NEON Water Sample Handling

v. 1.02

General

1. Receipt, handling, and analysis of NEON water samples should be conducted only by the SPATIAL Facility Manager or a designated analyst who has received training in protocols and procedures specific to the NEON project.

Sample Receipt

1. The designated SIRFER/SPATIAL point of contact (POC, the SPATIAL Facility Manager) will receive an advance email notification of each NEON sample shipment, including a shipment manifest and tracking number. This email and attachments should be filed in the POC's university email account in a designated NEON project folder.
2. Monitor tracking information for the sample shipment and collect the package from the Geology & Geophysics Department office on the day of receipt.
3. Upon receipt, inspect the sample package for damage and any severe external damage to the packaging materials noted and photographically documented.
4. Open the sample packaging and inspect the condition of the samples. Note any damage to the sample bottles, unreadable label information, or other conditions that might compromise the samples.
5. Run the "neon_receipt" function in the CRDS_utils R-package to log the receipt and condition of all samples. Refer to the SOP "CRDS Data Processing R Scripts".
6. Submit the updated manifest via the NEON Data Portal.
7. Immediately transfer sample vials to the 'To Be Analyzed' storage area of the lab refrigerator.

Sample Analysis

1. Samples should be analyzed according to their place in the first-in first-out queue, as indicated by the job number sequence. Analysis of NEON samples should occur no later than 90 days following sample receipt.
2. Sample analysis should follow all procedures specified in the SOP "CRDS Water Isotope Analyzer Operation".
3. NEON samples can be comingled with samples from other projects in an analysis sequence, if necessary, but should be grouped together in the analysis sequence.

Data Reduction and Reporting

1. Data reduction and evaluation of quality control metrics will be conducted by the Facility Manager following the procedures specified in the SOPs "CRDS Water Isotope Analyzer Operation" and "CRDS Data Processing R Scripts".

2. A NEON-formatted data report will be generated for each job after all samples associated with the SIRFER job number have been analyzed. The report consists of two CSV files containing sample and QC information, and is generated using the CRDS_utils R-package (refer to the SOP "CRDS Data Processing R Scripts")
3. The Facility Manager will email each completed report to the SPATIAL PI (Gabe Bowen), who will review and then upload the report via the NEON Data Portal.
4. After the report is uploaded, the SPATIAL PI will notify the Facility Manger, who will close the SIRFER job and submit the job to the SIRFER Accountant for invoicing.

Sample Archival

1. After completion of the job and submission of the data report, the Facility Manger will transfer sample bottles to the NEON Archive space in the SPATIAL facility.
2. Samples bottles must be retained for at least six months following the date when the sample analysis data were reported to NEON.
3. Samples vials that have been retained beyond the 6-month archival period can be drained and discarded in accordance with standard lab safety procedures.

Change Log

Version	Date	Changes	By
1.00	4/2015	Original version	Gabe Bowen
1.01	4/2017	Update to add controlled vocabulary	Gabe Bowen
1.02	4/2022	Update to reflect new CRDSutils package	Gabe Bowen

CRDS Water Isotope Analyzer Operation

v. 1.02

Part 1 – Sample Preparation

1. Fill standard and sample vials
    a. Pipette samples
        i. Pipette 0.5 mL from sample container into 2mL crimp-top vial. Use a separate, clean pipette tip for each sample. Discard used tips into a beaker for washing and re-use.
        ii. Use crimper to seal lid. Check to make sure the lid is tight (i.e. does not rotate on the top of the vial) and cleanly crimped. If the crimper is not creating a tight seal, you can adjust it with an Allen wrench.
        iii. Pipette samples 8 at a time, writing each sample name or a unique abbreviation of each sample name on each 2 mL vial with a sharpie.
        iv. Place samples in the sample tray leaving the first four plate locations empty and leaving one plate location blank between each group of eight samples. Empty locations will be used for reference waters. A maximum of 56 samples should be run at a time.
    b. Pipette reference water
        i. In order to limit evaporation, minimize the amount of time the reference waters are out of the refrigerator and the amount of time the cap is off of the reference water bottles. After pipetting reference waters, immediately replace the cap securely on the bottle and parafilm tightly around the cap.
        ii. Pipette 0.5 mL from container into 2mL crimp-top vial. Use a separate, clean pipette tip for each reference water. Discard used tips into a beaker for washing and re-use.
        iii. Use crimper to seal lid. Check to make sure the lid is tight (i.e. does not rotate on the top of the vial) and cleanly crimped.
        iv. Fill 1 vial with primary reference water PZ and 1 with primary reference water UT2. These primary references are used to calibrate each run.
        v. Fill 1 vial with secondary reference water EV to put at the beginning of the run, 1 additional vial to run before every 8 samples, and 1 to be run in the last plate location. This secondary reference water is used to quality check the accuracy of the calibration regression and to generate a drift correction in each run. An example plate map is shown below.

Table 1. Example plate map with maximum plate locations filled

64	Sample54	65	Sample55	66	Sample56	67	EV	68		69		70	
57	Sample48	58	EV	59	Sample49	60	Sample50	61	Sample51	62	Sample52	63	Sample53
50	Sample41	51	Sample42	52	Sample43	53	Sample44	54	Sample45	55	Sample46	56	Sample47
43	Sample35	44	Sample36	45	Sample37	46	Sample38	47	Sample39	48	Sample40	49	EV
36	Sample29	37	Sample30	38	Sample31	39	Sample32	40	EV	41	Sample33	42	Sample34
29	Sample23	30	Sample24	31	EV	32	Sample25	33	Sample26	34	Sample27	35	Sample28
22	EV	23	Sample17	24	Sample18	25	Sample19	26	Sample20	27	Sample21	28	Sample22
15	Sample10	16	Sample11	17	Sample12	18	Sample13	19	Sample14	20	Sample15	21	Sample16
8	Sample4	9	Sample5	10	Sample6	11	Sample7	12	Sample8	13	EV	14	Sample9
1	EV	2	PZ	3	UT2	4	EV	5	Sample1	6	Sample2	7	Sample3

