Determination of the $\delta(^{34}S/^{32}S)$ of Sulfate in Water: RSIL Lab Code 1951

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

Techniques and Methods 10-C10

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

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By Kinga Révész and Haiping Qi

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GALE A. NORTON, Secretary

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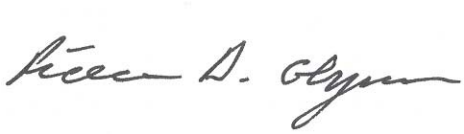
Foreword

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 Glynn
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Conversion Factors, Acronyms, and Abbreviations

Multiply	By	To Obtain
	Length	
millimeter (mm)	0.03937	inch
centimeter (cm)	0.3937	inch
meter (m)	3.281	foot
	Volume	
micro liter (µL)	0.0610210^{-3}	cubic inch
milliliter (mL)	0.06102	cubic inch
cubic centimeter (cm^3)	0.06102	cubic inch
	Mass	
nanogram (ng) = 10^{-3} µg	3.527×10^{-11}	ounce
microgram (µg) = 10^{-3} mg	3.527×10^{-8}	ounce
milligram (mg) = 10^{-3} g	3.527×10^{-5}	ounce
gram (g) = 10^{-3} (kg)	3.527×10^{-2}	ounce
kilogram = 10^3 g; 10^6 mg; 10^9 µg; 10^{12} ng	2.205	pound
	Density	
gram per cubic centimeter (g/cm^3)	0.5780	ounce per cubic inch
	Temperature	
Celsius (°C)	°F = 9/5 (°C) + 32	Fahrenheit (°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°F

ANSI	American National Safety Institute
ASR	analytical services request
CF-IRMS	continuous flow isotope-ratio mass spectrometer
DIW	deionized water
DOS	dissolved organic sulfur
EA	elemental analyzer
GC	gas chromatograph
IAEA	International Atomic Energy Agency
IRMS	isotope-ratio mass spectrometer
LIMS-LSI	Laboratory Information Management System for Light Stable Isotopes
mg/L	milligram per liter

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 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	United States Geological Survey
VCDT	Vienna Cañon Diablo Troilite

Determination of the $\delta(^{34}S/^{32}S)$ of Sulfate in Water: RSIL Lab Code 1951

By Kinga Révész and Haiping Qi

Summary of Procedure

The purpose of Reston Stable Isotope Laboratory (RSIL) lab code 1951 is to determine the $\delta^{34}S$ of dissolved sulfate. Dissolved sulfate is collected in the field and precipitated with $BaCl_2$ at pH 3 to 4 as $BaSO_4$ in the laboratory. However, the dissolved organic sulfur (DOS) is oxidized to SO_2, and the carbonate is acidified to CO_2. Both are degassed from the water sample before the sulfate is precipitated. The precipitated $BaSO_4$ is filtered and dried before introduction into an elemental analyzer (EA)(Carlo Erba NC 2500). The EA is used to convert S in a $BaSO_4$ solid sample into SO_2 gas, and the EA is connected to a continuous flow isotope-ratio mass spectrometer (CF-IRMS), which determines the differences in the isotope–amount ratios of stable sulfur isotopes ($^{34}S/^{32}S$) of the product 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 He atmosphere containing an excess of oxygen gas at the oxidation zone at the top of the reaction tube. Combustion products are transported by a He 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 CO_2, N_2, and SO_2, are separated by a gas chromatograph (GC). The gas is then introduced into the isotope-ratio mass spectrometer (IRMS) through a Finnigan ConFlo II interface, which also is used to inject SO_2 reference gas and He for sample dilution. The IRMS is a Finnigan Delta^{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 SO_2 are as follows: m/z 64 = SO_2 = $^{32}S^{16}O^{16}O$; 66 = SO_2 = $^{34}S^{16}O^{16}O$ primarily.

Reporting Units and Operational Range

Variations in stable isotope–amount ratios typically are small. Stable isotope–amount ratios commonly are determined as the relative difference in the ratio of the less abundant isotope (usually the heavy isotope) to the amount of more abundant isotope (usually the light isotope) of a sample with respect to a reference. This relative difference is designated $\delta(^{i}E)$, and it is defined according to equation 1:

$$\delta\left(^{i}\mathrm{E}\right) = \frac{n_{\mathrm{X}}\left(^{i}\mathrm{E}\right)/n_{\mathrm{X}}\left(^{j}\mathrm{E}\right) - n_{\mathrm{ref}}\left(^{i}\mathrm{E}\right)/n_{\mathrm{ref}}\left(^{j}\mathrm{E}\right)}{n_{\mathrm{ref}}\left(^{i}\mathrm{E}\right)/n_{\mathrm{ref}}\left(^{j}\mathrm{E}\right)} \qquad \textbf{(1)}$$

