

Measuring gas concentrations of small samples with Trace Gas Analyzers

The LI-7810, LI-7815, and LI-7820 Trace Gas Analyzers are designed for high-precision and high-accuracy measurements of CH₄, CO₂, and N₂O gases, respectively. For example, at a concentration of 2 ppm methane, the LI-7810, precision is 0.6 ppb with 1 second averaging and 0.25 ppb with 5 second averaging. Other LI-COR Trace Gas Analyzers offer high-precision measurements of their respective gases. This precision makes the analyzers ideal for long-term atmospheric methane, carbon dioxide, and nitrous oxide concentration measurements and chamber-based soil gas flux measurements.

In addition, the analyzers can be used to measure gas concentrations of small air samples when the volume of the air sample is too small for continuous flow-through measurements. As long as the air sample can be drawn into a syringe, the concentration can be measured precisely with the LI-7810, LI-7815, and LI-7820 analyzers. In addition, using small air samples allows the measurement of gas concentrations that are outside of the specified range of the instruments. In this application note we describe two methods that can be used to measure gas concentration of small air samples: closed-loop and open-loop. The examples use CH₄ gas and the LI-7810 but the same procedures and considerations apply to other gases measured by LI-COR Trace Gas Analyzers.

The small volume sample kit (part number 7800-110) includes all the parts for the closed-loop and open-loop methods. The kit has the following parts:

Description	Quantity	Part #
3-way Compression Fitting	1	9881-181
3-way Quick Connector	1	300-07385
4-way Toggle Valve	1	300-02562
Silicon Septum	8	300-08998
Ferrule and Nut Set (1/4")	6	300-15025
Bev-a-line Tubing (1/8" ID)	3.6 meters	222-01824
Hose Barb	2	300-17717

Closed-loop method

The example uses CH₄, but you can follow the same procedure using CO₂ or N₂O and other LI-COR Trace Gas Analyzers.

A 3-way T-shaped compression fitting and a 4-way toggle valve connect the inlet and outlet of the analyzer (Figure 1). The calibration gas and sample gas are injected via the septum on the T-shaped compression fitting with a precision syringe. Port 1 on the 4-way toggle valve connects to the outlet of the analyzer, and port 4 connects to the T-shaped compression fitting. Ports 2 and 5 remain open to ambient air. When the toggle is at the port 1 side, air is circulated from the analyzer, in to port 1, out of port 4, through the T-shaped compression fitting and back to the analyzer. The 4-way valve is used to release air injected into the closed-loop. By switching the toggle to the port 2 side, ambient air will be pumped into the analyzer through port 5 and released back to ambient air through port 2.

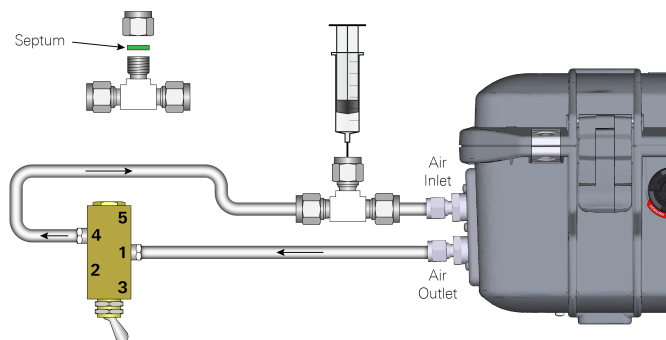


Figure 1. Illustration of the setup for the closed-loop method. When the toggle is on the port 1 side, the system is a closed loop. When the toggle is on the port 2 side, the loop is open to ambient air.

