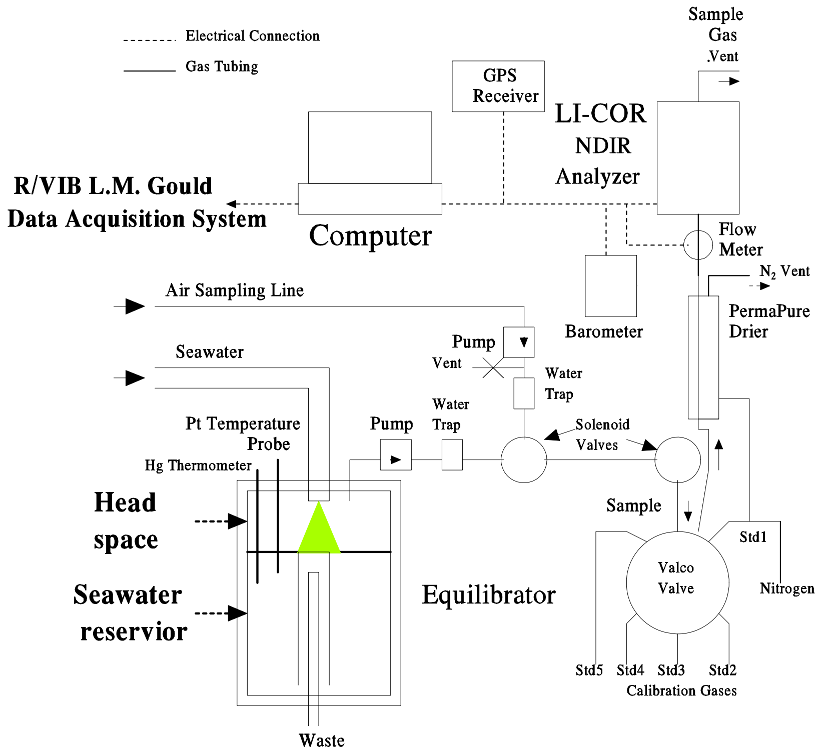
pCO$_2$ Equilibrator Users Manual



Lamont – Doherty Earth Observatory
CO$_2$ Group
205 Geoscience
Rt 9W Palisades, NY 10964
(914) 365-8768
csweeney@ldeo.columbia.edu

Table of Contents

Quick Start

1. Plug in CO_2 analyzer power box.
   - Air pumps should not be on.
2. Turn IR box "on":
   - Toggle forward-most switch up.
3. Check flow for **nitrogen reference gas**:
   - Go to **STEP 2** and turn flowmeter selection output to reference gas outlet and set for ~90 ml/min.
4. Set flows for **standard gases**:
   - Energize solenoid valve while going to **STEP 4** through 10 (even # only).
   - Set flow rates at ~60 ml/min.
5. Turn on pumps and check flow:
   - Go to **HOME**. Equilibrator and atmospheric air should be flowing at 45 ml/min.
6. Set flow of seawater to equilibrator
   - Bubbles from spray should extend at least 3 inches down from water line ~10 L/min.
7. Check for uw_pco2.ini in C:\pco2 subdirectory.
   - Make sure that all gas concentrations and serial # match the positions.
8. Check for C:\pco2\data subdirectory in C:\pco2 subdirectory
9. Start up program
   - C:\pco2>palmeruw
   - Press "F9" to send data to floppy drive (A:).

Daily Checks

1. Flow rates of gases
   - nitrogen 90 ml/min
   - standards 60 ml/min
   - equil. & atm. 45 ml/min
2. Water in Manometer
3. Flow of equilibrator
4. Check floppy disk space (if using)
5. Make sure computer time is near GMT
6. Log any changes to system in GMT

Less frequent tasks

1. Check floppy disk space (every two weeks).
2. Record offset between temperature readout and calibrated thermometer in equilibrator.
3. Send data to csweeney@ldeo.columbia.edu (every two weeks).

System Description

The pCO_2 analysis system consists of two major components- a seawater/air equilibrator and an automated analysis system that uses a LI-COR infrared analyzer to measure the concentration of CO_2 gas in seawater. The partial pressure of CO_2 is calculated using pressure and temperature at the time of measurement. The prototype of this system was operated on the WOCE S4P leg in the Pacific sector of the Southern Ocean (R/V Akademik Ioffe, Feb.-Apr. 1992) and since May 1992 has been operating continuously on the R/V Ewing, but has not previously been described.

