MODEL AS-C3

DISSOLVED INORGANIC CARBON ANALYZER

INSTRUCTION MANUAL

V2016.01

Apollo SciTech, LLC

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CAUTION!

1. **Please read this instruction manual before using the Dissolved Inorganic Carbon Analyzer.**

2. **This product is designed for a laboratory environment.**

3. **Ensure the correct voltage is supplied to the instrument and the correct fuses are installed.**

This instrument requires a PC computer running Microsoft Windows to operate. We recommend that the PC is used to control of this instrument only. Connection to the Internet should be avoided. Virus protection software or Internet backdoor software (which constantly checks a website) may interfere with the execution of the analysis.

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A. UNPACKING AND INITIAL INSPECTION

A.1. Inspect the package

The Total Dissolved Inorganic Carbon Analyzer (referred to as: “the DIC Analyzer” or “the Analyzer”) was carefully packed in a sturdy carton box, with cushioning materials to withstand shock during shipping. Inspect the exterior of the package for possible damage upon receipt. If damage to the exterior of the package is apparent, contact the shipping company immediately. The Analyzer is insured for its full price with the shipping company. Apollo SciTech LLC. will not be liable for damage caused by the shipping carrier.

A.2. Unpack the package

Open the top of the package carefully and inspect for any signs of interior shipping damage. Please forward a report of any damages to Apollo SciTech LLC., in addition to contacting the shipping carrier.

When unpacking the instrument from the package, please ensure that the package contains all the items indicated on the Packing List. Please report any items on the Packing List which were not included in the shipment promptly to Apollo SciTech LLC.

B. INSTALLATION

B.1. Preparing to install your Dissolved Inorganic Carbon (DIC) Analyzer

For DIC analysis, you need a carrier gas, a reacting solution and a waste solution container.

B.1.1. Carrier gas: Nitrogen should be used as the carrier gas (not included with instrument). The nitrogen should be of 99.998% purity or better with constant pressure. A high-quality two-stage regulator capable of delivery a stable 15-16 psi (~1 atm) pressure is required. Full-scale pressure for this regulator is typically ~30 psi. The Harris Regulator is a good choice (Model No. 92SS-15, available from Fisher or VWR). Fluctuation of the carrier gas pressure will reduce the accuracy of the analysis.
If you suspect that the quality of your N_2 gas is low (generally not a problem in the U.S.), installing a chemical filter to remove CO_2 or H_2O in the N_2 gas is recommended. Also you may also install a PTFE filter (similar that supplied by Li Cor) before channel A.

B.1.2. Acid solution: Use a 6% H_3PO_4 acid plus 10% NaCl solution to convert all dissolved inorganic carbon to free CO_2 (i.e., 0.94L H_2O + 60mL H_3PO_4 + 0.10 kg NaCl).

B.1.3. Waste solution container: Since the Analyzer discharges before and after each measurement, place a container (for example, a plastic bottle 1 to 5 L) behind the Analyzer and run the waste tubing into the container.

Note 1: It is recommended that the waste solution collector be positioned below the Analyzer's waste outlet, ideally on the floor below the Analyzer. Check the waste container periodically, emptying as needed. Note that the waste solution is a relatively strong acid. Please discard it with sufficient dilution and follow local environmental protection regulations.

Note 2: The waste discharge valve inside the DIC Analyzer is normally open. It is necessary to keep the waste discharge tubing placed inside the waste container. The connector marked "Waste" on the back panel of the DIC Analyzer is also fitted with an internal shut-off valve; disconnecting the plug from the connector will stop the discharge. You may do so (or keep the end of tubing in a plastic bag) when transporting the Analyzer to another location to avoid spilling acid during transport. Make sure that the waste tubing is reconnected and waste solution flow is open before use (see the end of section B.2 for more information).

A Windows®-equipped laptop PC and a USB-serial converter (from USB to two RS232 serial ports) are included with the Analyzer. If the user chooses to supply their own computer, a similar laptop or desktop PC and USB-serial converter are required. A Windows®-equipped personal computer with two serial ports (RS232C) can also be used.

B.2. Familiarizing yourself with the Analyzer

Your DIC Analyzer is composed of three main parts: a digital pump on the left hand side, a *LI-COR* CO_2 analyzer (model LI-7000) on the lower right side and the main DIC Analyzer unit on the upper-right. Refer to Figure 1. Inside the upper-right compartment are the CO_2 gas extraction reactor, flow control devices, and the electronic control units. On the front panel are power switch and a temperature indicator for the reactor. A bubble/foam monitoring window is also installed on the left edge of the front panel.

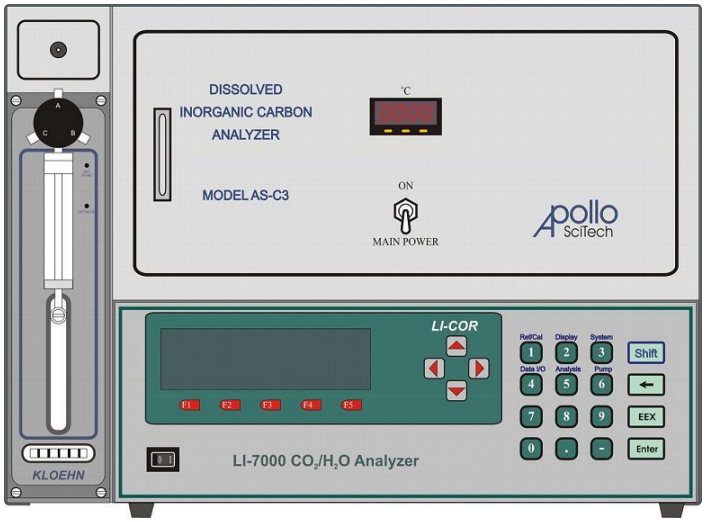


Fig. 1 Front view of the DIC Analyzer model AS-C3

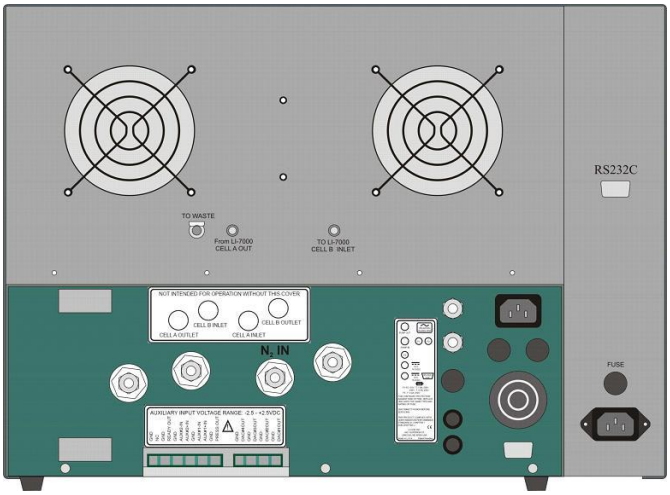


Fig. 2a Back-view of the DIC Analyzer without tubing

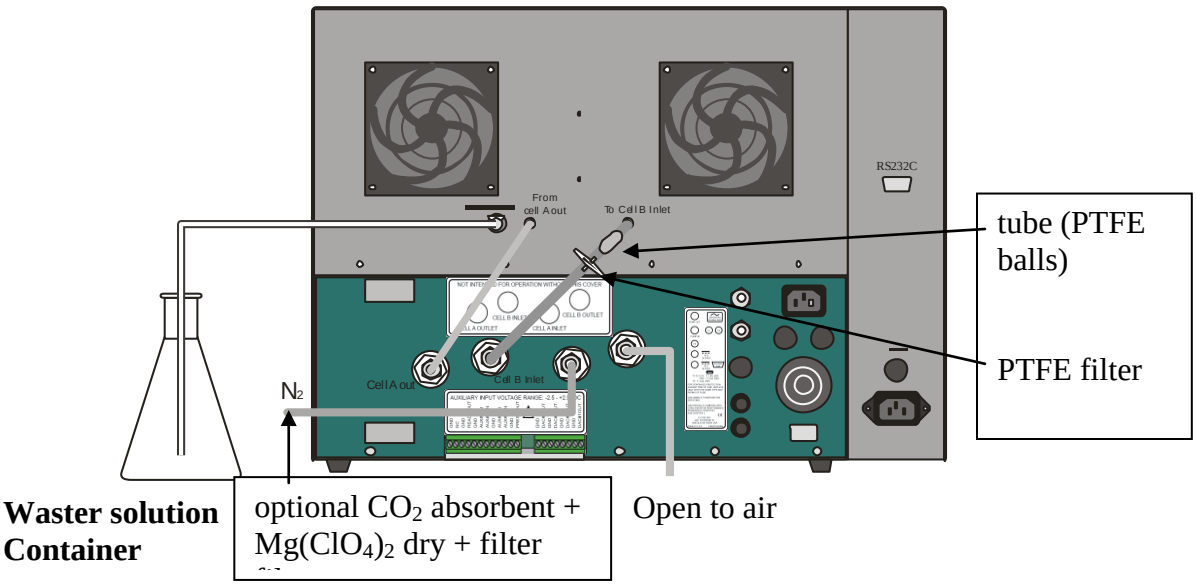


Fig. 2b Back-view of the DIC Analyzer with tubing (note a filter must be installed before Li7000 cell B inlet. Also another filter may be added before N_2 IN to prevent any particle to go inside the Licor's optical cell). A dryer tube (before cell b inlet) is included but filling the chemical, $Mg(ClO_4)_2$, is not required.

