



LOS GATOS RESEARCH



DLT-100

Liquid-Water Isotope Analyzer

Automated Injection

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Instrument Setup

AutoInjector Setup

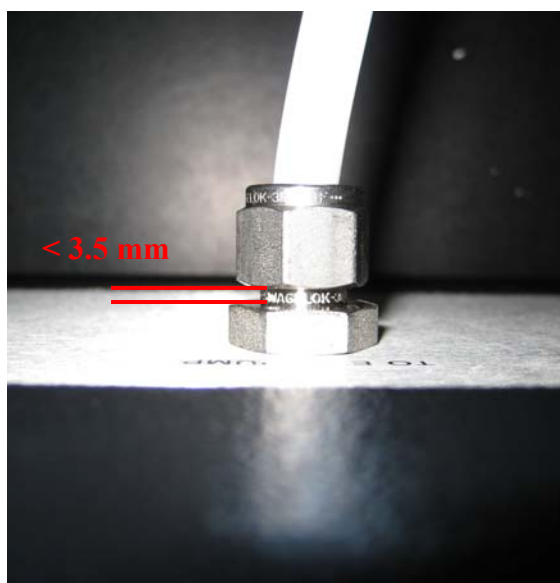
1. Assemble Injection Unit, Keypad terminal, Safety Shield, and Power Supply as per instructions in **Chapter 6 of the LC PAL User Manual**. Place autoloader on the right side of the DLT, and attach keypad to the left side of the autoloader.
2. Setup Trayholder reference position as per instructions in **Chapter 7 of the LC PAL User Manual**. Do NOT have a syringe installed for this step (breakage is possible).
3. Setup septum reference position as per instructions in **Chapter 7 of the LC PAL User Manual**. Use injector “LCVlv1” as the septum location and do NOT have a syringe installed for this step (breakage is possible).
4. Insert syringe as per instructions in **Chapter 8 of the LC PAL User Manual**. Manual priming is not necessary for this syringe. Confirm that the syringe has some resistance when manually actuated. If there is little to no resistance, tighten the syringe nut slightly. When inserting the syringe holder into the Autoinjector, extra caution is required to assure that the syringe needle does not bend.

LWIA Setup

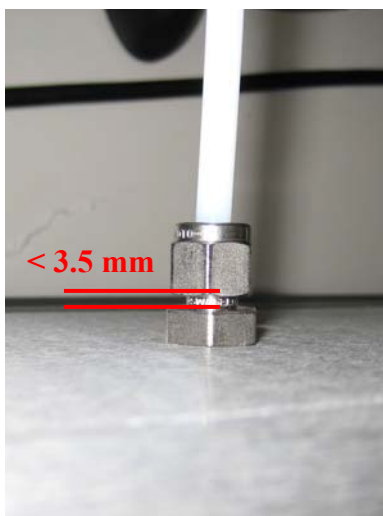
1. Connect the instrument power cord to switched power entry module and the pump power cord to the slave outlet labeled “Ext. Pump Power” on the LWIA. Use the voltage selection switch to select the line voltage (e.g. 115 VAC or 210 VAC).



2. Connect the 3/8" pump connection to labeled 3/8" Swagelok port labeled "To Ext. Pump" on the LWIA via the provided Teflon tubing. The connection should be tightened to 1/4 - 1/2 turn past finger-tight using a wrench and leave a gap of < 3.5 mm.



3. Connect the Drierite Laboratory Gas Drying unit to the labeled 1/4" Swagelok port on LWIA labeled "Dry Gas Inlet" via the provided 1/4" Teflon tubing. The connection should be tightened to 1/4 - 1/2 turn past finger-tight using a wrench and leave a gap of < 3.5 mm. **Remove the plastic gas plug.** (NOTE – if using dry gas from a cylinder or house dry gas system, make sure that the inlet pressure is between 0 – 5 psig).



4. Connect the septum heater plug and 1/8" Teflon tube with filter assembly from the Autoinjector septum block to the back of the LWIA. The connection should be tightened to 1/4 - 1/2 turn past finger-tight using a wrench and leave a gap of < 3.5 mm.



5. Connect the serial communications cable from the Autoinjector to the LWIA serial connector labeled "LC-PAL".

Daily Operation Checklist

Every 1 – 2 days:

1. Change the septum in the autoinjector septum block as described in the “Changing Septa” section.
2. Remove the syringe from the autoinjector and manually rinse with de-ionized water to remove any salt build-up or septum residue that has collected in the syringe. Confirm that the syringe has some resistance when manually actuated. If there is little to no resistance, tighten the syringe nut slightly. When inserting the syringe holder into the Autoinjector, extra caution is required to assure that the syringe needle does not bend.

Every 3 – 6 days:

1. Adjust the Laser Offset, if necessary (as described in the “Adjusting Laser Offset” section).
2. Clean the sample transfer line and filter assembly as described in the “Cleaning the Sample Transfer Line and Filter Assembly” section.

Measuring Samples

NOTE: The below example outlines the measurement of 3 samples with 3 reference standards interspersed between the samples. Each vial is injected 6 times.

The reference standards should be replaced at the beginning of each run to prevent a change in their isotope ratios due to evaporation.

1. Load Tray 1(lower left Tray) with the reference standards (“REF 1” – “REF 3”) in positions 1 – 3.
2. Load Tray 1 with the unknown samples (“SAMPLE 1” – “SAMPLE 3”) in positions 4 – 6.
3. Upon instrument startup, the Run Configuration screen should be displayed:

The screenshot displays the Run Configuration interface with three main sections: Sample List, Run List, and Standard Scripts.

Sample List: A table with columns Name, S/N, Tray, and Position. It contains one entry: Null, 060929-T1-01, 01, 01. Below the table are buttons for Insert, Delete, and Select All, and a Populate Tray section with checkboxes for Tray01, Tray02, Tray03, and Tray04.

Run List: A table with columns Name, S/N, Tray, and Position. It contains one entry: Null, 060929-T1-01, 01, 01. Below the table is a dropdown for Injections per sample set to 1.

Standard Scripts: A section titled Standards To Run with a table having columns Name, S/N, Tray, and Position. It contains one entry: Null, 060929-T2-01, 02, 01. Below this are fields for Run standards after (set to 0) and Start with (set to Samples).

Bottom Bar: Contains icons for Configure, Run, and Spectrum, a status display showing h2o_20060929_000.txt, 10:06:25, 0.0 °C, and 0.000 us, and icons for File Transfer, Setup, and Exit.

- Depress the “INSERT” button 5 times to add 5 additional samples to the SAMPLE LIST:

Sample List | Standard List

Name	S/N	Tray	Position
Null	060929-T1-01	01	01
Null	060929-T1-02	01	02
Null	060929-T1-03	01	03
Null	060929-T1-04	01	04
Null	060929-T1-05	01	05
Null	060929-T1-06	01	06

Up
Down

Insert Delete Select All

Populate Tray ☐ Tray01 ☐ Tray03 ☐ Tray02 ☐ Tray04

Run List

Name	S/N	Tray	Position
Null	060929-T1-01	01	01

Up
Down

Standard Scripts

Standards To Run

Name	S/N	Tray	Position
Null	060929-T2-01	02	01

Up
Down

Run standards after Samples

Start with Samples

Configure Run Spectrum

h2o_20060929_000.txt 10:06:58
0.0 °C 0.000 us

File Transfer Setup Exit

- Using the mouse and keyboard, rename the first 3 samples as the references (“REF 1” – “REF 3”) and last 3 samples appropriately (“SAMPLE 1” – “SAMPLE 3”):

Sample List | Standard List

Name	S/N	Tray	Position
REF 1	060929-T1-01	01	01
REF 2	060929-T1-02	01	02
REF 3	060929-T1-03	01	03
Sample 1	060929-T1-04	01	04
Sample 2	060929-T1-05	01	05
Sample 3	060929-T1-06	01	06