Part 2 – Instrument Preparation

2. Clean syringe
    a. Unplug Autosampler and carefully remove syringe
    b. Don gloves (latex or nitrile), a lab coat, and safety goggles
    c. Open chemical fume hood sash, turn on light, and ensure that it is functioning properly with adequate air flow
    d. Lay down 2 Kimwipes; one to lay syringe on and another for ejecting solvent onto
    e. Use solvent (1-methyl-2-pyrrolidinone) from cabinet below hood to clean the syringe
        i. Insert syringe through the septum on solvent bottle, preferably targeting a previously punctured location. Be careful not to bend the syringe tip.
        ii. Extract solvent with syringe to capacity by moving plunger slowly until it comes out of the syringe. Rotate the plunger as you remove it to thoroughly clean the syringe. Rotating may also help to free the plunger if it becomes stuck.
        iii. Remove syringe from solvent bottle and eject solvent from syringe onto Kimwipe by replacing the plunger in the syringe and fully depressing it.
        iv. Repeat process at least three times or as many times as necessary until the plunger moves smoothly and easily in the syringe. If you cannot get the plunger to move freely it might need to be replaced. Note that broken syringes must be discarded in the sharps container.
        v. Once complete, re-cap the solvent bottle and return to storage under hood. Leave the Kimwipe with the ejected solvent in the fume hood until the solvent has completely evaporated before discarding.
    f. Use deionized water to rinse the syringe three times, fully filling and emptying the syringe each time
    g. Dry syringe
        i. Remove the plunger from the syringe, wiping it with a Kimwipe
        ii. Insert tip of syringe into the piece of blue tubing near the compressed air station, preferably locating a pre-existing hole and being careful not to bend the syringe
        iii. Place the opening of the tubing loosely against the air nozzle (do not try to force tubing over the nozzle)
        iv. Turn the air on and let it run until any water has been blown out of the syringe

v. Check the syringe to ensure that no water droplets remain and then replace the plunger. This eliminates the possibility of air bubbles that might affect the fill volume of the syringe.

h. Replace Syringe
    i. Plug the power supply to the autosampler back in
    ii. On the CRDS computer desktop, open the Autosampler Controller and press Chg Syringe button and wait for the syringe holder to move into position
    iii. Place syringe in syringe holder, making sure body and plunger are in holding locations
    iv. Press Swap Done button on Autosampler Controller

3. Fill out instrument log
    a. Open the sample log file on the desktop of the CRDS instrument computer
    b. Input the following information: date, time, initials, project name, number of samples, number of injections, N_2 pressure from the primary regulator on the N_2 tank
        i. N_2 pressure on the primary regulator should be > 150 psi. If the value is lower do not start the run. Wait for all instruments to finish their runs and then replace the tank will a full one. If no full spare tanks remain on the rack alert the SPATIAL facility manager who will order replacements.
        ii. N_2 pressure on the red, secondary regulator (on the bench top near the tanks) should be 2 (+/- 0.3) psi. If outside this range alert the SPATIAL facility manger. This value does not need to be recorded in the log.
    c. Look at the previous row to determine whether the septum should be changed – the septum should be changed every 300 injections. See section 5 for instructions on changing the septum. Indicate with an "X" if you have changed the septum or syringe.
4. Fill out sample ID file
    a. Open "Sample_list_template.csv" from desktop
    b. In the runfiles folder, save as "YYMMDD_project_HIDS20XX"
    c. Fill out template with sample IDs; record the project identifier for each sample in the "Sample ID 2" column
5. Change septum
    a. The septum needs to be changed every 300 injections. Check run log to see if it needs to be replaced.
    b. Unscrew the injection port of the vaporizer, using fingers or tool that sits on top of the injection port to grasp and turn the ceramic top of the port. Caution: ceramic surface is warm, but metal parts at base of injection port will be hot.
    c. Remove old septum, replace with new septum. Check to see that new septum is centered.
    d. Replace injection port and hand-tighten
6. Check glass wool
    a. Make sure the glass wool container remains dry and no condensation is apparent in the vial. Check to make sure that the aquarium pump is working correctly and air is being forced through the opening at the top of the vial.

7. Check that background H_2O concentration reported in the data viewer window is below 100 ppm. If not, check that the N_2 tank regulator valve is open and the primary and secondary regulator pressures are correct (see #3).
8. Open Coordinator Launcher
    a. Don't press launch yet
    b. Make sure High Precision program ("AI High Precision" on some instruments) is selected
9. Open Autosampler Control
    a. Check that the following settings are correct:
        i. Row 1 is set for samples 1-4 and ten injections
        ii. Row 2 is set for samples 5-67 and four injections
        iii. If running less than 67 vials, update number in row 2 to match the position of the final sample in the autosampler tray
        iv. Method should be set as 'GJB rinse' (see Appendix)
    b. Click the Run button
10. After clicking Run in Autosampler Control, click the Launch button in Coordinator Launcher
11. Watch first few samples before leaving lab to ensure no problems at start of analysis
12. **Do not open OpenOffice files while run in progress, otherwise raw data will be lost and not saved to .csv file**

