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Application Note 133

Going beyond the requirements of US EPA Method TO-15: Innovative cryogen-free ambient air monitoring of trace-level air toxics at high humidity

Summary

This Application Note describes the GC–MS analysis of trace-level ‘air toxics’ in humidified canister air, using Markes’ ground-breaking cryogen-free Dry-Focus3 pre-concentration technology. We show that this system is able to detect 65 target compounds ranging from propene to naphthalene, with method detection limits as low as 0.7 pptv in SIM mode, making it compliant both with standard TO-15 methods, and with ‘trace TO-15’ methods stipulating lower detection limits.

Introduction

With growing concerns over the harmful effects of long-term exposure to low levels of hazardous air pollutants (‘air toxics’), there is increasing demand for analytical laboratories to detect ever-lower levels of analyte concentrations in ambient air. Unfortunately, the detection limit criteria on the analytical instrumentation set by the widely used US EPA Method TO-15[1] is not always able to address such needs. Therefore, some state environmental protection agencies in the US have developed new standard methods for low-level air toxics.

One of these, released by the New Jersey Department of Environmental Protection, and known as ‘Low-level US EPA Method TO-15’ (NJDEP LL TO-15),[2] sets lower reporting limits for the majority of the air toxics in US EPA Method TO-15, and in doing so moves the reporting limits for some compounds closer to health-based criteria.

Although traditional canister preconcentration technologies have long been used to quantitatively determine air toxics, significant challenges are posed by the ever-greater range of analytes and concentrations of interest, and by the range of temperatures and humidities at sampling locations. Dealing with high levels of humidity is particularly important, because the ingress of water to the analytical instrument can negatively impact analyte response and repeatability, as well as reduce the lifetime of the column and detector.

In this Application Note, we show how a canister autosampler (using innovative cryogen-free water-removal technology) and thermal desorption–gas chromatography–mass spectrometry (TD–GC–MS) together allow the analysis of a range of trace-level air toxics from air at 100% relative humidity (RH), in accordance with US EPA Method TO-15 and related methods with lower detection limits.

Analytical equipment

The analytical system used for this study was a CIA *Advantage*-xr™ canister autosampler and UNITY-xr™ thermal desorber with a Kori-xr™ water removal device, coupled to a GC–MS system (Figures 1 and 2). This system harnesses Dry-Focus3™ technology – a unique, three-stage focusing and water-management mechanism that operates entirely without liquid cryogen.

Figure 1: The UNITY–Kori–CIA *Advantage*-xr system used in the current study.

