



# **Determination of the $\delta^{34}\text{S}$ of Low-Concentration Sulfate in Water; RSIL Lab Code 1949**

Chapter 8 of  
Section C, Stable Isotope-Ratio Methods  
**Book 10, Methods of the Reston Stable Isotope  
Laboratory**

Techniques and Methods 10–C8

**U.S. Department of the Interior  
U.S. Geological Survey**

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By Kinga Révész, Haiping Qi, and Tyler B. Coplen

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Edited by Kinga Révész and Tyler B. Coplen

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**U.S. Department of the Interior  
U.S. Geological Survey**

**U.S. Department of the Interior**  
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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 hydrogen, nitrogen, oxygen, carbon, and sulfur 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 water-supply sustainability, groundwater/surface-water interactions, paleoclimate history, biologic cycling of nutrients, groundwater 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 Glynn  
Chief, Branch of Regional Research, Eastern Region

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## Conversion Factors

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

## Acronyms and Abbreviations

ANSI	American National Standards Institute
CF-IRMS	continuous flow isotope-ratio mass spectrometer
cm	centimeter
DIW	deionized water
EA	elemental analyzer
GC	gas chromatograph
IRMS	isotope-ratio mass spectrometer

kPa	kilopascal
LIMS-LSI	Laboratory Information Management System for Light Stable Isotopes
mg	milligram
mg/L	milligram per liter
min	minute
mL	milliliter
mL/min	milliliter per minute
MSDS	Material Safety Data Sheets
NBS	National Bureau of Standards
NFPA	National Fire Protection Association
NWQL	National Water-Quality Laboratory (USGS)
PCM	polycarbonate membrane
per mil, ‰	one part in one thousand parts, with value $10^{-3}$
pF	picofarad
QA	quality assurance
QC	quality control
QC/QA	quality control/quality assurance
RSIL	Reston Stable Isotope Laboratory
SOP	standard operating procedure
std	international measurement standard
USGS	U.S. Geological Survey
VCDT	Vienna Cañon Diablo Troilite
µg	microgram

## Symbols

$\Omega$	ohm
<	less than
$\leq$	less than or equal

# Determination of the $\delta^{34}\text{S}$ of Low-Concentration Sulfate in Water; RSIL Lab Code 1949

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## Summary of Procedure

The purpose of the Reston Stable Isotope Laboratory (RSIL) lab code 1949 is to determine the  $\delta(^{34}\text{S}/^{32}\text{S})$ , abbreviated as  $\delta^{34}\text{S}$ , of dissolved sulfate having a concentration less than 20 milligrams per liter (mg/L). Dissolved sulfate is collected on an anion-exchange resin in the field, eluted in the laboratory with 3 M KCl, and precipitated with  $\text{BaCl}_2$  at pH 3 to 4 as  $\text{BaSO}_4$ . The precipitated  $\text{BaSO}_4$  is filtered and dried before introduction into an elemental analyzer (EA) Carlo Erba NC 2500. The EA is used to convert sulfur in a  $\text{BaSO}_4$  solid sample into  $\text{SO}_2$  gas, and the EA is connected to a continuous flow isotope-ratio mass spectrometer (CF-IRMS), which determines differences in the isotope-amount ratios of stable sulfur isotopes ( $^{34}\text{S}/^{32}\text{S}$ ) of the product  $\text{SO}_2$  gas. The combustion is quantitative; no isotopic fractionation is involved. Samples are placed in a tin capsule and loaded into the Costech Zero Blank Autosampler of the EA. Under computer control, samples are dropped into a heated tube reaction tube that combines the oxidation and reduction reactions. The combustion takes place in a helium atmosphere containing an excess of oxygen gas at the oxidation zone at the top of the reaction tube. Combustion products are transported by a helium carrier through the reduction zone at the bottom of the reaction tube to remove excess oxygen and through a separate drying tube to remove any water. The gas-phase products, mainly  $\text{CO}_2$ ,  $\text{N}_2$ , and  $\text{SO}_2$ , are separated by a gas chromatograph (GC). The gas is then introduced into the isotope-ratio mass spectrometer (IRMS) through a Finnigan MAT (now Thermo Scientific) ConFlo II interface, which is also used to inject  $\text{SO}_2$  reference gas and helium for sample dilution. The IRMS is a Thermo Scientific Delta V Plus CF-IRMS. It has a universal triple collector with two wide cups and a narrow cup in the middle. It is capable of measuring mass/charge ( $m/z$ ) 64 and 66 simultaneously. The ion beams from  $\text{SO}_2$  are as follows:  $m/z$  64 =  $\text{SO}_2 = ^{32}\text{S}^{16}\text{O}^{16}\text{O}$ ;  $m/z$  66 =  $\text{SO}_2 = ^{34}\text{S}^{16}\text{O}^{16}\text{O}$  primarily.

## Reporting Units and Operational Range

Variations in stable isotope ratios typically are small. Stable isotope 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 the measurement standard, std (Coplen, 2011). This relative difference is designated  $\delta^i\text{E}$ , which is a shortened form of  $\delta(^i\text{E}/^j\text{E})$  or  $\delta(^i\text{E})$ , and is defined according to equation 1 (Coplen, 2011):

$$\delta^i\text{E} = \delta(^i\text{E}) = \delta(^i\text{E}/^j\text{E}) = \frac{N(^i\text{E})_{\text{P}}/N(^j\text{E})_{\text{P}} - N(^i\text{E})_{\text{std}}/N(^j\text{E})_{\text{std}}}{N(^i\text{E})_{\text{std}}/N(^j\text{E})_{\text{std}}} \quad (1)$$

where  $N(^i\text{E})_{\text{P}}$  and  $N(^j\text{E})_{\text{P}}$  are the numbers of the two isotopes  $^i\text{E}$  and  $^j\text{E}$  of element E in specimen P and equivalent parameters follow for the international measurement standard, “std.” A positive  $\delta^i\text{E}$  value indicates that the specimen is enriched in the heavy isotope,  $^i\text{E}$ , relative to the std. A negative  $\delta^i\text{E}$  value indicates that the specimen is depleted in the heavy isotope,  $^i\text{E}$ , relative to the std. For stable sulfur

isotope-amount ratios,  $\delta^{34}\text{S}$  is defined as follows:

$$\delta^{34}\text{S} = \delta(^{34}\text{S}) = \delta(^{34}\text{S}/^{32}\text{S}) = \frac{N(^{34}\text{S})_{\text{P}}/N(^{32}\text{S})_{\text{P}} - N(^{34}\text{S})_{\text{std}}/N(^{32}\text{S})_{\text{std}}}{N(^{34}\text{S})_{\text{std}}/N(^{32}\text{S})_{\text{std}}} \quad (2)$$

The primary reference material for relative sulfur isotope-ratio measurements ( $\delta^{34}\text{S}$ ) is IAEA-S-1, which has a consensus  $\delta^{34}\text{S}$  value of  $-0.3$  ‰ relative to Vienna Cañon Diablo Troilite (VCDT)(Robinson, 1995; Krouse and Coplen, 1997; Coplen and Krouse, 1998). By interspersing isotopic reference materials with accepted isotopic compositions among unknown samples,  $\delta^{34}\text{S}$  values can be determined. These  $\delta^{34}\text{S}$  measurements are made with a CF-IRMS, which measures the isotope-amount ratios of the sample  $\text{SO}_2$  gas and one or more injections of the “working reference”  $\text{SO}_2$  gas. Values of  $\delta^{34}\text{S}$  typically are reported in parts per thousand (‰).

The system was tested by analyzing  $\text{BaSO}_4$  samples with known  $\delta^{34}\text{S}$  values. The routine analysis requires a minimum of 40 micrograms ( $\mu\text{g}$ ) of sample as sulfur; however, the system is capable of analyzing samples as small as 19  $\mu\text{g}$  of sulfur in one sample aliquot with reduced analytical precision. The  $\delta^{34}\text{S}$  values of test samples ranged from approximately  $-34$  to  $+21$  ‰, which covers the range of  $\delta^{34}\text{S}$  of most sulfate in natural water. The precision and accuracy of the results were acceptable ( $\pm 0.2$  ‰), and no memory effects were observed.

## Reference Materials and Documentation

### Reference Materials Used, Storage Requirements, and Shelf Life

The primary reference material for  $\delta^{34}\text{S}$  measurements is IAEA-S-1, which has a consensus  $\delta^{34}\text{S}$  value of  $-0.3$  ‰ relative to VCDT (Robinson, 1995; Krouse and Coplen, 1997; Coplen and Krouse, 1998). Other internationally distributed reference materials that are used have a wide range of  $\delta^{34}\text{S}$  values. In the procedure reported herein, barium sulfates ( $\text{BaSO}_4$ ) that are used for isotopic analysis of inorganic samples include NBS127 with a  $\delta^{34}\text{S}$  of  $+21.1$  ‰, IAEA-SO-5 with  $\delta^{34}\text{S}$  of  $+0.5$  ‰, and IAEA-SO-6 with  $\delta^{34}\text{S}$  of  $-34.05$  ‰. No locally prepared isotopic reference materials are used in this method.