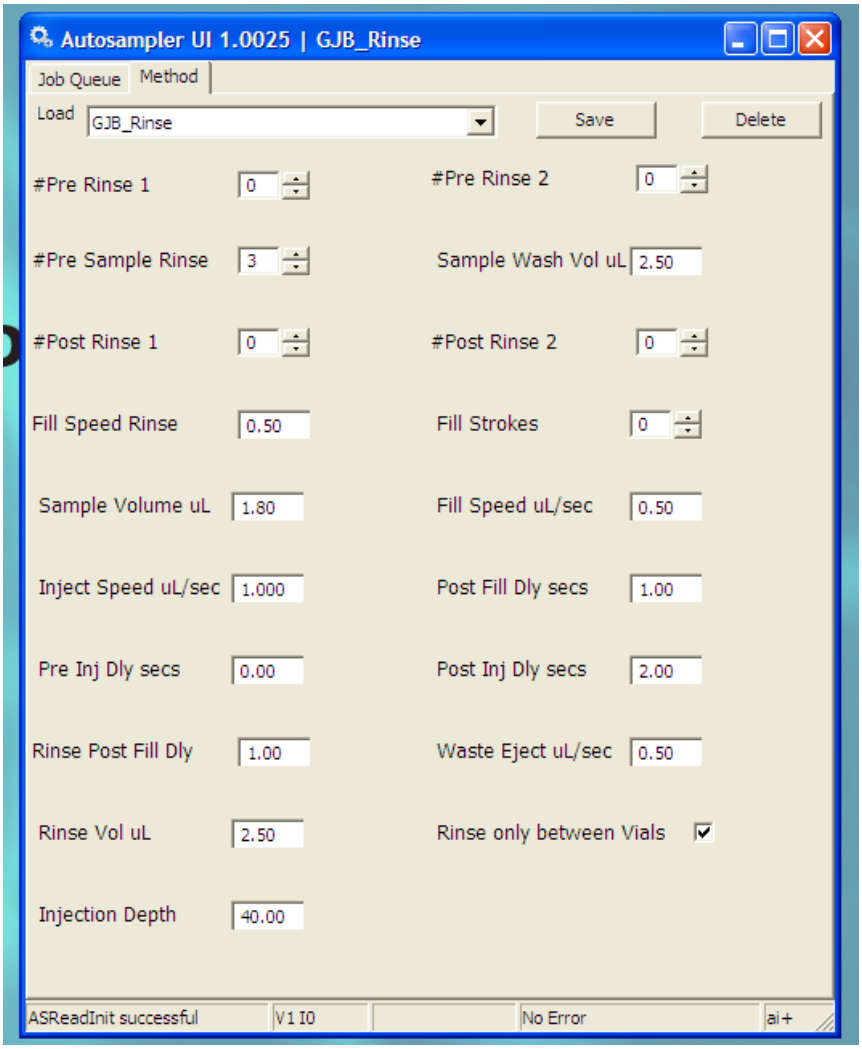
Part 3 – Data Processing

13. Run ChemCorrect
    a. After analysis has completed, close the Coordinator Launcher and Autosampler Control and open ChemCorrect from the desktop of the Picarro computer
    b. Click the Source button and navigate to the file with the correct date
    c. Click the 'OK' button to run ChemCorrect
    d. Examine the results to ensure that no samples show evidence for contamination, as indicated by red highlighting in the results window. Any samples flagged for contamination should be treated with activated charcoal and re-run.
        i. Uncap sample vial, add 0.5 mg activated charcoal, recap, and invert 3 times.
        ii. Allow treated sample to rest for 12 or more hours before re-analyzing.
        iii. If the same sample is flagged for contamination by ChemCorrect a second time, the sample should be transferred to the SIRFER lab for analysis by IRMS.
14. Process data
    a. Refer to SOP "CRDS Data Processing R Scripts" for instructions.

Part 4 – Sample Disposal

15. Keep 2 mL sample vials in fridge for two weeks after returning data in case some need to be re-run. After this window, discard used sample vials in Broken Glass box.

Appendix – GJB_rinse autosampler method



Change Log

Version	Date	Changes	By
1.00	2015	Original version	Crystal Tulley-Cordova
1.01	5/2017	Update to add details	Gabe Bowen
1.02	1/2023	Link to CRDS Data Processing R Scripts SOP	Gabe Bowen

CRDS Calibration, Standardization, and QC Monitoring

v.1.03

General

1. The SPATIAL facility manager is the primary party responsible for quality assurance of CRDS liquid water isotope measurements, including the maintenance of reference materials and regular monitoring of instrument performance.

Maintaining SPATIAL Reference Waters

1. The SPATIAL facility maintains a collection of reference waters which have been calibrated relative to international isotope standards. These waters must always be stored and handled in such a way that they are not subjected to evaporation or contamination. In addition, the facility maintains a stock of certified international standard waters (USGS47, VSLAP, VSMOW2). For standards received in large volume ampules, upon opening these waters are split among GC sample vials, filled completely, and the closures sealed with paraffin wax. The stock of calibrated standards should be replenished by ordering new waters every 3 years or when the inventory of vials falls below 5 for any standard, whichever occurs first.
2. Archive volumes of the SPATIAL reference waters are stored in large bottles or sealed, pressurized kegs. The number and duration of openings of these containers should be minimized. Only one container should be opened at a time, and care should be taken not to mix lids or fittings among containers.
3. Working volumes of the waters are stored in smaller (125 ml) HDPE bottles. These should be stored in the lab refrigerator, and the closures sealed with parafilm, when not in use. Care should be taken to not cross-contaminate reference water bottles.
    a. Working reference water containers should be refilled from the archive volume once every 3 months or when the bottle is half-full, whichever is first. The date when the bottle was re-filled should be recorded on the bottle label.
    b. Working reference bottles should refilled one at a time so that any changes in the instrument calibration and QC parameters associated with replenishing the working volume of a particular reference water can be easily identified.
    c. The SPATIAL facility manager should closely monitor the instrument calibration parameters (slope, intercept) and QC sample values (EV mean values) to identify any systematic shift following the re-filling of a reference water bottle. If a significant shift is identified sample analyses should be discontinued while the manager conducts testing to check the working bottle values against values of the reference water taken directly

from the archive container. If a discrepancy is found, the working volume should be discarded and a new working volume seeded directly from the archive bottle.

