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## NATIONAL WATER QUALITY LABORATORY SUPPLEMENTARY TECHNICAL MEMORANDUM 1997-04S

April 7, 1997

From: Peter F. Rogerson, Chief  
National Water Quality Laboratory  
Branch of Analytical Services

Subject: Collection, processing, and analysis of ground-water samples for tritium/helium-3 dating

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Supplemental: This technical memorandum contains supplementary information for NWQL Tech Memo 97.04

### SCOPE

The National Water Quality Laboratory (NWQL) of the U.S. Geological Survey (USGS) has contracted with the Lamont-Doherty Earth Observatory of Columbia University, Palisades, New York, for the analysis of low-level tritium ( $^3\text{H}$ ), total dissolved helium (He), total dissolved neon (Ne), and the helium-3/helium-4 isotope ratio ( $^3\text{He}/^4\text{He}$ ) of dissolved helium for purposes of ground-water dating based on the tritium/helium-3 ( $^3\text{H}/^3\text{He}$ ) method. The precisions of the measurements are, for tritium,  $\pm 4$  percent ( $2\sigma$ ) or  $\pm 0.01$  Tritium Units (TU)<sup>1</sup>, for the helium isotope ratio,  $^3\text{He}/^4\text{He}$ ,  $\pm 0.4$  percent to  $\pm 2$  percent ( $2\sigma$ ), and for the He and Ne concentrations,  $\pm 1.0$  percent ( $2\sigma$ ).

$^3\text{H}/^3\text{He}$  dating of ground water applies to the time elapsed since recharge and isolation from the atmosphere. The method is based on the radioactive decay of  $^3\text{H}$  to  $^3\text{He}$ . As these substances are virtually inert in ground water, unaffected by ground-water chemistry and unaffected by contamination from most anthropogenic sources,  $^3\text{H}/^3\text{He}$  dating can be applied to a wide range of hydrologic investigations.  $^3\text{H}/^3\text{He}$  dating complements existing capabilities within the U.S. Geological Survey for dating of young ground water, such as, uses of chlorofluorocarbons (see joint Office of Water Quality and Office of Ground Water Technical Memorandum No 95.02 and attachments, dated December 29, 1994) and can be applied to dating waters recharged within the past approximately 30 years. The purpose of this Memorandum is to define procedures for submittal of  $^3\text{H}/^3\text{He}$  samples, describe collection procedures, compare and contrast  $^3\text{H}/^3\text{He}$  dating with other methods for dating young ground water (0-50 year time scale), and provide some technical specifics

on the  $^3\text{H}/^3\text{He}$  dating method and interpretation of ages from the analytical results. The following table summarizes the available analyses and lab codes.

<b>Available Analyses and Lab Codes</b>		
<b>Schedule</b>	<b>Lab Code</b>	<b>Determination</b>
1033	2120	Total dissolved He in cc at STP per g water
	2121	Precision of the He determination (in percent $2\sigma$ )
	2122	Total dissolved Ne in cc at STP per g water
	2123	Precision of the Ne determination (in percent $2\sigma$ )
	2124	$^3\text{He}/^4\text{He}$ isotopic ratio for total dissolved He (corrected to date of sample collection, if $^3\text{H}$ is determined on sample; otherwise, reported for the date of extraction of the He from the water)
	2145	Precision of the $^3\text{He}/^4\text{He}$ isotopic ratio (in percent $2\sigma$ )
<b>Lab Codes for tritium determination by the helium ingrowth method</b>		
	2112	Tritium by helium ingrowth, in TU
	2113	Precision of the tritium determination (in TU, $2\sigma$ )

<sup>1</sup>One TU is equal to 1  $^3\text{H}$  atom in  $10^{18}$  atoms of H, or 3.24 picocuries per liter, pCi/L. One liter of water with a concentration of 1 TU produces 7.2 disintegrations per minute (dpm) or 0.12 becquerel (Bq); one Bq corresponds to 1 disintegration per second (dps); one curie (Ci) is equal to  $3.7 \times 10^{10}$  Bq.

### **PLANNING FOR $^3\text{H}/^3\text{He}$ SAMPLING-- CONSIDERATION OF EXPECTED OR KNOWN $^3\text{H}$ CONCENTRATIONS**

As indicated in the preceding table, determination of the  $^3\text{H}/^3\text{He}$  age requires use of Schedule 1033 which includes Lab Codes 2120, 2122, and 2124 and determination of tritium. If tritium is to be determined by the  $^3\text{He}$  ingrowth method, select Lab Code 2112. Prior to submission of the tritium sample for determination of tritium by the  $^3\text{He}$  ingrowth method, careful consideration should be given to estimate the tritium content of the water. This information must be provided to the contract lab at time of submission of the sample and will be used by the lab to determine the amount of water that needs to be degassed and stored for a prescribed helium ingrowth period.

In most samples, the water used for the  $^3\text{He}$  ingrowth determination of tritium will be the approximately 40 cc of water remaining from the original water sample after degassing on the high-vacuum extraction line. In this case, water samples containing more than about 7 TU would need an ingrowth period of approximately 1 month to attain the reported precision of 0.01 TU, and for 40-cc water samples containing 3, 2 or 1 TU, ingrowth periods of 2, 4, and 6 months, respectively, are required to attain the reported precision. For water samples with tritium content estimated to be less than 1-2 TU, the contract laboratory will degas approximately 400 cc of water from the 500-cc sample supplied and flame-seal this sample into a 1-liter glass bulb. If the tritium content of the water sample is more than 1 TU, 30 days ingrowth period for a 400-cc water sample should be sufficient to attain the reported precision. For tritium concentrations in the range of 0.2 to 1 TU, a 4-month ingrowth period is needed for a 400-cc water sample. For tritium contents expected to be less than 0.2 TU, ingrowth periods of 8 to 12 months can be expected.

Most ground-water samples recharged since the mid-1960s will contain sufficient tritium for attainment of the reported precision for ingrowth periods of 1-2 months using the 40-cc water sample from the helium extraction line. Exceptions would be waters recharged prior to about 1964

and young waters that have mixed with relatively large fractions of old, tritium-free water, in which case larger ingrowth sample volumes and possibly longer ingrowth periods would be required. If the reported precision cannot be attained in tritium from a 40-cc sample, the contract lab will repeat the determination using a 400-cc water sample from the 500-cc sample originally supplied to the laboratory.

