorporating ammonia and hydrogen sulfide; for open ocean use the total concentrations of these are essentially equal to zero.

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[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:

$$f = [H^+]/[H'] \; ; \qquad (A.1)$$

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

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

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

Equation (6) is rewritten as:

$$A_T - C_T\left(\frac{K_1 f[H'] + 2K_1 K_2}{(f[H'])^2 + K_1 f[H'] + K_1 K_2}\right) - B_T\left(\frac{1}{1 + (f[H'])/K_B}\right)$$

$$-P_T\left(\frac{K_{1P}K_{2P}(f[H']) + 2K_{1P}K_{2P}K_{3P} - (f[H'])^3}{(f[H'])^3 + K_{1P}(f[H'])^2 + K_{1P}K_{2P}(f[H']) + K_{1P}K_{2P}K_{3P}}\right)$$

$$- Si_T\left(\frac{1}{1 + (f[H'])/K_{Si}}\right) - NH_{3T}\left(\frac{1}{1 + (f[H'])/K_{NH3}}\right)$$

$$- H_2S_T\left(\frac{1}{1 + (f[H'])/K_{H2S}}\right) + S_T\left(\frac{1}{1 + K_S Z/(f[H'])}\right)$$

$$+ F_T\left(\frac{1}{1 + K_F/(f[H'])}\right) + \left(\frac{m_0 + m}{m_0}\right)\left(\frac{f[H']}{Z} - \frac{K_W}{f[H']}\right) - \frac{m}{m_0}C$$

$$= 0 \qquad (A.3)$$

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:

$$[H^+]_F = [H^+]/Z \; ; \qquad (A.4)$$

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:

$$C_T = [CO_2^*] + [HCO_3^-] + [CO_3^{2-}] \tag{A.5}$$

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

$$S_T = [HSO_4^-] + [SO_4^{2-}] \tag{A.7}$$

$$F_T = [HF] + [F^-] \tag{A.8}$$

$$P_T = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] \tag{A.9}$$

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

$$NH_{3\,T} = [NH_4^+] + [NH_3] \tag{A.11}$$

$$H_2S_T = [H_2S] + [HS^-] \tag{A.12}$$

Equilibrium constants:[a]

$$K_1 = [H^+][HCO_3^-]/[CO_2^*] \tag{A.13}$$

$$K_2 = [H^+][CO_3^{2-}]/[HCO_3^-] \tag{A.14}$$

$$K_W = [H^+][OH^-] \tag{A.15}$$

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

$$K_S = [H^+]_F [SO_4^{2-}]/[HSO_4^-] \tag{A.17}$$

$$K_F = [H^+][F^-]/[HF] \tag{A.18}$$

$$K_{1P} = [H^+][H_2PO_4^-]/[H_3PO_4] \tag{A.19}$$

$$K_{2P} = [H^+][HPO_4^{2-}]/[H_2PO_4^-] \tag{A.20}$$

$$K_{3P} = [H^+][PO_4^{3-}]/[HPO_4^{2-}] \tag{A.21}$$

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

$$K_{NH3} = [H^+][NH_3]/[NH_4^+] \tag{A.23}$$

$$K_{H2S} = [H^+][HS^-]/[H_2S] \tag{A.24}$$

Additional definitions:

$$Z = 1 + S_T/K_S \tag{A.25}$$

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).

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

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

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

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

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

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

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

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

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

$$[\text{NH}_3] = NH_{3\,T} / (1 + [\text{H}^+]/K_{\text{NH3}}) \tag{A.35}$$

$$[\text{HS}^-] = H_2 S_T / (1 + [\text{H}^+]/K_{\text{H2S}}) \tag{A.36}$$

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

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

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

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 ≠ 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.

```
                            ┌────────────┐
                            │    main    │
                            └────────────┘

  ┌──────────┐      ┌──────────┐    ╭──────────╮    ┌──────────┐
  │  Input   │      │  SetUp   │    │ MINPACK  │    │  Output  │
  └──────────┘      └──────────┘    │ LMDIF1   │    └──────────┘
                                    ╰──────────╯
                                          │
                                    ┌──────────┐
                                    │   FCN    │
                                    └──────────┘

  ┌──────────┐      ┌──────────┐    ┌──────────┐
  │ DensSW   │      │ DensNaCl │    │ EstimE0  │
  ├──────────┤      ├──────────┤    └──────────┘
  │ ConcnsSW │      │ ConstsNaCl│
  ├──────────┤      └──────────┘
  │ ConstsSW │
  └──────────┘
```
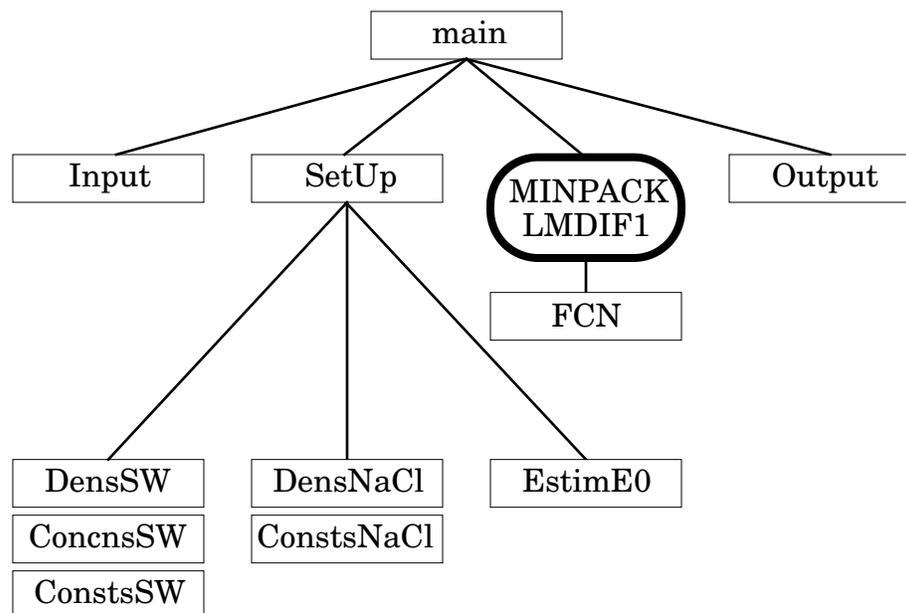
A machine readable version of this code is available from

> Dr. Andrew G. Dickson
> Marine Physical Laboratory – 0902
> University of California, San Diego
> 9500 Gilman Drive
> La Jolla, CA 92093-0902, U. S. A.
> Telefax: 1-619-456-9079

---

[20] J. J. Moré, B. S. Garbow, & K. E. Hillstrom (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      µmol/kg   total phosphate
SiT   = 0.0      µmol/kg   total silicate

T     = 20.05    oC        temperature of sample when titrated
W0    = 165.391  cm3       volume of sample titrated
C     = 0.20455  mol/kg    concentration of acid titrant
DACID = 1.02409  g/cm3     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   µmol/kg
SiT   =     0.00   µmol/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  µmol/kg
CT    =   2344.26  µmol/kg
pK1   =   5.9090

s     =   1.209 µmol/kg
```

V/cm3	E/V	-log[H]	ΔH/(µmol/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)

*    Inititialize 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 adust X so as to mimize 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 containg residuals (calculated by FCN)
```

```
*       TOL    - tolerance for fitting
*       INFO   - flag indicating if minimization was successsful
*       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*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)

*    Uppstrom (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 cloride 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,
*    appropriateto 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
```

SOP 4

Determination of *p*(CO₂) in air that is in equilibrium with a discrete sample of sea water

1. Scope and field of application

This procedure describes a method for the determination of the partial pressure of carbon dioxide in air that is in equilibrium with a discrete sample of seawater. The partial pressure of carbon dioxide is expressed as microatmospheres. The method is suitable for the assay of air in equilibrium with oceanic water samples (250–2000 µatm at 20 °C).

2. Definition

The partial pressure of carbon dioxide in air that is in equilibrium with a sample of seawater is defined as the product of the mole fraction of CO_2 in the equilibrated gas phase and the total pressure of equilibration:

$$p(CO_2) = x(CO_2) \cdot p \quad . \tag{1}$$

It is a temperature dependent property of the sea water sample; thus it is important to record the temperature at equilibrium.

3. Principle

A known amount of sea water is isolated in a closed system containing a small known volume of air (containing a known initial amount of carbon dioxide) and maintained at a constant, known temperature and pressure. Once the water and air are in equilibrium (Note 1) a sample of the air is analyzed for carbon dioxide content using a gas chromatograph (Note 2) in which the carbon dioxide is catalytically reduced to methane which is detected using a flame ionization detector.

---

[1] Typically the gas and liquid phases are mixed thoroughly to speed this process up. The approach commonly used is to recirculate the air through a frit immersed in the sea water sample—thus creating small bubbles—while simultaneously stirring the sea water.

The partial pressure, $p(\text{CO}_2)$, is calculated from (1). To use this measurement together with other measurements of the other parameters of the carbon dioxide system in sea water, it is necessary to convert it to the fugacity, $f(\text{CO}_2)$:

$$f(\text{CO}_2) \; = \; x(\text{CO}_2)\,p \, \exp\!\left(\int_{0}^{p} \frac{(V(\text{CO}_2) - RT/p')\,dp'}{RT} \right) \quad . \qquad (2)$$

(see Chapter 2). The calculations required to do this are outlined in SOP 24.

4.   Apparatus (Note 3)

4.1   Gas chromatograph system

4.1.1   Gas chromatograph with temperature controlled oven.

4.1.2   Computer-controlled 10-port valve with 1 cm³ sample loop for sample injection and column switching

4.1.3   2.0 m chromatographic column and 0.2 m precolumn packed with porous polystyrene (60–80 mesh) (Chromosorb 102 or Porapak Q).

4.1.4   Catalytic system to convert carbon dioxide to methane (Ruthenium on Chromosorb W support).

4.1.5   Flame-ionization detector.

4.1.6   Programmable chromatographic integrator.

4.2   CO₂ equilibration system

4.2.1   Constant-temperature bath

4.2.2   Air recirculation pump(s)

4.2.3   Thermometer (± 0.02 °C)

---

[2]   A non-dispersive infra-red detector can also be used to quantify the amount of CO_2 and can be used to assess the rate of approach to equilibrium (see *e.g.* Wanninkhof & Thoning, 1993).

However, such a detector requires a larger air/water ratio—and thus involves a larger and less reliable correction for CO_2 exchange (see § 8.2)— also infra-red detectors are non-linear and thus require more elaborate calibration for use over such a wide range of CO_2 concentrations. In addition, it is important to take account of the effect of H_2O vapor on the infra-red performance of the instrument.

[3]   The system described here is based on that used at the Lamont-Doherty Earth Observatory. A schematic diagram of that apparatus is provided in the Annexe to this procedure.

4.3   Calibration system

4.3.1   Remotely operated valve allowing selection between the three calibration gases.

4.3.2   Normally-closed solenoid shut-off valve used to control the flow of calibration gas.

4.3.3   Barometer, accurate to $\pm$ 50 Pa (0.5 mbar), with computer interface

4.4   System control

4.4.1   Microcomputer for data logging

4.4.2   Digital interface board to control valves *etc.*

5.   Reagents

5.1   Compressed gases

5.1.1   Carrier gas: hydrocarbon-free hydrogen (*e.g.* from hydrogen generator)

5.1.2   FID oxidant gas: hydrocarbon-free air (*e.g.* from pure air generator)

5.1.3   Three calibration gas mixtures of CO_2 in air: well-known CO_2 concentrations chosen to span the range of measured values: $x(CO_2) = 250–2000 \times 10^{-6}$.

6.   Sampling

It is essential that samples are collected, poisoned and stored according to the procedure detailed in SOP 1. However, for this analysis the sample bottles are 500 cm^3 volumetric flasks with screw caps which have internal plastic conical liners. Samples are equilibrated in the same bottles in which they are collected, eliminating one transfer operation.

7.   Procedures

7.1   Introduction

The normal sequence of analyses is designed to compensate for changes in the response of the detector with time. A full set of three calibration gases are analyzed, followed by a set of unknowns (two equilibrations of each of two sea water samples);

the same three calibration gases are then analyzed a second time, followed by the next set of unknowns and so on. The response of the detector to each calibration gas at the time of analysis of each of the four unknowns is interpolated from the pairs of measurements of each of the three calibration gases that bracket the sample analyses.

7.2 System start-up

To reduce the time required for the gas chromatograph to stabilize at the beginning of an analytical session, analyze laboratory air repeatedly rather than equilibrated air as follows:

7.2.1 Disconnect the lines leading to and from the equilibrators, so that the pumps will fill the sample loop with room air rather than equilibrated air.

7.2.2 Use a separate subroutine of the operating program to run these analyses without the use of calibration gases, thus conserving the calibration gases.

Calculation of $p(CO_2)$ for a set of samples requires knowledge of the concentration of CO_2 in the head-space gas prior to starting the equilibration. This is estimated—in part—from the $p(CO_2)$ of the previous sample analysis.

Thus at the initial start, after reconnecting the lines to the equilibrators (see above) analyze two start-up (or practice) samples prior to running the main suite of analyses. Subsequently, the final samples from an analysis session can be left in place until the next set of analyses are begun (see § 7.5).

7.3 Loading of new samples

As each sample analysis is completed (see § 7.4), replace the previous sample flask with a fresh sample as described below. This will create a head-space with a known volume and a known CO_2 concentration

7.3.1 Bring the next sample to the equilibration temperature prior to analysis (*e.g.* by placing it in the same thermostat bath used to maintain the analysis temperature).

7.3.2 Turn off the recirculation pump for the equilibrator. This minimizes the exchange of laboratory air with the air currently in the pump and tubing and prevents sample water from being forced into the return line leading to the gas chromatograph.

7.3.3 Open the drain valve for the equilibrator and insert the stopper with gas disperser, return line and drain line into the next sample flask.

7.3.4 Force sample water out from the flask through the drain line using air of known CO_2 concentration admitted to the flask through the return line.

7.3.5 Stop the flow of air once the water level reaches the bottom end of the drain tube and close the drain valve.

7.3.6 Turn the recirculation air pump back on.

7.4 Acceptance criterion

Analyze each sample in duplicate (two consecutive equilibrations of the same water sample). Compare the integrated detector peak areas for the CO_2 from the two analyses; if the difference between the two areas is less than 0.25% of the mean of the two areas, accept the results and replace the sample flask by a fresh sample as described in § 7.3 above.

If the two analyses differ by more than this amount, do not replace the flask, but re-analyze it as part of the next sequence. After any sample has been analyzed a third and fourth time, it is replaced whether or not it has attained the acceptance criterion.

Repeated failure of samples to attain this criterion on a particular equilibrator suggests that is necessary to clean the system, as aerosol particles of salt or water may be restricting the air flows or interfering with the action of the recirculation pump.

7.5 Termination of analytical session

Following the analysis of the final samples of a given session (including the final set of calibration analyses), the two flasks are left in place connected to the two equilibrators. This serves to prevent drying of the gas dispersers and to provide start-up samples to establish the concentration of CO_2 in the pumps and gas lines before the analysis of fresh samples. In addition, use of such samples—with known $p(CO_2)$—provides a check on the system prior to the analysis of fresh samples.

8. Calculation and expression of results

8.1 Calculation of GC response

The response of a flame ionization detector is almost linear over a large dynamic range. However, the response varies with changes in ambient temperature and with the flow rates of the hydrogen and oxygen reaching the flame. A quadratic curve will fit the actual response closely at any given time.

To account for changes in the response with time, the detector peak area (A_x) corresponding to the CO_2 content—$x(CO_2)$—of each of the three calibration gases is linearly interpolated in time between a pair of measurements (made at times t_1 and t_2) to estimate the response of the system at the time (t) of measurement of each unknown:

$$A_x(t) \; = \; A_x(t_1) + \frac{t - t_1}{t_2 - t_1}(A_x(t_2) - A_x(t_1)) \quad . \tag{3}$$

A separate response curve is then calculated at the time of measurement of each unknown (t):

$$x(CO_2) \cdot p \; = \; a_0 + a_1 \cdot A_x(t) + a_2 \cdot (A_x(t))^2 \quad ; \tag{4}$$

p is the measured atmospheric pressure (Note 4). Equation (4) is then used to calculate the partial pressure of CO_2 in the air that is equilibrated with the water samples from their respective measured peak areas.

8.2 Corrections for sample perturbation during equilibration.

Some CO_2 will be exchanged between the sea water sample and the air of the head-space during the process of equilibration. This process will alter the total dissolved inorganic carbon (C_T) in the sea water sample while leaving the total alkalinity (A_T) constant. The measured partial pressure will be in equilibrium with this modified sample. A mass balance approach is used to estimate the partial pressure of carbon dioxide in air that would have been in equilibrium with the original, unchanged sample.

---

[4]   The pressure in the loop is controlled at atmospheric pressure which is measured at the time of injection. The calibration gases are vented directly to the atmosphere to achieve this; air in equilibrium with the sample is in pressure equilibrium with the atmosphere through a flexible rubber diaphragm. Thus, the measured response curve relates partial pressures of CO_2 (rather than concentrations) to peak areas.

8.2.1 Calculation of ΔC_T

The change in the number of moles of CO_2—$\Delta n(CO_2)$—in the equilibrator head-space can be calculated (assuming ideal behavior):

$$\Delta n(CO_2) = \frac{(p(CO_2)_1 - p(CO_2)_2)V(\text{head-space})}{RT} \qquad (5)$$

where V(head-space) is the volume of air in the head-space and the subscripts 1 and 2 refer to values measured before and after the equilibration process respectively. Note that the temperature of the system and the head-space volume are assumed to remain constant throughout. The change in C_T can then be calculated:

$$\Delta C_T = \frac{\Delta n(CO_2)}{\rho \cdot V(\text{sample})} \quad , \qquad (6)$$

where V(sample) is the volume of sea water of density ρ that was equilibrated with the head-space gas.

8.2.2 Calculation of corrected p(CO₂)

(a) If the C_T of the unperturbed sample is known:

- Assume that $f(CO_2) \approx p(CO_2)$ (Note 5).
- Calculate the C_T of the perturbed water sample and use this together with $f(CO_2)$ to calculate the value of A_T for the sea water sample (see Annexe to Chapter 2). The equilibrium constants used should be appropriate to the equilibration temperature and the salinity of the sample being equilibrated (Note 6).
- Calculate $p(CO_2)$ ($\approx f(CO_2)$) for the unperturbed sea water from the knowledge of A_T and C_T (see Annexe to Chapter 2).

(b) If the A_T of the original sample is known:

- Assume that $f(CO_2) \approx p(CO_2)$ (Note 5).
- Use this together with A_T to calculate the C_T of the perturbed water sample (see Annexe to Chapter 2). The equilibrium constants used should be appropriate to the

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[5]   Strictly, it is the fugacity of CO_2 that is in equilibrium with a sample of sea water. However, assuming that CO_2 behaves ideally for the calculation of this correction will not make a significant difference to the final result as the same assumption is made in both the forward and back calculations.

[6]   As the same equilibrium constants (see Appendix to this Handbook) are used for the forward and back calculation, errors due to uncertainties in these will be small.

equilibration temperature and the salinity of the sample being equilibrated (Note 6).

- Use equation (6) to estimate C_T in the unperturbed sample.
- Calculate $p(CO_2)$ $(\approx f(CO_2))$ for the unperturbed sea water from the knowledge of A_T and C_T (see Annexe to Chapter 2).

8.3   Correction for water vapor pressure.

If the equilibrated air is injected into the gas chromatograph without removal of water vapor, the calculation outlined in § 8.2 will give the final value of $p(CO_2)$. If water vapor was removed from the equilibrated air prior to injection into the gas chromatograph, it is necessary to correct for this. The partial pressure of CO_2 in the dried air must be reduced by a factor which accounts for the increase in concentration of CO_2 in the air resulting from the removal of the water vapor.

$$p(CO_2) \ = \ p(CO_2 \text{ in dry air}) \times (1 - VP(H_2O)) \quad , \qquad (7)$$

where $VP(H_2O)$ is the water vapor pressure over a sea water sample of a given salinity at the temperature of equilibration (Note 7)—see Chapter 5, § 3.

8.4   Calculation of $f(CO_2)$ from corrected $p(CO_2)$

See SOP 24.

8.5   Example calculation

Flask volume = 525 cm^3
Flask head-space = 45 cm^3
Residual system volume (lines & pump) = 13 cm^3
Fill gas (used to displace head-space), $x(CO_2) = 750 \times 10^{-6}$
Residual gas (lines & pump), $x(CO_2) = 535 \times 10^{-6}$
Temperature of gas in head-space = 25 °C
Salinity of sample = 35
C_T of sample (before equilibration) = 2050 µmol·kg-soln^{-1}
Equilibration pressure = 995 mbar (99.5 kPa)
Equilibration temperature = 20 °C
Measured $x(CO_2)$ for sample = 350×10^{-6}.

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[7]   Equation (7) assumes that the water vapor behaves ideally.

From equation (5), for the head-space

$$\Delta n(\mathrm{CO_2}) = \frac{(750 \times 10^{-6} - 350 \times 10^{-6}) \times 45 \times 10^{-6} \times 99500}{8.31451 \times 298.15}$$

$$= 7.22 \times 10^{-7} \text{ mol },$$

and for the residual gas in the lines and pump

$$\Delta n(\mathrm{CO_2}) = \frac{(535 \times 10^{-6} - 350 \times 10^{-6}) \times 13 \times 10^{-6} \times 99500}{8.31451 \times 298.15}$$

$$= 9.65 \times 10^{-8} \text{ mol}.$$

Then at $S = 35$ and $t = 20\ °C$, $\rho_{SW} = 1024.76 \text{ kg·m}^{-3}$ and from equation (6):

$$\Delta C_T = \frac{7.22 \times 10^{-7} + 9.65 \times 10^{-8}}{1024.76 \times (525 - 45) \times 10^{-6}} = 1.67 \times 10^{-6} \text{ mol·kg}^{-1} \ ;$$

thus

C_T (after equilibration) $= 2050 + 1.67 = 2051.67\ \mu\text{mol·kg}^{-1}$.

Total alkalinity (A_T) in the sample is calculated from the post-equilibration values of $p(\mathrm{CO_2})$ (see Note 5)

$$p(\mathrm{CO_2}) = (350 \times 10^{-6}) \times (99.5 / 101.325) = 343.7\ \mu\text{atm} \ .$$

and $C_T = 2051.67\ \mu\text{mol·kg}^{-1}$, using the equations in the Annexe to Chapter 2 together with the thermodynamic data in Chapter 5:

$$A_T = 2368.10\ \mu\text{mol·kg}^{-1}.$$

The $p(\mathrm{CO_2})$ of the sample before equilibration (see Note 5) is then estimated from this value for A_T and $C_T = 2050\ \mu\text{mol·kg}^{-1}$ (again using the equations in the Annexe to Chapter 2 together with the thermodynamic data in Chapter 5):

$$p(\mathrm{CO_2}) = 341.1\ \mu\text{atm} \ .$$

9.　Quality assurance

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

9.2　Specific applications of analytical quality control

9.2.1　Stability of the response of gas chromatograph
The performance of the gas chromatograph can be monitored by means of control charts (SOP 22) which give a visual indication of

any significant change in the response of the instrument to injections of nearly constant amounts of CO$_2$ calibration gases.

