



Determination of the $\delta(^2\text{H}/^1\text{H})$ of Water: RSIL Lab Code 1574

Chapter 1 of
Book 10, Methods of the Reston Stable Isotope
Laboratory
Section C, Stable Isotope-Ratio Methods

Techniques and Methods 10–C1

U.S. Department of the Interior
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By Kinga Révész and T.B. Coplen

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DIRK KEMTHORNE, Secretary

U.S. Geological Survey
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Foreword

The Reston Stable Isotope Laboratory (RSIL) provides stable isotope analyses on a routine basis for a large user community within the U.S. Geological Survey (USGS) and elsewhere. The RSIL also serves the USGS National Research Program (NRP) through its project on Stable Isotope Fractionation in Hydrologic Processes. The NRP conducts basic and problem-oriented hydrologic research in support of the mission of the USGS. The stable isotope project conducts research on the use of isotope-ratio measurements in studies of water resources and environmental quality. One objective of this project is to develop new techniques for isotopic analysis of H, N, O, C, and S in environmental samples. New analytical techniques expand the range of tools available for studying the movement of those elements in hydrologic and biogeochemical systems. Another objective of the project is to test new applications of isotope measurements in specific field settings. Field studies of isotope behavior have contributed to understanding of water-supply sustainability, ground-water/surface-water interactions, paleoclimate history, biologic cycling of nutrients, ground-water contamination, and natural remediation. This project also contributes to the improvement of measurement science and the development of isotope databases.

Book 10 of the Techniques and Methods Series of the USGS contains detailed descriptions of methods of the RSIL, including routine analytical methods called standard operating procedures (SOPs), along with safety guidelines, maintenance procedures, and other information about the operation of the RSIL. Section C of Book 10 contains the SOPs for a variety of methods to measure stable isotope ratios, each of which constitutes a chapter. Each chapter is limited to a narrow field of subject matter to permit flexibility in revision as the need arises.



Pierre D. Glynn
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Conversion Factors

| Multiply | By | To Obtain |
|--|--|--|
| Length | | |
| micrometer (μm) | 0.00003937 | inch (in.) |
| millimeter (mm) | 0.03937 | inch (in.) |
| centimeter (cm) | 0.3937 | inch (in.) |
| meter (m) | 3.281 | foot (ft) |
| Volume | | |
| microliter (μL) | 0.0610210^{-3} | cubic inch (in^3) |
| milliliter (mL) | 0.06102 | cubic inch (in^3) |
| cubic centimeter (cm^3) | 0.06102 | cubic inch (in^3) |
| liter (L) | 61.02 | cubic inch (in^3) |
| Mass | | |
| nanogram (ng) = 10^{-3} μg | 3.527×10^{-11} | ounce (oz) |
| microgram (μg) = 10^{-3} mg | 3.527×10^{-8} | ounce (oz) |
| milligram (mg) = 10^{-3} g | 3.527×10^{-5} | ounce (oz) |
| gram (g) = 10^{-3} (kg) | 3.527×10^{-2} | ounce (oz) |
| kilogram (kg) = 10^3 g; 10^6 mg; 10^9 μg ; 10^{12} ng | 2.205 | pound (lb) |
| Density | | |
| gram per cubic centimeter (g/cm^3) | 0.5780 | ounce per cubic inch (oz/in^3) |
| Temperature | | |
| Celsius ($^{\circ}\text{C}$) | $^{\circ}\text{F} = 9/5 (^{\circ}\text{C}) + 32$ | Fahrenheit ($^{\circ}\text{F}$) |
| Pressure (force/area) | | |
| kilopascal (kPa) | 9.869×10^{-3} | atmosphere, standard (atm) |
| kilopascal (kPa) | 1.450×10^{-1} | pound-force/square inch (psi) |
| kilopascal (kPa) | 1.000×10^{-2} | bar |
| kilopascal (kPa) | 2.961×10^{-1} | inches of mercury at 60 $^{\circ}\text{F}$ |

Acronyms and Abbreviations

| | |
|---------|--|
| ANSI | American National Standards Institute |
| ASR | analytical services request |
| DI-IRMS | dual inlet isotope-ratio mass spectrometer |
| DIW | deionized water |

| | |
|-------------|--|
| IAEA | International Atomic Energy Agency |
| IRMS | isotope-ratio mass spectrometer |
| LIMS-LSI | Laboratory Information Management System for Light Stable Isotopes |
| MSDS | Material Safety Data Sheets |
| <i>m/z</i> | mass-to-charge ratio |
| NBS | National Bureau of Standards |
| NFPA | National Fire Protection Association |
| NIST | National Institute of Standards and Technology |
| NWIS | National Water Information System |
| NWQL | National Water-Quality Laboratory (USGS) |
| per mill, ‰ | 1/1000 |
| pF | picofarad |
| QA | quality assurance |
| QC | quality control |
| QC/QA | quality control/quality assurance |
| RSIL | Reston Stable Isotope Laboratory |
| SOP | standard operating procedure |
| USGS | U.S. Geological Survey |
| VSMOW | Vienna Standard Mean Ocean Water |
| SLAP | Standard Light Antarctic Precipitation |

Symbols

| | |
|----------|-----------------------|
| Ω | ohm |
| < | less than |
| > | greater than |
| \leq | less than or equal |
| \geq | greater than or equal |

Determination of the $\delta(^2\text{H}/^1\text{H})$ of Water: RSIL Lab Code 1574

By Kinga Révész and T.B. Coplen

Summary of Procedure

Reston Stable Isotope Laboratory (RSIL) lab code 1574 describes a method used to determine the relative hydrogen isotope-ratio $\delta(^2\text{H}, ^1\text{H})$, abbreviated hereafter as $\delta^2\text{H}$ of water. The $\delta^2\text{H}$ measurement of water also is a component of the National Water Quality Laboratory (NWQL) schedules 1142 and 1172. The water is collected unfiltered in a 60-mL glass bottle and capped with a Polyseal cap. In the laboratory, the water sample is equilibrated with gaseous hydrogen using a platinum catalyst (Horita, 1988; Horita and others, 1989; Coplen and others, 1991). The reaction for the exchange of one hydrogen atom is shown in equation 1:



The number ratio $N(^2\text{H})/N(^1\text{H})$ of the equilibrated hydrogen is related to that of the water through an isotopic fractionation factor $\alpha_{\text{hydrogen gas, water}}$

$$\alpha_{\text{hydrogen gas, water}} = \frac{N_{\text{hydrogen gas}}(^2\text{H})/N_{\text{hydrogen gas}}(^1\text{H})}{N_{\text{water}}(^2\text{H})/N_{\text{water}}(^1\text{H})} \quad (2)$$

The value of $\alpha_{\text{hydrogen gas, water}}$ is constant at a given temperature. Because reference waters and unknowns are interspersed and analyzed at the same temperature, the isotopic fractionation factor cancels and does not need to be known. Water and platinum catalyst are placed in glass tubes on a manifold in the equilibration system. The temperature in the equilibration system is held constant to keep the isotopic fractionation constant between gaseous hydrogen and water samples and references. Under computer control, the air from each sample vessel is exhausted, and the vessels are filled with gaseous hydrogen. The equilibrated hydrogen from each sample vessel is expanded under computer control into a dual inlet isotope-ratio mass spectrometer (DI-IRMS), which determines stable hydrogen isotopic composition. The RSIL uses a VG Micromass 602 hydrogen isotope-ratio mass spectrometer (IRMS). It has two Faraday cup collectors and is capable of measuring mass/charge (m/z) 2 and 3 simultaneously. The ion beams from H_2 are as follows: m/z 2 = $\text{H}_2^+ = ^1\text{H}^1\text{H}^+$; 3 = $\text{H}_2 = ^2\text{H}^1\text{H}^+$ and $^1\text{H}^1\text{H}^1\text{H}^+$. The isotopic compositions of unknowns are determined by normalizing data to that of isotopic reference waters analyzed with unknowns.

