

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

Summary

This Application Note describes validation of a cryogen-free thermal desorption (TD) system with dual-column GC–FID detection 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. Using the new Kori-xr system for analyte focusing and water removal, we demonstrate excellent chromatographic performance, linearities and reproducibilities for a 59-component standard mix, and apply this method to a real air sample.



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 interest recently growing 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 (January 2018), the proposed list of target compounds for the re-engineered PAMS program comprises 28 ‘priority compounds’ and 35 ‘optional compounds’. 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.

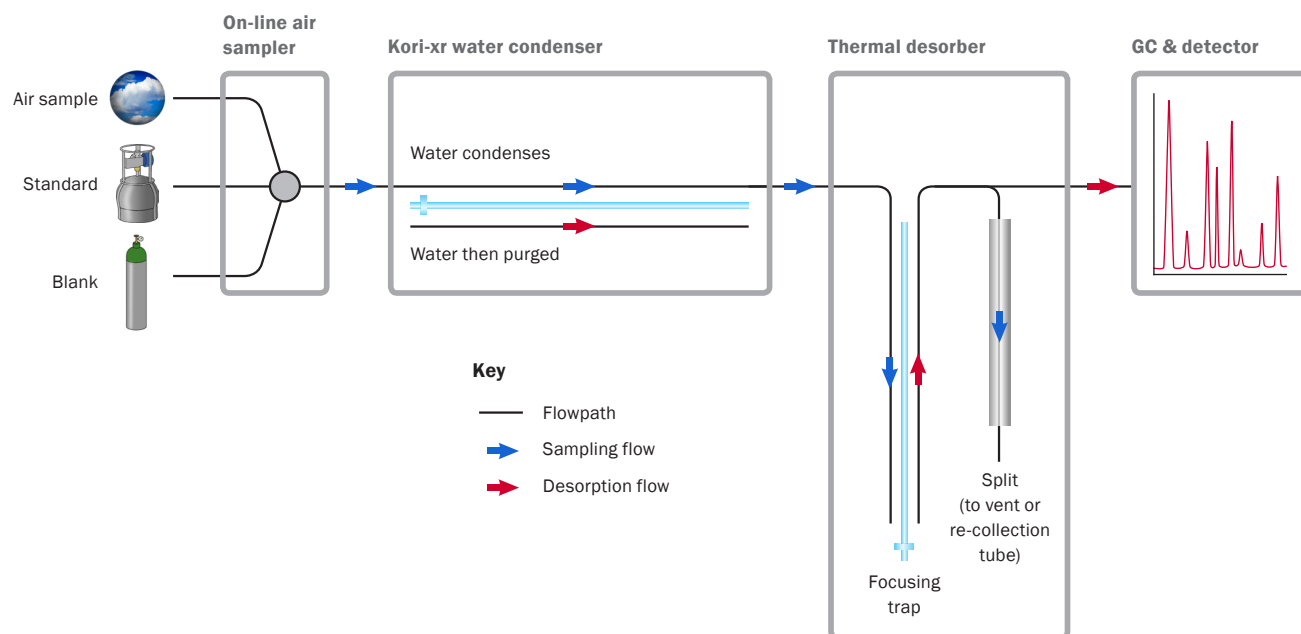


Figure 1: TD instrument configuration.

These dryers work by using a hydrophilic co-polymer to adsorb water, 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 the use of on-line thermal desorption system with dual-column GC–FID that overcomes this difficulty by combining efficient analyte focusing with use of an innovative, cryogen-free water-removal device. This approach results in improved performance for an extended range of analytes in a single run, including hydrocarbons, polar species and monoterpenes.

