Effects of Temperature and Pressure on Sample Loop Volume in Gas Analysis

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January 25, 2018

Accuracy of analytical results in gas chromatography is critically dependent on several factors:

- Accuracy of standards.
- Stability of the chromatography process,
- Consistency of detector performance, especially noise and drift,
- Uniformity of injection volumes, especially with standards and a variety of samples.

Quantitation of target analytes is gas chromatography is most often performed by ratioing detector response of unknown samples to corresponding peaks in standards, run under matching chromatographic conditions. In gas analysis, two parameters must be well controlled to provide consistent results, especially when surroundings of samples vary, such as sample containers and their physical character, including pressure in the container. The sample loop, used to dose a constant volume into the process, must have temperature and pressure consistent at the time of injection. Both are governed by the Basic Gas Law: PV=nRT, where P is the pressure in the loop at time of injection, V is the loop volume, n is the number of "molecules" (effectively concentration), R is a constant to correct units of the other factors and T is the temperature of the loop. If we maintain these variables constant, expected accuracy of the measurement will be more likely be achieved. Volume is fixed by the volume of the sample loop. The sample loading process to the loop must remain constant over multiple runs, including all samples analyzed, to keep Pressure and Temperature stable. Any changes in these two parameters result in systematic errors that would not likely be detected by consecutive runs of the same sample.

Temperature of the sample loop impacts the effective injection volume by a reciprocal relationship - Charles' Law. Doubling the loop temperature, in units of ºKevin, cuts the concentration in half from thermal expansion of the loaded gas. Figures 1 and 2 illustrate changes over a range of temperature. For example, a loop temperature that ranges over 80 ºC ± 5 ºC will change the effective volume by ± 1.4%. Reducing the possible temperature span to < ± 0.1 ºC improves the volume consistency to < ± 0.028%, significantly lower than all other possible contributors to errors. Figure 3 shows typical variations in loop temperatures for a high performance gas chromatograph. This achievement mandates that the sample loop is mounted in an oven at a setting well above room temperature to minimize the effects of varying ambient changes, and that the zone is controlled by Proportional/Integral/Derivative (PID) circuitry.

Pressure in the sample container up for analysis can alter the process required to ensure that the sample loop always reaches a constant pressure for all standards and samples, independent of the container and its initial pressure. Three common types of sample containers include Tedlar™ bags, canisters above ambient pressure, and canisters below ambient pressure.

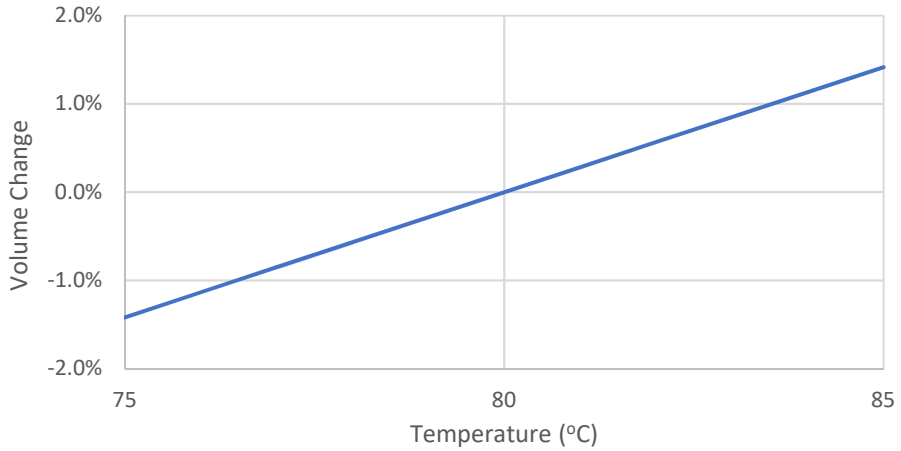

Figure 1. Temperature directly effects the apparent volume in a sample loop by Charles' Law. In this example, a target temperature of 80 °C, with a tolerance range of ± 5 °C, can result in a systematic error in the sample volume 2.8% at the extremes.

