

SOP 5

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

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

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

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

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

(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 $6\text{--}8 \text{ dm}^3 \cdot \text{min}^{-1}$ 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

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 $6 \text{ dm}^3 \cdot \text{min}^{-1}$. 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.

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 $p(\text{CO}_2)$ 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: $x(\text{CO}_2) = 250\text{--}500 \times 10^{-6}$.

- 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 ($\sim 75 \text{ cm}^3 \cdot \text{min}^{-1}$) to control the rate of flow of gases through the sample cell.
- 4.4.4 Mass flow controller ($\sim 50 \text{ cm}^3 \cdot \text{min}^{-1}$) to control the rate of flow of reference gas through the reference cell (Note 7).
- 4.4.5 Barometer accurate to $\pm 30 \text{ Pa}$. 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).

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 equilibrators 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: $x(\text{CO}_2) = 250\text{--}500 \times 10^{-6}$.

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

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:

$$n(\text{CO}_2) = \frac{x(\text{CO}_2) \cdot p \cdot V(\text{cell})}{RT} \times \phi \quad , \quad (3)$$

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.

$$x(\text{CO}_2) - x(\text{CO}_2)_{\text{REF}} = \left(a_1 \cdot (V - V_R) \frac{P^\circ}{P} + a_2 \cdot \left((V - V_R) \frac{P^\circ}{P} \right)^2 \right) \frac{T}{T^\circ} \quad ; \quad (4)$$

the various terms are

- $x(\text{CO}_2)$ = mole fraction of CO_2 of gas in sample cell,
- $x(\text{CO}_2)_{\text{REF}}$ = 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, $x(\text{CO}_2)$ 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):

$$p(\text{CO}_2) = x(\text{CO}_2) \cdot p_{\text{ATM}} \quad . \quad (5)$$

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:

¹³ Over a wider range of $x(\text{CO}_2)$ 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

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

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

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

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

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

$$\begin{aligned} \text{Standard 1 } (x(\text{CO}_2)) &= 305.56 \times 10^{-6} \text{ — reference gas} \\ V &= 0.07400 \text{ V} \\ T &= 304.61 \text{ K } (31.46 \text{ }^\circ\text{C}) \\ p &= 101.788 \text{ kPa} \end{aligned}$$

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 $|T_S - T_E| < 1 \text{ K}$, as is the case for most measurement systems.

$$\text{Standard 2 } (x(\text{CO}_2) = 356.20 \times 10^{-6})$$

$$V = 0.63300 \text{ V}$$

$$T = 304.61 \text{ K } (31.46 \text{ }^\circ\text{C})$$

$$p = 101.804 \text{ kPa}$$

$$\text{Standard 3 } (x(\text{CO}_2) = 404.73 \times 10^{-6})$$

$$V = 1.14167 \text{ V}$$

$$T = 304.61 \text{ K } (31.46 \text{ }^\circ\text{C})$$

$$p = 1017.97 \text{ kPa}$$

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

$$a_0 = 88.493 \times 10^{-6}$$

$$a_1 = 4.540 \times 10^{-6} .$$

8.5.2 Measurement of $p(\text{CO}_2)$

$$V = 0.67467 \text{ V}$$

$$T = 304.61 \text{ K } (31.61 \text{ }^\circ\text{C})$$

$$p = 101.802 \text{ kPa}$$

$$\Delta x(\text{CO}_2) = 88.493 \times 10^{-6} (0.67467 - 0.07400) \frac{101.325}{101.802} +$$

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

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

Thus

$$x(\text{CO}_2) = 305.56 \times 10^{-6} + 36.03 \times 10^{-6} = 341.59 \times 10^{-6},$$

and from equation (5)

$$p(\text{CO}_2 \text{ in dry air}) = (341.59 \times 10^{-6})(10180.2) = 34.773 \text{ Pa}$$

$$= 343.18 \text{ } \mu\text{atm} .$$

8.5.3 Correction to 100% humidity

The water in the equilibrator has

$$S = 35$$

$$T_E = 298.15 \text{ K } (25.00 \text{ }^\circ\text{C}) ;$$

thus

$$VP(\text{H}_2\text{O}) = 3.1094 \text{ kPa (Chapter 5)}$$

$$= 0.0307 \text{ atm}$$

and from equation (6)

$$p(\text{CO}_2) = 343.18 \times (1 - 0.0307) = 332.65 \mu\text{atm} .$$

8.5.4 Correction to sea surface temperature

The sea surface temperature

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

thus from equation (7)

$$\begin{aligned} p(\text{CO}_2, T_S) &= 332.65 \times \exp(0.0423 (297.85 - 298.15)) \\ &= 328.46 \mu\text{atm} . \end{aligned}$$

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 $0.3 \mu\text{atm}$ for ambient air and less than $1 \mu\text{atm}$ for air from the equilibrator.

References

Butler J. H., J. W. Elkins, C. M. Brunson, K. B. Egan, T. M. Thompson, T. J. Conway & B. D. Hall (1988) Trace gases in and over the West Pacific and East Indian Oceans during the El Niño–Southern Oscillation event of 1987. *NOAA Data Report*, ERL-ARL-16, 104 pp. Air Resources Laboratory, Silver Spring, Md.

- Copin-Montegut C. (1988) A new formula for the effect of temperature on the partial pressure of CO_2 in seawater. *Marine Chemistry* **25**, 29–37.
- Goyet C., F. J. Millero, A. Poisson & D. Schafer (1993) Temperature dependence of CO_2 fugacity in seawater. *Marine Chemistry* **44**, 205–219.
- LI-COR (1992) LI-6251 CO_2 analyzer operating and service manual. LI-COR, inc. Publication No. 8712-56, Revision 1.
- Robertson J. E. & A. J. Watson (1992) Surface thermal skin effect and the uptake of atmospheric CO_2 by the ocean. *Nature* **358**, 738–740.
- Robertson J. E., A. J. Watson, C. Langdon, R. D. Ling & J. Wood (1993) Diurnal variation in surface $p\text{CO}_2$ and O_2 at 60°N and 20°W in the North Atlantic. *Deep-Sea Research* **40**, 409–423.
- Takahashi, T., J. Olafsson, J. G. Goddard, D. W. Chipman & S. C. Sutherland (1993) Seasonal variation of CO_2 and nutrients in the high-latitude surface oceans: a comparative study. *Global Biogeochemical Cycles* **7**, 843–878.
- 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.
- Weiss R. F., R. A. Jahnke & C. D. Keeling (1982) Seasonal effects of temperature and salinity on the partial pressure of carbon dioxide in seawater. *Nature* **300**, 511–513.
- Weiss R. F., F. A. Van Woy & P. K. Salameh (1992) Surface water and atmospheric carbon dioxide and nitrous oxide observations by shipboard automated gas chromatography: Results from expeditions between 1977 and 1990. Scripps Institution of Oceanography Reference 92-11. ORNL/CDIAC-59 NDP-044. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 144 pp.

Annexe

Schematic showing the layout of the analytical system described here (based on Wanninkhof & Thoning, 1993). (The cold trap—at $\sim 5^\circ\text{C}$ —that is used to reduce the water vapor in air and head-space lines is not shown in this diagram.)

