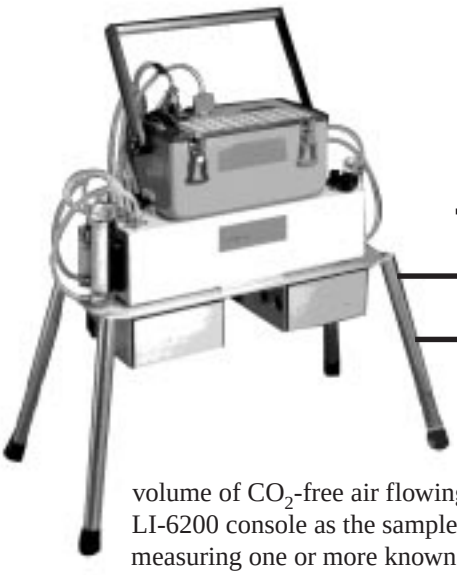


Measuring Small Volumes Of CO_2 With the LI-COR LI-6200 System

Application Note #121

The LI-6200 system can be easily modified to measure CO_2 in applications where only small volumes of gas are available (e.g. 10 ml or less when measuring soil CO_2 concentrations). A small sample volume is drawn into a syringe and injected into a buffer volume of CO_2-free air flowing into the Infrared Gas Analyzer (IRGA). The rise and fall of CO_2 are logged by the LI-6200 console as the sample gas flows through the IRGA. The user must first generate a 'calibration curve' by measuring one or more known gases. By selecting the appropriate buffer and/or injection volumes, and flow rates, a wide range of CO_2 concentrations can be measured.

Figure 1 shows the setup for measuring small volumes of gas. The implementation can be very simple, involving no more than adding a buffer volume (e.g. an empty soda lime scrub tube), a 'T' piece just before the soda lime scrub tube, and a short piece of gum (soft) rubber tubing to act as a septum.

The buffer volume is placed in series between the existing soda lime tube and desiccant tube on the left hand side of the analyzer. The septum for injecting the sample is placed just before the buffer volume. The purpose of adding a 'T' piece before the soda lime scrub tube is to bleed off most of the flow to the atmosphere and slow down the rate at which the injected sample is flushed through the IRGA. This is necessary to accommodate the slow sampling rate of the LI-6200 console (approximately once every 1.5 seconds), so that it can adequately sample the rise and fall of the injected CO_2 sample.

A calibration curve is established either by plotting the integral of the CO_2 (with respect to time) against the concentration for each standard, or by plotting the measured peak CO_2 concentration against the actual sample CO_2 concentration injected into the system. Programming the LI-6200 to give integrated CO_2 concentrations is described in Example 8 (page 4-19) of the LI-6200 Technical Reference manual. The CO_2 peak concentration can be obtained from the 'Range' parameter (FCT: 6E) which is part of the standard output of the LI-6200 software, and requires no additional programming.

Theoretically, using the integral of the area under the CO_2 versus time curve should be less technique dependent than the peak value method, because it gives an absolute value of the amount of CO_2 in the sample. Also, the integration technique should not require the establishment of a prior calibration curve. In practice, however, it can take a long time to completely flush out all the sample CO_2 from the system, and the CO_2 versus time curve can have a long tail. If there are any zero offsets, significant errors can accumulate when the integration time is long (as in this case, because of the relatively slow data acquisition rate of the LI-6200 console, and the low flow rates necessary to accommodate the slow logging rate). Also, the calculation of the total integrated sample CO_2 requires accurate calibration of the flow meter. Because of these difficulties, a standard curve should be established even when using the total integrated CO_2. With the setup shown in Figure 1, both calibration techniques worked equally well, but both required a prior calibration.

To set up the system, set PUMP ON, SCRUB ON, DES ON, and turn the desiccant flow control knob all the way clockwise (to maximum flow). With a buffer volume of about 80 to 100 ml (one standard soda lime scrub tube used in the LI-6200 system), the free end of the 'T' piece should allow around 90% of the flow generated by the pump to vent to the atmosphere, so that the flow rate is no more than about 150 µmol/second. The operating parameters should be set to:

```
CHANNEL = 10     (Observations based on time)
CHANGE = 100     (100 seconds for an observation)
#OBS = 1
```

Figure 2 shows the rise and fall of CO_2 injected into the system during calibration with known standard gases and measurement of CO_2 concentration in human breath. The total buffer volume (magnesium perchlorate chemical tube and the empty chemical tube) was about 90 ml. Figure 3 shows the calibration curve obtained from the standard gases. Although we used 3 different gases, Figure 3 indicates that one would have been adequate.