4. The SPATIAL facility manager will monitor the amount of water remaining in the archive volume of each reference water. The stock of archived water should not be allowed to fall below 500 ml. Before the archive volume of any reference water reaches this level, the manager should establish a new archive volume of 8 or more liters of an isotopically similar reference water and calibrate the new reference water relative to international standards (see Annual Calibration Check below).
5. Only clean, dionized waters or similarly low ionic strength waters should be used as SPATIAL facility reference waters. Reference waters used in routine operation of the CRDS instruments should span the majority of the range of isotope ratios normally encountered in unknown samples, nominally between -150‰ and +10‰ for $\delta^{2}H$ and -15‰ and 0‰ for $\delta^{18}O$.

Monthly Monitoring

1. As a component of the lab's quality assurance practices, the SPATIAL facility manager should review CRDS instrument calibration and QC parameters stored in the "Spatial_WI" database at the end of each calendar month. These values are stored in the table "Parameters_table" and a set of functions for analyzing and reviewing parameters can be run using the "Parameters_analysis.R" script.
    a. Values of the memory correction parameters should be checked for stability (for the first two, largest, correction terms for each element the standard deviation should be no more than 20% of the average parameter value across the month). Memory correction terms will increase as the vaporizers accumulate solutes, and when any memory correction term exceeds 12% the quality control metrics for that instrument should be monitored closely and vaporizer cleaning scheduled.
    b. Secondary reference water (QC reference) values for runs that have passed quality control screening should not vary by more than 0.9‰ for $\delta^{2}H$ and 0.12‰ for $\delta^{18}O$ (1 standard deviation). If monthly values exceed these thresholds the data from individual runs should be reviewed to identify and remedy potential errors in data processing or any systematic changes in instrument performance and their cause.
2. The number of 'bad' runs (analysis batches rejected based on QC results) on each instrument during the previous month should be checked. Unless unusual sample types (e.g., samples with high solute loads, plant extracts) were being run no more than 5 – 10 % of all runs should be expected to be flagged as bad (i.e. 1 or 2 per month on any instrument). Numbers in excess of this may indicate deterioration in instrument performance due to contamination of the vaporizer or laser ageing. Troubleshooting should be conducted and corrective action taken before additional sample analyses are run.
3. Vaporizer cleaning instructions and hardware provided by Picarro are available in the lab's CRDS work area and should be used to remove solutes from the vaporizer chamber when memory correction parameter values exceed tolerances and a reduction in instrument precision is noted based on the number of 'bad' runs or poor reproducibility of QC reference water values.

Annual Calibration Check

1. SPATIAL reference water values should be checked against international standards at the beginning of each calendar year (ideally in the first half of January).
2. Separate vials of the international standard waters should be run as 'unknown' samples in at least 4 analysis batches on 2 different instruments (if operational) over a period of 2 weeks. Data should be evaluated using the normal SPATIAL data reduction procedures.
3. Average measured values for δ^2H and $\delta^{18}O$ of the VSMOW and USGS47 standards serve as the primary criteria for evaluation of the check. These should be within 0.1‰ and 0.9‰ of the certified values for $\delta^{18}O$ and δ^2H, respectively. SLAP values lie well outside of the range of isotopic values for samples normally analyzed at the SPATIAL facility and should be used as a secondary qualitative check.
4. If the check values lie outside of the accepted range sample analyses should be stopped and a recalibration of the SPATIAL reference water values should be conducted according to the following guidelines.
    a. Reduced international standard data from the reference check runs should be used to calculate average and standard deviation values for each of the international standards.
    b. These values should be input to the R script "Recal_script.R", which when run will calculate updated SPATIAL reference water values based on a 3-point linear calibration to the international standard values and conduct a numerical propagation of uncertainty for those values.
    c. New calibrated SPATIAL reference water values can be adopted when the combined uncertainty of the calibrated values is better than 0.1‰ for $\delta^{18}O$ and 0.9‰ for δ^2H. If these targets are not achieved additional check runs should be conducted until the criteria are reached.
5. Recalibrated reference water values should be updated in the "CRDS_liquid_parameters.csv" file in the Dropbox share Reference_materials folder. An archive copy of the previous version of the file should be saved, noting the date of depreciation of the previous values.

Change Log

Version	Date	Changes	By
1.00	2015	Original version	Gabe Bowen
1.01	1/2020	Annual calibration to use normal analytical setup and treat standards as unknowns	Gabe Bowen
1.02	1/2021	Change maximum period of storage for calibrated standards from 5 years to 3 years; clarify that separate vials should be used for each analysis batch in annual calibration checks.	Gabe Bowen
1.03	1/2023	Update to reflect use of USGS47 in place of GISP, which is no longer available.	Gabe Bowen

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QUALITY ASSURANCE MANAGEMENT PLAN

OCTOBER 2017

The approaches and practices described within are used to ensure that the SIRFER laboratory is providing data that are accurate, precise, and meet the requirements expected in a high quality stable isotope analysis laboratory.

TABLE OF CONTENTS

Contents

SIRFER – QUALITY ASSURANCE MANAGEMENT PLAN

Introduction

PREFACE

The Stable Isotope Ratio Facility for Environmental Research (SIRFER) at the University of Utah in Salt Lake City, UT, USA was established to provide the scientific community with the highest quality stable isotope ratio analyses of hydrogen, carbon, nitrogen, oxygen, and sulfur. This quality assurance management plan (QAMP) addresses the quality control and quality assurance measures required for the operation of SIRFER. The approaches and practices described here are used to ensure that the SIRFER laboratory is providing data that are accurate, precise, and meet the requirements expected in a high quality stable isotope analysis laboratory. This manual is structured to satisfy U.S. Environmental Protection Agency guidelines as described in the Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans, QAMS-005/80.

PURPOSE

The purpose of this manual is to describe how quality assurance (QA) and quality control (QC program) activities are applied to SIRFER laboratory practices in order to generate the most precise and accurate data possible. The ultimate goal of SIRFER is to produce quality data that are both accurate and precise. The QAMP is designed to control and monitor laboratory activities, ensuring the laboratory meets these data quality objectives.

