Identification of Hydrocarbons in Ambient Air

Randall Bramston-Cook and **Edward Bramston-Cook**
Lotus Consulting
5781 Campo Walk, Long Beach, Ca 90803
310/569-0128
ebramstoncook@msn.com

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Extended Abstract # 53

Randall Bramston-Cook and Edward Bramston-Cook
Lotus Consulting, 5781 Campo Walk, Long Beach, California 90803

INTRODUCTION

Volatile non-methane hydrocarbons in ambient air are the principal precursors of photochemical smog. Some are more reactive than others, especially olefins and aromatics, with Maximum Incremental Reactivity (MIR) values[1] ranging from 0.31 for Ethane to 16.33 for 2-Butyne. A full assessment of their impact on creation of ozone necessitates complete chromatographic speciation of hydrocarbons and their accurate identification in the chromatogram. Over 300 hydrocarbon species can be found in ambient air, making proper labeling of peaks critically important and often a daunting task.

Gas chromatography with flame ionization detection is the technique of choice for this measurement, as nearly all of these hydrocarbons can be fully resolved and adequately detected. However, peak identifications are accomplished only by retention times on the column. Other detection techniques, such as mass spectrometry, can provide some characterization of the eluting compounds, but they require special operator skills in matching spectra with libraries. Also, mass fragments generated during the process most often differ for each compound, mandating that a standard for each one be available to properly determine concentrations. With so many compounds involved, this process is not practical, as commercially available standards typically possess up to 55 components, and miss many of the hydrocarbons found in ambient air.

Using high performance flame ionization detectors, all non-methane hydrocarbons found in ambient air respond equally when basing their concentrations on the number of carbon atoms per molecule (ppb Carbon).[2] This performance can be achieved even with olefins and aromatics. However, this detector is unable to provide positive identification of chemical structures. Only retention times on the column are employed as the usual mechanism to distinguish peak identities.

Various important additional approaches to determining the classification of every hydrocarbon detected in ambient air are compared, including use of reference chromatograms, standard mixes, especially comparing their relative concentrations, and Kovats indices, also called Relative Retention Index.

EXPERIMENTAL METHODS

A single capillary column cannot fully resolve all hydrocarbons from Ethane to Tridecane. For example, dimethylpolysiloxane stationary phase (Chrompak CP5 and VF1, and J&W DB1) separates compounds very roughly by their boiling points and is the column of choice for separating hydrocarbons from Hexane to Tridecane (see Figure 1), but performs poorly in resolving the lighter ones, especially the C_2, C_3 and C_4 alkenes from their equivalent alkanes.

Figure 1. Typical Mid-Range Chromatogram for Ambient Air.
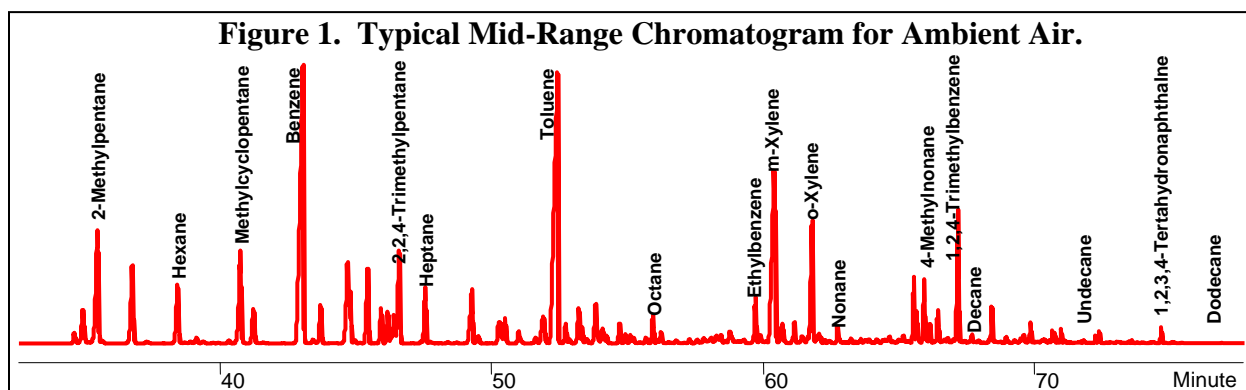
The preferred column for these is the Alumina-SO$_4$ Porous Layer Open Tubular (PLOT) column (Chrompak CP-Alumina-SO$_4$) where all of these "light" species are fully resolved to baseline (see Figure 2). Some peaks in the chromatogram are not labeled.

