SOP 4

Determination of $p(CO_2)$ 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 sea water. The partial pressure of carbon dioxide is expressed in microatmospheres. The method determines the dry mole fraction 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 sea water is defined as the product of the mole fraction of CO_2 in the equilibrated gas phase and the total pressure of equilibration:

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

The partial pressure of CO_2 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[1] a sample of the air is analyzed for carbon dioxide content using a gas chromatograph or infrared CO_2 detector which is capable of integrating a constant volume of CO_2.[2] The partial pressure, $p(CO_2)$, is calculated from (1).

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[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. The circulation of small air bubbles through the volume of water acts to not only equilibrate the water, but also stir it. The frit should be close to the surface.

[2] A non-dispersive infrared detector can also be used to quantify the amount of CO_2 and can be used to assess the rate of approach to equilibrium (see *e.g.*, Wanninkhof and Thoning, 1993). However, such a detector requires a larger air/water ratio—and thus

4. Apparatus[3]

4.1 Gas analyzer system

There are several ways to measure equilibrated headspace gas. This procedure focuses on the measurement of a constant volume of headspace gas which, once equilibrated with the sample water, is carried with CO_2-free gas (for flame ionization detection the carrier gas will need to be hydrocarbon free N_2).

4.1.1 Gas analyzer that is capable of accurately integrating the total amount of CO_2 in a sample loop

For best results using a gas chromatographic technique, the following are recommended:

- A 2.0 m chromatographic column and 0.2 m precolumn packed with porous polystyrene (60–80 mesh) (Chromosorb 102 or Porapak Q);
- A catalytic system to convert carbon dioxide to methane (Ruthenium on Chromosorb W support);
- A flame-ionization detector for methane quantification.

4.1.2 Computer-controlled 10-port 2-position valve with two 1 cm^3 sample loops for sample injection and column switching

This 10-port, 2-position valve should be contained in a temperature controlled box so that loops with known volume can be carefully temperature controlled and monitored. In this configuration one loop will always have the carrier gas flowing through it while the other loop will be in line with a selected sample equilibrator. Before the valve is switched, the flow of sample headspace gas must stop to allow the sample to be pressure and temperature equilibrated with the temperature controlled system.

4.1.3 Analog to digital integrator

Unless one can ensure that there is a predictable relationship between CO_2 concentration and the peak height of CO_2 passing through the analyzer, it is important to integrate the full area under the curve to account for peak broadening and carrier gas flow rate changes.

4.2 CO$_2$ equilibration system

The ideal equilibration system will be contained in a single temperature controlled water bath in close proximity to the selection valve and CO_2 gas analyzer to ensure minimal length of tubing in which the sample will be circulated. To avoid transferring samples from one container to another, each

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involves a larger and less reliable correction for CO_2 exchange (see section 8.2)— also infrared detectors are non-linear and thus require more elaborate calibration for use over such a wide range of CO_2 concentrations. In addition, it is important to take account of the effect of H_2O vapor on the infrared 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.

sample will be analyzed in the same sample container that it was collected. This can be done by recirculating headspace through a 0.5 L sample using a small air pump.

4.2.1 Constant-temperature bath

Because the partial pressure of CO_2 has a large sensitivity to changes in temperature, it is necessary to control the temperature and measure sample water temperature to less than 0.05 K at hourly time intervals. Because it may take up to an hour for the sample temperature to reach the bath temperature, and the air pumps used to circulate headspace air through the sample container are a source of heat, care must be taken to measure and record the sample temperature directly. Alternatively, with a good understanding of the temperature equilibration time of your system and the offset between bath temperature and sample temperature, given a typical air flow through the sample flask, corrections can be derived.

4.2.2 Air pumps for re-circulating headspace gas

It is important that the air pump does not pump more than 1.0 L min^{-1} at full speed and that the pump speed can be controlled to reduce the amount of aerosols and heat that are circulated through the headspace plumbing.

4.2.3 Thermometer (± 0.02°C)

Accurate temperature measurements are essential and should be recorded continuously throughout the measurement period.

4.2.4 Borosilicate glass flask (0.5 L) with 0.10 m extensions or long-neck sampling flasks (e.g., volumetric flask)

To provide adequate room for bubbles and froth from incoming air rising up through the sample, it is useful to have a long neck or extension on the sampling bottle. It should also be noted that the thinner walled flasks will equilibrate with the thermostat bath more quickly.

