Collection of ^{85}Kr and ^{39}Ar Samples

William M. Smethie, Jr.
Lamont Doherty Geological Observatory
Palisades, New York 10964 U.S.A.

1. Overview

The analysis of ^{85}Kr and ^{39}Ar in the ocean requires water volumes of about 250 liters and 1200 liters respectively. ^{85}Kr and ^{39}Ar samples can be collected using Gerard barrels, which have a volume of about 250 liters and have proven to be a reliable means of collecting such samples. A single Gerard barrel is required for a ^{85}Kr sample, and ve Gerard barrels are required for an ^{39}Ar sample. The dissolved gases in these water samples must be extracted at sea and returned to a shore-based lab for the ^{85}Kr and ^{39}Ar analysis. A large volume vacuum extraction system has been developed at Lamont-Doherty Geological Observatory (LDGO) for this purpose. A schematic diagram of this system is shown in Figure 1. Water is sprayed into a vacuum chamber where it rapidly degases from the small spray droplets and by owing through a column of small plastic cylinders. Degased water is continuously pumped out of the chamber as more water is pumped in, and the extracted gases are pumped through a condenser and several water traps to a previously evacuated cylinder. This system and the design criteria are discussed in detail in Smethie and Mathieu (1986) and the detailed operation procedure is given below.

2. Extraction Procedure

2.1 Preparation

Preparation of the extraction system should begin approximately one hour before the samples arrive on deck. Preparation steps are given below.

1. Remove all water from the glass water trap and the refrigerated water trap (RWT). Clean grease o of the gasket to the RWT and put fresh silicone grease on the gasket.
2. Turn on the diaphragm vacuum pump with valves V1, V2, and V3 closed, and V5 open to the atmosphere. Make sure that the top of the refrigerated water trap seals against its gasket. Turn on the RWT.
3. After the RWT has cooled for 30 minutes, turn on the high vacuum pump, close valve V4 and open valves V1 and V3 to evacuate the extraction chamber.
4. Pack the drying column with fresh Drierite and connect an evacuated sample cylinder to the system.