Up
Down

Insert Delete Select All

Populate Tray ☐ Tray01 ☐ Tray03 ☐ Tray02 ☐ Tray04

Run List

Name	S/N	Tray	Position
Null	060929-T1-01	01	01

Up
Down

Standard Scripts

Standards To Run

Name	S/N	Tray	Position
Null	060929-T2-01	02	01

Up
Down

Run standards after Samples

Start with Samples

Configure Run Spectrum

h2o_20060929_000.txt 10:07:37
0.0 °C 0.000 us

File Transfer Setup Exit

- Use the top set of arrow keys (“->”) to transfer samples from the SAMPLE LIST to the RUN LIST. Alternate between the references (“REF 1” ...) and the unknown samples (“SAMPLE 1” ...). After populating the RUN LIST, use the back arrow key (“<-“) to remove the top “NULL” entry. The resulting configuration screen is shown below:

Sample List | Standard List

Name	S/N	Tray	Position
REF 1	060929-T1-01	01	01
REF 2	060929-T1-02	01	02
REF 3	060929-T1-03	01	03
Sample 1	060929-T1-04	01	04
Sample 2	060929-T1-05	01	05
Sample 3	060929-T1-06	01	06

Run List

Name	S/N	Tray	Position
REF 1	060929-T1-01	01	01
Sample 1	060929-T1-04	01	04
REF 2	060929-T1-02	01	02
Sample 2	060929-T1-05	01	05
REF 3	060929-T1-03	01	03
Sample 3	060929-T1-06	01	06

Standard Scripts

Name	S/N	Tray	Position
Null	060929-T2-01	02	01

Run standards after: 0 Samples

Start with: Samples

Configure Run Spectrum File Transfer Setup Exit

h2o_20060929_000.txt 10:08:46 0.0 °C 0.000 us

- Increase the INJECTIONS PER SAMPLE to 6:

Sample List | Standard List

Name	S/N	Tray	Position
REF 1	060929-T1-01	01	01
REF 2	060929-T1-02	01	02
REF 3	060929-T1-03	01	03
Sample 1	060929-T1-04	01	04
Sample 2	060929-T1-05	01	05
Sample 3	060929-T1-06	01	06

Run List

Name	S/N	Tray	Position
REF 1	060929-T1-01	01	01
Sample 1	060929-T1-04	01	04
REF 2	060929-T1-02	01	02
Sample 2	060929-T1-05	01	05
REF 3	060929-T1-03	01	03
Sample 3	060929-T1-06	01	06

Standard Scripts

Name	S/N	Tray	Position
Null	060929-T2-01	02	01

Run standards after: 0 Samples

Start with: Samples

Configure Run Spectrum File Transfer Setup Exit

h2o_20060929_000.txt 10:09:13 0.0 °C 0.000 us

8. The run is now fully configured. Depress the “RUN” button to transfer to the expanded run screen. This screen shows the exact sequence of measurements that will be taking place.

The screenshot displays a software interface for configuring a measurement run. At the top, a table lists the sequence of measurements, including sample names, S/N numbers, tray positions, and DIH values. Below the table, there are fields for 'Testing Sample:', 'Tray xx - Index xx', and 'LCPalStatus'. A large play button is centered below these fields. At the bottom, a status bar shows the file 'h2o_20070313_000.txt', the time '15:40:39', and temperature '26.24 °C'. The bottom of the interface features a row of icons for 'Configure', 'Run', 'Spectrum', 'File Transfer', 'Setup', and 'Exit'.

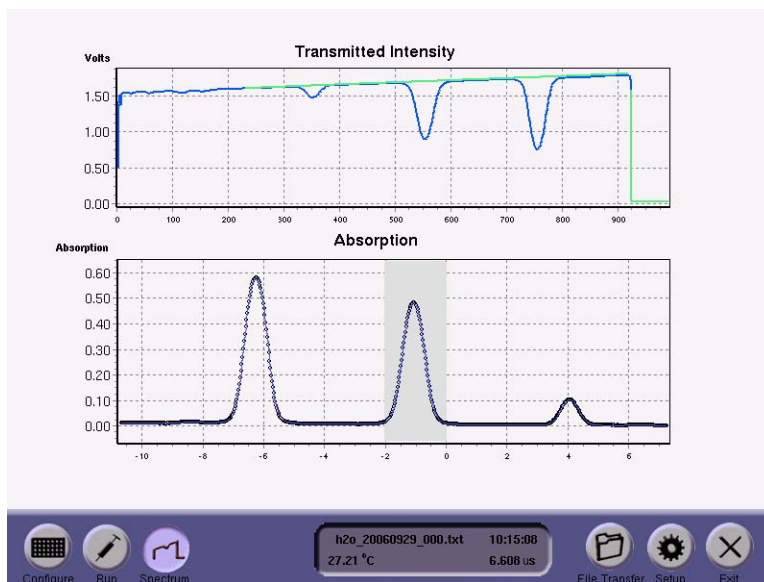
#	Sample Name	Sample S/N	Tray - Pos	DIH	H2O_N_cm3	O18/O16
01	REF 1	070319-T1-01	01-01	-	-	-
02	REF 1	070319-T1-01	01-01	-	-	-
03	REF 1	070319-T1-01	01-01	-	-	-
04	REF 1	070319-T1-01	01-01	-	-	-
05	REF 1	070319-T1-01	01-01	-	-	-
06	REF 1	070319-T1-01	01-01	-	-	-
07	SAMPLE 1	070319-T1-02	01-04	-	-	-
08	SAMPLE 1	070319-T1-02	01-04	-	-	-
09	SAMPLE 1	070319-T1-02	01-04	-	-	-
10	SAMPLE 1	070319-T1-02	01-04	-	-	-
11	SAMPLE 1	070319-T1-02	01-04	-	-	-
12	SAMPLE 1	070319-T1-02	01-04	-	-	-
13	REF 2	070319-T1-03	01-02	-	-	-
14	REF 2	070319-T1-03	01-02	-	-	-
15	REF 2	070319-T1-03	01-02	-	-	-
16	REF 2	070319-T1-03	01-02	-	-	-
17	REF 2	070319-T1-03	01-02	-	-	-
18	REF 2	070319-T1-03	01-02	-	-	-
19	SAMPLE 2	070319-T1-04	01-05	-	-	-
20	SAMPLE 2	070319-T1-04	01-05	-	-	-
21	SAMPLE 2	070319-T1-04	01-05	-	-	-

Testing Sample: Tray xx - Index xx LCPalStatus

h2o_20070313_000.txt 15:40:39
26.24 °C 8.021 us

Configure Run Spectrum File Transfer Setup Exit


9. Depress the PLAY button (play arrow) to start the measurements. The instrument will go through a series of flush cycles (e.g. filling with dry air and then evacuating) for ~ 2 minutes to purge residual water. The autoinjector will then move to position 1 on Tray 1 and transfer ~ 1 microliter of water into the injection port. The needle will remain in the port for 60 seconds, withdraw, and wait 10 seconds to assure complete sample evaporation. The instrument will then start taking data. If the “SPECTRUM” button is depressed, the measured spectrum will be shown. The observed spectrum should be similar to that shown below. Note that the transmission (top panel) should be 0.3 – 3.0 Volts and show marked dips due to the water injection. The absorption spectrum (bottom panel) should show absorption on the order of 10 – 60 %. The large, central peak near -1.0 GHz should be roughly centered in shaded grey box.




10. Over the course of the run, switching back to “RUN” mode will show the measurement list being populated as subsequent samples are measured.



