

Analysis of US EPA TO-15 for Ambient Air Monitoring Using Cryogen-Free Thermal Desorption and Gas Chromatography Coupled to a Single Quadrupole Mass Spectrometer (GC/MSD)

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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 out 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 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 online 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-15.¹

Despite the popularity of canister sampling, traditional canister preconcentration technologies are challenged 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 will show 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 at a range of humidities, in

accordance with US EPA method TO-15. It should be noted that, 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

The key operations are summarized below.

1. **Sampling:** After cleaning and evacuating the canister, it is brought to the sampling site. The canister valve is opened, and a flow controller draws air through a filter into the canister. After the sampling time corresponding to the set constant flow rate is reached, the canister valve is closed, and sealed with caps.
2. **Storage:** The sample is kept at ambient temperature, and should be analyzed as soon as possible, and no later than 20 days after sampling.
3. **Sample analysis:** 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. The 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, and then focused in a small volume by trapping on a reduced-temperature trap or a small volume multisorbent trap. The sample is then released from the trap by thermal desorption and transferred onto a gas chromatographic column for separation.

4. **Compound identification and quantitation:** Method TO-15 uses GC/MS for qualitative and quantitative analysis of the sample. For linear quadrupole MS, monitoring of a wide m/z range (SCAN mode), or ion-selective scanning (SIM mode) patterns can be used to monitor the relevant target compounds. The mass spectra of the individual peaks in the total ion chromatogram are examined, and VOCs identified on the basis of the intensities of quantifier and qualifier ions. The acquired mass spectra are then compared with library spectra (taken under similar conditions), in order to identify the compound. For any given compound, the abundance of the quantifier ion is compared to its abundance for the compound at known concentrations, to determine the concentration of the compound in the sample.

Experimental

Instrumentation

The analytical system used for this study was a CIA Advantage-xr canister autosampler with a Kori-xr water removal device and UNITY-xr thermal desorber, coupled to an Agilent 7890B or 8890 GC and 5977B single quadrupole GC/MSD system with an extractor EI source and 6 mm lens (p/n: G3870-20448).

Tables 1 and 2 display the canister, TD, GC, and MS parameters.

Table 1. GC & TD parameters.

Parameter	Value
Gas Chromatograph	Agilent 7890B or 8890 GC
Column	Agilent J&W DB-624, 60 m × 0.32 mm × 1.80 μm (p/n 123-1364)
Constant Flow	1.5 mL/min
Back SS Inlet He	Splitless
Inlet Temperature	250 °C
Oven Temperature Program	30 °C (5 min) 5 °C/min to 230 °C (0 min)
Total Run Time	45 min
MS Transfer Line Temperature	230 °C
Injection Volume	N/A
Carrier Gas	Helium, 1.5 mL/min
Canister Sampling	
Instrument	CIA Advantage-xr (Markes International)
Sample Volume	Up to 400 mL (for samples of 50 to 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 min
Loop Equilibration	0.1 min
Is Loop Injection	1.0 min at 50 mL/min
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
Cold Trap	Air toxics (p/n U-T15ATA-2S)

Standard preparation

A 1 ppm standard containing 65 'air toxics' compounds at 1 ppm was diluted in 6 L canisters with nitrogen balance gas to 10 ppbv, unless otherwise stated. Relative humidities of 50, 75, or 100% were achieved by injecting an appropriate volume of water into the canister.

MS acquisition method

Table 2. MS parameters.

Parameter	Value
MSD	Agilent 5977B
Mode	Electron ionization, 70 eV
Source Temperature	300 °C
Quadrupole Temperature	200 °C
Scan Range	m/z 30 to 300

Results and discussion

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

Chromatography

Figure 1 shows typical analyses of the 10 ppbv TO-15 standard at 50, 75, and 100% relative humidity (RH), and Figure 2 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.

An additional noteworthy aspect is that (as expected) the three highest-boiling components have responses substantially higher than the lower-boiling compounds, with no loss of intensity at higher humidities (Figure 3).

