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Application Note 159

The impact of COVID-19 lockdowns on New York City's air quality: continuous, cryogen-free on-line monitoring of PAMS in ambient air using hydrogen carrier gas

Summary

This study demonstrates the advantages of using Markes' Multi-Gas thermal desorption (TD) with gas chromatography (GC) and hydrogen carrier gas for the analysis of ozone precursors in air. Also presented is a case study and some new findings possible thanks to the reduced traffic pollution during lockdown periods.

Introduction

Helium is commonly used as GC carrier gas but is a finite resource that is increasingly expensive and difficult to source. It must be extracted and stored before being shipped around the world, giving it a high carbon footprint. Hydrogen, on the other hand, is simple to generate on-site and on-demand using water and electricity, so seems to be the obvious environmentally friendly alternative. Securing against helium shortages in the long term and offering immediate cost and operational savings, hydrogen also promises shorter analytical cycle times and faster sample throughput whilst being the optimum choice in remote locations where access is limited.

Markes' world leading -xr range of TD instruments are now certified for safe operation with hydrogen carrier gas as well as helium and nitrogen. In these new systems, no TD features or functions are compromised by using hydrogen, and all thermal desorbers for tube-based, on-line and canister TD–GC–MS analysis can be configured with any choice of carrier gas without changing system hardware.

Hydrogen can clearly be used to future-proof against dwindling helium sources but it is also ideal for monitoring ambient air at remote locations or from mobile laboratories. This type of sampling normally requires a portable source of carrier gas, and a hydrogen generator would be an advantage, particularly for its consistent hydrogen supply, low maintenance requirements and ease of use.

The US EPA Photochemical Assessment Monitoring Stations (PAMS)[1] are a network of ozone precursor monitoring stations that were set up to meet the requirements of the Clean Air Act.[2] The requirements are reviewed regularly, but the main objective is to form a database of ozone precursors and meteorological measurements to support the development of an ozone model and to track any trends with the identified compounds and their concentrations. The TD–GC requirements include continuous hourly monitoring of volatile organic compounds (VOCs) of which there is a list of 59 compounds for priority and optional monitoring.[3] More information on the setup of US EPA PAMS with Markes' thermal desorbers can be found in Application Note 016[4] (GC–FID) and Application Note 129[5] (GC–MS).

This application note focuses on the impact of switching regulated TD–GC air monitoring methods to hydrogen carrier gas following the US EPA PAMS method. Faster run times while maintaining separation of critical compounds and excellent system stability are shown. A case study from the New York Botanic Gardens located in the Bronx, New York City, showcases the benefits of using Multi-Gas enabled TD during the COVID-19 city-wide lockdown, highlighting the advantages of using hydrogen as a carrier gas in remote locations and the subsequent results during this unique air monitoring opportunity.

Analytical system

The analytical system used for this study comprised Multi-Gas enabled instruments including a CIA *Advantage*-xr™ autosampler with a Kori-xr™ water condenser and UNITY-xr™ thermal desorber (Figure 1), coupled with a dual-column GC–FID system. The entire system is cryogen-free and can be controlled remotely, making it ideal for unattended operation in remote field locations.

Figure 1: Multi-Gas enabled UNITY–Kori–CIA *Advantage*-xr™.

