Measuring Small Volume Gas Concentrations with the SSIM

PICARRO

APPLICATION NOTE (AN038)
SMALL SAMPLE INTRODUCTION MODULE

Summary

The Picarro Small Sample Introduction Module (SSIM) is designed for processing small volumes of gas samples through a Picarro analyzer. The SSIM is composed of a 20 mL sample chamber, five solenoid valves, an external vacuum pump, and an internal pressure sensor. It requires a pressurized supply of dry gas. Memory effects between samples are reduced due to efficient purge cycles, the pressure sensor within the SSIM chamber allows for controlled 4- or 8-minute sampling intervals, and the dry air provides an option for sample dilution.

Previously, a single sample introduction could achieve a maximum concentration of only 94% of its original concentration, due to injection volumes between 1-20 mL from bags or syringes and limitations in the SSIM design. For example, a 1000 ppm CO_2 sample will be measured as ~940 ppm at best. With a minor modification of the method, we can now expand the functionality of the SSIM so that more accurate concentration measurements can be performed on both isotopic and concentration analyzers (see tables on page 3). The dilution effects inherent in the SSIM design are reduced further, meaning that sample measurements can now achieve concentration values of up to 99.4% of their original concentration; with no trade-offs in isotopic precision. This document serves as a method guide so that accurate and precise measurement can be made.

Compatibility and Updated Requirements

Analyzers	Currently, this method is compatible with iCO_2, iCH_4 (G2101-*i*, G2121-*i*, G2131-*i*, G2132-*i*, G2201-*i*), and select iN_2O instruments (G5101-*i* and the G5131-*i*), and two concentrations analyzers (G2308, G2508).
Sample Volume	The minimum sample volume requirements range from 20 to 25 mL (*see 'Injection Procedure' on next page*).
Sample Delivery	A syringe is required to perform the injection of sample gas. Only the G5131-*i* analyzer remains compatible with syringe and bag delivery.
Hardware	A septum port is preferred. On concentration analyzers a flow restrictor must be installed.

NOTE: The modified method outlined in this document does not support the 16-port. If the 16-port is used, additional sample volume will be required to fulfil the injection pressure requirement – *see 'Injection Procedure' on next page*. The 16-port may be used with the G5131-*i*.

Setup Modifications

1. Minimizing the path-length between the SSIM sample port and your sample is a strict requirement for the concentration method. We recommend that a septum port is purchased and attached directly to the port. If a septum port is not used, less than 5 cm of tubing with a stop-cock is required.

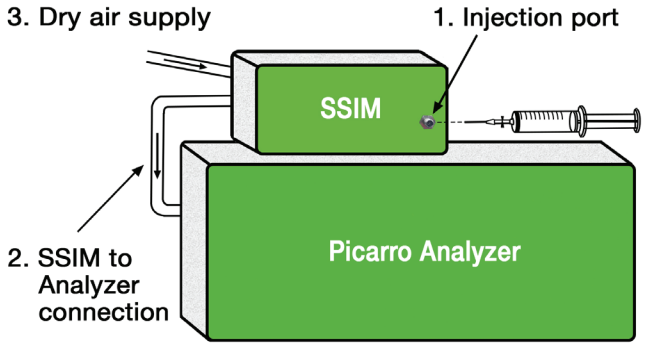
   Either setup **must** be leak-proof. If this requirement is not met, the sample injection pressure requirement will not be met, and additional sample volume well be required – *see following section.*

   Recommended nut, septum, and septum support for the 1/8" male Swagelok connector on the SSIM: https://www.vici.com/vfit/sepnut.php

   As with a single injection on the SSIM, the syringe should have a stop-cock. These are available from several manufacturers. Example: http://www.qosina.com/stopcocks

2. For **Picarro Isotopic Analyzers** the SSIM to analyzer connection remains unchanged. For **Picarro Concentration Analyzers,** an AN-6 flow restrictor (*supplied by Picarro*) is attached to the analyzer inlet port to reduce the flow rate from 250 mL/min to ~20 mL/min.

