

Application Note 016

Round-the-clock, on-line and cryogen-free monitoring of hydrocarbons from acetylene to trimethylbenzene in ambient air

Summary

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



Introduction

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 butadiene). 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.

Background to the analytical methodology

The UNITY-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.

In summary, sample air is pulled directly onto an electrically-cooled, sorbent-packed focusing trap at a controlled flow rate. No liquid cryogen is 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 vapour. This transfer may be performed splitless for maximum sensitivity. Once the trap has desorbed, it re-cools, re-equilibrates to the trapping temperature and begins collection of the next sample while analysis of the previous sample is ongoing. The UNITY-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.

In May 2016, Markes International launched the 'xr' series of thermal desorption instruments, which offer extended re-collection capability, extended analyte range and extended reliability.

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 employed). Table A1 (see Appendix) provides the full 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 for many reasons. The narrow-bore design of the UNITY 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.

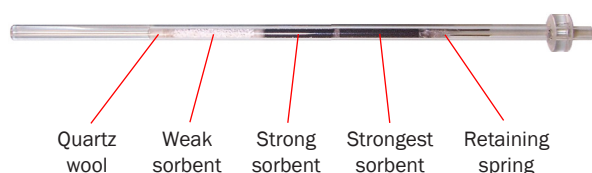


Figure 1: Design of the focusing trap. Note the narrow-bore outlet and the long sorbent bed.

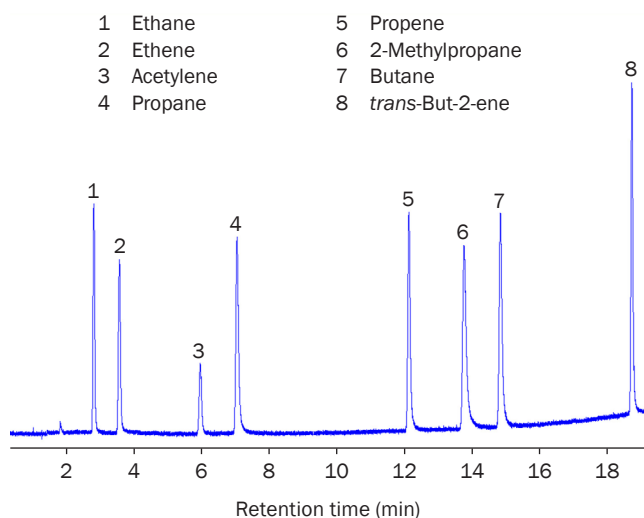


Figure 2: Chromatogram showing a splitless injection of 500 mL of the calibration standard.

Experimental

(a) Breakthrough tests

TD:

Prepurge time:	1 min
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 min
Flow path temp.:	80 °C

GC:

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

(b) Two-column Deans switch GC system

TD:

Prepurge time:	2 min
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 min
Flow path temp.:	80 °C

GC-FID:

Inlet pressure:	44.9 psi
Midpoint pressure:	21.26 psi
GC oven program:	30 °C (hold 12 min), then 5 °C/min to 170 °C, then 15 °C/min to 200 °C
Switching time:	17.5 min
FID temp.:	250 °C
Air flow:	400 mL/min
H ₂ flow:	40 mL/min

Results and discussion

(a) Breakthrough tests

All the C₂ hydrocarbons are highly volatile species. Acetylene (ethyne) has a boiling point of -84 °C and is the most difficult to trap, and to quantitatively retain it without liquid cryogen 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 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, *i.e.* there is negligible breakthrough.