The QAMP will be carried out under the direction of the Facility Manager who reports directly to the SIRFER Steering Committee. The QAMP covers all aspects of the laboratory including:

- Sample collection/receipt and storage
- Sample preparation
- Sample analysis
- Result reporting

SIRFER – QUALITY ASSURANCE MANAGEMENT PLAN

ORGANIZATION AND RESPONSIBILITIES

Steering Committee

The Steering Committee is ultimately responsible for ensuring that the data produced at SIRFER meet the criteria set forth in the QAMP. The Steering Committee is responsible for all operational activities within the laboratory and is accountable for all data generated by the laboratory. QA responsibilities for the Steering Committee consist of:

- Final authority on all analytical procedures and SOPs used by laboratory personnel.
- Coordination with the Facility Manager to implement the QAMP.
- Auditing the QAMP to ensure that all objectives and procedures are being followed.

Facility Manager

The Facility Manager is responsible for the daily operation of SIRFER, including instrument maintenance, training of new personnel, and instrument/method development. Key QA/QC responsibilities of the Facility Manager include:

- Participation in preparing the QAMP.
- Method development, preparation and analysis of samples, and data analysis.
- Documentation of QC activities associated with a project.
- Identification and initiation of any appropriate corrective actions as determined by QC procedures.
- Interaction with the Steering Committee regarding QA/QC.

Analysts.

Analysts perform routine daily tasks, including sample preparation and sample analysis. Analysts are responsible for ensuring the quality of the results during analytical procedures. Key QA/QC responsibilities and duties for an Analyst include:

- The use of established SIRFER methods and procedures, such as SOPs, and documentation of any deviations that occurred during sample analysis.
- Documentation of any preventive maintenance performed.
- Maintenance of up-to-date laboratory notebooks and other record-keeping systems.
- Reporting to the Facility Manager all QC problems encountered and the corrective actions taken in response.

SIRFER – QUALITY ASSURANCE MANAGEMENT PLAN

Analytical Capabilities

ANALYSES PERFORMED

SIRFER can perform the following isotope ratio analyses:

- Hydrogen isotope ratio analysis of gases, liquids, and organic and inorganic solids.
- Oxygen isotope ratio analysis of gases, liquids, and organic and inorganic solids.
- Carbon isotope ratio analysis of gases and organic and inorganic solids.
- Nitrogen isotope ratio analysis of gases and organic and inorganic solids and liquids.
- Sulfur isotope ratio analysis of organic and inorganic materials.

OVERVIEW OF PROCEDURES

When samples are collected by or received at SIRFER, the following procedures are followed:

Samples are logged into a database, which assigns a unique SIRFER laboratory number to each sample. This unique identifier is used to track the sample during preparation and analysis.

Samples are prepared for isotopic analysis using established procedures, followed by analysis for isotopic composition.

After isotope ratio analysis, the measured data are corrected using a series of established templates. Data are corrected using primary laboratory reference materials (PLRMs) that were analyzed alongside the samples. Corrected data are reported on accepted international scales.

EQUIPMENT AT SIRFER

Sample Preparation and Analysis Equipment

Device, with manufacturer information	Quantity
Finnigan MAT 253 Isotope Ratio Mass Spectrometer	1
Thermo Finnigan Delta Plus Advantage Isotope Ratio Mass Spectrometer	1
Thermo Finnigan Delta Plus XL Isotope Ratio Mass Spectrometer	2
Thermo Finnigan Delta Plus Isotope Ratio Mass Spectrometer	1
Thermo Finnigan Delta V Isotope Ratio Mass Spectrometer	2
Carla Erba 1108 Elemental Analyzer	2
Carla Erba 1110 Elemental Analyzer	1
Costech Analytical 4010 Elemental Analyzer	1
Thermo Fisher IRMS Flush EA (CNS)	1
Thermo Finnigan Trace Gas Chromatograph/Trace Mass Spectrometer	1
Thermo Finnigan Trace Gas Chromatograph	2
Thermo Finnigan High Termperature/Conversion Elemental Analyzer	4
CTC Analytics GC PAL Autosampler	4
LabConCo Freeze Zone Freeze Dry System	1
Retsch MM-200 Mixer Mill	1
Waters Delta 600 HPLC System	1
Beckman Coulter Allegra 64R Centrifuge	2
LabLine Orbit Environ Shaker	1
Linberg/Blue M Muffle Furnace	2
Sartorius MC-5 Microbalance	2
Perkin-Elmer AD-4 Autobalance	1
Picarro cavity ring-down water analyzer	2

Isotope Ratio Mass Spectrometers

Model	Options/ Peripherals	Element	Gas Form
Finnigan	Dual inlet	^{2}H	H_2
Delta Plus	Elemental analyzer	^{34}S	SO_2
XL	Laser analyzer	^{13}C, ^{18}O	CO_2
Finnigan	Dual inlet	^{13}C, ^{15}N, ^{18}O, ^{2}H	CO_2, N_2, H_2
Delta Plus	GC/GP interface	^{13}C, ^{18}O	CO_2
Advantage	Elemental analyzer	^{13}C, ^{15}N	CO_2, N_2
Finnigan	Elemental analyzer	^{13}C, ^{15}N, ^{18}O	CO_2, N_2
Delta Plus	Gas bench	^{13}C, ^{18}O	CO_2
Finnigan	TC/EA (solid)	^{2}H, ^{18}O	CO, H_2
Delta Plus	GC-C	^{13}C	CO_2
XL	GC-TC (solid)	^{2}H	H_2
Finnigan	Dual inlet	^{13}C, ^{15}N, ^{18}O, ^{2}H	CO_2, N_2, H_2
Delta Plus	TC/EA (solid)	^{2}H, ^{18}O	CO, H_2
XL	TC/EA (liquid)	^{2}H, ^{18}O	CO, H_2
Finnigan	Dual inlet	^{13}C, ^{15}N, ^{18}O	CO_2, N_2
MAT 253	GasBench	^{13}C, ^{18}O, ^{2}H	CO_2, water
	Elemental analyzer	^{13}C, ^{15}N	CO_2, N_2
	GasBench	^{15}N, ^{18}O	N_2O, water
Finnigan	GC-C		CO_2
Delta V	TC/EA (liquid)	^{2}H, ^{18}O	CO, H_2
	GC-TC	^{2}H	H_2
Finnigan	TC/EA (solid)	^{2}H, ^{18}O	CO, H_2
Delta V	IRMS Flash EA	^{13}C, ^{15}N, ^{34}S	CO_2, N_2, SO_2

