



## SAMPLING AND MEASURING HELIUM ISOTOPES AND TRITIUM IN SEAWATER

W. J. Jenkins, D. E. Lott, K. Cahill, J. Curtice, P. Landry

Woods Hole Oceanographic Institution

Woods Hole, Massachusetts 02543 U.S.A. e-mail: wjenkins@whoi.edu, dlott@whoi.edu, kcahill@whoi.edu, jcurtice@whoi.edu, plandry@whoi.edu

### 1. INTRODUCTION

This document is meant to describe the essential elements of sampling and measuring helium isotopes and tritium in seawater. The methods described are those that have been used in our laboratory, and should not be regarded as the only means of making such measurements. Rather, they are provided as a guide for those interested in evaluating or comparing such techniques with others and for understanding the limits of the measurements and the resulting data. Other summaries of experimental procedures are available in the literature (Jenkins and Clarke, 1976; Clarke et al., 1976; Jenkins, 1981; Lott and Jenkins, 1984; Bayer et al., 1989; Lott and Jenkins, 1998; Stanley, 2007; Stanley et al., 2009).

Helium isotopes are extracted from sea water and analyzed by mass spectrometry. Tritium is determined by first degassing the seawater, storing it *in vacuo* for several months or more, and mass spectrometrically measuring the  $^3\text{He}$  that grows in from tritium decay. This regrowth technique yields results consistent with “direct” measurement via gas-proportional counting (Bayer et al., 1989), but with substantially lower detection limits (Jenkins et al., 1983; Lott and Jenkins, 1998).

### 2. TAKING SAMPLES AT SEA

We describe here three basic sampling methodologies for helium isotopes, and one for tritium. The helium isotope sampling methods include either sample storage in copper-tubing for shore-based gas extraction, or at-sea extraction of dissolved gases into glass ampoules. Tritium water samples are transferred to pre-treated, argon filled, flint glass bottles and sealed with high density polyethylene caps secured with black plastic electrical tape.

#### 2.1 Helium Isotope Samples

Samples taken at sea for helium isotope analysis must be stored in sealed containers which have a low permeability for that element. This restricts the choice of materials to soft metals (e.g., copper) or special kinds of glass. The former is the more generally used material at sea. Samples are generally taken in copper tubing, a metal which is sufficiently soft to make a good, helium leak-tight seal. The seal is made either by clamping the tube to provide a non-welded metal-metal seal, or crimped to form a pressure welded seal. Dehydrated, soft annealed, refrigeration-grade copper tubing (typically 0.95 cm OD) is used to collect clamped tube helium samples. The copper is cut into about 1 m lengths and mounted in an channel and clamp assembly consisting of an aluminum channel with steel clamps mounted a few centimeters from either end. In the past, plumber's pinch-clamps were used (Imperial Eastman No. 105), but experience indicates that these clamps do not perform well

under repeated use (they warp, increasing their gaps), the bolts tend to shear easily, and they are susceptible to salt-water induced corrosion. Better clamps can be custom-fabricated from case-hardened mild steel with optimum gap width (0.4 to 0.8 mm) and minimal creep fatigue. Good corrosion resistance is achieved by metal plating. The clamps (Figure 1) are attached to the channel by screws and are partially closed to secure the copper tube during shipment.

Typically, a shorter length of larger diameter tubing is used when samples are cold-weld sealed. Diameters of 1.6 to 1.9 cm have been used, with a length sufficient to provide a water sample of 30 to 90 cc. The tubing must be soft annealed OFHC copper, with a very clean inside surface to facilitate cold welding. On some larger diameter tubing, the surface must be mechanically cleaned to obtain good results.

During many of the WOCE/CLIVAR cruises, samples were gas extracted at sea. Although requiring more equipment and more work at sea, the method offers the advantage of eliminating the time-consuming shore-based step of sample extraction.

Samples are transferred from the Niskin (or other sampling) bottle to the copper tubing using a gravity-feed technique through lengths of plastic tubing (see Figure 2). Although plastic is relatively permeable to helium, the seawater does not spend sufficient time in the tubing to be appreciably compromised. The clear tubing has the advantage of making air bubbles visible. It is advisable to soak and store the plastic tubing prior to initial use in a bucket of sea water, as this appears to reduce the tendency for small air bubbles to stick to the inner surface of the tubing. It is important during sampling to eliminate air bubbles because of helium's very low solubility: a small amount of air inclusion will result in a large helium contamination, particularly if "tank helium" is being used on the ship (see below). Moreover, helium's relatively high molecular diffusivity makes it prone to rapid equilibration of the flowing water with such air bubbles.

*Clamped Copper Tubing:* To draw a sample, two pieces of tubing are attached to the ends of the copper tube, and the lower end is attached to the spigot on the Niskin bottle. The sample is held vertically above the water level in the Niskin bottle, the valve is opened to establish flow, and the sample is lowered over a ten- to twenty-second period to establish gravity flow. The relatively slow entry of the water into the container minimizes trapped air and bubble formation in the container. The amount of water flushed through the copper tube should be at least five or six volumes. During the "flush" period, the container is tapped (usually with a wooden baton or a wrench) to remove bubbles. For clamped samples, the seal is made by tightening the top clamp first, and then the bottom clamp. The clamps should be tightened until the edges meet where the bolts transect the clamp (Figure 1). Prior to tightening, the copper tubing should be situated near the center of the clamp. It is also important to insure that the sealing surface of the clamps are free from grit or foreign materials, as this may lead to fracturing the copper pinch seal or making it brittle. After sampling and prior to storage in shipping containers, all salt water should be removed from the containers. Best practice is to dunk both ends of the sampler in a bucket of fresh water, then rinse the inside of both ends twice with distilled water, and once with isopropanol using squirt bottles, shaking liquid out of the ends between rinses.

*Cold-weld Sampling:* For the cold weld samples, which have a larger diameter, an adapter is needed to connect to the smaller diameter plastic tubing. Also, the filling procedure is terminated using pinch clamps on the plastic tubing. The sampler is then placed in the cold welder and the seals are immediately made. The cold welder consists of a set of hydraulically actuated jaws. The hydraulics

may be powered either by a manual pump, or a pneumatically driven system. The jaws are commercially available "knife edges", or more usually lengths of 1.25 cm diameter tungsten carbide dowel pins. Experience indicates that the jaw surfaces must be kept in good condition: scratch and corrosion free, well lubricated, and free of grit, salt and dirt. Prior to sampling, a small portion of the cold weld sample tube is flattened to reduce internal volume slightly. After sealing, that portion is re-rounded to increase internal volume, and maintain the copper seal at a negative pressure. The containers should also be rinsed free of salt water and dried prior to storage.

