Validating Instrument Performance for Measurement of Hydrocarbons in Ambient Air with a Gas Chromatograph and Dual Flame Ionization Detectors

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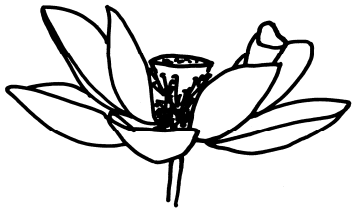

Full speciation of hydrocarbons in ambient air involved in the USEPA Photochemical Assessment Monitoring Stations (PAMS) Program[1] is undoubtedly one of the most difficult analyses in gas chromatography.[2] Ambient levels are well below detection by direct injection with flame ionization detectors. Samples must be concentrated from typically 300 ml into a small volume to enhance detection into measurable range of the detectors. A very large number of possible hydrocarbons (>300) must be "fully" resolved to avoid improperly assigning concentrations to nearby and overlapping peaks. And the full gamut of peaks must be identified and quantified with limited standards (typically NIST or NIST-traceable Propane and Benzene).

The system involves a high-performance gas chromatograph with cryogenic trapping, four automated valves, a 16-position automated sampler, three capillary columns, pneumatic controllers, two flame ionization detectors, a mass flow controller to set the sample flow, cryogenic concentrator, and one workstation to fully speciate the full range of hydrocarbons to compute their concentrations. A single column is not sufficient to fully resolve all hydrocarbons within the C_2-C_{13} range, since a "boiling point" column (dimethylpolysiloxane) cannot fully resolve the very light hydrocarbons, especially Ethane/Ethene/Ethyne, Propane/Propene and Butanes/Butenes, and still separate the heavier hydrocarbons. A second column - Alumina Porous Layer Open Tubular (PLOT) - is added to fully separate the light hydrocarbons. A column switching valve and a short precolumn is installed to perform a coarse separation of the "Light-End" hydrocarbons (C_2-C_5) from the "Mid-Range" ones (C_6+).[3] Appropriate valve timing is selected to place proper analytes (typically a column switch just after 2,2-Dimethylbutane) onto the suitable columns. Typical Light-End and Mid-Range chromatograms of ambient air are presented in Figures 1 and 2. Such a complex analysis requires assurances that the data values are valid, that the system is fully functional and ready for use, and that the ultimate performance is achievable.

The process to establish optimal working conditions for the measurement involves specific steps to ensure accurate and reproducible results. These include establishment of consistent retention times to ensure accurate identification of eluting peaks, setting up linear range and detection limits, and assurances of results' quality. The instrument setup is not simple and involves operations that can potentially fail to achieve expected results.

Specific tests required to validate this system include:

- Assignment of peak identifications.
- Establishment of a clean instrument blank using nitrogen gas as a sample.
- Performance of a multi-point calibration over a minimum range of 1 ppbC[4] to 100 ppbC using primary NIST standards, especially for propane and benzene.
- Proof of even detector responses for Ethane through Decane.
- Determination of detection limits by conducting repetitive runs within five times the expected detection limit, anticipated to be near 0.2 ppbC.
- Confirmation of stability of retention times and reported concentrations with a multi-component gas mixture over an extended time interval.
- Substantiating minimal carryover of high concentration samples into a following blank.

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1 See: www.epa.gov/air/oaqps/pams.

2 An established method protocol for PAMS hydrocarbons can be found at www.arb.ca.gov/aaqm/sop/sop032.pdf.

3 The split between the two columns can occur between the Butanes and Pentanes, or between Pentanes and Hexanes. The latter places Methylbuta-1,3-diene (Isoprene) on the PLOT column for full separation of it from Pentane.

4 Concentrations for hydrocarbons are often reported in units of ppbCarbon (ppbC) to facilitate direct comparison of the total carbon concentrations. The conversion from ppbVolume is ppbC = ppbV * number of carbons in molecule; for example 1 ppbV Hexane becomes 6 ppbC.

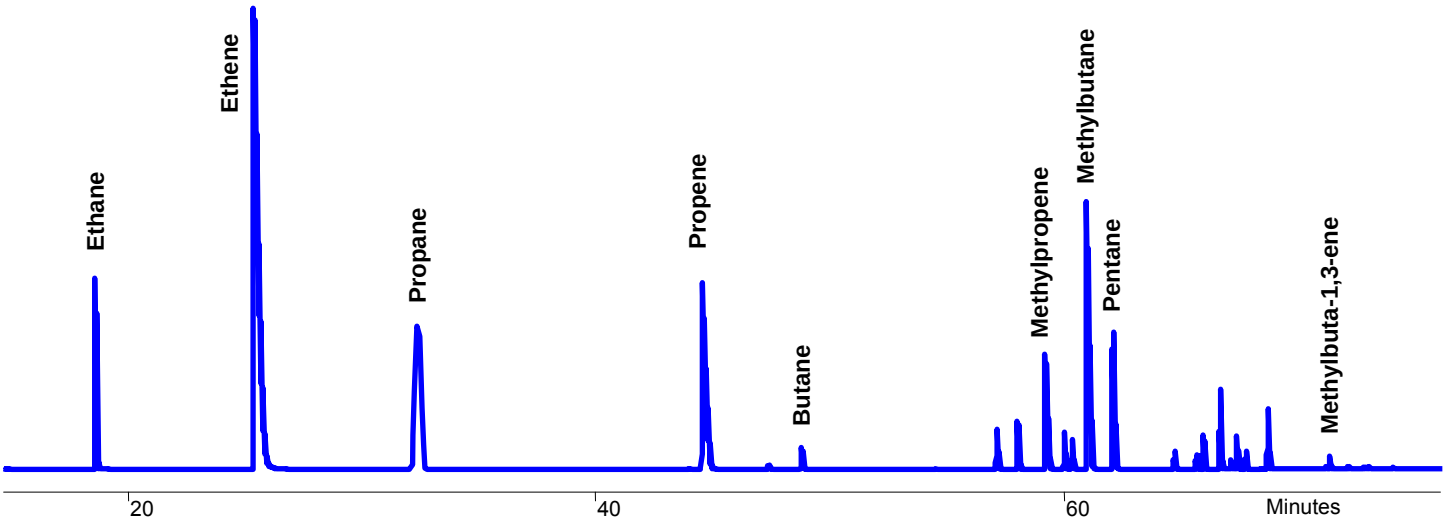

Figure 1. Typical Light-End chromatogram for ambient air.

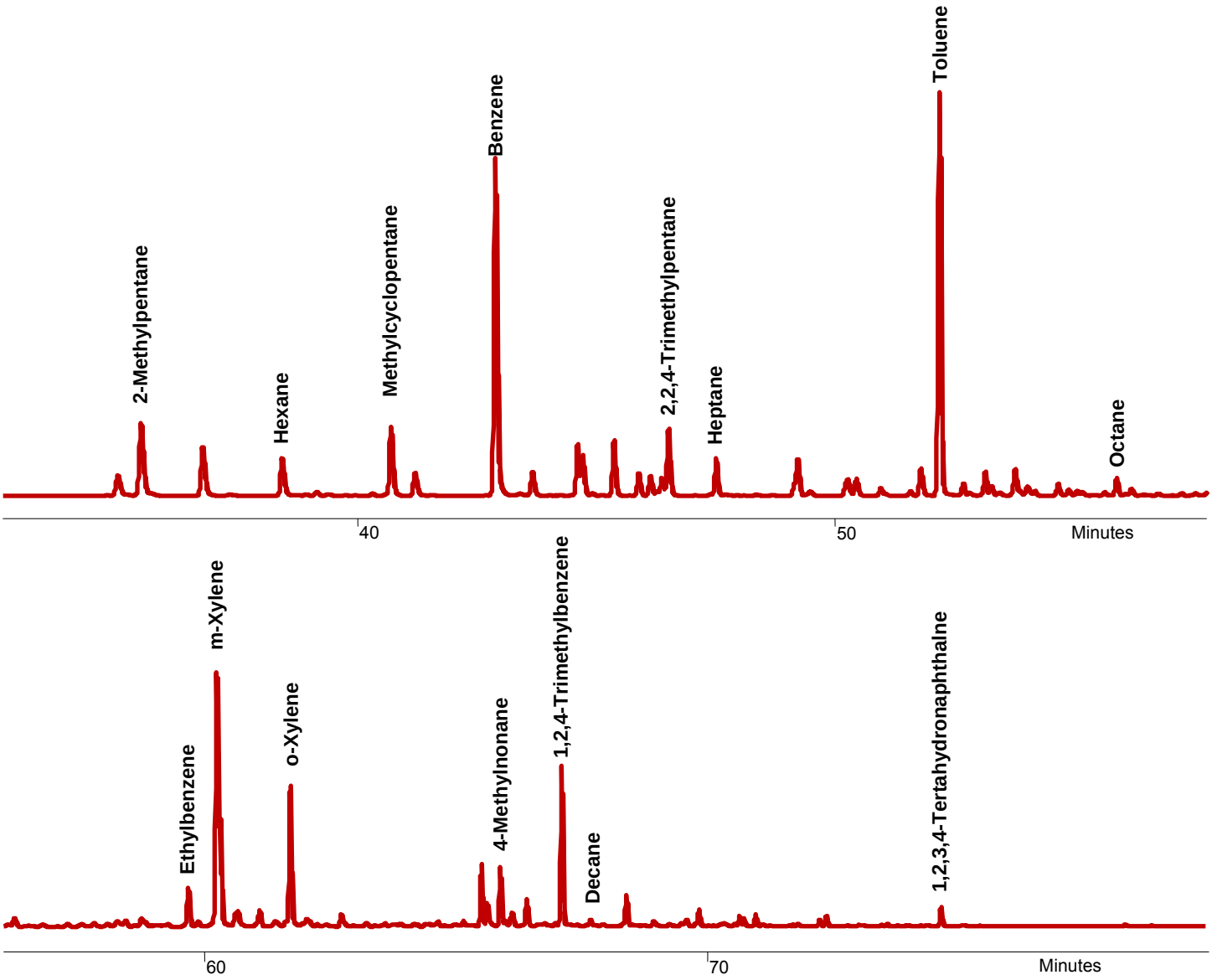

Figure 2. Typical Mid-Range chromatogram for ambient air.

I. IUPAC Compound Labeling

Many hydrocarbons are called by multiple names, and numerous can be confused with differing tags. An example is But-1-ene (following IUPAC protocol) with common names of 1-Butene, Ethylethylene, 1-Butylene, and α-Butylene. This monograph lists all hydrocarbons by their names established by the International Union of Pure and Applied Chemistry (IUPAC).[5]

II. Compromise in Resolution, Speed and Sample Capacity

Measurement of hydrocarbons in ambient air involves utilization of the full power of capillary columns. Many target analytes have very close retention times. If not fully resolved, significant errors in quantitation will occur when single peaks combine multiple hydrocarbon species. To achieve accurate results for each analyte, the columns employed must be pushed nearly to their limits. The column conditions suggested in this monograph result in a total analysis time of 80 minutes to avoid most coelutions of the target compounds. And the film thicknesses of the employed columns allow a wide range of concentrations before distortion occurs from overloading these columns. The aim here is to maximize resolution of the peaks, at the sacrifice of speed and somewhat of sample capacity (or how much each analyte can be loaded onto the column). This optimization involves a long, narrow-bore column (Light-End- 50 meters, 0.32 mm ID, Mid-Range - 60 meters, 0.32mm ID), with a medium thick phase coating (1 micron film thickness), and a slow column temperature ramp and a moderate flow rate. The total analysis time becomes 80 minutes, with the first ten minutes applied to sample loading and concentrating. A shorter run time will noticeably impact both resolution of peaks and sample capacity of the column. Decreasing the analysis time by using rapid column temperature programming, or faster column flow rates, or shorter columns, or narrower columns will result in peaks overlapping, and column overloadings that can dramatically distort peak shapes and shift retention times and limit the dynamic range of concentrations. The column choices listed here (see Section V) are a good compromise in generating nearly complete separations and in handling expected concentrations in ambient air samples. The trade-off is the total analysis time.

III. Water Management

As water-saturated air contains about 2% water by volume at 20 ^{o}C and sea level[6], a sample loading of 300 ml of ambient air with 50% humidity yields ~2 µL of ice in the cryotrap - more than enough to generate an ice plug either within the trap confines, or at the head of the column. An appropriate mechanism for hydrocarbons analyses to strip off water is installation of a Nafion dryer in the sample path.[7] The process involves passing the "wet" sample through a special polymer tube that allows water to permeate through its walls into a counter flow of dry gas, typically from headspace from liquid nitrogen, set to 100 ml/minute. All hydrocarbons, including aromatics, are excluded from the permeation process, but oxygenates, such as alcohols and ketones, are not and are nearly fully extracted from the sample stream. Since the Photochemical Assessment Monitoring Stations (PAMS) Program measurement lists only hydrocarbons, the loss of these oxygenates does not affect the final reporting. Unfortunately the physical properties of water place it right in the middle of the hydrocarbon chromatography, and must be removed prior to trapping.

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[5] See: old.iupac.org/publications/compendium/. On-line Wikipedia provides ready access to all labels in IUPAC format, as well as their common names. See for example: en.wikipedia.org/wiki/1-Butene.

[6] See: en.wikipedia.org/wiki/Water_vapor.

[7] Source for Nafion dryers is Perma Pure LLC website: 64.13.252.116/wp/wp-content/uploads/MD-Series-gas-dryer.pdf?ind=science&prod=449.

IV. Measurement Effects from Carbon Dioxide in the Sample Matrix

Presently, ambient air possesses 385 ppmV Carbon Dioxide[8] - and climbing. Since this analysis system employs a cryogenic trap at -180 ^{o}C to ensnare the full range of hydrocarbons, especially Ethane, any Carbon Dioxide is also trapped here. Fortunately, this level of Carbon Dioxide yields only 0.1 µl solid dry ice when cryogenically trapped and is not sufficient to generate a blockage either in the trap or in the column, especially if the column remains above -78 ^{o}C, the sublimation point of Carbon Dioxide.