The Project Office should consider the turnaround time necessary to obtain the desired  $^3\text{H} / ^3\text{He}$  age, especially when planning studies of short duration. Delivery of results will require a minimum of 6 months; however, depending on the time required for helium ingrowth, delivery times could approach 1 year. Further complications can arise in interpretation of age--if, for example, the sample contains a large amount of excess (radiogenic) helium (see technical details below). Although the measurements can be quite precise, users should realize that as with any dating procedure, interpretation of a tracer-based age is not always straightforward.

An alternative means of using this contract to obtain  $^3\text{H} / ^3\text{He}$  ages is to submit samples for the helium isotope analyses (Schedule 1033) and use one of the existing NWQL Lab Codes, 1565 (MDL 0.3TU) or 1043 (MDL 0.1TU), for tritium determination by liquid scintillation and/or gas proportional counting. An ingrowth period is not needed for tritium determination by liquid scintillation and/or gas proportional counting. A limitation is that the precision normally obtained by beta-counting procedures is not as high as that obtained from the helium ingrowth method. (The NWQL cost schedule lists precisions that can be obtained for various beta-counting procedures.) Consequently, larger error bars must normally be assigned to  $^3\text{H} / ^3\text{He}$  ages based on data in which the tritium content is determined by beta-counting procedures. One final consideration is that the contract lab cannot be responsible for determination of age when tritium data are not available.

## **UNACCEPTABLE SAMPLES**

Water samples containing more than 500 TU seriously risk contamination of the low-level tritium laboratory and cannot be submitted to the contract lab for tritium determination by the  $^3\text{He}$  ingrowth method. Dating by  $^3\text{H} / ^3\text{He}$  should not be attempted for waters containing tritium sources in addition to that of normal atmospheric precipitation. Pre-screening via beta-counting of any sample suspected to be contaminated with tritium is required. All personnel involved in water sampling and subsequent handling of water samples for tritium determination must avoid use of watches and other devices with luminescent tritium dials which are known to contaminate tritium samples and tritium laboratories. The Project Office submitting the samples assumes financial responsibility for tritium contamination problems at the contract laboratory caused by submission of inappropriate samples.

## **SAMPLE COLLECTION**

Proper collection of a water sample for  $^3\text{H} / ^3\text{He}$  age determination requires:

1. Filling a special copper sample tube which is used for helium and neon analyses, determination of the  $^3\text{H} / ^3\text{He}$  isotope ratio of dissolved helium, and in most cases, determination of tritium.
2. Filling a 500-cc bottle, which may be used for tritium determination by helium ingrowth (for samples with low (<1-2 TU) tritium content).

Safety-coated 500-cc glass bottles with polycone seals are recommended for the alternative tritium sample, though high-density polyethylene bottles with polycone seals may be substituted. If glass

bottles are used, a headspace of several cc's should be left in the bottle to prevent breakage on warming (expansion). The water samples for helium, neon, and tritium determinations are collected in special pinch-off copper tubes (3/8-inch diameter, 30-inch length, containing about 40 cc of water, and fitted with stainless steel pinch-off clamps at each end). These sample tubes are prepared and owned by Lamont-Doherty Earth Observatory who maintains a stock of them with the National Water Quality Laboratory, Arvada, Colorado.

Both the tritium and helium samples should be collected in duplicate. The duplicate water sample for tritium determination (duplicate 500-cc bottle) should be retained at the Project Office, but both copper tubes should be returned for each sample. The project should request the appropriate number of copper sample tubes from the NWQL who will ship them to the Project Office.

The project will be billed for each set of two sample tubes requested from the NWQL and will be credited in full for each sample returned for analysis. Unused sample tubes remain the property of Lamont-Doherty Earth Observatory and can be returned to the NWQL for credit.

The copper tube for He and Ne determinations can normally be flushed and filled within 5 minutes. Remove and discard the plastic caps that cover the ends of the copper tube, taking care not to scratch or bend or otherwise damage the ends of the copper tube. Damage to the ends of the copper tube may prevent proper attachment of the sample tube to the vacuum extraction line for sample preparation at the contract laboratory. The copper tube, which is fixed in an aluminum channel holding the stainless steel pinch-off clamps, is connected to a closed path from the well or pump. The connection to the well or pump can be of almost any material including plastic, rubber, or metal tubing, providing that all connections are airtight and will not come loose when back pressure is applied during closing of the copper tubes. Clear plastic tubing (Tygon) is preferred because one can visually observe whether air bubbles are present in the water line. It is recommended that connections be secured with stainless steel hose clamps, again being careful not to damage the end of the copper tube. The length of the path from the well or pump discharge should not exceed about 5 feet to minimize the possibility of gas separation from the water sample prior to sealing the copper tube.

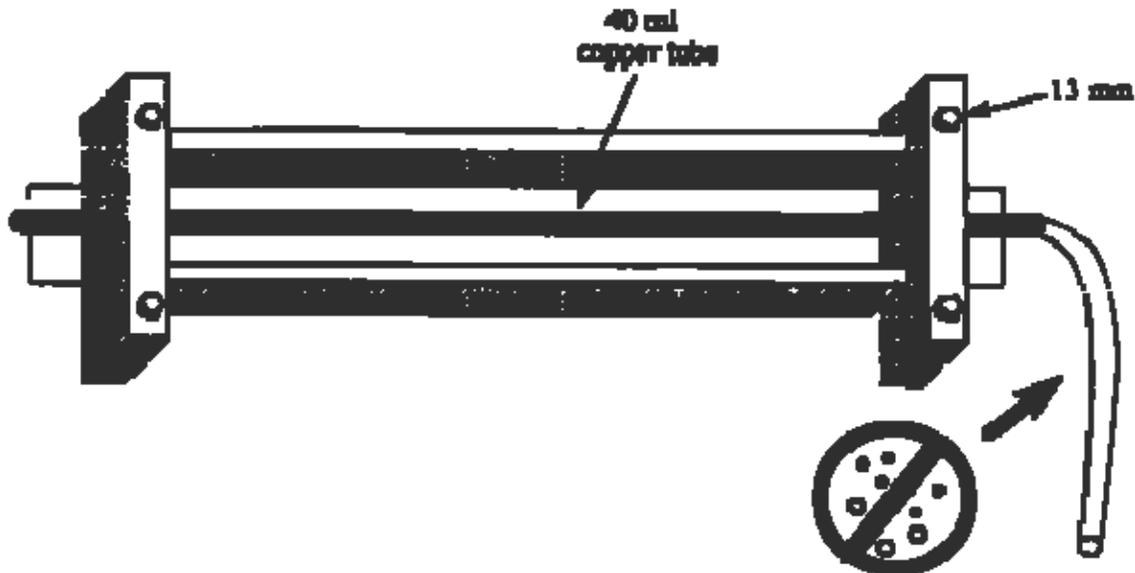
Any trapped air or formation of gas bubbles in the helium water sample will produce erroneous results. Back pressure is normally applied to the discharge end of the copper tube during filling. The Project Office will need to obtain a small valve and suitable compression type fittings to attach the valve to the discharge end of the copper tube. Figures 1 and 2 show diagrams of the copper tube and back pressure valve assembly, respectively. The symbols for "no bubbles" show areas where clear plastic tubing can be inserted to observe inflow to the copper tube (Figure 1) and discharge from the copper tube (Figure 2) before the back pressure valve to check for bubble formation. Both water flow and back pressure on the sample should be increased if gas bubble formation is observed in either clear plastic tubing. The valve should not be closed completely during filling because a steady flow of water must be maintained through the copper tube during sealing. Suitable parts to make the back pressure valve assembly are:

Whitey valve SS-1RS6, 3/8-inch stainless steel valve  
Swagelok 3/8-inch Nylon ferrules set, NY-600 sets (10 each)

These items are available through the Swagelok Companies. Check local listings for suppliers of Swagelok products or equivalent. An over-pressure of approximately 1 atmosphere, 14 psi, is normally sufficient to prevent gas bubble formation in the ground-water sample. However, in

general, to prevent gas bubble formation, the back pressure applied must exceed the internal pressure of the dissolved gases in the water sample.

**FIGURE 1**



**FIGURE 2**

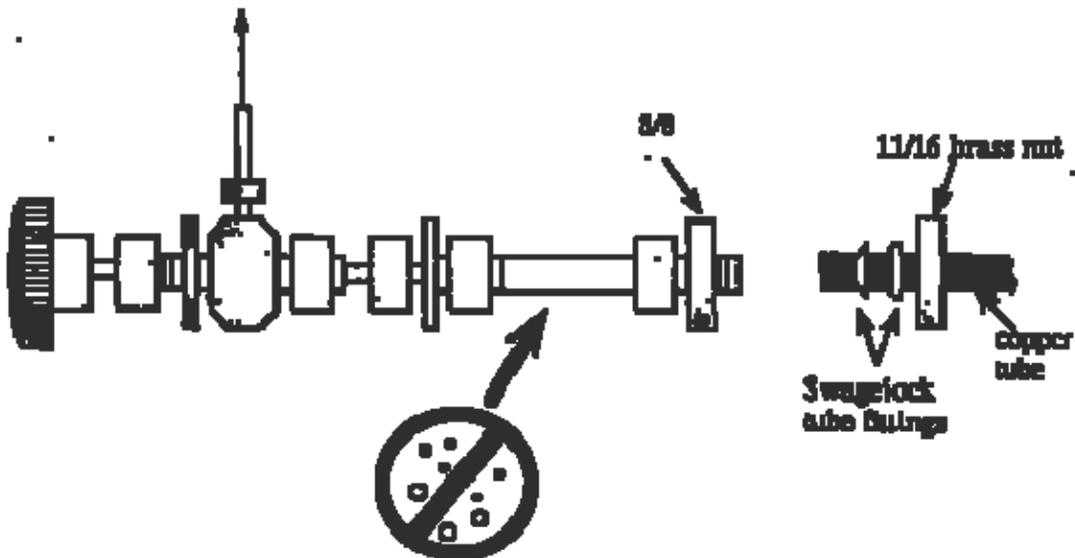


Figure 3 (A-D) shows photographs of the equipment used to take the noble gas and tritium sample. Figure 3A shows the copper tube in an aluminum channel with stainless steel pinch-off clamps, a 1/4-inch copper tube used to connect to the pump, and back-pressure value. Figure 3B shows the parts of Figure 3A connected for sampling and a 500-ml safety coated glass bottle with polycone seal for collection of a tritium sample. Note that in this case, clear plastic tubing was not inserted at the inflow and outflow ends of the copper tube and thus, in this case, there is no opportunity to check if gas bubbles are forming inside the tubing. Figure 3C shows the back-pressure valve connected to the end of the copper tube. Figure 3D shows the ends of properly sealed copper tubes (note the centering of the tubes in the pinch-off clamps).

A socket wrench with 13-mm (note metric bolt) socket is used to turn the bolts that close the pinch-off clamps. Prior to turning the bolts, the entire line from the well through the copper tube should be tapped forcibly to dislodge any gas bubbles that may be in the line or copper tube. During the tapping process, the copper tube should be held at an approximate 45-degree angle with discharge pointing up, to assure that gas bubbles, if present, will be completely flushed. This tapping procedure normally requires about 1 minute to complete. Once satisfied that water flowing through the copper tube is free of any gas bubbles, the socket wrench is used to close the bolts on the pinch-off clamps, beginning with the bolts at the discharge end. Before turning the bolts, be sure to position the copper tube in the approximate center of the pinch-off clamp. There are two bolts on each clamp. Turn the bolts in successive order (back and forth approximately four (4) times until firmly closed) so that the blades of the pinch-off clamp close approximately evenly. The pinch-off clamps are machined to leave about a 1-mm space when the bolts are turned all the way down; however, care should be taken not to overtighten and strip the threads on the bolts. After tightening the discharge end bolts, tighten the upstream bolts in the same manner, again centering the copper tube between the blade. When done, doublecheck to be sure that all bolts are tight. The sample is then complete and the copper tube can be disconnected from the well or pump.

Remove the back-pressure valve from the discharge end of the copper tube. Precautions should be taken not to scratch or otherwise damage the ends of the copper tubes. If waters are corrosive, such as seawater or other saline or acidic waters, the ends of the copper tubes should be washed with dilute water to prevent corrosion, which might prevent obtaining a proper seal when extracting the noble gases. Care should be taken not to further bend the ends of the sealed copper tubes because they can easily break off. If the tubes were received with plastic caps protecting the ends, do not replace the caps after filling. Additional instructions on ground-water sampling for noble gases provided by Lamont-Doherty Earth Observatory appear at the end of this document.

