

Measuring Helium Isotopes and Tritium in Seawater Samples

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1. Introduction

This document is meant to describe the essential elements of measuring helium isotopes and tritium in seawater samples. The methods described are those 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). 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 many months, and mass spectrometrically measuring the ^3He 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).

2. Preparation For Taking Samples At Sea

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. 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 put into a channel and clamp assembly consisting of a three-sided aluminum channel with clamps mounted a few centimeters from either end. In the past, plumber’s pinch-off clamps were used (Imperial Eastman No. 105ff), but experience indicates that these clamps do not perform well under repeated use (they warp), the bolts tend to shear off easily, and they are susceptible to corrosion. Clamps can be custom-fabricated from case-hardened mild

steel with optimum gap width (0.4 to 0.8 mm), minimal creep fatigue, and good corrosion resistance. The clamps 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 1.8 cm are used, with a length sufficient to provide a water sample of 40 to 100 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.

2.2 Large Volume Tritium Samples

We generally use flint glass bottles of 1 to 4 liter capacity, sealed with caps fitted with high density polyethylene cones to minimize water vapor transpiration. To achieve a minimum contamination, the bottles should be pretreated to remove adsorbed water. This is achieved by baking the bottles for a few hours at about 180° C in a pre-purified argon atmosphere. The inside of the bottle is purged by capillary tubes inserted into the bottle to displace the inside gas many times during the process. The bottles are cooled and sealed with argon inside.

Polyseal caps (plastic caps with high density polyethylene inserts) for the bottles are placed in a desiccator attached to a vacuum pump and an argon supply. The desiccator is evacuated and backfilled with argon. This procedure is repeated once. The caps are secured on the bottles after bakeout using black plastic electrical tape which is applied with tension to keep caps tight.

3. At-Sea Sampling

Until recently, all helium and tritium samples were stored in containers and returned to shore based facilities for gas extraction and degassing. New techniques for processing these samples at sea are currently under development, but will not be discussed here because they are still experimental.

3.1 Helium Samples

Samples are transferred from the Niskin (or other sampling) bottle to the copper tubing using a gravity feed technique through lengths of plastic tubing. 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 best to soak the 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. 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).

To draw a sample, two pieces of tubing are attached to the ends of a tube, and one 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. The amount of water flushed through the copper tube is about six volumes. During the “flush” period, the container is tapped to remove bubbles. For clamped samples, the seal is made by tightening the top clamp and then the bottom clamp until the edges meet. The ends must be thoroughly rinsed with fresh water to avoid excessive corrosion (figures 1 and 2).

For the cold weld samples, which have a large diameter, some 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 rerounded 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.

3.2 Large Volume Tritium Samples

The sealed bottles are untaped just before using, and any bottles with loose or damaged caps are not used. The bottle is never 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 within a cm or two of the top. The head space is retained to permit expansion during warming. The cap is immediately replaced, and taped (such that there is a closing torque provided by the tape).

