

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

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## 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 ethyne (acetylene) to trimethylbenzene, and are generally referred to as 'ozone precursors'. Vehicle emissions are thought to be the main source of these compounds.

European and US regulations<sup>1,2</sup> 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 1,3-butadiene).



C<sub>2</sub> to C<sub>10</sub> hydrocarbons, originating from car exhausts, have been identified as precursors to the formation of street-level ozone and urban smog. US, European and other regulators require round-the-clock monitoring of these compounds in major urban centers during the summer months. 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.



Figure 1: UNITY 2-Air Server system (left) and canister (right)

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.

## Ozone precursor analysis

### Experimental

- Using a UNITY 2-Air Server system, sample air is pulled from the sample container (e.g. a canister; see Figure 1) through an optionally incorporated permeable membrane dryer, directly onto an electrically-cooled, sorbent-packed focusing trap at a controlled flow rate. No liquid cryogen is required. The membrane dryer selectively eliminates water and other low molecular weight polar components; this reduces the risk of interference from unknown species and facilitates 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.

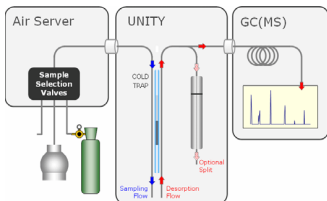


Figure 2: Schematic showing the sampling options with the UNITY 2-Air Server system and the subsequent flow of sample through the system

- 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 2-Air Server also offers automatic interchange between three sample channels (typically sample, reference and blank) for remote system calibration/validation as per user requirements. An 8-channel option is also available.

## Results: Breakthrough

All the C<sub>2</sub> hydrocarbons are highly volatile species. Ethyne (acetylene), has a boiling point of -89°C and is the most difficult to trap. To quantitatively retain it without liquid cryogen requires careful selection of the focusing trap sorbent(s) and focusing temperature. The focusing trap design is also important to allow injection of compounds into a narrow band of vapour even when splitless analysis is required. This true splitless analysis allows -low levels of detection to be achieved.



Breakthrough volume experiments were performed on the selected focusing 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 detector response against sampled volume was plotted. Breakthrough occurs when the data deviates from a linear relationship, i.e. when the species of interest are no longer quantitatively retained. Data from the low volumes of standard introduced were also used to estimate detection limits.

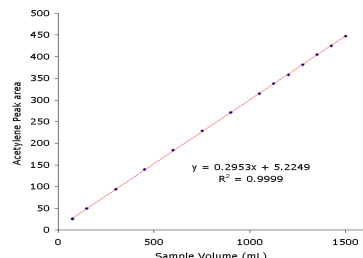


Figure 3: Peak area versus volume sampled for acetylene.

Figure 3 shows that there is good reproducibility and negligible breakthrough for acetylene even at 1500 mL of sampled gas. Field sampling volumes up to 1500 mL (30 min sampling at 50 mL/min) may therefore be used.

## Results: Real air samples

Analysers performance for unattended field operation was evaluated during a five-day trial. Figure 4 shows a sequence of ambient air profiles running from before dawn through to the height of rush hour in a semi-rural environment. These data were collected at the end of the trial, and show that good analytical performance was maintained. No user intervention was required during the trial. Detection limits in this relatively clean environment were also satisfactory.

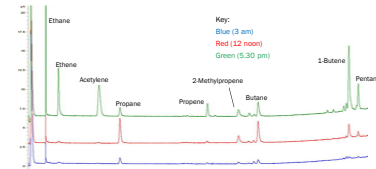


Figure 4: Online monitoring of semi-rural ambient air showing how the profile changes over time

The column used in all previous tests was a 30 m x 0.32 mm i.d. Agilent J&W GS-GasPro. Unfortunately, this column did not allow full resolution of the C<sub>4</sub> and C<sub>5</sub> components in the standard mixture. Therefore, to effect better separation of the C<sub>4</sub> and C<sub>5</sub> components a two-column system with a Deans switch was used. All the effluent from the focusing trap of the desorber was directed into the dimethylpolysiloxane column at 40°C. The C<sub>2</sub>-C<sub>5</sub> 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.

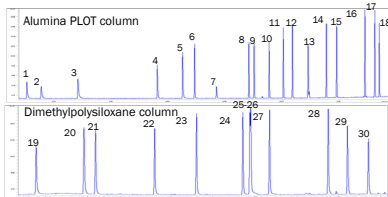


Figure 5: 30-component calibration gas injection on two-column analytical system (for compound index see Table 1)

For the first 12–13 minutes of the run, the Deans switch between the primary and secondary columns works in this direction. At this point, the compounds eluting from the primary column are C<sub>6</sub> and are well resolved. The Deans switch then activates, directing effluent from the primary column to the deactivated uncoated fused-silica link and the other FID. From this point on, two chromatograms are produced in parallel on each FID – the C<sub>2</sub>-C<sub>5</sub> compounds from the alumina PLOT column (FID 1) and the C<sub>6</sub>-C<sub>10</sub> compounds from the dimethylpolysiloxane column (FID 2). Figure 5 shows the plot for the 30-component ozone precursor mixture.

Compound	Peak number	Compound	Peak number
Ethane	1	2-Methylpentane	16
Ethene	2	Isoprene	17
Propane	3	n-Hexane	18
Propene	4	n-Heptane	19
2-Methylpropane	5	Benzene	20
n-Butane	6	2,2,4-Trimethylpentane	21
Acetylene (Ethyne)	7	Octane	22
trans-2-Butene	8	Toluene	23
But-1-ene	9	Ethylbenzene	24
cis-2-Butene	10	m- + p-Xylene	25 + 26
2-Methylbutane	11	o-Xylene	27
Pentane	12	1,3,5-Trimethylbenzene	28
1,3-Butadiene	13	1,2,4-Trimethylbenzene	29
trans-2-Pentene	14	1,2,3-Trimethylbenzene	30
Pent-1-Ene	15		

Table 1. 30 ozone precursors

## Conclusions

A reliable, continuous, cryogen-free sampling and GC-FID analysis system has been demonstrated for this challenging and complex mix of volatile and very volatile hydrocarbons. Markes' series 2 TD systems offer splitless desorption and uniquely high cryogen-free retention volumes for ultra-volatiles such as acetylene and ethane. Systems can be operated in remote, unattended monitoring stations, with data accessed via telemetry and processed/validated at remote network control centers.

References  
 1. Council Directive 96/62/EC (on ambient air quality assessment and management), and its "daughter" directive 2000/69/EC, (relating to limit values for benzene and carbon monoxide in ambient air).  
 2. 1990 US Clean Air Act Amendments.