# Mass Flow Controllers and Carbon Dioxide

# - Their Effects on Quantitation

**by**

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Concentration measurements in gas chromatography are relative calculations. The size of the eluting peak for an unknown is normally directly proportional to the corresponding size of a standard peak collected under identical conditions.

$$\text{Response Factor} = \frac{\text{Area of Standard}}{[\text{Standard}]}$$

This determination is very reliant on knowing the injection volume.

$$[\text{Unknown}] = \frac{\text{Area of Unknown}}{\text{Response Factor}} \times \frac{\text{Injection Volume of Sample}}{\text{Injection Volume of Standard}}$$

Standard procedures in chromatography mandate a verification of system linearity to ensure that the relationship given above applies to a range of concentrations. One process is to inject standards over a range of concentrations to establish that the response factor remains constant over a concentration range. In gas analysis, this process to generate accurate standards of various concentrations can be very tedious and subject to errors in the dilution process, or it can be very expensive with an inventory of multiple-level standard cylinders required.

Mass flow controllers can be employed in an analytical gas system to set a sample flow rate into the injection process, typically into cold trapping systems. By timing the sample loading into the trap with a given flow rate, the injection volume is determined. For example, a flow rate of 50 ml/min for 3 minutes yields an injection volume of 150 ml.

| Loading Time | Volume Loaded | Effective Concentration |
|---|---|---|
| 12.00 minutes | 600 ml | 8.00 ppb |
| 6.00 minutes | 300 ml | 4.00 ppb |
| 3.00 minutes | 150 ml | 2.00 ppb |
| 2.00 minutes | 100 ml | 1.33 ppb |
| 1.00 minutes | 50 ml | 0.67 ppb |
| 0.50 minutes | 25 ml | 0.33 ppb |

A multipoint calibration is readily generated from one standard by simply varying the timing for the standard loading. The table above illustrates a typical application of a multipoint calibration using a single standard with a concentration of 2 ppb, based on a loading volume of 150 ml. And Figure 1 demonstrates typical results generated with the various sampling times of a single standard.

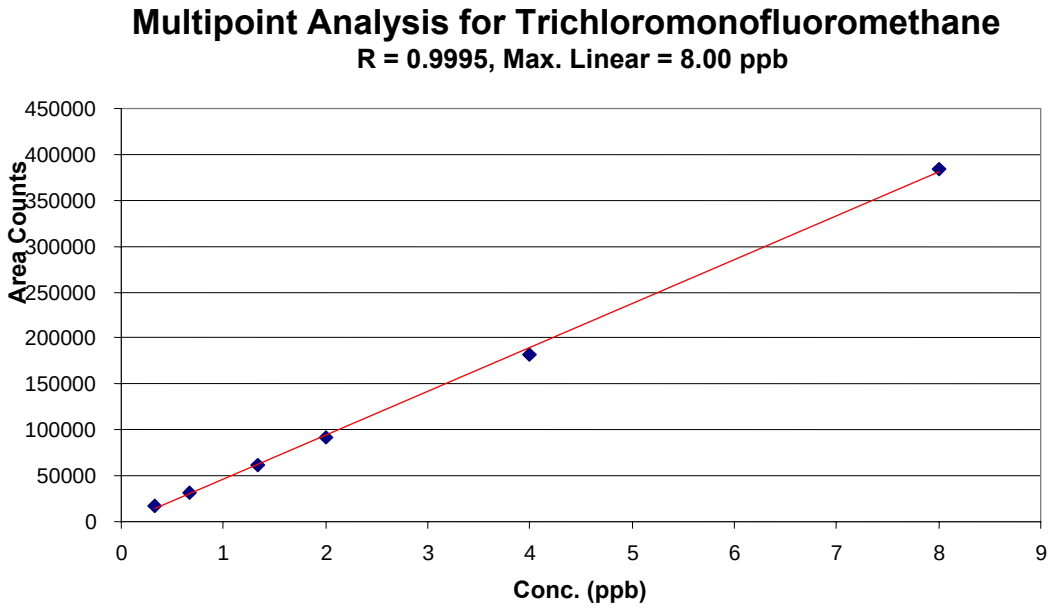


**Figure 1. A nice advantage of Mass Flow Controllers is that they can be used to generate multiple level calibrations, all based on a single standard. As the sample flow to the cold trap remains constant, the sampling time is varied to yield the different concentrations. The graph above illustrates the linearity from 0.33 ppb to 8.00 ppb by setting the MFC to 50 ml/min and varying the sampling time from 0.5 minutes to 12 minutes.**