3.3 Contamination Issues

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

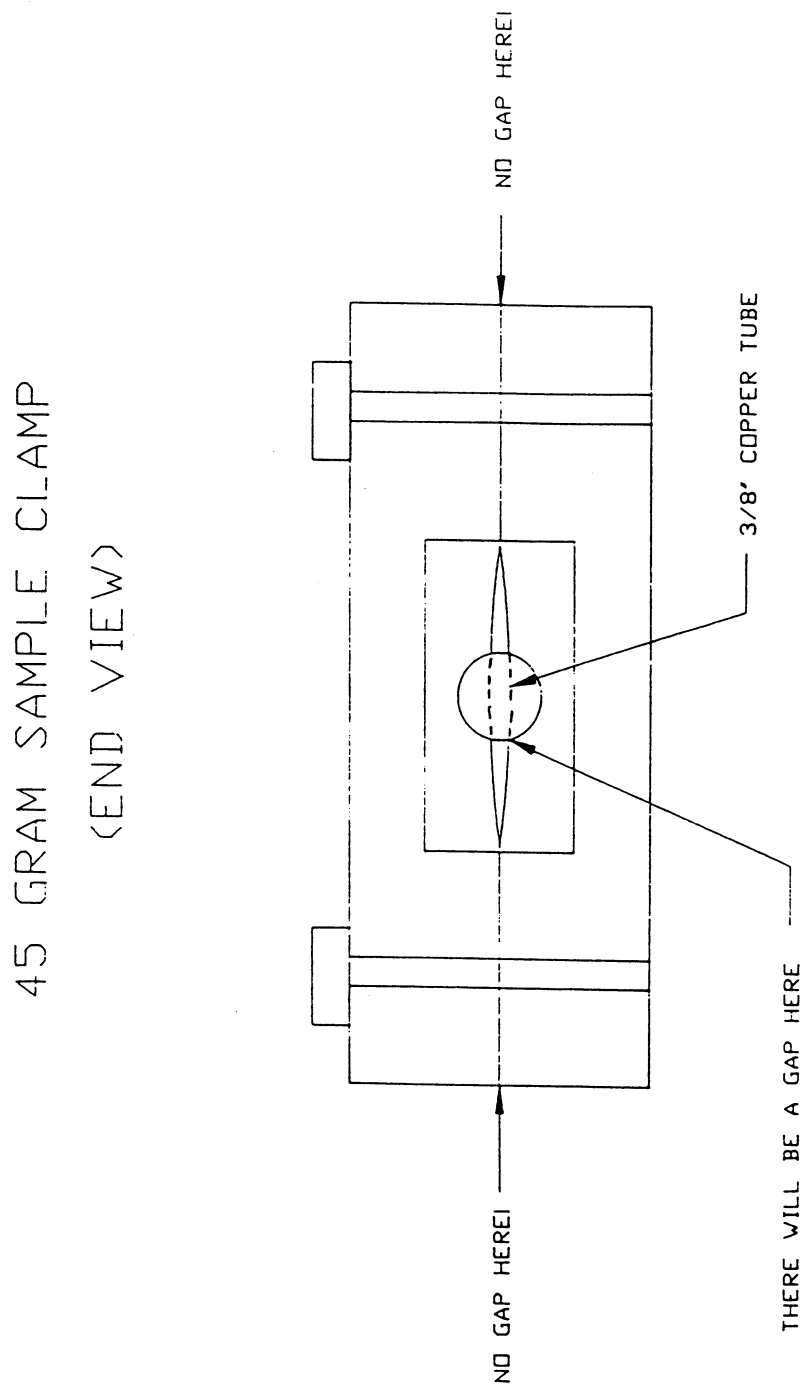


Figure 1: Sample clamp (end view)

COPPER SAMPLE TUBE FILL PROCEDURE

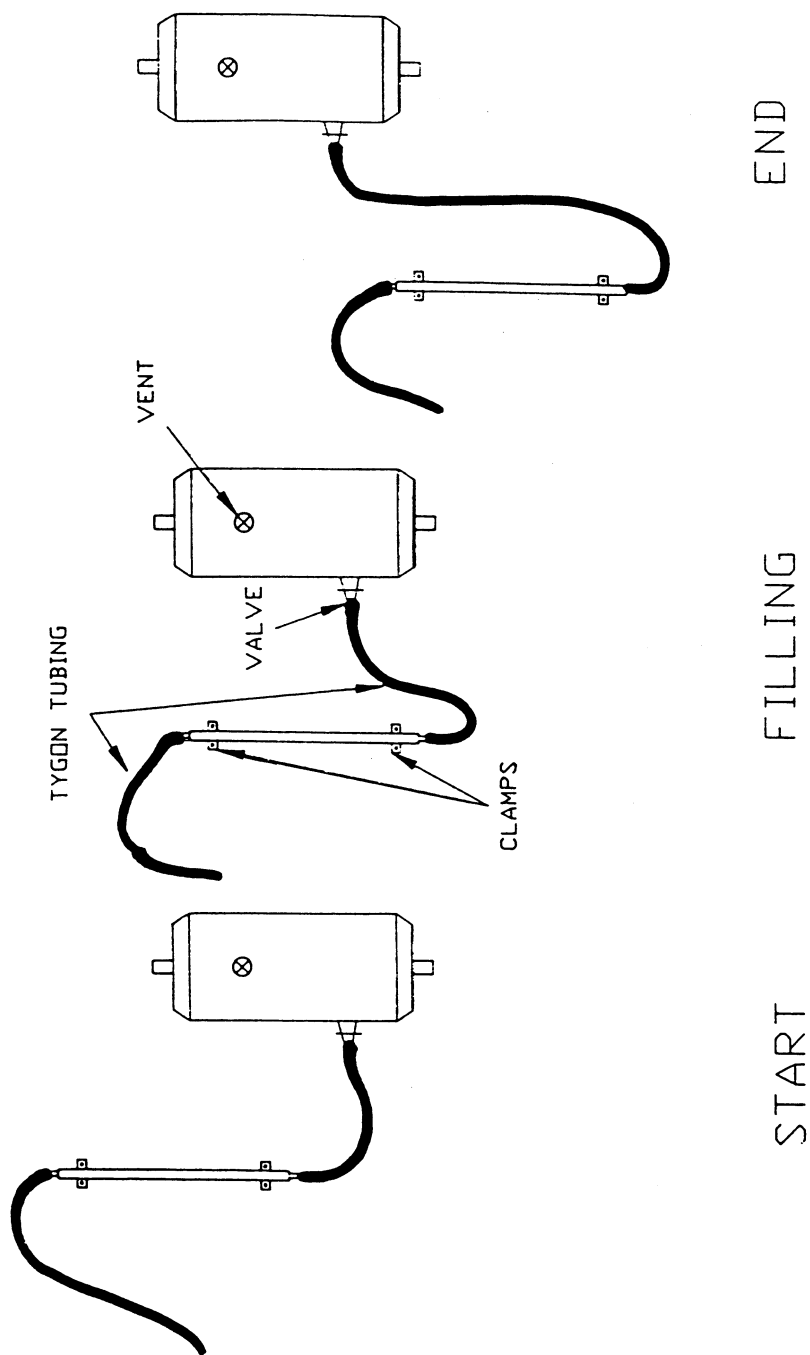


Figure 2: Copper sample tube fill procedure

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 the sampling for tritiums, 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. An additional source of contamination is the use of tritiated compounds in bio-labelling 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.