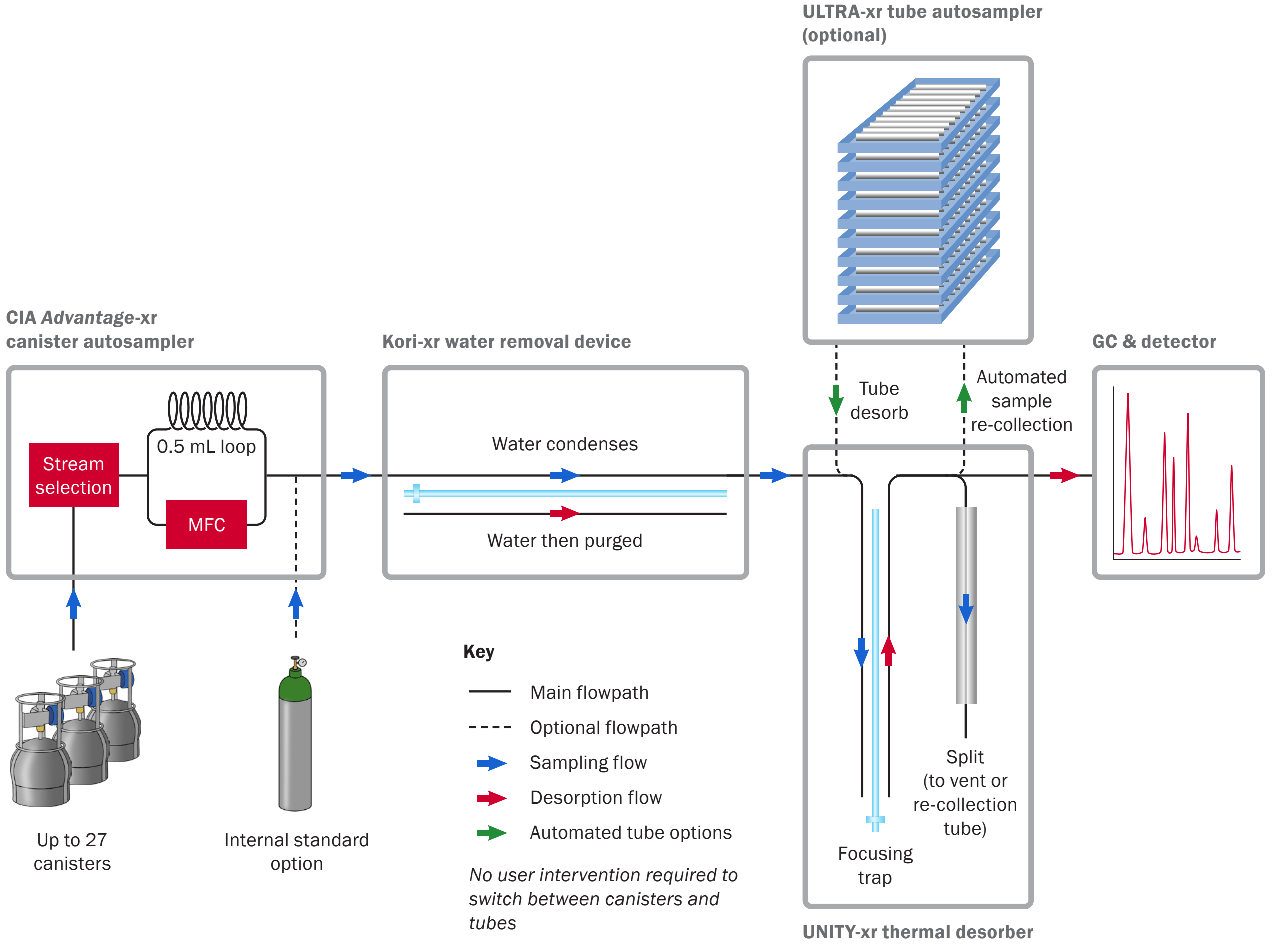


Figure 2: Equipment configuration.

The **CIA *Advantage*-xr** is an autosampler for the analysis of VOCs in up to 27 canisters (or bags), using either a 0.5 mL sample loop or a mass flow controller (MFC). These sampling options allow the automated analysis of both high- and low-concentration samples in a single automated sequence, avoiding the need to resort to dilution of high-concentration samples, and the associated increase in analytical uncertainty and the risk of contaminant introduction. It also overcomes the limitations of traditional cryogen-cooled technology for canister air analysis, such as high costs and flow path blocking caused by ice formation. 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% RH ambient air, the amount of residual water reaching the GC–MS system must be very low. For this reason Markes has developed the Dry-Focus3 approach, as well as a new focusing trap that is optimised for the cryogen-free analysis of VOCs, VVOCs and oxygenates in humid air using canisters.

The operation of this system is as follows. Ambient air samples first pass through a **Kori-xr** device that, without use of liquid cryogen, efficiently removes humidity from the air stream while preserving the compounds of interest (Figure 3). Note that as well as canisters and bags, Kori-xr can also be applied to on-line samples.

With the majority of excess water removed, samples then pass into the **UNITY-xr** thermal desorber, containing the newly-developed ‘Trace TO-15’ focusing trap (part no. U-TO15-KXR). This narrow, electrically-cooled trap is filled with separate beds of porous polymer, graphitised carbon black and molecular sieve sorbents. The different strength of these sorbents ensures that compounds over a wide volatility range are quantitatively trapped.

After sample collection at a trap temperature of –30°C, the temperature is initially elevated to 25°C, and the trap is purged with carrier gas in the sampling direction to eliminate oxygen and further reduce water from the focusing trap, without any loss or breakthrough of the analytes retained. Finally, the flow of gas through the focusing trap is reversed, and the trap is heated rapidly (up to 100°C/s), to inject the analytes onto the GC column.

1 Air sampling and water removal

Canister or whole-air samples pass through the drying trap (where vapour-phase water is selectively deposited as ice), before being concentrated on the focusing trap.

2 Purging of residual water

Optional temperature-programmed dry-purging of the focusing trap with carrier gas (between –30°C and 50°C) selectively eliminates any residual water while retaining 100% of target analytes.

3 Trap desorption

The focusing trap is rapidly heated in a reverse flow of carrier gas, to transfer analytes to the GC. Simultaneously, the drying trap is heated in a flow of gas to expel the trapped ice and regenerate it for the next sample.

