Radiocarbon

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1. Background

In nature, production of ^{14}C takes place in the upper atmosphere where cosmic rays interact with atmospheric particles to produce large numbers of high-energy neutrons. These high-energy neutrons are rapidly reduced to thermal neutrons through repeated collisions with atmospheric gases. Most of the thermal neutrons are finally captured by ^{14}N in the reaction:

$$^{14}_{7}N + ^{1}_{0}n \rightarrow ^{14}_{6}C + ^{1}_{1}H$$

This process creates about two radiocarbon atoms per square centimeter of earth surface per second.

Oxygen and ozone rapidly react with the ^{14}C to produce $^{14}CO_2$ which mixes with ordinary $^{12}CO_2$ and is distributed into the lower atmosphere by eddy diffusion. Once in the lower atmosphere radiocarbon is mixed into the various natural carbon reservoirs (Table 1).

Table 1: Carbon content of natural-exchange reservoirs
(after Riley and Skirrow, 1965)

Carbon Reservoir	Carbon Content (g/cm^2 of earth's surface)
Atmosphere	0.125
Humus	0.19
Biosphere (land)	0.06
Biosphere (marine)	0.002
Oceanic dissolved organic carbon	0.533 [1]
Oceanic inorganic carbon (above thermocline)	0.20
Oceanic inorganic carbon (below thermocline)	7.25

[1] The true value may be at least twice this number in light of new evidence using high temperature combustion techniques. (Sugimura and Suzuki, *Marine Chemistry*, 1988.

When surface water is removed from contact with the atmosphere, radiocarbon activity will decrease. The time since submergence is not, however, a simple decay calculation. Mixing with adjacent water masses of different origin and activity gives rise to water of intermediate activity. Decaying organic matter in equilibrium with surface water of relatively high radiocarbon content can fall into older, deeper water. Oxidation of this organic matter ultimately gives bicarbonate which will alter the apparent age of the lower waters. Burning fossil fuels and atomic weapons testing respectively decrease and increase the atmospheric $^{14}C/^{12}C$ ratio. Finally, CO_2 injection into the ocean is not uniform over the earth's surface.

Approximate time scales for many of the transfer processes within the carbon system can be estimated by measuring the ^{14}C distribution. ^{14}C decays by β emission and has a half-life of 5730 ±30 years. Once the specific activity of carbon in a reservoir and the ^{14}C production rate are known, it is possible to estimate the reservoir turnover and mixing times.

Since the GEOSECS expeditions, both natural and man-made radionuclides have come to play an important role in oceanography. The most fruitful application of the data has been through the use of oceanographic models ranging from simple box models to three-dimensional, general-circulation models. The ocean-atmosphere system is not in equilibrium with respect to ^{14}C. The degree of disequilibrium is controlled by physical, chemical, and biological processes. Each of these can complicate interpretation of ^{14}C data; however, this involvement also increases the ultimate value of ^{14}C as a tracer.

2. Outline of General Method

During WOCE two methods will be used for ^{14}C analysis: accelerator mass spectrometry (AMS) and traditional beta counting. Samples for AMS analysis will primarily be collected in the main thermocline where bomb-produced ^{14}C has elevated concentrations significantly above natural levels. Large volume samples for beta counting will be collected throughout the water column, but will primarily be taken from the deeper regions.

AMS ^{14}C samples will be collected in 500 ml in glass bottles with ground glass stoppers. The collection technique is essentially that used for total CO_2 or dissolved O_2. After collection, the samples are poisoned with $100\mu\ell HgCl_2$. The detailed collection and analysis procedure can be found elsewhere in this manual (*Measuring ^{14}C in Seawater ΣCO_2 by Accelerator Mass Spectrometry*, A. P. McNichol and G. A. Jones).

Seawater samples which will be analyzed for ^{14}C by beta counting are normally collected in 270 liter Gerard-Ewing barrels. Once aboard ship, the water is acidified to convert carbonate and bicarbonate to CO_2. The CO_2 is then extracted either by purging with N_2 or by vacuum extraction. Vacuum extraction is faster than nitrogen purging and is equally efficient; however due to equipment availability, nitrogen purging will be the primary WOCE technique. CO_2 is quantitatively absorbed from the extracted gas by passing through a NaOH solution to produce Na_2CO_3. The Na_2CO_3 solution is returned to shore for determination of the $^{14}C/^{12}C$ ratio. A detailed description of this extraction technique is given below. The beta analysis technique has been thoroughly documented in the literature.

3. Sample Contamination and Sources of Error

During GEOSECS the atmospheric ^{14}C level was significantly higher than today due to nuclear weapons testing in the mid-1960s. The procedure described below was designed to minimize atmospheric contamination. Some of the precautions originally built into the procedure amount to "overkill" with today's atmospheric levels, but have been left in for extra safety.