Analytical equipment

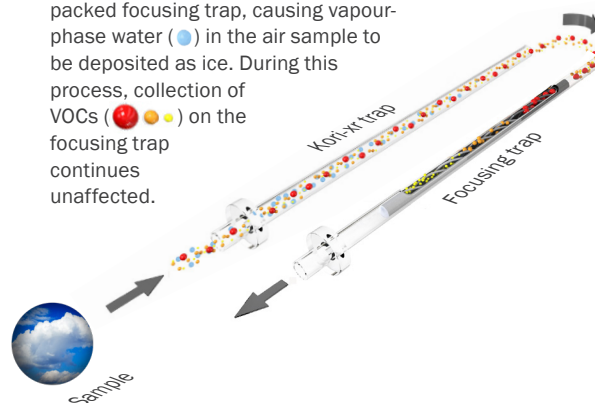
The analytical system used for this study was an Air Server-xr on-line sampler with a Kori-xr water condenser and UNITY-xr thermal desorber, coupled to a dual-column GC–FID system¹⁵ (Figure 1). The entire system is cryogen-free and can be controlled remotely, making it ideal for unattended operation 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). In addition to 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

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.

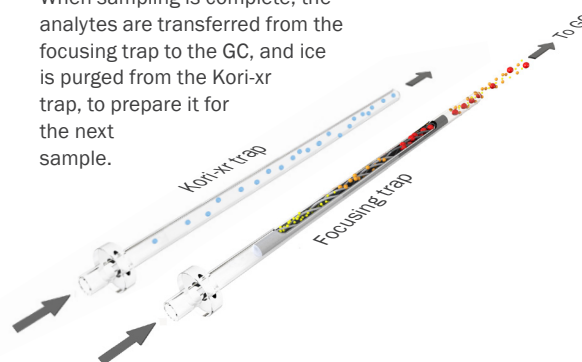


Figure 2: Operation of the Kori-xr device for removing water from humid air streams.

that as well as on-line monitoring, Kori-xr can also be applied to canister and bag samples, as part of the Dry-Focus3™ approach involving water removal, analyte focusing and a trap dry-purge.

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, 59-component gas standard, humidified to 100% RH by an injection of an appropriate amount of water. The real air sample (with a relative humidity of ~75%) was taken in August 2017 at a light-industrial location in Llantrisant, UK.

Sampling:

Instrument: Air Server-xr (Markes International)
 Sample purge: 4 min at 25 mL/min
 Sampling rate: 25 mL/min
 Sampling time: Various
 Line flush: 5 min at 75 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’ (part no. U-T20PAM-2S)
 Cold trap low: -30°C
 Cold trap high: 300°C
 Cold trap hold: 5 min
 Flow path temp.: 80°C
 Trap purge: 2 min at 50 mL/min
 Split flow: 2 mL/min

GC:

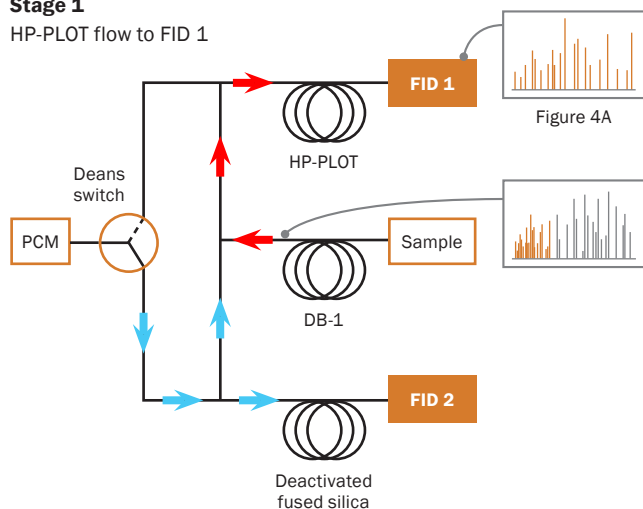
Column 1: DB-1™ (polydimethylsiloxane), 60 m × 0.25 mm × 1 μm
 Column flow: 2.4 mL/min (helium)
 Pressure: 45.6 psi (constant)
 Column 2: HP-PLOT™ (Al₂O₃ S), 50 m × 0.32 mm × 8 μm
 Column flow: 3.2 mL/min (helium)
 Pressure: 22.4 psi (constant)
 Oven ramp: 35°C (12 min), then 5°C/min to 170°C (10 min), then 15°C/min to 200°C (5 min)
 GC run time: 46 min
 Deans switch: On for 15.5 min, then off (see Figure 3 for the column/detector setup)