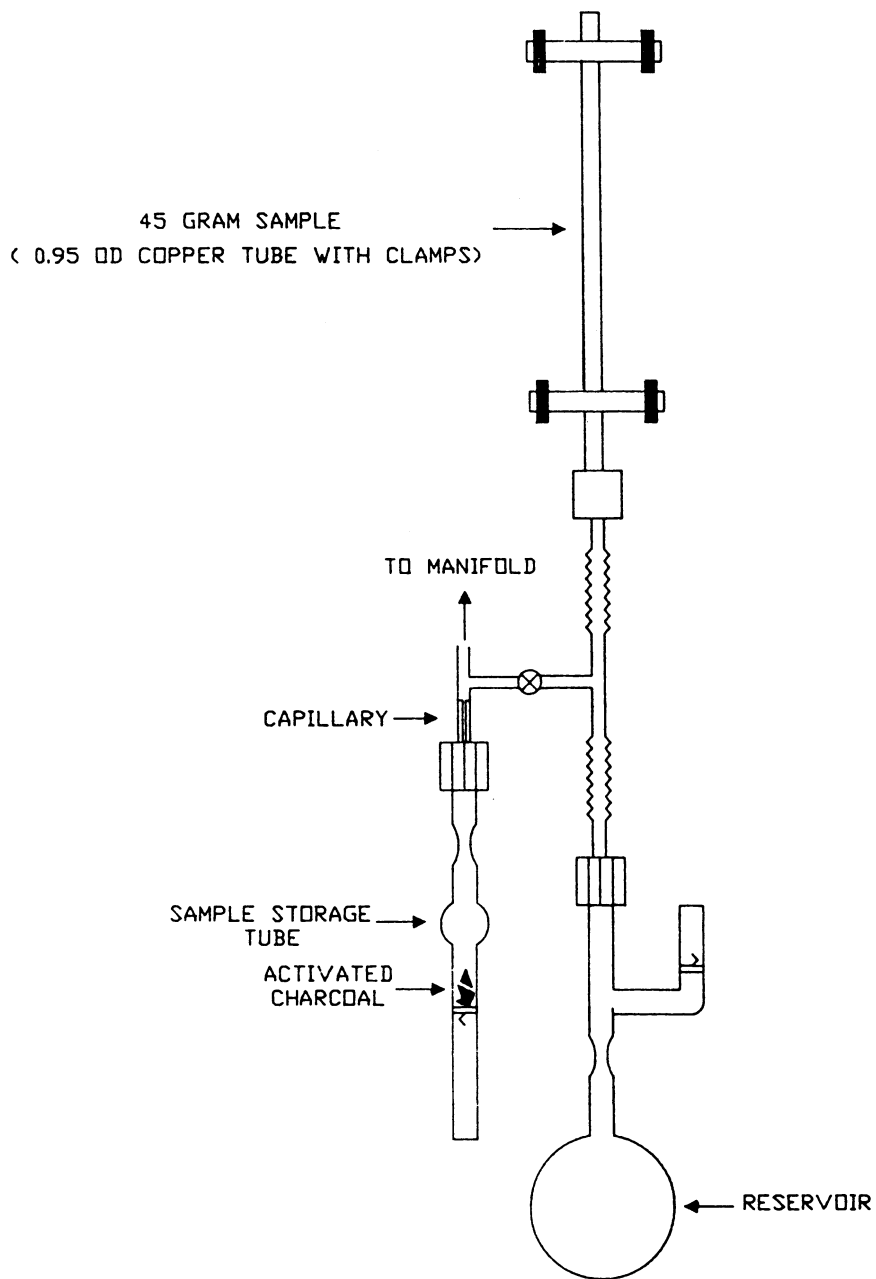
4. Extraction/Degassing Procedures

In general, the extraction and degassing procedures are executed with several (6–8) samples in parallel, with extraction or degassing sections coupled to a common vacuum manifold. The same samples extracted for helium are often stored for tritium analysis by ^3He regrowth, although low level (large volume) tritium samples must be processed separately.

4.1 Helium Extraction Procedure

Prior to extraction, the copper sample tube is removed from the aluminum shipping channel, weighed, and the ends cleaned if necessary. Clamped samples are 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 of order 10^{-6} Torr range 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. The system is isolated from the pump, and the sample introduced by removing the clamp, and using it to reround the copper seal. The copper tube must be gently flamed with a torch to force the water down into the sample reservoir.

The sample is stirred by shaking the reservoir for a period of 10–15 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



45 GRAM EXTRACTION SECTION

Figure 3: Clamped sample extraction section

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 ensure 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. 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.

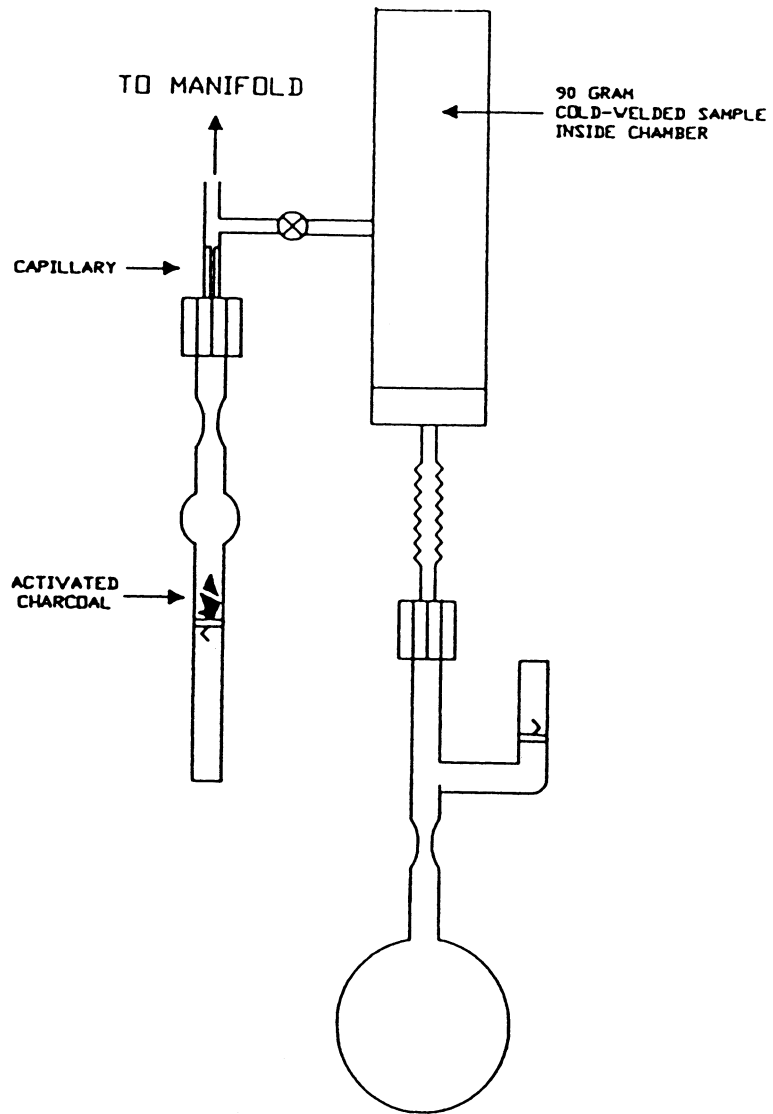
After extraction, the empty copper tube samples are weighed to determine the water weight, and the tritium flasks (which were weighed prior to being used) are weighed full. The extraction sections are rinsed with distilled water and alcohol, blown out with compressed air and re-evacuated with new sample 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 (figure 5). The manifold is a 3.8 cm O.D. 304 stainless steel tube with 7 cm Varian conflat flanges 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 thermocouple 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.