The largest potential source of contamination today is other scientific activity aboard ship–either current or previous. Studies of primary productivity often use ^{14}C as a tracer. The activity levels used in these studies are many orders of magnitude higher than natural levels. An accidental spill during a spike experiment can be totally negligible with respect to the spike experiment levels or to health considerations, yet high enough to be disastrous for a program trying to measure natural water column activity. One such accident during the TTO program raised background levels aboard the ship by 5 orders of magnitude and required that all decks be acid washed before water column ^{14}C measurements could begin. Any ship being used to collect ^{14}C samples for WOCE must be checked for contamination prior to sailing. Dr. Göte Ostlund at the University of Miami, RSMAS, is currently (1991) in charge of the ship monitoring program (SWAB). In general, it should be remembered that ^{14}C is a trace element in the ocean. Care should be taken to keep all parts of the collection and extraction equipment as clean as possible.

Contamination of NaOH reagent by atmospheric CO_2 is likely in improperly sealed reagent bottles. Often these bottles will contain excessive amounts of precipitate. Any such bottles, or those with broken lids, should not be used. Prior to collecting a NaOH-carbonate sample, the reagent bottle lid must be thoroughly rinsed with dilute acid, then distilled water, and dried. After collection of the NaOH-carbonate sample, the lid must be replaced tightly, and secured with electrical tape. This is important since samples may not be analyzed for many months after collection.

Air contamination should be minimized. An empty extraction barrel containing 200 liters of air has enough $^{14}CO_2$ (relative to normal carbon) to raise the $^{14}C/^{12}C$ ratio in a 200 liter seawater sample by 0.2%. The accuracy of the beta technique is 0.4%. Since it is unlikely that all of the $^{14}CO_2$ would go into the sample, this contamination is not large.

Water samples can be transferred from the Gerard barrels to the extraction barrels either by pumping or by applying a positive pressure head to the Gerard barrel with CO_2 free air. The latter method is a bit slower, but preferred. If a pump is used, there should be no air leaks between the Gerard and the extraction tank, and the pump should be designed so that cavitation does not occur. Clear tubing is used for plumbing between the Gerard and extraction tank so that any bubbles caused by pump cavitation or air leaks can be easily identified.

4. Theoretical and Actual Stripping Efficiency

After acidification, dissolved CO_2 is removed from the water sample contained in the extraction barrel by purging with N_2 gas. If equilibrium is reached between the N_2 carrier gas bubbles and the dissolved CO_2, then the extraction should proceed according to a first order Raleigh curve. The characteristic time τ required to reduce the concentration of CO_2 gas in solution by the factor 1/e is given by:

$$\tau = \frac{\beta_{CO_2} V P}{F}$$

where:

β_{CO_2} is the Bateman solubility coefficient of CO_2 at the sample temperature at extraction time (atm_1);
V is the sample water volume ($\sim$ 200 liters);
F is the volume flow rate of N_2 carrier gas at STP ($\sim$ 300 liters/hr);
P is the pressure inside the stripper ($\sim$ 1.05 atmosphere).

This equation gives the characteristic extraction time for the liquid phase only. The characteristic flushing time for a well mixed gas volume (V_g) such as the head space above the water sample is simply V_g/F.

Table 2 demonstrates actual extractor system efficiency relative to theoretical. The difference between theoretical and actual extraction times are ~15% at 0° C, ~24% at 20° C, and ~2% at 30° C. During WOCE operations, the extractors should be operated long enough to assure that at least 98% of the CO_2 has been removed.

Table 2

β_{CO_2} **and** $\tau_{theoretical}$ **at various temperatures compared** τ_{actual} **values**[2]

β_{CO_2}	Temperature °C	$\tau_{theoretical}$ (minutes)	τ_{actual} (minutes)
1.49	0°C	61.5	71
1.2	5	49.4	–
1.0	10	41.3	–
0.74	20	30.5	38
0.64	25	26.4	–
0.57	30	23.5	24

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[2] The actual stripping times were determined by analysis of discrete samples for ΣCO_2 at various times during the course of an extraction. The ΣCO_2 concentrations were determined by gas chromatography. Note that the 30° C data is questionable.

The characteristic stripping time is directly proportional to the gas solubility in the liquid phase and inversely proportional to the sample temperature and carrier gas flow rate. An upper limit on flow rate is imposed by equipment design. Extraction time also varies directly with internal system pressure and sample volume, but these variables are constrained by equipment design and contamination considerations and are, therefore, fixed to a narrow range.

For the analyst doing the extractions, a more useful expression than that given above is:

$$t = -\frac{ln(f)\beta V P}{F}$$

Where t is the time required for the extraction and f is the fraction of CO_2 remaining in the sample (*i.e.* for 98% extractions, $f = .02$). The following conversions may also be useful (please forgive the units mix).

55 gal. - 20 liter head space = 188 liters = V

0.7 psi over pressure = 1.05 atm; 1.0 psi over pressure = 1.07 atm

1 ft^3 = 28.3 liters

1 ft^3/hr = 0.472 liter/min

$-ln(.02) = 3.912$

For a flowmeter which reads in ft^3/hr (F) and an over pressure of 1.0 psi, then the amount of time in minutes to achieve 98% extraction is:

$$t = \frac{1668\beta}{F}$$

Figure 1 demonstrates the effect on extraction time of sample temperature and carrier gas flow rate.