*At Sea-Extractions:* Samples are drawn from the Niskin bottles using the same techniques as above, but using type 316 stainless steel sample cylinders. The cylinders are constructed from 2.54 cm O.D. stainless steel tubing welded to plug valves (Nupro SS-4P4T-3571) via custom made diameter reducing adapters. The internal volumes of these units are typically 90 cc. The plug valves are either modified by drilling a 0.094 inch hole through one side of the plug into the bore, or the plugs are replaced with plugs with pump-out holes (Nupro SS-P4V-K9) to permit cleaning and pumping out the bore on the extraction system while the sample is isolated in the cylinder. Care must be taken during flushing to "exercise" the plug valves to release trapped air. This must be done several times until bubbles cease to appear in the effluent tube. Similar to the clamped copper tube samples, the ends of the cylinder must be carefully rinsed with fresh water and isopropanol after filling.

## 2.2 Large Volume Tritium Samples

We generally use flint glass bottles of 0.5 to 1 liter capacity, sealed with plastic caps fitted with high density polyethylene cones to minimize water vapor transpiration. To minimize contamination, the bottles should be pretreated to remove adsorbed water and filled with dry argon. This is achieved by baking the bottles for at least two hours at about 180°C in a pre-purified argon atmosphere. The inside of the bottle is continuously purged by argon flow through metal capillary tubes inserted into the bottle to displace the inside gas many times during the process. After baking, the bottles are cooled to room temperature while gas flow is continuously maintained and sealed with the caps with argon inside.

The caps are prepared by repeated evacuation and back-filling with argon in a desiccator and held under an argon atmosphere for several hours. The caps are secured on the bottles after bake-out using black plastic electrical tape which is applied with tension to keep caps tight.

At sea, the sealed bottles are un-taped just before using, and any bottles with loose or damaged caps are not used. The bottle should never be tipped or inverted, since argon will "pour" out. The sample is introduced into the bottle with a short length of plastic tubing, which has been soaked in seawater. After opening the Niskin spigot, water is allowed to overflow the tube (held vertically) to rinse off the outside end, then it is inserted part way into the bottle. The bottle is filled, but neither rinsed nor allowed to overflow, to approximately 2 cm from the top. The head space is retained to permit expansion during warming. The cap is immediately replaced and taped with black plastic electrical tape such that there is a closing torque provided by the tape.

## 3. CONTAMINATION THREATS

There are a number of potential contamination hazards while sampling for helium and tritium. "Tank helium" is commonly used for TIG welding, as a carrier gas in some gas chromatographs, and for gas stripping of samples (e.g., for radon). It has an isotopic ratio drastically different from

atmosphere. The primary contamination problem is when materials (glass, plastics, etc.) are soaked in this gas and are subsequently used to take helium samples. It is also important to beware of bubbles trapped in samples, as they may contain more than just air. It is, therefore, best to avoid the use of this gas on board while sampling for helium, or to exercise extreme caution. Sample in an open area, and avoid soaking the Niskin bottles with the helium.

During tritium sampling, since you are working with an open container (the bottle), you must avoid the introduction of environmental water. Be careful to protect the sample from rain or sea spray, drips from decks above, other samplers, or from the outside of the Niskin bottle itself. A far more serious contamination threat is the proliferation of luminous dial watches (and now tritiated emergency signs). The amount of tritium contained in such devices is comparable to the amount of tritium analyzed in our laboratory over the course of a hundred million years. Luminous dial watches should be banned from the sampling area, and should never be worn by tritium sampling personnel during a cruise. Also, be aware of the exhaust vents from the engine room; numerous tritiated dials are used there and the air exhaust is likely high in tritiated water vapor. Avoid placing equipment or sampling in the immediate area.

An additional source of contamination is the use of tritiated compounds in bio-labeling experiments. Residual activity may occur from previous cruises on the vessel, so that if spills have occurred, or contamination is suspected, swab tests should be performed. As with helium, one should never use unknown materials to sample with.

#### 4. EXTRACTION/DEGASSING PROCEDURES

In general, the extraction and degassing procedures are executed with several (8) samples in parallel, with extraction or degassing sections coupled to a common vacuum manifold. The same samples extracted for helium may be stored for tritium analysis by  $^3\text{He}$  regrowth, although lower level (larger volume) tritium samples must be sampled and processed separately.

##### 4.1 Shore-based Helium Extraction Procedure

Prior to extraction, the copper sample tube is removed from the aluminum shipping channel and the ends cleaned with dilute nitric acid, distilled water, and isopropanol if necessary. Before mounting on the extraction system, the full samplers are weighed. Clamped samples are then attached to a stainless steel vacuum system using polymer O-ring compression fittings. The glass sample storage tube (Figure 3) and the reservoir are made with low diffusivity aluminosilicate glass (Corning type 1724 or equivalent). The system is diffusion pumped down to a vacuum better than  $10^{-6}$  Torr, usually overnight to remove atmospheric helium, provide sensitivity to atmospheric leaks, and to remove ambient water vapor. Prior to sample introduction, the sample tube is immersed in liquid nitrogen (up to the "bulb" portion) and the valve between it and the sample closed. Recently, we have demonstrated that the break-seal-charcoal unit can be replaced with a simple 25-30 cc aluminosilicate glass bulb with seal-off capillary similar to the ASEX ampoules (see next subsection). Chilling this bulb with liquid nitrogen achieves quantitative extraction for all the noble gases in a 40 minute period.

Each section is isolated from the pumping manifold by closing its isolation valve, the cross valve is closed, and the sample introduced by removing the clamp and using it to re-round the copper seal slightly. It is important not to compress the seal too much in this operation as it can crack. It should

be “opened” just enough to achieve a modest trickle of water into the waiting reservoir. After the drainage appears to stop, the copper tube must be gently flamed with a torch to force the water down into the sample reservoir.

The sample is stirred either by shaking the reservoir (which would be on a bellows) or with a magnetic stir-bar. Initially, it is stirred for a period of about 10 minutes to exsolve gases into the head-space. With typical volumes in the system, more than 99.5% of the helium should reside in the head-space at equilibrium. At the end of the shaking period, the cross-valve is opened. The transfer of water vapor from the sample reservoir effectively sweeps over the head-space gases, most of which are adsorbed on the activated charcoal in the sample tube. The non-adsorbed gases (principally helium and neon) are kept in the tube by the water vapor pressure drop across the capillary. During the transfer period, the reservoir is continuously shaken to facilitate the further exsolution of gases remaining in the water. Also, the system is periodically flamed with a torch to thermally stir the gases in the system, and hence make sure that gases are not trapped in “dead end” parts of the section (e.g., the copper tube sampler). The transfer period is typically 15-25 minutes for helium isotopes, or 40 minutes if measuring all the noble gases. Extraction is terminated by flame-sealing the capillary with a torch. The transfer is then checked by measuring the pressure surge through a liquid nitrogen chilled trap (to remove water vapor) on an ion gauge. This effectively diagnoses problems associated with incomplete extraction or atmospheric leaks. If the remaining water is to be stored for tritium analysis (in which case the reservoir is a storage flask), the flask is flame sealed as well and stored. After extraction, the empty copper tube samples are weighed to determine the water weight, and the tritium flasks (which were weighed prior to being used) are weighed full. The extraction sections are rinsed with distilled water and alcohol, blown out with compressed air and re-evacuated with new sample tubes and flasks.

