

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

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

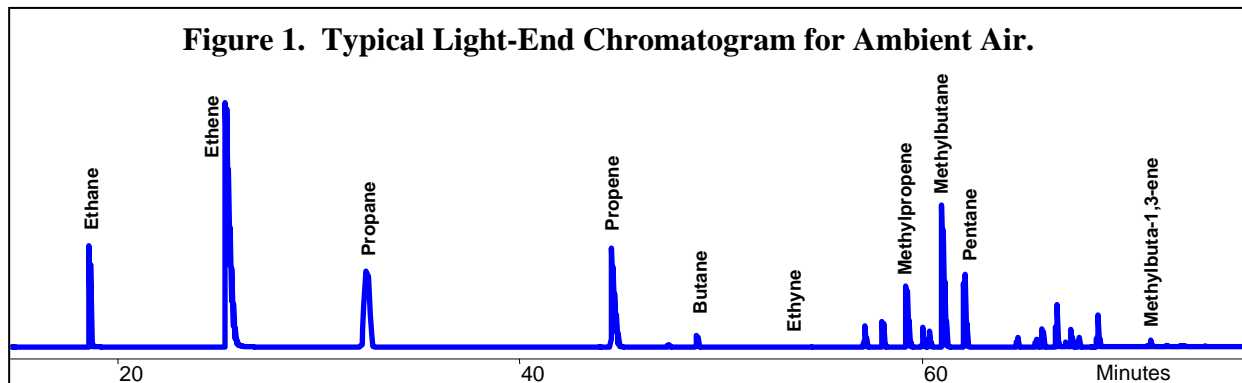
Extended Abstract # 35

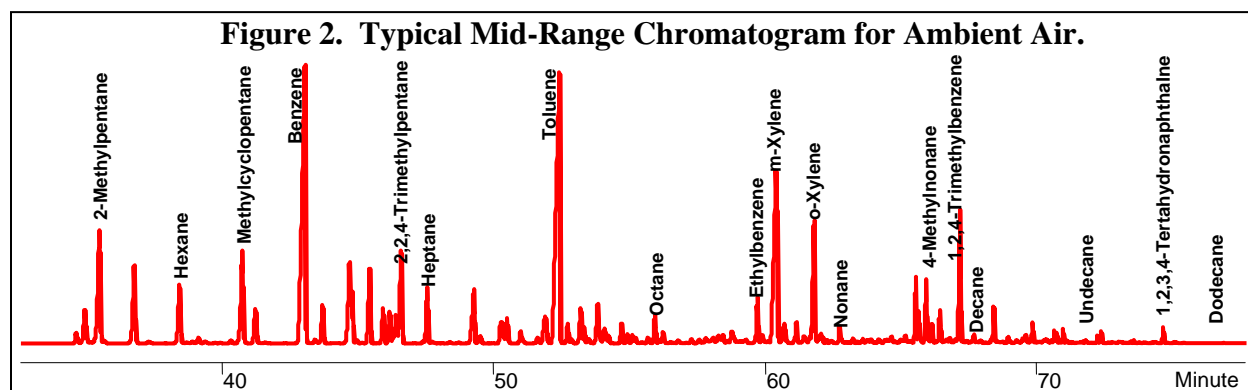
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## INTRODUCTION

Full speciation of hydrocarbons in ambient air involved in the USEPA Photochemical Assessment Monitoring Stations (PAMS) Program is undoubtedly one of the most difficult analyses in gas chromatography. 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).

A single column is not sufficient to fully resolve all hydrocarbons within the C<sub>2</sub>-C<sub>13</sub> 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<sub>2</sub>-C<sub>5</sub>) from the “Mid-Range” ones (C<sub>6</sub>+). 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. 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:

- Retention Time Reproducibility
- Assignment of Peak Identifications.
- Establishment of clean instrument blank
- Performance of a multi-point calibration over a minimum range of 1 ppbC to 100 ppbC.
- 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 for reported concentrations
- Substantiating minimal carryover of high concentration samples into a following blank.

## EXPERIMENTAL METHODS

All chromatograms displayed are generated on Varian 3800 (Walnut Creek, CA) and Bruker 450 (Fremont, CA) Gas Chromatographs, adapted for measurement of trace hydrocarbons in air by Lotus Consulting (Long Beach, CA) with cryogenic trap to concentrate air samples into the operating range of the detectors, mass flow controller for sample loading, Nafion dryer to control sample moisture prior to trapping, required valving to direct a measured aliquot of sample to the trap, and then on to the column set and two independent flame ionization detectors. Typically 300 ml of sample are trapped. A short precolumn (Chrompak CP5 CB, 15 m, 0.32 mm ID, 1  $\mu$  film) performs a coarse separation of the Light-End hydrocarbons from the Mid-Range ones. The lights are passed on to the Alumina PLOT (Chrompak Alumina SO<sub>4</sub>, 50 m, 0.32 mm ID) and to one of the detectors. At the appropriate time, determined by experiment, a column switching valve is activated to then direct the Mid-Range components left on the pre-column to the dimethylpolysiloxane column (Chrompak CP5 CB, 60 m, 0.32 mm ID, 1  $\mu$  film) and the second detector. Data collection and complete instrument control is performed with Varian Star Workstation and Bruker MS Workstation. All operations follow California Air Resources Board protocol (SOP 032).<sup>1</sup>

## RESULTS AND DISCUSSION

### 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 are listed in Table I for 12 consecutive runs on the same instrument. The pair with the closest elution is m-Xylene and p-Xylene, with a separation of 0.069 minutes. The demonstrated performance here is capable of keeping them properly identified over multiple runs.