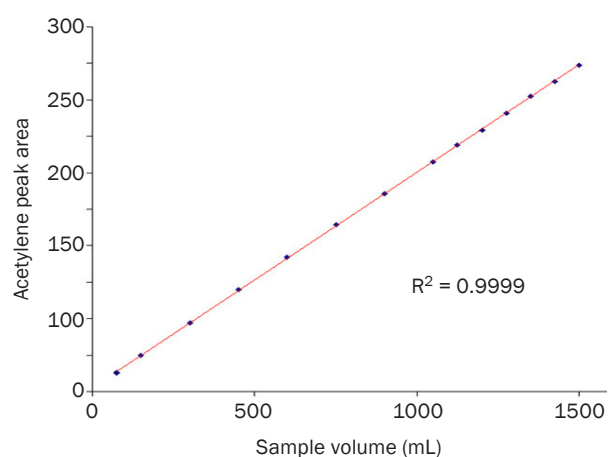


Figure 3: Plot of peak area against volume sampled for acetylene. *Image courtesy of Ecole des Mines de Douai.*

(b) Two-column Deans switch GC system

The column used in all previous tests was a 30 m × 0.32 mm i.d. J&W GS-GasPro. Unfortunately, this column did not allow full resolution of the C₄ and C₅ 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).

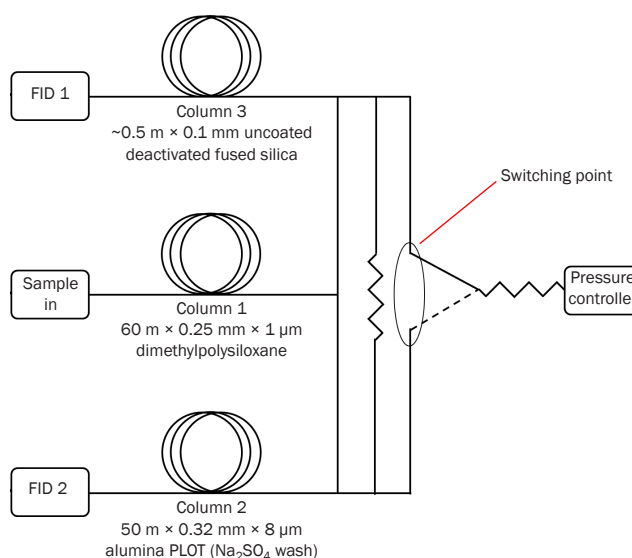


Figure 4: Schematic representation of the two-column ozone precursor analytical system.

All the effluent from the focusing trap of the desorber was directed into the dimethylpolysiloxane column at 40 °C. The C₂-C₅ compounds are unresolved on this column at this temperature, and are passed, *via* 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 C₆ and higher, and are well-resolved. The Deans switch is thus activated, directing effluent from the primary column to the deactivated, uncoated fused silica link and to the other FID.

From this point on, two chromatograms are produced in parallel; the C₆₊ compounds from the dimethylpolysiloxane column (labelled FID 1), and the C₂-C₆ compounds from the alumina PLOT column (labelled 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	7 Acetylene	13 Butadiene	19 Benzene	25] <i>m</i> - and <i>p</i> -Xylene
2 Ethene	8 <i>trans</i> -But-2-ene	14 <i>trans</i> -Pent-2-ene	20 2,2,4-Trimethylpentane	26] <i>m</i> - and <i>p</i> -Xylene
3 Propane	9 But-1-ene	15 Pent-1-ene	21 <i>n</i> -Heptane	27 <i>o</i> -Xylene
4 Propene	10 <i>cis</i> -But-2-ene	16 2-Methylpentane	22 Toluene	28 1,3,5-Trimethylbenzene
5 2-Methylpropane	11 2-Methylbutane	17 Isoprene	23 Octane	29 1,2,4-Trimethylbenzene
6 <i>n</i> -Butane	12 Pentane	18 <i>n</i> -Hexane	24 Ethylbenzene	30 1,2,3-Trimethylbenzene

