LOS GATOS RESEARCH

CO_2 Carbon Isotope Analyzer

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Quick Start Guide (Standard Instrument)

Set up the CO_2 Carbon Isotope Analyzer

- Connect the instrument to main power.
- Remove the gas inlet cap.
- Remove the gas outlet cap and attach the provided vacuum pump.
- Attach the desired data connections to the rear panel of the instrument.
- Install the Nafion gas drier (see page 8) if the sample is known to contain water.
- Start the analyzer via the power switch. The startup process takes approximately one minute.
- Allow the instrument cell temperature to stabilize at around 45 degrees Celsius. This may take 1-2 hours and the exact final temperature will be instrument specific.

Calibrate the CO_2 Carbon Isotope Analyzer

- Enter the “Setup” panel and click the “Calibrate” button.
- Follow the on-screen directions for calibration.
- Attach a tube to the inlet, regulated at a pressure just slightly above ambient atmosphere (<10 psig), from a local gas standard.
- Enter the known total CO_2 concentration in ppm and isotopic ratio in ‰.
- Disconnect the gas standard when prompted by the on-screen directions.

Starting measurement

- Attach a tube from the gas sample to the gas inlet port.
    - If the optional ‘Dynamic Dilution System’ is being used, see page 25.
    - If the optional ‘Batch Mode’ is being used, see page 28.
- If the instrument is already on, a new file can be started by entering the “Setup” panel and then exiting.
- Note the filename being written as data is taken.
- Download the data (one of the two following options) when measurement is complete.
    - Insert a USB memory device and go to the “File Transfer” menu.
    - Download through the LAN Ethernet connection if it is enabled during startup (see Appendix A – Accessing data via a LAN Ethernet Connection).

Installation

The Los Gatos Research (LGR) CO_2 Carbon Isotope Analyzer is comprised of several components. Be sure to check that each of the system components has arrived before beginning the installation procedure.

For the basic, free-flow system you should have received:

- CO_2 Carbon Isotope Analyzer
- Instrument power cord
- Users guide (this document)
- USB flash drive
- External pump
- Pump slave power cord
- Pump connection tubes
- Serial port connection cable (null modem type)
- Nafion/Drierite gas drier w/ inlet and pump port tubing

For the Dynamic Dilution System (Optional):

- DCS-200 dilution system
- BNC connection cable for control signal
- Sample connection tubing with flow-thru 'Tee'
- Diluter power cord

For the Batch Mode Operation (Optional):

- Syringe body
- Needle pack and centering needle/tool
- Septum pack and tool

If you have not received all of these components, please contact LGR (650-965-7772 or sales@lgrinc.com).

Electrical Power Connection

In order to operate the CO_2 Carbon Isotope Analyzer, it must be connected to main power via the fused power entry module on the back of the unit. The unit can be switched from 115 VAC operation to 230 VAC operation via a voltage selection switch on the rear panel near the power entry module (see Figure 1). If operation from any other voltage source is desired, please contact LGR.

Figure 1: AC power entry module with fuse, power switch, and AC voltage selection switch

Data Interface Connections

The CO_2 Carbon Isotope Analyzer has a variety of data interface connection ports on the back panel (see Figure 2). These can vary slightly from instrument to instrument depending on the ordered configuration.

- "USB" ports are utilized for file transfer to USB memory devices and connecting peripherals.
- "Serial" port is utilized for real-time measurement output directly to a computer.
- "Ethernet" connection allows the instrument to be connected to a Local Area Network (LAN) and the data directory is made available as a Windows™ network shared directory (see Appendix A – Accessing data via a LAN Ethernet Connection).
- "Analog" port is not configured for this instrument at this time.
- "VGA" port allows for connection to an external monitor.
- "Control Out" (not labeled) is a BNC connection to the Dynamic Dilution System (Optional).
- 24-pin data port for connection to the Multi-Port Input Unit (optional).

The functionality of the data interface connections is described in the relevant sections later in this manual.

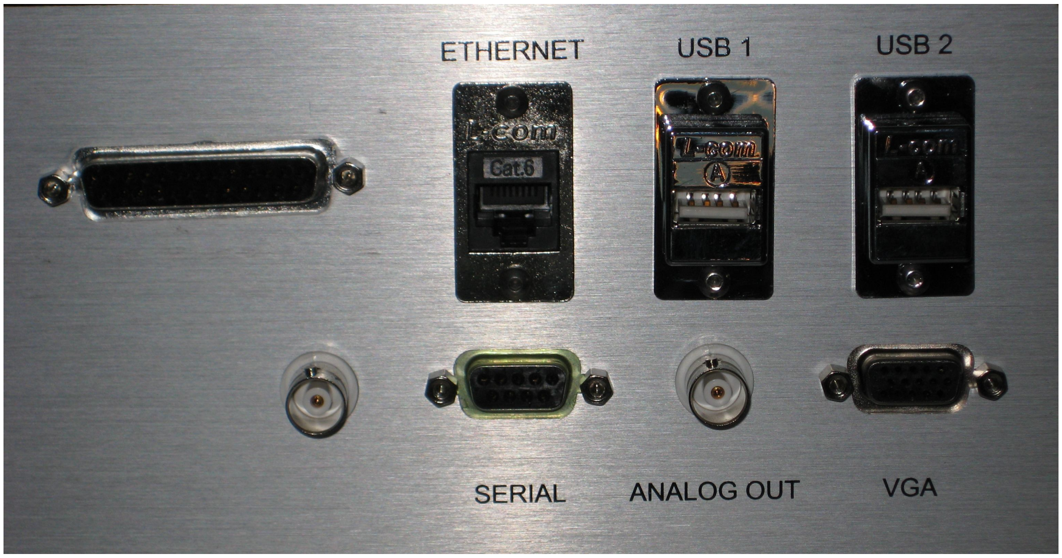

Figure 2: Data interface connections

Gas Inlet / Outlet Connections (Standard Instrument)

The gas inlet and outlet ports of the instrument are on the rear panel (see Figure 3 and Figure 4). The unit is shipped with all inlets and outlets plugged for protection during transit.

Figure 3: External pump connection (3/8"). The internal pump exhaust port is not used if the instrument has an external pump.

Figure 4: Gas sample inlet connection (1/4"), care must be taken to not over-pressurize.

In the normal mode of operation, the provided external pump draws sample through the instrument from the inlet (1/4" Swagelok). The inlet gas pressure range is 0 to 10 psig. The external pump is connected to the instrument with the provided 3/8” tubing and Swagelok connectors. Proper Swagelok connection requires using either a 9/16” wrench (for 1/4" tube) or an 11/16” wrench (for 3/8” tube) to tighten the connection 1/4-1/2 turn past finger-tight, leaving a gap of < 3.5mm (see Figure 5).

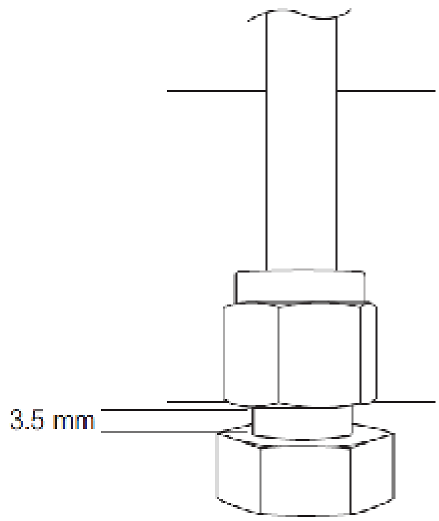

Figure 5: Swagelok connections should be tightened to 1/4-1/2 turn past finger tight, leaving a gap of < 3.5mm. Use a 9/16" wrench for 1/4" tubing, and an 11/16" wrench for 3/8" tubing.

The external pump slave power cord should be plugged into the outlet on the back panel of the instrument labeled “External Pump Power” (see Figure 6), and connected to the power connection on the pump. Make sure the pump power switch is left in the “ON” position, and that the speed control knob on the pump is turned to approximately 2/3 speed (indicator at approximately a 2 o’clock position).

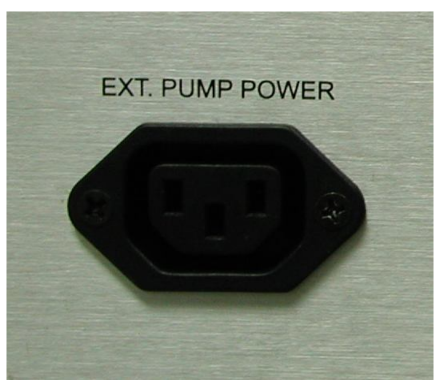

Figure 6: External pump power connection.

Nafion Gas Drier

The presence of water in the sample gas can introduce systematic effects in the isotopic measurement. This results from slight variations in the absorption lineshape due to collisional effects with water. Lab measurements have shown a shift on the order of -0.4‰ per 1000ppm of water. LGR recommends drying the gas sample in order to remove this effect. Other methods include calibration with a reference that has similar water content to the sample.

To aid in mitigating this effect for free-flow (standard) operation, LGR provides a Nafion filter system which reduces the water content while not perturbing the isotopic measurement. The Nafion filter operates by exchanging water in the sample across a membrane with dry 'backing' air. In a modified-reflux configuration, we use the dry instrument exhaust post-measurement with additional drying provided by a Drierite filter. The entire system is diagrammed in Figure 7:

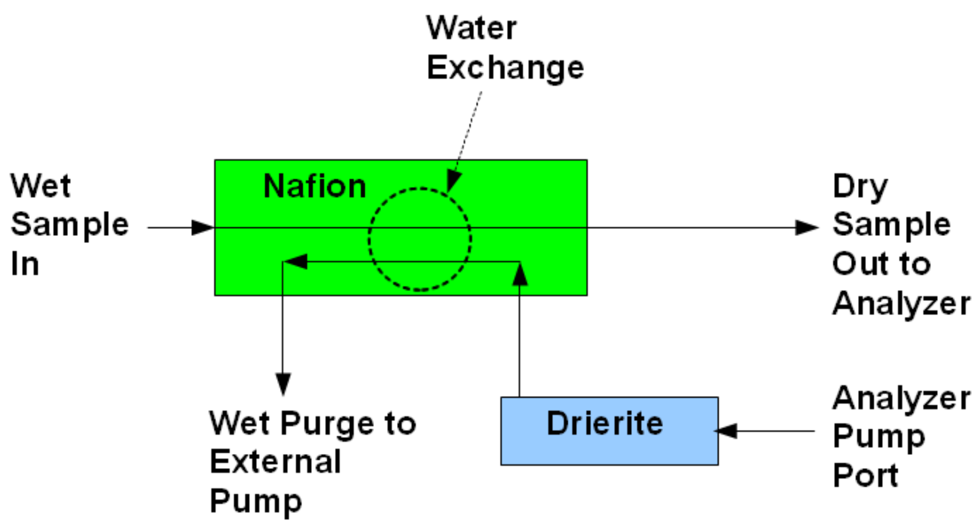

Figure 7: Schematic of Nafion filter system for drying input air sample.

