# TDTS 16

## Round-the-Clock, On-Line, and Cryogen-Free Monitoring of Hydrocarbons from Acetylene to Trimethylbenzene in Ambient Air

## Application Note

**MARKES**
international

### Abstract

This application note describes the validation of a thermal desorption system for on-line monitoring of a complex mix of volatile and very volatile hydrocarbons (ozone precursors) in air.

The presence of volatile hydrocarbons in urban atmospheres is believed to contribute to the formation of ground-level ozone, one of the main constituents of urban smog. The compounds of interest range in volatility from acetylene (ethyne) to trimethylbenzene, and are generally referred to as ozone precursors. Vehicle emissions are thought to be the main source of these compounds. Recent European and US regulations [1,2] require round-the-clock monitoring of target species in all major urban centers to establish and monitor the link between periods of high traffic density and high pollution levels (key compounds include benzene, toluene, xylene, and buta-1,3-diene). Continuous real-time monitoring provides an insight into emission episodes from local industry, and can be used to monitor the effect of weather conditions such as wind direction, precipitation, and temperature inversion.

### Introduction

The UNITY 2 Air Server is a cost-effective system for round-the-clock speciated measurement of multiple trace-level volatile organic compounds (VOCs) in air or pure gases. It combines automated, controlled-flow sampling with cryogen-free concentration technology. The system connects to standard GC and GC/MS technology, and is designed for unattended operation in remote field locations.

**Agilent Technologies**

In summary, sample air is pulled directly onto an electrically cooled, sorbent-packed focusing trap at a controlled flow rate. Liquid cryogen is not required. An optional membrane dryer selectively eliminates water and other low-molecular-weight polar components, reducing the risk of interference from unknown species, and facilitating the use of FID rather than MS detection.

Sampling flows are controlled by an electronic mass flow controller and pump, located downstream of the focusing trap to avoid contamination. All sampling parameters are selected by the user, and monitored by system software as an integral part of the analytical method. After sample collection, the flow path is purged with carrier gas to prevent carryover and eliminate oxygen from the focusing trap. The trap then heats rapidly, at rates approaching 100 °C/min, to inject retained analytes into the capillary column as a highly concentrated band of vapor. This transfer may be performed splitless for maximum sensitivity. Once the trap has desorbed, it recools, reequilibrates to the trapping temperature, and begins collection of the next sample while analysis of the previous sample is ongoing. The UNITY 2 Air Server also offers automatic interchange between a minimum of three sample channels (typically sample, reference, and blank) for remote system calibration/validation as per user requirements.

This application note describes validation of the system for on-line monitoring of the 27 ozone precursors specified by European regulators, with the addition of 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, and isoprene (present in the gas standard used). Table A1 (see Appendix) provides the list of 30 compounds. Key factors taken into account when developing this method included the need for a system that could operate round-the-clock unattended, so cryogen-free operation was essential. The system also needed to allow hourly sample collection, with as much of the hour as possible dedicated to sampling. Finally, detection limits needed to be below 0.5 ppb (ideally 0.1 ppb).

## Defining the ideal focusing trap

The design and packing of the trap is crucial for this application. The narrow-bore design of the UNITY 2 trap (Figure 1) allows true splitless operation, allowing transfer of the whole sample to the GC system, giving increased sensitivity for low concentration compounds. The narrow-bore design also gives the best possible peak shape for early-eluting compounds (Figure 2).

The sorbents chosen are also crucial, as they permit increased retention of very volatile compounds, thereby increasing the sample volume taken, and allowing lower levels to be detected.
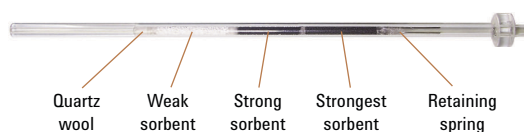


Quartz wool | Weak sorbent | Strong sorbent | Strongest sorbent | Retaining spring

Figure 1. Design of the focusing trap. Note the narrow-bore outlet and the long sorbent bed.



1  Ethane
2  Ethene
3  Acetylene
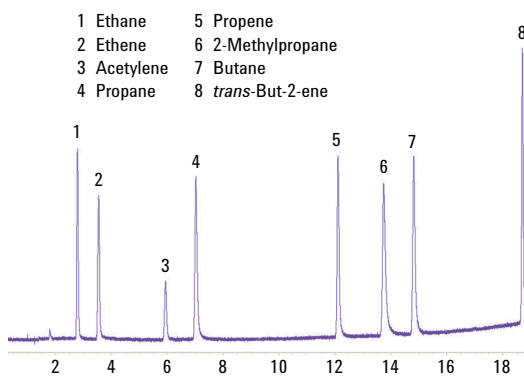4  Propane
5  Propene
6  2-Methylpropane
7  Butane
8  *trans*-But-2-ene

Figure 2. Chromatogram showing a splitless injection of 500 mL of the calibration standard.