#	Sample Name	Sample S/N	Tray - Pos	D/H	H ₂ O_N ₂ _cm3	O18/O16
01	REF 1	070319-T1-01	01-01	1.58295e-04	3.06334e+16	2.04993e-03
02	REF 1	070319-T1-01	01-01	-	-	-
03	REF 1	070319-T1-01	01-01	-	-	-
04	REF 1	070319-T1-01	01-01	-	-	-
05	REF 1	070319-T1-01	01-01	-	-	-
06	REF 1	070319-T1-01	01-01	-	-	-
07	SAMPLE 1	070319-T1-02	01-04	-	-	-
08	SAMPLE 1	070319-T1-02	01-04	-	-	-
09	SAMPLE 1	070319-T1-02	01-04	-	-	-
10	SAMPLE 1	070319-T1-02	01-04	-	-	-
11	SAMPLE 1	070319-T1-02	01-04	-	-	-
12	SAMPLE 1	070319-T1-02	01-04	-	-	-
13	REF 2	070319-T1-03	01-02	-	-	-
14	REF 2	070319-T1-03	01-02	-	-	-
15	REF 2	070319-T1-03	01-02	-	-	-
16	REF 2	070319-T1-03	01-02	-	-	-
17	REF 2	070319-T1-03	01-02	-	-	-
18	REF 2	070319-T1-03	01-02	-	-	-
19	SAMPLE 2	070319-T1-04	01-05	-	-	-
20	SAMPLE 2	070319-T1-04	01-05	-	-	-
21	SAMPLE 2	070319-T1-04	01-05	-	-	-

Testing Sample: 01 - REF 1 - 070319-T1-01 Tray 01 - Index 01 Flushing Cavity







h2o_20070319_001.txt 15:49:43
26.45 °C 7.884 us

11. The sample run can be stopped or paused at any time via the indicated buttons in the RUN Mode. Note that the current sample will be completed prior to pausing/stopping.
12. Once the run is complete (or prematurely stopped), the data will be saved to the file indicated in the center of the control panel (“h2o_20070319_001.txt”). The data analysis procedure is outlined in a separate section.

Analyzing the Data

Note: An example data analysis procedure presented below. This procedure may be optimized as necessary, depending on the types of samples used.

1. The instrument saves three data files for each run:
 - a. “h2o_(date)_(file #).txt” – This file contains all of the data necessary to determine the δD and $\delta^{18}O$ isotope ratios.
 - b. “h2o_(date)_(file #).lgr.txt” – This file is for diagnostic purposes and can be sent to Los Gatos Research if necessary. It is not needed for regular data analysis.
 - c. “h2o_(date)_(file#).spectrum.txt.bz2” – This file is also for diagnostic purposes and can be sent to Los Gatos Research if necessary. It is not needed for regular data analysis.
2. In the “h2o_(date)_(file#).txt” file, there are 17 columns of data. They contain:
 - a. “Inj_” – The injection number.
 - b. “Sample_name” – The sample name entered in the Run Configuration menu.
 - c. “Sample_S_N” – The sample serial number entered in the Run Configuration menu.
 - d. “Sample_Info” – Not used at this time.
 - e. “Time_sec” – Time elapsed (in seconds) since the run was started. Note that each injection typically requires ~ 300 seconds (5 minutes).
 - f. “Temp_Celsius” – The gas temperature of the water vapor inside the instrument. **Note that the gas temperature should not change at rate faster than 0.3 °C / hour, and show minimal oscillation during the run.** This typically corresponds to a lab temperature change of less than 2 – 3 °C / hour.
 - g. “stdv_Celsius” – The standard deviation of the gas temperature for each measurement. **Note that this parameter should typically be less than 0.004 °C, and a significantly higher value (e.g. 0.01 °C) indicates that the laboratory temperature is changing too rapidly.**
 - h. “H2O_N_cm3” – The number density (molecules/cm³) of water molecules inside the cavity during each measurement. **This number should typically be ~ 2 – 4 × 10¹⁶ molecules/cm³ and should not fluctuate by more than 2 – 4 % (rms fluctuation) over the entire run. A higher fluctuation is indicative of leaking at either the syringe or septum. In this case, replace the septum, remove the syringe, clean and retighten the syringe nut, and re-insert the syringe. If the syringe can be no longer be tightened to give a “silky” feel, replace the syringe.**
 - i. “stdv_H2O” – The standard deviation of the water molecule density for each measurement. Typically this number should be ~1000 times smaller than the

injected water density. A larger standard deviation may be indicative of leaking and will require a septum change and syringe adjustment (see above).

- j. “HOD_H2O” – The measured molecular ratio of $\text{H}^{16}\text{OD}/\text{H}_2^{16}\text{O}$. This number is converted to a D/H atomic ratio and listed in another column.
 - k. “stdv_HOD_HOH” – The standard deviation of the measured $\text{H}^{16}\text{OD}/\text{H}_2^{16}\text{O}$ molecular ratio for each measurement.
 - l. “H2O18_H2O” – The measured molecular ratio of $\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$. This number is converted to a $^{18}\text{O}/^{16}\text{O}$ atomic ratio and listed in another column.
 - m. “stdH2O18_H2O” – The standard deviation of the measured $\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$ molecular ratio for each measurement.
 - n. “D_H” – The measured D/H atomic ratio for each injection. As described below, this number will be converted into an actual D/H atomic ratio using the measured standards and finally converted into δD (‰). **For most natural samples, the D/H atomic ratio should range from $0.9 - 1.6 \times 10^{-4}$.**
 - o. “stdD_H” – The standard deviation of the measured D/H atomic ratio for each measurement. **This number should be ~1000 times smaller than the measured D/H atomic ratio.** Note that multiple measurements (typically 20) are made for every injection and used to determine the D/H ratio; therefore, the actual uncertainty in the measured D/H is substantially smaller than this listed standard deviation.
 - p. “O18_O16” – The measured $^{18}\text{O}/^{16}\text{O}$ atomic ratio for each injection. As described below, this number will be converted into an actual $^{18}\text{O}/^{16}\text{O}$ atomic ratio using the measured standards and finally converted into $\delta^{18}\text{O}$ (‰). **For most natural samples, the $^{18}\text{O}/^{16}\text{O}$ atomic ratio should range from $1.9 - 2.0 \times 10^{-3}$.**
 - q. “stdO18_O16” – The standard deviation of the measured $^{18}\text{O}/^{16}\text{O}$ atomic ratio for each measurement. **This number should be ~3000 times smaller than the measured $^{18}\text{O}/^{16}\text{O}$ atomic ratio.** Note that multiple measurements (typically 20) are made for every injection and used to determine the $^{18}\text{O}/^{16}\text{O}$ ratio; therefore, the actual uncertainty in the measured $^{18}\text{O}/^{16}\text{O}$ is substantially smaller (typically 4.5 times smaller) than this listed standard deviation.
3. Prior to analysis, confirm that Cavity Temperature (“Temp_Celsius”) and injected volume (“H2O_N_cm3”) are within the specifications described above.

4. The only columns required for data analysis are “Sample_name”, “D_H” and “O18_O16”. Example data is shown below for a run that consisted of 5 standards (“Std 10”, “TRIN”, “LGR”, “GSDI”, and “Std 7”) interspersed amongst 5 unknowns (“1”, “2”, “3”, “4”, and “5”). There are 6 injections for each vial:

Sample_name	D_H	O18_O16
Std 10	0.000094369	0.00191978
Std 10	0.000094173	0.00191947
Std 10	0.000094151	0.00191929
Std 10	0.000094035	0.00191939
Std 10	0.000094048	0.00191925
Std 10	0.000094042	0.00191912
1	0.000113518	0.00195421
1	0.000114382	0.00195543
1	0.000114511	0.00195562
1	0.000114625	0.00195576
1	0.000114542	0.00195567
1	0.000114556	0.00195554
TRIN	0.000132183	0.0019844
TRIN	0.000132875	0.00198507
TRIN	0.000133091	0.00198544
TRIN	0.000133148	0.00198545
TRIN	0.000133319	0.0019858
TRIN	0.000133247	0.00198584
2	0.000115629	0.00195685
2	0.000114970	0.00195624
2	0.000114770	0.001956
2	0.000114785	0.00195591
2	0.000114783	0.00195617
2	0.000114646	0.00195603
LGR	0.000140948	0.00199829
LGR	0.000142087	0.00199964
LGR	0.000142211	0.00199954
LGR	0.000142383	0.00200001
LGR	0.000142351	0.00199962
LGR	0.000142411	0.00199991
3	0.000116022	0.00195749
3	0.000114836	0.00195646
3	0.000114529	0.00195674
3	0.000114457	0.00195657
3	0.000114374	0.00195679
3	0.000114385	0.00195701
GSDI	0.000143764	0.00200585
GSDI	0.000145076	0.00200751
GSDI	0.000145346	0.00200746
GSDI	0.000145392	0.00200766
GSDI	0.000145394	0.00200787
GSDI	0.000145578	0.00200744
4	0.000116087	0.00195831
4	0.000114840	0.00195707
4	0.000114513	0.00195707
4	0.000114650	0.00195695
4	0.000114513	0.00195683
4	0.000114652	0.00195639
Std 7	0.000151267	0.00202024
Std 7	0.000152812	0.00202251
Std 7	0.000152988	0.00202325
Std 7	0.000153181	0.0020233
Std 7	0.000153290	0.00202317
Std 7	0.000153381	0.00202381
5	0.000117112	0.00195916
5	0.000115477	0.00195723
5	0.000115064	0.00195692
5	0.000115015	0.00195703
5	0.000114885	0.00195637
5	0.000114903	0.00195645

5. In order to mitigate “memory” effects due to contamination from previously injected samples, the first 3 injections of each sample will be ignored.