Attached to the digital pump is a 3-way distribution valve with a 2.5-mL syringe, which is used to transfer reagent and standard solution/sample for measurement. The digital pump is controlled through a PC by the original manufacturer's program. For more information about the digital pump please refer to the WinPump® User's Manual.

For detailed information regarding the *LI-COR* CO_2 Analyzer, please refer to the LI-7000 CO_2 analyzer instruction manual.
Figure 2 is a view of the back of the DIC Analyzer, shown with (b) or without (a) tubing connections. See B.1.3 Note 2 for more information about the waste discharge.

A flow monitoring window is added to the front panel in recent units. Some users may want to analyze the DIC of samples that have high organic matter and surfactant levels (such as soil pore fluid). Bubbles/foams may be formed during the analysis. Such bubbles may go through the gas line and damage the LI7000 (see Section D.7 for more information). Therefore, if bubbles or liquid is found in the window, one must stop the analysis until the problem is solved. Note you may open the case and clean the gas lines by flushing DI water through the window and drying it with N_2 gas if bubbles are found inside the window.

B.3. Carrier gas connection

Install a high-quality regulator capable of delivering 15 psi (1 atm, full scale is ~30 psi) to a pure nitrogen tank. Connect a piece of ¼" Tygon® tubing from the regulator to the "N_2 IN" connector on the back of the Analyzer (the same connector labeled "CELL A INLET" on the LI-7000 analyzer, see Figure 2). Set the regulator outlet to 15 psi or slightly higher (<17) and check for N_2 leakage. Fix any leakages.

Due to possible impurity (e.g., H_2O), we highly recommend installation of a $Mg(ClO_4)_2$ dry + PTFE filter (a dry tube is included in the LI7000 spare parts box) before the N_2 gas goes into Li7000 cell A. If you suspect there is also CO_2 in the N_2 gas, you may also add soda lime (or ascarite II) in the same tube (before $Mg(ClO_4)_2$) to remove CO_2.

WARNING: Do not set the carrier gas pressure too low or too high. If the pressure is too low, it will not open the internal mass-flow-controller. If the pressure is too high, it may burst connections within the system. A stable gas flow is critical. Inside the instrument, a mass flow controller regulates the N_2 flow to a constant rate between 250-300 mL/min.

B.4. Acid solution and standard/sample solution supply

Place the acid solution (i.e. 6% H_3PO_4) bottle to the left of the digital syringe. Connect a piece of 1/16" ID Tygon® tubing to port "C" of the digital pump (see Figure 1), and place the tubing into the reacting solution. Note that the end of the tubing should be completely submerged into the acid solution.

Attach a 1/32" ID Tygon® tubing to port "B" of the digital syringe on the Analyzer (see Figure 1). Place the tubing into your standard or sample for measurement (refer to Figure 3 below). Alternatively, use a glass/plastic syringe to withdraw standard solution or sample (take care not to introduce air into the syringe), then connect the syringe to the Tygon® tubing attached the port "B" of the digital syringe via an 1/16" ID Tygon tubing. Leave any valves or stopcocks between the syringe and the digital syringe open as the action of the digital syringe will draw the standard/sample solution directly from the glass syringe.

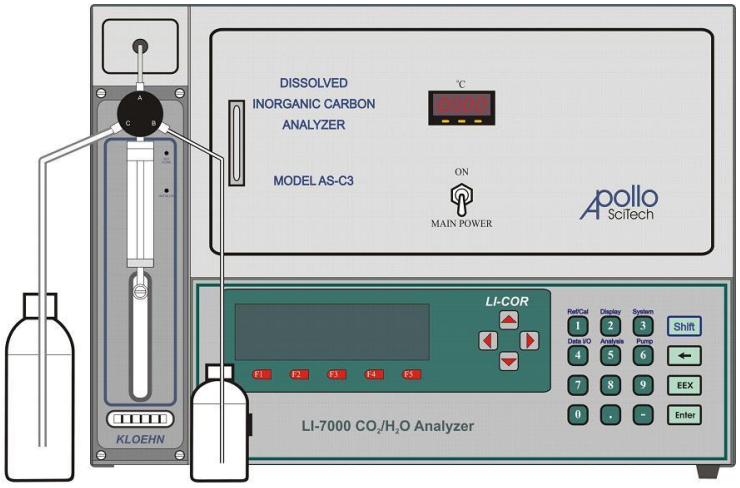


Fig. 3 Reagent and standard/sample solution tubing connection

When the sample volume is very limited, such as a total of 1-2 mL of porewater, supplying the sample directly from a syringe via a piece of short tubing is recommended. Supplying water via a syringe may also be preferred if CO_2 degassing from a limited volume sample is a concern. When plenty of the sample is available in a vial or bottle, withdrawing the sample via a capillary tubing is the preferred method (as illustrated in Figure 3). The inlet of the tubing should be well below the liquid level to minimize the effect of CO_2 loss.

B.5. Computer connection

A Windows® operation system laptop PC is used to control the Analyzer. It is connected to the Analyzer via a USB port with a USB-serial converter (from USB in the PC to two RS232 serial ports on the Analyzer). If the user chooses to supply a computer, a similar laptop or desktop PC running Windows® operation system is required.

We recommend that the PC is dedicated to control of this instrument only. Connection to the Internet should be avoided. Virus protection software or Internet backdoor software (which constantly checks a website) may interfere with the execution of the analysis.

A desktop PC with two serial ports may also be used. Connect the PC's first COM port to the 9-pin D-connector on the back of the digital syringe, using the RS232C cable with male/female connectors. Connect the second PC serial port to the 9-pin D-connector on the back of the LI-7000 analyzer, using the cable with female connectors on both ends. Both RS232C cables are included. If the RS232C cable does not match your computer, use a standard converter.

Refer to the LI-7000 manual and the digital pump manual for pin assignments.

The default setup of the DIC Analyzer program is that COM1 leads from the #1 serial port on the PC to the DIC main body, and COM2 leads from the #2 serial port on the PC to the LI-7000 analyzer. These settings can be changed within the DIC Analyzer software.

B.6. Power supply connection

Check that all of the power switches are in the "OFF" position before connecting the wall outlet.

Your AS-C3 is supplied with a Y-shaped AC power cord (or two power cables). One is for the LI-7000 and the other is for the AS-C3 main unit (both have a universal power setting). Connect the AC power cord from the DIC Analyzer and the LI-7000 to a wall outlet. A surge protector may be used to protect the instrument.

B.7. Computer program installation

Note that the supplied laptop PC has been installed with the control software and the USB-serial converter driver, and thus the following description only applies to users who supply their own computer.

The Analyzer comes with a CD or a USB Flash Drive (memory stick) containing all software programs. Copy all the files to the hard disk in your computer into one directory. There are two programs, DIC7INST.exe and DIC-LI7000.exe. The function of the DIC7INST.exe program is to transfer pump control sequences into the digital pump, which will be saved into the permanent (non-volatile) memory. This program has been pre-installed into the digital pump during factory testing. However, if the Analyzer has experienced a malfunction or memory loss due to a power surge or other reasons, you may reinstall the software by running this program.

