SOP 5

Determination of $p(CO_2)$ 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 sea water, *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 (250–550 μatm).

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, $x(CO_2)$, in the equilibrated gas phase and the total pressure (p) of equilibration:

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

It is a temperature-dependent property of the sea water sample; thus it is important to record the *in situ* water temperature as well as 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[1]. As the volume of sea water that flows through the equilibrator is essentially infinite compared to the volume of air, the CO_2 content of the air adjusts to equilibrium with the sea water without altering the CO_2 content of the sea water appreciably. The air is circulated through a non-

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[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). The apparatus described in this SOP also uses a rain type equilibrator, but it has approximately one tenth of the volume (~1.3 dm^3) of the original Weiss design.

dispersive infra-red analyzer to measure its CO_2 content[2]. The analyzer is calibrated using gases of known CO_2 concentration (mole fraction).

The partial pressure, $p(CO_2)$, is then calculated from (1). To use this measurement together with other parameters of the carbon dioxide system in sea water, it is necessary to convert the mole fraction to fugacity, $f(CO_2)$, to account for the fact that CO_2 does not strictly follow Henry's Law for ideal gases:

$$f(CO_2) = x(CO_2)\frac{p}{RT}\exp\left(\int_0^p V(CO_2) - RT/p'\,dp'\right) \tag{2}$$

(see Chapter 2). The calculations required are outlined in SOP 24.

4. Apparatus

The apparatus described here is intended to serve as an example of a commonly used system. It is based on a standardized design that is currently used on over a dozen ships at the time of writing[3]. Some of the details of flow rates and timing are "tuned" to this system and may need to be adjusted for systems with different components.

4.1 Outside air intake

A tube, typically Synflex® (formerly Dekoron®) type "1300", is run from the measurement system to a location where uncontaminated outside air can be sampled. If the measurement system is located on board a ship, this line will typically be led to the bow of the ship[4]. The air is continually pumped at a rate of $2–3$ dm^3 min^{-1} to ensure constant flushing of the tubing. During sampling, a fraction ($60–80$ cm^3 min^{-1}) of the air stream is diverted through a dryer to the analyzer.

4.2 Equilibrator

The most common type of equilibrator involves a chamber where sea water is exposed to a headspace of air maintained at the ambient atmospheric pressure[5].

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[2] A gas chromatographic system can be used successfully for this measurement (see *e.g.*, Weiss, 1981; Weiss *et al.,* 1982; Robertson *et al.,* 1993; Weiss *et al.*, 1992). Although the gas chromatograph 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 infrared approach is recommended here as being potentially more rugged and simpler to implement.

[3] A schematic of the layout described here is given in the Annexe to this procedure.

[4] It is important to record the relative wind 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.

[5] Some equilibrator designs (*e.g.*, bubble or membrane type equilibrators) equilibrate at pressures different from ambient atmospheric pressure. These systems either need to

Rapid exchange of CO_2 is facilitated by enhancing the surface area of water exposed to the headspace air (*e.g.*, raining sea water droplets through the headspace into a sea water reservoir at the bottom of the equilibrator). The water flow rate is 2–5 $dm^3 min^{-1}$ and can be dispersed using a standard gardening spray head. The sea water is removed from the reservoir using a gravity drain and a series of water traps to minimize air exchange between the lab and the equilibrator headspace. Ambient air pressure is maintained in the headspace with a vent tube that is open to the outside air. The vent tube should have a volume of at least 10% of the headspace volume so small high-frequency pressure fluctuations just move the headspace air in and out of the vent tube but do not draw in outside air. This can be accomplished by attaching a long tube to the vent that extends outside the ship. This also provides fresh air for the headspace rather than high-CO_2 lab air. A better option for ensuring that the uptake of air through the vent line does not significantly affect the headspace gas is to include a pre-equilibration chamber on the vent line. This is particularly important for equilibrators with a small headspace volume (< 2 dm^3). The pre-equilibration chamber is a small chamber with sea water raining through it so any air brought into the headspace is already close to equilibrium with the sea water. During sampling, the headspace air is pumped through a dryer and the infrared detector at a rate of 60–80 $cm^3 min^{-1}$. After passing through the detector, the equilibrated air is returned to the headspace to minimize the need for replacement air from the vent. It is important to keep track of temperature and pressure in the equilibrator at all times.