4.2.5 Three-hole stopper, nylon tubing and frit to carry headspace gas through equilibrators

The equilibration is done in a closed loop by pushing air from the pump to just below the water level of each sample flask through a nylon tube and frit. Air passes out of the sample cell through a second nylon tube flush with the stopper. A third tube provides an opening to ensure that the samples are at ambient pressure. The longer the tube, the less likely it is that the headspace will be contaminated by room air. A net flow of gas into or out of the third opening is an indication of a leak in the system.

4.2.6 0.5 μm syringe filters

Filters are used to capture aerosols and water droplets on the downstream side of the equilibrator.

4.3   Calibration system

- Remotely operated valve allowing selection between the three calibration gases,
- Normally closed solenoid shut-off valve used to control the flow of calibration gas,
- Barometer, accurate to ± 50 Pa (0.5 mbar), with computer interface.

4.4   System control

- Microcomputer for data logging,
- Digital interface board to control valves, *etc*.

5.   Reagents

5.1   Compressed gases

- Carrier gas: hydrocarbon-free nitrogen,
- FID gases: hydrocarbon-free hydrogen (*e.g.*, from a hydrogen generator) and air (*e.g.*, from a pure air generator),
- Three calibration gas mixtures of CO_2 in air: well-known CO_2 concentrations chosen to span the range of measured values: $x(CO_2) = 250–2000 \times 10^{-6}$.

6.   Sampling

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

7.   Procedure

7.1   Introduction

This procedure has been designed to maximize the sample analysis while accounting for drifts in the system and allowing for both temperature and head space equilibration of CO_2 in each sample. The normal sequence of analysis accounts for changes in the response of the detector with time by running a set of standards (typically three) through the analyzer before and after a set of four samples has been run. To ensure full air–water equilibration of CO_2 in headspace volumes of ~ 0.04 L with 0.5 L of sea water with flow rates of ~ 0.2 L min^{-1}, it is necessary to circulate the air for 8 minutes. In extreme conditions, it may take an hour to equilibrate sample temperatures to bath temperatures. To ensure temperature equilibration, samples should be stored near measurement temperatures, and the sample in the temperature-controlled bath replaced immediately after the previous sample has been analyzed.

7.2   System start-up

To begin a sample analysis run it is important to ensure that the system is stable. To save standards it is possible to run laboratory air samples as follows:

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

7.2.2   Run these analyses without the use of calibration gases, thus conserving the calibration gases (this can be achieved by using a separate subroutine in the operating program).

Calculation of p(CO$_2$) for a set of samples requires knowledge of the concentration of CO$_2$ in the headspace gas prior to starting the equilibration. This is estimated—in part—from the p(CO$_2$) of the previous sample analysis. Thus, after reconnecting the lines to the equilibrators (see above), analyze two dummy (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 begins (see section 7.5).

7.3   Loading of new samples

As each sample analysis is completed (see section 7.4), replace the previous sample flask with a fresh sample as described below.   The immediate replacement of a recently analyzed sample will ensure that the headspace has a known CO$_2$ concentration at the start of the equilibration time period.

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).   As mentioned above, it is important to pre-equilibrate the sample temperature to ensure that the sample is at the thermostat bath temperature when the headspace gas is analyzed.

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 analyzer.

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 (see diagram).

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   Equilibration of sample

Full equilibration with the headspace can take as long as 8 minutes, depending on the total headspace and loop size. It is therefore necessary to ensure that air being captured in the sample gas loop has circulated for an adequate amount of time before capturing the sample and moving on to the next sample.

7.5   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 section 7.3.

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

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

7.6   Termination of analytical session

Following the analysis of the final samples of a given session (including the final set of calibration analyses), the two flasks are left in place connected to the two equilibrators. This serves to prevent drying of the gas dispersers and to provide start-up samples to establish the concentration of CO$_2$ in the pumps and gas lines before the analysis of fresh samples. In addition, use of such samples—with known p(CO$_2$)—provides a check on the system prior to the analysis of fresh samples.

8.   Calculation and expression of results

8.1   Calculation of gas chromatograph 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. With an infrared analyzer, which is not as linear, it will be necessary to run more than three standards to reduce the potential errors for concentrations not well represented by standards.

The detector peak area (A_x) corresponds to the dry CO$_2$ content—x(CO$_2$)—of each of the three calibration gases. The peak area 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:

$$A_x(t) = A_x(t_1) + \frac{t - t_1}{t_2 - t_1}[A_x(t_2) - A_x(t_1)]. \tag{2}$$

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

$$x(CO_2) \cdot p = a_0 + a_1 \cdot A_x(t) + a_2 \cdot [A_x(t)]^2 \tag{3}$$

where p is the measured atmospheric pressure[4].