The absolute peak areas for the three calibration gases (normalized to a constant pressure and temperature) should be plotted against time and deviations of more than 2% should be investigated. As a rapid check on the functioning of the instrument, the values of the response function coefficients a_0, a_1 and a_2 can be printed with the calculated value of $p(CO_2)$ for each analysis.

*9.2.2 Reproducibility of equilibrated samples*
Use of the acceptance criterion given in § 7.4: replicate samples should agree within 0.25%, will give a rapid indication of deteriorating performance of the equilibration system. The fraction of analyses from each analytical session that fail to meet the criterion should be entered on a control chart, and any significant increase in these fractions investigated. As a further check on the functioning of the two equilibrators of the system, occasional duplicate samples should be taken from the same water sampler and run as a pair on the two equilibrators. Differences of greater than 0.5% in the corrected values should be cause for concern.

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Annexe

Schematic showing the gas-water equilibrator and gas chromatographic system for the equilibration of $p(CO_2)$ in discrete samples (Chipman *et al.*, 1992)
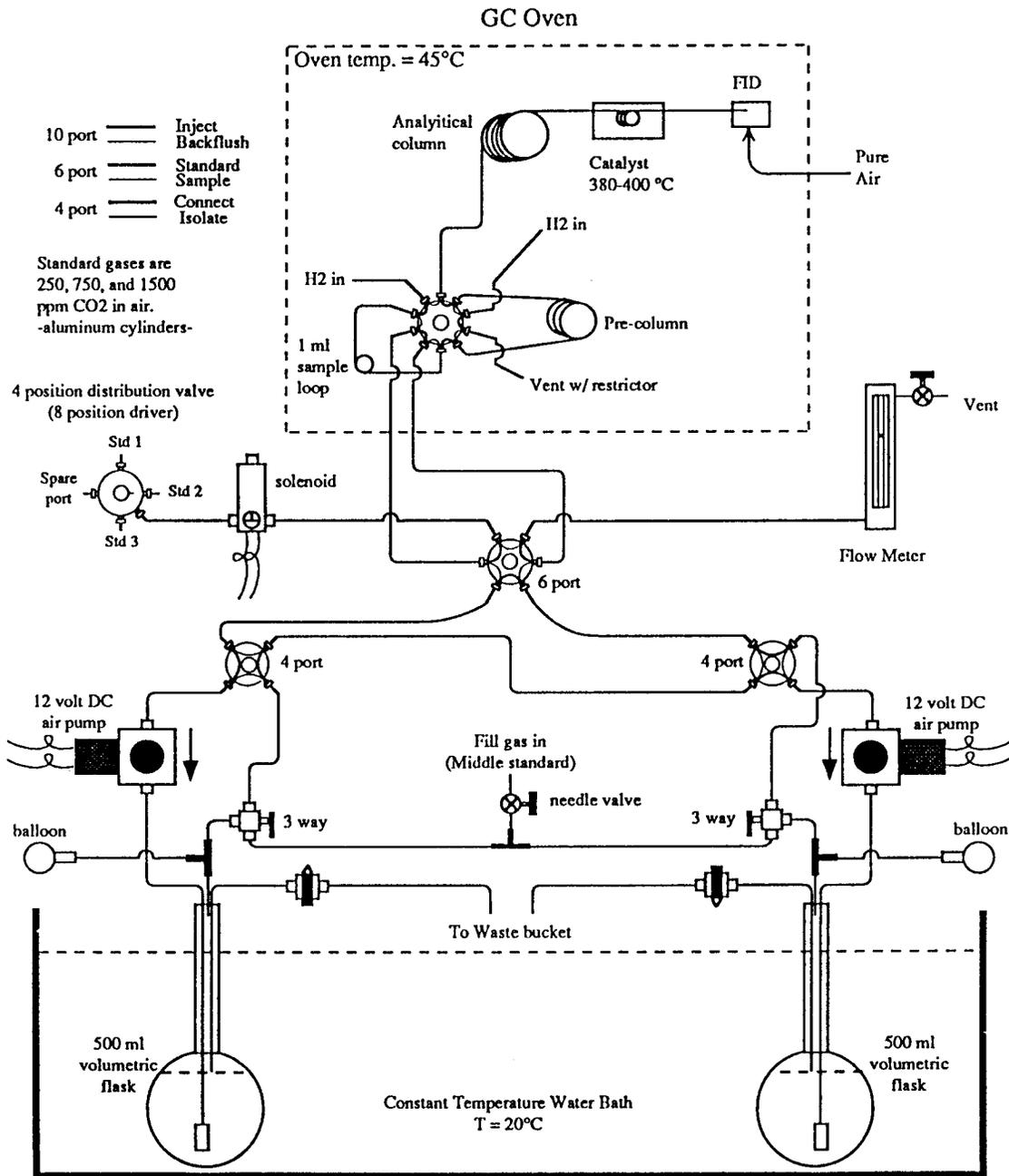
SOP 5

Determination of $p(CO_2)$ in air that is in equilibrium with a continuous stream of sea water

1.   Scope and field of application

This procedure describes a method for the determination of the partial pressure of carbon dioxide in air that is in equilibrium with a flowing stream of seawater, *e.g.* that obtained by pumping surface sea water from the bow of a ship for underway analysis. The partial pressure of carbon dioxide is expressed as microatmospheres. The method is suitable for the assay of air in equilibrium with oceanic water samples (250–500 µatm).

2.   Definition

The partial pressure of carbon dioxide in air that is in equilibrium with a sample of seawater is defined as the product of the mole fraction of CO_2 in the equilibrated gas phase and the total pressure of equilibration:

$$p(CO_2) = x(CO_2) \cdot p \quad .\tag{1}$$

It is a temperature dependent property of the sea water sample; thus it is important to record the water temperature in the equilibrator at the time of measurement.

3.   Principle

A fixed volume of air is equilibrated with a stream of sea water that flows through an equilibrator (Note 1). The system is maintained at the ambient atmospheric pressure. As the volume of sea water that flows through the equilibrator is essentially infinite in comparison with that of the air, the CO_2 content of the air adjusts to remain in equilibrium with the sea water without altering the CO_2 content of the sea water appreciably. The air is

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[1]   A number of effective designs exist for such an equilibrator. The most common is that designed by Dr. Ray Weiss at the Scripps Institution of Oceanography and described in a report by Butler *et al.* (1988).

recirculated through a non-dispersive infra-red analyzer to measure its CO_2 content (Note 2). The analyzer is calibrated using gases of known CO_2 concentration (mole fraction).

The partial pressure, $p(CO_2)$, is then calculated from (1). To use this measurement together with other measurements of the other parameters of the carbon dioxide system in sea water, it is necessary to convert it to the fugacity, $f(CO_2)$:

$$f(CO_2) \;=\; x(CO_2)p \, \exp\left(\int_0^p \frac{(V(CO_2) - RT/p')dp'}{RT} \right) \quad . \qquad (2)$$

(see Chapter 2). The calculations required are outlined in SOP 24.

4. Apparatus (Note 3)

4.1 *Outside air intake*

A tube is run from the location of the measurement system so as to be able to sample uncontaminated outside air. If the measurement system is located on board a ship, this line will typically be led to the bow of the ship (Note 4). The air is pumped at a rate of 6–8 $dm^3 \cdot min^{-1}$ to ensure continual flushing of the tubing. The air stream is sampled through a dryer to the analyzer system when needed.

4.2 *Equilibrator*

An equilibrator is used to ensure that the air in the equilibrator head-space is at equilibrium with sea water stream—particularly in regard to the water and CO_2 content. A key feature of a

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[2] A gas chromatographic system can be used successfully for this measurement (see *e.g.* Weiss, 1981; Weiss *et al.,* 1982; Robertson *et al.,* 1992; Weiss *et al.*, 1992). Although the GC approach has a number of advantages in that it requires smaller amounts of both sample and calibration gas and is not sensitive to the O_2 / N_2 ratio of the gas being measured, the infra-red approach is recommended here as being potentially more rugged and simpler to implement.

[3] A schematic of the layout described here (which is based on that of Wanninkhof & Thoning, 1993) is given in the Annexe to this procedure.

[4] It is important to record the relative wind's speed and direction to confirm that the air being sampled represents uncontaminated marine air and does not contain any stack gas from the ship.

Some investigators have reported that they believe that this air intake line can, in time, become contaminated with sea salt aerosols and then bleed CO_2 slowly into the gas stream.

successful design is that the volume of air in the head-space remains approximately constant regardless of the ship's motion and that this air is not exchanged very quickly with the outside air even though there is an open tube to ensure that the equilibration is carried out at atmospheric pressure. Air from the equilibrator is recirculated through a pump at a rate of about 6 $dm^3 \cdot min^{-1}$. The air stream is sampled and dried as needed. It is important to keep track of temperature and pressure in the equilibrator at all times (Note 5).

4.3 Drying system (Note 6)

It is desirable to dry the air streams going to the detector (both outside air and air from the equilibrator). The drying system should be placed on the low-pressure side of any pump. Drying the air eliminates the possibility of condensation in the tubing leading to the analyzer; it also improves the sensitivity and the accuracy of the infra-red analysis as it eliminates the need to correct for the pressure broadening of the CO_2 band resulting from the presence of the water. (The calibration gases are typically dry air containing known mole fractions of CO_2.)

A number of approaches can be used:

- Cooling the air to a specified dew point using a refrigeration unit. This necessitates emptying the traps of the accumulated water (or ice) on a regular basis.
- Using a chemical drying agent, *e.g.* Aquasorb™—a solid support impregnated with P_2O_5 and containing a colored indicator (dew point –96 °C). This drying agent will need to be replaced on a regular basis.

The system described here uses both these approaches.

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[5] Robertson *et al*. (1992) use a closed equilibrator system that is not vented to atmosphere. They do not measure the pressure in the equilibrator, and thus measure $p(CO_2)$ directly using their GC system (see SOP 4); this approach can be problematic for an infra-red based system (see Note 12).

[6] Some systems in use (*e.g.* the LI-COR Model 6262) do not dry the gases, rather they use a two-channel infra-red detector system to measure both the water and CO_2 contents. Although this is more convenient, there are potential problems with water condensation in the tubing leading to the detector and with correcting the measured CO_2 content of the air to 100% humidity to compare it with the measured CO_2 content of the water.

4.4 Calibration system

A system that allows selection of one of a set of three calibration gases. These are based on dry air and cover the range of concentrations: $x(CO_2) = 250\text{–}500 \times 10^{-6}$.

4.4.1 High-purity two-stage gas cylinder pressure regulators.

4.4.2 Remotely operable valve allowing selection between the three calibration gases.

4.4.3 Mass flow controller (~ 75 cm³·min⁻¹) to control the rate of flow of gases through the sample cell.

4.4.4 Mass flow controller (~ 50 cm³·min⁻¹) to control the rate of flow of reference gas through the reference cell (Note 7).

4.4.5 Barometer accurate to ±30 Pa. This is used to monitor atmospheric pressure (Note 8).

4.5 Detector system

It is essential to know the temperature (and also the pressure) of the gas in the infra-red absorption cells at the time of the various measurements. In the system described here, sample and reference cells are assumed to be at the same temperature (which is monitored) and low flow rates from both cells are vented to atmosphere, thus keeping the cell pressures at the atmospheric value (which is also monitored).

4.5.1 Non-dispersive infra-red analyzer with a temperature probe mounted on the cell *(Note 9)*.

4.5.2 Reference cell, flushed regularly with gas containing a known amount of CO_2 (Note 7).

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[7] In the system described in this SOP, the reference cell is flushed with air containing a precisely known mole fraction of CO_2 (*i.e.* a reference gas). An alternate approach is to use air with the CO_2 removed from it, *e.g.* by scrubbing with soda-lime, as a reference. This latter approach has the advantages that the signal is not sensitive to temperature and pressure fluctuations in the reference compartment and it saves on the use of calibrated gas; the disadvantage is that instrument sensitivity is reduced by measuring relative to zero rather than relative to a fixed CO_2 concentration comparable to that of the samples being measured.

[8] It is desirable to monitor the pressure in the cells and the pressure in the equilibrator directly; however, as these are both vented to atmosphere it is more usual to measure the atmospheric pressure as a proxy for both.

[9] Suitable instruments are available from LI-COR Inc., P. O. Box 4425, Lincoln, Nebraska 68504, U.S.A.

4.6 System control etc.

4.6.1 Microcomputer for data logging

4.6.2 Digital interface board to control valves *etc.*

5. Reagents

5.1 Compressed gases

5.1.1 Three calibration gas mixtures of CO_2 in air: well-known CO_2 concentrations chosen to span the range of measured values: $x(CO_2) = 250–500 \times 10^{-6}$.

5.1.2 Chemical drying agent (if used).

5.1.3 CO_2 removal agent (if CO_2 free air used as reference gas).

6. Sampling

As this procedure is for underway measurements, the sampling is done as part of the analysis. The important features are to ensure that the air line samples uncontaminated marine air (§ 4.1) and that the equilibrator samples uncontaminated surface sea water. As the $p(CO_2)$ is very dependent on the water temperature it is important that the water in the equilibrator be as close to sea surface temperature as possible. This is achieved by using a high flow rate of sea water to reduce the extent of the inevitable warming or cooling that occurs during passage from the water intake to the equilibrator. It is important to record the water intake temperature and salinity, *e.g.* using a thermosalinograph system as well as the equilibrator temperature.

7. Procedures

7.1 Introduction

The sequence of analyses outlined below is designed to measure both the marine air and the equilibrator in a cycle together with the calibration gases (Note 10). The frequency of analysis is determined by the length-scale of the phenomena that are being observed (compared to the ship's speed) and by the desire to conserve calibration gases.

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[10] The timing detailed here is that of Wanninkhof & Thoning, 1993).

7.2 *Cycle of analyses*

The procedure described here is based on a one hour cycle. The temperature and pressure of the air in the infra-red absorption cell is measured as well as the detector output voltage.

7.2.1 Measure the ambient air concentration of CO_2 for 22 min. Record the average of measurements over a 1 min period for further processing. (Discard the results from the first 3 minutes to ensure adequate flushing of the detector cell.)

7.2.2 Measure the concentration of CO_2 in air from the equilibrator for 23 min. Record the average of measurements over a 1 min period for further processing. (Discard the results from the first 3 minutes to ensure adequate flushing of the detector cell.)

7.2.3 Measure the suite of three calibration gases for 5 min each. Record the average of measurements over a 1 min period for further processing. (Discard the results from the first 3 minutes to ensure adequate flushing of the detector cell.)

8. Calculation and expression of results

8.1 *Calculation of infra-red detector response*

The response of a non-dispersive infra-red absorption detector is appreciably non-linear, even over the restricted range of CO_2 concentrations that apply here. Furthermore, the detector signal depends in part on the number of moles of CO_2 in the cell, not on the mole fraction. This is given by the gas law:

$$n(CO_2) = \frac{x(CO_2) \cdot p \cdot V(\text{cell})}{RT} \times \phi \quad , \tag{3}$$

where ϕ is an approximately constant term (Note 11) that accounts for the non-ideality of the gas phase and p and T refer to the pressure and temperature respectively of the gas in the absorption cell, which has a volume $V(\text{cell})$—(Note 12).

The results from the three calibration runs are used to calculate the coefficients a_1 and a_2 of the quadratic function (Note 13):

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[11] Provided that the temperature, pressure and composition remain approximately constant. This is typically the case for this procedure.

[12] However, the absorption per mole of CO_2 also increases with pressure and it has been found empirically (LI-COR, 1992) that (at a constant temperature) the pressure affects the signal voltage in a linear fashion.

$$x(CO_2) - x(CO_2)_{REF} =$$

$$\left(a_1 \cdot (V - V_R)\frac{P^\circ}{P} + a_2 \cdot \left((V - V_R)\frac{P^\circ}{P}\right)^2 \right)\frac{T}{T^\circ} \quad ; \quad (4)$$

the various terms are

$x(CO_2)$	= mole fraction of CO_2 of gas in sample cell,
$x(CO_2)_{REF}$	= mole fraction of CO_2 of gas in reference cell,
V	= detector output voltage (V)
V_R	= detector output voltage when the reference gas is also flowing through the sample cell (V),
P	= atmospheric pressure,
P°	= standard atmospheric pressure (101.325 kPa),
T	= temperature of the cell assembly (K),
T°	= standard temperature (K) to which results are adjusted; most conveniently the calibration temperature.

When only three gases are used—and when one of these is also used as the reference gas— a_1 and a_2 can be calculated algebraically, otherwise a least-squares procedure should be used.

Equation (4) is then used to calculate the mole fraction, $x(CO_2)$ in each of the dried air samples in turn: the ambient air and the air from the equilibrator (Note 14). If the partial pressure of CO_2 in dry air is required, it is necessary to multiply this quantity by the atmospheric pressure p_{ATM} (the pressure of equilibration):

$$p(CO_2) = x(CO_2) \cdot p_{ATM} \quad . \quad\quad (5)$$

8.2   Correction for water vapor pressure.

Air in the equilibrator—like air at the sea surface—is assumed to be at 100% humidity. The partial pressure of CO_2 measured in dried air must therefore be reduced by a factor which accounts for the increase in concentration of CO_2 in the air resulting from the removal of the water vapor:

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[13]   Over a wider range of $x(CO_2)$ a cubic function has been found to be more appropriate — see LI-COR (1992).

[14]   Some investigators interpolate their calibrations in time to try to represent more closely the exact behavior of the infra-red analyzer at the time of sample measurements (see *e.g.* the procedure adopted in SOP 4, §8). The difference is not expected to be significant when the calibration is performed reasonably frequently (as here) and when temperature and pressure variation is explicitly allowed for.

Thus

$$p(\text{CO}_2) \approx p(\text{CO}_2 \text{ in dry air}) \times (1 - VP(H_2O)) \quad , \qquad (6)$$

where $VP(\text{H}_2\text{O})$ is the water vapor pressure over a sea water sample of a given salinity at the temperature of equilibration (Note 15)—see Chapter 5.

8.3   Correction of p(CO$_2$) to sea surface temperature

The $p(\text{CO}_2)$ measured in the equilibrator is appropriate to the temperature of the water in the equilibrator. To use this as information about gas exchange at the sea surface it is necessary to correct the value obtained to the measured sea-surface temperature:

$$p(\text{CO}_2, T_S) = p(\text{CO}_2, T_E) \times \exp(0.0423(T_S - T_E)) \quad , \qquad (7)$$

where T_S is the sea-surface temperature—typically the bulk temperature of the mixed layer(Note 16)—and T_E is the temperature measured in the equilibrator (Note 17).

8.4   Calculation of f(CO$_2$) from corrected p(CO$_2$)

If the $p(\text{CO}_2)$ of the sea water is to be used to calculate—or compare with—the other parameters of the CO_2 system it is necessary to calculate the fugacity, $f(\text{CO}_2)$—see SOP 24.

8.5   Example calculations

8.5.1   Calibration data

The measured data for the calibration cycle are

Standard 1 ($x(\text{CO}_2) = 305.56 \times 10^{-6}$ — reference gas)

$V = 0.07400$ V

$T = 304.61$ K (31.46 °C)

$p = 101.788$ kPa

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[15]   Equation (6) assumes that the water vapor behaves ideally.

[16]   There is still some discussion as to whether the appropriate choice of sea-surface temperature that should be used to study air-sea exchange is that measured on the ship's underway system (typically the bulk temperature of the mixed layer), or whether a "skin temperature" should be determined and used (see Robertson & Watson, 1992).

[17]   The factor of 0.0423 has been determined experimentally (Takahashi *et al.*, 1993). A more elaborate correction procedure is possible (see for example Weiss *et al.,* 1982; Copin-Montegut, 1988; Goyet *et al.,* 1993) however it is unnecessary provided that $|T_S - T_E| < 1$ K, as is the case for most measurement systems.

Standard 2 ($x(CO_2) = 356.20 \times 10^{-6}$)

V = 0.63300 V

T = 304.61 K (31.46 °C)

p = 101.804 kPa

Standard 3 ($x(CO_2) = 404.73 \times 10^{-6}$)

V = 1.14167 V

T = 304.61 K (31.46 °C)

p = 1017.97 kPa

Thus (setting the standard temperature to 304.61 K), equation (4) can be used to obtain the simultaneous equations

$50.64 \times 10^{-6} = 0.55637\, a_1 + 0.30955\, a_2$

$99.17 \times 10^{-6} = 1.06272\, a_1 + 1.12937\, a_2$.

These are solved to give

a_0 = 88.493×10^{-6}

a_1 = 4.540×10^{-6} .

8.5.2 Measurement of p(CO₂)

V = 0.67467 V

T = 304.61 K (31.61 °C)

p = 101.802 kPa

$$\Delta x(CO_2) = 88.493 \times 10^{-6}(0.67467 - 0.07400)\frac{101.325}{101.802} +$$

$$4.540 \times 10^{-6}\left((0.67467 - 0.07400)\frac{101.325}{101.802}\right)^2$$

$$= 36.03 \times 10^{-6}$$

Thus

$$x(CO_2) = 305.56 \times 10^{-6} + 36.03 \times 10^{-6} = 341.59 \times 10^{-6},$$

and from equation (5)

$p(CO_2$ in dry air$) = (341.59 \times 10^{-6})(10180.2) = 34.773$ Pa

= 343.18 µatm .

8.5.3 Correction to 100% humidity

The water in the equilibrator has

S = 35

T_E = 298.15 K (25.00 °C) ;

thus

$VP(H_2O)$ = 3.1094 kPa (Chapter 5)

= 0.0307 atm

and from equation (6)

$$p(CO_2) = 343.18 \times (1 - 0.0307) = 332.65 \text{ µatm} .$$

8.5.4 Correction to sea surface temperature
The sea surface temperature

$$T_S = 297.85 \text{ K } (25.00 \text{ °C}) ;$$

thus from equation (7)

$$p(CO_2, T_S) = 332.65 \times \exp(0.0423 (297.85 - 298.15))$$
$$= 328.46 \text{ µatm} .$$

9.   Quality assurance

*9.1 For general principles of analytical quality control see
Chapter 3.*

9.2 Specific applications of analytical quality control

9.2.1 Stability of the response of the infra-red analyzer
The performance of the infra-red analyzer can be monitored by
means of control charts (SOP 22) which give a visual indication of
any significant change in the response of the instrument to CO_2.
The offset between the cells should remain near zero. The values
of the coefficients a_1 and a_2 should remain fairly stable.

9.2.2 Reproducibility of equilibrated samples
An estimate of the reproducibility of the instrument can be
obtained in areas where the rate of change is slow. For marine air
samples, this should extend over wide areas; for water it is most
striking in the central gyres. The standard deviation of the
measurement can be calculated over the approximately 20 min
period that either ambient air or air from the equilibrator is being
measured. The standard deviation should be monitored carefully,
it should be less than 0.3 µatm for ambient air and less than
1 µatm for air from the equilibrator.