4.3   Drying system

It is desirable to dry all of the air streams going to the detector[6]. 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 infrared analysis as it eliminates the need to correct for the pressure broadening of the CO_2 band resulting from the presence of water. Also, the calibration gases are typically dry air, so it is preferable to also analyze the unknown samples under the same dry air conditions.

A number of approaches can be used to dry the air:

- Cooling the air to a specified dew point using a refrigeration unit (*e.g.*, Peltier cooler). 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.
- Passing the wet sample gas through water permeable tubing (*e.g.*, Nafion®) with drying gas on the outside of the tubing to carry away the water vapor

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use a second-stage equilibrator maintained at ambient pressure or apply a pressure correction term to adjust the values to ambient conditions.

[6] Some systems do not dry the gas streams. Instead, they use a two-channel infrared detector (*e.g.*, the LI-COR® Model 7000) to measure both the water and CO_2 content, then correct for the water vapor in the final calculations. The advantage of these systems is the elimination of a complicated and potentially labor-intensive gas drying procedure.

and maintain a humidity gradient between the inside and the outside of the tubing.

The system described here combines a Peltier cooler and Nafion® tubing to dry the gases, but the analyses are made with a LI-COR® analyzer containing a water channel to ensure a complete accounting of any remaining water vapor.

4.4 Calibration system

Because the infrared detector has a non-linear response to changing CO_2 concentrations, it is recommended that multiple standards (3–6) be analyzed for the most accurate characterization of the response curve. Depending on whether the analyzer is run in absolute mode (*i.e.*, the reference cell is circulated with a closed loop of zero CO_2 air) or in differential mode (*i.e.*, the reference cell is flushed with a known standard gas), it may be desirable to run the reference gas through the sample cell to "zero" the instrument. High-purity two-stage gas cylinder pressure regulators are needed for each of the standard gases, as well as a remotely operable valve for selecting between the different gas sources.

4.5 Detector system

High quality infrared detectors can be purchased commercially. For operation on a ship, it is essential that the instrument not be sensitive to motion or vibration[7]. It is important to keep track of the temperature and pressure of the gas in the infrared absorption cells at the time of the measurements. If a water vapor correction is to be applied, then a detector with a water channel must be used.

4.6 System control

Since the system is intended to operate in "underway" mode, there should be a program for autonomously controlling valve switching, monitoring flow rates and logging the necessary data. This program will require a microcomputer as well as digital and analog interface boards for controlling valves, solenoids and necessary sensors.

5. Reagents

5.1 Compressed gases

The standards should be mixtures of CO_2 in natural air (*i.e.*, containing N_2, O_2, and trace gases) that bracket the expected concentrations of the samples as closely as possible (typically $250–550 \times 10^{-6}$ for open ocean applications). CO_2 concentrations have been found to be most stable in aluminum cylinders. The gases must be calibrated to better than the desired accuracy of the final measurements (*i.e.*, typically beyond the accuracy offered by commercial gas suppliers) and should be traceable to the World Meteorological Organization scale.

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[7] Suitable instruments are available from LI-COR Environmental, 4647 Superior Street, P.O. Box 4425, Lincoln, NE 68504-0425, U.S.A.

5.2 Drying agents

Chemical drying agents are the most reliable way to ensure that the sample gas is dry. Even if condensing systems or drying tubes are used to primarily dry the gas, many systems also run the sample gas through a chemical drying agent as a final confirmation that the sample is dry. Some common drying agents are Aquasorb®, magnesium perchlorate or silica gel.