6. The D/H and $^{18}\text{O}/^{16}\text{O}$ values for the 4th – 6th injection for each sample will be averaged together to yield:

Sample_name	Measured D H	Measured O18 O16
Std 10	0.0000940420	0.0019192500
1	0.0001145740	0.0019556600
TRIN	0.0001332380	0.0019857000
2	0.0001147380	0.0019560400
LGR	0.0001423820	0.0019998800
3	0.0001144050	0.0019567900
GSDI	0.0001454550	0.0020076600
4	0.0001146050	0.0019567200
Std 7	0.0001532840	0.0020234300
5	0.0001149340	0.0019566200

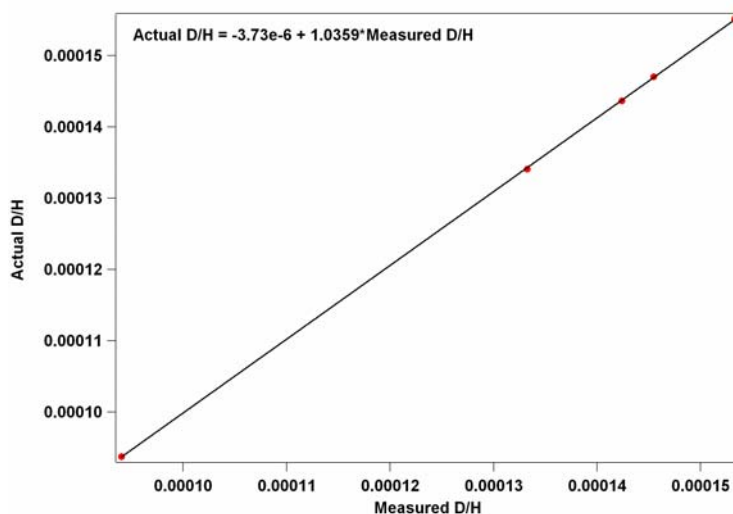
7. Using the known isotope ratios for the standards, δD (‰) and $\delta^{18}\text{O}$ (‰), determine the actual D/H and $^{18}\text{O}/^{16}\text{O}$ atomic ratios for the standards:

$$\frac{\text{D}}{\text{H}} = \left(\frac{\delta\text{D}}{1000} + 1 \right) * 155.76 \times 10^{-6}$$

$$\frac{^{18}\text{O}}{^{16}\text{O}} = \left(\frac{\delta^{18}\text{O}}{1000} + 1 \right) * 2005.2 \times 10^{-6}$$

Sample_name	δD (‰)	Actual D/H	$\delta^{18}\text{O}$ (‰)	Actual $^{18}\text{O}/^{16}\text{O}$
Std 10	-398.1	9.37519e-05	-50.94	0.00190306
1				
TRIN	-139.16	0.000134084	-18.23	0.00196865
2				
LGR	-77.5	0.000143689	-11.55	0.00198204
3				
GSDI	-55.78	0.000147072	-7.97	0.00198922
4				
Std 7	-4.0	0.000155137	-0.071	0.00200506
5				

8. Make a graph of “Actual D/H” versus “Measured D/H” for the standards and fit it to a line. The equation for this line is the relationship between the D/H measured by the instrument and the actual D/H.



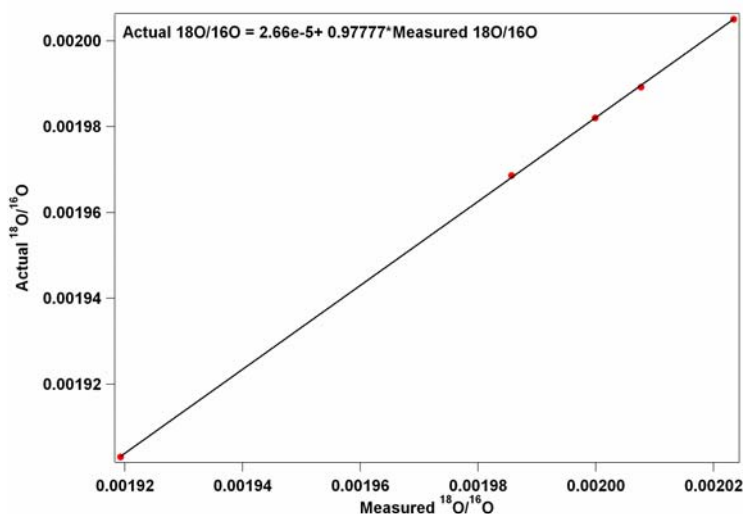
9. Use this relationship to calculate the “Determined D/H” for all of the samples. This determined D/H can be readily converted to δD (‰) for both the standards and samples:

$$\delta D = \left(\frac{\left(\frac{D}{H} \right)}{155.76 \times 10^{-6}} - 1 \right) * 1000$$

Sample_name	δD (‰)	Actual D/H	Determined D/H	Determined δD (‰)
Std 10	-398.1	9.37519e-05	9.36863e-05	-398.521
1			0.000114955	-261.97
TRIN	-139.16	0.000134084	0.000134289	-137.85
2			0.000115125	-260.88
LGR	-77.5	0.000143689	0.000143761	-77.04
3			0.00011478	-263.10
GSDI	-55.78	0.000147072	0.000146944	-56.60
4			0.000114987	-261.77
Std 7	-4.0	0.000155137	0.000155054	-4.53
5			0.000115328	-259.58

Note that the deviation between the Determined δD (‰) and the Actual δD (‰) for the standards is ± 0.88 ‰ (in this case, dominated by inconsistencies in the standards). **This value should be $< \pm 1$ ‰ for the known standards.**

10. Make a graph of “Actual $^{18}\text{O}/^{16}\text{O}$ ” versus “Measured $^{18}\text{O}/^{16}\text{O}$ ” for the standards and fit it to a line. The equation for this line is the relationship between the $^{18}\text{O}/^{16}\text{O}$ measured by the instrument and the actual $^{18}\text{O}/^{16}\text{O}$.



11. Use this relationship to calculate the “Determined $^{18}\text{O}/^{16}\text{O}$ ” for all of the samples. This determined $^{18}\text{O}/^{16}\text{O}$ can be readily converted to $\delta^{18}\text{O}$ (‰) for both the standards and samples:

$$\delta^{18}\text{O} = \left(\frac{\left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)}{2005.2 \times 10^{-6}} - 1 \right) * 1000$$