Determining the effective volume of the closed loop

V_{eff} (cm³) is defined as the total volume of air in the closed-loop before the injection at a certain pressure and temperature. Injecting a specific volume (V_{cal} , cm³) of known calibration CH₄ gas (CH_{4_cal} , ppb), you will see the CH₄ concentration increase from the baseline (CH_{4_base} , ppb) to a new concentration (CH_{4_post} , ppb). The effective volume can be estimated with equation 1b.

$$\frac{V_{eff} \times CH_{4_base} + V_{cal} \times CH_{4_cal}}{V_{eff} + V_{cal}} = CH_{4_post} \quad 1a$$

$$V_{eff} = \frac{V_{cal} \times (CH_{4_cal} - CH_{4_post})}{\Delta CH_4} \quad 1b$$

With ΔCH_4 (ppb) being the difference between CH_{4_post} and CH_{4_base} . The analyzer outputs CH_4 concentration data at 1 Hz (Figure 2). An average of 10 data points from a 10-second time interval is sufficient for estimating ΔCH_4 . To understand the procedure, ensure repeatability, and acquire a good average of V_{eff} , you should perform this multiple times (~5 times) on the same calibration gas.

It is necessary to release the extra air injected into the loop after each sample to keep the effective volume constant between samples. Switch the toggle to the side of port 2 for 5 seconds to open the loop. Depending on the length of the bev-a-line tubing used to setup the closed-loop, V_{eff} should be around 27-28 cm^3 .

If CH_4 calibration gas is not available, CH_4 -free gas or CO_2 calibration gas can also be used to estimate the effective volume using equations 1a and 1b. (Do not power on the instrument with CH_4 -free air.)

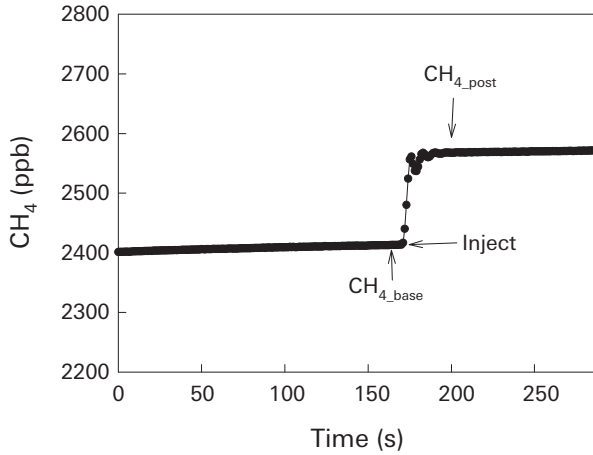


Figure 2. An example of time series of CH_4 concentration dataset from an injection of 0.05 cm^3 of 98.889 ppm CH_4 calibration gas.

Inject a specific volume of sample air

When injecting the sample (V_{sam} , cm^3) of unknown CH_4 concentration, you will see a step change in CH_4 , similar to the example shown in Figure 2. Once the readings are stable, a ΔCH_4 (ppb) can be computed. From this, you should be able to estimate the CH_4 concentration of the sample air (CH_{4_sam} , ppb) based on the V_{eff} determined previously, ΔCH_4 , using the equation 2b.

$$\frac{V_{eff} \times CH_{4_base} + V_{sam} \times CH_{4_sam}}{V_{eff} + V_{sam}} = CH_{4_post} \quad 2a$$

$$CH_{4_sam} = \frac{(V_{sam} \times CH_{4_post}) + (V_{eff} \times \Delta CH_4)}{V_{sam}} \quad 2b$$

To test the validity of equations 2a and 2b, we tried three different CH_4 concentrations of calibration gases (10.747 ppm, 50.530 ppm, and 98.889 ppm) and each with three different volumes (0.25 cm^3 , 0.50 cm^3 , 0.75 cm^3) with the closed-loop method. Figure 3 shows the excellent linearity between the product of ΔCH_4 and the sum of V_{eff} and V_{cal} and the product of the methane concentration difference between the calibration gas and the base line ($CH_{4_cal} - CH_{4_base}$) and V_{cal} . The calibration line has a slope of 0.982 and R^2 of 0.999. The close 1-to-1 linearity and high R-squared value demonstrates the validity and the robustness of equations 2a and 2b. One nice feature for using equation 2b is that the volume of calibration gas and sample air can be different.