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Annexe

Schematic showing the layout of the analytical system described here (based on Wanninkhof & Thoning, 1993). (The cold trap—at ~5 °C—that is used to reduce the water vapor in air and head-space lines is not shown in this diagram.)
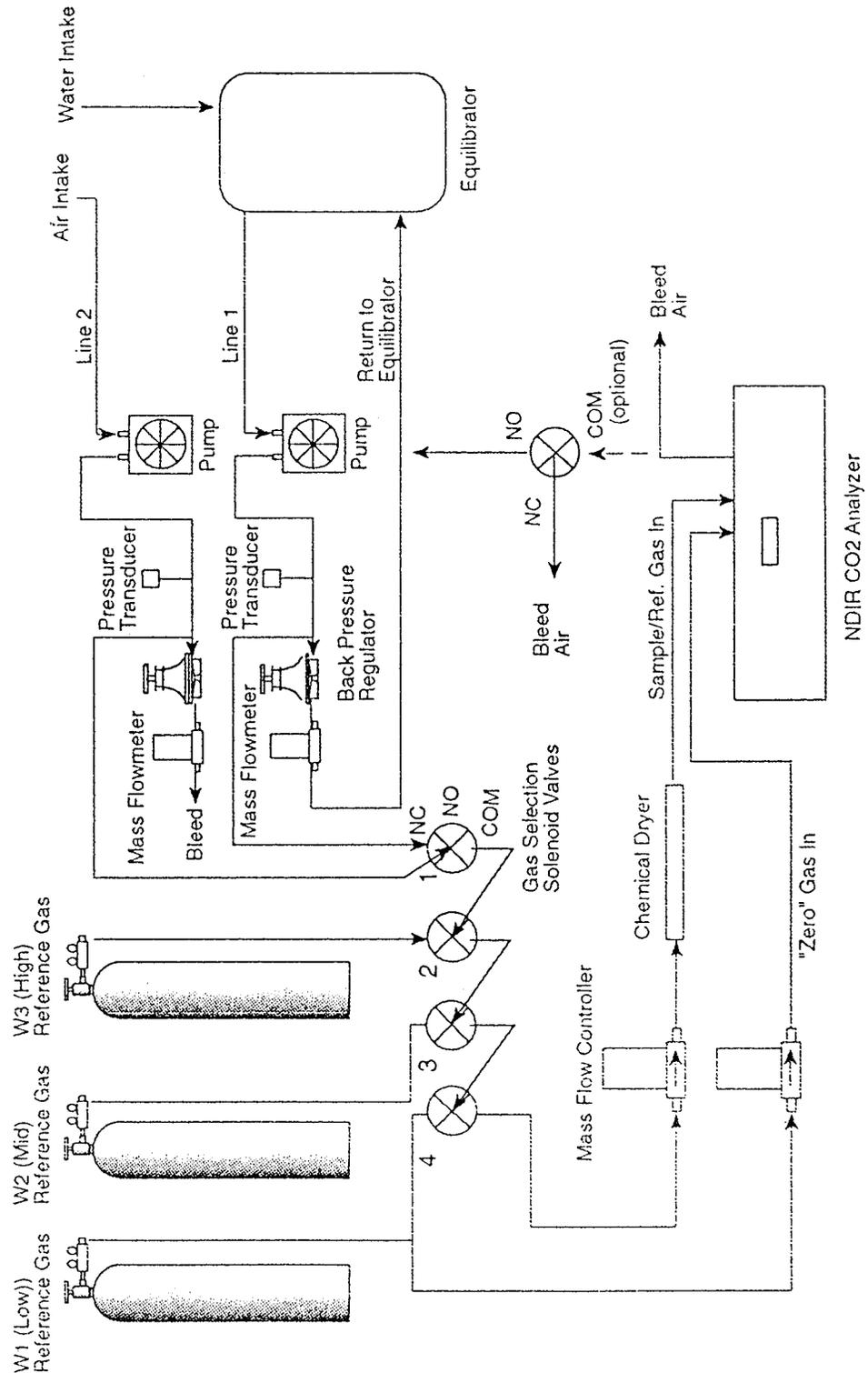
SOP 6

Determination of the pH of sea water using a glass / reference electrode cell

1. Scope and field of application

This procedure describes a method for the potentiometric determination of the pH of seawater on the total hydrogen ion concentration pH scale. The total hydrogen ion concentration, $[H^+]$, is expressed as moles per kilogram of sea water.

2. Definition

The total hydrogen ion concentration of sea water includes the contribution of the medium ion sulfate and is defined as

$$[H^+] = [H^+]_F (1 + S_T / K_S)$$
$$\approx [H^+]_F + [HSO_4^-] \; ; \tag{1}$$

$[H^+]_F$ is the *free* concentration of hydrogen ion in sea water, S_T is the total sulfate concentration ($[HSO_4^-] + [SO_4^{2-}]$) and K_S is the acid dissociation constant for HSO_4^-. The pH is then defined as the negative of the base 10 logarithm of the hydrogen ion concentration:

$$pH = -\log\left(\frac{[H^+]}{\text{mol·kg-soln}^{-1}}\right). \tag{2}$$

3. Principle

Values of pH are determined experimentally from sequential measurements of the e.m.f. (E) of the cell

| reference electrode | concentrated KCl solution | test solution | glass (H$^+$) electrode |
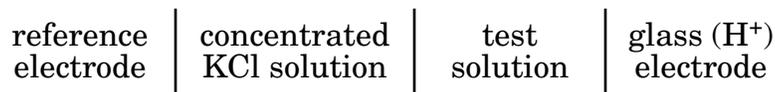
in a standard buffer (S) of known (defined) pH and in the sea water sample (X).

The operational pH is defined by the expression

$$pH\,(X) = pH(S) + \frac{E_S - E_X}{RT\,\ln 10/F} \quad . \tag{3}$$

Residual liquid-junction error is minimized by matching the composition of the standard buffer to the sea water sample, *i.e.* by making the buffer up in synthetic sea water.

Values of pH(S) have been assigned to various standard buffers in synthetic sea water. These are based on careful laboratory measurements made using cells without liquid junction.

4. Apparatus

4.1 pH cell

A combination glass / reference electrode is typically the most convenient cell to use; however, measurement quality can often be improved by using separate glass and reference electrodes.

4.2 Voltmeter with high input impedance

The e.m.f. of the glass / reference electrode cell can be measured with a pH meter or other voltmeter with a high input impedance ($>10^{13}$ Ω). If a pH meter with a sensitivity of ±0.1 mV is used to measure the e.m.f., the sensitivity in determining the pH is ±0.002 pH units. The use of a $5^1/_2$ digit voltmeter with a high input impedance (Note 1) can improve the sensitivity to better than ± 0.001 pH units. (The accuracy of the measurement is dependent upon the reliability of the assignment of pH(S) values to the calibration buffers used.)

4.3 Closed measurement container

It is necessary to measure the pH on a sample that has not had the opportunity to exchange CO_2 with the atmosphere so as to ensure reliable pH results.

4.4 Thermometer (accurate to ± 0.05 °C)

The temperature should be known or controlled to within 0.1 °C during the measurement.

---

1   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. Reagents

5.1 Synthetic seawater

5.1.1   Reagent grade NaCl (dried in an oven at 110 °C)

5.1.2   Reagent grade Na_2SO_4 (dried in an oven at 110 °C)

5.1.3   Reagent grade KCl (dried in an oven at 110 °C)

5.1.4   Calibrated solution of reagent grade $MgCl_2$ (Note 2)

5.1.5   Calibrated solution of reagent grade $CaCl_2$ (Note 2)

5.1.6   Deionized water

5.2 Buffer substances

5.2.1   Calibrated solution of HCl prepared from redistilled reagent grade HCl. Its concentration should be known to within 0.1% (Note 3).

5.2.2   2-amino-2-hydroxymethyl-1,3-propanediol ("tris"), crushed and dried in a desiccator at room temperature over phosphorus (V) oxide before use.

5.2.3   2-aminopyridine, recrystallized from a benzene–petroleum ether mixture, crushed and dried in a desiccator at room temperature over phosphorus (V) oxide before use.

6. Sampling

It is essential that the samples analyzed are collected, poisoned, and stored according to the procedures detailed in SOP 1. Care should be taken to avoid the exchange of CO_2 with the atmosphere both during sampling and during subsequent manipulation.

7. Procedures

7.1 Preparation of buffers in synthetic sea water

The compositions of a tris/HCl buffer and of a 2-aminopyridine/HCl buffer in a synthetic sea water with a salinity of 35 are given

---

[2]   Solutions of $MgCl_2$ and $CaCl_2$ can be analyzed either by measuring the density of the stock solution, by titrating with a calibrated silver nitrate solution (*e.g.* using K_2CrO_4 as an indicator) or by gravimetric precipitation of chloride.

[3]   Solutions of HCl can be analyzed accurately by coulometric titration, by a careful titration against a standard base (*e.g.* tris—NIST 723)or by gravimetric precipitation of chloride.

in Table 1. This recipe is based on a synthetic sea water (see Chapter 5, Table 6.3) in which 0.04 mol/kg-H_2O of NaCl has been replaced with HCl, and contains a total of 0.08 mol/kg-H_2O of the desired base. The simplest way to prepare this buffer accurately, is first to weigh out the hydrochloric acid and then to scale the amounts of the other constituents to match the exact amount of HCl that was weighed out. Such buffers can be stored for a few weeks, in a sealed, almost full, container.

Table 1: Composition of a buffer solution for pH in a synthetic sea water of salinity 35 (weights based on 1000 g of H_2O).

Constituent	Moles	Weight (g)[a]
NaCl	0.38762[b]	22.6446
KCl	0.01058	0.7884
$MgCl_2$	0.05474	—
$CaCl_2$	0.01075	—
Na_2SO_4	0.02927	4.1563
HCl	0.04000	—
One of:		
2-amino-2-hydroxymethyl-1,3-propanediol (tris)	0.08000	9.6837
2-aminopyridine	0.08000	7.5231
Total weight of solution containing:		
2-amino-2-hydroxymethyl-1,3-propanediol (tris)		1044.09
2-aminopyridine		1041.93

a. Weight in air at sea level (*i.e.* not corrected to mass). If a weight is not given, the component is added as the appropriate amount of a calibrated solution.
b. $m(\text{NaCl}) = 0.42762 - 0.04$ mol/kg-H_2O, *i.e.* replacing NaCl with HCl.

To compute the composition for a buffer with a salinity different to 35 (Note 4), first compute the composition of the basic artificial sea water—containing no base or HCl and with the full amount of NaCl—corresponding to the new salinity, S:

$$m_S = m_{35} \times \frac{25.5695S}{1000 - 1.0019S} \ , \tag{4}$$

---

[4]   The magnitude of the error involved in using a salinity 35 buffer for most oceanic measurements (*i.e.* in the salinity range 33–37) is probably less than 0.005 in pH. For a more complete discussion of this error see Whitfield *et al.* (1985) and Butler *et al.* (1985).

then adjust the m(NaCl) down by 0.04 mol/kg-H_2O and add 0.08 mol/kg-H_2O of base.

7.2 *Confirm response of pH cell (Note 5)*

Before a pH cell (a glass electrode / reference electrode pair) is used to measure pH, it should be tested to ensure that it is performing properly, *i.e.* that it has an ideal Nernst response.

Bring both buffers (tris and 2-aminopyridine) to the same, known temperature (*e.g.* 25 °C). Measure and record the e.m.f. of the pH cell in each buffer. The difference in the e.m.f.s is used to check the response of the pH cell (§ 8.1). If the response is not theoretical (within the experimental uncertainty), the electrodes should be rejected. E.m.f. readings obtained with a well-behaved pH cell should be stable with time (drift < 0.05 mV·min^{-1}).

7.3 *Measurement of pH*

Bring the tris buffer and the sea water samples to be measured to the same, known temperature (*e.g.* 25 °C). The e.m.f. of the pH cell is then measured, first in the tris buffer (E_S) and then in the sea water sample (E_X). Care should be taken to minimize any exposure of the sea water samples to the atmosphere so as to limit loss or gain of CO_2.

8. Calculation and expression of results

8.1 *Calculation of response of pH cell*

The defined pH values of the two buffers recommended for use in this procedure are:

2-amino-2-hydroxy-1,3-propanediol (tris)

$$
\text{pH(S)} = \frac{11997.0 + 3.7669S + 0.00178S^2}{T/K} - 381.3088 - 0.011634S
$$

$$
+ 67.63163 \ \ln(T/K) - 0.121538(T/K) - \log(1 - 0.00106S) \quad .
$$

$$
(5)
$$

---

[5] Some investigators make use of the titration curve obtained from titrating a sodium chloride solution with HCl (see SOP 3) to confirm that the electrode pair has the theoretical 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 better to verify the response of the electrode pair used with suitable buffers as is done here.

2-aminopyridine (AMP)

$$pH(S) = \frac{111.35 + 5.44875S}{T/K} + 41.6775 - 0.015683S$$

$$- 6.20815 \ln(T/K) - \log(1 - 0.00106S) \ . \qquad (6)$$

The electrode response (s) can then be calculated:

$$s = \frac{E_{AMP} - E_{TRIS}}{pH(S)_{TRIS} - pH(S)_{AMP}} \ , \qquad (7)$$

and compared with the ideal Nernst value: $RT \ln 10 / F$. If it is more than about 0.3% different the pH cell should be replaced.

8.2 *Calculation of pH*

Values of pH are calculated from the expression

$$pH(X) = pH(S) + \frac{E_S - E_X}{RT\ln 10/F} \ . \qquad (8)$$

where pH(S), the pH of tris buffer (Table 1) on the total hydrogen ion scale (expressed in mol/kg-soln) is given by Equation (5).

8.3 *Example calculations*

Input data:

$$t \quad = \quad 25\ °C\ (\textit{i.e. } T = 298.15\ K)\ ,$$
$$S \quad = \quad 35\ ,$$
$$E_{TRIS} \ = \ -0.0720\ V\ ,$$
$$E_{AMP} \ = \ 0.0049\ V\ ,$$
$$E_X \quad = \ -0.0670\ V\ .$$

Hence

$$pH(S)_{TRIS} = 8.089_3;$$
$$pH(S)_{AMP} = 6.786_6;$$
$$RT \ln 10 / F = 0.05916\ V / pH\ unit\ .$$

Thus

$$s = \frac{0.0049 - (-0.0720)}{8.0893 - 6.7866} = 0.05903\ \ V / pH\ unit\ ;$$

and

$$pH(X) = 8.0893 + \frac{-0.0720 - (-0.0670)}{0.05916} = 8.0048\ \ .$$

9. Quality assurance

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

9.2 Specific applications of analytical quality control

9.2.1 Ideality of pH cell behavior

The measured electrode response (s) should be compared with ideal Nernst behavior on a regular basis (see § 7.2). If the value is more than 0.3% from theoretical, try cleaning the glass electrode of surface deposits and measuring again. If the discrepancy persists, the electrode should be replaced.

The value of E_S in tris buffer when measured at a constant temperature (*e.g.* 25 °C) should remain stable to within a few mV. A sudden change in E_S is indicative of potential problems. Similarly, the e.m.f. of a well-behaved pH cell immersed in a thermostated buffer should be stable (drift < 0.05 mV / min).

9.2.2 Precision

A precision of 0.003 pH units (1 std. dev.) is possible with care. Plot the results of duplicate analyses on a range control chart (SOP 22).

9.2.3 Bias

The bias of potentiometric pH measurements depends on the care with which the buffer was prepared, especially with regard to the ratio between the tris and the HCl, and on the accuracy with which the values of pH(S) were originally assigned. This latter value has been estimated as being within 0.004 pH units.

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SOP 7

Determination of the pH of sea water using the indicator dye *m*-cresol purple

1. Scope and field of application

This procedure describes a method for the spectrophotometric determination of the pH of seawater on the total hydrogen ion concentration pH scale. The total hydrogen ion concentration, $[H^+]$, is expressed as moles per kilogram of sea water.

2. Definition

The total hydrogen ion concentration of sea water includes the contribution of the medium ion sulfate and is defined as

$$[H^+] = [H^+]_F (1 + S_T/K_S)$$
$$\approx [H^+]_F + [HSO_4^-] \; ; \tag{1}$$

$[H^+]_F$ is the *free* concentration of hydrogen ion in sea water, S_T is the total sulfate concentration ($[HSO_4^-] + [SO_4^{2-}]$) and K_S is the acid dissociation constant for HSO_4^-. The pH is then defined as the negative of the base 10 logarithm of the hydrogen ion concentration:

$$pH = -\log\left(\frac{[H^+]}{mol \cdot kg\text{-}soln^{-1}}\right). \tag{2}$$

3. Principle

The values of pH are determined by adding an indicator dye to sea water. For the sulfonephthalein indicators such as *m*-cresol purple the reaction of interest at sea water pH is the second dissociation

$$HI^-(aq) = H^+(aq) + I^{2-}(aq) \; ; \tag{3}$$
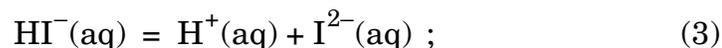
the indicator being present at a low level in a sea water sample. The total hydrogen ion concentration of the sample can then be determined:

$$\text{pH} = \text{p}K^*(\text{HI}) + \log\frac{[\text{I}^{2-}]}{[\text{HI}^-]} \quad . \tag{4}$$

The principle of this approach uses the fact that the different forms of the indicator have substantially different absorption spectra. Thus the information contained in the composite spectrum can be used to estimate $[\text{I}^{2-}]/[\text{HI}^-]$.

At an individual wavelength, λ, the measured absorbance in a cell with a path length, l, is given by the Beer-Lambert law as:

$$\frac{A_\lambda}{l} = \varepsilon_\lambda(\text{HI}^-)[\text{HI}^-] + \varepsilon_\lambda(\text{I}^{2-})[\text{I}^{2-}] + B_\lambda + e \quad , \tag{5}$$

where B_λ corresponds to the background absorbance of the sample and e is an error term due to instrumental noise. Provided that the values of the extinction coefficients: $\varepsilon_\lambda(\text{HI}^-)$ and $\varepsilon_\lambda(\text{HI}^{2-})$ have been measured as a function of wavelength, absorbance measurements made at two or more wavelengths can be used to estimate the ratio $[\text{I}^{2-}]/[\text{HI}^-]$.

In the case that only two wavelengths are used, and provided that the background can be eliminated effectively by a subtractive procedure, (5) can be rearranged to give (assuming no instrumental error):

$$\frac{[\text{I}^{2-}]}{[\text{HI}^-]} = \frac{A_1/A_2 - \varepsilon_1(\text{HI}^-)/\varepsilon_2(\text{HI}^-)}{\varepsilon_1(\text{I}^{2-})/\varepsilon_2(\text{HI}^-) - (A_1/A_2)\varepsilon_2(\text{I}^{2-})/\varepsilon_2(\text{HI}^-)} \quad ; \tag{6}$$

the numbers 1 and 2 refer to the wavelengths chosen. For the best sensitivity the wavelengths corresponding to the absorbance maxima of the base (I^{2-}) and acid (HI^-) forms respectively are used. The various terms ε are the extinction coefficients of the specified species at wavelengths 1 and 2 respectively.

4. Apparatus

4.1 *Flexible drawing tube*

Approximately 40 cm long, sized to fit snugly over cell port. Silicone rubber is suitable for this (see Note 1 in SOP 1).

4.2   Spectrophotometric cells

These should be made of optical glass with a 10 cm path-length, two ports and PTFE stoppers. A sufficient number of cells is needed to collect all the samples that will be analyzed from a particular cast (see § 6).

4.3   Micropipette

This is used to add the dye to the cell. It should be of ~0.1 cm^3 capacity with a narrow PTFE tube attached to act as a nozzle.

4.4   High-quality spectrophotometer

For work of the highest sensitivity and precision a double-beam spectrophotometer is desirable. However, good results can be obtained with a high-quality single-beam instrument.

4.5   Temperature-control system for spectrophotometer cell

Commercially-manufactured, thermostated spectrophotometer compartments that can accommodate 10 cm cells are rarely available and one will probably have to be custom-made. The temperature should be regulated to better than 0.1 °C.

4.6   System to warm samples to measurement temperature

Although it is possible to warm up the cells containing samples in Ziploc$^®$ bags in a thermostat bath, this is inconvenient. It is much better to build a custom-made thermostated compartment that can hold ~12 cells at once without getting them wet.

4.7   Thermostat bath (±0.05 °C)

This is used to regulate the temperature of the cell compartment and also the temperature of the system in § 4.6.

5.   Reagents

5.1   Solution of m-*cresol purple*

A concentrated (at least 2 mmol·dm^{-3}) dye solution of known pH adjusted to be in the range 7.9 ± 0.1 pH units— chosen to match pH measurements from an oceanic profile—is required; this implies for *m*-cresol purple that $A_1/A_2 \approx 1.6$ (Note 1).

---

[1]   The absorbance ratio of a concentrated dye solution can be measured using a cell with a short path length (0.5 mm).

6.   Sampling

Draw the sample—using the drawing tube—directly from the Niskin bottle (or other water sampler) into the optical cell. After flushing with several hundred cm^3 of seawater—a flushing time of 15–20 seconds— seal the cell with the PTFE caps ensuring that there is no head-space. Since the pH samples must be analyzed immediately, there is no long-term storage or preservation protocol. However, while awaiting analysis store the samples in the dark at room temperature.

7.   Procedures

7.1   Warm sample cell to 25.0 °C (± 0.1 °C).

This is done in by placing a number of cells in a thermostated compartment (see § 4.6) for some hours.

7.2   Measure absorbances for the cell + seawater.

Clean and dry the exterior of the cell; place the cell in the thermostated sample compartment of the spectrophotometer. Measure and record the absorbances at three wavelengths: a non-absorbing wavelength (730 nm for *m*-cresol purple) and at the wavelengths corresponding to the absorption maxima of the base (I^{2-}) and acid (HI^-) forms of the dye respectively (578 and 434 nm).

7.3   Inject dye into cell.

Remove one of the cell caps, add approximately 0.05 to 0.1 cm^3 of concentrated dye (~2 mmol·dm^{-3}) to the sample, replace the cap and shake the cell to mix the sea water and dye. The amount of dye required is that which will produce absorbance values of between 0.4 and 1.0 at each of the two absorbance peaks.

7.4   Measure absorbances of cell + sea water + dye.

Return the cell to the spectrophotometer and again measure the absorbances at the three wavelengths used in § 7.2.

8.   Calculation and expression of results

8.1   Correction of measured absorbances

At each of the three wavelengths, subtract the absorbances measured for the background measurement (without dye) from

the corresponding absorbances measured for the system containing dye.

In addition, the absorbance measured at a non-absorbing wavelength is used to monitor and correct for any baseline shift due to error in repositioning the cell, instrumental shifts, *etc.* (Note 2). This assumes that the magnitude of any observed baseline shift is identical across the visible spectrum. To do this, subtract the measured shift from the background corrected absorbances at wavelengths 1 and 2 to obtain the final corrected absorbance value at each wavelength.

These final absorbance values, corrected for background absorbances *and* any observed baseline shifts, are used to calculate A_1/A_2, the absorbance ratio which describes the extent of protonation of the dye.

8.2   Calculation of the pH of the sea water + dye

The pH of the sea water and dye in the cell is computed from

$$
\text{pH} = \text{p}K_2 + \log\left(\frac{A_1/A_2 - \varepsilon_1(\text{HI}^-)/\varepsilon_2(\text{HI}^-)}{\varepsilon_1(\text{I}^{2-})/\varepsilon_2(\text{HI}^-) - (A_1/A_2)\varepsilon_2(\text{I}^{2-})/\varepsilon_2(\text{HI}^-)}\right) \;;
$$

$$(7)$$

$\text{p}K_2$ is the acid dissociation constant for the species HI^- (expressed on the total hydrogen ion concentration scale in mol/kg-soln), A_1 and A_2 are the corrected absorbances measured at the wavelengths corresponding to the absorbance maxima of the base and acid forms respectively. The various extinction coefficient terms ε correspond to values measured for the specified species at wavelengths 1 and 2 respectively.