Equilibrator

The equilibrator, shown diagrammatically in figure 1, is based on the design used by Takahashi during the GEOSECS expedition (Takahashi, 1966). A continuous flow of seawater enters a closed equilibration chamber through a fine nozzle, producing a fine spray, which enhances the rate of gas exchange between water and the overlying air. A small pump continuously re-circulates the headspace air, and a small amount of the air (nominally 30-50 ml min^{-1}) is diverted to the analyzer for analysis. The air removed for analysis is replaced by means of a "controlled leak" into the equilibrator through a water-manometer, which allows the rate of replacement to be monitored and which further assures that the pressure within the equilibrator headspace cannot differ significantly from the ambient pressure in the laboratory, which is continuously monitored. The temperature of the water in the equilibrator is measured with a platinum resistance thermometer, which is calibrated against a high-precision mercury thermometer traceable to N.I.S.T. The flow of water into the equilibrator is kept great enough that the residence time for water is less than five minutes (preferably less than two minutes, ~ 10 L/min), while the residence time for air is approximately five hours.

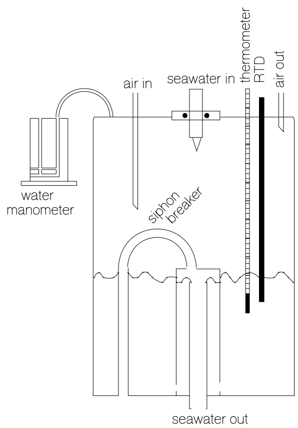


Figure 1. pCO_2 equilibrator

A second air pump draws a sample of outside air from an inlet mounted as high and far forward as possible (to avoid contamination with stack gas) for analysis as a sample of the ambient atmosphere.

pCO_2 analyzer box

Figure 2 shows the components of the analyzer box. Air from the equilibrator passes through the normally-open ports of two computer-controlled solenoid valves (plumbed in series) and subsequently through a countercurrent flow permeation dryer prior to entering the sample cell of the LI-COR IR analyzer (Model 6251, Lincoln, Nebraska). The output from the sample cell is directed through a digital flowmeter, to verify the complete flushing of the cell between analyses. If the first solenoid valve is energized, the equilibrated air is blocked and outside air pumped from the forward mast is directed through the dryer and IR cell. At intervals of no more than every one hour, five calibration gas mixtures (CO_2-free nitrogen and CO2 in air) are used to determine the response of the LI-COR analyzer. The CO_2-free nitrogen is also continuously flowed through the reference side of the IR cell, and the output of the reference side is used to flush the region of the chopper before being used as the drying gas in the permeation dryer. In order to insure complete drying of the sample gases, the **rate of the reference/drying gas flow is kept at least twice that of the sample gases**. In order to eliminate any possible excess pressure in the sample cell, the sample gas flows are stopped for several seconds prior to reading the CO2 signal voltage. The ambient pressure (which equals the cell pressure with the flow stopped) is measured using a high-precision electronic barometer (Setra Model 270, Acton, Massachusetts) each time a sample or calibration gas is analyzed. IR cell temperature is monitored, but is not required for the calculation of CO2 concentration.

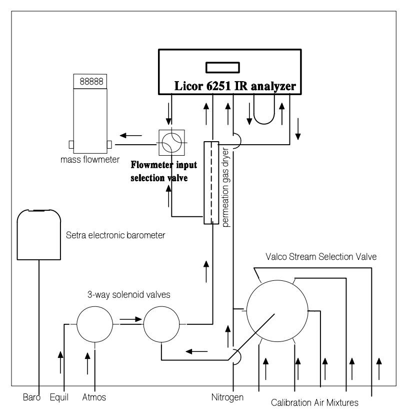


Figure 2. pCO_2 analyzer box

The output of each of the sensors (IR CO2 signal and cell temperature, barometric pressure, sample flowrate and equilibrator temperature) is converted to a digital value using separate A/D converters (modules 1 through 5 respectively) (MetraByte, Models 1131 and 1411, Taunton, Massachusetts). The modules are daisy-chained into the serial port of a laptop computer. Digital outputs on two of the A/D modules allow the computer also to control the operation of the solenoid and stream-selection valve.

