Hydrogen Isotope Analyses of Waters

Procedure ID: YMP-LBNL-TIP/TT-9.0, Rev.0, Mod.2 *Effective:02/09/2006*

1. PURPOSE

This Technical Implementing Procedure (TIP) describes a method for hydrogen isotope analyses of water for the Yucca Mountain Project (YMP) at Lawrence Berkeley National Laboratory (LBNL).

2. SCOPE

This procedure shall be used by all LBNL personnel (or contractor personnel following LBNL procedures) involved in YMP activities whenever they are required to analyze the hydrogen isotopic composition (δD value) of water samples. Prior to conducting work described in section 3.0 of this procedure, personnel require training in this procedure.

For all technical activities, data collected using this procedure and any equipment calibrations or recalibrations that may be required shall be in accordance with this TIP and in full compliance with LP-12.1Q-BSC, *Control of Measuring and Test Equipment.* Documentation resulting from actions taken under this TIP shall be recorded in scientific notebooks as described in LP-SIII.11Q-BSC, *Scientific Notebooks.* Electronic data maintenance, controls and transfers shall comply with YMP-LBNL-Quality Implementing Procedure (QIP)-SV.0, *Control of the Electronic Management of Data.*

If this procedure cannot be implemented as written, YMP-LBNL personnel shall notify the responsible Principal Investigator (PI) or designee. If it is determined that a portion of the work cannot be accomplished as described in this TIP, or would produce undesirable results, that portion of the work shall be stopped and not resumed until this procedure is modified per YMP-LBNL-QIP-5.2, *Preparing Quality & Technical Implementing Procedures*.

If the responsible PI or designee determines that a modification or a revision to the TIP would cause an unreasonable delay in proceeding with the task, then an expedited change to the procedure, including documentation of deviation from the approved procedure, can be made according to YMP-LBNL-QIP-5.2. Such changes are subject to review, usually after the task has proceeded, and thus work performed under TIPs with expedited changes is done at risk of future invalidation.

Employees may use copies of this procedure printed from the controlled document electronic file; however, employees are responsible for assuring that the correct revision of this procedure is used. When this procedure becomes obsolete or superseded, it must be destroyed or marked superseded to ensure that this document is not used to perform work.

3. PROCEDURE

3.1 Principle

This procedure outlines a technique for converting liquid H_2O to H_2 gas for stable hydrogen isotope analysis. This is accomplished by injecting the water into a 6 mm outer diameter glass tube with zinc metal, sealing the tube with a glass blowing torch and then heating the tubes to 500°C. This results in the following reaction:

$$H_2O \text{ (liquid)} + Zn \rightarrow H_2 \text{ (gas)} + ZnO$$

The δD value of the H_2 is then measured using the Center for Isotope Geochemistry's (CIG) VG Isotech Prism Series II Isotope Ratio Mass Spectrometer (Prism).

3.2 Materials/Equipment Required

- Zinc metal shavings (obtained from Indiana University Biogeochemical Society)
- 6 mm o.d. glass tubes, ~12" long, sealed at one end
- Specialized fittings for injecting water into glass tubes with zinc metal (see Attachment 1)
- 3/8" to 3/8" Cajon unions
- Glass vacuum line (Attachment 2)
- Heat gun
- 10 µl gas-tight syringe
- Dewars
- Liquid N_2 (LN)
- Glass blowing torch
- Muffle furnace
- Aluminum rack
- VG Isotech Prism Series II Isotope Ratio Mass Spectrometer (Prism)
- Water standards (NIST standards VSMOW, GISP and SLAP and internally calibrated water standards).

3.3 Sample Preparation

3.3.1 Records generated as a result of this TIP shall be entered into the appropriate YMP scientific notebook in accordance with LP-SIII.11Q-BSC. Applicable elements of the laboratory notebooks are incorporated into the scientific notebook.

3.3.2 Prepare glass tubes for loading samples by sealing one end of 12" lengths of 6 mm o.d. tubing with a glass blowing torch. After sealing the end of the tubes, anneal them at 500°C for 2 hours and store them in a drying oven at 100°C prior to use.