5. Equipment Description, Set-up, and Check-out

The equipment necessary to collect, extract, and concentrate ^{14}C at sea is composed of: (1) collection equipment, (2) extraction barrels, (3) a CO_2-free air generator, (4) a N_2 gas source, and (5) NaOH absorber units. Proper set-up requires that each part be adequately cleaned and secured. All connections and valves in the gas circulation loop must be leak tight.

5.1 Collection Equipment

During WOCE most large volume samples will be collected with 270 liter Gerard barrels. Deployment strategy and sampling order are discussed in another part of this

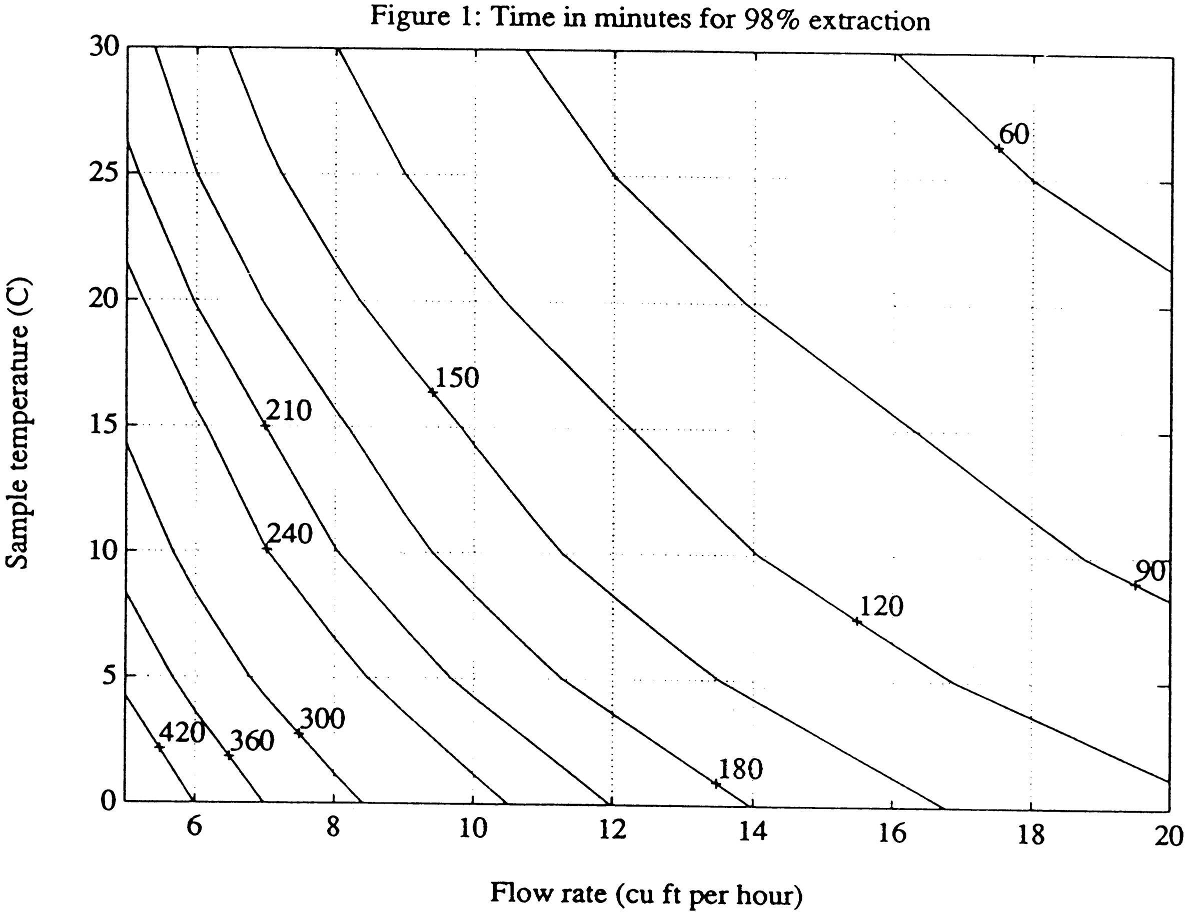

Figure 1: Time in minutes for 98% extraction

document (*Large Volume Sampling,* R. M. Key). In general, maintenance and operation of this U. S. equipment will be provided by Scripps Ocean Data Facility personnel. The scientist providing support for the large volume program is required to provide at least one person to assist with deployment and to be in charge of selecting sampling depths, stations, *etc.*.

On most ships, the Gerard barrels are stored in racks which are bolted or welded to the deck in close proximity to the A-frame used for deployment. The rest of the ^{14}C equipment should be located as close to this areas as is practical.

Care must be taken before the expedition to assure that the tubing used to drain the Gerard barrels into the extraction barrels has fittings compatible wit those on the Gerard barrels and extractor barrels. If the water is transferred by applying head pressure with CO_2-free air to the Gerard barrel, then these fittings must also be checked. If the water is pumped between the Gerard and extractor, the pump must be appropriately sized for the tubing, leak tight, and not cavitate.