Table 1: Extinction coefficient ratios for *m*-cresol purple;
$\lambda_1 = 578$ nm ; $\lambda_2 = 434$ nm.

$\varepsilon_1(\text{HI}^-)/\varepsilon_2(\text{HI}^-)$	0.0069_1
$\varepsilon_1(\text{I}^{2-})/\varepsilon_2(\text{HI}^-)$	2.222_0
$\varepsilon_2(\text{I}^{2-})/\varepsilon_2(\text{HI}^-)$	0.133_1

---

[2]   The difference between the baseline absorbance (sea water only) and the absorbance of the sample + dye at 730 nm should be no greater than ± 0.001; if this value is exceeded, the cell should be removed and the optical windows cleaned before the absorbances are measured again.

The equilibrium constant K_2 is a function of salinity and temperature and has been determined by careful laboratory measurements. For m-cresol purple,

$$\text{p}K_2 = \frac{1245.69}{(T/\text{K})} + 3.8275 + 0.00211(35 - S) \ , \tag{8}$$

where $293 \leq T/\text{K} \leq 303$ and $30 \leq S \leq 37$.

8.3   Correction for pH change resulting from addition of the dye

The addition of indicator dye to the sea water sample will perturb the pH (another acid-base system has been added!). Although care is taken to minimize this (by adjusting the dye solution pH), it is desirable to correct for the addition of dye to obtain the best pH measurements.

Although, in principle, the pH perturbation could be calculated from a knowledge of the equilibrium chemistry of the sample and the dye, it is simpler to evaluate the magnitude of the correction empirically. A pair of additions of dye are made to each of a series sea water samples with different pHs, and the change in the measured ratio A_1/A_2 with the second addition of indicator solution is determined as a function of the measured value (A_1/A_2) determined after the first addition of dye using a least-squares procedure (SOP 23):

$$\frac{\Delta(A_1/A_2)}{V} = a + b(A_1/A_2) \ , \tag{9}$$

where V is the volume of dye added at each addition. The final, corrected, absorbance ratio:

$$(A_1/A_2)_{corr} = (A_1/A_2) - V(a + b(A_1/A_2)) \tag{10}$$

8.4   An example calculation

$t \quad = \quad 25\,°\text{C} \ ;$

$S \quad = \quad 35 \ ;$

$\text{p}K_2 = \quad 8.0056 \ ;$

and for indicator stock solution with $A_1/A_2 = 1.6$,

$$\frac{\Delta(A_1/A_2)}{V} = 0.125 - 0.147(A_1/A_2) \ .$$

Measured absorbances:

Sea water: $A_{434} = 0.02433 \ ; A_{578} = 0.01936 \ ; A_{730} = 0.08365$

Dye + sea water: $A_{434} = 0.45123 \ ; A_{578} = 0.84574 \ ; A_{730} = 0.08298$

Then after addition of dye:

$$A_1 / A_2 = \frac{0.84574 - 0.01936 - (0.08298 - 0.08365)}{0.45123 - 0.02433 - (0.08298 - 0.08365)} = 1.93430 \ ;$$

corrected to zero dye addition ($V = 0.08 \text{ cm}^3$),

$$
\begin{aligned}
(A_1 / A_2)_{corr} &= 1.93430 - 0.08(0.125 - 0.147(1.93430)) \\
&= 1.94705
\end{aligned}
\tag{11}
$$

and thus

$$\text{pH} = 8.0056 + \log\left(\frac{1.94705 - 0.00691}{2.2220 - 1.94705 \times 0.1331}\right) = 8.0005 \ .$$

9. Quality assurance

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

9.2   Specific applications of analytical quality control

9.2.1   Spectrophotometer performance

The spectrophotometric performance of the instrument used can be confirmed using reference materials that are available from the U. S. National Institute for Standards and Technology (NIST). SRM 2034 is a holmium oxide solution in a sealed cuvette that allows the wavelength accuracy of the spectrophotometer to be determined; SRM 930d is a set of absorbance filters that allows the absorbance measurement accuracy to be verified. Property control charts should be maintained of these measurements and the spectrophotometer adjusted if it goes out of tolerance. (Nevertheless, the procedure detailed here is fairly insensitive to minor changes in spectrophotometer performance.)

A more important concern is that the spectrometer have a high stability. This can be confirmed by making a series of repeated measurements on a system of constant absorbance (*e.g.* SRM 930d or a thermostated buffer solution containing indicator dye) and computing the standard deviation at the wavelengths of interest.

9.2.2   Precision

A precision of better than 0.001 pH units (1 std. dev.) is possible with care—particularly in regard to the sample handling. The results of duplicate analyses should be plotted on a range control chart (SOP 22).

9.2.3 Bias

The bias of spectrophotometric pH measurements depends on the accuracy with which the various extinction coefficient ratios were determined, and on the accuracy of the values assigned to the values of pK_2. A significant advantage of spectrophotometric measurements is that, if more accurate information becomes available for these parameters at a later time, the pH results obtained can be adjusted without any degradation in precision., provided that the original data are retained. At present, the likely bias is estimated to be less than than 0.005 pH units.

References

Byrne R. H. & J. A. Breland (1989) High precision multiwavelength pH determinations in seawater using cresol red. *Deep-Sea Research* **36**, 803–810.

Byrne R. H., G. Robert-Baldo, S. W. Thompson & C. T. A. Chen (1988) Seawater pH measurements: an at-sea comparison of spectrophotometric and potentiometric methods. *Deep-Sea Research* **35**, 1405–1410.

Clayton T. D. & R. H. Byrne (1993) Spectrophotometric seawater pH measurements: total hydrogen ion concentration scale calibration of m-cresol purple and at-sea results. *Deep-Sea Research* **40**, 2115–2129.

Dickson A. G. (1993) The measurement of sea water pH. *Marine Chemistry* **44**, 131–142.

SOP 11

Gravimetric calibration of the volume of a gas loop using mercury

1. Scope and field of application

This procedure describes how to calibrate the volume of a length of stainless steel tubing coiled as a loop. Such loops are used together with a valve system to deliver known amounts of pure carbon dioxide to calibrate the coulometer used in the extraction / coulometric procedure for determining total dissolved inorganic carbon in sea water (SOP 2). This procedure is capable of achieving a reproducibility of about 0.01% (1 relative standard deviation). A procedure is also detailed for computing the volume of the loop, in the valve assembly, at temperatures different from the calibration temperature.

2. Principle

The loop is weighed empty and full of mercury and its volume at the calibration temperature is computed from the mass of mercury contained. The volume at another temperature can then be calculated by allowing for the thermal expansion of the tubing.

3. Apparatus

3.1 Analytical balance, capacity 100 g, sensitivity 0.1 mg

3.2 Thermometer accurate to ± 0.2 °C

3.3 Length of 316 stainless steel tubing $^1/_{16}$ inch outside diameter, electropolished on the inside and coiled as a loop. The ends of the tubing must be cut perfectly square (Note 1).

---

[1] Using $^1/_{16}$ inch tubing minimizes the size of the inlet ports in the chromatography valve used with the gas loop as well as errors due to the mercury meniscus. The square ends are needed to ensure that the tubing fits perfectly into the valve ports.

4. Reagents

4.1 Clean mercury (Note 2)

4.2 Acetone (analytical grade)

4.3 Supply of clean, dry, gas

4.4 Source of vacuum

5. Procedure

5.1 Clean the loop prior to weighing

It is essential that the loop be scrupulously clean before the measurement and that it remain that way. This can be achieved as follows: rinse the exterior of the loop and flush the interior of the loop repeatedly with acetone. Then blow the loop dry using clean dry gas. Use gloves or tongs to handle the loop at all times to maintain its cleanliness. If a gas with a density different from air is used to dry the loop (*e.g.* helium), it is important that this gas be flushed out of the tube with laboratory air prior to weighing.

5.2 Weigh the empty loop on an analytical balance

5.3 Fill the loop with mercury prior to reweighing (Note 3)

Immerse one end of the loop in a beaker of clean mercury (Note 4). The other end of the loop should also be maintained below the mercury level. Fill the loop with mercury by sucking it through the loop using a piece of flexible, transparent, plastic tubing (*e.g.* Tygon®) connected to a vacuum pump. Once the stainless steel loop is full, disconnect the plastic tubing from the loop and allow the mercury to continue syphoning through the loop to ensure that no air bubbles remain in the tube.

---

[2] Mercury can be cleaned satisfactorily by washing it thoroughly with dilute nitric acid and dilute sodium hydroxide, then rinsing it with copious amounts of deionized water. The mercury is dried by dabbing the excess water off the top using a piece of filter paper then filtering it through a pinhole in a filter paper.

[3] Mercury vapor is potentially hazardous and mercury should be handled appropriately. In particular, efforts should be made to minimize spillage and to contain such spills as occur.

[4] Both the mercury and stainless steel loop must be allowed to equilibrate with the room temperature before starting this procedure.

Once at least one loop volume has siphoned through, close the ends of the loop with the fingertips—wearing disposable plastic gloves—and invert the loop so that the open ends are upward.

Top the loop off with small droplets of mercury which are picked up using a syringe needle. Examine the ends closely to ensure that they are filled correctly (Note 5). Replace the disposable gloves before handling the loop further (Note 6).

Note the temperature of the mercury and weigh the filled loop.

5.4 *Empty the loop of mercury*

Provided that the loop is scrupulously clean, the mercury will siphon out cleanly. If on reweighing, the loop is still thought to contain mercury, the loop should be blown through with a clean dry gas, taking care to catch the mercury droplets that are blown out. Again, make sure the loop is filled with laboratory air before reweighing.

5.5 *Assemble the valve*

Once accurate volumes have been obtained for both loops, mount the loops on the valve. It is essential that the stainless steel tubing fit perfectly into the valve ports and that the tubing is held firmly while tightening the fittings.

6.   Calculation and expression of results

6.1 *Volume of the tubing used as the loop*

The weight of the mercury contained is computed from the difference between the filled and empty loop weights:

$$w(\text{Hg}) \; = \; w(\text{filled loop}) \; - \; w(\text{empty loop}) \quad .$$

The mass of mercury contained is computed from the weight, correcting for air buoyancy (see SOP 21). The volume of the loop at the temperature of weighing is given by the expression

$$V(t) = \; m(\text{Hg}) \, / \, \rho(\text{Hg}) \quad .$$

---

[5]   One method of achieving this is to use two small transparent plastic weighing boats which are used to flatten and observe the mercury meniscus.

[6]   Small droplets of mercury adhering to the outside of the loop are a significant cause of contamination and must be avoided. This is a precaution to help achieve this.

The density of mercury over the range $0 - 40$ °C is given by:

$$\rho(\text{Hg}) = 13.5955 \left[1 - \alpha_V(\text{Hg}) \left(\frac{t}{°C} \right) \right] \text{g} \cdot \text{cm}^{-3} \quad ;$$

where t is the temperature. The volumetric coefficient of expansion

$$\alpha_V(\text{Hg}) = \left(181792 + 0.175 \left(\frac{t}{°C} \right) + 0.035116 \left(\frac{t}{°C} \right)^2 \right) \times 10^{-9}$$

Weast (1975). The temperature of the mercury, t, must be known to within 0.5 °C to achieve an accuracy of better than 1 part in 10^4.

6.2 *Volume in the valve configuration*

The volume of the coiled tubing is not the only contribution to the volume of a loop on a chromatography valve. Although it is possible to plumb an eight port chromatography valve so that the path through the valve rotor is not part of the loop (see Annexe A to SOP 2), allowance needs to be made for the volume of the valve inlet ports. This information is typically available from the manufacturer.

6.3 *Volume at an alternate temperature*

The thermal expansion of the tubing being used must be taken into account to convert volume measured at one temperature (t) to a standard or alternate temperature (θ). For 316 stainless steel the coefficient of linear expansion α_l is about 1.73×10^{-5} K^{-1} (Weast, 1975). The coefficient of volumetric expansion,

$$\alpha_V = (1 + \alpha_l)^3 - 1 \approx 3 \, \alpha_l \quad ,$$

is used to calculate the volume at the alternate temperature:

$$V(\theta) = V(t) \left\{ 1 + \alpha_V (\theta - t) \right\} \quad .$$

6.4 *Example calculation*

The following data were used for this calculation:

> weighing conditions
>> $\rho(\text{air}) = 0.0012$ g·cm^{-3} (Note 7),
>> $\rho(\text{weights}) = 8.0$ g·cm^{-3} ,
>
> calibration temperature = 23.0 °C ,

---

[7]   This value is appropriate to measurements of moderate accuracy made at sea level pressure (1 atm) and at normal laboratory temperatures (~20 °C). For a more accurate value see SOP 21, equation (1).

$w(\text{Hg}) = 15.0000 \text{ g}$,
$\rho(\text{Hg, 23.0 °C}) = 13.5386 \text{ g·cm}^{-3}$,
$V(\text{inlet port}) = 1.6 \times 10^{-4} \text{ cm}^3$,
temperature of use $\theta = 30.0$ °C .

6.4.1 Correct weight of mercury to mass:

$m(\text{Hg}) = 14.9991 \text{ g}$.

6.4.2 Compute volume of stainless steel tubing at $t = 23.0$ °C:

$V(t) = 1.10791 \text{ cm}^3$.

6.4.3 Compute volume of loop at $t = 23.0$ °C
(*i.e.* including two inlet ports):

$V(\text{loop}, t) = 1.10823 \text{ cm}^3$.

6.4.4 Compute volume of loop at $\theta = 30.0$ °C:

$V(\text{loop}, \theta) = 1.10863 \text{ cm}^3$.

7. Quality asurance

The following points should be noted:

- The weights for the stainless steel tubing (empty of mercury) obtained at each measurement should agree with each other to ± 1 mg. This confirms that the tubing is being cleaned adequately before each weighing.
- Measurements of the volume of the stainless steel tubing made on different days should agree with each other when corrected to a standard temperature.
- The ratio of measured loop volumes from a pair of loops should agree with the ratio of the amounts of CO_2 gas delivered as determined by the coulometer.

References

Weast, R. F. (1975) *CRC Handbook of chemistry and physics*, 56th edition, Chemical Rubber Company.

SOP 12

Gravimetric calibration of volume delivered using water

1.   Scope and field of application

This procedure describes how to calibrate the volume of water delivered by a volumetric pipette—or similar device such as a Knudsen style pipette, a syringe or a piston burette. This is expressed as the volume delivered at a standard temperature (20.0 °C). This procedure is capable of achieving a reproducibility of better than 0.01% (1 relative standard deviation).

2.   Principle

The mass of water delivered by the device at a measured calibration temperature is used to compute the volume of water delivered at that temperature. The volume that would be delivered at the standard temperature (20 °C) can be calculated by taking account of the volumetric expansion of the dispenser. The volume of liquid delivered at any desired temperature can be calculated in a similar fashion.

3.   Apparatus

3.1   Analytical balance capable of weighing the quantity of water delivered with a resolution of 1 part in 10^5 while having sufficient capacity to weigh the water together with the glass container used to collect it.

3.2   Clean dry glass containers with suitable closures (Note 1)

3.3   Thermometer accurate to ± 0.1 °C

3.4   Timer

---

[1]   If the container and water will be weighed shortly after delivery then an ungreased ground glass stopper, or even a screw cap, is suitable. If it will be some time before the water delivered is weighed, as when samples are delivered on board ship, it is essential that the closure chosen be both air and water-tight.

4. Reagents

4.1 Deionized water

5. Procedure

5.1 Weigh the clean, dry, empty container together with the associated closure.

5.2 Fill the clean pipette or other apparatus being calibrated with deionized water. Allow the temperature of the pipette and water to reach an equilibrium value. Note this temperature.

5.3 Allow the water to drain into the pre-weighed container for a controlled time (60 seconds).

5.4 Close the container and reweigh it.

6. Calculation and expression of results

6.1 Volume of water delivered at the calibration temperature

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

$$w(\text{H}_2\text{O}) \;=\; w(\text{filled container}) - w(\text{empty container}) \,. \qquad (1)$$

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

$$m(\text{H}_2\text{O}) \;=\; w(\text{H}_2\text{O})\left(\frac{1 - \rho(\text{air})/\rho(\text{weights})}{1 - \rho(\text{air})/\rho(\text{sample})}\right) \,. \qquad (2)$$

The volume dispensed at the temperature noted (t) is

$$V(t) = \; m(\text{H}_2\text{O}) \,/\, \rho(\text{H}_2\text{O}, t) \,. \qquad (3)$$

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

$$\rho_\text{W} \,/\, (\text{kg·m}^{-3}) \;=\; 999.84847 + \; 6.337563 \times 10^{-2} \, (t/\text{°C})$$

$$- \; 8.523829 \times 10^{-3} \, (t/\text{°C})^2 \; + 6.943248 \times 10^{-5} \, (t/\text{°C})^3$$

$$- \; 3.821216 \times 10^{-7} \, (t/\text{°C})^4 \,, \qquad (4)$$

where t is the temperature on ITS 90 (Note 2). To achieve an accuracy of 1 part in 10^4, t must be known to within 0.5 °C.

6.2 Volume that would be delivered at an alternate temperature

To convert the volume dispensed at one temperature (t_1) to the volume that would be delivered at a standard or alternate temperature (t_2), we need to take account of the thermal expansion of the dispenser being used. For pyrex-like glasses (Corning 7740, Kimble KG-33, Schott Duran, Wheaton 200, *etc.*) the coefficient of linear expansion α_l is 32.5×10^{-7} K^{-1}; for glasses such as Kimble KG-35, α_l is about 55×10^{-7} K^{-1}. The coefficient of volumetric expansion,

$$\alpha_V = (1 + \alpha_l)^3 - 1 \approx 3\,\alpha_l\ , \tag{5}$$

is used to calculate the corrected volume at the alternate temperature:

$$V(t_2) = V(t_1)\left\{1 + \alpha_V\,(t_2 - t_1)\right\} . \tag{6}$$

This correction is negligible for all except the most precise work unless $(t_2 - t_1)$ exceeds 10 °C.

6.3 Example calculation

6.3.1   The following data were used for this calculation:

$$w(\text{H}_2\text{O}) = 30.0000 \text{ g} ,$$
calibration temperature = 23.0 °C ,
$$\rho(\text{H}_2\text{O}, 23.0\text{ °C}) = 0.997535 \text{ g·cm}^{-3} ,$$
$$\alpha_l = 32.5 \times 10^{-7} \text{ K}^{-1} ,$$
weighing conditions
$$\rho(\text{air}) = 0.0012 \text{ g·cm}^{-3} \text{ (Note 3)} ,$$
$$\rho(\text{weights}) = 8.0 \text{ g·cm}^{-3} .$$

6.3.2   Correct weight of water to mass:

$$m(\text{H}_2\text{O}) = 30.0000 \times \frac{1 - 0.0012/8.0}{1 - 0.0012/0.997541}$$

$$= 30.0316 \text{ g} .$$

---

[2]   The International Practical Temperature Scale of 1968 (IPTS 68) has recently been superceded by the International Temperature Scale of 1990 (ITS 90). A simple equation can be used to relate the two over the oceanographic temperature range 0 to 40 °C (Jones & Harris, 1992):

$$t_{90} = 0.0002 + 0.99975\ t_{68} .$$

The small difference in temperature scales is typically not important to the calibration of glassware for the procedures in this Handbook.

[3]   This value is appropriate to measurements of moderate accuracy made at sea level pressure (1 atm) and at normal laboratory temperatures (~20 °C). For a more accurate value see SOP 21, Equation (1).

6.3.3   Compute volume of water delivered at the calibration temperature of 23.0 °C:

$$V(23.0\ °C)\ =\ 30.0316 / 0.997535$$
$$=\ 30.1058\ cm^3\ .$$

6.3.4   Compute volume that would be dispensed at the standard temperature of 20.0 °C, *i.e.* the standard calibrated volume.

$$V(20.0\ °C)\ =\ 30.1058\ \{1 + 3\,(32.5 \times 10^{-7})(20.0 - 23.0)\}$$
$$=\ 30.1049\ cm^3\ .$$

6.3.5   Compute volume that is dispensed at 25 °C.

$$V(25.0\ °C)\ =\ 30.1049\ \{1 + 3\,(32.5 \times 10^{-7})(25.0 - 20.0)\}$$
$$=\ 30.1064\ cm^3\ .$$

7.   Quality assurance

To ensure that the volume dispensed is in control, the amount dispensed should be measured regularly and a property control chart maintained of the volume as corrected to 20 °C (see SOP 22).

References

Jones F. E. & G. L. Harris (1992) ITS-90 density of water formulation for volumetric standards calibration. *Journal of Research of the National Institute of Standards and Technology* **97**, 335–340.

SOP 13

Gravimetric calibration of volume contained using water

1.   Scope and field of application

This procedure describes how to calibrate the volume of solution contained by a volumetric flask or other container capable of being filled to a reproducible mark. This is expressed as the volume contained at a standard temperature (20.0 °C). This procedure is capable of achieving a reproducibility of better than 0.01% (1 relative standard deviation).

2.   Principle

The mass of water contained by the flask at a measured calibration temperature is used to compute the volume of water contained at that temperature. The volume that would be contained at the standard temperature (20 °C) can be calculated by taking account of the volumetric expansion of the flask. The volume of liquid contained at any desired temperature can be calculated in a similar fashion.

3.   Apparatus

3.1   Analytical balance capable of weighing the quantity of water contained with a sensitivity of 1 part in 10^5 while having the capacity to weigh the water together with the container being calibrated.

3.2   Thermometer accurate to ± 0.1 °C

4.   Reagents

4.1   Deionized water

5. Procedure

5.1 Weigh the clean dry empty container together with the associated closure.

5.2 Fill the container being calibrated to the mark with deionized water, allowing the temperature of the container and contained water to reach an equilibrium value. Note this temperature.

5.3 Close the container and reweigh it.

6. Calculation and expression of results

6.1 Volume of the water contained at the calibration temperature

Compute the weight of the water contained from the difference between weights of the filled and empty container:

$$w(\text{H}_2\text{O}) \ = \ w(\text{filled container}) \ - \ w(\text{empty container}) \,. \qquad (1)$$

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

$$m(\text{H}_2\text{O}) \ = \ w(\text{H}_2\text{O})\left(\frac{1 - \rho(\text{air})/\rho(\text{weights})}{1 - \rho(\text{air})/\rho(\text{sample})}\right) \quad . \qquad (2)$$

The volume contained at the noted temperature, t, is

$$V(t) = \ m(\text{H}_2\text{O}) \, / \, \rho(\text{H}_2\text{O}, t) \,. \qquad (3)$$

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

$$\rho_\text{W} \, / \, (\text{kg·m}^{-3}) \ = \ 999.84847 \ + \ 6.337563 \times 10^{-2} \, (t/^\circ\text{C})$$
$$- \ 8.523829 \times 10^{-3} \, (t/^\circ\text{C})^2 \ + 6.943248 \times 10^{-5} \, (t/^\circ\text{C})^3$$
$$- \ 3.821216 \times 10^{-7} \, (t/^\circ\text{C})^4 \,, \qquad (4)$$

where t is the temperature on ITS 90 (Note 1). To achieve an accuracy of 1 part in 10^4, t must be known to within 0.5 °C.