CO_2 Analyzer Box

Power up

To start up, unplug air pumps until gasses are turned on and drying incoming air. Meanwhile plug computer and pCO_2 analyzer box into appropriate power sources. There are no separate power switches for the pumps or pCO_2 analyzer box, although the IR analyzer itself has a power switch on the lower left side, which must be turned ON (up) AFTER the pCO_2 analyzer box has been connected to power. LED position indicator on Valco valve driver control should be illuminated once power cable to pCO_2 analyzer box has been turned on. Digital flow meter should initially read above 200 (off scale), but reading should drop to approximately 25 within a few seconds. When IR analyzer is turned on, the sound of fan should be heard, and within a few minutes a green LED on the front of the IR analyzer should light up, showing that the reading is stable. If pressed, each of the momentary solenoid control switches should cause the appropriate solenoid to operate. Valco valve position selection switch will drive valve ahead one position (STEP) or to position 1 (HOME).

CO_2 standards and N_2 gas hook up

Turn on the cylinders of nitrogen (valve position 2) and calibration gases (positions 4, 6, 8, 10 and possibly 12). The nitrogen connection has a T connection immediately upon entering the box but no flow controller. It should be the second connection from the back and the top row (IR and VALCO 6-position value should be at front of box). The consecutive positions (i.e. #2, #4, and #6) should be located on the top row from back to front in increasing order. The consecutive order continues on the bottom row from front to back (i.e. #8 in front of #10). We do not have a 5th standard for position #12.

Using the valve position selection switch and the standard gas solenoid switch, set the **gases to flow at approximately 60 ml/min (90 ml/min for nitrogen)**, as indicated on the digital flowmeter, by adjusting the pressure regulators on each cylinder. Hold the gas solenoid switch for about 10 seconds to get an accurate flow reading.

Note

Refer to the Reference Sheet inside the cover of the pCO2 Box for proper flow settings.

Once all calibration gas flows are set, turn flowmeter input selection valve (Figure 2) to the reference gas position (handle horizontal) and check that the nitrogen reference gas flows at approximately twice that of the nitrogen (>100 ml/min). The flow of this gas is set by means of a crimp restrictor in the line between the Tee and the filter, and can be reset only by adjusting the crimp. This can be reset by using a vise-grip pliers and a pair of drill bits to reduce the flow or vise-grip pliers alone, at right angles to the crimp, to increase the flow **but should only be done under the direction of Colm Sweeney when the system is being totally overhauled.** After checking the flow of reference gas, be sure to **return the flowmeter input selection valve to the "sample gas" position** (handle vertical).

Connection of equilibrator sample line and air sample line.

Next, set the flows of equilibrated and ambient air. (When the Standard gas solenoid is **not** energized, equilibrated air will flow through the cell, unless the air solenoid is energized to allow ambient air to flow.) **Maintaining these flows at their proper values is the key to obtaining accurate analysis and is one of the most difficult aspects of operating the system**. Since the outputs of the pumps are fixed, and are much too great to be fed through the analyzer directly, a complicated system of restrictions (fixed and variable) and shunts or vents are used to reduce the flows. Aerosol (water and/or salt) and condensate can collect in the pumps and restrictors, causing changes in the flowrates, requiring fairly frequent adjustment of the variable restrictions to balance the flows.

Ambient Air
The flow of ambient air is likely to have fewer problems. In order to keep the bow line well flushed with air, the full pumping rate of the pump is utilized, with most of the flow being subsequently discharged before reaching the IR analysis system. A Tee with a slightly restricted vent provides the slight backpressure necessary to give a reasonable flow through the analyzer. The flow for this is tested by pressing the atmospheric (labeled "atmos") solenoid switch. Adjustments to this flow are made using the needle valve inside the CO_2 analyzer box (figure 2); gross adjustments require changing the restriction to the vent downstream from the pump. **Keep the ambient air flow between 35 and 50 ml/min.**

Equilibrated air flow
Since this air contains fairly large amounts of aerosol, and is saturated with water vapor at equilibrator temperature, changes in the flow are more common. In order to keep the residence time of air in the equilibrator long, excess air cannot be vented, but must be returned to the equilibrator. Only that portion of the air, which passes through the analyzer, is discharged. In order to keep the pressures in the vicinity of the pump close to ambient, simple restrictions to reduce the flow cannot be used, and a variable shunt between the input and output sides of the pump is used (Figure 3). The shunt should be opened enough so that less than ~150 ml/min ofair is being circulated to and from the equilibrator. Low flow will cut down on moisture and aerosol build up in the sample lines.