where $\delta(^{i}E)$ refers to the delta value of isotope number i of element E of sample X relative to the reference (ref), and $n_X(^{i}E)/n_X(^{j}E)$ and $n_{ref}(^{i}E)/n_{ref}(^{j}E)$ are the ratios of the isotope amounts in unknown X and a reference ref and $\delta = [(R_x - R_{ref})/R_{ref}]$. A positive $\delta(^{i}E)$ value indicates that the unknown is more enriched in the amount of the heavy isotope than the reference. A negative $\delta(^{i}E)$ value indicates that the unknown is depleted in the amount of the heavy isotope relative to the reference. The $\delta(^{i}E)$ 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 sulfur isotope–amount ratios, this is written as follows:

$$\delta\left({}^{34}S\right) = \delta^{34}S = \frac{n_X\left({}^{34}S\right)/n_X\left({}^{32}S\right) - n_{ref}\left({}^{34}S\right)/n_{ref}\left({}^{32}S\right)}{n_{ref}\left({}^{34}S\right)/n_{ref}\left({}^{32}S\right)} \quad \textbf{(2)}$$

The primary reference material for relative sulfur isotope-ratio measurements ($\delta^{34}S$) is IAEA-S-1, which is assigned a $\delta^{34}S$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 with unknown samples, sulfur isotope ratios can be determined. These isotope ratios are made with a CF-IRMS, which measures the ratios of the unknown SO_2 gas and one or more injections of the "working reference" SO_2 gas.

The system was tested by analyzing $BaSO_4$ samples with known $\delta^{34}S$ values. The routine analysis requires a minimum of 40 µg of sample as sulfur; however, the system is capable of analyzing samples as small as 19 µg of S in one sample aliquot with reduced analytical precision. The $\delta^{34}S$ values of test samples ranged from approximately –34 to +21 ‰, which covers the range of $\delta^{34}S$ values of most sulfate in natural water. The precision and accuracy of the results were acceptable (± 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 $\delta^{34}S$ measurements is IAEA-S-1, which is assigned a $\delta^{34}S$ 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 isotopic compositions. In the procedure reported herein, barium sulfates ($BaSO_4$) that are used for isotopic analysis of inorganic sample include NBS127 with a $\delta^{34}S$ = +21.1 ‰, IAEA-SO-5 with $\delta^{34}S$ = +0.5 ‰, and IAEA-SO-6 with $\delta^{34}S$ = –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, 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, reagents, and apparatus include 20 weight % $BaCl_2$ solutions, beakers, a stirring hot plate with stir bar, a watch glass, a thermometer, a filtering apparatus with 0.2-µm Millipore GTTP polycarbonate membrane (PCM) filter, tin capsules, and a microbalance capable of measuring samples with 0.0001-mg precision. The analytical apparatus consists of four different segments: (1) EA, (2) ConFlo 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 He flow (90 mL/min). The sample immediately reacts with a measured amount of oxygen from a 5-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 $BaSO_4$ has a decomposition temperature of 1580°C, it is critical to synchronize the He flow, the oxygen flow, and the timing of the sample drop to achieve quantitative combustion (Révész, 1998; also see in this work the section titled "Troubleshooting and Bench Notes"). To boost the combustion, 0.8 ± 0.3 mg V_2O_5 is added to each sample (Yanagisawa and Sakai, 1983). The combustion gases are first carried by He through an oxidative catalyst layer (tungsten oxide, WO_3, on alumina) in the top of the reaction tube, where oxidation is completed, and then through a reduction agent (Cu) packed on the bottom of the

