QUANTITATION OF HYDROCARBONS IN VEHICLE EXHAUST AND AMBIENT AIR

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ABSTRACT

Ironically, one of the most complex analyses in gas chromatography involves the simplest computation to generate concentrations. The difficult determination of hydrocarbons in vehicle exhaust and ambient air involves separation of over 200 compounds, requires cryogenic concentration to bring expected concentrations into a detectable range, and mandates usage of multiple columns and intricate valving. Yet, quantitation of these hydrocarbons can be calibrated with only one or two component standards and a simple mathematical operation.

Requirements for meeting this goal include: (1) even detector responses for all hydrocarbons from ethane to n-tridecane (including olefins and aromatics), (2) accurate and reproducible measure of the sample injection volumes, (3) maximizing trap, column and detector performances, and (4) minimizing sample carry-over. Importance of these factors and how they can be implemented in routine measurements are presented with examples from vehicle exhaust and ambient air analyses.

TEXT

Hydrocarbons remain a major pollutant in our atmosphere. Much of the problem generated is from incomplete combustion and unburned fuel in vehicle exhaust. Accurate measure of atmospheric and exhaust levels for hydrocarbons is on-going in many facilities in the world. This analysis is undoubtedly one of the most complex in chromatography due to large number of individual hydrocarbon components found, the low levels required to be measured, and high concentrations of potential inferences to the measuring process. Well over 200 hydrocarbon species are often detectable in ambient air samples and over 300 peaks are assigned in chromatograms from vehicle exhaust. Levels to less than 1 ppb Carbon are needed for the final report – well below direct detection by normal chromatographic methods. A concentrating step is required to bring these levels into the normal range of the flame ionization detector. Both exhaust and ambient air possess major constituents that can effect problems in the measurement, including water, carbon dioxide, carbon monoxide, nitrogen oxides, nitrogen and oxygen. The measurement process must not allow these components to interfere with the final hydrocarbon tally.

The range of hydrocarbons usually speciated in ambient air and vehicle exhaust is from Ethane to n-Tridecane. These components represent very wide boiling points from –88 ^{o}C to +235 ^{o}C. They are not adequately separated within a single capillary column, especially the C_2s, C_3s and the C_4 olefins. The analysis should be completed on two columns for more optimal speciation – one alumina PLOT wide-bore capillary column (0.32 mm ID) for "light-end" components from Ethane to n-Hexane, and a second non-polar wide-bore capillary column (0.32 mm ID) for the "mid-range" from n-Hexane to n-Tridecane. To achieve the needed detection levels, samples are concentrated on a cold trap and are processed through a system with complex valving hardware.

However, quantitation of hydrocarbons becomes very simple if all detected hydrocarbons possess an even response. Then the calibration standard need not possess every component. In fact, no standard is presently available with every component to be measured at the trace levels. With even responses, a standard with only propane (or propane and benzene) can be employed with the measured response factor(s) applied to every peak.

The flame ionization detector (FID) employed in high performance gas chromatographs is a very effective carbon counter for most hydrocarbons. Its response is nearly even for all hydrocarbons detected in ambient air and exhaust when component concentrations are converted to "ppb Carbon" (or "ppb Volume/Volume times Carbon Number" - for example 1 ppmV/V Propane becomes 3 ppm Carbon). FID responses can be verified with examination of NIST standards for selected hydrocarbons from Ethane to n-Decane. Other responses are checked with other available standards. Experimental results can be achieved to a variation over the range of less than 5% off from the Propane response for most hydrocarbons, as shown in Figure 1. Deviations from an even response can be attributed to cold spots in the sampling process, component loss in sampling containers and insufficient trapping capacity. All sample lines and valving must be kept sufficiently warm to avoid loss of particularly the heavier components, such as n-Tridecane. Component loss in canisters can be minimized by injection of water to coat reactive surfaces.[1] And trapping can be effective for a large range of components by cryogenically cooling the trap to –180 ^{o}C and then heating it as rapidly as possible to release the hydrocarbons to the columns for speciation.

Temperature control of the initial temperature setting for the trap is critical to properly trapping Ethane but not oxygen and Methane. A small temperature variation of only ±5 ^{o}C from the optimum can readily cause either the improper trapping of oxygen and Methane or a significant loss of Ethane. Figure 2 illustrates the trapping efficiencies for several compounds versus trap temperature. A properly designed proportional heating/cooling trap is effective in maintaining a consistent setting and yields good recovery for all light-end components.

Another advantage for the FID is its non-response to many of the major components in the matrix, including no response to nitrogen, carbon monoxide, carbon dioxide and nitrogen oxides, and very low response to oxygen and water. Its extremely wide linear range (of > 10^7) permits small peaks to be detected along with major ones in the same measurement. In addition, with sample concentration prior to inject into the column, detectable levels to less than 1 ppb Carbon are possible.

Sample lines and tubing can have a major effect on proper recovery for hydrocarbons. Some materials, such as stainless steel, are very reactive and can tie up hydrocarbons, especially the heavier ones. Other materials, such as silica-lined stainless steel are purported to be very inert to hydrocarbons.[2] Other possible materials for sample lines and loops include nickel and glass. These various materials have been examined as sample loops for even response to a range of hydrocarbons. Results are summarized in Figure 3. Stainless steel, as might be expected, showed significant loss in hydrocarbons across the range. Fused silica lined stainless steel yielded higher factors than anticipated; the enhancement is likely due to the very rough surface of silica rods and selective retention of heavier hydrocarbons on this surface and their subsequent release to the trap. Nickel tubing showed better performance and glass loops generated the most even response factors across the range.