Leaks in the circulation system will be shown by excessive flow of replacement air into the equilibrator through the water manometer (leak on high-pressure side of pump) or flow of equilibrated air out through the manometer (leak on low-pressure side of pump). When the equilibrated air is flowing through the IR cell, the replacement rate through the manometer should nearly match that of the flowmeter; when the equilibrated air is blocked (as during calibration periods) there should be little or no flow through the manometer. (Excessive rolling of the ship may cause this comparison to be difficult or impossible to make!) **As with the ambient air, the flow of equilibrated air through the IR cell should be kept between 35 and 50 ml/min.** This value is displayed on the LCD display inside the pCO2 analyzer box as sample flows into the IR analyzer with brief (~30 second) interruptions when actual reading are being taken by the IR analyzer.

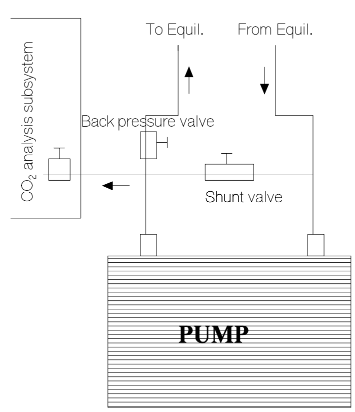


Figure 3. Equilibrator air circulation pump.

Connect Thermistor and GPS

The temperature probe (Figure 1) is connected to the CO_2 analyzer box by a gray data line. This is connected to a MetraByte A/D module marked "Thermistor". When the GPS is being used it is connected to the laptop through the PCMIA slot.

Setting up uw_pco2.ini file

This file specifies many of the operating parameters for the operating program of the underway system. Bring DOS screen up and go into pco2 subdirectory by typing:

C:> **cd pco2 <Enter>**

Now type: C:> **edit uw_pco2.ini <Enter>**

The file should look as shown in Figure 4.

```
32 , 5 , 90 , 70
13.576 , .10732 , 3.110E-5,0,0
3
Nitrogen, 0
ca02231, 236.29
ca02235, 100.00
cc15551, 362.78
ca02205, 495.18
02-18-1999  17:38:22
```

Figure 4. uw_pco2.ini File display use DOS edit

Starting with the first line: It is set for **32** samples between single runs of **5** standards. Air from the equilibrator will flow for **90** seconds and the standards will flow for **70** seconds. The double precision numbers in the second line are the coefficients for the last calibration that was made and will be updated with each set of standards. The third line contains the order of the polynomial (**3**rd) used to fit the standards. The fourth through the second from last lines are the standard IDs and concentrations. The date at the bottom of the INI file is the last time it was accessed by the NBP_PCO2.EXE program.

When finished editing press the alt key followed by the down arrow to select quit. The edit program will prompt you to save changes.

Software Start up

To start the system operating, turn on the laptop computer, check that the computer date and time are correct (use GMT), and place a formatted empty disk in drive A. Drive C should have the pco2 program (c:\palmeruw.exe) and the initial file (c:\uw_pco2.ini). Start the program by typing:

C:\pco2> **palmeruw <Enter>**

Within a few seconds the Valco valve should drive to position 2 and the standard gas solenoid should click (signaling energizing of second solenoid in series) as the first calibration gas flows. The program is completely automatic from this point. The following commands will help:

F10 To stop the program. This exit procedure will make certain that the valves are in the proper shutdown position before ending.

F9 To toggle switch that prints data to floppy. Is **off** when program starts.

F7 To determine the amount of disk space remaining. **The high-density floppy disk in drive A: will need to be replaced every two weeks.**

F3 To toggle switch that prints data to ships data acquisition system. Is **on** when program starts.

The program gives the user the option to save each day's data to a single disk file (F9), assigning a new name each day. There should be enough room on the disk for roughly two weeks worth of data; to determine the amount of disk space remaining, the F7 key from within the program. If less space remains than is required for a single data file (approximately 70,000 bytes), end the program (F10), replace the data disk with another high density, formatted disk and restart the program as above.

Maintenance

Flow rates

Once the underway CO_2 system is started there is very little that needs to be done except keep an eye on the flow rates of the gases. Since the equilibrator sample contains large amounts of aerosol, and is saturated with water vapor at equilibrator temperature, changes in the flow are more common. In addition to the flowrates, the aerosol trap (equilibrated air line) and condensate traps (both lines) need to be checked periodically and emptied as needed.

