

Application Note 128

Extending the analysis of ozone precursors – Continuous, unattended, cryogen-free on-line monitoring of PAMS hydrocarbons and polar VOCs in ambient air by TD–GC–MS

Summary

This Application Note describes validation of a cryogen-free thermal desorption (TD)–GC–MS system for on-line monitoring of an extended range of very volatile species in ambient air, which includes 'ozone precursors' (as specified by the US PAMS program), polar compounds and monoterpenes. In addition to analysis of a 61-component standard mix and a real air sample, we demonstrate low method detection limits using the new trap-based Kori-xr system for eliminating water from the air stream.



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 to trimethylbenzene, and are generally referred to as 'ozone precursors'.

There is currently growing interest in carrying out continuous time-resolved measurement ('on-line monitoring') of ozone precursors and other compounds, for source apportionment and in order to better understand the factors that influence their concentrations. This is particularly the case in Asia, with recent strong growth in on-line monitoring of industrial emissions in China,^{1,2,3} following the mandating of a nationwide real-time air monitoring system in the 13th Five-Year Plan, and numerous regional controls on industrial VOC emissions. On-line industrial air monitoring is also experiencing a high level of interest in South Korea,^{4,5,6} while other areas also receiving attention include emissions from road vehicles^{7,8,9} and long-range transport of pollutants.^{10,11}

For many years, however, the main user of technology for on-line monitoring of emissions from industrial and urban sources has been the US, through its network of Photochemical Assessment Monitoring Stations (PAMS). Since 1993, this program has required US states and local environmental agencies to measure ozone precursors in areas affected by significant ground-level ozone pollution.

Much of the air monitoring equipment in the current network uses older technology not capable of handling present-day analytical requirements, so the US EPA commissioned independent laboratory and field trials in order to inform the choice of the best automated GC technologies for the purpose. The reports on these trials¹² describe excellent performance for the two systems containing Markes' instrumentation – in particular, they were able to report on 100% of the target compounds, had very low levels of instrumental bias, and showed excellent precision between replicate measurements. Monitoring using the new systems is expected to begin in June 2019.

The PAMS scheme recommends¹³ that hourly speciated VOC measurements are taken using automated gas chromatography (GC) with pre-concentration by thermal desorption (TD). As indicated in recent guidance for the implementation of the 'PAMS re-engineering' plan,¹⁴ this stipulation will remain, with decisions on the new instrumentation to be used being referred to the individual monitoring agencies.

At the time of writing (July 2017), the proposed list of target compounds for the re-engineered PAMS program comprises 28 'priority compounds' and 35 'optional compounds'.¹⁴ These are all aliphatic or aromatic hydrocarbons except for formaldehyde, acetaldehyde and acetone (priority) and ethanol, benzaldehyde, carbon tetrachloride, tetrachloroethene, α -pinene and β -pinene (optional). However, it is widely recognised that numerous polar compounds (including oxygenated species such as alcohols, aldehydes, ketones and esters) and terpenoids play an important role in atmospheric chemistry, including in the formation of ozone and secondary organic aerosols.

As a result, there is a growing desire to 'future-proof' on-line GC systems for VOC monitoring, by ensuring that polar compounds as well as hydrocarbons can be monitored simultaneously. This has historically presented a challenge to analysts because of the tendency for volatile polar species and monoterpenes to be lost when conventional Nafion™ dryers are used to remove humidity from the air stream.