FID (1 and 2):

Heater: 250°C
 H₂ flow: 40 mL/min
 Air flow: 400 mL/min

Stage 1

HP-PLOT flow to FID 1



Stage 2

DB-1 flow to FID 2

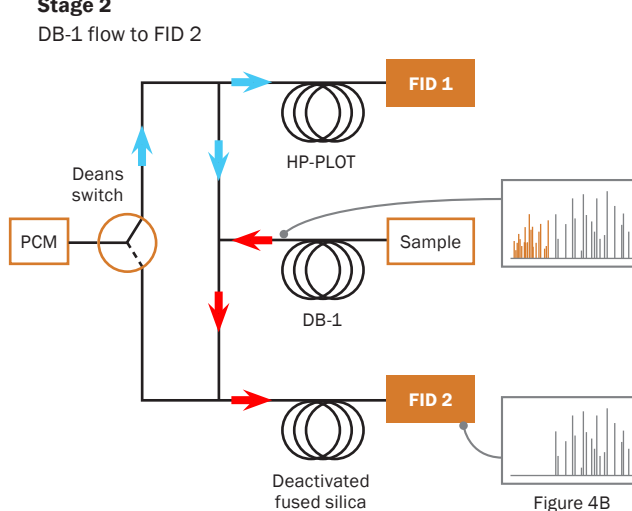


Figure 3: Dual-column GC–FID instrument operation. → = Analyte flow. → = Gas flow. PCM = Pneumatic control module.

Results and discussion

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

1. Breakthrough tests

The most volatile compounds monitored under the PAMS scheme – the C₂ hydrocarbons – have very low boiling points, requiring careful selection of the cold trap sorbent(s) and focusing temperature in order to achieve quantitative retention without liquid cryogen.

The conditions selected were assessed by sequentially sampling increasing volumes of gas standard (up to 2 L) and plotting detector response against sample volume. All the compounds were found to give linear responses up to at least 1.5 L, except for acetylene (the most volatile C₂ compound), which gave a non-linear response for sample volumes of 1 L and above.