Figure 2. Typical Light-End Chromatogram for Ambient Air.
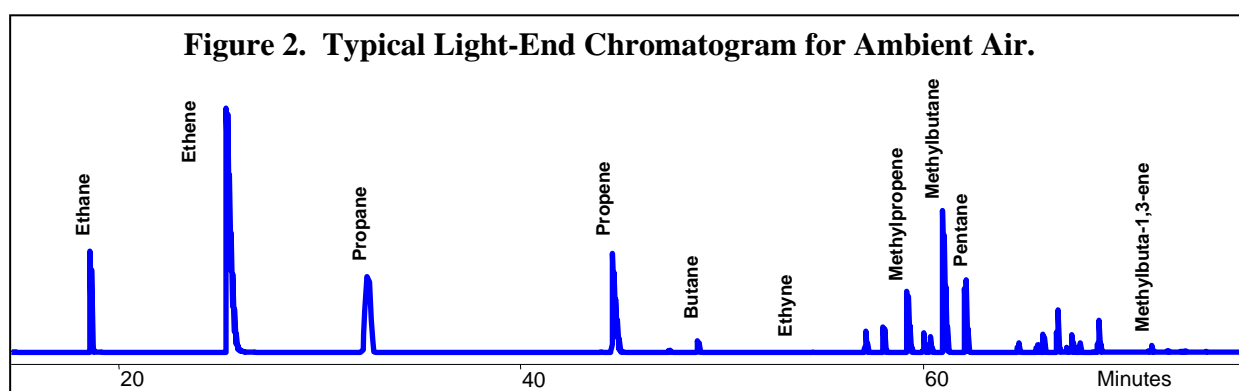

All chromatograms displayed are generated on Varian 3800 (Walnut Creek, CA) and Bruker 450 (Fremont, CA) Gas Chromatographs adapted for measurement of trace hydrocarbons in air by Lotus Consulting (Long Beach, CA) with cryogenic trap to concentrate air samples into the operating range of the detectors, 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. A short precolumn (Chrompak CP5 CB, 15 m, 0.32 mm ID, 1 μ 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$_4$, 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 μ 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 SOP 032.[3]

Retention time data summarized below are generated by 15 different chromatographic systems with varying experimental conditions, including column dimensions, temperature programming and flow rates are. Sources for standards used in setting peak assignments include NIST 1800, Scott Marin, Scott Specially Gases, Restek and Spectra Gas Supply. Many peak assignments are also confirmed with mass spectrometric measurements with pure chemicals diluted into ambient concentration ranges.[4]

RESULTS AND DISCUSSION

Peak Assignments for Light-end Hydrocarbons (C_2-C_5)

Peaks detected with the Alumina PLOT are easily characterized since only 18 peaks are monitored here, and are fully resolved from each other. In addition, Ethyne is readily picked out by its characteristic peak shape as if it were distorted by column overload, but exhibits this shape even at low concentrations (Figure 3). Performance of this column easily degrades when exposed to moisture, especially from the sample. Retention times for these light analytes will shift to shorter elutions, and most dramatically for Propene and Ethyne. Regeneration of the column is accomplished by heating the column to 200 °C overnight and then retention times usually return to their initial values. No other analyte is found in this region, dramatically simplifying peak labeling for these eluents.

Figure 3. Ethyne is picked out by its distinguishing peak shape.
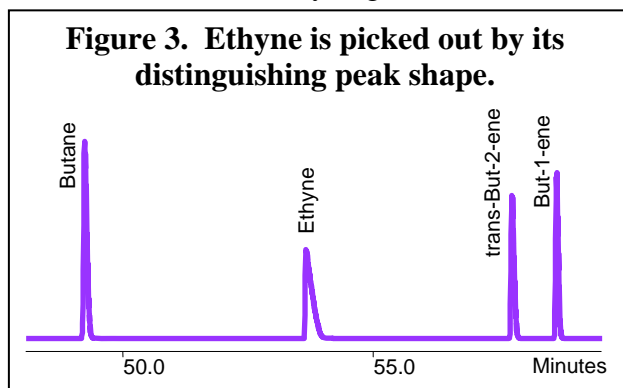
Peak Assignments for Mid-Range Hydrocarbons (C_6-C_{13})

The column used in the chromatography of Mid-Range components (C_6-C_{13}) separates them roughly by their boiling points. Figure 4 illustrates the correspondence between retention time and boiling points. Unfortunately, this column yields many exceptions to a direct correlation,