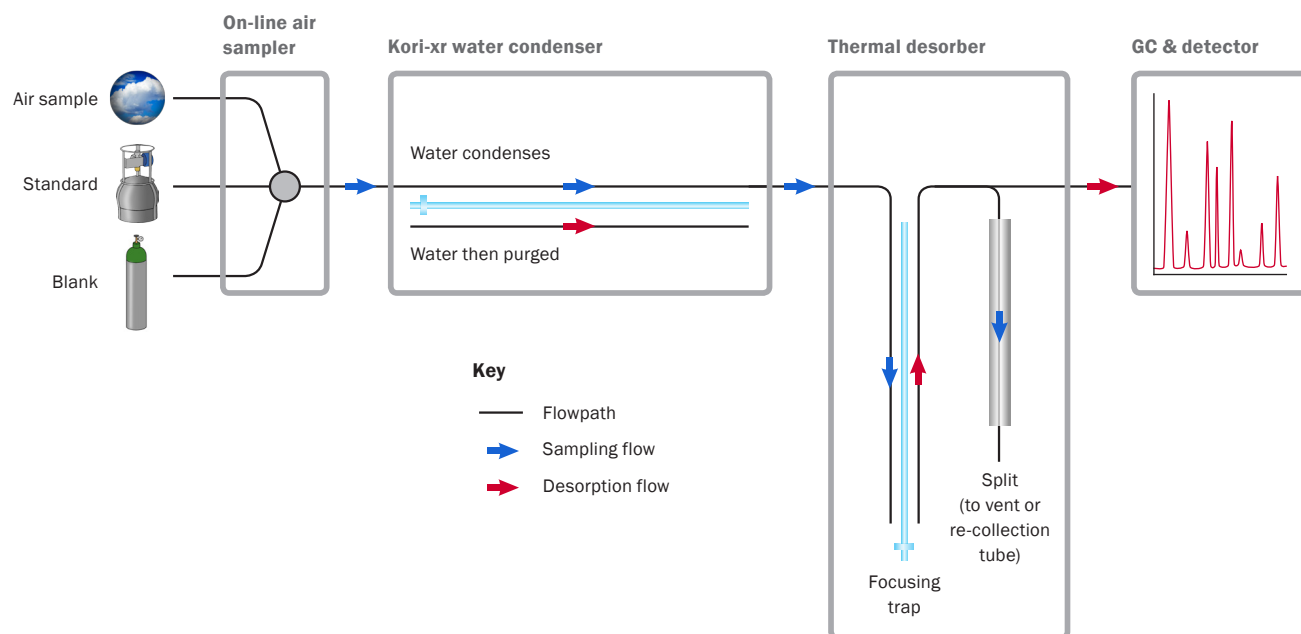


Figure 1: Equipment configuration.

These dryers work by using a hydrophilic co-polymer to adsorb water from the air stream, which, driven by the humidity gradient, passes through to be removed by a stream of purge gas. However, the presence of strongly acidic groups on the polymer surface means that most polar compounds and monoterpenes also migrate through and are completely lost at the same time as the water.

This Application Note describes an on-line thermal desorption (TD)-GC-MS system that overcomes this difficulty by using an innovative, cryogen-free water-removal device upstream of the thermal desorption focusing trap. The result is improved performance for an extended range of analytes that includes hydrocarbons, polar species and monoterpenes.

Analytical equipment

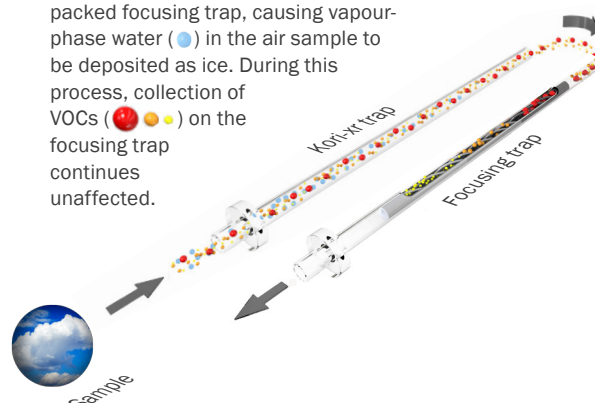
The analytical system used for this study was an Air Server-xr on-line sampler with a Kori-xr water condenser and UNITY-xr thermal desorber, coupled to a GC-MS system¹⁵ (Figure 1). The entire system is cryogen-free and can be controlled remotely, making it ideal for unattended operation in remote field locations. The individual components of the system are briefly described below.

The **Air Server-xr™** instrument for on-line sampling allows air/gas to be sampled at a controlled rate, with automatic interchange between three or eight sample channels allowing remote system calibration or validation.

Before entering the thermal desorber, samples pass through a **Kori-xr™** device that efficiently removes humidity from the air stream (Figure 2). As well as eliminating the risk of poor chromatography caused by water interference, this allows lower temperatures to be used in the focusing trap without risk of water retention, allowing VOCs, VVOCs, oxygenates and monoterpenes in humid air to be quantitatively retained. Note that as well as on-line monitoring, Kori-xr can also be applied to canister and bag samples.

1 Air sampling and water removal:

The empty Kori-xr trap, held below 0°C, sits in-between the sample inlet and the sorbent-packed focusing trap, causing vapour-phase water (●) in the air sample to be deposited as ice. During this process, collection of VOCs (●●●) on the focusing trap continues unaffected.



2 Trap desorption and water purging:

When sampling is complete, the analytes are transferred from the focusing trap to the GC, and ice is purged from the Kori-xr trap, to prepare it for the next sample.

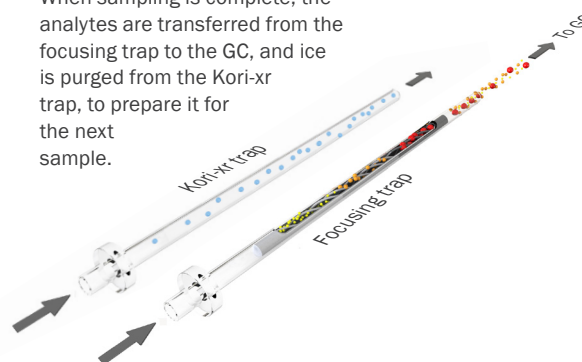


Figure 2: Operation of the Kori-xr device for removing water from humid air streams.

With excess water removed, samples pass into the **UNITY-xr™** thermal desorber. This contains a narrow focusing trap, electrically cooled to 0°C or below,¹⁶ and filled with separate beds of porous polymer, graphitised carbon black and carbonised molecular sieve sorbents.¹⁷ This combination of sorbents of different strengths ensures that compounds over a wide volatility range are quantitatively trapped. Once the analytes are trapped, the flow of gas is reversed, and the trap is heated rapidly (up to 100°C/s), to ‘backflush’ the analytes onto the GC column.

Note that sampling through the entire Air Server–Kori–UNITY-xr system is performed using an electronic mass flow controller and pump, located downstream of the focusing trap to avoid contamination. Once the trap has desorbed, the system re-equilibrates and begins collection of the next sample, while analysis of the previous sample continues. In conjunction with an appropriate GC run time, this allows samples to be acquired at intervals of an hour or less, as required under the PAMS scheme.