Data Management

DATA VALIDATION

SIRFER makes extensive use of a laboratory information management system (LIMS) to control sample processing and data analysis. LIMS records information about the samples, stores the analytical raw results, corrects the analytical results using standardized algorithms and templates, and normalizes the results to international scales. LIMS monitors instrument parameters and can provides notification to the Analyst of abnormalities. The LIMS provides statistics on laboratory reference materials (long-term precision and reproducibility) plus a record of all correction factors.

Validation of data consists of a three-step process:

- Step 1 – Analyst Review
- Step 2 – LIMS Validation
- Step 3 – QA Approval

Analyst Review is the primary responsibility of the Analyst. The Analyst monitors instrument stability and is responsible for the initial examination of the measured isotope ratio data. The Analyst assesses the quality of the analysis based upon the following guidelines:

- The appropriate sample preparation and analysis SOPs have been followed.
- Sample preparation is correct and complete.
- Analytical results are correct and complete.
- QC sample data are within established acceptable limits.

LIMS Validation identifies data outliers, assesses instrument stability, notifies the Analyst of non-conforming instrument parameters, and verifies that the corrected/normalized data meet the criteria set forth in the appropriate SOP.

QA Approval is the final assessment of the data before acceptance. QA Approval is an independent assessment of the corrected and normalized isotope ratio data by a SIRFER employee other than the Analyst and must confirm the following:

- The reported results meet tolerances specified in the appropriate SOPs.
- The reported results are traceable to internationally accepted standards.
- The results for a given sample are traceable throughout the entire analytical process.

CF-IRMS Results

Following continuous flow-isotope ratio mass spectrometry (CF-IRMS) analysis, a LIMS-based template is used to correct raw isotope data. All measured results outside the acceptable tolerances are subject to review/re-analysis. Those tolerances are:

- Linearity isotope correction, based on the slope of a simple linear equation between the defined (known) and measured isotope ratios of two primary laboratory reference materials (PLRMs). Tolerance: ± 5 %**.**
- Linearity isotope/area correction, based on the slope of a simple linear equation between peak areas and the measured isotope ratios of all PLRMs and secondary laboratory reference materials (SLRMs). Tolerance: ± 10%.
- Precision of PLRMs, based on the standard uncertainty of all linearity corrected PLRMs within an analytical run.
- Accuracy of SLRM(s), based on the standard uncertainty of all SLRMs corrected using the PLRMs within an analytical run.

DI-IRMS Results

Following dual inlet-isotope ratio mass spectrometry (DI-IRMS) analysis, a LIMS-based template is used to correct raw isotope data. All measured results outside the acceptable tolerances are subject to review/re-analysis. Those tolerances are based on the standard uncertainty of the PLRM(s) within an analytical run and are defined as:

- The standard uncertainty (1-sigma) for carbon isotopes is ± 0.05 ‰.
- The standard uncertainty (1 sigma) for nitrogen isotope is ± 0.08 ‰.
- The standard uncertainty (1-sigma) for oxygen isotopes is ± 0.15 ‰.
- The standard uncertainty (1-sigma) for hydrogen isotopes is ± 2.0 ‰.
- The standard uncertainty (1-sigma) for sulfur isotopes is ± 0.4 ‰

CORRECTIVE MEASURES

When analytical anomalies are encountered, corrective action is necessary. The need for corrective action can be identified in a number of ways:

- QC data lying outside acceptable limits for a given analytical run
- Unusual deviations in reference gas isotope ratios
- CF-IRMS timing problems
- Deficiencies detected by reviewing analytical data such as double dropped samples and incorrectly entered information
- Poor chromatography

It is generally the responsibility of the Analyst to identify anomalies and take corrective action. If the analyst cannot correct the problem, the matter is referred to the Facility Manager. The following corrective action steps are then taken:

- Identification of the problem
- Investigation and determination of the cause of the problem
- Corrective action determined to eliminate the problem
- Assignment of responsibility for implementing corrective action
- Evaluation of the effectiveness of the corrective action
- Verification that the corrective action has eliminated the problem
- Documentation of the problem and corrective action taken

Data Reporting

UNCERTAINTY

Using QUAM2000[1] as a guide, the following definitions apply to the measurement of uncertainty at SIRFER:

Standard uncertainty

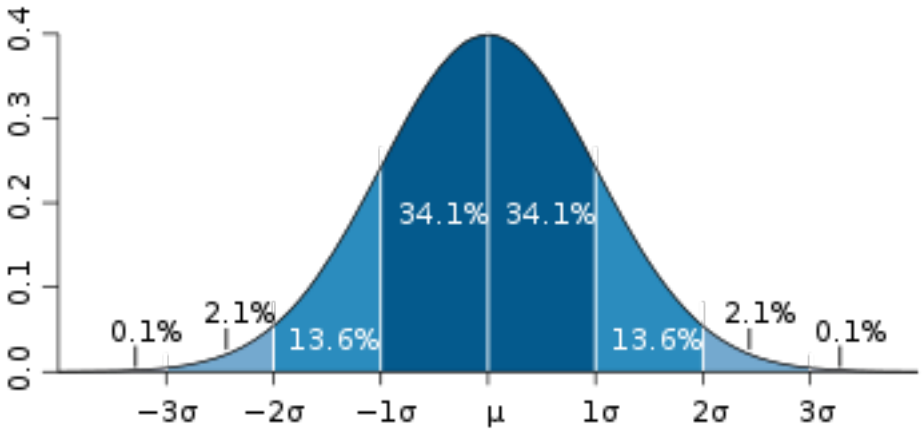
The statistically estimated standard deviation of the mean.