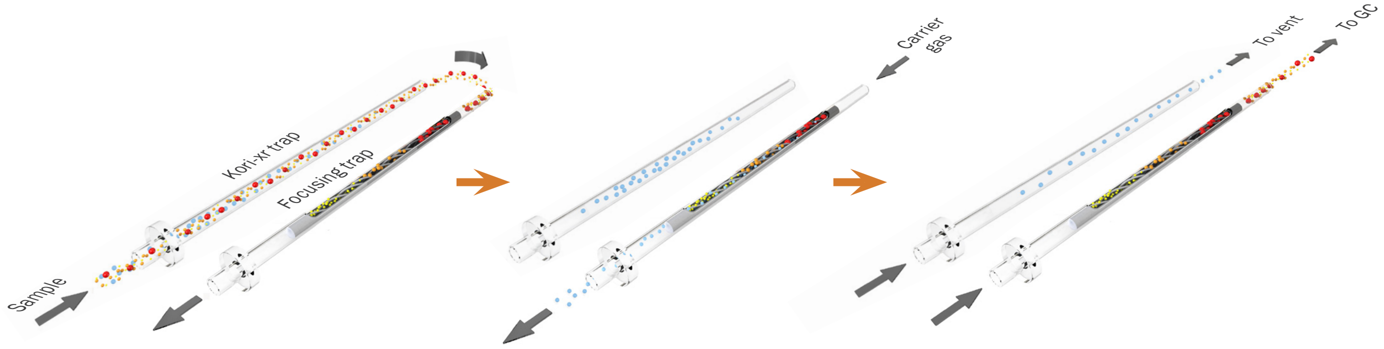


Figure 3: Operation of Dry-Focus3.

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 at a later time (although it should be noted that sorbent tubes are not able to retain very volatile compounds such as acetylene). The above process of sample splitting and re-collection can be fully automated by adding an **ULTRA-xr™** tube autosampler.

Experimental

The experimental parameters are listed below. The minimal amount of residual water resulting from use of Markes' cryogen-free Dry-Focus3 approach allows the GC oven temperature to start at a relatively high temperature of 35°C, for more efficient operation without compromising analyte peak shape.

Standards:
The 0.05 ppbv TO-15 standard was prepared by diluting 1 mL of a 1 ppbm standard (Restek catalogue no. 34436) with nitrogen, pressurised to 35 psig and contained in 6 L canisters (SilcoCan®, Restek). 100% RH was achieved by injecting 365 µL pure water into the canister at ambient laboratory temperature (21°C).

Canister sampling:

Instrument:	CIA *Advantage*-xr (Markes International)
Sample volume:	Up to 1000 mL

Water removal:

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

TD:

Instrument:	UNITY-xr (Markes International)
Flow path:	120°C
Sample flow:	50 mL/min
Post-sampling line purge:	5 min at 50 mL/min (with Kori-xr)
Trap purge:	1.0 min at 50 mL/min at 25°C
Focusing trap:	'Trace TO-15' (part no. U-TO15-KXR). *We suggest that this trap is only used in conjunction with Kori-xr*
Focusing trap low:	–30°C, then +25°C for dry-purge
Focusing trap high:	300°C (2 min)
Outlet split:	2 mL/min
Trap heat rate:	40°C/s

GC:

Column:	J&W DB-624™, 60 m × 0.32 mm × 1.80 µm
Constant flow:	2 mL/min
Oven:	35°C (5 min), 10°C/min to 160°C (0 min), 25°C/min to 230°C (5 min)

