

SOP 4

Determination of $p(\text{CO}_2)$ 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:

$$p(\text{CO}_2) = x(\text{CO}_2) \cdot p \quad (1)$$

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, $f(\text{CO}_2)$:

$$f(\text{CO}_2) = \alpha(\text{CO}_2)p \exp\left(\int_0^p \frac{(V(\text{CO}_2) - RT/p')dp'}{RT}\right) . \quad (2)$$

(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 CO₂ 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 CO₂ 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 CO₂ concentrations. In addition, it is important to take account of the effect of H₂O 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 ± 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: $x(\text{CO}_2) = 250\text{--}2000 \times 10^{-6}$.

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 cm³ 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 $p(\text{CO}_2)$ 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 $p(\text{CO}_2)$ 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 it 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 $p(\text{CO}_2)$ —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— $x(\text{CO}_2)$ —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:

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

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

$$x(\text{CO}_2) \cdot p = a_0 + a_1 \cdot A_x(t) + a_2 \cdot (A_x(t))^2 \quad ; \quad (4)$$

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 — $\Delta n(\text{CO}_2)$ —in the equilibrator head-space can be calculated (assuming ideal behavior):

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

where $V(\text{head-space})$ 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:

$$\Delta C_T = \frac{\Delta n(\text{CO}_2)}{\rho \cdot V(\text{sample})} \quad (6)$$

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

8.2.2 Calculation of corrected $p(\text{CO}_2)$

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

- Assume that $f(\text{CO}_2) \approx p(\text{CO}_2)$ (Note 5).
- Calculate the C_T of the perturbed water sample and use this together with $f(\text{CO}_2)$ 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 $p(\text{CO}_2) (\approx f(\text{CO}_2))$ 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 $f(\text{CO}_2) \approx p(\text{CO}_2)$ (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

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 $p(\text{CO}_2)$ ($\approx f(\text{CO}_2)$) 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 $p(\text{CO}_2)$. 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.

$$p(\text{CO}_2) = p(\text{CO}_2 \text{ in dry air}) \times (1 - VP(\text{H}_2\text{O})) \quad , \quad (7)$$

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 7)—see Chapter 5, § 3.

8.4 Calculation of $f(\text{CO}_2)$ from corrected $p(\text{CO}_2)$

See SOP 24.

8.5 Example calculation

Flask volume = 525 cm³

Flask head-space = 45 cm³

Residual system volume (lines & pump) = 13 cm³

Fill gas (used to displace head-space), $x(\text{CO}_2) = 750 \times 10^{-6}$

Residual gas (lines & pump), $x(\text{CO}_2) = 535 \times 10^{-6}$

Temperature of gas in head-space = 25 °C

Salinity of sample = 35

C_T of sample (before equilibration) = 2050 $\mu\text{mol}\cdot\text{kg}\cdot\text{soln}^{-1}$

Equilibration pressure = 995 mbar (99.5 kPa)

Equilibration temperature = 20 °C

Measured $x(\text{CO}_2)$ for sample = 350×10^{-6} .

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

From equation (5), for the head-space

$$\begin{aligned}\Delta n(\text{CO}_2) &= \frac{(750 \times 10^{-6} - 350 \times 10^{-6}) \times 45 \times 10^{-6} \times 99500}{8.31451 \times 298.15} \\ &= 7.22 \times 10^{-7} \text{ mol ,}\end{aligned}$$

and for the residual gas in the lines and pump

$$\begin{aligned}\Delta n(\text{CO}_2) &= \frac{(535 \times 10^{-6} - 350 \times 10^{-6}) \times 13 \times 10^{-6} \times 99500}{8.31451 \times 298.15} \\ &= 9.65 \times 10^{-8} \text{ mol.}\end{aligned}$$

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

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

thus

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

Total alkalinity (A_{T}) in the sample is calculated from the post-equilibration values of $p(\text{CO}_2)$ (see Note 5)

$$p(\text{CO}_2) = (350 \times 10^{-6}) \times (99.5 / 101.325) = 343.7 \text{ }\mu\text{atm} .$$

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

$$A_{\text{T}} = 2368.10 \text{ }\mu\text{mol}\cdot\text{kg}^{-1}.$$

The $p(\text{CO}_2)$ of the sample before equilibration (see Note 5) is then estimated from this value for A_{T} and $C_{\text{T}} = 2050 \text{ }\mu\text{mol}\cdot\text{kg}^{-1}$ (again using the equations in the Annexe to Chapter 2 together with the thermodynamic data in Chapter 5):

$$p(\text{CO}_2) = 341.1 \text{ }\mu\text{atm} .$$

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 $p(\text{CO}_2)$ 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.

References

- Chipman D. W., T. Takahashi, D. Breger & S. C. Sutherland (1992) Investigation of carbon dioxide in the South Atlantic and Northern Weddell Sea areas (WOCE sections A-12 and A-21) during the Meteor Expedition 11/5, January–March, 1990. Lamont-Doherty Geological Observatory of Columbia University. Final technical report for Grant No. DE-FG02-90ER60943.
- Wanninkhof R. & K. Thoning (1993) Measurement of fugacity of CO_2 in surface water using continuous and discrete methods. *Marine Chemistry* **44**, 189–204.
- Weiss R. F. (1981) Determinations of carbon dioxide and methane by dual catalyst flame ionization chromatography and nitrous oxide by electron capture chromatography. *Journal of Chromatographic Science* **19**, 611–616.

Annexe

Schematic showing the gas-water equilibrator and gas chromatographic system for the equilibration of $p(\text{CO}_2)$ in discrete samples (Chipman *et al.*, 1992)