90 GRAM EXTRACTION SECTION

Figure 4: Cold weld extraction section

4.2 Large-Volume Tritium Degassing

The tritium samples are degassed for ^3He regrowth analysis in large (1–2 liter) aluminosilicate glass storage flasks connected via compression fittings to an all metal vacuum system. As with the helium extraction systems, the sections (figure 6) 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 pumpout are initially a fraction of a Torr (determined by system pumping speed), reducing to the order of 10^{-7} Torr on the final pumpout. 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 pumpout, the samples are flame-sealed off, and their final sealoff 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).

4.3 Tritium Flask Preparation and Storage

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. The flasks are evacuated and filled with nitrogen gas several times before placement in the oven. Better results are obtained when nitrogen is fed into the flasks during baking through stainless steel capillary tubes, with a gas flow sufficient to displace flasks' interior volumes many times during the bakeout. To further reduce helium diffusion from the glass during storage, the samples are stored in a freezer (-20°C) to lower the diffusion rate.

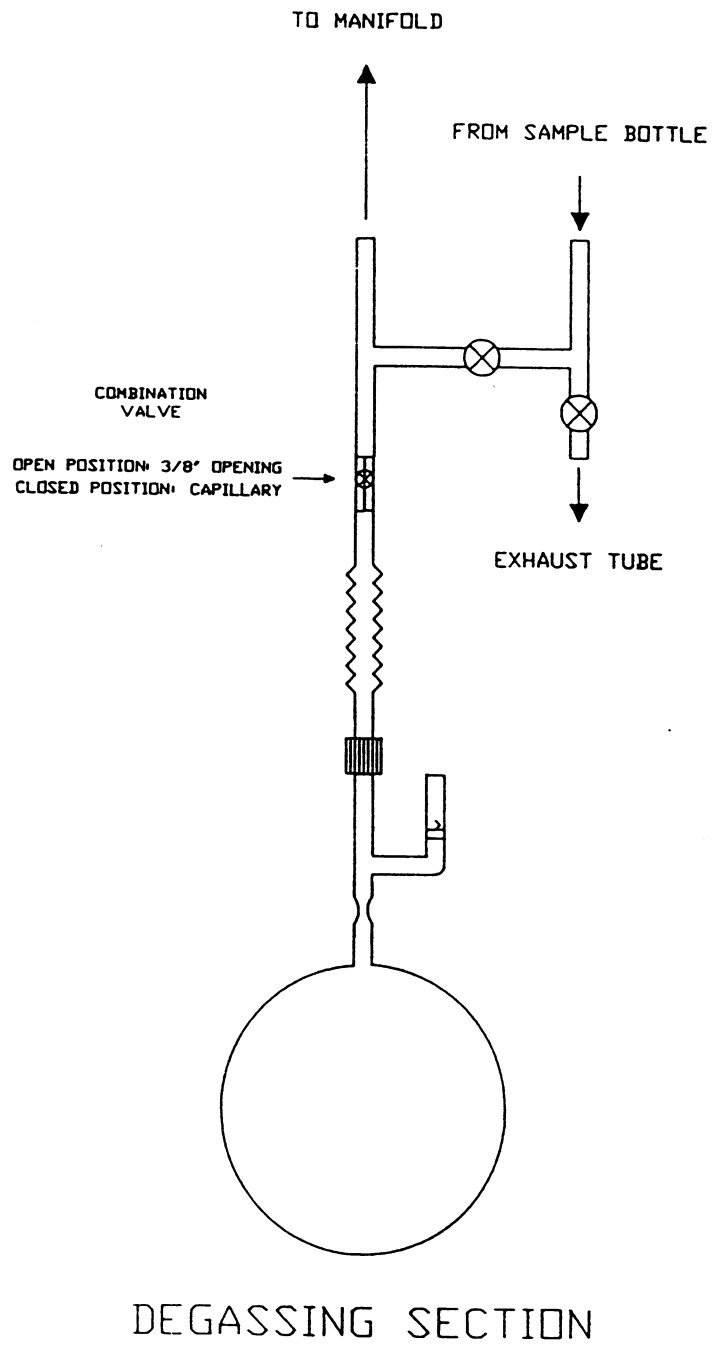


Figure 6: Degassing section

For very low level samples, it is important to shield them from cosmic rays. A simple calculation shows that at sea level, an unshielded sample will have a production of ^3He by cosmic rays of about 50 atoms per gram 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 sufficient shielding 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.