Reporting Units and Operational Range

Variations in isotopic compositions typically are small. Stable isotope–number ratios commonly are measured and expressed as the relative difference in the ratio of the number of the less abundant isotope (usually the heavy isotope) to the number of the more abundant isotope (usually the light isotope) of a sample with respect to a reference. This relative difference is designated $\delta(E)$, and it is defined according to equation 3:

$$\delta^i E = \delta^i(E) = \delta^i(E, jE) = \frac{N_B(iE)/N_B(jE) - N_{std}(iE)/N_{std}(jE)}{N_{std}(iE)/N_{std}(jE)} \quad (3)$$

where $\delta^i(E)$ refers to the delta value of isotope number i and j (heavy and light isotopes, respectively) of element E of sample B relative to an international measurement standard (std), $N_B(iE)/N_B(jE)$ and $N_{std}(iE)/N_{std}(jE)$ are the ratios of the number of isotopes in unknown B and the international measurement standard. A positive $\delta^i(E)$ value indicates that the unknown is more enriched in the heavy isotope than the international measurement standard. A negative $\delta^i(E)$ value indicates that the unknown is depleted in the heavy isotope relative than the international measurement standard. The symbol $\delta^i(E)$ is commonly shortened to $\delta^i E$ and has been reported in parts per hundred (‰ or percent), parts per thousand (‰ or per mill), and parts per ten thousand. For stable hydrogen isotope–number ratios, δ^2H (sometimes written in the literature as δD) is written as follows:

$$\delta^2H = \delta^2(H) = \delta^2(2H, 1H) = \frac{N_B(2H)/N_B(1H) - N_{std}(2H)/N_{std}(1H)}{N_{std}(2H)/N_{std}(1H)} \quad (4)$$

The international measurement standards are Vienna Standard Mean Ocean Water (VSMOW) and Standard Light Antarctic Precipitation (SLAP) (Coplen, 1988; Coplen, 1994). By interspersing local laboratory isotopic reference waters with isotopic compositions calibrated with international reference waters VSMOW and SLAP (Coplen, 1996) among the unknowns, the δ^2H values can be determined. The δ^2H measurements are made with a DI-IRMS, which alternatively measures 10 cycles of the isotope–number ratios of the unknown H_2 gas and of the “working reference” H_2 gas.

The system was tested by analyzing water samples with known δ^2H values. The δ^2H values of test samples range from approximately -428 to $+2120$ ‰ (Coplen and others, 1991), which includes the range of δ^2H of not only natural water but water artificially enriched in 2H as well. The routine analysis requires 1.5 mL of water; however, the system is capable of analyzing samples as small as 0.2 mL with minimal reduction in accuracy. The precision and accuracy of the results are acceptable (± 1 ‰) (Coplen and Harper, 1994), and memory between sample vessels is below detection (± 1 ‰).

Reference Materials and Documentation

Reference Materials Used, Storage Requirements, and Shelf Life

The international measurement standards for δ^2H measurements are VSMOW (distributed by the National Institute of Standards and Technology (NIST) as RM 8535) and SLAP (distributed by NIST as RM 8537) (Coplen, 1994). They are assigned a δ^2H value of 0 ‰ and -428 ‰, respectively. The RSIL has used VSMOW and SLAP reference waters to calibrate local laboratory reference waters as needed. These include deionized water (DIW) with a δ^2H value of approximately -65 ‰ and Antarctic water with a

value of approximately -400‰ . Approximately 40 L of DIW water was homogenized in a large container and was stored in 250-mL glass bottles with Polyseal caps. As aliquots are removed for analysis as local laboratory reference water, the water level decreases; however, it is never allowed to go below two-thirds full to minimize changes in isotopic composition caused by loss of water vapor, which is depleted in ^2H . Approximately 40 L of homogenized Antarctic water was sealed in 10-mL glass ampoules with an automatic ampoule-filling device. The ampoules were sterilized to minimize growth of algae and to identify any ampoules with pinhole leaks. These local laboratory reference waters are stored in the RSIL, and their shelf life is indefinite.

Documentation

All calibration results are stored in the Laboratory Information Management System for Light Stable Isotopes (LIMS-LSI) (Coplen, 2000) under sample identifiers with a prefix of W. Local laboratory reference waters, which include W-62000 and W-63333 (DIW and Antarctic water, respectively), are analyzed daily.

Labware, Instrumentation, and Reagents

The apparatus consists of three components: (1) hydrogen-water equilibration unit, (2) mass spectrometer, and (3) computer software. The equilibration unit (fig. 1) (Coplen and others, 1991) is constructed to hold 60 samples and has an air bath that ensures a temporal and spatial temperature variation of less than $\pm 0.007\text{ °C}$. The gas-handling system is constructed of four 3/8-in. stainless steel manifolds (Cajon 316L-1-ASYV-02387), each connected to 15 sample-port valves. All valves are pneumatically actuated to minimize heat production. Computer control of each valve is achieved by driving 12-V solenoid-operated valves (Parker Pneutronics Model 11104BB12) with complementary metal oxide semiconductor circuitry. The unit has two pump systems to achieve 10^{-3} Pa . Sample vessels consist of $13 \times 100\text{ mm}$ culture tubes (Corning model 9820-13). The equilibration is promoted with a hydrophobic-based (Teflon or styrene divinyl benzene) platinum catalyst (“Hokko beads” 3 % Pt by weight, 125–250 μm diameter, manufactured by Shoko Co. Ltd., Japan; Horita, 1988). The catalyst is glued to a 4-mm diameter glass rod 101 mm long with clear silicone household glue and sealed in a band covering a 10-mm length of the rod from $28 \pm 5\text{ mm}$ from one end. The meniscus of a 2-mL water sample is positioned in the center of this band.

The IRMS (fig. 2) is a VG Micromass 602 hydrogen dual inlet, double-collecting, isotope-ratio mass spectrometer. In the IRMS, H_2 gas molecules are ionized in a source by electrons emitted from a hot filament. The ions are accelerated into an analyzer, separated in a magnetic field, and collected in a Faraday cup collector. The ion-beam intensities are measured with electrometers. Two computer-controlled sample pistons (Coplen, 1981) feed a single sample capillary alternately to increase sample throughput. One computer-controlled working reference piston feeds the reference capillary. Working reference H_2 gas is chosen with an isotopic composition near -750‰ relative to VSMOW to minimize error caused by H^{3+} contribution (Coplen and others, 1991). The Microsoft Visual Basic data acquisition and control software is designed to (1) control the sample preparation unit, (2) control the DI-IRMS, (3) acquire data from the DI-IRMS, and (4) process and store data directly to LIMS-LSI.

