

Round-the-clock, online and cryogen-free monitoring of VOC hydrocarbons in ambient air using GC-MS

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Key words

EPA air quality, PAMS assessment, air sampling, ambient air monitoring, VOC emissions, thermal desorption, continuous monitoring

Goal

To describe the evaluation and validation of a thermal desorption gas chromatography-mass spectrometry (TD-GC-MS) system for online monitoring of a complex mix of volatile organic compounds (VOC) designated as ozone precursors in ambient air.

Introduction

The presence of VOCs 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, although industrial activity and oil and gas refining play significant roles. 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). These continuous real-time monitoring efforts provide 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 on the formation of ozone.

This application note reviews the evaluation and validation of a TD-GC-MS system for online monitoring of the 59 ozone precursors specified by the US Environmental Protection Agency (USEPA). Efforts to update photochemical assessment monitoring station (PAMS) requirements and capabilities have been initiated and include a revised list of monitored compounds split in to two parts, priority (25) and optional (29) compounds, with the proposed addition of five new priority compounds. Table A1 (see Appendix) provides the full list. PAMS site requirements dictate which instrumentation can be used in this application, including the need for a system that can collect and analyze samples unattended round-the-clock, making cryogen-free operation essential. Additionally, the system also requires hourly sample collection capabilities, with as much time as possible in each sampling hour dedicated to sampling. Finally, the required detection limits for analysis are below 0.5 ppb (ideally 0.1 ppb) or less. System evaluation was completed in collaboration with the EPA as part of an effort to evaluate and determine the effectiveness and performance attributes of the TD-GC-MS system for replacement of legacy Auto-GCs at future EPA PAMS sites.

Experimental

Analytical methodology

The UNITY-xr™ Air Server-xr™ was employed for round-the-clock collection of ambient air samples for speciated measurement of multiple trace-level VOCs. To complete ambient air monitoring cycles, sample air was pulled directly onto an electrically cooled, sorbent-packed focusing trap at a controlled flow rate. To further extend the applicability of the instrumentation, a dehydration trap, Kori-xr™ was used for water removal. Using the Kori-xr allowed analysis of polar and pinene compounds, which are typically removed when using Nafion® dryers. It is important to note that no liquid cryogen was required in the instrumentation setup.

Sampling flows were controlled by an electronic mass flow controller and pump, located downstream of the focusing trap to avoid contamination. Following sample collection, the flow path was purged with carrier gas to prevent carryover and eliminate oxygen from the focusing trap. The trap was then heated rapidly, at rates approaching 100 °C/min, to immediately transfer retained analytes as a

highly concentrated band of vapor into the GC-MS system. A Thermo Scientific™ TRACE™ 1310 gas chromatograph was coupled to a Thermo Scientific™ ISQ™ LT mass spectrometer for detection and quantitation of the VOC compounds. A 30 m × 0.32 mm I.D. × 10 µm Thermo Scientific™ TraceGOLD™ Bond Q analytical column was used to separate and resolve VOC compounds.

Once desorbed, the trap was re-cooled and re-equilibrated to the trapping temperature to begin collection of the next sample while the initial sample was analyzed by the GC-MS. Additional analytical parameters are listed in Tables 1 and 2.

Table 1. Focusing trap breakthrough test parameters.

UNITY-xr™ TD Instrument	
Prepurge time	1 min
Sampling rate	25 mL/min
Sampling time	Various
Focusing trap	U-T20PAM-2S (ozone precursor mix)
Focusing trap low	-30 °C
Focusing trap high	270 °C
Focusing trap hold	5 min
Flow path temp	80 °C

Table 2. GC-MS instrument operating parameters for EPA evaluation - lab and field.

TRACE 1310 GC Parameters	
Column	TraceGOLD™ Bond Q 30 m × 0.32 mm I.D. × 10 µm
Mode	Splitless
He flow	2.5 mL/min
GC oven temperature program	Initial 37 °C for 6.75 min
	Ramp 7 °C/min - 240 °C
	Ramp 12 °C/min - 260 °C, hold 10 min
ISQ Mass Spectrometer Parameters	
Transfer line	230 °C
Ionization type	EI
Ion source	310 °C
Emission current	50 µA
Acquisition mode	Full scan
Range	22–300 <i>m/z</i>
	35–300 <i>m/z</i>

Defining the ideal focusing trap

The design and packing of the trap was critical for this application for many reasons. The narrow-bore design of the UNITY-xr trap (Figure 1) allowed true splitless operation and transfer of the entire sample volume to the GC system, thereby enabling increased sensitivity for low-concentration compounds. The narrow-bore design also provided the best possible peak shape for early-eluting compounds (Figure 2).