The bulk of the water in the sample is removed by the Nafion and expelled in the filter wet purge. Whatever amount remains is further removed by the Drierite after the isotopic measurement before it enters the Nafion exchanger. Once the Drierite is consumed (blue to pink), it must be either replaced or recharged as detailed on the container. Maximum drying efficiency is obtained by running the sample in the opposite direction to the dry gas purge.

NOTE: Care must be taken to make sure water does not condense within the Nafion filter; the dewpoint of the sample must be less than the temperature of the drier. If the filter becomes saturated with water, it will cease to function and must be dried out. Please see manufacturer's instruction for further details..

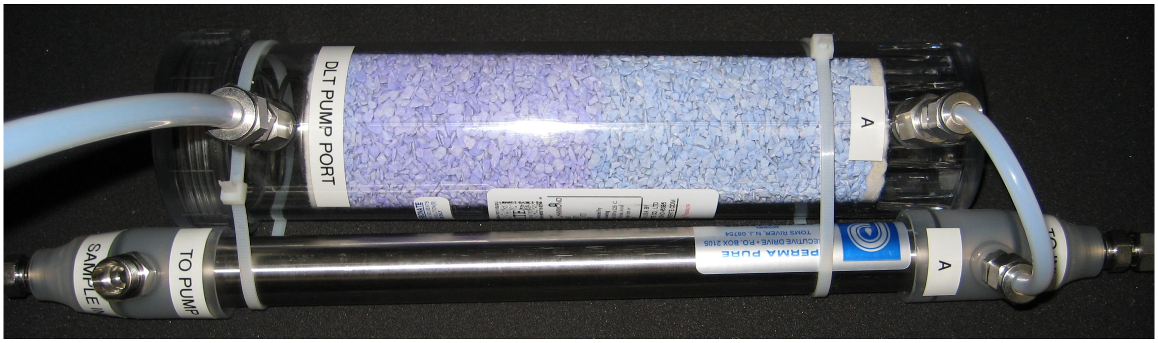

Figure 8: Nafion and Drierite filters for drying gas sample.


Figure 9: Attachment of Nafion filter to the analyzer.

Tubing is provided to connect the drying filter to the inlet, the Drierite to the instrument pump port, and the external pump to the filter purge. Appropriate connections are labeled on the filter assembly. The instrument flow rate may vary depending on the pressure of the inlet with slower flow coinciding with larger inlet pressure. This is due to the Nafion tubing expanding and constricting instrument flow in the purge. LGR recommends keeping the inlet pressure under 10 psig to avoid damaging the internal pressure controller. Reducing inlet pressure further will increase instrument flow rate,

NOTE: Care must be taken to insure than the sample flow direction is opposite to the purge flow of the pump.

Instrument Startup / Shutdown

When the appropriate electrical, gas, and data connections are in place, the instrument may be started via the power switch on the rear power entry module (see Figure 1). The internal computer will boot, and automatically load and start the instrument control software. The startup process takes approximately 1 minute. Operation of the instrument is described in the next section.

Isotopic measurements require a stable environment with minimal temperature fluctuations if possible; the instrument measurement cell is temperature stabilized to help accomplish this.

NOTE: LGR recommends waiting for the cell temperature to stabilize (around 45 degrees Celsius) before starting work. The exact final cell temperature will be instrument specific.

Shutdown of the instrument is accomplished by exiting the operating software, waiting for the instrument to shut down, and turning off the power switch. Please refer to the more detailed Startup/Shutdown section on page 16.

Operation

The Los Gatos Research (LGR) CO_2 Carbon Isotope Analyzer is easily operated via the user interface as described in this section.

Main Panel

Display Modes

When the instrument is turned on, it will automatically go through a one minute initialization cycle with the Los Gatos Research logo and "Please Wait" message on the screen. After initialization is complete, the instrument will begin to draw in gas and to display results in the "Spectrum" mode (see Figure 10). This display shows the laser transmission through the ICOS measurement cell (Figure 10, top frame) recorded as the laser wavelength is tuned across the selected wavelength region near 2.05 microns. The CO_2 absorption lineshapes that result from a detailed analysis of the measured transmission signal are shown in the bottom frame of Figure 10.

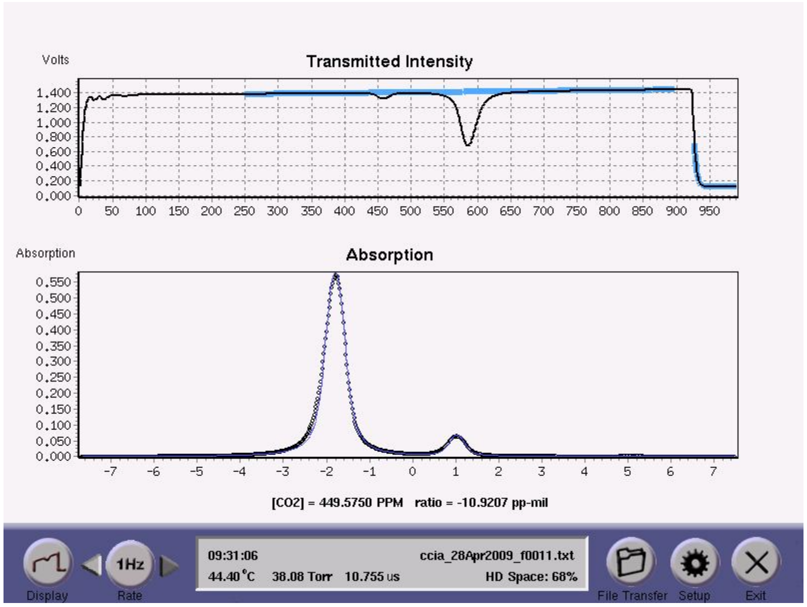

Figure 10: The spectrum display consists of two graphs: the top shows the voltage from the photodetector as the laser scans across the CO_2 absorption features, the bottom shows the optical absorption fraction due to CO_2 in black, and the peak fit resulting from signal analysis in blue.

The total CO_2 concentration ($^{12}CO_2$ + $^{13}CO_2$) is shown in parts-per-million (ppm). The isotope ratio is shown in parts-per-thousand (‰ or pp-mil). The isotope ratio is reported relative to Pee Dee Belemnite (PDB) as shown in Equation 1.

$$\delta^{13}C = \left[\frac{{}^{13}C_{Sample} / {}^{12}C_{Sample}}{{}^{13}C_{PDB} / {}^{12}C_{PDB}} - 1 \right] \times 1000$$

Equation 1: Definition of isotope ratio $\delta^{13}C$ vs. Pee Dee Belemnite (PDB). PDB is defined to be $^{13}C/^{12}C = 0.0112372$.

The user may toggle the “Display” button to see time-charts of CO_2 concentration and isotopic ratio as shown in Figure 11.

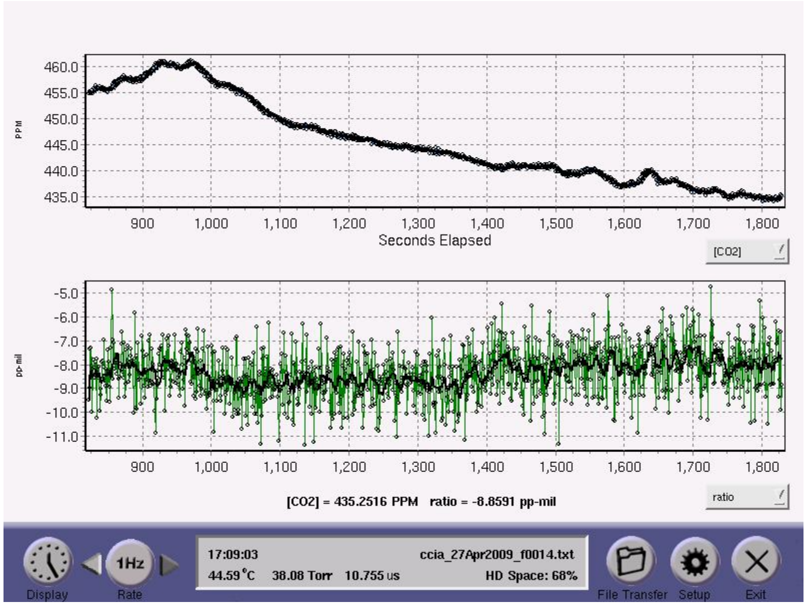

Figure 11: The time chart shows a continuous record of CO_2 concentration and isotopic ratio $\delta^{13}C$ over time. A 10-point running average (in black) is shown going through the raw data (in color).

The user may use the drop down box in the lower right of either window to toggle displays of CO_2 concentration and isotope ratio $\delta^{13}C$. These data are also being saved to the file indicated in the upper right corner of the parameter window (located at the bottom middle of the screen). The parameter window also displays the current time, cell temperature, cell pressure, and cell ring-down which are also written to the file. In addition, the parameter window shows the available hard-drive space left on the instrument. The user may change the rate at which data are written to the log file by selecting the Left or Right arrows next to the Rate indicator. In normal mode, data will be acquired at a 1 Hz rate and averaged for a selected interval (1 to 100 seconds) before being written to the data file and plotted on the time chart. Longer averaging periods (or equivalently, slower data acquisition rates) will yield better measurement precision than shorter averaging periods; so the user may trade off precision in concentration and isotope ratio for precision in time.