Proper calibration also relies on clean system blanks and no (or at least very low) carryover from previous samples or standards. Detected components not attributable to the sample can lead to invalid results. The best approach to verify a clean system is examination of a sample directly from the headspace of liquid nitrogen. Any hydrocarbons originally in the headspace are effectively condensed into the liquid nitrogen at –196 ^{o}C and are not present in the blank sample. A likely source for detected

contamination can be from impurities in the carrier and purge gases employed. Contamination is greatly minimized by using helium carrier gas of 99.9999% purity. Purge flows, used to transfer samples to the trap, can be effectively scrubbed by innovative precleansing of the purge gas through a cryogenic trap and then venting the impurities off later in the analysis. Another possible source for artifacts is from material employed in the trap. Some organic trapping materials can react with nitrogen oxides in samples and unexpectedly yield Ethene and other hydrocarbons.[3] Also, repeated temperature cycling of some organic trapping materials can release hydrocarbons, notably benzene.[4] And the very wide range of hydrocarbons makes the choice of trapping absorbents difficult to insure effective trapping of light-end compounds and still permit quantitative release the very heavy ones. Use of liquid nitrogen cryogen and empty nickel tubing or nickel tubing packed with glass beads for traps is a very effective approach to complete trapping. Rapid temperature ramping to at least 250 ^{o}C/minute with these materials guarantees full release without measurable artifacts. Carryover can be minimized by keeping all flow paths continually flushed with purge gas, even when the system is idle. When a sample is to be loaded, it is first flushed through its sampling lines prior to loading onto the trap. After the loading, purge gas again flushes all lines to prevent any residues from appearing in the next run.

Detectable concentrations of hydrocarbons in ambient air and vehicle exhaust can vary well over four orders of magnitude (10,000) within one sample. To avoid sample dilution and rerunning to measure the higher concentrations, an analyzer needs to perform properly over the wide range. Although the FID is effectively linear over a wider range, other experimental conditions can restrict accurate quantitation to a more limited range. Wide–bore columns (with 0.32 mm ID) start to exhibit overloaded peaks at a level below the capacity of the FID and the column's sample capacity becomes the major limit to the operating range. Peak coelutions and underlying peak contaminations can render low concentration levels non-linear due to contributions from hydrocarbons other than the compound of interest. Electronic signal processing, including electrometers and analog-to-digital converters, can also limit operations when their maximum is exceeded. Newer electrometers, however, have extended the ability to detect small and large peaks together without the need to switch range settings.

Very often linear ranges are displayed with linear plots of area counts versus concentration, as shown in Figure 4, and performance is measured as the slope, intercept and a statistical fit. This scheme becomes easy to visualize but is hampered by dynamics of a large concentration range possible. Usually, higher concentrations dominate the graph and low levels are condensed into a small, unreadable region. A better approach to handle the four orders of magnitudes possible in this measurement is to plot the effective response factor (area counts/concentration) versus log [concentration]. Figure 5 demonstrates this method for charting. Deviations outside a specified linearity are readily portrayed with this presentation.

Generation of peaks as large as possible makes their detection easier and more accurate. Readability is enhanced by injecting large sample volumes, typically 10-100 ml for vehicle exhaust and 50–800 ml for ambient air. However, these volumes cannot be loaded directly into a wide-bore capillary column effectively. The large volumes must be reduced to an injection of less than 100 µl to maintain the performance of the capillary column. Other approaches to enhancing the peak size include the employment of narrow-bore flame tips (+52% over conventional flame tips), use of nitrogen as the detector make-up (+65% over helium make-up), and isolating the trap while it is heating to yield a sharp transfer of the sample from trap to column (+41% over non-isolation). Narrow-bore columns (~0.18 mm ID) generate sharper and taller peaks (+31% over wide-bore columns), but it is much more susceptible to column overloading with higher component concentrations. They are severely limited in their upper range of measurement.

Aliquots of samples can be loaded into the chromatograph through three commonly employed mechanisms – (1) direct injection of a fixed volume loop, (2) concentrating on a trap with a mass flow controller and (3) concentrating on a trap from a fixed volume loop. Direct injection has the advantages of simpler instrument hardware and it is a true volume measurement with no systematic errors created with changes in the bulk gas composition. However, volumes injected directly into a capillary are limited 0.1 ml or less to avoid degradation of the column performance, and the low volume severely hampers detection limits.