8.2   Corrections for sample perturbation during equilibration

Some CO_2 will be exchanged between the sea water sample and the air of the headspace 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. Although it is useful to have measurements of C_T, rough estimates will suffice for this calculation.

8.2.1   Calculation of ΔC_T

The change in the number of moles of CO_2—$\Delta n(CO_2)$—in the equilibrator headspace can be calculated (assuming ideal behavior),

$$\Delta n(CO_2) = \frac{[p(CO_2)_1 - p(CO_2)_2]V_H}{RT} \tag{4}$$

where V_H is the volume of air in the headspace 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 headspace volume are assumed to remain constant throughout. The change in C_T can then be calculated,

$$\Delta C_T = \frac{\Delta n(CO_2)}{\rho \cdot V_S} \tag{5}$$

where V_S is the volume of sea water of density ρ that was equilibrated with the headspace gas.

8.2.2   Calculation of corrected $p(CO_2)$

If the C_T of the unperturbed sample is known:

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[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 pressure of CO_2 (rather than concentration) to peak area.

- Calculate the C_T of the perturbed water sample and use this together with $p(CO_2)$ to calculate the value of A_T for the sea water sample (see Annexe to Chapter 2)[5]. The equilibrium constants used should be appropriate to the equilibration temperature and the salinity of the sample being equilibrated[6].

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

If the A_T of the original sample is known:

- Use $p(CO_2)$ together with A_T to calculate the C_T of the perturbed water sample (see Annexe to Chapter 2)[5]. The equilibrium constants used should be appropriate to the equilibration temperature and the salinity of the sample being equilibrated[6].

- Use equation (5) to estimate C_T in the unperturbed sample.

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

8.3   Correction for water vapor pressure

If the equilibrated air is injected into the gas chromatograph without removal of water vapor, the calculation outlined in section 8.2 will give the final value of $p(CO_2)$ at equilibration pressure.

If water vapor was removed from the equilibrated air prior to injection into the gas chromatograph, it is necessary to correct for this. The partial pressure of CO_2 in the dried air must be reduced by a factor which accounts for the increase in concentration of CO_2 in the air resulting from the removal of the water vapor.

$$p(CO_2) = p(CO_2 \text{ in dry air}) \times [1 - p_\sigma(H_2O)] \qquad (6)$$

where $p_\sigma(H_2O)$ is the water vapor pressure over a sea water sample of a given salinity at the temperature of equilibration[7]—see Chapter 5, section 3.

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

See SOP 24.

8.5   Example calculation

Flask volume = 525 cm^3,
Flask headspace = 45 cm^3,
Residual system volume (lines and pump) = 13 cm^3,

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[5] If desired it can be assumed that $f(CO_2) \approx p(CO_2)$ for this calculation. Assuming that CO_2 behaves ideally will not make a significant difference to the final result as long as the same assumption is made in both the forward and back calculations.

[6] As the same equilibrium constants (see Chapter 5) are used for the forward and back calculations, errors due to uncertainties in these will be small.

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

Fill gas (used to displace headspace), $x(CO_2) = 750 \times 10^{-6}$,
Residual gas (lines and pump), $x(CO_2) = 535 \times 10^{-6}$,
Temperature of gas in headspace = 25°C,
Salinity of sample = 35,
C_T of sample (before equilibration) = 2050 μmol kg-soln^{-1},
Equilibration pressure = 995 mbar (99.5 kPa),
Equilibration temperature = 20°C,
Measured $x(CO_2)$ for sample = 350×10^{-6}.

From equation (4), for the headspace,

$$\Delta n(CO_2) = \frac{(750 \times 10^{-6} - 350 \times 10^{-6}) \times 45 \times 10^{-6} \times 99500}{8.31447 \times 298.15}$$
$$= 7.225 \times 10^{-7} \, mol \,,$$

and for the residual gas in the lines and pump,

$$\Delta n(CO_2) = \frac{(535 \times 10^{-6} - 350 \times 10^{-6}) \times 13 \times 10^{-6} \times 99500}{8.31447 \times 298.15}$$
$$= 9.653 \times 10^{-8} \, mol \,.$$

Then at $S = 35$ and $T = 20$°C, $\rho_{SW} = 1024.76$ kg m^{-3} and from equation (5)

$$\Delta C_T = \frac{7.225 \times 10^{-7} + 9.653 \times 10^{-8}}{1024.76 \times (525 - 45) \times 10^{-6}} = 1.665 \times 10^{-6} \, mol \ kg^{-1} \,,$$

thus

$\qquad$ C_T (after equilibration) = 2050 + 1.665 = 2051.67 μmol kg^{-1}.