All is good when the sample bulk gas matches the standard matrix. Mass flow controllers are calibrated by the manufacturer to a preset bulk gas, typically "air".[1] But if the composition of the bulk gas deviates from the calibrated basis, systematic errors are introduced.[2] Errors generated from various concentrations of carbon dioxide in air are given in Figure 2. Adjustments are possible, but the new matrix composition must be known and correction factors applied mathematically, albeit subject to induced calculation errors.[3] The error can be significant if the carbon dioxide level exceeds 5% of the matrix (with balance air).

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[1] "Air" and nitrogen have identical responses with mass flow controllers - *Operator's Manual, Sierra Series 830/840/860 Side-Trak and Auto-Trak Mass Flow Meters and Controllers*, Sierra Instruments, Monterey, CA, 1994, A-6.

[2] *Ibid.*, A-2.

[3] "Important note about K-Factors (corrections to MFC calibrations): Please note that if you have a transducer calibrated for a gas such as methane and wish to use the K-factors to measure a gas such as air, the inaccuracy of the measurement can range from ±5 to 10%. The use of K-factors is, at best, only a rough approximation and should not used in applications that require a better than ±5 to 10% accuracy." *Ibid.*, A-5.

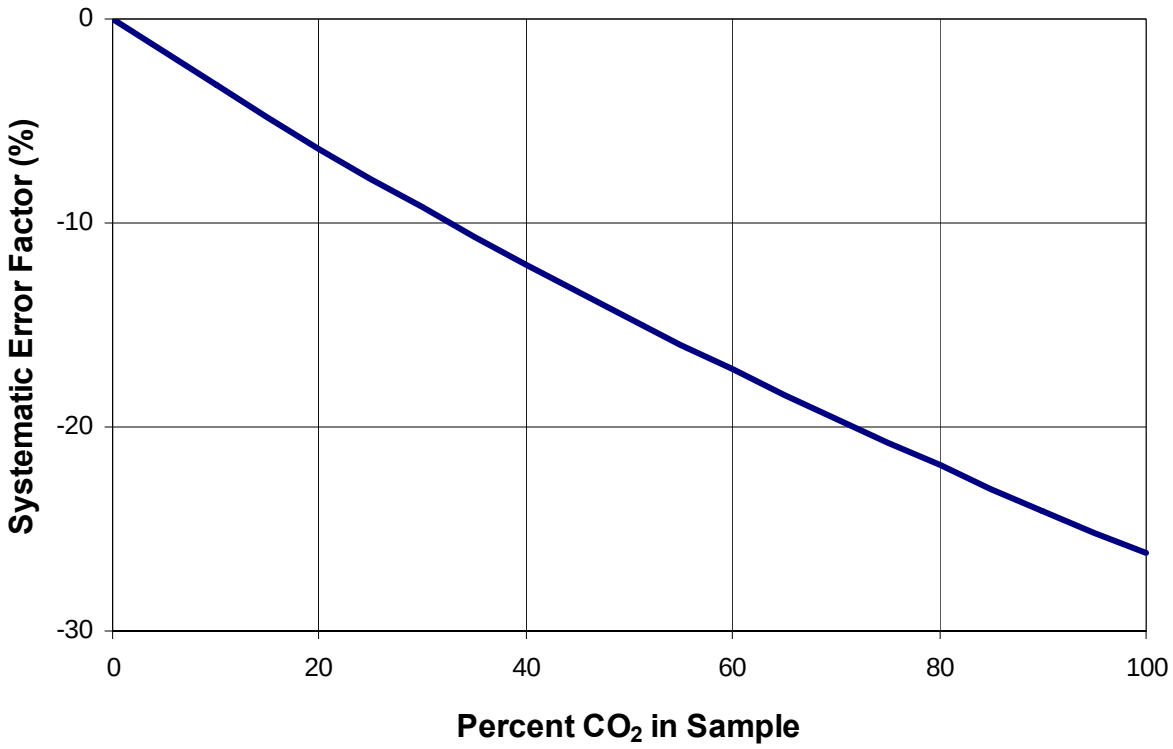
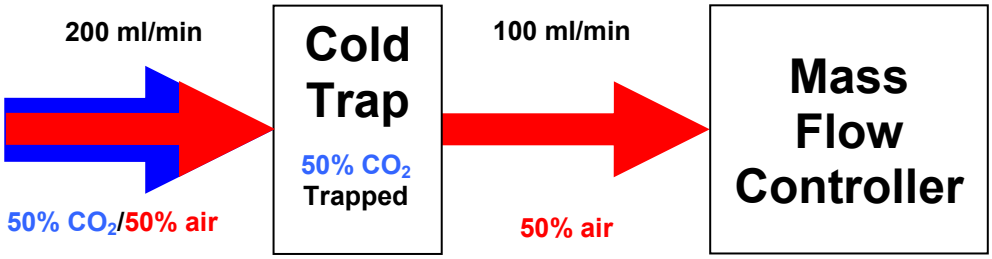