Very large volumes can be measured by mass flow controllers (MFC). A sample flow rate transferred to a trap over a time period yields a volume measure for that interval. Various volumes are selected by altering the sample time interval. Achievable volumes can range from 5 ml to 1,000 ml. These volumes necessitate use of a concentrator to maintain optimum capillary performance. Calibrations for mass flow controllers are altered with changes in their ambient temperature.[5] The control head must be maintained at constant temperature for best consistencies of volume. Moreover, they do possess an error from varying input pressures. A pressure regulator in-line with the controller is recommended to minimize this error.[6] In addition, major volume errors can be realized with changes in the bulk gas of the sample, as mass flow controllers are calibrated to a specific gas, typically nitrogen or air. Alterations in the overall thermal conductivity of the sample, such as the inclusion of carbon dioxide or water, can greatly effect a change in the sample thermal conductivity and modify the volume that is loaded.[7] Figure 6 illustrates graphing for the estimated error from various carbon dioxide levels when the mass flow controller is installed <u>upstream</u> from the trap. For example, a 50% carbon dioxide sample can generate a systematic error of approximately 15% in volume due to the change in sample conductivity. The error is not usually correctable as the composition of each sample must be known precisely and predictions for the resulting conductivity – hence volume - are accurate to no better than 10% relative.[8]

When the mass flow controller is mounted <u>downstream</u> from the trap, some of the major components in the sample can be trapped out and the controller only meters the remaining gas. 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 MFC will be +100%. Figure 7 graphs the errors possible for various carbon dioxide levels with a mass flow controller downstream from the trap. In addition, reproducibities for the volume measurement with a mass flow controller are typically in the range of 5% - 10% and are not up with performance possible from a fixed volume loop.

The best reproducibility performance is achieved with a fixed volume loop. Reasonable volumes can be loaded when used with a focusing trap prior to column injection. Typical precision performance is ±2% for levels above detection limits. The volume metered is independent of the bulk gas composition - it is a true volumetric measure. However, very large loop volumes are not realistic due to their very massive physical bulk. Practical volumes range from 10 μl to 100 ml.

From the Boyle-Mariotte Gas Law, volumes in a loop have a direct relationship with pressure. Doubling of the sample pressure in the loop yields a twofold increase in its effective volume to the trap. Figure 8 illustrates the possible errors with different sample inlet pressures. For example, a sample loop pressure of 1.2 atmospheres (3 psi) can generate an effective volume error of 20%. Prior to the trap transfer, a sample loop should be allowed to come to a consistent pressure, such as atmospheric pressure, to accomplish better reproducibilities for peak areas. Subtle changes of atmospheric pressure over a day rarely exceed 0.1%[9]- well below other contributing errors.

Similarly, the Charles-Gay-Lussac Gas Law defines the relationship between volume and temperature. A five (5) degree Celsius change in the loop temperature can generate nearly a 2% change in the effective loop volume, as indicated from data presented in Figure 9. Holding a loop at constant temperature in an oven can minimize the error and enhance the volume precision. With the loop maintained at +150 ^{o}C, for example, a 1 ^{o}C change in this temperature will effect a minimal change of volume of 0.2% - again way below the overall experimental error.

Achieving the best results from this complex analytical measurement requires attention to many facets of the instrumental set-up and run conditions. Proper design of the system can reduce quantitation errors. Awareness by the operator of potential systematic errors can yield optimum results for a wide range of hydrocarbons.

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[4] Tsou, G. 1995. California Air Resources Board, El Monte, CA*, personal communication.*

[5] *Instruction Manual for Sierra Series 830/840/860 Side-Trak Mass Flow Meters and Controllers*, Sierra Instruments, Inc., Monterey, CA 93940, June 1996, p. 55.

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[7] *Instruction Manual for Sierra Series 830/840/860 Side-Trak Mass Flow Meters and Controllers*, Sierra Instruments, Inc., Monterey, CA 93940, June 1996, p. 56.

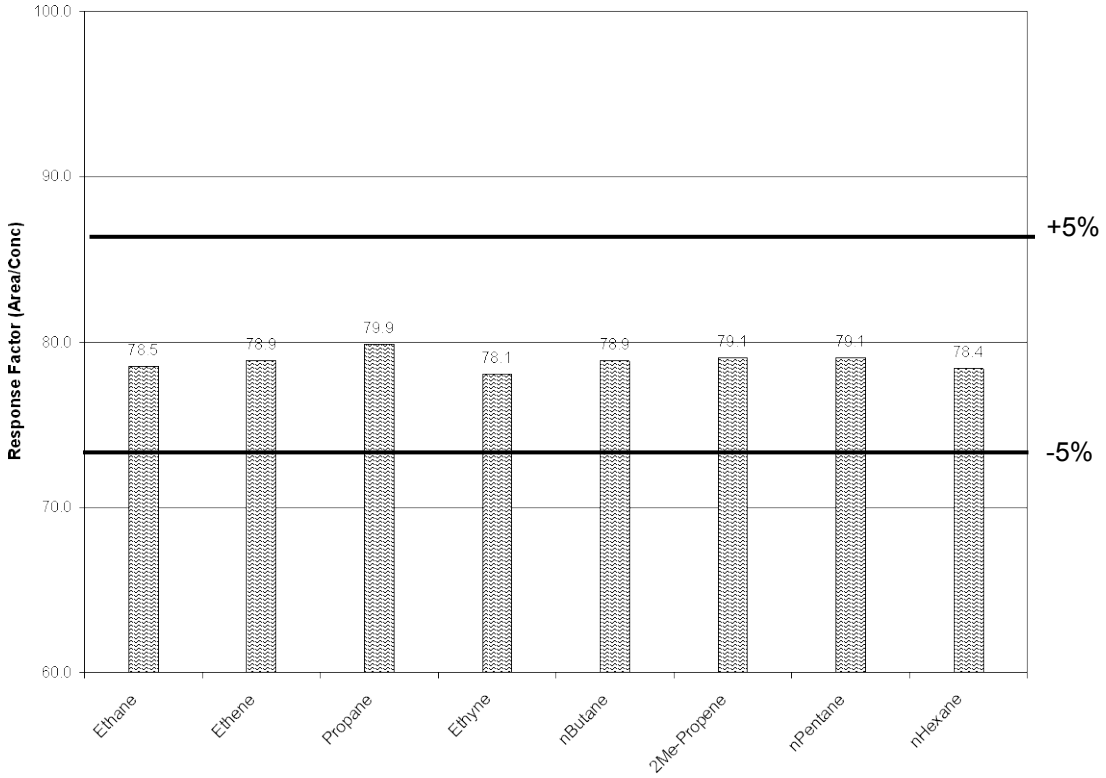
[8] *Instruction Manual for Sierra Series 830/840/860 Side-Trak Mass Flow Meters and Controllers*, Sierra Instruments, Inc., Monterey, CA 93940, June 1996, p. 59.