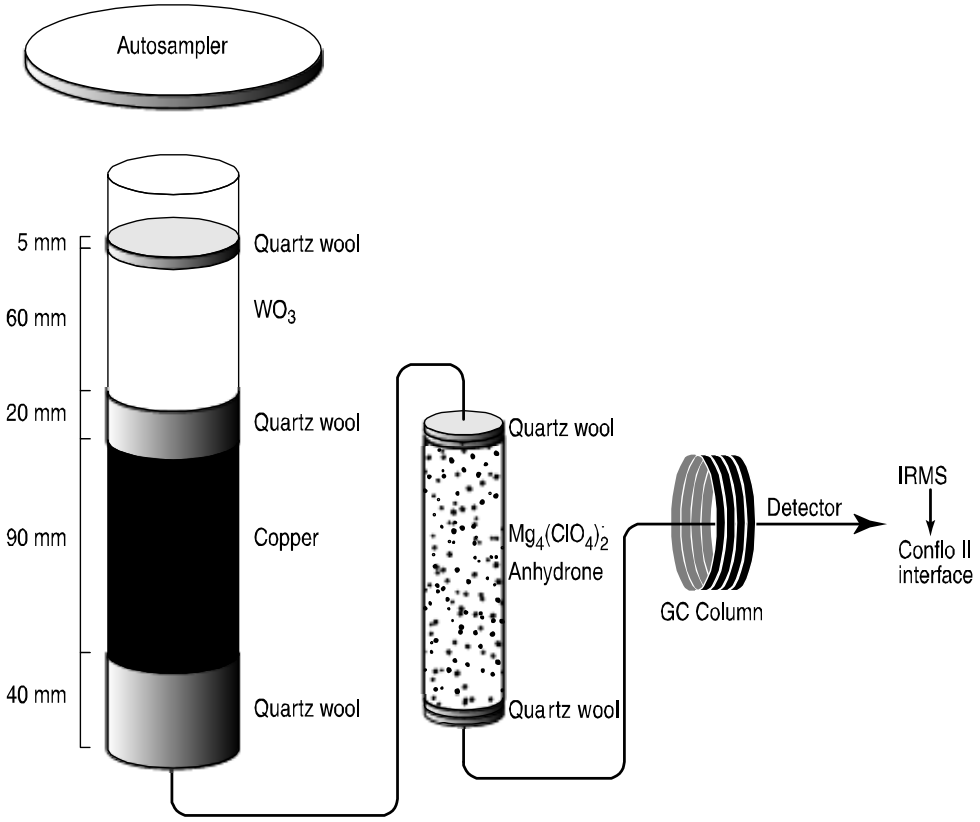

Figure 1. Diagram of the Carlo Erba Instruments NC 2500 (CE NC 2500) Elemental Analyzer (used with permission of Thermo Electron Co.).

reaction tube where any excess oxygen gas is consumed. At the outlet of the reaction tube, the gas mixture (N_2, CO_2, SO_2, and H_2O) enters a trap containing Anhydrone, which absorbs water. The gas mixture, now N_2, CO_2, and SO_2, flows through a Teflon tubing gas chromatograph column (0.8-m Poraplot W kept at 90°C), which separates the gases and ensures that pure SO_2 gas passes separately through the thermal conductivity detector, through the ConFlo II open split, and into the IRMS.

The Finnigan ConFlo II 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 He flow needed to operate the EA to a 0.3 mL/min He 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 He 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 He 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 He if the sample is too large (or to direct gases away by dilution if they are too large to ensure total separation).

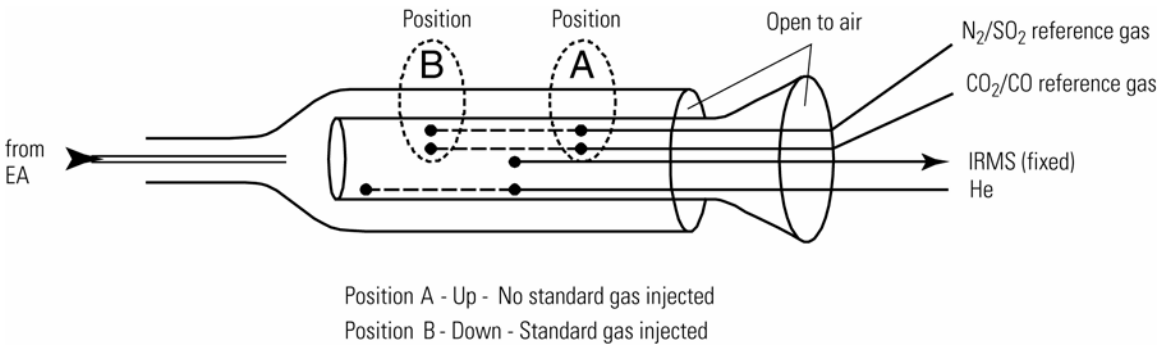

Figure 2. Diagram of a Finnigan ConFlo II Open Split (used with permission of Thermo Electron Co.).

The IRMS is a Finnigan Delta^{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, δ 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 a Faraday cup collector. 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 3×10^8 Ω and 680 pF. At the high-mass cup, it is 3.5×10^{10} Ω and 5 pF. The instrument is capable of measuring *m*/*z* 64 and 66 simultaneously.

The Finnigan ISODAT 2.0 software is designed (1) to advance the autosampler carousel, (2) to control the 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.

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 δ^{34}S values. Sulfate and sulfide concentration should be determined in the field by ion chromatograph or spectrophotometer. Each sample that contains more than 20 mg/L

