Ultimate Performance in Gas Chromatography

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Successful measurements in gas chromatography are critically dependent on accuracy of standards employed, on how well the experiment can be repeated, and on having large enough peaks to enhance readability and minimize effects of detector noise. Degradation in any one of these will render the measurement inadequate to report results to the full ability of the instrument.

Quantitation in gas chromatography is performed by comparing detector response for an unknown with results generated by a standard of the same analyte, preferably in the same matrix. Uncertainty in label concentrations for standards translates directly into the accuracy of results for unknowns. Thus, for example, if a standard is certified by NIST[1] to be accurate to ±1%, then reported concentrations cannot be reported with any tighter accuracy.

Also impacting the quality of results is how well the measurement can be duplicated. Reproducibility that is worse than the accuracy of the standard will yield answers poorer than the quality of that standard. To achieve proper results, reproducibility must be better than the accuracy of reference materials.

Another factor in generating the best results is to insure that peak responses are maximized and well above any impact of uncertainty from detector noise. This mandates that the detector be operated under its optimum conditions,[2] and the digital conversion of the detector signal be performed without degradation.

Measurement of concentrations for gaseous analytes by gas chromatography have special laws that must be obeyed to yield the ultimate performance. Back in 1662, Robert Boyle published that pressure is inversely proportional to volume, resulting in Boyle-Mariotte Law. Then 1787, Jacques Charles wrote that gas volume is directly proportional to temperature, referred to as Charles-Gay-Lussac Law. Later in 1834, Clapeyron combined these into the Ideal Gas Law –

$$\mathbf{PV = nRT}$$

where **P** is pressure of the gas, **V** is volume holding the gas, **n** is the number of gas molecules, **R** is a constant to correct units from the other factors, and **T** is temperature of the gas. If we maintain all of these variables constant, we will achieve a consistent number of molecules – the reproducibility of the gas measurement.

The challenge then becomes how consistent can results be with routine measurements.

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[1] National Institute of Standards and Technology, Gaitherburg, MD 20899, www.nist.gov

[2] This optimization is not discussed here. The reader is referred to other references from GC manufacturers for optimizing specific detectors.

One approach to introduce a sample into a gas chromatograph is to inject the gas sample with a fixed volume sample loop attached to a gas sample valve (GSV). This process assures that one variable in the Ideal Gas Law - VOLUME - remains very consistent and eliminates the effect of varying volumes on reproducibility of concentrations.

When a sample is loaded into a sample loop, its pressure at injection must be made consistent from run to run, and from standard to sample, to yield consistent results. One mechanism is to always vent the sample loop to atmosphere just prior to injection into the chromatograph. This operation must be designed to handle pressurized samples, as well as samples naturally at atmospheric pressure, such as Tedlar® bags or ambient samples that are sucked in by vacuum.

Obvious this approach does not work for samples below atmospheric pressure as once the sample loop is opened to atmosphere, room air will be sucked back into the void and significantly alter the sample composition. In this case, the loop must be evacuated first and then filled with sample, with the sample pressure in the loop upon injection being accurately measured without venting and then applied as a correction to results, or the sample can be pressurized above atmospheric with an inert gas diluent and a correction applied to the results to account for the dilution through the Lotus Consulting PS1 Pressure Station.

Interestingly, atmospheric pressure ***does*** change over a day. And when measurements are made over an extended time period, this deviation can impact the quality of results. Corrections become mandatory if this variation exceeds the required precision of the measurement, and if the measurement span for standards and samples is more than a few hours, especially if the barometer changes due to an approaching storm or post-storm clearing.