**Figure 2. Alterations in the overall coefficient of specific heat of the sample matrix, such as the inclusion of carbon dioxide, can greatly effect a change in the volume that is loaded into a trap with a mass flow controller. The estimated systematic error when the mass flow controller is installed upstream from the trap is plotted for various carbon dioxide levels. For example, a 50% carbon dioxide sample can generate an approximate error of 15% in volume due to the change in sample conductivity.**

When trapping gas samples into a cold trap warm enough to allow carbon dioxide to pass on through, the magnitude of the flow rate error is indicated above. If the trap is colder, normally below -78 $^{o}$C, carbon dioxide is frozen out, held in the trap and taken out of the flow stream. The resulting flow into the mass flow controller is then less than anticipated, as illustrated below and in Figures 3 and 4. As a result, the indicated flow for the mass flow controller is not accurate, with the magnitude dependent on the concentration of carbon dioxide in the sample.



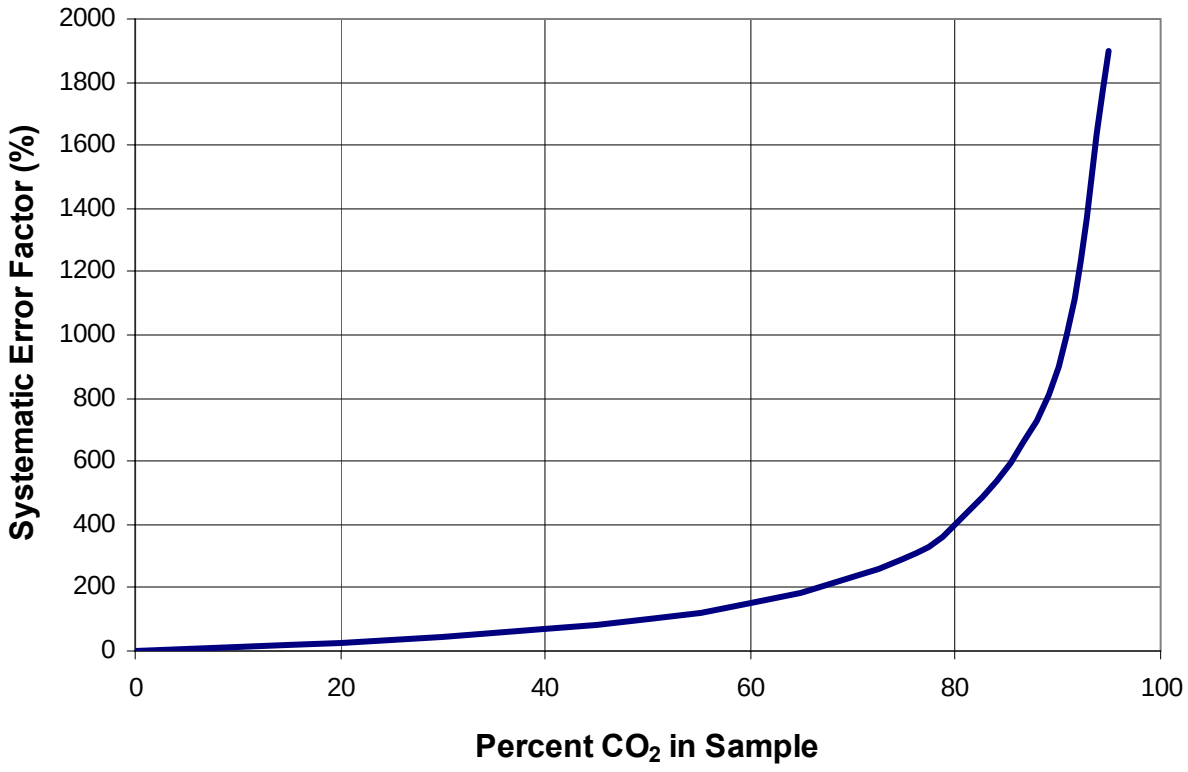



**Figure 3. When the mass flow controller is mounted <u>downstream</u> from the trap and the trap is cold enough to freeze out carbon dioxide (< -78 $^{o}$C), the carbon dioxide component in the sample is snared out of the sample stream and the controller only meters the remaining gas. Possible systematic errors are charted for various carbon dioxide levels with a mass flow controller downstream from the trap. For example, if a sample possesses 50% carbon dioxide and if the trap is cold enough to trap out this carbon dioxide, the mass flow controller effectively "sees" only half of the sample and the resulting volume error measured by the mass flow controller will be +100%.**