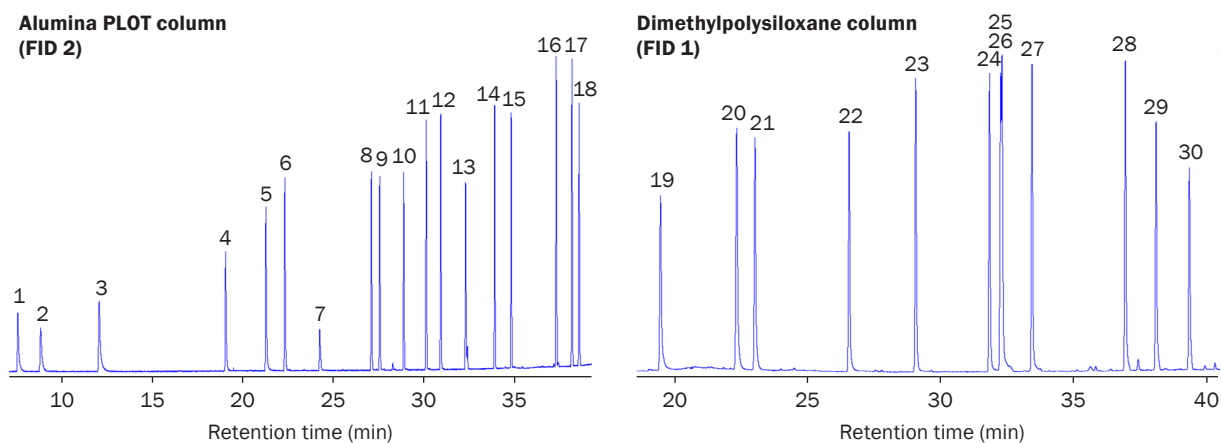


Figure 5: Chromatograms for the ppb-level 30-component calibration standard (generated by NPL) on the two-column analytical system. All components had a concentration in the range 3.83–4.16 ppb, with uncertainties for each of ± 0.08 ppb.

