

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

2. Definition

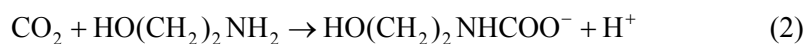
The total dissolved inorganic carbon content of sea water is defined as

$$C_T = [\text{CO}_2^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (1)$$

where brackets represent total concentrations of these constituents in solution (in mol kg^{-1}) and $[\text{CO}_2^*]$ represents the total concentration of all unionized carbon dioxide, whether present as H_2CO_3 or as CO_2 .

3. Principle

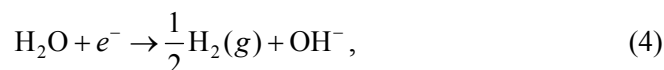
A known amount of sea water is dispensed into a stripping chamber where it is acidified and purged with an inert gas. The presence of solid carbonates, such as CaCO_3 , thus constitutes an interference in the method. The amount of CO_2 in the resulting gas stream is determined by trapping the CO_2 in 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



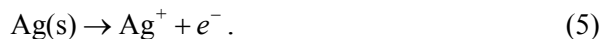
and



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



while silver is dissolved at the anode:



The overall efficiency of the coulometric procedure is calibrated using known amounts of CO₂ gas or from Na₂CO₃ solutions.

4. Apparatus

In the late 1980s, a system called the Single Operator Multi-parameter Metabolic Analyzer (SOMMA) was developed to interface with a coulometer to make high precision C_T measurements (Johnson *et al.*, 1985; 1987; 1993). The system was produced commercially for a few years in the early 1990s and became the standard for automated coulometric C_T measurements. The original manufacturer of the SOMMA system is no longer in operation, but this approach still represents the most common technique for C_T measurements.

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 CO₂ with the atmosphere¹. If a controlled volume of water is dispensed, its temperature must be known to within $\pm 0.4^\circ\text{C}$.

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 CO₂ by bubbling the carrier gas through a fine frit submerged in the acidified sample. Carrier gas leaving the stripping chamber is treated to prevent acid droplets from reaching the coulometer cell.

4.3 Coulometer system

A UIC Model 5011 or 5012 CO₂ coulometer (UIC Inc., P.O. Box 863, Joliet, IL 60434, U.S.A.) is the most common system used. This system uses a coulometer cell with a platinum spiral cathode and silver rod anode (both available from UIC). It is desirable to control the temperature of this cell to within $\pm 0.2^\circ\text{C}$. 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

¹ There are two principal means of achieving 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 system.

an analysis will cause an error. The magnitude of this error is about 200 counts per degree Celsius per 100 cm³ of cathode solution. Although this is rarely significant for a sea water sample, it complicates accurate measurement of the background titration rate.

4.4 Gas loop calibration system

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, the most common way of calibrating the system and is strongly recommended. Typically, two stainless steel loops of a known volume (within $\pm 0.02\%$)² are mounted to an 8-port chromatography valve³ inside of an enclosure to control the temperature. Thermometers accurate to $\pm 0.05^\circ\text{C}$ and a barometer accurate to ± 20 Pa (± 0.2 mbar) are necessary to determine the number of moles of gas in the loops at the time of calibration.

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 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

A CO₂ free carrier gas stream is needed to transfer the CO₂ from the stripper to the coulometer cell. This gas can be produced locally using a pure air generator, or dispersed from a compressed gas cylinder (*e.g.*, nitrogen > 99.995% pure). A standard “A cylinder” of carrier gas will last approximately 3 weeks with continuous use on a SOMMA system under normal operating conditions. If gas loops are used for calibration, then a small cylinder (*e.g.*, Scotty 48 cylinder) of pure (> 99.99% pure) carbon dioxide is needed.

5.2 Removal of CO₂ from the carrier gas

The carrier gas is run through a column of CO₂ absorbent (*e.g.*, Ascarite II[®] or Malcosorb[®]) to ensure that there is no CO₂ in the stream as this will affect the cell blank. If the carrier gas is truly CO₂-free, then these chemicals should not need to be replaced very frequently.

² The loops can be calibrated with water while mounted on the valve (see SOP 11).

³ A plumbing diagram for the Valco 8-port valve (W type) is shown in the Annexe to this procedure.