[9] Barometric data obtained from U.S. Department of Commerce, National Oceanic and Atmospheric Administration, National Weather Service Office, San Diego, CA 92127.

KEY WORDS

Quantitation of Hydrocarbons, Hydrocarbons in Vehicle Exhaust, Hydrocarbons in Ambient Air, Speciation of Hydrocarbons

Figure 1. Even responses are achievable from Ethane to n-Dodecane. Response factors for selected hydrocarbons are shown for light-end components (Ethane to n-Hexane) and for mid-range components (n-Hexane to Tridecane). Nearly all components lie well within 5% of the Propane response, with the exception of n-Tridecane. The label value for the n-Tridecane standard was "unanalyzed" and can be in error. Response factors for the two sets differ due to dissimilar injection volumes. Bars for ±5% of the Propane response are attached. These even responses allow a single standard to be employed for the complete calibration.



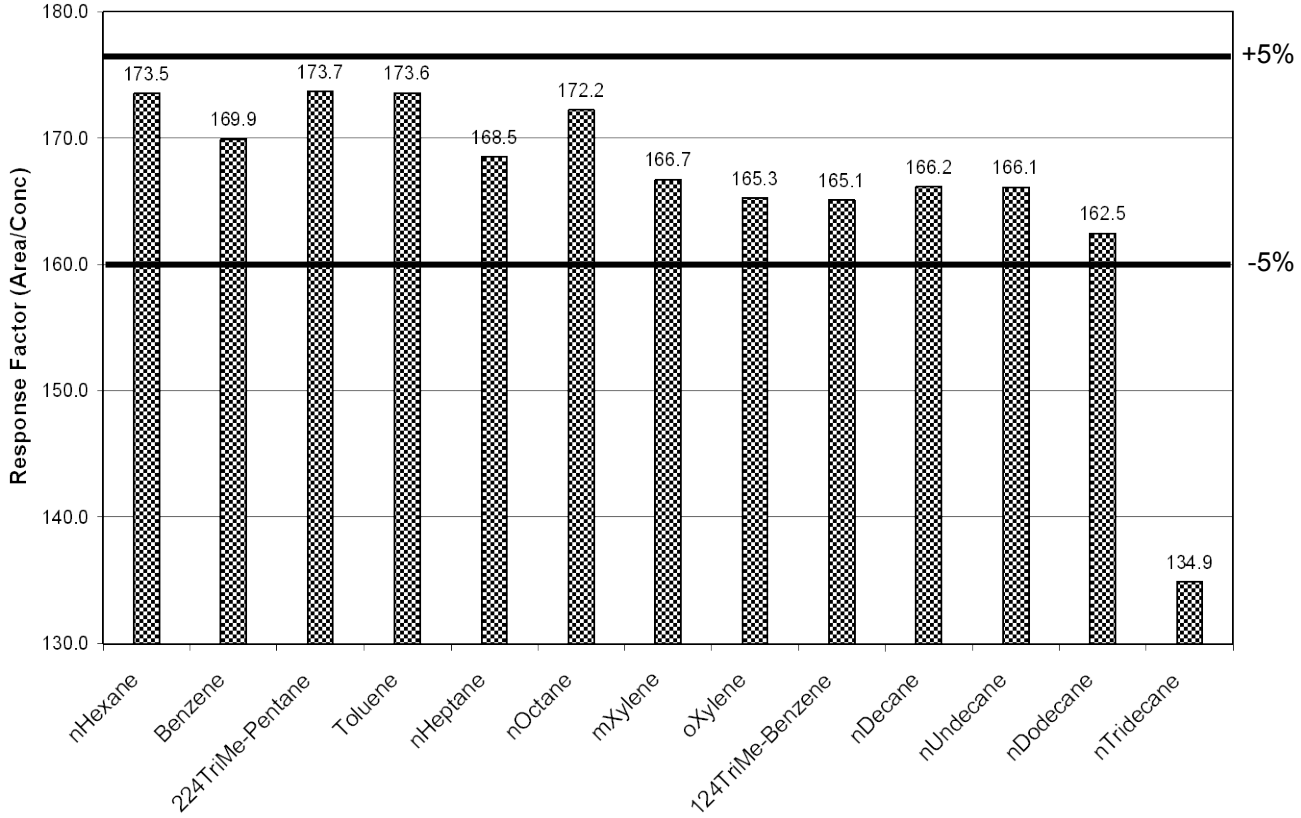


Figure 2. Trapping efficiencies for several compounds are shown plotted against trap temperatures. To effectively trap Ethane and allow Methane and oxygen to pass, the trap temperature must be maintained within ±5°C. Wider variations in temperatures can even cause loss in Ethene and Propane.