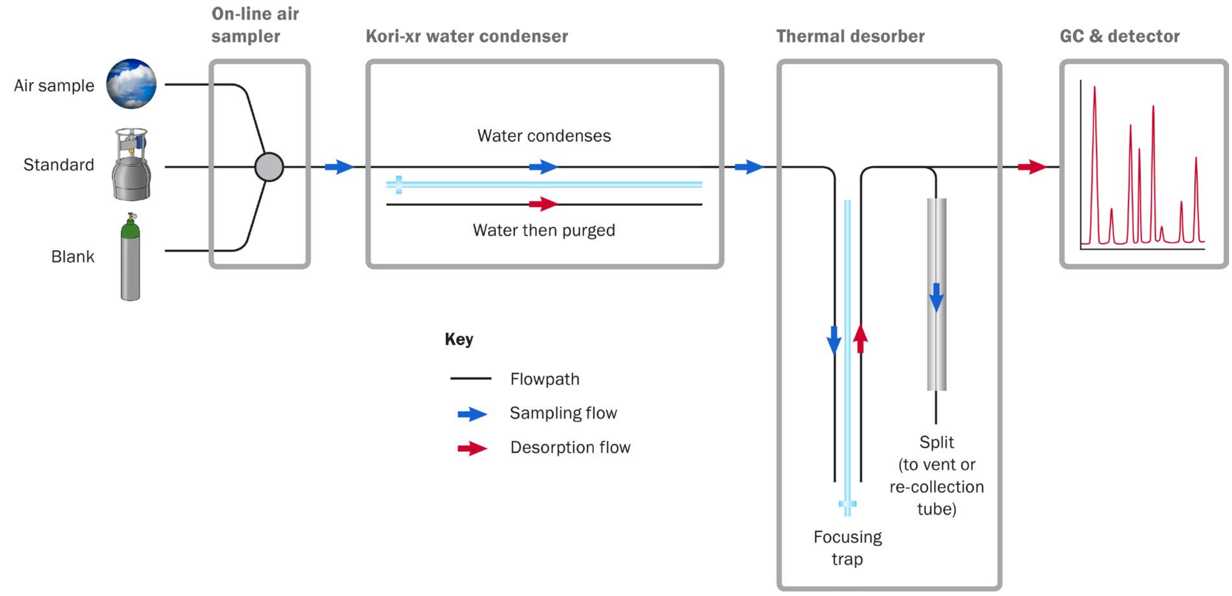

Figure 2: TD–GC–FID configuration.

The individual components of the system are briefly described next.

The CIA *Advantage*-xr is a versatile four-channel autosampler for round-the-clock speciated measurement of multiple trace-level VOCs in air or pure gases, either on-line or with canister or bag sampling. The four channels automate the sequencing between sample, calibration and blank, and can be upgraded to 17 channels with the CIA Satellite-xr. This combines controlled-flow sampling with cryogen-free concentration technology, which overcomes the limitations of cryogen-cooled systems such as high cost and flow-path blockages caused by ice. The CIA *Advantage*-xr also offers internal standard addition *via* a 1-mL loop, which allows a small volume of a high-concentration internal standard gas to be used, reducing the need for dilution and saving on the consumption of expensive standard gases.

To achieve optimum results for 100% relative humidity (%RH) ambient air,[5] the amount of residual water reaching the GC–FID system must be very low. For this reason, Markes has developed the Dry-Focus3™ approach. With this system, ambient air samples pass through a Kori-xr device that, without liquid cryogen, efficiently removes humidity from the air stream while preserving the compounds of interest (Figure 2). With most of the excess water removed, samples then pass into the trap of the UNITY-xr thermal desorber, held at -30°C, where the analytes are quantitatively trapped. The trap is then purged with carrier gas in the sampling direction to eliminate oxygen and further reduce water without any loss or breakthrough of the analytes retained. Finally, the flow of carrier gas through the focusing trap is reversed, and it is heated rapidly (up to 100°C/s) to inject the analytes onto the GC column.

At this point, there is the ability to split the sample, either to vent or onto a clean sorbent tube for storage and re-analysis later (although it should be noted that sorbent tubes are not able to retain very volatile compounds such as acetylene). The process of sample splitting and re-collection can be fully automated by adding an ULTRA-xr™ tube autosampler.

Experimental

The UNITY–Kori–CIA *Advantage*-xr Trace system was installed onto a GC–FID located at the New York Botanic Gardens in the Bronx, New York City. The real air samples were taken continuously throughout the monitoring season, during all weathers, with samples expected to be 30–90%RH.

The chromatograms in Figure 3 and Figure 4 display results for the 56-component mix of the US EPA Ozone Precursor standard with compounds ranging from ethane to dodecane (Restek part number 34420-PI).