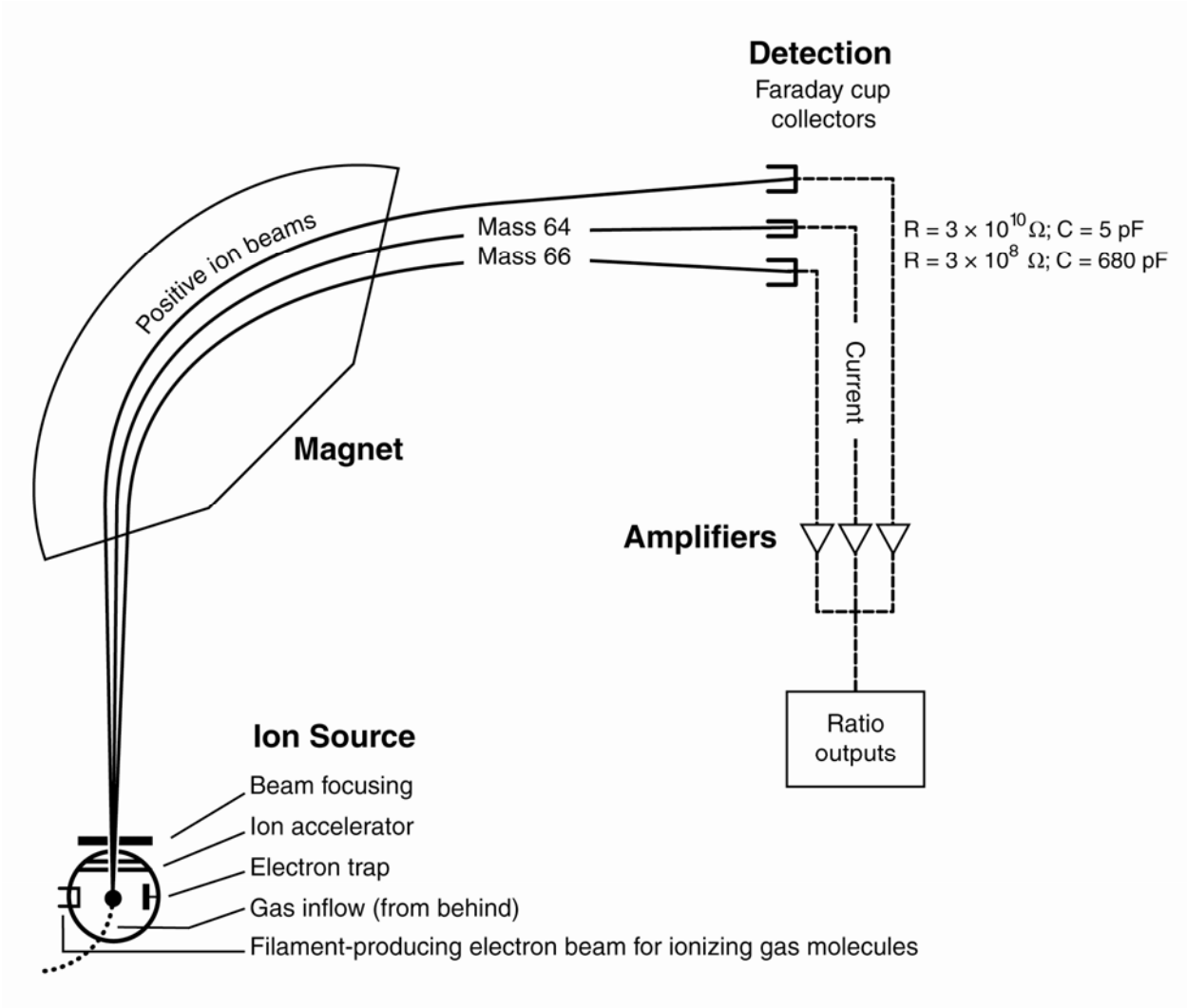

Figure 3. Schematic of a continuous flow isotope-ratio mass spectrometer (CF-IRMS) (modified from Clark and Fritz, 1997).

sulfate and does not contain sulfide is filtered with a 47-mm diameter 0.4-µm PCM filter. Each sample should be collected in 1-L (or smaller) glass or plastic bottles. An amount of 50 mg of $BaSO_4$ is required. Containers should be labeled with isotopes whose concentrations are to be determined and with the respective laboratory code or schedule number.

Sulfate concentrations lower than 20 mg/L can be analyzed; however, a different collection technique is required. Consult SOP 1949 or contact the laboratory for further information.

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 should be stripped with N_2 gas to remove sulfide before the sample is collected. Trace oxidized sulfide could seriously alter the $\delta^{34}S$ of sulfate. The sulfide stripping is done by filling a 10-L bucket with a water sample, acidifying it to pH 3 to 4 with 1 M HCl, immersing the outlet of the N_2 flow into the bottom, covering the system loosely with plastic wrap, and purging with an N_2 flow rate of 8 L/min until the sulfide concentration is less than 0.01 mg/L. This usually takes less than 10 to 20 min.

No treatment, preservation, or special shipping is required.

Sample Preparation and Time Requirements

Sample preparation involves logging in samples to the LIMS-LSI, processing samples to precipitate $BaSO_4$, 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."

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 a 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. Copies of the ASR forms are mailed to NWQL. Step-by-step procedures are given in Appendix A.

The processing of samples involves the precipitation of pure $BaSO_4$ from the sample (modified from Carmody and others, 1998). The $BaSO_4$ is precipitated by acidifying an amount of water sufficient to yield 50 mg of $BaSO_4$ to pH 3 to 4 by adding 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_2 gas from the sample. If the samples contain organic material, 6 mL of 6 % H_2O_2 are added along with the acid to oxidize the dissolved organic sulfur to SO_2 and oxidize any dissolved organic carbon to CO_2, which are then degassed from the samples. At the last minute, 5 mL of 20 % $BaCl_2$ solution is added to the sample to precipitate the $BaSO_4$. The solution is cooled slowly to 50°C or lower and usually allowed to settle overnight. The liquid containing the $BaSO_4$ precipitate is filtered through a preweighed 0.2-µm GTTP PCM filter, rinsed with deionized water (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 $BaSO_4$ 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 B

An Excel sample workbook is generated. The step-by-step procedures are shown in Appendix C. Sample weighing includes balance conditioning, weighing approximately 0.30 mg of sample into a capsule, recording the weight on the template, adding approximately 600 µg of V_2O_5 to the capsule, and closing the capsule by folding it. Step-by-step procedures are given in Appendix D. The time required for sample preparation is approximately 5 to 8 days.