## Experimental

### Breakthrough tests

**TD**

| | |
|---|---|
| Prepurge time: | 1 minute |
| Sampling rate: | 25 mL/min |
| Sampling time: | Various |
| Cold trap: | U-T17O3P-2S (Ozone precursor) |
| Cold trap low: | –30 °C |
| Cold trap high: | 325 °C |
| Cold trap hold: | 5 minutes |
| Flow path temperature: | 80 °C |

**GC**

| | |
|---|---|
| Column: | Agilent J&W GS-GasPro, 30 m × 0.32 mm |
| GC program: | 40 °C (hold 6 minutes), then 20 °C/min to 200 °C (hold 1 minute) |

### Two-column Deans switch GC sytem

**TD**

| | |
|---|---|
| Prepurge time: | 2 minutes |
| Sampling rate: | 25 mL/min |
| Sampling time: | Various |
| Cold trap: | U-T17O3P-2S (Ozone precursor) |
| Cold trap low: | –30 °C |
| Cold trap high: | 325 °C |
| Cold trap hold: | 5 minutes |
| Flow path temperature: | 80 °C |

**GC/FID**

| | |
|---|---|
| Inlet pressure: | 44.9 psi |
| Midpoint pressure: | 21.26 psi |
| GC oven program: | 30 °C (hold 12 minutes), then 5 °C/min to 170 °C, then 15 °C/min to 200 °C |
| Switching time: | 17.5 minutes |
| FID temperature: | 250 °C |
| Air flow: | 400 mL/min |
| $H_2$ flow: | 40 mL/min |

## Results and Discussion

### Breakthrough tests

All $C_2$ hydrocarbons are highly volatile species. Acetylene (ethyne) has a boiling point of –84 °C, and is the most difficult to trap and quantitatively retain without liquid cryogen. It requires careful selection of the cold trap sorbent(s) and focusing temperature. Experiments to determine the limit of quantitative retention (the breakthrough volume) were performed on an ozone precursor cold trap using the ppb-level certified gas standard generated by the National Physical Laboratory (Teddington, UK). Steadily increasing volumes of the gas standard were introduced, and a graph of detector response against sampled volume was plotted.

Figure 3 is a plot of the peak area against the sampled volume of calibration gas for acetylene, and shows that even at 1.5 L of sampled gas, there is no deviation from linearity, that is, there is negligible breakthrough.
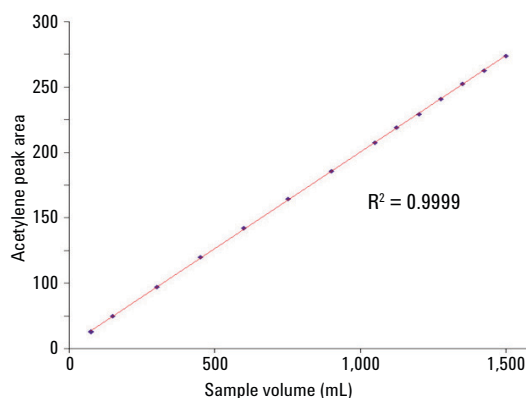


Figure 3. Plot of peak area against volume sampled for acetylene. Image courtesy of Ecole des Mines de Douai.

## Two-column Deans switch GC system

The column used in all previous tests was an Agilent J&W GS-GasPro, 30 m × 0.32 mm. Unfortunately, this column did not allow full resolution of the $C_4$ and $C_5$ components in the standard mixture. For better separation of these components, it was necessary to use a two-column system with a Deans switch (schematically illustrated in Figure 4).
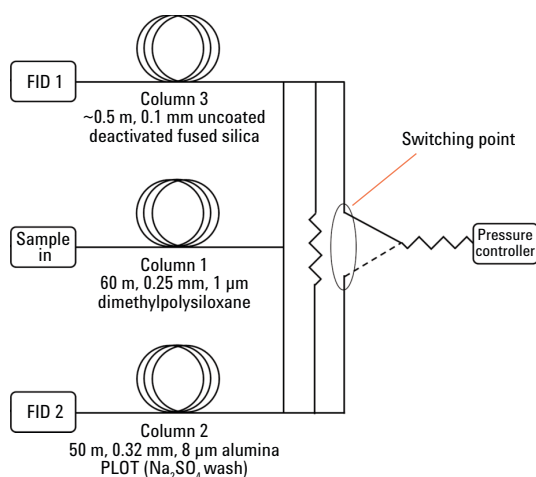


Figure 4. Schematic representation of the two-column ozone precursor analytical system.