The DIC-LI7000.exe program is the main analytical program which controls the instrument (refer to section E.4 for more information).

C. DIC MEASUREMENT PRINCIPLE

In a typical water sample, the species of dissolved inorganic carbon are CO_{2aq} + H_2CO_3, HCO_3^- and CO_3^{2-}. Upon the addition of a strong acid by the Analyzer, all of the species are converted to CO_2 according to the reactions below:

$$CO_3^{2-} + 2H^+ \rightarrow H_2CO_3$$

$$HCO_3^- + H^+ \rightarrow H_2CO_3$$

$$H_2CO_3 \leftrightarrow H_2O + CO_2$$

The resulting CO_2 gas is purged from the water sample by the pure nitrogen (N_2) carrier gas. The N_2 gas flow carries the CO_2 from the sample through a drying system that includes an electronic cooling pad surrounding the reactor and a Nafion tube to reduce water vapor. No chemical is used for drying. This helps to protect the environment and reduce operation cost. If you prefer to employ a chemical drier, a dryer tube is include with the shipment. Please fill $Mg(ClO_4)_2$ anhydrite in it and install it before the filter which goes to the LI7000 B cell (see Fig. 2 back view).

The concentration of dried CO_2 gas is then measured with the LI-7000 CO_2 analyzer. The total amount of CO_2 in your sample is quantified as the integrated area under the concentration-time curve. The LI-7000 CO_2 analyzer is a differential, non-dispersive, infrared gas analyzer. It is stable when maintained properly. For more detailed information about the LI-7000 CO_2 analyzer, refer to the LI-7000 CO_2 Analyzer INSTRUCTION MANUAL included on CD.

D. OPERATION

⚠ ***Caution:*** *During every measurement cycle* ***the waste solution in the reactor is discharged both during the end of an analysis and at the beginning of the next analysis****. If it does not, stop running the program and check for waste discharge problems (such as blockages in the waste tubing). Do not run the Analyzer until the problem is solved!*

D.1. Warming up

Turn the Analyzer's main power switch on, then turn the LI-7000 CO_2 analyzer power on. Wait until the LI-7000 passes its self-test (the self-test is when the LI-7000 is checking its internal conditions before the instrument is ready to use). Refer to the LI-7000 manual if the self-test fails.

Let the Analyzer warm up for 60 minutes or longer. (One user used a timer to turn the LI7000 on early morning, 3 hours before turning on the DIC main system). The temperature display on the front panel of the Analyzer should show 3°C. Turn the two-stage regulator valves of the carrier gas (N_2) on with an output pressure of 101 kPa (or 1 atm or 15 psi) or slightly higher. Make sure **the gas exit valve in the back is open (Fig. 2b: Open to air)**. This valve should be open sufficiently to sustain a flow rate of 250 mL/min, which is regulated to a constant value (within ± 2 mL/min) by a mass flow controller inside the Analyzer. Note in a dust-free lab environment, you may leave this valve open all the time.

D.2. Zero and span settings

In general, it should not be necessary to adjust the zero and span settings of the LI-7000 for two reasons. First, they have been set in the factory. Second, the Analyzer will measure each peak's area relative to a baseline (the CO_2 reading when running N_2 gas through the LI-7000 directly), regardless if the LI-7000 is reading zero CO_2 or not. However, if for any reason the baseline has drifted away from zero significantly (for example over 10 ppm, which may occur over a long period of use), we suggest resetting the zero and possibly even the span. The DIC Analyzer is not particularly sensitive to the CO_2 concentration of the span gas, as all samples are calibrated against a DIC standard solution (i.e., the Certified Reference Material or seawater with known DIC concentration). Thus, the span gas does not have to be highly accurate.

D.3. Digital pump HOME position setting

When you receive the DIC Analyzer, the HOME position of the digital pump is already set at the correct position. Unless absolute necessary, do not try to reset it.

If the zero volume position of the piston in the syringe has been changed and is more than 2 mm from the top, reset the HOME position (the newer version has only a very small gap of <0.5 mm). The procedure of resetting the digital pump HOME position is:

1. After powering up the DIC Analyzer, push the "INITIALIZE" button on the front panel of the digital pump.

   *Note: the piston position after initialization is **NOT** the **"HOME"** position.*

2. Observe the top position of the piston inside the syringe while adjusting the thumb wheel on the lower level of the front panel until the piston is approximately 0.5 mm away from the top of the syringe. (or move the piston all the way to touch the top by turning the thumb wheel to the left, then, turn piston down or the wheel to right for about 1/16 turn)

   Note: If the piston is too close to the top of the syringe, the syringe may be damaged when pushed too hard by the piston.

3. Push the "HOME" key on the front panel of the digital pump to complete the HOME position setting.

WARNING: Whenever the thumbwheel is moved- whether the power is on or not- a new HOME position must be set to avoid possible damage to the digital pump's syringe.

D.4. Running the analytical program

Under Windows system, click "Start" in bottom left corner, then "All Programs", select DIC/DIC. The program will start, and show a window as in Fig. 4. Or click the icon "A/DIC" on your PC's screen to start. Note many of the steps below are already set in attached laptop and thus are not needed.

Click button "Parameter" to input communication port numbers and the volume of sample to be measure in ml as in Fig. 5. Once the com-ports are typed in with correct numbers, click the Connect button on the top left corner on the tool bar to create the communication with DIC analyzer and LI-7000, to initialize the pump and LI-7000 (default setting: COM1 for the DIC unit and COM2 for the LI-7000 analyzer) (Refer to Fig 5).