The focusing trap sorbents chosen were also crucial, as they permitted increased retention of very volatile compounds, thereby increasing the sample volume taken and allowing lower levels to be detected. Use of a proprietary sorbent mix designed specifically for ozone precursor analysis allowed examination of compounds that typically react/convert³ on standard graphitized carbon black sorbents that are used in some legacy systems.

Results and discussion

Breakthrough tests

All the C₂ hydrocarbons are highly volatile species. Acetylene (ethyne) possesses a boiling point of -84 °C and is often the most difficult analyte to trap and quantitatively retain without liquid cryogen. Because of these properties, careful selection of the cold trap sorbent(s) and focusing temperature were required. Experiments to determine the limit of quantitative retention (the breakthrough volume) were performed on an 'ozone precursor' custom 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 to measure the detector response against sampled volume.

Figure 3 is a plot of the peak area against the sampled volume of calibration gas for acetylene, showing that even at 0.5 L of sampled gas, there was no deviation from linearity, i.e. there was negligible breakthrough.



Figure 1. Design of the focusing trap. Note the narrow-bore outlet and the long sorbent bed. Sampling occurs from left to right. Desorption occurs from right to left.

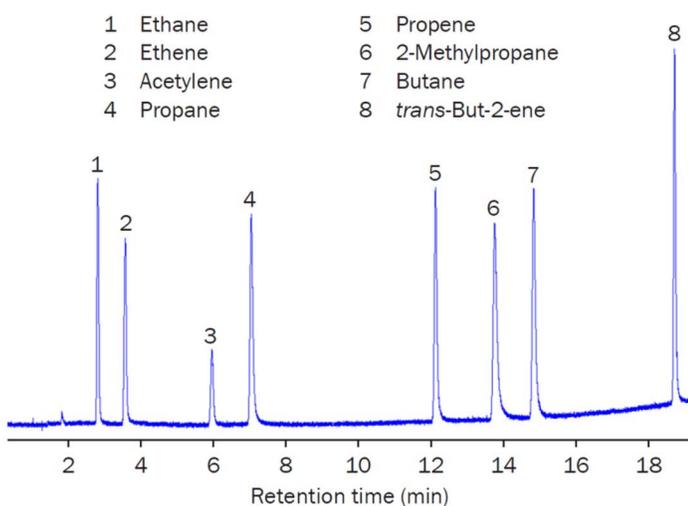


Figure 2. Chromatogram showing a splitless injection of 500 mL of the calibration standard.

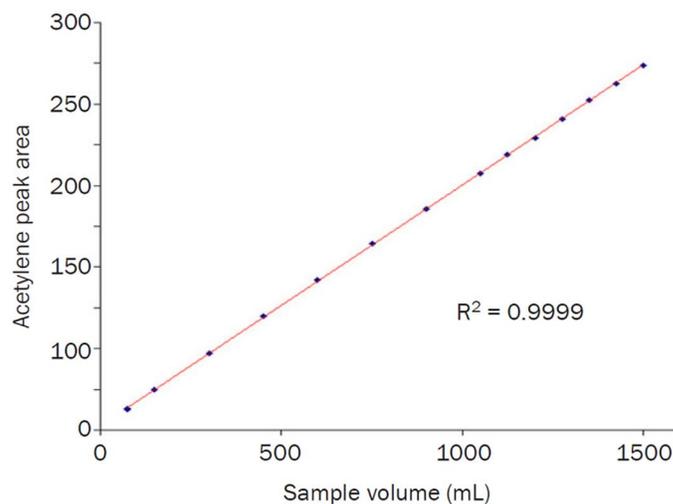


Figure 3. Plot of peak area against volume sampled for acetylene. Image courtesy of Ecole des Mines de Douai.