All the effluent from the focusing trap of the desorber was directed into the dimethylpolysiloxane column at 40 °C. The $C_2$–$C_5$ compounds are unresolved on this column at this temperature, and are passed through the Deans switch into the alumina PLOT column as they elute from the primary column. For the first 17.5 minutes of the run, the Deans switch between the primary and secondary columns works in this direction. At this point, all the compounds eluting from the primary column are $C_6$ and higher, and are well-resolved. The Deans switch is activated, directing effluent from the primary column to the deactivated, uncoated fused silica link, and to the other FID.

Going forward, two chromatograms are produced in parallel: the $C_{6+}$ compounds from the dimethylpolysiloxane column (labeled FID 1), and the $C_2$–$C_6$ compounds from the alumina PLOT column (labeled FID 2).

Figure 5 shows a plot for the calibration gas run through the two-column system, and Figure 6 shows the equivalent plot for the 56-component US EPA ozone precursor mix.

1. Ethane
2. Ethene
3. Propane
4. Propene
5. 2-Methylpropane
6. *n*-Butane
7. Acetylene
8. *trans*-But-2-ene
9. But-1-ene
10. *cis*-But-2-ene
11. 2-Methylbutane
12. Pentane
13. Buta-1,3-diene
14. *trans*-Pent-2-ene
15. Pent-1-ene
16. 2-Methylpentane
17. Isoprene
18. *n*-Hexane
19. Benzene
20. 2,2,4-Trimethylpentane
21. *n*-Heptane
22. Toluene
23. Octane
24. Ethylbenzene
25. *m*- and *p*-Xylene
26. *m*- and *p*-Xylene
27. *o*-Xylene
28. 1,3,5-Trimethylbenzene
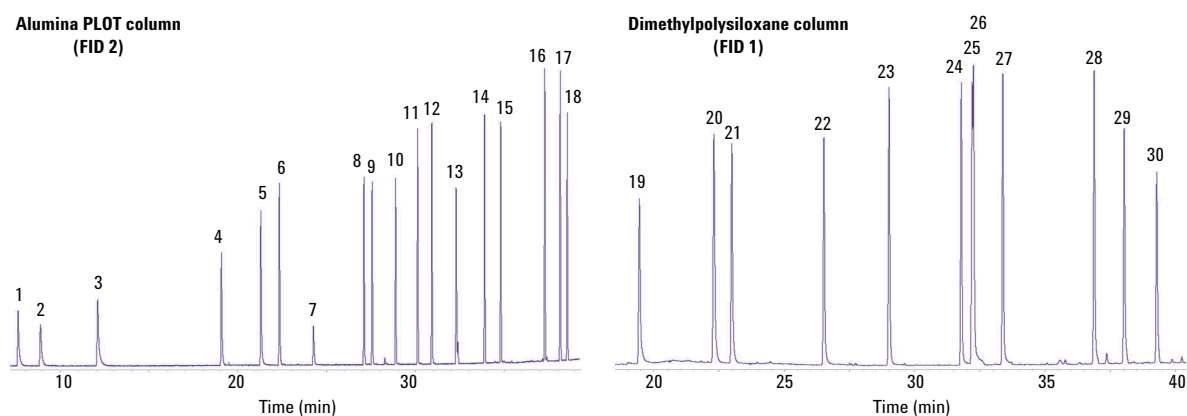29. 1,2,4-Trimethylbenzene
30. 1,2,3-Trimethylbenzene



Figure 5. Chromatograms for the ppb-level 30-component calibration standard (generated by NPL) on the two column analytical system. All components had a concentration in the range 3.83–4.16 ppb, with uncertainties for each of ±0.08 ppb.

1. Ethane
2. Ethene
3. Propane
4. Propene
5. 2-Methylpropane
6. *n*-Butane
7. Acetylene
8. *trans*-But-2-ene
9. But-1-ene
10. *cis*-But-2-ene
11. Cyclopentane
12. 2-Methylbutane
13. Pentane
14. *trans*-Pent-2-ene
15. Pent-1-ene
16. *cis*-Pent-2-ene
17. 2,2-Dimethylbutane
18. 2,3-Dimethylbutane
19. 2-Methylpentane
20. 3-Methylpentane
21. Isoprene
22. 2-Methylpent-1-ene
23. *n*-Hexane
24. Methylcyclopentane
25. 2,4-Dimethylpentane
26. Benzene
27. Cyclohexane
28. 2-Methylhexane
29. 2,3-Dimethylpentane
30. 3-Methylhexane
31. 2,2,4-Trimethylpentane
32. Heptane
33. Methylcyclohexane
34. 2,3,4-Trimethylpentane
35. Toluene
36. 2-Methylheptane