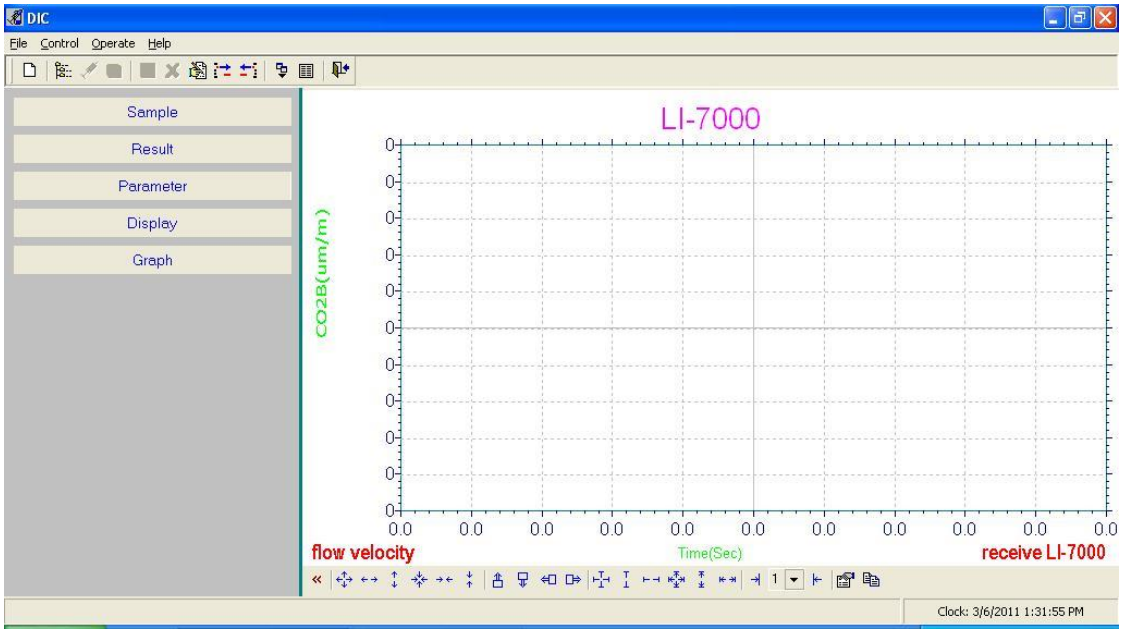


Fig. 4 DIC program interface

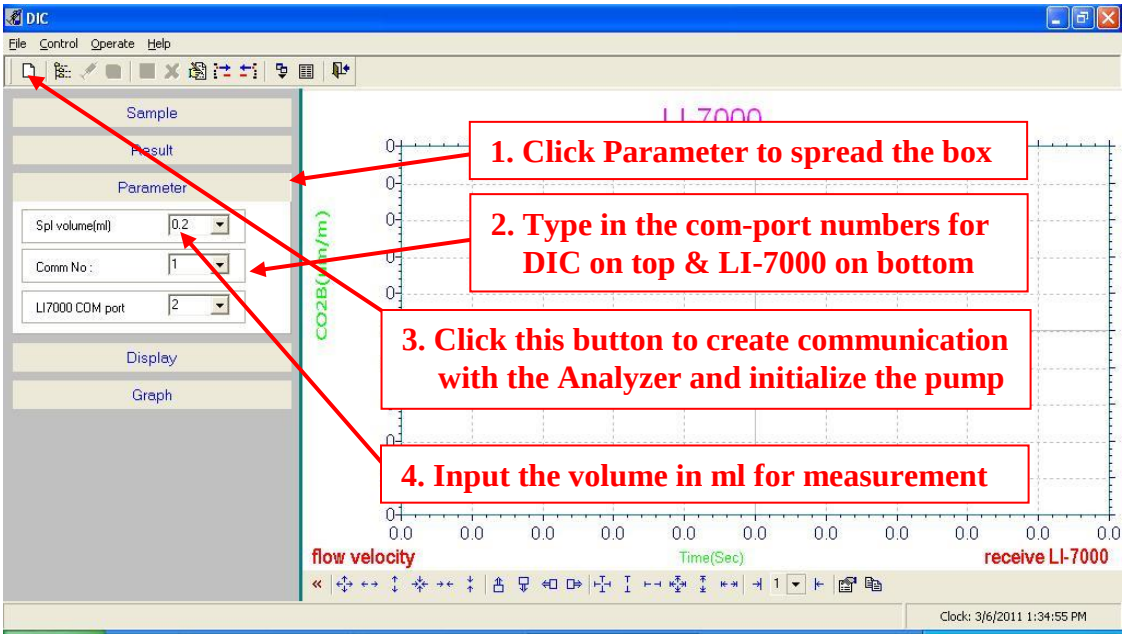


Fig. 5 DIC program Parameter setup box

If the COM-ports of the computer are not COM1 and COM2, you may reassign the computer's COM port numbers by opening Windows's Control Panel. Then follow the path: Control Panel → System → Device Manager → Ports → Ports Setting → Advanced → COM-port number selection. Select the desired port number from this window.

Once the communication is created, the window will show the N_2 flow rate and the CO_2 reading from LI-7000, as shown in Fig 6.

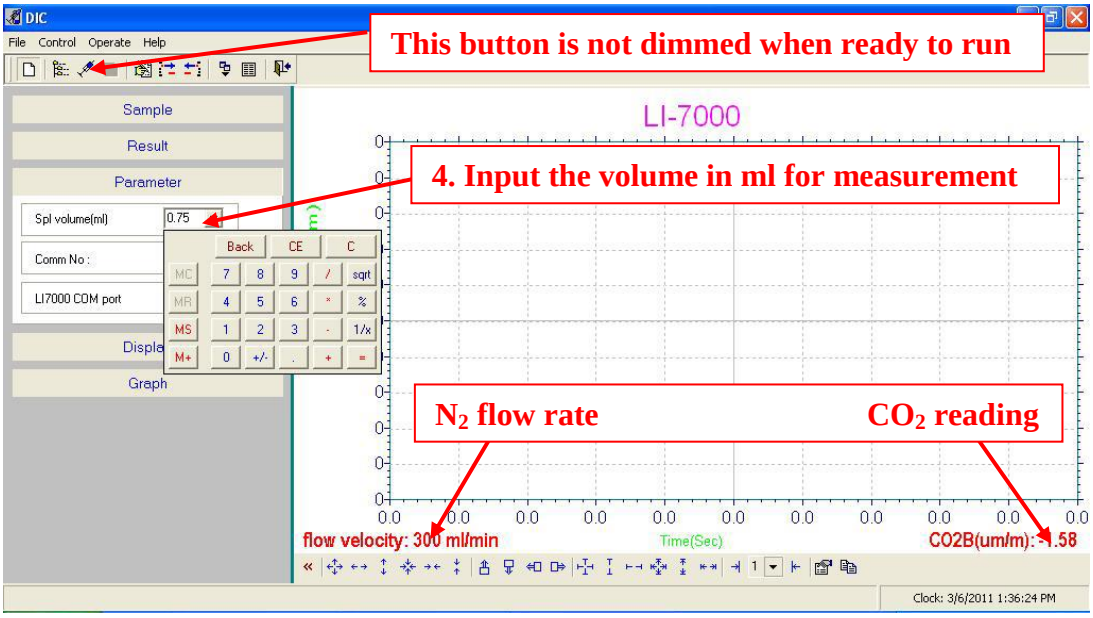


Fig. 6 DIC program communication created and sampling volume box (note in newer unit the flow rate is set to 200 ml/min.

D.5. Analytical procedure

Place the tubing from port "B" of the digital pump into a standard solution or water sample, or connect the tubing to a glass syringe containing a standard solution or sample. Then click "Spl volume(ml)" cell or pull-down button to open a key pad to input a volume of the sample/ standard to be measured. See Fig. 6. The value of the previous measurement is shown in the cell. The allowable range of the volume is from 0 to 1.5 mL (preferred range is within 0.2 to 1.2 mL). A volume of 0.8 or 1.0 mL is recommended for seawater samples.

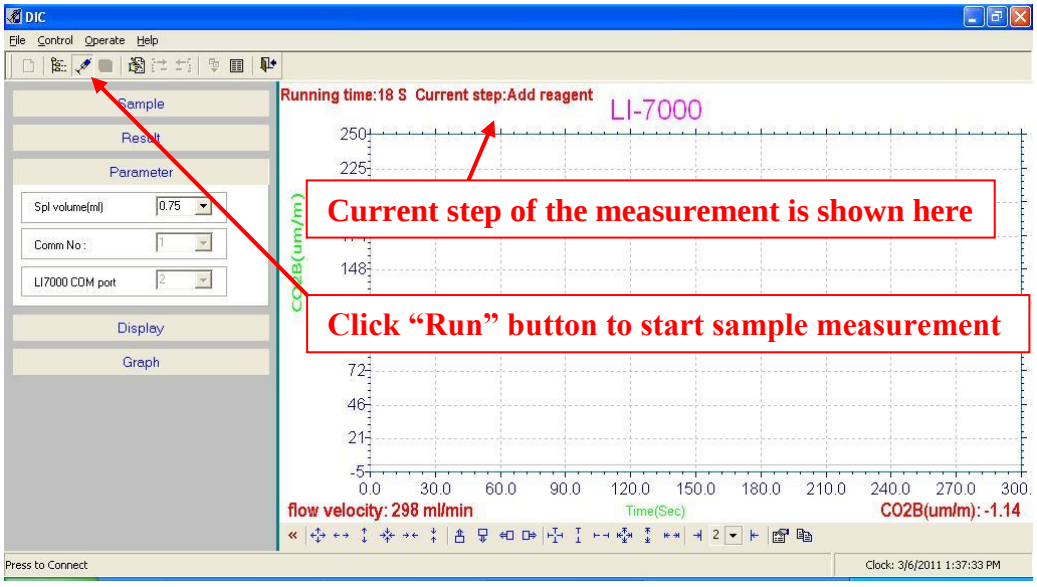


Fig. 7 Run sample measurement

Click the "Run" (with a symbol of "syringe") button on the tool bar to start measurement (Fig. 7). After pumping the reagent and sample solutions, the Analyzer will start to integrate the CO_2 produced over time. Once the integration has started, the plot window on the right hand side will start drawing the curve of the CO_2 reading from LI-7000 until the integration is completed. The result is shown in the "Result" box, with the integration area, and DIC value if the calibration has been completed (Fig. 8).