A serious problem is generated for samples from emission sources, such as vehicle emissions or smoke stacks, where Carbon Dioxide levels can reach into the high percentage levels. For example, if the sample possesses 20% Carbon Dioxide, 49 µl of dry ice will form and nearly fill the cryotrap. No device like a Nafion dryer is available to preferentially extract Carbon Dioxide from the sample and leave the hydrocarbons intact. Instead, an absorbent trap must be incorporated to hang on to the hydrocarbons at near ambient temperature and allow Carbon Dioxide to pass on through with the other bulk gases.

Then the issue becomes the effect on the calibration of the mass flow controller for sample loading. This controller is calibrated for a specific bulk gas, typically nitrogen or air. A significant change in the gas composition will alter the accuracy of the device due to an alteration in the specific heat of the sample matrix. The consequence depends on the location of the controller relative to the concentrator trap. If the controller is situated prior to the trap, the impact will reduce the effective flow by 15% for a sample with 50% Carbon Dioxide, due to the change in specific heat from nitrogen only.

If the mass flow controller is located downstream of the cryotrap, and with the trap cold enough to freeze out Carbon Dioxide, the controller will not see the entire sample matrix and will compensate this loss by upping the effective flow through the trap. For example, if the sample has 50% Carbon Dioxide with balance air, half of the sample volume would not be seen by the controller because it is frozen out prior to reaching it. The result would effectively double sample flow through the trap. With an intended flow of 50 ml/min, the mass flow controller will measure out this flow with half of the bulk gas lost to the trap, and the actual flow into the trap will become 100 ml/min and resulting in an error of 100%. Because standards are normally made up in bulk nitrogen, reported results for unknowns will be wrong by a factor of two. Since Carbon Dioxide does not always remain constant in every source sample, a mathematical correction is not realistic.

As air possesses mostly nitrogen and the specific heat of nitrogen (1.04 *kJ/kg ^{o}K*) and air (1.01 *kJ/kg ^{o}K)* are very close, this effect on mass flow controllers is minimal when comparing standards in nitrogen with samples in ambient air.

The proper means to generate accurate volumes when the bulk matrices change is to measure the sample aliquot with a fixed volume sample loop to ensure reproducible and accurate volumes. However, the design of the apparatus to measure a volume of 300 ml must consider eddy currents that impact carryover, and flushing to ensure that the entire loop contents are passed off to the trap. And since the sample loop is fixed in volume, the handy feature of the mass flow controller with easily generated, predictable variation in loaded volume is disabled (see discussion in Section XIII).

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[8] See: cdiac.ornl.gov/pns/current_ghg.html

V. Suggested Operating Conditions for Measurement of Hydrocarbons in Ambient Air

Columns: Stripper - Varian CP5 CB, 15 meters, 0.32 mm ID, 1 micron film, P/N CP8540.
Light-End - Varian Alumina-SO_4 PLOT, 50 meters, 0.32 mm ID, P/N CP7565.
Mid-Range - Varian CP5 CB, 60 meters, 0.32 mm ID, 1 micron film, P/N CP8870.

Sample Loading: 50 ml/minute for 6 minutes - total 300 ml

Trapping: -179 ^oC, hold for 9.10 minutes, ramp to 203 ^oC at 300 ^oC/minute.

Column Temperature Program:
50 ^oC, hold for 0.01 minutes, ramp to -20 ^oC at 100 ^oC/minute, hold for 12.29 minute, ramp to 90 ^oC at 2.5 ^oC/minute to 90 ^oC, ramp to 200 ^oC at 5.0 ^oC/minute and hold for 1.00 minute; total - 80 minutes.

Column carrier: Helium, 3.0 ml/minute, true flow controlled, not calculated from pressure for both columns.

On-column injection: at 10 minutes.

Detector: Light-End - Front - Flame tip - 0.01", make-up (N_2) - 22 ml/minute, H_2 - 25 ml/minute, air - 300 ml/minute; range - 12.
Mid-Range - Middle - Flame tip - 0.02", make-up (N_2) - 27 ml/minute, H_2 - 30 ml/minute, air - 300 ml/minute; range - 12.

Detector Bunch Rate: 16 points (2.5 Hz) - Varian 3800; 32 points (3.1 Hz) - Bruker 450

Detector Full Scale: 1000 volts.

VI. True Flow Control versus Pressure Control with Calculated Flow for Carrier Gases

To generate a full chromatogram of C_2-C_{13} hydrocarbons, the column set must be temperature programmed from a low starting point to fully resolve the early peaks and provide some refocusing of analytes at the head of the column, and then are ramped to a higher temperature to progressively flush through the hydrocarbons, roughly by their boiling points.

During this programming process, column flow can be severely impacted if the column headpressure were to remain constant. Helium viscosity is proportional to temperature. During a temperature program, this change in viscosity causes a decrease in flow if the headpressure were held constant, or an increase in backpressure if the column flow were held steady. Flow-controlled pneumatics is the mode of choice to keep flow at its optimum throughout the run. Programmable electronic pressure control has been utilized to provide carrier flow, and computes the anticipated flow based on column dimensions, carrier viscosity and column temperature. A critical factor is flow's relationship to pressure with various column internal diameters. Hagen-Poiseuille equation establishes that flow calculated from pressure is dependent on the diameter of the column to the fourth power.[9] Typically, column internal diameters have a dimension tolerance of ±4.8%. Unless the precise value is entered, an error of up to ±21% in flow rate can be realized just from the electronics computing flow with a slightly inaccurate diameter. This error can provide a major departure from the expected flow without warning or indication and can cause a shift in expected retention times of up to 56% when compared with another column using isothermal conditions. Column temperature programming reduces this error somewhat. Flow controlled devices, including true electronic flow controllers always maintain their flows by automatic adjustment of the column backpressure and do not rely on any computations and their consequential errors. Backpressures generated with flow controllers become a useful diagnostic for monitoring operations, as a leak will give lower than expected pressures, and a plug in the carrier pathway will yield excessive pressures. Pressure-regulated systems will always provide the specified pressure, with no indication of a leak or a plug.

9 See: en.wikipedia.org/wiki/Hagen–Poiseuille_equation

VII. Determination of Time for Column Switch

A single column cannot fully resolve all of the hydrocarbons found in ambient air. A dimethylpolysiloxane column (for example Varian CP5 or VF1) separates compounds primarily by their boiling points, but does a terrible job with the light hydrocarbons, notably Ethane/Ethene/Ethyne, Propane/Propene and the Butenes, as illustrated in Figure 3. The preferred column for these is the Alumina PLOT deactivated with Na_2SO_4, as shown in chromatograms in Figures 1 and 9. Unfortunately this column's performance, with a limit of only 200 ^oC, cannot rapidly elute the heavier hydrocarbons. To protect this column, a short 15 meter CP5 or VF1 is installed upstream of a column switching valve to hold up the heavy hydrocarbons and allow the lighter components to pass onto the alumina PLOT column and to the first flame ionization detector. At an appropriate time, the valve is activated to direct the heavier hydrocarbons to the full 60 meter CP5 or VF1 column and then to the second flame ionization detector (see Figure 4). Since the valve switch must occur before the analytes elute from the columns, the timing must be determined by performing a series of runs with differing settings. Fortunately, the elution of hydrocarbons from a short CP5 or VF1 column yields gaps in the chromatography to allow easy column switching without splitting peaks between the two columns.

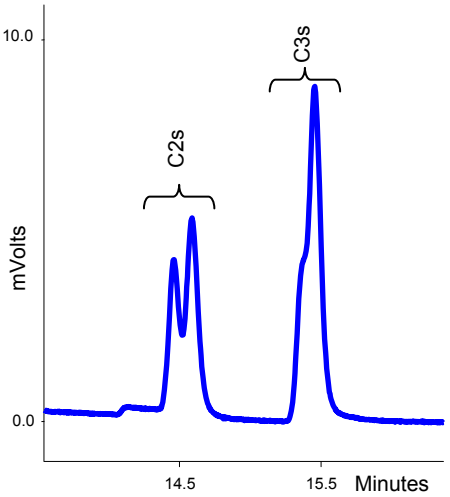

Figure 3. Poor separations of Ethane/Ethene/Ethyne (C_2s) and Propane/Propene (C_3s) with CP5 capillary column, even with a starting column temperature at -20 ^oC.

Any changes to column dimensions, flow rates, and temperature programming will shift elution of hydrocarbons dramatically and will necessitate a reevaluation of the column switching timing, as illustrated in Figure 5.

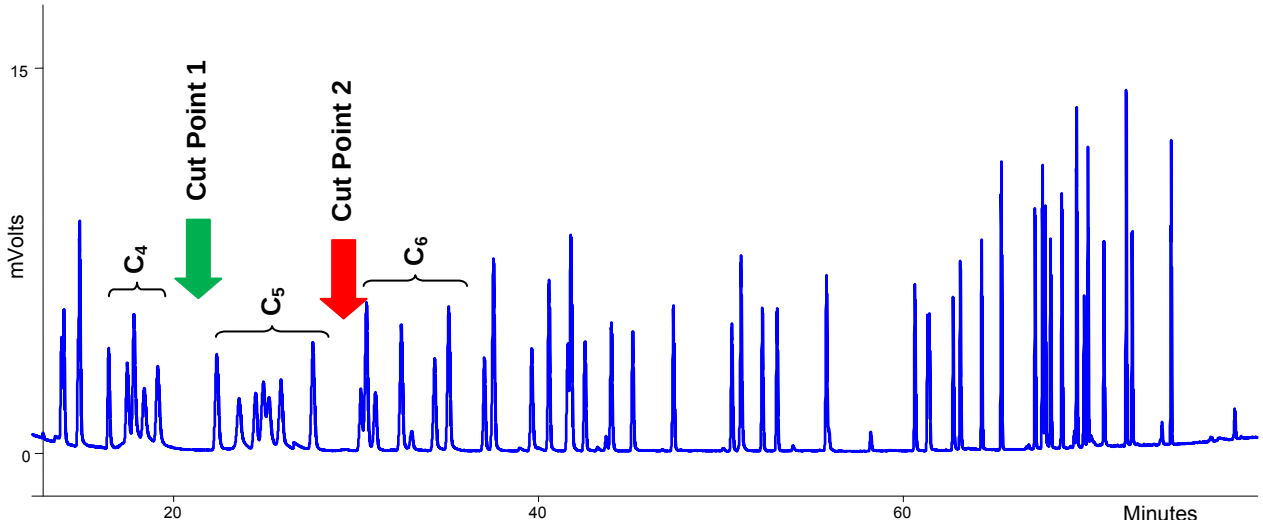

Figure 4. Complete Mid-Range chromatographic run of 56 C_2-C_{12} Hydrocarbons illustrates elution gaps appropriate for column switching between the Alumina-SO_4 PLOT column and the dimethylpolysyloxane column. Cut Point 2 is often selected to ensure that Isoprene is fully separated from Pentane on the PLOT column.

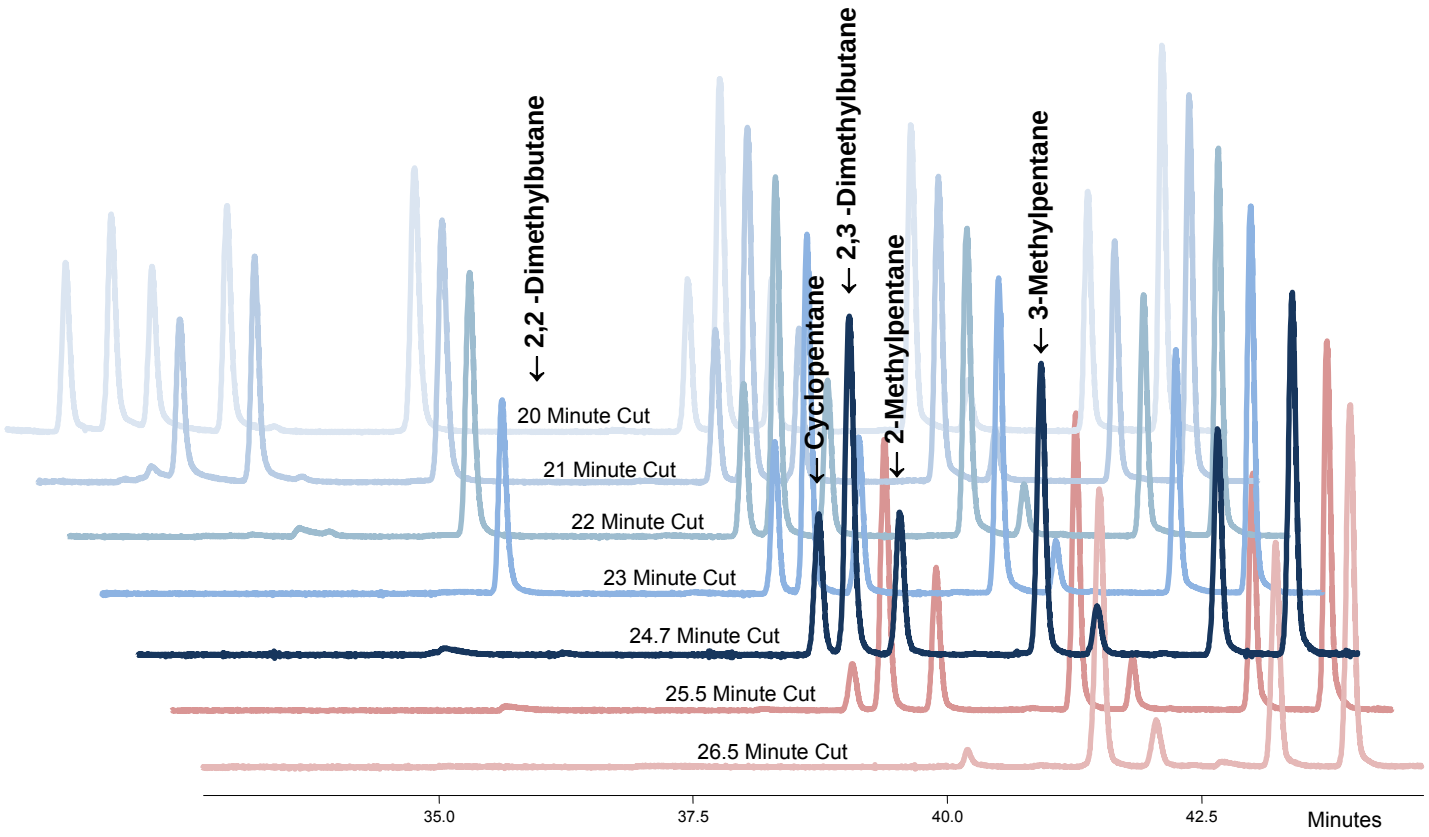

Figure 5. Subtle changes in column switching timing impact the cut of analytes between the Alumina PLOT (Light End) and dimethylpolysyloxane (Mid-Range) columns. Illustrated here are chromatograms from the Mid-Range column, with small adjustments in cut times. The "24.7" setting properly assigns Pentanes, 2,2-Dimethylbutane and Methylbuta-1,3-diene (Isoprene) to the Alumina PLOT, and Hexanes+ to the Mid-Range column. If the cut is too late, some of the "Hexanes" are improperly loaded onto the Alumina PLOT column.

