Measuring ^{14}C in Seawater DIC by Accelerator Mass Spectrometry

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1. Introduction

The radiocarbon content of seawater dissolved inorganic carbon ($DI^{14}C$) is measured by extracting the inorganic carbon as CO_2 gas, converting the gas to graphite, and counting the number of ^{14}C atoms in the sample directly using an accelerator mass spectrometer. The sampling procedure described below is straightforward, but it is important to stress the need for clean sampling techniques as ^{14}C contamination is not obvious.

The use of an accelerator mass spectrometer (AMS) to measure ^{14}C in seawater samples greatly reduced the size of the sample required for radiocarbon analysis, but it also greatly increased the importance of collecting the sample in a clean, ^{14}C-free, environment. Contamination of a sample container can arise from collecting and handling the sample on a contaminated surface or from exchange of the CO_2 in the sample with atmospheric CO_2. Radiocarbon is used in the laboratory and at sea to measure oceanic productivity and inadvertent spills can leave isolated spots that are severely contaminated. The levels typically used in tracer experiments can be several million times modern levels and infinitesimally small residual amounts on sampling surfaces can ruin the collection of samples for the measurement of natural levels of ^{14}C.

Programs such as Operation Swab based at the University of Miami will ensure an environment is not grossly contaminated but cannot guarantee the level of cleanliness we require. Their detection limit is 10^2 to 10^3 higher than what NOSAMS measures. "Operation Swab" clean means that, with proper precautions, uncompromised radiocarbon samples can be collected. In order to avoid contamination, we recommend that surfaces where the samples are collected or handled be covered with fresh disposable sheets of plastic and that disposable gloves (changed often) be worn during sampling. Access to sample handling areas should be limited to those persons processing the samples. The pre-cruise preparations should not be performed in a laboratory in which ^{14}C has been used as a spike. In order to minimize exchange with atmospheric CO_2, sample transfers must be as rapid as possible.

For the CLIVAR program, clean bottles are provided by NOSAMS in plastic boxes containing 16 bottles. Each NOSAMS box and each bottle have unique ID numbers. These numbers should be used as the sample identifier. The instructions pertain to cruises where NOSAMS is **not** providing the sampling bottles.

2. Bottle Cleaning Procedure

The bottle used for the collection of seawater is a 500 ml Pyrex (or Pyrex-equivalent) reagent bottle with a 29/26 standard taper ground glass joint and a solid stopper. Teflon tape or a piece of laboratory wipe is essential for preventing the stopper from seizing when shipping the bottles. Prior to packing for use at sea, the bottle must be cleaned.

To clean the bottles, first wipe any excess grease from the stopper and ground glass joint on the bottle. In a hood, further clean the stopper and joint with laboratory wipes soaked in xylenes and acetone to prevent transfer of grease from the stopper region to the inside of the bottle. After washing with solvents, allow the pieces to dry in a well-ventilated area. When using xylene, solvent-impermeable gloves should be worn. The above steps are not necessary for bottles fresh from the factory.

The following steps are necessary for all bottles, unless an arrangement has been made with the factory to provide bottles cleaned in the same manner. When the labels and grease have been removed and solvents have evaporated, wash the bottles and stoppers with a dilute soap solution, rinse well with warm tap water, rinse the bottles and stoppers with 10% HCl, and finally rinse three times with distilled water. From this point on, do not leave bottles upright without covering the opening with clean aluminum foil. The foil can be rinsed with distilled water. Bake the glassware overnight in a 450^{o} C oven. When the bottles and stoppers are dry and cool, place tape or laboratory wipe in the ground glass joint of each bottle. Part of the tape should extend over the lip of the joint. Finally, place the stopper in the bottle.