All of these reference materials are stored in the RSIL at room temperature in glass bottles capped with Teflon-coated or cone-shaped caps to keep moisture out. Their shelf life is indefinite.

### Documentation

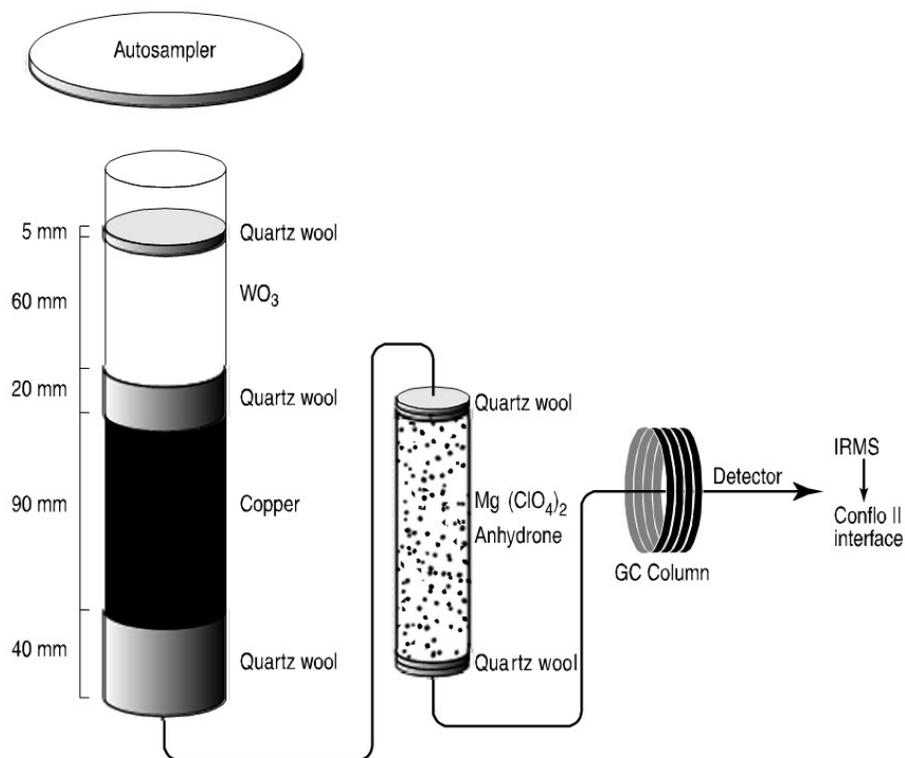
All calibration results are stored in the Laboratory Information Management System for Light Stable Isotopes (LIMS-LSI) (Coplen, 2000) under the following sample identifiers: S-1301 (IAEA-SO-5); S-97 (NBS127); and S-1302 (IAEA-SO-6).

## Labware, Instrumentation, and Reagents

Preparatory labware, instrumentation, and reagents, include (Amberlite IRA-400 ( $\text{RN}(\text{CH}_3)_3 + \text{Cl}$ ) anion-exchange resin, 3 M KCl solution, 1 M HCl, 20-weight-percent  $\text{BaCl}_2$  solutions, beakers, a stirring hot plate with stir bar, a watch glass, a thermometer, a filtering apparatus with 0.2- $\mu\text{m}$  Millipore GTTP polycarbonate membrane (PCM) filter, tin capsules, and a microbalance capable of measuring samples with 0.001-mg precision. The analytical apparatus consists of four different segments: (1) EA,

(2) ConFlo II interface, (3) IRMS, and (4) computer software.

The EA is a Carlo Erba Instruments NC 2500 (CE NC 2500) system, and it has a Costech “Zero Blank” Autosampler that holds 49 samples enclosed in tin capsules (fig. 1). Each tin capsule falls into the reaction tube, which is kept at 1020 °C and is under constant helium flow (90 milliliters per minute (mL/min)). The sample immediately reacts with a measured amount of oxygen from a 5-milliliter (mL) loop purged at 35 mL/min. The reaction of oxygen with the tin capsule is exothermic, resulting in localized temperatures of up to 1800 °C, thus ensuring complete and instantaneous sample combustion. This is called “dynamic flash combustion.” Because the BaSO<sub>4</sub> has a decomposition temperature of 1580 °C, it is critical to synchronize the helium flow, the oxygen flow, and the timing of the sample drop to achieve quantitative combustion (Révész, 1998; also see in the present report the section titled “Troubleshooting and Bench Notes”). To boost the combustion, 0.8 ± 0.3 mg V<sub>2</sub>O<sub>5</sub> is added to each sample (Yanagisawa and Sakai, 1983). The combustion gases are first carried by helium through an oxidative catalyst layer (tungsten oxide, WO<sub>3</sub>, on alumina) in the top of the reaction tube, where oxidation



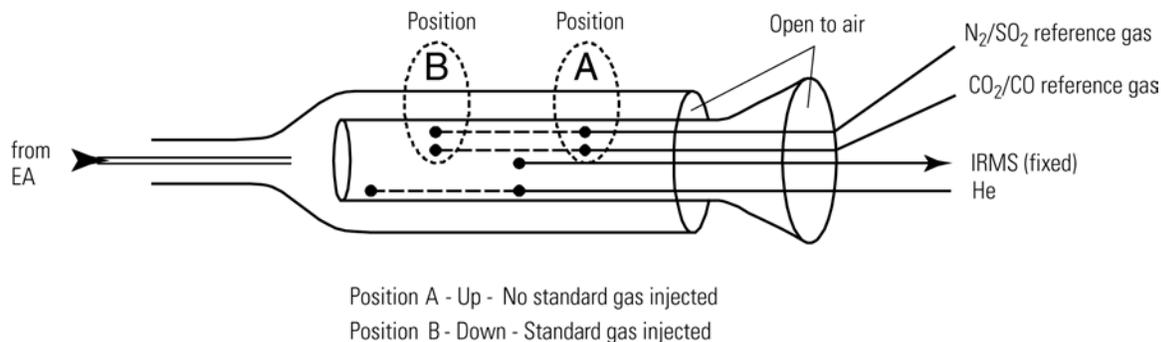
**Figure 1.** Diagram of the Carlo Erba Instruments NC 2500 E (CE NC 2500) elemental analyzer (used with permission from Thermo Scientific).

is completed, and then through a reduction agent (Cu) packed on the bottom of the reaction tube where any excess oxygen gas is consumed. At the outlet of the reaction tube, the gas mixture (N<sub>2</sub>, CO<sub>2</sub>, SO<sub>2</sub>, and H<sub>2</sub>O) enters a trap containing Anhydron, which absorbs water. The gas mixture, now N<sub>2</sub>, CO<sub>2</sub>, and SO<sub>2</sub>, flows through a Teflon tubing gas chromatograph column (0.8-m Porapak Q kept at 90 °C), which separates the gases and ensures that pure sulfur dioxide gas passes separately through the thermal conductivity detector, through the Finnigan MAT ConFlo II open split, and into the IRMS.