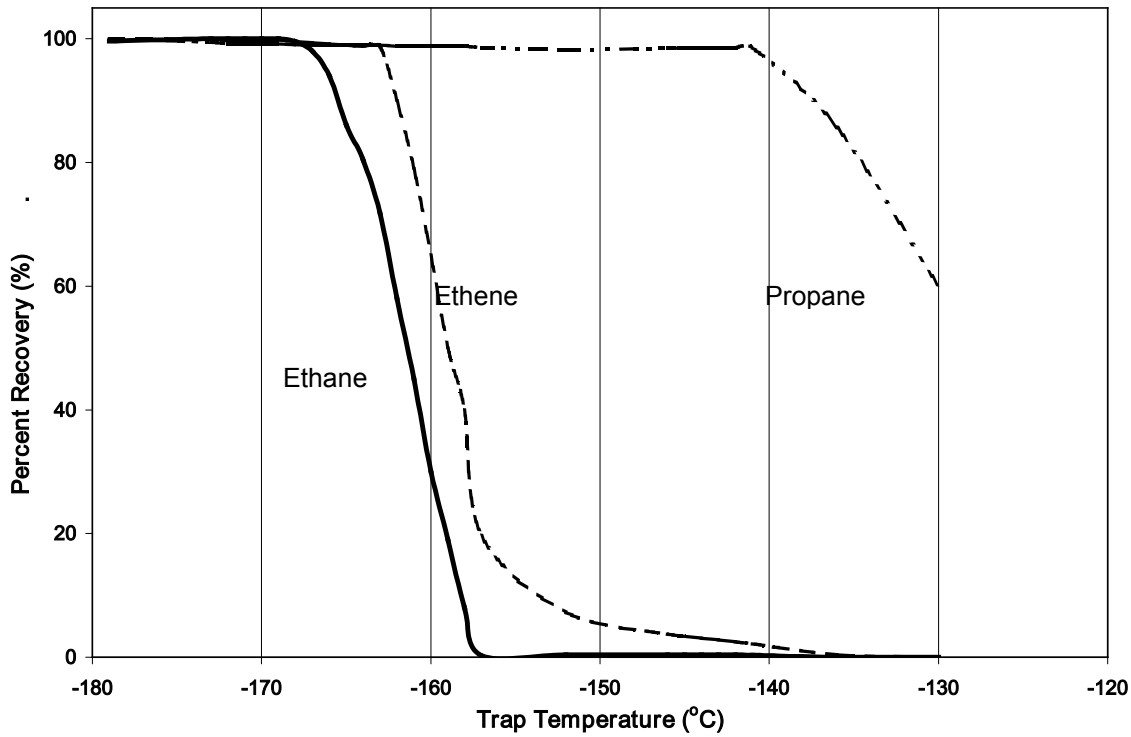


Figure 3. Materials used for sample loops and tubing can have major effects on proper recovery for hydrocarbons. Performance for several common materials is summarized by plotting response factors against hydrocarbon retention time. This chart has all responses normalized to Propane. A glass sample loop yields the most consistent response factors over the hydrocarbon range.