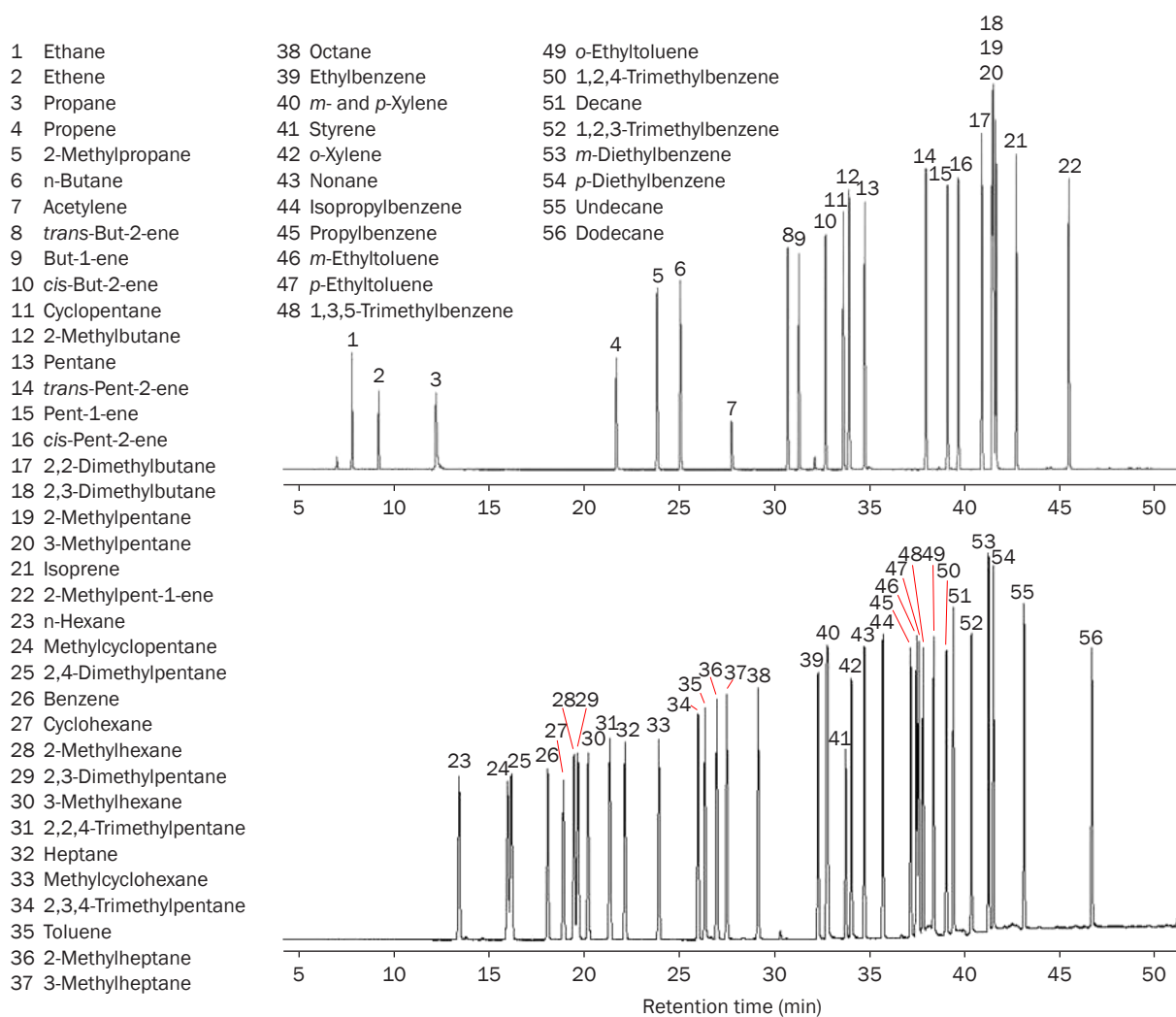


Figure 6: Chromatograms for the ppb-level 56-component calibration standard (from the US EPA) on the two-column analytical system. Data courtesy of ITC, Korea.

Reproducibility of retention time

Due to the nature of the two-column set-up, 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-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 0.04–0.32%.

Reliability study – multipoint calibrations

In order 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.

As can be seen, the repeat analyses appear identical, but to confirm this numerically, a 5-point calibration curve was generated, and five replicates at each level were analysed (see Table A3 in the Appendix). Nearly all the relative standard deviations were below 1%, demonstrating the reliability of the method.