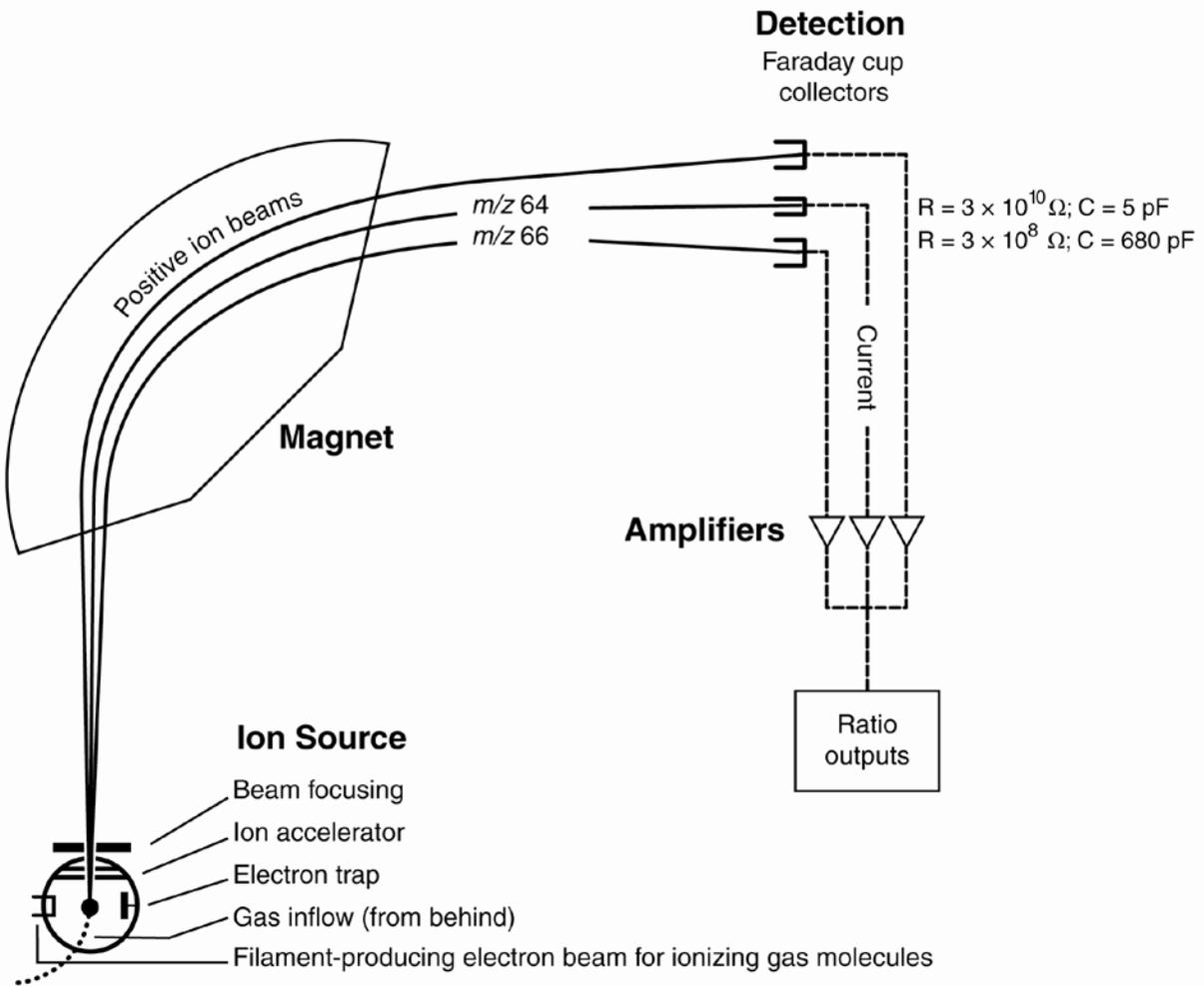
The Finnigan MAT ConFlo II interface provides the means for coupling the EA to the CF-IRMS with an open-split arrangement (fig. 2). The principle of an open split is that it reduces the 90 mL/min helium flow needed to operate the EA to a 0.3 mL/min helium flow needed to operate the IRMS. This is achieved by placing the end of the capillary that leads to the IRMS directly in the flow of helium coming from the EA. The narrow diameter and length of this capillary limit the flow of gas into the IRMS. Furthermore, extra capillaries carrying reference gas or helium gas can be added to the open split, thereby making it possible to inject reference gas into the IRMS or to dilute the sample with extra helium if the sample is too large (or to direct gases away by dilution if they are too large to ensure total separation).

The IRMS is a Thermo Scientific Delta V Plus CF-IRMS (fig. 3). The fundamental principle of the CF-IRMS technique is that a carrier gas transports the analyte through an initial stage of online chemistry for conversion to a form acceptable by the IRMS (Brenna and others, 1997). This is an automated system generating online, high-precision,  $\delta$  values of bulk solid and nonvolatile liquid samples. In the IRMS, 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 Faraday cup collectors. The ion beam intensities are measured with electrometers. This IRMS has a universal triple collector with two wide cups and a narrow cup in the middle. The resistor-capacitor combination on the electrometer of the low-mass cup is  $3 \times 10^8$  ohms ( $\Omega$ ) and 680 picofarads (pF). At the high-mass cup, it is  $3 \times 10^{10}$   $\Omega$  and 5 pF. The instrument is capable of measuring  $m/z$  64 and 66 simultaneously.

The Thermo Scientific ISODAT 2.0 software is designed (1) to advance the autosampler carousel, (2) to control the Finnigan MAT ConFlo II interface to inject reference gases at the desired time and dilute the sample if desired, (3) to operate the IRMS, (4) to acquire data from the IRMS, and (5) to calculate delta values.



**Figure 2.** Diagram of a Finnigan MAT (now Thermo Scientific) ConFlo II Open Split (used with permission of Thermo Scientific).



**Figure 3.** Schematic of a continuous flow isotope-ratio mass spectrometer (CF-IRMS) (modified from Clark and Fritz, 1997).

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

### Sample Containers, Preservation, and Handling Requirements

Carmody and others (1998) discuss in detail sample collection of dissolved sulfate samples for determination of  $\delta^{34}\text{S}$  values. Sulfate and sulfide concentration should be determined in the field by ion chromatograph or spectrophotometer. Each sample that contains less than 20 mg/L of sulfate is collected on a column containing approximately 20 mL anion-exchange resin (Amberlite IRA-400  $(\text{RN}(\text{CH}_3)_3 +$

Cl<sup>-</sup>), which is provided by RSIL (see <http://isotopes.usgs.gov/>). The RSIL is responsible for removing any

trace SO<sub>4</sub><sup>2-</sup> from the resin by rinsing 500 g resin with 2 L of 3 M KCl and rinsing it with 3 L of deionized water (DIW). The sample is collected in the field in a large 10-L bucket and acidified with 1 M HCl to pH 3 to 4. The sample is then pumped by a peristaltic pump through the ion-exchange column at a speed of 0.4 L/min. It is critical not to exceed the capacity of the resin. The resin column provided by the RSIL has the capacity of holding 2.3 g sulfate, which is substantially greater than the capacity needed. Thus, it can collect sulfate safely from 2 L of water with a sulfate concentration of 10 mg/L, 4 L of water with a sulfate concentration of 5 mg/L, and 20 L of water with a sulfate concentration of 1 mg/L. Resin columns must be labeled in the field with isotopes whose delta values are to be determined and with the respective laboratory code or schedule number.

If a water sample contains dissolved sulfide, care should be taken during collection not to expose the sample to air to minimize oxidation of sulfide to sulfate. Alternatively, each sample that contains more than 0.01 mg/L sulfide or has a sulfate/sulfide ratio less than 40 must be bubbled with N<sub>2</sub> gas to strip sulfide from it prior to collection of sulfate. Trace oxidized sulfide could seriously alter the δ<sup>34</sup>S of sulfate. Sulfide is stripped by filling a 10-L bucket with the water sample, acidifying it to pH 3 to 4 with 1 M HCl, immersing the outlet of the N<sub>2</sub> flow into the bottom, covering the system loosely with plastic wrap, and purging for 10 to 20 minutes (min) with an N<sub>2</sub> flow rate of 8 L/min until the sulfide concentration is less than 0.01 mg/L.

No treatment, preservation, or special shipping is required.

## Sample Preparation and Time Requirements

Sample preparation involves logging in samples to the LIMS-LSI (see appendix A), processing samples to precipitate BaSO<sub>4</sub>, creating a sample work-order sheet, and weighing samples into capsules.

The logging-in procedure involves logging samples in batches to LIMS-LSI 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.”

The processing of samples involves (1) the elution of sulfate from resin, and (2) the precipitation of pure BaSO<sub>4</sub> from the eluant (modified from Carmody and others, 1998). The resin is eluted with 150 mL of 3 M KCl at a flow rate of 3 mL/min. Step-by-step procedures are given in appendix B. The BaSO<sub>4</sub> is precipitated by acidifying the eluant to pH 3 to 4 by addition of approximately four drops of 1 M HCl, heating it at 90 °C, and stirring continuously for 45 min. This process removes all the carbonate as CO<sub>2</sub> gas from the sample. If the samples contain organic material, 6 mL of 6-percent H<sub>2</sub>O<sub>2</sub> are added along with the acid to oxidize the dissolved organic sulfur to SO<sub>2</sub> and oxidize any dissolved organic carbon to CO<sub>2</sub>, which are then degassed from the samples. At the last minute, 5 mL of 20-weight-percent BaCl<sub>2</sub> solution is added to the sample to precipitate the BaSO<sub>4</sub>. The solution is cooled slowly to 50 °C or lower and usually allowed to settle overnight. The liquid containing the BaSO<sub>4</sub> precipitate is filtered through a preweighed 0.2-µm GTTP PCM filter, rinsed with DIW, and dried in a sulfate-free oven at 90 °C. After weighing the dried precipitate and the filter, the yield is determined for reassurance of quantitative precipitation of sulfate. The BaSO<sub>4</sub> precipitate is scraped off the filter into a vial, homogenized with a spatula, and stored for analysis. It is recommended that samples be dried overnight at 90 °C and be put into sealed vials as soon as they are removed from the oven. Before weighing, a sample in a vial must be homogenized with a spatula or with an agate mortar and pestle. If more than a single filter paper is used for the same sample, the precipitates must be combined and homogenized. The detailed procedure can be found in appendix C.