Water management

Legacy Auto-GC systems designed for PAMS analysis used permeable membrane dryers such as Nafion dryers. These were great for GC-flame ionized detection (FID) analysis, as they removed not only the water but also possible interferences from the sample to avoid co-elutions and simplify the chromatography. With the re-engineered PAMS program, new priority compounds have been added to the list that would also be removed by the Nafion dryers. As an effect, a new way to manage water was required. Markes developed Kori-xr™, a water abstraction device that was placed between the Air Server-xr and UNITY-xr as shown in Figure 4.

Kori-xr dehydrated the sample stream to remove water using an immediate phase transition from gas to solid, effectively minimizing the loss of any polar compounds while removing the majority of the water present in the sample.

Tests were performed to compare the Kori-xr system to a system fitted with a Nafion dryer for a selection of the new priority compounds and other polar species that could be present in an ambient air sample (Figure 5).

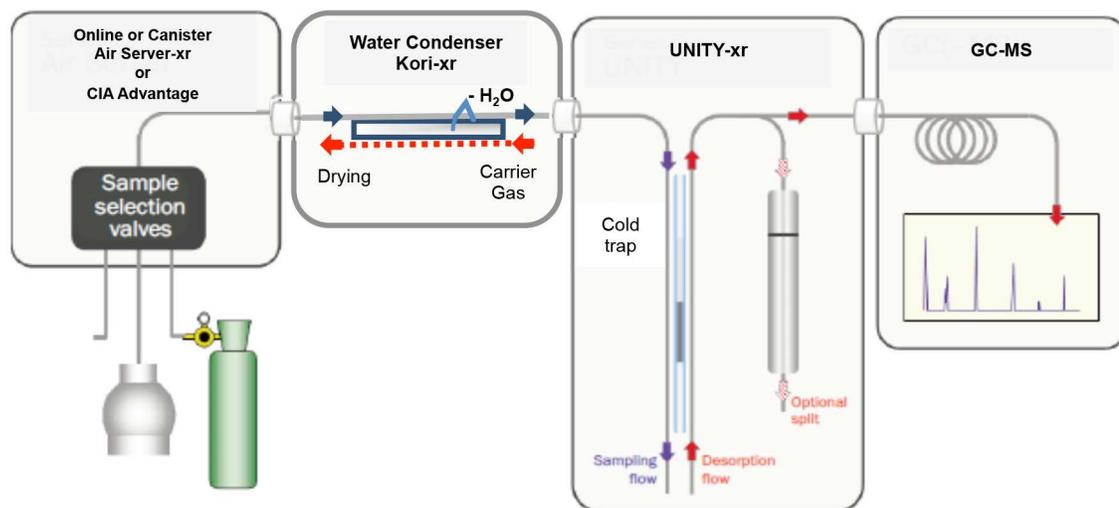


Figure 4. Schematic of the TD-GC-MS setup including the Kori-xr water abstraction device.

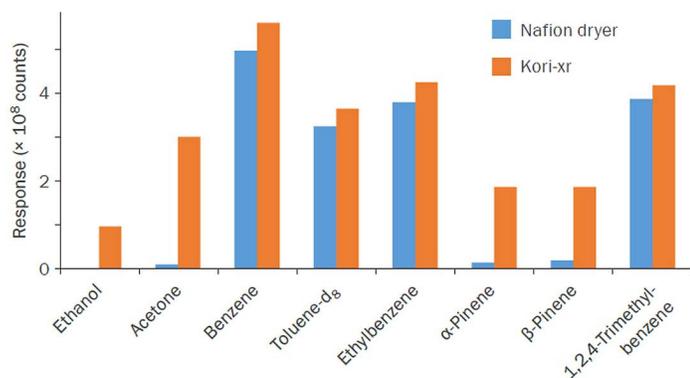


Figure 5. Chart comparing key priority compounds and other polar compounds using Nafion and Kori-xr in an 80% relative humidity (RH) sample.