3.3.3 Load 50-100 mg of zinc into the glass tubes by sight – Zn shavings should fill the bottom ~2 cm of the tube. While loading the zinc into the tubes **do not touch the zinc** (the moisture on your hands will significantly affect the accuracy of the analyses). If any zinc falls on the table or onto the ground, discard it. When not in use, the zinc shall be stored under a vacuum.

3.3.4 Insert the glass tubes with the zinc into #7 Ace threaded joints on the specialized fittings used for loading the water into the tubes (Attachment 1) by placing an O-ring ~1 cm from the top of the tube. Then slide the tube into the black nylon bushing and screw bushing into the threaded joint. Connect the fittings onto a sample port on the vacuum line (Attachment 2) with a 3/8" to 3/8" Cajon union. Evacuate the air in the tubes by opening the valves above the sample ports and the valves between the sample manifolds and the vacuum pump.

3.3.5 Heat the zinc with a heat gun about 1 minute until a silvery halo of zinc vapor condenses on the lower part of the tube. Continue to evacuate the tubes for at least 1 hour after heating the zinc.

3.3.6 Loosen the black nylon bushing and carefully slide the tube up until it reaches the top of the glass fitting, just below the septa. Evacuate the tubes for an extra 5 minutes if the pressure reading on the thermocouple gauges increases during this step (indicating that atmosphere leaked into the tubes).

3.3.7 Flush a 10 □l syringe 3 times with the sample to be injected. Draw up ~3 □l of sample, then draw air into the needle until an air bubble appears above the sample in the syringe and the total volume of water in the syringe can be measured. Record the actual amount of water in the laboratory notebook. Wipe the outside of the needle dry.

3.3.8 Close the valve between the glass fitting and the sample manifold. Insert the needle through the septa and into the sample tube inside the glass fitting. Depress the plunger. Leaving the needle in the tube, place a dewar of liquid nitrogen (LN) on the bottom 2.5 cm of the tube, just covering the zinc. Heat the glass fitting, making sure that any water frozen in the needle is removed. Heat the glass tube with the heat gun to move any water on the sides of the sample tube down into the bottom of the tube. When all the water is frozen into the LN, remove the syringe and check for water trapped in the needle by drawing air into the syringe. If there is any water remaining in the syringe, discard the sample and redo it.

3.3.9 After injecting 4 samples, raise the level of LN to the top of all 4 dewars. Close the valve between the manifold and the vacuum pump and open the valve between the manifold and the first sample tube. Record the pressure reading on the thermocouple gauge in the laboratory notebook. The reading should be <100 millitorr (if it is higher, replace the septa before using the fitting again). Pump away the noncondensable gases by opening the valve between the sample manifold and the vacuum pump. When the reading on the thermocouple gauge has dropped down to background, seal the tube with a glass blowing torch and write the sample number on the tube. Repeat this step with the next sample.

3.4 Reaction

3.4.1 Preheat the muffle furnace to 500°C. Place the sample tubes in the aluminum rack, noting the order of the samples in the rack (the original labels will burn off in the furnace). Place the rack with the samples into the furnace for 15-20 minutes. Remove the samples and re-label the tubes as soon as they have cooled. Reaction of the samples should be done within 4 hours of loading the waters into the reaction tubes with the zinc.

3.5 Analysis of the stable hydrogen isotopic composition of the hydrogen gas

3.5.1 The hydrogen isotopic ratio of H_2 (δD value) is analyzed using the VG Isotech Prism Series II Isotope Ratio Mass Spectrometer (Prism) in Room 4425 of Building 70A at LBNL. This analytical procedure is automated using the **Dual Inlet** software. The software used to control sample analysis with the mass spectrometer is an integral part of the mass spectrometer and thus controlled by LP-12.1Q-BSC. In essence, the H_2 gas is expanded into the sample bellows of the Prism and then bled into the ion source of the mass spectrometer through capillary tubing. In the ion source, the stream of H_2 gas is bombarded with a beam of electrons which cause a fraction (<1%) of the H_2 to become ionized to H_2^+. The H_2^+ ions are then

accelerated out of the ion source, through a series of electronic lenses which collimate the ions into a narrow beam. The ion beam is then passed through a strong magnetic field where it is bent. The amount that the H_2 ions are deflected by the magnetic field is a function of the mass of the ions (e.g., $^1H_2$ = mass 2 and $^1H^2H$ (or HD) = mass 3). As a result, the ion beam is separated into 2 beams. The relative intensities of these beams are then measured with Faraday cups positioned in the paths of the two ion beams. From the ratio of the intensity of beam 2 to beam 1, the δD value of the H_2 can be calculated.