An Excel sample workbook is generated. The step-by-step procedures are shown in appendix D. Sample weighing includes balance conditioning, weighing an appropriate amount of a sample into a capsule, recording the weight on the template, adding approximately 600 µg of V<sub>2</sub>O<sub>5</sub> to the capsule, and closing the capsule by folding it. Step-by-step procedures are given in appendix E. The time required for sample preparation is approximately 5 to 8 days.

## Performing the Analysis and Time Requirements

All BaSO<sub>4</sub> samples precipitated from water samples are prepared and analyzed in batches of a maximum of 80 per day, and all samples are analyzed in duplicate. Six aliquots of three internationally distributed isotopic reference materials with different δ<sup>34</sup>S values are analyzed at the beginning of a batch. Four of them are depleted in <sup>34</sup>S, one is enriched in <sup>34</sup>S, and one has an intermediate value. A set of these three reference materials also is interspersed among the samples. At least one reference material set is analyzed for every 10 unknowns. The amount of sulfur in the reference materials must be in the same range as that of the samples.

The procedure involves loading the autosampler carousel with capsules containing an appropriate amount of sample in sequence according to the “Template” (appendix F), loading a new sample heading (including sample weights) into the “Sequence Table” in ISODAT 2.0 of the IRMS software, choosing the appropriate “Method,” and starting sequence acquisition (appendix G). After the analyses are completed, data are exported (appendix H) to a Zip disk or “memory stick” from the ISODAT 2.0 database and transferred (appendix I) to the LIMS-LSI system and Data Back-Up computer. Final daily correction factors are determined by LIMS-LSI (appendix J), based on the daily analyses of reference materials using equations 3, 4, and 5, below, which are presented with example numerical values:

$$-34.05 \text{ ‰} = m \times \delta^{34}\text{S}_{\text{IAEA-SO-6/workingrefgas}} + b \quad (3)$$

$$+0.50 \text{ ‰} = m \times \delta^{34}\text{S}_{\text{IAEA-SO-5/workingrefgas}} + b \quad (4)$$

$$+21.10 \text{ ‰} = m \times \delta^{34}\text{S}_{\text{NBS127/workingrefgas}} + b \quad (5)$$

The values –34.05 ‰, +0.50 ‰, and +21.10 ‰ are the assigned values of the international reference materials IAEA-SO-6, IAEA-SO-5, and NBS 127, respectively. The δ<sup>34</sup>S<sub>ref/workingrefgas</sub> values in equations 3 to 5 are the daily mean delta values of the respective international reference materials relative to the working reference gas; *b* is the additive correction factor, and *m* is the expansion-coefficient correction factor. When two or more reference materials with different δ<sup>34</sup>S values are analyzed, the correction for sample blank does not need to be applied if the magnitude of the blank in the samples and reference materials is identical. However, if a single reference material is analyzed, only one-point calibration is possible; therefore, a blank correction must be applied.

If replicates do not agree within acceptable tolerances, they are analyzed until acceptable statistics are achieved. The computerized LIMS-LSI will not release data until the statistics are acceptable. The time required for performing the analyses is a minimum of 2 days.

No correction is made for the effect of sulfate δ<sup>18</sup>O value on the δ<sup>34</sup>S determination; V<sub>2</sub>O<sub>5</sub> is added to each sample to buffer the δ<sup>18</sup>O of SO<sub>2</sub> gas (Yanagisawa and Sakai, 1983).

The systematic procedure is listed in the “Lab Procedures” binder at RSIL. The supervisor reviews suggested changes before they are adopted.

## Problematic Samples

Problematic samples include those in which the sulfate concentration in the original water and the amount of water pumped through the resin are not provided. In this case, the sulfate concentration needs to be estimated after elution to be able to precipitate an appropriate amount of BaSO<sub>4</sub> for the analysis. This is done by precipitating 2 mL of sample and comparing its turbidity with a sample series ranging between 5 mg/L and 30 mg/L, which is prepared ahead of time. All the bottles should be the same size and color for proper comparison.

## Interferences

The  $\delta^{34}\text{S}$  of sulfate can be seriously altered if a water sample contains dissolved sulfide. The  $\delta^{34}\text{S}$  of sulfide can be as different as 65 ‰ from the  $\delta^{34}\text{S}$  of sulfate; therefore, trace oxidized sulfide could seriously alter the  $\delta^{34}\text{S}$  of sulfate.

## Troubleshooting and Bench Notes

The most common problems with this analytical technique are (1) incomplete combustion, (2) leakage in the system, particularly in the EA, and (3) insufficient linearity of the IRMS.

The fact that the melting point of the BaSO<sub>4</sub> is 1580 °C and the temperature of the reaction tube temperature is only 1020 °C could create insufficient combustion. The “flash point” has a higher temperature, approximately 1800 °C (because the tin oxidation reaction is exothermic); therefore, it is critical to create a sharp, sudden, bright, single flash. This can be done by coordinating (1) helium pressure and flow rate, (2) oxygen pressure and flow rate, and (3) sample “start time.” The system is so sensitive that even a 1-second difference in the sample dropping time can make a difference in the brightness of the flash, peak shape, peak area, and, consequently, the  $\delta^{34}\text{S}$  result. The optimum set-up parameters of the RSIL EA are cycle = 100, oxy = 60 (O<sub>2</sub> flow stops flowing into autosampler), sample start = 10, and sample stop = 40. The helium regulator is set for 150 kilopascals (kPa), and helium flow set up is 95 mL/min, which actually measures 120 mL/min at the vent. The oxygen regulator is set for 150 kPa, and the oxygen flow rate is 54 mL/min at purge. The oxygen loop is 5 mL. Oven temperature of the GC is 90 °C. Sample size is approximately 0.2 to 0.3 mg (BaSO<sub>4</sub>) (Révész, 1998). To improve analytical precision, 0.6 mg V<sub>2</sub>O<sub>5</sub> is added to each sample (Yanagisawa and Sakai, 1983).

Even a tiny leak can interfere with the result; it can create double peaks, an unstable analysis, and so forth. The high helium flow rate makes the system more sensitive to leaks (Bernoulli principle). Leaks can cause uncontrollable changes in the flow rate, which could prevent quantitative combustion, affecting the peak shape and peak area, and consequently, the  $\delta^{34}\text{S}$  value. Ash accumulation is also critical. Although tin oxide serves as a catalyst in the reaction, it also partially “clogs” the system, interfering with the flow rate, although not necessarily in a measurable manner. However, this assumes a nonrandom interference that causes the shift in  $\delta^{34}\text{S}$  value. By frequently analyzing reference materials, this shift can be corrected. However, after approximately 50 samples (one carousel), it is advisable to remove the ashes (Révész, 1998). The leak-checking procedure is given in appendix K. A leak is indicated in the IRMS when  $m/z$  28 and 29 are high and the ratios of  $m/z$  28, 32, and 40 (N<sub>2</sub>, O<sub>2</sub>, and argon) reflect atmospheric compositions. Acceptable levels for  $m/z$  28 and 29 are approximately 0.15 and 0.015 V, respectively, with typical IRMS settings. (See “Daily Checklist” in appendix L.)

Adjustment of the emission current is critical. The higher it is, the higher the signal will be, but the poorer the linearity will be. The IRMS is temperature sensitive; therefore, it must be operated in a temperature-controlled environment with all of the side panels on. The instrument is capable of measuring  $m/z$  64 and 66 simultaneously (fig. 3).

An internal precision check needs to be conducted using the “Zero Enrichment” method (standard gas

on/off 10 times), and it must give a standard deviation of 0.1 ‰ or better. The “Ratio Linearity” test must give 0.12 ‰/V or better linearity. An external precision check needs to be performed as needed, approximately every week or so; samples of the same amount need to be analyzed within  $\pm 0.010$  mg. The 1- $\sigma$  standard deviation must be 0.2 ‰ or better for  $n = 10$ . If either of these criteria has not been met, the IRMS cannot be used and must be refocused.

## **Maintenance and Maintenance Records**

Routine maintenance is necessary for the upkeep of the IRMS vacuum system, including (1) checking the pump performance from time to time, (2) changing the pump oil, and (3) changing the oil cartridge in each turbomolecular pump at 6-month intervals. Pump conditions, including date of oil changes, problems, and repairs to the pump, are listed in the pump database (file path: LIMS C:\RSIL\vacuum pumps). Maintenance of the EA includes (1) changing the insertion tube every day (appendix M), (2) changing the water trap approximately every 200 samples (appendix N), (3) changing reaction tubes approximately every 200 to 250 analyses (appendix O), and (4) cleaning the sample carousel every week. The IRMS also requires a daily check (appendix L). A logbook is kept for each IRMS, where notes of maintenance checks, history of normal settings, problems, and repairs are listed.

