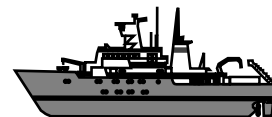# Advances in Analysis and Shipboard Processing of Tritium and Helium Samples

D.E. Lott, III, and W. J. Jenkins, Woods Hole Oceanographic Institution, Woods Hole, USA. wjenkins@whoi.edu

The World Ocean Circulation Experiment (WOCE) one-time hydrographic survey was aimed at the characterisation of the global distributions of properties for the purposes of describing and quantifying the large scale mean circulation and ventilation of the world's oceans. Our role in WOCE was to determine distributions of tritium, ^{3}He and the light noble gases (He and Ne). The large number of samples demanded a substantial increase in analytical capability, which is limited by both measurement throughput and sample handling capacity. Advances in automation and cryogenic techniques (e.g., Lott and Jenkins, 1984) have dramatically improved the former, but the latter had not changed substantially since the days of GEOSECS, nearly a quarter of a century before.

It immediately became clear that at-sea sample processing would be required. Once a water sample is obtained from a Niskin bottle, the gases must be extracted from the water and stored in aluminosilicate glass ampoules in preparation for mass spectrometric analysis of helium isotopes and neon. Additionally, water must be degassed and stored in aluminosilicate glass flasks for incubation and measurement of tritium by ^{3}He regrowth (e.g., see Clarke et al., 1976). Prior to WOCE, water samples were stored in clamped copper-tube samplers for He-Ne analysis, and argon-filled glass bottles for tritium analysis, both of which were shipped back for shore-based processing. For this programme, we developed a system which enabled the ship-board extraction of helium and neon from sea water samples, and the degassing of samples for ^{3}He regrowth measurement of tritium. This reduced the risk of contamination and sample loss, while speeding up the sample processing programme, reducing the amount of shore-based effort, and advancing the initiation of the tritium incubation period. The net result was more efficient processing and more reliable, better quality results.

The at-sea sample processing system

The sample processing system consisted of a self-contained 20 ft × 8 ft laboratory van which was shipped to the port of departure and mounted on the ship's deck. The van contained two vacuum systems, attendant instrumentation and computer control systems, a sink, drawers, cabinets and bench-top work-space. It required a single phase electrical source, compressed air, and fresh water supply, all of which were supplied through a common interface panel. In addition, a modest amount of crushed ice was required for sample extraction. No additional cryogens were required.

Separate water samples were drawn for tritium and helium from Niskin bottles through tygon tubing into valved, stainless steel sampling cylinders. On return to the van, the sample details were entered into a computer data base for tracking purposes. The sample cylinders were attached to their respective processing lines. There were two lines, a degassing line for tritium samples and an extraction line for helium/neon samples. These systems are described in more detail below. The samples are processed on the vacuum systems under computer control, and bar-code labels are automatically generated for glass ampoules or flasks containing the processed gas or water samples.

Helium and neon extraction

Sample cylinders were constructed from lengths of type 316 stainless steel tubing welded to custom-made diameter reducers and o-ring sealed plug valves on either end (see Fig. 1). The plug valves (Nupro SS-4P4T-3571) were modified by drilling a 0.094 in hole through the plug into the "bore" to permit cleaning and pumping out the bore while the sample was isolated within the cylinder. After connecting to the Niskin bottle with tygon tubing, the cylinder was flushed with several volumes of sample water from the Niskin, while the valves were repeatedly rotated to release air trapped in the valve bores and pump-out holes. Also, the cylinder was rapped sharply with a wooden "bat" to loosen any adhered bubbles during transfer. Once a bubble-free water stream was achieved, the cylinders were closed and disconnected from the Niskin and tubing. The salt water was immediately shaken out of the cylinder ends, and the ends were then flushed with fresh water and rinsed with isopropynol and allowed to air-dry.

The system consisted of eight identical extraction sections (Fig. 1, eight samples were processed at a time) attached to a pumping manifold which was evacuated through a cryogenic trap using first a rotary mechanical pump (Varian SD-200) and ultimately using an oil-based diffusion pump (Varian HS-2). The diffusion pump was backed by another rotary mechanical pump, and cooled using a closed-system water + ethylene glycol recirculation loop (Neslab CFT-33). The cryogenic trap was held at roughly -130°C using a PolyCold (P-75) refrigeration system. Vacuum pressure was measured by convection and ion gauges which were monitored by computer. The cryotrap was routinely warmed up and accumulated water removed after 25-50 extractions.

