

Large Volume Sampling

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1. Equipment

1.1 Large Volume Samplers

With the exception of ^{39}Ar , all of the WHP large-volume (LV) tracers require 200–300 liter samples (^{39}Ar requires ~ 1250 liters). This limits the choice of currently available samplers to either Gerard-Ewing bottles or 100-liter Niskin bottles hung in pairs. All of the major LV tracer expeditions of the past two decades have used Gerard barrels, and this is expected to continue throughout WOCE. The remainder of this discussion assumes that Gerard barrels will be used. If, instead, 100-liter Niskin bottles are used, they should be paired up (two bottles hung as close as possible per sample) and confirmatory samples (salt, *etc.*) should be drawn from each.

1. Design: All of the Gerard barrels currently in use have a volume of approximately 270 liters, are made of 300 series stainless steel and are designed to flush on the down cast while hung on wire rope. The barrels are closed either acoustically or with a messenger. Water is removed from the sampler by either gravity or pumping. If neither ^{39}Ar nor ^{85}Kr are being collected from the Gerard, then the water sample can also be forced from the Gerard by pressurizing the head space with CO_2 free air.
2. Contamination Considerations: The O-ring seal on the lid of each Gerard barrel must be made of material which is non-contaminating for all sample types to be collected. This is especially critical if chlorofluorocarbon samples are taken from the barrels. The only acceptable lubricant which may be applied to the O-rings is silicon stop cock grease (Dow Corning or equivalent). Hydrocarbon based lubricants (*e.g.* ApiezonTM) should not be used. Each bottle must be thoroughly cleaned before use. The cleaning is necessary in order to remove oils and greases which are often applied prior to storage to reduce corrosion. If either ^{85}Kr or ^{39}Ar samples are being collected, the head space created in the top of the barrel as the sample is removed must be replaced with a gas which is non-contaminating to all sample types. Nitrogen (99.998% pure) is well suited for this purpose. Helium should not be used if ^3H samples are being collected on the cruise.

Each bottle must be equipped with some means of recording *in situ* temperature and pressure at the trip time. This can be either the standard reversing thermometer arrangement mounted on the piggyback sampler or electronic sensors.

1.2 Piggyback Samplers

Piggyback samplers mounted on the LV samplers have one purpose: confirmation of proper trip on Gerard barrel.

Niskin bottles ranging upward in size from 1.2 liters are generally used with the size depending upon the samples needed. The technical group responsible for providing these bottles should be notified well in advance since changing bottle size requires minor fitting modifications. These bottles must be clean and equipped with O-rings and closure ‘springs’ which are non-contaminating to the samples being collected. If necessary, O-rings should be lubricated with silicon, not hydrocarbon-based grease. If chlorofluorocarbon samples are being collected from the piggyback Niskin bottles, then grease should not be used at all on the O-rings. Commercial Niskin bottles should not be acid washed since many of the fittings are made of nylon.

1.3 Cast Hanging

1. Wire: Large-volume casts should be hung using known, high-quality ‘new’ wire rope. Synthetic cable use is currently developing and may eventually replace the standard wire.
2. Bottle Distribution: There are two basic methods to hang an LV cast—dispersed and grouped. Each has advantages and disadvantages. General practice has been to hang no more than nine LV bottles on any cast due to wire strain considerations.
 - (a) Dispersed: This is the standard method where bottles are hung along the wire at the appropriate locations to sample the chosen water masses. This method has been thoroughly tested. Hung this way bottles can be tripped either acoustically or by a messenger. This method has the advantage that flushing occurs as the bottles are lowered and only one or two yoyo-ing winch motions are necessary at the maximum wire out distance to ensure proper sampling. The primary disadvantage is that the deck crew responsible for hanging the cast must be on hand for the entire cast.
 - (b) Grouped: With this method all of the bottles are hung near the terminal end of the wire. The primary advantage to this method is that the deck crew can work on other tasks while most of the wire is spooled out and retrieved. The disadvantages are that the Gerard bottles must be equipped with acoustic triggers; significant yoyo-ing is necessary to capture the desired water since closure is on the up cast; and the fact that the method has not been tested except by one group in the U.K.
3. ^{39}Ar Casts: One ^{39}Ar sample requires five Gerard bottles, and one profile requires ten samples. The general procedure is to hang ten bottles per cast in groups of five with an inner group spacing of 10 m. One cast is taken on each of five successive stations to produce a profile.