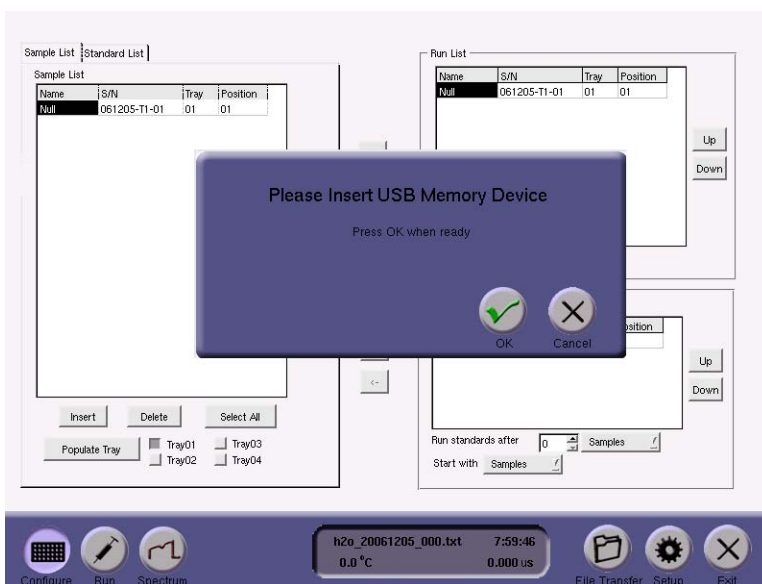
Sample_name	$\delta^{18}\text{O}$ (‰)	Actual $^{18}\text{O}/^{16}\text{O}$	Determined $^{18}\text{O}/^{16}\text{O}$	Determined δD (‰)
Std 10	-50.94	0.00190306	0.00190318	-50.8766
1			0.00193878	-33.12
TRIN	-18.23	0.00196865	0.00196815	-18.47
2			0.00193915	-32.94
LGR	-11.55	0.00198204	0.00198202	-11.56
3			0.00193989	-32.57
GSDI	-7.97	0.00198922	0.00198963	-7.77
4			0.00193982	-32.61
Std 7	-0.071	0.00200506	0.00200505	-0.077
5			0.00193972	-32.65

Note that the deviation between the Determined $^{18}\text{O}/^{16}\text{O}$ (‰) and the Actual $^{18}\text{O}/^{16}\text{O}$ (‰) for the standards is ± 0.16 ‰. **This value should be $< \pm 0.25$ ‰ for the known standards.**

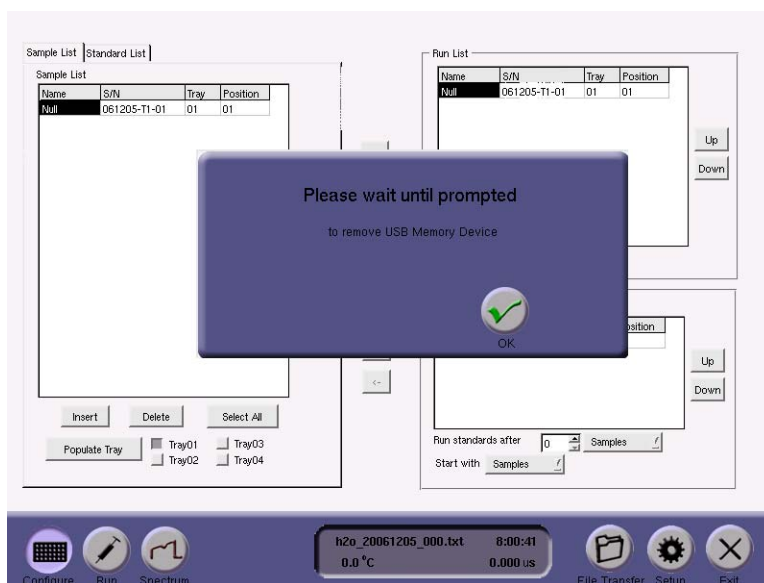
File Transfer

As noted above in the data analysis section, the instrument saves the measured results into files named “h2o_(date)_(file #).txt”, “h2o_(date)_(file #).lgr.txt”, and “h2o_(date)_(file #).txt.spectrum.bz2”. The user may transfer these data files from the instrument hard disk to a USB memory device by undertaking the file transfer process described below.

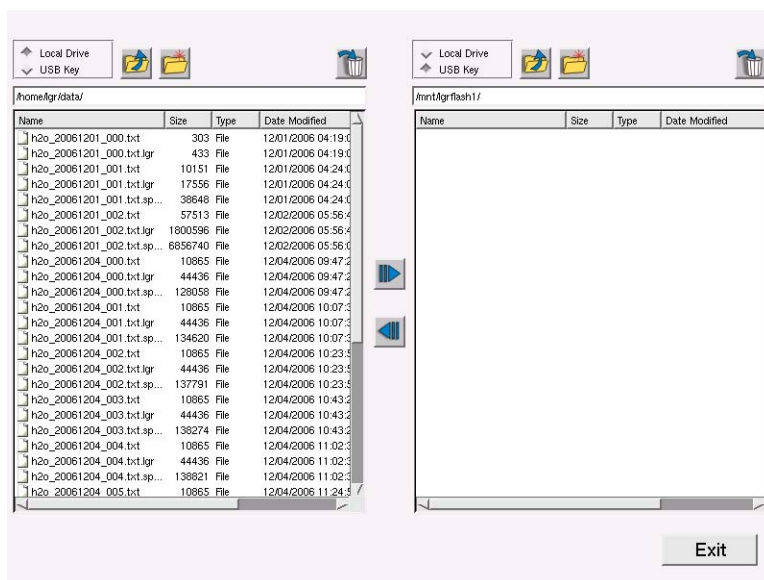
1. Upon instrument startup, the Run Configuration screen should be displayed. Select the “File Transfer” button to initiate the file transfer process. The instrument will prompt the user to insert a USB Memory Device.



2. Insert the USB memory device into the back of the instrument and depress “OK”. The instrument will warn the user to keep the USB device in the instrument until appropriately prompted. Depress “OK” to enter the file transfer screen.

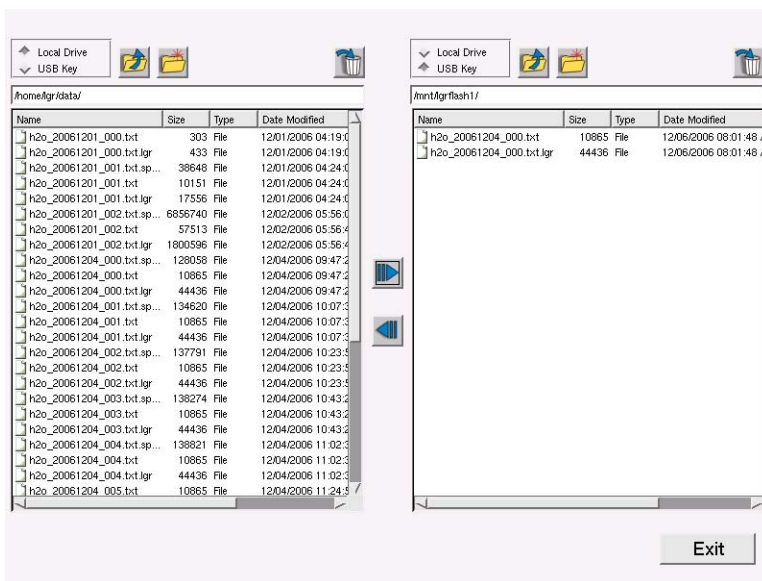


3. The user will see two file directory windows. The directory windows default to the local drive on the left screen and the USB memory device on the right. The directory windows can be changed by clicking the “Local Drive” or “USB Key” radio buttons.

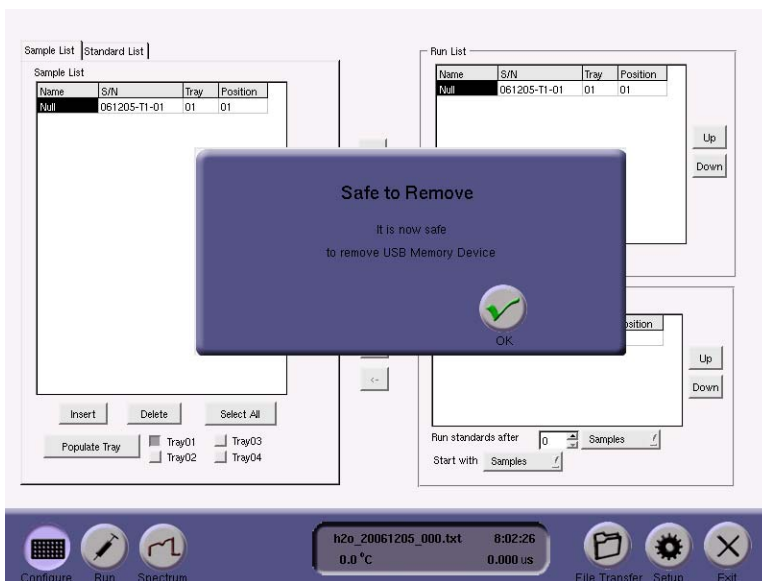


4. The user may use the left mouse button to highlight one or multiple files in the windows and the arrow buttons to copy the files between the directories. The user may also navigate through folders, create directories, and delete files and directories. Files may be managed within the local drive by selecting the “Local Drive” radio button above both directory windows. Files can then be organized into directories by creating a folder, copying the