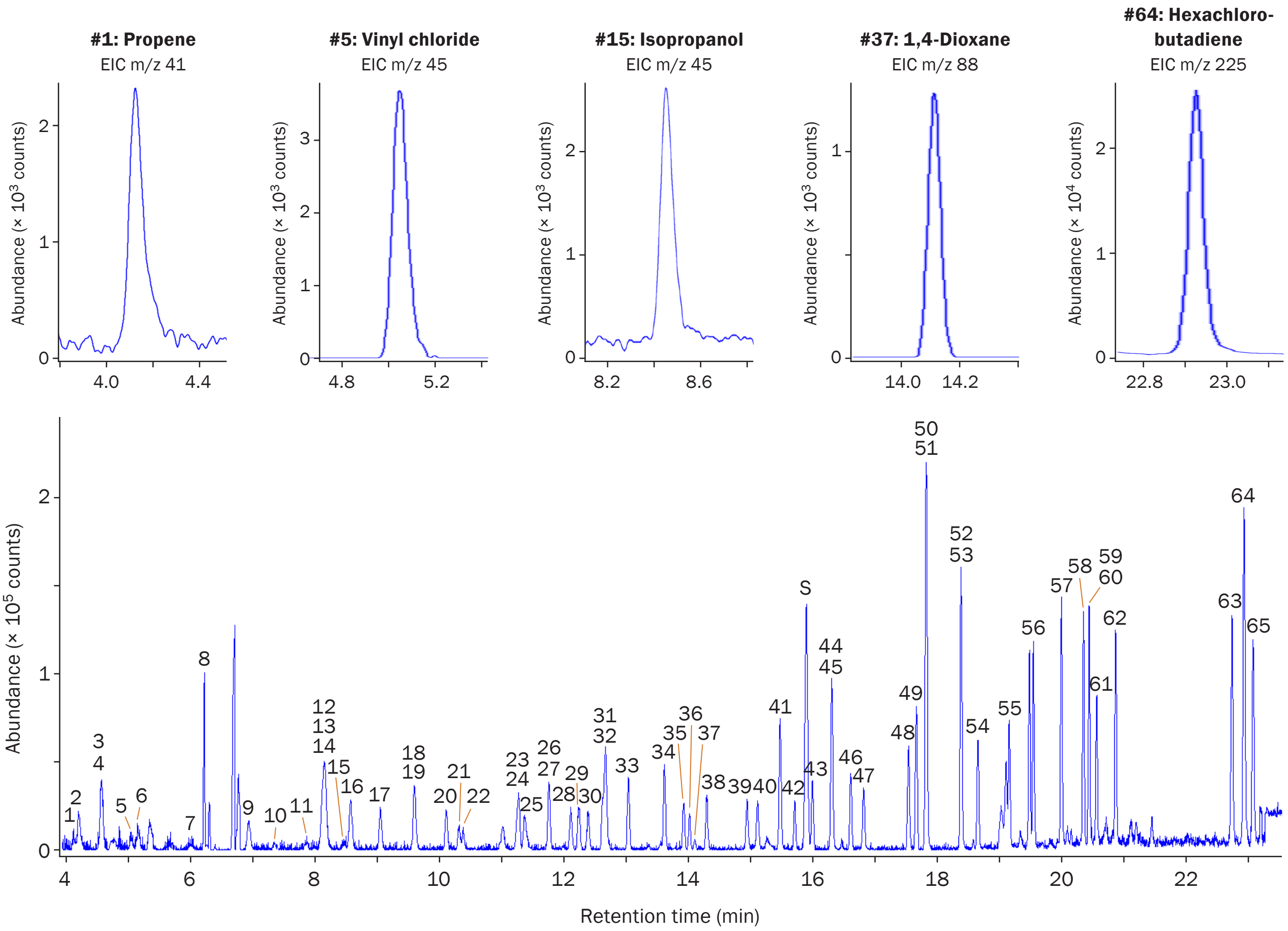
Quadrupole MS:

Source:	300°C
Transfer line:	200°C
Quadrupole:	200°C
Scan range:	m/z 35–300

Results and discussion

1. Chromatography

Figure 4 shows a typical total ion chromatogram for the ultra-low-level 0.05 ppbv TO-15 standard at 100% RH. Note the excellent peak shape of the early-eluting components propene and vinyl chloride, as well as highly polar compounds such as isopropanol and 1,4-dioxane, and the late-eluting high-boiling compound hexachlorobutadiene. These sharp, well-focused peaks demonstrate the high trap desorption efficiency and the effectiveness of the Dry-Focus3 approach for removing water at such low analyte concentrations and high humidity.



1 Propene
2 Dichlorodifluoromethane
3 Dichlorotetrafluoroethane
4 Chloromethane
5 Vinyl chloride
6 Butadiene
7 Bromomethane
8 Chloroethane
9 Trichlorofluoromethane
10 Ethanol
11 Acrolein
12 1,1-Dichloroethene
13 1,1,2-Trichloro-1,2,2-trifluoroethane
14 Acetone
15 Isopropanol
16 Carbon disulfide
17 Dichloromethane
18 1,2-Dichloroethene
19 *tert*-Butyl methyl ether
20 Hexane
21 1,1-Dichloroethane
22 Vinyl acetate
23 Methyl ethyl ketone
24 *trans*-1,2-Dichloroethene
25 Ethyl acetate
26 Tetrahydrofuran
27 Trichloromethane (Chloroform)
28 1,1,1-Trichloroethane
29 Cyclohexane
30 Tetrachloromethane
31 1,2-Dichloroethane
32 Benzene
33 Heptane
34 Trichloroethene
35 1,2-Dichloropropane
36 Methyl methacrylate
37 1,4-Dioxane
38 Bromodichloromethane
39 *cis*-1,3-Dichloropropene
40 4-Methylpentan-2-one
41 Toluene
42 *trans*-1,3-Dichloropropene
43 1,1,2-Trichloroethane
44 Tetrachloroethene
45 Methyl n-butyl ketone
46 Dibromochloromethane
47 1,2-Dibromoethane
48 Chlorobenzene
49 Ethylbenzene
50 *m*-Xylene
51 *p*-Xylene
52 *o*-Xylene
53 Styrene
54 Tribromomethane (Bromoform)
55 1,1,2,2-Tetrachloroethane
56 Benzyl chloride
57 4-Ethyltoluene
58 1,3,5-Trimethylbenzene
59 1,2,4-Trimethylbenzene
60 1,2-Dichlorobenzene
61 1,4-Dichlorobenzene
62 1,3-Dichlorobenzene
63 1,2,4-Trichlorobenzene
64 Hexachlorobutadiene
65 Naphthalene