Table 1 shows data collected during calibration of the system and measurement of CO_2 concentration in soil and in human breath. Flow rate after installing the 'T' piece was at about 132 µmoles/second. The volume injected in to the septum was 10 ml, for the standard gases and for soil air, but was only 1 ml for breath. Three replicate samples of each standard gas were injected into the septum. Using a graduated plastic syringe, the measured peak concentrations were repeatable to within 1%. The CO_2 concentration in breath varied, with the length of time breath was held (Table 1). The potted soil air CO_2 varied from about 7,210 ppm to about 12,170 ppm for samples collected within a few centimeters of each other within an 8 inch pot. Samples were taken with a syringe from a depth of about 7 cm. The pot was placed in a greenhouse and had been recently watered. The CO_2 concentration beneath a grass sward varied from 6,850 ppm to about 8,150 ppm for samples collected within about a 20 cm diameter area. The samples were taken on April 22, 1997, at LI-COR; the soil was cool and wet.

Table 1. Calibration data with known standard gases, and measurement of CO_2 in soil and in human breath (regression line through calibration data is: y = 9.9778x-1.22).

Sample Description	Sample Volume	Measured Peak (ppm)	Flow Rate (µmol/sec)	Calculated CO_2 Conc. (ppm)
Standard gases				
382 ppm	10 ml	38.4	132	-
760 ppm	"	77	"	-
1014 ppm	"	101.3	"	-
7 cm below surface of potted soil	10 ml	940 (avg. of 3 samples)	"	9,380
7 cm below a cool wet grass sward	10 ml	749 (avg. of 3 samples)	"	7,470
Human breath	1.0 ml	431	"	42,990
Breath held for 1 minute	1.0 ml	711	"	70,930