It is worth pointing out that 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.

Linearity

Linearities with respect to volume were calculated using 10, 25, 50, 100, 200, 300, and 400 mL samples from a 10 ppbv standard. Linearities with respect to concentration were calculated at 0.22, 0.55, 1.10, 2.21, 4.41, 6.62, 8.82, and 25 ppbv.

Excellent system linearities were obtained at all three humidity levels (Table A1), with mean R² values from 0.22 to 25 ppbv of 0.9993, 0.9987, and 0.9992 for 50, 75, and 100% RH, respectively. Figure 4 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.

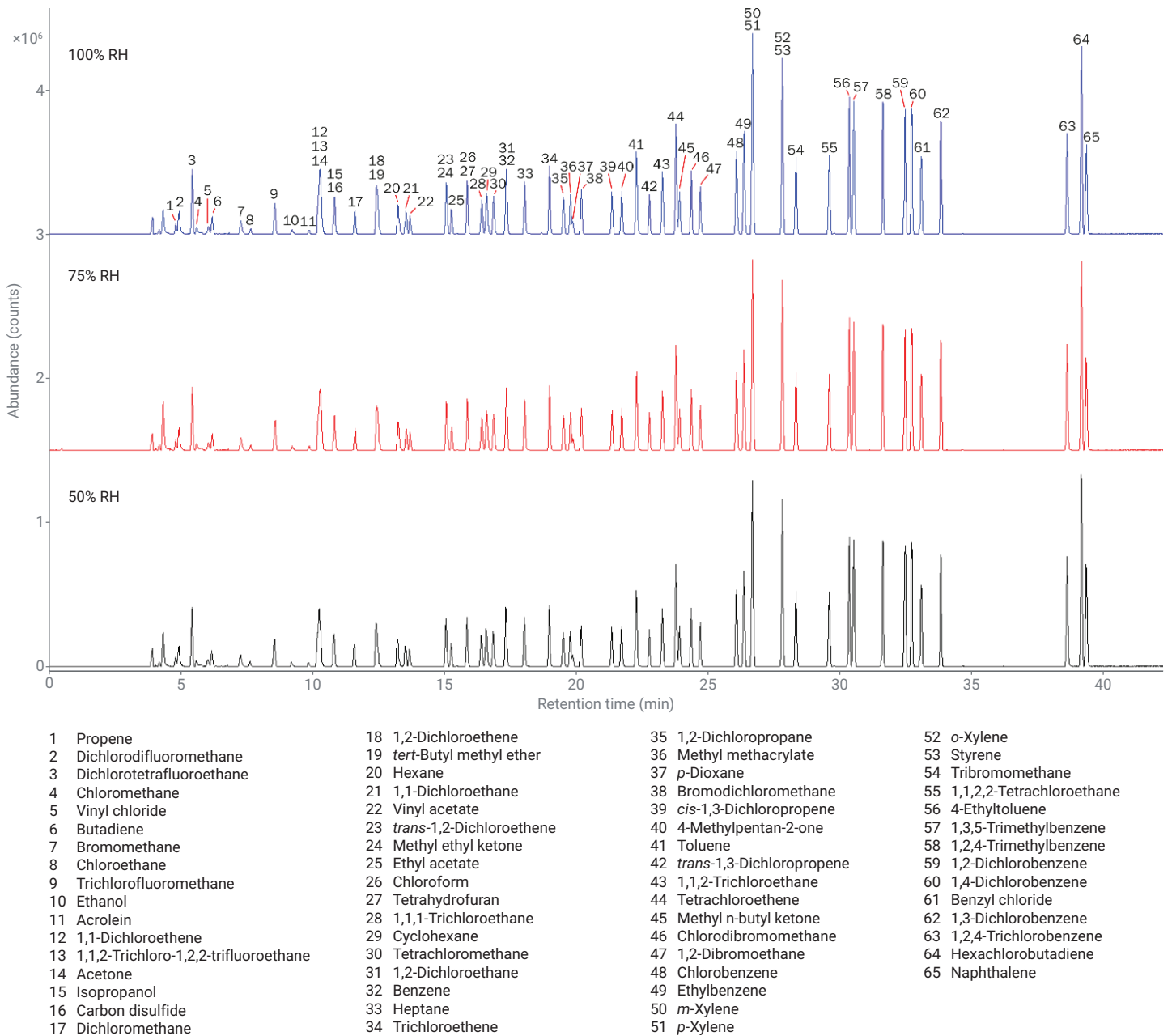


Figure 1. Analysis of 200 mL of a 10 ppbv 65-component TO-15 standard at 50% RH, 75% RH, and 100% RH. The upper two traces have been offset for clarity.