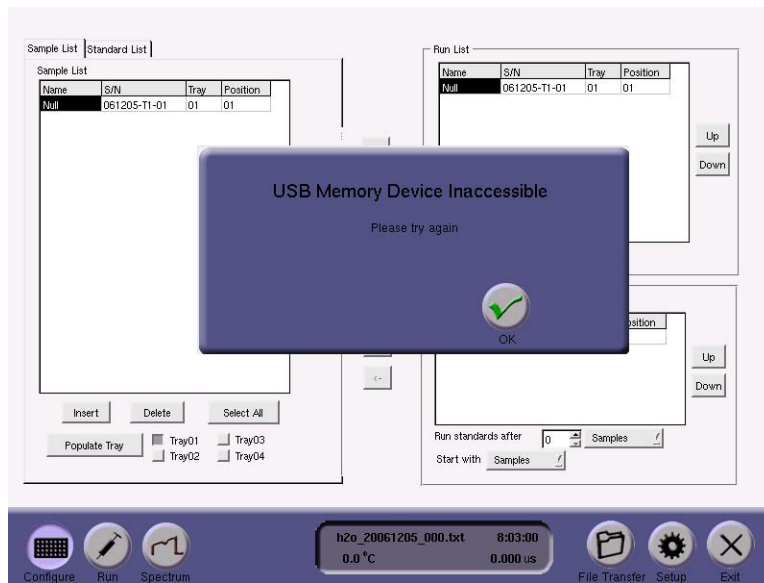
desired files to that folder, then deleting the original files. In the example shown here, “h2o_20061204_000.txt” and “h2o_20061204_000.lgr.txt” have been copied from the instrument hard drive to the USB memory device.



- Once the files have copied, select “Exit” to complete the file transfer process. Note that, if many files are being copied, the instrument may take several seconds to finish the transfer. Once complete, the instrument will prompt the user to remove the USB memory device. Depress “OK” and remove the USB device.



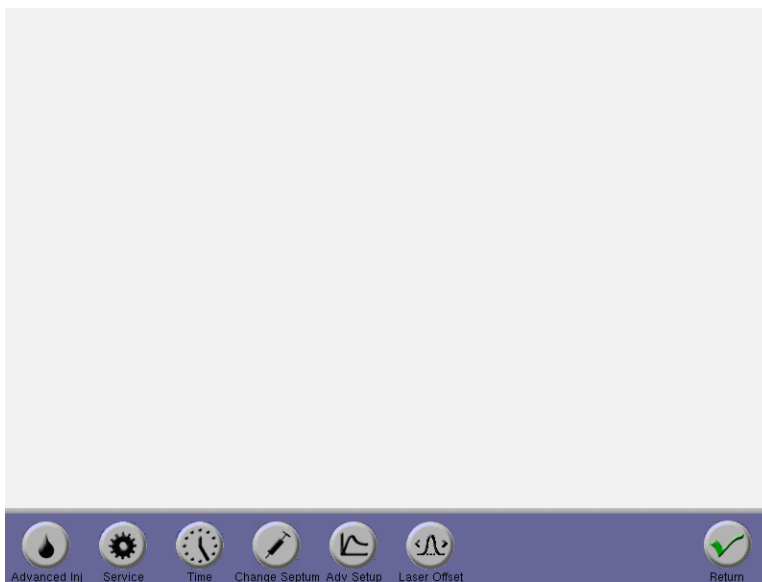
6. Note that, if there is a problem loading the USB device, or the device is not inserted, the instrument will display an error message and allow the user to retry the file transfer process.



Changing Septa

NOTE: Septa should be changed every 200 – 400 injections.

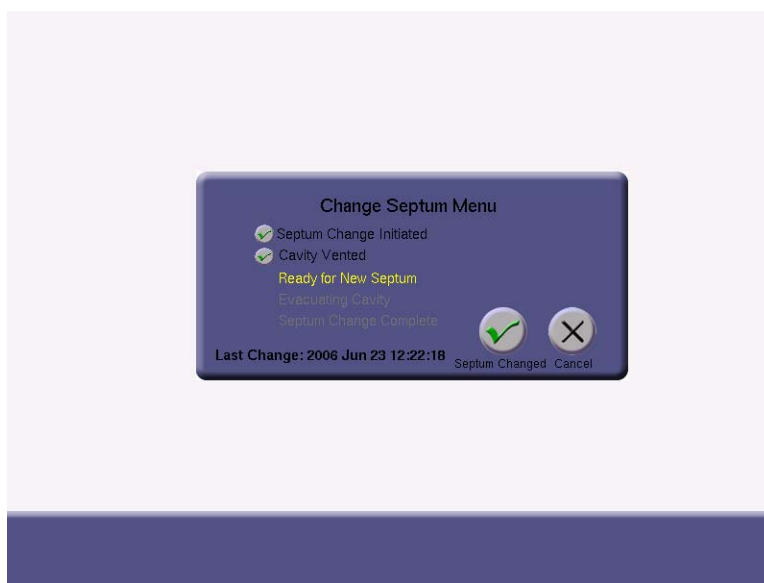
1. Upon instrument startup, the Run Configuration screen should be displayed. Select “SETUP” to enter SETUP MODE.



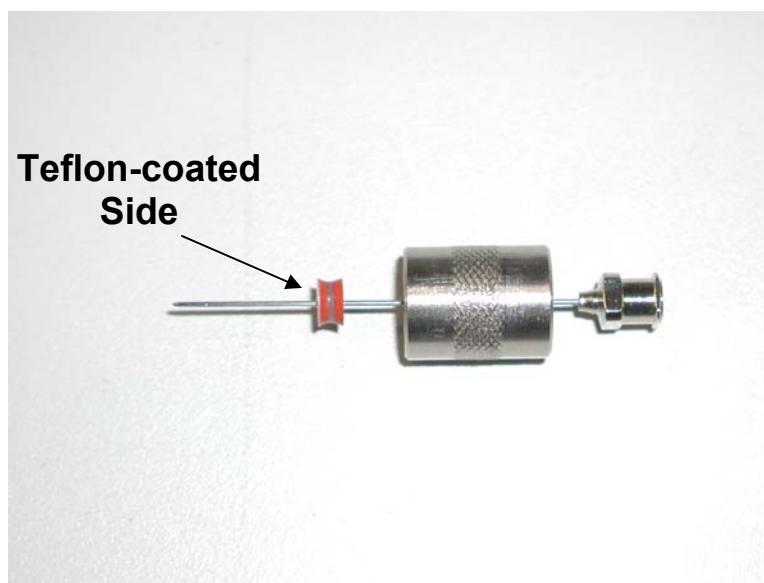
2. Select “CHANGE SEPTUM” to prepare for a septum change.