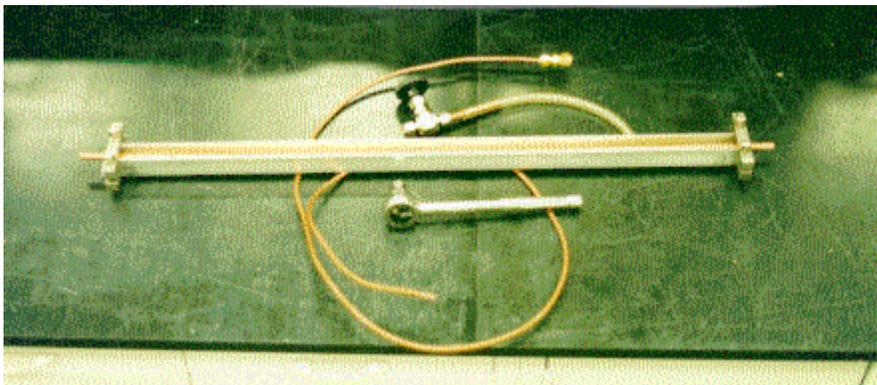


Figure 3a. Copper Tube in Aluminum Channel

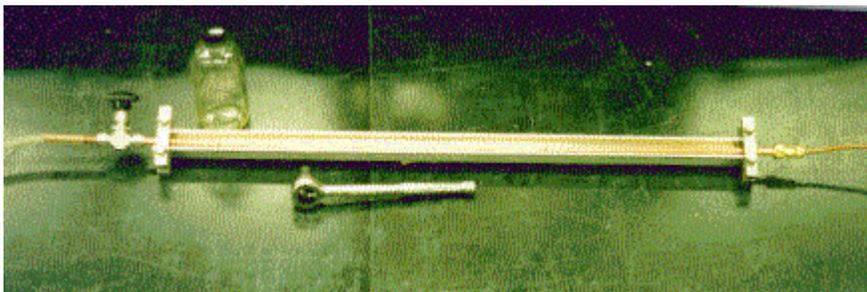


Figure 3b. Parts Connected for Sampling

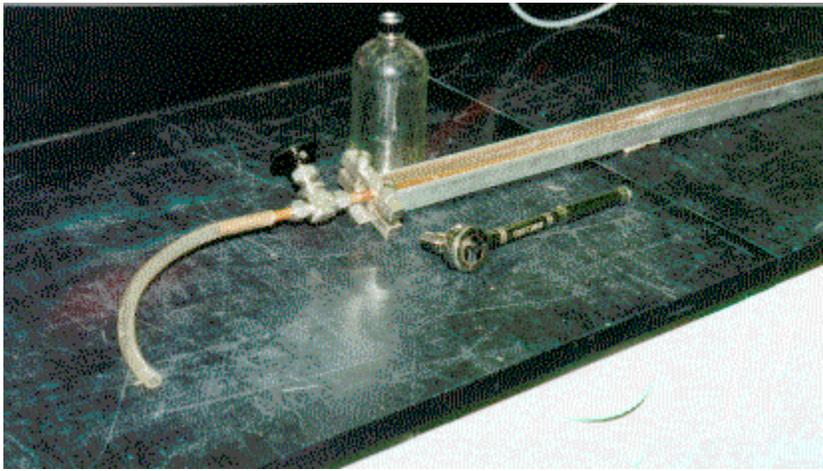


Figure 3c. Back-Pressure Valve Connected



Figure 3d. Properly Sealed Copper Tubes

USGS personnel will be responsible for proper collection of water samples, including (1) care in avoiding possible damage to ends of sample tubes which might preclude proper connection to laboratory high-vacuum extraction lines, and (2) exclusion of gas bubbles during sample collection. The contract lab will report samples that could not be extracted because of improperly sealed sample containers and/or damaged sample containers.

### **SUBMITTAL AND LOG-IN PROCEDURES**

After collection, the samples are retained at the Project Office until log-in numbers can be assigned by the NWQL. The submittal procedure is as follows:

1. The Project Office sends the ASR forms to the NWQL (ATTN: Ann Mullin) by either mail or fax ((303) 467-8240); contact (303) 467-8235.
2. The NWQL assigns log-in numbers for each sample and notifies the Project Office of the log-in numbers.

3. The Project Office is then responsible for writing the NWQL log-in number on each sample.
4. The Project Office ships the samples directly to the Noble Gas Laboratory at Lamont-Doherty Earth Observatory (see address below).
5. Duplicate copies of the NWQL ASR forms, showing the assigned log-in numbers, must accompany the water samples shipped to the Noble Gas Laboratory at Lamont-Doherty Earth Observatory.

The log-in process will automatically credit the Project Office for return of sample tubes. Unused sample tubes, or samples taken but not submitted for analysis, can be returned to the NWQL for credit. A nominal charge will be deducted from the deposit for replacement of filled or damaged copper tubes.

The submittal information sent to the Noble Gas Laboratory at Lamont-Doherty Earth Observatory must also include a cover letter with the following information:

1. Site I.D.
2. Date and time of collection.
3. Ground-water temperature.
4. Estimated, or known, tritium content.
5. Estimated, or known, elevation of the recharge area for the sample.
6. General description of the hydro-geologic environment, location, and well construction information.
7. Any information regarding possible tritium contamination of the sample.
8. The name, FAX number, e-mail address, and phone number of the Project Chief or person technically responsible for the samples.

There is no charge for samples that cannot be processed by the contract lab.

### **SHIPMENT OF SAMPLES**

Following the above log-in procedures, both copper tubes and one 500-cc water sample should be suitably packaged and shipped directly to:

Noble Gas Laboratory  
ATTN: Millie Klas  
Lamont-Doherty Earth Observatory of Columbia University  
Geochemistry 69  
Route 9W  
Palisades, New York 10964

The duplicate 500-cc water sample for tritium determination by helium ingrowth is retained at the Project Office until results are received. During cold periods, precautions should be taken to ensure that water samples do not freeze during shipment.

### **LABORATORY PROCESSING**

At the contract laboratory, helium isotopes are extracted quantitatively (>99.9 percent) from the water sealed in the copper tubes using a vacuum extraction line and transferred into flame-sealed

glass ampules. After separation of water vapor, neon, and other gases in several cryogenic traps, helium isotopes are measured on a VG 5400 mass spectrometer calibrated relative to standard air with a  $^3\text{He}/^4\text{He}$  isotopic ratio of  $1.384 \times 10^{-6}$ . Sample replicates normally agree within the analytical error of 2 percent for the  $^4\text{He}$  concentration and 1 percent for the  $^3\text{He}/^4\text{He}$  ratio. After release from the cryogenic trap, neon is measured in a quadrupole mass spectrometer with a precision of about 4 percent. The neon determination (together with a pressure measurement at the end of the extraction) provides a check on the extraction efficiency and a means of detecting radiogenic helium sources; i.e.,  $^4\text{He}$  produced through the U and Th decay series (Schlosser and others, 1989), or excess air.