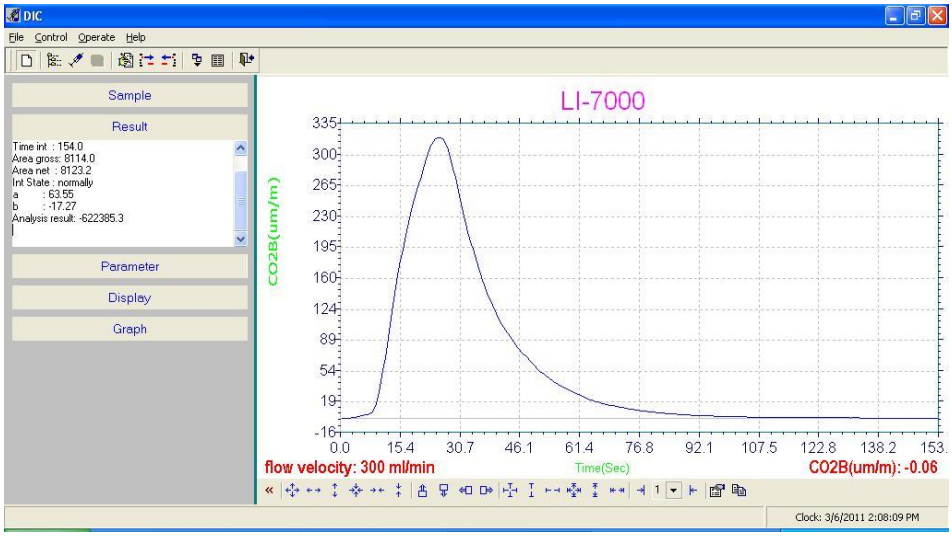


Fig. 8 Sample measurement result (curve could be in different shape)

We recommend discarding the first one peak area of each sample since the tubing system needs to be flushed completely with the solution before an accurate peak area can be produced. For the greatest accuracy, repeated measurements are essential. After flushing, the repeated analyses usually agree within ±0.1%. Following each measurement, record the result (peak area) and the volume measured.

Tip: Waiting for similar intervals (or idle times) between measurements, such as 20 seconds, will provide more precise results. Best is to use batch analysis (see below).

D.6. Standardization

Connect a standard solution of known DIC concentration to port "B" of the digital pump (refer to Section E.5).

You may run the standard as a sample, using different volumes of a primary standard you purchased or a secondary standard you prepared. It is recommended that three different volumes be measured for the standardization. Solution volumes between 0.20 and 1.0 mL are recommended (such as 0.60, 0.8 and 1.0 mL or 0.5, 0.8 and 1.1 mL, depending on the expected DIC concentration range of your samples). If you are analyzing open ocean seawater with a limited DIC range, use a tight range (for example, 0.7, 0.8 and 0.9 mL) is recommended. Repeat standard measurements several times for each volume (again, throw away the first analytical value when you first switched from sample to standard).

Standardization can be done manually or automated. First, let's use manual approach to illustrate the principle and procedure. You should write down the volume of the standard added and the CO_2 integration area each time.

After all standardization volumes have been completed, use a linear regression software program to determine the relationship between peak area and the DIC content by converting each volume of standard solution into DIC content. For example, if the standard solution DIC = 2000.0 µM, then 1.0 mL is equivalent to 2.0000 µmol of DIC (2000 µM*0.001 L) and 0.5 mL is equivalent to 1.0000 µmol of DIC (2000 µM*0.0005 L). As 1.0 mL is equivalent to a DIC concentration of 2000.0 µmol and 0.5 mL is equivalent to 1000.0 µmol if they are scaled to a total volume of 1 L, you may wish to make the linear regression equation directly to this unit (µmol/L or µM). Thus, if your sample volume is 1.0 mL, a direct inverse of the regression equation will give you the concentration of your sample (in µM/L). If your sample volume is 0.5 mL, a factor of two should be multiplied (see Example Calculations below). This can be performed conveniently on a spreadsheet program such as MS Excel® (as illustrated in Figure 9).

Example Calculation 1:
Sample volume: 1 mL (0.001 L)
Measured Peak Area: 6000
Regression equation: y (Peak Area) = 4.9755*x(DIC) + 92.128
Re-arranging the regression equation: DIC = (Peak Area – 92.128) / 4.9755
Calculation: DIC = (6000 – 92.128) / 4.9755 = 1187.4 µmol/mL
Volume Correction Factor (Scale to 1 L): 1187.4 µmol/mL / 1 mL = 1187.4 µmol/L

Example Calculation 2:
Sample volume: 0.75 mL (0.00075 L)
Measured Peak Area: 7631.5
Regression equation: y (Peak Area) = 4.9755 * x(DIC) + 92.128
Re-arranging the regression equation: DIC = (Peak Area – 92.128) / 4.9755
Calculation: DIC = (7631.5 – 92.128) / 4.9755 = 1515.3 µmol/mL
Volume Correction Factor (Scale to 1 L): 1515.3 µmol/mL / 0.75 mL = 2020.4 µmol/L

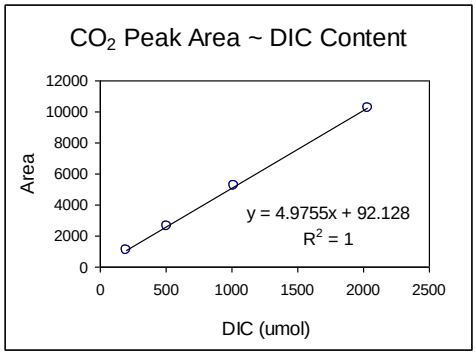


Fig. 9 Example of a standard curve (note the x-axis is converted to per 1-L volume unit). Four different volumes (0.1, 0.25, 0.5 and 1.0 mL) of the same standard solution were analyzed to generate this standardization curve. Results were obtained with an earlier version of the instrument.

For analysis of seawater samples, a standard solution of Certified Reference Material (CRM) is recommended. - CRM is prepared by Dr. A. Dickson of the Scripps Institution of Oceanography, La Jolla, CA 92093, U.S.A. (http://andrew.ucsd.edu/adickson/co2qc/). For low DIC freshwater samples, a very small volume (<0.1 mL) of the Dickson CRM may be used. For high DIC (>5 mM) sediment, porewater or groundwater samples, you may prefer to prepare custom DIC standards. Such a standard may be prepared from reagent grade Na_2CO_3 after baking at 285°C for two hours. It is recommended that any self-prepared DIC standard solutions be standardized against the CRM.

The above procedure is automated in the Analyzer and the user doesn't need to perform it. You can use the standardization function in the batch analysis mode or run CRM as samples of unknown and then make a standard curve as above in Excel.

D.7. Sample measurement

Replace the standard solution with a sample, either by moving the Tygon® tubing to the sample bottle or connecting it to a glass or plastic syringe with the sample. In the DIC computer program, select the desired volume for the measurement (0.8 mL is recommended). Then click "Run" button (Fig. 10) to start sample measurement. Record the result (Peak Area) displayed by the program and repeat until a consistent result is achieved. The first run of each sample should be discarded due to flushing of the tubing from the previous sample.

Note that the results will also be saved to a file. Click the short-cut button the result in Fig 10 to open the result sheet which you can export to either Excel file or text file.