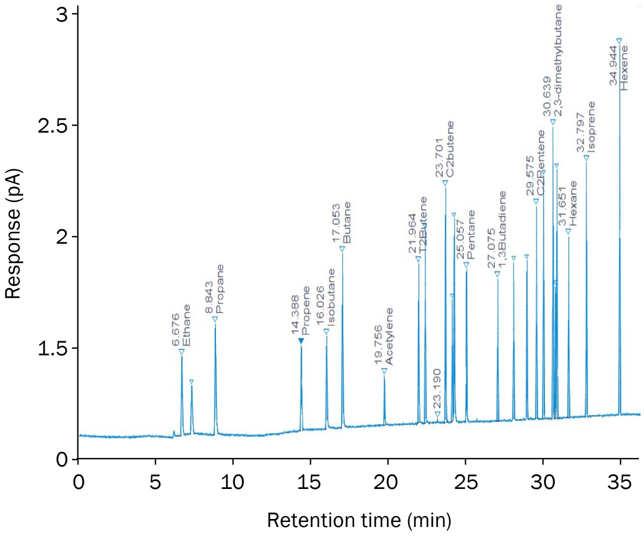

Figure 3: TD–GC–FID chromatogram from the PLOT column of the instrument.

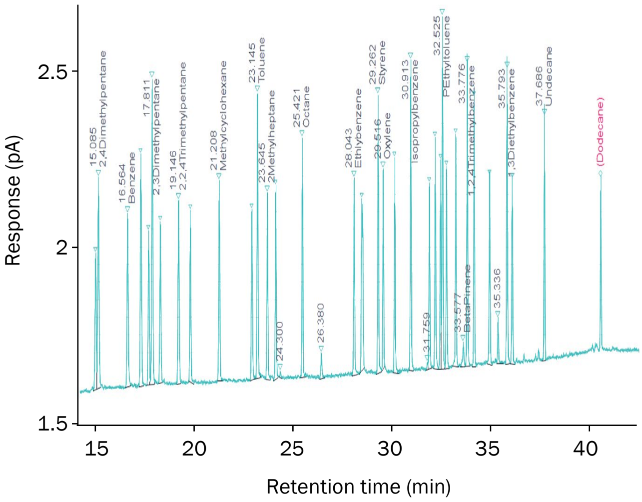

Figure 4: TD–GC–FID chromatogram from the BP-1 column of the instrument.

Sampling:

Instrument:	CIA *Advantage* Trace-xr
Sample volume:	800 mL
Sample purge:	2.0 min at 50 mL/min
Sampling rate:	20 mL/min
Sampling time:	40 min
Line flush:	2.0 min at 50 mL/min
Transfer line:	140°C

TD:

Instrument:	UNITY-xr
Flow path:	140°C
Post-sampling line purge:	2.0 min at 50 mL/min (with Kori-xr)
Trap purge:	4.0 min at 50 mL/min
Trap:	‘PAMS’ (part no. U-T20PAM-2S)
Trap low:	-30°C
Trap high:	330°C (1.0 min)
Outlet split:	12 mL/min
Trap heat rate:	Max

Water removal:

Instrument:	Kori-xr
Trap temperatures:	-30°C/300°C

GC:

Carrier gas type:	Hydrogen
Column 1:	BP-1™, 50 m x 0.22 mm x 1 µm
Constant column flow:	1.2 mL/min
Column 2:	HP-AL/S+PT, 50 m x 0.32 mm x 8 µm
Constant column flow:	4 mL/min
Oven ramp:	45°C (12 min), 5°C/min to 170, 10°C/min to 200°C (3 min)
GC runtime:	43 min
Deans switch:	On at 0.10 min for 14.4 min then off for remainder of analysis
Deans restrictor:	0.6 m x 0.1 mm i.d. deactivated fused silica

FID:

Heater 1:	200°C
Heater 2:	325°C
H_2 flow:	24 mL/min
Air flow:	300 mL/min

Results and discussion

With the dual column setup, two chromatograms are obtained with an optimum separation in accordance with the US EPA PAMS method. Full method compliance tests and results can be found in Application Note 016[4] and Application Note 129.[5]

Chromatography

Note the excellent peak shape across the range for all compounds from ethane to dodecane but particularly for acetylene, which can tail on a system that has some contamination or if water is not managed appropriately. In Figure 3, acetylene is shown as a sharp peak with no tailing at a retention time of 20 minutes on the PLOT column.