VIII. Peak Identifications

The preferred detector for hydrocarbons is flame ionization since it only responds to hydrocarbons, it is very sensitive to these compounds and it yields a very even response, in units of ppbCarbon,[10] across the board for Ethane through Tridecane, including olefins and aromatics. However, this detector can only identify them by retention time. Known standards must be run under identical chromatographic conditions to enable specific peaks to be picked out for accurate construction of the peak table. Retention time reproducibility is critical in ensuring that peak assignments based on a standard mixture apply to subsequent measurements of unknown samples. With over 300 hydrocarbon species possible in ambient air, with many eluting in close proximity to each other, accurate tagging can only occur with elution repeatability of less than 0.05 minutes.

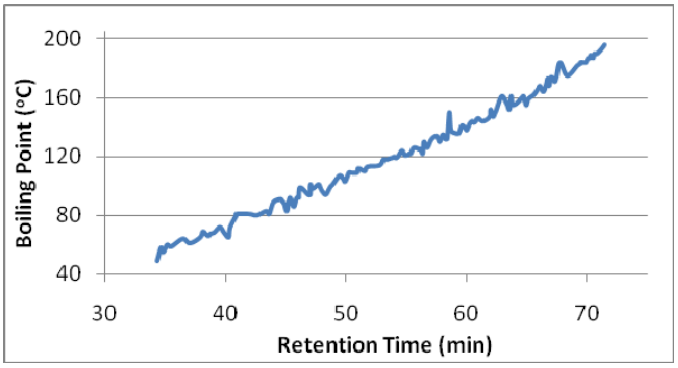

Figure 6. Plot of component boiling points versus retention time shows a rough correlation of the two, but with enough exceptions to limit its use to gross misassignments of peaks.

The column used in the chromatography of Mid-Range components (C_6-C_{13}) separates them roughly by their boiling points. Figure 6 illustrates the correspondence between retention time and boiling points. Unfortunately, this column yields many exceptions to a direct correlation, and explicit use of this association cannot provide positive identity of any peak. A comparison can only give a clue to a gross misassignment, such as labeling a peak as 2,3,4-Trimethylpentane (BP = 113 ^{o}C) in the n-Octane (BP = 126 ^{o}C) region of the chromatogram.

Mass spectrometry often provides the definitive identification of chromatographic peaks, but suffers somewhat when picking out hydrocarbons. Many hydrocarbons have very similar chemical structures, and, when ionized in the mass spectrometric process, break down into similar fragments and generate remarkably comparable spectra, even though they are different species.

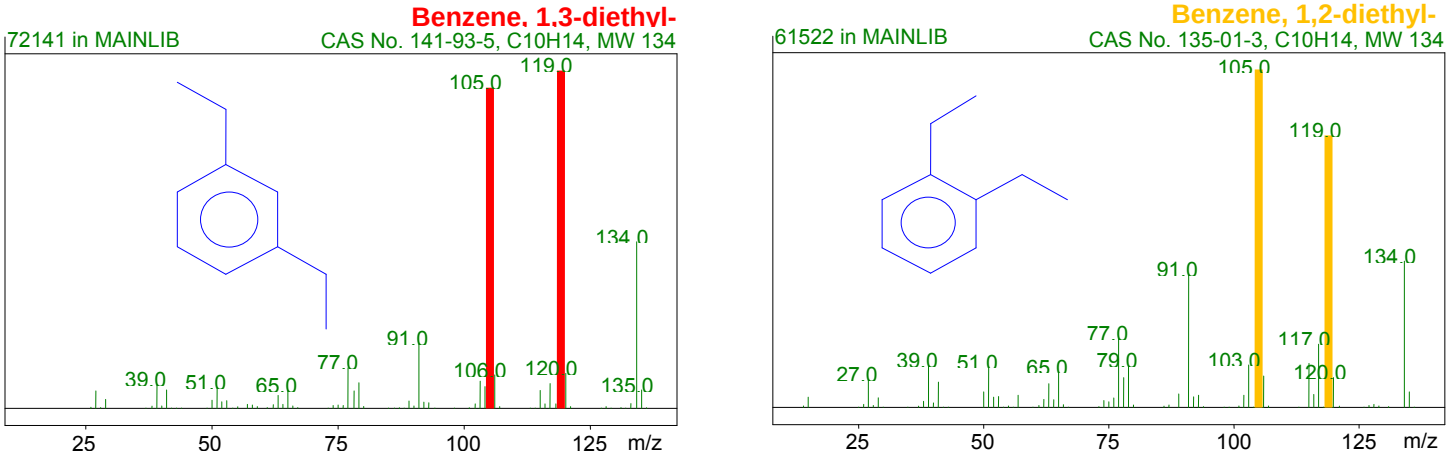

Figure 7. Hydrocarbons with similar chemical structure often generate mass spectra that are difficult to attribute to a single species. Here spectra of Diethylbenzenes are only distinguishable by very slight differences in the amplitudes of the 105 and 119 ions.

[10] Concentrations for hydrocarbons are usually reported as "part per billion Carbon" (ppbC), to allow direct totaling of all hydrocarbons in relation to methane. The conversion from ppbVolume is ppbC = ppbV * number of carbons in molecule; for example 1 ppbV Hexane becomes 6 ppbC.

Another issue is triggered by subtle disparities in ionization processes with dissimilar spectrometer types, particularly with different styles from those employed in the archived spectrum. Methyl groups are readily split off from the hydrocarbon backbone, making spectra of many straight-chained hydrocarbons remarkably similar; subtle changes in ionization conditions can dramatically alter these spectra. Figure 8 presents an example of a spectrum that differs significantly from the NIST library match. In the search of the library for a spectral match, the known peak - Hexane - at 31.601 minutes shows up as the 15th hit, not definitive for the identity of this hydrocarbon. Five other possible saturated hydrocarbons show up ahead of Hexane as more "likely" potential matches.

In addition, the ionization process in mass spectrometers produces a number of combined ions that are not consistent for all hydrocarbons. A single hydrocarbon standard cannot be used to calibrate the broad range of hydrocarbons found in ambient air, as occurs with the flame ionization detector (see Section XII). Individual standards must be invoked for each analyte, and those not in the standard mix cannot be quantified accurately.

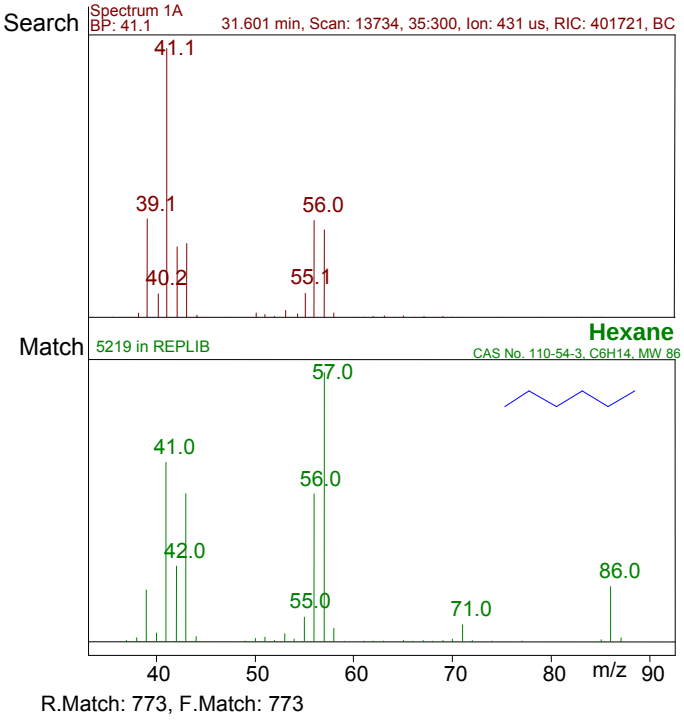

Figure 8. Library searches of hydrocarbon spectra often yield complete mismatches or relate results to many other possible compounds. Here the known peak at 31.601 does not come close to matching its equivalent in the NIST library.

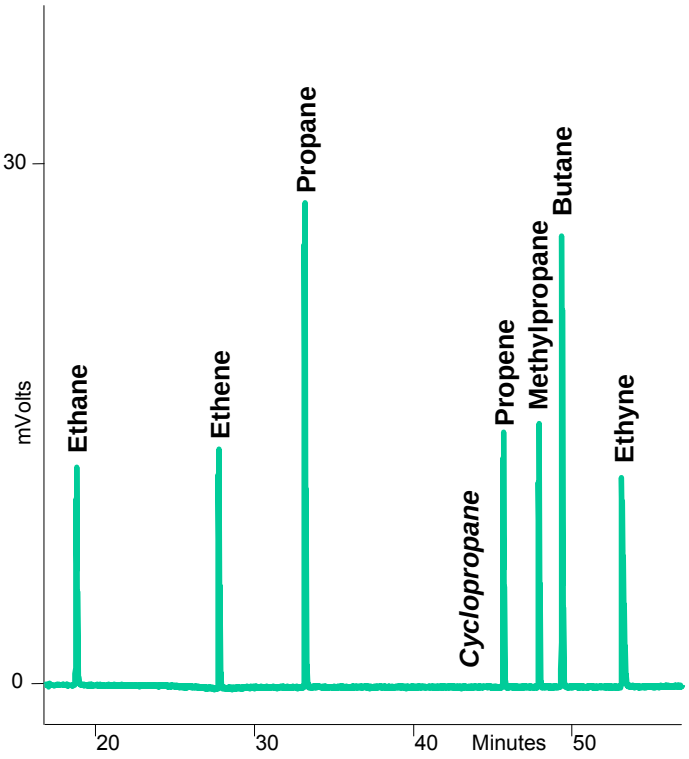

Figure 9. Alumina-SO_4 PLOT columns generate chromatograms with widely spaced peaks that are readily identifiable.

The elution order of the very light hydrocarbons with the Alumina SO_4 PLOT column is very predictable, even with some movement in retention times, since they are so widely spaced apart. This chromatography is dramatic improved over the single-column approach, shown in Figures 3 and 4. No other analyte is found in this region, dramatically simplifying peak labeling for these eluents.

Multi-component hydrocarbon standards with varying concentrations are available from several commercial sources.[11] Concentration levels in these standards are usually predetermined with uneven levels to assist in confirming peak assignments by comparing their measured sizes to expected values. Figure 10 shows a portion of a typical run of one of these standards illustrating this process, and Figures 11 and 12 demonstrate the validation of peak assignments by ratioing nominal label concentrations with measured values for each analyte. If the ratio remains near one, then the peak assignment is likely to be valid, if the standard was properly prepared, labeled and measured. Some excursions are possible due to the reactivity of some compounds with others, and with active metal surfaces in the gas cylinder and instrument. For example, Ethyne is measured in this example as over 30% of its label number, undoubtedly due to the inertness of the instrument used and underlabeling by the standard manufacturer. A similar situation probably applies to 2,4-Dimethylpentane. Another is the near complete loss of 1-Hexene - assessed at only 12% of its label. Olefins and aromatics are typically very reactive and their long term stability in a cylinder or canister is never assured.

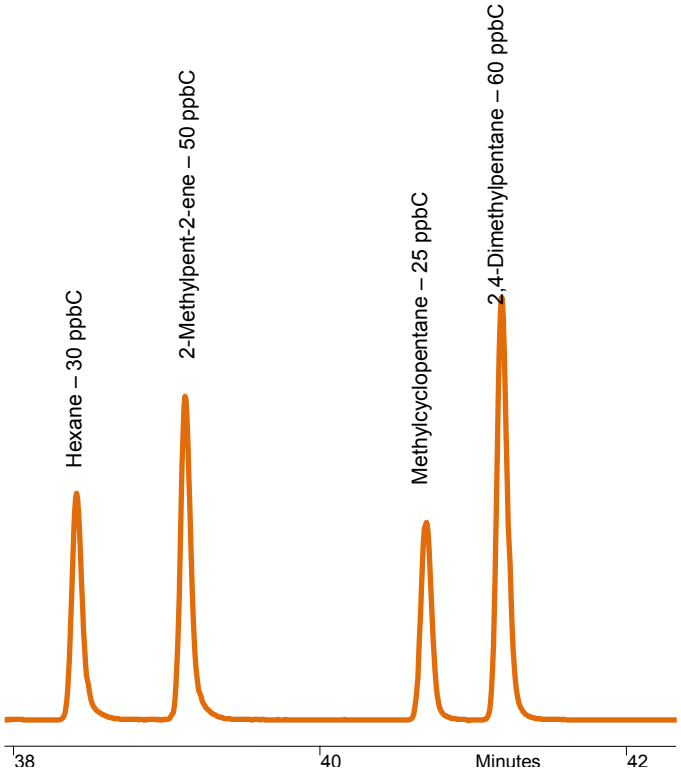

Figure 10. Identities of peaks in a standard are supported by comparing their relative sizes to nominal concentrations of the standard mixture.