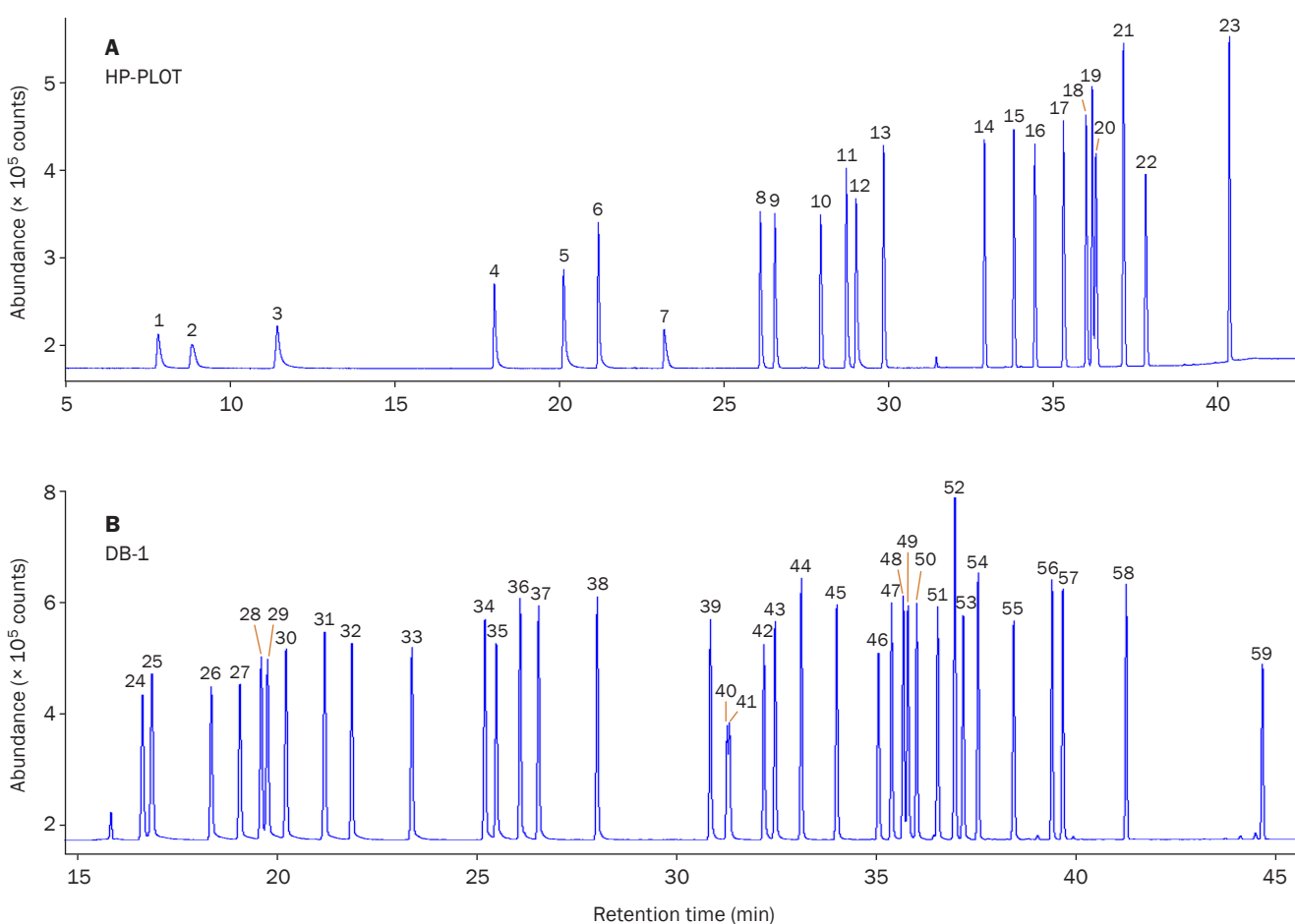
2. Analysis of a standard mix

Figure 4 shows analysis of 800 mL of the 10 ppb standard mix at 100% RH (relative humidity) using the TD-GC-FID system.

3. Reproducibility

The nature of the two-column set-up means that retention times can be affected by the pressure balance in the system. However, electronic carrier gas control (ECC) on the Air Server-UNITY-xr system, and the efficient removal of water using Kori-xr, means that stable retention times on both columns are achieved.

Reproducibilities for retention time and analyte response (relative to sample volume) were calculated using seven replicate measurements of 800 mL of the 100% RH standard mix, and are listed in Table A1.



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

Figure 4: Analysis of 800 mL of the 10 ppb, 100% RH 59-component standard using TD-dual-column GC-FID with Kori-xr water removal.

The mean retention-time RSD was 0.048%, with the highest value being 0.251% for acetylene (HP-PLOT column), and the lowest value being 0.002% for *m*-diethylbenzene (DB-1 column). This high degree of reproducibility makes it much easier to achieve precise automated quantitation, saving time when reviewing data.

The mean response RSD was 1.37%, with the highest value being 4.52% for *n*-dodecane (DB-1) and the lowest being 0.52% for 1,3,5-trimethylbenzene (DB-1).

4. Linearity

Linearities were calculated on the basis of analyses of the standard mix at five volumes from 100 to 800 mL, using two canisters to provide an overall concentration range of 0.5 to 50 ppb. R^2 values ≥ 0.995 were obtained for all compounds (with the exception of the two latest-eluting compounds, *n*-undecane and *n*-dodecane) from 0.5–50 ppb. Plots for five compounds are shown in Figure 5.

All ozone precursor target compounds, including polar compounds and terpenes, showed excellent linearity for air sample volumes up to at least 800 mL (see Table A1). This is well above the normal sampling range for PAMS monitoring, and allows quantitative detection to 0.1 ppb or below.