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[1] The International Practical Temperature Scale of 1968 (IPTS 68) has recently been superceded by the International Temperature Scale of 1990 (ITS 90). A simple equation can be used to relate the two over the oceanographic temperature range 0 to 40 °C (Jones & Harris, 1992):

$$t_{90} = 0.0002 + 0.99975 \, t_{68} \,.$$

The small difference in temperature scales is typically not important to the calibration of glassware for the procedures in this Handbook.

6.2 Volume that would be contained at an alternate temperature

To convert volume contained at one temperature (t_1) to a standard or alternate temperature (t_2), we need to take account of the thermal expansion of the container being used. For pyrex-like glasses (Corning 7740, Kimble KG-33, Schott Duran, Wheaton 200, *etc.*) the coefficient of linear expansion α_l is 32.5×10^{-7} K^{-1}; for glasses such as Kimble KG-35, α_l is about 55×10^{-7} K^{-1}.

The coefficient of volumetric expansion,

$$\alpha_V \;=\; (1 + \alpha_l)^3 - 1 \;\approx\; 3\,\alpha_l \;, \tag{5}$$

is used to calculate the corrected volume at the alternate temperature:

$$V(t_2) \;=\; V(t_1)\,\{1 + \alpha_V\,(t_2 - t_1)\} \quad . \tag{6}$$

This correction is negligible for all except the most precise work; unless $(t_2 - t_1)$ exceeds 10 °C or if plastic ware is used.

6.3 Example calculation

6.3.1 The following data were used for this calculation:

$w(\mathrm{H_2O}) \;=\; 996.55$ g ,
calibration temperature = 23.0 °C ,
$\rho(\mathrm{H_2O},\ 23.0\ °\mathrm{C}) \;=\; 0.997535$ g·cm^{-3} ,
α_l is 32.5×10^{-7} K^{-1} ,
weighing conditions
$\rho(\mathrm{air}) = 0.0012$ g·cm^{-3} (Note 2),
$\rho(\mathrm{weights}) = 8.0$ g·cm^{-3} .

6.3.2 Correct weight of water to mass:

$$m(\mathrm{H_2O}) \;=\; 996.55 \times \frac{1 - 0.0012/8.0}{1 - 0.0012/0.997535}$$

$$=\; 997.60\ \mathrm{g}\ .$$

6.3.3 Compute volume of water contained at the calibration temperature of 23.0 °C:

$$V(23.0\ °\mathrm{C}) \;=\; 997.60\,/\,0.997535$$

$$=\; 1000.07\ \mathrm{cm}^3\ .$$

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2 This value is appropriate to measurements of moderate accuracy made at sea level pressure (1 atm) and at normal laboratory temperatures (~20 °C). For a more accurate value see SOP 21, Equation (1).

6.3.4 Compute volume that would be contained at the standard temperature of 20.0 °C, *i.e.* the standard calibrated volume.

$$V(20.0\,°\mathrm{C}) = 1000.07\,\{1 + 3\,(32.5\times10^{-7})(20.0 - 23.0)\}$$
$$= 1000.04\ \mathrm{cm}^3\,.$$

6.3.5 Compute volume that would be contained at 25 °C.

$$V(25.0\,°\mathrm{C}) = 1000.04\,\{1 + 3\,(32.5\times10^{-7})(25.0 - 20.0)\}$$
$$= 1000.09\ \mathrm{cm}^3\,.$$

7. Quality assurance

To ensure that the volume contained is in control, the amount contained should be measured regularly and a property control chart maintained of the volume as corrected to 20 °C (see SOP 22).

References

Jones F. E. & G. L. Harris (1992) ITS-90 density of water formulation for volumetric standards calibration. *Journal of Research of the National Institute of Standards and Technology* **97**, 335–340.

SOP 14

Electronic calibration of the UIC Model 5011 coulometer

1. Scope and field of application

This procedure details how to determine the internal electronic calibration factor of the coulometer used in the determination of the total dissolved inorganic carbon in sea water (*i.e.* the UIC Model 5011—SOP 2). Doing this allows the performance of the current integrating circuitry of the coulometer to be assessed independently of any chemical procedures thus providing a valuable diagnostic check, particularly if there is a sudden unexplained change in calibration factor. Changes in the electronic calibration can indicate problems with the coulometer circuitry.

2. Principle

The internal circuitry of the coulometer uses a precision resistor in series with the external coulometer cell. The voltage across this resistor is input to a voltage to frequency converter module. This module then produces a stream of pulses whose frequency depends on the instantaneous voltage across the resistor, *i.e.* the current. The rate of pulse generation is adjusted at the factory to be $10\,000$ pulses s^{-1} when the current is 200 mA. The pulses are counted and the total number produced in a particular time interval is thus proportional to the total charge passed in that time interval.

To check the electronic calibration, the coulometer is adjusted to provide a constant current through an external precision resistor. This current is integrated by the coulometer for an accurately known time period. Simultaneously, the average voltage is measured across the external resistor.

The number of counts displayed is then compared with the number of counts that would correspond to the average current which is measured in the external circuit.

Measurements are carried out at at least two different current levels and the results obtained are used to assess the performance of the charge measuring circuitry in the coulometer. The simple calibration described here checks the current at two values: at ~50 mA and at ~2 mA. If desired, a more detailed calibration can be done using a variety of currents. The coulometer circuitry uses a different gain stage for measuring currents below and above 12 mA and thus a more detailed investigation may find that a slight change in the calibration occurs at that point.

3. Apparatus

3.1   Coulometer to be checked.

3.2   A high quality $5^1/_2$ digit voltmeter ($\pm$ 0.01%) which can be read from a computer at a frequency of at least 2 Hz. The voltmeter calibration should have been adjusted against a suitable voltage standard.

3.3   A high quality four-lead standard resistor (nominally 10 Ω) whose resistance (R_S) is *certified* to better than $\pm$ 0.01%. The value should be stable with respect to the self-heating caused by the passage of current (*i.e.* have a low temperature coefficient of resistance).

3.4   Computer with suitable interface for reading the digital voltmeter at a frequency of at least 2 Hz.

4. Procedure

4.1   Initial setup

4.1.1   Allow the coulometer and the digital voltmeter to warm up for at least one hour prior to making measurements.

4.1.2   Connect the standard 10 Ω resistor as part of the external coulometer circuit in place of the coulometer cell and connect the voltmeter to measure the voltage across it.

4.2   Measurement procedure using Mode 0 of the coulometer

Mode 0 of the UIC coulometer is the normal counts mode. Use of the thumbwheel controlled timer is not recommended in this mode. The coulometer is thus read under computer control, with the time interval measured by the computer. As the resolution of

the typical computer clock is ~0.01 s, a time period of 300 s is used to minimize timing uncertainties.

The following series of steps are repeated first for the "high" current (~50 mA—Note 1) and then for the "low" current (~2 mA —Note 2) settings of the coulometer. These currents can be obtained either by using the switch SW1 inside the coulometer or by adjusting the %T control on the coulometer front panel.

4.2.1   Set the coulometer in Mode 0.

4.2.2   Ensure that the TIME SET thumb-wheel is at 00.0.

4.2.3   Set the RUN/LATCH switch to the RUN position.

4.2.4   Set the desired current flowing (Note 3).

4.2.5   Reset the coulometer from the computer (ctrl-R).

4.2.6   Start the timer in the computer and read the coulometer immediately (ctrl-E).

4.2.7   Read the voltage across the standard resistor continuously during the period of measurement (~299 s).

4.2.8   Monitor the computer timer (Note 4). As soon as it reaches 300 s, read the coulometer again (ctrl-E).

4.2.9   The difference between the two coulometer readings is the number of pulses counted in the 300 s interval.

4.3   Alternate approach using Mode 15 of coulometer (Note 5)

Mode 15 of the UIC coulometer is optimized to provide an accurate timer function (1 in 100 000). The counter thus becomes an accurate frequency counter with the thumbwheel switch setting the gating period in seconds, and the pulses can be counted for a shorter time interval.

The following series of steps are repeated first for the "high" current (~50 mA—Note 1) and then for the "low" current (~2 mA —Note 2) settings of the coulometer. These can be obtained either

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[1]   The high current is adjusted to 50 mA (see coulometer instruction manual p. 22) to ensure optimal coulometer stability.

[2]   Caution, the voltage / frequency response of the coulometer circuitry becomes non-linear at currents below 2 mA.

[3]   Watch to make sure that the low current does not shut off during the measurement period.

[4]   To ensure an accurate time interval measurement, this should be done with a carefully optimized software.

[5]   The use of Mode 15 as described in the UIC coulometer manual cannot be used to verify the calibration as it employs no external standard.

by using the switch SW1 inside the coulometer or by adjusting the %T control on the coulometer front panel.

4.3.1 Set the coulometer to Mode 15.

4.3.2 Set the TIME SET thumb-wheels to 20.0 seconds.

4.3.3 Set the RUN/LATCH switch in the LATCH position.

4.3.4 Set the desired current flowing (Note 3).

4.3.5 Reset the coulometer using the front panel button (Note 6).

4.3.6 Read the voltage across the standard resistor continuously during the period of measurement (Note 7).

4.3.7 Write down the coulometer reading at the end of the time period (Note 8) for use in the subsequent calculations.

4.3.8 Ensure that the coulometer is returned to Mode 0, with the TIME/SET thumbwheels set to 00.0 and the RUN/LATCH switch to RUN before using the coulometer for normal measurements.

5.   Calculation and expression of results

5.1 Average current measured across standard resistor

The average current measured passing through the standard resistor in the external circuit over the time interval:

$$\bar{I} = \frac{\bar{V}}{R_S} \,, \tag{1}$$

where

$\bar{V}$ = the average voltage across the standard resistor:

$$\bar{V} = \frac{1}{n} \sum_{i=1}^{n} V_i \,, \tag{2}$$

R_S = the certified value of the standard resistor.

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[6]   The coulometer will not respond to serial commands in Mode 15.

[7]   This period will necessarily only approximate the period counted by the coulometer as the computer is independent from the coulometer.

[8]   As the coulometer has been optimized for time measurement it does not update the count total in real time. Instead the count total is displayed and latched at the end of the time period. The counter immediately proceeds to accumulate the next count in a free running manner.

5.2   Expected number of counts

The expected number of counts corresponding to an average current $\bar{I}$ passing for a time interval of t seconds:

$$N' = t \times \bar{I} \times 10^4 / 0.2 \quad , \tag{3}$$

where $10^4/0.2$ is the nominal conversion factor for the voltage to frequency converter (10^4 counts at 0.2 A).

5.3   Calculation of voltage / frequency performance

Ideally, the number of counts displayed by the coulometer (N) is equal to (or at least proportional to) the number of counts calculated from the measured current (N'). The slope and intercept for a straight line are thus calculated from the data:

$$N = a\, N' + b \quad . \tag{4}$$

Hence

$$a = \frac{N_{HI} - N_{LO}}{N'_{HI} - N'_{LO}} \tag{5}$$

$$b = N_{LO} - a\, N'_{LO} = N_{HI} - a\, N'_{HI} \, , \tag{6}$$

where the subscripts *HI* and *LO* refer to measurements at high and low current respectively. For the ideal case, $a = 1$ and $b = 0$ (Note 9). A value of the slope that is not exactly unity is not significant as the coulometer is calibrated for use with CO_2 directly. A value of the intercept that is far from zero is cause for concern (Note 10).

5.4   Example calculation

> Time period, t = 300 s
> Standard resistor, R_S = 10.00098 Ω
> Number of counts on low current setting, N_{LO} = 44 167
> Average voltage on low current setting, $\bar{V}_{LO}$ = 0.029408 V
> Number of counts on high current setting, N_{HI} = 751 858
> Average voltage on high current setting, $\bar{V}_{HI}$ = 0.500932 V

---

[9]   The slope and intercept can be adjusted in the coulometer circuitry. The slope is the voltage to frequency response (RV5) and the intercept the offset (RV6)— see pp. 24–25 in the coulometer manual.

[10]   The magnitude of the problem for the calculation of C_T can be seen by converting the value of the intercept (b) into units of μmol·min^{-1}: $b / (4825.54 \times 5)$. Note that this correction only applies for the period during which the titration current is above 2 mA.

Hence:

$$N'_{LO} = 300 \times \frac{0.029408}{10.00098} \times \frac{10^4}{0.2} = 44108 \ \text{counts} \ , \tag{7}$$

$$N'_{HI} = 300 \times \frac{0.500932}{10.00098} \times \frac{10^4}{0.2} = 751325 \ \text{counts} \ , \tag{8}$$

$$\tag{9}$$

and

$$a = \frac{751858 - 44167}{751325 - 44108} = 1.00067 \ ,$$

$$b = 751858 - 1.00067 \times 751325 = 29.6 \ ;$$

b is thus equivalent to a background of $0.0012 \ \mu\text{mol·min}^{-1}$.

6.   Quality assurance

The digital voltmeter and the external standard resistor are independently calibrated and certified. They thus provide an external standard against which the coulometer can be judged. Control charts should be kept of the values obtained for the slope and the intercept. Out of control behavior may indicate a problem with the coulometer circuitry.

References

Johnson, K. M., K. D. Wills, D. B. Butler, W. K. Johnson & C. S. Wong (1993) Coulometric total carbon dioxide analysis for marine studies: maximizing the performance of an automated continuous gas extraction system and coulometric detector. *Marine Chemistry* **44**, 167–187.

UIC Inc. (1985) Instruction manual; model 5011 CO_2 coulometer.

SOP 21

Applying air buoyancy corrections

1. Scope and field of application

The effect of air buoyancy is, if uncorrected, frequently the largest source of error in mass measurements. This procedure provides equations to be used to correct for the buoyant effect of air. An air buoyancy correction should be made in all high accuracy mass determinations.

2. Principle

The upthrust due to air buoyancy acts both on the sample being weighed and on the counter-balancing weights. If these are of different densities and hence of different volumes, it will be necessary to allow for the resulting difference in air buoyancy to obtain an accurate determination of mass.

3. Requirements

3.1 Knowledge of the air density at the time of weighing.

For the most accurate measurements, the air density is computed from a knowledge of pressure, temperature and relative humidity. Tolerances for the various measurements are:

	Uncertainty in computed air density	
Variable	± 0.1%	± 1.0%
Relative humidity	± 11.3%	. . .
Air Temperature	± 0.29 °C	± 2.9 °C
Air pressure	± 0.10 kPa	± 1.0 kPa

3.1.1 Barometer accurate to ± 0.05 kPa

3.1.2 Thermometer accurate to ± 0.1 °C

3.1.3 Hygrometer accurate to 10%

An error of 1% in air density results in an error of approximately 1 part in 10^5 in the mass corrected for air buoyancy. Although meteorological variability can result in variations of up to 3% in air density, the change of pressure (and hence of air density) with altitude can be much more significant. For measurements of moderate accuracy, made at sea level and at normal laboratory temperatures, an air density of 0.0012 g·cm^{-3} is often adequate.

3.2 Knowledge of the apparent mass scale used to calibrate the balance

There are two apparent mass scales in common use. The older one is based on the use of brass weights adjusted to a density of 8.4 g·cm^{-3}, the more recent one on the use of stainless steel weights adjusted to a density of 8.0 g·cm^{-3} (Note 1).

3.3 Knowledge of the density of the sample

The density of the sample being weighed is needed for this calculation.

4. Procedure

4.1 Computation of air density

The density of air in g·cm^{-3} can be computed from measurements of pressure, temperature and relative humidity (Jones, 1978):

$$\rho(\text{air}) = \frac{3.4848(p - 0.0037960U \cdot e_S)}{273.15 + t} \times 10^{-3} \tag{1}$$

where

p – air pressure (kPa),

U – relative humidity (%),

t – temperature (°C),

e_s – saturation vapor pressure (kPa):

$$e_s = 1.7526 \times 10^8 \exp\left(-5315.56 / (t + 273.15)\right). \tag{2}$$

---

[1]   Strictly, these densities apply only at 20 °C. The conversion factor from the "apparent mass" obtained by using these values to "true" mass is defined by the expression

$$Q = \frac{\rho(\text{weights})(D_{20} - 0.0012)}{D_{20}(\rho(\text{weights}) - 0.0012)}$$

where D_{20} is the apparent mass scale to which the weights are adjusted. This factor may be considered as unity for most purposes.

4.2   Computation of mass from weight

The mass m of a sample of weight w and density ρ(sample) is computed from the expression—see Annexe for derivation:

$$m = w\frac{1 - \rho(\text{air})/\rho(\text{weights})}{1 - \rho(\text{air})/\rho(\text{sample})} \ . \tag{3}$$

5.   Example computations

The following data were used for this calculation (Note 2):

weight of sample, w = 100.00000 g ,
density of sample, ρ(sample) = 1.0000 g·cm^{-3} ,
weighing conditions:

p = 101.325 kPa (1 atm) ,
U = 30.0% ,
t = 20.00 °C ,
ρ (weights) = 8.0000 g·cm^{-3} .

5.1   Computation of air density

e_s = 2.338 kPa ,
ρ(air) = 0.0012013 g·cm^{-3} .

5.2   Computation of mass

m = 100.10524 g .

References

Dean J. A. (1985) *Lange's handbook of chemistry*, McGraw-Hill Book Company, New York, 1792 pp.

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Schoonover R. M. & F. E. Jones (1981) Air buoyancy correction in high-accuracy weighing on analytical balances. *Analytical Chemistry* **53**, 900–902.

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---

[2]   The seemingly excessive number of decimal places is provided here so that users of this procedure can check their computation scheme.

Annexe

Derivation of the expression for buoyancy correction

An expression for the buoyancy correction can be derived from a consideration of the forces shown in Figure 1. Although the majority of balances nowadays are single-pan, the principles remain the same, the difference being that the forces are compared sequentially using a force sensor rather than simultaneously using a lever. At balance, the opposing forces are equal:

$$m_1 g - V_1 \rho(\text{air}) g = m_2 g - V_2 \rho(\text{air}) g , \tag{A.1}$$

where g is the acceleration due to gravity and $\rho(\text{air})$ is the density of the air at the temperature, pressure and humidity of the weighing operation. Note that m_2 is the "weight" of a sample whose true mass is m_1.

As

$$V = m / \rho , \tag{A.2}$$

we can rewrite (A.1) as

$$m_1 - m_1 \rho(\text{air}) / \rho_1 = m_2 - m_2 \rho(\text{air}) / \rho_2 . \tag{A.3}$$
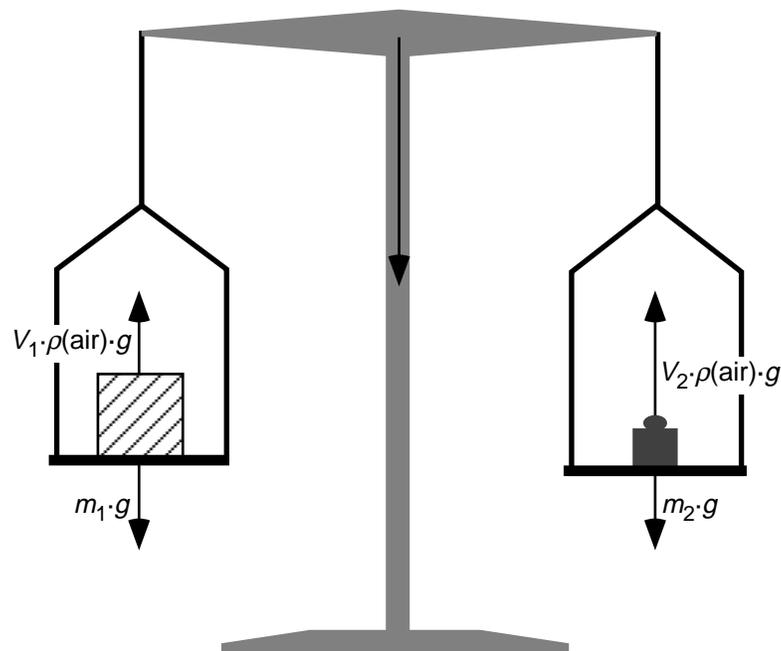

Figure 1. Forces on sample (1) and weights (2) when weighing in air.

This equation can be rearranged to obtain the expression:

$$m_1 = m_2 \frac{1 - \rho(\mathrm{air})/\rho_2}{1 - \rho(\mathrm{air})/\rho_1} \ . \qquad (A.4)$$

Equation (A.4) is the basis of the expression used for air buoyancy correction (Schoonover, 1981; Taylor & Oppermann, 1986):

$$m = w \frac{1 - \rho(\mathrm{air})/\rho(\mathrm{weights})}{1 - \rho(\mathrm{air})/\rho(\mathrm{sample})} \ , \qquad (A.5)$$

where w is the "weight" of the sample in air and m is the true mass.

Equation (A.3) can also be rearranged to give

$$m_1 = m_2 + m_2 \rho(\mathrm{air}) \left(\frac{m_1}{m_2} \frac{1}{\rho_1} - \frac{1}{\rho_2} \right) \ . \qquad (A.6)$$

As $m_1 \approx m_2$, equation (A.6) is almost identical to the commonly quoted expression for buoyancy correction:

$$m = w + w \rho(\mathrm{air}) \left(\frac{1}{\rho(\mathrm{sample})} - \frac{1}{\rho(\mathrm{weights})} \right) \qquad (A.7)$$

(Woodward & Redman, 1973; Dean, 1985). An approximate value of $\rho(\mathrm{air})$ (0.0012 g·cm^{-3}) is often used with this expression; this is appropriate to measurements of moderate accuracy made at sea level pressures and at normal laboratory temperatures.

SOP 22

Preparation of control charts

1.   Scope and field of application

This procedure details the preparation and use of property $(\overline{X})$ and range (R) control charts. The $\overline{X}$ chart is used to demonstrate whether a measurement mean is in control, the R chart is used to demonstrate whether measurement variability is in control. Such charts are basic tools for the quality assurance of analytical measurements. They can be used to document measurement uncertainty and to monitor a variety of aspects of a measurement process, such as blank levels or instrument sensitivity.

2.   Principle

The construction of a control chart is based on statistical principles, specifically on the normal distribution. The control limits are based on considerations of probability; thus decisions that a system is in control are supported. Similarly, the control limits can be used to warn of potential problems and reveal the need for corrective action. Control charts should be kept in real time so that such corrective action is taken promptly.

3.   Procedures

3.1   Statistical calculations

SOP 23 of this handbook provides all the necessary information to carry out the statistical calculations needed in this SOP.