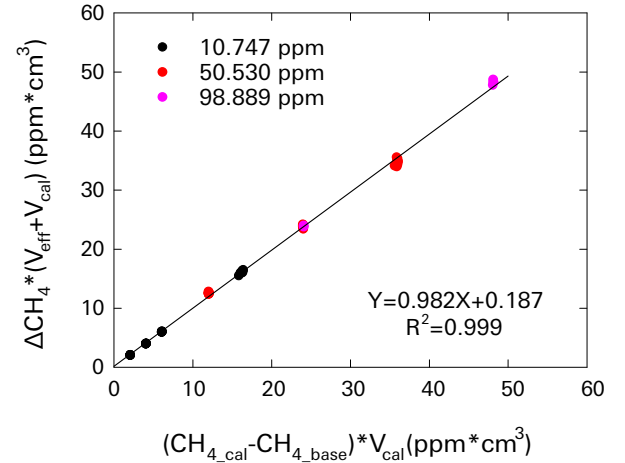


Figure 3. The linear relationship between the product of ΔCH_4 and the sum of effective volume (V_{eff}) and calibration gas volume (V_{cal}) and the product of the methane concentration difference between calibration gas and the base line ($CH_{4_cal} - CH_{4_base}$) and V_{cal} . Three different methane concentration of calibration gases (10.747 ppm, 50.530 ppm, and 98.889 ppm) and each with three different volume (0.25 cm^3 , 0.5 cm^3 , and 0.75 cm^3) were used in this closed-loop injection test

When using this closed-loop method, consider the following to minimize the uncertainties in your results.

First, when drawing the calibration gas or sample air into the syringe, slightly over-fill the syringe and expel some amount of air to the set-point volume just before injecting the needle into the septum.

Second, with the closed-loop configuration, the CH_4 reading before or after injection might not be as stable as you would expect. Changes can occur because the optical cavity of the analyzer operates at sub-ambient pressure of around 40 kPa. Any diffusion caused by the pressure gradient between the inside and outside of the optical cavity will likely cause small background level changes in the closed loop CH_4 reading. Normally, less than one minute is needed to finish one injection measurement. If the change of CH_4 concentration

(ΔCH_4) from the injection is larger (e.g., over 100 ppb), this small background level change can be ignored. However, if your ΔCH_4 is less than 10 ppb, ΔCH_4 should be corrected for the change based on the slope of CH_4 just before the injection.

Third, if the methane concentration of your sample air is very high, the CH_{4_post} is approaching 50 ppm, and the volume of the sample air is already very small ($\sim 0.1 \text{ cm}^3$), then an additional buffer volume can be added into the closed-loop. The buffer volume should be placed between the inlet of the analyzer and the 3-way T-shaped compression fitting. With an additional buffer volume, you would need to re-run a calibration gas to determine the new V_{eff} . In theory, with a buffer volume of 2 liters and sample air volume of 0.1 cm^3 , the closed-loop method can measure the concentration of the sample air up to 100% (v/v) of methane.

Fourth, if the temperature and pressure will change during your estimation of V_{eff} and your sample air measurements, you should normalize the volume of the calibration gas (V_{cal_std}) and sample air (V_{sam_std}) to the standard temperature and pressure ($0.0 \text{ }^\circ\text{C}$ and 101.3 kPa) using ideal gas law.

$$V_{sam_std} = \frac{273.15 \times P_{sam}}{(T_{sam} + 273.15) \times 101.3} V_{sam} \quad 3$$

With P_{sam} being the ambient pressure (kPa), and T_{sam} being the ambient temperature ($^\circ\text{C}$). Without this normalization, temperature of $10 \text{ }^\circ\text{C}$ difference can cause approximately 3% of error in your results, and an ambient pressure change of 1 kPa can cause approximately 1% of error in your results.

Open-loop method

The example uses CH_4 , but you can follow the same procedure using CO_2 or N_2O and other LI-COR Trace Gas Analyzers.

In the open-loop method the concentration of the injected sample is determined by constructing an empirical relationship between the observed area under the curve during injection and the corresponding change in CH_4 concentration. A carrier gas tank with a known CH_4 concentration and a 3-way T-shaped compression fitting are needed for this method. The methane concentration of the carrier gas can be at ambient level of around 2 ppm. The carrier gas must be non-zero CH_4 gas in air because the analyzer uses the CH_4 absorption line for parameter optimization during the gas concentration measurement.