Figure 4: Total ion chromatogram for a 1 L standard containing 0.05 ppbv air toxics, acquired cryogen-free and in full-scan mode using the CIA *Advantage*–Kori–UNITY-xr system with GC–MS, according to US EPA Method TO-15. The insets show the excellent peak shape for the extracted-ion chromatograms of five selected compounds. S = Siloxane (from column bleed).

2. Relative response factors and linearities

System linearity was assessed by sampling the 1 ppbv, 100% RH standard at 50, 100, 200, 400, 600, 800 and 1000 mL, equivalent to 1 L of a sample containing analytes at 0.05, 0.1, 0.2, 0.4, 0.6, 0.8 and 1 ppbv, respectively.

The relative response factors (RRFs) and their relative standard deviations (RSDs) were calculated using this linearity data, and are shown in Table A1 (see Appendix). The mean RSD is 6.0%, with no value being above 30% (as required by Method TO-15). This indicates that all the analytes are quantitatively retained and completely desorbed from the system. It is also important to note that the response for the most polar analytes – 1,4-dioxane for example – remains linear between 50 and 1000 mL, despite the significant increase in the volume of water sampled.

Linearities (R^2 values) are also listed in Table A1, and all these were >0.99, with an average of 0.9984. Figure 5 shows the excellent linearities for 10 compounds spanning the range of volatilities and polarities, indicating that up to 1 L can be sampled without any breakthrough.

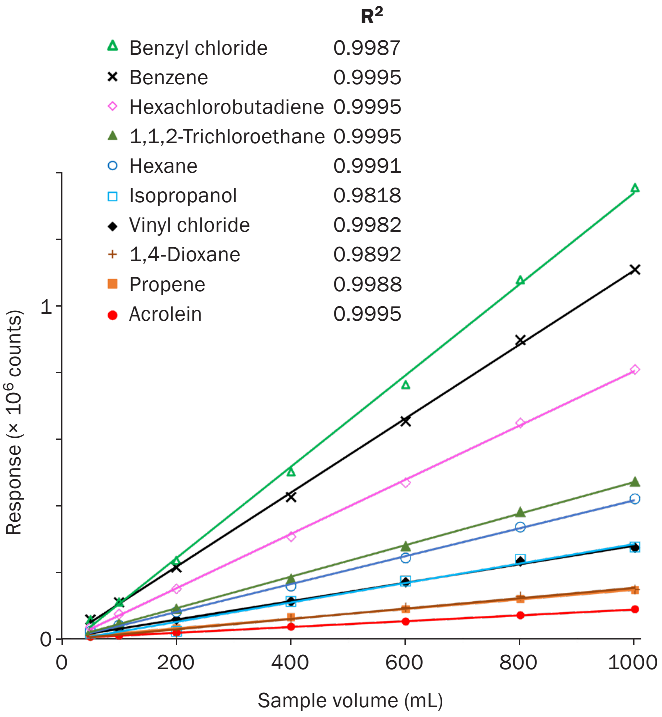


Figure 5: Linearities of 1 ppbv standard samples at 100% RH from 50–1000 mL for 10 compounds spanning the range of volatilities and polarities.

3. Background level and carryover

Systems suitable for analysing trace-level samples must display minimal carryover from previous higher-concentration samples, to avoid the need for multiple blanks between samples and the consequent negative impact on laboratory productivity. If carryover is significant, it could interfere with quantitation, and cause analytes in low-concentration samples to be over-estimated.

To assess carryover, a system blank was run by sampling 1 L nitrogen immediately after the highest-concentration sample in the linearity runs (Figure 6). Note that the dry nitrogen was sampled directly from the gas line to eliminate the background from the canisters.

Figure 6 shows that minimal carryover was detected at reportable levels in the TIC or in extracted-ion chromatograms (EICs) of high-boiling compounds such as hexachlorobutadiene. Negligible carryover is also demonstrated for toluene, trichloroethene and tetrachloroethene, which are often found in soil gas at high concentrations.

These results highlight the ability of the CIA *Advantage*–Kori–UNITY-xr system to recover quickly from being subjected to a high-concentration sample, with minimal carryover and a clean background for the next run.