4.4 Sample Transfer

After degassing or extraction, samples are stored in aluminosilicate glass ampoules with breakseals. In order to achieve reliable, automated processing of these samples, they are transferred to stainless steel containers with pneumatic valves (“bunnies”). Samples are transferred eight at a time on a vacuum system (figure 7) in the following fashion. Sample ampoules and empty bunnies are loaded onto the Transfer Line. The former are attached with Viton O-ring couplings while the latter are connected with VCR copper gaskets. The system is evacuated to a pressure less than 10^{-6} Torr, allowing at least 90 minutes to degas the Viton O-ring couplings. System integrity is checked prior to the transfer by a variety of tests. Starting at least 10 minutes before the transfer, the bunnies are chilled with liquid nitrogen. The sections are isolated from the pumping manifold, the bunnies closed, and the breakseals broken manually using hand magnets and iron slugs. Precisely 1 minute after isolation, the bunnies are opened, starting the transfer. Two minutes are allowed for the transfer (5 for the 1-liter and larger tritium flasks). Experiments demonstrate that this time is adequate for more than 99.9% transfer efficiency of the helium samples and head space gases for tritium. Correction for head space partitioning is made for the tritium samples (this correction ranges from about 0.39 to 0.80%).

The bunnies are subsequently closed and transferred to the mass spectrometer manifold for automated processing. The computer program which controls the transfer line automatically transfers the sample information and bunny serial numbers to the spectrometer control software, and schedules their analysis. Periodic blanks are run on the transfer line to verify system integrity, and to check for cross seat leakage on the manifold valves. The latter is accomplished by performing a blank run with air in the manifold. Less frequently, checks are made for cross seat leakage of the bunny valves themselves.

4.5 Sample Processing

The samples are stored on a vacuum system manifold to await processing. The sample processing line is pictured schematically in figure 8.

All valves are pneumatically operated ultra-high vacuum (UHV) stainless steel bellows valves (Nupro type SS4BW) which are controlled by the mass spectrometer computer *via* solid-state, relay-actuated, solenoid valves. The line is constructed of stainless steel, with UHV connections either of the ConFlat (Varian or substitute) or VCR (Cajon) type with copper or nickel gaskets. The water trap is cooled with a florence flask style double