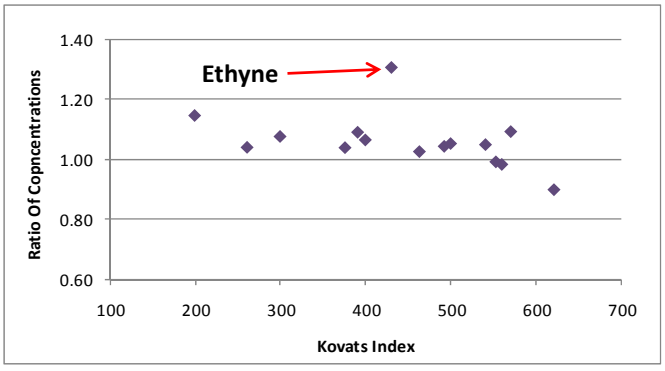

Figure 11. Ratios of measured concentration with nominal values for the Light-End hydrocarbons sustain their identity. Ethyne is a normal exception due to its frequent interaction with the measuring system.

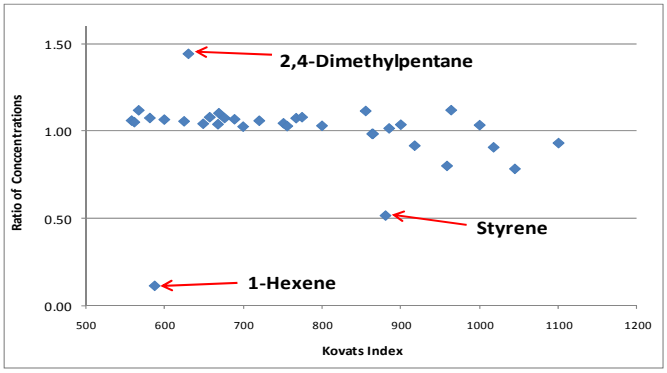

Figure 12. A similar display of ratios for the Mid-Range analytes helps affirm peak labeling. Ratios near one indicate good agreement with names from the standard certificate.

[11] Suggested vendors: Supelco P/N 41977U - www.sigmaaldrich.com/catalog/ProductDetail.do?lang=en&N4=41977U|SUPELCO&N5=SEARCH_CONCAT_PNO|BRAND_KEY&F=SPEC; Restek (www.restek.com/restek/prod/3946.asp); and Spectra Gases - www.spectragases.com/content/PAMS.htm.

An additional mechanism for peak identification involves use of Kovats indices, which relate relative elution of hydrocarbons to adjacent n-Alkanes.[12] This indicator allows peaks to be branded without having a standard to locate them. Remarkably these numbers remain independent of columns of the same type, with differing column dimensions, dissimilar column temperature programming, and various column flow rates. As an example, for dimethylpolysiloxane columns (Varian CP5 or VF1, or J&W DB-1), Benzene has a Kovats Index of 649 ± 2, which places it 49% of the distance between Hexane and Heptane. After examination of 14 chromatograms from eleven different column/ chromatographic systems, this index for Benzene has a standard deviation of ±2. An updated list, with over 300 hydrocarbons indices, is available from Lotus Consulting[13] for both columns employed in this analysis (Alumina-SO_4 PLOT for C_2-C_5, and dimethylpolysiloxane for C_6-C_{13}).

Retention times for Ethyne and Propene are notorious for moving around dramatically with changes in the condition of the Alumina PLOT column, especially from moisture degrading the column, and are found to have the widest deviation (±8 for Ethyne and ±6 for Propene) of all hydrocarbons. Most hydrocarbons have consistencies less than ±5, with many under ±1.

With all of the possible hydrocarbons measurable in ambient air, occasionally peak labeling can be mistakenly assigned by the gas standard supplier. Although the ratios of measured concentration to the label value are close to an ideal value of one for most of the peaks, their Kovats Indices may not always coincide with the tabulated values. Figure 13 shows significant deviations in the C_{10}-C_{11} regions where the Indices for most other hydrocarbons vary by less than ±3 units. A possible explanation is that another component was used to make the standard, and is mislabeled on the certificate. An example of this in a commercial gas standard is the labeling of 1,3-Diethylbenzene and 1,4-Diethylbenzene. Their Kovaks Index in the chromatogram is measured as 1045, or +6 units from the expected value of 1039 ±3, and 1052, or +7 units from the expected value of 1045 ±3. If, instead, these peaks are relabeled from the index listing, the deviations are greatly reduced, as shown in Figure 14. These corrections are detailed in Table I.

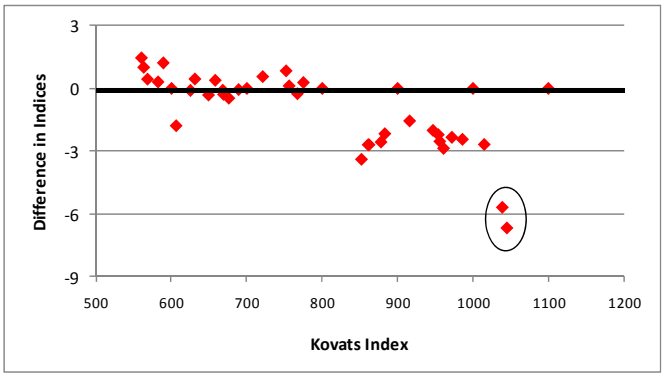

Figure 13. Comparing measured Kovaks Indices with tabulated values can provide additional support for valid peak assignments. A "zero" difference is a perfect match. Circled are two analytes with indices away from their expect values and are potentially mislabeled.

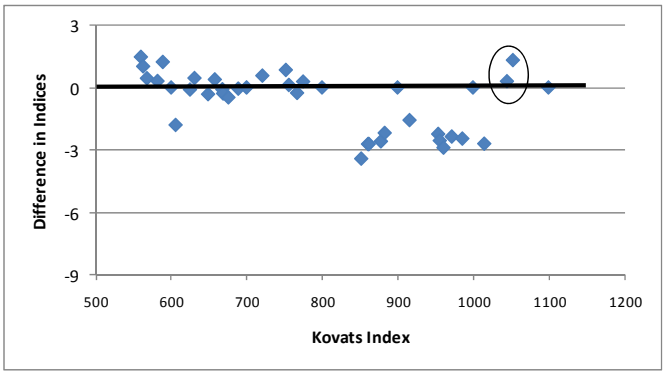

Figure 14. Reassignment of these two outliers to related compounds based on their measured indices returns the differences between measured and expected indices to near zero and promotes a judgment that these peaks were misidentified by the gas supplier.

[12] R. Bramston-Cook, "Using Kovats Indices to Identify Hydrocarbon Peaks in a Chromatogram", 2010, available on request from ebramstoncook@msn.com.

[13] R. Bramston-Cook, "Kovats Indices for C2-C13 Hydrocarbons and Selected Oxygenates/Halocarbons with 100% Dimethylpolysiloxane Columns", and "Kovats Indices for C2-C9 Hydrocarbons with Alumina PLOT Capillary Columns", 2010, both available on request from ebramstoncook@msn.com.

Labeled Analyte	Predicted Index	Difference	Measured Index	Revised Label	Predicted Index	Difference
1,2,3-Trimethylbenzene	1015 ±4	-3	1018			-3
1,3-Diethylbenzene	1039 ±3	**-6**	1045	**1,4-Diethylbenzene**	1045 ±3	**0**
1,4-Diethylbenzene	1045 ±3	**-7**	1052	**1,2-Diethylbenzene**	1053 ±3	**+1**
1,2-Diethylbenzene	1053 ±3	--	Not present on label			

Table I. Deviations from the expected Kovats Indices indicate that the certificate labeling for the Diethylbenzenes is not correct. If the "1,3" isomer were instead relabeled as "1,4", and the "1,4" becomes "1,2", then the differences in measured indices would more closely match tabulated values.

Several analytes have very characteristic peak structures that make them easily identifiable. Ethyne yields a distinctive peak shape that appears as if it were generated by a column overload, even at low concentrations. With the Alumina-SO_4 PLOT column, Ethyne elutes well separated from all other compounds. A typical peak is shown in Figure 15, with adjacent peaks.

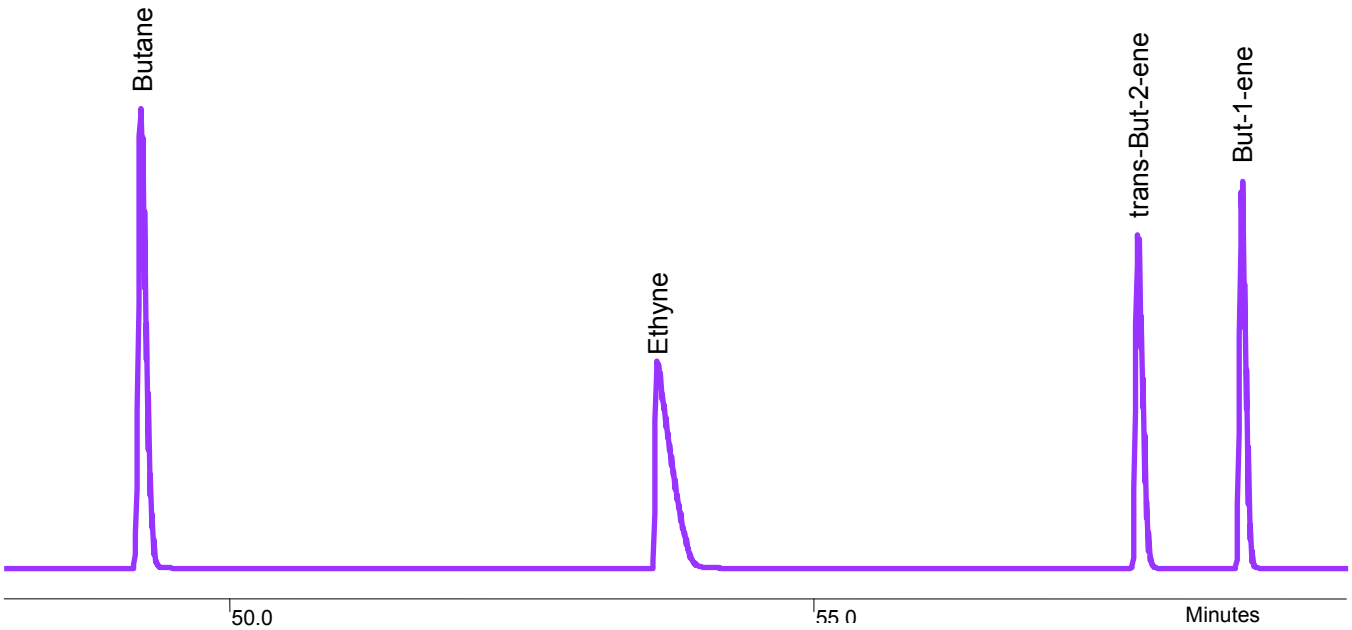

Figure 15. Ethyne is readily picked out from nearby peaks by its distinguishing peak shape as shown above.

Two isomers of Xylene – "1,3" (meta) and "1,4" (para) - nearly coleute, but often display two peaks with a valley in between. Since a major concentration of one can readily overwhelm a small companion, these two peaks are often reported as the combined concentrations and labeled as m&p-Xylenes. Figure 16 illustrates a normal separation of the two with nearby peaks included. These two are most likely to be the only fused peaks in this region of the chromatogram. Once this pair is located, adjacent peaks are readily assigned correctly.

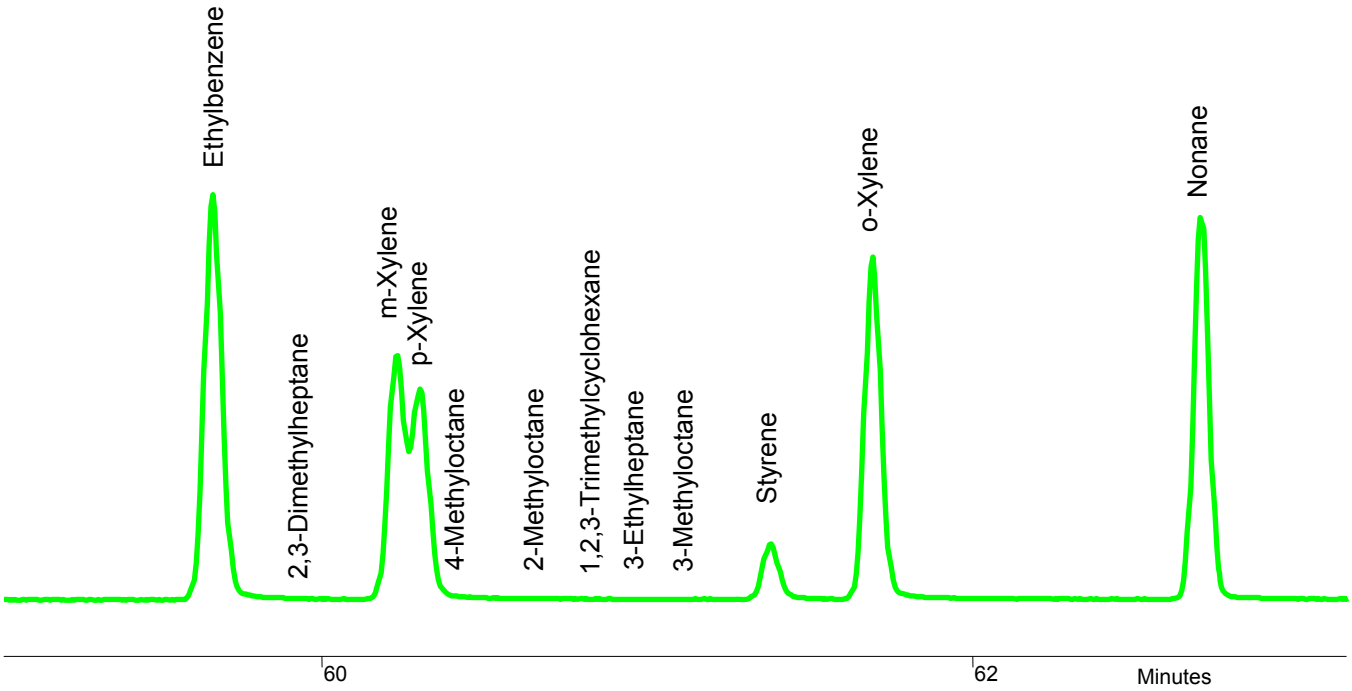

Figure 16. Both m-Xylene and p-Xylene normally exist together in ambient air and are distinguishable from other peaks by their close proximity to each other, even in a chromatographic region with many other analytes. Some column conditions result in their complete coelution, and the duet is then labeled as m&pXylenes.