At the point of trap desorption, there is the ability to split the sample, either to vent or onto a clean sorbent tube for storage and re-analysis at a later time (although it should be noted that sorbent tubes are not able to retain very volatile compounds such as acetylene). Optionally, this process of sample splitting and re-collection can be fully automated by adding an **ULTRA-xr™** 100-tube autosampler.

Experimental

Samples:

Analysis was performed on ppb-level mixtures generated by dilution of a 1 ppm, 61-component gas standard, humidified to 100% RH by injection of an appropriate amount of water. The real air sample (with a relative humidity of ~85%) was taken in March 2017 at a light-industrial location in Llantrisant, UK.

Sampling:

Instrument:	Air Server-xr (Markes International)
Sample purge:	2 min at 50 mL/min
Sampling rate:	25 mL/min
Sampling time:	Various
Line flush:	2 min at 50 mL/min
Transfer line:	75°C

Water removal:

Instrument:	Kori-xr (Markes International)
Trap temp.:	-30°C / +300°C

TD:

Instrument:	UNITY-xr (Markes International)
Cold trap:	‘PAMS’ (U-T20PAM-2S)
Cold trap low:	-30°C
Cold trap high:	325°C
Cold trap hold:	5 min
Flow path temp.:	120°C
Trap purge:	2 min

GC:

Column:	TracePLOT™ TG-BOND Q, 30 m × 0.32 mm × 10 µm
Oven ramp:	35°C (5 min), then 25°C/min to 115°C (2 min), then 15°C/min to 250°C, then 10°C/min to 270 (15 min)
Column flow:	2 mL/min
GC run time:	38 min

Quadrupole MS:

Source:	300°C
Transfer line:	200°C
Scan range:	$t_R < 5$ min: SIM (for the first five peaks, see Table A1 for acquired m/z values); $t_R \geq 5$ min: m/z 30–200

Results and discussion

A listing of results is provided in Table A1 (see Appendix).

1. Analysis of standard mix

Figure 3 shows analysis of a 4 ppb standard mix with 100% RH using the Kori-xr system.

2. Reproducibilities

Reproducibilities for retention time and analyte response were calculated using ten replicate measurements for 250 mL of the standard mix, and are listed in Table A1.

Mean retention-time RSDs were 0.022%, with all but three compounds being below 0.05%. This high degree of reproducibility makes it much easier to achieve precise automated quantitation, saving time when reviewing data.

Mean response RSDs were 3.6%, with a maximum of 12.6% for 1,3-diethylbenzene, still within the limits of the current PAMS recommendation of 15–25%.

1 Ethylene	14 Isopropanol	27 n-Hexane	40 3-Methylheptane	53 1,3,5-Trimethylbenzene
2 Acetylene	15 Pent-1-ene	28 Methylcyclopentane	41 n-Octane	54 β -Pinene
3 Ethane	16 <i>trans</i> -Pent-2-ene	29 Benzene	42 Ethylbenzene	55 1,2,3-Trimethylbenzene
4 Propylene	17 Isoprene	30 Cyclohexane	43 <i>m</i> -/ <i>p</i> -Xylene	56 1,2,4-Trimethylbenzene
5 Propane	18 <i>cis</i> -Pent-2-ene	31 2,4-Dimethylpentane	44 Styrene	57 n-Decane
6 Isobutane	19 n-Pentane	32 2-Methylhexane	45 <i>o</i> -Xylene	58 1,3-Diethylbenzene
7 But-1-ene	20 Cyclopentane	33 3-Methylhexane	46 n-Nonane	59 1,4-Diethylbenzene
8 n-Butane	21 2,2-Dimethylbutane	34 n-Heptane	47 Isopropylbenzene	60 n-Undecane
9 <i>cis</i> -But-2-ene	22 2,3-Dimethylbutane	35 Methylcyclohexane	48 1-Methyl-2-ethylbenzene	61 n-Dodecane
10 <i>trans</i> -But-2-ene	23 2-Methylpentane	36 Toluene	49 1-Methyl-4-ethylbenzene	
11 Ethanol	24 3-Methylpentane	37 2,2,4-Trimethylpentane	50 n-Propylbenzene	
12 Acetone	25 Hex-1-ene	38 2,3,4-Trimethylpentane	51 α -Pinene	
13 Isopentane	26 2,3-Dimethylpentane	39 2-Methylheptane	52 1-Methyl-3-ethylbenzene	