In addition, the presence of water in a sample is notorious for causing large retention times shifts in GC analysis. Because FID detection systems rely primarily on retention time stability to confidently identify compounds, a retention time shift can be catastrophic for peak identification. Using GC-MS, compound identification is still possible despite retention time shifts. During GC-MS analysis, spectral information is collected for each compound independent of retention time and compared to known spectra to confirm peak identification. Though this is a clear advantage of MS configurations, retention time shifts could cause problems with automatic reporting/data analysis requiring manual intervention and processing method adjustment. For high-throughput, around-the-clock monitoring this is not ideal. If water is managed correctly retention times remain consistent for each run, despite fluctuations in relative humidity (RH) of the sample. The Kori-xr system was repeatedly tested with an 80% RH sample and retention time was monitored for each run. An example for three compound peaks can be seen in Figure 6, which shows practically no retention time shifts despite the large amount of water present.

GC-MS system ISQ LT GC-MS

The use of the Kori-xr along with the TraceGOLD Bond Q analytical column allowed retention and separation of all compounds from C₂ through C₁₁. Legacy Auto-GC setup

with dual FID configuration required two segmented collections of the compounds, potentially using two separate analytical runs.

Legacy PAMS Auto-GC systems were composed of dual column, dual detection systems. FID was commonly employed and deemed the best solution for the compound list. With the updates to the monitoring program and list requirements, GC-MS has emerged as a compelling alternate to the legacy FID detector. As previously stated, there are unique advantages to GC-MS detection. In addition to using mass spectra in combination with retention time information for known compound identification, mass spectra or a fingerprint of unique fragmented ion masses for each compound can also be used to investigate the presence of unknown compounds. Unknown spectra can easily be compared to spectral reference libraries (i.e. NIST) of known spectra to aid in compound identification. As an added benefit, MS detection provides the ability to monitor single ions and ion ratios for VOC compounds, potentially increasing the accuracy of quantitation. Shown in Figure 7 is an example of the data processing using GC-MS software. Software suites such as Thermo Scientific™ TraceFinder™ or Thermo Scientific™ Chromeleon™ allow automated review of chromatograms, mass spectra, and extracted ions for each compound.

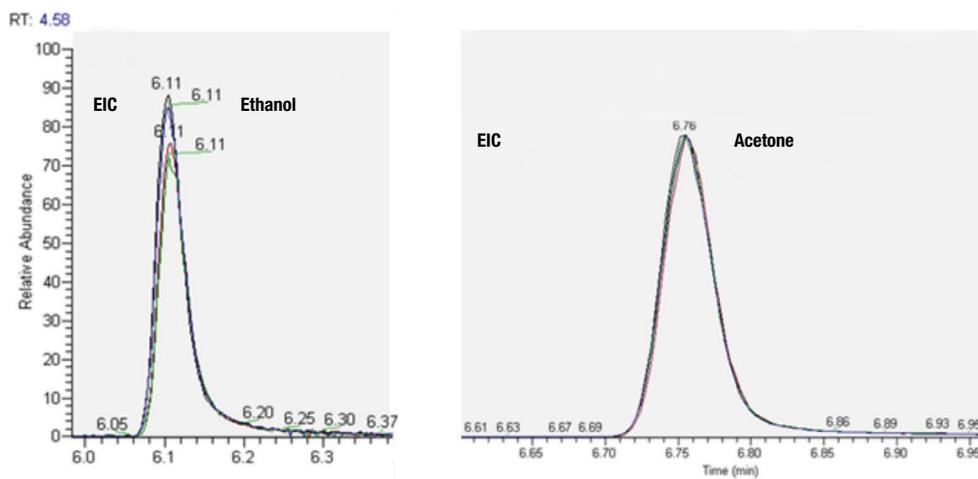


Figure 6. Four replicates of a 500 mL sample at 80% RH.