Maintenance of ISODAT 2.0 includes importing (transferring) results from the ISODAT 2.0 database to the LIMS-LSI computer hard disk and the Data Back-Up computer hard disk (appendix I).

## **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 ISODAT sample files from the IRMS computer are kept indefinitely on two different hard disks of the Data Back-Up computer. Paper reports are kept for a few weeks. Analytical results from the IRMS are transmitted to LIMS-LSI and 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 importing from the ISODAT database, (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 are ensured: (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 of errors in data reported to sample submitters. This database provides a complete record of information on how laboratory reference materials have been analyzed and provides a record of what correction factors have been used as an audit trail for the RSIL.

## Quality-Control (QC) Samples

Samples are prepared and analyzed in batches—a maximum of 80 daily. Each batch contains approximately six reference materials at the beginning, four enriched in  $^{34}\text{S}$ , one with an intermediate concentration, and one depleted in  $^{34}\text{S}$ . One set of three (depleted, intermediate, and enriched in  $^{34}\text{S}$ ) is analyzed for every 10 samples. The last analysis of a batch is one final set of the reference materials. All of these reference materials serve as QC samples.

Daily, the analyst (1) examines the computer printouts for indications of analytical problems, (2) determines the daily additive and expansion correction factors by the LIMS-LSI, and (3) applies corrections factors to isotopic data. These values with dates and analysis-number ranges are recorded manually in the laboratory “ $\delta^{34}\text{S}$  Correction Factor” three-ring binder even though the data are already in the LIMS-LSI. After printing the list of isotopic results from the “Table of Samples in Progress,” the analyst reviews the results and determines which samples need to be analyzed a third time to achieve acceptable results (i.e.,  $\Delta\delta \leq 0.2 \text{ ‰}$ ).

## Acceptance Criteria for All QC Samples

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

- If standard deviation is  $\leq 0.2 \text{ ‰}$ , use mean delta.
- If there are three or more analyses, delete the outlier and recalculate.
- If standard deviation of this recalculation is  $\leq 0.2 \text{ ‰}$ , use mean from this recalculation.
- If none of the above is the case, the result is not accepted, and corrective action is required.

The RSIL estimates the expanded uncertainty ( $U = 2\mu_c$ ) of  $\delta^{34}\text{S}$  measurement results. The expanded uncertainty provides an envelope that represents a 95-percent probability of encompassing the true value that has been determined from the aggregation of measurement results over a period of time. The expanded uncertainty can be determined using the guide to the expression of uncertainty (Joint Committee for Guides in Metrology, Working Group 1 (JCGM/WG1), 2010). The application of expanded uncertainty to the reporting of stable isotope measurements is discussed by Coplen and others (2006). The estimated expanded uncertainty of  $\delta^{34}\text{S}$  measurement results is  $\pm 0.4 \text{ ‰}$  unless otherwise specified, and this value is conservative. If any given sample were resubmitted to the RSIL for sulfur isotopic analysis, the measured value would fall within the uncertainty bounds of the previous result more than 95 percent of the time.

## Corrective Action Requirements

If the analyst finds any problem with the daily reference-sample data, the analyst contacts the supervisor. This process requires an evaluation and reanalysis of certain samples to ascertain 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.

## 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.

## Data Management and Records

In addition to evaluating daily sample analyses, every week an analyst evaluates the data project by project, reports results to the customers, and files final project data reports in the laboratory “Correspondence” binder (appendix P).

## Health, Safety, and Waste-Disposal Information

### Applicable Health and (or) 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 (MSDS); they are on file in the laboratory and at the URL <http://www.ilpi.com/msds/#Manufacturers>. This URL provides links to the MSDSs of most chemical companies.

#### 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). For more information, consult the U.S. Geological Survey’s *Safety and Environmental Health Handbook* (U.S. Geological Survey, 2002, sec. 4–4.1).

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

#### Chemical Hazards

The hazardous chemicals used in the process are  $\text{Cr}_2\text{O}_3$  and  $\text{Co}_3\text{O}_4$ , which are used in the oxidation reaction tube, and  $\text{V}_2\text{O}_5$ , which is used to boost combustion. Sometimes the reaction tube cracks, and the packing material leaks out. When this happens, protective gloves and a full-face mask are required during the cleanup process. All the materials, including gloves and any cleaning towels, need to be collected in a plastic bag and disposed of as hazardous waste. When handling  $\text{V}_2\text{O}_5$ , protective gloves and a full-face mask also are required. Upon receipt, all samples must be carefully inspected for indications of hazards.

The  $\text{SO}_2$  reference gas is colorless and has a suffocating odor. Exposure to  $\text{SO}_2$  can cause respiratory tract burns. Therefore, an appropriate ventilation unit must be installed in the Finnigan MAT ConFlo II interface. A leak test on the tank of gas and the line carrying  $\text{SO}_2$  to the Finnigan MAT ConFlo II interface be performed routinely.

#### Gas Cylinder Handling

Compressed gas cylinders must be handled and stored according to the U.S. Geological Survey’s *Safety and Environmental Health Handbook* (U.S. Geological Survey, 2002, sec. 4–4.5.1). 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**

The chemicals  $\text{Cr}_2\text{O}_3$ ,  $\text{Co}_3\text{O}_4$ , and  $\text{V}_2\text{O}_5$  must be collected in a separate, closed container. Ba from the waste  $\text{BaCl}_2$  solution must be precipitated with  $\text{Na}_2\text{SO}_4$  solution, and the solid  $\text{BaSO}_4$ , along with the other hazardous chemicals, must be given to the safety, health, and environment officer for disposal.

## Revision History

Publication Series and Series Number: Techniques and Methods 10–C8 (Book 10, Section C, Chapter 8)

Publication Title: Determination of the  $\delta^{34}\text{S}$  of Low-Concentration Sulfate in Water; RSIL Lab Code 1949

Publication Authorship: Révész, Kinga, Qi, Haiping, and Coplen, Tyler B.

Version 1.0, 2006

Version 1.1, 2007

Version 1.2, 2012

### Summary of Revised Product Components

Component	Description	Last revised in publication version	Date of last revision
Title	Replaced $\delta(^{34}\text{S}/^{32}\text{S})$ by $\delta^{34}\text{S}$ to be in accordance with recommendations of the Commission on Isotopic Abundances and Atomic Weights of the International Union of Pure and Applied Chemistry.	1.2	July 2012
Authorship	Tyler B. Coplen added as a coauthor.	1.2	July 2012
Summary of procedure	Updated text to reflect new instrumentation.	1.2	July 2012
Reporting units and operational range	Updated text to reflect expression of delta values with number ratios.	1.2	July 2012
Labware, instrumentation, and reagents	Updated text to reflect new instrumentation.	1.2	July 2012
Sample collection, preparation, analysis, retention times, and disposal	Updated text to reflect that samples are no longer submitted through the National Water Quality Laboratory (NWQL) and to document improved analytical techniques.	1.2	July 2012

Data acquisition, processing, evaluation, quality control, and quality assurance	Updated text to reflect that samples are no longer submitted through the National Water Quality Laboratory (NWQL).	1.2	July 2012
References cited	Added three references.	1.2	July 2012
Appendix A	Updated text to reflect that samples are no longer submitted through the National Water Quality Laboratory (NWQL)	1.2	July 2012
Appendix N	Updated text to reflect that samples are no longer submitted through the National Water Quality Laboratory (NWQL).	1.2	July 2012
Main text footer	Removed from document.	1.2	July 2012

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

1. For sample submitter:
  - a. Download “Standard Submission Excel Form” from the RSIL Web site at <http://isotopes.usgs.gov/>.
  - b. Fill out the requested sample information.
  - c. Send a diskette or CD and a hard copy along with the samples or e-mail the completed RSIL Excel worksheet to [isotopes@usgs.gov](mailto:isotopes@usgs.gov).
2. For RSIL personnel:
  - a. Match up information on sample bottles with the submitted “Standard Submission Excel Form.”
  - b. Enter all Standard Submission Excel Form information into LIMS-LSI by loading media. Submission date is the date samples are logged in.
  - c. Use “Import a New Project From Excel Submission” in LIMS-LSI to assign S#s.
  - d. Print out one project report and container labels (one for each sample).
  - e. Put a label on each sample bottle and cross-check Field IDs between bottles and Excel worksheet forms.
  - f. Punch holes in the original Excel worksheet and all the project information you have and put in “Samples-in-Progress” binder.

