Application Note 081

Innovative Cryogen-Free Ambient Air Monitoring in Compliance with US EPA Method TO-15

Application Note

Environmental, Canister, TO-15, Air Monitoring, Air Toxics

Abstract

This application note describes the GC/MS analysis of humidified canister air toxics samples at various relative humidities, using cryogen-free systems for thermal desorption preconcentration. Detection of 65 target compounds ranging in volatility from propene to naphthalene is demonstrated with excellent peak shape and performance well within the criteria set in US EPA Method TO-15, including method detection limits as low as 4 pptv.

Introduction

Monitoring of chemicals in ambient air is necessary to determine the effect they have on human health, the environment, and global climate. This has driven a number of national and international regulations to be developed, primarily in response to increased concern over potentially hazardous volatile organic compounds (VOCs) in ambient (primarily urban) air, industrial emissions, and landfill gas.

Analysis of these VOCs is carried out in accordance with a number of standard methods, which require the use of either sorbent tubes (pumped or passive), canisters, or on-line techniques. Each method has its own advantages and range of applicability, with canister sampling being most popular in the US and China. To achieve the required detection limits using this approach, preconcentration is required to focus analytes and selectively eliminate bulk constituents. This approach is mandated within the most popular standard method for canisters, US EPA Method TO-15. This protocol is used primarily in the US, but other countries also use canister sampling, and follow a similar methodology (such as Chinese EPA Method HJ 759).

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Despite the popularity of canister sampling, traditional canister preconcentration technologies are challenged by the ever increasing 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.

This application note shows how the use of a canister autosampler, an innovative trap-based water removal device, and thermal desorption gas chromatography mass spectrometry (TD-GC/MS) together allow the analysis of a range of volatile air toxics from canisters in a range of humidities, in accordance with US EPA Method TO-15. Although the term TO-15 is used by some to describe canister sampling in general, the focus of this work will be on compliance with the specific requirements of the method.

Overview of US EPA Method TO-15 [1]

Below are extracts from Method TO-15, summarizing the key parts of the process.

- The atmosphere is sampled by introduction of air into a specially-prepared stainless steel canister. Both subatmospheric pressure and pressurized sampling modes use an initially evacuated canister. A pump ventilated sampling line is used during sample collection with most commercially available samplers. Pressurized sampling requires an additional pump to provide positive pressure to the sample canister. A sample of air is drawn through a sampling train comprised of components that regulate the rate and duration of sampling into the pre-evacuated and passivated canister.

- After the air sample is collected, the canister valve is closed, an identification tag is attached to the canister, and the canister is transported to the laboratory for analysis.

- Upon receipt at the laboratory, the canister tag data is recorded, and the canister is stored until analysis. Storage times of up to 30 days have been demonstrated for many of the VOCs.

- To analyze the sample, a known volume of sample is directed from the canister through a solid multisorbent concentrator. A portion of the water vapor in the sample breaks through the concentrator during sampling, to a degree depending on the multisorbent composition, duration of sampling, and other factors. Water content of the sample can be further reduced by dry purging the concentrator with helium while retaining target compounds. After the concentration and drying steps are completed, the VOCs are thermally desorbed, entrained in a carrier gas stream, then focused in a small volume by trapping on a reduced temperature trap or small volume multisorbent trap. The sample is then released from the trap by thermal desorption, and carried onto a gas chromatographic column for separation.

- The analytical strategy for Compendium Method TO-15 involves using a high resolution gas chromatograph (GC) coupled to a mass spectrometer (MS). If the MS is a linear quadrupole system, it is operated either by continuously scanning a wide range of mass to charge ratios (SCAN mode), or by monitoring select ion monitoring mode (SIM) of compounds on the target list. If the MS is based on a standard ion trap design, only a scanning mode is used. Mass spectra for individual peaks in the total ion chromatogram are examined with respect to the fragmentation pattern of ions corresponding to various VOCs including the intensity of primary and secondary ions. To identify the compound, the fragmentation pattern is compared with stored spectra taken under similar conditions. For any given compound, the intensity of the primary fragment is compared with the system response to the primary fragment for known amounts of the compound. This establishes the compound concentration that exists in the sample.

Analytical Equipment

The analytical system used for this study was a CIA *Advantage* canister autosampler with a Kori-xr water condenser and a UNITY-xr thermal desorber, coupled to a GC/MS system (Figure 1). The individual components of the system are briefly described below.