The chromatography here is comparable to that shown using helium carrier gas in Application Note 016;[4] however, with hydrogen carrier gas, the compounds elute slightly earlier.

Also, note the addition of further compounds of interest such as dodecane. It is not an official PAMS ozone precursor but it is a compound of interest for monitoring system performance. Using the CIA *Advantage*-xr instrument enables the addition of these extra compounds for investigation because the heated inert flow path eliminates carryover and memory effects between analyses.

A typical air sample from the New York Botanic Gardens demonstrates the potential for misidentification of compounds if they do not have stable retention times (Figure 5). By using the Kori-xr and Dry-Focus3 water management steps, compounds of interest are constantly fully resolved to the baseline, and this enabled the detection of an additional peak eluting between the target compounds. This peak is often misidentified when water is not managed and subsequent retention times are not stable, so baseline resolutions and exceptional retention time stability are key features to verify in this application.

System stability

In a two-column set-up, retention time stability can be related to the pressure balance in the system. With electronic mass flow controllers on the UNITY–Kori–CIA *Advantage*-xr, stable retention times on both columns are achieved and are further facilitated by the water management provided by Kori-xr.

Retention time stability between runs was calculated based on 32 daily standard injections, which showed all compounds at a level of <0.5% over a one-month period. This can also be seen in the overlaid chromatograms in Figure 6, in which the 32 standard injections show peaks at consistent retention times, assisting with confident compound identification.

Early eluting compounds in the PLOT column can exhibit the most changes in retention time shifting when affected by humidity.

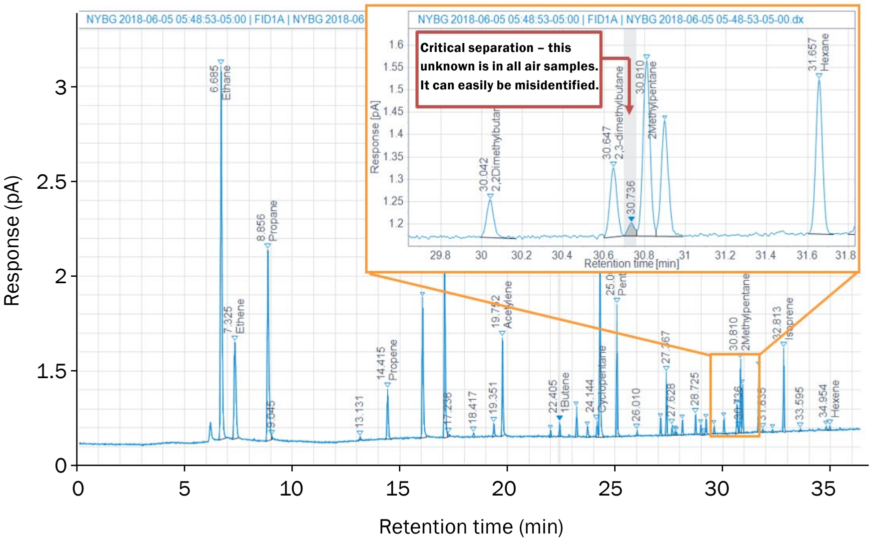

Figure 5: PLOT column showing a typical air sample analysed at the New York Botanic Gardens. The inset shows the critical separation of 2,3-dimethyl butane, 2-methylpentane and 3-methylpentane peaks with full baseline resolution and separation of additional non-target compounds.