IX. Baseline Noise

Excessive detector noise can severely hamper performance of the system, especially at low signal levels often observed in ambient air samples. The ability of the data system to distinguish real peaks from random noise is complicated when noise hinders the peak integration process and degrades detection limits. Typical noise expected with high performance flame detectors in the Varian 3800 is shown in Figure 17.

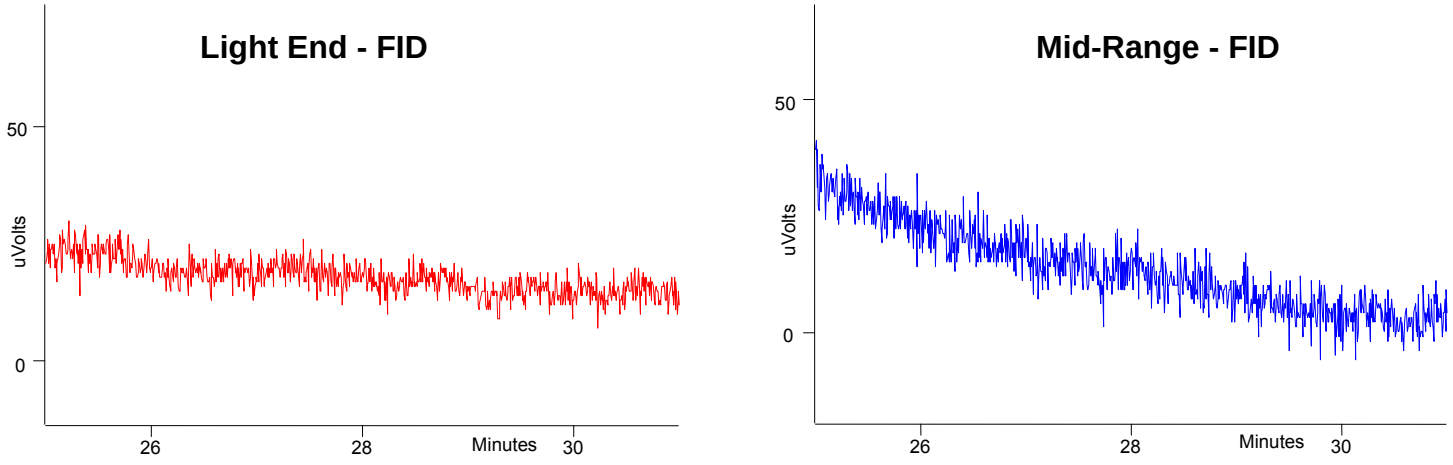

Figure 17. Typical noise levels for both detectors on a Varian 3800 are illustrated above. Data sampling rate is 2.5 Hz.

Noise displayed on a chromatogram is related to the detector bunch rate set by the data collection method. Character of the noise can be altered by careful selection of this parameter related to the expected peak width of the narrowest peak in the chromatogram.[14] Typical noise characteristics between the Varian 3800 and Bruker 450 are different, as the Varian 3800 uses a 4-point Finite Impulse Response (FIR) filter to quiet noise while still maintaining peak shapes, and for the 450, a 31-point Finite Impulse Response filter is employed because the chromatograph has a higher signal conversion rate and the resulting high frequency noise must be suppressed without peak distortions.[15]

Extreme deviations from the noise characteristics displayed here can indicate possible defects in the instrument system and should be corrected to enable achievement of the optimum results. Possible causes can include improper setting for detector bunch rate, impurities in any of the supply gases, contaminated detector, loose flame tip or cracked ferrule holding the tip, pulsations in detector supply gases, high signal backgrounds from excessive column bleed, or particles released by an aging Alumina PLOT column.

Noise levels displayed here are achieved with a typical instrument and offered only as guidelines. Some variation will occur with other systems. Noise levels should be tracked regularly to assist in evaluating status of the detectors. The Varian Star Workstation provides the result of noise monitored just prior to the start of each run, but the reported value also includes drift found during the this interval.

X. Detector Background

To achieve full performance of the analytical system and to minimize reporting hydrocarbon concentrations unrelated to the sample, the complete instrument must be free of any residual hydrocarbons. Carrier gas purity is validated with instrument blanks (see Section XI). A measure of the detector operation is through its generated background with the flame lit. A high background signal can be generated by contamination in the detector itself and from impurities in its supply gases of hydrogen, make-up gas and/or air. The Varian 3800 and 450 both have the controls to "Clear Autozero" and then display the flame background "signal" for a few moments. Flames generate an inherent signal from the combustion process involved, but a clean detector with high purity gases will give a minimal signal, typically less than 10 millivolts, and often in the range of 2-5 millivolts. A signal below 1 millivolt is sensed by the instrument as a flame-out and a fault message is triggered, halting operations until corrected. An excessively high background reading (above 10 millivolts) indicates a possible problem with a dirty flame-tip, or leaks around the tip, impure gas supplies, or fouled detector probes.

Defect	Corrective Action
Dirty Flame-tip	Replace tip
Leak at Flame Nut	Check for tightness and replace ferrule if cracked
Impure Gas Supplies	Use better grade, or install filter kit P/N CP736530
Fouled Detector Probes	Replace Probes
Contaminated Detector	Elevate detector temperature to 350 ^{o}C Temporarily, but first remove Alumina column

[14] R. Bramston-Cook, "Peak Detection with Varian Star Workstation for Varian 3800 and 450 Gas Chromatographs", Lotus Consulting, 2010.

[15] Ibid.

XI. Instrument Blank

Hydrocarbons are ubiquitous and can readily show up uninvited in systems when attempting to measure their concentrations at levels into the ppt Carbon range. Contamination can appear from impure supply gases and associated regulators and tubing, from cold spots in the sample pathways in the system, from inadequate conditioning of columns prior to every run, and from degradation of the column phase from repeated temperature cycling. The goal is to achieve a blank run with no peaks above the reported detection limit.

The purest nitrogen gas is normally generated from the headspace of liquid nitrogen, as any potential hydrocarbon contaminate is likely to be frozen out from the -196 ^{o}C environment. This source is usually perfect for purge flows in the instrument system and for make-up flows to the flame ionization detectors. In-line filtering with scrubbers is not generally required, unless clean blanks are not achieved. In some instrument designs, the nitrogen purge flow passes through a cryogenic cleansing process that is super cold during purging operations of the concentrator to ensnare any possible hydrocarbon and then any residue is flushed out to vent when the concentrator heats up to inject the target analytes into the column system.

Helium is available in a variety of purity grades, and labeling can vary among suppliers. The recommendation here is to use the best grade available, often called “Research Grade, or 99.9999%”, which is usually tested with total impurities (non-Argon) below 1 ppmV, and total hydrocarbons (THC) under 0.1 ppmV. In-line filtering with hydrocarbon traps for both helium carrier and nitrogen purge/detector gases is suggested to bring hydrocarbon impurities even lower. Typical nitrogen blank baselines for Light-End and Mid-Range detectors are shown in Figure 18.

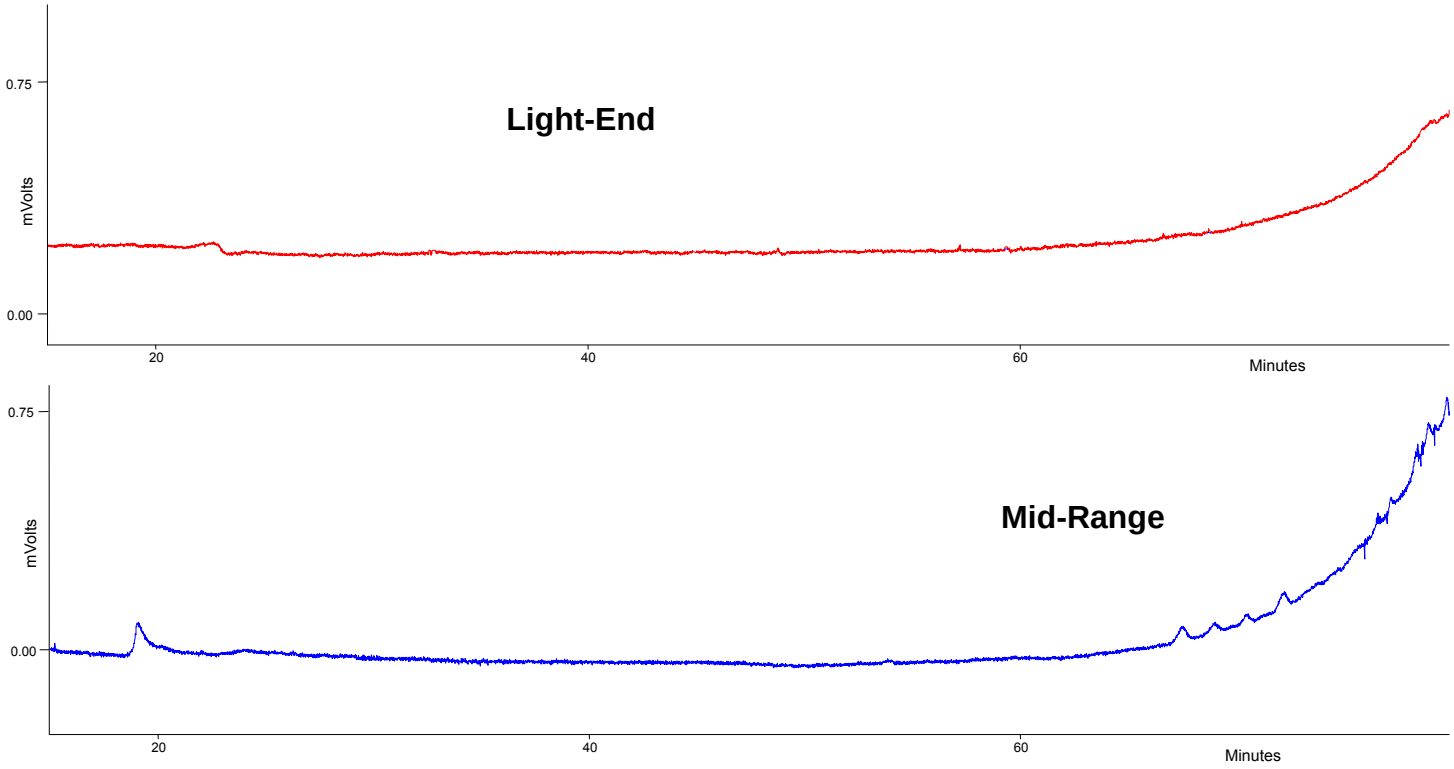

Figure 18. Typical nitrogen blank chromatograms for Light-End and Mid-Range detectors.

Discrepancies from this ideal can be traced by a testing series to track down the contamination source. For example, helium carrier can be validated as clean by performing a run without any valve operations; any peaks detected here can be attributed to either helium impurities or column bleed. Then by keeping the concentrator cold with carrier gas flowing through it prior to reaching the column and the result is a clean baseline, then the culprit can be assigned directly to impurities in carrier gas or related pneumatics and carrier gas filters upstream of this position in the plumbing. A more tedious process is to construct a special trap of coiled empty 1/16" tubing with appropriate fittings on the ends to be able to insert this trap at various locations in the plumbing pathways. Once installed, the coil can be dipped into a dewar with liquid nitrogen, and a run involving this path is performed. If the result is a clean baseline, the contamination source is upstream of this point. Subsequently, the trap can be removed and relocated to another spot for further diagnosing.

XII. Even Responses for Hydrocarbons with Flame Ionization Detection

Accurate standards are not available for every possible hydrocarbon found in ambient air. Reliance must be made on the uniform response of flame ionization detectors with hydrocarbons. Then, the response factor for a limited hydrocarbon set can be applied to all others measured with the same detector. Figure 18 illustrates the ability of high performance detectors to measure a wide range of hydrocarbons and still achieve even responses with the same detector. Then the response for Propane can be applied to all analytes measured with the Light-End detector, and Benzene for the Mid-Range ones, with confidence that correct concentrations for the full range of hydrocarbons are reported.