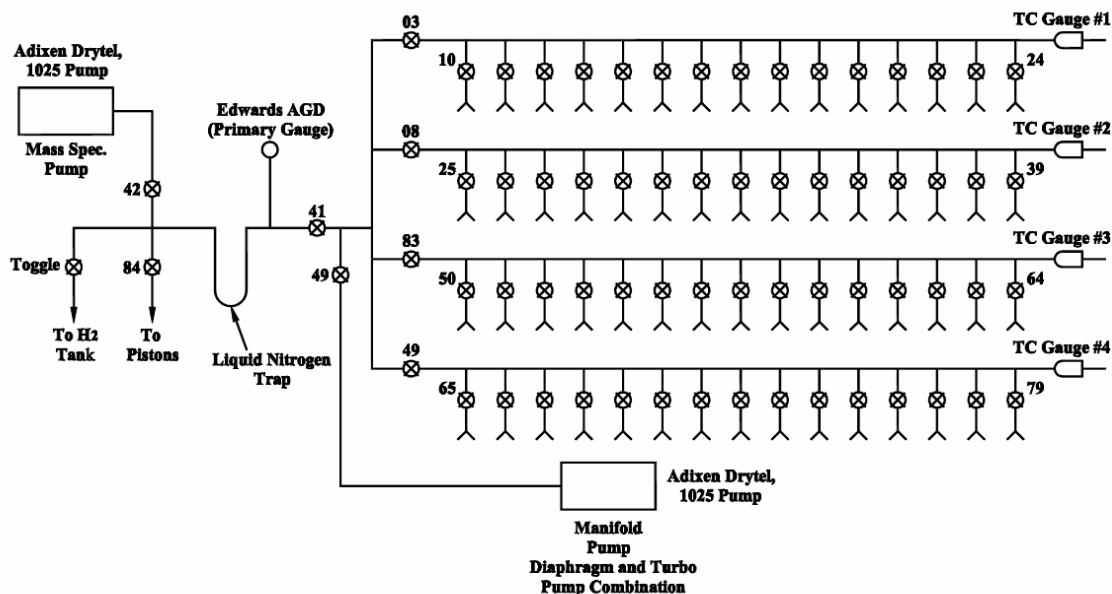


Figure 1. Diagram of water equilibration unit.

Sample Collection, Preparation, Analysis, Retention Times, and Disposal

Sample Containers, Preservation, and Handling Requirements

Each sample is collected in a 60-mL glass bottle with a Polyseal conical insert cap to minimize evaporation. Bottles are provided at no cost by the RSIL on request through e-mail: isotopes@usgs.gov. The bottles are labeled with isotopes whose concentrations are to be determined along with the respective laboratory code or schedule number. In the field, bottles should be filled with samples by overflowing directly from sample collection or processing devices, filtered or not filtered. No chemicals should be added for preservation. Before capping the bottles, some water should be poured out until the water level is at the bottle shoulder to prevent the bottle from breaking if it freezes during transit to RSIL. Samples could be collected in polyethylene bottles with no headspace. A minimum of 5 mL of water is required unless special arrangements are made in advance. Regardless of the amount of sample collected, the bottle size should be matched to the sample size; that is, bottles should be at least three-quarters full to minimize evaporation effects.

No treatment, preservation, or special shipping is required.

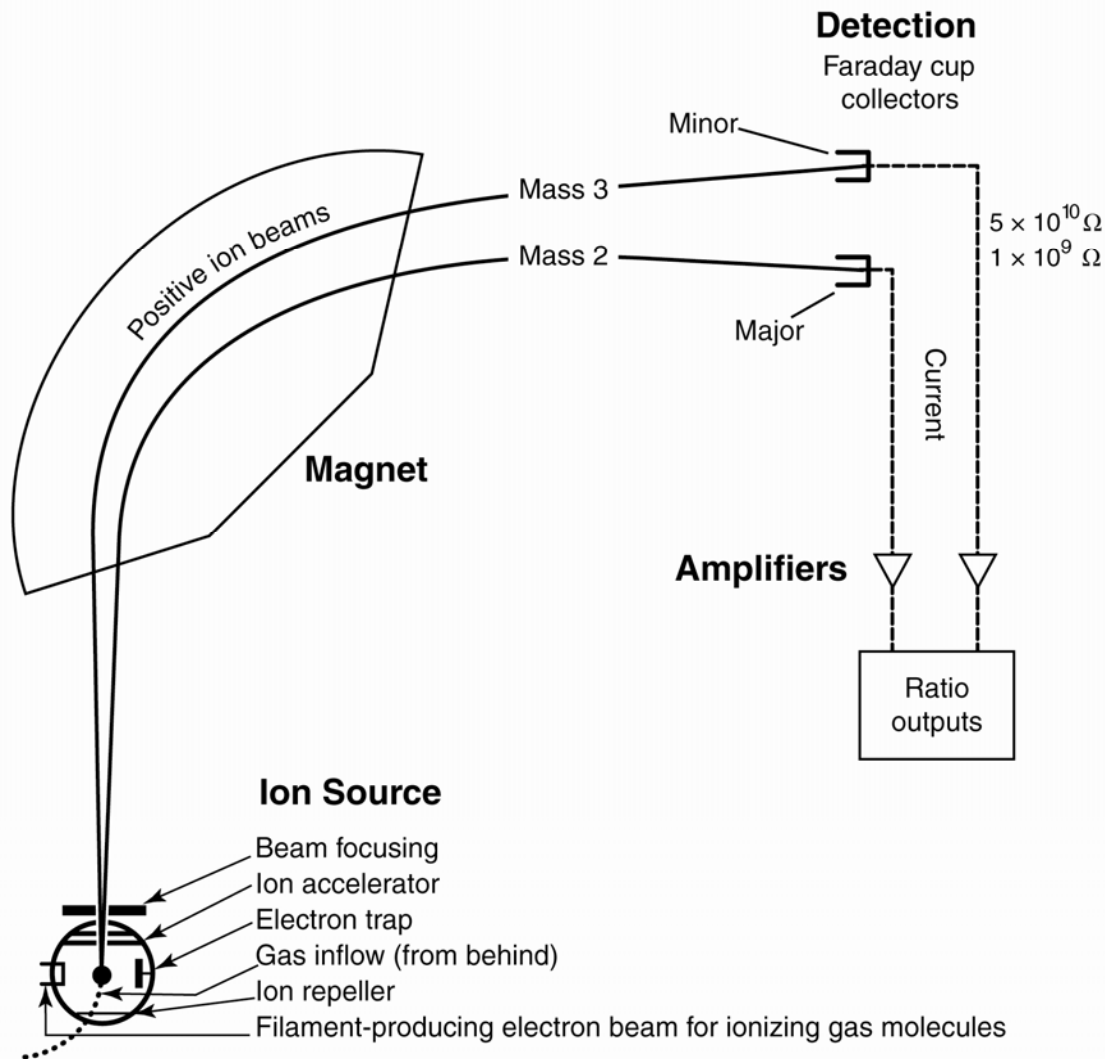


Figure 2. Schematic of a continuous flow isotope-ratio mass spectrometer (CF-IRMS) (modified from Clark and Fritz, 1997).

Sample Preparation and Time Requirements

Sample preparation involves logging in samples to LIMS-LSI in batches that could contain from 1 to 100 samples per batch (also called a project), printing labels for each sample, and printing a summary project report. Each sample label contains the Field ID (the identifier by which the sample submitter knows each sample) and the unique RSIL Lab ID assigned by the LIMS-LSI. The summary project report is inserted into a three-ring binder titled “Samples in Progress.”

If samples are submitted through the USGS National Water Quality Laboratory (NWQL), the Field ID is a unique number for each sample assigned according to NWQL guidelines; this unique number is written on the analytical services request (ASR) form accompanying the sample, and the ASR information is entered into the LIMS-LSI system. This information is e-mailed to the submitter of the samples for identification of any errors and subsequently e-mailed to NWQL. Paper copies of the ASR forms are mailed to NWQL. The step-by-step procedure to log in samples is given in Appendix A.

The processing of samples involves adding approximately 5 g of Cu metal granules to each sample to oxidize any sulfide in the sample. This is necessary because sulfide will poison the Pt catalyst needed for $\delta^2\text{H}$ analysis.

The time requirement for preparing the samples as described earlier is approximately 1 working day.