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 (see section 4.1) and that the equilibrator samples uncontaminated surface sea water. As the $p(CO_2)$ 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. One should strive to set the system up in such a way that the difference in the temperature observed in the equilibrator and that observed in the surrounding sea water is less than 0.5°C. 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. The sea water temperature should be monitored with a sensor in the equilibrator and a sensor at the ship's sea water intake (outboard of any pumps or flow restrictors) so any temperature differences can be accounted for (see section 8.3) in the data reduction sequence. Because $p(CO_2)$ is very sensitive to temperature, it is important to use high-quality sensors with confirmed accuracy by comparison with a National Institute of Standards ITS-90 traceable temperature sensor (confirmed calibration ± 0.0001 across the range)[8]. Comparison of the equilibrator and the sea surface temperature sensor readings can be done in a well stirred and insulated water bath either on the ship or in the laboratory, ideally over a range of temperatures with all sensors measuring at the same time. If the sensors vary from the traceable standard, then an offset can be applied.

7. Procedure

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. The exact sequence is not critical and can be optimized for the particular location and desired objectives of the study. In general, 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.

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[8] To prove temperature traceability, a continuous path of calibrated measurements must be "traced" back to a fixed point of reference. This path consists of comparison measurements between "transfer standards" to ensure a temperature indication is an accurate reflection of the ITS-90 definition of temperature (see Chapter 3).

7.2   System calibration

A full set of standards should be run every 2.5 to 3 hours. Each standard takes approximately 4.5 minutes to analyze. After the gas selector valve is switched to a new standard, the system is allowed to flush through the detector for approximately 4 minutes with flow rates similar to the sample flow rates (60–80 cm^3 min^{-1}). After the lines are flushed, the flow is stopped at a point before the detector (*i.e.*, the detector is still vented to the atmosphere). After a delay of 6 seconds to allow for pressure equilibration in the detector, a 1-second averaged reading is taken. The gas selector valve is then switched to the next standard.

7.3   Cycle of analyses

Once the system has been calibrated, it alternates between marine air and equilibrated air readings. In the open ocean, sea water $p(CO_2)$ generally has much larger variations than the marine air, so systems usually collect 5 to 10 times more equilibrator readings than marine air readings. Each time the gas selector valve is switched to a new gas, the air lines need to be thoroughly flushed with the new sample. After switching the gas selector valve to marine air, the detector is allowed to flush for 4 minutes. After flushing, the flow is stopped for 6 seconds and a 1-second averaged reading is taken. Flow is started again and the system is allowed to flush for 30 seconds before the flow is stopped for another reading. After 10 marine air readings are collected, the gas selector valve switches to equilibrator air and is allowed to flush for 4 minutes. After flushing, the flow is stopped for 6 seconds and the reading is taken. Flow is started again and the system is allowed to flush for 1 minute before the flow is stopped again for another reading. After 60 equilibrator readings, the system switches back to marine air.   The sequence continues until it is time to standardize the system again.

8.   Calculation and expression of results

8.1   Calculation of infrared detector response

The response of a non-dispersive infrared 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

$$n(CO_2) = \frac{x(CO_2) \cdot p \cdot V(\text{cell})}{RT} \cdot \phi \tag{3}$$

where ϕ is an approximately constant term[9] that accounts for the non-ideality of the gas phase and p and T are the pressure and temperature of the gas, respectively, in the absorption cell, which has a volume $V(\text{cell})$[10].

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[9] Provided that the temperature, pressure and composition remain approximately constant. This is typically the case for this procedure.

[10] 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.

Two approaches are commonly used to evaluate the mole fraction of an unknown sample, based on standards with a known mole fraction. The first approach is based on a factory-calibrated response curve for the instrument. The LI-COR[®] instruments come from the factory with a built-in response function. This response function is tuned for the particular environmental conditions by setting the "zero" and "span" parameters using standard gases (see LI-COR, 1992 for details). While this approach gives reasonable values over a very wide range of conditions, more accurate values can be achieved over the limited range of conditions observed in the open ocean.