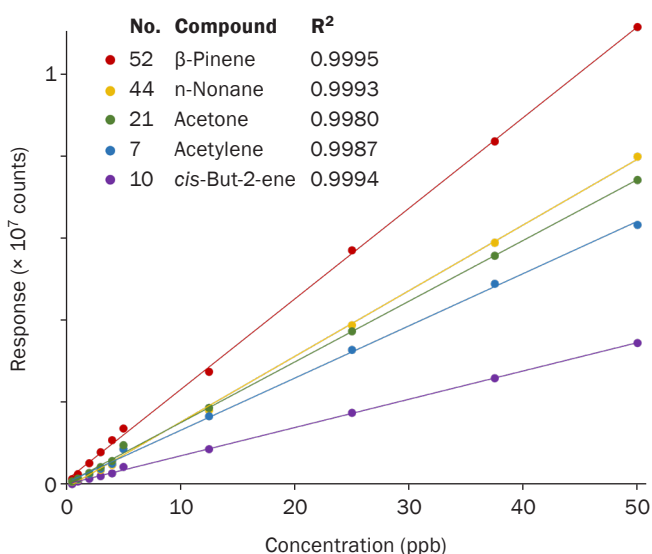


Figure 5: Linearities from 0.5–50 ppb for five target compounds from the 100% RH 59-component standard. β -Pinene and *n*-nonane were analysed on the DB-1 column; acetone, acetylene and *cis*-but-2-ene were analysed on the HP-PLOT column. It should be noted that β -pinene and acetone cannot be quantitatively analysed using Nafion dryers.¹⁸

5. Method detection limits (MDLs)

MDLs were calculated based on the analysis of seven repeat analyses of the standard mix at 0.1 ppb and 0.5 ppb using 800 mL of sample.²⁵

Our calculations gave a mean MDL of 26.7 ppt (Table A1), with values for 41 out of the 59 compounds being at 30 ppt or below. Values ranged from 6.51 ppt for 2-methylheptane to 112 ppt for ethane.

6. 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 10 ppb standard under standard instrument conditions.

As demonstrated previously for the analysis of a PAMS ozone precursors mix using TD-GC-MS (see [Application Note 128](#)), use of Kori-xr results in a much cleaner system than would be expected with a Nafion dryer. The majority of compounds showed carryover values below 1%, with higher values being obtained for certain less volatile compounds such as *n*-undecane and *n*-dodecane. The same experiment, performed using a Nafion dryer, resulted in carryover values for *n*-undecane and *n*-dodecane that were 1.3 and 1.7 times higher, respectively.

7. Background

In order to achieve reliable air analysis and accurate quantitation, blank levels need to be as low as possible. To assess this, system blanks were carried out at the beginning of the study, by running 800 mL of nitrogen from the gas line (Figure 6). Blank levels were at 0.035 ppb or below, with the sole exception of benzene (0.096 ppb).

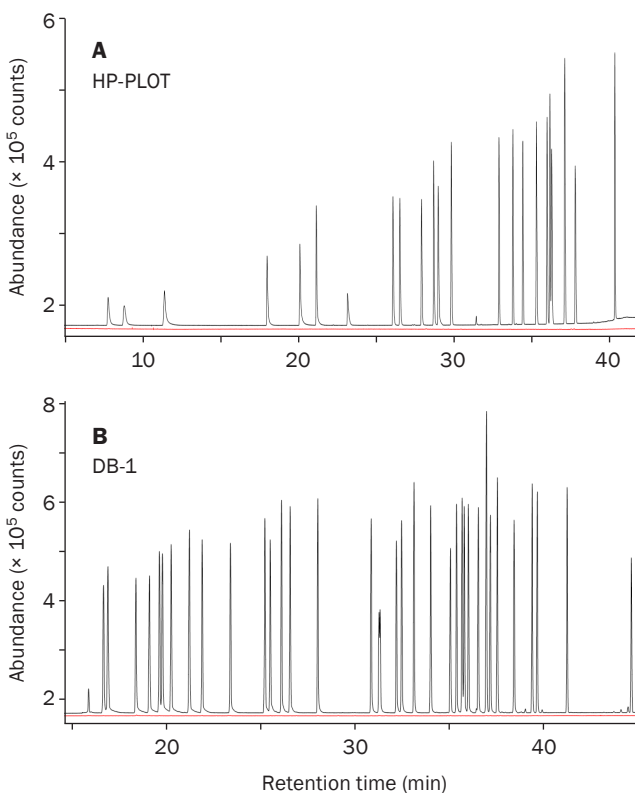


Figure 6: Analysis of 800 mL of the 10 ppb, 100% RH 59-component standard (black) compared to an 800 mL nitrogen blank (red).