Performing the Analysis and Time Requirements

As many as 60 water samples are analyzed daily. Using the sample work order/worksheet, which is created by LIMS-LSI by printing a "Template" from the "Samples to be Analyzed Form" (step-by-step procedure is found in Appendix B), the analyst sets up the unknowns and reference waters to be analyzed. Each sample vessel is loaded with 2 mL of water, and a Hokko-bead rod is put into each sample vessel. The Hokko-bead rods are numbered so that they can be tracked and removed in case they are poisoned. To remove the air from sample vessels, they are evacuated through built-in capillaries in groups of four for 60 s under computer control. After satisfactory evacuation, H_2 is added simultaneously to all 60 vessels to a pressure of 100 kPa. The temperature controller is powered on and maintains the temperature at 27.48 ± 0.03 °C. The system procedure is listed in the "Lab Procedures" binder. The supervisor reviews any suggested changes before they are instituted. The current procedure, which includes the sections "System Preparation," "Water Sample Preparation," and "Starting Analysis," is given in Appendix C.

Before starting isotopic analyses of the samples, the analyst checks to make sure that the DI-IRMS and its preparation system are functioning properly by checking off items (in ink) on the "Hydrogen Mass Spectrometer Checklist," which is provided in Appendix D. This checklist is replaced weekly and saved for analytical audits.

The samples are equilibrated for a minimum of 1 h, primarily to allow the system to reach temperature stability. For each sample analysis, the pneumatically actuated valve is opened to the sample piston for 15 s, releasing more than 90% of the H_2 from the sample vessel. Trace water is removed from the H_2 by trapping with a U-tube trap filled with liquid nitrogen. The water is pumped away after all analysis is completed. Pressure adjustment in the sample piston is performed with an absolute pressure transducer; finer adjustment is performed with the $m/z = 2$ ion-beam voltage. Samples are analyzed in turn. They are corrected for mismatch between sample and reference $m/z = 2$ ion-beam voltages. The $\delta^2\text{H}$ values are normalized to the VSMOW-SLAP scale by the mass spectrometric software using the equation $\delta^2\text{H}$ relative to VSMOW equals $1.0083 \delta^2\text{H} - 32.36$. This calculated delta value is called the penultimate delta and is saved in real time in the LIMS-LSI database.

An analyst at the LIMS-LSI determines daily correction factors using the $\delta^2\text{H}$ values of the secondary water references using equations similar to the following:

$$-62.3 \text{‰} = m \times \delta_{\text{W-50000,VSMOW}}^2\text{H} + b \quad (5)$$

$$-399.8 \text{‰} = m \times \delta_{\text{W-63333,VSMOW}}^2\text{H} + b \quad (6)$$

The values -62.3‰ and -399.8‰ are the values of secondary reference waters that have been calibrated using the international reference waters VSMOW and SLAP. The $\delta^2\text{H}$ values in equations 5 and 6 are the mean daily delta values of the respective secondary reference water relative to VSMOW; b is the additive correction factor; m is the expansion coefficient correction factor. The procedure to apply correction factors is given in Appendix E.

All samples are prepared and analyzed in duplicate on different days. Different Hokko-bead rods and ports typically are used for the duplicates; this minimizes errors due to misidentification and erratic analytical problems. If the replicates do not agree within acceptable tolerances, the samples are reanalyzed until acceptable statistics are achieved. The computerized LIMS-LSI will not release data until

the statistics are acceptable. The time requirement for performing the analyses described earlier is a minimum of 2 days.

Problematic Samples

Problematic samples include those from landfills, which contain substantial amounts of organic material. The organic material interferes with equilibration of the hydrogen. Sometimes activated charcoal can be added to a water sample to absorb the organic material (Coplen and Harper, 1994). Organic material can be dissolved in hot paraffin in contact with the water.

Samples that contain H₂S are also problematic. The H₂S must be removed (commonly using Cu granules) before isotopic analysis or the Pt catalyst will be poisoned.

Interferences

Organic material can also be an interference, as discussed earlier. Evaporation alters the isotopic composition of the water; therefore, improperly capped samples are noted and sent back to the sample submitter.

Troubleshooting and Bench Notes

The most common problem is degradation of the Hokko-bead rods. They deteriorate because either the Hokko beads fall off over time, or the Hokko beads are poisoned. At approximately quarterly intervals, the same water is analyzed in all 60 sample vessels to identify Hokko-bead rods that no longer provide satisfactory $\delta^2\text{H}$ values.

After every set of analyses, the analyst should inspect the data sheets. If the sample volume is too small, the analyst should make a note of the port number and notify the supervisor.

Maintenance and Maintenance Records

The major maintenance is equivalent to the maintenance of a vacuum line. This includes checking pump performance from time to time, changing the diaphragm and pump head, and cleaning and greasing stopcocks and O-rings in fittings on a regular basis. Pump conditions are listed, such as date of diaphragm change, problems, and repairs in a pump logbook as well as in a database (File path: LIMS C:\RSIL\vacuum pumps). The DI-IRMS does not require regular maintenance; however, it requires a daily maintenance check (Appendix D). A logbook is kept for each DI-IRMS; notes about maintenance checks, normal settings, problems, and repairs are included.

Sample Retention Time and Disposal

Samples are retained in the RSIL for at least 6 months after reporting data. Samples are then discarded unless the submitter has requested that the samples be returned.

The sample-analysis files from the DI-IRMS computer are kept indefinitely on two different hard disks of the data backup computer. Paper reports are kept for a few weeks.

Analytical results from the DI-IRMS are transmitted to LIMS-LSI and are kept indefinitely. No data are entered by hand and no manual calculations are performed on the data.

Data Acquisition, Processing, Evaluation, Quality Control, and Quality Assurance

Laboratory Information Management System for Light Stable Isotopes (LIMS-LSI)

In the RSIL, the LIMS-LSI (Coplen, 2000) is used for data acquisition, processing, and evaluation. This system is a database program capable of (1) storing information about samples, (2) storing the results of mass spectrometric delta values of samples after analysis, (3) calculating analytical results using standardized algorithms stored in a database, (4) normalizing delta values using isotopic reference materials, and (5) generating templates for convenient sample placement to facilitate loading of automated mass spectrometer sample preparation manifolds. With this system, the following can be achieved: (1) quality assurance (QA), (2) laboratory efficiency, (3) reduction of workload and errors owing to the elimination of retyping of data by laboratory personnel, and (4) a decrease in errors in data reported to sample submitters. This database provides a complete record of information on how laboratory reference materials have been analyzed, a record of what correction factors have been used, and an audit trail for the RSIL.

Quality-Control (QC) Samples

Samples commonly are loaded in four groups of 15 samples each, because each manifold has 15 ports. Approximately 11 laboratory reference waters are analyzed daily with the samples. Two of these are Antarctic waters that are highly depleted in ^2H , and the others are laboratory DIW with normal ^2H concentration. Many reference water positions in a sample template are randomly located among samples by LIMS-LSI. The randomized locations allow the analyst to detect problem ports, including defective Hokko-bead rods, leaks, and other problems. Nevertheless, the analytical result from an occasional reference water is ignored unless the error is persistent or its frequency increases greatly. For NWQL samples, one QC sample is analyzed for every 50 samples submitted. The NWQL provides these QC samples, and their isotope-ratio values are unknown to the RSIL. If the NWQL finds any problem with the QC sample data, it reports the problem to the RSIL, and the QC sample in question is reanalyzed along with the other samples analyzed in the same period. This is an infrequent occurrence.