The cold welded samples are extracted using essentially the same procedure, except that the copper tube sample must be opened inside a vacuum chamber attached to the extraction section (Figure 4). Prior to insertion in the chamber, the sample must be cleaned to minimize outgassing and reduce the ultimate pressure of the line. Opening of the sample tube is achieved using a bellows sealed side actuated crushing mechanism which squeezes the seal open. Other methods are possible. It appears especially important to heat the chamber during the extraction processes to ensure complete extraction.

A schematic showing the manifold, sample chambers, and pumps that comprise the vacuum system is shown in Figure 5. The manifold is a 3.8 cm O.D. 304 stainless steel tube with 7 cm Varian ConFlat angles welded on each end and male VCR fittings welded along the tube. Each of the sample chambers can be isolated from the manifold by an all-metal 0.64 cm valve. The oil-filled, rotary mechanical pump is connected in series with a liquid nitrogen trap and a 3.8 cm right angle valve. The water-cooled diffusion pump also has a liquid nitrogen trap and a 3.8 cm right angle valve separating it from the manifold. The forepump for the diffusion pump is a direct-drive mechanical pump. The pressure is measured by a convectron gauge (to  $10^{-3}$  Torr) and an ionization gauge (from  $10^{-3}$  to  $10^{-8}$  Torr). A dry, nitrogen backfill line is connected to the manifold through a VCR fitting.

#### 4.2 At-Sea Helium Extraction (ASEX)

We have developed an at-sea extraction procedure that does not rely on cryogenics (e.g., liquid nitrogen). Water samples are transferred from the Niskin rosette into stainless steel sample cylinders sealed with plug valves. Sample storage in these containers is limited to the order of a day or so, as

experiments indicate that the equilibration rate of the dissolved helium is equivalent to 0.25% per day. Thus a sample with a helium isotope ratio anomaly of 10% will be reduced by 0.025% after a day's storage.

The sample cylinders are mounted on a manifold that holds 8 extraction units and evacuated to a pressure of better than  $10^{-6}$  Torr (see Figure 6). Pumping is accomplished using a diffusion pump "protected" from water vapor by a mechanically cooled trap (typically run at -130C). At the beginning of the extraction, iced water is placed on the aluminosilicate glass bulbs, the sections are isolated from the pumping manifold by plug valves, and the samples introduced into the extraction reservoir by opening the cylinder valves, and the heaters are turned on (100 watt cylinder heaters inserted into aluminum clamps holding the bottoms of the reservoirs). After 3-4 minutes, a visible jet of water and accumulation appears in the bulbs. Boiling occurs in the reservoirs, and is aided by the presence of small stainless steel nuts (#3) that act as boiling chips. This establishes strong mixing of the sample. The extraction is completed at the 10 minute mark when the aluminosilicate bulb is flame-sealed off. A ½ inch stainless steel nut slipped over the top of the bulb when it is first mounted insures that the bulb, once flame sealed off, settles safely into the iced water bath on sealing.

Laboratory experiments have demonstrated quantitative extraction for helium and neon (Lott and Jenkins, 1998), and for the other noble gases (Ar, Kr, and Xe; see Stanley, 2007). After cleaning of the vacuum system and remounting of the next set of cylinders, the next extraction typically can occur in about 2 hours after the first one.

#### 4.3 Large-Volume Tritium Degassing

The tritium samples are degassed for  $^3\text{He}$  regrowth analysis in large (1 liter) aluminosilicate glass storage flasks connected via compression fittings to an all metal vacuum system. As with the helium extraction systems, the sections (Figure 7) are evacuated to about  $10^{-6}$  Torr to remove ambient water vapor and check for atmospheric leaks. The samples are introduced under an "argon blanket", that is with a flow of pre-purified argon filling the head-space of the bottle as the sample is transferred, so that the remaining water may be resealed in the bottle for possible future re-analysis. The water is transferred to the system using plastic tubing, with a fraction of the sample allowed to flow through the tubing into a three-way valve, and flushed to waste. The remainder of the sample is introduced to the storage flask, typically half filling it, and the valve closed. A flow restricting valve (orifice about 1 mm diameter) is closed, and the head-space is pumped on (for about 2 minutes) using a liquid nitrogen trapped mechanical rotary pump to remove the already exsolved gases. Experiments show that if the sample introduction is done carefully, more than 95% of the dissolved helium is removed in this step.

The samples are then agitated for a period of 15-30 minutes, and then pumped on again for a period of 2-3 minutes. This process is repeated two more times, but with the pumping being done with a liquid nitrogen trapped diffusion pump. Pressure surges associated with the pump-out are initially a fraction of a Torr (determined by system pumping speed), reducing to the order of  $10^{-7}$  Torr on the final pump-out. It is important to make sure that agitation is sufficient to achieve good degassing. Experimentation is necessary to establish the appropriate times and procedures. Tests show that typically less than  $10^{-10}$  cc (STP) helium remains after this procedure. Prior to all pumping sessions, the glass capillaries must be inspected for liquid water blockage, and the sections flamed down to ensure a clear pumping path. Individual sections can be pumped on to test for possible vacuum

breaches or other problems. On the final pump-out, the samples are flame-sealed off, and their final seal-off pressure noted. The sample flasks are weighed both empty and full to determine water weight. During the procedure, about 2-3 g of water is pumped away per sample, producing a slight tritium enrichment which must be corrected for in the final calculations (cf. Clarke et al., 1976).

Prior to use, the tritium flasks are baked at 600 C for several hours in a helium free atmosphere to remove dissolved helium. This helium would normally diffuse into the sample during the long storage period and reduce measurement precision. A good source of low-helium gas is the head-space nitrogen produced from liquid nitrogen; boiling within the container self-sparges the liquid nitrogen to remove any dissolved He during storage and shipping to the laboratory. Helium-free nitrogen gas is fed into the flasks during baking through stainless steel capillary tubes, with a gas flow sufficient to displace the flasks' interior volumes many times during the bake-out. To further reduce helium diffusion from the glass during storage, the samples may be stored in a freezer (-20 °C) to lower the diffusion rate.

For very low level samples, it is important to shield them from cosmic rays during storage. A simple calculation shows that at sea level in mid latitudes, an unshielded sample will suffer a production of  $^3\text{He}$  by cosmic rays of about 50 atoms per gram of water per year, equivalent to an apparent tritium concentration of about .016 T.U. In our current situation, the freezer is in the basement of a four storey concrete building, which provides shielding sufficient to reduce this effect by about a factor of 5. The residual "ghost tritium" effect must be monitored using tritium free water, and corrected for. Tritium free water is usually obtained from "old" ground water aquifers that have been determined to be tritium free, or inferred so by radiocarbon or  $^{36}\text{Cl}$  measurements.