The CIA *Advantage* 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. This avoids the need to resort to dilution of high-concentration samples, the associated increase in analytical uncertainty, and the risks 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* also offers internal standard addition through a 1 mL loop, which allows a small volume of a high-concentration internal standard gas to be used. This reduces the need for dilution and the consumption of expensive standard gases.
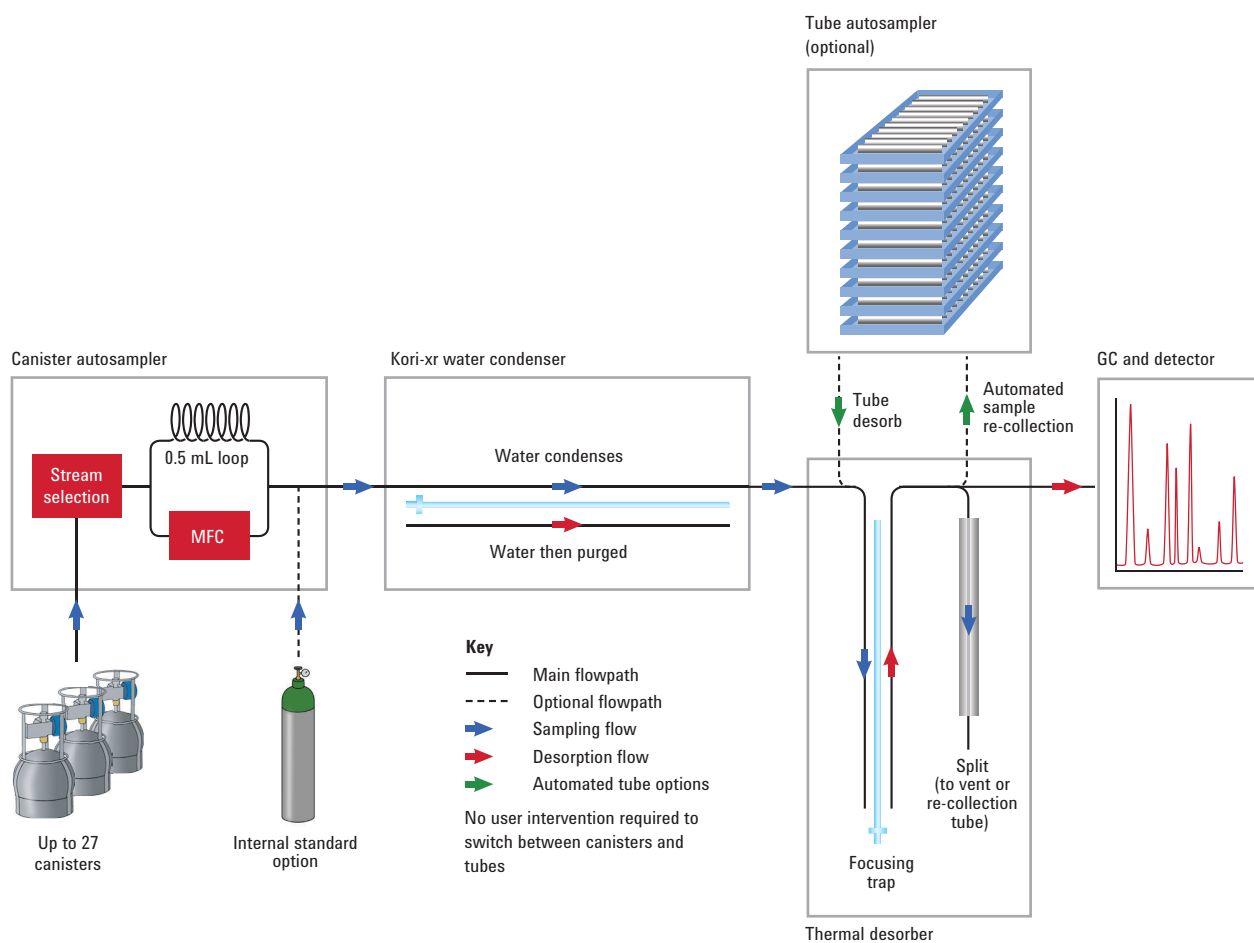

Figure 1. Equipment configuration.

Before entering the thermal desorber, samples pass through a Kori-xr device that efficiently removes humidity from the air stream (Figure 2). Note that as well as canisters and bags, Kori-xr can also be applied to on-line samples.

1 Air sampling and water removal:

The Kori-xr trap, held at –30 °C, sits between the sample inlet and the sorbent-packed focusing trap, causing vapor-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.
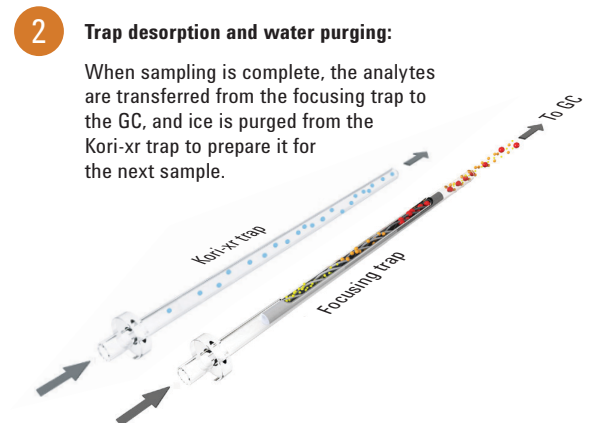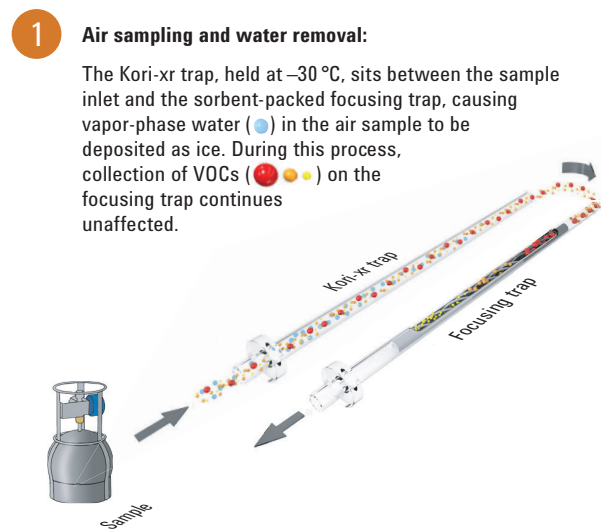
Figure 2. Operation of the Kori-xr device for removing water from humid air streams.