File Transfer Menu

Each time the instrument is re-started, and each time the user enters and then exits the "File Transfer" menu or "Setup" panel, a new data file is created with a filename of the form "ccia_DDMMMYYYY_fxxxx.txt". This filename has a time stamp consisting of day (DD), month (MMM), and year (YYYY) and is followed by a 4-digit serial number (xxxx); i.e., ccia_27Apr2009_f0010. The serial number counts upward to provide up to 10000 unique file names each day. If the instrument is left in continuous operation, a new data file will automatically be created in order to keep data file sizes manageable. The time period between creation of new files is set in the "File Settings" menu as described later. The data files are written in text (ASCII) format and contain labeled columns as shown in Figure 12.

```
2009 Apr 27 19:04:02
                     Time,       [12CO2],    [12CO2]_se,       [13CO2],    [13CO2]_se,         [CO2],      [CO2]_se,
                    2.998,  4.28346e+02,  0.00000e+00,  4.68362e+00,  0.00000e+00,  4.33029e+02,  0.00000e+00,
                    4.012,  4.27779e+02,  0.00000e+00,  4.63975e+00,  0.00000e+00,  4.32419e+02,  0.00000e+00,
                    5.015,  4.25845e+02,  0.00000e+00,  4.59844e+00,  0.00000e+00,  4.30444e+02,  0.00000e+00,
                    6.033,  4.23859e+02,  0.00000e+00,  4.56978e+00,  0.00000e+00,  4.28429e+02,  0.00000e+00,
                    7.038,  4.22924e+02,  0.00000e+00,  4.54627e+00,  0.00000e+00,  4.27470e+02,  0.00000e+00,
                    8.047,  4.23569e+02,  0.00000e+00,  4.55571e+00,  0.00000e+00,  4.28125e+02,  0.00000e+00,
                    9.057,  4.24586e+02,  0.00000e+00,  4.57601e+00,  0.00000e+00,  4.29162e+02,  0.00000e+00,
                   10.125,  4.24631e+02,  0.00000e+00,  4.60155e+00,  0.00000e+00,  4.29232e+02,  0.00000e+00,
                   11.062,  4.25895e+02,  0.00000e+00,  4.64139e+00,  0.00000e+00,  4.30537e+02,  0.00000e+00,
                   12.064,  4.25727e+02,  0.00000e+00,  4.64951e+00,  0.00000e+00,  4.30377e+02,  0.00000e+00,
                   13.069,  4.26351e+02,  0.00000e+00,  4.67263e+00,  0.00000e+00,  4.31024e+02,  0.00000e+00,
                   14.070,  4.26487e+02,  0.00000e+00,  4.68150e+00,  0.00000e+00,  4.31169e+02,  0.00000e+00,
                   15.077,  4.26400e+02,  0.00000e+00,  4.69525e+00,  0.00000e+00,  4.31096e+02,  0.00000e+00,
                   16.086,  4.26533e+02,  0.00000e+00,  4.70891e+00,  0.00000e+00,  4.31242e+02,  0.00000e+00,
                   17.143,  4.26893e+02,  0.00000e+00,  4.71610e+00,  0.00000e+00,  4.31609e+02,  0.00000e+00,
                   18.106,  4.26901e+02,  0.00000e+00,  4.72244e+00,  0.00000e+00,  4.31623e+02,  0.00000e+00,
                   19.122,  4.26692e+02,  0.00000e+00,  4.72241e+00,  0.00000e+00,  4.31414e+02,  0.00000e+00,
                   20.179,  4.27244e+02,  0.00000e+00,  4.72338e+00,  0.00000e+00,  4.31967e+02,  0.00000e+00,
                   21.156,  4.26253e+02,  0.00000e+00,  4.71875e+00,  0.00000e+00,  4.30972e+02,  0.00000e+00,
-----BEGIN PGP MESSAGE-----
Version: GnuPG v1.2.3 (GNU/Linux)

jAOEAwMCcsOrUPUNti5gyewGsrkikHUNTxCQvY4tOgQA/9FCFtgYBOpStjxIpKGG
k2j5fY+bYAsPEljaFJDbWkbED3TtzAUyXY3pKlGruV886hWP6SGUQHeu/W28N6Bl
ykm4xXU01385F/PUhoQb52G4JfJ86BtgSNMAQ4tloykOiOFnwYQYk6FJN8K7zYOZ
WRCkwWe+zuiaLqzvY8IxloCNmlYjxAFRphVcUmVxU/amK6xZ+Y1byt4HAOnP7kKd
```

Figure 12: A typical data file showing just a few of the data columns. Instrument settings are encoded at the end of the file after the data columns.

The "Time" column reports the time stamp of each recorded measurement; its format is set by the user in the "Setup" menu (see page 19). Also reported are:

- [$^{12}CO_2$] (ppm)
- [$^{13}CO_2$] (ppm)
- [CO_2] (ppm) = [$^{12}CO_2$] + [$^{13}CO_2$]
- Isotope ratio = delta (pp-mil)
- [CO_2]_sample (ppm) estimated input into dynamic dilution system (optional). Without the diluter, this is either the same as total [CO_2] or zero depending on the software version.
- Cell pressure (Torr)
- Cell temperature (Celsius)
- Cell ring-down (μsecs)
- … and further fit parameters

For each of these measurements there is an additional adjacent column reporting the standard error of the measurement (designated with '_se' tag). The standard error is zero when the instrument is running at 1 Hz, as no averaging of data has taken place. At speeds slower than 1 Hz, the standard error of the average is reported. Additional columns may be present depending on the instrument settings and options. These columns contain details regarding the instrument analysis and, if present, are stored in case LGR scientists wish to evaluate the instrument performance. At the end of each data file are encrypted listings of settings used by the instrument for that data file. The settings are stored in case LGR scientists wish to re-analyze a data set to study instrument performance.

The user may transfer data files from the instrument hard disk to a USB memory device by selecting the "File Transfer" button. The instrument will remind the user to insert a USB memory device into the instrument USB port before proceeding (Figure 13).

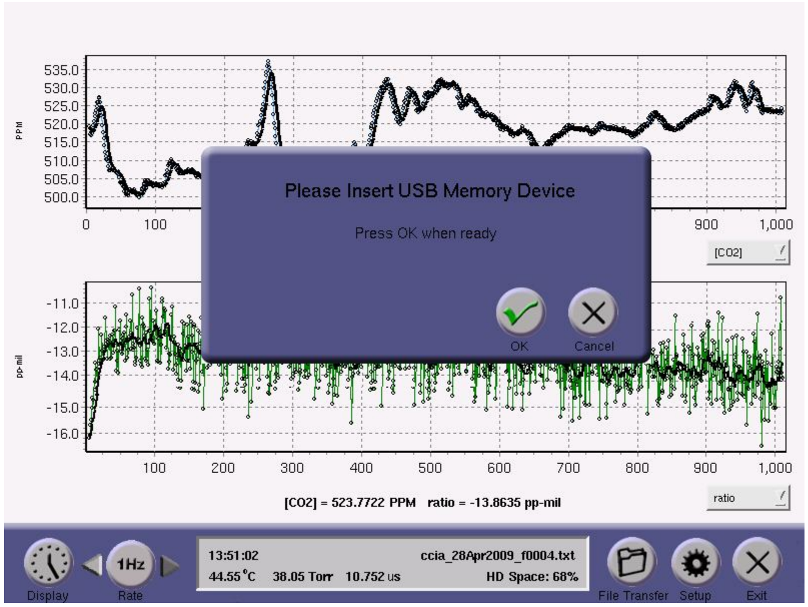

Figure 13: Reminder to insert USB memory device into the instrument.

After OK is pressed, data acquisition will halt, and the user will see two file directory windows as shown in Figure 14. 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. 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.

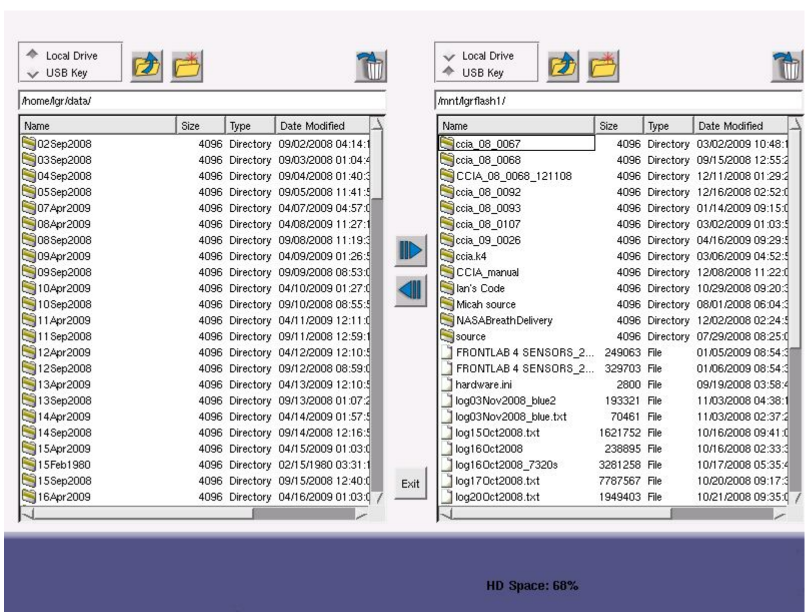

Figure 14: File transfer windows. Highlight the files to copy and click the appropriate arrow. Click the new folder icon to create directories and click the trash can to delete files.

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.

Instrument data is automatically stored within the /home/lgr/data/ directory to a directory named by date of data acquisition. Data is further organized into 'batch' and 'flow' directories depending on the specific instrument mode and option ordered. The ‘flow’ files are typically 'zipped' to keep disk usage to a minimum. Files for ‘flow’ mode are labeled with a ‘fxxxx’ serial number while ‘batch’ mode files are labeled with a ‘bxxxx’ serial number.

When finished transferring files, the user must click the “Exit” button and wait for the “Safe to Remove USB Memory Device” message prior to removing the USB memory device to ensure proper un-mounting of the file system.

WARNING: Removal of the USB memory device before prompted to do so may result in loss of data.

If the user forgets to insert a USB device before entering the “File Transfer” mode, or if the USB device is not recognized, the instrument will display a warning and will automatically restart data acquisition (Figure 15).

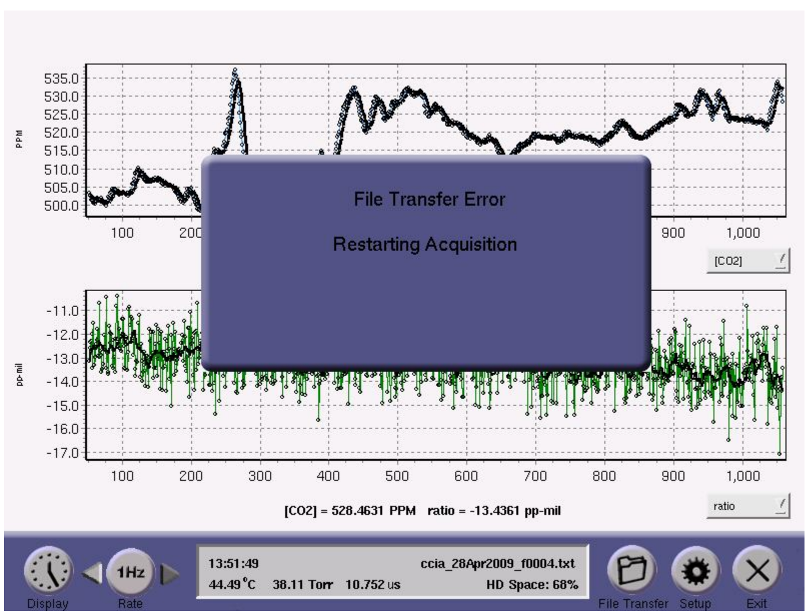

Figure 15: File transfer error. User forgot to insert a USB device, or the device was not recognized. Please try again with a USB device correctly inserted or with a different USB device.

The amount of hard drive space left on the instrument is shown in the main instrument parameter window, lower right corner.

Startup / Shutdown

The internal computer will boot, then automatically load and start the instrument control software once the proper power connections are made and the switch is set to the ON position. The startup process takes approximately 1 minute. Once a month, the instrument automatically performs a thorough file system integrity check during boot-up. The display shown in Figure 16 appears and the instrument will take approximately 1-2 minutes to complete the integrity check before continuing with loading the software. Do not turn off the computer during this maintenance.

Figure 16: The Routine Maintenance Screen appears during boot-up once a month. Normal operation will automatically continue after the maintenance is complete. Please do not turn off the instrument during maintenance.

The "Exit" button will prompt the user for verification prior to shutting down the instrument. This prevents accidental button presses from causing interruption in data acquisition. The "OK" button will halt data acquisition, close the current data file, and display the shutdown screen (Figure 17). After the progress bar completes, the instrument will switch to a text-based output as it completes shutting down. The user must wait until after the "Power Down" command is displayed as shown in Figure 18 before turning off the instrument. Failure to do so may result in file system instability.