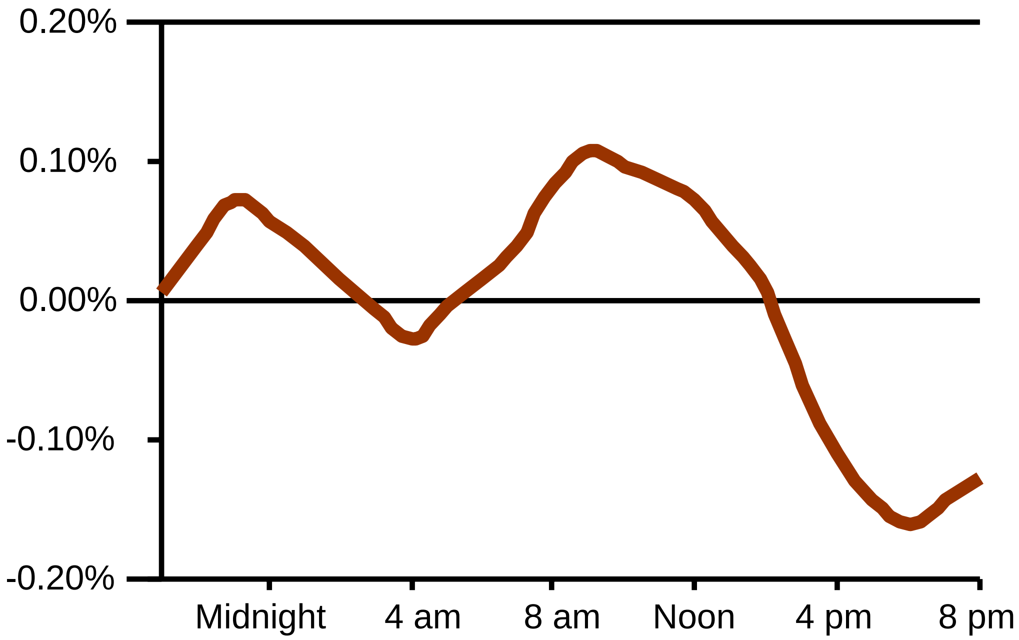

Figure 1. Hourly barometric pressure readings of a typical summer day at Long Beach Airport illustrate routine variations realized over a 24 hour period. Average pressure over the day was 1011 hPa, with the two extremes of 1013 hPa and 1009 hPa. Percentage change in sample loop volume over the day, due to the change in barometric pressure, becomes 0.27% at the extremes.

Temperature of the loop at injection remains as a variable in the Gas Law. If the measurement is not crucial, temperature at the loop can vary somewhat. However, to achieve the ultimate performance, temperature of the loop must remain very constant, as any variation directly impacts the sample volume. A change in loop temperature, between the time when calibrating the system with a standard and then later running a sample, directly influences the consistency of the measurement.