The approach described here starts with the output mole fraction determined by the internal functions provided by the LI-COR[®] instruments as described in the first approach, then modifies the output based on a series of calibration standards analyzed as part of the sampling sequence. This approach is recommended for those using LI-COR[®] instruments because:

1) the $x(CO_2)$ signal from RS-232 has better averaging (*i.e.*, the mV signal for the newer LI-COR[®] instruments is a converted digital signal that is not filtered or averaged);
2) the $x(CO_2)$ signal is internally corrected for band broadening;
3) the $x(CO_2)$ signal automatically takes cell pressure and temperature changes into account[11].

Ideally, the instrument should be calibrated using the built-in zero and span functions at least once at the beginning of the cruise. Additional calibrations during the cruise should be bracketed by analyses of the full set of standards to document the change in nominal $x(CO_2)$ output.

Following the analysis sequence outlined in section 7 provides nominal $x(CO_2)$ values for the unknown samples bracketed in time by the analysis of a series of known standards. The proposed measurement cycle necessarily performs the measurements on each calibration gas, and on each sample of air, at different times. To ensure the highest measurement quality, it is necessary to interpolate the measurements on calibration gases so as to infer the appropriate calibration function at the exact time of the measurement of a sample of air (either atmospheric or from the equilibrator). This is achieved using a piecewise linear interpolation in time. The measured nominal $x(CO_2)$ appropriate to a particular time t is estimated for each of the standard gases from values measured at times t_0 and t_1 that bracket time t:

$$C_0 + (C_1 - C_0)\frac{(t - t_0)}{(t_1 - t_0)} . \qquad (4)$$

C_0 is the nominal concentration of the particular standard gas measured at time t_0, and C_1 that measured at time t_1. This set of values is then used, together with the associated set of assigned $x(CO_2)$ values for the standard gases, to estimate the coefficients of a linear calibration function appropriate to time t. This information is then used to calculate the nominal value of $x(CO_2)$ for the air sample measured at time t:

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[11] This requires an internal pressure transducer which some LI-COR[®] models may not have. In this case the pressure is a pre-set value.

$$y_s = A + Bx_s \tag{5}$$

where x_s and y_s are, respectively, the nominal value of $x(CO_2)$ for the air sample and "true" value calculated from the calibration curve, and A and B are regression coefficients determined by a linear least-squares fit of the standards.

If the partial pressure of CO_2 in dry air is required, it is necessary to multiply the corrected sample $x(CO_2)$ by the equilibrator pressure P_{eq} (the pressure at the time of equilibration):

$$p(CO_2)_{T_E,\text{dry}} = x(CO_2) \cdot P_{eq} \tag{6}$$

where T_E is the temperature measured in the equilibrator.

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 equilibrator 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.

Thus

$$p(CO_2)_{T_E,\text{wet}} = x(CO_2)\left[P_{eq} - VP(H_2O)\right] \tag{7}$$

where $VP(H_2O)$ is the water vapor pressure over a sea water sample of a given salinity at the temperature of equilibration[12]—see Chapter 5.

8.3 Calculation of _ƒ_(CO₂) from _p_(CO₂)

If the $p(CO_2)$ of the sea water is to be used to calculate—or compared with—the other parameters of the CO_2 system, it is necessary to calculate the fugacity, $f(CO_2)$—see SOP 24:

$$f(CO_2)_{T_E} = p(CO_2)_{T_E,\text{wet}} \cdot \exp\left[\frac{\left(B(CO_2)_{T_E} + 2 \cdot \delta(CO_2)_{T_E}\right)p_{\text{atm}}}{R \cdot T_E}\right] \tag{8}$$

where p_{atm} is the atmospheric pressure and B and δ are defined in SOP 24. The term $(x_C)^2$ is approximately equal to 1.

8.4 Correction of _ƒ_(CO₂) to sea surface temperature

The $f(CO_2)$ 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:

$$f(CO_2)_{T_S,\text{wet}} = f(CO_2)_{T_S,\text{wet}} \cdot \exp\left[0.0423(T_S - T_E)\right] \tag{9}$$

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

where T_S is the sea surface temperature—typically the bulk temperature of the mixed layer[13]—and T_E is the temperature measured in the equilibrator[14].