## 5. SAMPLE ANALYSIS

Due to the difference in sample size and character, we discuss the measurement of helium isotopes and tritium separately. But first, we describe the common elements of both procedures. Extracted helium samples or degassed tritium samples are stored in aluminosilicate glass ampoules. These ampoules may have traditional breakseals that are coupled to an appropriate vacuum system or mass spectrometer using an o-ring compression fitting and breached by magnetically actuated pistons. More commonly, the samples are introduced into the vacuum system by inserting the capillary seal-off stub into the chamber through a compression fitting, and breaking the stub off with a side-ways actuated piston. Prior to insertion, the glass is scored with a glass-blower's knife to control the break-point. The break-off actuator usually consists of a modified bellows-sealed valve with the stem-tip replaced by a suitable "jaw". These valves can be either manually or pneumatically actuated.

The samples may be transferred using water vapor sweeping into stainless steel valved containers for subsequent automatic processing on the mass spectrometer (e.g., see Lott and Jenkins, 1984), or they may be coupled directly to the mass spectrometer (e.g., see Stanley, 2007; Stanley et al., 2009). Samples are subsequently purified by some combination of cryogenic trapping (at 180 K to block water vapor), removal of methane by catalytic oxidation, chemical "gettering" using Zr-Al-Ti-V alloys at elevated temperature to consume reactive gases, and subsequent cryogenic separation (see Stanley et al., 2009 and Stanley, 2007 for a complete discussion). The primary objective is to provide a quantitatively pure He sample to the mass spectrometer.

Sample processing and analysis is done under complete computer control, where monitoring of system pressures, temperatures, etc permit safe and reproducible operation on a 24/7 basis. Valve

operation is accomplished by computer-solid state relay-solenoid valve-pneumatic UHV valve combination. Prior to admission into the isotope ratio mass spectrometer, a small ( $\sim 1\%$ ) aliquot of the helium sample is “previewed” using a quadrupole mass spectrometer (QMS) to insure that inadvertently large samples (due to vacuum failure, incomplete degassing, bubble inclusion, etc) are prevented from being introduced into the instrument. This step improves instrument stability and reduces memory effects. Additionally, the same QMS may be used in parallel to quantify the other noble gases by peak-height manometry with reasonable precision (e.g., see Stanley, 2007). After screening, the essentially pure helium sample is introduced into the magnetic sector instrument through a pneumatically controlled valve after the instrument is isolated from its vacuum pumps. Thus the sample is analyzed “statically”.

A 25 cm radius, dual collecting, all metal, single focusing,  $\pi/2$  magnetic sector mass spectrometer is used in “the static mode”, with a “Nier style” electron impact ion source, a faraday cup collector for  $^4\text{He}$ , and a secondary electron multiplier (continuous dynode “channeltron”) operated in the pulse counting mode is used for  $^3\text{He}$ . A series of retardation potential slits or an electrostatic analyzer may be used before the  $^3\text{He}$  detector to reduce background for this isotope due to other, more abundant ions scattering off neutrals. Due to the ubiquitous presence of hydrogen due to exsolution from the metal vacuum envelope and other parts, one or more Zr-Al-V or Ti sponges are included in the static volume to pump  $\text{H}_2$  and thereby reduce the potential interference by  $\text{H}_3$ -HD near the  $^3\text{He}$  peak. The dual collector instrument is operated in static mode, whereby vacuum pumping on the flight tube, collectors, and ion source is arrested and the sample expanded into the spectrometer. The mass spectrometer is calibrated with air standards (see next section) that are interspersed with actual samples, and are processed in an identical fashion. The frequency with which air standards are measured depends on the stability of the mass spectrometer and the need for precision.

## 5.1 Helium Isotope Analysis

For a typical sized seawater sample (and comparably sized air standards), ion currents are of the order of a few nano-amperes for  $^4\text{He}$ , and a few thousand ions per second for  $^3\text{He}$ . With a well designed system, the corresponding  $\text{H}_3$ -HD composite peak is much smaller than and well resolved from the  $^3\text{He}$  peak. Background due to low angle ion scattering off resident neutrals in the flight tube is typically monitored by voltage jumping to the high mass side of the  $^3\text{He}$  peak, and is typically a very small fraction of the  $^3\text{He}$  peak. Typically, an analysis consists of approximately 1000 second integration of the  $^3\text{He}$  ion beam split up into a number (say 10 or 20) blocks interspersed with shorter background integrations. After analysis, the sample is usually ion pumped away by opening the instrument’s main pump valves.

The precision of the  $^3\text{He}/^4\text{He}$  measurement is limited by  $^3\text{He}$  ion counting statistics, the stability of the mass spectrometer, and the frequency of standardization. For water samples of order 40-90g, one accumulates several million  $^3\text{He}$  ions during an analysis, so counting statistical limits are of order 0.1% or less. When the instrument is working well, precisions of order 0.15% are routinely achievable. Typically, an air standard is analyzed every 3<sup>rd</sup> or 4<sup>th</sup> sample.

A running air standard is prepared by evacuation of a large (10-15 liter) helium-leak-tight reservoir with a UHV metal-sealed valve on it. The evacuated reservoir is situated on the beach with a shoreward breeze and allowed to thermally equilibrate for an hour. The reservoir is filled by opening the valve and allowing pressure equilibrium (a few minutes) while the temperature, barometric pressure, and humidity are monitored. Temperature is determined using an ASTM certified



thermometer accurate to 0.1 C, and pressure determined using an aneroid barometer (Pennwalt Model FA185260D). Relative humidity is determined using a hydrometer (Lufit Model 4007), to an accuracy of 5% and the vapor pressure of water is corrected for, using standard tables. The tank is then closed and the reservoir returned to the laboratory where it is mounted on the mass spectrometer system inside a temperature stabilized metal enclosure. In this enclosure is a pair of metal aliquot volumes, one about 10% of the size of the other, that are used to aliquot air standards into the vacuum system. The volumes of the aliquots are calibrated by inter-comparison with glass aliquots that have been calibrated gravimetrically with Hg, and they are trimmed in size by insertion of precisely known metal “slugs” (determined densimetrically). Their volumes are adjusted such that a standard consisting of one aliquot of each size adds to the target sample size. The air aliquot size is calculated from the known temperature, pressure (corrected for water vapor), and volume of the aliquots. Corrections for depletion (due to aliquot removal) are made over the course of a standard’s life-time.

The mass spectrometer is calibrated at regular intervals for an apparent isotopic ratio dependence on sample size, as well as non-linearity in ion beam intensity to the amount of sample introduced. Linearity curves are determined on an approximately weekly basis, and deviations from ideal response are fit to a quadratic function of sample size. Normal corrections are typically less than analytical precision, (i.e., 1 standard deviation), and rarely exceed double that value. In addition to the “running” air standards, there exists a second, independent system consisting of a 2 l air tank and single aliquot volume, which is used on a regular basis to monitor and cross check the main standards. This process is also used to establish a “chain of evidence” by inter-comparing the running air standards when a new standard is “brought on line.”