Expanded standard uncertainty

A measure of the uncertainty surrounding a measurement within which the true value should lie. The expanded standard uncertainty is obtained by multiplying the standard uncertainty by a coverage factor.

Coverage factor

The desired level of confidence of a measurement; the coverage factor is typically 2 – 3. When working with normal distributions, the coverage factor can be generally defined as 'sigma' (see figure below).



[1] EURACHEM / CITAC Guide CG 4: Quantifying Uncertainty in Analytical Measurement, Second Edition.

Based on duplicate analyses of SLRM within an IRMS analysis, the calculated standard uncertainty of the SLRM is used to estimate the uncertainty of the IRMS measurements. If the standard uncertainty is greater than the tolerance listed in the appropriate SOP, all samples within the analysis are re-analyzed. Re-analyzed samples must meet the criteria such that the expanded standard uncertainty of duplicate SLRM measurements is better than the 2× the tolerance listed in the appropriate SOP.

Thus, there is an ~ 95 % probability the re-analysis of any given unknown would be within a 2-sigma tolerance of the original result.

INTERNATIONAL STANDARDS

The international stable isotope analysis community has defined several standards to be used to reference isotope measurements:

Standard	Isotope Ratio	Isotope Ratio Value
Vienna Pee Dee Belemnite (VPDB)	$^{13}C/^{12}C$	0.0112372
	$^{18}O/^{16}O$	0.0020671
Vienna Standard Mean Ocean Water (VSMOW)	$^{18}O/^{16}O$	0.0020052
	$^{2}H/H$	0.00015576
Atmospheric Air (AIR)	$^{15}N/^{14}N$	0.0036765
Vienna Canyon Diablo Troilite (VCDT)	$^{34}S/^{32}S$	0.04500451

By definition, the isotopic composition of VPDB, VSMOW, AIR, and VCDT is $\delta = 0$ ‰.

The International Atomic Energy Agency (IAEA), the National Institute of Standards and Technology (NIST), and the U.S. Geological Survey (USGS) are responsible for the distribution of certified reference materials that have been calibrated to these international standards. There certified materials are typically available only in small quantities. These international reference materials can be used to calibrate “in-house” reference materials for day-to-day operation.

LABORATORY REFERENCE MATERIALS

SIRFER uses a variety of laboratory reference materials in day-to-day operation.

Primary laboratory reference materials

Primary laboratory reference materials are materials that have been directly calibrated against internationally-available reference materials. During analysis, primary laboratory reference materials are used that have a sufficiently broad isotope and/or elemental composition range such that measured sample data are bracketed by the values of two primary laboratory reference materials. These primary laboratory reference materials are the basis upon which the measured data are normalized and corrected to international isotope scales.

Secondary laboratory reference materials

Secondary laboratory reference materials are materials included in the analytical run and treated as unknown samples for the purpose of assessing the accuracy of the data corrections completed using the primary laboratory reference materials. During LIMS Validation, corrected data from secondary laboratory reference materials are compared to the values established for those materials. Before any data can be accepted, the values for the secondary laboratory reference materials must fall within established and expected limits. If the results fall outside those limits, some or all of the sample results are unacceptable. Corrective steps are then taken and filed with the Facility Manager. After the corrective action, the suspect samples are re-analyzed.

Primary laboratory reference gases

Primary laboratory reference gases consist of gases that have been calibrated against internationally-available reference materials. During a DI-IRMS analysis, a primary laboratory reference gas is selected that has an isotope composition similar to that of the sample isotope value. These primary laboratory reference gases are the basis upon which the samples are corrected to international scales.

VERIFICATION OF PLRM AND SLRM DATA

All PLRMs and SLRMs are compared to appropriate international reference materials at regular, scheduled intervals to confirm that the accepted PLRM and SLRM isotope values have not changed. Long-term records of these comparisons are maintained for QA purposes.

The accuracy of the PLRM and SLRM review is defined as samples analyzed in dual-inlet mode with the following uncertainties –

- The standard uncertainty (1-sigma) for carbon isotopes: ± 0.05 ‰.
- The standard uncertainty (1 sigma) for nitrogen isotopes: ± 0.08 ‰.
- The standard uncertainty (1-sigma) for oxygen isotopes: ± 0.15 ‰.
- The standard uncertainty (1-sigma) for hydrogen isotopes: ± 2.0 ‰.
- The standard uncertainty (1-sigma) for sulfur isotopes: ± 0.4 ‰.

PROCEDURES FOR UNACCEPTABLE DATA

In the event that the SIRFER laboratory cannot provide certified isotope results to the end-user due to sample issues (heterogeneity, evaporation of liquids, etc.), SIRFER procedures are as follows:

The Facility Manager shall contact the end-user about replacement of the samples before re-analysis.

If replacing the samples is not possible or if data generated during re-analysis are still deemed unacceptable:

The end-user can accept uncertified data after the Facility Manager has informed the end-user of the sample problems encountered and what corrective actions were taken in an attempt to certify the results.

In the event that neither of the above options is possible, the Facility Manager shall:

Inform the end-user that SIRFER was not able to successfully measure the isotope composition of the samples. All remaining sample material shall then be returned to the end-user.