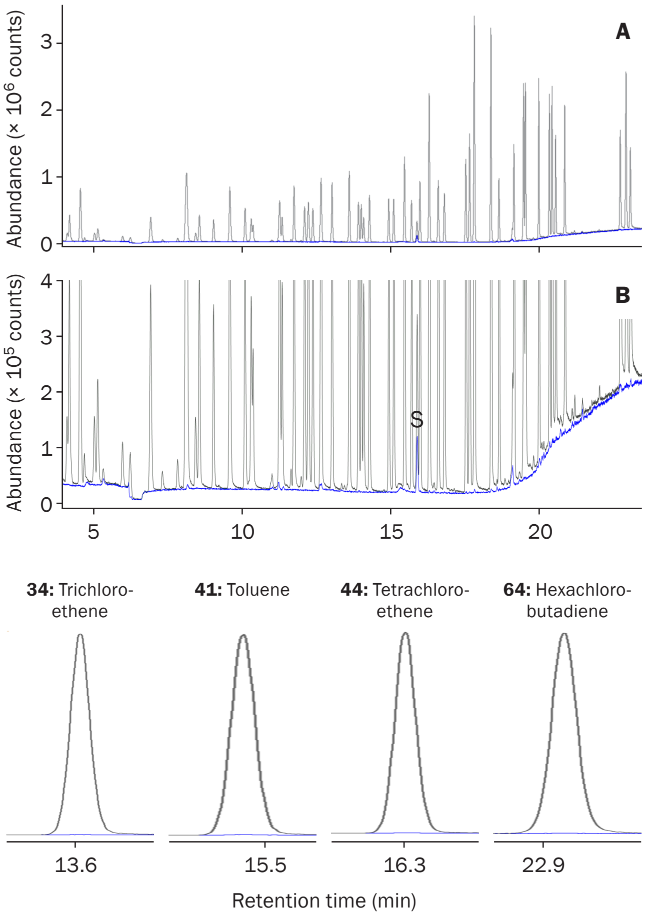


Figure 6: Analysis of 1 L of the 1 ppbv standard at 100% RH (grey), with a subsequent blank run of 1 L nitrogen (blue). (**A**) Full scale. (**B**) Vertical expansion. (**C**) EICs of compounds commonly found at high levels. S = Siloxane (from column bleed).

4. Method detection limits

Method detection limits (MDLs) are defined by the US EPA as "the minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results".[3]

MDLs are calculated on the basis of seven replicate samples with a concentration near the detection limit. To comply with Method TO-15, MDLs are required to be ≤0.5 ppbv. However, this reporting limit is too high for the analysis of trace-level air toxics encountered in a number of programs, and the NJDEP LL TO-15 Method stipulates that MDLs should be ≤0.2 ppbv for the majority of the TO-15 compounds.

In this study, the MDLs were determined for seven replicates using (a) 1 L of the 0.05 ppbv, 100% RH standard with full-scan mode, and (b) 1 L of the 0.01 ppbv, 100% RH standard with SIM mode. The results are listed in Table A1.

For the full-scan analysis, the mean MDL was 0.18 ppbv, with all but three values in the range 0.006–0.040 ppbv (the three outliers are ascribed to canister background contamination). Note that the NJDEP LL TO-15 Method requires a clean canister certification level of 0.20 ppbv – much higher than the 0.05 ppbv standards used for the MDL calculations in this work.

For the SIM analysis, the mean MDL was 0.0039 ppbv, with all values in the range 0.0007–0.0443 ppbv, and all but three compounds below 0.01 ppbv. These values are all significantly lower than the requirement of ≤0.2 ppbv stated by the NJDEP LL TO-15 Method.

5. Reproducibility

System reproducibility was investigated using the results of seven replicate runs of the 0.05 ppbv standard at 100% RH. The results are listed in Table A1, and show mean retention-time RSDs of 0.021%, with all but four compounds being 0.07% or below. This high degree of reproducibility makes it much easier to achieve precise automated quantitation, saving time when reviewing data.

The consistency in retention time, peak shape and abundance achieved indicates that the system is robust and stable, even for challenging lighter and polar compounds.

Conclusions

A system for trace-level canister analysis of 'air toxics' in humid environments is described, comprising the CIA *Advantage*–Kori–UNITY-xr preconcentrator with new Dry-Focus3 technology and 'Trace TO-15' focusing trap.

This system allows confident GC–MS of a wide range of analytes in humid air in accordance both with US EPA Method TO-15 and (due to its significantly increased sensitivity) with more stringent protocols such as the NJDEP LL TO-15 Method.