## 5.2 Tritium Analysis

For the tritium analyses, a similar procedure is followed, with some changes due to the smaller and more variable sample sizes. Because the amounts of helium are substantially smaller than the helium isotope analysis above, the ion beams are correspondingly weaker. Typically,  $^4\text{He}$  beams are a fraction of a picoampere or smaller, and  $^3\text{He}$  beams are a few ions per second or less. When the  $^3\text{He}$  ion beams are sufficiently small, it becomes more appropriate to spend a greater fraction of integration time on the background. Overall, measurement precision is limited more by  $^3\text{He}$  ion counting statistics than instrument stability. Consequently, the precision and detection limit is governed by a combination of water sample size, sample storage time, storage vessel integrity, and efficiency of degassing. With the latter two, introduction of non-tritiogenic  $^3\text{He}$  due to small leaks, incomplete degassing, or exsolution from the storage vessel can significantly degrade measurement quality. Even if the isotopic ratio of the “exogenous” He were perfectly known, Poisson statistical dilution will limit the intrinsic measurement precision. Thus extreme care must be exercised to minimize these effects. Typically, measurement precision is of order 0.5% with an overall “detection limit” somewhat less than 0.005 TU.

We also use air standards for this measurement, although it is possible to use an enriched  $^3\text{He}$  standard for improved statistics. This running standard, however, must be tied either to an atmospheric standard or the NIST standard. We typically use an air standard. To do this, we prepare an air standard by evacuating the 15 l tank, and also a smaller (ca. 40 cc) calibrated valved tank. The smaller tank is filled with marine air of known temperature, pressure and relative humidity, and then expanded into the larger tank. Using the same aliquoting system, the running standard size is approximately  $5 \times 10^{-9} \text{ cm}^3$  (STP) He. Because of the inherently larger range in sample size, the

standard curve is determined over a large range, from  $1 \times 10^{-9} \text{ cm}^3$  through  $20 \times 10^{-9} \text{ cm}^3$ . As with the seawater helium isotope analyses, standard curves are determined on an approximately weekly basis.

## 6. REFERENCES

- Bayer, R., P. Schlosser, et al. 1989. Performance and blank components of a mass spectrometric system for routine measurement of helium isotopes and tritium by  $^3\text{He}$  ingrowth method. *Sitzungsberichte der Heidelberger Akademie der Wissenschaften Mathematisch-naturwissenschaftliche Klasse* 5: 241-279.
- Clarke, W. B., W. J. Jenkins and Z. Top. 1976. Determination of tritium by mass spectrometric measurement of  $^3\text{He}$ . *Int. J. Appl. Rad. Isotopes* 27, pp. 217-225.
- Jenkins, W. J. 1981. *Mass spectrometric measurement of tritium and  $^3\text{He}$  in low level tritium measurement*. IAEA-TECDOC-246. Int. Atomic Energy Agency, Vienna, pp. 179-190
- Jenkins, W. J., D. E. Lott, M.W. Pratt, and R.D. Boudreau. 1983. Anthropogenic tritium in South Atlantic bottom water. *Nature* 305: 45-46.
- Lott, D. E. 2001. Improvements in noble gas separation methodology: a nude cryogenic trap. *Geochemistry, Geophysics, Geosystems* 2: 10.129/2001GC000202.
- Lott, D. E. and W. J. Jenkins. 1984. An automated cryogenic charcoal trap system for helium isotope mass spectrometry. *Rev. Sci. Inst.* 55, pp. 1982-1988.
- Lott, D. E. and W. J. Jenkins. 1998. *Advances in the analysis and shipboard processing of tritium and helium samples*. International WOCE Newsletter 30: 27-30.
- Stanley, R. H. R. 2007. A Determination of Air-Sea Gas Exchange Processes and Upper Ocean Biological Production From Five Noble Gases and Tritiogenic Helium-3. Department of Marine Chemistry and Geochemistry. Woods Hole, MA, MIT-WHOI Joint Program in Chemical Oceanography. PhD: 224.
- Stanley, R. H. R., B. Baschek, D.E. Lott, and W.J. Jenkins. 2009. A new automated method for measuring noble gases and their isotopic ratios in water samples. *Geochemistry Geophysics Geosystems* 10(5): Q05008, doi:10.1029/2009GC002429.

# 45 GRAM SAMPLE CLAMP

(END VIEW)

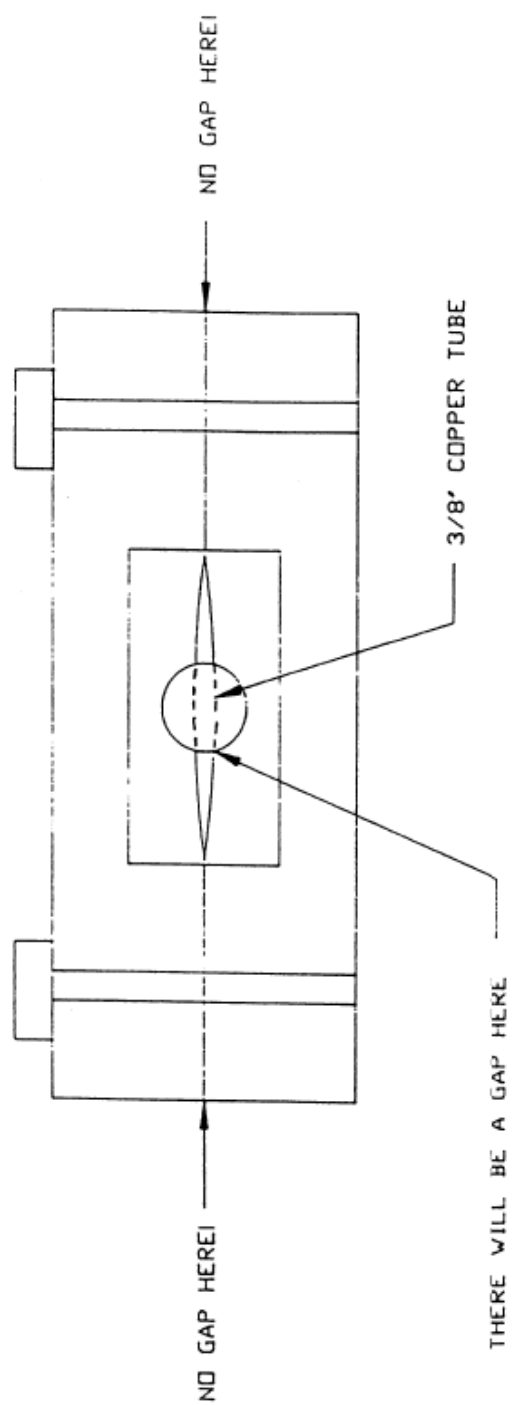


Figure 1: Sample clamp (end view)