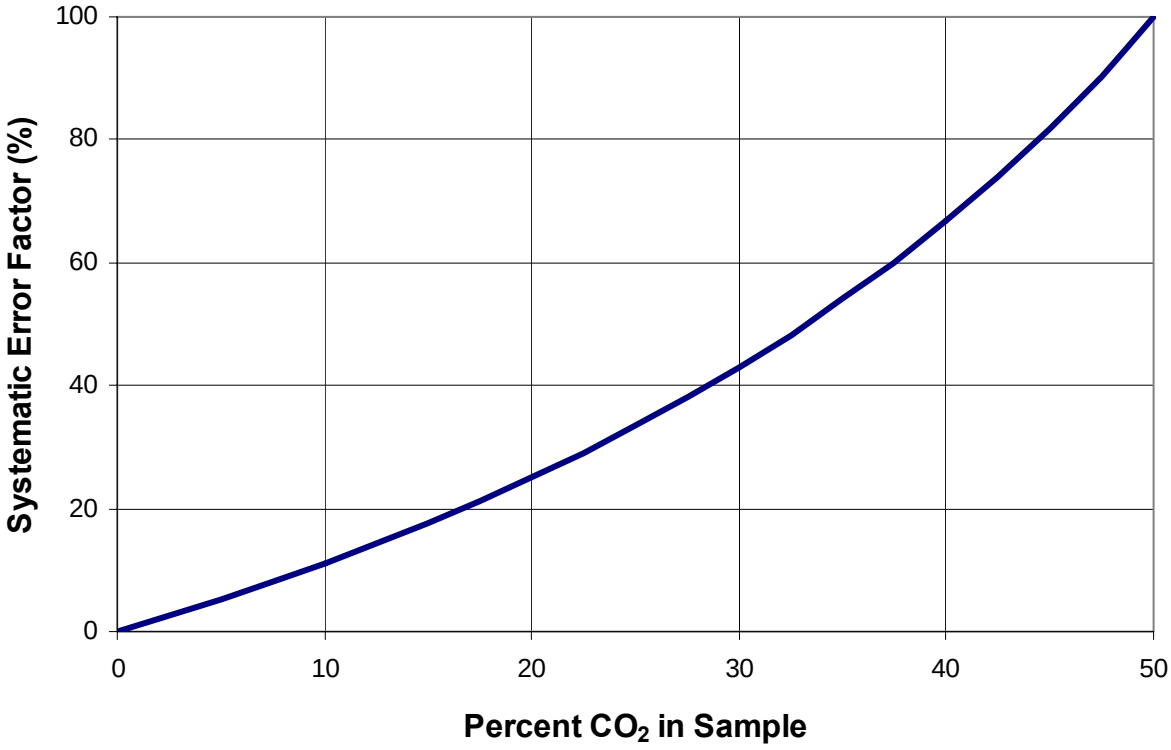



**Figure 4. While the magnitude of the error is catastrophic at high concentrations of carbon dioxide, when the mass flow controller is located downstream of the trap and carbon dioxide is frozen out of the stream (from Figure3), the error is still significant even at modest concentrations. For example, at a CO2 concentration of 20%, the flow passing into the trap is 25% higher than the flow measured by the controller.**

If the sample matrix is ambient air, no corrections are required since the mass flow controller will indeed measure the actual loading volume properly.[4]

With samples from combustion sources, such as vehicle exhaust or stack emissions, both possessing sizeable and variable levels of carbon dioxide, corrections for these errors become difficult to generate. An accurate assessment of the carbon dioxide concentration must be determined and then mathematical manipulations, outlined above and listed in Table II, are applied to yield the corrected injection volume and the effect on the results. Even then, an accumulation of errors can severely impact the accuracy of the final corrected results.

These errors are not canceled out from the calibration sequence. The standard matrix is frequently either nitrogen or air; unlikely is the standard to possess the same carbon diode level as exhaust or stack emission samples. Besides, the carbon dioxide level can vary from sample to sample. Table I illustrates the possible systematic errors realized with a 50% carbon dioxide matrix.

| Concentration of Sample in Air | Same Sample with 50% CO2 | Relative Error | Same Sample with 50% CO2 and MFC after Trap | Relative Error |
|---|---|---|---|---|
| 2.00 ppb | 1.70 ppb | -15% | 4.00 ppb | +100% |

**Table I. The magnitude of possible errors is demonstrated for a 2.00 ppb sample in a matrix with 50% $CO_2$. The position of the cold trap relative to the mass flow controller alters the effect.