Samples that contain large excesses of helium may need to be split prior to injection into the mass spectrometer and will likely have reported errors that are greater than 1 percent ( $2\sigma$ ) and will be identified as such by the contract lab. Because of unexpected concentrations of helium, some samples may be lost during processing. If that occurs, the contract lab may use the duplicate sample or report that the sample cannot be analyzed because of excess helium. Projects will not be billed for samples that are not analyzed.

Tritium is determined mass spectrometrically by the  $^3\text{He}$  ingrowth method (Clarke and others, 1976) from water samples that have been degassed of all helium on a high-vacuum line and sealed in containers with low helium permeability (e.g., Corning type-1720 glass ampules, or equivalent). Prior to use, the glass ampules are baked at  $400^\circ\text{C}$  in helium-free nitrogen to minimize the concentration of helium in the glass. After sealing, the ampules are stored under refrigeration at approximately  $-20^\circ\text{C}$  for a period of at least several days to as long as 12 months (depending on tritium content of the sample) to allow time for  $^3\text{He}$  ingrowth. The methods conform generally to those of Clarke and others (1976), Bayer and others (1989), and Solomon and others (1992).

## **DELIVERY**

Delivery is 6 months for Schedule 1033, Lab Codes 2120, 2122, and 2124 (helium and neon measurements only). If tritium is determined by helium ingrowth, Lab Code 2112, delivery can be longer than 6 months, depending on the duration of the ingrowth period and time needed for processing and interpretation of age; but for most samples in which ages are requested (Schedule 1033 and Lab Code 2112), delivery will be within 6-8 months. The turnaround time might increase in cases of unexpected equipment breakdown at the laboratory. The Project Office may be contacted by Lamont-Doherty Earth Observatory personnel for further hydrogeologic information to aid in interpretation of age.

The contract specifies that for Schedule 1033, the contract lab will provide the date of extraction of the helium from the water sample. The date of extraction will be used by the Project Office in special cases in which, for example, tritium was determined by beta counting at another laboratory. In this case, the contract lab will report the  $^3\text{He}/^4\text{He}$  ratio at time of extraction and the Project Office will make the necessary corrections to determine the  $^3\text{He}/^4\text{He}$  isotope ratio at date of sampling. It is recommended, however, that the Project Office report the tritium analyses, analytical precision, and date of collection of the tritium sample to Lamont-Doherty Earth Observatory for their use in interpretation of age. It is highly recommended that the tritium and helium samples be collected at the same time.

## **TECHNICAL QUESTIONS**

Technical questions may be referred to Niel Plummer (703) 648-5841. Questions pertaining to the contract turnaround times, reporting of results, sample shipping, sample tracking, etc., will be directed to Ann Mullin (303) 467-8235.

## BACKGROUND INFORMATION ON DATING YOUNG GROUNDWATER (<sup>3</sup>H/<sup>3</sup>He AND CHLOROFLUOROCARBONS)

(From: Plummer and others, 1993; Szabo and others, 1995; Plummer and others, in prep.)

### <sup>3</sup>H/<sup>3</sup>He DATING

Tritium (<sup>3</sup>H, half-life of 12.43 years (Unterweger and others, 1980)) has provided an excellent tracer of young waters. Tritium input to ground water has occurred in a series of spikes following periods of atmospheric testing of nuclear devices that began in 1952 and reached a maximum in 1963-1964. Concentrations of <sup>3</sup>H in precipitation have decreased since the mid-1960s bomb peak, except for some small increases from French and Chinese tests in the late 1970s. Radioactive decay of <sup>3</sup>H produces the noble gas helium-3 (<sup>3</sup>He). Tritium measurements alone can be used to locate the depth of the mid-1960s bomb peak, but, because of radioactive decay, many samples may need to be collected and analyzed today to locate its position. And for waters younger than the mid-1960s, the bomb peak will not be present. Although initial <sup>3</sup>H concentrations have decreased because of radioactive decay, measurements of <sup>3</sup>H and tritiogenic <sup>3</sup>He define a quasi-stable tracer of initial <sup>3</sup>H input to ground water and may be used to determine the position of the mid-1960s bomb peak in recharge areas. Additionally, location of the mid-1960s bomb peak provides independent information on recharge rate (Schlosser and others, 1988, 1989; Solomon and Sudicky, 1991; Solomon and others, 1992, 1993; Ekwurzel and others, 1994).

Locating the position of the mid-1960s bomb peak is difficult due to the required relatively high density of vertical sampling and, therefore, is often an impractical means of obtaining ground-water age information. On the other hand, determination of the <sup>3</sup>H/<sup>3</sup>He ratio can be used to calculate the <sup>3</sup>H/<sup>3</sup>He apparent age of ground water from a single water sample (Schlosser and others, 1988; 1989; Poreda and others, 1988; Solomon and others, 1992, 1993). As with CFCs, the <sup>3</sup>H/<sup>3</sup>He age is defined as the time elapsed since the parcel of water was isolated from the atmosphere following recharge. If the <sup>4</sup>He concentration of the water can be attributed solely to atmospheric sources (by equilibration with air during recharge and "excess air"), it can be assumed that <sup>3</sup>He in the water is of atmospheric and tritiogenic origin. For samples that are not affected by radiogenic helium, the tritiogenic <sup>3</sup>He concentration in the water sample is, in this case (Schlosser and others, 1988),

$${}^3\text{He}_{\text{trit}} = 4.021 \cdot 10^{14} \cdot \left[ {}^4\text{He}_s \cdot (R_s - R_a) + {}^4\text{He}_{\text{eq}} \cdot R_a \cdot (1 - \alpha) \right]$$

where <sup>3</sup>He<sub>trit</sub> is the tritiogenic <sup>3</sup>He in TU, <sup>4</sup>He<sub>s</sub> is the measured <sup>4</sup>He content of the sample in ccSTP/g water, <sup>4</sup>He<sub>eq</sub> is the <sup>4</sup>He content of air-equilibrated water at the recharge temperature in ccSTP/g water, R<sub>s</sub> is the measured <sup>3</sup>He/<sup>4</sup>He ratio of the sample, R<sub>a</sub> is the <sup>3</sup>He/<sup>4</sup>He ratio of air (1.384x10<sup>-6</sup> Clarke and others, 1976), and α is the equilibrium isotope fractionation factor (0.983, Benson and Krause, 1980). The constant 4.021·10<sup>14</sup> converts the unit ccSTP/g water to TU.