Figure 17: Instrument shutdown screen.

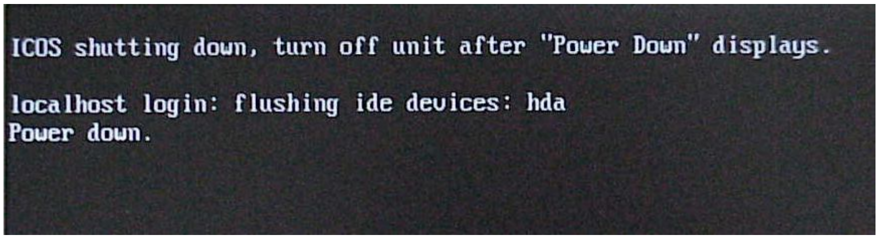

Figure 18: Final shutdown screen.

Setup Panel

The "Setup" button will prompt the user for verification prior to entering "Setup" mode as shown in Figure 19. This prevents accidental button presses from causing interruption in data acquisition. The "OK" button will halt data acquisition, close the current data file, and display the Setup Panel shown in Figure 20. From this panel the user may configure the file saving settings, re-calibrate the instrument to a local CO_2 gas standard, configure the Serial Output, enter the service mode, and adjust the current time/date settings.

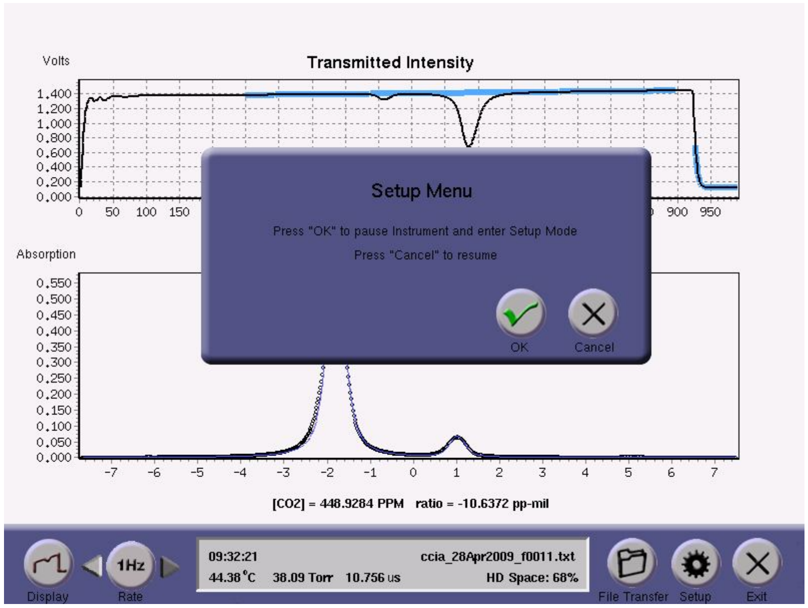

Figure 19: Pressing the Setup button prompts the user for further input.

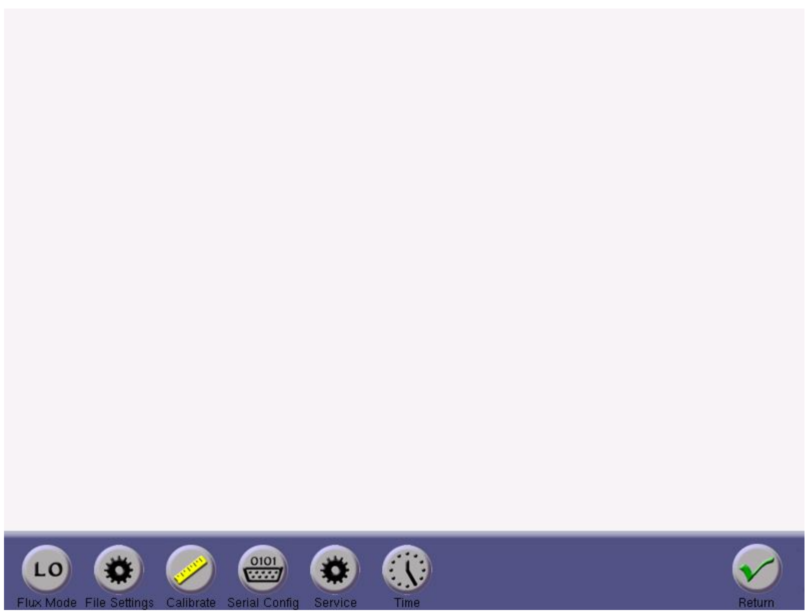

Figure 20: The Setup panel allows the user to select the instrument mode, configure file settings, calibrate, configure serial output, enter service mode, and configure the instrument time.

Flux Mode (Flow / Batch)

For a “free flow” CO_2 Carbon Isotope Analyzer this mode is permanently set in the low (LO) state. If the instrument has been ordered with “batch” capability, this state can be toggled from free flow (LO) to various pre-defined batch states which are described in the section Batch Mode Operation (Optional) on page 28.

File Settings Menu

The "File Settings" menu (Figure 21) allows the user to adjust the time stamp format of the data files and the new file creation interval (when running continuously). The available time stamp formats are the same as for the serial output settings (see Table 1: Available Time Stamp Formats).

Figure 21: The File Settings menu.

Calibration Menu

The CO_2 Carbon Isotope Analyzer is equipped with a calibration routine. Los Gatos Research recommends regular calibration to ensure measurement accuracy and consistency. Calibration can be achieved by attaching a tube, regulated at a pressure just slightly above ambient atmosphere (< 10 psig), from a local gas standard to the instrument inlet. The sequence of calibration steps is illustrated from Figure 22 through Figure 27.

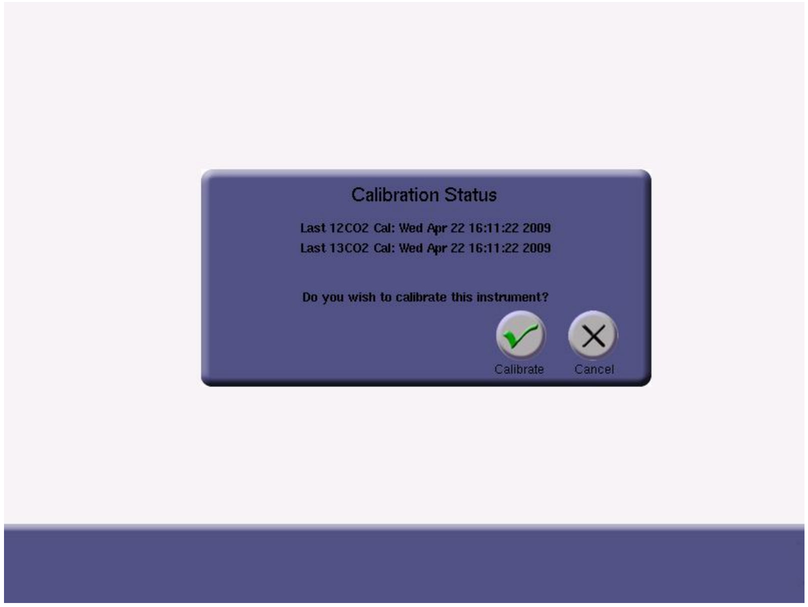

Figure 22: Initial Calibration prompt.

Click the "Calibrate" button on the "Setup" panel to bring up information on the most recent calibration (Figure 22). Click the "Calibrate" button on the pop-up window and another screen will pop up indicating that calibration will begin when the "Setup" menu is exited (Figure 23). Exit "Setup" mode and another screen will confirm that calibration is desired (Figure 24). Enter the known total concentration of CO_2 in ppm and value of $\delta^{13}C$ in pp-mil (relative to PDB) for the local gas standard into the box labeled "Enter Calibration Data" (Figure 25). A screen will pop up indicating that the instrument is ready to calibrate (Figure 26). Click "OK" when consistent flow has been established, the transfer tube is fully flushed with the calibration gas, and you are ready to begin calibration. If "OK" is not clicked within 60 seconds, calibration will be aborted and standard gas measurement will continue. The instrument will run the calibration routine for approximately two minutes. A screen will pop up indicating when the calibration is finished and that the user should disconnect the calibration gas (Figure 27). The time of latest calibration is also stored in the instrument configuration files for future reference.

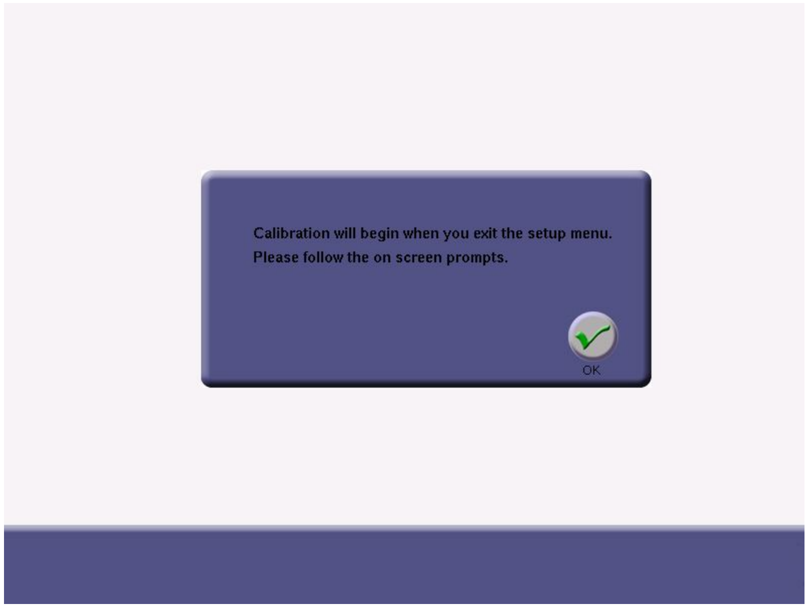

Figure 23: Verification of calibration.

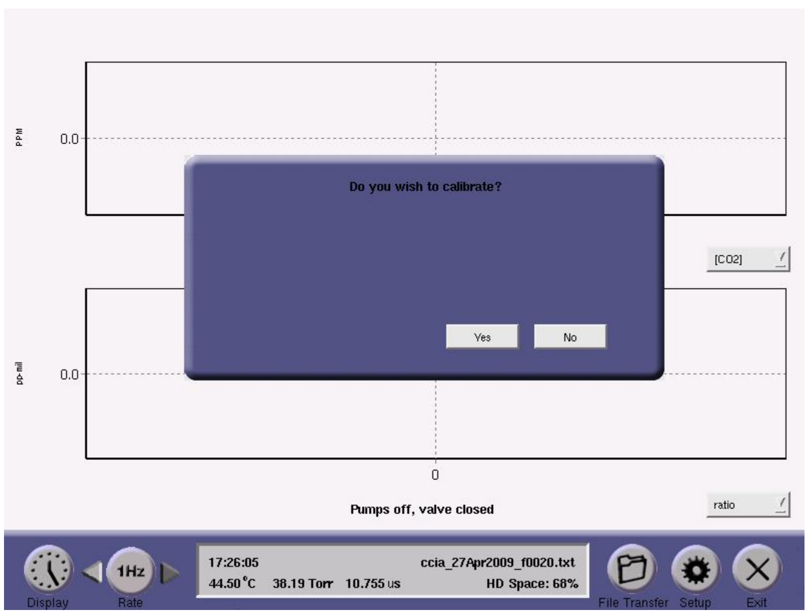

Figure 24: Calibration prompt before measurement.