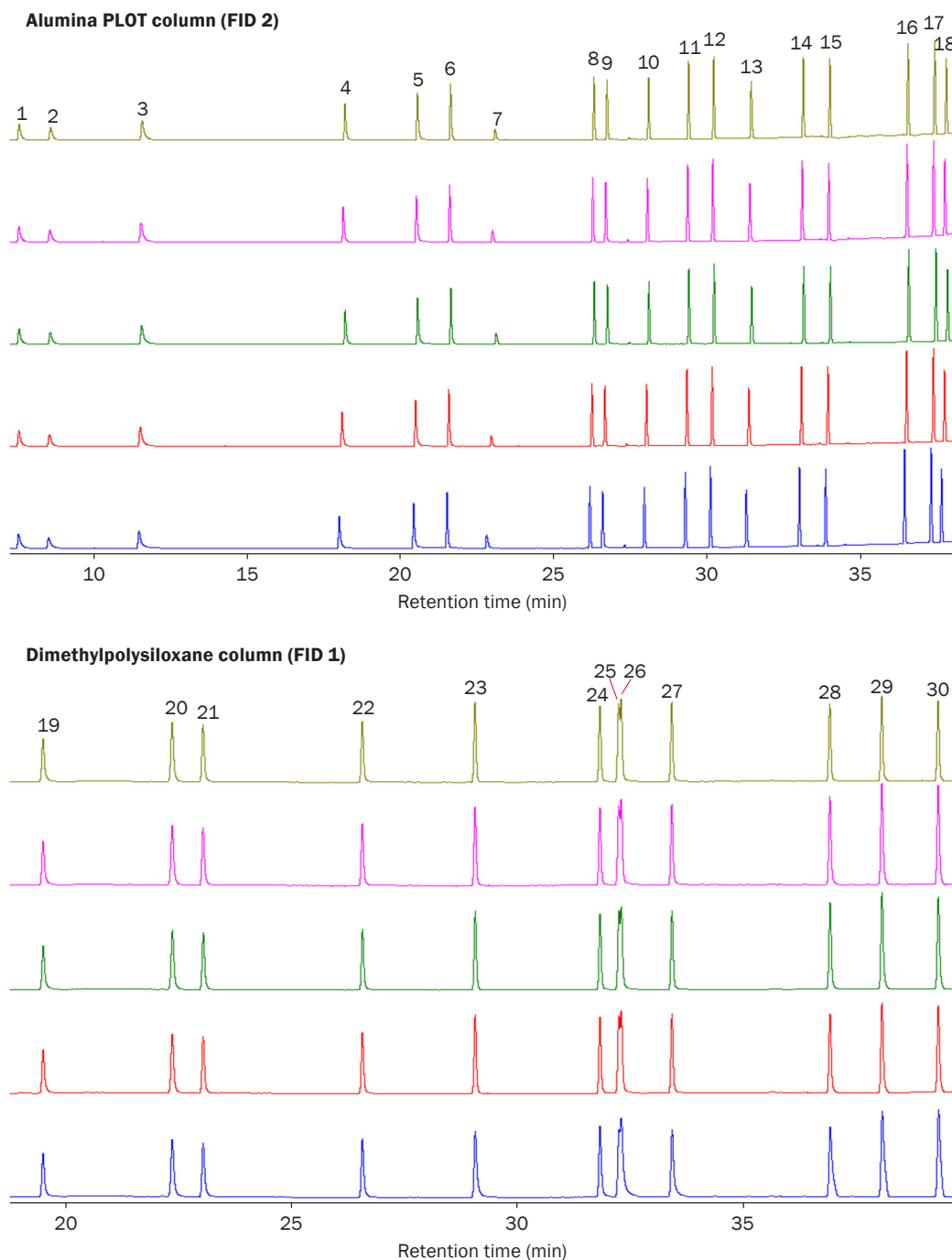


Figure 7: Repeat analysis of a splitless gas injection of a 500 mL sample of gas standard.

Each of the repeat calibrations was then plotted and a linear relationship derived; the corresponding R^2 values are provided in Table A4 (see Appendix). 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 (α) 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.

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; quantitation: 0.1 ppb

C_{4+} hydrocarbons:

Detection: 0.03 ppb; quantitation: 0.06 ppb

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
<i>trans</i> -But-2-ene	0.178
But-1-ene	0.466
<i>cis</i> -But-2-ene	1.713
2-Methylbutane	0.373
Pentane	0.417
Butadiene	0.388
<i>trans</i> -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
<i>m</i> -Xylene	3.186
<i>p</i> -Xylene	
<i>o</i> -Xylene	2.381
1,3,5-Trimethylbenzene	2.813
1,2,4-Trimethylbenzene	0.952
1,2,3-Trimethylbenzene	3.958

Table 1: F -test values.