## Appendix B. Step-by-Step Procedure to Prepare Resin for Field Collection and Elute Sulfate from Resin after Field Collection

1. Prepare resin cartridge for field collection:
  - a. Clean “sulfate-free” commercially available anion (Amberlite IRA-400 (RN(CH<sub>3</sub>)<sub>3</sub> + Cl<sup>-</sup>) resin:
    - i. Add DIW to 500 g of resin and load it into a 6-centimeter (cm) × 50-cm column, cover with 2 cm of quartz wool. Make sure there are no air bubbles in the resin.
    - ii. Prepare 3 M KCl solution:
      - (1) Weigh 223.74 g KCl in 1000 mL volumetric flask; add DIW to make 1000 mL.
      - (2) Pour 2 L of 3 M KCl through the resin at a flow rate of 10 mL/min.
      - (3) Rinse resin with 3 L of DIW.
2. Distribute clean resin into 1.5-cm × 15-cm column, plugged with 1 cm of glass wool to hold the resin in place.
3. Elute sulfate from resin:
  - a. Open the drying tube at one end, remove glass wool and transfer the resin to a 1.5-cm × 30-cm glass column by DIW. Put the glass wool on top of the resin. Rinse with 20 mL DIW. Make sure there are no air bubbles in the column.
  - b. Place a 250-mL beaker beneath the column and close the stopcock.
  - c. Measure 150 mL of 3 M KCl solution and pour it into the column.
  - d. Open the stopcock, and let the solution elute the resin at a flow rate of 3 mL/min.
  - e. Collect last 1 mL of eluant in a 5-mL beaker that contains a few drops of BaCl<sub>2</sub> to check the completion of elution of SO<sub>4</sub><sup>2-</sup>. If small amount of BaSO<sub>4</sub> precipitate can be observed, elute the column with an additional 10 mL of 3 M KCl. Repeat this step until no BaSO<sub>4</sub> precipitate can be observed.

## Appendix C. Step-by-Step Procedure to Precipitate BaSO<sub>4</sub>

1. Acidify an amount of water to yield 50 mg of BaSO<sub>4</sub> with four drops of 1 M HCl to convert carbonate to CO<sub>2</sub> gas. (The 1 M HCl can be prepared by pouring 40.4 mL of 38-percent commercial HCl solution into 500 mL of DIW.)
2. Add H<sub>2</sub>O<sub>2</sub> to oxidize dissolved organic sulfur and any resin in case it leaked through during elution:
  - a. Add 6 mL of 6-percent H<sub>2</sub>O<sub>2</sub> to sample. (The 6-weight-percent H<sub>2</sub>O<sub>2</sub> can be prepared by adding 95.5 mL of 30-percent H<sub>2</sub>O<sub>2</sub> to 404.5 mL of DIW.) Put beaker with sample onto the hot plate with stir bar and set temperature controller to 200 °C. Cover the beaker with a watch glass.
  - b. Remove all the samples from the hot plate after 45 min.
3. Precipitate sulfate:
  - a. Add 5 mL of 20-weight-percent BaCl<sub>2</sub> solution. (The 20-weight-percent BaCl<sub>2</sub> can be prepared by dissolving 117.3 g BaCl<sub>2</sub>·2H<sub>2</sub>O solids in 441 mL DIW.) Let the solution cool slowly to 50 °C or lower, usually overnight.
4. Filter BaSO<sub>4</sub> precipitate:
  - a. Place a 0.2-µm Isopore PCM filter paper into an empty, clean, labeled sample bottle. Weigh the sample bottle with filter paper without the cap. Record weight on the Dissolved Sulfate Precipitation form.
  - b. Set up filtration apparatus:
    - i. Clean filtration apparatus equipment thoroughly with DIW and then set up the filtration apparatus.
    - ii. Put a coarse-fritted glass support base (with stopper) onto a 1000-mL filtering glass flask.
    - iii. Place tubing accordingly in a peristalsis pump. Attach the vacuum end of the tubing to the 1000-mL filtering glass flask.
    - iv. Moisten the coarse-fritted glass support base with some DIW. Place a 0.2-µm Isopore PCM filter paper (shiny side face up) centered on the coarse-fritted glass support base.
    - v. Place a 300-mL graduated funnel onto the coarse-fritted glass support base and then clamp the two together with an aluminum clamp.
    - vi. Turn peristaltic pump on. Add a small amount of DIW into the 300-mL graduated funnel to check for any leaking.
  - c. Pour sample into 300-mL graduated funnel until the entire sample has filtered into the 1000-mL flask.
  - d. Turn off pump. Remove the tubing attached to the 1000-mL filtering glass flask. Take off the clamp and remove the 300-mL flask from the coarse-fritted glass support base.
  - e. Remove filter paper with precipitate and put it back in its container.
  - f. Take the coarse-fritted glass support base off the 1000-mL filtering glass flask.
  - g. Test the filtrate for sulfate by adding BaCl<sub>2</sub> solution. If no turbidity shows, discard the filtrate. If there is some turbidity, filter the solution again on a different filter paper and combine the two precipitates.
  - h. Clean all of apparatus thoroughly. Repeat procedure for the remaining samples.
5. Dry each precipitate at 90 °C in an oven overnight.
6. Weigh the sample bottle with filter paper that has BaSO<sub>4</sub> on it and record it on the Dissolved Sulfate Precipitation form.
7. Scrape off the dried BaSO<sub>4</sub> from filter into the vial and homogenize the sample with a spatula in the vial. Store them on the shelf for isotopic analysis. Discard the filter.

## DISSOLVED SULFATE PREPARATION FORM

S-#		Date	
NWQL-#		Project Chief	
Field ID		Location	

Reported $\text{SO}_4^{2-}$ concentration:	
Volume submitted:	
Volume used	

### PRE-FILTRATION Comments

Pore diameter of polycarbonate membrane:	
--	--

### ACIDIFICATION: (pH = 2.75 to 3.25)

pH before acidification:		approx. _____ mL HCl used
pH after acidification:		

Began heating sample at: \_\_\_\_\_

### OXIDATION

Oxidizing agent:	6 mL 6-percent $\text{H}_2\text{O}_2$	Comments:
volume used:		

### PRECIPITATION

Approx. _____ mL $\text{BaCl}_2$ , added at: _____	Comments:

### FILTRATION AND YIELD

Use 0.2  $\mu$ -pore-diameter polycarbonate membrane: \_\_\_\_\_

weight of PCM, $\text{BaSO}_4$ , dish		Yield/Concentration:
weight of PCM, dish		
weight of $\text{BaSO}_4$		

- 1 mL of 20-weight-percent  $\text{BaCl}_2$  added to ensure complete precipitation of  $\text{BaSO}_4$ .
- No further precipitation observed after 10 min; precipitation complete.
- Continued precipitation; further filtering required.

## **Appendix D. Step-by-Step Procedure to Create an Excel Sample-List Workbook and Print a Sample List**

### **Excel Sample-List Workbook**

1. Use default worksheet-weighing template and add samples to be analyzed.
2. Fill the appropriate amount in the cells of the rows labeled "Set weight mg."
3. Print first worksheet in workbook.
4. Write the tray ID and the date on both the diskette and paper template.
5. Put them near the balance.

### **Sample List**

1. Use "Create a Sample List -->" in LIMS-LSI.
2. Select appropriate template for EA and mass spectrometer.
3. Select "Create Sample List for Mass Spec" (dialog box informs user how many samples are waiting to be analyzed).
4. Click "OK."
5. Click "Save and 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 paper template.
9. Put them near the balance.
10. Exit LIMS-LSI.

Worksheet 1. Weighing template.

[International reference materials are in bold font]

		1	2	3	4	5	6	7	8	9	10	11	12
	Our Lab ID	<b>S-97</b>	<b>S-97</b>	<b>S-97</b>	<b>S-97</b>	<b>S-1301</b>	<b>S-1302</b>	S-9031	S-9031	S-9032	S-9032	S-9033	S-9033
A	Set weight mg	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
	Actual weight, mg	0.3	0.29	0.31	0.31	0.304	0.298	0.299	0.302	0.305	0.303	0.305	0.303
	Comment	NBS-127	NBS-127	NBS-127	NBS-127	IAEA-SO-5	IAEA-SO-6						
	Our Lab ID	S-9034	S-9034	S-9035	S-9035	<b>S-97</b>	<b>S-1301</b>	<b>S-1302</b>	S-9037	S-9037	S-9038	S-9038	S-9039
B	Set weight mg	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
	Actual weight, mg	0.301	0.302	0.295	0.303	0.299	0.295	0.301	0.299	0.293	0.304	0.301	0.304
	Comment					NBS-127	IAEA-SO-5	IAEA-SO-6					
	Our Lab ID	S-9039	S-9040	S-9040	S-9041	S-9041	<b>S-97</b>	<b>S-1301</b>	<b>S-1302</b>	S-9043	S-9043	S-9044	S-9044
C	Set weight mg	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
	Actual weight, mg	0.301	0.301	0.295	0.306	0.297	0.302	0.3	0.305	0.304	0.297	0.304	0.301
	Comment						NBS-127	IAEA-SO-5	IAEA-SO-6				
	Our Lab ID	S-9045	S-9045	S-9046	S-9046	S-9047	S-9047	<b>S-97</b>	<b>S-1301</b>	<b>S-1302</b>	S-9049	S-9049	S-9050
D	Set weight mg	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
	Actual weight, mg	0.295	0.303	0.32	0.299	0.298	0.296	0.303	0.305	0.305	0.297	0.302	0.296
	Comment							NBS-127	IAEA-SO-5	IAEA-SO-6			
	Our Lab ID	S-9050	S-9051	S-9051	S-9052	S-9052	S-9053	S-9053	<b>S-97</b>	<b>S-1301</b>	<b>S-1302</b>		
E	Set weight mg	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3		
	Actual weight, mg	0.296	0.296	0.295	0.299	0.305	0.305	0.299	0.302	0.297	0.304		
	Comment								NBS-127	IAEA-SO-5	IAEA-SO-6		

Worksheet 2. Samples to be analyzed.