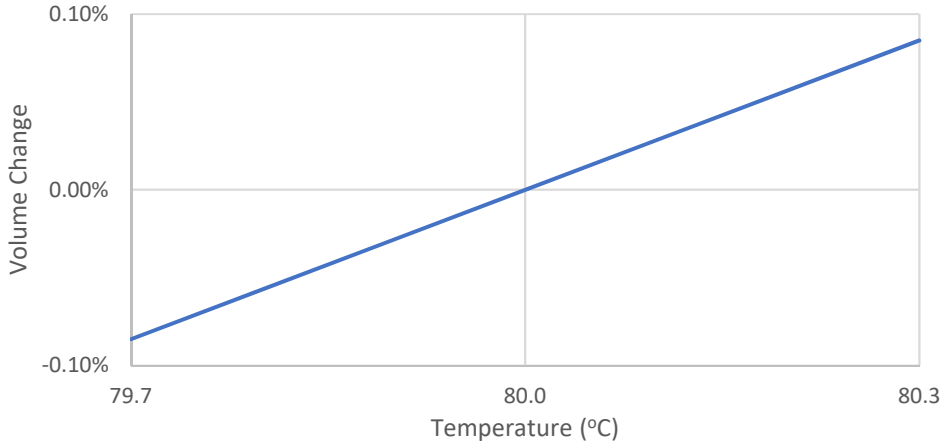

Figure 2. In this graph, a target temperature of 80 °C, with a tolerance range of ± 0.3 °C can result in a systematic error in the sample volume 0.17%.

Figure 3. Live monitor of temperature of oven with sample loop. Target temperature is 80.0 °C. Average temperature of monitor interval is 80.000 °C, standard deviation of ± 0.047 °C. This range gives a volume change for the sample volume of 0.026 ml for the extremes.

Tedlar™ Bags

Pressure inside a Tedlar™ bag is always one atmosphere, typically 14.7 psiA,[1] (if not full to almost bursting), as the bag collapses to maintain that pressure. Since the sample will not flow out of the bag unassisted, a sample vacuum pump is required to pull the sample out of the bag. With this method, the sample vacuum creates a pressure gradient across a 1 ml sample loop that generates an effective loop volume of 0.80 ml by Charles' Law, as depicted in Figure 4.

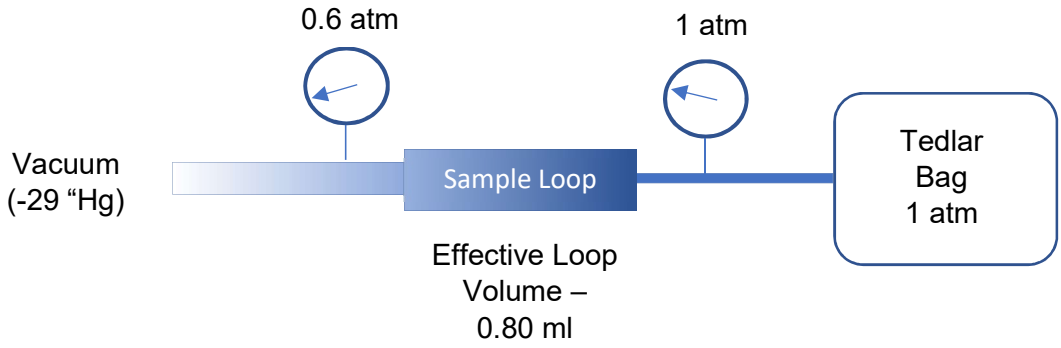

Figure 4. Pulling a sample out of a Tedlar bag with a vacuum pump generates a vacuum gradient across the loop that reduces the 1 ml loop to 0.80 ml.

To allow the sample loop to reach a steady, reproducible pressure, the vacuum pump must be turned off prior to loop injection to allow the loop to come to atmospheric pressure from the collapsing bag.[2] Otherwise, the vacuum side of the loop will have pressure below the inlet side and a lower effective volume.