When an adequate vacuum pressure was achieved (less than 3×10^{-7} torr), indicating the lack of significant vacuum leaks, beakers of water with crushed ice were mounted to cool the glass ampoules. Then the sections were isolated from the pumping manifold and the water was allowed to drain into the reservoirs by opening the cylinder valves. 100 watt heaters, which were clamped to the bottom

of the reservoirs, were then turned on. After a few minutes, when the water temperature rose above a critical value, water transfer to the ampoule commenced. Boiling of the water sample, aided by stainless steel "boiling chips" effectively stripped dissolved gases from the water sample, and the water vapour transfer quantitatively swept the gases into the ampoule. The constant vapour stream prevented back-streaming of accumulated gas through the capillary back into the system. Over the course of the extraction, several grammes of water would be transferred, and a significant water transfer rate was observable by the downward deflection of the accumulating water's surface. After 10 minutes (from the time the heater was turned on) the sample was sealed off by applying a glass blowing torch to the capillary. The samples were subsequently labelled and stored, and the vacuum sections removed, rinsed with fresh water and isopropynol and dried using a compressed air flow. With care, and barring significant problems, extractions could be done at a rate of approximately one every two hours.

Through extensive experimentation, using prototype systems attached directly to a mass spectrometer, we established that quantitative (>99.8%) extraction was achieved with this procedure. One consideration, however, was the potential for compromise of the water sample due to diffusion through the polymer seals during storage in the sample cylinder. We performed a series of tests by storing degassed water in these sample cylinders for various periods
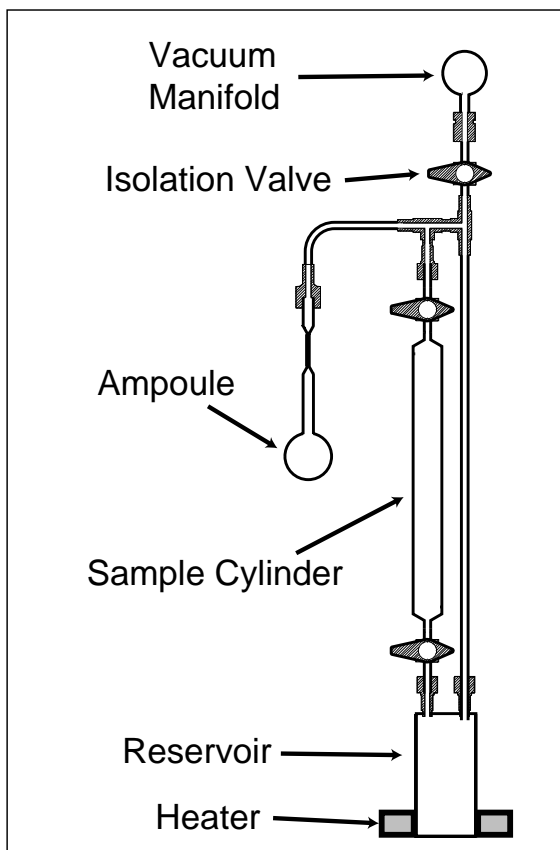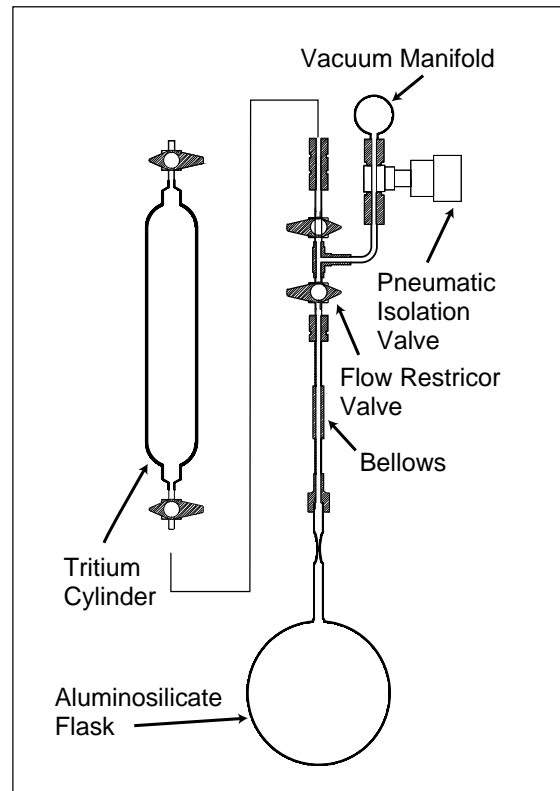

Figure 2. Degassing line section schematic.

of time. The observed rate of He increase in the cylinders was 0.019 0.003% per hour. Thus a sample of Pacific deep water, with a helium isotope ratio anomaly of 30%, stored for about 12 hours (typically the maximum that we stored samples at sea) would have its isotope ratio lowered by only about one half our analytical uncertainty, and could in principle be corrected since we tracked sample acquisition and processing times. For neon, the rate of contamination was much lower, being 0.004 0.002% per hour. Inasmuch as dissolved neon concentrations rarely departed from equilibrium more than a few percent, the corresponding errors were infinitesimal.