5.2 Extraction Barrels

The extraction barrels are 55 gal. plastic drums with two bung ports on the top. Since they weight 200 kg each when full, they must be secured prior to being filled. The general procedure is to strap them in groups to some structure which is either bolted or permanently affixed to the deck. They should be mounted as close to the Gerard barrels and the NaOH absorber units as is possible. If this is impractical, it is more important to have the barrels close to the absorber equipment than the Gerard barrels because of all the plumbing connections. Figure 2 is a schematic of an extractor barrel and associated fittings.

During set-up, the barrels should be cleaned prior to removing the bungs. The water fill - drain leg should be inspected for cracks, loose fittings, or other damage. The tygon sleeve at the end of the leg should be adjusted so that it will reach the bottom of the barrel. The acid fill - gas dispersion leg should be similarly inspected and cleaned. Special attention should be given to the air stone (or similar dispersion device) to make sure that it is functional and securely attached. It is a good practice to occasionally check the air stone during long cruises. In addition to a pump problem, a malfunctioning air stone is a high probability factor whenever gas flow rate decreases during an extraction.

Each extractor is connected to a NaOH absorber unit with a length of twin flexible tubing *via* a manifold. This twin tubing is shockingly expensive (∼\$4/ft) and degrades in direct sunlight. Any sort of simple insulation which block UV light will slow degradation. Under extreme conditions, it is also necessary to insulate this tubing sufficiently to maintain a reasonable temperature range (∼5-30° C). With all of the connections which result in a multi-barrel - Multi-absorber set-up, the possibility of gas leaks is high. Therefore, it is good practice to secure the twin tubing on the barrel fittings (wire, tie-wrap, hose clamp, or equivalent).