8. 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 eight components from the PAMS listing were found to be at quantifiable levels (Figure 7).

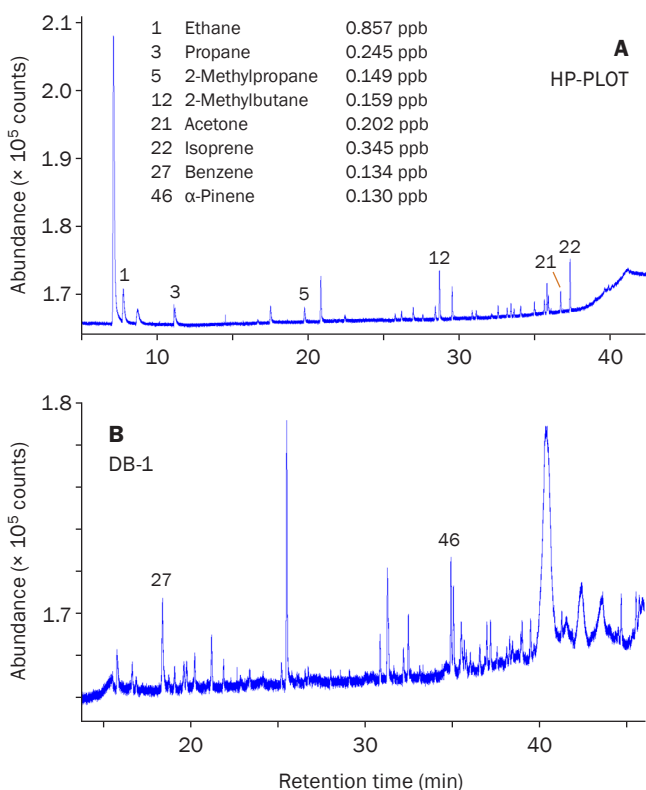


Figure 7: Analysis of 800 mL air at a light-industrial location in UK, using the conditions previously described. Compounds from the PAMS listing are indicated.

Conclusions

In summary, the UNITY–Air Server-xr pre-concentration system allows confident on-line dual-column GC–FID 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 efficiency by Kori-xr allows unattended analysis of polar species and oxygenates, and avoids the difficulties often encountered when using Nafion dryers to remove airborne humidity prior to GC analysis.
- Analysis of a wide range of PAMS target compounds in humid ambient air with excellent linearities and reproducibilities is demonstrated, for increased data quality and rapid, unattended reporting.
- Electrical trap cooling (both in the UNITY-xr thermal desorber and the Kori-xr water condenser) makes 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.

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.

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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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14. Quality assurance guidance: PAMS required quality assurance implementation plan, US EPA, October 2016, www3.epa.gov/ttnamti1/pamsguidance.html.
15. The current PAMS guidance does not stipulate whether flame ionisation detection (FID) or mass spectrometry (MS) should be used. FID, although having lower sensitivity than MS and not allowing identification of unknowns, does not require quantitation to be conducted using a standard containing all analytes. Detailed validation of a TD–GC–MS system using Kori-xr is the subject of [Application Note 128](#), and 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.^{21,22,23,24}
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25. MDLs were calculated on the basis of 99% confidence for seven values ($MDL = 3.143 \times \text{standard deviation} \times \text{concentration}$).

Trademarks

Air Server-xr™, Dry-Focus3™, Kori-xr™, ULTRA-xr™ and UNITY-xr™ are trademarks of Markes International.

DB-1™ and HP-PLOT™ are trademarks of Agilent Corporation.