Performing the Analysis and Time Requirements

All $BaSO_4$ 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 $\delta^{34}S$ values are analyzed at the beginning of a batch. Four of them are depleted in ^{34}S, one is enriched in ^{34}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 E), 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 F). After the analyses are completed, data are exported (Appendix G) to a Zip disk or "memory stick" from the ISODAT 2.0 database and transferred (Appendix H) to the LIMS-LSI system and Data Back-Up computer. Final daily correction factors are determined by LIMS-LSI (Appendix I), based on the daily analyses of reference materials using equations 3, 4, and 5 below, which are presented with numerical values:

$$-34.05\ ‰ = m\left(\delta^{34}S_{\text{NBS127/workingrefgas}}\right) + b/1000 \quad \textbf{(3)}$$

$$+0.50\ ‰ = m\left(\delta^{34}S_{\text{IAEA-SO-5/workingrefgas}}\right) + b/1000 \quad \textbf{(4)}$$

$$+21.10\ ‰ = m\left(\delta^{34}S_{\text{IAEA-SO-6/workingrefgas}}\right) + b/1000 \quad \textbf{(5)}$$

The values –34.05 ‰, +0.5 ‰, and +21.1 ‰ are the values of the international reference materials NBS127, IAEA-SO-5, and IAEA-SO-6, respectively. The δ^{34}S values in equations 3–5 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 isotopic compositions 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^{18}O value on the δ^{34}S determination; V_2O_5 is added to each sample to buffer the δ^{18}O of SO_2 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 is not provided. In this case, the sulfate concentration needs to be estimated to be able to precipitate an appropriate amount of $BaSO_4$ (50 mg) 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 bottles should be the same size and color for proper comparison.

Interferences

The δ^{34}S of sulfate can be seriously altered if a water sample contains dissolved sulfide. The δ^{34}S of sulfide can be as different as 65 ‰ from the δ^{34}S of sulfate; therefore, trace oxidized sulfide could seriously alter the δ^{34}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 $BaSO_4$ is 1580°C and 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) He pressure and flow rate, (2) oxygen pressure and flow rate, and (3) sample "start time." The system is so sensitive that even a 1-s difference in the sample dropping time can make a difference in the brightness of the flash, peak shape, peak area, and, consequently, the δ^{34}S value. The optimum set-up parameters of the RSIL EA are cycle = 100, oxy = 60 (O_2 flow stops flowing into autosampler), sample start = 10, and sample stop = 40. The helium regulator is set for 150 kPa, and He flow setup 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 ($BaSO_4$) (Révész, 1998). To improve analytical precision, 0.8 mg ± 0.3 mgV_2O_5 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 He flow rate makes the system more sensitive to leaks (Bernoulli principle). Leaks can cause uncontrollable changes in the flow rate, which could interfere in the quantitative combustion, in the peak shape, in the peak area, and consequently, in the isotope-ratio 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 δ^{34}S value. This shift can be corrected by frequently analyzing reference materials. However, after approximately 50 samples (one carousel), it is advisable to remove the ashes (Révész, 1998). The leak-checking procedure is given in Appendix J. 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_2, O_2, and Ar) reflect atmospheric compositions. Acceptable levels for *m*/*z* 28 and 29 are 40 to 50 mV with typical IRMS settings. (See "Daily Checklist" in Appendix K.)

The IRMS must be focused carefully. The analyst should start with the original factory setting. In the RSIL, the settings (in priority order) are as follows: Extraction = 7.00; X focusing = 4.8; Voltage = 8.00; Trap = 5.7; Electron = 7.8; Y1 focusing = 3.00; Y2 focusing = 3.8; X deflection = 6.4; Extraction = 5.6; and X-focusing symmetry = 3. Emission current is critical. The higher it is, the higher the signal is but the poorer the linearity is. The IRMS is temperature sensitive; therefore, it must be operated in a temperature-controlled environment with all of the side panels on. The resistor–capacitor combination at the low-mass cup is 3×10^8 Ω and 680 pF. At the high-mass cup, the combination is 3.5×10^{10} Ω and 5 pF. 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 approximately every week; samples of the same size need to be analyzed within ± 0.010 mg. The 1 – σ 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 L), (2) changing the water trap approximately every 200 samples (Appendix M), (3) changing reaction tubes approximately every 200 to 250 analyses (Appendix N), and (4) cleaning the sample carousel every week. The IRMS also requires a daily check (Appendix K). 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 G).