3.2   The $\overline{X}$ chart

Values obtained for repetitive measurements of a control sample are plotted sequentially to evaluate the stability of the measurement process (see figure 1). Such control samples must be very similar to the test samples of interest, otherwise it is not

possible to draw conclusions about the performance of the system on test samples from this information.
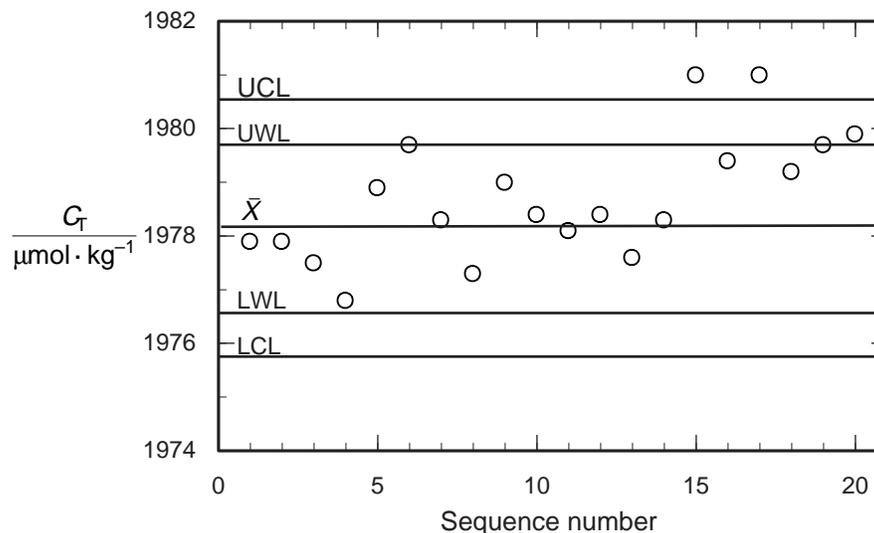

Figure 1. Example of a property control chart showing a trend in the data with time; control limits were calculated from the first 12 points. This chart indicates that the measurement process is not in control.

The results from at least twelve measurements—with never more than one measurement made on the same day—are used to compute estimates of the mean and standard deviation of the data in accordance with the standard expressions (SOP 23).

The central line is the mean value, $\bar{x}$, the control limits are based on the sample standard deviation, s:

upper control limit	UCL	$= \bar{x} + 3s$
upper warning limit	UWL	$= \bar{x} + 2s$
lower warning limit	LWL	$= \bar{x} - 2s$
lower control limit	LCL	$= \bar{x} - 3s$

When so set, approximately 95% of the plotted points should fall between the warning limits (UWL and LWL) and rarely should any fall outside the control limits (UCL and LCL).

3.3 The R chart

The absolute differences (R) of duplicate measurements are plotted sequentially to evaluate the precision of the measurement process (see figure 2). The average range $\bar{R}$ is related to the short-term standard deviation (or repeatability, s_R) of the measurement

process (SOP 23). At least 12 measurements should be used to compute $\bar{R}$. The control limits for duplicate measurements are

$$
\begin{aligned}
\text{UCL} &= 3.267\,\bar{R} \\
\text{UWL} &= 2.512\,\bar{R} \\
\text{LWL} &= 0 \\
\text{LCL} &= 0\,.
\end{aligned}
$$
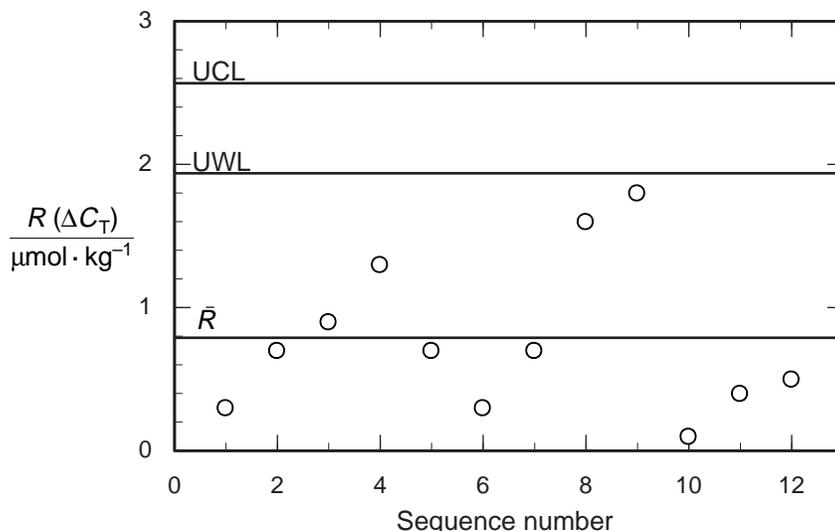
Figure 2. Example of a range control chart; control limits were calculated using all the data shown. The measurement precision is in control.

3.4 *Updating control charts*

After additional control data have been accumulated—at least as much as was used originally—the control limits may be updated. A t test is made to assess whether $\bar{x}$ for the second set of data is significantly different from that for the first (SOP 23). If not, all the data may be used to compute a new estimate of $\bar{x}$, otherwise only the second set of data should be used to revise the control chart.

The value of the sample standard deviation, s, should also be calculated for the second set of data. It should be compared with the estimate from the first set of data, using the F test (SOP 23) to decide whether to pool it with the first, or to use it separately in setting new control limits.

If the values of R show no significant trends and if $\bar{R}$ has not changed significantly, all of the values of R should be combined to obtain an updated estimate of $\bar{R}$ from which updated control

limits can be computed. Judgement of the significance of changes in $\bar{R}$ are best judged by computing the corresponding values of the short-term standard deviation (the repeatability) and conducting an F test.

3.5   *Interpretation of control chart data*

Points plotted on a control chart should be randomly distributed within the warning limits when the system is in a state of statistical control. If a plotted point lies outside of the warning limits, a second set of measurements should be made. If this point also lies outside the warning limits, corrective action is required and demonstrated attainment of control is necessary before measurements may be reported with confidence. Barring blunders, one point outside of the control limits is reason for corrective action. The nature of the corrective action to be taken will depend, in either case, on the kind of measurement made. If the X point is outside the limits but the R point is not, a source of bias should be sought and eliminated. If the R point is outside of limits, X probably will be as well. Sources of extraordinary random error should be sought and eliminated before any possible bias can be detected.

Control charts may be used to evaluate the uncertainty of measurement in some cases. When an appropriate control chart is maintained, an $\bar{X}$ chart may be used to evaluate bias and to document the standard deviation of the measurement process. Then the values of s on which the control limits are based may be used in calculating confidence limits for measurement values.

References

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SOP 23

Statistical techniques used in quality assessment

1. Scope and field of application

This procedure describes various statistical calculations used in quality assessment. Calculations are detailed which allow the computation of the mean and standard deviation of a set of values, the computation of a standard deviation from a set of duplicate measurements, the computation of the confidence interval for a mean, the examination of the values of two means or of two standard deviations to assess if they are significantly different at some chosen level of probability, and the computation of the least-squares estimates of the slope and intercept of a straight line.

2. Principle

These calculations are based on statistical principles, specifically on the normal distribution. More details of the relevant statistical background are given in the references.

3. Procedures

3.1 Estimation of the mean and the standard deviation from a series of measurements

Given n measurements

$$x_1, x_2, x_3, \ldots, x_n ,$$

the mean, $\bar{x}$, is given by

$$\bar{x} = \frac{1}{n} \sum_{i=1}^{n} x_i , \tag{1}$$

and an estimate of the standard deviation, s, is given by

$$s = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}} . \tag{2}$$

3.2 Estimation of the standard deviation from the difference of sets of duplicate measurements

Given k differences of duplicate measurements

$$d_1, d_2, d_3, \ldots, d_k \, ,$$

an estimate of the standard deviation, s, is given by

$$s \; = \; \sqrt{\frac{\displaystyle\sum_{i=1} d_i^2}{2k}} \; .$$
(3)

This is a measure of the short term standard deviation, or repeatability of measurements (Note 1).

3.3 Confidence interval for a mean

The formula for use is

$$\bar{x} \; \pm \; \frac{ts}{\sqrt{n}} \; ,$$
(4)

where

$\bar{x}$ = sample mean,

n = number of measurements on which the mean is based,

s = estimate of the standard deviation (Note 2),

t = Student's t value, *i.e.* the probability factor for the desired confidence limit and the number of degrees of freedom associated with s. (For numerical values see Table A.1 in the annexe to this procedure.)

3.4 Comparing values of two means

Case 1. No reason to believe that the standard deviations differ

Step 1:   Choose α, the desired probability level (*i.e.* the significance level) of the test.

---

1   The International Organization for Standardization (ISO) applies two descriptions of precision: (1) the *reproducibility*, the closeness of agreement between individual results obtained with the same method but under different conditions (*e.g.* in different laboratories) and (2) the *repeatability*, the closeness of agreement between successive results obtained with the same method and under the same conditions.

2   If $\bar{x}$ and s are based on the same data set, the number of degrees of freedom, df = $n - 1$. However, if s is based on additional evidence, such as a system under statistical control (judged by a control chart) then the degrees of freedom on which the estimate of s is based may be used to determine t. In such a case, one can calculate a confidence interval for even a single measurement.

Step 2: Calculate a pooled standard deviation from the two estimates to obtain a better estimate of the standard deviation:

$$s_{\mathrm{p}} = \sqrt{\frac{\nu_{\mathrm{A}} s_{\mathrm{A}}^2 + \nu_{\mathrm{B}} s_{\mathrm{B}}^2}{\nu_{\mathrm{A}} + \nu_{\mathrm{B}}}} \; ; \tag{5}$$

ν_{A} and ν_{B} are the number of degrees of freedom associated with s_{A} and s_{B} respectively. s_{p} will thus be based on $\nu_{\mathrm{A}} + \nu_{\mathrm{B}}$ degrees of freedom.

Step 3: Calculate the uncertainty, U, of the differences:

$$U = t s_{\mathrm{p}} \sqrt{\frac{1}{n_{\mathrm{A}}} + \frac{1}{n_{\mathrm{B}}}} \;, \tag{6}$$

where t is the appropriate Student's t value.

Step 4: Compare $\Delta = \left| \bar{x}_A - \bar{x}_B \right|$ with U. If $\Delta \le$ U, there is no reason to believe that the means disagree.

Case 2. The standard deviations differ significantly (see § 3.5)

Step 1: Choose α, the significance level of the test.

Step 2: Compute the estimated variance of each mean using the individual estimates of the standard deviations:

$$V_{\mathrm{A}} = s_{\mathrm{A}}^2 / n_{\mathrm{A}}, \quad V_{\mathrm{B}} = s_{\mathrm{B}}^2 / n_{\mathrm{B}}. \tag{7}$$

Step 3: Compute the effective number of degrees of freedom (Note 3)

$$\mathrm{f}^* = \frac{(V_{\mathrm{A}} + V_{\mathrm{B}})^2}{V_{\mathrm{A}}^2 / (n_{\mathrm{A}} + 1) + V_{\mathrm{B}}^2 / (n_{\mathrm{B}} + 1)} - 2 \quad . \tag{8}$$

Step 4: Calculate the uncertainty, U, of the differences:

$$U = t^* \sqrt{V_{\mathrm{A}} + V_{\mathrm{B}}} \;, \tag{9}$$

where t^* is the effective value of t based on f^* degrees of freedom and the choice of significance level, α (Annexe—Table 1).

Step 5: Compare $\Delta = \left| \bar{x}_A - \bar{x}_B \right|$ with U. If $\Delta \le$ U, there is no reason to believe that the means disagree.

---

[3]   A number of expressions exist in the literature for this calculation with some authors even arguing that such a pooling of the variances is inappropriate. The expression used here comes from Taylor (1987).

3.5 Comparing estimates of a standard deviation (F test)

This test may be used to decide whether there is sufficient reason to believe that two estimates of a standard deviation are significantly different. It consists of calculating the ratio of the variances and comparing it with tabulated values. Unless the computed ratio is larger than the tabulated value, there is no reason to believe that the respective standard deviations are significantly different.

The F ratio is calculated as

$$F = s_L^2 / s_S^2 , \tag{10}$$

where s_L is the larger value and s_S is the smaller of the two estimates under consideration. The critical value of F will depend on the significance level chosen and on the degrees of freedom associated with s_L and s_S (Annexe—Table 2).

3.6 Computation of least squares estimates

For the linear model

$$y_i = \beta_0 + \beta_1 x_i + \varepsilon_i , \tag{11}$$

where x is essentially without error (for data with errors in x and y—see York, 1966) and the error ε_i is normally distributed with a constant variance, least squares estimates of the coefficients β_0 and β_1 are given by the expressions:

$$\beta_1 = \frac{\sum_i (x_i - \bar{x})(y_i - \bar{y})}{\sum_i (x_i - \bar{x})^2} , \tag{12}$$

$$\beta_0 = \bar{y} - \beta_1 \bar{x} . \tag{13}$$

An estimate of the experimental error variance is then given by

$$s^2 = \frac{\sum_i (y_i - \beta_0 - \beta_1 x_i)^2}{n - 2} ; \tag{14}$$

and estimates of the standard errors of the coefficients by

$$\text{S.E.}(\beta_0) = s \left(\frac{1}{n} + \frac{\bar{x}^2}{\sum_i (x_i - \bar{x})^2} \right)^{1/2} , \tag{15}$$

$$\text{S.E.}(\beta_1) \; = \; \frac{s}{\left(\sum_i (x_i - \bar{x})^2\right)^{1/2}} \quad . \tag{16}$$

4. Example calculations

4.1 Estimation of the mean and the standard deviation from a series of measurements.

Given the following 9 measurements:

> 1977.67, 1977.98, 1977.29, 1978.60, 1979.48, 1979.14, 1979.33, 1979.95, 1979.99,

the mean is 1978.83 and the standard deviation is 0.99.

4.2 Estimation of the standard deviation from the difference of sets of duplicate measurements.

Given 10 pairs of measurements:

> 1976.8, 1979.3,   1978.9, 1979.6,   1979.6, 1979.8
> 1978.3, 1978.6,   1981.2, 1979.8,   1977.6, 1977.8
> 1976.2, 1976.8,   1978.6, 1977.0,   1976.6, 1978.9
> 1978.3, 1978.9,

the standard deviation calculated using (3) is 0.93.

4.3 Confidence interval for a mean

The 95% confidence interval for the mean calculated in § 4.1 is

$$1978.83 \pm \frac{(2.306)(0.99)}{\sqrt{9}} \; = \; 1978.83 \pm 0.76 \quad .$$

4.4 Comparing values for two means

Case 1: No reason to believe that the standard deviations differ

$$\bar{x}_A = 1978.78, \quad s_A = 0.93, \quad n_A = 9$$
$$\bar{x}_B = 1981.74, \quad s_B = 0.87, \quad n_B = 18$$

Step 1:   Require 95% confidence in decision
Step 2:   Pooled standard deviation

$$s_p = \sqrt{\frac{8(0.93)^2 + 17(0.87)^2}{8 + 17}}$$
$$= 0.89$$

Step 3: Calculate U:

$$U = 2.060(0.89)\sqrt{\frac{1}{9} + \frac{1}{18}}$$

$$= 0.75$$

Step 4: As Δ (= 1981.74 − 1978.78 = 2.96) is larger than U, the means disagree at the 95% confidence level.

Case 2: The standard deviations differ significantly

$$\bar{x}_A = 1978.78, \quad s_A = 0.93, \quad n_A = 9$$
$$\bar{x}_B = 1981.74, \quad s_B = 2.75, \quad n_B = 16$$

Step 1: Require 95% confidence in decision

Step 2: Compute the estimated variance of each mean

$$V_A = (0.93)^2/9 = 0.0961$$
$$V_B = (2.75)^2/16 = 0.4727$$

Step 3: Compute the effective number of degrees of freedom

$$f^* = \left(\frac{(0.0961 + 0.4727)^2}{\frac{(0.0961)^2}{9+1} + \frac{(0.4727)^2}{16+1}} \right) - 2 \approx 21$$

Step 4: Calculate U:

$$U = 2.08\sqrt{0.0961 + 0.4727} = 1.57$$

Step 5: As Δ (= 1981.74 − 1978.78 = 2.96) is larger than U, the means disagree at the 95% confidence level.

4.5 Comparing estimates of a standard deviation

$$\bar{x}_A = 1978.78, \quad s_A = 0.93, \quad n_A = 9$$
$$\bar{x}_B = 1975.35, \quad s_B = 1.71, \quad n_B = 12$$

Calculate F

$$F = \frac{(1.71)^2}{(0.93)^2} = 3.38$$

The tabulated value of F—with 8 degrees of freedom in the numerator and 11 degrees of freedom in the denominator—is 3.7. As the computed value is smaller than the tabulated value, there is no reason to believe that the two standard deviations are significantly different.

4.6 Computation of least squares estimates

Given 6 pairs of measurements of x and y:

0.0	1892
498.8	66537
1001.9	130818
1500.8	195216
2002.5	260068
2497.1	323456

Linear regression gives:

$$\beta_0 = 2017.77$$
$$\beta_1 = 128.765 \quad .$$

The error estimates are:

$$s = 221.77$$
$$\text{S.E.}(\beta_0) = 160.55$$
$$\text{S.E.}(\beta_1) = 0.106 \quad .$$

References

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Annexe

Table 1. Student's t values for 95% and 99% confidence intervals

	Probability level for two-sided confidence interval	
df [a]	95%	99%
1	12.706	63.657
2	4.303	9.925
3	3.182	5.841
4	2.776	4.604
5	2.571	4.032
6	2.447	3.707
7	2.365	3.499
8	2.306	3.355
9	2.262	3.250
10	2.228	3.169
11	2.201	3.106
12	2.179	3.055
13	2.160	3.012
14	2.145	2.977
15	2.131	2.947
16	2.120	2.921
17	2.110	2.898
18	2.101	2.878
19	2.093	2.861
20	2.086	2.845
25	2.060	2.787
40	2.021	2.704
60	2.000	2.660
∞	1.960	2.576

a. degrees of freedom $(n - 1)$

Table 2. Critical values for the F test for use for a two tailed test of equality of standard deviation at 95% level of confidence

	df_N									
df_D	1	2	4	6	8	10	15	20	30	40
1	648	800	900	937	957	969	983	993	1001	1006
2	38.5	39.0	39.2	39.3	39.4	39.4	39.4	39.4	39.5	39.5
4	12.2	10.6	9.6	9.2	9.0	8.8	8.7	8.6	8.5	8.4
6	8.8	7.3	6.2	5.8	5.6	5.5	5.3	5.2	5.1	5.0
8	7.6	6.1	5.0	4.6	4.4	4.3	4.1	4.0	3.9	3.8
10	6.9	5.5	4.5	4.1	3.8	3.7	3.5	3.4	3.3	3.3
15	6.2	4.8	3.8	3.4	3.2	3.1	2.9	2.8	2.6	2.6
20	5.9	4.5	3.5	3.1	2.9	2.8	2.6	2.5	2.4	2.3
30	5.6	4.2	3.2	2.9	2.6	2.5	2.3	2.2	2.1	2.0
40	5.4	4.0	3.1	2.7	2.5	2.4	2.2	2.1	1.9	1.9
60	5.3	3.9	3.0	2.6	2.4	2.3	2.1	1.9	1.8	1.7
120	5.2	3.8	2.9	2.5	2.3	2.2	1.9	1.8	1.7	1.6
∞	5.0	3.7	2.8	2.4	2.2	2.1	1.8	1.7	1.6	1.5

df_D — degrees of freedom of the variance in the denominator
df_N — degrees of freedom of the variance in the numerator

SOP 24

Calculation of the fugacity of carbon dioxide in the pure gas or in air.

1. Scope and field of application

This procedure describes a method for the calculation of the fugacity of carbon dioxide in the pure gas or in air. The fugacity, $f(CO_2)$, is expressed either in Pascals or in atmospheres (Note 1).

2. Definition

The chemical potential (μ_B) of an individual component of a vapor phase can be expressed in terms of its fugacity (f_B). This is defined by the equation

$$RT \ln f_B = \mu_B - \lim_{p \to 0} (\mu_B - RT \ln(x_B p / p^\circ)) \qquad (1)$$

where x_B is the mole fraction of B in the gaseous mixture and thus $x_B p$ is the partial pressure of B (p_B) in the vapor phase and p° is astandard pressure (typically 101325 Pa, *i.e.* 1 atm). The term

$$\lim_{p \to 0} (\mu_B - RT \ln(x_B p / p^\circ)) \qquad (2)$$

is thus a standard chemical potential, $\mu_B^\circ(T)$.

3. Principle

The vapor phase fugacity of either a pure gas $(x_B = 1)$ or of a component in a mixture of gases can be calculated from the equation

$$f_B = x_B p \exp\left(\int_0^p \frac{(V_B - RT/p')dp'}{RT} \right) . \qquad (3)$$

---

1   1 atm = 101325 Pa.

V_B is obtained from

$$V_B = \left(\frac{\partial V}{\partial n_B}\right)_{T,p} \quad , \tag{4}$$

where V is given by an equation of state for the vapor:

$$V = f(T, p) \quad . \tag{5}$$

3.1 The ideal gas equation

The simplest equation of state is the expression for a perfect gas mixture

$$V = (\textstyle\sum_B n_B) RT/p \quad . \tag{6}$$

The integral in equation (3) is then equal to zero and

$$f_B = x_B p \quad . \tag{7}$$

3.2 The virial equation

More generally the equation of state can be represented by a virial expression:

$$\frac{pV_B}{RT} = 1 + \frac{B(T)}{V_B} + \frac{C(T)}{V_B^2} + \ldots \tag{8}$$

This equation, truncated after the second virial coefficient is usually adequate to represent p–V–T properties at pressures up to a few atmospheres. It also has the advantage that the coefficient $B(T)$ can be related to the intermolecular potential energy function of the molecules concerned.

In a mixture of gases,

$$B(T) = \sum_l \sum_m x_l x_m B_{lm}(T) \quad , \tag{9}$$

where $B_{lm} = B_{ml}$. The total volume can then be written

$$V = \sum_k n_k V_k = \sum_k n_k \frac{RT}{p} + \frac{\displaystyle\sum_l \sum_m n_l n_m B_{lm}(T)}{\displaystyle\sum_k n_k} \quad . \tag{10}$$

The partial molar volume of an individual component

$$V_B = \frac{RT}{p} - \frac{\displaystyle\sum_l \sum_m n_l n_m B_{lm}(T)}{\left(\displaystyle\sum_k n_k\right)^2} + \frac{2\displaystyle\sum_m n_m B_{Bm}(T)}{\displaystyle\sum_k n_k} \tag{11}$$

and thus

$$V_{\mathrm{B}} \;=\; \frac{RT}{p} + \sum_l \sum_m x_l x_m (2B_{\mathrm{B}m}(T) - B_{lm}(T))p \quad .\qquad (12)$$

The fugacity is then given by

$$f_{\mathrm{B}} \;=\; x_{\mathrm{B}} p \exp\!\left(\frac{\sum_l \sum_m x_l x_m (2B_{\mathrm{B}m}(T) - B_{lm}(T))p}{RT} \right) \quad .\qquad (13)$$

For a pure gas this reduces to

$$f_{\mathrm{B}} \;=\; p \exp\!\left(\frac{B_{\mathrm{BB}}(T)p}{RT} \right) \;,\qquad (14)$$

where $B_{\mathrm{BB}}(T)$ is the virial coefficient for the pure gas B.

A further particular case of equation (13) is the expression for a component of a binary mixture

$$f_{\mathrm{B}} \;=\; x_{\mathrm{B}} p \exp\!\left(\frac{(B_{\mathrm{BB}}(T) + 2x_C^2 \delta_{\mathrm{B-C}}(T))p}{RT} \right) \;,\qquad (15)$$

where

$$\delta_{\mathrm{B-C}} \;=\; B_{\mathrm{BC}} - \tfrac{1}{2}(B_{\mathrm{BB}} + B_{\mathrm{CC}}) \;.\qquad (16)$$

Many of the cross virial coefficients for the practical computation of fugacity in vapor mixtures have never been measured experimentally. However a number of empirical approaches can be used.