Nafion™ is a trademark of the Chemours Company.

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]	Column	t _R (min)	t _R RSD (%) ^[b]	Response RSD (%) ^[b]	R ² (0.5–50 ppb)	MDL (ppt) ^[c]	Spiked level (ppb)
1	Ethane	C ₂	P	HP-PLOT	7.86	0.048	1.41	0.9974	111.5	0.5
2	Ethylene	C ₂	P	HP-PLOT	8.72	0.149	2.04	0.9990	91.2	0.5
3	Propane	C ₃	P	HP-PLOT	11.80	0.129	1.22	0.9990	73.4	0.5
4	Propylene	C ₃	P	HP-PLOT	18.60	0.217	1.81	0.9991	31.1	0.1
5	2-Methylpropane	C ₅	N	HP-PLOT	20.16	0.123	1.27	0.9986	66.1	0.1
6	n-Butane	C ₄	P	HP-PLOT	21.23	0.108	1.74	0.9989	10.6	0.5
7	Acetylene	C ₂	O	HP-PLOT	23.25	0.251	3.84	0.9987	23.3	0.1
8	trans-But-2-ene	C ₄	P	HP-PLOT	26.05	0.110	1.47	0.9990	15.8	0.1
9	But-1-ene	C ₄	P	HP-PLOT	26.53	0.004	0.88	0.9994	19.4	0.5
10	cis-But-2-ene	C ₄	P	HP-PLOT	27.90	0.105	1.80	0.9994	9.22	0.5
11	Cyclopentane	C ₅	O	HP-PLOT	28.70	0.086	0.62	0.9981	18.3	0.5
12	2-Methylbutane	C ₅	N	HP-PLOT	29.01	0.073	1.13	0.9993	11.8	0.5
13	n-Pentane	C ₅	P	HP-PLOT	29.85	0.075	0.77	0.9993	17.2	0.5
14	trans-Pent-2-ene	C ₅	O	HP-PLOT	32.91	0.085	0.88	0.9992	16.3	0.1
15	Pent-1-ene	C ₅	O	HP-PLOT	33.81	0.093	1.01	0.9994	13.5	0.5
16	cis-Pent-2-ene	C ₅	O	HP-PLOT	34.44	0.004	0.88	0.9986	10.6	0.1
17	2,2-Dimethylbutane	C ₆	O	HP-PLOT	35.31	0.083	2.28	0.9974	12.6	0.5
18	2,3-Dimethylbutane	C ₆	O	HP-PLOT	36.00	0.091	1.79	0.9957	17.4	0.1
19	2-Methylpentane	C ₆	O	HP-PLOT	36.18	0.080	1.97	0.9991	13.2	0.1
20	3-Methylpentane	C ₆	O	HP-PLOT	36.30	0.097	0.72	0.9979	8.81	0.1
21	Acetone	Polar	P	HP-PLOT	37.14	0.005	1.01	0.9980	7.69	0.1
22	Isoprene	C ₅	P	HP-PLOT	37.81	0.116	0.79	0.9993	9.32	0.1
23	2-Methylpent-1-ene	C ₆	N	HP-PLOT	40.35	0.116	0.82	0.9993	10.2	0.1
24	n-Hexane	C ₆	P	DB-1	16.64	0.104	0.53	0.9991	43.4	0.1
25	Methylcyclopentane	C ₆	O	DB-1	16.87	0.010	2.57	0.9977	7.32	0.1
26	2,4-Dimethylpentane	C ₇	O	DB-1	18.35	0.011	0.76	0.9980	7.83	0.1
27	Benzene	C ₆	P	DB-1	19.07	0.009	0.56	0.9993	96.5	0.1
28	Cyclohexane	C ₆	O	DB-1	19.60	0.009	0.63	0.9960	14.6	0.1
29	2-Methylhexane	C ₇	O	DB-1	19.76	0.008	0.58	0.9991	17.1	0.1
30	2,3-Dimethylpentane	C ₇	O	DB-1	20.23	0.008	0.73	0.9986	25.0	0.5
31	3-Methylhexane	C ₇	O	DB-1	21.19	0.008	1.21	0.9991	15.5	0.5