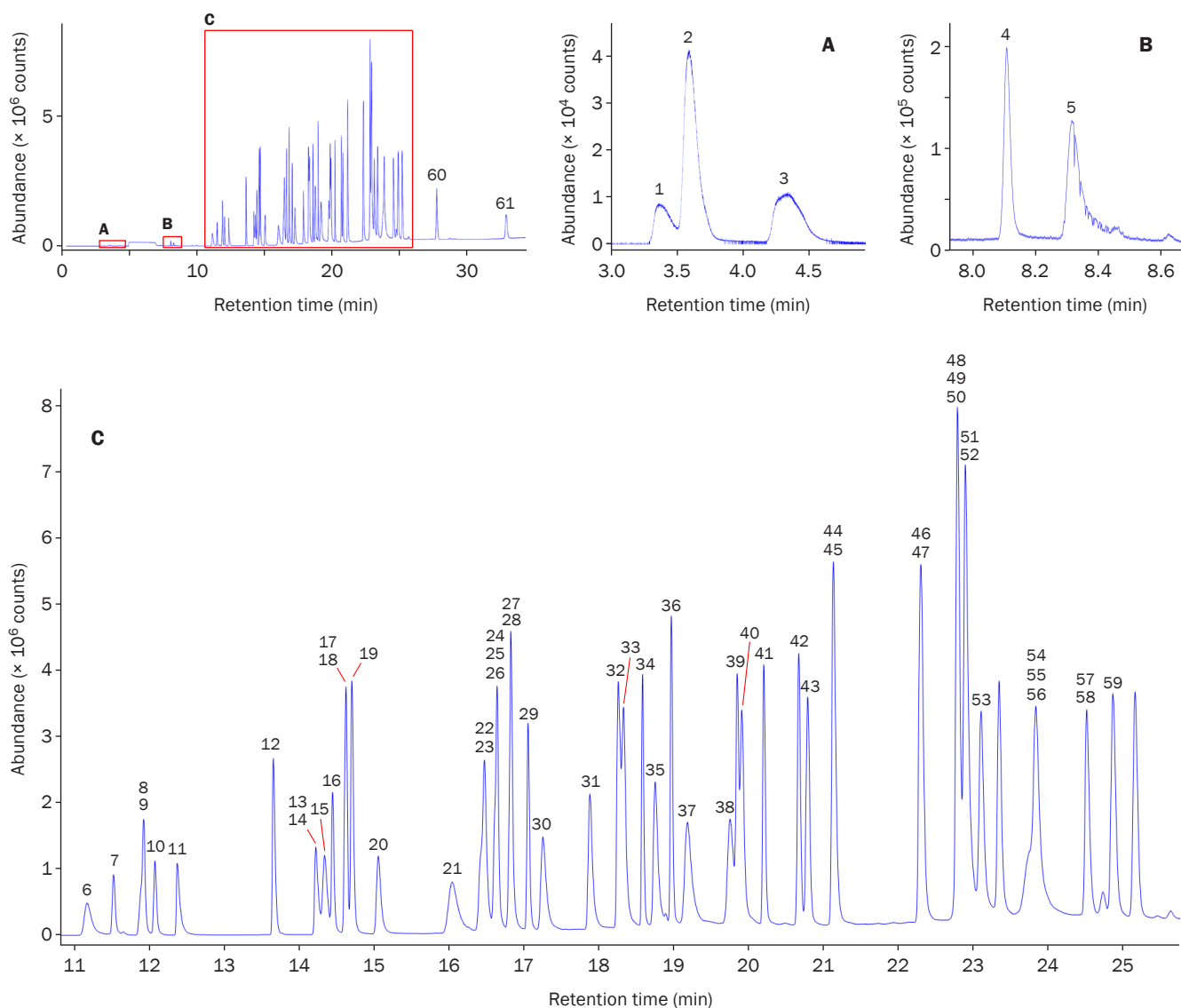


Figure 3: Analysis of 800 mL of the 4 ppb, 100% RH, 61-component standard using TD-GC-MS with Kori-xr water removal.

3. Linearities

Linearities were calculated on the basis of analyses of the standard mix at nine volumes from 50 to 1500 mL, and 47 of the 61 compounds gave R^2 values >0.99 for data across this full volume range. Plots for four target compounds are shown in Figure 4.

All ozone precursor target compounds, including the most volatile species (acetylene, ethane and ethane), showed excellent linearity for air sample volumes up to at least 800 mL. This is well above the normal sampling range for PAMS monitoring, and allows quantitative detection to 0.1 ppb or below.

4. Method detection limits (MDLs)

MDLs were calculated on the basis of seven repeat analyses of the standard mix at 0.5 ppb using 800 mL of sample.²⁵ Our calculations, performed using the Student's t-test value, gave a mean MDL of 47.5 ppt (Table A1), with values for 58 out of the 61 compounds being below 100 ppt, and 37 being below 50 ppt. The vast majority of values obtained are therefore substantially lower than the typical PAMS requirement of 0.1–0.5 ppb.

5. Carryover

Carryover of analytes from one run to the next is often observed when using Nafion dryers. To assess the reduced levels of carryover achieved using Kori-xr, blank runs were performed immediately after analysis of a 4 ppb standard under standard instrument conditions (Figure 5), using either Kori-xr or a Nafion dryer. It is clear from this comparison that the use of Kori-xr results in a much cleaner system.

In addition, quantitation indicated carryover levels for the Nafion dryer experiment that were above 0.15 ppb for ethane, 2,2-dimethylbutane, o-xylene, 1,4-diethylbenzene, n-decane, n-undecane and n-dodecane. This would significantly impact the validity of quantitation for those compounds. Note that the Kori-xr experiment shows no carryover for polar species and monoterpenes, while those compounds cannot be quantitatively analysed using Nafion dryers.

6. Real air sample

To illustrate the performance of the system for a real air sample, air at a light-industrial location in the UK was analysed under the same conditions as described previously, and 10 components from the PAMS listing were found to be at quantifiable levels (Figure 6).