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 [2], and filled with separate beds of porous polymer, graphitized carbon black, and molecular sieve sorbents. This combination of sorbents of different strengths ensures that compounds over a wide volatility range are quantitatively trapped. In configurations using Kori-xr, lower temperatures can be used in the focusing trap without risk of water retention, allowing VOCs, VVOCs, oxygenates, and monoterpenes in humid air to be

quantitatively retained. 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.

At this point, there is an 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

Standards: The chromatograms shown in Figures 3-5 result from the analysis of 200 mL of a 65-component TO-15 air toxics standard at 10 ppbv, pressurized to 15 psig (nominal), and contained in 6 L canisters [3].

In all experiments, relative humidities of 50%, 75%, and 100% were obtained by injecting an appropriate volume of water into the canister.

Instrument parameters

| Parameter	Value
Canister sampling	
Instrument:	CIA *Advantage* (Markes International)
Sample volume:	Up to 400 mL (for samples of 50-100% RH)
Water removal	
Instrument:	Kori-xr (Markes International)
Trap temperatures:	–30 °C/+300 °C
TD	
Instrument:	UNITY-xr (Markes International)
Flow path:	160 °C
IS loop fill:	1.0 minute
Loop equilibration:	0.1 minutes
IS loop injection:	1.0 minute at 50 mL/min
Sample flow:	50 mL/min
Post-sampling	
Line purge:	5 minutes at 50 mL/min (with Kori-xr)
Trap purge:	1.0 minute at 50 mL/min
Cold trap:	Air toxics (p/n U-T15ATA-2S)
GC	
Column:	Agilent J&W DB-624, 60 m × 0.32 mm, 1.80 μm
Constant flow:	1.5 mL/min
Oven:	30 °C (5 minutes), 5 °C/min to 230 °C (0 minutes)
Quadrupole MS	
Source:	300 °C
Transfer line:	200 °C
Scan range:	*m/z* 30-300

Results and Discussion

Table A1 provides a listing of results (see Appendix).