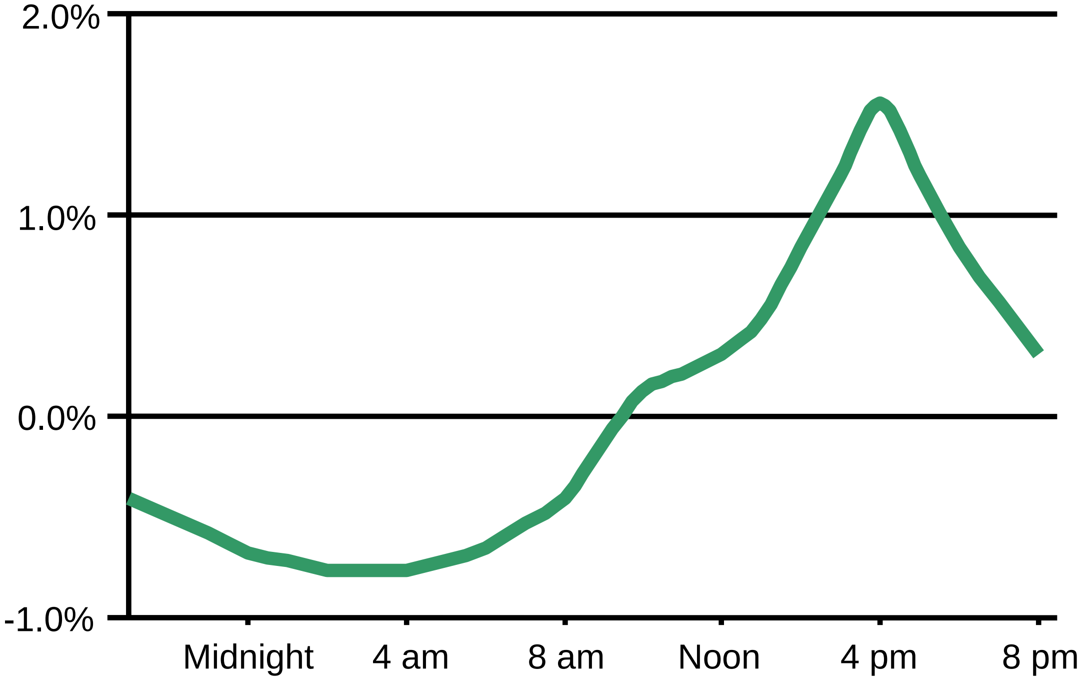

Figure 2. Temperature variations over a typical summer day at Long Beach Airport range from a low of 18.8 ^{o}C to a high of 26.1 ^{o}C, with an average of 21.2 ^{o}C. If a sample loop were to follow this profile, the loop volume would change by as much as 2.5%, significantly impacting sample reproducibility, especially with runs over the day. Obviously, a larger swing in temperatures will have a greater effect.

THE ULTIMATE PERFOMANCE

To achieve the best reproducibility of gas measurements, pressure and temperature of sample in the loop, just prior to injection, must be maintained with very tight tolerances to minimize their effects in precision of the measurement, or at least corrections be made for the variation. If the loop were held at 120 ^{o}C, a 1 ^{o}C change in that temperature would alter the effective loop volume by 0.25%; a 0.1 ^{o}C change would impact the volume by 0.025%. For pressure to yield a similar low impact, it must be controlled or corrected to 1 hPa [3] to yield just a 0.1% volume change. To get down to 0.01%, pressure must be maintained or corrected to better than 0.1 hPa.

TEMPERATURE CONTROL

To minimize any thermal variation in the sample loop, the loop must be installed in a zone where temperature can be maintained with very tight controls. And heat applied to that zone must be proportionally controlled so that the block preserves a very consistent temperature and does not have wild swings as the heater circuit cycles on and off. A proportional controller provides full heat to bring the zone up to temperature, but then is throttled back to provide just enough heat to maintain that temperature.

A special valve oven has been manufactured from copper instead of conventional aluminum; copper was selected for its better thermal conductivity and thermal mass over aluminum. A cavity, with a cover, is provided to hold a sample loop inside the block to keep loop environs under very tight thermal control. This same block can be used to mount the gas sample valve (GSV), so that interconnecting lines to the loop are as short as possible and maintained in temperature as closely as possible to the block temperature. The purpose is to keep the loop in a very tightly controlled thermal zone, independent of any outside influences, including changes in ambient conditions.