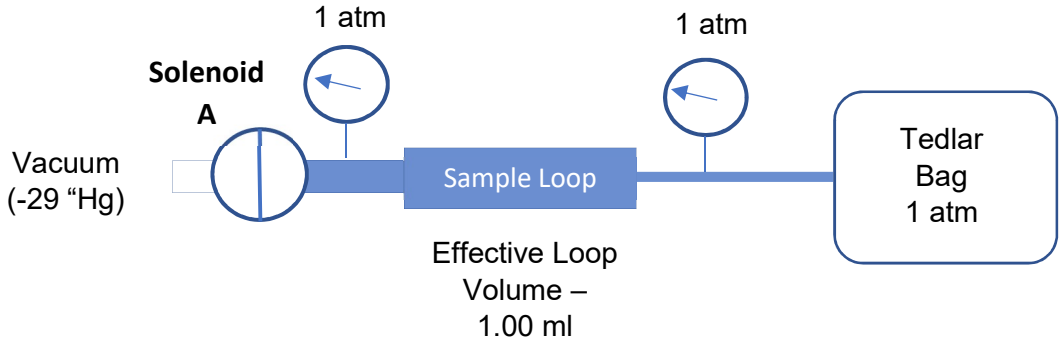

Figure 5. After the sample is pulled into the sample and then the vacuum pump is isolated by turning off Solenoid A, the Tedlar bag collapses to bring the sample loop to 1 atm. The sample loop is then the full aliquot of 1 ml.

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[1] The unit "psiA", or pounds per square inch absolute, relates to pressure relative to an absolute vacuum, and is linked to the unit "atm" by psiA/14.7.

[2] Atmospheric pressure does vary over the day with a diurnal pattern, especially when weather fronts approach. A typical variation for a summer day in Long Beach, California, amounts to a change of 0.27% at the extremes for the day.

Canister with Positive Atmospheric Pressure

In this case, sample flow is automatically generated by the native canister pressure. If nothing is performed to adjust the loop pressure, the pressure gradient across the loop, effectively doubles the injection volume when the canister pressure is 33 psiG[3] at the inlet and vacuum on the opposite side. To ensure that the sample loop always reaches a consistent pressure, independent of canister pressure, the sample loop must be exposed to atmospheric pressure, allowing the loop to release excess pressure. Then the injection is made. Suggested sequence is illustrated in Figures 7-9.

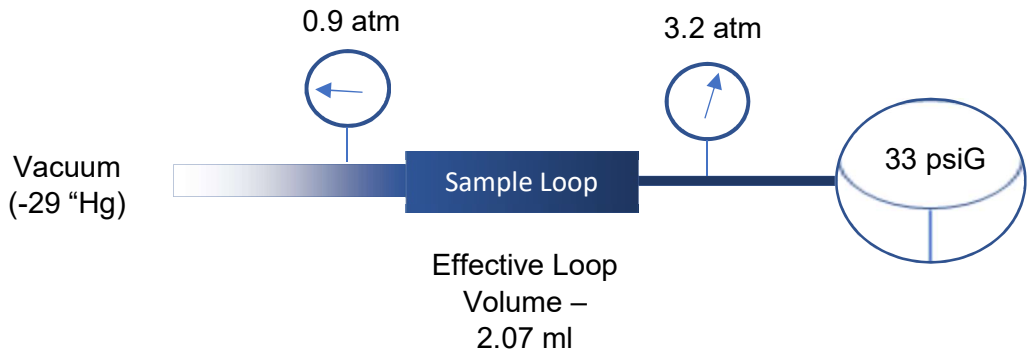

Figure 6. Pulling a sample out of a pressurized canister bag with a vacuum pump generates a vacuum gradient across the loop that changes the effective volume for a 1 ml loop to 2.07 ml.

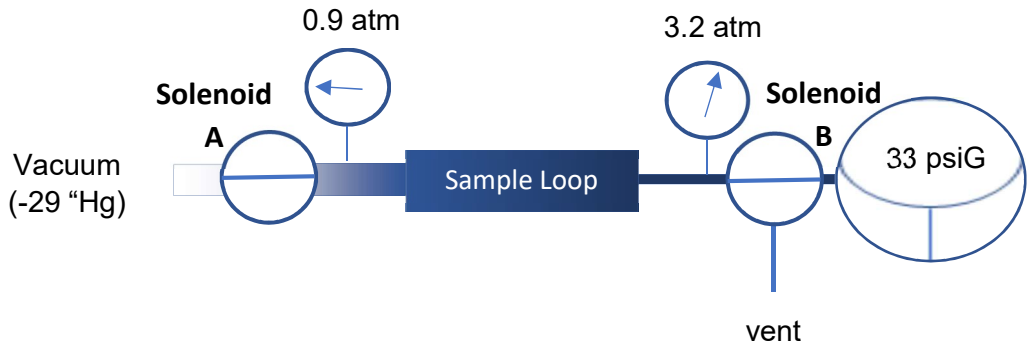

Figure 7. Step 1: to bring the sample loop to its full aliquot of 1 ml, the sample line is flushed out with the new sample by turning on Solenoids A and B.