Total alkalinity (A_T) in the sample is calculated from this together with the post-equilibration values of $p(CO_2)$ (see Footnote 5).

As $p(CO_2) = (350 \times 10^{-6}) \times (99.5/101.325) = 343.7$ μatm and $C_T = 2051.67$ μmol kg^{-1}, using the equations in the Annexe to Chapter 2 together with the thermodynamic data in Chapter 5[8],

$\qquad$ $A_T = 2348.21$ μmol kg^{-1}.

The $p(CO_2)$ of the sample before equilibration is then estimated from this value for A_T and $C_T = 2050$ μmol kg^{-1} (again, using the equations in the Annexe to Chapter 2 together with the thermodynamic data in Chapter 5) to give

$\qquad$ $p(CO_2) = 341.0$ μatm.

9. Quality assurance

For general principles of analytical quality control see Chapter 3.

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[8] If $f(CO_2)$ is assumed $\approx p(CO_2)$, the calculated $A_T = 2347.35$ μmol kg^{-1}.

9.1　Stability of the response of the gas chromatograph

The performance of the gas chromatograph can be monitored by means of control charts (SOP 22) which give a visual indication of any significant change in the response of the instrument to injections of nearly constant amounts of CO_2 calibration gases.

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

9.2　Reproducibility of equilibrated samples

Replicate samples should agree within 0.25% (see section 7.5); this test will give a rapid indication of deteriorating performance of the equilibration system. The fraction of analyses from each analytical session that fails 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.

10.　Bibliography

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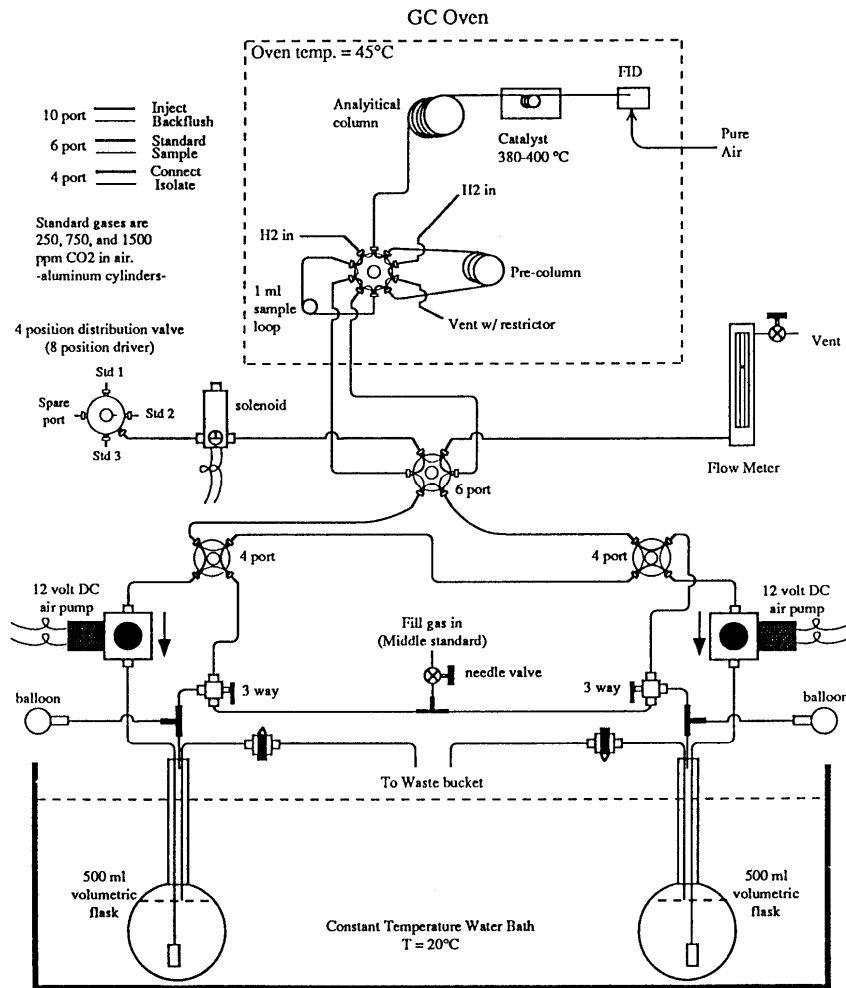
Annexe

Fig. 1   Schematic showing the gas–water equilibrator and gas chromatographic system for the equilibration of $p(CO_2)$ in discrete samples (Chipman *et al.*, 1992).