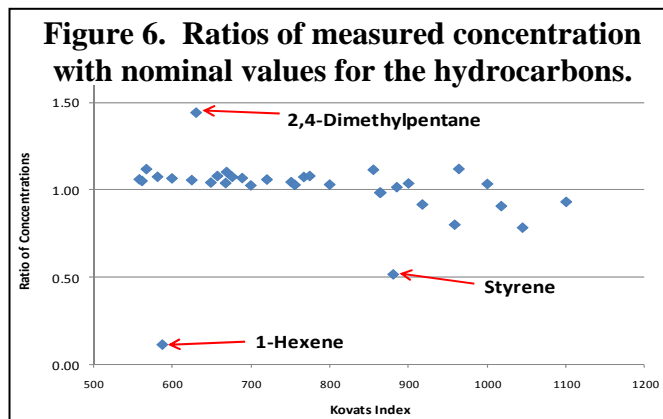**Figure 4. Plot of Component Boiling Point versus Retention Time**
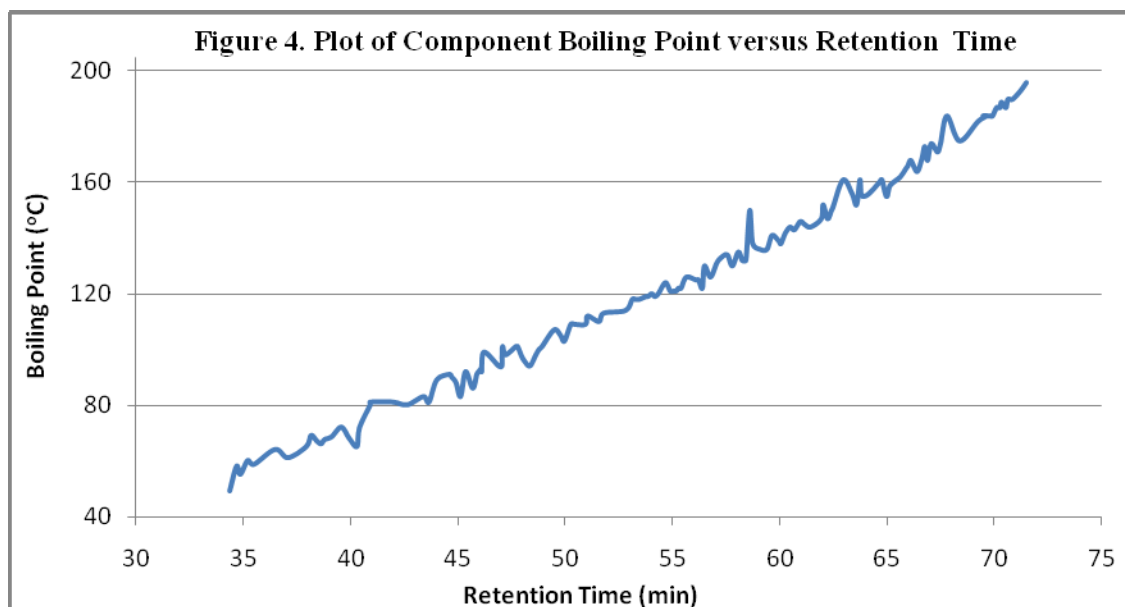
and explicit use of this association cannot provide positive identity of any peak. A comparison can only give a clue to a gross misassignment, such as labeling a peak as 2,3,4-Trimethylpentane (BP = 113 °C) in the Octane (BP = 126 °C) region of the chromatogram.

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. 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. In a typical search of the library for a spectral match (Figure 5), a 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. Individual standards must be invoked for each analyte, and those not in the standard mix cannot be quantified accurately.