An analyst examines the mass spectrometric analysis reports daily for problems. Additive correction factors and expansion factors are determined daily with LIMS-LSI and applied to isotopic data. After printing the isotopic results from the "Table of Samples in Progress," the analyst reviews the results, determines which samples need to be reanalyzed to achieve acceptable statistics (e.g., $\leq 2\text{‰}$), and adds those samples back to the "Table of Samples to be Analyzed" so that they will appear on a sample template.

For each batch of samples completed, a graph is made of $\delta^2\text{H}$ versus $\delta^{18}\text{O}$ ($\delta^{18}\text{O}$ analyses are usually also requested for water samples). The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of naturally occurring waters commonly have a high natural correlation coefficient; the loci of points defines the "meteoric waterline." Outliers are noted and reanalyzed for both $\delta^2\text{H}$ and $\delta^{18}\text{O}$ because these are either interesting research findings or laboratory errors, such as a mix-up on a sample template.

Every few years, the RSIL participates in an International Atomic Energy Agency (IAEA) interlaboratory calibration. This is a good check of the calibration of the DI-IRMS, the laboratory reference waters, and the computer data-management systems.

Acceptance Criteria for All QC Samples

Acceptance criteria for QC samples are the same as acceptance criteria for other samples. The rules are as follows:

- If standard deviation is smaller than $\pm 1.55 \text{ ‰}$, use mean delta.
- If there are three or more analyses, delete the outlier and recalculate.
- If standard deviation of this recalculation is less than or equal to $\pm 1.8 \text{ ‰}$, use the mean of this recalculation.
- If recalculation was performed on exactly three analyses and if the recalculation mean is $\pm 2.5 \text{ ‰}$ or less, use it.
- If the difference between the original standard deviation and the recalculated standard deviation is larger than 1.1 and the recalculated standard deviation is less than 3 ‰ , use the mean of the recalculated standard deviation.
- If none of the above is the case, the result is not accepted.

A comparison of the precision of pairs of references analyzed on the same day shows that the $\Delta\delta$ is 1 ‰ for $n = 364$. The comparison of the precision of two aliquots analyzed on different days shows that $\Delta\delta$ is better than 1.3 ‰ for $n = 368$. These numbers represent a 1-year period; only outliers where the analyses were flagged for problems were omitted from comparison.

Corrective Action Requirements

If the analyst finds any problem with the daily reference-sample data, the analyst contacts the supervisor. The trouble-shooting process requires an evaluation and reanalysis of certain samples to identify the origin of the problem.

If samples do not give satisfactory results after three or more separate analyses, the analyst averages all the data and reports the mean value. Such analytical results are indicated with a comment, and the customer will be advised by e-mail or other means. If the sample was submitted through the NWQL, it is the responsibility of the customer to determine whether the data need to be qualified. If so, the NWQL will mark the result appropriately in the USGS databases.

Responsible Parties for All QA/QC Functions for Procedures Covered in RSIL SOPs

The analyst, with supervisory approval, is responsible for qualifying data and notifying customers about problematic results.

Data Management and Records

In addition to evaluating daily sample analyses, an analyst evaluates the data weekly project by project, reports results to the customers, and files final project data reports in the laboratory "Correspondence" binder (Appendix F).

Health, Safety, and Waste-Disposal Information

Applicable Health and Safety Issues

Personal Protection

Safety glasses and protective gloves are recommended whenever samples are handled, especially when the samples are of biological origin. For other precautions and safety procedures, consult Material Safety Data Sheets (MSDSs), which are on file in the laboratory, and <http://www.ilpi.com/msds/#Manufacturers>. This URL provides links to the MSDSs of most chemicals.

Electrical Hazards

Electrical systems must conform to the National Electric Code, National Fire Protection Association Code (NFPA 70–1971), and the American National Standards Institute (ANSI) Code (C1-1971). Consult the U.S. Geological Survey’s Safety and Environmental Health Handbook (U.S. Geological Survey, 2002).

Shock hazards exist inside the instruments. Only an authorized service representative or an individual with training in electronic repair may remove panels or circuit boards where voltages are greater than 20 V. The instruments require a third-wire protective grounding conductor. Three-to-two wire adapters are unsafe for these instruments.

Chemical Hazards

Mercury is used in the pistons of the DI-IRMS. All samples should be carefully inspected on receipt for obvious indications of hazards.

Gas Cylinder Handling

Compressed gas cylinders must be handled and stored according to the Safety and Environmental Health Handbook (U.S. Geological Survey, 2002). Each cylinder must be (1) carefully inspected when received; (2) securely fastened at all times with an approved chain assembly or belt; (3) capped at all times when not in use; (4) capped when transported; (5) transported only by a properly designed vehicle (hand truck); and (6) stored separately with other full, empty, flammable, or oxidizing tanks of gas, as appropriate.

Specific Waste-Disposal Requirements

Sample containers must be emptied before disposal. Samples to be discarded should be emptied into a container in a sink. The container can catch any Cu granules to prevent them from clogging the sink drain. Cu granules that have been collected from samples should be poured into a bottle and given to the safety health and environment officer for disposal.

Revision History

Publication Series and Series Number: Techniques and Methods 10–C1 (Book 10, Section C, Chapter 1)

Publication Title: Determination of the $\delta(^2\text{H}/^1\text{H})$ of Water: RSIL Lab Code 1574

Publication Authorship: Révész, Kinga, and Coplen, T.B.

First Version and Date of First Release: December 2008

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Summary of Product Components

| Component | Description | Last Revised In Publication Version | Date of Last Revision |
|-----------|-------------|--|--------------------------|
| | | | |
| | | | |
| | | | |

List of Revisions (latest version first):

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Appendix A. Step-by-Step Procedure to Log In Samples to LIMS-LSI

Submittal Types

1. Samples submitted to RSIL for analysis are sent either through the NWQL or directly to RSIL by the person or agency requesting an analysis.
2. There are two primary types of submittals:
 - a. ASR, which uses ASR forms for each sample submitted.
 - b. Direct, in which all sample information is submitted via diskette, CD, or e-mail.

ASR Submittal

1. Match the information on the sample bottles with the information on the ASR forms by spreading out the ASR forms and placing each bottle on its respective ASR form. Each sample must have a corresponding ASR form.
2. At this time, check for any broken or damaged sample bottles.

Assign National Water Information System (NWIS) Numbers to Samples

1. Use the format 00 (year) 000 (Julian date) 95 (standard #) 00 (sample #).
2. The Julian date is found on the standard-issue calendar used in the laboratory. It refers to the number of the day of the year.
3. The sample number is derived from the number of samples submitted, starting with 00 for the first sample, 01 for the second sample, 02 for the third sample, and so on.
4. An example of format would be as follows: 071389504: 07 for the year 2007, 138 for the 18th of May, 95 (which is a standard number), and 04 to indicate the fifth sample in the group.
5. If there are two or more groups of samples logged in on the same day, the sample number(s) will be different for each group. If the last sample of the first group that was logged in is 071389504, then the first sample of the second group would be 071389505.
6. Add any QC samples to the group (explained in next section) and assign NWIS number(s).
7. Write the NWIS numbers, assigned in step 2, in the space provided on the top left-hand side of the ASR form marked NWIS RECORD NUMBER, SAMPLE TRACKING ID.

QC Samples (NWQL Samples Only)

1. QC samples must be checked before logging samples into the LIMS database.
2. For every 50 samples submitted through NWQL, a QC sample must be added (see the laboratory supervisor for the location of QC samples).
3. An additional Julian date (explained in the next section) will need to be created as a placeholder for the QC sample to be correctly added to the LIMS database.
4. To determine whether a QC sample is required, reference the yellow QC sample log sheet located on the wall to the right of the LIMS printer.
 - a. There are four columns on the QC sample log sheet: project date, start W#, end W#, and # of samples.
 - b. QC sample numbers begin with the prefix QC followed by three "0s," that is, QC-00038, QC-00040, QC-000120, and so forth.
 - c. Add up the numbers in the "# of Samples" column from the last QC number.
 - d. After the 50th submitted sample, a QC sample must be added.