5.3 Acidification of sample

Reagent grade phosphoric acid is needed to acidify the sample in the stripping chamber. Typically 85% acid is diluted with deionized water by a factor of 10:1 (to ~ 8.5%). Approximately 1.5 cm³ of diluted acid is used per sample.

5.4 Sample gas stream purification

After the CO₂ is removed from the sea water sample in the stripper, the excess water vapor and non-CO₂ acid gases must be removed (see section 4.2). This is accomplished in the SOMMA system with a cold condensing chamber followed by a chemical column of Dehydrite[®] (magnesium perchlorate) to remove the water vapor, then a column of activated silica gel, ORBO-53[®] from Supelco, Inc., to trap the non-CO₂ acid vapors⁴.

For samples that contain H₂S, an additional scrubber is needed. Dissolve 3 g of silver nitrate (AgNO₃) into 100 cm³ of deionized water. Acidify the solution to approximately pH 3 by adding several drops of 70% sulfuric acid. When using this scrubber solution, add approximately 1 cm³ of 30% hydrogen peroxide (H₂O₂) to 15 cm³ of scrubber solution on a daily basis. The precipitate formed in this solution by the absorption of H₂S or SO₂ is black in color. This scrubber will also remove halogens. The precipitate of halogens will generally be dull gray or yellowish in color.

5.5 Coulometer cell solutions

The primary chamber of the coulometer cell is filled with approximately 100 cm³ of cathode solution (available from UIC Inc.), a proprietary mixture which contains water, ethanolamine, tetra-ethyl-ammonium bromide, and thymolphthalein in solution in dimethyl sulfoxide (DMSO)⁵. The side arm of the coulometer cell is filled with anode solution (available from UIC Inc.) to be approximately 1 cm below the liquid level of the cathode solution. The anode solution contains saturated potassium iodide in water and DMSO. To ensure that the anode solution remains saturated, reagent-grade potassium iodide crystals are added to the side arm of the coulometer cell.

⁴ 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 aerosols from the gas stream by impacting them either on Pyrex[®] wool or on a Teflon[®] filter, rather than removing them by chemical means.

⁵ 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.

6. Sampling

It is essential that the samples to be analyzed are collected, poisoned and stored according to the procedure detailed in SOP 1. Care must be taken to avoid the exchange of CO₂ with the atmosphere during both sampling and subsequent manipulation. When using a 36 place rosette to sample the water column, it is recommended that 3 sets of duplicate samples be collected. One set of duplicates is collected in the deep water, one is collected near the surface, and one set is collected at intermediate depths (typically near the oxygen minimum zone). Analysis of these duplicates is interspersed in the analysis sequence to confirm the stability of the cell.

7. Procedure

7.1 Introduction

An analysis session, starting with fresh solutions in the coulometer⁶, consists of the sequence of activities outlined in Table 1. 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 section 9). Once the initial tests are complete, water samples can be analyzed. The calibration factor is verified during the course of the sequence of analyses and again at the end before the cell solutions are discarded⁷.

Table 1 Recommended sequence of activities in an analysis session.

Activity	Section
Document pipette delivery volume (beginning of cruise)	SOP 12
Fill cell with fresh anode and cathode solutions	5.5
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 either with loops, reference material, or with sample duplicates	7.4, 7.5
Analyze further samples	7.5
Confirm calibration either with loops, reference material, or with sample duplicates	7.4, 7.5
Discard cell solutions	Footnote 5
Clean cell and electrodes	7.6

⁶ 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).

⁷ The cell solutions should be replaced either after 12 hours of use, after a cumulative total of 2 mmol CO₂ have been titrated, or after the change in calibration factor is considered excessive (see section 9). The cell solutions should be disposed of safely (see Footnote 5).

7.2 Check of sea water dispensing system calibration

At the beginning of a cruise, after the system has been set up on the ship, and again at the end of a cruise, before the system is packed away, the pipette delivery volume should be confirmed by collecting several replicate samples that can be returned to the shore-based laboratory to be weighed. 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.

7.3 Determination of the background level

Run CO₂ 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 the total number of counts on the coulometer over a 10-minute period. If the background level is within the specified tolerance (see section 9), note its value and begin the various analyses. If the background level is too high, run another background check or troubleshoot the system.