3. Select the “INITIATE” button. The instrument will start venting and take 180 seconds to come to pressure. Once the cavity has vented, the “READY FOR NEW SEPTUM” line will flash:



4. Unscrew the septum nut. Note that, since the septum holder is heated to $\sim 70\text{ }^{\circ}\text{C}$, appropriate care should be taken in handling the septum hardware. Remove the septum from the septum nut using the provided septum puller.
5. Slide the septum nut and new septum onto a blunt 22-gauge needle (e.g. Hamilton AS tip style or similar) **with the Teflon-coated side of the septum facing away from the septum nut.**



6. Place the whole assembly onto the autoinjector septum block and hand-tighten the septum nut firmly.



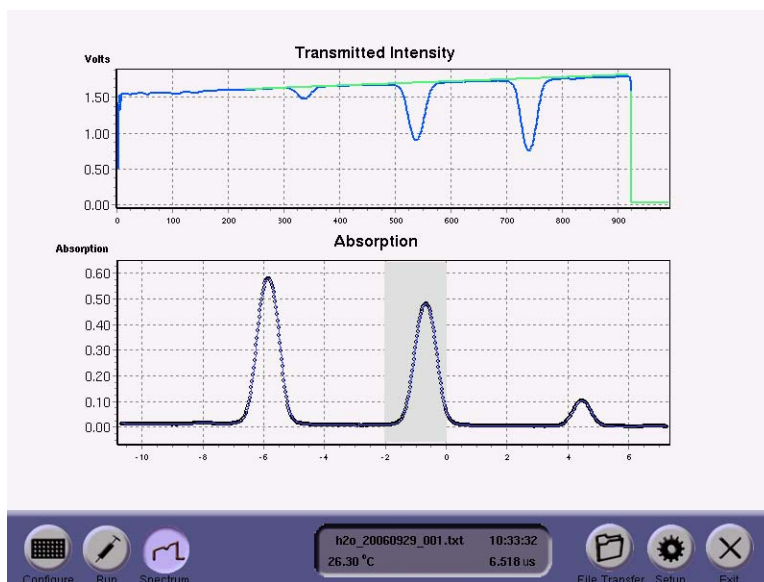
7. Manually actuate the blunt 2-gauge needle a few times to confirm that the septum is adequately pre-drilled.
8. Once the septum change procedure is complete, select the “SEPTUM CHANGED” button. The cell will then be evacuated for 120 seconds prior to the display of “SEPTUM CHANGE COMPLETE”. Hit OK to exit back to SETUP MODE and then RETURN to exit back to the Run Configuration screen.

Adjusting the Laser Offset

The user may need to adjust the laser offset approximately every 3 – 6 days.

NOTE: Do not adjust the laser offset, unless the central peak has drifted by more than $\frac{1}{2}$ division (0.25 GHz).

1. Assess if the laser offset needs to be changed. If the large, central peak shown in the “SPECTRUM” mode is centered in the grey box, there is no need to adjust the laser offset. Over several days, the spectrum will drift to the right. If the central peak has drifted by more than $\frac{1}{2}$ division (0.25 GHz), the laser offset needs to be adjusted. For example, in the screenshot shown below, the central peak has drifted to the right by 1 division (0.50 GHz).



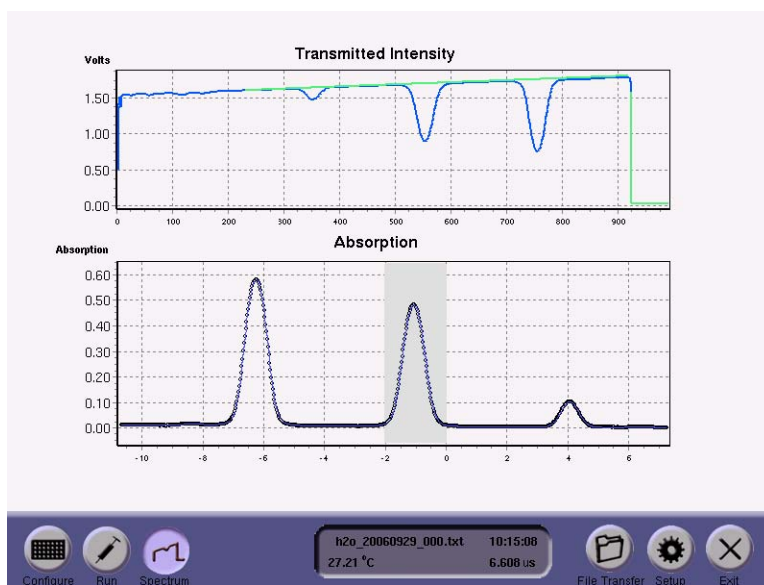
2. In order to adjust the laser offset, enter “SETUP” mode and select the “Laser Offset” button to enter the Laser Offset Adjustment Screen.



3. Depress the “>” softkey to move the central peak left. Since the peak has drifted by 1 division (0.50 GHz) to the right, the softkey must be depressed twice to shift the peaks by 0.50 GHz to the left. Note that the depicted number (“857”) is not relevant.



4. Once the wavelength has been adjusted, exit back to the run configuration screen. Upon injection of the next sample, the “SPECTRUM” mode should show a central peak that is well-centered in the grey box.



Cleaning the Sample Transfer Line and Filter Assembly

NOTE: Small pieces of septa will accumulate over time in the sample transfer line. After ~ 1 week of continuous use (e.g. 2000 – 4000 injections), the sample line and filter assembly should be cleaned to remove these pieces.

1. Shut down the instrument by depressing the “Exit” button. Shutdown will take 3 minutes and assures that the instrument is no longer at vacuum. Turn off the instrument power.
2. Remove the transfer line and filter assembly from the instrument by using a 9/16” wrench to disconnect the 1/4” Swagelok connection at the instrument back panel. **Do NOT unscrew the smaller Swagelok connection between the filter assembly and transfer line.**



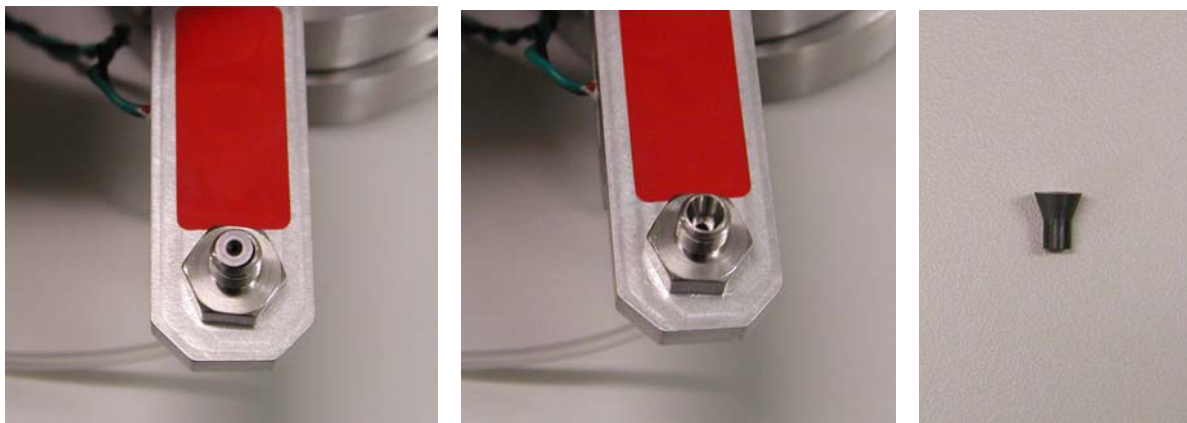
3. IMMEDEATELY cap the instrument using the provided 1/4" Swagelok Cap and fingertighten firmly. This step is critical in preventing dust from entering the instrument.



4. Unscrew the septum nut. Note that, since the septum holder is heated to $\sim 70\text{ }^{\circ}\text{C}$, appropriate care should be taken in handling the septum hardware. Remove the septum from the septum nut using the provided septum puller.
5. Using a clean, dry air canister, puff a single pulse of air through the filter assembly and transfer line.



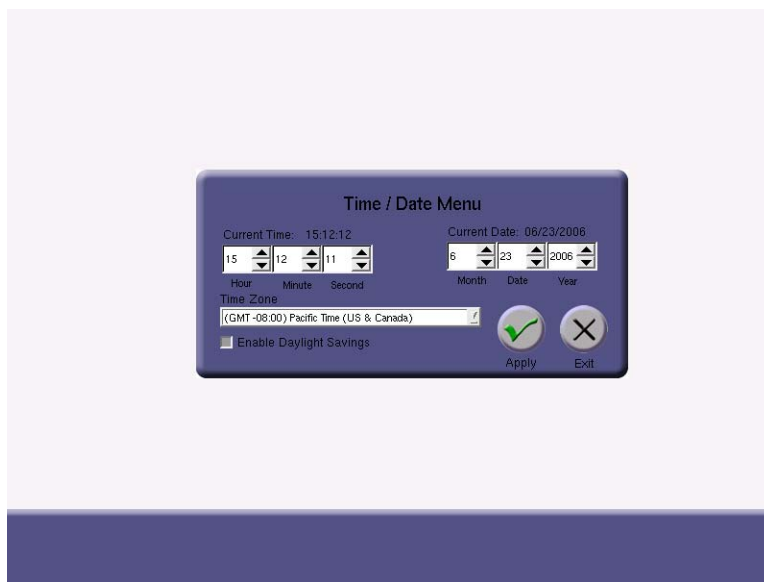
6. This will remove the black septum support. Carefully place the septum support aside.