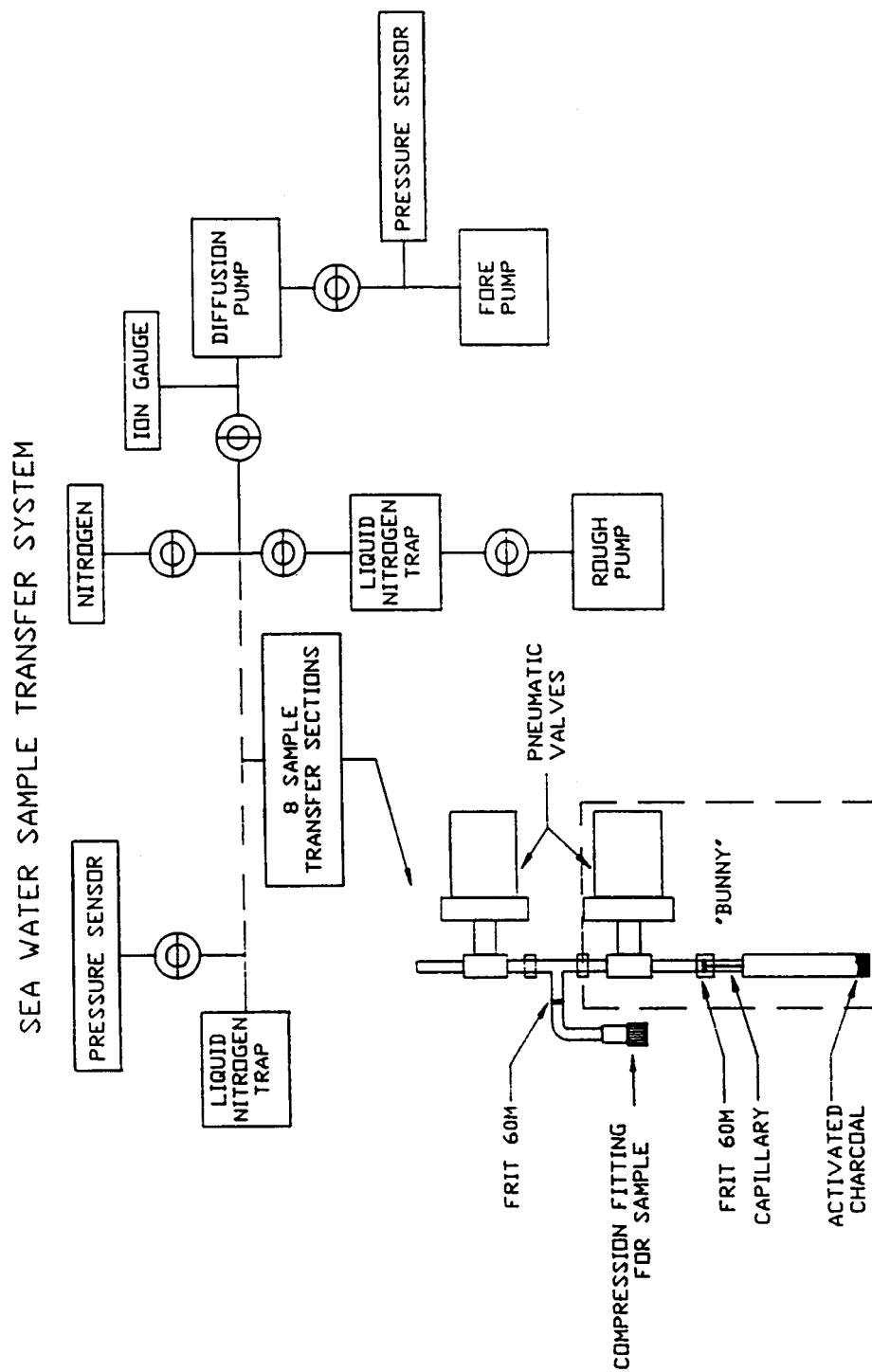


Figure 7: Sea water sample transfer system

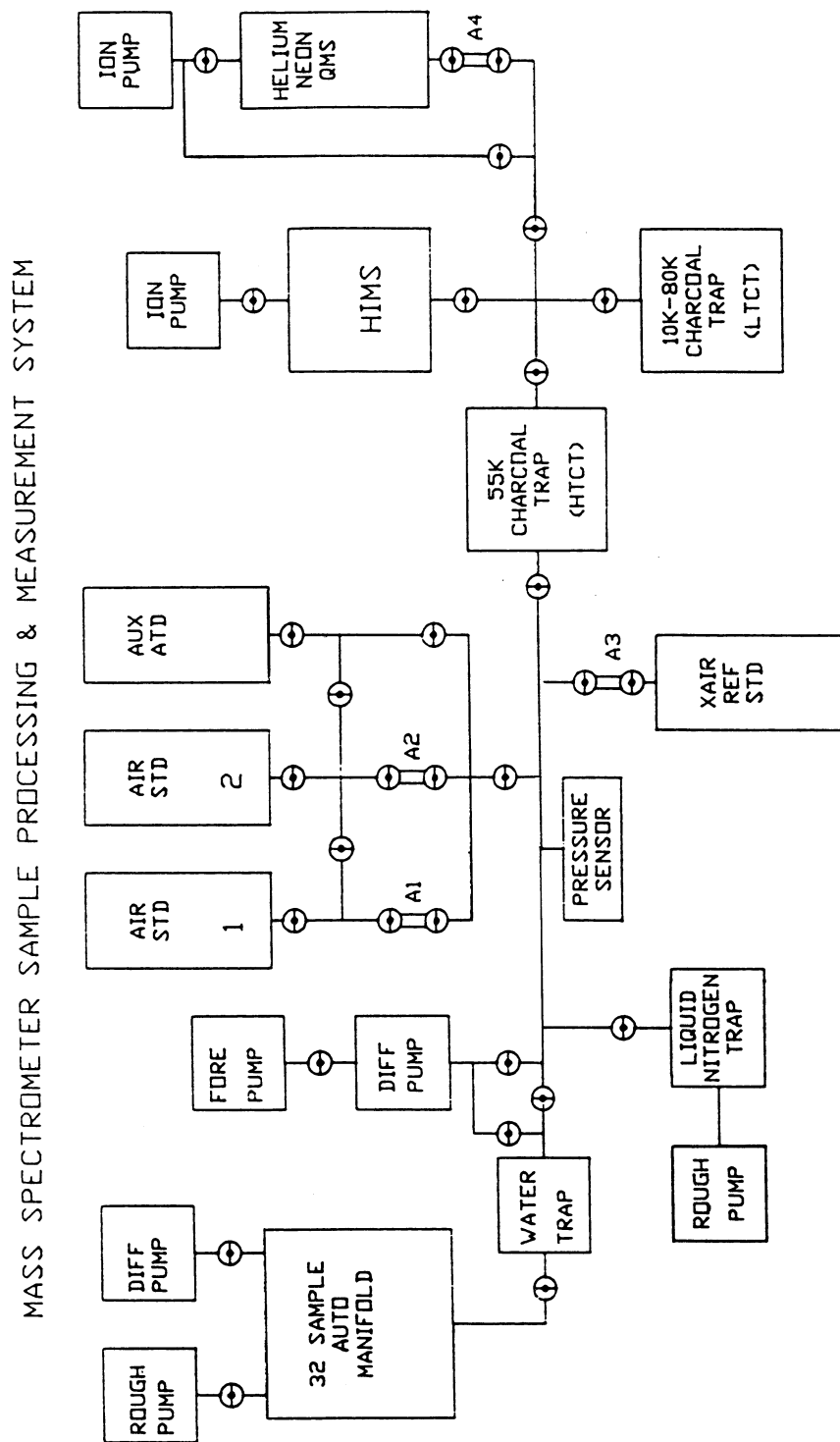


Figure 8: Mass spectrometer sample processing and measurement system

walled glass dewar filled with liquid nitrogen, and has a staying capacity of around three days, although it is filled daily. The trap is replaced every week with a “clean and dry” trap, since it will eventually fill with water. The other two cryotrap are cooled with a closed cycle helium refrigeration system (Air Products Compressor No. CSW-204), with a single stage expander (Model No. DE-102) for the “high temperature” cryotrap, and a double stage expander (Air Products Model DE-202) for the “low temperature” cryotrap. High temperature cryotrap (HTC) temperature is measured using an Au-Fe thermocouple, and low temperature cryotrap (LTC) temperature by a silicon diode thermometer. System pressures are monitored by thermocouple and ion gauges. All are monitored using a 16-channel multiplexed, 12-bit analog-to-digital converter (ADC) interface on the computer. In addition, the pneumatic pressure supply for the valves is monitored by a low pressure trip point. Details of the trap construction and performance as well as vacuum system design have been described by Lott and Jenkins (1984).

At the appropriate time, the vacuum pressure is measured by ion gauge and recorded, and the processing line is isolated from the diffusion pump. The sample is introduced into the system (the “bunny” valve is opened), and exposed to the water trap for 90 seconds (the time lapse is chosen to prevent “flash through” of water vapor to the cryotrap). Sample pressure in the line is measured statically *via* thermocouple gauge (Granville-Phillips Convector gauge), and if above an empirically determined limit, processing is aborted. The pressure is measured “downstream” of the water trap so that water vapor does not contribute to the measurement. After a total elapsed time of 130 seconds, the sample is introduced to the high temperature cryotrap (activated charcoal operated at 60 K) for a period of 30 seconds (again, to avoid flash through, this time for nitrogen and other gases). If the pressure does not drop below another empirically determined limit, the sample would be aborted at this point. The sample is then introduced to the low temperature cryotrap (LTC, activated charcoal operated at 10–15 K), and drawn for ten minutes. The high temperature cryotrap blocks all gases but helium and neon, which are drawn quantitatively onto the low temperature trap. The LTC is then isolated, and warmed to 40 K. At this point, the remainder of the vacuum system is opened to the diffusion pump manifold, and the bunny is closed.