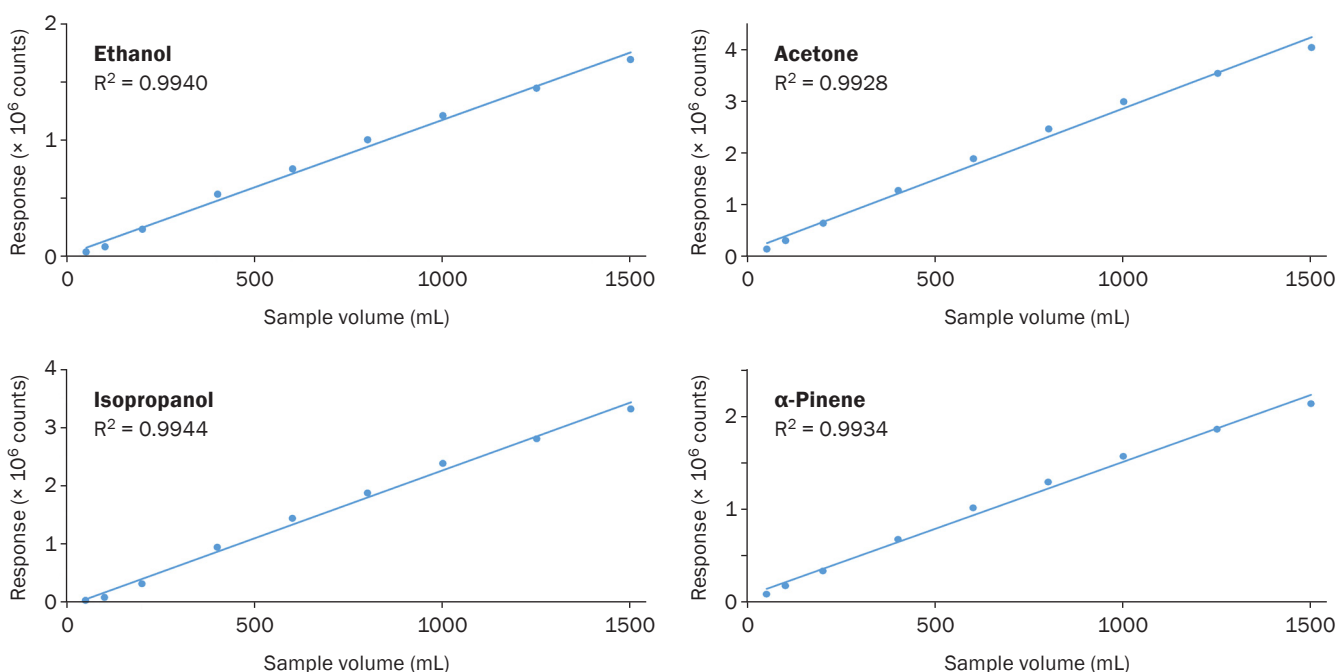


Figure 4: Linearities from 50–1500 mL for four target compounds from the 4 ppb, 100% RH, 61-component standard. It should be noted that these compounds cannot be quantitatively analysed using Nafion dryers.¹⁸