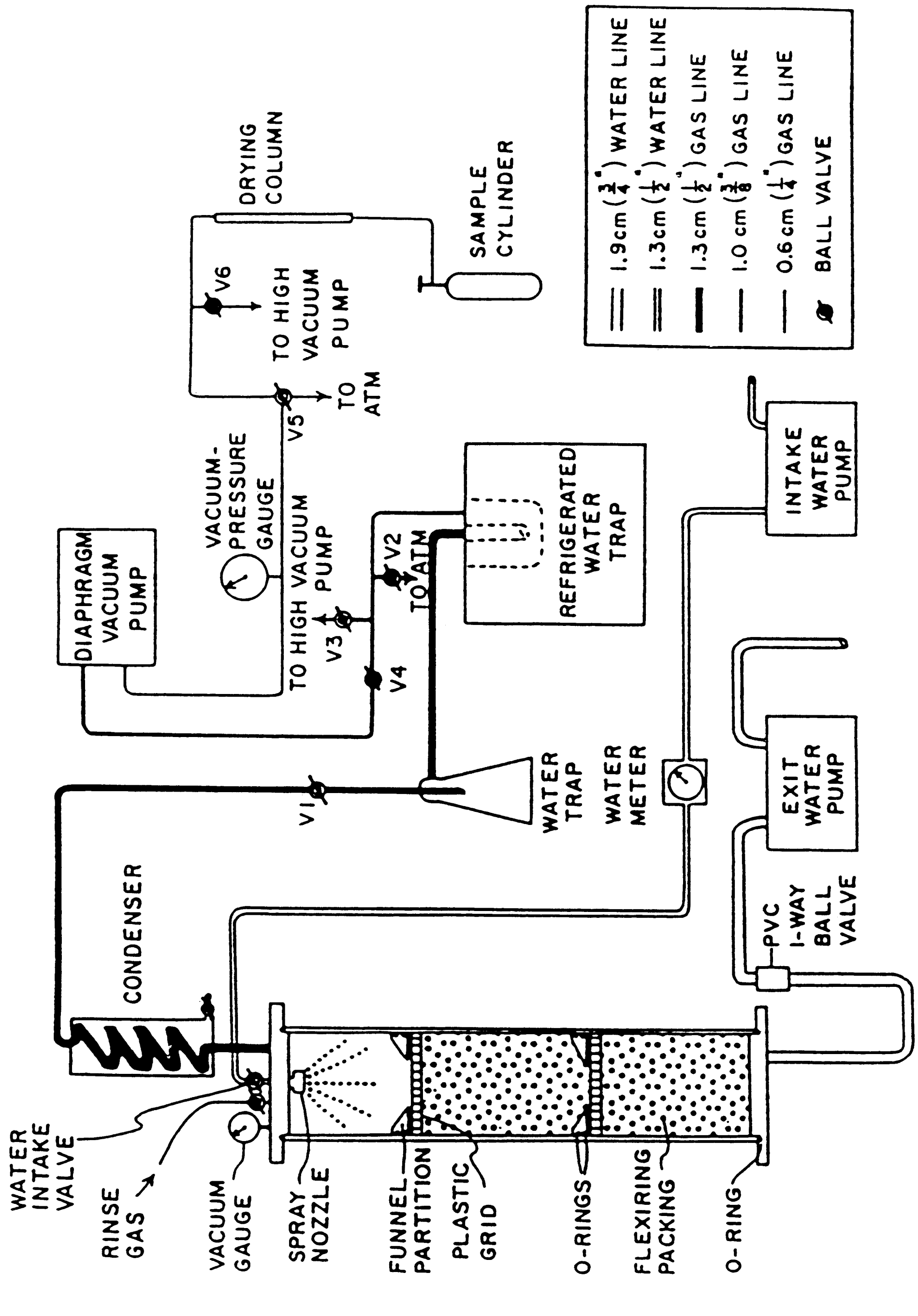

Figure 1: Schematic diagram of the L-DGO large volume vacuum extraction system.

5. After the extraction chamber has been evacuated for about 10 minutes close V3 and open V6 to evacuate the drying column.

6. Drain any water that may be in the condenser jacket and pack it with crushed ice. The system is now ready for a water sample.

2.2 Sample Extraction

1. Determine if the sample cylinder has been evacuated. This is done by closing V6, opening V5 to the sample cylinder, opening the sample cylinder valve and reading the pressure on the vacuum-pressure gauge. If the cylinder is not evacuated, open V6 to evacuate it.

2. The Gerard barrels are overpressured with nitrogen to prevent atmospheric contamination of the sample as it is drained from the Gerard barrel. Connect the overpressure line to the Gerard barrel to be processed by removing the pressure relief valve from the Gerard barrel and replacing it with an adapter that is then connected to a nitrogen line. Check the nitrogen pressure. It should be 3.5 kPa (0.5 psi).

3. Connect the extraction system water intake hose to the Gerard barrel and purge the connection with sample water by opening the Gerard barrel valve and the small valve on top of the connector.

4. Draw the salinity, total CO_2, and any other samples to be taken from the Gerard barrel through the small valve on top of the connector. Then open the intake hose valve.

5. Rinse the intake hose as follows. Close the sample cylinder valve. Valve V5 should be open to the sample cylinder. Valve V4 should be closed and valves V1 and V3 opened so that the extraction chamber is being evacuated by the high vacuum pump. Open the water intake valve at the top of the extraction chamber, turn on the water intake pump, and allow 7.6 liters (2 gallons) of water to ow into the chamber. Use the water meter to measure the volume. Then turn o the water intake pump and close the water intake valve. Never turn on the water intake pump with water intake valve closed or close the valve while the pump is running. If this happens, the water line between the intake pump and the extraction chamber will burst. Turn on the exit water pump to pump the 7.6 liters out of the extraction chamber, then turn the pump o . Do not run the water exit pump without water owing through it, or the pump will be damaged.

6. Rinse the extraction chamber as follows. Open the rinse gas valve on top of the extraction chamber and allow nitrogen to ow in until a pressure of 84.4 kPa (25 in. Hg) is obtained. Evacuate the chamber for about 10 minutes.

7. Check the system for leaks using the following procedure. Close valve V3, open valves V4 and V6. Valve V5 should be open to the sample cylinder. The entire extraction system is now being evacuated by the diaphragm vacuum pump and the high vacuum pump in series. The vacuum-pressure gauge should read 10^{7} torr if the system is completely evacuated. Close valve V5. The extraction chamber is now being evacuated

by the diaphragm vacuum pump into a dead volume of about 70 cm^3 connected to the vacuum-pressure gauge. If there is a leak, gases will accumulate in this dead volume and the pressure will increase. If there is no pressure change in 3 minutes, the system is leak tight and ready for the sample. If there is an increase, it may be caused by the chamber not being completely evacuated. Valve V5 should be opened to the sample cylinder and V3 opened to the high vacuum pump, the system evacuated for 5 minutes, and then leak tested again. If the pressure again increases there is a leak. See the trouble-shooting section for procedures to locate the leak and fix it.

8. Open the sample cylinder valve and valve V5 to the sample cylinder and close valves V3 and V6. Record the water meter reading, the initial pressure, and the time on the extraction log sheet. Open the water intake valve, turn on the intake water pump and turn on the exit water pump. This should be coordinated with the person doing ^{14}C since the water exiting the extraction system will be collected in a ^{14}C extraction barrel.