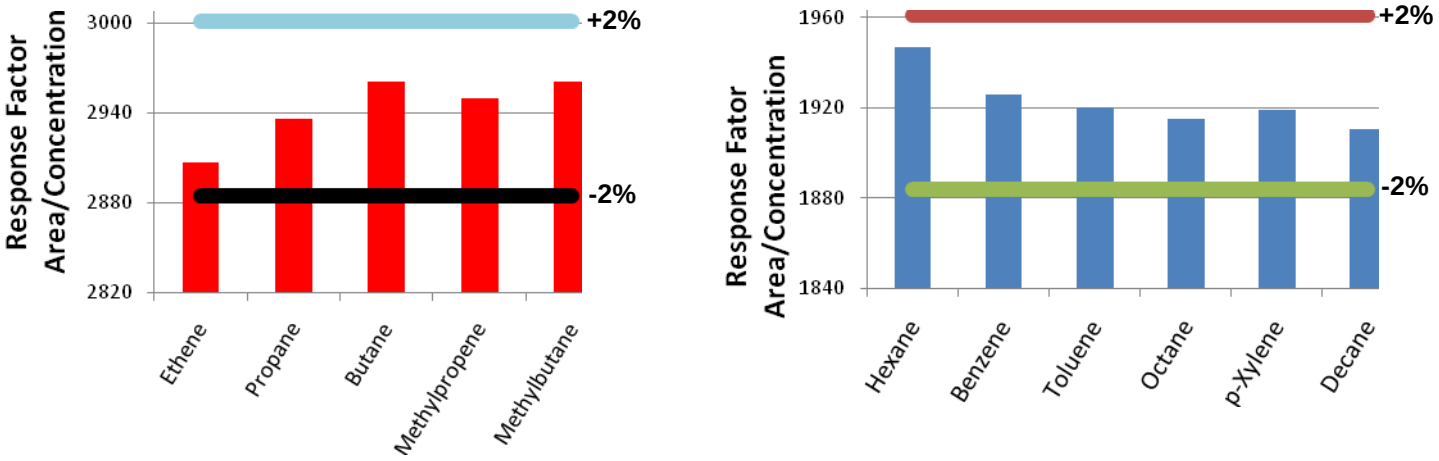

Figure 19. High performance flame ionization detectors yield uniform response factors over a range of analytes, as demonstrated with a 100 ppbCarbon NIST custom hydrocarbon blend certified to ±2%. The discontinuity between Light-End and Mid-Range response factors is due to the switch in detectors, with differing flame tips sizes (see Section XXIV). The solid lines represent ±2% deviations from the averages.

Divergence from this uniformity can be attributed to inaccurate standards, improper hydrogen/air/make-up flows to the flame detector, active sites in the sample pathways (including cold spots when the heavier ones are too low), loose flame tips, subtle leaks in the sample plumbing, particularly at the column inlet connection, and improper integration and baseline assignments of peaks.

XIII. Multi-point Calibration and Linear Range

A wonderful feature of the usual instrument design for measuring hydrocarbons in ambient air is the ability to generate multiple standard levels for calibration by simply keeping the sample flow into the concentrator constant with a mass flow controller and altering loading times. Thus, a single 100 ppbCarbon standard can be set up with sampling times from 0.1 to 6 minutes with a flow of 50 ml/min to yield calibration points from 1.7 to 100 ppbCarbon based on a sample loading of 300 ml (see Table II). A typical calibration curve for Propane is shown in Figure 20.

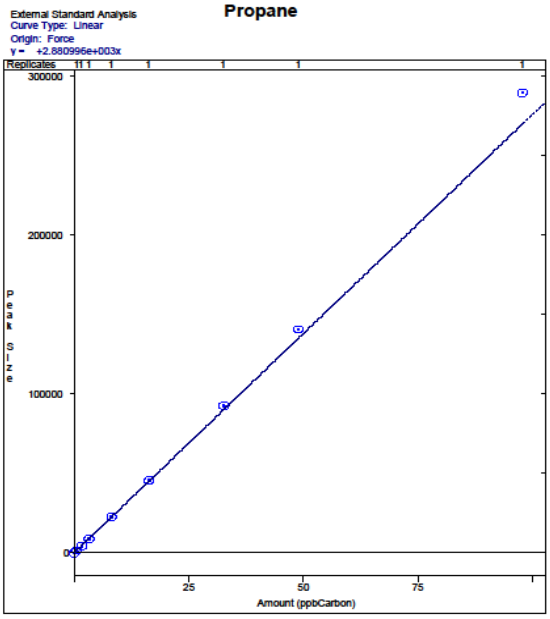

Figure 20. Cartesian plot of Area vs Concentration, showing compression of points at low concentrations.

Cartesian plots, as shown in Figure 20, display results nicely for limited concentration ranges - typically within a factor of ten, but become congested at the low end when used for concentrations over multiple orders of magnitude, common with hydrocarbon measurements. To illustrate the full dynamic range required for measurement of hydrocarbons in ambient air, a more meaningful display is to plot Response Factor versus log[Concentration], as depicted in Figure 21. Thus, maintenance of linearity can be visualized clearly at both low and high ends of the range.

U.S. National Institutes of Standards and Technology (NIST)[16] Standard Reference Material (SRM) 1800b Non-methane Hydrocarbon Compounds in Nitrogen (nominally 5 nanomoles/mole or 5 ppbV) is the definitive standard currently offered for low level hydrocarbons, with an accuracy of ±0.2 ppbV (±4%), although it is very pricey and presently (June 2010) out of stock.[17] This standard is the only one available with this accuracy for proper measurement of detection limits. Other gaseous standards are available from NIST, Supelco[18], Spectra Gases[19], and Restek[20] (in concentrations from 20-60 ppbCarbon, 100 ppbCarbon and 1,000 ppbCarbon for typically 56 components; these are nominally claimed to be accurate to ±5%).

To ensure repeatability with these low level calibration gases, one regulator should be dedicated to each standard cylinder to minimize sources for potential variances and possible cross contamination. Some of these components, notably Ethyne (Acetylene), are not stable, and they are not included in NIST standards for this reason. At the other end of the range, compounds above Decane can be reduced or lost due to cold spots in the sample pathway and from degradation in the cylinder. What is added into a cylinder by gravimetric processes must be validated by a chromatographic measurement to ensure that label concentrations are proper.

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16 See: www-s.nist.gov/srmors/view_detail.cfm?srm=1800B.

17 SRM 1800b is presently being restricted from sale while undergoing stability testing and/or revision.

18 See: www.sigmaaldrich.com/catalog/ProductDetail.do?lang=en&N4=41977U|SUPELCO&N5=SEARCH_CONCAT_PNO|BRAND_KEY&F=SPEC.

19 See: www.spectragases.com/content/upload/AssetMgmt/PDFs/environmental/ENV_VOCPAMSCalibrationStandards_030107.pdf.

20 See: www.restek.com/restek/prod/1288.asp and www.restek.com/restek/prod/3946.asp.

Low volume sample loading with a mass flow controller can be difficult to achieve, with too much sample measured in from extra volume effects in the sample path that are not flushed out prior to the next sample processing. Proper system design assures that these pathways are fully cleansed with nitrogen between sample loadings, and the next sample is allowed to first flow through to the mass flow controller bypassing the trap to wash out the previous sample and nitrogen in the lines, and then is directed to the trap for the set time interval for the actual volume measurement. These provisions can allow sample loadings down to 0.1 minute intervals, or 5 ml at 50 ml/min flow with sufficient accuracy (see Table II and Figure 21).

Standard (ppbCarbon)	Volume Loaded (ml)	Effective Concentration (ppbCarbon)
93 ±2.0	300	97.8
93 ±2.0	150	48.9
93 ±2.0	100	32.6
93 ±2.0	50	16.3
93 ±2.0	25	8.15
93 ±2.0	10	3.26
93 ±2.0	5	1.63
16.2 ±0.6	10	0.54
16.2 ±0.6	5	0.27

Table II. Multiple standards can be generated by simply varying the sample loading time to yield a wide range of *concentrations.*

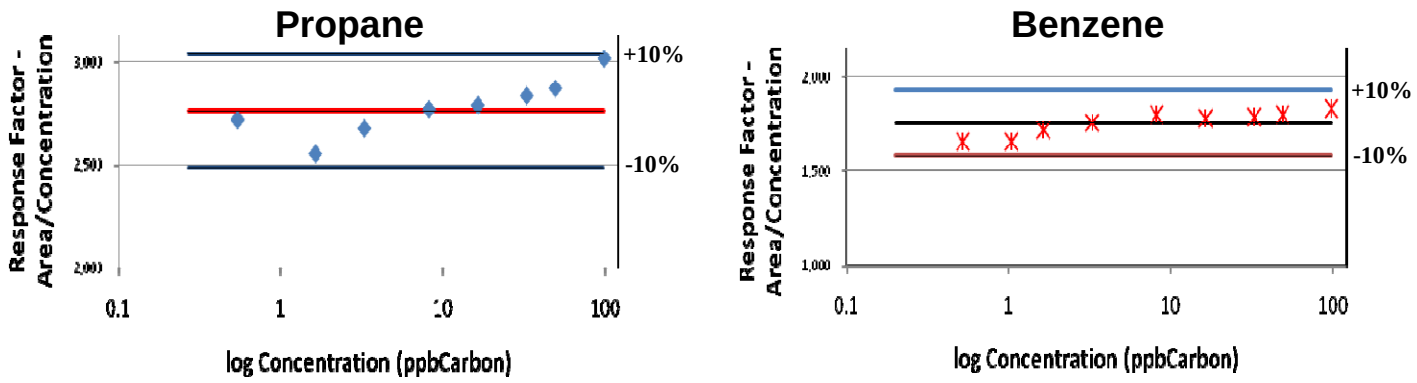


Figure 21. Plots of Area vs log[Concentration] for Propane and Benzene permit better visualization of conformity to linearity, including error bars for deviations at ±10%.

The upper end of the curve is limited solely by the sample loading interval. Some laboratories[21] have extended their sampling times to 48 minutes to illustrate linearity, but very rarely do ambient samples reach that concentration level. A more realistic practice is to keep the sample times at or below 6 minutes and employ appropriate standards to document linearity.

Deviations from the norm demonstrated here for linearity are likely caused by inadequate flushing of the new standard just prior to loading onto the concentrator trap, by inappropriate preparation standards (if multiple ones are involved), or by irreproducibility generated from a poorly performing system.

Linearity only demonstrates that concentrations are proportional to a given standard and does imply that results are true. Accuracy is strictly dependent on the quality of the primary standard(s) employed.

[21] California Air Resources Board, SOP No. MLD 032, 2001, www.arb.ca.gov/aaqm/sop/sop032.pdf, page 26.

XIV. Computation of Final Hydrocarbon Concentrations

Generation of results for normal chromatographic processes involves calculating response factors for ***each*** analyte based on known standards, and then using ***each*** factor to determine the individual outcome. Such a process is not realistic for reporting the expected wide range of hydrocarbons detectable in ambient air, since standards for every analyte are not practical. Since the flame ionization detector can be demonstrated to be a perfect carbon counter, especially for non-methanes (see Section XIII), the system can be calibrated with Propane for the Light-End (C_2-C_5) and Benzene for the Mid-Range (C_6-C_{13}). Then these two response factors can be applied to all other non-oxygenated/non-halogenated components without having a standard for each of the over 300 possible eluents. This criterion does not hold for oxygenates and halogenated analytes.

The operational sequence is:

1. Run a standard mix with the target components within the linear range of the measurement.

2. Compute "off-line" response factors for Propane and Benzene by the formula:

$$\boldsymbol{Response\ Factor_i = Area\ Counts_i / Concentration_i}$$

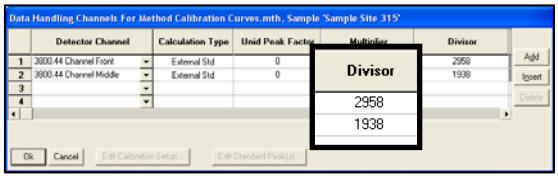
where *i* is each standard. For example, with Propane:

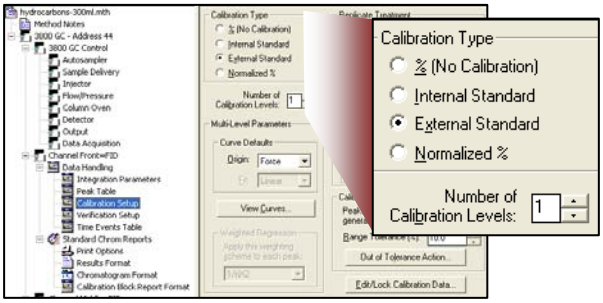
$$\boldsymbol{Response\ Factor_3 = 289{,}319/97.8 = 2{,}958}$$

And for benzene:

$$\boldsymbol{Response\ Factor_{27} = 180{,}228/93 = 1{,}938}$$

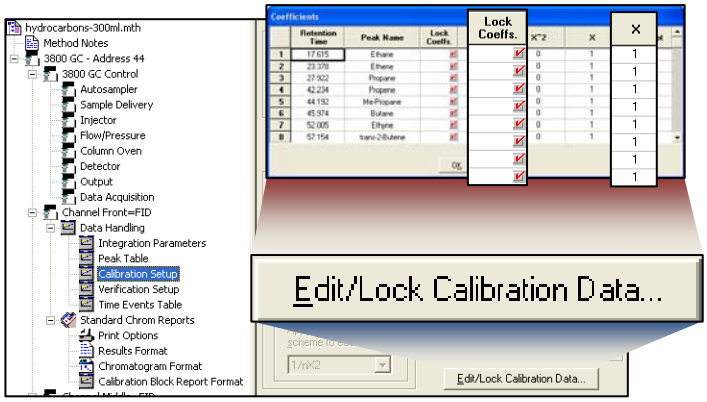
3. Enter these values into the SampleList as divisors for each detector in the MultiChannel/MultiStandard window, located on the far right of the SampleList.