The simplest of these is the Lewis and Randall rule

$$f_{\mathrm{B}} \;=\; x_{\mathrm{B}} f_{\mathrm{B}}^* \;,\qquad (17)$$

where f_{B}^* is the fugacity of pure component B at the same temperature and total pressure as the mixture—equation (14).

An alternate method of predicting $B(T)$, based on statistical-mechanical arguments, is to use the expression

$$B(T) \;=\; 2\pi L \int_0^\infty [1 - \exp\{-u(r)/kT\}] r^2 dr \quad ,\qquad (18)$$

where L is the Avogadro constant and k the Bolzmann constant. Here, $u(r)$—the pair-interaction energy—is assumed to depend only on the separation r of the centers of mass of two molecules.

4.   Calculation and expression of results

4.1 Virial coefficient of pure carbon dioxide

The first virial coefficient of CO_2, $B(CO_2, T)$, is given by the expression (Weiss, 1974) which is based on values reported by Levelt-Sengers, Klein, & Gallagher (1971)

$$\frac{B(CO_2, T)}{cm^3 \cdot mol^{-1}} = -1636.75 + 12.0408\left(\frac{T}{K}\right)$$

$$-3.27957 \times 10^{-2}\left(\frac{T}{K}\right)^2 + 3.16528 \times 10^{-5}\left(\frac{T}{K}\right)^3 , \quad (19)$$

where $265 < (T/K) < 320$.

This expression can then be used in equation (14) to calculate the fugacity of pure CO_2 provided that the pressure and temperature of the CO_2 are known.

4.2 Virial coefficient of carbon dioxide in air

In addition, Weiss used the Lennard-Jones (6–12) potential to estimate $u(r)$ and hence calculate values for δ_{BC} for the binary mixture: CO_2– air. He found that the temperature dependence of this parameter is represented by the equation

$$\frac{\delta(CO_2 - air)}{cm^3 \cdot mol^{-1}} = 57.7 - 0.118\left(\frac{T}{K}\right) , \quad (20)$$

where $273 < (T/K) < 313$.

This expression can then be used in equation (15), together with equation (19), to calculate the fugacity of CO_2 in air.

4.3 Example calculations

4.3.1 Fugacity of pure CO$_2$

$$T = 298.15 \text{ K} ;$$
$$p = 101.325 \text{ kPa (1 atm)} .$$

Then

$$B(T) = -123.2 \text{ cm}^3 \cdot \text{mol}^{-1} ,$$

$$f(CO_2) = 101325 \ \exp\left(\frac{-123.2 \times 10^{-6} \times 101325}{8.31451 \times 298.15}\right)$$

$$= 100.816 \text{ kPa} ,$$

or

$$f(CO_2) = 100.816/101.325 = 0.99498 \text{ atm} .$$

4.3.2   *Fugacity of CO$_2$ in air*

T = 298.15 K ;

p = 101.325 kPa (1 atm) ;

$x(CO_2) = 350 \times 10^{-6}$.

Then

$B(T) = -123.2 \text{ cm}^3 \cdot \text{mol}^{-1}$,

$\delta(CO_2\text{–air}) = 22.5 \text{ cm}^3 \cdot \text{mol}^{-1}$,

$$f(CO_2) = 350 \times 10^{-6}(101325) \times$$

$$\exp\left(\frac{(-123.2 \times 10^{-6} + 2(1 - 350 \times 10^{-6})^2 (22.5 \times 10^{-6})) \times 101325}{8.31451 \times 298.15}\right) ,$$

$$= 35.35 \text{ Pa} \quad (348.9 \times 10^{-6} \text{ atm}) .$$

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5

Physical and thermodynamic data

Table of Contents

1.   Values for various fundamental constants

$$R = 8.314510(70) \text{ J·K}^{-1}\text{·mol}^{-1}$$
$$F = 96485.309(29) \text{ C·mol}^{-1}$$
$$0 \text{ °C} = 273.15 \text{ K (defined)}$$
$$1 \text{ atm} = 101325 \text{ Pa (defined)}$$

(Cohen & Taylor, 1986). For each constant, the standard deviation uncertainty in the least significant digits is given in parentheses.

2.   Atomic Weights

Atomic weights are quoted here (Table 2.1) to five significant figures unless the dependable accuracy is more limited by either the combined uncertainties of the best published atomic weight determinations, or by the variability of isotopic composition in normal terrestial occurrences (the latter applied to elements **annotated r**). The last significant figure of each tabulated value is considered reliable to ±1 except when a larger single-digit uncertainty is inserted in parentheses following the atomic weight. Neither the highest or the lowest actual atomic weight of any normal sample is thought likely to differ from the tabulated value by more than the assigned uncertainty. However, the tabulated values do not apply either to samples of highly exceptional isotopic composition arising from most geological occurrences (for elements **annotated g**) or to those whose isotopic composition has been artificially altered. Such might even be found in commerce without disclosure of that modification (for elements **annotated m**). Elements annotated by an asterisk (*) have no stable isotope and are generally represented in this Table by just one of the element's commonly known radioisotopes, with a corresponding relative atomic mass in the atomic weight column. However, three such elements (Th, Pa and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated. For more detail, see the complete table (cited in IUPAC, 1993). Some atomic weights have been revised to reflect more recent determinations (IUPAC, 1994).

Table 2.1: IUPAC Table of standard atomic weights abridged to five significant figures. Scaled to the relative atomic mass $A(^{12}C) = 12$.

	Name	Symbol	Atomic weight	Annotations
1	Hydrogen	H	1.0079	g m
2	Helium	He	4.0026	
3	Lithium	Li	6.941(2)	g m r
4	Beryllium	Be	9.0122	
5	Boron	B	10.811(5)	g m r
6	Carbon	C	12.011	g r
7	Nitrogen	N	14.007	
8	Oxygen	O	15.999	
9	Fluorine	F	18.998	
10	Neon	Ne	20.180	m
11	Sodium (Natrium)	Na	22.990	
12	Magnesium	Mg	24.305	
13	Aluminium	Al	26.982	
14	Silicon	Si	28.086	
15	Phosphorus	P	30.974	
16	Sulfur	S	32.066(6)	g r
17	Chlorine	Cl	35.453	m
18	Argon	Ar	39.948	g r
19	Potassium (Kalium)	K	39.098	g
20	Calcium	Ca	40.078(4)	g
21	Scandium	Sc	44.956	
22	Titanium	Ti	47.867	
23	Vanadium	V	50.942	
24	Chromium	Cr	51.996	
25	Manganese	Mn	54.938	
26	Iron	Fe	55.845(2)	
27	Cobalt	Co	58.933	
28	Nickel	Ni	58.693	
29	Copper	Cu	63.546(3)	r
30	Zinc	Zn	65.39(2)	
31	Gallium	Ga	69.723	
32	Germanium	Ge	72.61(2)	
33	Arsenic	As	74.922	
34	Selenium	Se	78.96(3)	
35	Bromine	Br	79.904	
36	Krypton	Kr	83.80	g m
37	Rubidium	Rb	85.468	
38	Strontium	Sr	87.62	
39	Yttrium	Y	88.906	
40	Zirconium	Zr	91.224(2)	g
41	Niobium	Nb	92.906	
42	Molybdenum	Mo	95.94	g
43	Technetium*	^{99}Tc	98.906	
44	Ruthenium	Ru	101.07(2)	g
45	Rhodium	Rh	102.91	
46	Palladium	Pd	106.42	g
47	Silver	Ag	107.87	
48	Cadmium	Cd	112.41	
49	Indium	In	114.82	
50	Tin	Sn	118.71	
51	Antimony (Stibium)	Sb	121.76	g
52	Tellurium	Te	127.60	g

Table 2.1: IUPAC Table of standard atomic weights abridged to five
significant figures. Scaled to the relative atomic mass $A(^{12}C) = 12$.

	Name	Symbol	Atomic weight	Annotations
53	Iodine	I	126.90	
54	Xenon	Xe	131.29(2)	g m
55	Caesium	Cs	132.91	
56	Barium	Ba	137.33	
57	Lanthanum	La	138.91	
58	Cerium	Ce	140.12	g
59	Praesodymium	Pr	140.91	
60	Neodymium	Nd	144.24(3)	g
61	Promethium*	^{147}Pm	146.92	
62	Samarium	Sm	150.36	g
63	Europium	Eu	151.96	g
64	Gadolinium	Gd	157.25(3)	g
65	Terbium	Tb	158.93	
66	Dysprosium	Dy	162.50(3)	g
67	Holmium	Ho	164.93	
68	Erbium	Er	167.26	g
69	Thulium	Tm	168.93	
70	Ytterbium	Yb	173.04	
71	Lutetium	Lu	174.97	g
72	Hafnium	Hf	178.49	
73	Tantalum	Ta	180.95	
74	Tungsten(Wolfram)	W	183.84	
75	Rhenium	Re	186.21	
76	Osmium	Os	190.23(3)	g
77	Iridium	Ir	192.22	
78	Platinum	Pt	195.08(3)	
79	Gold	Au	196.97	
80	Mercury	Hg	200.59	
81	Thallium	Tl	204.38	
82	Lead	Pb	207.2	g r
83	Bismuth	Bi	208.98	
84	Polonium*	^{210}Po	209.98	
85	Astatine*	^{210}At	209.99	
86	Radon*	^{222}Rn	222.02	
87	Francium*	^{223}Fr	223.02	
88	Radium*	^{226}Ra	226.03	
89	Actinium*	^{227}Ac	227.03	
90	Thorium*	Th	232.04	g
91	Protoactinium*	Pa	231.04	
92	Uranium*	U	238.03	g m
93	Neptunium*	^{237}Np	237.05	
94	Plutonium*	^{239}Pu	239.05	
95	Americium*	^{241}Am	241.06	
96	Curium*	^{244}Cm	244.06	
97	Berkelium*	^{249}Bk	249.08	
98	Californium*	^{252}Cf	252.08	
99	Einsteinium*	^{252}Es	252.08	
100	Fermium*	^{257}Fm	257.10	
101	Mendelevium*	^{258}Md	258.10	
102	Nobelium*	^{259}No	259.10	
103	Lawrencium*	^{262}Lr	262.11	

3.   Vapor pressure of water

3.1 Pure water

The vapor pressure of pure water over the temperature range 273–648 K is represented by the Chebyshev polynomial (Ambrose and Lawrenson,1972):

$$\left(\frac{T}{\text{K}}\right)\log\left(\frac{VP(\text{H}_2\text{O})}{\text{kPa}}\right) = \tfrac{1}{2}a_0 + \left[\sum_{k=1}^{11} a_k E_k(x)\right] \quad, \qquad (3.1.1)$$

where $x = (2(T/\text{K}) - 921)/375$ and T is measured on the International Practical Temperature Scale of 1968 (Note 1). The Chebyshev coefficients are

$$
\begin{array}{ll}
a_0 = 2794.0144 & a_6 = 0.1371 \\
a_1 = 1430.6181 & a_7 = 0.0629 \\
a_2 = -18.2465 & a_8 = 0.0261 \\
a_3 = 7.6875 & a_9 = 0.0200 \\
a_4 = -0.0328 & a_{10} = 0.0117 \\
a_5 = 0.2728 & a_{11} = 0.0067 \;.
\end{array}
$$

At 25 °C (298.15 K), $VP(\text{H}_2\text{O}) = 3.1686$ kPa.

3.2 Sea water

The vapor pressure of water in sea water is related to that of pure water:

$$VP(\text{H}_2\text{O, s/w}) \approx VP(\text{H}_2\text{O}) \, \exp\left(-0.018\,\phi \sum_{\text{B}} m_\text{B}/m^\circ\right) , \qquad (3.2.1)$$

where

$VP(\text{H}_2\text{O})$ is the vapor pressure of pure water (3.1.1),

$\sum_{\text{B}} m_\text{B}$ is the total molality of dissolved species (3.2.2),

ϕ is the osmotic coefficient of sea water (3.2.3),

$m^\circ = 1\ \text{mol·kg-H}_2\text{O}^{-1}$.

For sea water (of the composition detailed in § 6.1)

$$\sum_{\text{B}} m_\text{B}/m^\circ = \frac{31.998\,S}{10^3 - 1.005\,S} \quad, \qquad (3.2.2)$$

---

[1]   The International Practical Temperature Scale of 1968 (IPTS 68) has recently been superseded by the International Temperature Scale of 1990 (ITS 90). A simple equation can be used to relate the two over the oceanographic temperature range 0 to 40 °C (Jones & Harris, 1992):

$$t_{90}\,/\,°\text{C} = 0.0002 + 0.99975\,t_{68}\,/\,°\text{C} \;.$$

and the osmotic coefficient at 25 °C is given by (Millero, 1974):

$$\phi = 0.90799 - 0.08992\left(\frac{\frac{1}{2}\sum_B m_B}{m^\circ}\right) + 0.18458\left(\frac{\frac{1}{2}\sum_B m_B}{m^\circ}\right)^2$$

$$- 0.07395\left(\frac{\frac{1}{2}\sum_B m_B}{m^\circ}\right)^3 - 0.00221\left(\frac{\frac{1}{2}\sum_B m_B}{m^\circ}\right)^4, \qquad (3.2.3)$$

for $I = 0.3 - 0.8$ mol·kg-H_2O^{-1} (S = 16–40) . (Although strictly ϕ is a function of temperature as well as of I, the change between 0 and 40 °C is typically about 1% and can be ignored here.)

At 25 °C and S = 35, $VP(H_2O, s/w)$ = 3.1094 kPa.

4.   Densities of various substances

4.1   Air-saturated water

The density of air-saturated water in the temperature range 5 to 40 °C—*i.e.* avoiding the temperature of maximum density—is given by the expression (Jones & Harris, 1992):

$$\rho_W / (kg·m^{-3}) = 999.84847 + 6.337563 \times 10^{-2} (t/°C)$$

$$- 8.523829 \times 10^{-3} (t/°C)^2 + 6.943248 \times 10^{-5} (t/°C)^3$$

$$- 3.821216 \times 10^{-7} (t/°C)^4, \qquad (4.1.1)$$

where t is the temperature on ITS 90 (see Note 1).

At 25 °C, ρ_W = 997.041 kg·m^{-3} = 0.997041 g·cm^{-3}.

4.2   Sea water

The density of sea water in the temperature range 0 to 40 °C (IPTS 68—see Note 1) and the salinity range 0 to 42 is given by the expression (Millero & Poisson, 1981):

$$\rho_{SW} / (kg·m^{-3}) = \rho_{SMOW} / (kg·m^{-3}) + A\,S + B\,S^{1.5} + C\,S^2 \qquad (4.2.1)$$

where (Note 2)

$$\rho_{SMOW} / (kg·m^{-3}) = 999.842594 + 6.793952 \times 10^{-2} (t/°C)$$

$$- 9.095290 \times 10^{-3} (t/°C)^2 + 1.001685 \times 10^{-4} (t/°C)^3$$

$$- 1.120083 \times 10^{-6} (t/°C)^4 + 6.536332 \times 10^{-9} (t/°C)^5, \qquad (4.2.2)$$

---

[2]   SMOW — Standard Mean Ocean Water (Craig, 1961)—is pure water with a specified isotopic composition and free of dissolved gases.

$$A = 8.24493 \times 10^{-1} - 4.0899 \times 10^{-3} \, (t/^\circ C)$$
$$+ \; 7.6438 \times 10^{-5} \, (t/^\circ C)^2 - 8.246\,7 \times 10^{-7} \, (t/^\circ C)^3$$
$$+ \; 5.3875 \times 10^{-9} \, (t/^\circ C)^4 \; , \tag{4.2.3}$$
$$B = -5.72466 \times 10^{-3} + 1.0227 \times 10^{-4} \, (t/^\circ C)$$
$$- \; 1.6546 \times 10^{-6} \, (t/^\circ C)^2 \; , \tag{4.2.4}$$
$$C = 4.8314 \times 10^{-4} \; ; \tag{4.2.5}$$

t is on IPTS 68 and S is the salinity.

At 25 °C (IPTS 68) and $S = 35$, $\rho_{SW} = 1023.343$ kg·m^{-3}.

4.3 Sodium chloride solutions

The density of a solution of sodium chloride in water in the temperature range 0 to 50 °C (IPTS 68—see Note 1) and the concentration range 0.1 mol·kg-H$_2$O^{-1} to saturation can be calculated from the expression (Lo Surdo *et al.*, 1982):

$$\frac{10^3(\rho(\text{NaCl}) - \rho_{\text{SMOW}})}{\text{g} \cdot \text{cm}^{-3}} = \left(\frac{m}{m^\circ}\right)\left(45.5655 - 0.2341\left(\frac{t}{^\circ C}\right)\right.$$
$$\left. + \; 3.4128 \times 10^{-3}\left(\frac{t}{^\circ C}\right)^2 - 2.7030 \times 10^{-5}\left(\frac{t}{^\circ C}\right)^3 + 1.4037 \times 10^{-7}\left(\frac{t}{^\circ C}\right)^4\right)$$
$$+ \left(\frac{m}{m^\circ}\right)^{3/2}\left(-1.8527 + 5.3956 \times 10^{-2}\left(\frac{t}{^\circ C}\right) - 6.2635 \times 10^{-4}\left(\frac{t}{^\circ C}\right)^2\right)$$
$$+ \left(\frac{m}{m^\circ}\right)^2\left(-1.6368 - 9.5653 \times 10^{-4}\left(\frac{t}{^\circ C}\right) + 5.2829 \times 10^{-5}\left(\frac{t}{^\circ C}\right)^2\right)$$
$$+ \; 0.2274\left(\frac{m}{m^\circ}\right)^{5/2} \tag{4.3.1}$$

where t is the temperature (IPTS 68), m the molality of the sodium chloride solution and $m^\circ = 1$ mol·kg-H$_2$O^{-1}. ρ_{SMOW} is calculated using equation (4.2.2)—see Note 3.

To convert the concentration of sodium chloride expressed in mol·kg-soln^{-1}—C(NaCl)—to mol·kg-H$_2$O^{-1} use the expression:

$$\frac{m(\text{NaCl})}{m^\circ} = \frac{10^3 \, C(\text{NaCl})}{10^3 - 58.443 \, C(\text{NaCl})} \; . \tag{4.3.2}$$

At 25 °C and $m = 0.725$ mol·kg-H$_2$O^{-1}, ρ(NaCl) = 1.02581 g·cm^{-3}.

---

[3]   In the original paper of Lo Surdo *et al.* (1982) an alternate formulation based on the work of Kell (1975) was used for the density of pure water. The difference is <10 ppm over the temperature range 0 to 50 °C.

4.4 A mixture of NaCl and HCl at 25 °C

An expression based on Young's rule has been developed for the density of a mixture of NaCl and HCl at a temperature of 25 °C (Millero, *personal communication*):

$$\rho_{mix}(25\,°C) \;=\; \frac{\rho_W(25\,°C)(10^3 + m_T\{m(HCl)+m(NaCl)\})}{10^3 + \varphi_{mix}\{m(HCl)+m(NaCl)\}(\rho_W(25\,°C))} \;,$$

$$(4.4.1)$$

where $\rho_W(25\,°C) = 0.99704$ g·cm^{-3} (Note 4),

$$m_T \;=\; \frac{36.46\,m(HCl) + 58.44\,m(NaCl)}{m(HCl)+m(NaCl)} \;, \qquad (4.4.2)$$

$$\varphi_{mix} \;=\; \frac{m(HCl)\,\varphi_{HCl} + m(NaCl)\,\varphi_{NaCl}}{m(HCl)+m(NaCl)} \;, \qquad (4.4.3)$$

and the apparent molar volumes at 25 °C:

$$\varphi_{HCl} \;=\; 17.854 + 1.460\sqrt{m} - 0.307\,m \;, \qquad (4.4.4)$$

$$\varphi_{NaCl} \;=\; 16.613 + 1.811\sqrt{m} + 0.094\,m \;, \qquad (4.4.5)$$

where $m = m(HCl) + m(NaCl)$. The concentrations $m(HCl)$ and $m(NaCl)$ are in mol·kg-H$_2$O^{-1}.

At $m(HCl) = 0.2$ mol·kg-H$_2$O^{-1} and $m(NaCl) = 0.5$ mol·kg-H$_2$O^{-1}, $\rho_{mix}(25\,°C) = 1.02056$ g·cm^{-3}.

4.5 Mercury

The density of mercury in the temperature range 0 to 50 °C is given by Weast (1975):

$$\rho(Hg) \;=\; 13.5955\left(1 - \alpha_V(Hg)\left(\frac{t}{°C}\right)\right)\,g\cdot cm^{-3} \;\;; \qquad (4.5.1)$$

where t is the temperature (presumably on IPTS 68). The volumetric coefficient of expansion

$$\alpha_V(Hg) \;=\; \left(181792 + 0.175\left(\frac{t}{°C}\right) + 0.035116\left(\frac{t}{°C}\right)^2\right)\times 10^{-9} \;\;. \quad (4.5.2)$$

At 25 °C, $\rho(Hg) = 13.5337$ g·cm^{-3}.

---

4   At temperatures other than 25 °C, equation (4.4.1) is not reliable.

4.6   Various solids

Data from Weast (1975).

   Potassium chloride
$$\rho(KCl) = 1.984 \text{ g·cm}^{-3} \qquad (4.6.1)$$

   Sodium chloride
$$\rho(NaCl) = 2.165 \text{ g·cm}^{-3} \qquad (4.6.2)$$

   Sodium carbonate
$$\rho(Na_2CO_3) = 2.532 \text{ g·cm}^{-3} \qquad (4.6.3)$$

   Sodium sulfate
$$\rho(Na_2SO_4) = 2.68 \text{ g·cm}^{-3} \qquad (4.6.4)$$

   Sodium tetraborate decahydrate (borax)
$$\rho(Na_2B_4O_7 \cdot 10H_2O) = 1.73 \text{ g·cm}^{-3} \qquad (4.6.5)$$

   2-amino-2-hydroxymethyl-1,3-propanediol ("tris")
$$\rho(H_2NC(CH_2OH)_3) = 1.35 \text{ g·cm}^{-3} \qquad (4.6.6)$$

   2-aminopyridine
$$\rho(C_5H_6N_2) = 1.24 \text{ g·cm}^{-3} \qquad (4.6.7)$$

5.   Virial coefficients for carbon dioxide

5.1   Pure carbon dioxide gas

The first virial coefficient of CO_2 is given by the expression (Weiss, 1974)

$$\frac{B(CO_2, T)}{\text{cm}^3 \cdot \text{mol}^{-1}} = -1636.75 + 12.0408\left(\frac{T}{K}\right)$$

$$- 3.27957 \times 10^{-2}\left(\frac{T}{K}\right)^2 + 3.16528 \times 10^{-5}\left(\frac{T}{K}\right)^3 , \quad (5.1.1)$$

where $265 < (T/K) < 320$.

At 25 °C (298.15 K), $B(CO_2, 298.15 \text{ K}) = -123.2 \text{ cm}^3 \cdot \text{mol}^{-1}$.