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[3] Unit "psiG" is pounds per square inch gauge, when zero is one atmosphere, and is related to the unit "atm" by (psiG+14.7)/14.7.

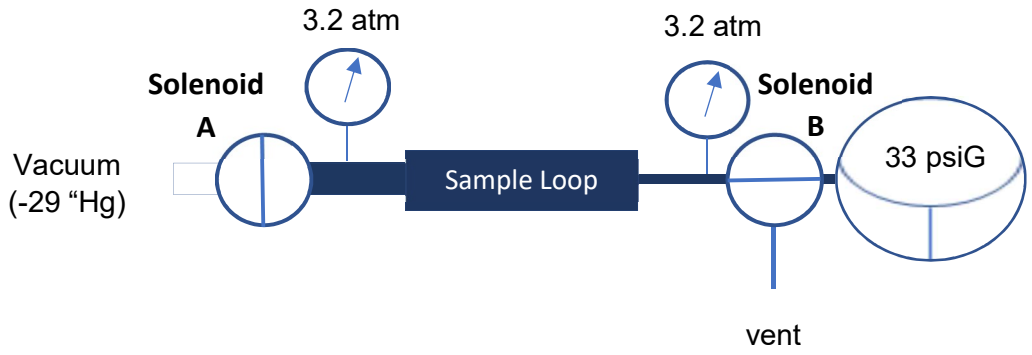

Figure 8. Step 2: after an adequate time is allowed for flushing, Solenoid A is turned off to allow the loop to reach a pressure equilibrium, matching the canister pressure.

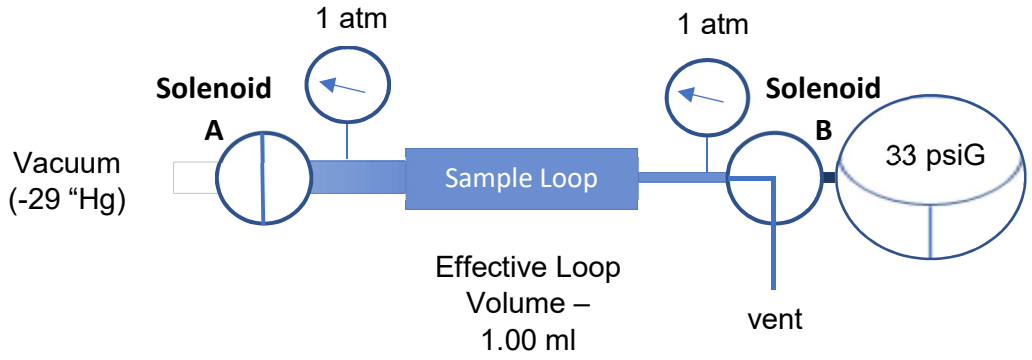

Figure 9. Step 3: then Solenoid B is turned off to release excess pressure in the sample loop to vent. This step brings the sample loop to its actual volume of 1.00 ml at 1 atm.

Canister with Subambient Pressure –

Sometimes sample collection creates canisters that are not at a positive pressure when received for analysis. Without precautions, samples could become contaminated. One possibility is backflow of room air into the canister if the sample path is not blocked off. Another possibility is residue from a previous sample in the active sample line can be sucked into the target sample, especially from previous high-level target analytes, inappropriately elevating reporting concentrations. The sample line into the gas chromatograph for low pressure canisters must be evacuated first before the canister on/off valve is opened, to reduce this carryover.

One solution is to pressurize the canister with an inert gas, such as nitrogen, to bring the canister to an elevated pressure. Then the initial and final pressures are noted and entered as divisor and multiplier respectively for each sample to account for the dilution. Lotus Consulting PS-1 Pressure Station performs this task, including automatic insertion of the factors into the sample list. Then steps illustrated in Figures 7-9 can be followed.

If such a subambient-pressure canister is loaded directly, without any preconditioning, through an evacuated sample line, and sample is pulled in by vacuum, a pressure gradient across the sample loop is formed and the effective loop volume is reduced to 0.31 ml. Since this decrease is a direct function of the canister pressure and how good the vacuum is, this approach does not yield a correct sample loop volume covering a variety of samples, from the inconsistent loop pressure.