37. 3-Methylheptane
38. Octane
39. Ethylbenzene
40. *m*- and *p*-Xylene
41. Styrene
42. *o*-Xylene
43. Nonane
44. Isopropylbenzene
45. Propylbenzene
46. *m*-Ethyltoluene
47. *p*-Ethyltoluene
48. 1,3,5-Trimethylbenzene
49. *o*-Ethyltoluene
50. 1,2,4-Trimethylbenzene

51. Decane
52. 1,2,3-Trimethylbenzene
53. *m*-Diethylbenzene
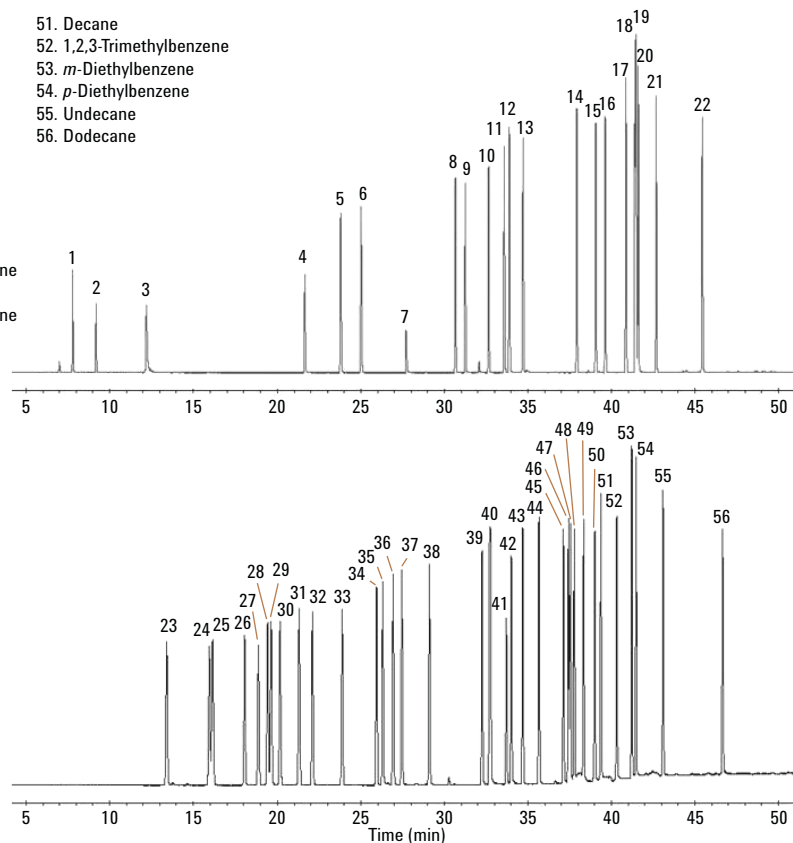54. *p*-Diethylbenzene
55. Undecane
56. Dodecane

Figure 6. Chromatograms for the ppb-level 56-component calibration standard (from the US EPA) on the two-column analytical system. Data courtesy of ITC, Korea.

## Reproducibility of retention time

Due to the nature of the two-column setup, the stability of the retention time can be related to the pressure balance in the system. With the added capability of electronic carrier gas control (ECC) on the UNITY 2 Air Server, stable retention times on both columns are achieved. Tables A1 and A2 (see Appendix) show the relative standard deviations for the compounds in the 30-component standard; those on the dimethylpolysiloxane column ($C_{6+}$ compounds) were close to 0.01%, and those in the alumina PLOT column ($C_2$–$C_6$ compounds) were in the range of 0.04–0.32%.

## Reliability study – multipoint calibrations

For a system to be reliable, stringent tests must be carried out. Figure 7 shows five repeat analyses of 500 mL of the ozone precursor calibration standard on the two-column system.