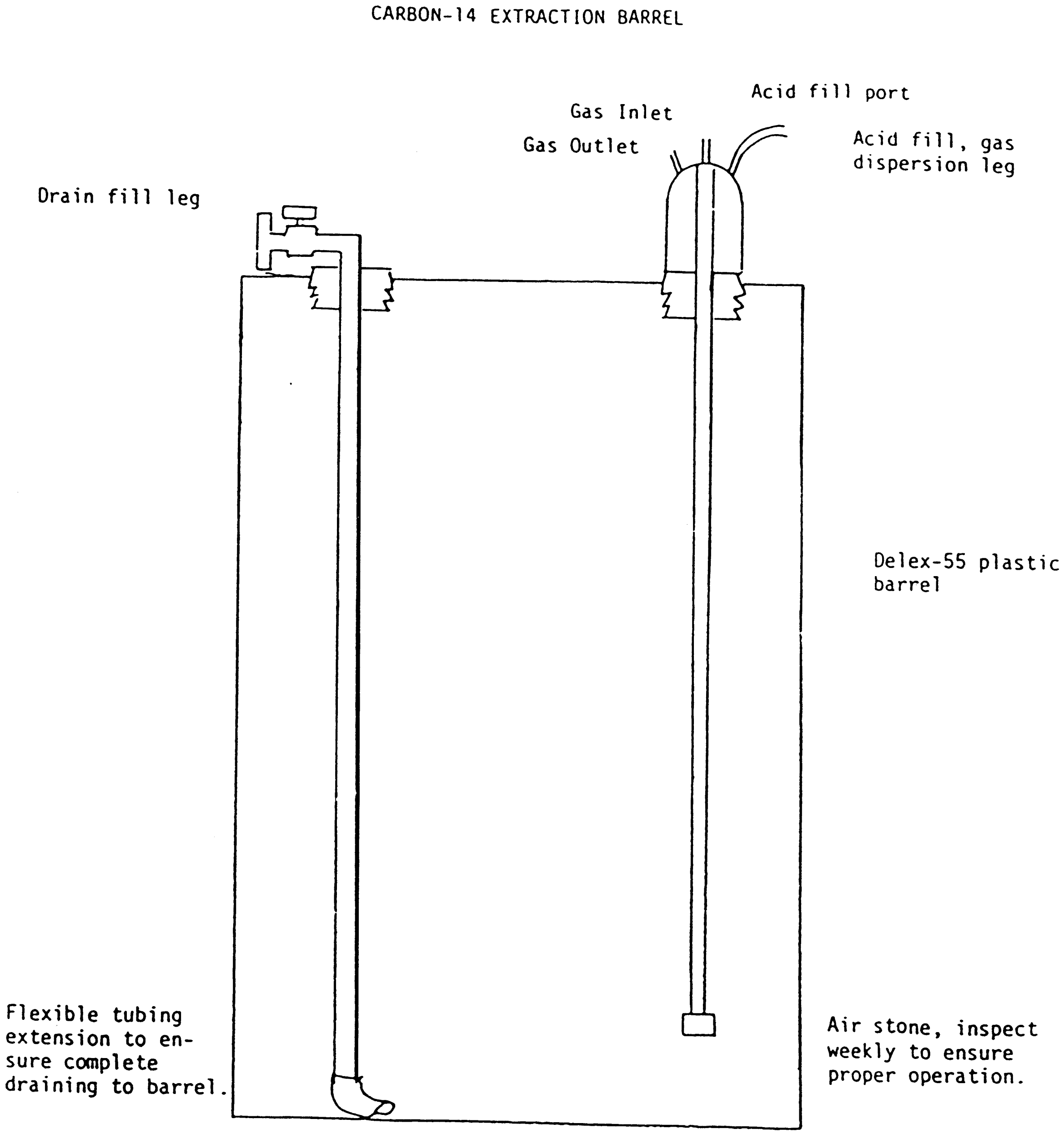

Figure 2: Carbon-14 Extraction Barrel

Prior to running samples, the Gerard barrels should be filled with seawater, the water transferred to the extractor barrels, and the entire degassing system tested for leaks, *etc.* This also provides an opportunity for the technician operating the system to practice the procedure. Distilled water should be used in place of NaOH solution in the absorber units for this test.

5.3 CO_2-Free Air Generator

A block diagram of the CO_2-free air generator is shown in Figure 3. The entire unit is packed in a shipping box. It is composed of an air pump, two 20 liter flint glass bottles, a PVC cylinder packed with glass wool, and flexible tubing to connect the components. Each bottle is filled with 10 liters of 1N NaOH. This solution should be changed after approximately 200 sample extractions (100 if the generator is used to transfer samples from the Gerard barrels to the extractor barrels). The entire system should be leak tight at operating pressure (5 - 10 psi). Prior to each station, the unit should be checked to make sure that the air dispersion devices inside the bottles are still secured and functional. In between cruises, the air pump should be thoroughly cleaned and checked because of the harsh operating environment.

The CO_2-free air generator is primarily used to pressurize the extractor barrels after they are filled with water in order to force out $\sim$20 liters of water for head space and to empty the extractor barrels after a sample has been finished. It can also be used to transfer water from the Gerard barrels to the extractor barrels by pressurizing at the top of the Gerard through the pressure relief port. If this technique is used, care must be taken to regulate the pressure (a pressure of 5 psi results in a total force of 1570 lbs. on each Gerard end plate).

5.4 N_2 Supply

N_2 is used to flush the absorber units and acts as the carrier gas during the stripping operation. One tank of compressed N_2 has enough gas for approximately 200 samples ($\sim$100 psi drop in tank pressure per 9 sample cast). If any significant leaks exist in the stripping loop, N_2 usage will appreciably increase in addition to losing sample.

5.5 NaOH Absorber Units

A schematic diagram of the NaOH absorber units is shown in Figure 4. The unit is essentially a bubble tower in which the CO_2 contained in the N_2 carrier gas reacts to produce Na_2CO_3. During operation the entire gas loop is kept at a positive pressure of 0.7 to 1 psi (5-7 kPa). The stripping tower, inlet trap, and outlet trap are glass and, therefore, must be securely mounted in a dry, safe location. Proximity to the extraction barrels is desirable. Each pair of absorbers is generally mounted in a wooden box which doubles as a shipping container. Obviously, spares must be available for all glass parts. Additionally, experience has shown that the small air circulation pumps have a relatively high failure