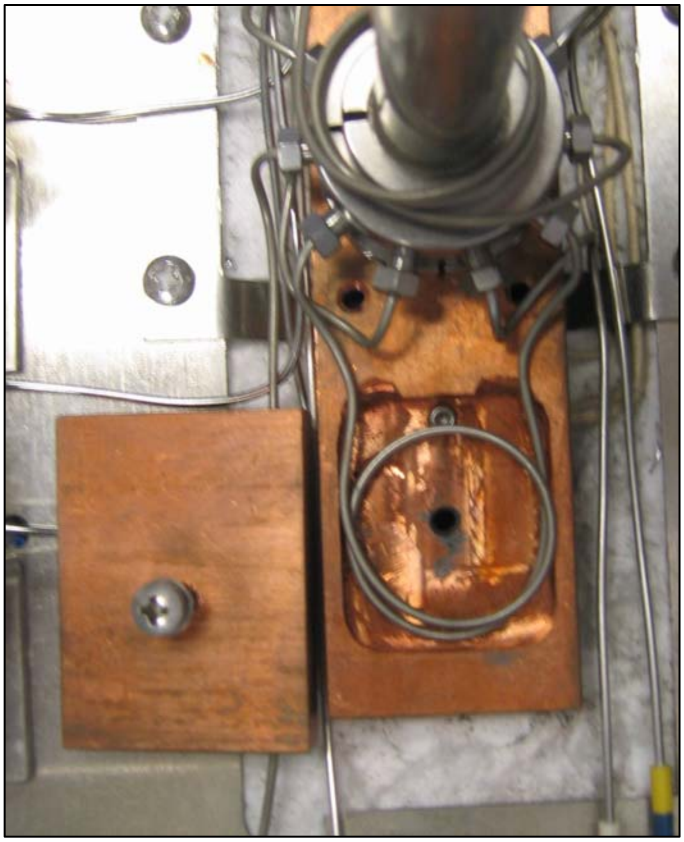

Figure 3. View from above of a special copper enclosure for a 200 micoliter sample loop to maintain thermal stability of the loop just prior to injection.

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[3] The SI unit for atmospheric pressure is now hectoPascals, or 100 pascals. One atmosphere at sea level and standard temperature and pressure is 1013.25 hPa.

PRESSURE CORRECTION

Pressure is a bit more difficult to handle, as achievement of a consistent loop pressure, independent of the sample container, mandates some correction. Atmospheric pressure does not remain consistent enough to use as a basis for uniformity over an extended series of measurements. The aim here is to attain the ultimate performance in reproducibility, but pressure variations realized in the normal experiment can readily overburden near perfect performance attained with control of other variables, including temperature and volume.

The process to handle both pressurized and ambient-pressure samples is to load the sample loop under vacuum, to flush the loop with new sample, and then turn off the vacuum to allow the sample loop to come to the pressure of the sample container, whether it be pressured or ambient. Once the loop is allowed to reach equilibrium, excess pressure from pressurized vessels is vented off to atmosphere just prior to injection. However, changes in atmospheric pressure can impart a systematic error in the effective sample volume in the loop.

To correct for this variation over an analysis cycle, barometric pressure must be monitored and automatically inserted into the SampleList or RecalcList as “multiplier” for the barometric reading for the calibration standard, and “divisor” for the sample reading just before injection. Thus, subtle changes in atmospheric pressure between standard and sample runs are compensated properly.

A special program (SPC - Sample Pressure Correction from Lotus Consulting) is available[4] to take continuous barometric readings from an appropriate digital instrument. This utility picks out atmospheric pressure readings at the times of injection for standards and for samples, and then automatically inserts them into a Varian Star RecalcList for correction of changes that occurred. Absolute accuracy of the barometer is not crucial, but readability and precision must be appropriate for the corrections incurred, as only the relative change is employed in this adjustment.

FINAL ACHIEVEMENT

To demonstrate performance achievable under careful control of all variables in gas measurements - volume, temperature and pressure -, a gaseous sample with Helium (1.3 %V/V), Hydrogen (7.3 %V/V), Oxygen (10 %V/V) and Nitrogen (33.6 %V/V), and balance Argon was measured six consecutive times over an hour. Resulting performance is displayed in Figures 4 and 5, and data for areas and retention times are summarized in Tables I and II.

The profound achievement of 0.015% relative standard deviation (RSD) for the Hydrogen peak over 6 consecutive runs demonstrates that temperature control of the sample loop must be well under 0.1 ^{o}C during that period, and atmospheric pressure stayed constant to less than 0.1 hPa.

Pressure corrections were not applied to this data, as the series of runs were made well within a time period where a change in barometric pressure is not likely to have much of an impact. If individual runs were separated by a larger time interval, then atmospheric pressure readings would need to be involved.

Of course, the sample volume (200 microliters) is fixed with a predetermined metal sample loop, and does not enter into the variable mix.

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[4] This program is not presently available for Varian Galaxie software.