The repeat analyses appear identical, but to confirm this numerically, a 5-point calibration curve was generated, and five replicates at each level were analyzed (see Table A3 in the Appendix). Nearly all the relative standard deviations were below 1%, demonstrating the reliability of the method.
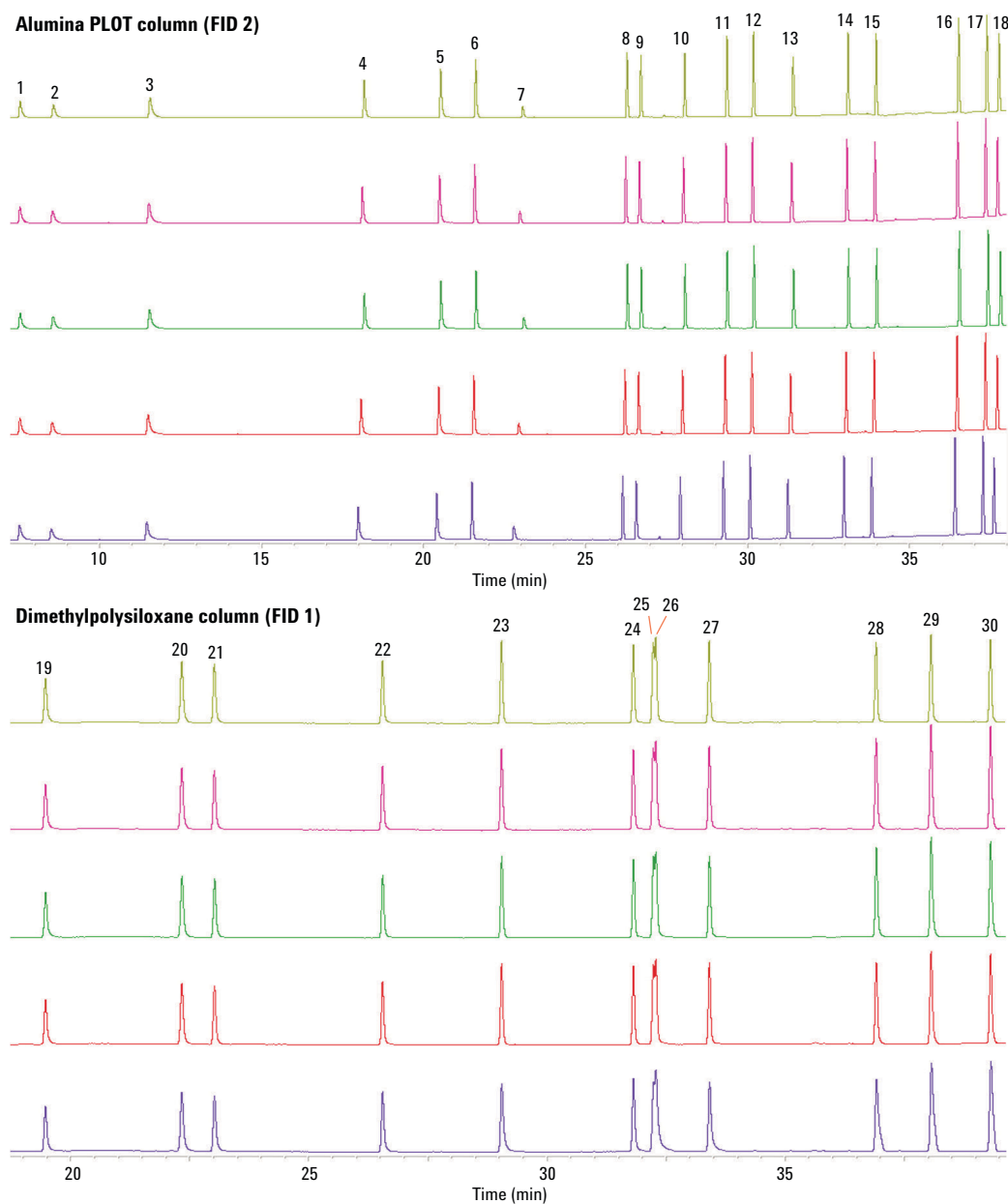
**Figure 7.** Repeat analysis of a splitless gas injection of a 500 mL sample of gas standard.

Each of the repeat calibrations was then plotted, and a linear relationship was derived. Table A4 (see Appendix) shows the corresponding $R^2$ values. $R^2$ values of 0.99 or above were seen for more than 98% of the data, confirming the reliability of the calibration.

French norm NF T90-2103 specifies a method for testing calibration data and systems in accordance with a stringent goodness-of-fit test. We used this F-test method to compare a theoretical calibration against the five 5-point experimental calibrations, assuming the homogeneity of the variances. The critical value ($F_{crit}$) corresponds to the value that F must exceed for this assumption to be incorrect, and in this case it is 4.103 at a risk level (a) of 1%.

Table 1 shows the F-values for each of the compounds, and they are all less than $F_{crit}$, so the calibration is acceptable.