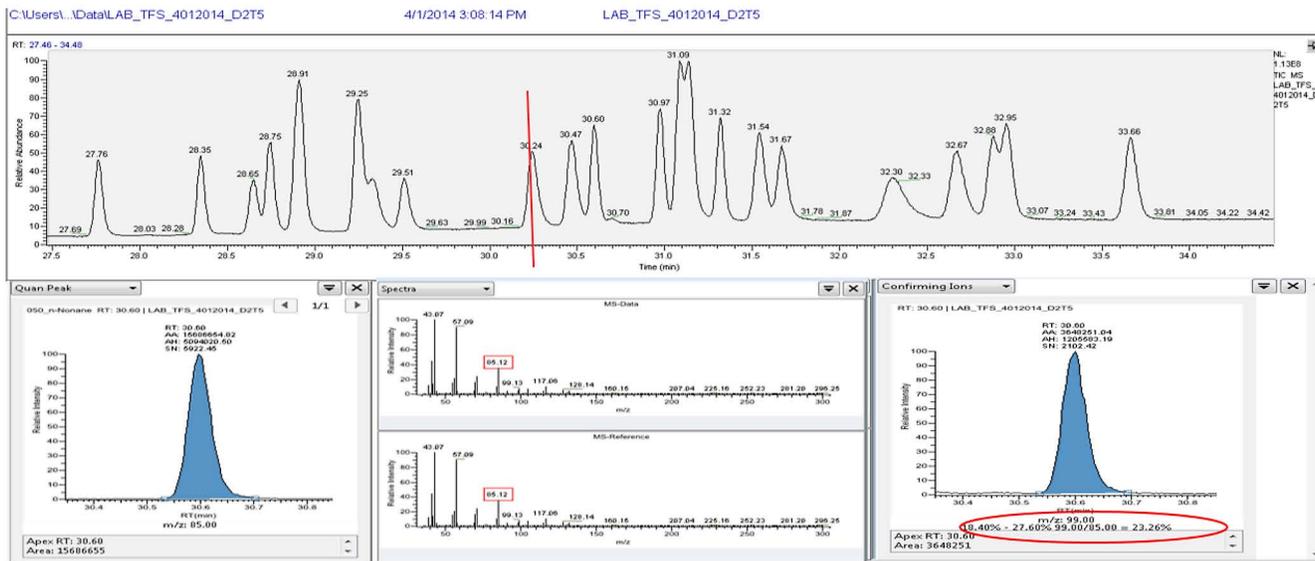


Figure 7. GC-MS data analysis showing 1 ppb ozone precursor standard blended with interferences. Extracted ion chromatograms on the lower left (m/z 85) and right (m/z 99). In the center is a comparison of the obtained spectra for *n*-nonane in agreement with the NIST reference spectra.

In legacy Auto-GC analysis, problematic compounds like carbon tetrachloride and tetrachloroethylene did not respond well to FID detection. Figure 8 demonstrates yet another advantage of GC-MS. Retention times of 27.71 and 31.68 min in Figure 8 correspond to these two compounds showing distinct peaks easily identified using MS detection.

Peak co-elutions

Also demonstrated in Figure 8 is the potential complexity of ambient air samples. During the evaluation phase of the validation, standards and interferences were combined and evaluated simultaneously using the ISQ LT GC-MS system. When using dual FID instrumentation in the presence of interferences, co-eluting compounds can influence the