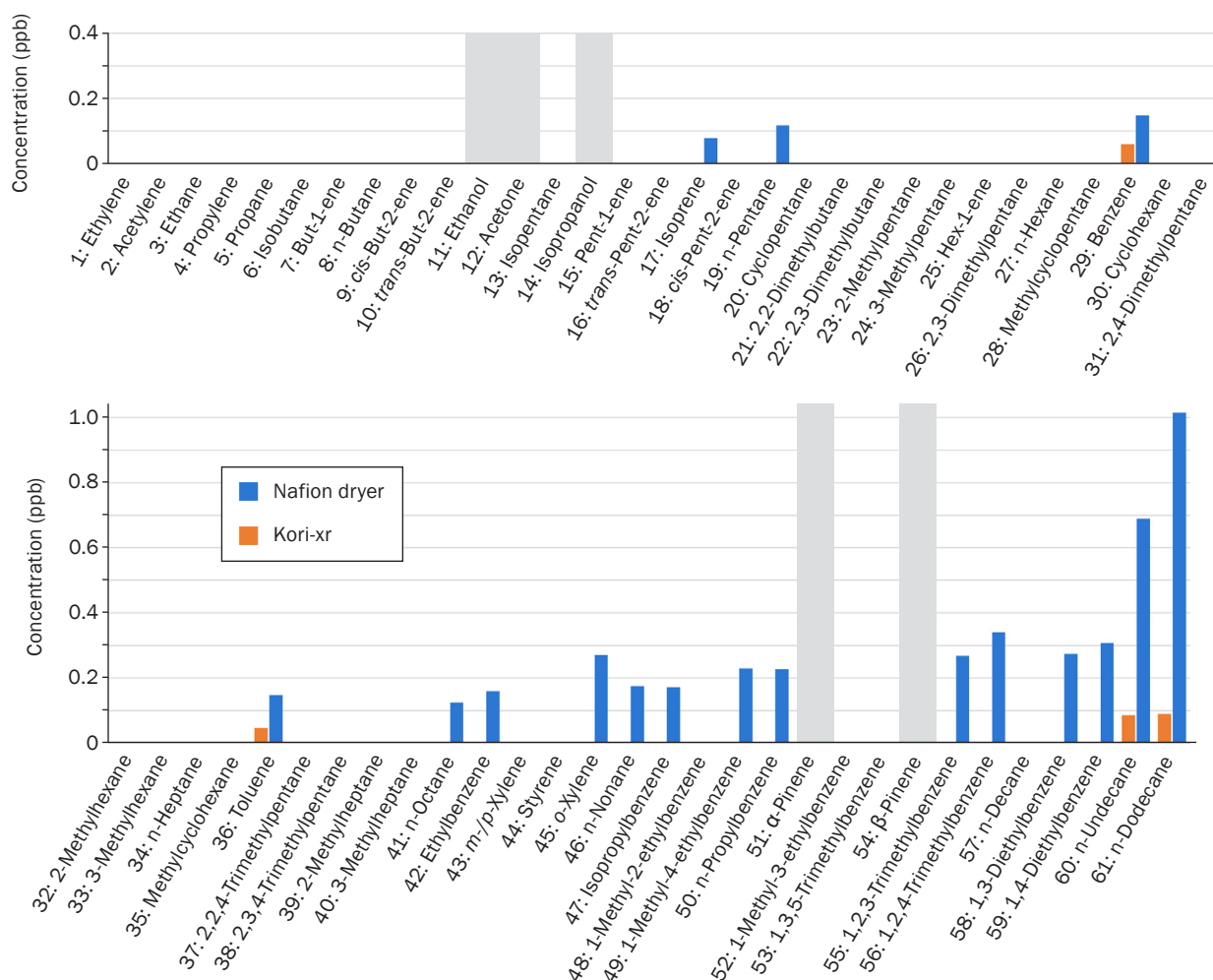


Figure 5: Assessment of carryover, by TD-GC-MS analysis of a 250 mL, dry nitrogen blank immediately following analysis of a 4 ppb, 100% RH, 61-component standard with water removal by Kori-xr (orange) or Nafion dryer (blue). Polar compounds and monoterpenes are shaded in grey (note that it is not possible to generate quantitative results for these compounds when using Nafion dryers).

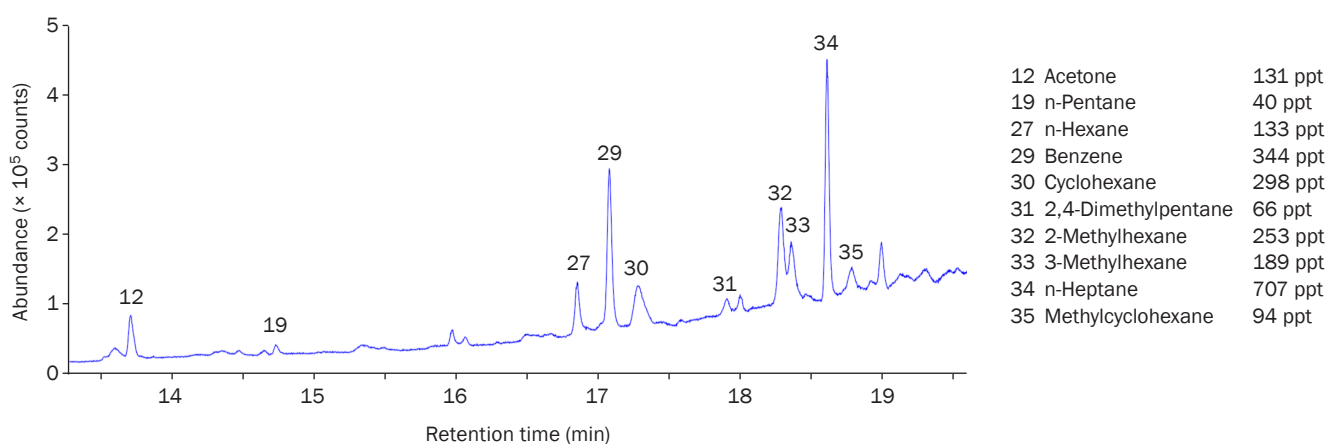


Figure 6: Analysis of 800 mL air at a light-industrial location in the UK, using the conditions previously described. Compounds from the PAMS listing are indicated.

Conclusions

In summary, the UNITY–Air Server-xr pre-concentration system with water removal by Kori-xr allows confident on-line GC–MS analysis of an extended range of ozone precursors in humid environments, in accordance with the recommendations of the US EPA PAMS technical assistance document.

Key results are:

- Unparalleled water removal, without loss of polar and oxygenated species. Reliable analysis of polar compounds (such as ethanol, isopropanol and acetone) and the monoterpenes α - and β -pinene is achieved, avoiding the difficulties often encountered when using Nafion dryers to remove airborne humidity prior to GC analysis.
- Cryogen-free analysis of the most volatile VVOCs, hydrocarbons, polar species and monoterpenes in humid ambient air with excellent linearities and reproducibilities, for increased data quality and rapid, unattended reporting.
- Electrical trap cooling (both in the UNITY-xr thermal desorber and the Kori-xr water condenser) make this system ideal for field monitoring in remote locations by eliminating the requirement for liquid cryogen.

Two additional features of all Markes' TD systems, including the UNITY–Air Server-xr system used in this study, are the ability to (a) run standard 3½" thermal desorption sample tubes, and (b) re-collect the split portions of samples onto clean sorbent tubes for easier method validation and sample storage.