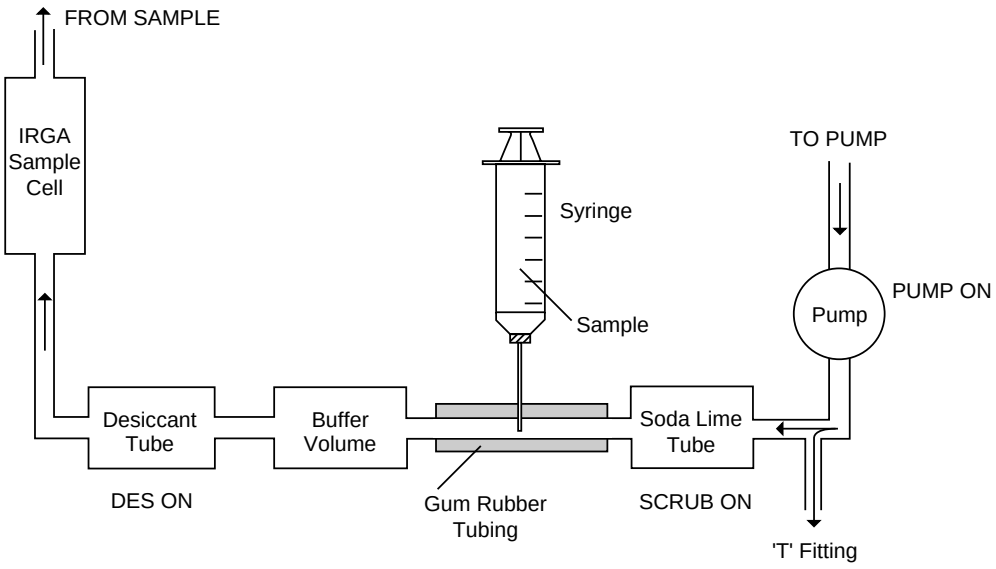
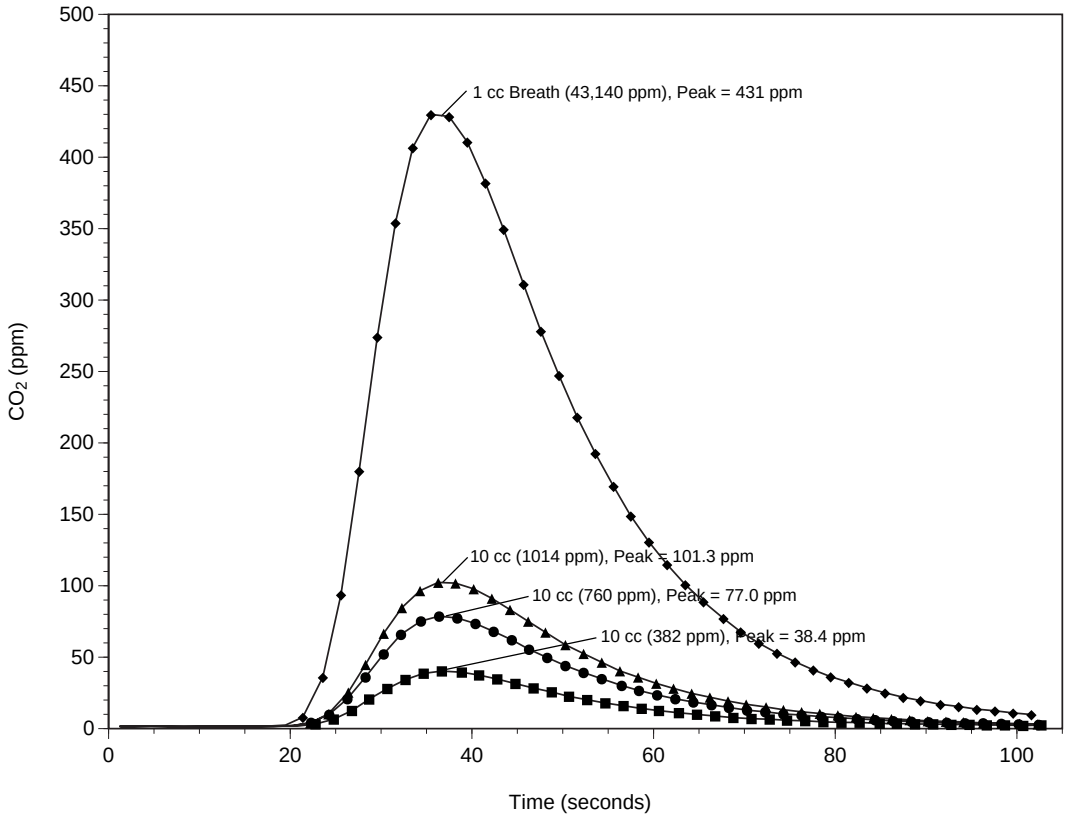
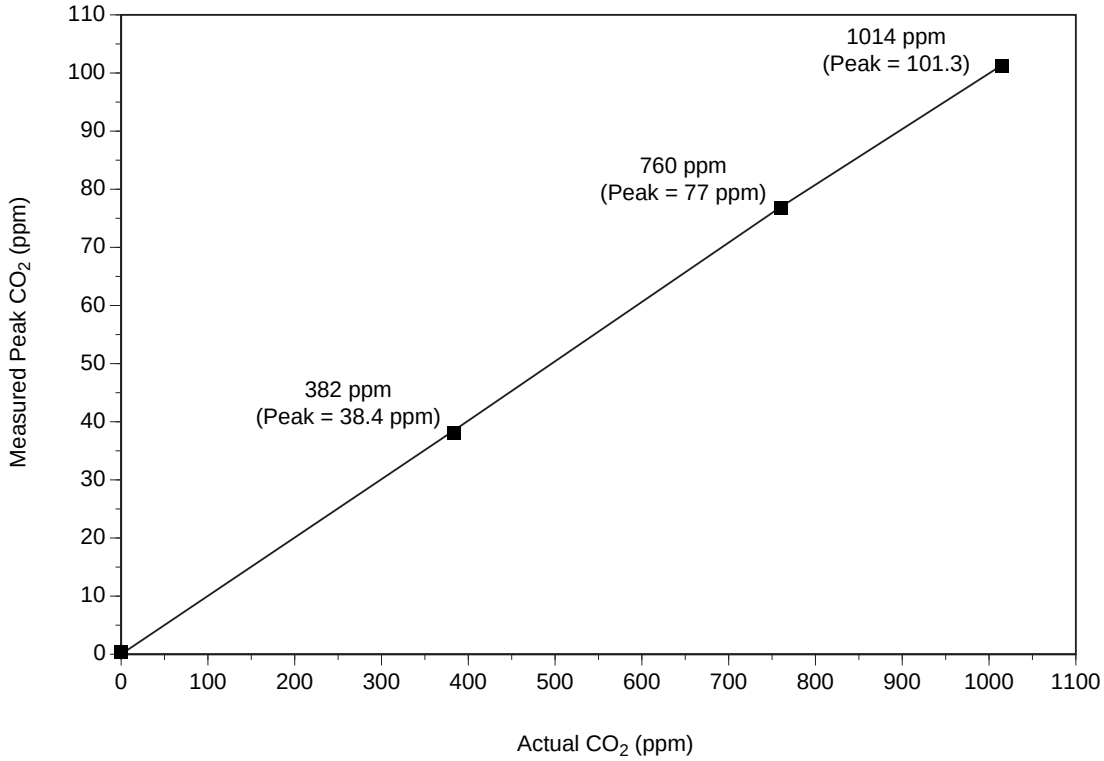


Figure 1. Schematic diagram of setup for measuring small volumes of CO_2.

LI-6200 Small Volume CO_2 Measurement



LI-6200 Small Volume Measurements Calibration Curve



LI-COR

LI-COR, inc. ● Environmental Division ● 4421 Superior Street ● P.O. Box 4425 ● Lincoln, Nebraska 68504 USA
Phone: 402-467-3576 ● FAX: 402-467-2819
Toll-free 1-800-447-3576 (U.S. & Canada)
E-mail: envsales@env.licor.com
Internet: http://www.licor.com

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