Chromatography

Figure 3 shows typical analyses of the 10 ppbv TO-15 standard at 50%, 75%, and 100% relative humidity (RH), and Figure 4 shows extracted-ion chromatograms (EICs) for nine components spanning the volatility range. Note the excellent peak shape, especially for lighter VOCs, and the high degree of similarity between the three humidity levels, indicating the effectiveness of the Kori-xr module for removing water prior to analyte trapping, across the entire humidity range.
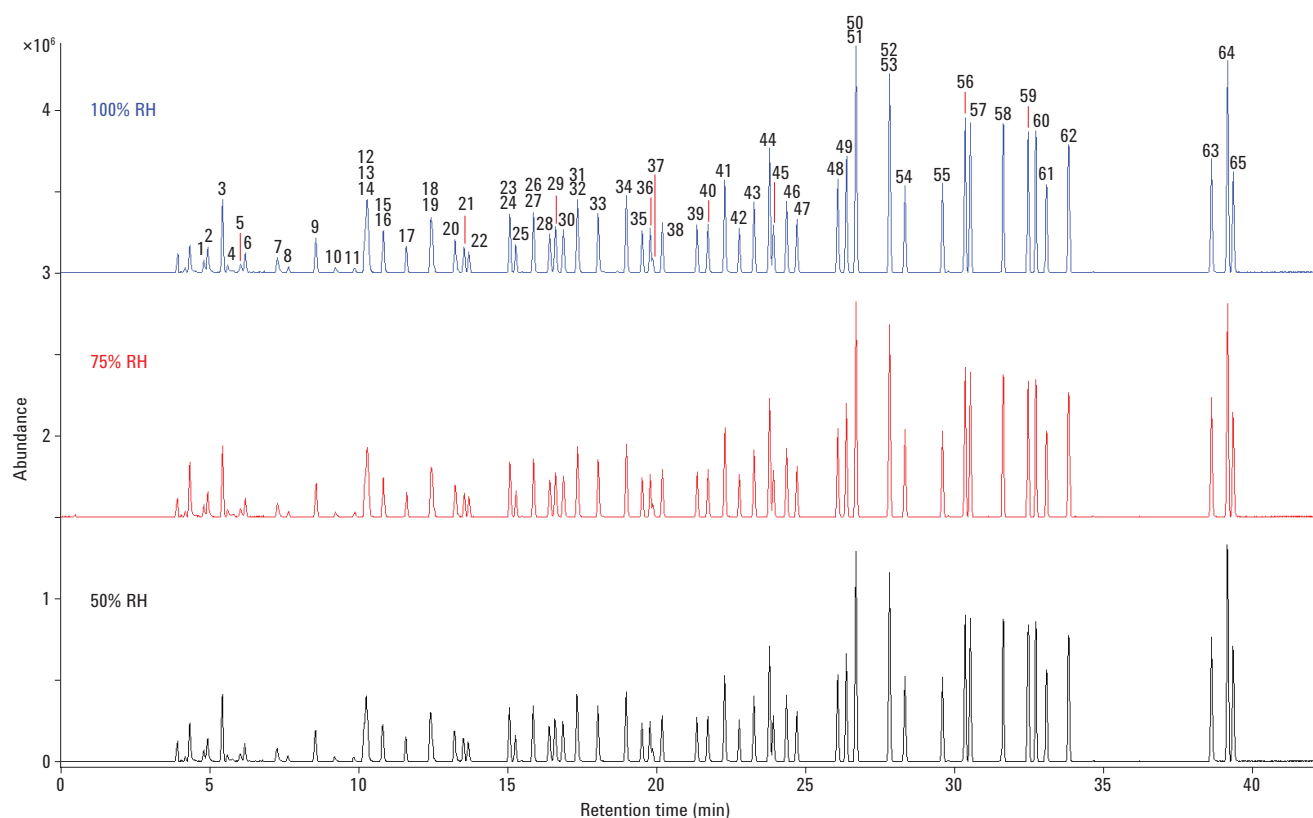
1. Propene	18. 1,2-Dichloroethene	35. 1,2-Dichloropropane	52. *o*-Xylene
2. Dichlorodifluoromethane	19. *tert*-Butyl methyl ether	36. Methyl methacrylate	53. Styrene
3. Dichlorotetrafluoroethane	20. Hexane	37. *p*-Dioxane	54. Tribromomethane
4.. Chloromethane	21. 1,1-Dichloroethane	38. Bromodichloromethane	55. 1,1,2,2-Tetrachloroethane
5 Vinyl chloride	22. Vinyl acetate	39. *cis*-1,3-Dichloropropene	56. 4-Ethyltoluene
6. Butadiene	23. *trans*-1,2-Dichloroethene	40. 4-Methylpentan-2-one	57. 1,3,5-Trimethylbenzene
7. Bromomethane	24. Methyl ethyl ketone	41. Toluene	58. 1,2,4-Trimethylbenzene
8. Chloroethane	25. Ethyl acetate	42. *trans*-1,3-Dichloropropene	59. 1,2-Dichlorobenzene
9. Trichlorofluoromethane	26. Chloroform	43. 1,1,2-Trichloroethane	60. 1,4-Dichlorobenzene
10. Ethanol	27. Tetrahydrofuran	44. Tetrachloroethene	61. Benzyl chloride
11. Acrolein	28. 1,1,1-Trichloroethane	45. Methyl *n*-butyl ketone	62. 1,3-Dichlorobenzene
12. 1,1-Dichlorethene	29. Cyclohexane	46. Chlorodibromomethane	63. 1,2,4-Trichlorobenzene
13. 1,1,2-Trichlorotrifluoroethane	30. Tetrachloromethane	47. 1,2-Dibromoethane	64. Hexachlorobutadiene
14. Acetone	31. 1,2-Dichloroethane	48. Chlorobenzene	65. Naphthalene
15. Isopropanol	32. Benzene	49. Ethylbenzene	
16. Carbon disulfide	33. Heptane	50. *m*-Xylene	
17. Dichloromethane	34. Trichloroethene	51. *p*-Xylene	

Figure 3. Analysis of 200 mL of a 10 ppbv 65-component TO-15 standard at 50% RH, 75% RH, and 100% RH. The upper two traces have been offset for clarity.

An additional noteworthy aspect is that the three highest-boiling components have responses substantially higher than the lower-boiling compounds, with no loss of intensity at higher humidities (Figure 5).