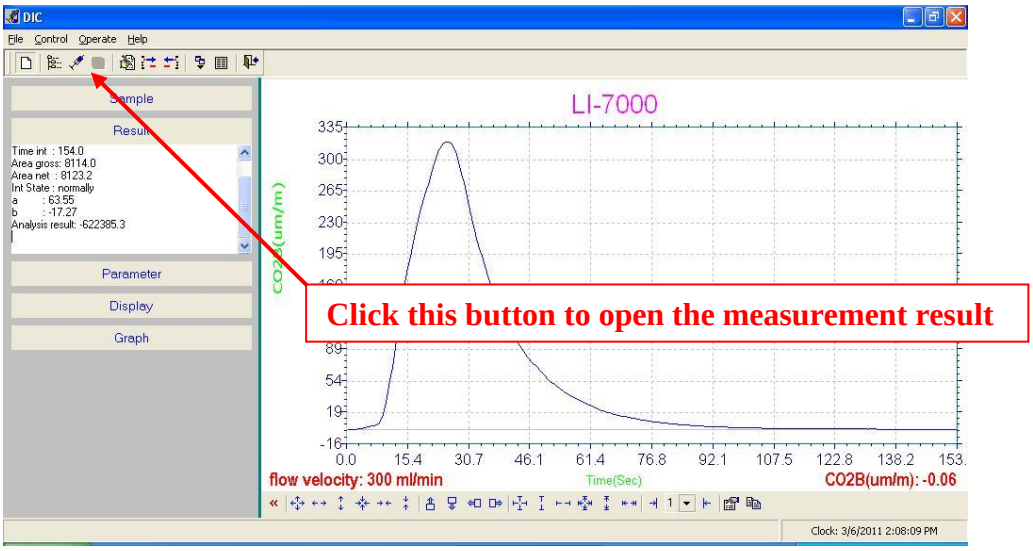


Fig. 10 Measurement result sheet quick open button

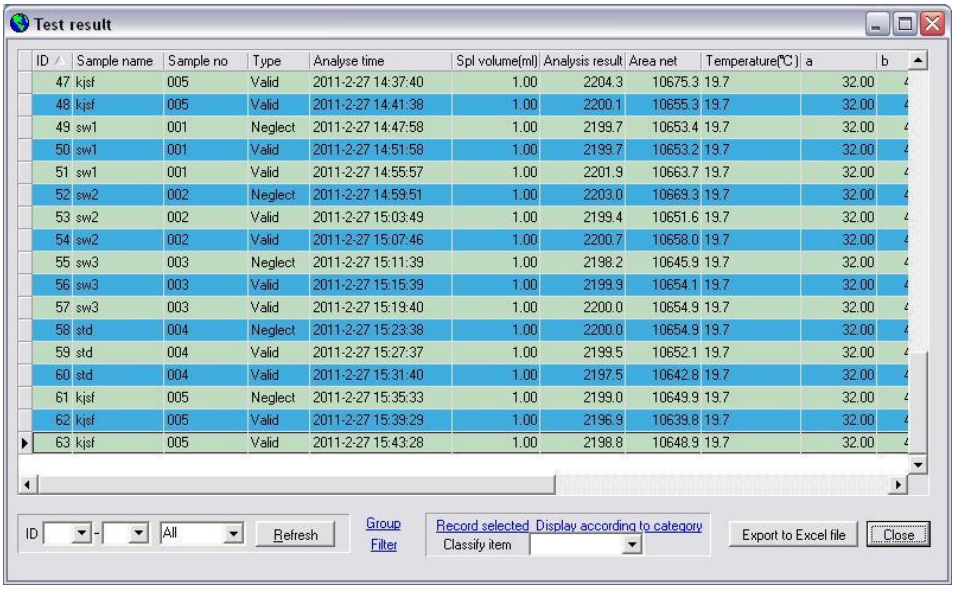


Fig. 11 Measurement result sheet

Calculate the DIC content according to the linear regression function obtained during standardization. This can be performed on a spreadsheet program such as MS Excel®. Alternatively, convert the final value directly into concentration units (µM or µmol/L), as illustrated in Figure 9. Again, this is automated in the Analyzer. Note it is preferred to run samples using the batch process below.

Record the room temperature of each measurement (sample or standard). This allows calculation of the sample density and conversion of units between µM/L and µmol/kg, according to this equation:

Density = (999.842594 + 0.06793952*T - 0.00909529*T^2 + 0.0001001685*T^3 -0.000001120083*T^4 + 0.000000006536332*T^5 + (0.824493-0.0040899*T + 0.000076438*T^2 - 0.00000082467*T^3 + 0.0000000053875*T^4)*S + (-0.00572466 + 0.00010227*T - 0.0000016546*T^2)*S^1.5 + 0.00048314*S^2)/1000 (check : at T=25°C, S=35, density = 1.02334)

Running samples with high surfactants: Some users may analyze the DIC of samples that have high surfactant content (such as soil pore fluid). Foams/bubbles may be formed during the analysis. Such bubbles may go through the gas line and into the LI7000 and damage it. While the instrument was not designed for this type of analysis, we have recognized the need to analyze such samples and have added flow monitoring window (on the front panel) to stop or delay the bubbles from entering the LI-7000. Great care must be exercised in analyzing high surfactant samples. If significant amounts of foams or bubbles are noticed inside the flow window, do not repeat the measurement of the same sample. Instead, remove the sample, place the sample intake line into DI water, and run the DI waster as a sample until the bubbles or liquid disappears. The liquid inside the flow monitoring window will be pushed automatically back through the reactor and discharged when the next measurement is run. Or open the case and flush the viewing window and tubing with DI water using a syringe.

D.8. Batch process for standard and sample measurement

There is a batch process function on the program, to do calibration and sample measurements. Click button "Batch Process" you will open the window as Fig 12.

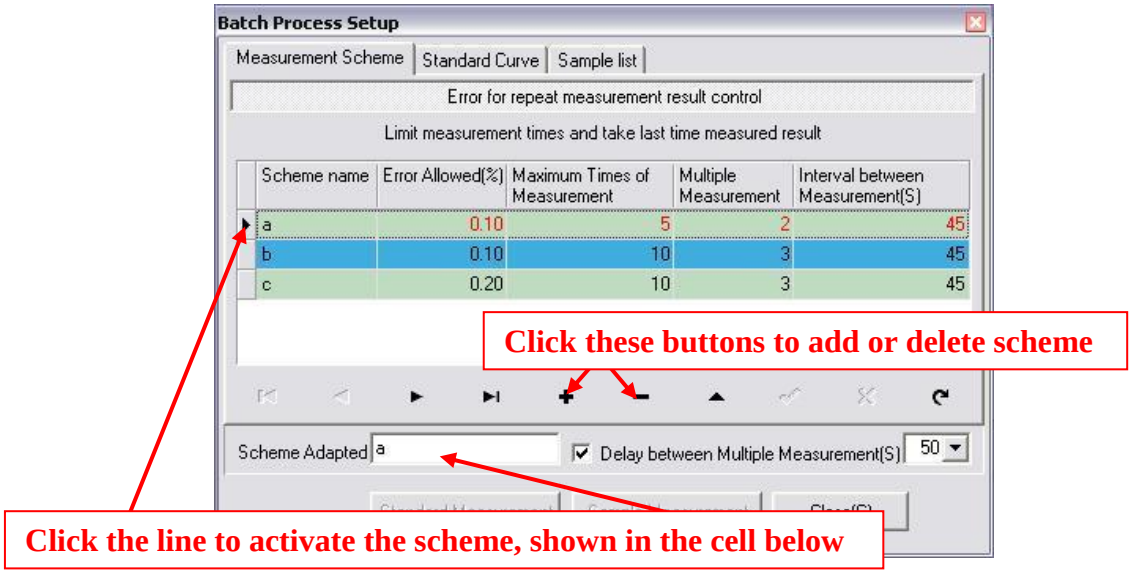


Fig. 12 Batch process window. Here "Maximum Times of Measurement" is the maximum times of repeated analysis while the "Multiple Measurement" means the times of repeated analysis when the allowed error (%) is met and when the analysis is ended. For example, for when 0.1%, 5 and 3 (or 2) are selected, a maximum of 5 repeated analysis is permitted but the analysis will end if 3 (or 2) of them met the set precision criteria of 0.1%. Note in newer version, the Interval between analysis is set to about 15 seconds.

There are three tabs on top of the window. The first one on the left is for setting up the criteria for the measurement. You may create as many schemes as you want by clicking the "+" button. For normal analysis, we recommend a "3 repeats out of 5 maximum" scheme.

Click the tab "Standard Curve" in the middle for calibration (Fig. 13).

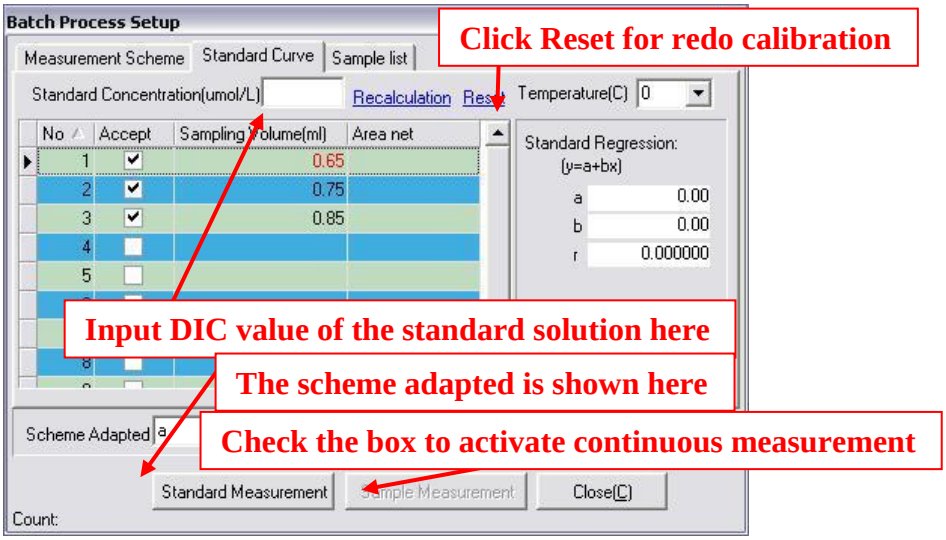


Fig. 13 Batch process for calibration

After all the information is input into the form and the standard solution is hooked on to port B of the digital pump, click the button "Standard Measurement" to start the calibration. The program will automatically draw the standard solution to run the measurement following the criteria of the scheme selected, until all the numbers of the standard accepted are done. The correlation of the result will be given on the right hand side, and also be saved.