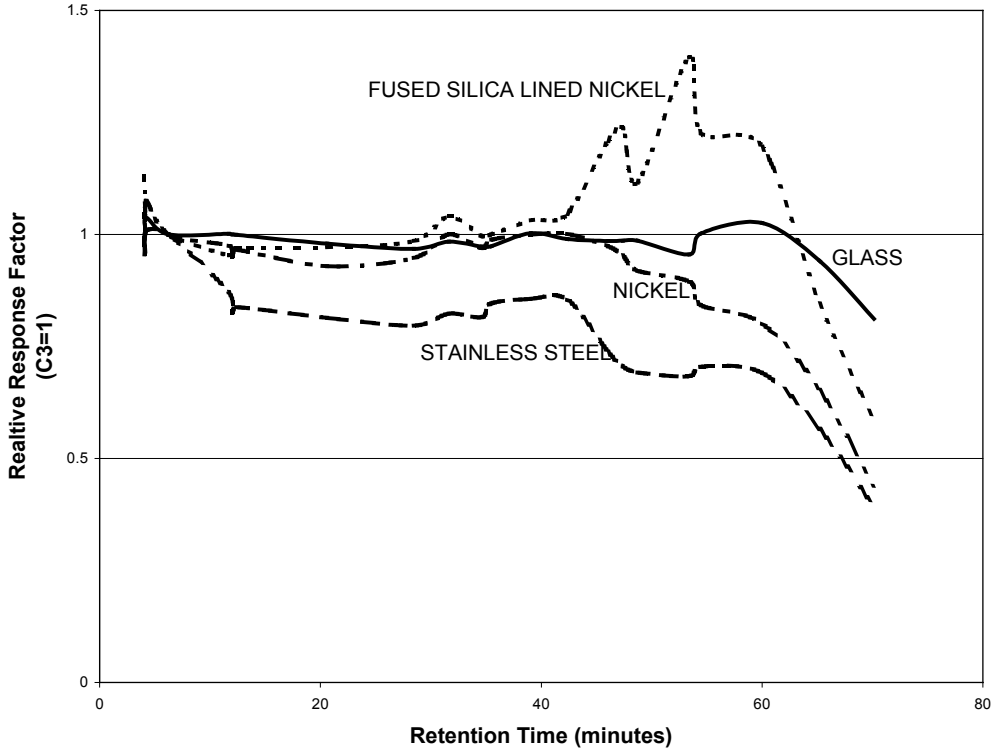


Figure 4. Typical linear plot of peak area counts versus concentration is shown. Linearity over wide concentration ranges is not easily displayed in this format. Deviations from linearity at the lower concentrations are difficult to discern. Error bars for a 5% tolerance in area counts are shown.

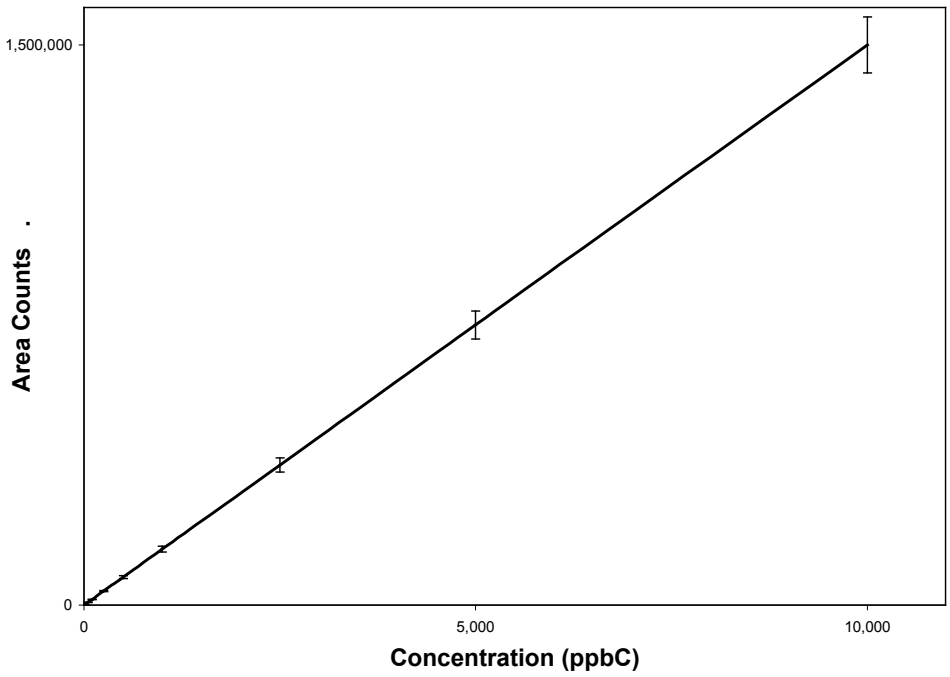


Figure 5. A more effective approach to handle the four orders of magnitudes possible in this measurement is to plot the response factor (area counts / concentration) versus log [concentration]. In this format, deviations outside a specified linearity (illustrated here as ±5%) are readily portrayed for all concentrations.