2. Sample Collection

The WHP sampling sequence is the same as that developed during the TTO and SAVE cruises. The procedure has been thoroughly tested and modified to minimize possible contamination sources. Obviously, sampling should be completed as soon as possible after a cast is on deck. It is imperative that anyone discovering a problem with a cast or individual sample notify *all* those working on that sample(s) as soon as possible. Any problems, or irregularities, must be recorded in the permanent record. Each sample collected must be tagged in some manner to the specific sample bottle used in order that histories can be developed for each sampler for quality control purposes.

2.1 Large-Volume Samples

Gerard barrel sample drawing follows the general sequence: ancillary samples (salinity *must* be sampled), $^{85}\text{Kr}/^{39}\text{Ar}$, ^{14}C , other. The sample path is shown schematically in Figure 1. This procedure is based upon TTO/SAVE cruise experience and may change somewhat depending on proposed extractor changes. With this technique, extreme care must be taken to avoid errors in sample routing and record keeping. One method to minimize this is to develop a routine among the technicians responsible so that everything is done repetitively and serially, *i.e.*, shallowest Gerard to lowest tank or extractor number, etc. Good communication between the technicians making diverse measurements is absolutely necessary.

2.2 Piggyback Samples

The sampling sequence for the piggyback samplers is the same as for Rosette samples, except that the sample suite will often be smaller. The sample set may include temperature, salinity, oxygen and nutrients. These samples are necessary to confirm a good trip and to avoid interpolation. Figure 2 shows the WHP sampling sequence for Rosette (piggyback) Niskin samples.

2.3 Surface Samples

Surface samples should be collected to accompany cast samples. These should be taken either by bucket or by lowering a hose to the surface and pumping. The ship's bow pump should not be used to collect these samples due to contamination and the fact that the intake for these pumps is significantly below the surface. This depth difference can lead to significant sampling error especially in high latitudes and near continents. Salinity, temperature, and nutrient measurements should be taken to accompany surface tracer samples.