Air standards (see next section) are interspersed with actual samples, and are prepared in an identical fashion, except that the air standards are not processed through the water trap. The frequency with which air standards are measured depends on the stability of the mass spectrometer, but typically four unknown samples are processed between standard analyses. Prior to analysis of a sample group (a set of eight samples arranged on one of the four sample manifolds), a manifold “blank” is performed to ensure that the manifold seals are leak tight. Processing of these samples is aborted if the blank is above a critical level. The appropriate level is dependent on the samples being run, which in turn determine the apparent processing blank due to memory effects. For tritium samples, this limit is usually set for the equivalent of a $1\text{--}2 \times 10^{-10}$ cc (STP) He. For helium isotope samples, it is usually ten times larger.

A period of 4 minutes is allowed for thermal equilibrium and stabilization of the trap. At this temperature, virtually all of the helium is released from the charcoal, while virtually all of the neon is retained. An aliquot (about 0.5%) of the sample is introduced into a quadruple mass spectrometer (QMS, Balzers Model QMG-112), and the amount of

helium is measured. The QMS mass is set using a 12 bit digital to analog converter (DAC), and the output monitored with the multiplexed 12 bit analog to digital converter (ADC). If the sample exceeds certain prescribed limits (usually a factor of two larger than normal sample size), the sample is volumetrically split between various parts of the vacuum line such that an appropriate amount of helium is let into the mass spectrometer.

The mass spectrometer is isolated from its ion pump system, and the sample introduced by expanding from the cryotrap section for a period of precisely 30 seconds. In this time 97.5% of the helium is introduced with no detectable isotopic fractionation (Lott and Jenkins, 1984), and only about 1% of the neon. Tests with neon enriched samples indicate that this level of contamination produces no significant measurement aberrations. During mass spectrometric analysis of helium isotopes, the LTC is further warmed to 75 K, allowing a total of 10 minutes to reach thermal equilibrium, and an aliquot of neon is introduced into the QMS for isotopic analysis. In addition to measuring masses 20 and 22, determinations of peaks at masses 18, 32, 40 and 44 are made to monitor sample purity and look for possible contributions from doubly charged Ar and CO₂. While the QMS neon analysis is proceeding, the LTC is ion pumped to remove the remaining Ne and any contaminating gases that may have “bled through” the HTC.

On a daily basis, the cryotrap are cycled up to approximately 200 K for about 90 minutes while being pumped, (less frequently during tritium analysis). The system is stopped on an approximately monthly basis to cycle the traps to room temperature overnight for a more thorough pumpout of both traps and vacuum jackets. The latter process is executed whenever significant degradation of system ultimate pressure or LTC minimum temperature occur.

4.6 Standardization

Standardization of the mass spectrometer, as well as monitoring of instrumental performance is accomplished by repeated measurements of air standards, interspersed between samples. Helium isotopic measurements are expressed as isotopic ratio anomalies relative to the atmospheric standard. The assumed value of the mole fraction of helium in dry air is 5.24×10^{-6} , and the adopted atmospheric ³He/⁴He ratio is 1.384×10^{-6} (Clarke *et al.*, 1976).

For normal seawater helium measurements, the air standards are obtained by evacuating a valved 15-liter stainless steel (helium leak tight) tank, which is subsequently filled with marine air at a known temperature, pressure and relative humidity. 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 (Lufft Model 4007), to an accuracy of 5% and the vapor pressure of water is corrected for, using standard tables. During use, the air standard tank and stainless steel aliquoting volumes are enclosed in an aluminum box bolted to the underside of the spectrometer table, ensuring thermal equilibrium between the aliquot volume and the tanks (there are two, 15 l tanks for cross comparison). This configuration also permits only very gradual temperature changes in the aliquoting system due to the large thermal mass of the spectrometer and table.

An air aliquot volume is custom made as a fixed bore volume between opposing valve seats compatible with our standard pneumatic UHV valves. Aliquots are calibrated by cross comparison with glass aliquot volumes placed in parallel using the same source tank. The glass aliquot volume (consisting of two glass stopcocks joined by glass tubing) are calibrated gravimetrically with triply distilled, ultrapure mercury.

The “running air standard” consists of two metal aliquot volumes operated in parallel from the 15 l source tank. Their “sizes” are adjusted as needed by insertion of metal slugs of known size (measured gravimetrically using a precisely determined density), so that in combination, their size approximates the median sample size. For example, their combined volume would be about 0.4 cm^3 for the analysis of helium samples extracted from 45 g water samples. The ratio of aliquot sizes is set so that simple combinations of numbers of aliquots generate air standards of differing sizes for “standard curves.” Typically, the ratio is 4:1, so that a simple standard curve of 80%, 100% and 120% of nominal size can be easily created. In addition, the relative size of the aliquot volumes can be readily checked by comparison of four small aliquots *versus* one large aliquot. The standard curve thus created permits a correction for apparent isotopic ratio dependence on sample size, as well as non-linearity in ion beam intensity. 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 intercomparing the running air standards when a new standard is “brought on line.”

For the tritium analyses, a similar procedure is followed, with some changes due to the smaller and more variable sample sizes. 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.