## Peak Identifications

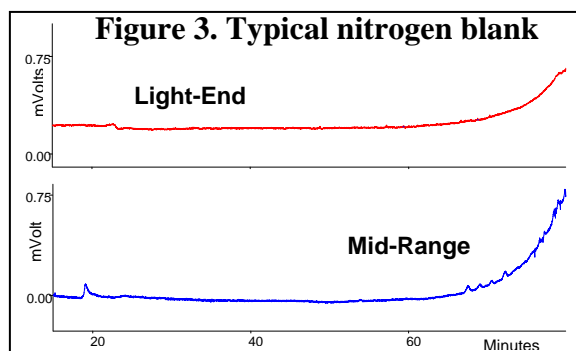
Flame ionization detectors can only identify peaks by retention time. Known standards must be run under identical chromatographic conditions to enable specific peaks to be picked out for accurate construction of the peak table. Retention time reproducibility is critical in ensuring that peak assignments 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. 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.<sup>2</sup>

An additional mechanism for peak identification for hydrocarbons involves use of Kovats indices, which relate relative elution of hydrocarbons to adjacent n-Alkanes.<sup>3,4</sup> 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, which places it 49% of the distance between Hexane and Heptane. After examination of 14 chromatograms from eleven chromatographic systems, this index for Benzene has a standard deviation of  $\pm 2$ . An updated list, with over 300 hydrocarbons indices, is available from Lotus Consulting for both columns employed in this analysis (Alumina-SO<sub>4</sub> PLOT for C<sub>2</sub>-C<sub>5</sub>, and dimethylpolysiloxane for C<sub>6</sub>-C<sub>13</sub>).<sup>5</sup>

## Blank Baseline

Hydrocarbons are ubiquitous and can readily show up uninvited in systems when attempting to measure concentrations at levels into the ppt Carbon range. These contaminants can add inappropriately to results and produce erroneous analyte concentrations. Typical nitrogen blank baselines for Light-End and Mid-Range detectors are shown in Figure 3. The goal is to achieve a blank run with no peaks above the reported detection limit.

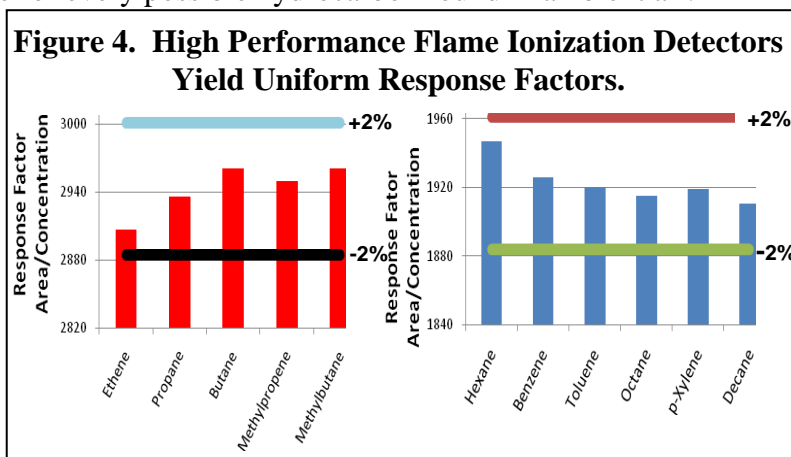
Compound	Retention Time (min.)	Standard Deviation (min.)
<b>Light-End</b>		
Ethane	20.964	0.017
Propane	34.959	0.021
But-1-ene	52.091	0.019
<b>Mid-Range</b>		
Cyclopentane	34.356	0.019
m-Xylene	59.989	0.023
p-Xylene	60.058	0.022
Undecane	71.491	0.015



## Even Detector Response

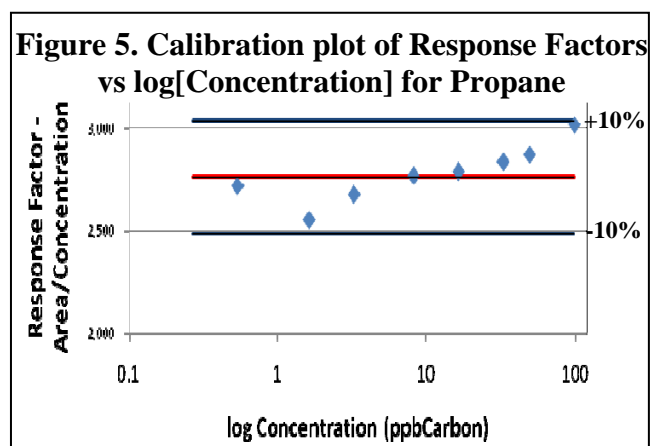
Accurate standards are not available for every possible hydrocarbon found in ambient air.