This level of sensitivity was obtained without the use of liquid cryogen, either for analyte trapping, or for refocusing components on the front of the GC column.
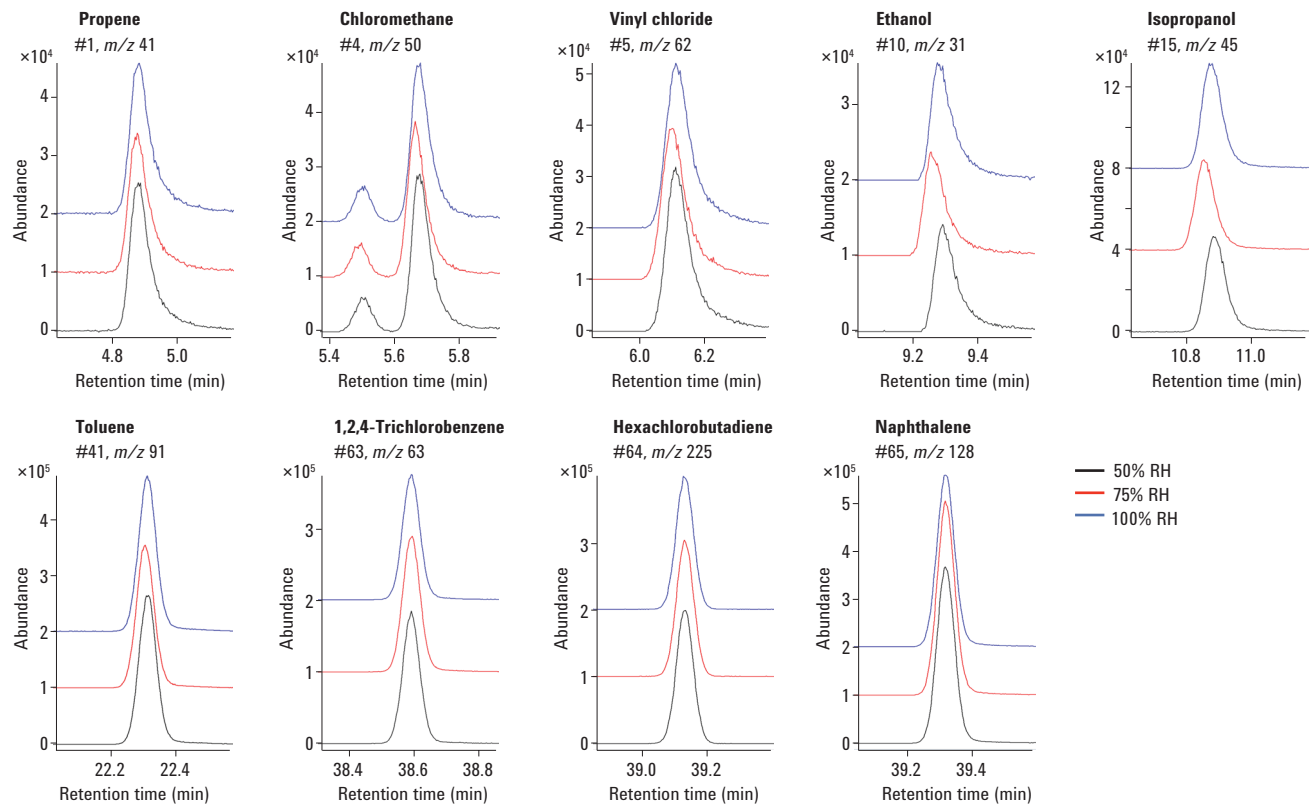

Figure 4. EICs for nine selected analytes from the analysis shown in Figure 3. The upper two traces in each case have been offset for clarity.
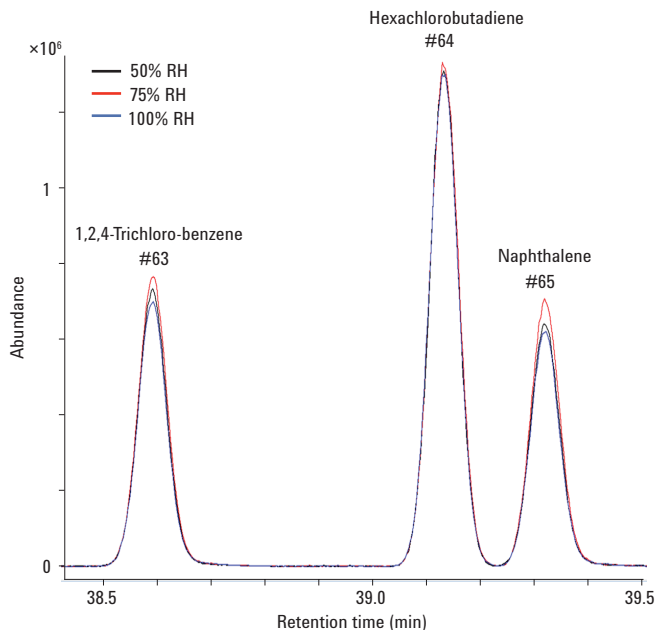
Figure 5. Expansion of Figure 3 (with zero offset), showing the similarity of the responses at the three humidities for the three least volatile compounds in the mix.

Linearity

Linearities were calculated using 10, 25, 50, 100, 200, 300, and 400 mL samples from a 10 ppbv standard at 15 psig (nominal), equivalent to 400 mL of a sample containing analytes at 0.22, 0.55, 1.10, 2.21, 4.41, 6.62, 8.82, and 25 ppbv, respectively.

Excellent system linearities were obtained at all three humidity levels (Table A1), with mean R^2 values from 0.1-25 ppbv of 0.9993, 0.9987, and 0.9992 for 50%, 75%, and 100% RH, respectively. Figure 6 shows linearity plots for the 100% RH sample for the set of nine compounds spanning the volatility range.