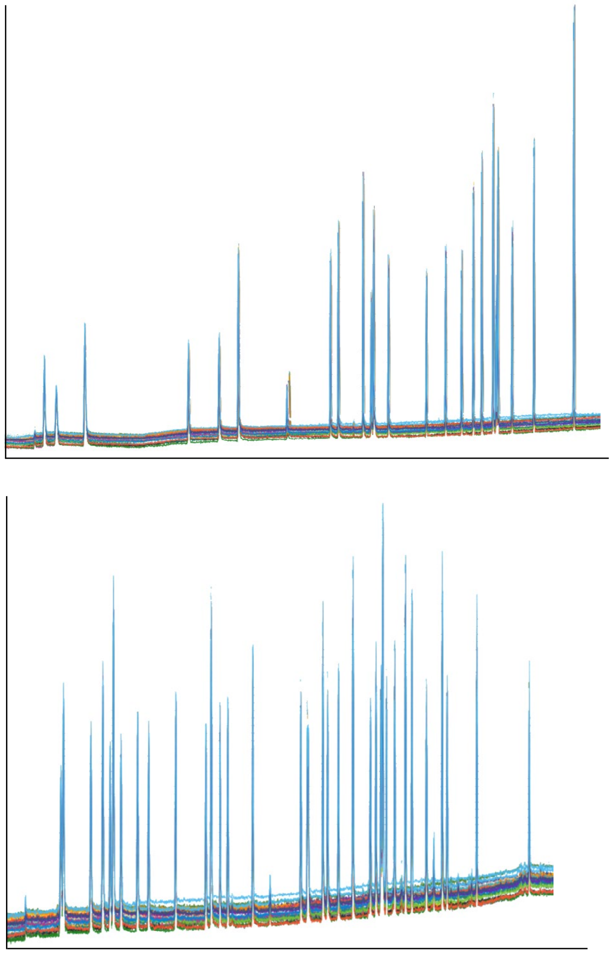

Figure 6: Overlaid chromatograms of the PLOT (top) and BP-1 (bottom) columns showing 32 days of standard analysis displaying excellent retention time stability for confident peak identification.

Figure 7 shows excellent retention time stability over 748 hourly injections of standards and samples covering a one-month continuous analysis period from 1 June to 2 July 2020, demonstrating the benefits of managing water effectively to achieve consistent high-quality data.

Response stability was also investigated over a 32-day period of standard injections. The concentration reproducibility of 56 of the 58 compounds was <10% RSD with the remaining two (heptane and β-pinene) below 30%, passing all method criteria of US EPA PAMS.

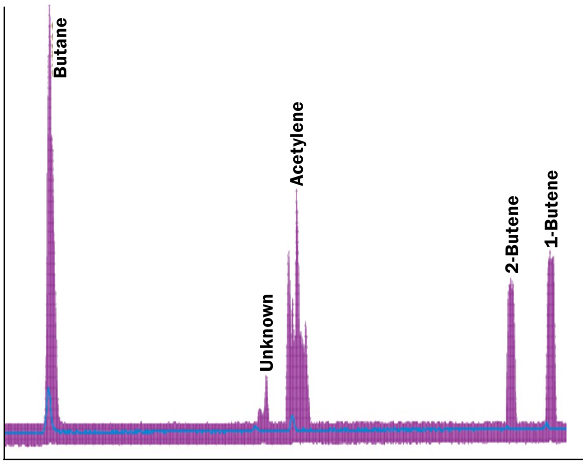

Figure 7: Overlay of 748 injections from a one-month period displaying excellent retention time stability even for this initial section of the most volatile compounds eluting on the PLOT column, including acetylene.

System background

The levels of PAMS compounds detected in ambient air at this location are very low, so system cleanliness is important for confident identification as well as reliable quantitation.

Figure 8 displays clean blanks with no significant peak presence at the retention times of any PAMS target compounds for both the PLOT and BP-1 columns. This is important because the method requires consistent hourly sampling and ensuring minimal interference from carryover between standards and samples or system contribution is key for data quality and confidence.