Logging Samples into the LIMS-LSI Database

1. Open the LIMS program.
2. Select “New Project Login.”
3. In the “New Project Login” window:
 - a. Submission date: The date samples are logged in (e.g., 5/21/07).
 - b. Customer: Type in or use drop-down menu to select. For NWQL samples, always select “Mullin, Ann H.” from the drop-down menu. This is not found on the ASR form.
 - c. Medium: This is determined by the type of sample submitted, that is, “01 Water.” This information is not found on the ASR form.
 - d. Project purpose or title: For example, Central Lab Samples, Schedule #, submitter or collectors name (District contact e-mail).
 - e. Location: Type in location of the samples if provided.
 - f. Country: Select from drop-down menu.
 - g. State and county: Select from drop-down menu.
 - h. NWQL media: Select from drop-down menu; this is indicated as “Medium Code” on the ASR sheet.
 - i. Lab code/schedule: This is on ASR form listed under “Analytical Work Requests.” The type of schedule submitted will determine whether the sample number will begin with a “W,” “G,” or “S.” Use “W” for hydrogen and oxygen isotopes of water samples.

Adding the QC Sample

1. The addition of the QC sample may fall at the beginning of the sample group, at the end of the sample group, or somewhere in the middle.
2. Treat the QC sample as one of the samples of the sample group and assign it a Julian date, just like the samples. The only difference is it will not have an ASR form.
3. While editing samples in the “Samples” window, delete the placeholder that was assigned to the QC sample in the “Field ID/NWQL Number” space and replace it with the QC number.

Generating Sample Numbers

1. In the “New Samples Log-In” window, click “Add Range.”
2. In the “Add Range” box, there are two fields: “From” and “To.”
3. Type in the NWQL numbers for that group from the lowest to the highest, that is “From” 071439500 “To” 071439507. Do not forget QC samples, if any.
4. Check that the information entered is correct, then click “Add.”
5. The “Add Range” window will pop up for confirmation of the number of rows (samples) added. If correct, click “Yes.”

Save Information into Project Record

1. When all information has been entered, click “Save” in the “Login New Samples” window.
2. In “LIMS” window, click “OK” to create a project record in the LIMS system.
3. If any of the information in the project record needs to be edited, go to the LIMS main page and click “Projects.”
4. In the “Find Project” window, select the project and double click to open.
5. From the “Projects” window, all information can be viewed and edited.

Entering Information for Each Sample

1. Information for each individual sample must be entered into LIMS from its corresponding ASR form.
2. From the LIMS main page, click “Projects.”
3. Select and double click the project to edit.
4. In the “Projects” window, click “Samples.”
5. In the “Samples” window, click “Edit.”
6. Fill in each sample’s information using the ASR form.
7. When the field has been completed, click “Save.”
8. Do this for each sample using the left or right arrow buttons found on either side of the sample number.
9. When all the samples have been entered, click “Close.”

Print Report

1. Print two copies of the Submission Report.
2. In the “Projects” window, click “Print Report” twice.
3. Update the QC log if any QC samples were added.

Print Sample Labels

1. Print two sets of labels, except for waterproof labels.
2. There are three options for printing labels:
 - a. “Print Labels”—blue labels, 30 per page.
 - b. “Print Small Labels,”—small white labels, 80 per page.
 - c. “Print Waterproof Labels,”—white labels, 27 per page.
3. The selection of labels will depend on the size of sample bottles submitted and whether samples need refrigeration where waterproof labels may be necessary. Ask the laboratory supervisor for guidance.
4. Blue labels are normally used for the ASR forms; white labels are used for small bottles.

NWQL Headings

1. Obtain a diskette.
2. Insert the diskette into the appropriate drive.
3. In the “Projects” window, click “NWQL Headings.”
4. Follow the directions on the computer.
5. When the data have been transferred, click “Close” to cancel the projects.
6. Leave the diskette in the drive at this time.

Print Sample Range

1. On the main LIMS page, click “Print Sample Range.”
2. Select a prefix, for example, “W” for water.
3. Type in the range from the lowest to the highest W #'s in the project in the “From” and “To” spaces provided.
4. Click print.
5. This information will be mailed back to NWQL.
6. The diskette can be removed at this time.

Placement of Labels

1. Place the correct label on the corresponding ASR form (blue labels) in the space in the upper right hand side marked "Lab Use Only," "NWQL Laboratory ID."
2. Place the other label on the corresponding sample bottle.
3. Crosscheck all information to ensure labels on ASR forms and bottles match.

Information to Be Mailed Back to NWQL

1. Photocopy all ASR forms.
2. The photocopied set goes into a manila envelope.
3. Include "Sample Range" printouts.
4. Place a preaddressed label to NWQL onto the front of the envelope.
5. Write mail stop 431 and the name of the laboratory supervisor in the top left corner.
6. Put in mail stop outbox.

E-Mail Headings to Sample Submitter

1. This information is on the diskette used in the NWQL headings section.
2. Access the correct drive on the computer and open the file with NotePad.
3. Right click in the NotePad window, click "Select All," right click again, and select "Copy."
4. Using Lotus Notes, open a "New Memo," right click, and select "Paste" to transfer all data into e-mail.
5. Delete the first three lines of the e-mail.
6. Enter the e-mail address of the submitter (District contact e-mail) and cc the laboratory supervisor (isotopes).
7. Print a copy of the e-mail and send.

Samples in Progress Binder

1. Take a printed copy of the e-mail along with a copy of the project report and place it in the "Samples in Progress" binder.
2. The projects are in order by date.
3. Arrange in the binder with the project report on top, copy of the e-mail second, and any other documentation received from the submitter last.
4. Place a divider after each project as it is placed in the binder.

Central Laboratory Sheets Binder

1. Place the project report and the original ASR forms in the back of the binder.
2. Use "write on" tape and record the submission date of the sample group. Place the tape on the edge of the project report to be used as a tab.

Direct Submittal Formats

1. RSIL Sample Submittal Form.
2. RSIL Alternative Sample Submittal Form.

3. Both types can be submitted via a CD, diskette, or e-mail.

Verifying Information

1. Place the submitted disk into the appropriate drive and print out the “Sample Submittal File” if the submitter has not already provided a paper copy.
2. Ensure that the information provided matches the information on the sample bottle labels.
3. Change the submission date on the submittal file to the date that the samples are actually being logged in.
4. Save any changes before exiting.

Logging Samples Into LIMS Database

1. Open the LIMS program.
2. From the LIMS main page, select “Import New Project.”
3. In the “Import Project” window, select the file being submitted.
4. In the “How Many Samples in Project” window, click “OK.”
5. In “LIMS” window click “OK.”

Getting a Password

1. A password is required if latitudes and longitudes are not provided in the submittal file.
2. See the laboratory supervisor for a password.
3. If some other information is missing and LIMS does not allow logging in the samples, send the diskette back to the customer for missing information.

Printing Report and Putting Samples into Template

1. On main LIMS page, select “Projects.”
2. Select and double click the project to edit.
3. Only one copy of the Submission Report needs to be printed.
4. In the “Projects” window, click “Print Report” once.
5. In the “Project” window, click “Templates” and then add the project to either the front or end of the queue for the appropriate mass spectrometer(s).

Printing Labels

Follow the instructions for “Print Sample Labels” except when only one set of labels needs to be printed.