Table 1. F-Test values.

| Compound | Calculated F-value |
|---|---|
| Ethane | 3.738 |
| Ethene | 2.063 |
| Propane | 1.172 |
| Propene | 3.422 |
| 2-Methylpropane | 0.132 |
| *n*-Butane | 3.149 |
| Acetylene | 3.199 |
| *trans*-But-2-ene | 0.178 |
| But-1-ene | 0.466 |
| *cis*-But-2-ene | 1.713 |
| 2-Methylbutane | 0.373 |
| Pentane | 0.417 |
| Buta-1,3-diene | 0.388 |
| *trans*-Pent-2-ene | 1.036 |
| Pent-1-ene | 0.309 |
| 2-Methylpentane | 0.433 |
| Isoprene | 1.221 |
| *n*-Hexane | 1.855 |
| *n*-Heptane | 1.456 |
| Benzene | 0.495 |
| 1,2,4-Trimethylpentane | 0.279 |
| Octane | 1.333 |
| Toluene | 1.267 |
| Ethylbenzene | 2.322 |
| *n*-Xylene | 3.186 |
| *n*-Xylene | 3.186 |
| *n*-Xylene | 2.381 |
| 1,3,5-Trimethylbenzene | 2.813 |
| 1,2,4-Trimethylbenzene | 0.952 |
| 1,2,3-Trimethylbenzene | 3.958 |

## Detection/quantitation limits

Signal-to-noise ratios for the 500 mL volume of standard using the two-column system are in the order of 250:1 for the light hydrocarbons at ~4 ppb, and 350:1 for compounds from *n*-butane upwards at ~4 ppb. Assuming a minimum detection signal of 3:1, approximate detection/quantitation limits for the 500 mL air samples were calculated as follows:

### $C_2$–$C_3$ hydrocarbons

Detection:          0.05 ppb

Quantification:  0.1 ppb

### $C_{4+}$ hydrocarbons

Detection:          0.03 ppb

Quantification:  0.06 ppb

## Suburban air monitoring

Analyzer performance for unattended field operation was evaluated in a forested semirural area, with high volumes of traffic during the working week and very few cars on weekends. Figure 8 shows a diurnal profile of various compounds from 16:40 on a Sunday through Monday evening. The difference between the two periods is distinct.

Most of the hydrocarbons were at low levels during the traffic-free periods, while rapid increases were seen during peak commuting hours. These data were collected at the end of the trial, and show that good analytical performance was maintained. Importantly, no user intervention was required during the trial, while detection limits, even in this relatively clean environment, were satisfactory.
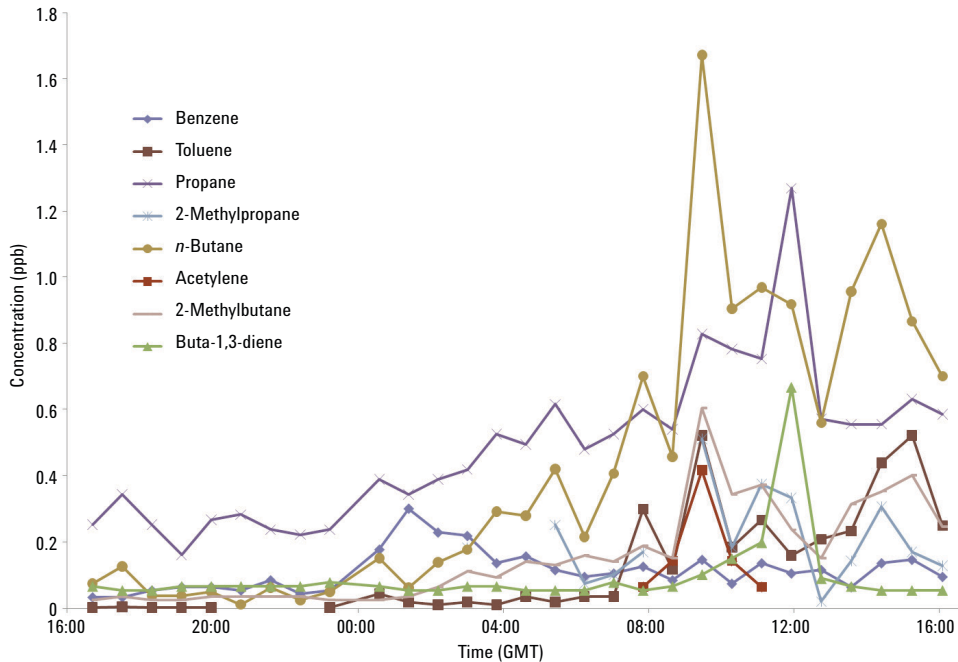
Figure 8. Diurnal profile of selected hydrocarbons, showing distinct differences between traffic-free and traffic-heavy periods.