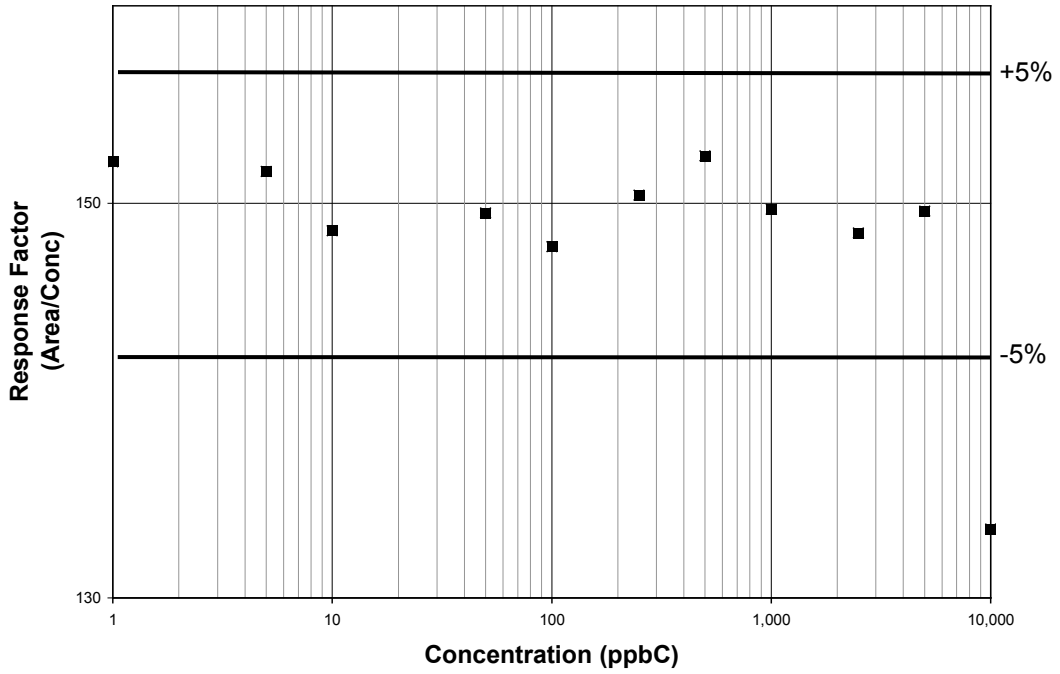


Figure 6. Alterations in the overall thermal conductivity of the sample, such as the addition of carbon dioxide or water, can greatly effect a change in the volume that is loaded with a mass flow controller. The estimated systematic error when the mass flow controller is installed upstream from the trap is plotted for various carbon dioxide levels. For example, a 50% carbon dioxide sample can generate an approximate error of 15% in volume due primarily to the change in sample conductivity.

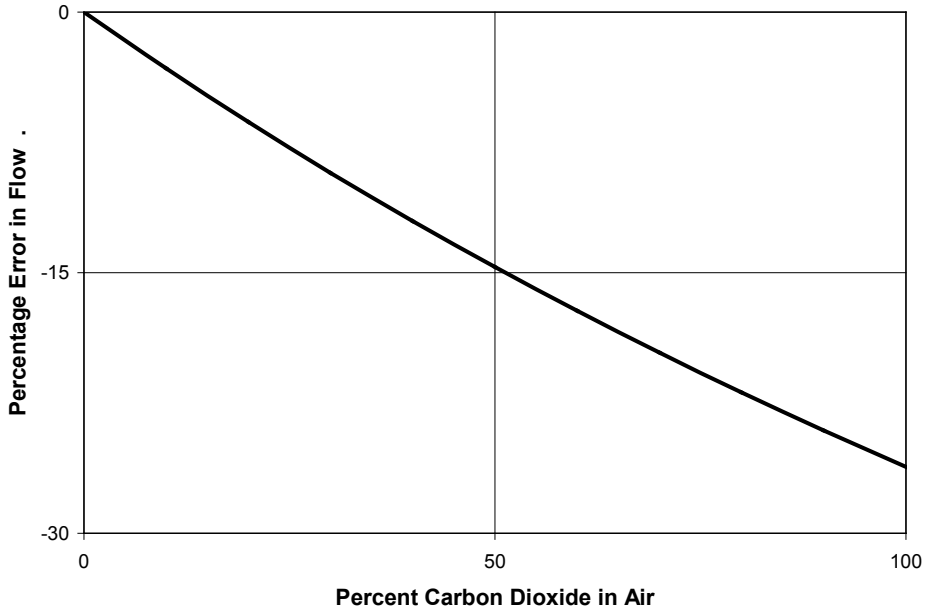


Figure 7. When the mass flow controller is mounted downstream from the trap, some of the major components in the sample can be trapped out and the controller only meters the remaining gas. Systematic errors possible is charted for various carbon dioxide levels with a mass flow controller downstream from 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%.

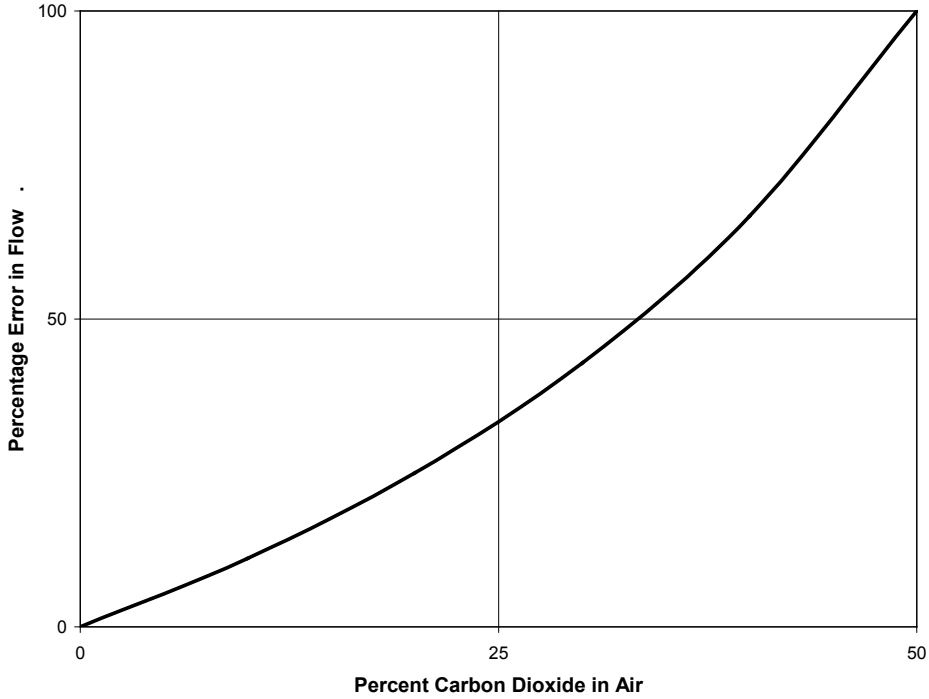


Figure 8. From the Boyle-Mariotte Gas Law, volumes in a loop have a direct relationship with pressure. Doubling of the sample pressure in the loop yields a twofold increase in its effective volume to the trap. Possible errors with different sample inlet pressures are graphed. For example, a sample loop pressure of just 1.2 atmospheres (or 3 psi) can generate an effective volume error of 20%.