After cleaning and capping, each bottle must have a label affixed. Spaces for the following information are suggested for the label:

1. Sample number or ID
2. Sample location
3. Cruise name and number, Leg number, Station/cast number (if collected at sea)
4. Depth
5. Date
6. Time

3. Shipping Preparation

When the bottles have been washed, dried, and labeled, weigh the bottle plus stopper and record the weight. If bottle weight is provided to us we can get the weight of the water by weighing the bottle + sample when it arrives at NOSAMS. Place them in a packing crate for shipping. The bottles should fit snugly in the crate and the crate should be sealed securely before shipping; each crate holds 16 bottles. In order to reduce the possibility of contamination during shipping and storage, the crates should be covered with a disposable plastic bag, which is closed with a reusable tie.

4. Sampling

a. Pre-sampling procedure

The integrity of DI^{14}C samples can only be guaranteed if the samples are collected using the proper procedures and collected in ^{14}C–free environment. The bottles should be handled as little as possible and removed from their packing crates only when necessary. A data sheet(s) should be kept for each crate of bottles. For CLIVAR, NOSAMS provides data sheets indicating the information we require for each sample (Appendix 1).

Additional information may include the following. Information regarding the history of each crate of bottles should be recorded on this sheet. This information should include identification of the laboratory in which the bottles were prepared, the shipping and storage history (dates and location) of each crate, information regarding the condition of laboratories and storage facilities (e.g. refrigerated or not) and identify other sampling programs in progress on the ship.

The items listed in Table 1 must be prepared before collection. The easiest and perhaps the safest way to prepare saturated $HgCl_2$ solutions for use at sea or in the field is to pre-weigh the $HgCl_2$ powder (ACS grade, crystal) into plastic bottles and add distilled water at sea. [1]The solubility of $HgCl_2$ is approximately 7g/100cc at 20°C; each sample requires 100 µl of solution. Thus, collection of 1000 water samples would require only 100 ml total solution.

Table 1: Items to be prepared for shipping with sample bottles.

1. Saturated aqueous $HgCl_2$* solution
2. 100 µl Eppendorf pipette with yellow tips
3. Plastic pipette with bulb, a cooking baster is ideal.
4. Swabbing tool (a stick with laboratory wipes attached)
5. Tygon drawing tube (pre-treat by soaking in clean seawater for at least one day)

Clean, disposable gloves should be worn any time the bottles are handled. When the bottles are removed from the crates, they should not be placed in direct contact with any surface on the ship either on deck or in the laboratory. Plastic sheets or garbage bags can be placed on any surfaces the bottles must touch. Bottles for each cast should be transferred from their packing crate to the plastic sample holder designed for use during transport and filling of the bottles. Prior to actually sampling the seawater, as much information as possible should be written on the bottle label or a data sheet; an example is included in the 1" sample log binder that is part of the sampling supply kit.

Data sheets should be used to record information regarding sea state at the time of sampling, other programs sampling simultaneously or sequentially from the WOCE water sampler, and any comments regarding unusual conditions.

c. Sample Transfer Procedure

The procedures described here are based on those used in C. David Keeling's laboratory for the collection of DIC samples (Peter Guenther, pers. Comm.) and assume that samples will be collected from a Niskin bottle. Prior to sampling, check to be sure that all the items in Table 1 are on hand and then proceed to collect the seawater samples.

Immediately prior to sampling, remove the glass stopper and the laboratory wipe (always make sure the strips of lab wipe or tie wrap have been removed before collecting any seawater). Place the tygon tubing on the Niskin bottle and flush the tubing with approx. 50 ml of water. Then place the tubing inside the sample bottle, making sure the tube reaches to the bottom of the bottle and the vent at the top of the Niskin bottle is open. Fill the bottle with approximately 50 ml of water; gently swirl around to rinse the sides of bottles and discard; repeat once more. With the tygon sampling tube at the bottom of the bottle, fill with enough water to fill the bottle 1.5 times (*Figure 1*); this can be accomplished by observing the amount of time it takes to fill the bottle and allowing the bottle to overflow for half this time, stopper the bottle with an ungreased stopper. Repeat this procedure for the remaining samples from the cast. If two samplers are available, have one sampling from the niskin and one in the lab poisoning/stoppering the bottles. That way you don't have to stopper the bottle twice. Using this procedure, an AMS water sample will require approximately 850 ml of water.