Figure 25: Calibration parameters queried.

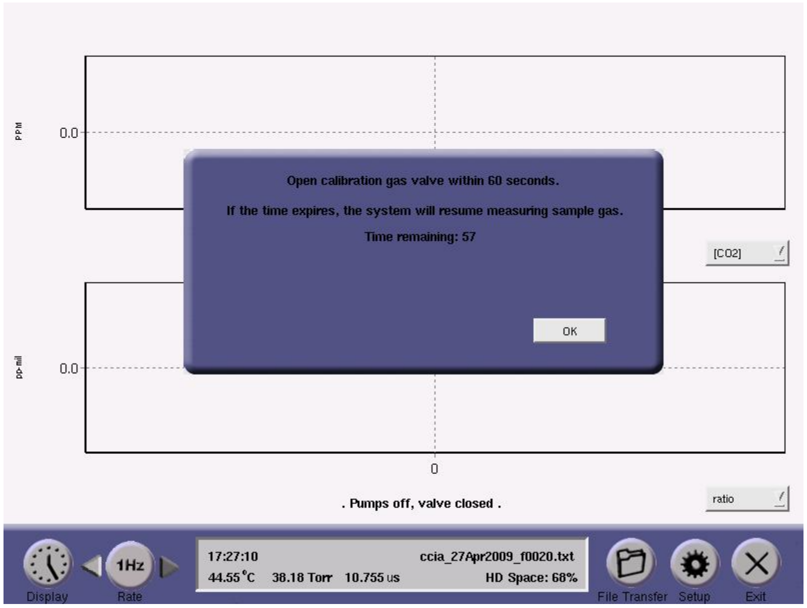

Figure 26: Calibration begins once user indicates reference gas is ready.

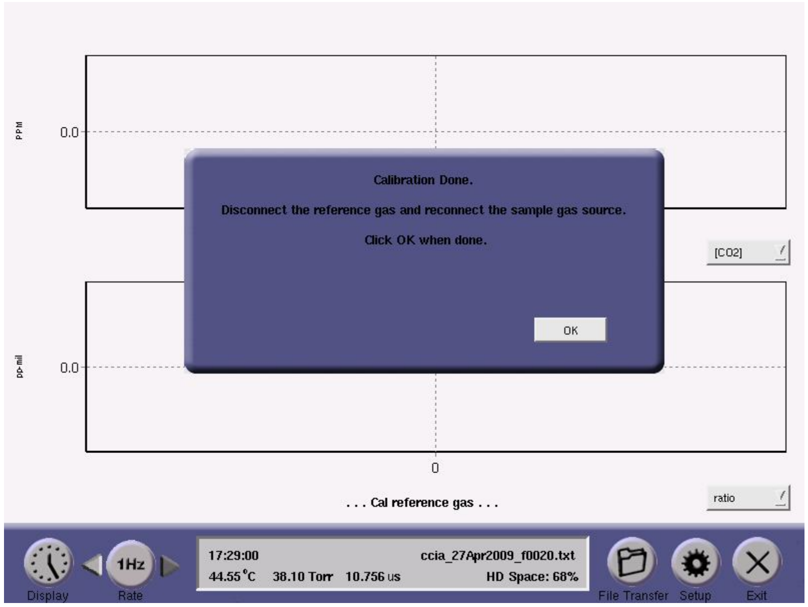

Figure 27: Calibration done.

NOTE: The calibration requires that the user input the total concentration of CO_2 in ppm. The analyzer reports the individual $^{12}CO_2$ and $^{13}CO_2$ concentrations in ppm. The total measured concentration, ignoring higher order isotopes, is reported as:

$[CO_2] = [^{12}CO_2] + [^{13}CO_2]$

Serial Configuration Menu

The Serial Configuration Menu (Figure 28) allows the user to change how the data reported at the RS-232 port is configured. Standard settings for Baud Rate, Parity, and Stop Bits are provided. The format of the Time Stamp (see Table 1) can be selected, the Delimiter chosen (comma, tab, space), and the Rate (1-10) specified. Note that the actual rate of serial output is equal to the Logged File Rate (i.e. 1 Hz) divided by the Rate specified in the Serial Configuration Menu. The data reported through the RS-232 port consists of:

- Time stamp
- $[^{12}CO_2]$ (ppm)
- $[^{13}CO_2]$ (ppm)
- $[CO_2]$ (ppm) = $[^{12}CO_2] + [^{13}CO_2]$
- Isotope ratio = delta (pp-mil)
- $[CO_2]$_sample (ppm) estimated input into dynamic dilution system if present, otherwise it should be ignored.
- Cell pressure (Torr)
- Cell temperature (Celsius)
- Instrument flag tagging data (0=Junk, 1=Calibration, 2=Adjusting spectra, 3=Measurement). Free-flow data will usually be tagged "3".
- Cell ring-down (μsecs)

NOTE: When connecting the serial port of the instrument to an external computer, a null modem type serial cable should be used.

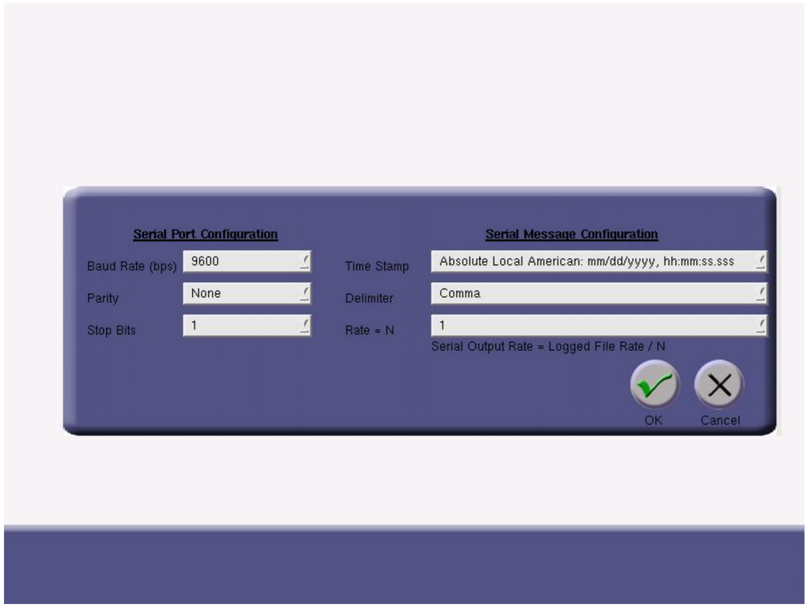

Figure 28: The serial configuration menu.

Absolute Local American	mm/dd/yyy, hh.:mm:ss.sss
Absolute Local European	dd/mm/yyyy, hh:mm:ss.sss
Absolute GMT American	mm/dd/yyy, hh.:mm:ss.sss
Absolute GMT European	dd/mm/yyyy, hh:mm:ss.sss
Relative Seconds After Power On	ssssss.sss
Relative Seconds in Hours, Minutes, Seconds	hh:mm:ss.sss

Table 1: Available Time Stamp Formats

Service Mode Menu

A password protected Service Mode (Figure 29) is available only for qualified technicians to make software upgrades or run instrument diagnostics.

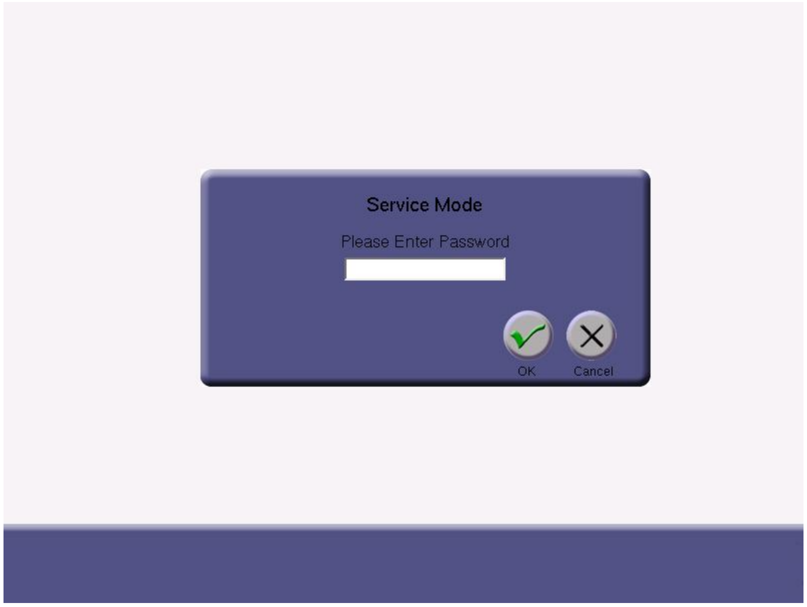

Figure 29: The Service menu.

Time Menu

The Time Menu lets the user adjust the current time and date settings of the instrument (Figure 30). The time zone and daylight savings enable / disable may also be set here.

Figure 30: The Time menu.

Dynamic Dilution System (Optional)

The CO_2 Carbon Isotope Analyzer can be factory equipped with an optional Dynamic Dilution System. This hardware option uses internal mass flow controllers to automatically dilute a flowing concentrated sample stream ($[CO_2]$ = 900ppm to 10%)

down to the top of the measurement range of the instrument (900 ppm). When a CO_2 Carbon Isotope Analyzer has been equipped with the Dynamic Dilution System, an additional unit (DCS-200) is provided as shown in Figure 31.

Figure 31: Dynamic Dilution System (Optional).

The back panel of the dilution system has gas ports for providing the CO_2 sample and the zero-air (CO_2 free) for dilution (see Figure 32). Both the sample and the zero air must be pressurized as indicated (15 to 50 psig) with a sample gas flow capability of 200 sccm and a zero-air flow capability of 2.2 slpm.

Figure 32: Back panel gas hook-ups for the Dynamic Dilution System (Optional). The sample and the zero-air must be provided with flow capability of 200 sccm and 2.2 slpm respectively.

The output of the diluter is then connected to the CO_2 Carbon Isotope Analyzer with a 'Tee' connector (provided with the DCS-200) that allows for steady flow past the inlet to the analyzer (Figure 33).

Figure 33: Inlet 'Tee' configuration for Dynamic Dilution System (Optional).

Connecting without a 'Tee' directly to the analyzer will not enable the mass flow controllers to maintain proper dilution.

NOTE: Depending on the sample concentration, sample flow can vary from 0 to 200 sccm, and zero-air flow can vary from 0 to 2.2 slpm as the mass flow controllers adjust the amount of dilution. Flow through the measurement cell will remain steady at approximately 180 sccm, with the excess flow vented out the 'Tee'.