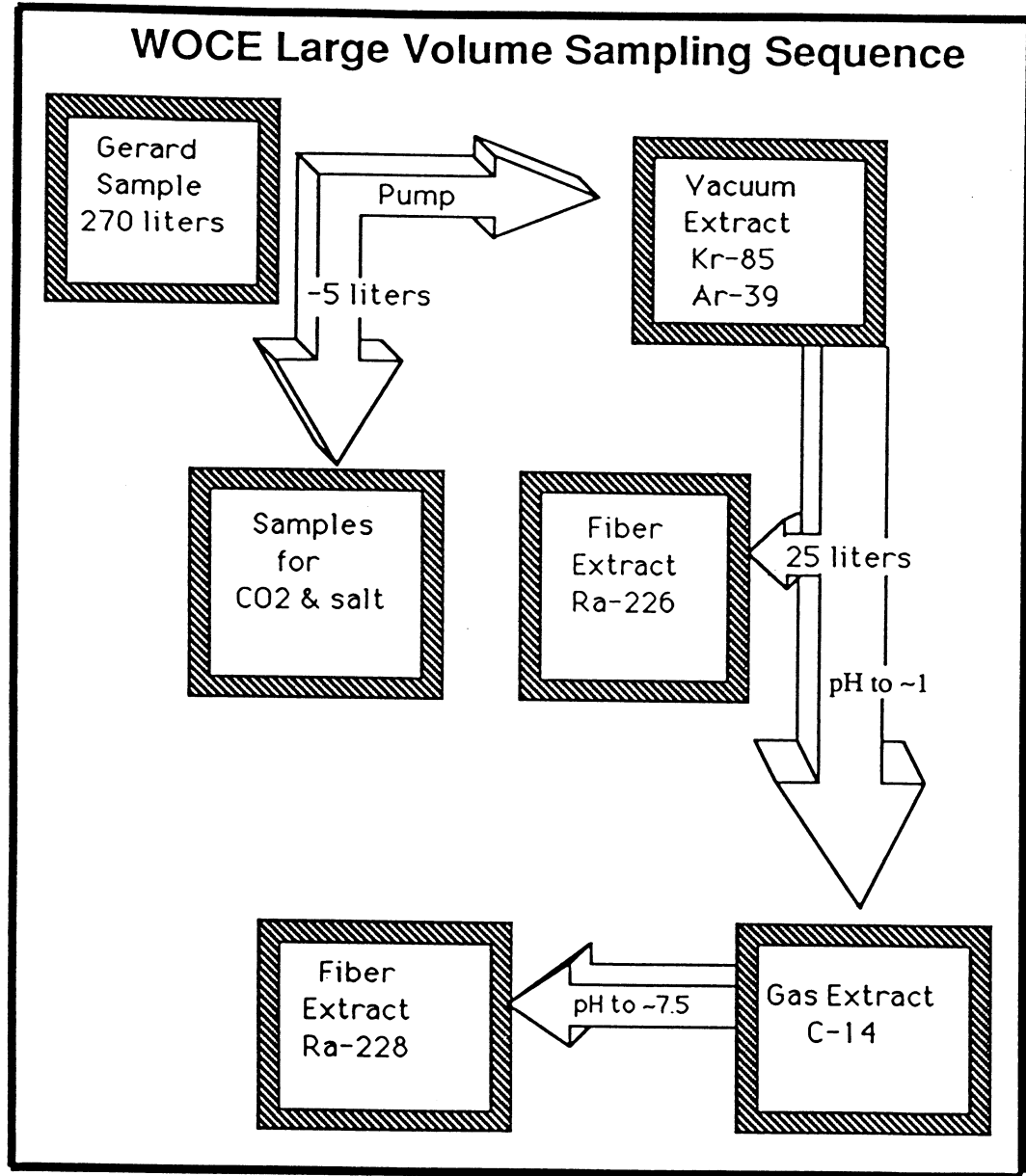


Figure 1: Large Volume Sample Drawing Sequence

SV SAMPLE DRAWING SEQUENCE

- **Chlorofluorocarbons**
- **Helium Isotopes**
- **Oxygen**
- **Total CO₂**
- **pCO₂ or Alkalinity**
- **AMS Carbon-14**
- **Tritium**
- **Nutrients**
- **Salinity**

Figure 2: Small Volume Sample Drawing Sequence

2.4 Sample Distribution

2.4.1 Areal

The *average* spacing for LV stations along WOCE tracks is 300 nm; however, the true distribution must be adjusted to adequately map open ocean gradient regions and continental boundary effects. The major goal of all LV sampling is to collect a representative global data set. Figure 3 illustrates adaptation of a similar distribution philosophy on an E-W SAVE transect along 47°S in the Atlantic Ocean. Note the close spaced stations along the western continental rise (looking for a deep western boundary current signal and continental effects in near surface waters) and the station separation increase as the track moved into the Argentine Basin. Principal Investigators responsible for LV sample collection should provide the Chief Scientist with station placement guidelines along with contingency plans and/or station priority lists and a brief explanation of the science behind the plan.

2.4.2 Depth

Depth selection philosophy for LV sampling is similar to a Rosette except that it is sparser. Bottle separation generally increases with depth through the thermocline to some near constant value for deep water. If ^{228}Ra samples are collected, near bottom sample density is increased. The sampling depths illustrated in Figure e were a compromise to accommodate the different distributions and sources of ^{14}C , $^{85}\text{Kr}/^{39}\text{Ar}$ and ^{228}Ra . It is statistically questionable, as well as extremely difficult (if not impossible), to sample very small-scale features which may appear on CTD traces.