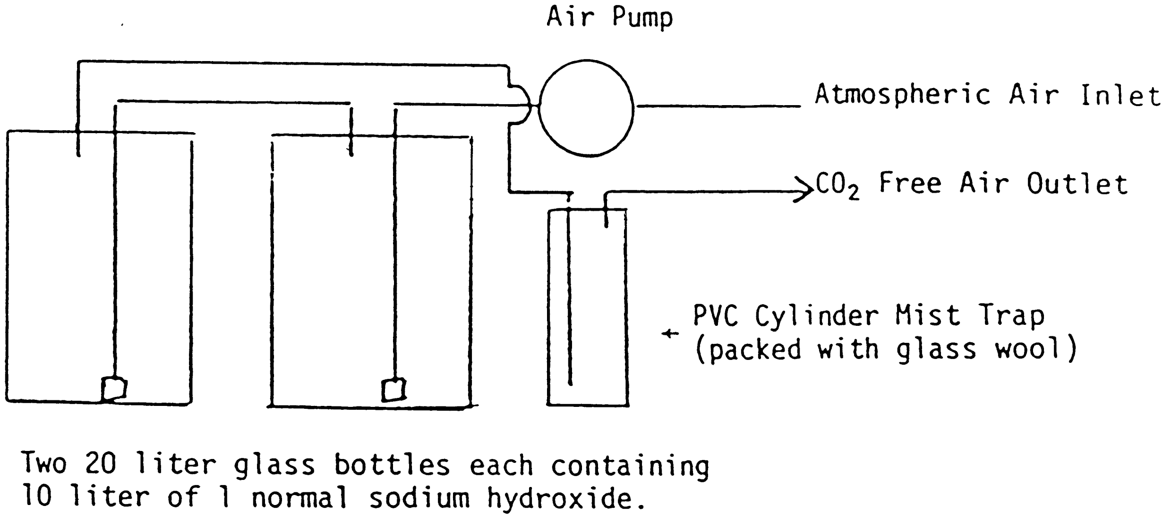

Figure 3: CO_2-Free Air Generator

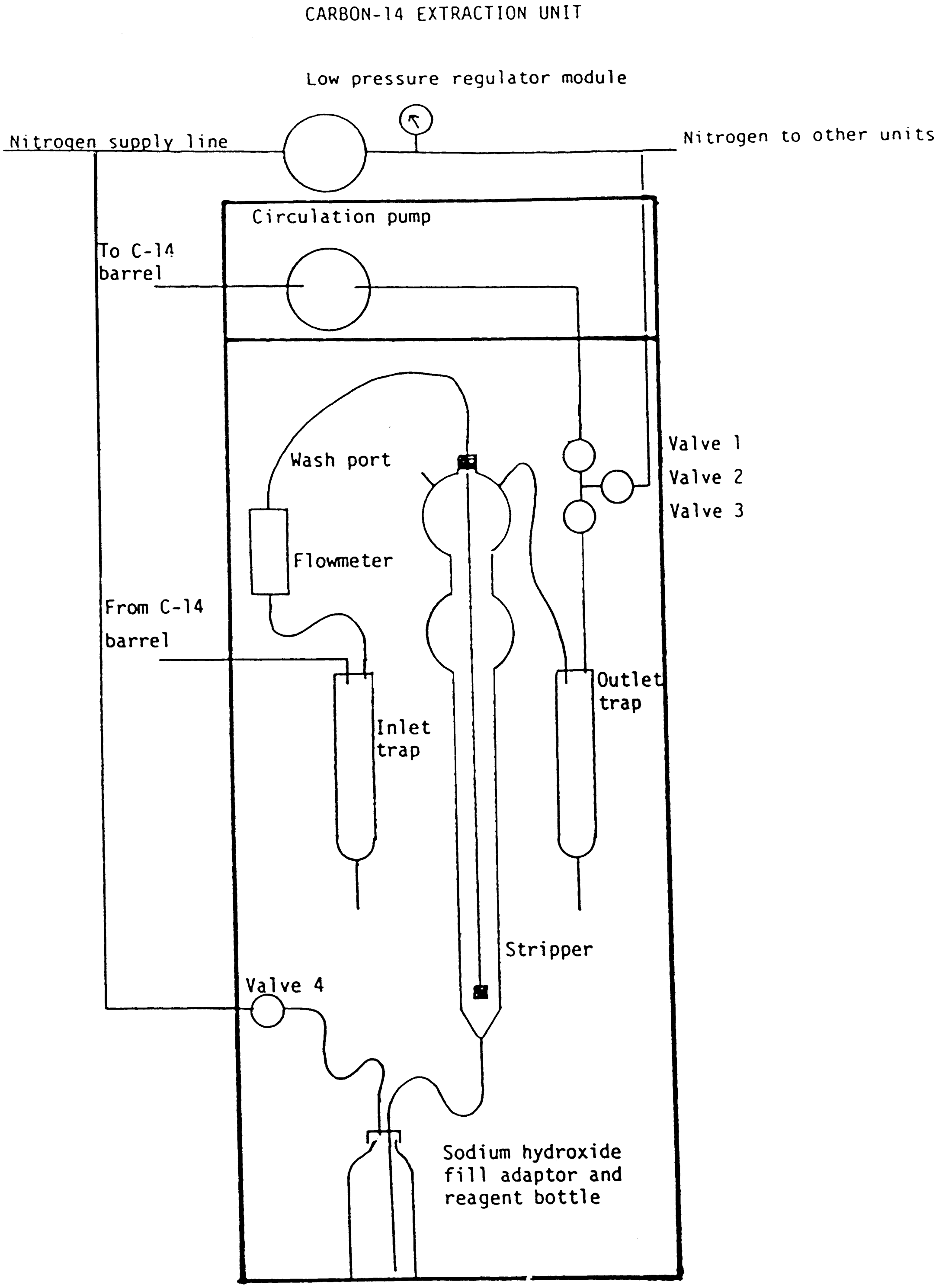

Figure 4: Carbon-14 Extraction Unit

rate. Careful cleaning of the air pumps and low pressure regulators is essential during shore maintenance, but can also be done at sea.

6. Leak Testing and Troubleshooting

The entire extraction system (Figure 5) must be leak free before any samples are processed in order to prevent sample loss and/or air contamination. The leak test is performed just as if a sample were being processed (*i.e.* the barrels are full of seawater except for the 20 liter head space) except that distilled water is substituted for the NaOH solution in the absorber units. The first test for a leak is that the system can be brought to equilibrium pressure. If no leaks are present, then N_2 flow as indicated by the flowmeter will stop in a relatively short time. A more sensitive test is to run the system with the N_2 supply turned off.