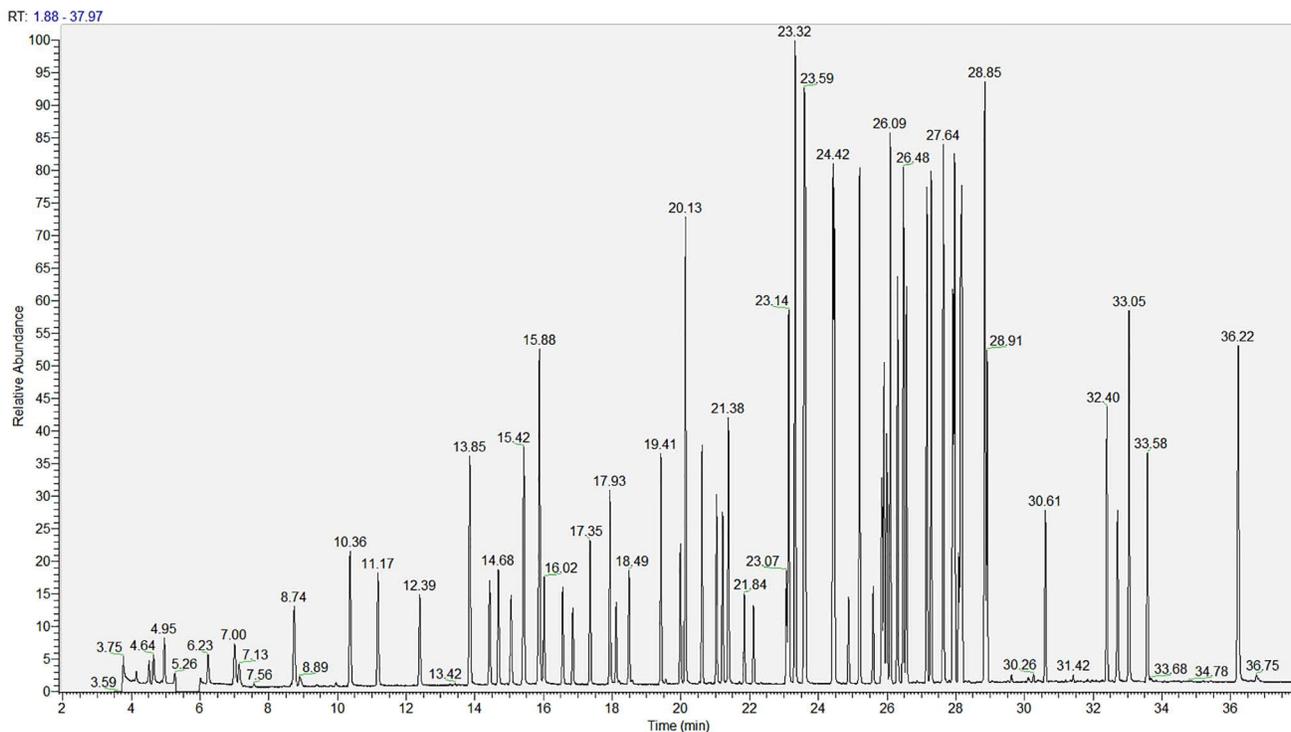


Figure 8. Chromatogram of an ozone precursor standard blended with interferences. Note: retention time 27.71 min for carbon tetrachloride and 31.68 min for tetrachloroethylene.

acceptability and validity of data collected. Typically, peaks that co-elute are not an issue when analyzing samples with MS detectors. Using MS, compounds are quantitated by extracting a single fragment ion (unique and highly abundant) from a compound's mass spectrum in an extracted ion chromatogram (EIC) that is collected during its retention window. This is illustrated in Figure 9 in which the top plot displays the total ion chromatogram (TIC) similar to a chromatogram obtained with a conventional GC detector like an FID. The two traces below are EICs of unique fragment ions (m/z 57 and m/z 134) from the co-eluting peaks in the top TIC plot. Extraction of ions for quantitation removes the effect of co-elution and increases the accuracy of quantitative results with less bias from retention time shifts.

Reliability study – multipoint calibrations and low method detection limits

During the EPA PAMS instrumentation evaluations, stringent tests were used to determine the reliability of the TD-GC-MS system. Evaluations involved multiple calibrations over several days at various levels of humidity. Resulting calibration R^2 values for linearity evaluations along with % relative standard deviation (RSD) for replicate injections are displayed in Table 3. Method detection limits were also determined from a series of repeated 0.5 ppb standard injections using the student t -test for final value calculation.

Troubleshooting the system – maintaining a GC-MS in the field is easy!

Troubleshooting any Auto-GC system is inevitable. At PAMS sites, Auto-GC systems are stationed in trailers with limited resources, while requiring short sampling durations, which can present unanticipated challenges. Due to this restrictive environment, instrument manufacturers must ensure that systems are easy to maintain and repair should a fault occur. For PAMS site evaluations, data captured during the allotted collection window must meet or exceed sampling requirements over 80% of the sampling time period to meet acceptance criteria. If faults occur that influence data acceptability over the 20% of the collection window threshold, entire data sets could be rejected.

An example of a fault impacting data acceptability could be carrier gas flow control errors. With standard GC systems there are many different components responsible for carrier gas flow, including pneumatics, electronic boards that control the pneumatics, wires, gas lines, filters, and other inlet components. Because of this complexity, in-depth system knowledge may be necessary to resolve carrier gas flow errors, including a large store of possible replacement components.