The last tab on the right hand side is for sample measurement, as shown in Fig. 14.

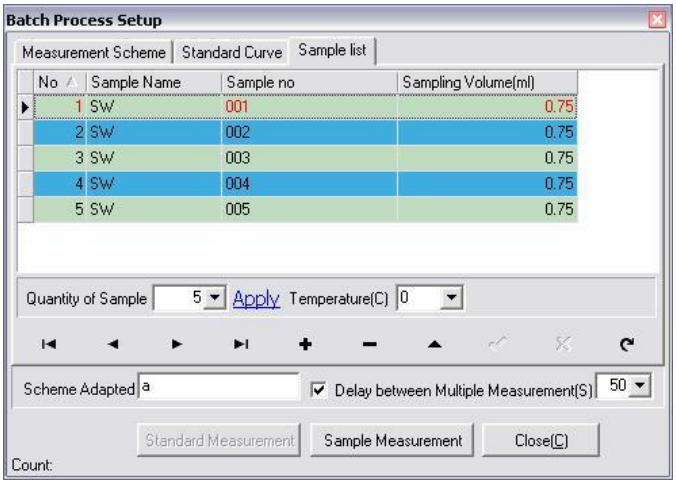


Fig. 14 Batch process for sample measurement

Add all the samples you want to measure at the time with the volume on the right column, clicking "+" to add lines. Press the button "Sample Measurement" to start the batch sample measurement. The program will finish all the samples according to the scheme selected, and the final result will be saved.

To view the result, click the short-cut button "Test Result" as shown in Fig. 10, a spreadsheet will be open with all the information saved. You may export the data either to program Excel (if you have installed Excel in the computer) or simply to Notepad in text format.

Note 1: Many users may find it easier to simply treat the standard as unknown samples (again use 3 volumes). At the beginning and end of analysis (or a day), after the Licor is warmed up, run a standard curve with 3 volumes. Then, insert the standard as an unknown every 5 to 8 samples using only one volume (the same as the samples). Then do the calculation in an Excel file. This is convenient for a few reasons. As the instrument will drift slightly with time, one cannot apply the same standard curve over a day, thus adjustment is needed. Also, one will have to convert the volume unit (μmol/L) to weight unit (μmol/kg) using sample salinity and room temperature, going to Excel is needed.

Note 2: Air bubbles may form inside the sample syringe on top of the piston or attached to the ceiling/top of the syringe). Small air bubbles of < 1mm in size do not seem to be a problem as they stay there stable most time. If you see large bubbles (3-4 mm), this is often the reason of large noise in the data as bubbles change size with time and with room temperature. First check if the digital syringe is not tight. Please tight it by turning the syringe clockwise using two fingers. Do not overtight it. If the syringe is tight, check if the two connectors are tight (if not tighten them, again use fingers are enough; no need to overtight). One may flush bubbles out by tapping the (bottom of the) syringe. One effective way to eliminate air bubbles is to use the Flush function (under Control Tab). Lift the acid tubing to air for a few seconds to create an air space in the syringe, which will eliminate all air bubbles.

Air bubbles may also form even if there is no leakage. This problem of bubble formation occurs most with river/estuarine samples (cold and fresh water is rich in dissolved air) inside a warm room. One option is to put bottles of samples and standard in cold water jackets.

Sometimes, it could be just an old leaking syringe problem (at the end of each day's work, flush with DI water will prolong the life of the syringe). Replace it. How to remove the syringe: 1) push Initialize button. 2) unscrew the lower screw rod using a screw driver. 3) unscrew the top with fingers.

How to install the syringe: (reverse the above procedure 3 and then do 2). The lower screw may not fit into the crew hole well, do not force it in but push the Initialize again. Or loose the upper screw a bit and try again or after tightening the lower screw, you should tighten the upper screw again. Finally, push Home button to finish the procedure.

D.9 Ending the measurement

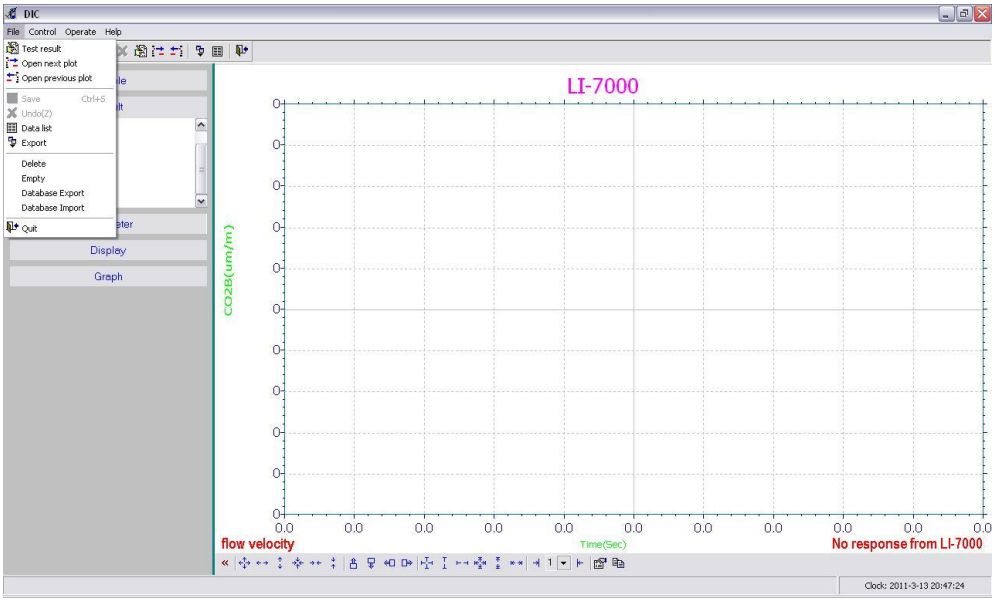
Reminder: Before shutting down the instrument, put the reagent/acid inlet into DI water and do the following:

Once the measurement is finished, click the short-cut button "Connect/Disconnect" to stop the program. A remind window will show up to ask you to replace the reagent/acid solution with DI water, press "Enter", the Analyzer will inject the DI water to rinse the tubing system, flush the reactor, and push the solution from the reactor into the waste container. After this is complete,

follow this sequence: turn the LI-COR CO_2 analyzer off, turn the DIC Analyzer main power off, then shut down the computer, and turn the N_2 gas off.

If you wish to store the Analyzer for a long period of time without using it or to transport the Analyzer, put both the sample and reagent inlets into DI water and run the Sample analysis procedure twice using a 1.5-mL volume, then leave both inlets in air and run the 1.5-mL Sample analysis procedure twice more. Then, press "Connect/Disconnect" button, followed by "Enter", keeping both inlets in air, and click the far-most on right short-cut button to stop the program.

Instead the short-cut buttons, you may use the pull-down menu to run the program, such as the figure shown below.