NOTE: If the sample to be measured will always remain below 900 ppm, it is not necessary to connect gas to the zero-air port, but the zero-air port must be capped.

The provided BNC connection cable is used to connect the CO_2 Carbon Isotope Analyzer to the DCS-200 so that the analyzer is able to control and maintain the proper diluted concentration. Please see Figure 34 and Figure 35.

Figure 34: "Control In" connection Dynamic Dilution System.

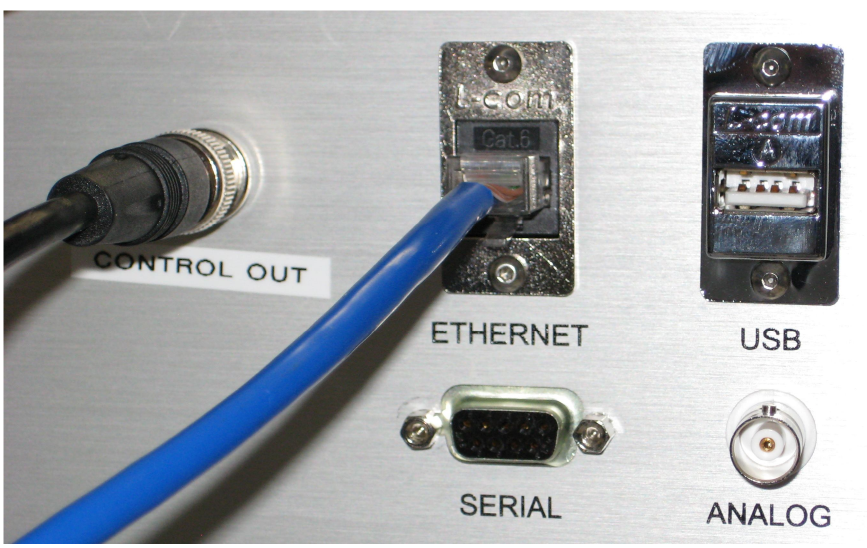

Figure 35: "Control Out" connection CO_2 Carbon Isotope Analyzer

With this Dynamic Dilution System, the instrument will automatically begin diluting the sample stream with zero-air whenever the concentration rises above 900 ppm, and will attempt to maintain the concentration at 900 ppm. The dilution system has a response time constant of approximately one minute, so a sudden rise in concentration will cause the concentration to "over-range" until the dilution system can adapt and return the concentration to 900 ppm. Whenever the cell concentration is temporarily above the 900 ppm limit of the measurement range, concentration and $\delta^{13}C$ will continue to be measured and recorded, but may be inaccurate.

NOTE: When the dilution system is actively diluting the sample stream, the CO_2 concentration displayed will be steady at approximately 900 ppm – representing the concentration in the cell after dilution, not the inlet sample concentration of the diluter. The data files contain a column with an ***approximate*** *value for the inlet sample concentration calculated from the measured cell concentration and the internally commanded dilution ratio.*

NOTE: When transitioning from a large CO_2 concentration to a lower CO_2 concentration, the user should be aware that there may be a "memory" effect resulting from residual CO_2 in the walls and surfaces of the lines and instrument. Care should be taken to make sure that the residual CO_2 from the previous sample has had time to exit the system. This could be aided by switching inlet lines, using short line lengths, and flushing lines with zero-air and/or vacuum.

Batch Mode Operation (Optional)

The CO_2 Carbon Isotope Analyzer can be factory equipped with an optional batch mode system. This system allows the user to introduce individual samples to the system via a syringe port mounted on the instrument. When the instrument has been equipped with the batch mode system, the back panel configuration of the instrument is modified to add a zero-air inlet port (1/4" Swagelok) as shown in Figure 36. In this configuration, zero-air (i.e. CO_2 and H_2O free air) must be supplied to the instrument at 15 to 150 psig.

Figure 36: Zero-Air connection port for a CO_2 Carbon Isotope Analyzer equipped with the optional batch mode system.

NOTE: The zero-air must be a proper air mixture (N_2 and O_2). Using only N_2 will give a systematic change in the CO_2 absorption lineshape resulting in systematic errors in the *isotope measurement. LGR has observed ~10 pp-mil (‰) shift when measuring CO_2 in air versus pure N_2 background.*

The instrument is also modified to add a syringe injection port arm and instrument gas port as shown in Figure 37.

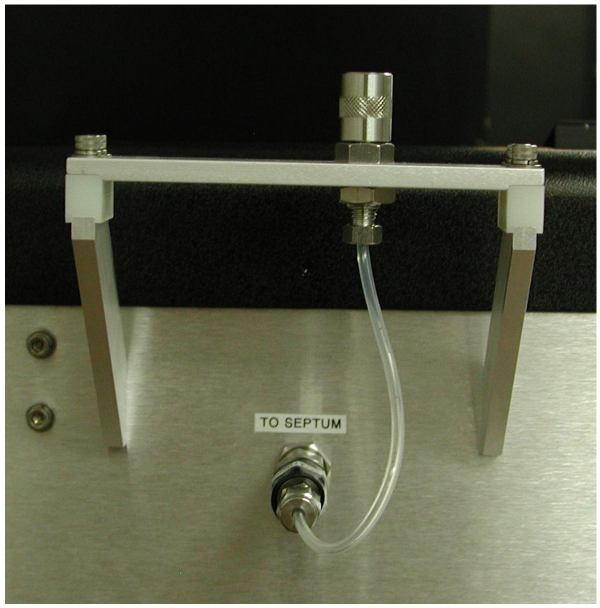

Figure 37: Syringe injection port arm and instrument gas connection for a CO_2 Carbon Isotope Analyzer equipped with the optional batch mode system.

Using this optional batch mode system, the user can measure individual gas samples via a supplied gas-tight 140 ml syringe. There are two user selectable separate batch modes (described below) that can be used in this configuration: ‘normal injection mode’, for samples with CO_2 concentration in the instrument range of 350-1000 ppm, and injection with ‘fixed dilution mode’ for samples with CO_2 concentration between 1000-3000 ppm.

Normal Injection Mode

If the optional batch mode system has been installed in the CO_2 Carbon Isotope Analyzer, the instrument may be switched into batch injection mode via the setup panel. Depressing the leftmost button on the Setup menu (Figure 38) will cycle the operational mode of the instrument from ‘flow through’ (top) to ‘normal injection’ (middle) to ‘injection with fixed dilution’ (bottom) and back to ‘flow through’ mode.

Figure 38: Setup panels displaying various flux modes with the optional batch system installed. Flow through mode (top – LO icon), normal injection (middle – syringe icon), and injection with fixed dilution (bottom – syringe with "D" icon).

For discrete samples with a CO_2 concentration of up to 1000 ppm, normal injection mode should be used. For normal injection mode, select the syringe icon (middle panel above) and return to the main panel. Upon returning to the main panel, the instrument will close off the sample inlet, and begin preparing to accept a sample via the syringe port. The first step entails pumping out the measurement (ICOS) cell and the internal sample tank (Figure 39), and purging the cell and sample tank with zero air. After a couple of purge cycles, the instrument will continue pumping until the pressure in the measurement cell falls below approximately 3.5 Torr (this can take several minutes).

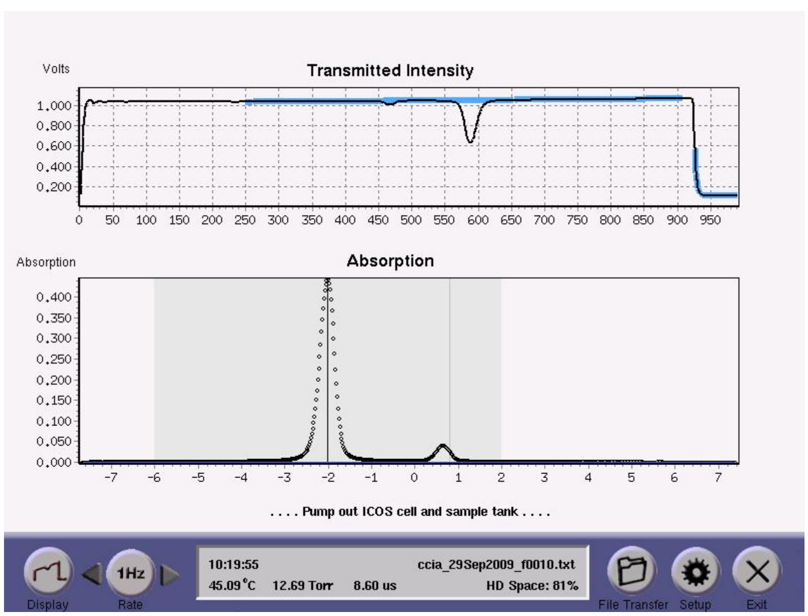

Figure 39: Display indicating that the instrument is pumping out the measurement (ICOS) cell and internal sample tank in preparation for a syringe injection of sample gas. The instrument will pump down to roughly 6 Torr and flush with zero air twice before fully pumping down for sample injection.

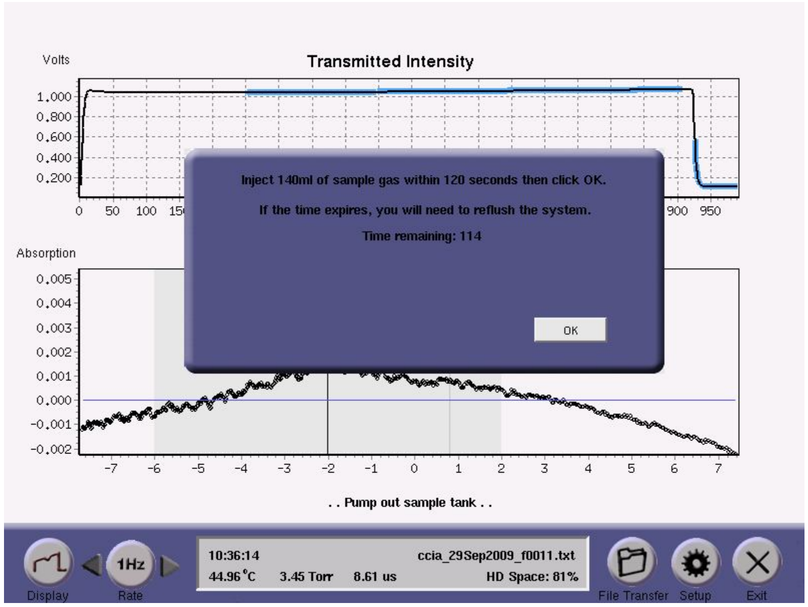

Figure 40: Display prompt indicating that the user should inject the gas sample via the syringe port, and click OK.

The user will then be prompted to inject sample gas via the syringe port (Figure 40). An injection volume of around 140 ml is recommended. The user then has 120 seconds to fill the syringe with the sample gas, and insert the syringe needle into the septum port as shown in Figure 41.