During analysis of the samples, the isotopic ratios of the gas will be shifted slightly and the sensitivity of the machine will drift. To correct for these systematic errors, a standard gas with known isotopic ratios is analyzed at the same time as the sample (in 10-12 alternating blocks of 10-20 seconds each). The data for the sample is then corrected relative to the data for the standard. The procedure for calibrating the standard gas is discussed in detail in YMP-LBNL-TIP/TT-11.0, *Calibration of a Mass Spectrometer for Isotopic Measurements of CO_2 and H_2.*

3.5.2 To analyze the isotopic ratios of the H_2 samples generated using the method outlined in Sections 3.3 and 3.4, load up to 20 glass tubes containing the H_2 samples into the multiport of the Prism. Before loading the tubes, score each one lightly with the glass scoring tool at about the point where they will be broken by the cracker on the multiport (~2" from the end of the tube). While loading the samples, be sure to check the O-rings, making sure they have no particles of glass on them, that they are lightly greased with Apezion N grease, and that they are seated correctly on the fitting. In every run of unknowns, ~30% samples of H_2 gas from standard waters should be analyzed to calibrate the raw hydrogen isotope data obtained from the Prism. If possible, the standards should be loaded into the reaction tubes with the zinc and reacted at the same time as the unknowns. The specific number of samples from standard waters shall be noted in the scientific notebook.

3.5.3 When all the samples for the run have been loaded into the multiport, open the valves between the ports and the multiport manifold, then open the valves between the manifold and the low-vacuum pump. Once the reading on Pirani gauge 2 has dropped to less than 1e-2, switch from low vacuum to high vacuum. Be sure that none of the sample tubes slip out of the fitting when they are evacuated.

3.5.4 Enter the sample run data in the Manifold set up file.

3.5.5 Check the tuning of the mass spectrometer by letting standard gas into the mass spectrometer and doing a peak center (Control C). If the sensitivity is low (for a beam 1 reading of 5e-9 amps, the ion gauge reading shall be less than or equal to 3e-7) or the peak shape is bad (not symmetric or choppy), adjust the tuning of the mass spectrometer or find someone who is able to do that.

3.5.6 When the tuning is set, make sure there is adequate standard gas for the sample run (for beam 1 of 5e-9 amps, the position of the standard bellows shall be less than or equal to 2000), check that valve N7 between the multiport and the sample inlet is open and start the autorun.

3.5.7 When the run is finished, enter the run data in the Prism log book.

3.6 Data reduction

3.6.1 Check all the data output to make sure that the ion gauge readings of the sample and the reference gas were equal and that the ratios were stable during the analyses. Reject any samples that do not meet these criteria.

3.6.2 To correct the data, plot the measured isotopic ratios of the standards versus the average measured values of the standards. Use a best fit line through this data as a correction curve with which to correct the data for the unknowns.

3.7 Safety Considerations

Safety considerations for this procedure are the following:

- Care must be taken whenever dealing with depressurized glass lines. Turn on-line valves only when supporting the connection of the valve to the line with the other hand. Be cautious not to jolt the line unnecessarily.

- Use all required safety precautions when using liquid nitrogen: heavy gloves, full length pants, closed toed shoes, lab coat, and face shield.

- Be aware that the heat gun can reach very high temperatures and avoid contact with the gun when hot. Always turn the heat to low and allow it to cool before turning it off.

- When using the glassblowing torch to seal off tubes be sure to wear glassblowing glasses to filter out harmful rays. Also, be cautious of the flame, as the high temperature zone of the flame extends past the visible flame.

- When operating the muffle furnace, be sure to set the proper temperature (500°C) as a higher temperature can cause the tubes to melt.

- Be careful when removing tubes from the muffle furnace, as they will be hot.

- When scoring tubes for the cracker on the Prism, do not exert too much force on the tube so as to prevent shattering.