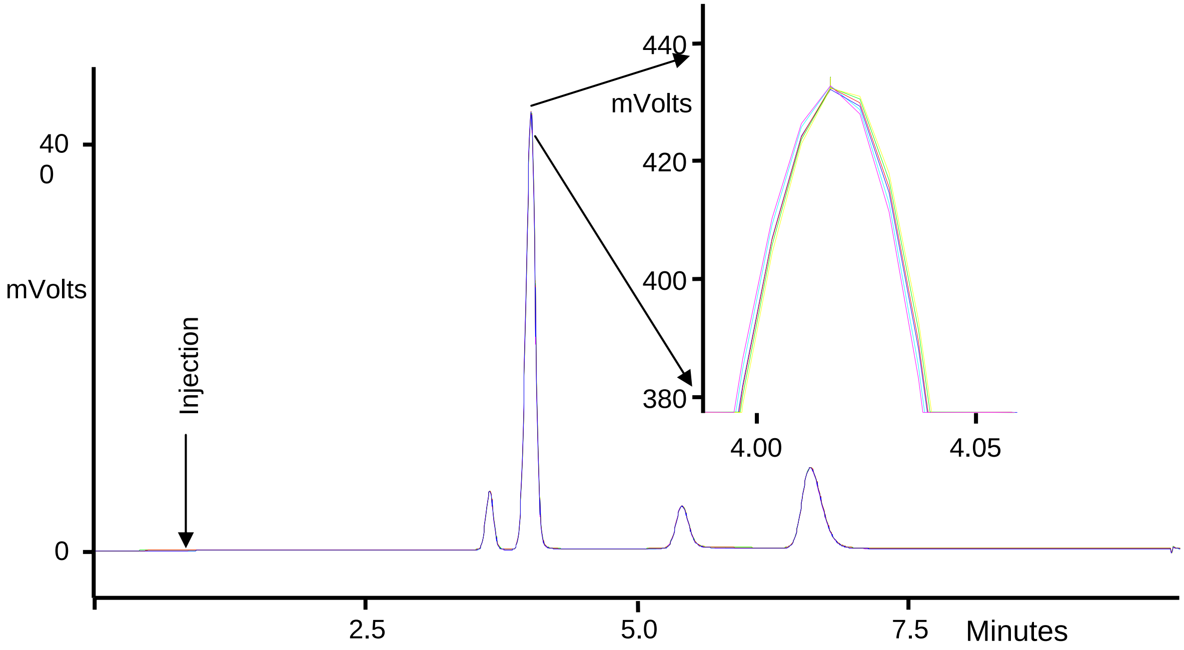

Figure 4. Six consecutive runs of a gaseous mixture[5] **are displayed overlaid to illustrate precision obtained with equalizing pressure to atmosphere just before injection and maintaining the sample loop inside a very well controlled thermal chamber.** Top of the major peak is expanded in the inset to visualize subtle differences in peak shapes at the apex.