[International reference materials are in bold font]

Line	Identifier	Port	Comment	Amount	Amt Unit
1	<b>S-97</b>	A1	NBS-127	0.3	mg
2	<b>S-97</b>	A2	NBS-127	0.29	mg
3	<b>S-97</b>	A3	NBS-127	0.31	mg
4	<b>S-97</b>	A4	NBS-127	0.31	mg
5	<b>S-1301</b>	A5	IAEA-SO-5	0.304	mg
6	<b>S-1302</b>	A6	IAEA-SO-6	0.298	mg
7	S-9031	A7		0.299	mg
8	S-9031	A8		0.302	mg
9	S-9032	A9		0.305	mg
10	S-9032	A10		0.303	mg
11	S-9033	A11		0.305	mg
12	S-9033	A12		0.303	mg
13	S-9034	B1		0.301	mg
14	S-9034	B2		0.302	mg
15	S-9035	B3		0.295	mg
16	S-9035	B4		0.303	mg
17	<b>S-97</b>	B5	NBS-127	0.299	mg
18	<b>S-1301</b>	B6	IAEA-SO-5	0.295	mg
19	<b>S-1302</b>	B7	IAEA-SO-6	0.301	mg
20	S-9037	B8		0.299	mg
21	S-9037	B9		0.293	mg
22	S-9038	B10		0.304	mg
23	S-9038	B11		0.301	mg
24	S-9039	B12		0.304	mg
25	S-9039	C1		0.301	mg
26	S-9040	C2		0.301	mg
27	S-9040	C3		0.295	mg
28	S-9041	C4		0.306	mg
29	S-9041	C5		0.297	mg
30	<b>S-97</b>	C6	NBS-127	0.302	mg
31	<b>S-1301</b>	C7	IAEA-SO-5	0.3	mg
32	<b>S-1302</b>	C8	IAEA-SO-6	0.305	mg
33	S-9043	C9		0.304	mg
34	S-9043	C10		0.297	mg
35	S-9044	C11		0.304	mg
36	S-9044	C12		0.301	mg
37	S-9045	D1		0.395	mg
38	S-9045	D2		0.303	mg
39	S-9046	D3		0.32	mg
40	S-9046	D4		0.299	mg

Line	Identifier	Port	Comment	Amount	Amt Unit
41	S-9047	D5		0.298	mg
42	S-9047	D6		0.296	mg
43	<b>S-97</b>	D7	NBS-127	0.303	mg
44	<b>S-1301</b>	D8	IAEA-SO-5	0.305	mg
45	<b>S-1302</b>	D9	IAEA-SO-6	0.305	mg
46	S-9049	D10		0.297	mg
47	S-9049	D11		0.302	mg
48	S-9050	D12		0.296	mg
49	S-9050	E1		0.296	mg
50	S-9051	E2		0.296	mg
51	S-9051	E3		0.295	mg
52	S-9052	E4		0.299	mg
53	S-9052	E5		0.305	mg
54	S-9053	E6		0.305	mg
55	S-9053	E7		0.299	mg
56	<b>S-97</b>	E8	NBS-127	0.302	mg
57	<b>S-1301</b>	E9	IAEA-SO-5	0.297	mg
58	<b>S-1302</b>	E10	IAEA-SO-6	0.304	mg

## Appendix E. Step-by-Step Procedure for Weighing and Storing Samples

1. Samples should be homogenized and dried.
2. Insert template diskette in the computer connected to the microbalance.
3. Condition balance (this step should be performed once a day):
  - a. Place empty capsule on balance and close door. Wait for reading to stabilize (the “mg” on the display appears). Tare the balance.
  - b. Remove and replace capsule and make sure the stabilized weight is 0.000 mg.
  - c. Repeat these steps until the balance is stable.
4. Remove capsule from balance, add sample, and weigh the filled capsule. Repeat until you have the desired weight ( $300 \pm 10 \mu\text{g}$ ).
5. Enter sample mass on the template.
6. Add  $600 \mu\text{g} \pm 100 \mu\text{g}$  of  $\text{V}_2\text{O}_5$  to the sample.
7. Fold cup, secure sample in it.
8. Repeat steps 4 to 7 for every sample.
9. Note:
  - a. Do not cross-contaminate samples.
  - b. Make sure the spatula and sample area are cleaned using Kimwipes between each sample.
  - c. Always allow balance to stabilize before removing capsule.

## Appendix F. Step-by-Step Procedure of Zero Blank Autosampler Operation

1. Before opening the lid, make sure the isolation valve (between sample chamber and reaction tube) is closed (arrow towards you) and make sure the helium purge isolation valve (on the left) is closed.
2. Open the purge vent on the top of the autosampler to vent the sample chamber.
3. Release the three fittings holding the lid closed and open the lid.
4. Place your samples in the autosampler and close the lid. Load 49 samples for a 50-position carousel, leaving the first hole empty.
5. Secure the lid with three bolts. Screw in all three bolts finger tight, and then lightly tighten two bolts at a time, moving around the lid until they are all completely tight to minimize stress and warping of the lid.
6. Open the helium purge isolation valve (screw down), purge the sample chamber for 5 min at a helium flow rate of 298 mL/min. Make sure the purge vent valve (on top) is open. Press your finger on top of the vent valve for 2 s, then release; you should hear the sound of a pressure release.
7. Close the helium purge vent valve (screw down), wait for 2 min for gas pressure at sample chamber and a helium flow rate to stabilize. Close the helium purge isolation valve.
8. Open the isolation valve (arrow toward up). Wait for 2 min for stabilized baseline. With a helium carrier flow rate of 90 mL/min, one should observe  $m/z$  28 on cup 1 at about 50 millivolts,  $m/z$  29 on cup 2 at about 50 to 60 millivolts and  $m/z$  30 on cup 3 at about 140 millivolts to 1 volt (appendix L).

## **Appendix G. Step-by-Step Procedure to Add Sample Information to Sequence Table**

1. Insert diskette with “Weighing Template” on it.
2. Open “Sequence File” under “EA configuration.”
3. Open “Weighing Template” in Excel.
4. “Copy” and “Paste” the list of Sample IDs and sample weight from the template to sequence table.
5. Select appropriate “method” for each sample.
6. Define the reference line and blank line.
7. Start.
8. Give Folder Name: Comment
  - a. Select pre: “Date.”
9. Give File Name:
  - a. Select pre: “Analyzes #.”
  - b. Select post: “Identifier 1.”
  - c. Select: “Print Result.”
10. Click “OK.”
11. Wait for first sample to be analyzed.

## **Appendix H. Step-by-Step Procedure to Retrieve Data from ISODAT 2.0 for LIMS-LSI and for Data Back-Up**

1. For LIMS-LSI:
  - a. Select “Result” in ISODAT 2.0.
  - b. Select the result folder you wish to export data from.
  - c. Select all the individual analyses you want to retrieve by right clicking the selected file.
  - d. Select “Reprocess.”
  - e. Give a file name.
  - f. Add export template previously designed.
  - g. Open.
  - h. Click “OK.” (Reprocessing takes 1–2 min)
  - i. Open Excel.
  - j. Find the file you reprocessed (E-drive, Finnigan, ISODAT 2.0, Global, User, CONFLO II, Interface, Result: File name).
  - k. Open it in Excel.
    1. Save as: “A” drive. Keep in Lotus format.
  - m. Define all reference peaks by adding #1 under column “Is Ref.?”
  - n. Now the file can be imported to LIMS-LSI.
2. For Data Back-Up computer:
  - a. Go to Windows Explorer in ISODAT 2.0 computer.
  - b. Find the drive where the data are (D).
  - c. Choose: “Finnigan.”
  - d. Choose: “User.”
  - e. Choose the inlet system where you have data (Gas Bench or EA).
  - f. Choose “Result folder.”
  - g. Transfer data to memory stick.