Sample Retention Time and Disposal

Samples are retained in the RSIL for at least 4 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 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 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. It provides 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}S, one with an intermediate concentration, and one depleted in ^{34}S. One set of three (depleted, intermediate, and enriched in ^{34}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. The preparation and analytical cost of these isotopic reference materials is the responsibility of RSIL. Both RSIL and NWQL monitor these results. Quarterly, RSIL prepares a summary of results and makes them available to NWQL.

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 "$\delta^{34}S$ 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., $\Delta\delta \leq 0.2$ ‰).

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

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. 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 in USGS databases appropriately.

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 O).

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 (MSDS); they are on file in the laboratory, and http://www.ilpi.com/msds/#Manufacturers provides links to 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). Consult 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 must 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

The hazardous chemicals used in the process are Cr_2O_3 and Co_3O_4, which are used in the oxidation reaction tube, and V_2O_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 V_2O_5, protective gloves and a full-face mask also are required. All samples must be carefully inspected upon receipt for obvious indications of hazards.

The SO_2 reference gas is colorless and has a suffocating odor. Exposure to SO_2 can cause respiratory tract burns. Therefore, an appropriate ventilation unit must be installed in the ConFlo unit. A leak test on the tank of gas and the line carrying SO_2 to the ConFlo must be performed routinely.

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

The chemicals Cr_2O_3, Co_3O_4, and V_2O_5 must be collected in a separate, closed container. Ba from the waste $BaCl_2$ solution must be precipitated with Na_2SO_4 solution, and the solid $BaSO_4$, along with the other hazardous chemicals, must be given to the safety, health, and environment officer for disposal.

Revision History

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Publication Authorship: Révész, Kinga, and Qi, Haiping

First Version and Date of First Release: May 2006
Current Version and Date of Current Release: May 2006
Summary of Product Components

Component	Description	Last Revised In Publication Version	Date of Last Revision

History List of Revisions (latest version first):

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

1. For samples submitted through NWQL:
   a. Match up information on sample bottles with information on ASR forms by spreading out ASR forms and placing each bottle on its respective ASR form. Check for broken bottles.
   b. Assign NWQL #s based on the Julian date of the Monday following the submission date. Check note on bulletin board for "Next NWQL #." Write NWQL #s on ASR forms, then update "Next NWQL #" on bulletin board.
   c. Use "New Project Log-In" in LIMS-LSI to assign S-#s; field IDs are the Station IDs. Submission date is the date samples are logged in.
   d. Enter all ASR information into LIMS-LSI, sample by sample.
   e. Print out two Project Reports, Labels (two for each sample), and Sample Range forms.
   f. Put a label on a sample bottle and on the corresponding ASR form; crosscheck Field IDs between bottles and ASR forms.
   g. Make one photocopy of each ASR form.
   h. Enter S-# range into the appropriate template.
   i. Proofread information on Sample Range forms against ASR forms (recruit help if necessary). Make corrections in LIMS-LSI, if necessary and print out corrected Sample Range Forms. Initial and date both Project Reports to indicate that proofreading is complete.
   j. In LIMS-LSI, save NWQL Headings to a diskette.
   k. In ISOTOPES e-mail on the common-use PC, copy headings into new message from diskette by opening headings-file in Notepad and copying/pasting to new message. Print copy of headings and e-mail to each project chief for information review and NWQL [Attn: Jeanne Hatcher (jhatcher@usgs.gov)].
   l. Mail copies (not originals) of ASR forms and corrected Sample Range forms to NWQL [National Water Quality Laboratory, Attn: Jeanne Hatcher, U.S. Geological Survey, P.O. Pax 25708, MS 407, Building 95, Denver Federal Center, Denver, CO 80225-0608 (Tel: 303-236-3481)]. Envelope should be mailed every Friday.
   m. Punch holes in original ASRs and put in "Central Lab" binder along with project reports and date on piece of tape. Punch holes in NWQL headings and other project report and place in "Samples-in-Progress" binder.
   n. Add samples to the "Table of Samples to Be Analyzed" in LIMS-LSI.
      i. Click the "Projects" button of LIMS-LSI.
      ii. Select the project that was logged in.
      iii. Click the "Templates" button.
      iv. Select "EA for S."
      v. Click "Add" and close LIMS-LSI.
   o. Put samples in cabinets for storage until analyzed.
2. For samples submitted directly to RSIL:
   a. For sample submitter:
      i. Download "RSIL Excel Worksheet" from RSIL website at http://isotopes.usgs.gov/.
      ii. Fill out the requested sample information.
      iii. Send diskette and a hard copy along with the samples.
   b. For RSIL personnel:
      i. Match up information on sample bottles with submitted "Excel Worksheet."
      ii. Enter all Excel Worksheet information into LIMS-LSI by loading the diskette. Submission date is the date samples are logged in.
      iii. Use "New Project Log-In" in LIMS-LSI to assign S-#s; field IDs are the Station IDs.
      iv. Print out one Project Reports and container labels (one for each sample).

v. Put a label on a sample bottle and crosscheck Field ID's between bottles and Excel Worksheet forms.
vi. Enter S-# range into the appropriate template.
vii. Punch holes in original Excel Worksheet and all the information for the project and put in "Samples-in-Progress" binder.
viii. Add samples to the "Table of Samples to Be Analyzed" in LIMS-LSI.
    1. Click the "Projects" button of LIMS-LSI.
    2. Select the project that was logged in.
    3. Click the "Templates" button.
    4. Select "EA for S."
    5. Click "Add" and close LIMS-LSI.
ix. Put samples in cabinets for storage until analyzed.