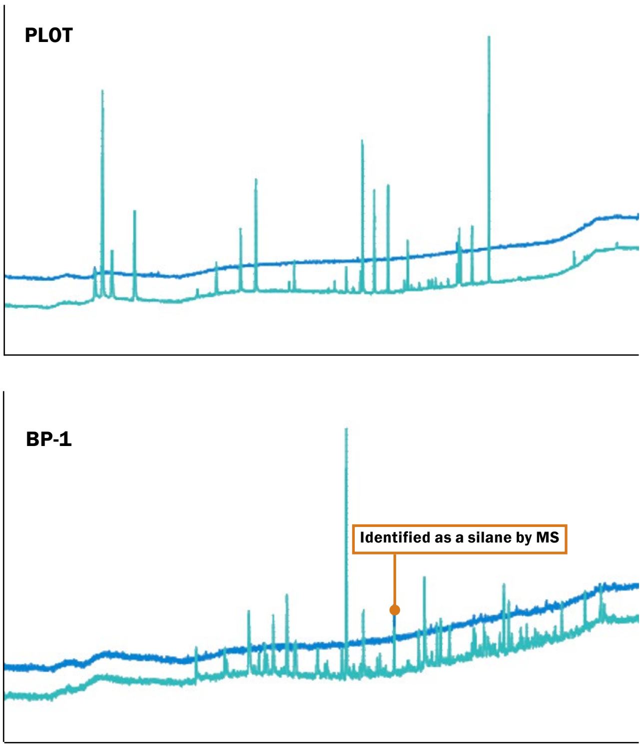

Figure 8: PLOT (top) and BP-1 (bottom) columns for an air sample and a blank run directly afterwards, ensuring no system interference or memory effect, providing confidence in results.

COVID-19 impact study

Since early 2020, the world has been affected by the COVID-19 pandemic with mass lockdowns amongst the actions taken to limit the spread of the virus. In New York City, as in many other places, only essential travel was permitted during lockdown, with non-essential workforces ordered to work from home, and non-essential businesses closing for extended periods of time, resulting in a significant change to traffic and footfall in cities.

During this time, the PAMS station in the New York Botanic Gardens maintained its continuous air monitoring analyses by TD–GC using hydrogen as a carrier gas. This presented a unique opportunity to investigate target compound concentrations without the impact of automotive contributions, which would usually interfere with the data.

During lockdown monitoring, the results showed numerous compounds spiking at random times of the day that were not seen before. These compounds included isobutane, butane, isopentane, pentane and propene (Figure 9 and Figure 10).