SIRFER – QUALITY ASSURANCE MANAGEMENT PLAN

Quality Assurance

REFERENCE MATERIALS

$\delta^{13}C$, $\delta^{15}N$, $\delta^{2}H$, $\delta^{18}O$, $\delta^{34}S$: Solids, Continuous Flow

Two different primary laboratory reference materials (PLRM) of known isotopic composition are included in every run for normalization purposes. In addition, quality control secondary laboratory reference materials (SLRM) are included in each analytical run. For $\delta^{13}C$, $\delta^{15}N$, $\delta^{2}H$, $\delta^{18}O$, and $\delta^{34}S$ analysis there is at least one PLRM for every twelve unknowns. For $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$ analysis of solid material, individual samples are analyzed once during an analytical run with the following exception: two unknown samples are run in duplicate during an analytical run. For $\delta^{18}O$ and $\delta^{2}H$ analysis of solid material, all samples are analyzed in duplicate during an analytical run.

$\delta^{13}C$: Liquids, Continuous Flow

Two different primary laboratory reference materials (PLRM) of known isotopic composition are included with the samples for normalization purposes. In addition, quality control secondary laboratory reference materials (SLRM) are included. Individual samples are analyzed in duplicate during an analytical run.

$\delta^{2}H$ and $\delta^{18}O$: Water, Continuous Flow

Waters of known isotopic signatures are included in every run for normalization purposes, including PLRM and SLRM. These reference materials have been calibrated against accepted internationally-available water reference materials. These PLRM and SLRM are analyzed after ten samples with the order of analysis reversed every set to allow LIMS to correct for memory effects and signal drift. All sample vials are analyzed in duplicate during an analytical run.

$\delta^{13}C$, $\delta^{15}N$, $\delta^{18}O$, $\delta^{2}H$: Pure Gases, Dual Inlet

Samples are compared to two PLRM gases of known isotopic composition using dual inlet methods. The PLRM gases are generated offline via in-tube combustion followed by cryogenic trapping and collection of the product gas. All gases (PLRM and unknown) are run against calibrated reference gases. The reference gases have been calibrated against accepted internationally-available reference materials.

$\delta^{13}C$ and $\delta^{18}O$: Atmospheric Gas

Samples are analyzed for $\delta^{13}C$ and $\delta^{18}O$ using continuous flow methods and the samples are compared to multiple atmospheric PLRM of known isotopic signatures and CO_2 concentrations. The $\delta^{13}C$ and $\delta^{18}O$ isotopic composition of the PLRM is measured by extracting the CO_2 from the mixture and comparing this extracted CO_2 to pure gases of known isotopic composition using DI-IRMS.

The CO_2 concentrations of the primary cylinders have been measured by the NOAA/CMDL/CCGG (National Oceanic and Atmospheric Administration / Climate Monitoring and Diagnostics Laboratory / Carbon Cycle Gases Group). This measurement by NOAA/CMDL places SIRFER on the WMO (World Meteorological Organization) CO_2 mole fraction scale.

Note on N_2O:

Correcting atmospheric CO_2 for the presence of N_2O is necessary if the $\delta^{13}C$ and $\delta^{18}O$ values of CO_2 need to be measured accurately because the raw CO_2 isotopic data contains a N_2O contribution, which accounts for about 0.2% of the mass 44 signal.

SIRFER employs the following method to eliminate N_2O:

Gas chromatography separation of N_2O and CO_2. This method results in complete separation of N_2O and CO_2 using a packed Porapak Q column. The method allows automated on-line applications and is invaluable for samples with high and/or variable N_2O content.

Definitions and Terms

CONTINUOUS FLOW IRMS (CF-IRMS)

A system for the introduction of a sample into the isotope ratio mass spectrometer using a helium carrier gas. Prior to introduction, the sample is converted to a gas using various automated sample preparation devices, including, but not limited to, elemental analyzers (EA) and gas chromatographs (GC).

DELTA VALUES

The notation used for expressing isotope results, represented by the Greek symbol δ. Delta values are typically presented in units of per mil (‰). One per mil represents a one-part-per-thousand difference between a sample and an international standard.

DUAL INLET IRMS (DI-IRMS)

A system for the introduction of a pure gas sample into the isotope ratio mass spectrometer. Samples are prepared (i.e., converted into simple gases) off-line. Once prepared, the pure gas is admitted into the mass spectrometer where comparisons are made between the isotopic compositions of the gas sample of interest relative to that of a reference gas.

ISOTOPE RATIO MASS SPECTROMETRY (IRMS)

An analytical technique for the precise and accurate measurement of variation in the natural isotopic abundance of light stable isotopes within samples. Measurements are completed using specialized isotope ratio mass spectrometers.

LABORATORY INFORMATION MANAGEMENT SYSTEM (LIMS)

The integrated system used for the management of samples, laboratory users, instruments, reference materials, and other laboratory functions. LIMS includes a software-based component and a process-based component.

PRIMARY LABORATORY REFERENCE MATERIAL (PLRM)

A material that has been directly calibrated against international stable isotope reference materials.

SIRFER – QUALITY ASSURANCE MANAGEMENT PLAN

QUALITY ASSURANCE (QA)

The integrated program that provides SIRFER's customers the assurance that measurement data meet defined standards of quality with a stated level of confidence. QA is essentially the management system for ensuring credible results.

QUALITY CONTROL (QC)

The application of procedures to control the quality of the data generated at SIRFER. The QC system consists of day-to-day activities such as: the following of written protocols; up-to-date and suitable training of personnel; the use of reliable, well maintained and calibrated equipment; the regular use of QC samples; and record keeping. QC operates as a feedback system throughout the analytical process.

SECONDARY LABORATORY REFERENCE MATERIAL (SLRM)

Any material included in an analytical run for the purpose of assessing the accuracy of data corrections completed using the PLRM.

STANDARD OPERATING PROCEDURE (SOP)

A detailed written procedure designed to standardize a sample preparation or sample analysis method or protocol.

SIRFER – QUALITY ASSURANCE MANAGEMENT PLAN

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