References and notes

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12. (a) *Final Report: Gas Chromatograph Evaluation Study – Laboratory Evaluation Phase*, US EPA, October 2014 (in this report systems containing Markes' TD instruments correspond to Vendor 1 and Vendor 3); (b) *Final Report: Gas Chromatograph Evaluation Study – Field Deployment Evaluation Phase*, US EPA, February 2017 (in this report systems containing Markes' TD instruments correspond to Vendor D and Vendor E). Both reports are available at www3.epa.gov/ttnamti1/pamsreeng.html, and a summary of the results can be found at www.markes.com/news/air-monitoring-equipment-from-markes-comes-top-in-us-epa-field-trials.aspx.
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15. The current PAMS guidance does not stipulate whether flame ionisation detection (FID) or mass spectrometry (MS) should be used. MS, although requiring quantitation to be conducted using a standard containing all analytes (as shown in this document), offers the advantage of easier analyte speciation and reduced sensitivity to interference compared to FID. Detailed validation of a TD-GC-dual FID system using Kori-xr will be the subject of a future application note. An e-seminar covering detector choice, presented by a PAMS analyst, is available: <http://webinar.sepscience.com/hourly-monitoring-of-nmhcs-by-autogc-for-pams>.
16. Older systems for on-line analysis use liquid cryogen in order to trap very volatile compounds. Markes' systems are specifically designed to use electrical (Peltier) cooling, allowing quantitative retention of the most volatile compounds from large sample volumes. This avoids the considerable cost of liquid nitrogen, and the inconvenience or impracticality of using it, especially in field locations.
17. The design and packing of the trap is crucial for this application for several reasons. The narrow-bore design of the UNITY-xr trap 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. The sorbents chosen and sorbent bed length 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.
18. The manufacturers of Nafion tubing, PermaPure, state that alcohols are "all actively removed by Nafion", that ketones are removed after undergoing acid-catalysed enolisation, and that compounds with double/triple bonds involving carbon or with steric stress (*i.e.* including pinenes), are converted into other compounds.¹⁹ Similarly, US EPA Method TO-14A notes that "Polar organic compounds permeate this membrane in a manner similar to water vapor and rearrangements can occur in some hydrocarbons due to the acid nature of the dryer."²⁰ A number of earlier publications also report the loss of these types of compounds using Nafion.²¹⁻²⁴
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25. MDLs were calculated on the basis of 99% confidence for seven values (MDL = 3.143 × standard deviation × concentration).

Trademarks

Air Server-xr™, Kori-xr™, ULTRA-xr™ and UNITY-xr™ are trademarks of Markes International.

Nafion™ is a trademark of the Chemours Company.

TracePLOT™ is a trademark of ThermoFisher Scientific.

Acknowledgement

Kori-xr was developed in collaboration with the National Centre for Atmospheric Science (NCAS) at the University of York. It was co-funded by the UK's innovation agency (Innovate UK), the Natural Environment Research Council (NERC) and the Welsh Government under the Knowledge Transfer Partnership program.