## Conclusions

A reliable, semicontinuous, cryogen-free sampling and analysis system has been demonstrated for a challenging and complex mix of volatile and very volatile hydrocarbons, confirming Markes' UNITY 2 Air Server system as an excellent choice for those wishing to quantify ozone precursors in ambient air.

## References

1. Council Directive 96/62/EC of 27 September 1996 on ambient air quality assessment and management, Council of the European Parliament, 1996; and its 'daughter' directive, Directive 2000/69/EC of the European Parliament and of the Council of 16 November 2000 relating to limit values for benzene and carbon monoxide in ambient air, Council of the European Parliament, 2000. See http://ec.europa.eu/environment/air/legis.htm for more details.

2. Provisions for attainment and maintenance of national ambient air quality standards (US Clean Air Act Amendments of 1990). See http://www.epa.gov/air/caa/ for more details.

3. Revision de la norme NF T90-210: Qualite de l'eau. Protocole d'évaluation initiale des performances d'une méthode dans un laboratoire, Association Francaise de Normalisation, 2009. Available from http://www.boutique. afnor.org/NEL5DetailNormeEnLigne.aspx?&nivCtx= NELZ NELZ1A10A101A107&ts=3162565& CLE_ART=FA160221.

# Appendix

Table A1. Retention time stability on the dimethylpolysiloxane column ($C_{6+}$ compounds).

| Compound | Retention time RSD (%) (n = 15) |
|---|---|
| Benzene | 0.0090 |
| 2,2,4-Trimethylpentane | 0.0122 |
| *n*-Heptane | 0.0119 |
| Toluene | 0.0123 |
| Octane | 0.0127 |
| Ethylbenzene | 0.0121 |
| *m*- and *p*-Xylene | 0.0131 |
| *o*-Xylene | 0.0133 |
| 1,3,5-Trimethylbenzene | 0.0119 |
| 1,2,4-Trimethylbenzene | 0.0108 |
| 1,2,3-Trimethylbenzene | 0.0104 |

Table A2. Retention time stability on the alumina PLOT column ($C_2$–$C_6$ compounds).

| Compound | Retention time RSD (%) (n = 15) |
|---|---|
| Ethane | 0.0413 |
| Ethene | 0.1375 |
| Propane | 0.1695 |
| Propene | 0.2976 |
| 2-Methylpropane | 0.1776 |
| *n*-Butane | 0.1600 |
| Acetylene | 0.3204 |
| *trans*-But-2-ene | 0.1644 |
| But-1-ene | 0.1552 |
| *cis*-But-2-ene | 0.1360 |
| 2-Methylbutane | 0.1339 |
| Pentane | 0.1217 |
| Buta-1,3-diene | 0.1558 |
| *trans*-Pent-2-ene | 0.1013 |
| Pent-1-ene | 0.1145 |
| 2-Methylpentane | 0.1008 |
| Isoprene | 0.0972 |
| *n*-Hexane | 0.1313 |

Table A3. Reproducibility of the 30-component gas standard for five sample volumes.

| Compound | Response RSD (%) (n = 5) | | | | |
|---|---|---|---|---|---|
| | 250 mL | 375 mL | 500 mL | 625 mL | 750 mL |
| Ethane | 0.8 | 0.4 | 0.3 | 0.4 | 0.9 |
| Ethene | 0.6 | 0.4 | 1.2 | 1.2 | 0.5 |
| Propane | 0.3 | 2.0 | 1.4 | 1.5 | 1.6 |
| Propene | 0.7 | 0.3 | 0.2 | 0.7 | 0.6 |
| 2-Methylpropane | 1.0 | 0.8 | 0.5 | 0.3 | 0.5 |
| *n*-Butane | 1.3 | 0.8 | 0.5 | 1.2 | 0.6 |
| Acetylene | 3.4 | 2.9 | 2.2 | 3.5 | 0.8 |
| *trans*-But-2-ene | 0.7 | 0.5 | 0.4 | 0.3 | 0.6 |
| But-1-ene | 0.4 | 0.9 | 0.8 | 0.9 | 1.9 |
| *cis*-But-2-ene | 0.5 | 0.6 | 0.2 | 0.5 | 0.4 |
| 2-Methylbutane | 0.5 | 0.3 | 0.3 | 0.3 | 0.3 |
| Pentane | 0.5 | 0.3 | 0.4 | 0.3 | 0.4 |
| Buta-1,3-diene | 0.9 | 0.9 | 0.8 | 0.5 | 0.4 |
| *trans*-Pent-2-ene | 0.8 | 0.5 | 0.2 | 0.3 | 0.4 |
| Pent-1-ene | 0.5 | 0.5 | 0.2 | 0.4 | 0.4 |
| 2-Methylpentane | 1.2 | 0.5 | 0.6 | 0.7 | 0.6 |
| Isoprene | 0.7 | 0.4 | 1.0 | 0.4 | 0.3 |
| *n*-Hexane | 0.3 | 0.4 | 0.5 | 0.4 | 0.5 |
| Benzene | 0.8 | 0.5 | 0.6 | 0.6 | 0.5 |
| 2,2,4-Trimethylpentane | 0.2 | 0.4 | 0.5 | 0.5 | 0.6 |
| *n*-Heptane | 1.0 | 0.4 | 0.7 | 0.7 | 0.9 |
| Toluene | 0.8 | 0.8 | 0.6 | 0.9 | 1.2 |
| Octane | 1.1 | 1.2 | 1.0 | 1.4 | 1.4 |
| Ethylbenzene | 0.5 | 1.0 | 1.2 | 0.9 | 2.1 |
| *m*- and *p*-Xylene | 1.3 | 0.3 | 0.5 | 2.8 | 0.4 |
| *o*-Xylene | 3.8 | 2.2 | 2.1 | 2.9 | 3.2 |
| 1,3,5-Trimethylbenzene | 1.9 | 1.2 | 4.3 | 3.1 | 1.3 |
| 1,2,4-Trimethylbenzene | 5.5 | 1.7 | 1.8 | 2.0 | 2.7 |
| 1,2,3-Trimethylbenzene | 4.5 | 1.6 | 2.3 | 2.5 | 2.0 |