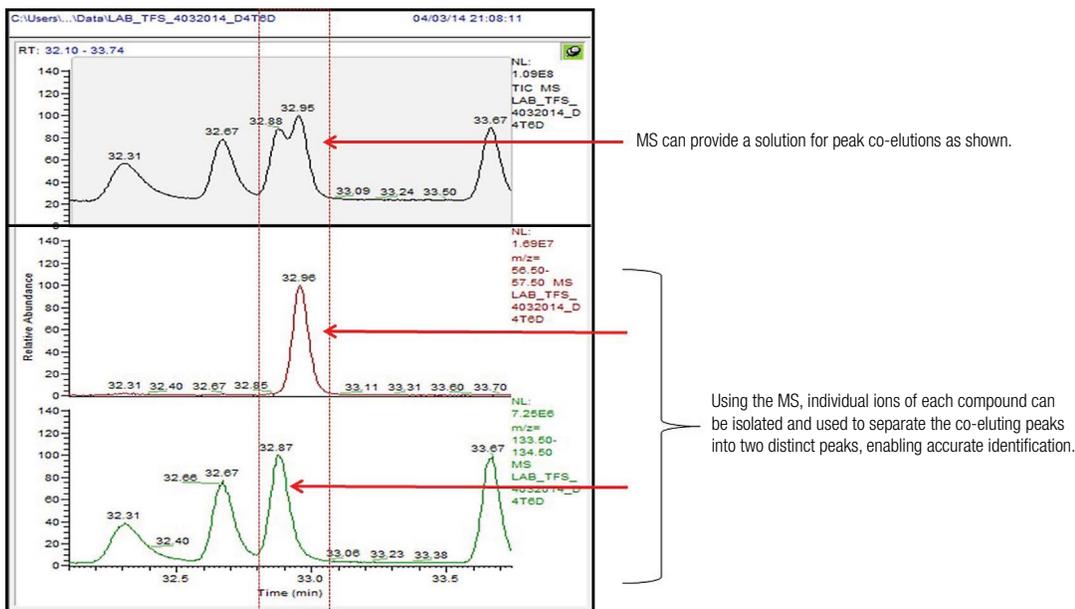


Figure 9. TIC (top) and extracted ions m/z 57 (middle) and m/z 134 (bottom).

Table 3. Calibration fit (R²), %RSD, and MDL for the target ozone precursor compounds.

Compound	R ²	%RSD	MDL	Compound	R ²	%RSD	MDL
Ethylene	0.9995	1.886	0.286	Carbon tetrachloride	0.9999	0.829	0.103
Ethane	0.9991	2.578	0.402	Benzene	0.9998	1.215	0.029
Propylene	0.9999	0.743	0.113	Tetrachloroethylene	0.9995	2.049	0.02
Propane	0.9997	1.385	0.153	Toluene	0.9998	1.136	0.024
Isobutane	0.9998	1.254	0.157	2,2,4-Trimethylpentane	0.9975	2.289	0.083
<i>cis</i> -2-Butene	1.0000	0.081	0.024	Ethylbenzene	0.9995	1.907	0.029
1,3-Butadiene	0.9998	1.129	0.018	<i>m,p</i> -Xylene	0.9991	2.56	0.038
<i>n</i> -Butane	0.9998	1.205	0.045	Styrene	0.9998	1.34	0.019
1-Butene	0.9998	1.323	0.019	<i>o</i> -Xylene	0.9998	1.456	0.022
<i>trans</i> -2-Butene	0.9998	1.527	0.016	<i>m</i> -Ethyltoluene	0.9997	1.511	0.026
Isopentane	0.9999	0.795	0.092	<i>p</i> -Ethyltoluene	0.9924	7.471	0.116
Isoprene	0.9989	3.032	0.098	1,2,4-Trimethylbenzene	0.9909	8.698	0.086
<i>n</i> -Pentane	0.9997	1.574	0.077	<i>o</i> -Ethyltoluene	0.9996	1.684	0.043
<i>n</i> -Hexane	0.9999	0.742	0.022	1,2,3-Trimethylbenzene	0.9998	1.312	0.089

Using the TRACE 1310 GC Instant Connect Split/Splitless (SSL) inlet module, the entire inlet, including all flow control assemblies, can be replaced with limited training in less than two minutes (Figure 10). The modularity of the TRACE 1310 GC drastically reduces troubleshooting providing additional time for collecting sample data.



Figure 10. TRACE 1310 Instant Connect capability. Instant Connect modules are quickly replaced without special training or tools.