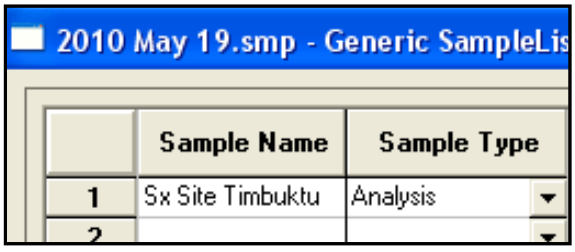




4. Set Calibration Type to "External Standard" and Number of Calibration Levels to "1".

5. Lock all coefficients for peaks and set all "X" coefficients to "1", with the rest remaining at "0". Special note: the first time a method is used, an internal flag must be set with a dummy calibration run to indicate that a standard had been run, or the error "Wrong Calibration Type" appears in the report and Area% numbers are listed.





6. Set Sample Type to "Analysis" and fill in other pertinent information related to the sample.

7. Run unknown samples.

XV. Detection Limit

How low components can be detected are explicitly defined in current regulatory protocols[22] as at least seven replicate runs at or near (within five times) the anticipated detection limit, and computed as 3.14 times the computed standard deviation of that series.[23] NIST SRM 1800 low-level primary standard was developed specifically to perform this test. Since its label concentrations are well above the anticipated limit of 0.2 ppbC, its injected concentration can be reduced by loading a smaller volume through a shorter trapping interval and by serial dilution with nitrogen. Typical results for Propane are shown in Table III and Figure 22, and for Benzene in Table IV.

Raw Area Counts
872
823
926
943
873
886
898
1074

3 * Std Dev = 224
÷ 3,019 = **0.07 ppbCarbon**

Table III. Computation of Propane detection limit with a 0.27 ppbCarbon standard.

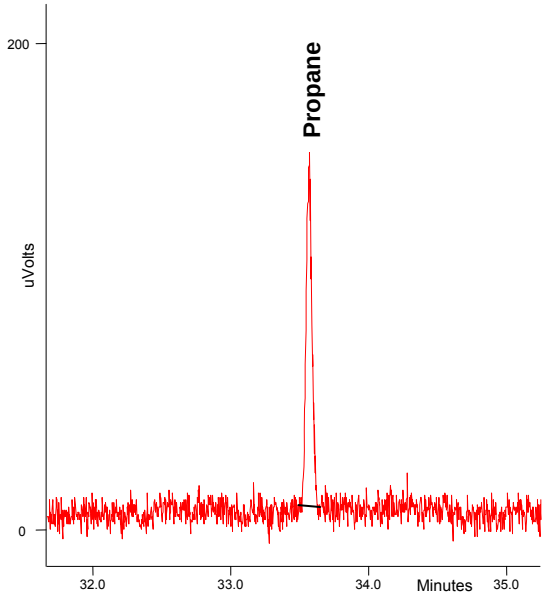


Figure 22. Typical Propane peak generated with a 0.27 ppbCarbon standard.

Raw Area Counts
1100
992
1021
897
1005
940
913
1012

3 * Std Dev = 199
÷ 1832 = **0.11 ppbCarbon**

Table IV. Computation of Benzene detection limit with a 0.54 ppbCarbon standard.

Failure to achieve a detection limit near this value can be triggered by excessive detector noise from contamination, poor chromatography, reactive sites in the sample pathway, improper baseline assignment or peak integration, and leaks in the system, especially around the sample loading process or related to column connections.

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[22] Code of Federal Regulations, April 16, 2010, ecfr.gpoaccess.gov/cgi/t/text/text-idx?c=ecfr&sid=5ec3715e1862a7010265d3fbb70b45c0&rgn=div9&view=text&node=40:22.0.1.1.1.0.1.7.2&idno=40.

[23] Detection limits are too often reported as some factor times the measured detector noise, often by a factor of two, converted to concentration by a suitable response factor. Since modern instruments and data systems can readily perform digital filtering, measured noise can be manipulated to yield any value desired, frequently to the degradation of the chromatography. Statistical analysis, as illustrated, eliminates this bias.

XVI. Control Sample for Retention Time Reproducibility

Since identification of peaks is extremely dependent on retention times, consistency in these times is critical in accurately reporting results. Subtle shifts in peak elution times can erroneously assign peaks labels. Typical results for representative peaks on the Mid-Range column are listed in Table V. The pair with the closest elution is m-Xylene and p-Xylene with a separation of 0.069 minutes, and the demonstrated performance here is well capable of keeping them properly identified over multiple runs.

Variations in retention times can be caused by leaks in the column system, irreproducible column flow rates, lack of stability in important temperature zones, including column oven and pneumatic components, especially flow controllers, inadequate removal of water with Nafion dryer (see Section III), and column not fully conditioned, especially with the water-sensitive Alumina PLOT column. A stabilization time setting can be set to help steady column flows prior to the start of each run, although these flows naturally reach their set points during the sample trapping process of typically 10 minutes after the start of the run and before the sample is loaded onto the column.

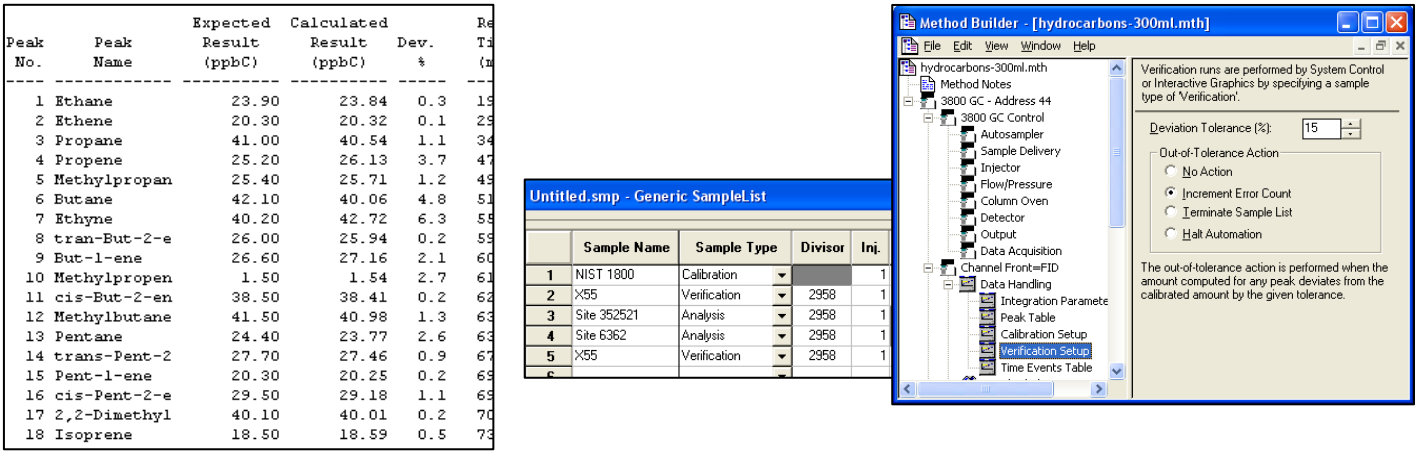
Table V. Typical retention time reproducibility for selected Light-End analytes. Data shown is a summary of 12 consecutive runs with instrument conditions listed in Section V.

	Ret Time (min.)	Std Dev (min.)		Ret Time (min.)	Std Dev (min.)		Ret Time (min.)	Std Dev (min.)
Cyclopentane	34.346	0.019	3-Methylhexane	45.101	0.025	Nonane	62.484	0.020
2,3-Dimethylbutane	34.679	0.021	2,2,4-Trimethylpentane	46.239	0.026	Cumene	63.345	0.020
2-Methylpentane	35.194	0.021	Heptane	47.242	0.025	Propylbenzene	64.915	0.019
3-Methylpentane	36.475	0.023	Methylcyclohexane	48.939	0.026	1-Ethyl-3-methylbenzene	65.272	0.018
2-Methylpent-1-ene	37.038	0.023	2,3,4-Trimethylpentane	51.521	0.025	1-Ethyl-4-methylbenzene	65.387	0.018
Hexane	38.146	0.024	Toluene	51.909	0.025	1,3,5-Trimethylbenzene	65.652	0.018
2-Methylpent2-pentene	38.854	0.024	2-Methylheptane	52.881	0.025	1-Ethyl-2-methylbenzene	66.170	0.017
Methylcyclopentane	40.416	0.024	3-Methylheptane	53.505	0.025	1,2,4-Trimethylbenzene	66.873	0.017
2,4-Dimethylpentane	40.921	0.024	Octane	55.629	0.025	Decane	67.461	0.016
Benzene	42.614	0.025	Ethylbenzene	59.416	0.023	1,2,3-Trimethylbenzene	68.158	0.017
Cyclohexane	43.369	0.025	m-Xylene	59.989	0.023	1,4-Diethylbenzene	69.252	0.016
2-Methylhexane	44.338	0.025	p-Xylene	60.058	0.022	1,2-Diethylbenzene	69.534	0.016
2,3-Dimethylpentane	44.440	0.025	Styrene	61.142	0.022	Undecane	71.491	0.016
			o-Xylene	61.454	0.021			

Table VI. Typical retention time reproducibility for selected Mid-Range analytes. Data shown is a summary of 12 consecutive runs with instrument conditions listed in Section V.

XVII. Daily Calibration Verification Runs - Area Count Reproducibility

The calibration process for this analysis is a very tedious and time-consuming procedure as it normally involves at least 5 calibration runs with about 80 minutes per run. Once this task is performed, a simple control check on the stability of the calibration validates that the quantitation remains legitimate. Use of a "verification" run type permits a single control sample to be compared to expected concentrations. The resulting report lists both the expected values and the calculated results, and then reports their percent deviation (Dev %), as shown in a partial report in Figure 23.



Peak No.	Peak Name	Expected Result (ppbC)	Calculated Result (ppbC)	Dev. %	Re Ti (m
1	Ethane	23.90	23.84	0.3	19
2	Ethene	20.30	20.32	0.1	29
3	Propane	41.00	40.54	1.1	34
4	Propene	25.20	26.13	3.7	47
5	Methylpropan	25.40	25.71	1.2	49
6	Butane	42.10	40.06	4.8	51
7	Ethyne	40.20	42.72	6.3	55
8	tran-But-2-e	26.00	25.94	0.2	59
9	But-1-ene	26.60	27.16	2.1	60
10	Methylpropen	1.50	1.54	2.7	61
11	cis-But-2-en	38.50	38.41	0.2	62
12	Methylbutane	41.50	40.98	1.3	63
13	Pentane	24.40	23.77	2.6	63
14	trans-Pent-2	27.70	27.46	0.9	67
15	Pent-1-ene	20.30	20.25	0.2	69
16	cis-Pent-2-e	29.50	29.18	1.1	69
17	2,2-Dimethyl	40.10	40.01	0.2	70
18	Isoprene	18.50	18.59	0.5	73

Figure 23. A "verification" sample type allows control sample results to be compared with expected ones, and an error is triggered if the deviation exceeds a specified tolerance, usually ±15%.

A daily calibration verification check should be run at the start and end of an analysis sequence to ensure that the calibration data remains intact. A high performance system must be able to maintain consistent responses for the wide range hydrocarbons found in ambient air to avoid the mandate to execute a complete recalibration. Some variation is expected, but the deviation must remain within acceptable constraints. Figure 24 illustrates a selected group of analytes from the early, middle and late portions of the chromatogram. The range of deviations is 0.7% to 6.9% (Light-End) and 1.7% to 4.7% (Mid-Range) for 55 major peaks.

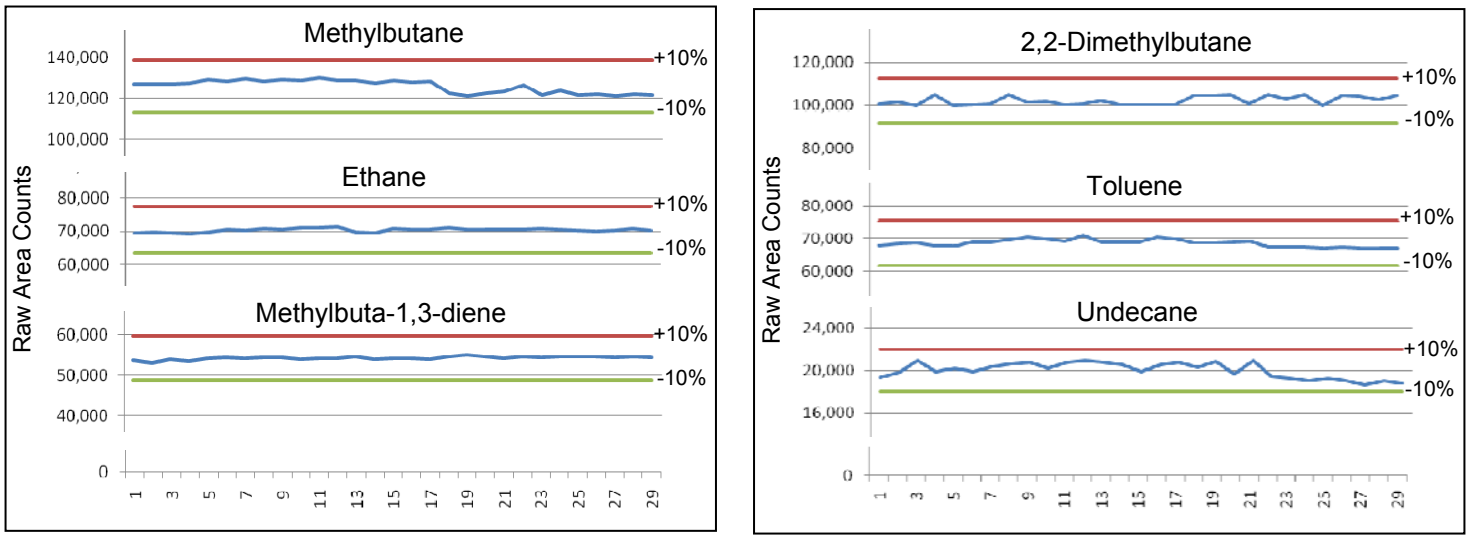


Figure 24. Typical reproducibilities of raw area counts for several Light-End and Mid-Range analytes are plotted with ±10% error bars. Data shown is a summary of 29 runs over 10 days

Since all compounds in the peak table are not found in control samples, a separate method with the limited peak table is usually employed only for this check. Then an off-line control chart (typically with Microsoft Excel) is constructed to monitor stability over extended operations. A suggested series of at least an initial set of 20 runs should be used to establish warning (±2σ) and failure limits (±3σ), and subsequent control runs are added to maintaining a running average. Active limits are set by the last 20 control runs. Some systems perform so consistently that an assigned "σ" of 5% must be implemented to avoid constant failures with small, minor changes in overall performance. This control sample should be run at the start of a sampling series and also at its end to confirm that the calibration remained intact throughout the interval. Excess deviations for the running mean can be attributed to natural instability of the control sample, to improper loading of the sample, to degradation in the performance of the instrument system and to inappropriate integration of the peak areas. Some compounds are much more sensitive to variations in concentrations over the extended times due to their inherent chemical reactivity, such as Ethyne and Methylbuta-1,3-diene (Isoprene), and due to new cold spots in the sample line through to the column, especially for components above Decane.