32	2,2,4-Trimethylpentane	C ₈	P	DB-1	21.87	0.007	1.20	0.9991	32.7	0.5
33	n-Heptane	C ₇	O	DB-1	23.37	0.011	0.97	0.9992	21.9	0.1
34	Methylcyclohexane	C ₇	O	DB-1	25.20	0.005	1.37	0.9987	17.0	0.5
35	2,3,4-Trimethylpentane	C ₈	O	DB-1	25.48	0.006	0.93	0.9992	7.74	0.1
36	Toluene	C ₇	P	DB-1	26.08	0.004	2.39	0.9992	16.5	0.5
37	2-Methylheptane	C ₈	O	DB-1	26.54	0.006	1.02	0.9990	6.51	0.5
38	3-Methylheptane	C ₈	O	DB-1	28.00	0.114	1.30	0.9993	7.04	0.1
39	n-Octane	C ₈	O	DB-1	30.83	0.004	1.63	0.9994	16.0	0.1
40	Ethylbenzene	C ₈	P	DB-1	31.25	0.006	0.81	0.9991	11.1	0.5
41	m-/p-Xylene	C ₈	P	DB-1	31.31	0.005	0.69	0.9991	36.1	0.5
42	Styrene	C ₈	P	DB-1	32.17	0.003	3.33	0.9969	36.7	0.1
43	o-Xylene	C ₈	P	DB-1	32.45	0.005	0.54	0.9994	21.1	0.5
44	n-Nonane	C ₉	O	DB-1	33.11	0.005	1.17	0.9993	16.3	0.1
45	Isopropylbenzene	C ₉	O	DB-1	33.99	0.005	0.71	0.9993	48.9	0.5
46	α-Pinene	Terpene	O	DB-1	35.03	0.095	0.99	0.9996	28.1	0.1
47	n-Propylbenzene	C ₉	O	DB-1	35.36	0.003	2.49	0.9987	6.83	0.1
48	1-Methyl-3-ethylbenzene	C ₉	P	DB-1	35.66	0.004	3.40	0.9983	26.8	0.5
49	1-Methyl-4-ethylbenzene	C ₉	P	DB-1	35.77	0.003	1.49	0.9961	34.5	0.5
50	1,3,5-Trimethylbenzene	C ₉	O	DB-1	35.99	0.004	0.52	0.9954	21.7	0.1
51	1-Methyl-2-ethylbenzene	C ₉	P	DB-1	36.51	0.004	0.90	0.9985	34.8	0.1
52	β-Pinene	Terpene	O	DB-1	36.95	0.003	1.00	0.9995	27.3	0.1
53	1,2,4-Trimethylbenzene	C ₉	P	DB-1	37.16	0.003	0.90	0.9975	34.1	0.5
54	n-Decane	C ₁₀	O	DB-1	37.53	0.097	0.76	0.9993	7.49	0.1
55	1,2,3-Trimethylbenzene	C ₉	P	DB-1	38.42	0.003	1.68	0.9977	44.0	0.5
56	1,3-Diethylbenzene	C ₈	O	DB-1	39.38	0.002	1.49	0.9965	38.5	0.1
57	1,4-Diethylbenzene	C ₈	O	DB-1	39.65	0.003	1.23	0.9949	8.70	0.5
58	n-Undecane	C ₁₁	O	DB-1	41.23	0.003	1.65	0.9941	35.1	0.5
59	n-Dodecane	C ₁₂	N	DB-1	44.64	0.004	4.52	0.9778	86.7	0.5
	Mean					0.016	1.35	0.9977	26.6	

Table A1: Data obtained for the 100% RH, 59-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), ethanol (O), formaldehyde (P), tetrachloromethane (O) and tetrachloroethene (O) are in the current PAMS target list but were not analysed in this study. ^[b] RSDs were based on seven replicates of an 800 mL, 10 ppb standard. ^[c] MDLs are based on analysis of seven replicates of 800 mL standards at 0.1 and 0.5 ppb.