If no leaks are present, then the system will maintain pressure during operation for at least 30 minutes. Any leaks must be located and corrected. Since the system operates at a slight positive pressure, liquid leak detector (soap solution or equivalent) can be used to find leaks. Patience is required for leak tests because of the small pressure differential and the large internal volume of the system. Leaks can also be isolated by closing off various portions of the circulation loop using the valves and/or pinch clamps.

Other than leaks, the other problem with the system is decreased flowrate during stripping. Decreased flow (as well as leaks) can be detected by monitoring the flow meter during the extraction. Decreased flow frequently occurs because of some malfunction with the small circulation pump. The most common pump problems are a leak due to a cracked head, plugged valves inside the pump head, and a worn or damaged diaphragm. Plugged valves can often be corrected by simply flushing a small amount of distilled water through the pump. The other problems require disassembly and part replacement. It is advisable to have extra complete pumps on hand in case of failure during a run. Three other common causes of decreased flowrate are kinked tubing, clogged air stones, and a sticking diaphragm on the low pressure regulator.

7. Detailed Procedure

The following is a moderately detailed recipe for transferring and extracting a sample and cleaning up afterwards. The recipe assumes that the filled Gerard is already on deck.

7.1 Sample Transfer and Equipment Preparation

7.1.1 Collect small volume samples from both piggyback Niskin bottle and Gerard barrel (salt, nutrients, *etc.*)

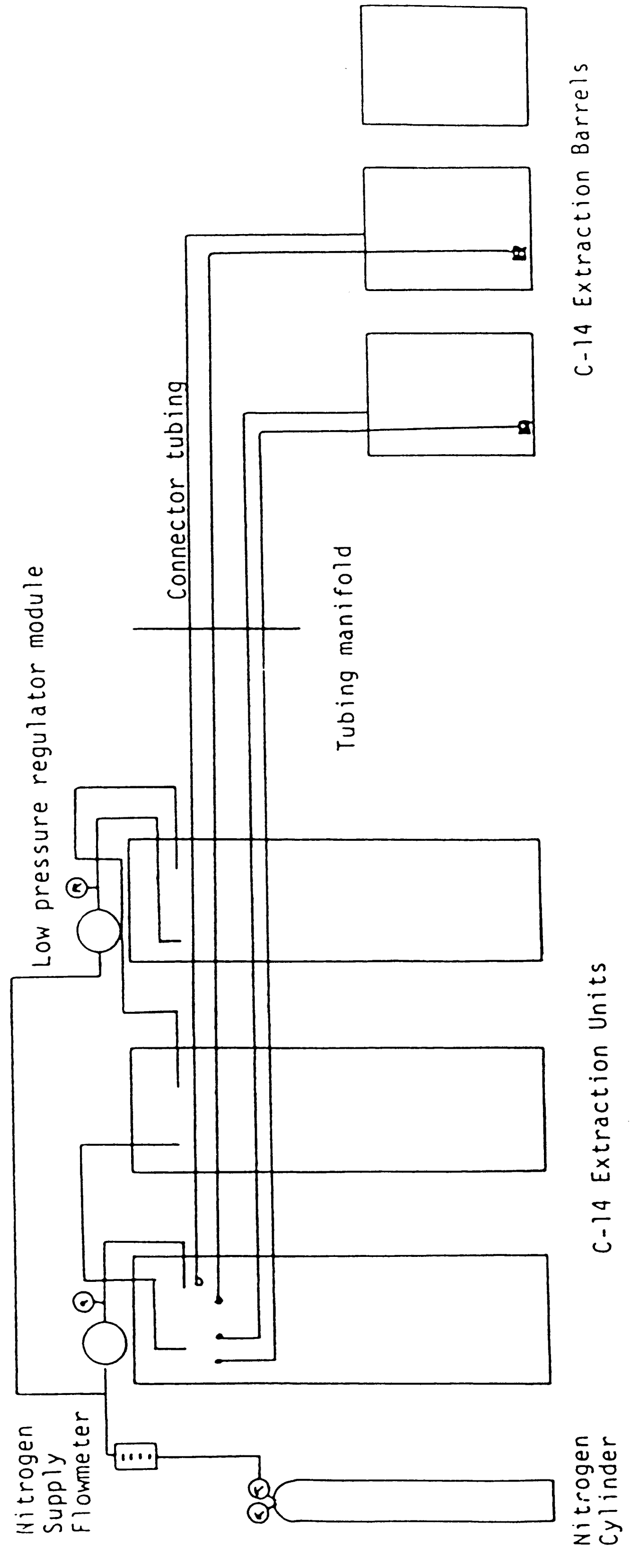

Figure 5: Carbon-14 Extraction System Layout

7.1.2 Transfer water from Gerard to extraction barrel (previously willed with CO_2-free air) until extraction barrel overflows by either pumping or application of pressure to Gerard barrel with CO_2-free air. Close all air and water ports to extraction barrel then proceed to next sample transfer. Continue until all samples from a cast have been transferred to the extraction barrels.