Tritium sample degassing

Prior to drawing water samples from the Niskin bottle, the tritium (500 cc) cylinders were dried and filled to a slight positive pressure with dry argon. Immediately prior to connecting the tygon tubing to the Niskin, the lower valve was opened, venting the argon through the tubing to displace ambient air. The cylinders were flushed with about two volumes of sample water, while the valves were actuated and the cylinder was rapped to remove adhering bubbles. After disconnecting, the cylinder ends were rinsed and dried prior to attaching to the degassing line. During this process the exposure of the water sample to ambient water vapour was minimised due to the risk of contamination. In particular, extreme care was used to avoid contact with devices (e.g., luminous dial watches) containing tritiated materials.

The degassing line (Fig. 2) consisted of six sections

Figure 1. Extraction line section schematic.

which are evacuated by a vacuum manifold virtually identical to that of the extraction system. The cryotrap was "cleaned" much more frequently, usually after every third degassing because water accumulation was much greater for degassings. This was due to the much longer pumping times and large volumes of water involved.

The samples were introduced into the 1 litre aluminosilicate glass storage ampoules after isolating the vacuum section from the pumping manifold. After the sample was drained into the flask, the isolation valve below the cylinder was closed so that the cylinder could be removed for cleaning and drying while the degassing proceeded. The capillary valve was turned to restrict water vapour loss, and the sample was initially pumped to remove the bulk of head space gases released by ex-solution during introduction into the flask.

Degassing of water samples for ^{3}He in-growth measurement of tritium required that at least 99.9995% of
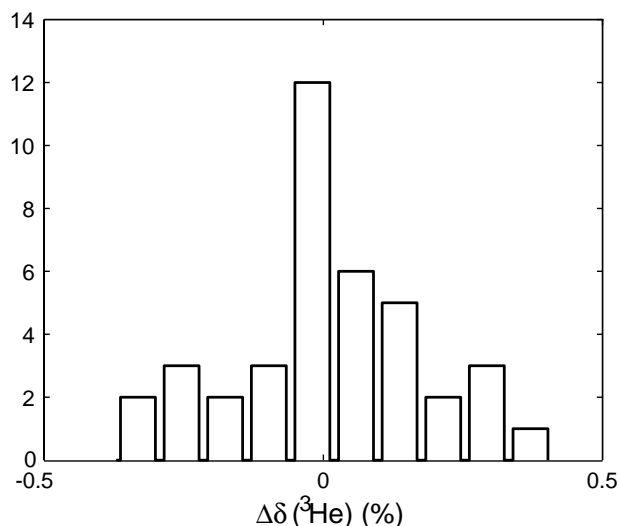

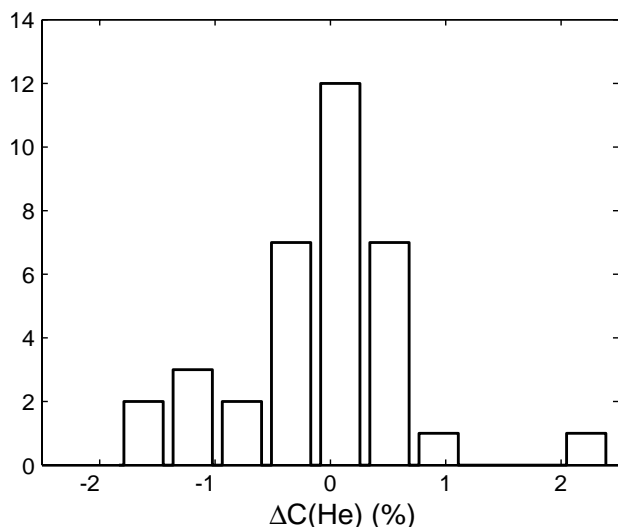*Figure 3. Histogram of helium isotope ratio anomaly differences between replicate samples.*

Figure 4. Histogram of helium concentration differences between replicate samples.

the normally dissolved helium was removed from the water sample. This was accomplished by repeated cycles of shaking (15 minutes) and pumping (2 minutes). Pumping was accomplished in the first three cycles with the mechanical vacuum pump, and by using a diffusion pump in the last two cycles. The pressure surges associated with pumping was measured via computer using convection and ion gauges to monitor degassing progress, and to alert the operator to leaks. Experiments indicated that 97–98% of the dissolved He was released into the head-space during the shaking cycle, and that the efficiency of its removal (from the head space) during pumping was much greater. Thus five shake and pump cycles, not including the initial degassing accomplished during introduction, in principle resulted in a minimum of 99.9999% degassing.