Flow rates:

Equil. and Atm. Samples:	35-50 ml/ min
Standards:	60 ml/min
Nitrogen	90 ml/min

Water Manometer

It is best if the water level in the water manometer (Figure 1) is checked daily to insure that it has not evaporated. The water level on the equilibrator side of the water manometer should not be higher than about 1/4 inch above the upper cross tube, or else the pressure in the equilibrator may be significantly below atmospheric pressure, and the calculated pCO_2 will be too low by the same factor. One inch of water is equivalent to almost 0.3% in pressure, or approximately 1 μatm at values close to atmospheric!

Equilibrator flow

There are relatively few adjustments that can be made on the equilibrator. A ball valve in the inlet line can be closed partially to reduce the rate of flow of seawater, or closed completely in the event of leaking or flooding. The nozzle is attached to a flange, which is itself attached to the equilibrator top plate by means of four stainless steel bolts and an O-ring seal. Remove the bolts and carefully withdraw the entire assembly, taking care not to drop the O-ring into the equilibrator. The nozzle can probably be cleaned sufficiently by turning the knurled cone to greatly increase the flow, open the ball valve with the nozzle loosely in the hole in the equilibrator top to rinse accumulated particulate matter from the nozzle, and readjust to give proper spray pattern. If absolutely necessary, the knurled cone can be removed by twisting in a counter-clockwise direction with vigor. The water drains from the equilibrator by means of gravity flow from the overflow in the inner tower; neither the drain line (large-diameter spiral plastic hose) nor the siphon breaker hole (in the bottom plate of the equilibrator) should be allowed to become restricted. In the event the siphon breaker tube becomes restricted, there is the great likelihood that water will siphon from the equilibrator due to periodic accumulation/draining of water in the drain line as the ship rolls. This will cause the pressure of air in the equilibrator to fluctuate greatly, causing excessive exchange ("breathing") between the equilibrator and the laboratory atmosphere. This will be shown by 2-way air exchange through the water manometer, in phase with the rolling of the ship. No meaningful measurements can be obtained until this situation is rectified (by reducing the restriction on the siphon breaker, re-routing the drain line to reduce the effect of rolling, or by reducing the flow rate of incoming water, so that the drain line can keep up with the input.)

A second drain line, with ball valve, allows the equilibrator to be completely emptied for servicing or cleaning. In general, this drain should not be opened except at the end of the cruise, to prepare for removal of the system.

Pumps

The KNF Neuberger air pumps have stainless steel heads, but some rust will form from contact with salt in the aerosol, particularly in the equilibrated air pump. It pays to occasionally remove the head and clean the head (using a "Scotch-Brite" pad wetted with water, dried with a paper wiper). Examine the diaphragm for leaks and the clear plastic valve plate for cracks at this time. Make sure all the parts are in their original orientation when reassembling. The four machine screws which hold it together are rather small diameter, and may "freeze" in the cast metal base, so a light coating of molybdenum disulfide grease on the threads should be added at this time as well, taking care not to get it inside the head.

Trouble shooting

Trouble shooting the CO_2 analysis system is like trouble shooting any other system. Work backwards from the symptom.

No sample flow

This is a common problem that results from aerosols that will clog up the equilibrator line. To adjust flow (section 3.1, Figure 3) start by opening up the pin valve inside the pCO_2 analyzer subs box. If this is not creating enough flow then shut down the shunt valve until the flow rate is high enough. Do not use the back pressure valve to increase flow because this may not allow circulation of air through the equilibrator. If non of these procedure give enough flow, then the equilibrator air line and pin valves should be rinsed through with DI water. Use N_2 gas to dry tubing and valves after rinsing.

Error #24

This is a devise time out error indicating that there was no response when the data was sent out to the data acquisition system on board. If this was to a printer it might indicate that there was something wrong with the printer.

Error #62

This is a end-of-file error that may show up when you first run the program. A miss-match between the specified number of standards and number of standards listed in the uw_pco2.ini file.

No communication between computer and CO_2 analyzer box.

In the event of loss of communication with the A/D module stack, check all connections on the modules and related connections on the terminal strip for breaks in continuity. Any loss of continuity in the daisy chain will prevent communication with all of the modules. By wiring the serial cable directly to any one module (black to GND, red to TRANSMIT and blue to RECEIVE), the individual module can be addressed using KERMIT (on the laptop C: drive) (N.B.- UPPERCASE LETTERS MUST BE USED WHEN COMMUNICATING WITH THE MODULES!). Typing "#1RS" from the laptop should cause the module (1) to respond with its setup configuration, as given in Table 1. See the MetraByte manual for further information if the modules need to be reprogrammed. See also the description of the use of the DEFAULT connection in case the modules will not communicate when connected directly to the serial cable.