A key feature of the results is the excellent chromatographic performance for the analysis of a 65-component TO-15 mix (including polar and non-polar VOCs) at 100% RH, far exceeding all method requirements. Crucially:

- This performance has been achieved for even the most volatile of components in the TO-15 mix. This is due to the capacity of the analytical system to efficiently and selectively remove water from humid air, without compromising the analysis of very volatile organic compounds or polar species.
- The system uses electrical trap cooling (both in the UNITY-xr thermal desorber and the Kori-xr water removal device), eliminating the cost and inconvenience associated with liquid cryogen.
- Up to 27 channels and cryogen-free operation enable low running costs, maximise instrument up-time, and guarantee unattended operation over extended periods.

Two additional features of all Markes' TD systems, including the UNITY–Kori–CIA *Advantage*-xr system used in this study, are the ability to (a) run sorbent-tube TD analysis in accordance with US EPA Method TO-17, and (b) re-collect the split portions of samples onto clean sorbent tubes for easier storage (and to release the canisters for sampling).

References

1. Compendium Method TO-15: Determination of volatile organic compounds (VOCs) in air collected in specially-prepared canisters and analyzed by gas chromatography/mass spectrometry (GC/MS), *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air* (second edition), US EPA, 1999, www.epa.gov/homeland-security-research/epa-air-method-toxic-organics-15-15-determination-volatile-organic.
2. NJDEP-SRP Low Level US EPA Method TO-15, Division of Remediation Management Response, New Jersey Department of Environmental Protection, www.nj.gov/dep/srp/guidance/vaporintrusion/newmethod2007/llto15.pdf.
3. Method Detection Limit – Frequent Questions, US EPA, www.epa.gov/cwa-methods/method-detection-limit-frequent-questions (accessed 4 September 2017).

Trademarks

CIA *Advantage*-xr™, Dry-Focus3™, Kori-xr™, ULTRA-xr™ and UNITY-xr™ are trademarks of Markes International.

DB-624™ is a trademark of Agilent Corporation.

SilcoCan® is a registered trademark of Restek.

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

Appendix

No.	Compound	RT (min)	RT RSD (%)	R^2	RSD RRF (%)	MDL (ppbv)	
						Full scan, 0.05 ppbv	SIM, 0.01 ppbv
1	Propene	4.124	0.083	0.9988	4.2	0.0118	0.0051
2	Dichlorodifluoromethane	4.182	0.084	0.9973	5.2	0.0118	0.0013
3	Dichlorotetrafluoroethane	4.531	0.070	0.9983	4.2	0.0094	0.0015
4	Chloromethane	4.686	0.101	0.9986	15.3	0.0201	0.0081
5	Vinyl chloride	5.029	0.062	0.9982	3.4	0.0134	0.0016
6	Butadiene	5.131	0.080	0.9999	2.4	0.0162	0.0027
7	Bromomethane	5.965	0.036	0.9955	9.0	0.0512	0.0067
8	Chloroethane	6.232	0.058	0.9996	3.0	0.0103	0.0030
9	Trichlorofluoromethane	6.914	0.049	0.9935	4.7	0.0221	0.0018
10	Ethanol	7.315	0.050	0.9823	27.6	0.1881	0.0443
11	Acrolein	7.813	0.052	0.9995	3.2	0.0223	0.0068
12	1,1-Dichloroethene	8.083	0.023	0.9997	1.9	0.0142	0.0016
13	1,1,2-Trichloro-1,2,2-trifluoroethane	8.128	0.034	0.9996	2.4	0.0146	0.0011
14	Acetone	8.142	0.026	0.9997	2.1	0.0346	0.0110
15	Isopropanol	8.423	0.027	0.9818	27.1	0.0565	0.0169
16	Carbon disulfide	8.546	0.029	0.9997	3.0	0.0173	0.0025
17	Dichloromethane	9.030	0.023	1.0000	1.9	0.0112	0.0059
18	*trans*-1,2-Dichloroethene	9.572	0.017	0.9997	1.7	0.0143	0.0022
19	*tert*-Butyl methyl ether	9.578	0.037	0.9992	4.0	0.0135	0.0015
20	Hexane	10.082	0.015	0.9991	2.8	0.0103	0.0035
21	1,1-Dichloroethane	10.292	0.025	0.9996	2.4	0.0108	0.0016
22	Vinyl acetate	10.357	0.027	0.9985	4.7	0.0094	0.0025
23	Methyl ethyl ketone	11.228	0.016	0.9948	7.8	0.0109	0.0050
24	*cis*-1,2-Dichloroethene	11.252	0.010	0.9995	5.3	0.0326	0.0024
25	Ethyl acetate	11.330	0.009	0.9995	7.9	0.0102	0.0079
26	Tetrahydrofuran	11.732	0.018	0.9996	2.3	0.0113	0.0009
27	Trichloromethane (Chloroform)	11.732	0.009	0.9985	6.3	0.0100	0.0038
28	1,1,1-Trichloroethane	12.085	0.018	0.9996	2.7	0.0111	0.0013
29	Cyclohexane	12.215	0.017	0.9992	2.8	0.0081	0.0021
30	Tetrachloromethane	12.359	0.022	0.9992	3.3	0.0139	0.0018
31	1,2-Dichloroethane	12.616	0.016	0.9997	2.4	0.0120	0.0011
32	Benzene	12.644	0.006	0.9995	2.5	0.0115	0.0017
33	Heptane	13.010	0.012	0.9995	3.9	0.0069	0.0037
34	Trichloroethene	13.590	0.008	0.9993	3.7	0.0100	0.0007
35	1,2-Dichloropropane	13.892	0.012	0.9997	1.9	0.0078	0.0023
36	Methyl methacrylate	13.994	0.011	0.9991	6.9	0.0110	0.0028
37	1,4-Dioxane	14.073	0.011	0.9892	19.0	0.0385	0.0053
38	Bromodichloromethane	14.272	0.008	0.9994	3.2	0.0075	0.0014
39	*cis*-1,3-Dichloropropene	14.913	0.009	0.9991	4.1	0.0078	0.0023
40	4-Methylpentan-2-one	15.085	0.012	0.9993	8.8	0.0063	0.0054
41	Toluene	15.452	0.008	0.9995	2.7	0.0132	0.0032
42	*trans*-1,3-Dichloropropene	15.685	0.010	0.9988	6.2	0.0081	0.0021
43	1,1,2-Trichloroethane	15.969	0.008	0.9995	2.9	0.0092	0.0017
44	Tetrachloroethene	16.278	0.008	0.9984	12.9	0.0064	0.0072
45	Methyl n-butyl ketone	16.281	0.009	0.9997	1.9	0.0085	0.0008
46	Dibromochloromethane	16.583	0.007	0.9995	4.6	0.0089	0.0018
47	1,2-Dibromoethane	16.789	0.005	0.9995	4.0	0.0099	0.0022
48	Chlorobenzene	17.509	0.006	0.9996	3.3	0.0107	0.0018
49	Ethylbenzene	17.643	0.006	0.9996	7.0	0.0116	0.0028
50	*m*-Xylene	17.797	0.004	0.9995	7.2	0.0157	0.0043