Additional He sources may be present in aquifers where the rocks are enriched in U or Th, or in ground-water samples in which young water has mixed with relatively old water containing radiogenic, and in some cases, mantle He. In these cases, the measured Ne content (assumed to be derived solely from the atmosphere) can be used to calculate the additional He (He<sub>rad</sub>; Schlosser and others, 1989)—

$${}^4\text{He}_{rad} = {}^4\text{He}_S - (N_{eS} - N_{e_{aq}}) \cdot \left( \frac{{}^4\text{He}}{\text{Ne}} \right)_{atm} - {}^4\text{He}_{aq}$$

where  ${}^4\text{He}_{rad}$  is the radiogenic  ${}^4\text{He}$  concentration,  $N_{eS}$  is the measured neon concentration in the sample,  $N_{e_{aq}}$  is the neon concentration in water in equilibrium with air, and  $({}^4\text{He}/\text{Ne})_{atm}$  is the atmospheric ratio (0.288). The  ${}^3\text{He}_{trit}$  then becomes

$${}^3\text{He}_{trit} = 4.021 \cdot 10^{14} \cdot \left[ {}^4\text{He}_S \cdot (R_S - R_\alpha) + {}^4\text{He}_{aq} \cdot R_\alpha \cdot (1 - \alpha) + {}^4\text{He}_{rad} \cdot (R_\alpha - R_{rad}) \right]$$

where  $R_{rad}$  is the  ${}^3\text{He}/{}^4\text{He}$  ratio of the radiogenic He source.  $R_{rad}$  has to be determined from the isotope measurements of tritium-free water in the aquifer under investigation. For dating studies of waters from crystalline rocks, or even for waters from alluvial aquifers associated with crystalline bedrock, it is best to sample several old (tritium-free) waters to aid in defining  $R_{rad}$  and interpretation of age. If the  ${}^3\text{He}_{trit}$  is confined in the aquifer, the apparent  ${}^3\text{H}/{}^3\text{He}$  age,  $\tau$  (in years) of the water can be calculated as follows (Schlosser and others, 1988):

$$\tau = \frac{T_{1/2}}{\ln 2} \cdot \ln \left[ 1 + \frac{{}^3\text{He}_{trit}}{{}^3\text{H}} \right]$$

where  $T_{1/2}$  is the  ${}^3\text{H}$  half-life.

Schlosser and others (1988, 1989) reported  ${}^3\text{H}/{}^3\text{He}$  dating of shallow ground water sampled from wells screened at multiple levels at Liedern/Bocholt, Germany. The  ${}^3\text{H}$  from 1963-64 atmospheric nuclear-bomb testing was clearly evident in the tritiogenic  ${}^3\text{He}$  at a depth of 5 to 10 meters in the saturated zone.  ${}^3\text{H}/{}^3\text{He}$  ages of the bomb-pulse waters were 3 to 5 years younger than the true age (1963). This difference was attributed to incomplete  ${}^3\text{He}$  confinement and dispersive mixing with deeper water. From estimates of the  ${}^3\text{H}$  infiltration, Schlosser and others (1988) estimated that approximately 80 percent of the tritiogenic  ${}^3\text{He}$  remained in the ground water at Liedern/ Bocholt. Calculations based on the "Vogel" model (Vogel 1967), as applied to shallow, homogeneous sand aquifers of isotropic hydraulic conductivity, showed that the shape of the bomb pulse will be detectable in tritiogenic  ${}^3\text{He}$  data for at least the next 40 years, long after the bomb pulse is lost in the  ${}^3\text{H}$  data because of radioactive decay and advection/dispersion (Schlosser and others 1989).

Helium-3 confinement has also been shown to be a function of the vertical flow velocity (recharge rate) and dispersivity. Schlosser and others (1989) calculated significant  ${}^3\text{He}$  loss across the water table to the atmosphere at vertical flow velocities of less than 0.25 to 0.5 m/yr. Although absolute  ${}^3\text{H}/{}^3\text{He}$  ages are less certain when recharge rates are small, location of the position of the bomb pulse, expressed in tritiogenic  ${}^3\text{He}$ , is of great value in hydrologic studies and can be used to determine ground-water velocities.

Solomon and Sudicky (1991, 1992) used numerical simulations of simple one- and two-dimensional flow systems in hypothetical unconfined, shallow sandy aquifers to investigate the sensitivity of calculated  ${}^3\text{H}/{}^3\text{He}$  ages to hydrodynamic dispersion. These authors showed that the magnitude of uncertainties in calculated  ${}^3\text{H}/{}^3\text{He}$  ages depends on the  ${}^3\text{H}$  input. When  ${}^3\text{H}$  input is nearly constant over time, such as the  ${}^3\text{H}$  input in recharge since the mid- to late 1970s, calculated  ${}^3\text{H}/{}^3\text{He}$  ages tend to be within 10 percent of true ages. However, under transient conditions, such as for waters recharged prior to the 1960s bomb pulse, dispersion can cause more than 50 percent differences

between calculated  $^3\text{H}/^3\text{He}$  ages and advective travel times. If the vertical velocity is rapid enough to maximize  $^3\text{He}$  confinement (Schlosser and others 1989),  $^3\text{H}/^3\text{He}$  ages determined near the water table should closely reflect the average vertical velocity.

Uncertainty in age because of analytic uncertainty is approximately  $\pm 0.5$  years. Larger uncertainties in age result from corrections in defining the tritiogenic  $^3\text{He}$ , the requirement that the parcel of water remain confined following infiltration, and mixing effects caused by hydrodynamic dispersion. If  $^3\text{He}$  is lost by diffusion to the unsaturated zone air, younger ages are derived.  $^3\text{He}$  can also be added to shallow ground water by dispersive transport.