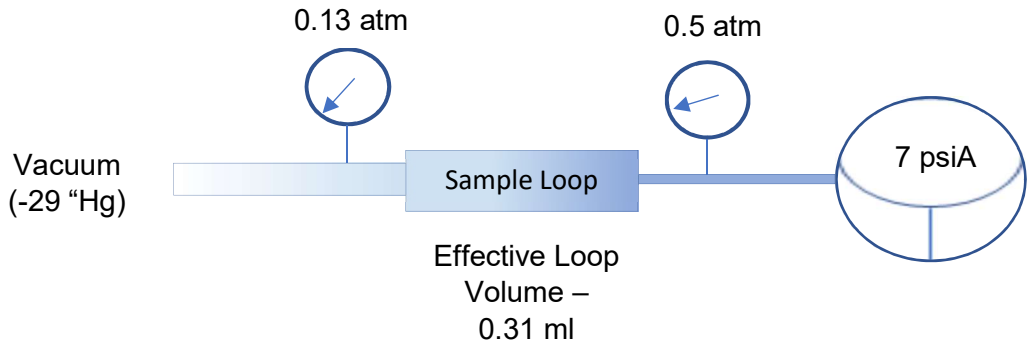

Figure 10. Pulling a sample out of a subambient canister with a vacuum pump generates a vacuum gradient across the loop that reduces the 1 ml loop to effectively 0.31 ml.

An alternative is to allow the sample to flow into an evacuated sample pathway, including a buffer volume of 5 ml. The buffer and loop is pressurized to slightly above ambient to compress the sample a bit, and then excess pressure is released to atmosphere. This process allows the sample volume is accurately maintained at 1.00 ml, without dilution of the sample. The recommended process is depicted in Figures 11-13.

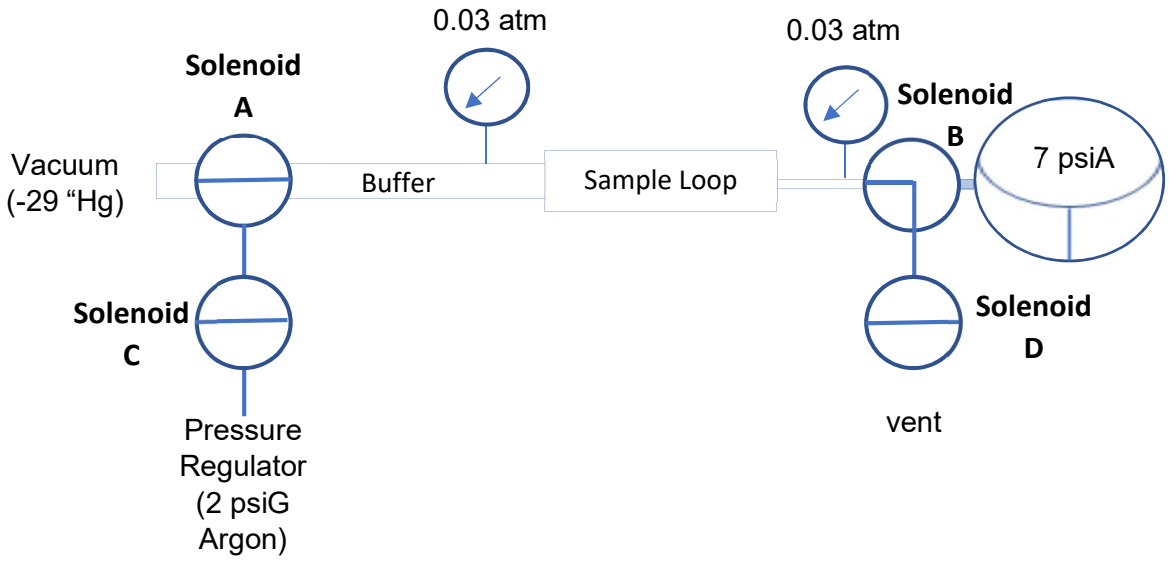

Figure 11. Step A: vacuum is pulled on the sample loop pathway with Solenoid A turned on. This ensures that any gas in the pathway is drained and not allowed to backflow into the sample canister.