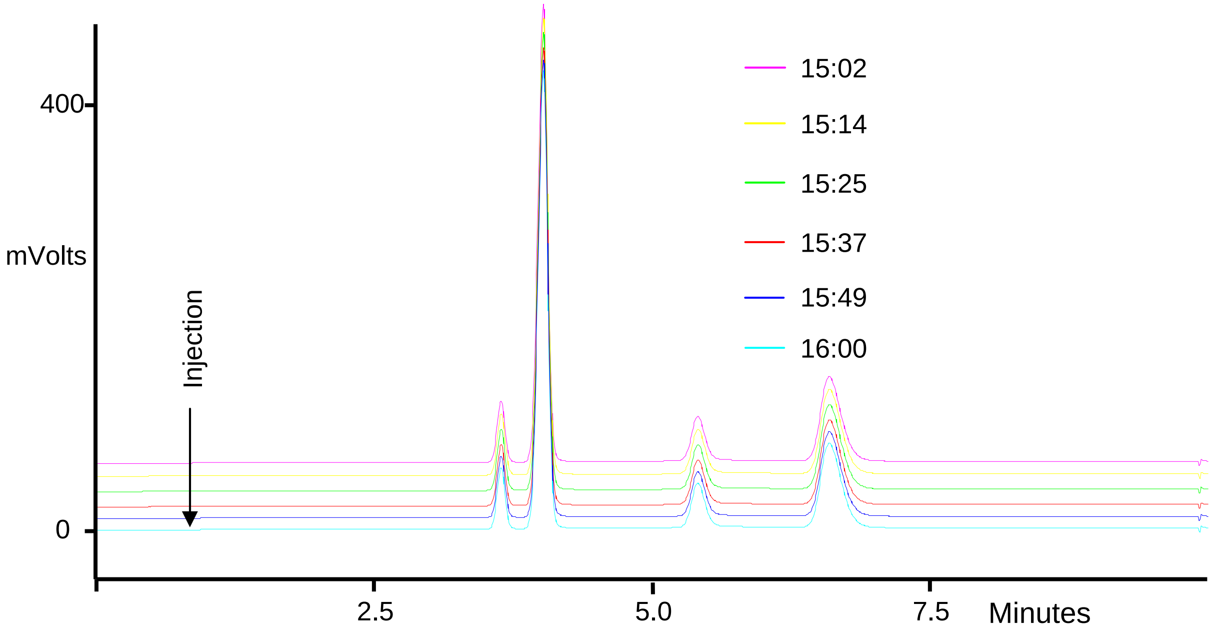

Figure 5. Each of six runs are separated slightly in the ordinate scale to demonstrate that each is indeed a separate run, with injection times noted.

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[5] Chromatographic conditions for this experiment are: injection volume - 200 microliters; columns - Hayesep N, 6 feet 1/8" ss, 60/80 mesh, plumbed in foreflush/backflush to vent, and Molecular Sieve 5A, 12 feet 1/8" ss, 45/60 mesh; Argon carrier, flow rate 20 ml/min; column temperature: 100 °C; valve and sample loop temperature: 120 °C; detector - TCD, block temperature: 120 °C, filament temperature: 230 °C, range - 0.5.

Table 1. Reproducibility of Raw Area Counts is listed for four analytes for each of six runs, with their relative standard deviations.

Raw Area Counts				
Injection Time	**Helium**	**Hydrogen**	**Oxygen**	**Nitrogen**
15:02	295830	2690045	355868	1046954
15:14	295858	2689354	356109	1046761
15:25	296008	2690487	355812	1046793
15:37	295853	2689919	355840	1046978
15:49	296058	2689518	355840	1046850
16:00	296087	2689609	355888	1046456
Average	295949	2689822	355918	1046799
%RSD	**0.039%**	**0.015%**	**0.032%**	**0.018%**

Retention times for the runs were so consistent over the series that no variation was observed for three peaks, into the fourth decimal place in minutes. This precision can be realized by maintaining the column at isothermal conditions, and employment of electronic flow controllers (EFC Type 3) or digital flow controllers. These true-flow devices maintain a very consistent flow over a series of runs, especially with isothermal column conditions.

Table II. Retention time precisions for the six runs are summarized with their computed relative standard deviations.

Retention Time (minutes)[6]				
Injection Time	**Helium**	**Hydrogen**	**Oxygen**	**Nitrogen**
15:02	3.6373	4.0167	5.4100	6.5900
15:14	3.6373	4.0167	5.4100	6.5900
15:25	3.6387	4.0167	5.4100	6.5900
15:37	3.6387	4.0167	5.4100	6.5900
15:49	3.6380	4.0167	5.4100	6.5900
16:00	3.6380	4.0167	5.4100	6.5900
Average	3.6379	4.0167	5.4100	6.5900
%RSD	**0.08%**	**0.00%**	**0.00%**	**0.00%**

**NOW THE TASK IS TO GET SUPPLIERS OF GAS STANDARDS
TO PROVIDE REFERENCE MATERIALS
WITH ACCURACIES COMMENSURATE
WITH PRECISIONS DEMONSTRATED HERE.**

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[6] The fourth decimal place is reported here from the cursor display in Varian Star Interactive Graphics. Normally the Star report indicates only three decimal places for retention time.