**

If the sample matrix matches the standard matrix and it corresponds to the calibration of the mass flow controller, a proper aliquot of sample is correctly loaded, with the cold trap located either prior or after to the mass flow controller. However, when the sample matrix is different, then serious errors can be introduced, resulting in invalid results. These errors are not detected with calibration sequences, as the errors are only realized with sample runs with differing major components.

The classical approach to eliminate any bias in results from the variation in matrix composition is to apportion the sample volume through a fixed volume sample loop. Now the sample loading is always measured volumetrically and is quite independent of the gas matrix. The only mandate is the precautions necessary to ensure that the sample loop is at constant temperature and the injection occurs when the loop has a consistent pressure for both standard and samples, due to the impact of the Gas Laws.[5]

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[4] Levels of CO2 in ambient air are much too low (< 400 ppm) to make a significant contribution (< 0.04%) to the flow measurement errors discussed here.

[5] From the Boyle-Mariotte Gas Law, volume in a loop has a direct relationship with pressure. Doubling of the sample pressure in the loop yields a twofold increase in its effective volume to the trap. Similarly, the Charles-Gay-Lussac Gas Law defines the relationship between volume and temperature. A five (5) degree Celsius increase in the loop temperature can generate nearly a 2% decrease in the effective loop volume.

| Error with MFC prior to Trap | Percent of $CO_2$ In Sample | Error with MFC after Trap |
|---|---|---|
| 0 | 0 % | 0 |
| - 3 % | 10 % | + 11 % |
| - 6 % | 20 % | + 25 % |
| - 9 % | 30 % | + 43 % |
| - 12 % | 40 % | + 67 % |
| - 15 % | 50 % | + 100 % |
| - 17 % | 60 % | + 150 % |
| - 20 % | 70 % | + 233 % |
| - 22 % | 80 % | + 400 % |
| - 24 % | 90 % | + 900 % |
| - 26 % | 100 % | + ∞ |

**Table II. The magnitude of systematic errors, in sample loading volume with a mass flow controller realized with various levels of carbon dioxide in the matrix, can be significant for even modest levels of $CO_2$.**

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