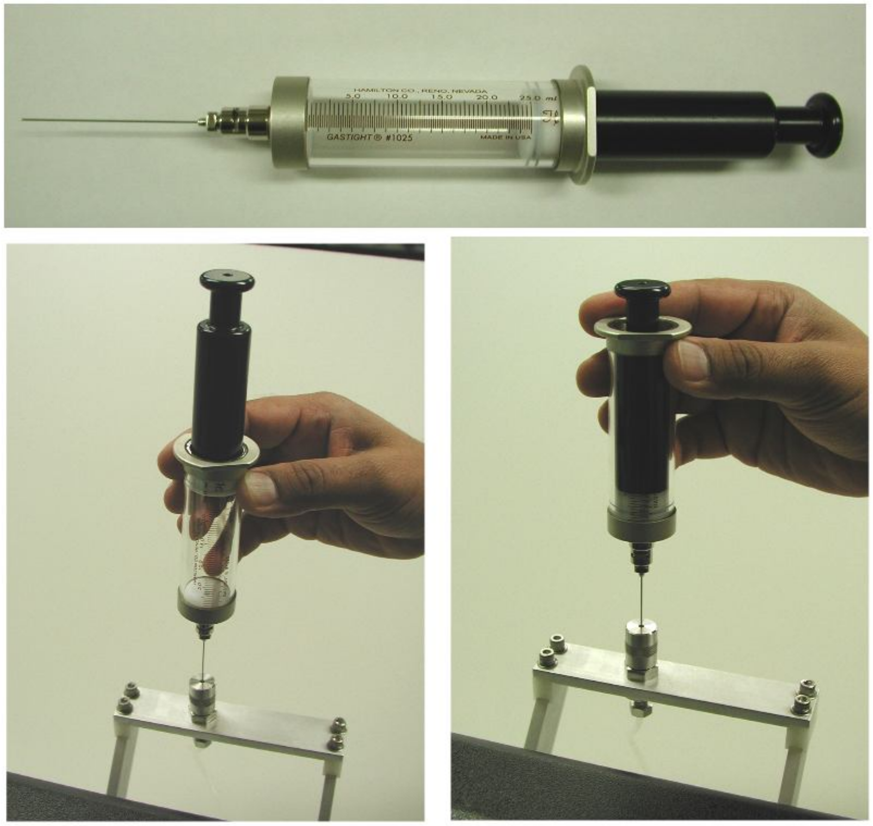

Figure 41: Syringe filled with sample gas (top) and injection into instrument septum port (left). It is not necessary to depress the syringe plunger to inject the gas into the instrument. The vacuum inside the internal sample tank will draw the gas from the syringe and "pull" the plunger down (right).

NOTE: It is not necessary to press the syringe plunger to inject the gas into the instrument. The vacuum inside the internal sample tank will draw the gas from the syringe and "pull" the plunger down. The user should wait until the plunger has been drawn to the bottom of the syringe, then remove the syringe and click the OK button on the dialog box.

If the injection is not completed within 120 seconds, the display will indicate a failed injection and ask the user to restart the process, as shown in Figure 42.

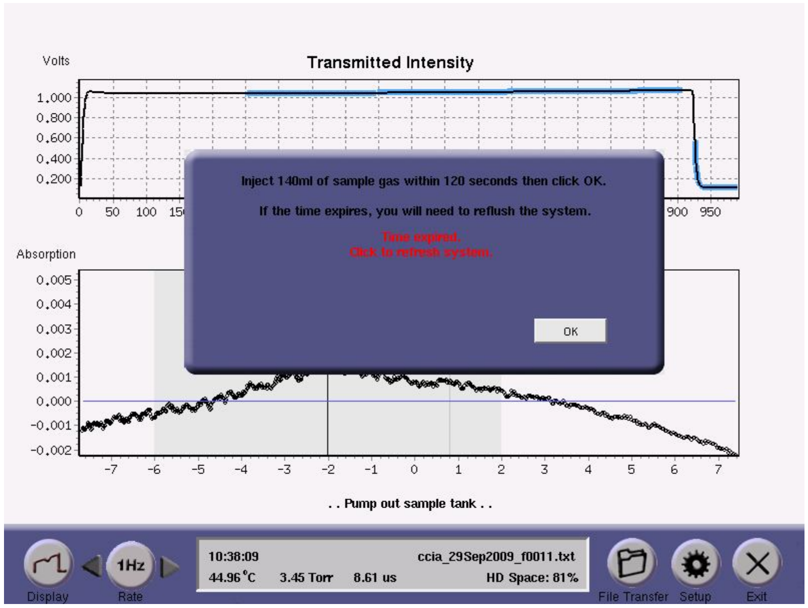

Figure 42: Timeout reached without a syringe injection. User should click OK when ready to restart the injection.

Once a sample has been successfully injected, the instrument will first flush the measurement cell (Figure 43) by "puffing" a portion of the sample gas into the measurement cell (you will hear a clicking sound as the sample introduction valve is pulsed open several times to introduce approximately 15 Torr of sample gas into the measurement cell). The instrument will then pump out the measurement cell to approximately 5 Torr (Figure 44). The purpose of this flush is to exchange any gas remaining from the previous injection with gas from the current sample (i.e. minimize sample memory from injection to injection). The flushing will be repeated twice.

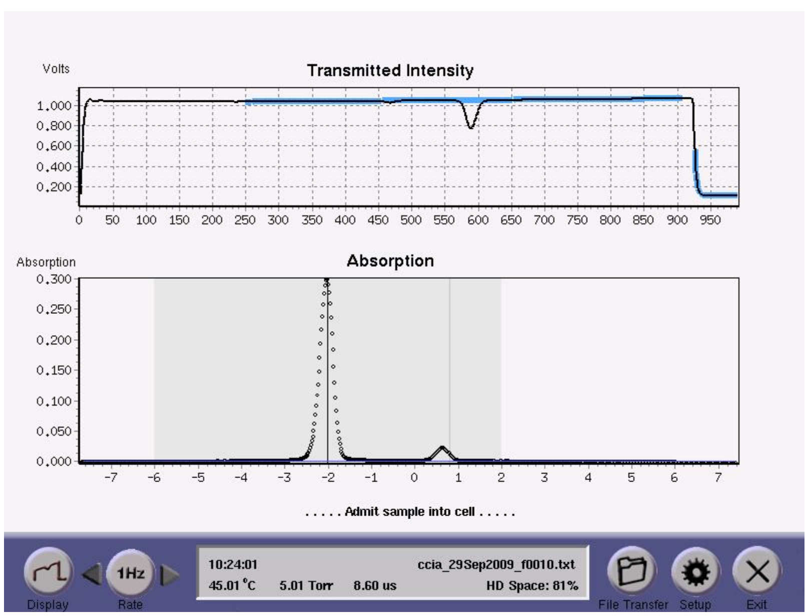

Figure 43: Flushing of sample gas into the measurement cell via "puffing" of the sample gas inlet valve.

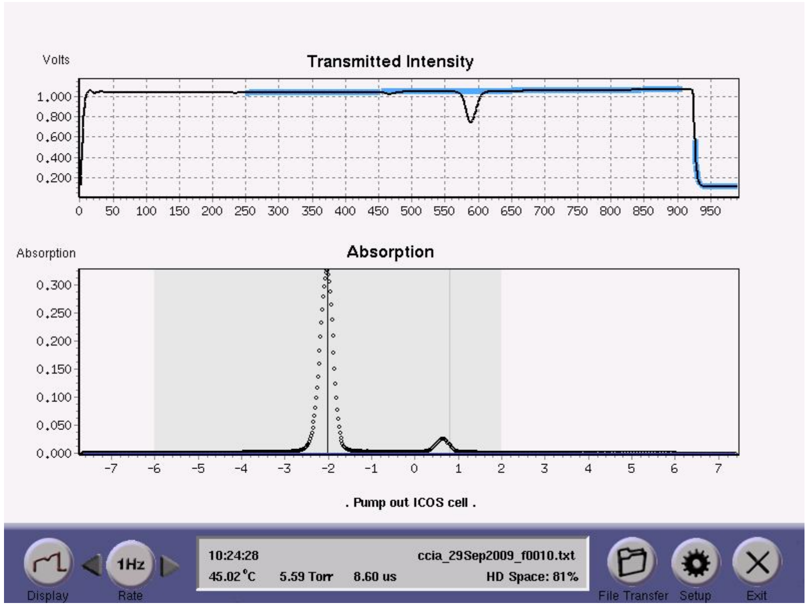

Figure 44: Pump out of the flush gas from the measurement (ICOS) cell.

After flushing twice, sample gas will again be admitted to the measurement cell until the measurement cell pressure has reached approximately 38 Torr. Once the sample has been loaded, the instrument will start taking measurements. There is some settling of the measurement as the gas equilibrates with the cell and the laser frequency is stabilized. For 'normal injection mode', the instrument will run for approximately 30 seconds and reset its data-log. After that, a full 90 second measurement of the sample will be taken and displayed with a dialog box for the user (Figure 45). The dialog box will also display the data file name to which the results will be saved, along with the option to save or discard these results. Once the Save or Discard button has been pressed, the instrument will begin preparation for the next sample and the process will repeat.

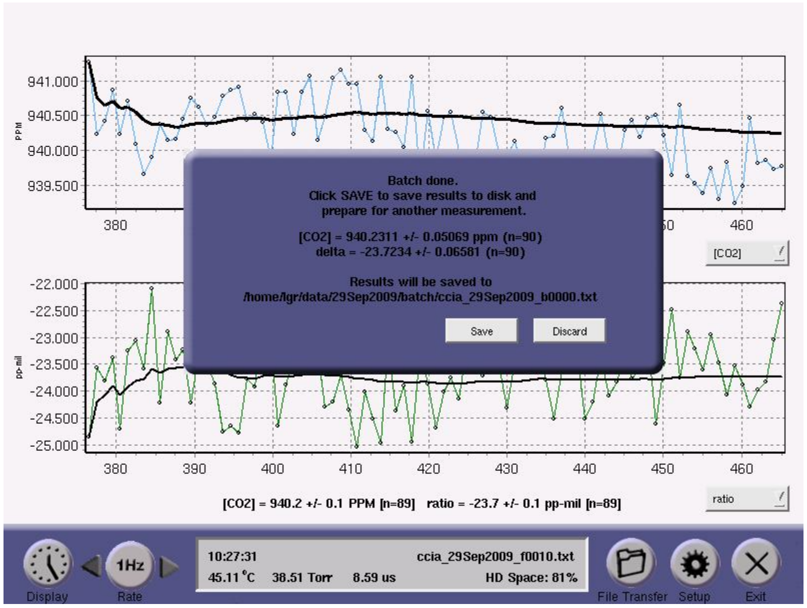

Figure 45: Results dialog for the sample injection.

Fixed Dilution Mode

For discrete samples with a CO_2 concentration in the range of 1000-3000 ppm the syringe injection with fixed dilution mode should be utilized. In this mode, the injected sample is internally diluted with zero-air gas by a fixed factor of approximately 3X to reduce the CO_2 concentration into the instrument measurement range. All other aspects of its operation are similar to the normal mode.