Another maintenance-related obstacle that could challenge round-the-clock operation is MS source maintenance. Unlike any other MS, the source of the ISQ LT system can be removed while the system is still under vacuum and at temperature in under 5 minutes. Depending on sample interferences and frequency of analysis, the MS source must be cleaned at regular intervals to maintain optimal sensitivity. In a realistic Auto-GC sampling environment, should any sensitivity issues arise, swapping sources could be used as a time-saving troubleshooting step or as a resolution to a detector that requires cleaning (Figure 11).



Figure 11. Schematic of ISQ LT ion source. Inset shows source being removed with the system under vacuum.

Conclusion

The combined Thermo Scientific – Markes International Auto TD-GC-MS system provides a reliable, semi-continuous, cryogen-free sampling and analysis system for this challenging and complex mix of VOCs. The Markes UNITY-xr Air Server-xr system provides optimal sampling control of moisture and breakthrough, ensuring the sampling reproducibility and accuracy needed for unattended round-the-clock monitoring in remote locations.

By combining the Kori-xr for moisture management with the UNITY-xr trap enabled for retention of very volatile compounds and the TG Bond Q analytical column for resolution and separation, VOC compounds from C₂ to C₁₁ were analyzed in a single sample collection, removing the need for Nafion dryers or cryogenic coolers, reducing sample collection steps, and resulting in an optimized workflow.

Using GC-MS detection enables the use of compound mass spectra for identification and quantitation of known compounds with the added benefit of spectral matching to investigate unknown compounds. These two capabilities can have a profound influence on data sets by providing a separation mechanism for co-eluting components that could prevent data disqualifications due to interferences and add to the relevance of the data set in future analysis models.

The integration of TraceFinder software or Chromeleon software into ambient air monitoring stations provides an essential tool for PAMS stations. These software packages allow automated sample collection and data analysis through an intuitive interface that can be easily managed remotely and operated by minimally skilled field technicians. Overall the Thermo Scientific – Markes International Auto TD-GC-MS System provides a productive and reliable new approach to monitoring VOC 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. Peters, R.J.B; Renesse, A.D.V, Duivenbode, V.; Duyzer, J.H.; Verhagen, H.L.M. The determination of terpenes in forest air, *Atmospheric Environment*, **1994**, 28, 2413–2419.

Appendix

Table A1. List of re-engineered USEPA PAMS compounds (correct as of September 2016).

Existing Priority Compounds	Optional Compounds	New Priority Compounds
1,2,3-Trimethylbenzene	1,3,5-Trimethylbenzene	α/β -Pinene
1,2,4-Trimethylbenzene	1-Pentene	1,3-Butadiene
1-Butene	2,2-Dimethylbutane	Benzaldehyde ^a
2,2,4-Trimethylpentane	2,3,4-Trimethylbenzene	Carbon tetrachloride
Acetaldehyde ^a	2,3-Dimethylbutane	Ethanol
Acetone ^a	2,3-Dimethylpentane	Tetrachloroethene
Benzene	2,4-Dimethylpentane	
<i>Cis</i> -2-Butene	2-Methylheptane	
Ethane	2-Methylhexane	
Ethylbenzene	2-Methylpentane	
Ethene	3-Methylheptane	
Formaldehyde ^a	3-Methylhexane	
Isobutane	3-Methylpentane	
Isopentane	Acetylene (Ethyne)	
Isoprene	<i>Cis</i> -2-pentene	
<i>m/p</i> -Xylene	Cyclohexane	
<i>m</i> -ethyltoluene	Cycloheptane	
<i>n</i> -Butane	Isopropylbenzene	
<i>n</i> -Hexane	<i>m</i> -Diethylbenzene	
<i>n</i> -Pentane	Methylcyclohexane	
<i>o</i> -Ethyltoluene	Methylcyclopentane	
<i>o</i> -Xylene	<i>n</i> -Decane	
<i>p</i> -Ethyltoluene	<i>n</i> -Heptane	
Propane	<i>n</i> -Nonane	
Propene	<i>n</i> -Octane	
Styrene	<i>n</i> -Propylbenzene	
Toluene	<i>n</i> -Undecane	
<i>Trans</i> -2-butene	<i>n</i> -Diethylbenzene	
	<i>Trans</i> -2-pentene	

^aThese compounds are carbonyls and are only required to be measured at PAMS sites in ozone non-attainment areas classified as serious or above the 8-hour ozone standard.

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