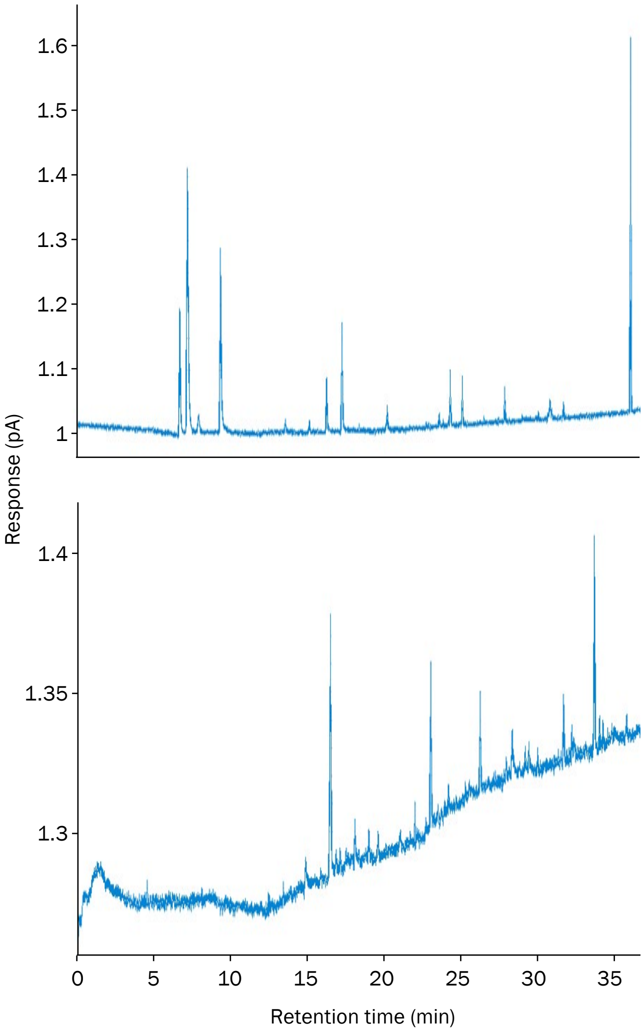

Figure 9: An ambient air sample taken at 2 am with the full COVID-19 lockdown in effect. Extremely clean air samples were observed when compared to historical PAMS monitoring data.

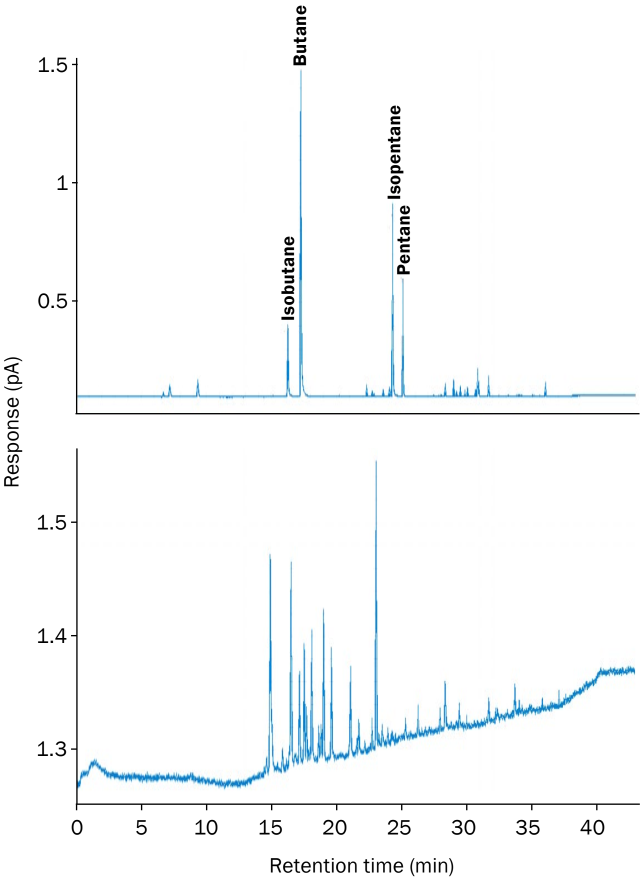

Figure 10: An ambient air sample taken at 3 am with the full COVID-19 lockdown in effect. Multiple peaks were detected at large concentrations compared to the previous hour.

In another study, the concentration profile for propene was plotted for the time between 1 April and 29 May 2020 and frequent spikes were observed (Figure 11).

This warranted further investigation so the concentration profile was compared with meteorological data, including wind direction, from the area surrounding the New York Botanic Gardens. The results suggested that the propene may have come from the direction of Staten Island, a heavily industrialised area in southwest NYC and southeast New Jersey. This area normally has high levels of traffic but because of the lockdown, traffic was ruled out as a reason for the high propene levels. Instead, it was suggested that the emissions came from an industrial source not identified previously.

Further investigations are now scheduled with the addition of another PAMS monitoring station in Staten Island. This will provide further information on the impact of emissions from this industrial area on the ambient air quality in the downstate area of New York City.