Filing Samples in Progress Binder

1. Take the printed copy of the Submission Report and Submittal File printout along with any other documentation and place in the “Samples in Progress” binder.
2. The projects are in order by date.
3. Arrange in the binder with Project Report first, along with any other documentation received from the submitter second.
4. Place a divider after each project as it is placed in the binder.

Placing Labels

1. Match the label to the sample bottle.
2. Ensure all information is correct using the submittal form.

Preparation of Samples (This Applies to All Samples)

1. Check to ensure that samples are labeled.
2. Check samples for hydrogen sulfide (H₂S) and organic material.
3. Using a suitable storage box (see Laboratory Supervisor), place samples in order.

Checking for H₂S

1. Open bottle and check cap to ensure it is a Polyseal type cap. Replace any caps that are not Polyseal caps.
2. Open bottle and add two scoops (0.70 g per scoop) of copper. This applies to all samples except precipitation samples.
3. Replace cap and shake.
4. Open bottle and sniff for H₂S (rotten egg smell).
5. Add more copper, shake sample, and check for H₂S smell again.
6. If the sample has an extremely strong H₂S smell, subdivide sample into a smaller (11-mL) bottle and add copper to that as before until no smell is present.
7. Print a duplicate label (the same as the original sample) and place it on the subsample bottle.
8. Use a rubber band to attach the subsample bottle to the original sample bottle.

Checking for Organic Material

1. Hold the sample up to light and check for cloudy or yellowish colored samples, which is an indication that organic material is present.
2. Using a small spatula, add up to two scoops (0.50 g per scoop) of granular activated charcoal.
3. Replace cap and shake.
4. Place sample in appropriate storage box in order by sample number.

Appendix B. Step-by-Step Procedure to Generate an Excel Sample Workbook or to Print a Template and a Samples-to-Be-Analyzed List

Template

1. Use “Print Template” in LIMS-LSI.
2. Select “appropriate template” “Pegasus” for water hydrogen and Micromass IRMS.
3. Select “New Template” (dialog box informs you how many samples are waiting to be analyzed).
4. Click “OK.”
5. Click “Print.”
6. Insert diskette to receive sample headings.
7. Click “OK.”
8. Write the day of the week that these samples should be analyzed on both the diskette and the paper template.
9. Put the diskette by the VG IRMS computer and the paper template in the sample preparation area.
10. Exit LIMS-LSI.

Samples to be Analyzed List

W-50000 and W-63333 are reference waters (Note that the in-house reference waters are in bold.)

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Pegasus Samples To Be Analyzed Hokko-Bead Tray: _____

| Port | Sample # | Amount | Sample Prep/Extract Info | Port | Sample # | Amount | Sample Prep/Extract Info |
|------|----------------|--------|--------------------------|------|----------------|--------|--------------------------|
| 10 | W-50000 | _____ | | 59 | W-94894 | _____ | |
| 11 | W-50000 | _____ | | | | | |
| 12 | W-94864 | _____ | | 60 | W-94895 | _____ | |
| 13 | W-94865 | _____ | | 61 | W-94896 | _____ | |
| 14 | W-94866 | _____ | | 62 | W-94897 | _____ | |
| | | | | 63 | W-94898 | _____ | |
| 15 | W-94867 | _____ | | 64 | W-94899 | _____ | |
| 16 | W-94868 | _____ | | | | | |
| 17 | W-94869 | _____ | | 65 | W-50000 | _____ | |
| 18 | W-50000 | _____ | | 66 | W-94900 | _____ | |
| 19 | W-94870 | _____ | | 67 | W-94901 | _____ | |
| | | | | 68 | W-94902 | _____ | |
| 20 | W-94871 | _____ | | 69 | W-50000 | _____ | |
| 21 | W-94872 | _____ | | | | | |
| 22 | W-94873 | _____ | | 70 | W-94903 | _____ | |
| 23 | W-94874 | _____ | | 71 | W-94904 | _____ | |
| 24 | W-50000 | _____ | | 72 | W-94905 | _____ | |
| | | | | 73 | W-50000 | _____ | |
| 25 | W-94875 | _____ | | 74 | W-94906 | _____ | |
| 26 | W-50000 | _____ | | | | | |
| 27 | W-94876 | _____ | | 75 | W-94907 | _____ | |
| 28 | W-94877 | _____ | | 76 | W-94908 | _____ | |
| 29 | W-94878 | _____ | | 77 | W-94909 | _____ | |
| | | | | 78 | W-94910 | _____ | |
| 30 | W-94879 | _____ | | 79 | W-94911 | _____ | |
| 31 | W-94880 | _____ | | | | | |
| 32 | W-63333 | _____ | | | | | |
| 33 | W-63333 | _____ | | | | | |
| 34 | W-94881 | _____ | | | | | |
| | | | | | | | |
| 35 | W-94882 | _____ | | | | | |
| 36 | W-94883 | _____ | | | | | |
| 37 | W-94884 | _____ | | | | | |
| 38 | W-94885 | _____ | | | | | |
| 39 | W-94886 | _____ | | | | | |
| | | | | | | | |
| 50 | W-94887 | _____ | | | | | |
| 51 | W-50000 | _____ | | | | | |
| 52 | W-94888 | _____ | | | | | |
| 53 | W-94889 | _____ | | | | | |
| 54 | W-94890 | _____ | | | | | |
| | | | | | | | |
| 55 | W-94891 | _____ | | | | | |
| 56 | W-94892 | _____ | | | | | |
| 57 | W-50000 | _____ | | | | | |
| 58 | W-94893 | _____ | | | | | |

[Local laboratory reference materials are in bold font.]

Actual Templates Showing the Port Numbers and Sample IDs

| | | |
|------------|------------|----------------------|
| 65/W-50000 | 66/W-94900 | 67/W-94901 |
| 50/W-94887 | 51/W-50000 | 52/W-94888 |
| 25/W-94875 | 26/W-50000 | 27/W-94876 |
| 10/W-50000 | 11/W-50000 | 12/W-94864 |
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| | | |
|------------|------------|----------------------|
| 68/W-94902 | 69/W-50000 | 70/W-94903 |
| 53/W-94889 | 54/W-94890 | 55/W-94891 |
| 28/W-94877 | 29/W-94878 | 30/W-94879 |
| 13/W-94865 | 14/W-94866 | 15/W-94867 |
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| | | |
|------------|------------|----------------------|
| 71/W-94904 | 72/W-94905 | 73/W-50000 |
| 56/W-94892 | 57/W-50000 | 58/W-94893 |
| 31/W-94880 | 32/W-63333 | 33/W-63333 |
| 16/W-94868 | 17/W-94869 | 18/W-50000 |
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| | | |
|------------|------------|----------------------|
| 74/W-94906 | 75/W-94907 | 76/W-94908 |
| 59/W-94894 | 60/W-94895 | 61/W-94896 |
| 34/W-94881 | 35/W-94882 | 36/W-94883 |
| 19/W-94870 | 20/W-94871 | 21/W-94872 |
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| | | |
|------------|------------|------------|
| 77/W-94909 | 78/W-94910 | 79/W-94911 |
| 62/W-94897 | 63/W-94898 | 64/W-94899 |
| 37/W-94884 | 38/W-94885 | 39/W-94886 |
| 22/W-94873 | 23/W-94874 | 24/W-50000 |

Pegasus

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Appendix C. Step-by-Step Procedure to Prepare and Analyze Samples on the Pt Equilibration Line

System Preparation

1. Wait until all water samples have been analyzed (Port 79 typically must have run).
2. Remove sample vessels from the oven (leave Hokko bead rods in oven).
3. Remove the water trap dewar.
4. Inspect analysis sheets to ensure samples were analyzed properly.
5. Turn off air-bath temperature controller.
6. Remove wing nuts and pins and open plastic doors of air-bath.
7. Evacuate condensate in valves by selecting “Multisample” and then selecting “Pump Condensate” from the controller display. Follow instructions on the display to remove vessels (by loosening Cajon fitting 1/8 turn), put in plugs, and begin evacuation of condensate. Special plug with capillary leak (ballast) goes in Port 10.
8. Transfer Hokko-bead rods to rack using tweezers and fingers. Keep the rods in order.
9. Rinse Hokko-bead rods in one rinse of tap water and soak 1 h in DIW. Do not put in the oven yet.
10. Rinse sample vessels with two rinses of tap water and one rinse of DIW using a rubber mat to hold them in the plastic rack.
11. Put analysis sheets away.
12. When condensate has been evacuated (~1.5 h or ~0.0066 V on thermocouple gauge), remove Hokko-bead rods from oven.
13. Remove plugs from valves.