# COPPER SAMPLE TUBE FILL PROCEDURE

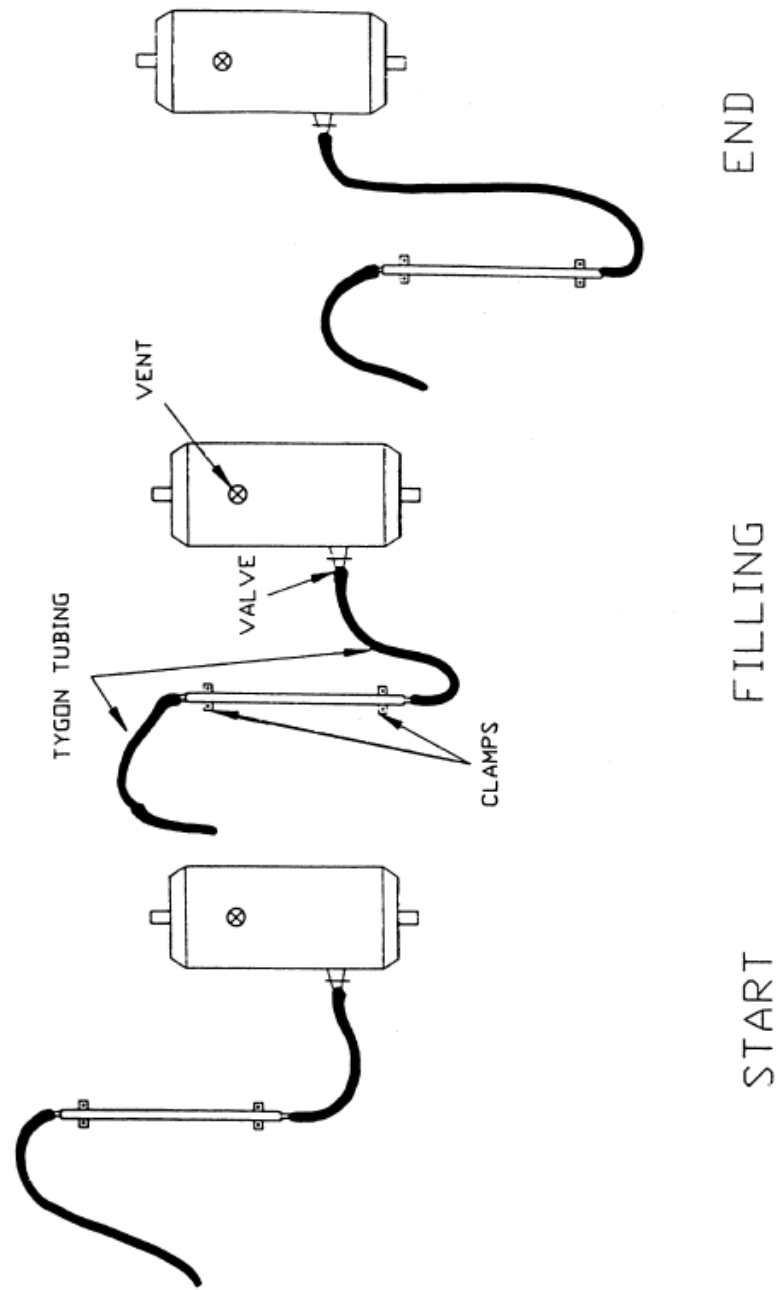


Figure 2: Copper sample tube fill procedure

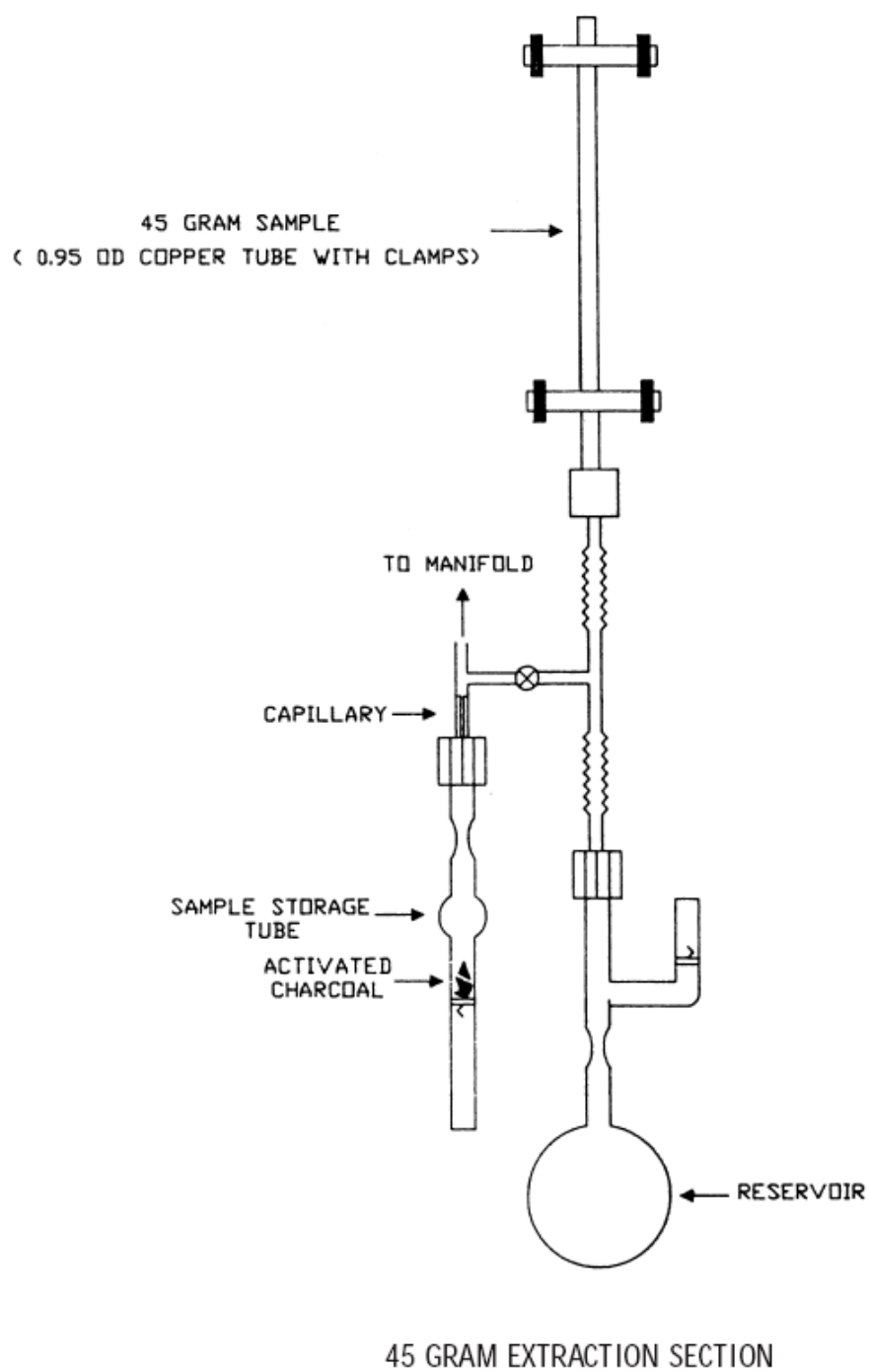
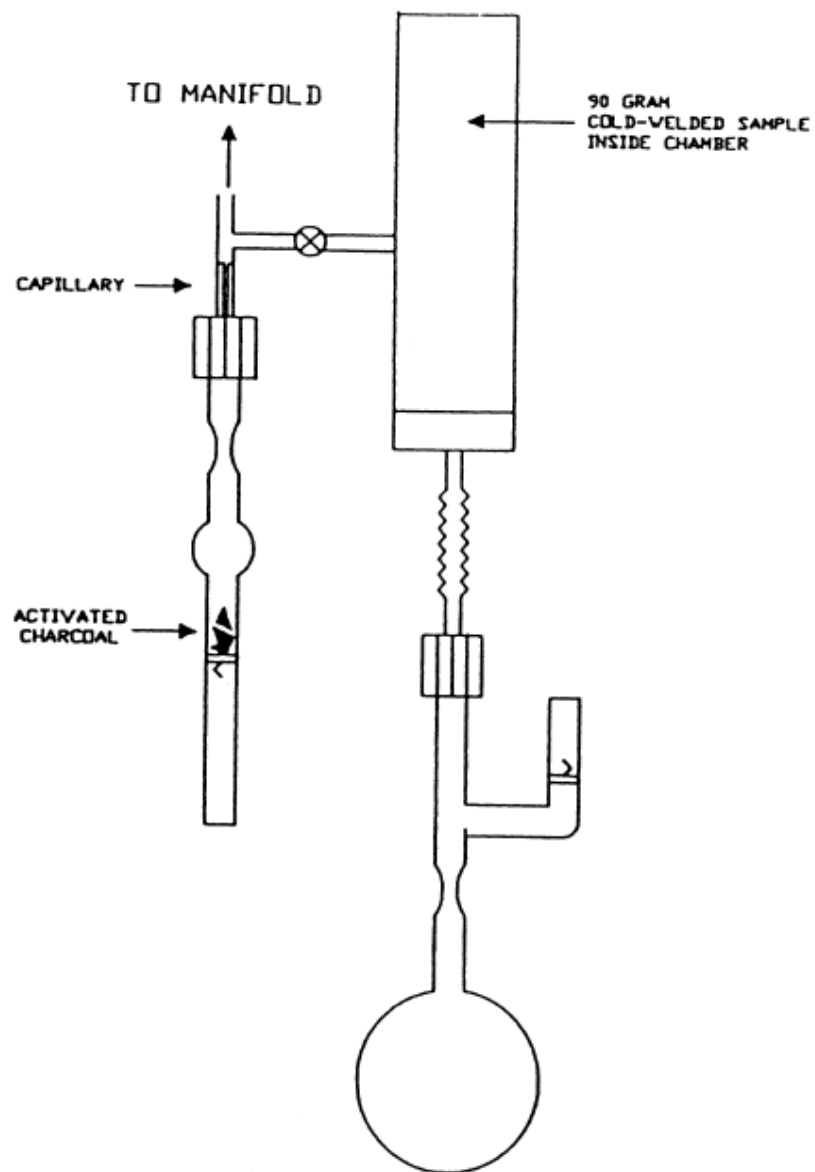