9. During the extraction process, the pressure will slowly build up. This should be recorded at approximately 10-minute intervals on the extraction log sheet. The water intake hose should be inspected for bubbles several times during extraction. If bubbles are present, there is either an air leak or the overpressure gas is not filling the Gerard barrel, and a vacuum is being pulled on the water causing it to degas. See trouble-shooting section.

10. The extraction chamber has a volume of about 38 liters, and a significant amount of extracted gases can reside in it at the end of an extraction, because the diaphragm vacuum pump will only reach a vacuum of about 10^{-6} torr (29.5 in. Hg). To minimize this loss, the chamber is allowed to fill with the last 38 liters (10 gallons) of the sample. Usually 250 liters (65 gallons) of water are extracted from a single Gerard barrel. When the water meter shows that 210 liters (55 gallons) have been pumped into the system, record the time and pressure on the extraction log sheet and turn the exit water pump off. Allow the chamber to fill to within about 1 inch of the top. Then turn off the intake water pump and close the water intake valve. If bubbles appear in the intake water hose before the chamber has filled, the Gerard barrel is empty and overpressure gas is entering the extraction chamber. Immediately turn off the intake water pump and close the water intake valve. Since the overpressure gas contains no krypton or argon, the sample does not become contaminated when this occurs, but it should be noted on the extraction log sheet.

11. Continue evacuating the extraction chamber for 3 minutes. Then record the time, the final pressure, and the final water meter reading on the extraction log sheet. Close the sample cylinder valve, switch valve V5 to the atmosphere, and remove the sample cylinder. Turn on the exit water pump and pump the water out of the extraction chamber.

12. To process another sample, connect an empty sample cylinder to the extraction system and repeat steps 1–11.

2.3 Argon-39 Samples

To collect an ^{39}Ar sample, ve or six Gerard barrels are hung at 10 m intervals on the trawl wire and tripped at the desired depth. The extraction procedure is basically the same described above for single Gerard barrel samples, except the extracted gases from the ve or six Gerard barrels are collected in a large sample cylinder. If two extraction systems are used for a single sample, they are connected together downstream of the drying columns just prior to the sample cylinder. Steps 1{12 of the extraction procedure should be followed, except that it is not necessary to rinse the water intake hose or the extraction chamber or perform the leak test between Gerard barrels processed for a single ^{39}Ar sample.

2.4 Shut Down Procedure

After completing extraction of a series of samples, the following procedure should be used to shut the system down.

1. Rinse water pumps and extraction chamber with fresh water. Place the end of the water intake hose in a bucket of fresh water and pump 7{10 liters into the extraction chamber. Then turn on the exit water pump and pump it out. Repeat this procedure once.
2. Shut o the diaphragm vacuum pump as follows. Close valve V1, open valve V5 to the atmosphere, and then open valve V2 so that air is being pumped through the diaphragm vacuum pump. Then turn the pump o . If the pump is turned o under a vacuum, it may rupture a diaphragm.
3. Open valve V3 and turn o high vacuum pump.
4. Turn o the refrigerated water tap (RWT).
5. If the extraction system will not be used for a week or more, the hoses should be disconnected from the water pumps and the pumps completely drained to prevent rust. Also, prior to processing samples again, water should be pumped through the intake water pump before it is connected to the extraction chamber to prevent any accumulated rust from being pumped into the extraction chamber.

3. Calculation of Recovery

The volume of gases extracted should be determined for each sample and compared to the volume expected. If things are working properly, the extraction e ciency is usually 90{95%. If the extraction e ciency exceeds this, either some overpressure gas got into the sample at the end of the extraction or there was a leak and the sample is contaminated with air. If the extraction e ciency is less than this, the gas line between the extraction chamber and the sample cylinder may be partly clogged.

The volume of gases extracted is determined from the volume of the sample cylinder and the final pressure from:

$$Vg = \left(1 + \frac{P}{14.7}\right)(V_C)\left(\frac{273}{T_R + 273}\right) \tag{1}$$

where Vg is the volume of gas recovered at 0°C, P is the final pressure in bars (1 bar = 10^5 Pa = 14.7 psi), V_C is the volume of the cylinder, and T_R is the room temperature in $^\circ$C. If pressure is measured in psi, divide P by 14.7 to get P in bars.

The volume of gas expected is calculated from:

$$V_E = [N_2 \text{ solubility} + \text{Ar solubility} + O_2 \text{ concentration} + 0.0005]V_W \tag{2}$$

where V_E is the volume expected in milliliters, V_W is the volume of water in liters, the solubilities and oxygen concentration are in milliliters/liter, and 0.0005 is the amount of CO_2 in milliliters extracted per liter of seawater. The oxygen concentration should be taken from measurements made on the Gerard barrel, if available, or interpolated from the rosette cast.