- Refer to all necessary safety training with respect to working with pressurized gas (LBNL EH&S Compressed Gas Safety Training).

4. RECORDS

The records listed below shall be collected and submitted to the Records Processing Center (RPC) in accordance with AP-17.1Q, *Records Management*, as individual records or included in a records package.

4.1 Quality Assurance (QA) Records

Records generated as a result of this TIP are entries in:

- Scientific notebooks or Supplements to such notebooks,

4.2 Non-QA Long Term Records

None

4.3 Non-QA Short-Term Records (three years or less retention)

None

5. RESPONSIBILITIES

5.1 The **Principal Investigator (PI)** or designee is responsible for assuring full compliance with this procedure and for providing training thereof. The PI or designee is also responsible for overseeing and coordinating the preparation, review, distribution, revision, and rescission of the TIP.

5.2 **Staff Members** are responsible for following this procedure and turning over related documentation to the Records Coordinator for submittal to the Records Processing Center in accordance with AP-17.1Q. Related data shall be turned over to the Technical Data Coordinator in accordance with AP-SIII.3Q, who will be responsible for submitting data to the YMP Technical Data Management System (TDMS).

6. ACRONYMS AND DEFINITIONS

6.1 Acronyms

CIG	Center for Isotope Geochemistry
CR	Condition Report
EA	Engineering Assurance
LBNL	Lawrence Berkeley National Laboratory
LN	Liquid nitrogen
OQA	Office of Quality Assurance
PI	Principal Investigator
QIP	Quality Implementing Procedure
TDMS	Technical Data Management System
TIP	Technical Implementing Procedure
YMP	Yucca Mountain Project

6.2 Definitions

Prism: VG Isotech Prism Series II Isotope Ratio Mass Spectrometer in Room 4425 of building 70A at LBNL.

Staff Member: Any scientist, engineer, research or technical associate, technician, or student research assistant performing quality-affecting work for YMP-LBNL.

Technical Implementing Procedure: Each TIP describes YMP-LBNL technical tasks that (1) are repetitive, (2) are standardized, and (3) can return different results if deviation from the sequence of steps occur.

7. REFERENCES

Vennemann, T.W., and OíNeil, J. R., 1993, A simple and inexpensive method of hydrogen isotope and water analyses of minerals and rocks based on zinc reagent: Chem. Geol. (Isotope Geoscience Sect.), v. 103, p. 227-234.

AP-17.1Q, *Records Management*

AP-SIII.3Q, *Submittal and Incorporation of Data to the Technical Data Management*

System

LP-12.1Q-BSC, *Control of Measuring and Test Equipment*

LP-SIII.11Q-BSC, *Scientific Notebooks*

YMP-LBNL-QIP-5.2, *Preparing Quality & Technical Implementing Procedure*

YMP-LBNL-QIP-SV.0, *Control of the Electronic Management of Data*

YMP-LBNL-TIP/TT-11.0, *Calibration of a Mass Spectrometer for Isotopic Measurements of CO_2 and H_2*

8. ATTACHMENTS

Attachment 1 - Schematic diagram of fittings used for loading water samples into glass tubes with zinc metal to be converted to H_2 gas for hydrogen isotope analysis.

Attachment 2 - Schematic diagram of the vacuum line used for loading water samples in glass tubes with zinc for reduction to H_2 gas.

9. REVISION HISTORY

09/30/98 - Revision 0, Modification 0:

This is the initial issue of this procedure. It is derived from a scientific notebook procedure "Hydrogen Isotope Analyses of Waters" in Notebooks YMP-LBNL-YWT-MC-1 and YMP-LBNL-JSW-MC-1.

03/31/05 - Revision 0, Modification 1:

Modified procedure to incorporate Corrective Action (CR) 4689 (identifying precautions/safety considerations). Also updated the references of the Administrative Procedures transitioned to Bechtel SAIC Company, LLC Line Procedures. Updated Format. Maintained PI and Technical Staff responsibilities only.

02/09/06 Revision 0, Modification 2:

Modified to remove reference to the Prism operating manual. No changes in response to condition report (CR) 6705.