Note that the larger sample volumes did not result in a drop-off in response for the most volatile components, indicating no problems with analyte breakthrough. However, where analyte responses are sufficiently high, using smaller sample volumes is beneficial because it reduces the amount of water that needs to be removed by the Kori-xr system.
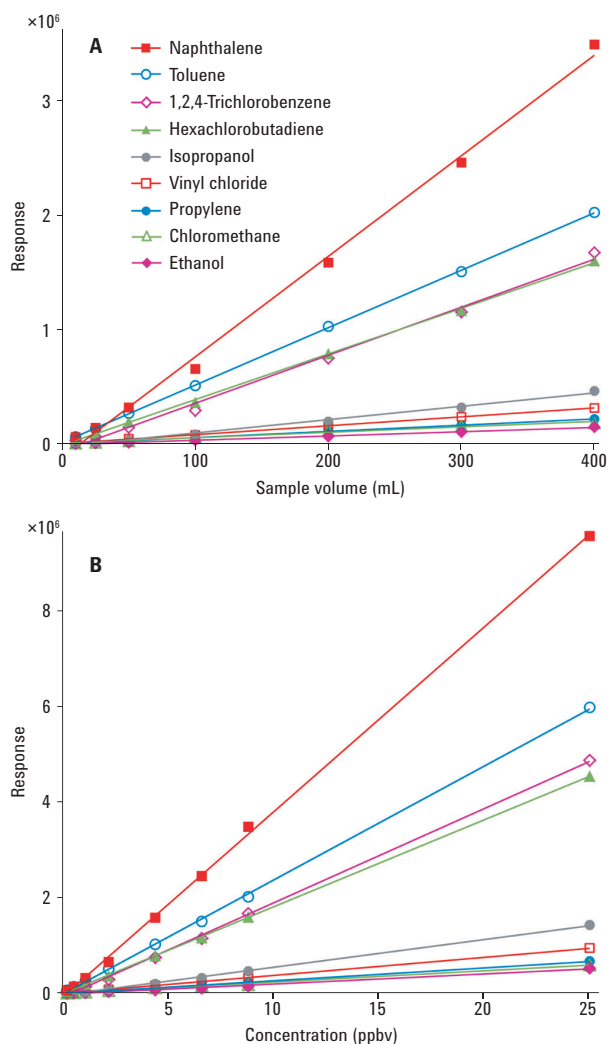

Figure 6. Linearities from (A) 10-400 mL and (B) 0.1-25 ppbv for nine compounds spanning the range of volatilities, from the 100% RH sample.

Method detection limits

Method detection limits (MDLs) were calculated on the basis of seven replicate samples at 0.1 ppbv [4]. To comply with Method TO-15, MDLs are required to be ≤0.5 ppbv.

Our calculations gave a mean MDL of 14 pptv (Table A1), with values for 54 out of the 65 compounds at 20 pptv or below. Values ranged from 4 pptv for dichlorotetrafluoroethane, tetrahydrofuran, 1,1,1-trichloroethane, and 1,2,4-trichlorobenzene, to 45 pptv for ethanol, with a solitary outlier at 95 pptv for propene. These values are all much lower than the requirement of ≤0.5 ppbv.

Reproducibility

Method TO-15 requires that the calculated RSDs for the relative response factors (RRFs) for each compound in the calibration table must be less than 30%, with at most two exceptions up to a limit of 40%.

Results were well within the requirements of Method TO-15 across the three humidity levels (Table A1). Mean values at the 50%, 75%, and 100% RH levels were 7.9%, 9.0%, and 8.5% respectively.

Real air sample

To illustrate the performance of the system for a real air sample, rural air was analyzed under the same conditions as described previously, and four components from the 65-member TO-15 list were found to be at quantifiable levels (Figure 7).
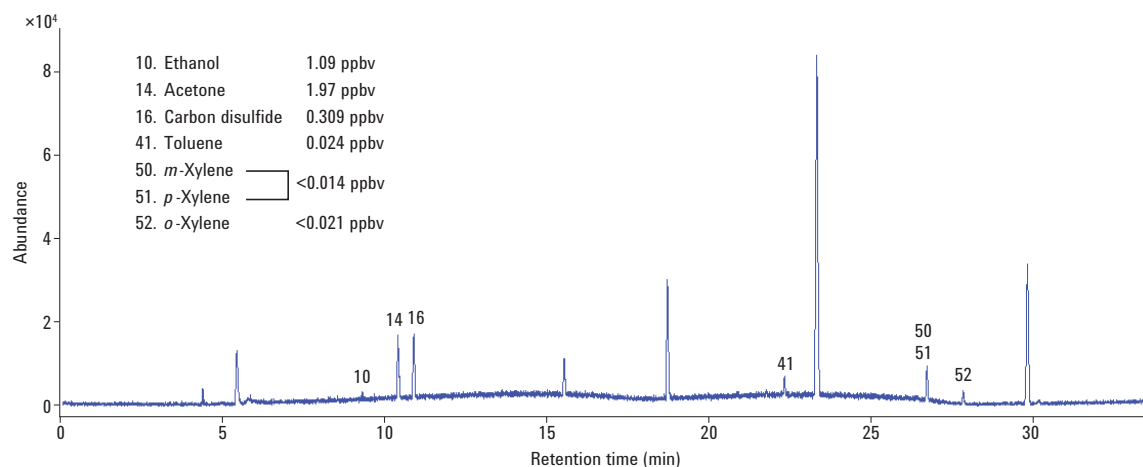

Figure 7. Real sample chromatogram generated from the analysis of 250 mL of rural air, using the conditions previously described. Compounds from the TO-15 listing are indicated.