Mass spectrometry

Helium isotope ratios were measured in a statically operated, $\pi/2$ magnetic sector, dual-collecting mass spectrometer with cryogenic processing (e.g., see Lott and Jenkins, 1984) against a reference air standard. A slight dependence of measured isotopic ratio size was monitored using isotopically identical standards of varying size, and the results corrected for this effect. The corrections were generally no more than about one s (i.e., within measurement error). Measurement precision, as determined by reproducibility of secondary vs. running standards, and reproducibility of running standards ranged from 0.10 to 0.13% in $\delta(^3$He), depending on the cruise. Systematic errors in the running air standard, as deduced by repeated comparisons with independent air standards, is less than 0.05%. Measurement reproducibility, based on replicate pairs of samples, as determined by the RMS difference between replicates (see Fig. 3) divided by $\sqrt{2}$, is 0.12%. The replicate $\delta(^3$He) differences are not statistically correlated with concentration differences, suggesting that bubble trapping during sampling and that any artefacts due to sample extraction are not significant contributors to isotope ratio anomaly errors. In addition, we obtained 3 groups of quadruplicate samples (helium samples drawn in quadruplicate from the same Niskin bottle). Measurement standard deviations for these three experiments averaged to 0.08%. In summary, measurement precision for the helium isotopic ratio was better than the stipulated WOCE requirement of 0.15% of analysis.

Helium concentrations were determined by ion current manometer, referenced to accurately determined aliquots of the reference air. The air standards were compared to multiple secondary gas standards at regular intervals and some adjustments made to bring the two into agreement. Replicate water sample reproducibility indicates an uncertainty in the dissolved gas concentrations of order 0.54% (Fig. 4), significantly larger than mass spectrometric analytical errors, but close to the WOCE target specifications for those measurements (0.5%). Mass spectrometric measurement uncertainties were of order 0.1%, with systematic uncertainties around 0.1% associated with

running standard calibration. We attribute the larger errors to sample handling, in particular the probable inclusion of trapped small air bubbles during sampling. The reproducibility is identical for *both* helium and neon, despite the fact that the gases are measured on two separate mass spectrometers: the He is measured on the branch-tube, magnetic sector instrument, while the Ne is measured using a quadrupole mass spectrometer. In addition, the ΔHe and ΔNe differences were highly correlated, with a slope statistically indistinguishable from air addition. Thus the variability is clearly due to the inadvertent addition of air (in the form of trapped bubbles either in the barrel of the sample cylinders or swept in from the tygon tubing). This additional air is automatically corrected for in the computation of the excess ^{3}He so that it does not add any significant error to the excess ^{3}He results.

Tritium was measured using the standard ^{3}He regrowth technique (e.g., Clarke et al., 1976; Jenkins, 1981; Jenkins et al., 1983). On return from sea, the degassed samples were stored in a shielded area (under 4 m of concrete) for at least one year, and the tritiugenic ^{3}He harvested for mass spectrometric analysis. During storage, a significant amount of ^{3}He can be generated by cosmic ray spallation of oxygen nuclei in the sample. In an unshielded sample stored at sea level, 43°N latitude, this production of ^{3}He results in an *apparent* tritium concentration of approximately 0.020 T.U. It should be noted that this is an apparent concentration, not an actual tritium contamination. Because of the shielding the production rate experienced by our samples is much smaller, generally around 0.002 T.U. However, because our at-sea degassed samples spend part of their time in a less-sheltered environment, some additional contribution due to cosmogenic ^{3}He production will "inflate" the blank level tritium measurements. The effect, which presents itself as a non-zero blank tritium determination, varies with the *ratio* of time spent in the exposed state to the total storage time. We monitored this cosmogenic interference by obtaining, processing and analysing almost 200 tritium samples that were "known" from hydrographic and radiocarbon measurements to be tritium-free. The mean cosmogenic blank effect is 2.1 ±0.3 mTU (1 mTU = 0.001 TU) for all but one of the WOCE Pacific cruises (P21), which had an observed blank of 6.1 ±0.6 mTU due to extended exposure during shipboard storage and surface shipping. We can correct the data for the cosmogenic interference blank to an accuracy better than 1 mTU (0.001 TU).

On the mass spectrometer, running-standards were cross-compared with external standards to an accuracy of order 0.1%, with systematic uncertainties of the same order. Measurement uncertainties were dominated by ion counting statistics, and vary with sample size, tritium concentration, incubation time, and other extraneous factors. Whereas for very small tritium concentrations the measurement uncertainty was close to the detection limit (1–2 mTU), the uncertainty increases with tritium concentration to as much as 7–10 mTU for the largest tritium concentrations (1–3 TU), which corresponds to an uncertainty of 0.5%. These are calculated on an individual basis, and reported with the tritium data.

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