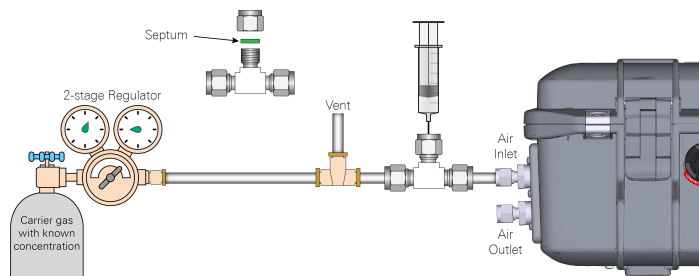


Figure 4. Illustration of the setup for the open-loop method using a carrier gas with a known concentration of the gas-of-interest.

Since the analyzer flow rate is about 0.28 liter per minute (lpm), the flow rate of carrier gas from the calibration tank should be set at a rate slightly higher than 0.28 lpm. A T-shape quick connector should be installed between the carrier gas tank and the 3-way T-shaped compression fitting so excess calibration gas can be vented.

In Figure 5, we plotted the area underneath the curve from injecting 0.2 cm^3 of 98.889 ppm calibration CH_4 gas against the products of the methane concentration difference between calibration gas and carrier gas ($CH_{4_cal} - CH_{4_base}$) and the volume of calibration gas (V_{cal}).

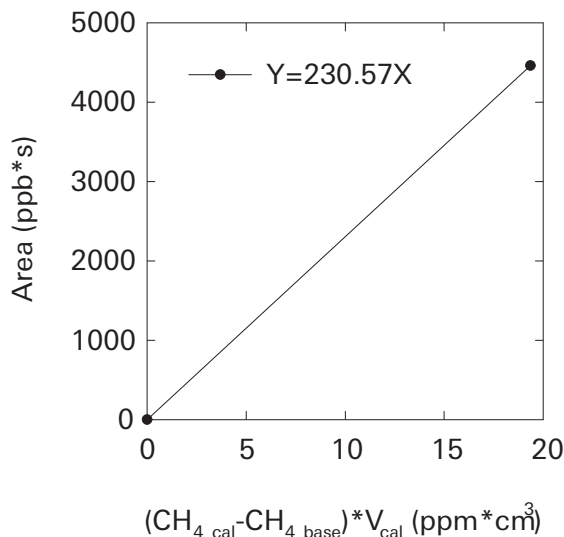


Figure 5. Calibration line for the open-loop method. This example is from injecting 0.2 cm^3 of 98.889 ppm calibration CH_4 gas.

As with the closed-loop method, it is a good idea to run this 4-5 times with the same volume and calibration gas to acquire a good average of the area underneath the pulse. Only one data point is needed to estimate the slope (α), since the calibration line must go through the origin when the concentration of calibration gas is the same as that of the carrier gas.

From the empirical relationship obtained in Figure 5, we have the following equation.

$$Area = \alpha \times (CH4_{cal} - CH4_{base}) \times V_{cal} \quad 4$$

Once you have the slope of the calibration line (α), and the area underneath the pulse from injecting sample air, the concentration of your sample air ($CH4_{sam}$) can be estimated using equation 5 below, with V_{sam} being the volume of the sample air.

$$CH4_{sam} = \frac{Area}{\alpha \times V_{sam}} + CH4_{base} \quad 5$$

In the example below, we used three calibration gases with three different CH_4 concentrations (10.747 ppm, 50.530 ppm, and 98.889 ppm) and each with four different volumes of calibration gas (0.2 cm^3 , 0.4 cm^3 , 0.6 cm^3 , and 0.8 cm^3) with the open-loop method. Results in Figure 6 illustrate the excellent linearity in the relationship between the area underneath the CH_4 pulse from injection and the product of the methane concentration difference between calibration gas and carrier gas ($CH4_{cal} - CH4_{base}$) and the volume of calibration gas (V_{cal}). This result also shows the robustness and the reliability of equation 5. One advantage of using equation 5 is that the volume of your sample air does not necessarily have to be always the same. In addition, only one data point is needed to obtain the slope, α .