Appendix B. Step-by-Step Procedure to Precipitate $BaSO_4$

1. Acidify an amount of water to yield 50 mg of $BaSO_4$ with 4 drops of 1 M HCl to convert carbonate to CO_2 gas. (The 1 M HCl can be prepared by pouring 40.4 mL of 38 % commercial HCl solution into 500 mL of DIW.)
2. Add H_2O_2 to oxidize dissolved organic sulfur:
   a. Add 6 mL of 6 % H_2O_2 to sample. (The 6 weight % H_2O_2 can be prepared by adding 95.5 mL of 30 % H_2O_2 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 % $BaCl_2$ solution. (The 20 weight % $BaCl_2$ can be prepared by dissolving 117.3 g $BaCl_2 \cdot 2H_2O$ solids in 441 mL DIW.) Let the solution cool slowly to 50°C or lower, usually overnight.
4. Filter $BaSO_4$ 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 $BaCl_2$ 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 $BaSO_4$ on it and record it on the Dissolved Sulfate Precipitation form.
7. Scrape off the dried $BaSO_4$ from filter into the vial and homogenize the sample with a spatula in the vial. Store them on the self for isotopic analysis. Discard the filter.

DISSOLVED SULFATE PREPARATION FORM

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

Reported 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 % H_2O_2	Comments:
volume used:		

PRECIPITATION:

Approx. _____ mL $BaCl_2$ added at: _____	Comments:

FILTRATION AND YIELD:

Use 0.2 µ-pore-diameter polycarbonate membrane: _____

weight of PCM, $BaSO_4$, dish		Yield/Concentration:
weight of PCM, dish		
weight of $BaSO_4$		

[ ] 1 mL of 20 weight % $BaCl_2$ added to ensure complete precipitation of $BaSO_4$.
[ ] No further precipitation observed after 10 min; precipitation complete.
[ ] Continued precipitation; further filtering required.

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

Excel Sample 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.

Template

1. Use “Print Template” in LIMS-LSI.
2. Select “appropriate template” for EA and “Delta Plus” 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 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	**S-97**	**S-97**	**S-97**	**S-97**	**S-1301**	**S-1302**	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	**S-97**	**S-1301**	**S-1302**	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						IAEA-SO-5	IAEA-SO-6					
	Our Lab ID	S-9039	S-9040	S-9040	S-9041	S-9041	**S-97**	**S-1301**	**S-1302**	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	**S-97**	**S-1301**	**S-1302**	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								IAEA-SO-5	IAEA-SO-6			
	Our Lab ID	S-9050	S-9051	S-9051	S-9052	S-9052	S-9053	S-9053	**S-97**	**S-1301**	**S-1302**		
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	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	**S-97**	A1	NBS 127	0.3	mg
2	**S-97**	A2	NBS 127	0.29	mg
3	**S-97**	A3	NBS 127	0.31	mg
4	**S-97**	A4	NBS 127	0.31	mg
5	**S-1301**	A5	IAEA-SO-5	0.304	mg
6	**S-1302**	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	**S-97**	B5	NBS 127	0.299	mg
18	**S-1301**	B6	IAEA-SO-5	0.295	mg
19	**S-1302**	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	**S-97**	C6	NBS 127	0.302	mg
31	**S-1301**	C7	IAEA-SO-5	0.3	mg
32	**S-1302**	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
41	S-9047	D5		0.298	mg

Line	Identifier	Port	Comment	Amount	Amt Unit
42	S-9047	D6		0.296	mg
43	**S-97**	D7	NBS 127	0.303	mg
44	**S-1301**	D8	IAEA-SO-5	0.305	mg
45	**S-1302**	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	**S-97**	E8	NBS 127	0.302	mg
57	**S-1301**	E9	IAEA-SO-5	0.297	mg
58	**S-1302**	E10	IAEA-SO-6	0.304	mg

Appendix D. 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 done 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 ± 10 µg).
5. Enter sample weight on the template.
6. Add 600 µg ± 100 µg of V_2O_5 to 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 E. Step-by-Step Procedure for Zero Blank Auto Sampler Operation