XVIII. Sample Carry-over

Valving design of high performance systems allows the active sample line to be purge with new sample prior to commencement of the trapping process. This operation significantly reduces the risk of the remnants of the previous sample being included in the new sample, especially when processing first a high level one followed by a very low one. In addition, all tubing involved in the sample train, through the Nafion dryer, valves and cryotrap is purged with either nitrogen or helium to ensure that these areas are cleansed to avoid carryover of analytes from one sample into the next. Figure 25 illustrates typical results for this test. Decane is often the worst case due to its higher boiling point. Most other analytes give carry-over under 0.02%

Hydrocarbon concentrations in ambient air rarely exceed 100 ppbCarbon. With carry-over under 0.1%, this residue is usually below detection limits.

Deviations from perfection can be caused by eddy currents generated from unswept deadvolumes in the sample pathways, dirty carrier gas, column bleed, cold spots in the sample pathway, and cross-contamination of samples prior to loading into the system.

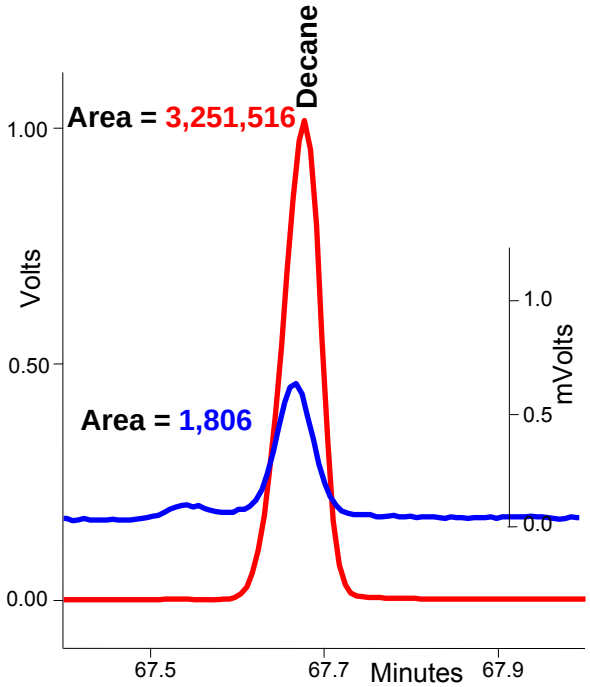


Figure 25. Sample carry-over is demonstrated by running a high standard (2,000 ppbCarbon) followed by a nitrogen blank. Ratio of the areas yields the carry-over, or 0.06%.

XIX. Effects of Varying Canister Pressures on Sample Volume and Corrective Action

Mass flow controllers work on the basis of a differential pressure between the inlet and outlet, and their factory calibration is set based on pressure values originally specified. Although many controllers can tolerate some variation in these pressures, large deviations result in inaccurate flows when the sample concentrator is placed in front of the mass flow controller from the compression of sample gases with Boyle-Mariotte Law.[24] Figure 26 illustrates the magnitude of the effect. Typically this problem is noticeable with daily control checks when an aliquot is taken regularly and slowly depletes the canister. Control charts show a small but perceptible drop in detector response, and when the canister is recharged with new standard, the original response returns.

[24] See discussions at en.wikipedia.org/wiki/Boyle's_law.

Unfortunately, pressures in sample canisters cannot be controlled and usually vary widely. Results can be significantly in error when responses are compared against standards of a different pressure. For example, if the calibration curve had been set up with a standard canister of 30 psiG, and the sample had only 10 psiG, the unknown concentrations would be reported too low by 33%. This effect can be mitigated by installation of a sample pressure regulator prior to the sample concentrator. When this regulator is set to a moderate pressure of 3-4 psiG, the volume measured by the mass flow controller becomes independent of the canister pressure, and results will match even with samples in Tedlar bags at atmospheric pressure. Critical to the operation of this regulator is the avoidance of carry-over due to the significant unswept deadvolume within the regulator and its gauge. Precautions are necessary to purge the device with nitrogen when not in use, and then allow the new sample to flow through prior to directing the sample to the concentrator. (See Section XVIII).

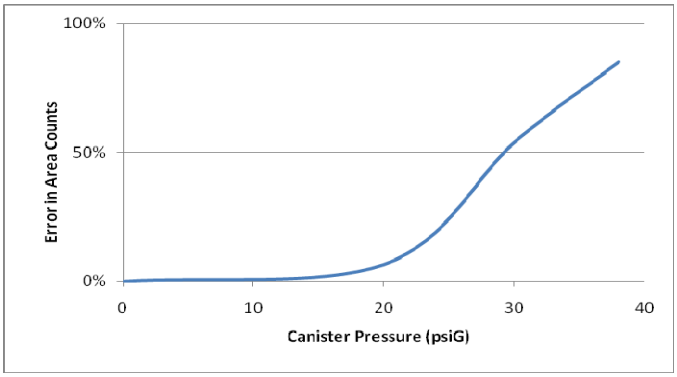


Figure 26. Effects of varying canister pressure on measured peak sizes with mass flow controller located downstream of sample concentrator.

XX. Addition of Water to Standard, Sample and Blank Canisters

To ensure that standards, low-humidity samples and blanks emulate processing conditions of typical ambient samples, 150 µl of HPLC grade water is added to empty 6 liter canisters to yield a 50% humidity level inside the canister.[25] The process is simply to load the dose of liquid water into the top of the canister valve, cap the valve and open the valve; the natural vacuum of the empty canister sucks in and distributes the water vapor. This procedure also minimizes active surface sites inside, especially for olefins, aromatics and heavier hydrocarbons, by producing a thin layer of water on the interior canister surface.

XXI. Canister Evacuation Requirements to Avoid Analyte Carryover

Canisters are often employed in storing ambient air samples, as they transport well, are normally inert to most analytes, and can be cleaned and reused. Their preparation involves multiple cycles of pressurization with clean nitrogen followed by evacuation with vacuum. Most EPA methods[26] mandate a final vacuum of less than 0.050 Torr (50 mTorr) to ensure no previous analyte remains in the canister to contaminate the next sample.

Some vacuum pumps can achieve the required performance with a single evacuation[27], while others with less capability require multiple cycles to flush out canisters below expected detection limits. Table VII lists requirements to achieve cleanliness below normal detection limits with various pump performances.

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[25] Air Resources Board SOP No MLD 032," Standard Operating Procedure for the Determination of Non-Methane Organic Compounds in Ambient Air by Gas Chromatography Using Dual Capillary Columns and Flame Ionization Detection", Section 5.10, (2001), www.arb.ca.gov/aaqm/sop/sop032.pdf.

[26] Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Method TO-15, 1999, www.epa.gov/ttn/amtic/files/ambient/airtox/tocomp99.pdf, Section 8.4.1.3.

[27] See for example: Varian/Agilent Triscroll 300 Dry Vacuum Pump, www.varianinc.com/cgi-bin/nav?products/vacuum/pumps/scroll/tri300/index&cid=LLQQQHLKFP.

Table VII. Performance Mandates to Evacuate Canisters with 100 ppbCarbon Contamination to below Typical Detection Limits. Entries in GREEN show achievement of levels below detection limits.

Vacuum Achieved ("Hg))	-29.9196	-29.918	-27	-25.5
Vacuum Achieved (Torr)	0.010	0.050	74	112
Carryover after 1 evacuation	**0.0013%**	**0.0066%**	10.0%	14.8%
Carryover after 2 evacuations	< 0.00001%	< 0.00001%	0.948%	2.18%
Carryover after 3 evacuations	<< 0.00001%	<< 0.00001%	0.092%	0.322%
Carryover after 4 evacuations	<< 0.00001%	<< 0.00001%	**0.0090%**	0.048%
Carryover after 5 evacuations	<< 0.00001%	<< 0.00001%	< 0.001%	**0.007%**
Cycles to yield concentrations < detection limit	1	1	4	5

XXII. Sub-atmospheric Pressure in Canisters

Canisters can come to the laboratory for analysis with pressures below atmospheric. Although mass flow controllers are calibrated at specific inlet and outlet pressures, the system will run the sample, but will not indicate quantitation errors due to differences in run conditions from the calibration series, and resulting discrepancies in the loaded volume, due to the controller's calibration pressure range differing from the actual sample.

Another potential difficulty occurs when the sub-atmospheric canister is opened up to a sample line that possesses a high concentration residual from the previous sample that is sucked into the new canister. The volume from that cross-contamination depends on the internal diameter of the sample line and its length and amount of vacuum in the canister.

For example, for a 6L canister hooked to a 1.5m sample line (1/8 OD), 5.6 ml aliquot of the previous sample could be pulled in and yield a 0.1% cross-contamination. In another case with a smaller 400 ml mini-canister attached to a 1.5 m sample line (1/16" and 0.040" ID), the sample corruption could amount to 0.4%.

Tubing Internal Diameter	Volume per length (µl/cm)
0.030"	4.6
0.040"	8.1
0.085"	36.6

A safer practice is to insure that all canisters are at positive pressures to ***push*** sample through its instrument pathway, to keep the mass flow controller in its calibrated mode, and to avoid alterations to the sample integrity from a previous sample. Sub-atmospheric canisters can be pressurized by adding in nitrogen and correcting the final results for the initial and final pressures, as these samples are proportional diluted by the added nitrogen following Boyle's Law.[28,29]

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[28] Op. Cit., en.wikipedia.org/wiki/Boyle's_law.

[29] See for example "Pressure Station by Lotus Consulting" brochure available on request from ebramstoncook@msn.com.

XXIII. Effects of Nitrogen as Make-up Gas for FID

By Graham's Law[30], Helium is 2.6 times more diffusive than Nitrogen and thus creates a larger, cooler flame than Nitrogen when used as the inert flow into a hydrogen-diffusion flame detector. Many chromatographs are set up with helium as the carrier gas, and with the same gas supply used to make up the flow into the detector appropriate to an optimum setting above the typical column flow. If Nitrogen were employed as the make-up gas instead, the flame becomes tighter and hotter, and yields an enhanced response to hydrocarbons, typically by a factor of two, with helium remaining as the carrier. And since Nitrogen is more abundant and less expensive, a cost savings is realized along with the increase in performance.

XXIV. Performance Enhancements with Narrow-bore Flame Tips

Flame tips for the flame ionization detector are available in two sizes - 0.01" ID and 0.02" ID; the latter is the standard size for instruments from the factory. The narrower one has the distinction of generating a tighter, hotter flame that provides a considerable enhancement in signal over the standard one. Figure 27 illustrates the differences in performance, showing a 59% larger peak simply by exchanging the flame tip and adjusting its flame gas flows. Combined with nitrogen make-up gas, an enhancement approaching a factor of 3 is achievable, with consequentially lower detection limits.

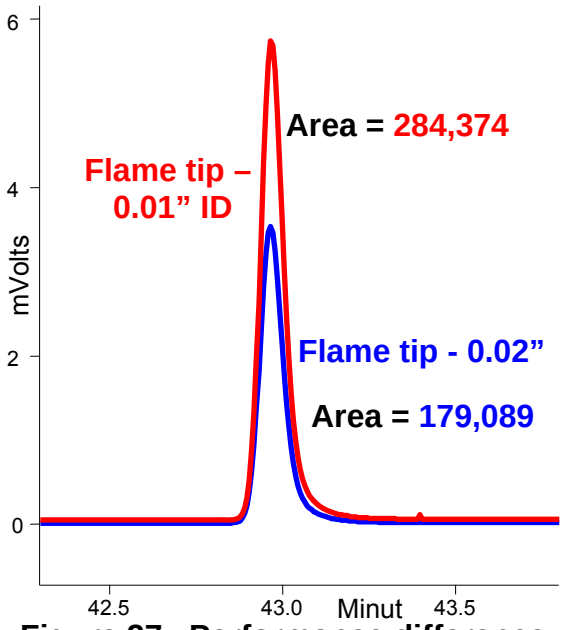

Figure 27. Performance difference between flame tip styles.

The narrow tip can be used effectively with the Light-End measurements where hydrocarbon responses are inherently smaller, with fewer carbon atoms per molecule, as this detector essentially counts carbon atoms. With the tighter flame, this tip is more susceptible to flame-out from elution of water and huge concentrations of analytes passing through. Accordingly, the appropriate tip for the Mid-Range portion is the 0.02" jet.

Optimum flows for these flame tips are listed in Table VIII. Actual flows should be verified with an external digital flowmeter to ensure accuracy.

	0.01" Flame Tip	0.02" Flame Tip
Carrier + Make-up	25 ml/min	30 ml/min
Hydrogen	25 ml/min	30 ml/min
Air	300 ml/min	300 ml/min

Table VIII. Optimum flows for flame tip styles.

[30] See: en.wikipedia.org/wiki/Graham's_law.

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