## **Appendix I. Step-by-Step Procedure to Transfer Data to LIMS-LSI, to Transfer Data to Back-Up Computer, and to Reevaluate Old Data**

1. Transfer data to LIMS-LSI:
  - a. Start LIMS.
  - b. Choose "Import Data From Instruments."
  - c. Choose mass spectrometer, for example "H --> Hercules."
  - d. Click "Import."
  - e. Select the file that will be imported.
  - f. Depending upon the mass spectrometer, the user may be given the opportunity to select the columns containing the isotope data. Enter column names as appropriate for the isotope or isotopes to be imported.
  - g. Click "Import." Note: Sample ID, sample weight, Peak Area, Analyses #s are automatically imported to LIMS-LSI.
2. Transfer data to Data Back-Up computer:
  - a. Go to Windows Explorer in the Data Back-Up computer.
  - b. Find the drive where your back ups are stored.
  - c. Choose: "RSIL."
  - d. Choose: "Mass. Spec. Analysis Back Up."
  - e. Choose the mass spectrometer. For example, "H," which stands for "Hercules," a Thermo Scientific Delta V Plus IRMS.
  - f. Under that folder create a new folder. The name of the folder should be the date range of the analyses that one wishes to back up.
  - g. Transfer data to that folder.
  - h. Make back ups every 2 weeks or so, as needed.
3. Reevaluate old data:
  - a. Find your samples in the Data Back-Up computer.
  - b. Transfer data by a memory stick to the computer where a virtual version of ISODAT 2.0 is installed.
  - c. Reevaluate your data.

## **Appendix J. Step-by-Step Procedure to Determine and Apply Correction Factors and Evaluate Data**

1. Open “Apply Data Normalization” in LIMS-LSI.
2. Select instrument and isotope, for example “H (Hercules) for 34S.”
3. Select “Query.”
4. Double click on the last sample analyzed on that day.
5. Evaluate data of the reference materials.
6. Choose “Normalize with all References.”
7. Click “Apply Normalization -->.”
8. Print out correction factor sheet.
9. Report daily reference values and correction factors along with date and range of analysis number to the “EA” binder.
10. Go back to LIMS-LSI main menu by closing open windows.
11. Choose “Print/Save Analyses in Progress”:
  - a. Choose appropriate isotope.
  - b. Choose appropriate prefix (W for water, N for nitrogen, S for sulfur).
  - c. Enter sample ID range from “Samples-to-Be-Analyzed” sheet.
  - d. Click Print.
12. Review results and identify samples that need to be re-analyzed.
13. Add the samples needing analyses to the Samples to Be Analyzed:
  - a. Go back to LIMS-LSI main menu.
  - b. Open “Create a Sample List -->.”
  - c. Select appropriate sample list for the mass spectrometer and the samples that are to be analyzed.
  - d. Find each sample in the “List of samples.”
  - e. Change entry in “Repeats” column from 0 to 1.
  - f. Close Windows and exit LIMS-LSI.

## **Appendix K. Step-by-Step Procedure to Check Elemental Analyzer for Leaks**

1. Close the VENT carrier output using the proper cap (provided).
2. Adjust the helium pressure to 150 kPa (regulator is on the front central panel), wait 3 min to equilibrate gas in the system.
3. Close the helium inlet valve by turning the above regulator counter clockwise.
4. If the gauge needle does not move, there is no leak.
5. If the gauge needle moves, indicating the lost of pressure, there is a leak in the system. The decreasing pressure rate accounts for the degree of leakage.
6. Locate the leak by separating and testing the system segment by segment, using the helium detector.

## Appendix L. Daily Checklist

Analyst in charge: \_\_\_\_\_ Date: \_\_\_\_\_

Weekly:

1. Change the working reference gas tank and the helium gas tank if the pressure is < 500 psi. Order new ones for a spare; the reference gas is SO<sub>2</sub> ANHY by Matheson, the helium carrier is zero grade, and the O<sub>2</sub> is research grade.
2. Change the water and CO<sub>2</sub> trap after approximately 8,000 samples, or when it is necessary.
3. Check and clean the autosampler carousel.
4. Change the reaction tube after approximately 200 or 250 samples, or when it is necessary.

THESE ITEMS ARE TO BE CHECKED OFF AS YOU CHECK THEM DAILY!

1. Check the helium, O<sub>2</sub>, and reference gas flow. [ ]
2. Check the EA reaction-tube temperature (1020 °C). [ ]
3. Change the insertion tube (ash-collector liner) in the reaction tube. [ ]
4. Check the background masses. [ ]

At emission current: 1.5 milliampere

Cups	Mass	Intensity (V)	Mass	Intensity (V)	Mass	Intensity (V)	Resistor (Ω)	Capacity (pF)
1	28	0.05	44	0	64	0.002	3 × 10 <sup>8</sup>	680
2	29	0.05	45	0	66	0.002	3.5 × 10 <sup>10</sup>	5
3	30	0.05–0.3	46	0.002			3 × 10 <sup>11</sup>	2

5. Check the peak center. [ ]
6. Analyze the Ref on/off method 10 times to stabilize the IRMS (standard deviation should be better than 0.1 ‰). [ ]

Optimal ConFlo II Pressure Setting SO <sub>2</sub> (bar)	SO <sub>2</sub> signal (V) Mass 66 on Cup 2
0.50	3.000

## Appendix M. Changing the Insertion Tube

The insertion tube needs to be changed before a template is run.

1. Manually close needle valve near the ion source.
2. On the menu of the Model 2500 EA under “Sp. Fun.,” choose “Std By” and press “enter.” The O<sub>2</sub> and helium gases should be turned off.
3. Unscrew the metal seals under the sample carousel to access the reaction tube.
4. Using the heat protective glove and the wire tool, remove the insertion tube from the reaction tube and place in the metal can. Be aware that the tube will be very hot!
5. Insert clean tube that has 0.5 cm of quartz wool packed at the bottom and tap it down with the wire tool.
6. Replace the carousel and tighten the metal seals with a wrench.
7. Turn the O<sub>2</sub> and the helium back on by pressing “enter” and return the screen to the temperature readout by pressing “Sp. Fun.”
8. Open the needle valve.

## Appendix N. Changing the Water Trap

Change the water trap after every 200 samples.

1. Retrieve quartz turnings, quartz wool, magnesium perchlorate, and a clean water trap from Delta V Plus supplies.
2. Under a hood, pack one end of the clean water trap with 1 cm of quartz wool.
3. On a piece of wax paper, create a mix by volume of approximately 70-percent magnesium perchlorate and 30-percent quartz turnings. Pack the mix into the water trap tube, leaving 1 cm of empty space.
4. Pack the open end of the water trap with quartz wool.
5. Unscrew the red plastic ends from the used water trap and replace it with the clean water trap; be sure to replace the rubber O-rings on the ends of the clean water trap and tighten the red ends.
6. Insert the plug into the vent and watch for any decrease in pressure to check for a leak in the system. If everything looks acceptable after 5 min, replace the vent line.
7. Under the “Sp. Fun.” menu of the model 2500 EA, choose “CNT” (counter) and zero “D” to set back the water-trap counter.
8. Clean the water trap by pushing all the mixture out of the tube into the trash can and use a clean cotton swab to wipe out the inside of the tube. Rinse the tube with DIW, and dry it in the oven. Return this tube to the water trap bag in the drawer.

## Appendix O. Changing the Reaction Tube

The reaction tube should be changed approximately every 200 to 250 samples.

1. Manually close the needle valve near the ion source.
2. Turn the Model 2500 EA to “Std By” with both gases off.
3. Lower the reaction tube temperature to less than 900 °C.
4. Retrieve the reaction tube from the cabinet.
5. Insert the insertion tube into the top of the reaction tube; there will already be a plastic tube in the reaction tube that should be removed. The bottom of the reaction tube has copper in it.
6. Place a black O-ring on the top of the reaction tube. Make sure that all O-ring connections are clean and free of any dust.
7. Loosen the top metal seal and remove the bottom metal seal. Go back and completely remove the top seal. It will be very hot! Use oven gloves!
8. Remove quartz reaction tube and place in metal can, place clean reaction tube in column. Make sure the O-ring is clean; then replace the top.
9. On the bottom, put on the metal piece with the metal O-ring first and then add the clean rubber O-ring. Raise the bottom portion and screw together. Then tighten the connection with wrenches and put the metal support back in place.
10. Turn the gases back on; then, go to “CNT” in the menu under “Sp. Fun.” and zero “B,” the oxidation reaction tube as well as “A” and “C,” to set back the counter.
11. Insert the plug into the vent and watch for any decrease in the pressure to check for a leak in the system. If everything looks okay after 3 min, replace the vent line.
12. Open the needle valve.

## **Appendix P. 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” print out.
4. Store data.
5. Go back to the main menu of LIMS-LSI.
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 the other documents in the “Samples In Progress” binder that are related to this project.