Due to the variable nature of the  $^3\text{H}$  input,  $^3\text{H}/^3\text{He}$  dating becomes less certain for waters older than the mid-1960s bomb pulse due to dispersive mixing. Consequently,  $^3\text{H}/^3\text{He}$  dating is most reliable only for the past 20 to 25 years (Solomon and others 1992) when  $^3\text{H}$  input has been relatively constant and therefore influenced to a lesser extent by hydrodynamic dispersion (Solomon and Sudicky 1991).

## **CHLOROFLUOROCARBON DATING**

Chlorofluorocarbons (CFCs) are stable synthetic organic compounds that are detectable to about one part in  $10^{15}$  (weight) in water and one part in  $10^{12}$  (volume) in air. CFCs were first manufactured in the 1930s and are entirely of anthropogenic origin. CFCs are ultimately released into the atmosphere and hydrosphere. The concentrations of CFCs in water vary as a function of the atmospheric partial pressures of CFCs and the water temperature. The use of CFC concentrations in natural waters as a potential dating tool was recognized in the 1970s (Thompson, 1976; Thompson and Hayes, 1979), and developed and refined more recently (Busenberg and Plummer, 1992).

The CFC-model recharge age refers to the time since the recharge water was isolated from air. CFCs can be detected in post-1940 ground water. The presence of CFCs in ground water indicates recharge after 1940 or mixing of older waters with post-1940 water. The CFC model age is determined by comparing calculated concentrations of CFCs that would be in air in equilibrium with the ground-water concentration to CFC concentrations measured in air from Niwot Ridge, Colorado (Elkins and others, 1993), after adjustment for the recharge elevation.

The recharge temperature is required in CFC dating to calculate the Henry's Law solubility constants that relate ground-water CFC concentrations to air concentrations. Relatively small errors in CFC dating are introduced by uncertainties in recharge temperature. Warmer recharge temperatures lead to younger CFC-model ages. An age error of 2-3 years results from uncertainties of  $\pm 2^\circ\text{C}$  for waters recharged in the 1980s and early 1990s. CFC-model age uncertainties due to uncertainties in recharge temperature are usually less than 1 year for waters recharged prior to approximately 1975 (Busenberg and others, 1993). Other limitations to CFC dating result from processes that can alter CFC concentrations established by air-water equilibrium, such as contamination from other sources, microbial degradation, and sorption (see for example, Dunkle and others, 1993; Cook and others, 1995). Sampling artifacts resulting in CFC contamination can cause a "young" bias. Waters contaminated with VOCs may also be contaminated with CFCs and thus not suited for CFC dating. For further information on CFC dating, see joint Office of Water Quality and Office of Ground Water Technical Memorandum No. 95.02 and associated attachments, dated December 29, 1994.

## **MULTI-TRACER APPROACH--CFC AND $^3\text{H}/^3\text{He}$ DATING**

The CFC and  $^3\text{H}/^3\text{He}$  dating techniques are complimentary in their strengths and weaknesses; therefore, their combined use may help eliminate some uncertainties in ground-water age

determinations (Szabo and others, 1996). Input of CFCs has increased relatively smoothly, while tritium input is dominated by the "bomb" peak. Hence dispersion may have minimal effect on CFC-determined apparent ages (Plummer and others, 1993; Ekwurzel and others, 1994) while dispersion of the "bomb" peak can result in apparent ages that are too young for ground water at depths just below the position of the "bomb" peak (Schlosser and others, 1988; 1989). CFC concentrations in ground water are sometimes contaminated from local, near-surface sources, such as domestic septic tanks, other sources associated with industrial or urban development, or from contaminated sampling equipment; but tritium concentrations in ground water are not normally contaminated from local sources (though there are exceptions in some landfills and other waste sites).

The ranges of  $^3\text{H}/^3\text{He}$  and CFC dating are not identical. CFC dating has potentially the longest dating period of the two transient tracers, extending to 1940 for CFC-12 and approximately 1947 for CFC-11. Applications of  $^3\text{H}/^3\text{He}$  dating have recognized waters recharged over the past 30 years (Schlosser and others 1988; Solomon and others, 1992; Ekwurzel and others, 1994). Recently, Szabo and others (1995) reported agreement in  $^3\text{H}/^3\text{He}$  and CFC ages of 33 to 40 years for waters below the bomb peak. However, it is expected that the usefulness of  $^3\text{H}/^3\text{He}$  dating will decrease in the future as the mid-60s bomb pulse dissipates due to decay and dispersive mixing (Schlosser, et al, 1989).

Greater confidence can be placed in concurring apparent ages obtained from the use of these two different tracers. Plummer and others (1993) discuss details of  $^3\text{H}/^3\text{He}$  and CFC dating, and contrast advantages and limitations of dating procedures for young ground water.

### **GROUND-WATER MIXTURES--CFCs vs $^3\text{H}/^3\text{He}$**

Practical applications of environmental tracers to dating young ground water often depend on sampling from pre-existing domestic, industrial, and municipal-supply wells that, because of their construction, intercept relatively large open intervals and can produce mixed waters. The age of the young fraction(s) in ground-water mixtures can be particularly useful when assessing the susceptibility of ground-water resources to contamination from anthropogenic sources. There are fundamental differences between dating the young fraction in ground-water mixtures with CFCs and with  $^3\text{H}/^3\text{He}$ . In the case of simple binary mixtures of old (>50 years) water and young water, the source of CFCs and  $^3\text{H}$  can be almost entirely attributed to the young fraction. In some mixtures, the CFC age of the young fraction could be determined from the ratio of CFC-11 to CFC-12 in the water sample, and mixing fractions based on the ratio of observed to expected CFC concentrations in the water sample. This approach is limited in application to young fractions recharged between the late-1940s and the mid-1970s, because, since the mid-1970s, the CFC-11/CFC-12 ratio has been nearly constant in the troposphere. Other limitations result when the CFC concentrations in the young fraction are altered from air-water equilibrium values by additional (contaminant) sources or by microbial degradation or other geochemical processes that remove CFCs from the water.

Because of these limitations, ground-water dating using CFCs is usually performed independently for each CFC compound measured. In this case, the CFC concentration in the ground-water sample must be divided by the fraction of young water in the mixture before age of the young fraction can be estimated. The CFC age of the young fraction is then computed by comparing air concentrations that would be in equilibrium with the CFC concentration in the young fraction with historical air concentrations (Busenberg and Plummer, 1992). If the mixture contains multiple fractions of young water, the resulting age is regarded as a mean age of the young fraction(s) in the mixture.