Hardware details

A/D modules

The MetraByte A/D modules are stacked in the lower left portion of the analyzer enclosure, in numerical order from the bottom of the stack. Table 1 gives the details of the use and configuration of the modules.

Solenoids

The solenoid bodies are constructed largely of stainless steel, but some internal parts will rust when in contact with the salt in the aerosol from the equilibrator. Once this happens, the oxide will begin to interact chemically with the CO_2 of the air passing through. The effect appears to be chromatographic and reversible. When cool, the oxide will adsorb carbon dioxide, which it will then release when heated. Since the "standard" solenoid is held on for approximately six minutes

during the calibration sequence, it will heat up significantly and will add CO_2 to the calibration gas passing through. When turned off at the end of the calibration sequence, the solenoid will cool and the oxide will again adsorb CO_2 from the sample gas passing through, lowering the observed concentration in the first one or several samples. The solenoids should be examined for corrosion occasionally, and cleaned (or more realistically, replaced) if a significant amount is found.
modules.

Table 1 (see MetraByte manual for discussion of modules)
(all modules set for 9600 baud and ECHO ON)

Module #	Signal	Configuration (setup)	Digital Output 0	Digital Output 1
1	CO2 level	310205C2		
2	Cell Temp	320205C2		
3	Barometer	330205C2		
4	Flowmeter	340205C2		
5	Equil Temp	35020DC2		

Digital output:

Module #	0	1
1.	Valco valve STEP	Valco valve HOME
2.	Standard Solenoid	Air Solenoid
3.	---------	---------
4.	---------	---------
5.	---------	---------

Table 2. Terminal strip connections (top=1 bottom=12)

connection	color	pos	color	connection
A/D module 3 -V	gray	1	white	Setra barometer
A/D module 3 +V	yellow	2	green	Setra barometer
jumper to 6	red	3	red	Setra barometer
		3	red	power supply +12V
jumper to 9	black	4	black	Setra barometer
		4	black	power supply -12V
jumper to 10	grn/wht	5	grn/wht	power supply 12V common
		5	black	flowmeter 0V excitation
jumper to 3	red	6	red	flowmeter +12V excitation
A/D module 4 -V	green	7	green	flowmeter signal gnd
A/D module 4 +V	orange	8	white	flowmeter signal 0-5VDC
jumper to 4	black	9	black	A/D daisy chain gnd
serial cable gnd	black	9		
jumper to 5	grn/wht	10	red	A/D daisy chain +V
serial cable RD	red	11	grey	A/D module 5 xmit
serial cable SD	blue	12	blue	A/D module 1 receive

MetraBytes A/D modules

The modules are "daisychained" together, with the communication output (transmit) of one connected to the input (receive) of the next in line. The computer serial port "send data" line is connected to the input of the first module, and the serial port "receive data" line is connected to the output of the final module in the chain. This being the case, the computer can "talk" directly only to the first module, and communication is only possible with the other modules because each is programmed to echo anything received on its input to its output (and thus to the next module in the chain). The result of this echoing is that any command (mostly requests for readings, or to turn digital outputs on or off) will be sent through the entire chain and will then appear on the input of the computer that sent the command in the first place. If the command is recognized as valid, the addressed module will then send the requested reading (if that was the command). Anytime the program requests a reading from a module, the result should be the appearance of TWO strings at the serial port input- first the echo of the command, then the reading. Anytime the program requests a change in the state of one or more of the digital outputs, ONE string will be received by the computer (the echo only), even though no response is required by the program. The result is the buffer that holds the characters received by the serial port will often contain much unneeded information. Therefore, it is necessary to empty the buffer before requesting a module reading, and then to "throw away" the first string received after making the request (the echo of the command). For this reason, the program will be seen to clear the buffer (by means of an "input" command, with the string read being ignored) before requesting any reading (the commands to PRINT to the serial port). After requesting the reading, the program will take TWO inputs from the serial port, with both being assigned to the same string (q$), so that only the second input is actually used. The number of characters in the input buffer can be checked without removal by examining the value of the variable "loc(1)" (if the serial port was opened as #1), but anytime the data in the buffer is read with an INPUT command, the buffer will be emptied as it is read.