1. Before opening lid, make sure the isolation valve (between sample chamber and reaction tube) is closed (arrow toward you), and make sure the He purge isolation valve (on the left) is closed.
2. Open the purge vent on the top of the auto sampler to vent the sample chamber.
3. Release the three fittings holding the lid close and open the lid.
4. Place your samples and close the lid. Load 49 samples for 50-position carousel, leave the first hole empty.
5. Secure the lid with three bolts. Start all three bolts, and then lightly tighten two at a time, moving around the lid until they are all completely tight.
6. Open He purge isolation valve (slide to left); purge the sample chamber for 5 min at He 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 He purge vent valve (screw down), wait for 2 min for gas pressure at sample chamber and He flow rate to stabilize. Close He purge isolation valve.
8. Open isolation valve (arrow towards up).Wait for 2 min for stabilized baseline. Normally when the emission current set at 0.54 mA/0.48 mA, with He carrier flow rate of 90 mL/min, one should see *m*/*z* 28 on cup 1 at approximately 10 mV, *m*/*z* 29 on cup 2 at approximately 8 to 12 mV, and *m*/*z* 30 on cup 3 at approximately 140 mV to 1V (Appendix K).

Appendix F. 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 ID, sample weight from template to sequence table.
5. Select appropriate “method” for each sample.
6. Define 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 G. 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.
   l. 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 Zip disk or “memory stick.”

Appendix H. 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 Analysis.”
   c. Choose IRMS “Delta Plus.”
   d. Click “Import.”
   e. Select the file that will be imported.
   f. Select columns containing δ^{34}S data. Check the boxes to import these two columns.
   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 your back ups are stored.
   c. Choose: “RSIL.”
   d. Choose: “Mass. Spec. Analysis Back Up.”
   e. Choose: “P.” (Stands for Delta^{Plus} IRMS).
   f. Under that folder create a new folder. The name of the folder should be the date range when those analyses were done that you want to back up.
   g. Transfer data to that folder.
   h. Make back ups every 2 weeks or so, as required.
3. Reevaluate old data:
   a. Find your samples in the Data Back-Up computer.
   b. Transfer data by a Zip disk or “memory stick” to the computer where a virtual version of ISODAT 2.0 is installed.
   c. Reevaluate your data.

Appendix I. 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 “P (Delta Plus) 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. 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 “EA” binder.
10. Go back to LIMS-LSI main menu by closing open windows.
11. Choose “Print Samples in Progress,”
    a. Open “Sample in Progress.”
    b. Choose appropriate isotope.
    c. Choose appropriate prefix (W for water, N for nitrogen, S for sulfur).
    d. Put in sample ID range from “Samples-to-Be-Analyzed” sheet. Click Print.
12. Review results; determine repeats.
13. Put repeats back to 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 J. Step-by-Step Procedure to Check Elemental Analyzer for Leaks

1. Close the VENT carrier output using the proper cap (provided).
2. Adjust the He pressure to 150 kPa (regulator is on the front central panel), wait 3 min to equilibrate gas in the system.
3. Close He 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 He detector.

Appendix K. Daily Checklist

Analyst in charge: _____Date: _____

Weekly:

1. Change working reference gas tank and He gas tank if the pressure is < 500 psi. Order new ones for a spare; reference gas is SO_2 ANHY by Matheson, He carrier is zero grade, oxygen gas is research grade.
2. Change water and CO_2 trap after approximately 200 samples or when it is necessary.
3. Check and clean 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 He, O_2, and reference gas flow. [ ]
2. Check EA reaction-tube temperature (1020 °C)
3. Change insertion tube (ash-collector liner) in the reaction tube. [ ]
4. Check background masses. [ ]

Typical Background at N_2/CO_2 Configuration
Emission Current: 0.54 mA/0.48 mA

Cups	Mass	Intensity (V)	Mass	Intensity (V)	Mass	Intensity (V)	Resistor (Ω)	Capacity (pF)
1	28	0.010	44	0	64	0.002	3×10^8	680
2	29	0.007	45	0	65	0.002	3.5×10^{10}	5
3	30	0.140	46	0.002			3×10^{11}	2

5. Perform Ref on/off method three times to stabilize IRMS. [ ]
6. Check peak center. If it is off default value by more than 50, do mass calibration. [ ]
7. Analyze Ref on/off method 10 times to stabilize IRMS (standard deviation should be better than ±0.1 ‰). [ ]

Optimal ConFlo Pressure Setting SO_2 (bar)	SO_2 signal (V) Mass 66 on Cup 2
0.50	3.000

8. Check paper in printer. [ ]

Appendix L. 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 “Spc. Fun.,” choose “Std By” and press “enter.” The O_2 and He 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_2 and He back on by pressing “enter” and return the screen to the temperature readout by pressing “Spc. Fun.”
8. Open the needle valve.

Appendix M. 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^{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 of approximately 70 % magnesium perchlorate and 30 % 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 “Spc. 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 N. 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 “Spc. Fun.” Set to zero the counter of the reaction tube “B.”
11. Insert the plug into the vent and close the He supply. Watch for any decrease in the pressure to check for a leak in the system. If everything looks okay after 3 min, open the He supply and replace the vent line.
12. Open the needle valve.

Appendix O. 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 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.