Figure 3: Clamped sample extraction section



90 GRAM EXTRATION SECTION

Figure 4: Cold weld extraction section

# GENERAL VACUUM MANIFOLD

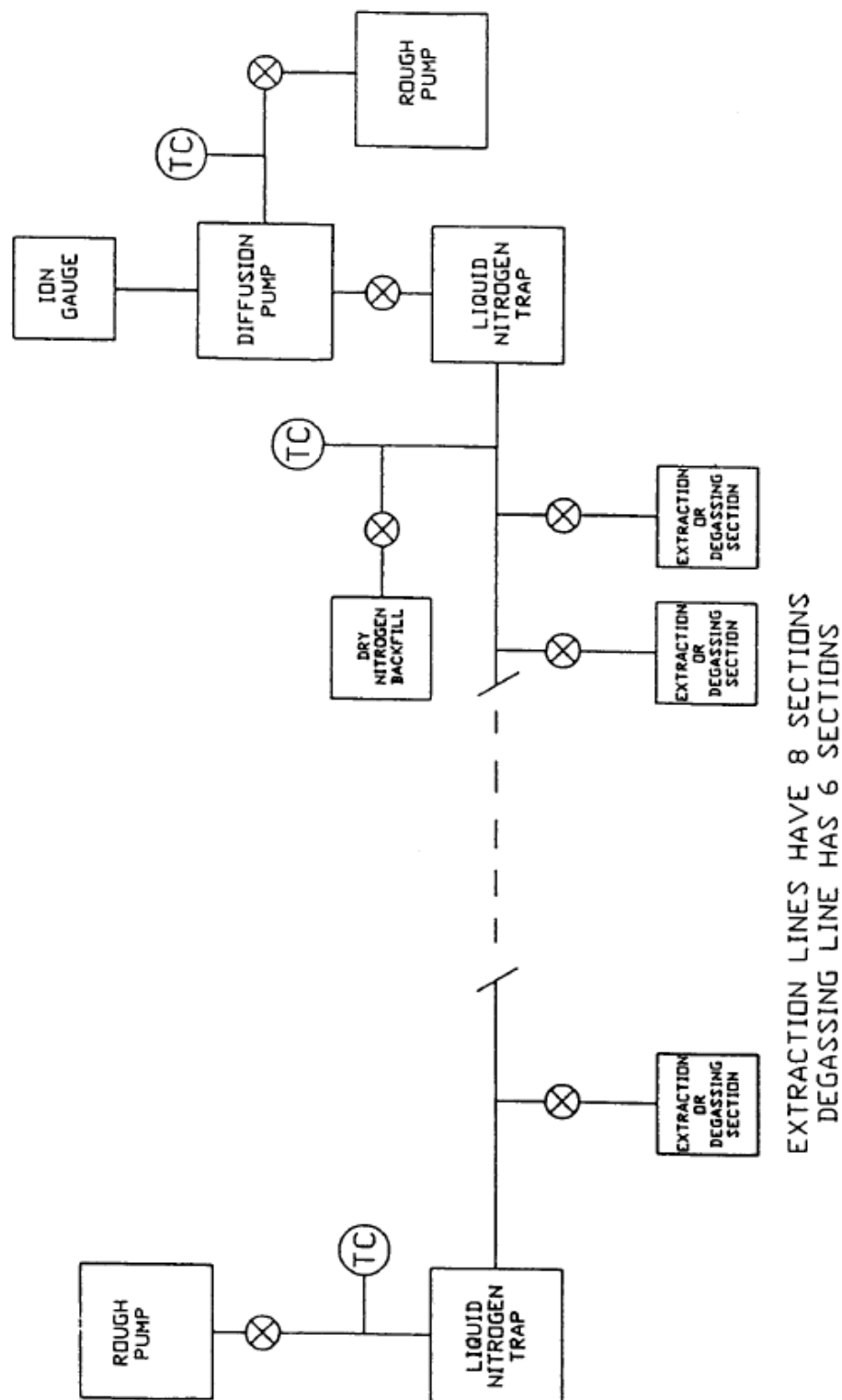