Figure 5. Library Search Comparison of Sample versus NIST Library
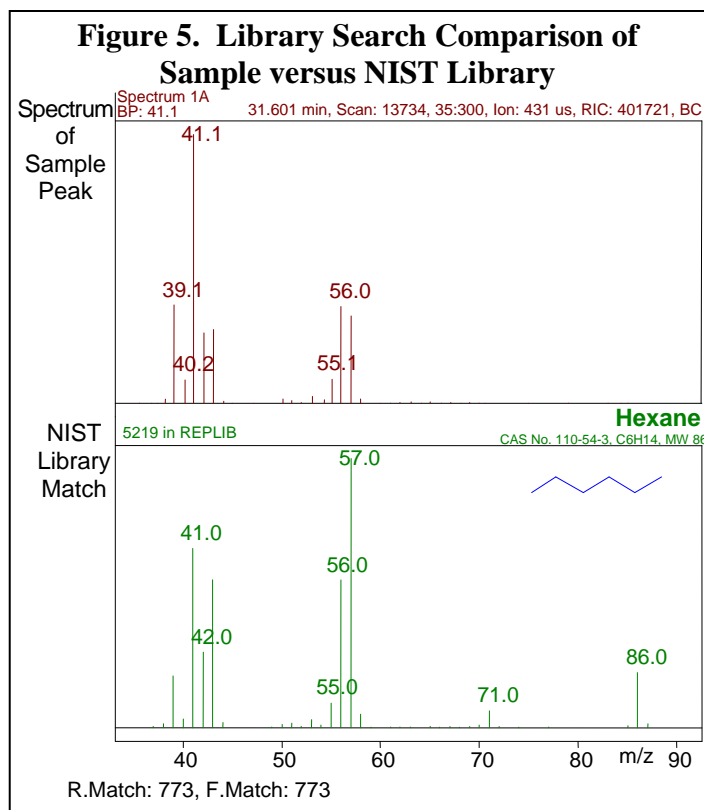
Multi-component hydrocarbon standards with varying concentrations are available from several commercial sources. Concentration levels in these standards are usually predetermined with uneven levels to assist in confirming peak assignments by comparing their measured sizes to expected values. Figure 6 demonstrates 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, 2,4-Dimethylpentane can be measured as over 45% of its label number, undoubtedly

Figure 6. Ratios of measured concentration with nominal values for the hydrocarbons.

due to the inertness of the instrument used and underlabeling by the standard manufacturer. Another case is the near complete loss of 1-Hexene - assessed at only 12% of its label, and Styrene - 50% off label. Olefins and aromatics are typically very reactive and their long term stability in a cylinder or canister is never assured.

An additional mechanism for peak identification involves use of Kovats indices[4, 5, 6, 7, 8], which relate relative elution of hydrocarbons to adjacent n-Alkanes. 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 (Chrompak 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 15 chromatograms from eleven different chromatographic systems, this index for Benzene has a standard deviation of ± 2. 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 in Kovats Indices (± 8 for Ethyne and ± 6 for Propene) of all hydrocarbons. Most hydrocarbons have consistencies less than ± 3, 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 7 shows significant deviations in the C_{10}-C_{11} regions (index range of 1000 to 1100) when 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 Indices in the chromatogram are 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,

Figure 7. Comparing Measured Kovaks Indices with Tabulated Values.

these peaks are relabeled from the Kovats Index listing as 1,4-Diethylbenzene and 1,2-Diethylbenzene, the deviations are greatly reduced, confirming that the compounds are likely to have been mislabeled on the certificate.
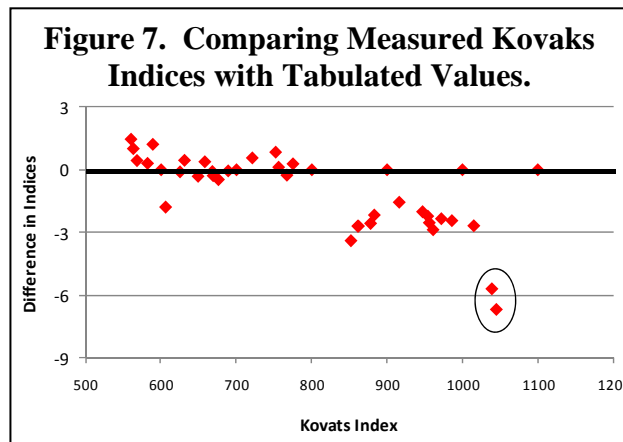
SUMMARY

Full speciation and identification of hydrocarbons in ambient air are critical to properly reporting their concentrations, as their impact on smog development is very dependent on the species available. The process can be overwhelming due to the multiple hydrocarbons detectable.

Retention time alone is not always the most accurate parameter to use for labeling peaks. Various additional processes can be employed to confirm identities, including Kovats Indices, mass spectral information, and ratio of measured concentrations for standards versus the corresponding label values. Compromising the full separation of hydrocarbons by shortening the analysis time with higher column flow rates and faster column temperature programming risks increased coelutions and the subsequent reporting of individual hydrocarbon concentrations higher than their true values.

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