Table A4. $R^2$ values for five repeats of the 5-point calibration.

| Compound | Calibration 1 | Calibration 2 | Calibration 3 | Calibration 4 | Calibration 5 |
|---|---|---|---|---|---|
| Ethane | 0.9999 | 0.9997 | 1.0000 | 0.9997 | 0.9997 |
| Ethene | 0.9996 | 0.9997 | 0.9984 | 0.9989 | 0.9998 |
| Propane | 0.9998 | 0.9991 | 0.9987 | 0.9998 | 0.9999 |
| Propene | 1.0000 | 0.9999 | 0.9998 | 0.9997 | 0.9997 |
| 2-Methylpropane | 0.9999 | 1.0000 | 0.9999 | 0.9999 | 0.9999 |
| *n*-Butane | 0.9996 | 0.9995 | 0.9996 | 0.9997 | 0.9998 |
| Acetylene | 0.9994 | 0.9973 | 0.9992 | 0.9897 | 0.9911 |
| *trans*-But-2-ene | 0.9998 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| But-1-ene | 0.9999 | 1.0000 | 0.9999 | 1.0000 | 1.0000 |
| *cis*-But-2-ene | 0.9998 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2-Methylbutane | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| Pentane | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| Buta-1,3-diene | 0.9999 | 1.0000 | 0.9999 | 1.0000 | 1.0000 |
| *trans*-Pent-2-ene | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| Pent-1-ene | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2-Methylpentane | 1.0000 | 1.0000 | 0.9999 | 0.9998 | 0.9999 |
| Isoprene | 0.9997 | 0.9999 | 0.9999 | 1.0000 | 0.9998 |
| *n*-Hexane | 0.9999 | 1.0000 | 0.9999 | 0.9998 | 0.9999 |
| Benzene | 0.9997 | 1.0000 | 0.9999 | 1.0000 | 0.9999 |
| 2,2,4-Trimethylpentane | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| *n*-Heptane | 1.0000 | 1.0000 | 0.9999 | 1.0000 | 1.0000 |
| Toluene | 1.0000 | 0.9999 | 1.0000 | 0.9998 | 1.0000 |
| Octane | 0.9999 | 1.0000 | 1.0000 | 0.9999 | 1.0000 |
| Ethylbenzene | 0.9993 | 0.9998 | 1.0000 | 0.9996 | 0.9995 |
| *m*- and *p*-Xylene | 0.9934 | 0.9992 | 0.9995 | 0.9998 | 1.0000 |
| *o*-Xylene | 0.9996 | 0.9988 | 0.9990 | 0.9985 | 0.9998 |
| 1,3,5-Trimethylbenzene | 0.9994 | 0.9967 | 0.9916 | 0.9850 | 0.9860 |
| 1,2,4-Trimethylbenzene | 0.9991 | 0.9927 | 0.9994 | 0.9986 | 0.9957 |
| 1,2,3-Trimethylbenzene | 0.9945 | 0.9998 | 0.9968 | 0.9901 | 0.9992 |

# For More Information

These data represent typical results. For more information on our products and services, visit our Web site at www.agilent.com/chem.

www.agilent.com/chem

**Agilent Technologies**