SOP 1

Water sampling for the parameters of the oceanic carbon dioxide system

1. Scope and field of application

This chapter describes how to collect samples—from a Niskin bottle or other water sampler—that are suitable for the analysis of the various parameters of the oceanic carbon dioxide system: total dissolved inorganic carbon, total alkalinity, pH and fugacity of CO_2 in equilibrium with a water sample.

2. Principle

The sample of sea water is collected in a clean borosilicate glass container in a manner designed to minimize gas exchange with the atmosphere (however, exchange of CO_2 gas does not affect alkalinity measurements). The sample is then treated with mercuric chloride to poison it thus preventing further biological activity and the container is closed to prevent any further exchange of carbon dioxide or water vapor with the atmosphere.

3. Apparatus

3.1 Flexible plastic drawing tube (Note 1), long enough to reach from the drain on the water sampler to the bottom of the sample bottle

3.2 Clean glass sample bottles with stoppers (Note 2)

3.3 Pipette to dispense the mercuric chloride solution

3.4 Sampling log book

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[1] Tygon® tubing is normally used for this purpose. However, if samples are being taken for measurement of dissolved organic carbon, they will be contaminated by the use of Tygon tubing and silicone rubber tubing should be used instead. The drawing tube can be pre-treated by soaking in clean sea water for at least one day. This minimizes the amount of bubble formation in the tube when drawing a sample.

4.   Reagents

4.1   Solution of mercuric chloride (Note 3)

4.2   Apiezon® L grease (if using ground glass stoppers) (Note 4)

5.   Procedures

5.1   Introduction

Collection of water at sea from the Niskin bottle or other sampler, must be done soon after opening the sampler and before much other water has been removed from it. This is necessary to minimize exchange of CO_2 with the head space in the sampler which typically results in a loss of CO_2. Samples for the various carbon dioxide parameters are not the first priority on the WOCE Hydrographic Program as samples to be analyzed for other gases are even more susceptible to contamination from gas exchange; it is however desirable that samples for all parameters, with the exception of total alkalinity (for which gas exchange is not a problem), be drawn before half of the Niskin bottle has been drained and within ten minutes of it being first opened.

5.2   Filling procedure

Rinse the sample bottle—If the bottle is not already clean, rinse it twice with 30 to 50 cm^3 of sample so as to remove any traces of a previous sample.

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[2]   *Bottle type* — High quality glass bottles, preferably made from borosilicate glass such as Schott Duran (l.c.e. 32×10^{-7}), are recommended for both temporary and longer term storage. The bottles should be sealed using greased ground glass stoppers held in place with some form of positive closure, or in some alternate gas-tight fashion.

   Bottle preparation — Bottles should be cleaned carefully before use. An established method is "ashing" at ~550 °C, followed by rinsing with deionized water. Chemical cleaning using a detergent has also been successful, when combined with careful rinsing. Bottles used for the temporary storage of samples before analysis at sea can be reused after adequate rinsing with the new sea water.

[3]   Saturated solutions of mercuric chloride are commonly used but have been found to clog certain repeating pipettes. Equivalent amounts of more dilute solutions (*e.g.* 50% saturated) can also be used successfully.

[4]   Although this grease has been found by experience to be suitable for this use, other greases may well be equivalent. However, the use of grease to provide an air-tight seal is inconvenient and further investigation of alternate closure systems is needed.

Fill the sample bottle—Fill the bottle smoothly from the bottom using a drawing tube which extends from the Niskin drain to the bottom of the glass sample bottle. Overflow the water by at least a half, and preferably by a full, bottle volume (Note 5).

Adjust the head-space—A head-space of 1% of the bottle volume is left to allow for water expansion (see Annexe to this procedure), *i.e.* 2.5 cm^3 for a 250 cm^3 bottle. This can be achieved by removing excess water using a plastic pipette with a bulb.

Add mercuric chloride—Mercuric chloride is added to poison the sample; the recommended minimum amount is about 0.02% by volume of a saturated aqueous solution. Thus to poison a 250 cm^3 sample requires 0.05 cm^3 (50 µL) of saturated mercuric chloride (or 0.10 cm^3 of a 50% saturated solution).

Close the bottle—Seal the bottle carefully to ensure that it remains gas-tight. If it is to be sealed using a greased ground glass stopper (Note 6), first wipe the excess water from the ground glass in the bottle neck, then insert the stopper completely, and finally twist the stopper to squeeze the air out of the grease to make a good seal. Finally, secure the clip—or other positive closure—and shake the bottle to disperse the mercuric chloride solution thoroughly.

5.3   Sample storage

The samples should be stored in a cool, dark, location (preferably refrigerated but not frozen) until use.

5.4   Sample documentation

The following information must be recorded in the sampling log book at the time of sampling.

- Time and date when taken
- Full name of person who took sample
- Location: an unambiguous designation of the station, cast, and bottle number from which the sample was taken

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[5] The amount of overflow water can be estimated by measuring how long it takes to fill a sample bottle, and allowing the water to flow for a period of 1.5 times that.

[6] The recommended procedure for re-greasing (or greasing) a stopper is as follows: (a) wipe the stopper with a tissue to remove as much grease as possible, (b) grease the stopper with 4 strips of grease, each strip extending ^{2}/$_3$ of the way from the top towards the bottom of the ground portion of the stopper. This provides a path for air to escape when the stopper is inserted into the neck of the bottle.

- Container designation: a number or alphanumeric symbol unique to the sample container
- Comments: additional information such as conditions when sampling, problems with sample collection, *etc.*

6. Quality assurance

Some duplicate sampling is recommended, both from the same sampler (*e.g.* Niskin bottle) and, if possible, from two samplers tripped together at the same depth, to assess the quality of the sampling procedures.