10. APPROVAL

(SIGNATURE ON FILE)

Preparer: Kate Woods — Date

(SIGNATURE ON FILE)

Technical Review/PI: Mark Conrad — Date

(SIGNATURE ON FILE)

Technical Review: Yvonne Tsang — Date

(SIGNATURE ON FILE)

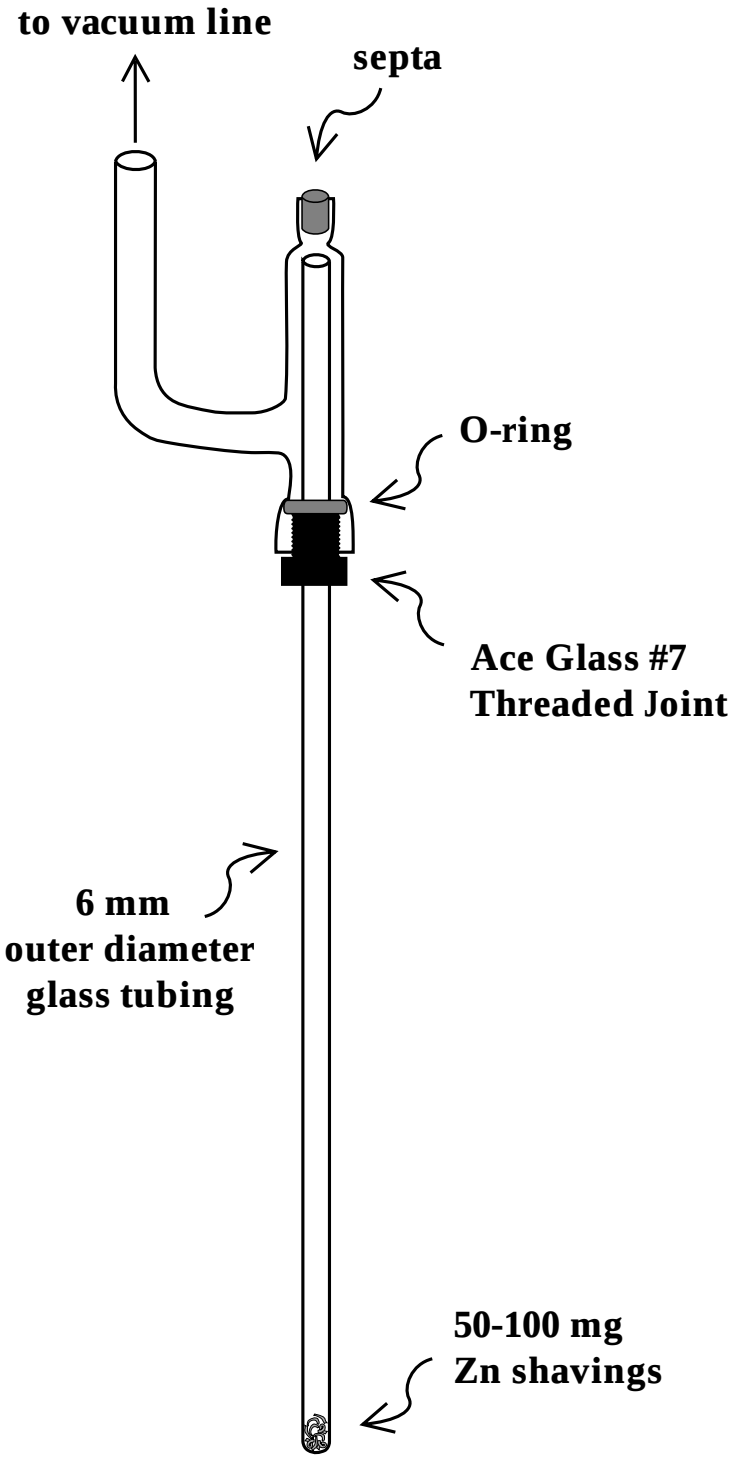
EA Review: Vivi Fissekidou — Date

(SIGNATURE ON FILE)