Figure 5: General vacuum manifold

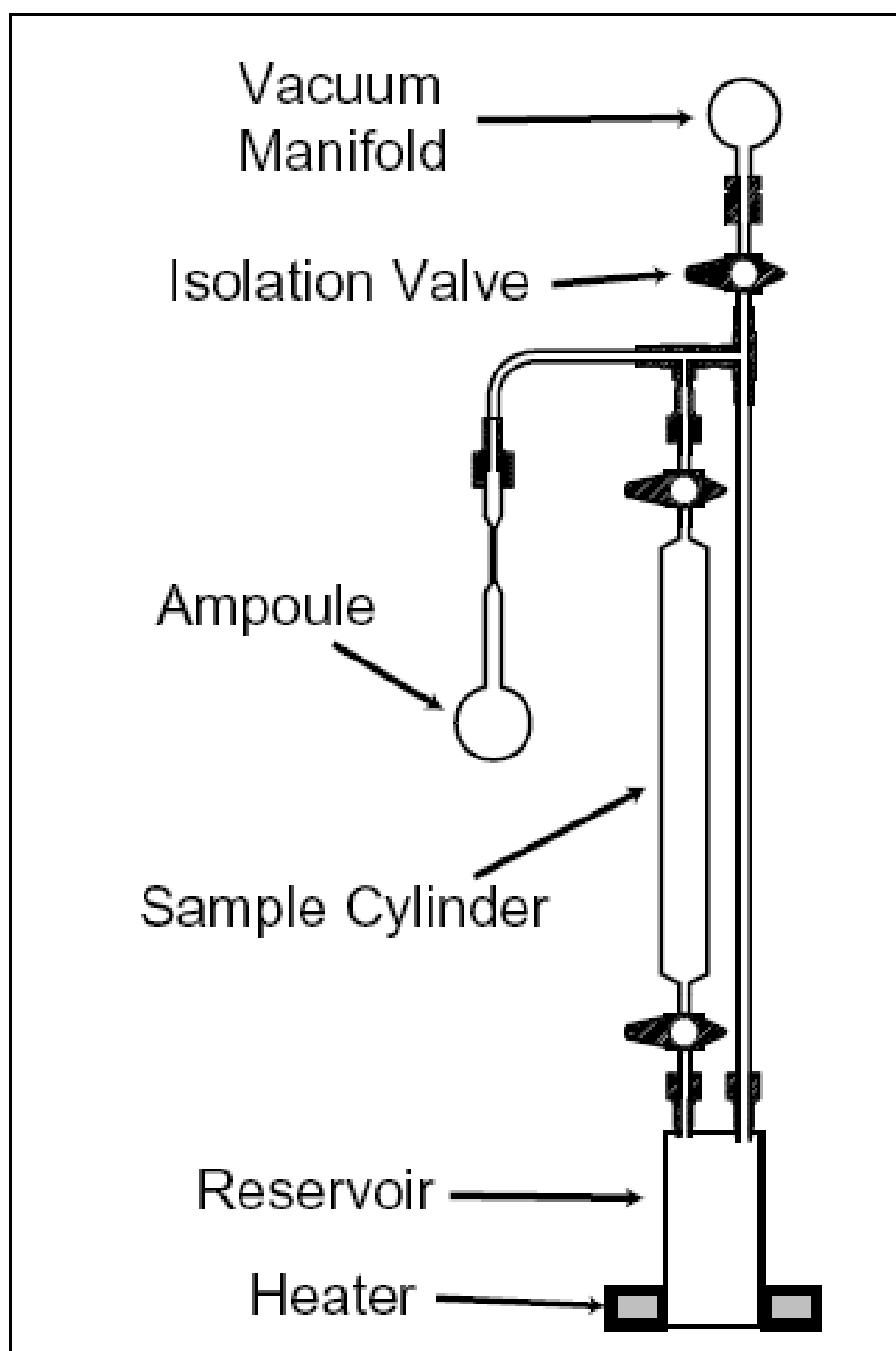


Figure 6: At-Sea Extraction (ASEX) section



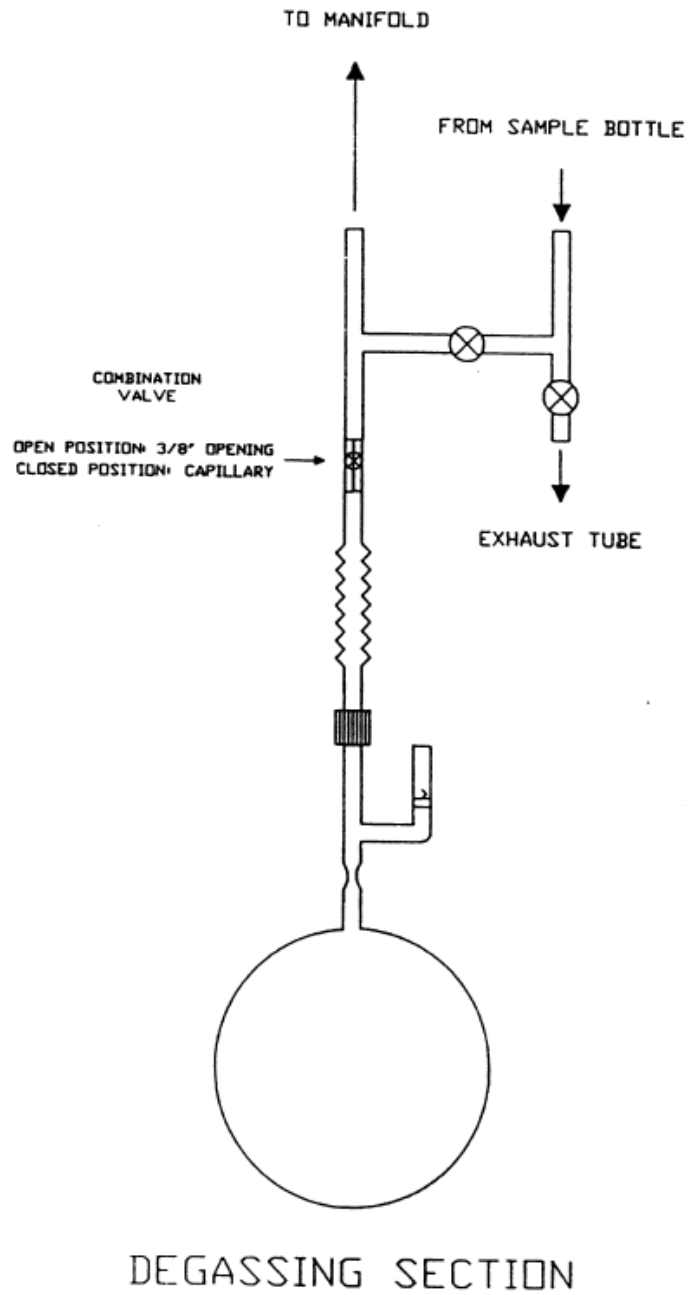


Figure 7: Tritium degassing section