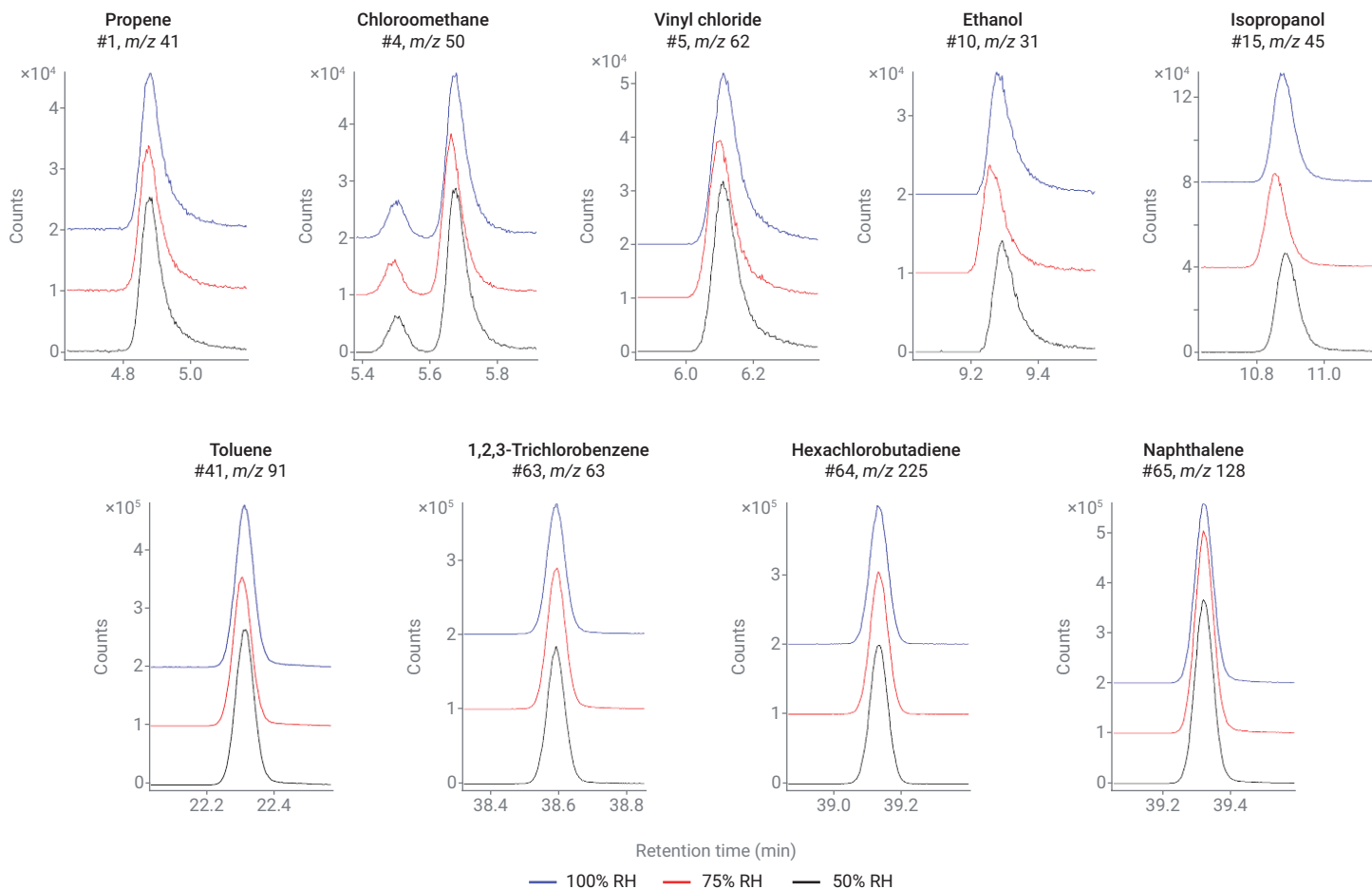


Figure 2. Extracted ion chromatograms for nine selected analytes from the analysis shown in Figure 3. The upper two traces in each case have been offset for clarity.

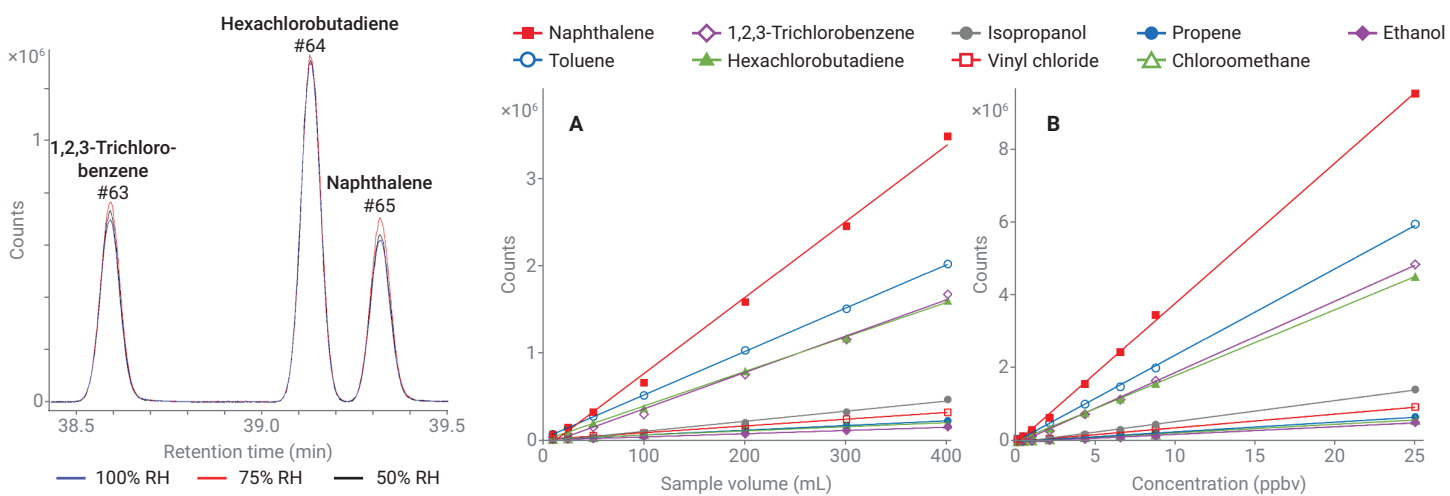


Figure 3. Expansion of Figure 3 (with zero offset), showing the similarity of the responses at the three humidities for the three least-volatile compounds in the mix.

Figure 4. Linearities from (A) 10 to 400 mL and (B) 0.22 to 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.² 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 being 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 very 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 5).