5.2   Carbon dioxide in air

For a binary mixture (B–C), it is possible to define a cross virial coefficient:

$$\delta_{B-C} = B_{BC} - \tfrac{1}{2}(B_{BB} - B_{CC}) \quad . \qquad (5.2.1)$$

Weiss (1974) used the Lennard-Jones (6–12) potential to calculate values for the cross-virial coefficient δ for the binary mixture: CO_2–air (see also SOP 24). He found that the temperature dependence of this parameter could be represented by the equation

$$\frac{\delta(CO_2 - air)}{cm^3 \cdot mol^{-1}} = 57.7 - 0.118\left(\frac{T}{K}\right) , \qquad (5.2.2)$$

where $273 < (T/K) < 313$.

At 25 °C (298.15 K), $\delta(CO_2$–air) = 22.5 $cm^3 \cdot mol^{-1}$.

6.   Salinity and the composition of sea water

6.1   The major ion composition of sea water

Traditionally the parameter salinity, S, has been used to give a measure of the total dissolved solids in sea water. Originally this was intended to be an analytical parameter with the units $g \cdot kg^{-1}$, but this direct approach was quickly superseded by the practice of estimating salinity from alternative, simpler procedures (*e.g.* the measurement of chlorinity or conductivity ratio). The concept of a "constant composition of sea water" is then invoked to relate these parameters to salinity (UNESCO, 1966).

Although the idea of "constant composition of sea water" is recognized as being not strictly accurate, it is a useful device in simplifying the study of the various physicochemical properties of sea water. One example of this is the treatment of sea water as a two component system—water and sea-salt—to represent its thermodynamic properties (*e. g* osmotic coefficient or density, see § 3.2 and § 4.2). Another is the treatment of sea water as a constant ionic medium in which the thermodynamics of various chemical process involving minor constituents can be studied (*e. g.* gas solubility or acid–base equilibria).

Analytical results for the other major components of sea water are usually expressed relative to chlorinity (Table 6.1) and a standard mean chemical composition of sea water (Table 6.2) can be calculated using the equilibrium constants for the dissociation of water, carbonic and boric acids.

Table 6.1: Standard mean analytical composition of
sea water with S = 35, chlorinity = 19.374.

Component	Relative Concentration[a]	mol·kg-soln^{-1}	Reference
Chloride	0.99889	0.54586	calculated from chlorinity
Sulfate	0.1400	0.02824	Morris & Riley (1966)
Bromide	0.003473	0.00084	Morris & Riley (1966)
Fluoride	0.000067	0.00007	Riley (1965)
Sodium	0.55661	0.46906	from charge balance
Magnesium	0.06626	0.05282	Carpenter & Manella (1973)
Calcium	0.02127	0.01028	Riley & Tongudai (1967)
Potassium	0.0206	0.01021	Riley & Tongudai (1967)
Strontium	0.00041	0.00009	Riley & Tongudai (1967)
Boron	0.000232	0.000416	Uppström (1974)
Total alkalinity		0.002400	average surface water
pH = 8.1		$10^{-8.1}$	average surface water

a. Expressed relative to the chlorinity (= S/1.80655). Thus the total sulfate (molar mass 96.062 g) at a salinity S is given by:

$$S_T = \left(\frac{0.1400}{96.062}\right)\times\left(\frac{S}{1.80655}\right) \text{ mol·kg-soln}^{-1}.$$

Table 6.2: Standard mean chemical composition of sea water (S = 35)

Species	mol·kg-soln^{-1}	g·kg-soln^{-1}	mol·kg-H$_2$O^{-1}	g·kg-H$_2$O^{-1}
Cl^-	0.54586	19.3524	0.56576	20.0579
SO_4^{2-}	0.02824	2.7123	0.02927	2.8117
Br^-	0.00084	0.0673	0.00087	0.0695
F^-	0.00007	0.0013	0.00007	0.0013
Na^+	0.46906	10.7837	0.48616	11.1768
Mg^{2+}	0.05282	1.2837	0.05475	1.3307
Ca^{2+}	0.01028	0.4121	0.01065	0.4268
K^+	0.01021	0.3991	0.01058	0.4137
Sr^{2+}	0.00009	0.0079	0.00009	0.0079
$B(OH)_3$	0.00032	0.0198	0.00033	0.0204
$B(OH)_4^-$	0.00010	0.0079	0.00010	0.0079
CO_2^*	0.00001	0.0004	0.00001	0.0004
HCO_3^-	0.00177	0.1080	0.00183	0.1117
CO_3^{2-}	0.00026	0.0156	0.00027	0.0162
OH^-	0.00001	0.0002	0.00001	0.0002
sum of column	1.11994	35.1717	1.16075	36.4531
ionic strength	0.69734		0.72275	

6.2 A simplified synthetic sea water recipe

A simplified artificial sea water recipe can be obtained from the recipe in Table 6.2 as follows: replace bromide, fluoride, and total alkalinity with chloride and replace strontium with calcium. The resultant composition (Table 6.3) is the basis of the synthetic sea water that has been used to determine a variety of equilibrium constants for use in sea water (*e. g.* Dickson, 1990; Roy *et al.,* 1993):

Table 6.3: Simplified artificial sea water composition ($S = 35$)[a]

Species	mol·kg-soln^{-1}	g·kg-soln^{-1}	mol·kg-H$_2$O^{-1}	g·kg-H$_2$O^{-1}
Cl$^-$	0.54922	19.4715	0.56918	20.1791
SO$_4^{2-}$	0.02824	2.7128	0.02927	2.8117
Na$^+$	0.46911	10.7848	0.48616	11.1768
Mg^{2+}	0.05283	1.2840	0.05475	1.3307
Ca^{2+}	0.01036	0.4152	0.01074	0.4304
K$^+$	0.01021	0.3992	0.01058	0.4137
sum of column	1.11997	35.0675	1.16068	36.3424
ionic strength	0.69713		0.72248	

a. The composition here is very slightly different from that used by Dickson (1990) or Roy *et al.,* (1993). This is the result of minor changes in the molar masses used to compute the various concentrations.

7. Equilibrium constants

All the equations for the equilibrium constants presented here use concentrations expressed in moles per kilogram of solution. In addition, with the exception of that for bisulfate ion, all acid dissociation constants are expressed in terms of "total" hydrogen ion concentration (see Chapter 2).

7.1 Solubility of carbon dioxide in sea water

The equilibrium constant for the process

$$CO_2(g) = CO_2^*(aq) \quad, \tag{7.1.1}$$
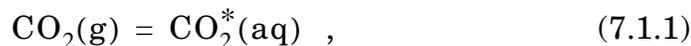
i. e.

$$K_0 = [CO_2^*]/f(CO_2) \quad, \tag{7.1.2}$$

is given by the expression (Weiss, 1974):

$$\ln(K_0/k^\circ) = 93.4517\left(\frac{100}{T/K}\right) - 60.2409 + 23.3585\ln\left(\frac{T/K}{100}\right)$$
$$+ S\left(0.023517 - 0.023656\left(\frac{T/K}{100}\right) + 0.0047036\left(\frac{T/K}{100}\right)^2\right),$$

(7.1.3)

The fugacity of CO_2 gas (see Chapter 2) is expressed in atm; $k^\circ = 1$ mol·kg-soln^{-1}.

At $S = 35$ and $t = 25$ °C (298.15 K), $\ln(K_0/k^\circ) = -3.5617$.

7.2   Acid-base reactions in sea water

BISULFATE ION
The equilibrium constant for the reaction

$$HSO_4^- = H^+ + SO_4^{2-} \ ,$$ (7.2.1)
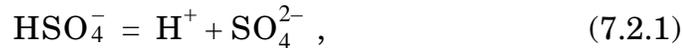
i. e.

$$K_S = [H^+]_F[SO_4^{2-}]/[HSO_4^-] \ ,$$ (7.2.2)

is given by the expression (Dickson, 1990a):

$$\ln(K_S/k^\circ) = \frac{-4276.1}{(T/K)} + 141.328 - 23.093 \ln(T/K)$$
$$+ \left(\frac{-13856}{(T/K)} + 324.57 - 47.986 \ln(T/K)\right) \times \left(\frac{I}{m^\circ}\right)^{1/2}$$
$$+ \left(\frac{35474}{(T/K)} - 771.54 + 114.723 \ln(T/K)\right) \times \left(\frac{I}{m^\circ}\right)$$
$$- \frac{2698}{(T/K)}\left(\frac{I}{m^\circ}\right)^{3/2} + \frac{1776}{(T/K)}\left(\frac{I}{m^\circ}\right)^2 + \ln(1 - 0.001005 \ S) \quad .$$

(7.2.3)

$k^\circ = 1$ mol·kg-soln^{-1} and hydrogen ion concentration is expressed on the "free" scale. The ionic strength is calculated from the expression

$$I/m^\circ = \frac{19.924S}{1000 - 1.005S} \ ;$$ (7.2.4)

The term $\ln(1 - 0.001005S)$ converts the value of K_S from mol·kg-H_2O^{-1} (used in the paper of Dickson) to mol·kg-soln^{-1}.

At $S = 35$ and $t = 25$ °C (298.15K), $\ln(K_S/k^\circ) = -2.30$.

BORIC ACID

The equilibrium constant for the reaction

$$B(OH)_3 + H_2O = H^+ + B(OH)_4^- \ , \tag{7.2.5}$$

i. e.

$$K_B = [H^+][B(OH)_4^-]/[B(OH)_3] \ , \tag{7.2.6}$$

is given by the expression (Dickson,1990b):

$$\ln\left(\frac{K_B}{k^\circ}\right) = \frac{-8966.90 - 2890.53 \, S^{1/2} - 77.942 \, S + 1.728 \, S^{3/2} - 0.0996 \, S^2}{(T/K)}$$

$$+ (148.0248 + 137.1942 \, S^{1/2} + 1.62142 S)$$

$$+ (-24.4344 - 25.085 \, S^{1/2} - 0.2474 \, S)\ln(T/K)$$

$$+ 0.053105 \, S^{1/2}(T/K) \ ; \tag{7.2.7}$$

k° = 1 mol·kg-soln^{-1}. This equation is in excellent agreement with the measurements made by Roy *et al.* (1993a); it is also in reasonable agreement with the results of Hansson (1973a).

At $S = 35$ and $t = 25\ °C$ (298.15 K), $\ln(K_B/k^\circ) = -19.7964$.

CARBONIC ACID

The equilibrium constants used here are from Roy *et al.* (1993b). These constants are in excellent agreement with those measured by Goyet & Poisson (1989), and in reasonable agreement with those of Hansson (1973b) and Mehrbach *et al.*(1973).

The equilibrium constant for the reaction

$$CO_2^*(aq) + H_2O(l) = H^+(aq) + HCO_3^-(aq) \ , \tag{7.2.8}$$
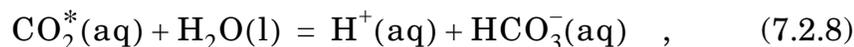
i. e.

$$K_1 = [H^+][HCO_3^-]/[CO_2^*] \tag{7.2.9}$$

is given by the expression (Roy *et al.*, 1993):

$$\ln(K_1/k^\circ) = \frac{-2307.1266}{(T/K)} + 2.83655 - 1.5529413 \ln(T/K)$$

$$+ \left(\frac{-4.0484}{(T/K)} - 0.20760841 \right)S^{1/2} + 0.08468345 \, S$$

$$- 0.00654208 \, S^{3/2} + \ln(1 - 0.001005 \, S) \ ; \tag{7.2.10}$$

where k° = 1 mol·kg-soln^{-1}.

The term $\ln(1 - 0.001005\,S)$ converts the value of K_1 from $mol \cdot kg\text{-}H_2O^{-1}$ (in the original paper of Roy *et al.*) to $mol \cdot kg\text{-}soln^{-1}$.

At $S = 35$ and $t = 25\ °C$ (298.15 K), $\ln(K_1/k°) = -13.4847$.

The equilibrium constant for the reaction

$$HCO_3^-(aq) \;=\; H^+(aq) + CO_3^{2-}(aq) \quad , \qquad (7.2.11)$$
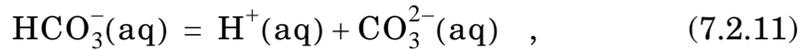
i. e.

$$K_2 \;=\; [H^+][CO_3^{2-}]/[HCO_3^-] \qquad (7.2.12)$$

is given by the expression (Roy *et al.,* 1993):

$$\ln(K_2/k°) \;=\; \frac{-3351.6106}{(T/K)} - 9.226508 - 0.2005743\,\ln(T/K)$$

$$+ \left(\frac{-23.9722}{(T/K)} - 0.106901773\right)S^{1/2} + 0.1130822\,S$$

$$- 0.00846934\,S^{3/2} + \ln(1 - 0.001005\,S)\ ; \qquad (7.2.13)$$

where $k° = 1\ mol \cdot kg\text{-}soln^{-1}$. The term $\ln(1 - 0.001005\,S)$ converts the value of K_1 from $mol \cdot kg\text{-}H_2O^{-1}$ (in the paper of Roy *et al.*) to $mol \cdot kg\text{-}soln^{-1}$.

At $S = 35$ and $t = 25\ °C$ (298.15 K), $\ln(K_2/k°) = -20.5504$.

HYDROGEN FLUORIDE
The equilibrium constant for the reaction

$$HF(aq) \;=\; H^+(aq) + F^-(aq) \quad , \qquad (7.2.14)$$
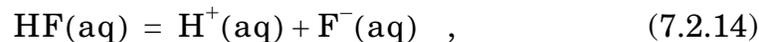
i. e.

$$K_F \;=\; [H^+][F^-]/[HF] \quad , \qquad (7.2.15)$$

is given by the expression (Dickson & Riley, 1979a)

$$\ln(K_F/k°) \;=\; \frac{1590.2}{(T/K)} - 12.641 + 1.525(I/m°)^{1/2}$$

$$+ \ \ln(1 - 0.001005\,S) + \ln(1 + S_T/K_S)\ ; \qquad (7.2.16)$$

where $k° = 1\ mol \cdot kg\text{-}soln^{-1}$. The ionic strength is calculated from

$$I/m° \;=\; \frac{19.924S}{1000 - 1.005S}\ ; \qquad (7.2.17)$$

The term $\ln(1 - 0.001005\,S)$ converts the value of K_F from $mol \cdot kg\text{-}H_2O^{-1}$ (in the paper of Dickson & Riley) to $mol \cdot kg\text{-}soln^{-1}$;

and the term $\ln(1 + S_T/K_S)$ converts from the "free" hydrogen ion concentration scale to the "total" scale—see Table 6.1 for S_T

At $S = 35$ and $t = 25\ °C$ (289.15K), $\ln(K_F/k°) = -5.80$.

PHOSPHORIC ACID

The expressions below are from Millero (1995)—Note 5—and are a composite of measurements by Kester & Pytkowicz (1967), by Dickson & Riley (1979b) and by Johansson & Wedborg (1979).

The equilibrium constant for the reaction

$$H_3PO_4(aq) = H^+(aq) + H_2PO_4^-(aq) \quad , \qquad (7.2.18)$$

i. e.

$$K_{1P} = [H^+][H_2PO_4^-]/[H_3PO_4] \quad , \qquad (7.2.19)$$

is given by the expression

$$\ln(K_{1P}/k°) = \frac{-4576.752}{T/K} + 115.525 - 18.453 \ln(T/K) +$$

$$\left(\frac{-106.736}{(T/K)} + 0.69171\right)S^{1/2} + \left(-\frac{0.65643}{(T/K)} - 0.01844\right)S \quad ; \qquad (7.2.20)$$

where $k° = 1\ \mathrm{mol \cdot kg\text{-}soln^{-1}}$.

At $S = 35$ and $t = 25\ °C$ (298.15 K), $\ln(K_{1P}/k°) = -3.71$.

The equilibrium constant for the reaction

$$H_2PO_4^-(aq) = H^+(aq) + HPO_4^{2-}(aq) \quad , \qquad (7.2.21)$$

i. e.

$$K_{2P} = [H^+][HPO_4^{2-}]/[H_2PO_4^-] \quad , \qquad (7.2.22)$$

is given by the expression

$$\ln(K_{2P}/k°) = \frac{-8814.715}{T/K} + 172.0883 - 27.927 \ln(T/K) +$$

$$\left(\frac{-160.340}{(T/K)} + 1.3566\right)S^{1/2} + \left(\frac{0.37335}{(T/K)} - 0.05778\right)S \quad ; \qquad (7.2.23)$$

where $k° = 1\ \mathrm{mol \cdot kg\text{-}soln^{-1}}$.

At $S = 35$ and $t = 25\ °C$ (298.15 K), $\ln(K_{2P}/k°) = -13.727$.

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[5]   0.015 has been subtracted from the constant term in each of these expressions: (7.2.20), (7.2.23), (7.2.26) to convert—approximately—from the SWS pH scale (including HF) used by Millero (1995) to the "total" hydrogen ion scale used here.

The equilibrium constant for the reaction

$$HPO_4^{2-}(aq) = H^+(aq) + PO_4^{3-}(aq) \quad , \qquad (7.2.24)$$

i. e.

$$K_{3P} = [H^+][PO_4^{3-}]/[HPO_4^{2-}] \quad , \qquad (7.2.25)$$

is given by the expression

$$\ln(K_{3P}/k^\circ) = \frac{-3070.75}{T/K} - 18.141 +$$

$$\left(\frac{17.27039}{T/K} + 2.81197\right)S^{1/2} + \left(\frac{-44.99486}{T/K} - 0.09984\right)S \; ;$$

$$(7.2.26)$$

where k° = 1 mol·kg-soln^{-1}.

At $S = 35$ and t = 25 °C (298.15 K), ln (K_{3P}/k°) = −20.24 .

SILICIC ACID
The equilibrium constant for the reaction

$$Si(OH)_4(aq) = H^+(aq) + SiO(OH)_3^-(aq) \quad , \qquad (7.2.27)$$

i. e.

$$K_{Si} = [H^+][SiO(OH)_3^-]/[Si(OH)_4] \quad , \qquad (7.2.28)$$

is given by the expression (Millero, 1995):

$$\ln(K_{Si}/k^\circ) = \frac{-8904.2}{(T/K)} + 117.385 - 19.334\ln(T/K) +$$

$$+ \left(\frac{-458.79}{(T/K)} + 3.5913\right)(I/m^\circ)^{1/2} + \left(\frac{188.74}{(T/K)} - 1.5998\right)(I/m^\circ) \quad (7.2.29)$$

$$+ \left(\frac{-12.1652}{(T/K)} + 0.07871\right)(I/m^\circ)^2 + \ln(1 - 0.001005S);$$

where k° = 1 mol·kg-soln^{-1}. This expression is based on the results of Sjöberg *et al.* (1981) and the review by Baes & Mesmer (1976); 0.015 has been subtracted from the constant (see Note 5). The ionic strength is calculated from the expression

$$I/m^\circ = \frac{19.924S}{1000 - 1.005S} \approx 0.02S \; ; \qquad (7.2.30)$$

The term ln $(1 - 0.001005S)$ converts the value of K_{Si} from mol·kg-H$_2$O^{-1} to mol·kg-soln^{-1}.

At $S = 35$ and t = 25 °C (298.15 K), ln (K_{Si}/k°) = −21.61 .

WATER

The equilibrium constant for the reaction

$$H_2O(aq) = H^+(aq) + OH^-(aq) \quad, \qquad (7.2.31)$$
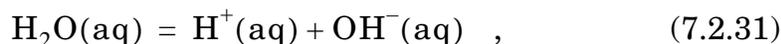
i. e.

$$K_W = [H^+][OH^-] \quad, \qquad (7.2.32)$$

is given by the expression (Millero, 1995):

$$\ln(K_W/(k°)^2) = \frac{-13847.26}{(T/K)} + 148.9652 - 23.6521\ln(T/K),$$

$$+ \left(\frac{118.67}{(T/K)} - 5.977 + 1.0495\ln(T/K)\right)S^{1/2} - 0.01615S \quad; $$

$$(7.2.33)$$

where $k° = 1$ mol·kg-soln^{-1}. This expression is based on results published by Hansson (1973a), by Culberson & Pytkowicz (1973) and by Dickson & Riley (1979a). Note that 0.015 has been subtracted from the constant term (see Note 5).

At $S = 35$ and $t = 25$ °C (298.15 K), ln $(K_W/(k°)^2) = -30.434$.

7.3 Acid-base reactions in sodium chloride media

The values given here are appropriate to a background medium with $C(NaCl) = 0.7$ mol·kg-soln^{-1} and at a temperature of 25 °C.

CARBONIC ACID

The values given here are from Dyrssen & Hansson (1973).

The equilibrium constant for the reaction

$$CO_2^*(aq) + H_2O(l) = H^+(aq) + HCO_3^-(aq) \quad, \qquad (7.3.1)$$
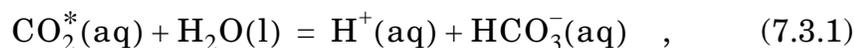
i. e.

$$K_1 = [H^+][HCO_3^-]/[CO_2^*] \qquad (7.3.2)$$

at $C(NaCl) = 0.7$ mol·kg-soln^{-1} and $t = 25$ °C is

$$\ln(K_1/k°) = -13.82 \ . \qquad (7.3.3)$$

The equilibrium constant for the reaction

$$HCO_3^-(aq) = H^+(aq) + CO_3^{2-}(aq) \quad, \qquad (7.3.4)$$
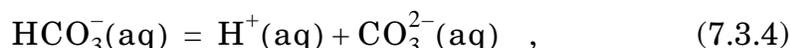
i. e.

$$K_2 = [H^+][CO_3^{2-}]/[HCO_3^-] \qquad (7.3.5)$$

at $C(NaCl) = 0.7$ mol·kg-soln^{-1} and $t = 25$ °C is

$$\ln(K_2/k°) = -21.97 \ . \qquad (7.3.6)$$

2-AMINO-2-HYDROXYMETHYL-1,3-PROPANEDIOL
The equilibrium constant for the reaction

$$H_3NC(CH_2OH)_3^+(aq) \;=\; H^+(aq) + H_2NC(CH_2OH)_3(aq) \quad , \tag{7.3.7}$$
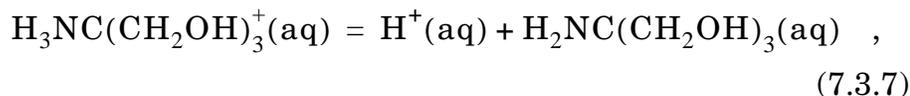
i. e.

$$K_{tris} \;=\; [H^+][H_2NC(CH_2OH)_3]/[H_3NC(CH_2OH)_3^+] \tag{7.3.8}$$

at $C(NaCl) = C(NaCl) = 0.7$ mol·kg-soln^{-1} and $t = 25\ °C$ is

$$\ln(K_{tris}/k°) = -18.90 \;, \tag{7.3.9}$$

(Millero *et al.*, 1987).

WATER
The equilibrium constant for the reaction

$$H_2O(aq) \;=\; H^+(aq) + OH^-(aq) \quad , \tag{7.3.10}$$
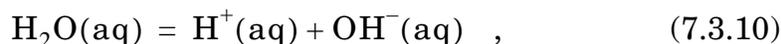
i. e.

$$K_W \;=\; [H^+][OH^-] \;, \tag{7.3.11}$$

at $C(NaCl) = 0.7$ mol·kg-soln^{-1} and $t = 25\ °C$ is

$$\ln(K_W/(k°)^2) = -31.71 \;, \tag{7.3.12}$$

(Dyrssen & Hansson, 1973).

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