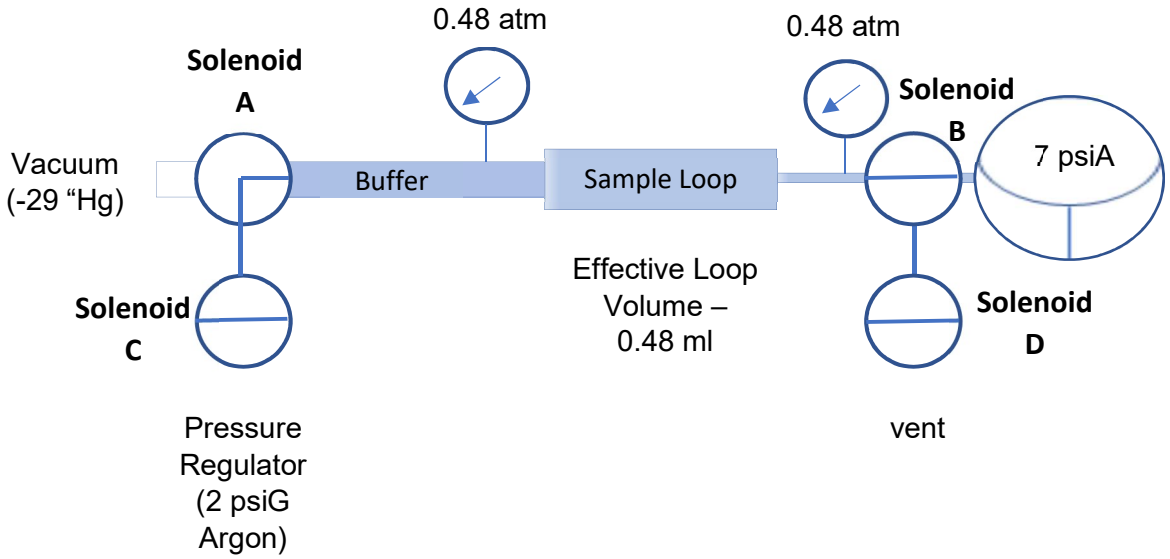

Figure 12. Step B: sample is allowed to flow into the evacuated path by turning off Solenoid A and activating Solenoid B. The buffer volume of 5 ml is also filled with sample.

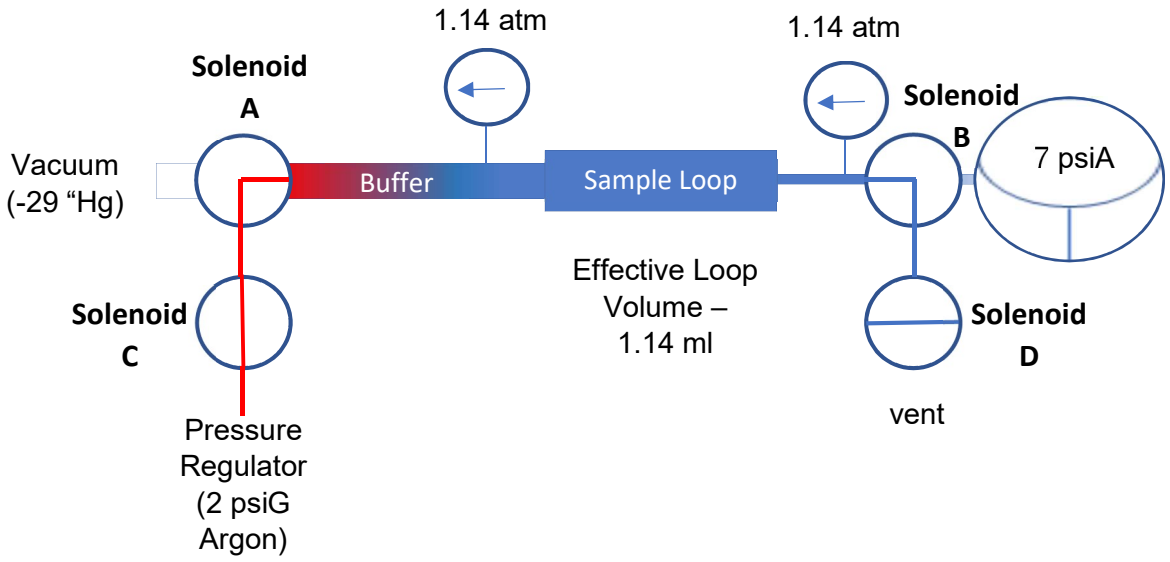

Figure 13. Step C: Solenoid B is turned off and Solenoid C is triggered to set up the path to be pressurized by 2 psiG argon. Argon pushes on the sample in the 5 ml buffer volume to compress the sample into the 1 ml loop at a pressure slightly above ambient.