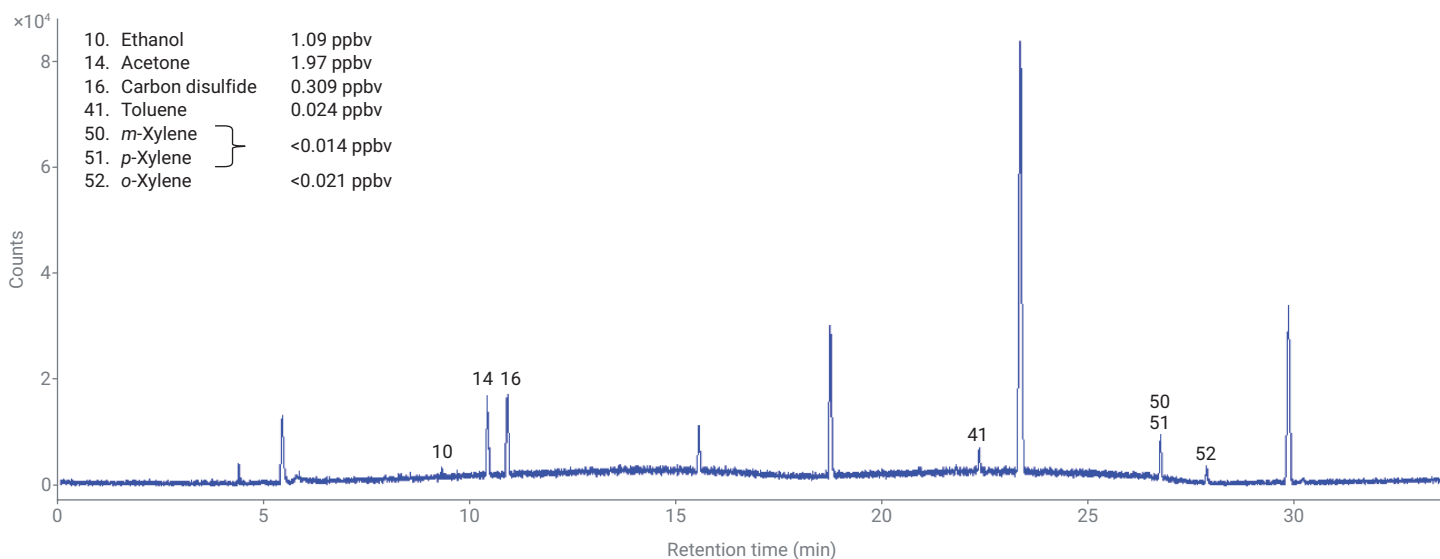


Figure 5. Real sample chromatogram generated from analysis of 250 mL of rural air, using the conditions previously described. Compounds from the TO-15 listing are indicated.

Conclusion

In summary, the 7890B or 8890 GC coupled to the 5977B single quadrupole MS and CIA Advantage–Kori-xr–UNITY-xr preconcentration system described allows confident analysis of ‘air toxics’ in humid environments, in accordance with US EPA method TO-15.

Key features of the results are 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 method detection limits 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 efficient and selective removal of 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, eliminating the cost and inconvenience associated with liquid cryogen. The robustness and reliability of the GC/MSD allows for long-term operation of the system while generating data in compliance with US EPA TO-15 requirements.

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

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 0.22 to 25 ppbv.

No.	Compound	RT (min)	50% RH			75% RH		100% RH	
			R^2	RRF RSD (%)	MDL (ppbv)	R^2	RRF RSD (%)	R^2	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-Dichloroethene	10.258	0.9993	3.7	0.006	0.9994	5.1	0.9998	1.2
13	1,1,2-Trichloro-1,2,2-trifluoroethane	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	<i>tert</i> -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	<i>trans</i> -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	<i>p</i> -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	<i>cis</i> -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

No.	Compound	RT (min)	50% RH			75% RH		100% RH	
			R ²	RRF RSD (%)	MDL (ppbv)	R ²	RRF RSD (%)	R ²	RRF RSD (%)
41	Toluene	22.326	0.9996	7.8	0.021	0.9997	11.0	0.9999	16.3
42	<i>trans</i> -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
44	Tetrachloroethene	23.828	0.9995	8.6	0.007	0.9995	10.1	1.0000	8.8
45	Methyl <i>n</i> -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	<i>m</i> -Xylene	26.732	1.0000	8.0	0.014	0.9996	9.4	1.0000	20.8
51	<i>p</i> -Xylene	26.732	1.0000	8.0	0.014	0.9996	9.4	1.0000	20.8
52	<i>o</i> -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

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