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 $\mu mol \cdot kg^{-1}$) and also for higher levels such as are found in the Black Sea (3800–4300 $\mu mol \cdot kg^{-1}$).

2. Definition

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

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

where brackets represent total concentrations of these constituents in solution (in $mol \cdot kg^{-1}$) 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:

$$CO_2 + HO(CH_2)_2NH_2 \rightarrow HO(CH_2)_2NHCOO^- + H^+ \tag{2}$$

and

$$H^+ + OH^- \rightarrow H_2O \ . \tag{3}$$

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

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

while silver is dissolved at the anode:

$$Ag(s) \rightarrow Ag^+ + e^- \ . \tag{5}$$

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 (~30 cm^3) into the stripping chamber and acidify it with phosphoric acid (~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·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):

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

where

$\quad N_b$ = 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

$$N_c = \text{the coulometer reading for the gas sample (counts),}$$
$$b = \text{the background level of the system (counts / min),}$$
$$t = \text{the time required to measure that sample (min),}$$
$$n(CO_2) = \text{the amount of } CO_2 \text{ dispensed from the loop (mol),}$$

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

$V(T)$ 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

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

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

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:

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

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[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 ;
$V(298.15\ K)$ = 1.5000 cm^3 ;
$B(CO_2, 298.15\ K)$ = −123.2 cm^3·mol^{-1} ;
N_c = 294033 counts in 15 minutes ;

Thus

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

and

$$n(CO_2) \ = \ 1.5 / 24341.7 \ \ mol$$
$$= \ 61.6226 \ \mu mol \ .$$

Hence

$$c \ = \ \frac{294033 - 10 \times 15}{61.6226 \times 10^{-6}}$$
$$= \ 4.76908 \times 10^9 \ \ counts \ / \ mol \ .$$

8.4.3   Calculation of the calibration factor using 6 Na$_2$CO$_3$
       solutions

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

M_1 =   0.0 μmol·dm^{-3} ; N_s =   1892 counts in 15 min
M_2 =   498.8 μmol·dm^{-3} ; N_s =   66537 counts in 15 min
M_3 = 1001.9 μmol·dm^{-3} ; N_s = 130818 counts in 15 min
M_4 = 1500.8 μmol·dm^{-3} ; N_s = 195216 counts in 15 min
M_5 = 2002.5 μmol·dm^{-3} ; N_s = 260068 counts in 15 min
M_6 = 2497.1 μmol·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.

slope $= 4.76908 \times 10^9$ counts / mol

intercept $= 67695.1$ counts / dm^3.

Thus

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

and hence

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

8.4.4 Calculation for a sea water sample:

$S = 35.00$; $t = 25.0$ °C ; $\rho(S, t) = 1.02334$ g·cm^3 ;

$V_\text{s} = 27.0000$ cm^3 ;

$a = 40$ counts ; $b = 10$ counts / min ;

$N_\text{s} = 289\,874$ counts in 15 minutes .

Then

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

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

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

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

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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[22]   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

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).
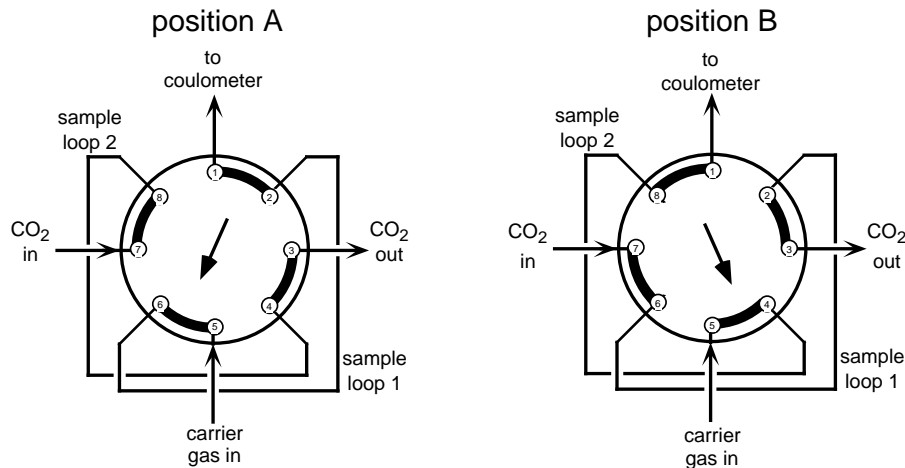
Annexe B

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 $\pm$ 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):

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

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):

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

5.3   Sample calculation

$w(Na_2CO_3) = 0.21230$ g ;
$V(\text{flask}) = 1.0001$ dm^3 ;
$\rho(\text{weights}) = 8.0$ g·cm^{-3} ;
$\rho(Na_2CO_3) = 2.532$ g·cm^{-3} ;
purity of $Na_2CO_3 = 99.95\%$.

Thus

$$m(Na_2CO_3) = 0.21230\left(\frac{1 - 0.0012/8.0}{1 - 0.0012/2.532}\right)$$

$$= 0.21237 \text{ g}$$

and

$$c(Na_2CO_3) = \frac{0.21237}{105.988} \times \frac{1}{1.0001} \times 0.9995$$

$$= 2002.5 \ \mu\text{mol·dm}^{-3} \ .$$

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.

References

Goyet, C. and Hacker, S. D. (1992) Procedure for calibration of a coulometric system used for total inorganic carbon measurements. *Marine Chemistry* **38**, 37–51.

IUPAC (1969) Sodium carbonate and sulphamic acid as acid-base primary standards. *Pure & Applied Chemistry* **18**, 445–455.