In previous dating studies (see, for example, Dunkle and others, 1993; Katz and others, 1994; Cook and others, 1995), waters have been sampled from relatively narrow intervals in shallow recharge

areas of surficial aquifers, where the fraction of young water in the sample is nearly unity and the water is nearly homogeneous in CFC composition over the depth interval sampled. In such cases, no correction for dilution is needed, and the resulting apparent age can be compared with results from other dating techniques and with travel times computed from numerical models (Reilly and others, 1995; Szabo and others, 1996) without further adjustment. However, if the fraction of young water in a ground-water mixture is not known and a mixing fraction of unity is assumed, the "apparent" CFC age is a maximum for the young fraction and a minimum age for the older fraction.

Effects of mixing can be more significant when waters are sampled from relatively large intervals in aquifers. Mixing, if it occurs, may not be readily apparent if the concentration of a particular constituent (such as dissolved  $\text{Cl}^-$  or  $\text{Ca}^{2+}$ ) in the aquifer is uniform over the depth interval sampled. When sampling young ground water or mixtures containing young ground water for transient tracers such as CFCs and  $^3\text{H}/^3\text{He}$ , there will almost always be compositional gradients, especially when ground water is sampled from relatively large intervals in aquifers.

In any mixture containing a fraction of post-bomb water and a fraction of pre-bomb water, the detectable  $^3\text{H}$  and  $^3\text{He}_{\text{trit}}$  is attributed to the young water fraction. Compared to  $^3\text{H}$  and  $^3\text{He}$  derived from the young water fraction, any contribution of  $^3\text{H}$  and  $^3\text{He}$  from the old water fraction is, to a good approximation, negligible and the calculated  $^3\text{H}/^3\text{He}$  age applies to the post-bomb fraction of the mixture. If mixtures of more than one post-bomb water fraction of different age occur, the calculated  $^3\text{H}/^3\text{He}$  age will be intermediate to the ages of the post-bomb fractions. There is usually insufficient data for resolving mixtures of more than one post-bomb water in ground-water mixtures, and consequently, the reported ages (both  $^3\text{H}/^3\text{He}$ - and CFC-based ages) should be regarded as mixed ages for the young fraction(s) in each sample. Plummer and others (in preparation) investigate dating of the young fraction in ground-water mixtures in the Upper Floridan aquifer near Valdosta, Georgia, using CFCs and  $^3\text{H}/^3\text{He}$ .

**Attachments** (Noble Gas Document)

**Impact on Data Base:** None

**Supplements:** NWQL Tech Memo 97-04

**Supersedes:** None

**Key words:** Groundwater Dating,  $^3\text{H}/^3\text{He}$ , Tritium/Helium-3

**Distribution:** <http://wwwnwql.cr.usgs.gov/>

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## **Attachment**

### **Additional Information from Lamont-Doherty L-DEO, July 20, 1994**

~~**WARNING.**- Watch out for gas bubbles in the plastic tubing! Make sure there is no contact of the water with air before you take the sample.

#### **1. SAMPLER PREPARATION**

Write the sample location, date, and time on the aluminum channels with a waterproof marker. Mark the channels before you begin to draw water through the sample container. Whenever possible, take duplicate samples.

Both ends of the aluminum channel have clamps to hold a piece of copper tube. They may rattle loose during shipment. These clamps should be finger-tightened to hold the copper tube firmly on center in the aluminum channel (Figure 1).

For sampling water under high pressure, you need to install a pressure valve on one end of the copper tube. Slide a brass nut over the copper tube as shown in Figure 2. Next, slide two "Swagelock" nylon fittings on the tube so they rest inside the nut (see Figure 2, watch the orientation!). Screw the pressure valve into the brass nut and tighten by hand. Be careful not to break the plexiglass tube.

Place a piece of inner braided PVC tubing onto one end of the copper tube and fix it with a hose clamp. Make sure that you do not deform the copper tube by tightening the hose clamp. Connect the other end of the tubing to the pump discharge.

#### **2. FLUSHING**

Open the pressure valve completely. Hold the copper sampler vertically (pressure valve UP) with one hand and the ratchet wrench with the other hand. Allow the water to run at least 1 minute through the system to flush the sample tube. Keep the pressure in the system as high as possible (it is safe up to 10 bars). Watch the PVC tubing and the plexiglass tube near the valve (Figure 2) for bubbles. Bubbles do preferentially form near fittings. If bubbles are present, squeeze the tube or knock against the tube to get rid of the bubbles. You may also try to increase the pressure further by reducing the flow through the copper tube by partially closing the brass valve. During flushing, bang the side of the aluminum channel with the ratchet handle to remove trapped air bubbles from the copper tube. Watch again the plexiglass tube between the valve and the sample container for bubbles (Figure 2). Close the pressure valve completely. Make sure that the sample container was flushed at least 1 minute with bubble-free water. If you cannot avoid formation of bubbles, take the sample anyway, and mark the sample container accordingly.

#### **3. SEALING**

Once flushing is complete and no air bubbles appear in the PVC tubing, the copper tube may be closed off. Close the valve completely. Tighten the clamp which is closer to the pressure valve (top clamp, outflow) first. Tighten each screw a little at a time until the outer edges of the clamp touch. You have tightened the clamps sufficiently when you notice that it is getting much harder (almost

impossible) to tighten the clamp further. Do not worry, it is not easy to shear the bolts. The clamp will bow somewhat around the copper, so that it maintains a constant pressure on the copper seal. Watch the plastic tubing for bubbles while tightening the top clamp. Tighten the bottom clamp and remove the plastic tubing. If you think there are bubbles inside the copper tube after it has been clamped, write "BUBBLES?" on the aluminum channel. Remove the pressure valve. You can reuse the nylon fittings and the brass nut.

#### **4. SAMPLER STORAGE**

Shake the sample container a little to remove the excess water from the ends. If the water is very corrosive (high salt content), rinse the inside of the copper tube ends by spraying low salinity water into them and shaking out the excess.

Sampler should be returned to the box immediately after cleaning and then stored out of the weather. The ends of the copper tube are very fragile after the tube is squeezed.

#### **POINTS TO REMEMBER**

1. Avoid bubbles.
2. Close clamp at outflow end first.
3. Copper tube ends are very fragile after clamp is tight.
4. If you think there are bubbles inside the copper tube after it has been clamped, write "BUBBLES?" on the aluminum channel.
5. Make sure that the sample container is properly marked (date, time, location).
6. Take duplicates whenever possible!

Good Luck!!!

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