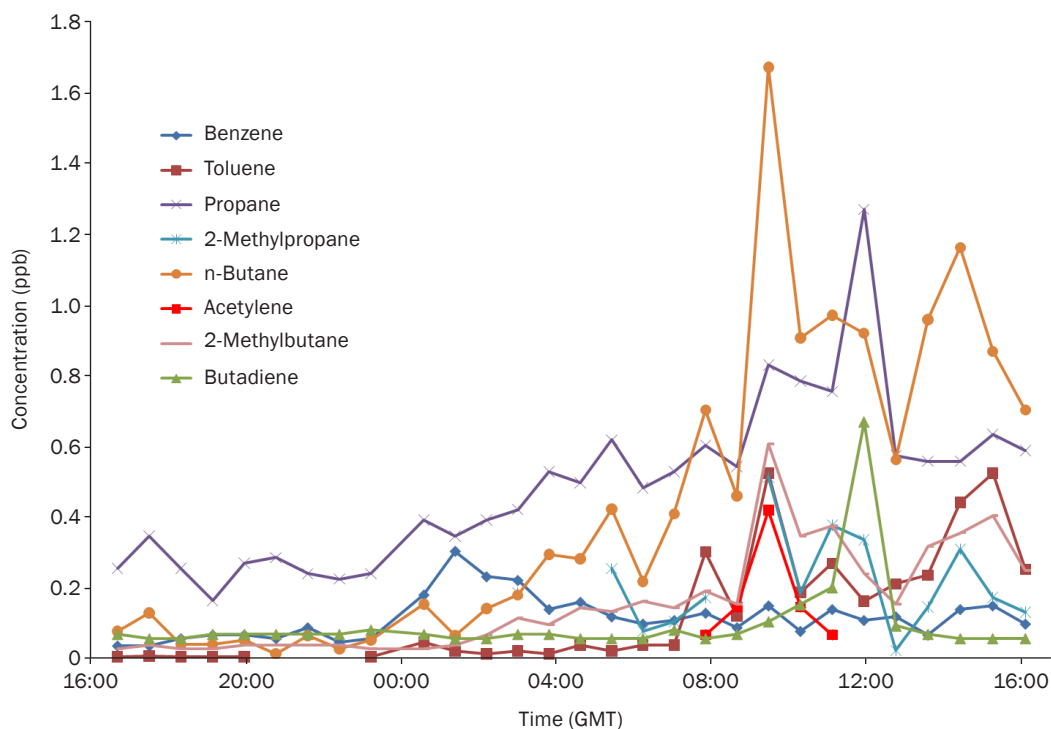


Figure 8: Diurnal profile of selected hydrocarbons, showing distinct differences between traffic-free and traffic-heavy periods.

Suburban air monitoring

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

Most of the hydrocarbons were at low levels during the traffic-free periods, whilst 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 also satisfactory.

Conclusions

A reliable, semi-continuous, cryogen-free sampling and analysis system has been demonstrated for this challenging and complex mix of volatile and very volatile hydrocarbons, confirming Markes' UNITY-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/norme/nf-t90-210/qualite-de-l-eau-protocole-d-evaluation-initiale-des-performances-d-une-methode-dans-un-laboratoire/article/771330/fa160221>.

Trademarks

Air Server™ and UNITY™ are trademarks of Markes International.

Applications were performed under the stated analytical conditions. Operation under different conditions, or with incompatible sample matrices, may impact the performance shown.

Appendix

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
<i>m</i> - and <i>p</i> -Xylene	0.0131
<i>o</i> -Xylene	0.0133
1,3,5-Trimethylbenzene	0.0119
1,2,4-Trimethylbenzene	0.0108
1,2,3-Trimethylbenzene	0.0104

Table A1: Retention time stability on the dimethylpolysiloxane column (C₆₊ 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
<i>trans</i> -But-2-ene	0.1644
But-1-ene	0.1552
<i>cis</i> -But-2-ene	0.1360
2-Methylbutane	0.1339
Pentane	0.1217
Butadiene	0.1558
<i>trans</i> -Pent-2-ene	0.1013
Pent-1-ene	0.1145
2-Methylpentane	0.1008
Isoprene	0.0972
n-Hexane	0.1313

Table A2: Retention time stability on the alumina PLOT column (C₂-C₆ compounds).

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
<i>trans</i> -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
<i>cis</i> -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
Butadiene	0.9	0.9	0.8	0.5	0.4
<i>trans</i> -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
<i>m</i> - and <i>p</i> -Xylene	1.3	0.3	0.5	2.8	0.4
<i>o</i> -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 A3: Reproducibility of the 30-component gas standard for five sample volumes.

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
<i>trans</i> -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
<i>cis</i> -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
Butadiene	0.9999	1.0000	0.9999	1.0000	1.0000
<i>trans</i> -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
<i>m</i> - and <i>p</i> -Xylene	0.9934	0.9992	0.9995	0.9998	1.0000
<i>o</i> -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

Table A4: R² values for five repeats of the five-point calibration.