Because the measurement range of the methane concentration of this analyzer is from 0.1 to 50 ppm, with this method the highest methane concentration that can be measured is limited to 6000 ppm (0.6%, v/v) when using 0.05 cm^3 sample air volume.

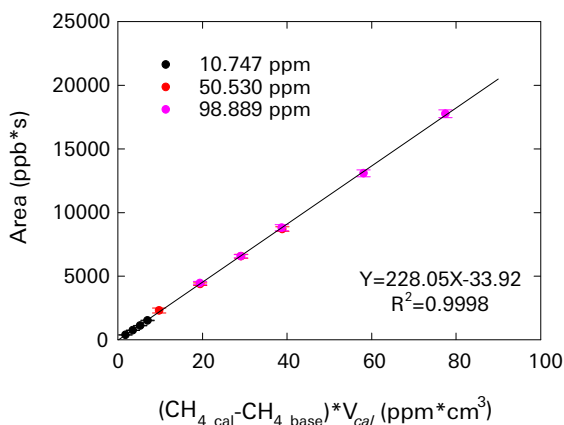


Figure 6. The linear relationship between the area underneath the pulse from injection and the product of the methane concentration difference between calibration gas and carrier gas ($CH4_{cal} - CH4_{base}$) and the volume of calibration gas (V_{cal}). Three different methane concentrations of calibration gases (10.747 ppm, 50.530 ppm, and 98.889 ppm) and each with four different volumes (0.2 cm^3 , 0.4 cm^3 , 0.6 cm^3 , and 0.8 cm^3) were used in this open-loop injection test. Data points represent the mean and standard deviation with sample size of 10 ($m \pm std, n = 10$).

The methane analyzer outputs data at the rate of 1 Hz. From the example shown in Figure 7, one might feel that the 1-Hz output rate is not fast enough to characterize the pulse from injection. However, our testing shows the 1-Hz output rate is sufficient because the fundamental measurement frequency of the analyzer is 4 Hz. It uses block averaging to output the data at the rate of 1 Hz. In Figure 7, the pulse from 4-Hz data points is shown for comparison. As expected, the 4-Hz dataset characterized the pulse much better and smoother than the pulse from the 1-hz dataset.

However, the area underneath the pulses from 1-Hz and 4-Hz datasets are exactly the same because of the block averaging. So no additional error will be introduced with 1-Hz dataset in quantifying the area underneath the pulse.

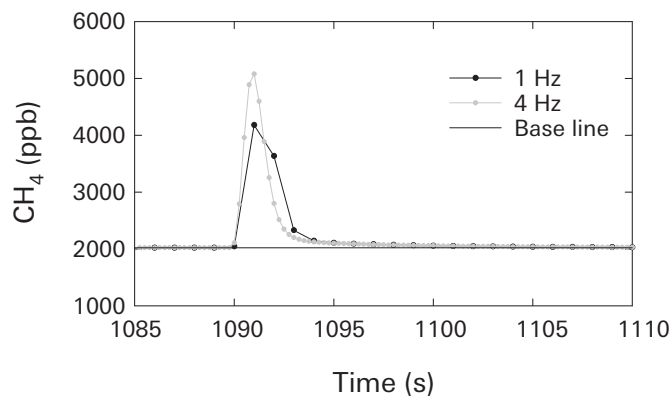


Figure 7. An example of the open-loop method, showing the CH_4 pulse from injecting 0.4 cm^3 of 50.530 ppm CH_4 calibration gas. The carrier gas is compressed air which has a CH_4 concentration of 2022.8 ppb. Both 1-Hz and 4-Hz data points are shown. The area (ppb \times s) underneath the CH_4 concentration pulse and above the base line will be used to estimate the sample air concentration. Normally, 25 seconds is sufficient to determine the area.

When using this open-loop method, consider the following to minimize the uncertainties in your results. First, inject the sample into the 3-way T-shaped compression fitting quickly to minimize the technique-induced uncertainties. Second, if the temperature and pressure will change from when you obtain the calibration line and do your air sample measurements, you should normalize the volume of calibration gas and sample air to the standard temperature and pressure, see the sections above for details.

Depending on the range of concentrations of the gas-of-interest in the air sample and the availability of a suitable carrier gas, a user can decide which method to use.



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