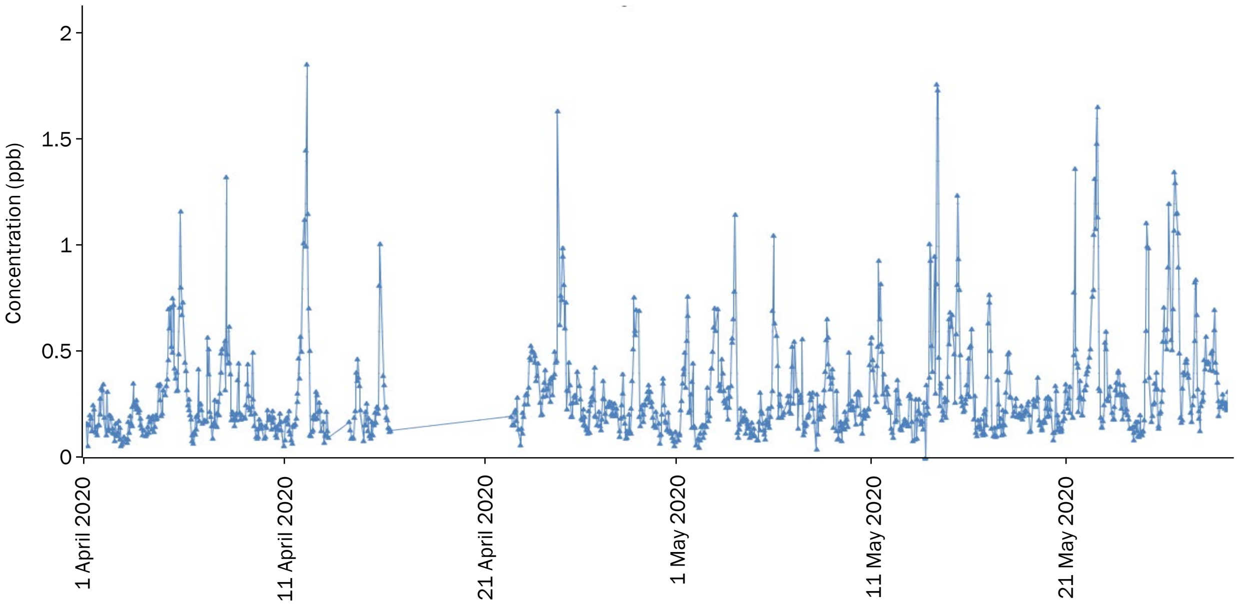

Figure 11: Profile of propene concentrations over the analysis period demonstrating spikes in response that were not identified prior to COVID-19 lockdowns.

Conclusion

In summary, this study demonstrates that the criteria cited in the US EPA PAMS method, including critical separation of compounds, retention time stability and management of water, can be comfortably met using a Multi-Gas enabled thermal desorber operating with hydrogen carrier gas.

Sampling at remote locations is easy because a generator can provide a continuous hydrogen supply. Generators are easy to maintain as they only require water top-ups, so even in times of limited access (such as city-wide lockdowns), the system can continue to gather data. Not only does this improve consistency of the gas supply in times of restricted travel, but it also reduces costs and carbon footprint. Also, using hydrogen is a way of future-proofing laboratories against helium shortages.

Both the TD–GC–FID and generator are also suitable for use from mobile laboratories as well as from fixed locations, establishing Multi-Gas enabled TD systems as the optimum choice for continuous ambient air monitoring.

Acknowledgments

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References

1. Ambient Monitoring Technology Information Center (AMTIC) Photochemical Assessment Monitoring Stations (PAMS): https://www.epa.gov/amtic/photochemical-assessment-monitoring-stations-pams.
2. Clean Air Act.
3. Standard operating procedure for the analysis of photochemical assessment monitoring stations (PAMS) volatile organic compounds (VOCs) in ambient air via Markes' UNITY-xr thermal desorber with Agilent 7890B auto-gas chromatograph with flame Ionisation detection (auto-GC–FID), found in the methods section of the following website: https://www.epa.gov/amtic/photochemical-assessment-monitoring-stations-pams.
4. Application Note 016: Round-the-clock, on-line and cryogen-free monitoring of hydrocarbons from acetylene to trimethylbenzene in ambient air.
5. Application Note 129: Extending the analysis of ozone precursors – Continuous, unattended, cryogen-free on-line monitoring of PAMS hydrocarbons and polar VOCs in ambient air by dual-column TD–GC–FID.

Trademarks

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