Water Sample Preparation

1. Load sample vessels as follows:
 - a. Put 15 sample vessels in the first (front) row of red plastic sample preparation rack.
 - b. Use 2.5 mL pipetman and appropriate 2,500 μ L Eppendorf tips.
 - (1) Put first pipette tip on pipetter.
 - (2) Mix sample bottle by inversion.
 - (3) Remove cap from first bottle.
 - (4) Withdraw a 1.5-mL (0.5 mL for small samples) sample from bottle and transfer into first sample vessel, being careful to minimize drops on the wall of the vessel. Remove any drops on the wall of the vessel using a clean cotton-tipped applicator and discard applicator. Water must reach but not surpass catalyst on glass rod.
 - (5) Eject pipette tip into trash container. Alternatively, save tips and rinse later (once) with DIW, shake, let air-dry).
 - (6) Move first sample vessel from the first to the second row of the rack.
 - (7) Put a plastic cover on first sample vessel.
 - (8) Secure cap on bottle to eliminate any evaporation.
 - (9) Move sample bottle to left of sample preparation area, (or put away in box as you work).
 - c. Repeat above for the remaining 14 samples in the rack. Reference samples in ampoules can be opened by enclosing them in a paper towel (or pipettes tip labeled “breaker” and stored with pens in work area) to protect skin during breaking.
 - d. Remove covers and insert Hokko-bead rods into all 15 sample vessels. Preserve the order of Hokko-bead rods: rod 10 goes in Port 10’s sample vessel, and so forth.

- e. Load samples into ports, twisting as you insert. Load as though you were reading a book—start at top left and go full right, and then move to bottom left and go full right.
2. Repeat these steps for the other three sets of samples.
3. Check to see that water level is within band of catalyst on each of the 60 Hokko-bead rods.
4. Close plastic doors to air bath and secure with pins and wing nuts.
5. Turn on temperature controller.
6. Evacuate air from samples by selecting “Multisample” and then selecting “Evacuate Air From Samples” from the controller display. Follow instructions on the display.
7. Set up the next template with samples, if available.
8. Put away old samples and recycle old template.
9. Put wet Hokko-bead rods and sample vessels into oven.
10. Record Hokko bead tray used that day on “Samples to be Analyzed List.”

Adding Hydrogen

1. Wait until air has been evacuated from all 60 sample vessels.
2. Add hydrogen by selecting “Multisample” and then selecting “Add Hydrogen” from the controller display. Follow instructions on the display.

Starting Analyses

1. Load new headings from daily diskette by loading diskette and then selecting “Data” and selecting “Load New Headings” from the controller display.
2. If any samples on the template have been changed, edit the list by selecting “Data” and selecting “Edit Headings” from the controller display.
3. Print new headings by selecting “Data” and then selecting “Print Headings” from the controller display.
4. Go through the VG mass spectrometer checklist.
5. Start analysis program by selecting “Multisample” and then selecting “Analyze samples” from the controller display. Select Pump Away Sample in piston, if necessary. Select 1-h equilibration time.
6. Three-hole punch “Sample to be Analyzed List” and file by date in “Daily Master List” binder.

Appendix D. Step-by-Step Procedure for Hydrogen Mass Spectrometer Checklist

Hydrogen Mass Spectrometer Checklist

Analyst in charge _____ Monday Date _____

- ___ 1. Check or regrease O-rings 1st Monday of each month
- ___ 2. Notify supervisor if working standard gas will not last the week

THESE ITEMS ARE TO BE CHECKED OFF AS YOU CHECK THEM

| | MON | TUE | WED | THU | FRI | SAT | SUN |
|---|-----|-----|-----|-----|-----|-----|-----|
| 1. Hydrogen toggle valve closed. | | | | | | | |
| 2. Box temperature 2.7 V. | | | | | | | |
| 3. All valves on AUTO. | | | | | | | |
| 4. Make sure all piston Hoke valves open. | | | | | | | |
| 5. Make sure piston pressure set to 5 psi. | | | | | | | |
| 6. Make sure piston lights are on (all 4). | | | | | | | |
| 7. Add paper to printer. | | | | | | | |
| 8. Put samples away and clear workspace. | | | | | | | |
| 9. Put Hokko beads in oven. | | | | | | | |
| 10. LN ₂ dewar filled at the end of day. | | | | | | | |
| 11. Check on first sample. | | | | | | | |

Appendix E. Step-by-Step Procedure to Determine and Apply Correction Factors and Evaluate Data

1. Open “Correction Factors and Normalization Equations” in LIMS-LSI.
2. Select the IRMS and isotope, such as “Pegasus for H.”
3. Select “Query.”
4. Double click on the last sample analyzed on that day.
5. Evaluate data of the reference materials. Ignore outliers; there should not be more than one or two outliers.
6. Choose “Normalize with all References.”
7. Accept “Expansion Correction and Additive Correction factors.”
8. Print out correction factor sheet.
9. Report daily reference values and correction factors along with date and range of analysis number to the “H” binder.
10. Go back to LIMS-LSI main menu by closing open windows.
11. Choose “Print Samples in Progress” and
 - a. Open “Sample in Progress.”
 - b. Choose appropriate isotope.
 - c. Choose appropriate prefix (W for water).
 - d. Put in sample ID range from “Samples-to-Be-Analyzed” sheet. Click Print.
12. Review results; determine repeats.
13. Put repeats back in “Table of Samples to Be Analyzed.”
 - a. Go back to LIMS-LSI main menu.
 - b. Open “Print Templates.”
 - c. Select appropriate template name for the IRMS with which the samples are analyzed.
 - d. Find the sample in the “List of Samples.”
 - e. Change “Repeats” from 0 to 1.
 - f. Close windows and exit LIMS-LSI.

Appendix F. Step-by-Step Procedure to Report Data

1. Open “Store Samples in Progress” in LIMS-LSI.
2. Choose the appropriate isotope.
3. Choose sample ID range from “Sample in Progress” printout.
4. Store data.
5. Go back to the LIMS-LSI main menu.
6. Open “Project” and find the appropriate project in the list.
7. Select “Print Report” and check whether the project report contains all the results. If not, search for the missing results in the database.
8. Select “Results,” transfer data in Excel format or (and) text format to a diskette, and report data to customer through e-mail.
9. Click “Print Report” to print a project report and put it in the “Correspondence” binder along with all other documents in the “Samples in Progress” binder that are related to this project.
10. If the samples were submitted through the NWQL, click “NWQL Export” and transfer data in NWQL format to a disc; report these data to the NWQL by e-mail. Print a copy of the NWQL export file and save in the “Correspondence” binder with the project report printed in the step above.