During many WHP cruises, upper water column ^{14}C samples will be small volume (for AMS analysis). This means that unless ^{85}Kr or ^{228}Ra sampling is planned, all of the LV samples will be concentrated in the lower water column. When this happens, the small volume cast (Rosette) ^{14}C sampling depths should overlap with the shallowest large-volume cast ^{14}C samples. For early expeditions, the shift-over point from small to large samples for ^{14}C should be that depth where the tritium concentration approaches the detection limit. In the Pacific this corresponds approximately to the surface $\sigma_\theta = 27.1$.

If upper water column samples are required for ^{85}Kr or ^{228}Ra , or if ^{14}C samples are to be counted using traditional techniques, then the two LV casts must be spread over the entire water column. This will provide a profile of 19–21 samples. Figure 3 is a reasonable example of this type sampling.

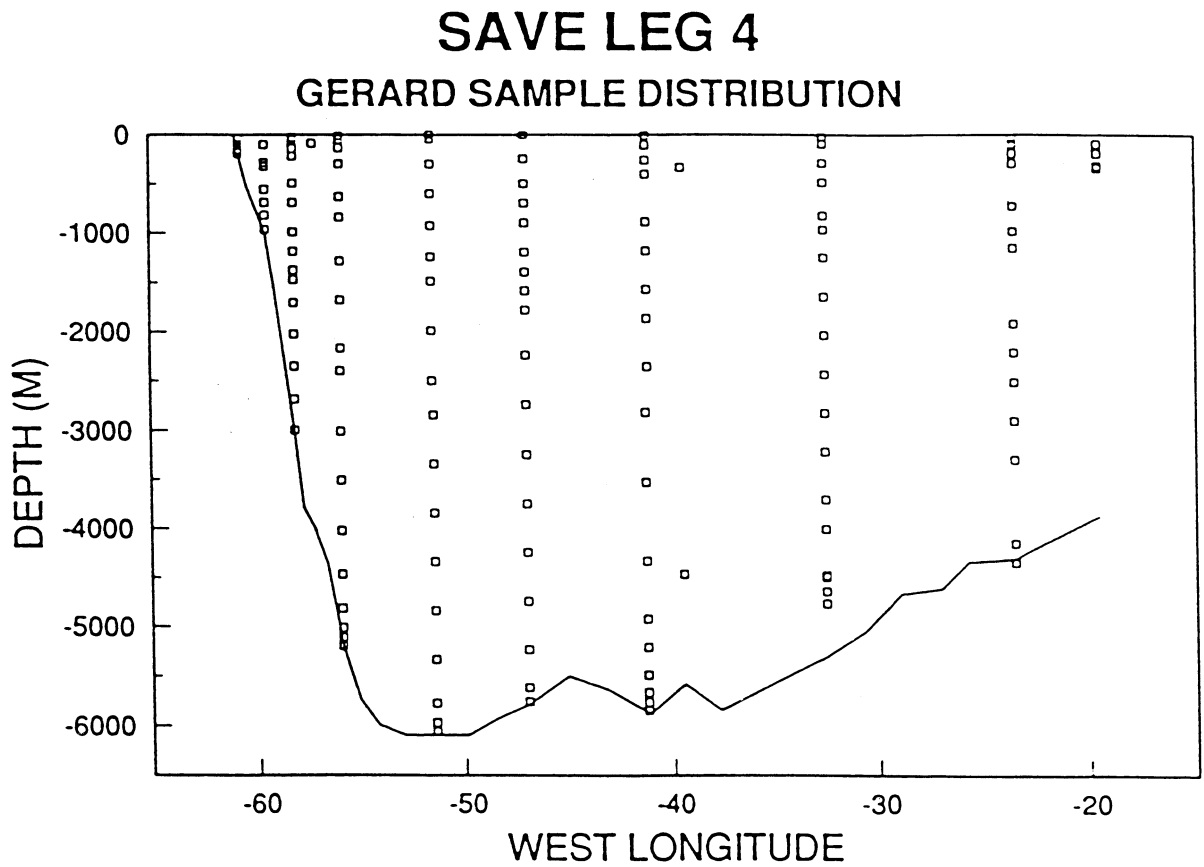


Figure 3: An example of the distribution of large volume samples from a SAVE section across the South Atlantic