For syringe injection with fixed dilution mode, enter setup mode and select the syringe with "D" icon (Figure 38, bottom panel) and return to the main panel. Upon returning to the main panel, the instrument will close off the sample inlet, and begin preparing to accept a sample via syringe in the same fashion as the normal injection described in the previous section. The cell will be pumped down and flushed twice with zero air before prompting the user for the gas sample (see Figure 39 through Figure 42 from the previous section).

Once a sample has been successfully injected, the instrument will flush the cell twice with sample gas (up to 15 Torr) just as normal mode. Following pump-down, the sample will be 'puffed' in to ~13 Torr followed by zero air up to the operating pressure of ~38 Torr. This gives a rough factor of 3x dilution (Figure 46). You will hear a clicking sound as the zero-air introduction valve is pulsed open several times to reach approximately 38 Torr in the measurement cell).

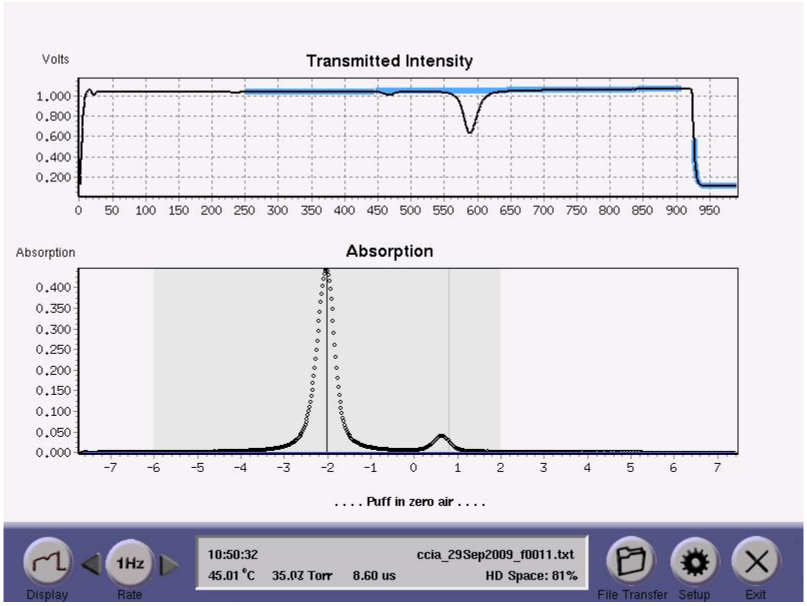

Figure 46: Dilution of sample gas in the measurement cell via "puffing" of the zero-air gas inlet valve.

Once the sample has been loaded and diluted, the instrument will take and discard 4 minutes of data allowing for the diluted gas to thoroughly mix inside the cell (see Figure 47).

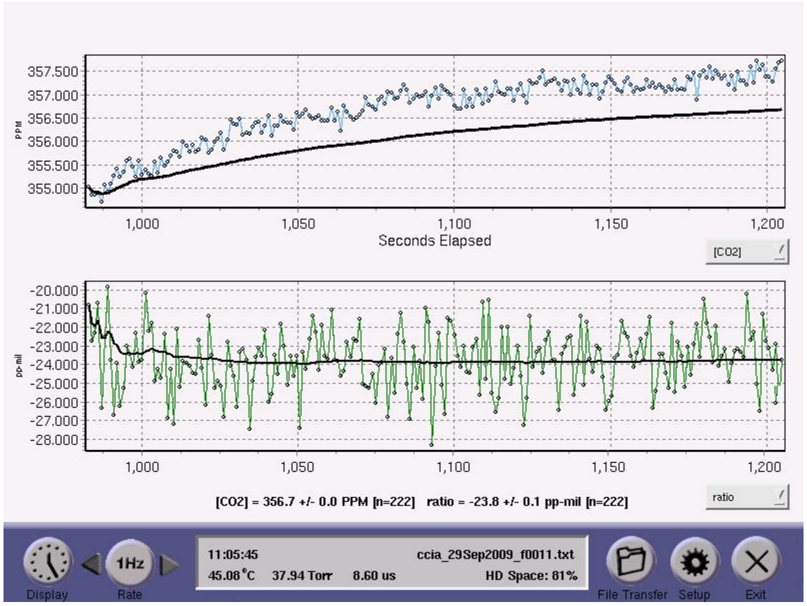

Figure 47: Equilibration of gas mixture after zero-air dilution. After 4 minutes of collection, the data log will reset to start a 90 second collection.

Following the equilibration, a 90 second measurement is taken and the results are displayed in a dialog box for the user (Figure 48). The dialog box will also display the data file name to which the results will be saved, along with the option to save or discard these results.

NOTE: The fixed dilution ratio of 3 is only approximate, and will vary from injection to injection. As such, the reported concentration should be treated as only approximately 3X less than the original sample value. The reported $\delta^{13}C$ value, however, will be accurate.

Once the Save or Discard button has been pressed, the instrument will begin preparation for the next sample and the process will repeat.

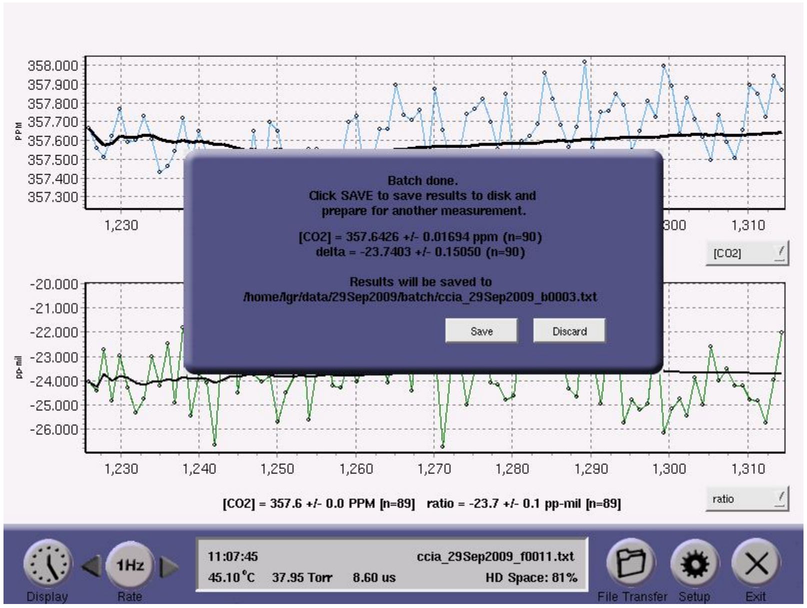

Figure 48: Results dialog for the sample injection.

Syringe Dilution

For discrete samples with a CO_2 concentration greater than 3000 ppm, it is possible to measure these samples via a two step dilution/injection process. A smaller, more concentrated sample is injected first followed by an injection of zero air such that the total gas volume is approximately 140 ml. LGR recommends running in 'normal batch mode' and using two different syringes with adequate volume precision. For example, a 140 μl sample of pure CO_2 followed by 140 ml of zero air can achieve a 1000:1 dilution giving a measurement sample on the order of 1000 ppm. Of course it is critical to have zero air that is thoroughly free of CO_2 if this level of dilution is needed.

NOTE: LGR recommends injecting sample first followed by zero air in order to insure that the entire sample has been thoroughly transferred through the input lines into the instrument.

Appendix

The following Appendices give additional information on the instrument configuration and operation.

Appendix A – 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.

Appendix B – Mirror ring-down time and maintenance

The mirrors of the measurement cell are protected from contamination by an internal inlet filter. However, it is possible over time and with continued use that the mirrors may gradually decline in reflectivity. This will not create errors in the CO_2 concentration or the isotopic measurement, because the mirror reflectivity is continually monitored and the measurement is compensated using the mirror ring-down time. However, if a significant change occurs in the mirror ring-down time (for example, greater than 20% reduction), the precision of the instrument may be reduced. Users should occasionally take note of the ring-down time and request instrument service (mirror cleaning) from LGR if a significant reduction in ring-down time occurs.

Appendix C – Changing septa on the syringe injection port (optional)

If your CO_2 Carbon Isotope Analyzer is equipped with an optional batch mode system for syringe injection of discrete samples, the septa on the syringe injection port requires periodic replacement. Depending on use, the septa should last a minimum of 100 injections. This procedure describes how to replace the septa.

First, make sure the instrument is in flow through mode (Setup panel, Figure 38 top). Remove the septum nut from the injection port as shown in Figure 49.

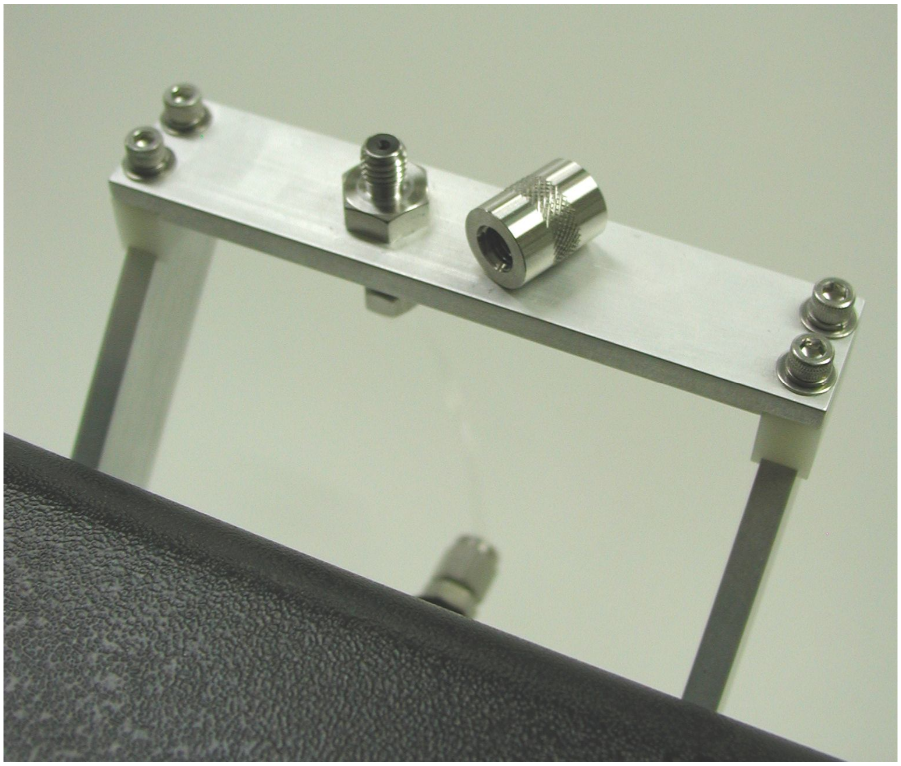

Figure 49: Syringe port with septum nut removed.

Remove the septa from the septum nut, and replace with a new septa from the package included with your instrument. Make sure the septa is installed so that the Teflon side (white) is facing out (i.e. will contact the injection port surface) as shown in Figure 50. A needle can be used to center the septa by inserting the needle through the septum nut and septa; the entire nut/septa/needle assembly can then be re-installed on the syringe port before removing the needle.

Figure 50: Position of septa within septum nut. Make sure that the Teflon side (white) is facing out.

Appendix D – LGR Contact Information:

For questions regarding the operation of this instrument, please contact:

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