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 4 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 one, with confidence that correct concentrations for the full range of hydrocarbons are reported.



## Multi-point Calibration

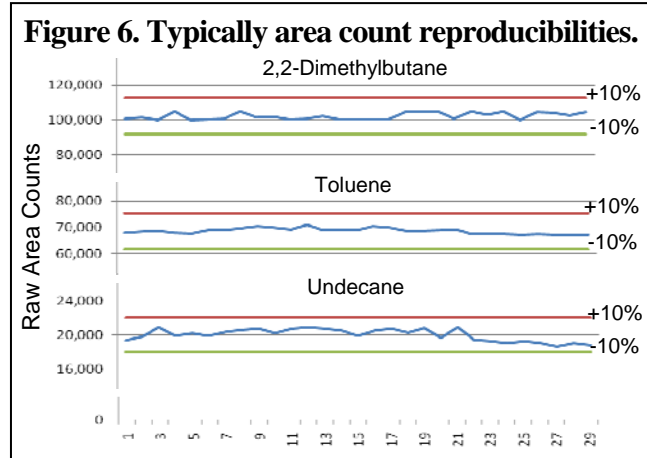
A wonderful feature of the usual instrument design for measuring hydrocarbons in ambient air is the ability to generate multiple standard levels for system calibration by simply keeping the sample flow into the concentrator constant with a mass flow controller and altering loading times. Thus, a single 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 multiple calibration points from 1.7 to 100 ppbCarbon based on a sample loading of 300 ml. Calibration curves are usually shown as a Cartesian plot. These plots 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  $\log[\text{Concentration}]$ , as depicted in Figure 5. Thus, maintenance of linearity can be visualized clearly at both low and high ends of the range.



## Concentration Reproducibility

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 6 illustrates a selected group of analytes from the early, middle and late portions of the chromatogram for 29 tests performed over 10 days. The range of deviations is 0.7% to 6.9% (Light-End) and 1.7% to 4.7% (Mid-Range) for 55 major peaks.



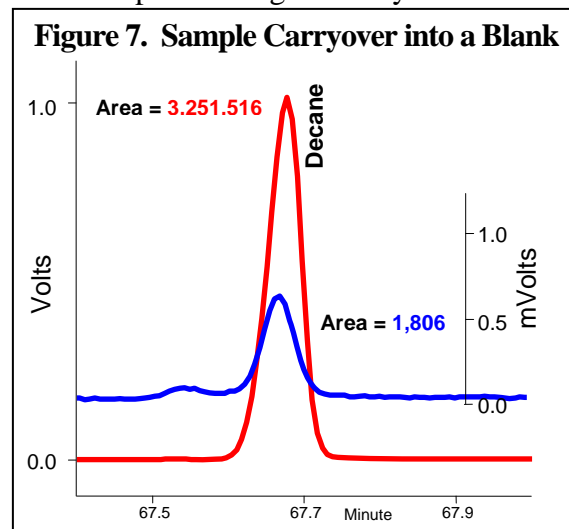
## Detection Limit

How low components can be detected is explicitly defined in current regulatory protocols<sup>6</sup> for 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. 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 0.3 ppbCarbon Propane are shown in Table II, based on the average Light End response factor in Figure 5.

Table II. Detection Limit Calculation	
Raw Area Counts	Calculation
872	$3 \times \text{Standard Deviation} = 224 \text{ area counts}$ $\text{Detection Limit} = \frac{224 \text{ area counts}}{2,763 \text{ area counts/ppbCarbon}}$ $= 0.08 \text{ ppbCarbon}$
823	
926	
943	
873	
886	
898	
1,074	

## Test for Carryover

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 remnants from 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 7 illustrates typical results for this test with Decane at 2,000 ppbCarbon followed by a nitrogen blank. Results show carryover of 0.06%. 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 carryover under 0.1%, these residues are usually below method detection limits.

## SUMMARY

Following steps outlined above, measurement of hydrocarbons in ambient air can be fully validated. Concentrations for specified analytes should be reported as accurately as possible. Since concentrations in chromatography are determined exclusively with external standards, the absolute accuracies of the results are strictly dependent on the legitimacy of calibration standards. Other system performance criteria can also alter the quality of the measurements. Avoidable errors in reporting hydrocarbon values include measure of retention times, assignment of peak identifications, added contributions from system contamination, changes in response across the full range of analytes, detection limits, and component carryover. Minimizing the effects of all of these factors ensures that the final results are valid.

## REFERENCES

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