E. SPECIFICATIONS

Power supply: 100 - 240 VAC (universal power， auto-switch)
Carrier gas required: N_2, ~15 psi (1 atm) exiting pressure
Repeatability: ± 0.1% at DIC concentrations ~ 2000 μmol/L
Sample volume: 0.2 - 1.5 mL per measurement
Time required: < 5 minutes per measurement
PC requirement: 80486 or up
PC operating system: Windows XP®
Communication: RS232C or USB (a USB-RS232 converter is included)
LI-COR setup
Baud rate: 9600

Data Bits:	8
Stop Bits:	1
Parity:	None
Environment Required:	Indoor
Temperature:	Room temperature (steady at 15-28°C) preferred. Temperature fluctuations will affect the precision of the measurement
Humidity:	Up to 85%
Positioning:	Upright use. No angle greater than ±15 degrees from vertical is allowed.
Dimensions:	12.5” x 17.4” x 10.4” (H x W x D) (31.8 cm x 44.2 cm x 26.5 cm)

F. MAINTENANCE

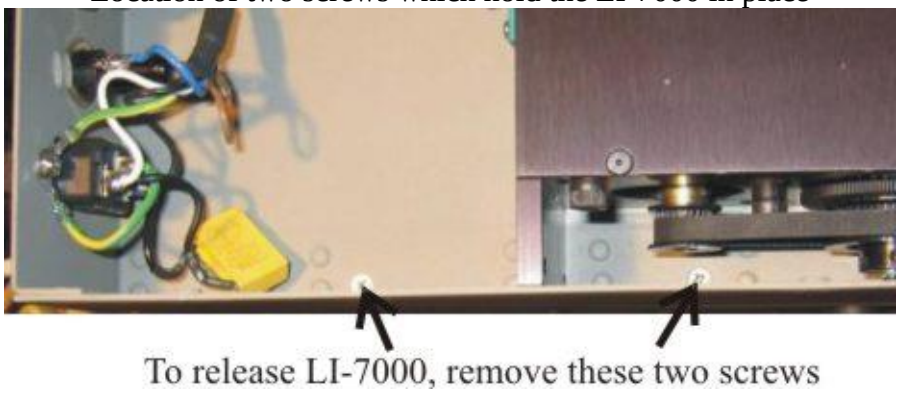
F.1. LI-7000 maintenance

⚠ ***Caution:*** *Disconnect the AC power supply before opening the cover. The AC power is high voltage which is hazardous!*

To service the LI-7000, detach the LI-7000 from the DIC Analyzer first. Follow the procedure below:

1. Turn off the device. Shut off the N_2 flow. Disconnect the main power supply.
2. Remove the 2 screws on the bottom part of the left-hand side panel (below the KLOEHN digital pump) with a Philips screw driver.
3. Remove another 4 screws underneath the opposite right-hand side panel.
4. Remove 6 screws on the top of the instrument cover.
5. Grip the bottoms of the two side panels, and flex them away from each other and away from the main body of the instrument. The cover and side panels are sheet metal and should flex with a minimal amount of force. When the bottoms of the two side panels are clear of the main body of the instrument, carefully move the entire cover upwards until it is clear of the instrument. There are two (2) screws inside the device on the left-hand side. They are located near the bottom and they hold the LI-7000 in place. Refer to the picture below to find the location of the screws, and remove them.
6. The LI-7000 can now be removed.
7. Reverse this procedure to reinstall the LI-7000.

Location of two screws which hold the LI-7000 in place



G. TROUBLESHOOTING

G.1. Common problems

The DIC Analyzer was completely checked during and after manufacturing and assembly operations. It was carefully packed to prevent damage during shipment. If the Analyzer is not functioning properly, check for the following common problems first:

Are all cables connected correctly?

Are there any gas and/or liquid leaks?

Does your power supply outlet match the selected value?

Were the cable connector pin-outs matched properly?

G.2. Troubleshooting guide

G.2.1. Power supply problems

1. Check the power supply cord to ensure it is connected properly.
2. Check the fuses, and replace any fuses that are burned out. If the DIC Analyzer's main power switch works but the LI-COR does not get power when switched on, check the LI-COR fuse.
3. Verify that the power supply setting matches the supply outlet voltage.

   Note: If the voltage supplied to the instrument is greater than the selected value on the power cord switch, the Analyzer could be damaged.

G.2.2. LI-7000 CO_2 analyzer problems

Refer to the LI-COR CO_2 analyzer instruction manual.

G.2.3. Software problems

G.2.3.1. DIC Program does not run

Check that your computer is an IBM/Windows compatible, 80486 or better system. Ensure your computer has enough memory (RAM) to run the program.

If the DIC program displays "Disk is full" and then stops, check your hard disk and ensure that there is enough free space to save the measurement record.

G.2.3.2. No communication between the computer and the Analyzer

1. Check the communication cables (RS232 cables). There are two cables required for communication between the DIC Analyzer and the computer. One is for the main DIC system, and the other is for the LI-7000 CO_2 analyzer. Use the cables that come with the Analyzer. If the "D" connector plugs do not fit your computer, use standard connector converters to match your computer's communication ports. Note that all the pin-outs should have good contact.
2. Check that the correct communication port numbers have been selected in the DIC program. The default setup is COM1 for the DIC system and COM2 for the LI-7000 analyzer.
3. Check the communication parameters. The program uses the following parameters:
   Baud rate: 9600
   Data bits: 8
   Stop bits: 1
   Parity: None
   Make sure the Baud rate of the LI-COR CO_2 analyzer has been set to the same value as the DIC program. Refer to the LI-COR CO_2 analyzer instruction manual for instructions to set the Baud rate.
4. If you are using a USB port for communication with the instrument, a USB-RS232 converter is required. Run the DIC program with Windows XP®. When the USB-RS232 converter's driver is installed, it may assign the RS232 ports to various COM port numbers. Check to make sure the RS232 ports are assigned to COM1 and COM2 by clicking Control Panel → Performance & Maintenance → System Properties →Device Manager → Ports → Ports Setting → Advanced → COM-port number selection, and then set the desired port number.

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G.2.4. Cooling system problems

1. Make sure the ambient room temperature is not too high.
2. Check the cooling fans to see if they are blocked by foreign objects or dust.

G.2.5. Measurement stability problems

G.2.5.1. Carrier gas N_2 flow rate not stable

1. Check the N_2 supply pressure. Confirm that the pressure is ~15 psi (1atm) or slightly high (<17 psi). If the pressure is too low, it will not open the mass-flow-controller's valve. If the pressure is set too high, it will burst fittings within the system.
2. Make sure the regulator valve for the N_2 gas is open enough to supply the flow rate of 300 mL/min.
3. The pressure of N_2 gas should be stable with no fluctuation.

G.2.5.2. Solution problems

1. Check that the reagent/acid tubing is immersed into the solution and that no air bubbles are trapped inside the tubing.

2. Ensure that the sample solution is homogeneous- mix or stir if obvious separation is visible.
3. Samples with suspended particulates should be avoided since they may block the tubing.

G.2.5.3. Digital pump problems

1. If you accidentally pressed the "Home" button on the front panel of the digital pump and set the syringe to an incorrect home position, reset the home position. Follow the "WinPump® Software User's Manual" to set home for the digital pump, and also see section D.3 of this manual.
2. Check that the programs stored in the pump are not corrupted. Re-install the programs if necessary (see Section B.7).

   How to remove the syringe: 1) push Initialize button. 2) unscrew the lower screw rod using a screw driver. 3) unscrew the top with fingers.

   How to install the syringe: (reserve the above procedure 3 and then do 2). The lower screw may not fit into the crew hole well, do not force it in but push the Initialize again. Or loose the upper screw a bit and try again or after tightening the lower screw, you should tighten the upper screw again. Finally, push Home button to finish the procedure.

H. WARRANTY

Apollo SciTech offers a one year full warranty on the Dissolved Inorganic Carbon Analyzer against defects in parts and workmanship from the date of purchase. Apollo SciTech's sole obligation under this warranty shall be to repair or replace any part of the instrument which Apollo SciTech's examination discloses to have been defective in material or workmanship without charge and only under the following conditions:

1. The defects are reported to Apollo SciTech in writing within one year after the shipping date of the instrument.
2. The instrument has not been maintained, repaired, or altered by anyone who was not approved by Apollo SciTech.
3. The instrument was used in a normal, proper, and ordinary manner and has not been abused, altered, misused, neglected, involved in an accident or damaged by act of God or other casualty.
4. The purchaser packs and ships or delivers the instrument to Apollo SciTech within 20 days after Apollo SciTech has received the written notice of the defect.
5. No-charge repair parts may be sent at Apollo SciTech's sole discretion to the purchaser for installation by purchaser.
6. Apollo SciTech's liability is limited to repair or replace any part of the instrument without charge if Apollo SciTech's examination discloses that part to have been defective in material or workmanship.

This warranty defines the obligation of Apollo SciTech and no other warranties expressed or implied are recognized.