4.7 Mass Spectrometry

Helium isotope measurements are made using a statically operated, dual collecting, all metal, 90° magnetic sector mass spectrometer (*cf.* Jenkins and Clarke, 1976). Generally, a modified Nier type source is used, although a Bauer source has also been employed. Source sensitivity is typically on the order of $1\text{--}3 \times 10^{-4}$ amps/Torr for He, with an internal volume of about 1 l. Nominal resolution is 1:625, and in practice, amounts to a contribution to the center of the ^3He mass position of about 10^{-5} of the $\text{H}_3\text{-HD}$ peak. The instrument is “tuned” by adjustment of ion gun plate voltages and movement of the source

and analyzer magnet positions. Criteria used in this process are ion beam intensity, peak shape (determined by scanning the beam across the detector), and the “depth” of the ion intensity minimum between the H₃-HD and the ³He peaks.

The ⁴He beam is measured using a Faraday cup detector in combination with a solid state (or vibrating reed) electrometer. The ³He beam is measured with an electron multiplier (typically 20-stage focused mesh), operated either in the pulse counting or integrated current mode. The former is preferred, since it permits some degree of multiplier gain independence, along with the possibility of optimizing performance for the style of measurement. For a given ion beam intensity, output count rate exhibits a “plateau” (a range of relatively low slope) *versus* dynode voltage. At the low voltage end, count rate is a strong function of dynode voltage. At the high voltage end, count rate rapidly increases due to electron cascading and increased noise current. For seawater helium analyses, it is preferable to operate at the high end of the plateau to take maximum advantage of the higher count rates. For the tritium determinations, background count rates are minimized by operating at the low end of the plateau. Precise determination of the gain *versus* dynode voltage and the noise *versus* dynode voltage curves permit one to choose optimum operating characteristics.

It is important to minimize the hydrogen (and hence the H₃-HD) background in the instrument. This is accomplished in three ways: construction of the instrument with hydrogen-free metal, high temperature bake-out, and the use of bulk titanium pumps within the static volume.

After inlet, the ion beam is centered on the collector slit by adjusting the magnetic field so that the ³He ion beam decreases by the same amount for incrementing and decrementing the ion acceleration voltage (approximately 3 kV) by a small amount (*ca.* 2V). Analysis consists of 10 “integration” time periods of ³He (and ⁴He) ion beam averaging bracketed by baseline measurements. The total integration time is approximately 1500 seconds, and the ratio of peak to baseline time is optimized to sample size. For seawater helium isotope determinations, the ratio is typically around six, whereas for tritium determinations, it is about two.

4.8 Software Control

The approach used in this laboratory for computer operation of the mass spectrometer system is described here. Other methods are used elsewhere, but the philosophy used here may be of general interest.

Different aspects of sample processing and analysis need to proceed in parallel to make effective use of system resources and time. For example, while a sample is being analyzed in the mass spectrometer, the neon fraction will be measured in the QMS, and the next sample is being prepared in the vacuum system. Since these processes need to occur in a more-or-less asynchronous sequence, each is controlled by individual programs operating under a real-time operating system (TSX-PLUS) with a priority sensitive adaptive scheduling protocol. Interprocess communication is achieved through the operating system’s message handling services and semaphores, providing the ability to transfer information such as sample name and other operating parameters, and allowing “hand shaking”

where necessary. Several system processes operate continuously, and a number of “human interface” programs are used to communicate with them. The programs are written in FORTRAN-77, while some of the more machine dependent aspects were coded in assembly language as part of a “system subroutine library”. Samples are scheduled automatically as they are loaded onto the mass spectrometer, and various types of processing protocols are accommodated by the programs. Many checks of critical system parameters are made routinely by the programs (*e.g.*, thermal performance of the cryogenics, vacuum pressures, pneumatic pressures) to ensure correct functioning. If parameters fall outside “nominal” values, the system shuts down gracefully.

4.9 Data Storage and Reduction

Data from each analysis is stored in a binary, direct access file on hard disk, with one record per sample, and one file per day. Files are backed up on a daily basis to a floppy disk, and copied to the central computer over the network. There, the daily file is processed for preliminary results and stored on hard disk. A final backup copy from the central computer is made on removable hard disk or tape.

Data is processed on a daily basis. The original (raw) data is never modified, but computed data is added to the data file once it has been processed. A first order memory effect correction is made using an empirically determined function of the previous sample's ion beam intensity. The sample processing blank (performed on a daily basis) is then subtracted from all the air standard analyses, and the $^3\text{He}/^4\text{He}$ ratios and ^4He ion beam intensities are subsequently regressed *versus* time with polynomials. The polynomial regressions are used to interpolate instrument response (sensitivity and discrimination) for all analyses, and the scatter of air standards about the regression is used to estimate measurement precision. Sample size is computed from the interpolated standard response and the ^4He ion beam intensity using the air standard size, corrected for depletion. For helium isotope ratio determinations, the isotope ratio anomaly is computed from the measured ratio and the interpolated standard ratio. For the tritium determinations, the amount of excess ^3He is computed.

An analytical series generally lasts several months, and consists of several thousand sample and standard analyses. Upon its completion, linearity curves (*i.e.*, apparent sizes and isotopic ratios of otherwise identical air standards) are processed, and the linearity factors (usually expressed as quadratic functions of sample size centered on the running standard size) are fit as a function of time and applied to the data.

For tritium determinations, air standard sensitivity and discrimination are recalculated and fit on a longer than daily time basis, since fitting statistics are improved for the longer time series. The uncertainty associated with a given analysis is composed of two factors: uncertainty in instrument calibration and ion counting statistics for the individual sample. The former depends on instrumental stability and frequency of standardization, and contributes less than 1% to the error. The latter depends on integrated ^3He ion beam, *i.e.*, the total number of ^3He ions collected during the analysis. Both are accounted for in estimation of sample uncertainty.

5. References

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