4. Troubleshooting

4.1 Water Pumps

The water pumps have proven to be very reliable as long as they are rinsed with fresh water after use. If a pump fails to work properly, it should be replaced with a spare. There are also pump repair kits. Note that the intake water pump and exit water pump are different models, # 33201 for the intake water pump, and # 34401 for the exit water pump.

4.2 High Vacuum Pump

The oil in this pump should be checked daily. Occasionally, water vapor will enter the pump and form an emulsion with the oil. When this occurs, the oil should be changed.

4.3 Diaphragm Vacuum Pump

Occasionally, the diaphragm will rupture. A large leak will develop when this occurs and the pressure will rapidly increase. Valve V5 should be opened to the atmosphere and the pump turned off. The diaphragm should be replaced.

These pumps also have metal flappers in the heads which can become damaged, particularly if water accidently gets into the pump. If the pump appears to have an internal leak or is not pumping efficiently, the flappers should be inspected and replaced if necessary.

Leaks can occur where the head is connected to the body of the pump. To fix such a leak, first try tightening the head bolts. If the leak persists, remove the head and install a new gasket. The newer model pumps have a thin head which is not quite rigid enough to form a good seal against the gasket and it may be necessary to use some silicone cement to achieve a good seal.

4.4 Clogs

Clogs in the gas line at the top of the condenser and within the RWT can occur as the result of ice formation. When this happens, the pressure on the vacuum gauge on top of the extraction chamber will increase as gases accumulate in the chamber, while the pressure on the vacuum-pressure gauge remains constant. A clog at the top of the condenser can be cleared by heating the top of the condenser with a hair dryer. If the RWT clogs, turn the unit o , remove the top and heat with a hair dryer to speed thawing. Clean all ice and water from trap, reassemble it, evacuate and leak check. If the RWT is cold when it is initially evacuated, small ice crystals may form on the gasket and prevent a good seal.

Salt deposits may build up in the bottom of the condenser. If the condenser is clogged after being heated, this is probably the cause. The condenser should be removed and ushed with fresh water to dissolve the salt.

4.5 Leaks in the Gas Line

If the leak test described in step 7 of the extraction procedure shows a leak to be present, it can be isolated using the following procedure. Close valve V4 and perform leak test. If a leak is present, it is in the diaphragm vacuum pump or any ttings between the diaphragm vacuum pump and V4. If there is no leak, open valve V4 with valve V1 closed, to check for leaks in the water traps. If no leaks are found, open valve V1 to determine if the leak is in the extraction chamber or condenser. Some initial places to check for leaks are the gasket on the RWT, the O-rings in the Cajon ttings, and the exit pipe connection at the bottom of the extraction chamber. A leak at the exit pipe connection can be identi ed by pumping about 4 liters (1 gallon) of water into the chamber and checking to see if bubbles enter the chamber from the exit pipe opening. O-rings on the Cajon ttings leak if they become nicked, or dried out and brittle, and should be replaced if these conditions exist. A very small amount of silicone grease applied to an O-ring may also create a better seal.

Circumstances may arise where a small leak develops while running samples. If the leak cannot be quickly found and xed, it will be necessary to process the samples with the leak. In this case the leak rate should be determined so a correction for atmospheric contamination can be applied later. To determine the leak rate, perform the leak test for about 10 minutes and record the pressure change during that time interval. The amount of gas that would leak into a sample during a 40-minute extraction can then be calculated from:

$$Vg = \frac{\quad}{30} (70) \frac{40}{t} \qquad (3)$$

where is the change in pressure in in.Hg, and t is the length of time in minutes that the test was performed.

4.6 Leaks in the Water Line

If bubbles appear in the intake water hose, air is leaking in. If overpressure gas is not owing to the Gerard barrel, a partial vacuum will occur in the Gerard barrel and water lines connecting the Gerard barrel to the extraction system. This can cause air leakage at the hose connection to the Gerard barrel. Check to see that this connection is tight and that overpressure gas is owing to the Gerard barrel.

4.7 Other Problems

Sometime the one-way ball valve between the extraction chamber and the exit water pump sticks and water cannot be pumped from the extraction chamber. Try tapping the valve to unstick it. If this does not work, close valve V1 and ow a couple of gallons of water into the extraction chamber. Then bleed rinse gas into the extraction chamber with the exit pump running. When the valve opens, close the rinse gas valve and open valves V1 and V3 to evacuate rinse gas.

5. Reference

Smethie, W. M., Jr. and G. Mathieu, 1986. Measurement of krypton-85 in the ocean. Mar. Chem., 18, 17{33.