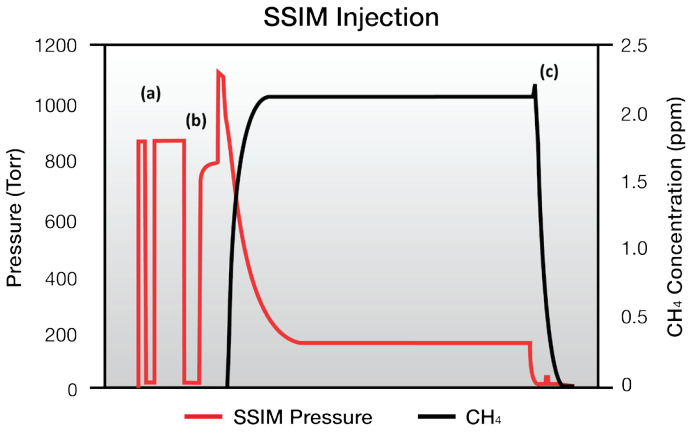
3. Zero-air or N_2 supply to the SSIM remains unchanged.



Injection Procedure

To begin the injection procedure, first select "Read SSIM Pressure" from the desktop and run the SSIM Coordinator. Once the SSIM setup screen is open, choose the Syringe Injection. For the G5131-*i*, you can select manual and automatic delivery as it is compatible with both bag and syringe measurements.

'SSIM pressure' is a critical parameter that lets the user determine the quality of the injection, as well as helps identify leaks in the SSIM. The following figure illustrates a typical analysis of a single sample of 2 ppm CH_4 gas on a G2308 gas concentration analyzer. The injection will look identical on an isotopic analyzer.



NOTE: If you are unsure about the basic operation of the coordinator, please refer to the SSIM manual. The following points outline key steps that occur as part of the syringe sequence (above).

Step (a) – SSIM purge

Automated step – Every SSIM analysis begins with two purge cycles of the SSIM chamber using the attached dry air tank (a). During these purge cycles, the pressure inside the SSIM reflects the pressure setting on the dry air tank (2–3 psi = ~900 Torr). Before and after each purge, the vacuum pump evacuates the SSIM chamber, causing a drop in pressure to 0 Torr.

Step (b) – Injection

Manual step – The coordinator software will automatically engage the injection. Because the SSIM chamber is under vacuum, the air sample will be pulled out of the syringe, compressing the plunger. Not all the sample will be collected, as the air will equilibrate at 1 atmosphere (~760 Torr at sea level). Note the short plateau at 760 Torr. The user **must** push the remainder of the gas to reach a SSIM pressure reading of **at least 1100 Torr**. A 20–25 mL sample with a septum port should have no issues achieving this pressure. This 1100 Torr pressure will be more difficult to reach if the connection between your sample and the SSIM has a longer path length. More sample gas may be required. Once the injection of gas is complete the coordinator software will ask the user to click "Resume".

Step (c) – Completion

Automated step - After ~8 minutes, the sample collection will stop and a new SSIM purge cycle will begin. In the case of a fast measurement, the collection will last only ~4 minutes. The coordinator will automatically shade a portion of the flat plateau in red. This marks the data points from which concentration and/or isotopic averages will be calculated.

NOTE: We highly recommend you perform a test run with a gas standard of a known concentration. This initial test will help you become comfortable with the syringe injection procedure, the SSIM pressures after injection and it will help you identify any potential leaks in the system. Please refer to the SSIM manual for a guide on how "SSIM Pressure" may be used to determine leaks.

Injection Performance

TABLE 1- Typical performance of syringe injection SSIM measurements on a G2201-*i* (high-pressure CH_4 mode) and a G5131-*i*.

Variable	Units	Tank Value	Injections		
			SSIM Measurement	Precision*	% of Tank Value
CO_2	(ppm)	1008	1005	0.3	99.7
$\delta^{13}C$ (from CO_2)	(per mil)	-40.73	-40.76	0.05	NA
CH_4	(ppm)	9.86	9.84	0.001	99.8
$\delta^{13}C$ (from CH_4)	(per mil)	-40.3	-39.9	0.07	NA
N_2O	(ppb)	1000	998	0.5	99.8

**Precision measured as 1-sigma standard deviation of 20 replicates (CO_2 and CH_4) and 5 replicates (N_2O).*

TABLE 2 - Typical performance of syringe injection SSIM measurements on a G2508.

Variable	Units	Tank Value	Injections		
			SSIM Measurement	Precision*	% of Tank Value
CO_2	(ppm)	393	391	0.3	99.4
CH_4	(ppm)	1.98	1.97	0.001	99.4
N_2O	(ppb)	336	330	0.5	98.2

**Precision measured as 1-sigma standard deviation of 20 replicates.*

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