Conclusions

The CIA *Advantage*–Kori-xr–UNITY-xr preconcentration system allows confident GC/MS canister analysis of air toxics in humid environments, in accordance with US EPA Method TO-15.

A key feature of the results is the excellent chromatographic performance for the analysis of a 65-component TO-15 mix (from propene to naphthalene), at 50%, 75%, and 100% relative humidity. Performance was well within the requirements of Method TO-15, with MDLs as low as 4 pptv.

Crucially, this performance has been achieved for even the most volatile of components in the TO-15 mix, due to the ability of the Kori-xr module to efficiently and selectively remove water from humid air streams without compromising the analysis of very volatile organic compounds or polar species. In addition, the system uses electrical trap cooling (both in the UNITY-xr thermal desorber and the Kori-xr water condenser), eliminating the cost and inconvenience associated with liquid cryogen.

Two additional features of all Markes' TD systems, including the UNITY-xr–CIA *Advantage* system used in this study, are the ability to:

- Run standard 3½″ thermal desorption sample tubes

- 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. Many conventional systems for canister analysis use liquid cryogen in order to trap very volatile compounds. Markes' systems instead use electrical (Peltier) cooling, allowing quantitative retention of the most volatile compounds from large sample volumes, without incurring the cost of liquid cryogen.

3. Note that Method TO-15 states that any canister that has not tested clean (compared to direct analysis of humidified zero air of less than 0.2 ppbv of targeted VOCs) should not be used.

4. MDLs were calculated on the basis of 99% confidence for seven values (MDL = 3.143 × standard deviation × concentration).

Trademarks

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

DB-624™ is a trademark of Agilent Technologies.

Appendix

Table A1. Data obtained for TO-15 standards at 50%, 75%, and 100% relative humidity. Linearity (R^2) values were generated for the concentration range 0.1-25 ppbv.

No.	Compound	RT (min)	R^2	50% RH RRF RSD (%)	MDL (ppbv)	R^2	75% RH RRF RSD (%)	R^2	100% RH RRF RSD (%)
1	Propene	4.894	0.9989	3.4	0.094	0.9996	4.0	0.9997	6.3
2	Dichlorodifluoromethane	5.032	0.9993	8.2	0.011	0.9993	9.7	0.9998	5.6
3	Dichlorotetrafluoroethane	5.500	0.9994	9.6	0.004	0.9991	12.5	0.9997	7.7
4	Chloromethane	5.686	0.9965	14.8	0.028	0.9933	12.3	0.9808	11.0
5	Vinyl chloride	6.122	0.9992	7.2	0.019	0.9983	6.5	0.9994	4.6
6	Butadiene	6.276	0.9991	5.1	0.009	0.9989	6.0	0.9998	2.0
7	Bromomethane	7.346	0.9988	10.5	0.020	0.9993	13.5	0.9988	14.4
8	Chloroethane	7.723	0.9996	6.2	0.016	0.9980	8.8	0.9870	9.1
9	Trichlorofluoromethane	8.646	0.9993	7.5	0.008	0.9991	11.0	0.9999	6.2
10	Ethanol	9.299	0.9931	26.7	0.045	0.9866	13.4	0.9997	24.4
11	Acrolein	9.925	0.9984	14.2	0.033	0.9984	26.5	0.9993	9.3
12	1,1-Dichlorethene	10.258	0.9993	3.7	0.006	0.9994	5.1	0.9998	1.2
13	1,1,2-Trichlorotrifluoroethane	10.337	0.9993	6.8	0.005	0.9994	8.1	1.0000	4.8
14	Acetone	10.401	0.9980	6.3	0.024	0.9982	5.5	1.0000	2.7
15	Isopropanol	10.868	0.9979	23.4	0.016	0.9864	17.4	0.9981	18.8
16	Carbon disulfide	10.884	0.9994	2.8	0.007	0.9992	3.4	0.9999	0.9
17	Dichloromethane	11.657	0.9992	4.1	0.008	0.9996	4.4	0.9998	2.0
18	1,2-Dichloroethene	12.461	0.9996	3.6	0.005	0.9990	5.4	0.9999	1.6
19	*tert*-Butyl methyl ether	12.513	0.9985	7.8	0.008	0.9996	5.5	0.9997	4.2
20	Hexane	13.285	0.9984	16.8	0.022	0.9982	16.2	0.9956	13.6
21	1,1-Dichloroethane	13.578	0.9996	6.6	0.011	0.9992	9.6	1.0000	5.5
22	Vinyl acetate	13.737	0.9991	3.6	0.011	0.9991	5.2	0.9998	1.5
23	*trans*-1,2-Dichloroethene	15.112	0.9988	3.2	0.008	0.9995	8.6	0.9998	3.6
24	Methyl ethyl ketone	15.127	0.9995	4.6	0.034	0.9989	4.5	0.9998	9.2
25	Ethyl acetate	15.314	0.9995	2.8	0.025	0.9996	7.0	0.9999	5.5
26	Chloroform	15.904	0.9994	7.4	0.005	0.9995	9.5	0.9999	5.5
27	Tetrahydrofuran	15.912	0.9997	5.0	0.004	0.9995	10.5	0.9998	9.2
28	1,1,1-Trichloroethane	16.447	0.9992	10.8	0.004	0.9985	14.4	0.9999	8.2
29	Cyclohexane	16.637	0.9992	6.8	0.018	0.9973	7.8	0.9999	8.8
30	Tetrachloromethane	16.902	0.9993	9.3	0.005	0.9987	12.3	1.0000	7.4
31	1,2-Dichloroethane	17.378	0.9997	6.8	0.014	0.9993	7.9	1.0000	3.5
32	Benzene	17.390	0.9993	12.3	0.015	0.9997	10.2	0.9999	6.1
33	Heptane	18.075	0.9997	14.3	0.017	0.9998	16.5	0.9995	19.0
34	Trichloroethene	19.022	0.9993	7.7	0.009	0.9996	9.3	0.9999	5.1
35	1,2-Dichloropropane	19.557	0.9995	9.1	0.008	0.9995	11.3	0.9999	7.1
36	Methyl methacrylate	19.822	0.9994	4.7	0.017	0.9991	6.6	0.9989	2.9
37	*p*-Dioxane	19.914	0.9997	16.1	0.015	0.9982	6.8	0.9998	12.6
38	Bromodichloromethane	20.227	0.9994	7.6	0.011	0.9992	10.1	0.9999	6.2
39	*cis*-1,3-Dichloropropene	21.399	0.9993	7.3	0.006	0.9997	8.8	1.0000	4.5
40	4-Methylpentan-2-one	21.760	0.9997	4.0	0.007	0.9989	6.9	0.9999	2.8
41	Toluene	22.326	0.9996	7.8	0.021	0.9997	11.0	0.9999	16.3
42	*trans*-1,3-Dichloropropene	22.810	0.9994	6.0	0.009	0.9990	7.7	0.9997	2.9
43	1,1,2-Trichloroethane	23.305	0.9996	8.2	0.007	0.9990	11.9	1.0000	7.9