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 sooner). There are two principal means of achieving this: using a known amount of pure CO₂ 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 here⁸.

Calibration using gas loops — Stainless steel loops of a known volume are incorporated into a chromatography valve that can be controlled from a computer. Fill the loop with pure CO₂ 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.

⁸ The relative merits of these two approaches are still debated. Gas loops are difficult to calibrate initially (see Wilke *et al.*, 1993 and SOP 11) and their use requires accurate measurement of temperature and pressure (see section 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. The apparatus required is inexpensive and using such solutions calibrates the entire system response: delivery volume, extraction efficiency, and coulometer response.

The mean calibration factor—calculated as in section 8.2—obtained from a pair of loops that bracket the range of CO₂ 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 within tolerances (see section 9).

Calibration using sodium carbonate solutions — Sodium carbonate solutions (see SOP 14 for preparation procedure) are treated like sea water samples (see section 7.5). It is desirable to use a suite of solutions to measure the calibration factor⁹ although a single solution can be used to confirm the constancy of the calibration factor during a run. Compare the results—calculated as in section 8.2—with those obtained previously to ensure that the system remains within tolerances (see section 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 CO₂ exchange between the water sample and any headspace.

Dispense the sample (~ 30 cm³) into the stripping chamber and acidify it with phosphoric acid (~ 1.5 cm³). Ensure that the sample delivery system is rinsed adequately with fresh sample. The phosphoric acid must either be CO₂ free¹⁰ 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 ($\pm 0.4^\circ\text{C}$) and its salinity (± 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. Rinse and dry the cell cap and electrodes. Place the dried cell and cap in an oven at 50°C for 12 hours before use.

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.

⁹ Because of the experimental problems inherent in weighing and transferring small amounts of Na₂CO₃ crystals, and because of the ubiquitous CO₂ background in deionized water, it is typically not possible to make up a single solution with an uncertainty of less than 1 $\mu\text{mol kg}^{-1}$. By using a series of such solutions, the resultant error in the calibration factor is minimized.

¹⁰ If the acid is dispensed into the stripping cell prior to the addition of sea water, it can be purged of CO₂ *in situ*.

8. Calculation and expression of results

8.1 Calculation of the background titration rate

Compute the background titration rate—expressed in counts min^{-1} :¹¹

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

where

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

8.2 Calculation of the calibration factor

8.2.1 Based on a single loop

Compute the calibration factor (c)—expressed in counts mol^{-1} —from the coulometer reading for the analysis of $n(\text{CO}_2)$ moles of CO_2 dispensed from a gas loop of known volume, at a known temperature and pressure:

$$c = \frac{N_c - bt}{n(\text{CO}_2)} \quad (7)$$

where

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

b = the background level of the system (counts min^{-1}),

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

$n(\text{CO}_2)$ = the amount of CO_2 dispensed from the loop (mol),

$$n(\text{CO}_2) = \frac{V(T)}{V(\text{CO}_2)}. \quad (8)$$

$V(T)$ is the volume of the loop at the calibration temperature T (see SOP 11, section 4.4); $V(\text{CO}_2)$ is the molar volume of pure CO_2 at the temperature (T) and pressure (p) of the calibration and is calculated iteratively from the expression

$$V(\text{CO}_2) = \frac{RT}{p} \left(1 + \frac{B(\text{CO}_2, T)}{V(\text{CO}_2)} \right). \quad (9)$$

Values of the virial coefficient $B(\text{CO}_2, T)$ are given by the expression

$$\frac{B(\text{CO}_2, T)}{\text{cm}^3 \text{mol}^{-1}} = -1636.75 + 12.0408 \left(\frac{T}{\text{K}} \right) - 3.27957 \times 10^{-2} \left(\frac{T}{\text{K}} \right)^2 + 3.16528 \times 10^{-5} \left(\frac{T}{\text{K}} \right)^3 \quad (10)$$

where $265 < T/\text{K} < 320$ (see Chapter 5 for check value).

¹¹ The unit counts (mode 0) corresponds to the most sensitive setting of the coulometer. The results obtained using other settings, such as $\mu\text{g C}$ (e.g., mode 2), can also be interpreted as arbitrary units for use in these equations.