Annexe

How large a head-space should be left in a sample bottle?

The volume of the head-space is chosen so as to leave room for expansion of the sea water on warming, while being sufficiently small to minimize the amount of gas exchange between the head space and the bulk of the sample. The closure system must be adequate to retain the pressure exerted by the expansion.

The apparent change in the volume of a fixed mass of sea water can be calculated by allowing for the change in the density of the sea water and the expansion of the glass container. The total change over the temperature range 0–40 °C is about 1%. (The effect of expansion on the volume of the borosilicate glass bottle is only 0.04% over this range.) One third of this expansion occurs on heating the sea water from 0 to 20 °C, the remaining two thirds on heating it from 20 to 40 °C.

The pressure in the head-space of a container heated from a temperature t_1 to t_2 can be estimated allowing for the following:

- the expansion of the sea water in the bottle,
- the change in solubility of gases such as N_2, O_2, Ar,
- the thermal expansion of the gas phase,
- the change in the vapor pressure of H_2O above the sea water contained

Defining the initial head-space ratio

$$r = \frac{V(\text{head-space})}{V(\text{sea water})} \ ,\qquad\qquad \text{(A.1)}$$
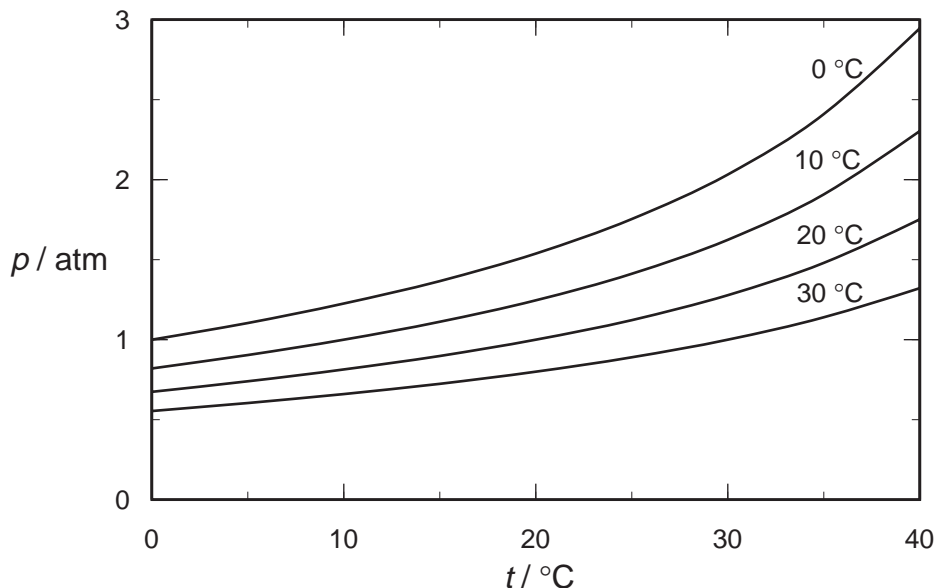
Figure 1. Pressure in head-space, with $r = 0.01$, as a function of temperature for various initial temperatures. In calculating this, it was assumed that the gases—N_2, O_2, Ar, H_2O—were initially at solubility equilibrium with sea water at the starting temperature, that they behaved ideally and that the initial pressure in the bottle at the indicated temperature was 1 atm.

allows the calculation of the approximate pressure in the head-space of a closed container as a function of temperature (Figure 1).

Clearly, if cold samples (< 10 °C) are likely to be heated above 30 °C, there is a risk of them leaking if the head-space ratio is significantly less than 1%.

There is, however, an additional factor to be taken into account when determining the optimal head-space size: gas exchange with the head-space. The change in total dissolved inorganic carbon (ΔC_T) resulting from this gas exchange can be derived from mass balance considerations:

$$\Delta C_T = \frac{\left(\dfrac{p(CO_2)V}{T}\right)_{\text{inital}} - \left(\dfrac{p(CO_2)V}{T}\right)_{\text{final}}}{R \cdot m(\text{sample})} \quad ; \qquad \text{(A.2)}$$

where $p(CO_2)$ is the partial pressure of CO_2 in a head-space of volume V and at a temperature T corresponding to the inital condition (when the bottle is closed) and the final condition (when the bottle is analyzed), R is the gas constant and $m(\text{sample})$ is the mass of the sample.

The volume of the head-space decreases as the contents heat up (due to the expansion of the sea water) partially compensating for

the decrease in the solubility of the various gases, thus the greatest loss of CO_2 will occur if the sea water has a high $p(CO_2)$ but does not warm up significantly in the container. Even then, provided that the head-space ratio is less than 0.01, ΔC_T will be less than 0.5 $\mu mol \cdot kg^{-1}$.

Gain or loss of CO_2 gas is not significant when collecting discrete samples for alkalinity measurement; however, if $p(CO_2)$ is to be measured the so-called "buffer factor" comes into play and the resultant relative error in $p(CO_2)$ is approximately 10 times that in C_T, *i.e.* for an change of –0.5 $\mu mol \cdot kg^{-1}$ in C_T the change in $p(CO_2)$ is about –0.25%. This corresponds to a change in pH of about +0.001.

A head-space of 1% is thus optimal for the collection of CO_2 samples provided one can be sure that they will not be exposed to temperature changes of 30 °C or more. If this cannot be assured, it might be preferable to allow a larger head-space and to estimate the appropriate correction.