8.5 Example calculations

8.5.1 *Calibration data*

The calibrated $x(CO_2)$ values for 4 standards are:

305.00, 370.00, 405.00 and 500.00 $\times 10^{-6}$.

The measured $x(CO_2)$ values at time t_0 are:

12:05 = 305.06 $\times 10^{-6}$,
12:10 = 370.10 $\times 10^{-6}$,
12:15 = 405.21 $\times 10^{-6}$,
12:20 = 500.33 $\times 10^{-6}$.

The measured $x(CO_2)$ values at time t_1 are:

15:05 = 305.56 $\times 10^{-6}$,
15:10 = 370.60 $\times 10^{-6}$,
15:15 = 405.71 $\times 10^{-6}$,
15:20 = 500.83 $\times 10^{-6}$.

The interpolated $x(CO_2)$ values at 13:00 are:

$$305.06 + (305.56 - 305.06) \cdot \left(\frac{55}{180} \right) = 305.21 \times 10^{-6},$$

$$370.10 + (370.60 - 370.10) \cdot \left(\frac{50}{180} \right) = 370.24 \times 10^{-6},$$

$$405.21 + (405.71 - 405.21) \cdot \left(\frac{45}{180} \right) = 405.34 \times 10^{-6},$$

$$500.33 + (500.83 - 500.33) \cdot \left(\frac{40}{180} \right) = 500.44 \times 10^{-6}.$$

8.5.2 *Correction of nominal sample value*

The nominal equilibrator air $x(CO_2)$ was 378.45 $\times 10^{-6}$ at 13:00.

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[13] 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 and Watson, 1992).

[14] The factor of 0.0423 has been determined experimentally (Takahashi *et al.*, 1993). A more elaborate correction procedure is possible (see, *e.g.*, Copin-Montegut, 1988; Goyet *et al.*, 1993); however, it is unnecessary provided that $|T_S–T_E| < 1$ K, as is the case for most measurement systems.

$A = 0.1813$, $B = 0.99876$ from linear fit,
$y_s = 0.99876 \cdot 378.45 + 0.1813 = 378.16 \times 10^{-6}$.

The final calibrated $x(CO_2)$ value is 378.16×10^{-6}.

8.5.3   Conversion to $p(CO_2)$

The calibrated $x(CO_2)$ value was 378.16×10^{-6} at $P_{eq} = 101.802$ kPa (1.0047 atm).

Thus
$$p(CO_2)_{TE,\ dry} = (378.16 \times 10^{-6})(101802) = 38.498 \text{ Pa}$$
$$= 379.94\ \mu\text{atm}.$$

8.5.4   Correction to 100% humidity

The water in the equilibrator has $S = 35$ and $T_E = 298.15$ K (25.00°C).

Thus
$$p_\sigma(H_2O) = 3.1106 \text{ kPa (Chapter 5)}$$
$$= 0.0307 \text{ atm}$$

and from equation (7)
$$p(CO_2)_{TE,\ wet} = 378.16 \cdot (1.0047 - 0.0307)$$
$$= 368.33\ \mu\text{atm}.$$

8.5.5   Calculation of $f(CO_2)$

The equilibrator pressure is $P_{eq} = 101.802$ kPa and $T_E = 298.15$ K (25.0°C), then
$$B(CO_2)_{TE} = -123.20 \text{ cm}^3 \text{ mol}^{-1},$$
$$\delta(CO_2)_{TE} = 22.52 \text{ cm}^3 \text{ mol}^{-1}.$$

So, from equation (8),

$$f(CO_2)_{T_E,\text{wet}} = 368.33 \cdot \exp\left[\frac{\left(-123.20 \times 10^{-6} + 2(22.52 \times 10^{-6})\right) \times 101802}{8.314472 \times 298.15} \right]$$
$$= 367.15\mu\text{atm}.$$

8.5.6   Correction to sea surface temperature

The sea surface temperature, $T_S = 297.85$ K (24.70°C). Thus from equation (9),
$$f(CO_2)_{T_S,\text{wet}} = 367.17 \cdot \exp[0.0423 \cdot (297.85 - 298.15)]$$
$$= 362.52\ \mu\text{atm}.$$

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 the infrared analyzer

The performance of the infrared 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 nominal $x(CO_2)$ values of standards 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 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 μatm for ambient air and less than 1 μatm for air from the equilibrator.