7. Once the support has been removed, repeatedly pulse dry air through the filter assembly and transfer line to remove all visible septa pieces.
8. Using the dry air canister, blow septa pieces from the black carbon support and replace it into the heated injector block.
9. Using the dry air canister, blow septa pieces from the septum nut.
10. Replace the septum as described in the “Changing Septum” procedure.
11. Remove the 1/4” Swagelok cap from the instrument back panel and IMMEDEATELY replace the filter assembly and transfer line onto the instrument back panel.
12. Finger tighten the 1/4” Swagelok nut firmly and then use a 9/16” wrench to further tighten by 1/4 - 1/2 turn.
13. Confirm that the filter assembly and transfer line are securely attached to the back of the analyzer. Confirm that a new septum has been placed into the injection block.
14. Turn on the instrument and proceed to run samples.

Appendix 1: Changing Time Settings

1. Upon instrument startup, the Run Configuration screen should be displayed. Select the “SETUP” button to enter the SETUP MODE. Depress the “TIME” button to change the time settings.



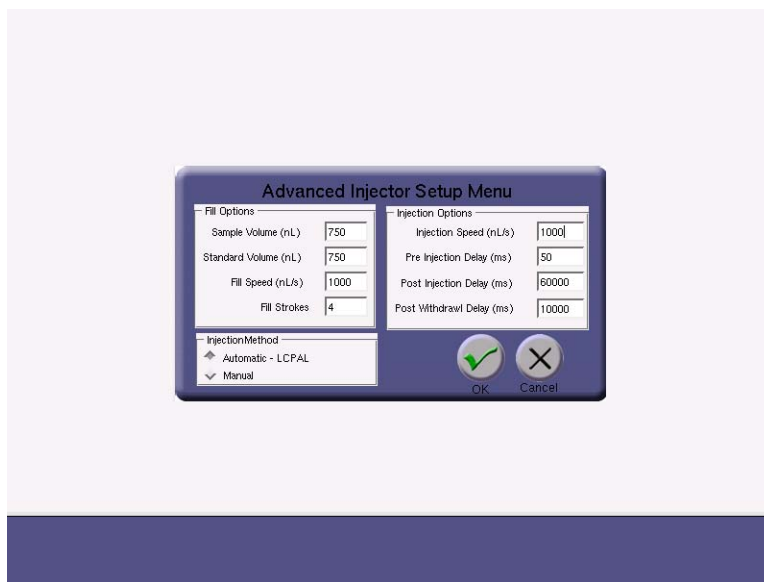
2. Adjust the Current Time, Date, and Time Zone and depress the “APPLY” button. Press the “RETURN” button to return to the run configuration screen.

Appendix 2: Advanced Controls

In addition to the instrument's standard operation, the user may also adjust several advanced parameters including injection settings and gas flush settings.

Note that these advanced settings have been optimized prior to the instrument's delivery and should only be adjusted by skilled users.

1. Upon instrument startup, the Run Configuration screen should be displayed. Depress the "SETUP" button to enter SETUP MODE. Depress "Advanced Inj" to adjust the injection settings.



Sample Volume:	The injected volume (in nL) for sample vials.
Standard Volume:	The injected volume (in nL) for reference standards.
Fill Speed:	The rate (in nL/s) at which the syringe is actuated during filling.
Fill Strokes:	The number of strokes used to help minimize air in the syringe.
Injection Speed:	The rate (in nL/s) at which liquid is injected into the instrument.
Pre Injection Delay:	The delay (in ms) prior to injecting the sample.
Post Injection Delay:	The delay (in ms) during which the syringe is held in the sample port. This period assures that the liquid sample is completely transferred into the instrument.
Post Withdrawal Delay:	The delay (in ms) after the syringe is withdrawn and before the measurements begin. This short delay assures that the system has adjusted to the rapid syringe removal.

Once the values have been appropriately adjusted, depress "OK" to exit back to the setup menu.

2. Depress "Adv Setup" to adjust the flush cycle and other miscellaneous settings.



Number Cycles:	The number of gas flush cycles between injections.
Initial Pumpdown:	The initial pumpdown time (in ms) that removes water prior to adding dry gas.
Purge Fill:	The purge fill time (in ms) during which dry gas is added to the cell.
Purge Pumpdown:	The pumpdown time (in ms) to remove the purge fill gas.
Final Pumpdown:	The finale pumdown time (in ms) prior to the next injection. This number must be sufficiently long to remove as much gas as possible.
Septum Vent Time:	The vent time (in ms) prior to a septum change. This period must be sufficiently long to allow the instrument to approach atmospheric pressure prior to the septum change.
Septum Evac Time:	The pumpdown time (in ms) after the septum has been changed. This time must be long enough to assure that the cell approached vacuum prior the sample injection.
Shutdown Vent Time:	The vent time (in ms) when the instrument is shutdown. Again, similar to the septum vent time, this number should be sufficiently long to assure that the instrument has reached atmospheric pressure.
Meas per Sample:	The number of time each injected sample is measured (e.g. the averaged spectra is analyzed to yield an isotope ratio). The standard deviations listed in the data files refer to the statistics resulting from these repeated measurements.
Ramps per Meas:	Each measurement involves averaging this many laser frequency ramps prior to analysis.

Once the values have been appropriately adjusted, depress “OK” to exit back to the setup menu.

Appendix 3: Accessing data via a LAN Ethernet Connection

This procedure describes how to access the analyzer data directory as a Windows™ Share via a Local Area Network (LAN) ethernet connection.

The data files stored on the internal hard disk drive of the analyzer may be accessed as a Windows™ Share via a Local Area Network (LAN) ethernet connection. The following prerequisites are necessary for this function to operate:

1. The analyzer must be connected to a Local Area Network (LAN) via the RJ-45 ethernet connection on the rear panel.
2. The analyzer must receive a response to a DHCP (Dynamic Host Configuration Protocol) request when the instrument is booted. If the analyzer does not receive a reply, it will disable the ethernet port and not attempt another DHCP request until the analyzer is restarted.

When these prerequisites are met, the data directory may be accessed via a Windows computer on the same LAN as follows:

1. Click “Start”, then “Run”, then type the following into the “Open” command field: \\LGR-XX-XXXX (where XX-XXXX is the serial number of the analyzer).
2. In a short time (usually between 10 and 60 seconds for the first access) a Windows share directory window will be displayed with a subdirectory named “lgrdata” displayed.
3. Double-click on the “lgrdata” directory, and you will see a listing of the data files stored on the internal hard disk drive of the analyzer. You may open or transfer any of the data files as you would with any Windows™ share drive.

ADDITIONAL NOTES:

1. The analyzer shared data directory may (or may not) be visible by “browsing” for it in the Windows “Network Neighborhood”. If it is, it will be in the workgroup called “LGR” and the computer name will be “LGR-XX-XXXX” where XX-XXXX is the analyzer serial number.
2. You can open the data file that is currently being written into by the analyzer without interrupting the analyzer operation (you will see a snapshot of the file as it was when you opened it). You will notice that the current data file is only updated occasionally (every 4 kB worth of data), so a new data file will appear empty until enough data is collected and written to disk.
3. If a LAN is not available, you may plug the analyzer into a simple standalone broadband router (such as a Netgear Model RP614 – approximately \$45). This will enable the analyzer to obtain a DHCP address from the router when the analyzer is started. You may then plug any Windows™ computer into the same broadband router and access the data directory.
4. A “crossover” ethernet cable will NOT allow an external computer to access the shared data directory, as the analyzer will not obtain a DHCP address at boot and will shut down its ethernet interface.

5. You may be able to access the shared analyzer data directory from computers running operating systems other than Windows™. The analyzer uses a Samba server to share the data directory, and it may be accessed by any appropriate Samba client application.