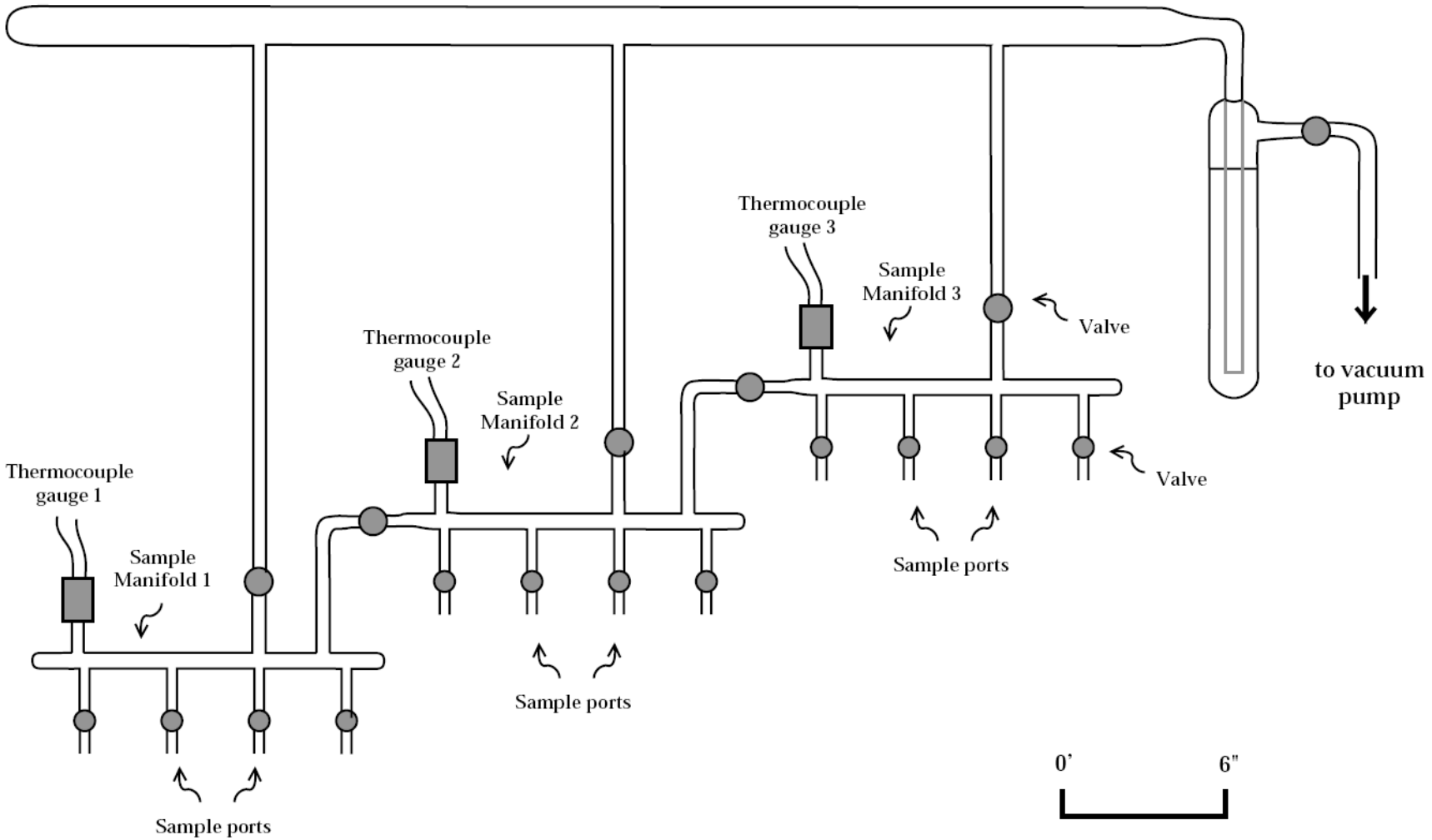
BSC QA Concurrence: Stephen D. Harris — Date

(SIGNATURE ON FILE)

Project Manager: Gudmundur S. Bodvarsson — Date



Attachment 1 - Schematic diagram of fittings used for loading water samples into glass tubes with zinc metal to be converted to H2 gas for hydrogen isotopic analysis



Attachment 2 - Schematic diagram of the vacuum line used for loading water samples in glass tubes with zinc for reduction to H_2 gas.