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

Appendix

No.	Compound	Type	PAMS status ^[a]	t _R (min)	t _R RSD (%)	Response RSD (%)	R ² (50–1500 mL)	MDL (ppt)	Quant ion (m/z)
1	Ethylene	C ₂	P	3.36	0.122	8.7	0.9059 ^[b]	83.4	26
2	Acetylene	C ₂	O	3.56	0.071	1.7	0.9897 ^[b]	92.9	26
3	Ethane	C ₂	P	4.25	0.112	3.0	0.9931 ^[b]	98.1	26
4	Propylene	C ₃	P	8.11	0.021	2.1	0.9990 ^[c]	7.8	41
5	Propane	C ₃	P	8.34	0.023	2.1	0.9923 ^[d]	91.2	44
6	Isobutane	C ₄	P	11.28	0.031	3.8	0.9966	47.6	43
7	But-1-ene	C ₄	P	11.60	0.016	2.6	0.9901 ^[c]	12.7	41
8	n-Butane	C ₄	P	11.95	0.015	2.2	0.9965	9.2	43
9	cis-But-2-ene	C ₄	P	11.96	0.016	2.6	0.9922	21.0	41
10	trans-But-2-ene	C ₄	P	12.11	0.025	3.3	0.9942 ^[c]	18.8	41
11	Ethanol	Polar	O	12.41	0.012	5.7	0.9940	96.1	31
12	Acetone	Polar	P	13.68	0.013	1.5	0.9928	21.7	43
13	Isopentane	C ₅	P	14.25	0.021	9.6	0.9941	14.6	43
14	Isopropanol	Polar	N	14.25	0.018	8.4	0.9944	112.6	45
15	Pent-1-ene	C ₅	O	14.35	0.018	5.9	0.9958	12.6	42
16	trans-Pent-2-ene	C ₅	O	14.46	0.019	3.4	0.9969	5.5	55
17	Isoprene	C ₅	P	14.63	0.010	2.3	0.9957	10.4	67
18	cis-Pent-2-ene	C ₅	O	14.65	0.016	3.6	0.9941	9.1	55
19	n-Pentane	C ₅	P	14.72	0.009	2.3	0.9944	10.6	43
20	Cyclopentane	C ₅	O	15.07	0.015	2.3	0.9953	9.5	42
21	2,2-Dimethylbutane	C ₆	O	16.06	0.048	1.9	0.9972	76.9	43
22	2,3-Dimethylbutane	C ₆	O	16.49	0.014	5.3	0.9959	82.6	43
23	2-Methylpentane	C ₆	O	16.49	0.014	11.7	0.9959	73.3	43
24	3-Methylpentane	C ₆	O	16.63	0.022	2.7	0.9952	18.0	57
25	Hex-1-ene	C ₆	N	16.66	0.013	2.1	0.9920	22.4	56
26	2,3-Dimethylpentane	C ₇	O	16.66	0.013	2.1	0.9920	15.6	56
27	n-Hexane	C ₆	P	16.81	0.009	2.4	0.9933	22.2	57
28	Methylcyclopentane	C ₆	O	16.84	0.011	9.7	0.9936	21.1	56
29	Benzene	C ₆	P	17.07	0.010	2.1	0.9946	50.5	78
30	Cyclohexane	C ₆	O	17.27	0.021	2.3	0.9944	98.2	56
31	2,4-Dimethylpentane	C ₇	O	17.90	0.013	2.0	0.9936	15.4	43
32	2-Methylhexane	C ₇	O	18.28	0.013	2.5	0.9934	19.8	43
33	3-Methylhexane	C ₇	O	18.35	0.015	11.5	0.9939 ^[c]	68.6	43
34	n-Heptane	C ₇	O	18.60	0.011	2.0	0.9908	21.7	43
35	Methylcyclohexane	C ₇	O	18.77	0.017	2.5	0.9955	23.9	83
36	Toluene	C ₇	P	18.98	0.009	2.2	0.9911	40.3	91
37	2,2,4-Trimethylpentane	C ₈	P	19.20	0.024	2.5	0.9905	27.1	57
38	2,3,4-Trimethylpentane	C ₈	O	19.77	0.017	3.0	0.9898	178.6	43
39	2-Methylheptane	C ₈	O	19.87	0.012	10.6	0.9777 ^[b]	26.6	43
40	3-Methylheptane	C ₈	O	19.93	0.020	9.5	0.9869 ^[b]	54.6	43
41	n-Octane	C ₈	O	20.23	0.010	1.8	0.9910	31.0	43
42	Ethylbenzene	C ₈	P	20.69	0.013	1.7	0.9939	41.0	91
43	m-/p-Xylene	C ₈	P	20.81	0.018	4.9	0.9924	36.1	91
44	Styrene	C ₈	P	21.15	0.015	1.9	0.9929	31.2	104
45	o-Xylene	C ₈	P	21.17	0.013	1.9	0.9916	82.8	91
46	n-Nonane	C ₉	O	22.32	0.014	2.0	0.9939	46.9	43
47	Isopropylbenzene	C ₉	O	22.33	0.013	2.2	0.9918	21.5	105
48	1-Methyl-2-ethylbenzene	C ₉	P	22.80	0.017	1.7	0.9923	43.3	105
49	1-Methyl-4-ethylbenzene	C ₉	P	22.81	0.017	1.7	0.9925	67.1	105
50	n-Propylbenzene	C ₉	O	22.83	0.015	1.5	0.9991 ^[b]	43.1	91
51	α-Pinene	Terpene	O	22.90	0.033	1.4	0.9934	24.8	93
52	1-Methyl-3-ethylbenzene	C ₉	P	22.92	0.009	3.0	0.9977 ^[c]	17.2	105
53	1,3,5-Trimethylbenzene	C ₉	O	23.12	0.015	1.6	0.9913	157.8	105
54	β-Pinene	Terpene	O	23.83	0.045	6.4	0.9865 ^[b]	71.5	93
55	1,2,3-Trimethylbenzene	C ₉	P	23.86	0.020	2.0	0.9961	81.1	105
56	1,2,4-Trimethylbenzene	C ₉	P	23.86	0.020	2.0	0.9961	72.7	105
57	n-Decane	C ₁₀	O	24.56	0.019	1.9	0.9982	68.7	57
58	1,3-Diethylbenzene	C ₁₀	O	24.60	0.018	12.6	0.9918 ^[b]	22.4	119
59	1,4-Diethylbenzene	C ₁₀	O	24.90	0.023	1.7	0.9974	59.6	119
60	n-Undecane	C ₁₁	O	27.75	0.016	1.2	0.9995	63.5	57
61	n-Dodecane	C ₁₂	N	32.89	0.029	3.1	0.9905	73.1	57
	Mean				0.022	3.6	0.9920	47.5	

Table A1: Data obtained for the 100% RH, 61-component standard. ^[a] Current status as indicated in ref. 14. P = Priority compound. O = Optional compound. N = Not listed. Acetaldehyde (P), benzaldehyde (O), butadiene (O), formaldehyde (P), tetrachloromethane (O) and tetrachloroethene (O) are in the current PAMS target list but were not analysed in this study. Acetaldehyde and formaldehyde are usually monitored using DNPH cartridges with HPLC detection. ^[b] Linearity for 50–800 mL. ^[c] Linearity for 50–1000 mL. ^[d] Linearity for 50–1250 mL.