If the calibration factors from the two loops agree well (see section 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:

$$\frac{N_S - b \cdot t - a}{V_S} = c \cdot dw + c \cdot M \quad (11)$$

where

- N_S = the coulometer reading for the Na_2CO_3 sample (counts),
- a = the acid blank (counts),¹²
- b = the background level of the system (counts min^{-1}),
- t = the time required to measure the Na_2CO_3 sample (min),
- V_S = the volume¹³ of the Na_2CO_3 sample (dm^3),
- dw = the background level of CO_2 in the deionized water used to prepare the samples (mol dm^{-3}),
- M = the nominal concentration of the Na_2CO_3 sample (mol dm^{-3}) computed from the mass of Na_2CO_3 used (see SOP 14).

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 $M = 0 \text{ mol dm}^{-3}$).

8.3 Calculation for a sea water sample

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

$$C_T' = \frac{N_S - b \cdot t - a}{c} \cdot \frac{1}{V_S \cdot \rho} \quad (12)$$

The various terms are:

- C_T' = the total dissolved inorganic carbon in the sample (mol kg^{-1}),
- N_S = the coulometer reading for the sea water sample (counts),
- a = the acid blank¹² (counts),
- b = the background level of the system (counts min^{-1}),
- c = the coulometer calibration factor (counts mol^{-1}),
- t = the time required to measure the water sample (min),

¹² 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.*, $a = 0$.

¹³ A comparison of equations (11) and (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 that this assumes that the Na_2CO_3 solution and the sea water are delivered at the same temperature.

- 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 Footnote 13.)
- ρ = the density of the sea water sample (g cm^{-3}) (see Chapter 5).

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 collected¹⁴ and for the exchange of CO_2 with the headspace in the sampling bottle¹⁵:

$$C_T = 1.0002(C'_T - \Delta C_T) \quad (13)$$

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

8.4 Example calculation¹⁶

8.4.1 Calculation of the blank

$$\begin{aligned} N_b &= 100 \text{ counts in 10 minutes,} \\ b &= 100 / 10 \\ &= 10 \text{ counts min}^{-1}. \end{aligned}$$

8.4.2 Calculation of the calibration factor for a single loop

$$\begin{aligned} T &= 298.15 \text{ K,} \\ p &= 101.325 \text{ kPa,} \\ V(298.15 \text{ K}) &= 1.5000 \text{ cm}^3, \\ B(\text{CO}_2, 298.15 \text{ K}) &= -123.2 \text{ cm}^3 \text{ mol}^{-1}, \\ N_c &= 294033 \text{ counts in 15 minutes.} \end{aligned}$$

Thus

$$V(\text{CO}_2) = 24341.6 \text{ cm}^3 \text{ mol}^{-1}$$

is calculated iteratively from (9) and

$$\begin{aligned} n(\text{CO}_2) &= 1.5/24341.6 \text{ mol} \\ &= 61.6229 \mu\text{mol}. \end{aligned}$$

Hence

$$\begin{aligned} c &= \frac{294033 - 10 \times 15}{61.6229 \times 10^{-6}} \\ &= 4.7691 \times 10^9 \text{ counts mol}^{-1}. \end{aligned}$$

¹⁴ The value 1.0002 assumes that 0.02% by volume saturated mercuric chloride was used; if a 50% saturated solution was used to preserve the sample, the minimum volume is 0.04% (see SOP 1).

¹⁵ See Annexe to SOP 1, equation (2).

¹⁶ The apparent excess of significant figures is provided to aid in checking computer implementations of these computations.

8.4.3 Calculation of the calibration factor using 6 Na_2CO_3 solutions

$b = 10 \text{ counts min}^{-1}$; $a = 40 \text{ counts}$; $V_S = 27.0000 \text{ cm}^3$;

$$M_1 = 0.0 \text{ } \mu\text{mol dm}^{-3}; \quad N_S = 1892 \text{ counts in 15 min}$$

$$M_2 = 498.8 \text{ } \mu\text{mol dm}^{-3}; \quad N_S = 66537 \text{ counts in 15 min}$$

$$M_3 = 1001.9 \text{ } \mu\text{mol dm}^{-3}; \quad N_S = 130818 \text{ counts in 15 min}$$

$$M_4 = 1500.8 \text{ } \mu\text{mol dm}^{-3}; \quad N_S = 195216 \text{ counts in 15 min}$$

$$M_5 = 2002.5 \text{ } \mu\text{mol dm}^{-3}; \quad N_S = 260068 \text{ counts in 15 min}$$

$$M_6 = 2497.1 \text{ } \mu\text{mol dm}^{-3}; \quad N_S = 323456 \text{ counts in 15 min}$$