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Annexe
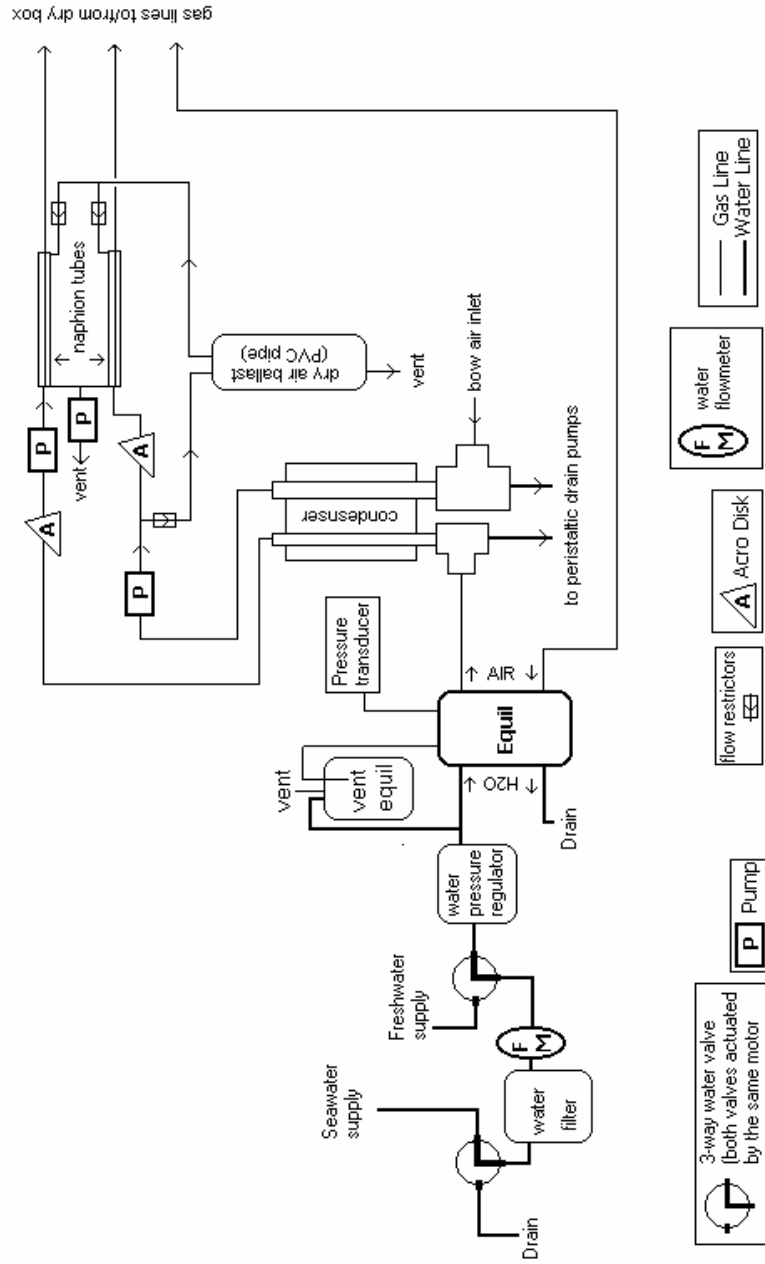
Fig. 1 Schematic showing the layout of the analytical system described here (based on system designed by Craig Neill, Bjerknes Center for Climate Research, Norway).