No.	Compound	RT (min)	50% RH			75% RH		100% RH	
			R^2	RRF RSD (%)	MDL (ppbv)	R^2	RRF RSD (%)	R^2	RRF RSD (%)
44	Tetrachloroethene	23.828	0.9995	8.6	0.007	0.9995	10.1	1.0000	8.8
45	Methyl *n*-butyl ketone	23.959	0.9997	4.3	0.008	0.9993	2.8	0.9998	2.5
46	Chlorodibromomethane	24.398	0.9992	6.3	0.009	0.9993	6.9	0.9999	4.7
47	1,2-Dibromoethane	24.735	0.9996	6.5	0.007	0.9994	7.4	1.0000	4.4
48	Chlorobenzene	26.102	0.9997	7.3	0.007	0.9995	9.4	1.0000	11.9
49	Ethylbenzene	26.407	0.9998	7.5	0.018	0.9995	8.8	0.9999	20.2
50	*m*-Xylene	26.732	1.0000	8.0	0.014	0.9996	9.4	1.0000	20.8
51	*p*-Xylene	26.732	1.0000	8.0	0.014	0.9996	9.4	1.0000	20.8
52	*o*-Xylene	27.837	0.9999	8.9	0.021	0.9997	9.8	1.0000	25.2
53	Styrene	27.857	0.9999	5.7	0.007	0.9992	7.4	0.9999	10.3
54	Tribromomethane	28.376	0.9991	5.3	0.006	0.9990	4.7	0.9998	4.4
55	1,1,2,2-Tetrachloroethane	29.624	0.9999	7.1	0.010	0.9995	10.2	0.9999	6.8
56	4-Ethyltoluene	30.385	1.0000	4.3	0.010	0.9994	5.4	0.9999	6.3
57	1,3,5-Trimethylbenzene	30.551	1.0000	5.1	0.023	0.9997	9.0	1.0000	19.6
58	1,2,4-Trimethylbenzene	31.653	1.0000	6.6	0.019	0.9995	8.2	1.0000	10.4
59	1,2-Dichlorobenzene	32.485	1.0000	3.5	0.016	0.9993	5.4	0.9999	3.9
60	1,4-Dichlorobenzene	32.738	1.0000	2.8	0.008	0.9994	2.9	0.9999	3.3
61	Benzyl chloride	33.107	0.9999	2.1	0.006	0.9991	2.9	0.9998	2.3
62	1,3-Dichlorobenzene	33.840	1.0000	6.7	0.006	0.9993	7.4	0.9999	7.4
63	1,2,4-Trichlorobenzene	38.594	0.9991	19.3	0.004	0.9972	16.1	0.9965	18.9
64	Hexachlorobutadiene	39.121	0.9999	4.9	0.010	0.9996	3.3	0.9997	9.4
65	Naphthalene	39.315	0.9994	16.4	0.010	0.9982	16.2	0.9975	19.7
	Mean values		**0.9993**	**7.9**	**0.014**	**0.9987**	**9.0**	**0.9992**	**8.5**

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

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