Table A1: Data obtained for TO-15 standards at 100% RH. Linearity values (R^2) and relative standard deviations of the relative response factors (RSD RRF) were generated for the 1 ppbv standard across the entire calibration range (50–1000 mL). *(Continued on next page)*

No.	Compound	RT (min)	RT RSD (%)	R^2	RSD RRF (%)	MDL (ppbv)	
						Full scan, 0.05 ppbv	SIM, 0.01 ppbv
51	*p*-Xylene	17.797	0.004	0.9995	7.2	0.0157	0.0043
52	*o*-Xylene	18.359	0.004	0.9996	5.5	0.0125	0.0026
53	Styrene	18.363	0.006	0.9990	10.6	0.0097	0.0020
54	Tribromomethane (Bromoform)	18.630	0.005	0.9992	2.5	0.0118	0.0030
55	1,1,2,2-Tetrachloroethane	19.134	0.006	0.9996	5.2	0.0097	0.0012
56	Benzyl chloride	19.528	0.001	0.9987	9.9	0.0234	0.0019
57	4-Ethyltoluene	19.974	0.005	0.9992	11.2	0.0323	0.0018
58	1,3,5-Trimethylbenzene	20.327	0.005	0.9992	7.7	0.0134	0.0022
59	1,2,4-Trimethylbenzene	20.423	0.004	0.9994	5.9	0.0138	0.0015
60	1,2-Dichlorobenzene	20.423	0.004	0.9995	6.4	0.0140	0.0016
61	1,4-Dichlorobenzene	20.547	0.004	0.9987	8.5	0.0149	0.0016
62	1,3-Dichlorobenzene	20.855	0.004	0.9995	5.1	0.0143	0.0016
63	1,2,4-Trichlorobenzene	22.720	0.006	0.9998	6.6	0.0296	0.0060
64	Hexachlorobutadiene	22.916	0.005	0.9995	6.2	0.0322	0.0023
65	Naphthalene	23.060	0.005	0.9986	8.3	0.0284	0.0055
	Mean values		**0.021**	**0.9984**	**6.0**	**0.0183**	**0.0039**

Table A1 *(Continued from previous page)*