7.1.3 Check to make sure that each extraction barrel is connected to the correct NaOH absorber unit.

7.1.4 Prepare: one 450 ml bottle of low CO_2, NaOH (4N) for each absorber units; ^{14}C extraction data sheet; one 40 ml aliquot of concentrated H_2SO_4 for each extractor barrel; wash bottle with dilute acid and wash bottle with distilled or deionized water for clean up.

7.1.5 Close valves on absorber unit and pinch clamp dual tubing connecting absorber unit to extractor barrel. This prevents sample from being forced into twin tubing as the head space is created.

7.1.6 Check N_2 supply and make sure valve is open.

7.1.7 Create 20 liter head space in each extractor barrel by applying pressure to acid inlet port with CO_2-free air generator. Measure water volume forced out water valve to determine sample volume.

7.1.8 Measure the temperature of the water forced out of the extractor. This temperature is used to determine the extraction time.

7.2 Sample Run

7.2.1 Acidify each sample using one 40 ml aliquot of concentrated H_2SO_4.

7.2.2 Remove pinch clamp on dual tubing (from 7.1.5).

7.2.3 Open valves 2 and 3 (Fig. 4), loosen pinch clamp on absorber wash port.

7.2.4 Clean NaOH adaptor dip leg with Double Distilled Water (DDW) and disposable wipes.

7.2.5 Open and immediately attach bottle of NaOH to adaptor.

7.2.6 Open stripper stop cock and gently close valve 4. Close stop cock when all NaOH has entered absorber tower.

7.2.7 Close valve 3 and clamp off wash port.

7.2.8 Open valve 1 and turn on circulation pump.

7.2.9 Use fingers to pinch off tubing connected to air dispersion tube in absorber tower. Release when sufficient pressure has developed to prevent NaOH from backing up bubbler tube.

7.2.10 Open valve 3 when bubbling begins in tower and record start time.

7.2.11 N_2 supply flowmeter reading should fall to zero as equilibrium is established. Continuing or subsequent flow indicates a leak somewhere in the system.

7.2.12 At equilibrium, flow rates of 280 liters/hour ($\sim$10 ft^3/hr) or greater are acceptable. Lower flow rates indicate poor pump performance or diminished air stone quality.

7.2.13 Clean NaOH bottle cap with dilute acid, DDW, and dry.

7.2.14 Label NaOH bottle including cruise, station, cast, and Gerard barrel information. Etching the glass bottle is one of the best methods of labeling.

7.2.15 Allow stripping to continue until 98% CO_2 extraction has been obtained (Fig. 1). Since the figure is based on theoretical extraction time, rounding should be up to account for any non-ideality in the extraction. Foaming often occurs with very cold samples. It can be decreased by either heating the water in the extractor or by heating the NaOH solution with a heat gun or heating tape. Heating the water has the added benefit of decreasing extraction time.

7.2.16 At end of extraction, turn off circulation pump and close valve 3.

7.2.17 Loosen NaOH adaptor and open stripper stop cock. Over-pressure will force NaOH solution into bottle. Slowly withdraw the adaptor leg as the bottle fills to avoid spattering. If the outlet trap has accumulated an appreciable amount of NaOH due to foaming, drain this into the bottle. Immediately insert the cap plug, secure the cap on the full bottle, and seal with electrical tape.

7.2.18 Close valves 1 and 2.

7.2.19 **Turn off N_2 supply.**

7.2.20 Measure the final sample temperature and make sure that all data have been correctly entered on the log sheet.

7.3 Clean Up

7.3.1 Disconnect twin tubing from manifold on the extractor barrel side and allow pressure in the extractor barrel to force any water out of the tubing. Pinch clamp dual tubing closed.

7.3.2 Open tower cleaning port and stop cock. Remove tygon tube from outlet side (top) of flowmeter to allow cleaning inside of bubbler tube. Rinse tower and bubbler tube with dilute acid followed by DDW water.

7.3.3 Rinse NaOH adaptor with dilute acid and DDW.

7.3.4 Drain traps if necessary, then clean with dilute acid and DDW.

7.3.5 Empty extractor barrel by applying pressure with CO_2-free air generator to acid inlet port, then make sure all barrel ports are closed.

8. Returning Samples to Shore

The NaOH-Na_2CO_3 solutions are packed in wooden crates for shipment to shore laboratories for analysis. Each crate should be checked to confirm that all samples have been correctly labeled and listed in both the log book and on duplicate packing lists. One copy of the packing list should be kept with the log book and the other with the crate of samples.

9. Procedure on Shore

Sample solutions of NaOH-Na_2CO_3 are treated with acid to liberate the CO_2. The evolved gas is then purified and beta counted. The volume of CO_2 extracted from the sample can be calculated from the gas equations after measuring the pressure and temperature in the known volume storage chamber.

^{13}C is determined using a mass spectrometer and the ^{14}C values are corrected for isotope fractionation effects using these results by assuming the ^{14}C effect is twice that of the ^{13}C effect. For further information see Ostlund, *et al.* (1974) and Stuiver, *et al.* (1974).

10. References

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