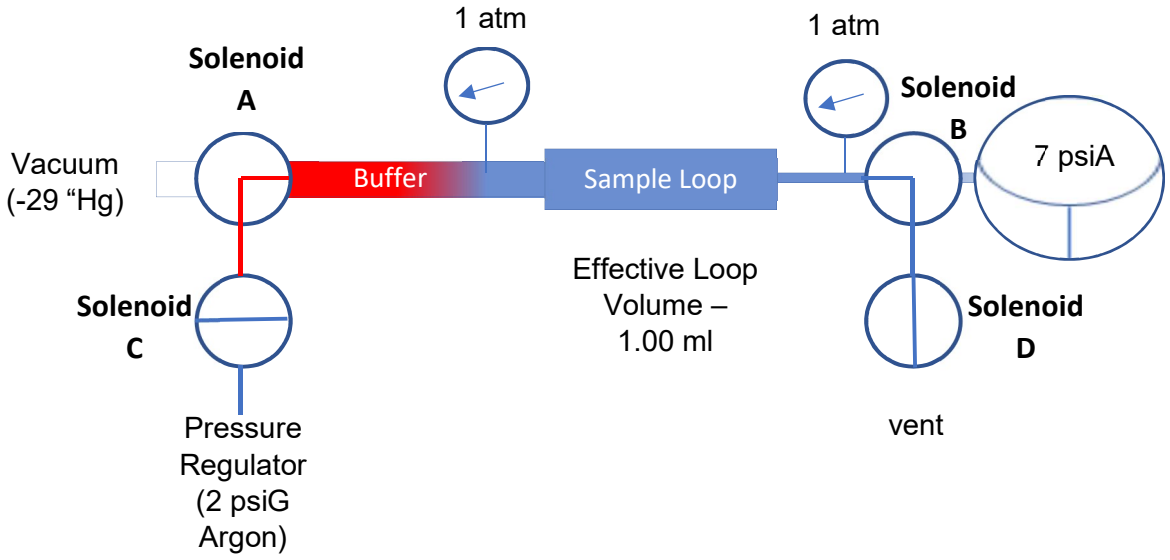

Figure 14. Step D: Solenoid C is turned off and Solenoid D is turned on to allow the excess pressure to be released to atmosphere. This sequence makes the effective volume equal to 1.00 ml.

Summary

Accuracy of results from a chromatographic measurement are critically dependent on consistent sampling conditions, notably with temperature and pressure values at the sample loop at the point of injection. Changes in these parameters between when standards are measured and when samples (and between samples) are examined result in systematic errors that typically do not become apparent from replicate runs of the same sample.

Table I. Summary of Volume Errors with Varying Temperatures.

Variable	Setpoint (°C)	Tolerance (°C)	Volume Error at Extremes
Ambient Temperature	~ 21[4]	± 5	3.4%
Temperature	80	± 5	2.8%
Temperature	80	± 0.3	0.17%

Table II. Summary of Volume Errors with Varying Pressures.

Variable	Container	Container Pressure	Effective Volume	Effective Volume
Pressure	Tedlar Bag	1 atm (14.7 psiA)	80% per Fig 4	100% per Fig 5
Pressure	Tedlar Bag	1.0047 atm (14.77 psiA)	100.5% per Fig 4	100.5% per Fig 5
Pressure	Canister	33 psiG (47.7 psiA)	207% per Fig 6	100% per Fig 9
Pressure	Canister	7 psiA (0.48 atm)	31% per Fig 10	100% per Fig 13

Typical reproducibility for measurement of a single gas sample is typically < ± 2% relative. If standards and samples are **not** examined under identical sample loop temperature and pressure, accuracy performance can dramatically deteriorate. To maintain this random error tolerance of ± 2% and the accuracy of standards, sample loop temperature must be maintained under ± 0.3 °C (error 0.17%), and its pressure under ± 0.0047 atm (error of ± 0.5%).

Configuration indicated in Figure 11 is appropriate for all container conditions discussed here, and is adjusted by activation of solenoids as needed.

Protocols must follow the processes outlined here to achieve of the best results.

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[4] Temperature variation is over a typical summer day at Long Beach Airport. This error occurs if the sample loop is exposed to typical ambient variation of temperatures over the day.

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