Linear regression (SOP 23) gives

$$\begin{aligned} \text{slope} &= 4.76908 \times 10^9 \text{ counts mol}^{-1}, \\ \text{intercept} &= 67695.1 \text{ counts dm}^{-3}. \end{aligned}$$

So, from (11),

$$c = 4.76908 \times 10^9 \text{ counts mol}^{-1}$$

and

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

8.4.4 Calculation for a sea water sample

$S = 35.00$; $t = 25.0^\circ\text{C}$; $\rho(S, t) = 1.02334 \text{ g cm}^3$;

$$V_S = 27.0000 \text{ cm}^3,$$

$$a = 40 \text{ counts}; \quad b = 10 \text{ counts min}^{-1},$$

$$N_S = 289874 \text{ counts in 15 minutes.}$$

From (12),

$$\begin{aligned} C'_T &= \frac{289874 - 10 \cdot 15 - 40}{4.76908 \times 10^9} \cdot \frac{1}{27 \cdot 1.02334} \\ &= 2197.64 \text{ } \mu\text{mol kg}^{-1}. \end{aligned}$$

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

$$C_T = 2198.07 \text{ } \mu\text{mol kg}^{-1}.$$

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. The targets that were set for the first world-wide CO_2 survey were: a maximum within cruise precision (1 SD) of $1.5 \text{ } \mu\text{mol kg}^{-1}$ and an overall between cruise (and between laboratory) range of

bias of less than $4 \mu\text{mol kg}^{-1}$. 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 $25 \text{ counts min}^{-1}$ ($0.05 \mu\text{g C min}^{-1}$) and should remain stable to within $\pm 10 \text{ counts min}^{-1}$. 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 material¹⁷ 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).

¹⁷ Reference materials available from Dr. Andrew G. Dickson, Marine Physical Laboratory, Scripps Institution of Oceanography, University of California, San Diego, 9500 Gilman Drive, La Jolla, CA 92093-0244, U.S.A. (fax: 1-858-822-2919; e-mail: co2crms@ucsd.edu).

10. Bibliography

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Annexe

Figure 1 illustrates the correct way to plumb an 8-port valve (e.g., W type valves from Valco Instruments Co. Inc., P.O. Box 55803, Houston, TX 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).

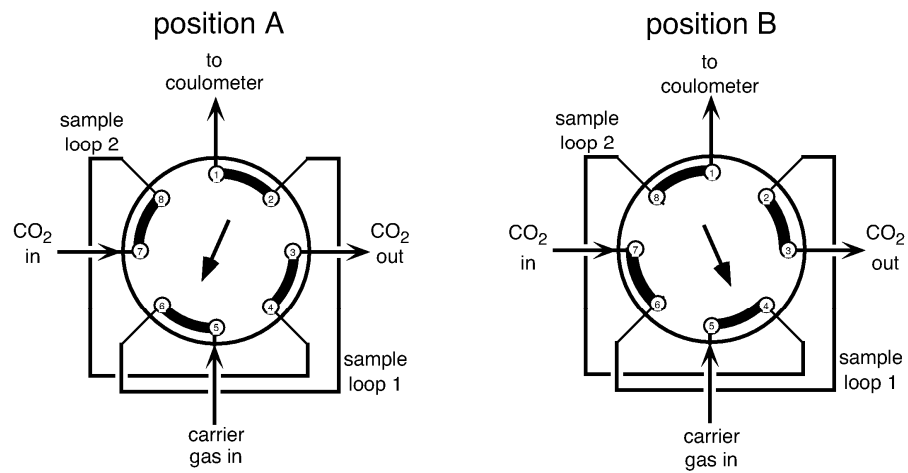


Fig. 1 Plumbing of a gas loop calibration valve.