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* The Merck index lists $HgCl_2$ as a "violent poison" for which 1 or 2 g is frequently fatal. After using $HgCl_2$ (either as a powder or in solution), the user should always wash thoroughly before eating or drinking. The powder should not be inhaled because it is corrosive to mucous membranes.

When all the bottles have been filled, remove them to a safe, dry place and continue preparing the samples for storage in the following manner. Remove the stopper; wipe clean and dry; using the grease syringe, apply a thin layer of grease in a wavy pattern around the stopper (*Figure 2*); set the stopper aside. Apiezon-M grease should be brought along for use. Using the large pipette or just by pouring, remove enough water for a 5-10 ml headspace to exist in the bottle; this level can be marked on the bottle; *Figure 3* shows a bottle with the right amount of headspace. Using the Eppendorf pipette, add 100 µl of the saturated $HgCl_2$ solution to the bottle. Carefully and completely wipe the inside of the ground glass joint dry using lab wipes and place the stopper in the bottle. Care must be taken not to put your finger in the sample. The joint **MUST BE DRY** for the grease seal to work properly! Twist the stopper around while applying pressure to ensure that a good seal is made. Secure the bottle top with one rubber band placed over the entire bottle. If a duplicate sample is to be taken, start filling the second bottle immediately using the same procedure. After both bottles are filled, capped, and secured with an elastic band, shake gently to mix poison in. After all samples from one cast have been taken and sealed, each label/data sheet should be checked to make sure it contains the necessary information, and the integrity of the greased seals should be checked.

d. CLIVAR Data Requirements

Information to include on the data sheet are: WHPID or transect, station number, latitude, longitude, date, cast, Niskin or rosette bottle number, sample depth or pressure, AMS bottle number, confirmation of the addition of poison, any comments and AMS box number. When the data for all the samples have been recorded properly, the samples should be transferred to the shipping crate. When time becomes available, data from all samples should be entered into a spreadsheet (format provided).

d. Sample Storage Procedures

The plastic shipping crate should be closed securely (use tie wraps to secure) and stored in a temperature-controlled environment (i.e. the ship's science hold). Seawater samples must not be exposed to extremes of temperature. Poisoned samples do not need to be refrigerated and should **NEVER BE FROZEN.** If the samples are frozen, the water will expand and either dislodge the cap or break the bottle. If the sample is stored at too high a temperature, the grease will melt and run into the sample, and the sample may expand enough to dislodge the cap. According to a manufacturer's bulletin (Biddle Instruments #43C) the optimum working temperatures for Apiezon greases L, M, and N are 15-25^{o}C. To maintain their integrity, samples must be stored in a van or environment that is capable of maintaining the temperature within this range. The samples should not be exposed to extreme temperatures during shipment either.

Please email Al Gagnon (agagnon@whoi.edu) or Ann McNichol (amcnichol@whoi.edu) if there are any questions or concerns regarding this procedure. We appreciate the time you are taking to collect our samples carefully.

Sampling kit

Each cruise has two sampling kits containing most of the materials listed below (quantities may vary).

Sample Kit #1

1 Box of 12 pencils

2 Pair Thick rubber gloves

1 Roll Duct Tape

1 Box Large Clear plastic bags

1 Box of 100 tyvex envelopes

2 Finn pipettes

1 Box of eppendorf pipette tips

“M” grease

1 roll scotch tape

1 Large storage bag containing roll of electric tape, MSDS (mercuric chloride), and vial of mercuric chloride powder

1 Binder containing about 100 deck log sheets

1 Storage bag containing pens, pencils, lab tape, markers, and electrical tape

lengths of tygon tubing (1 about 6 foot, 1 about 10 foot)

Tie down straps

Bag of vinyl gloves size M (100 gloves)

Bag of vinyl gloves size S (100 gloves)

1 Box Zip ties

1 Pair Wire Snips

Large rubber bands

Kim wipes