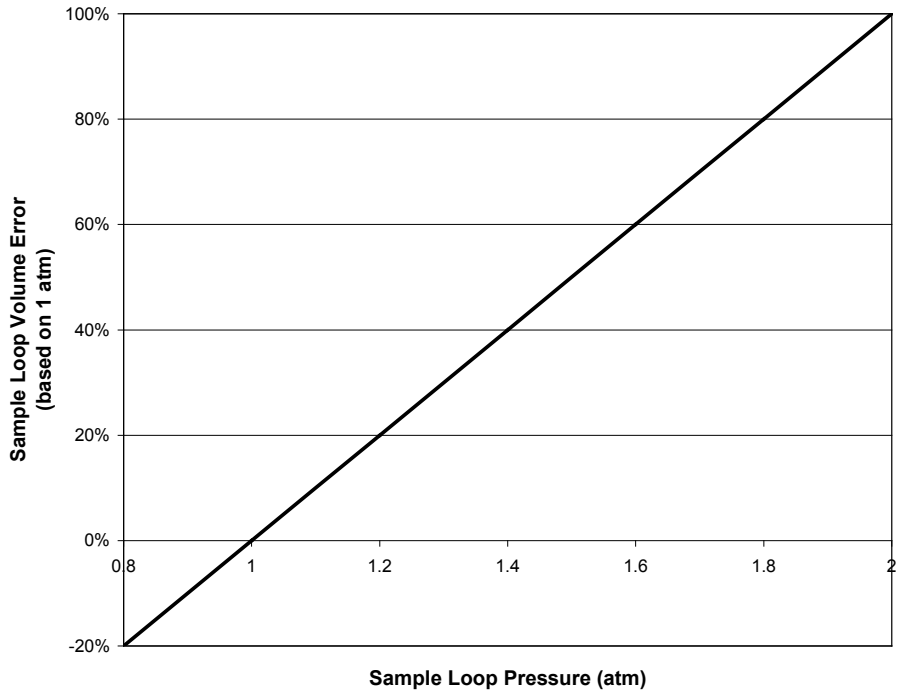
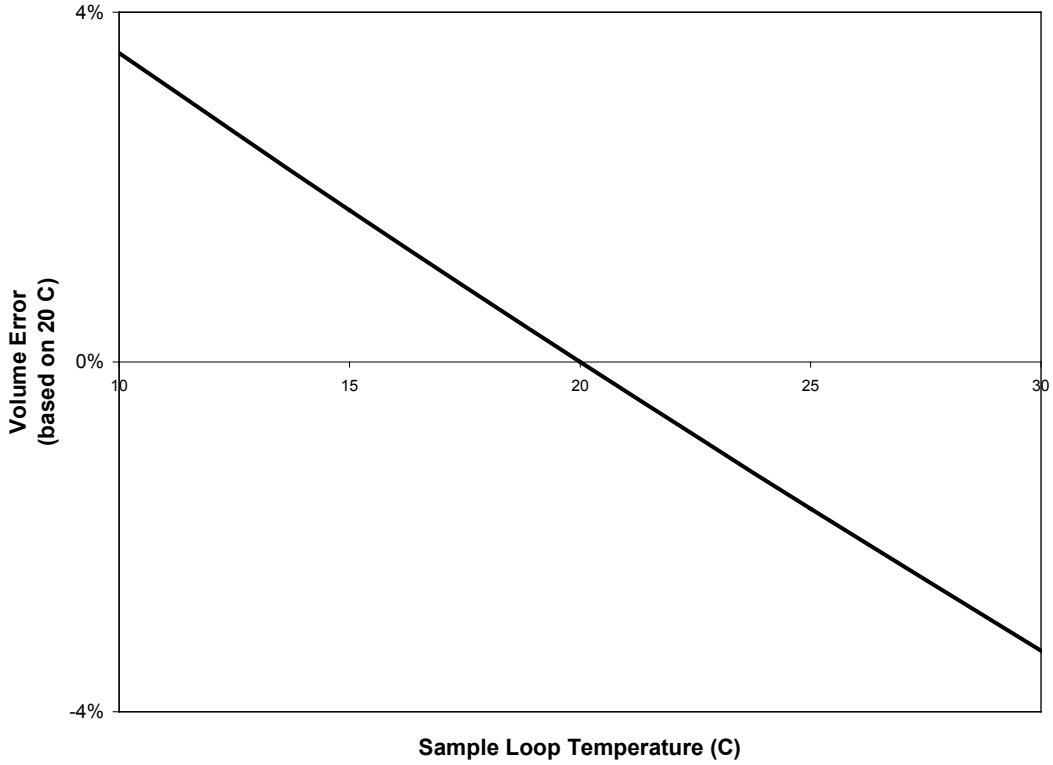



Figure 9. The Charles-Gay-Lussac Gas Law defines the relationship between loop volume and its temperature. A five (5) degree Celsius change in the loop temperature from 20 ^{o}C can generate nearly a 2% change in the effective loop volume as indicated in data presented here.