

EPA TO-15 Analysis Using Hydrogen Carrier Gas and the Agilent HydroInert Source

Ambient air testing using cryogen-free thermal desorption and gas chromatography coupled to a single quadrupole mass spectrometer (GC/MS) with hydrogen gas

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Abstract

Ambient air monitoring is commonly analyzed with gas chromatography/mass spectrometry (GC/MS) and helium carrier gas. Recent pressure on the helium supply has required organizations to actively investigate hydrogen carrier gas, but most GC/MS analyses have reduced sensitivity and hydrogenation or dechlorination in the sources. This application note describes the use of hydrogen carrier gas and the Agilent HydroInert source for GC/MS analysis of humidified canister "air toxics" samples at 100% relative humidity (RH), 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 U.S. Environmental Protection Agency (EPA) method Toxic Organics-15 (TO-15), including method detection limits (MDLs) as low as 11 parts per trillion by volume (pptv).

Introduction

Monitoring of chemicals in ambient air is necessary to determine the effect they have on the environment and global climate. This monitoring has driven the development of several national and international regulations, 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 few 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 U.S. and China. To achieve the required detection limits using this approach, preconcentration is required to focus analytes and to selectively eliminate bulk constituents. This approach is mandated within the most popular standard method for canisters, U.S. 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. The range of temperatures and humidities at sampling locations is also an issue. High levels of humidity are difficult 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.

The availability of helium has been a concern for several years, and interest in transitioning to alternative carrier gases such as hydrogen has significantly increased. However, existing MS systems have issues with dechlorination of heavily chlorinated compounds. These issues would alter the mass spectra of a peak in the total ion chromatogram (TIC) and lead to potential misidentification of compounds. A newly designed extractor source called the Agilent HydroInert source for the Agilent 5977B Inert Plus GC/MSD addresses these hydrogen-related issues and helps improve performance with hydrogen carrier gas in GC/MS. The HydroInert source with hydrogen carrier gas retains mass spectral fidelity and allows users to continue using existing helium-based mass spectral libraries and quantitative methods.

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 with hydrogen carrier gas and the HydroInert source, allow the analysis of a range of volatile "air toxics" from canisters at 100% RH, in accordance with U.S. EPA method TO-15. Note 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 U.S. 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, which is connected to the canister autosampler through a water removal unit and into the multisorbent focusing trap within the concentrator system. The water removal unit will remove most of the water from the sample, and any water vapor remaining in the sample can further be reduced through purging the trap. After the concentration and drying steps are completed, the VOCs are thermally desorbed, entrained in a carrier gas stream, and transferred onto a GC column for separation.
4. **Compound identification and quantitation:** Method TO-15 uses GC/MS for qualitative and quantitative analysis of samples. 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 TIC are examined, and VOCs are identified based on the intensities of quantifier and qualifier ions. The acquired mass spectra are then compared with library spectra (taken under similar conditions) 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 multigas CIA Advantage-xr canister autosampler with a Kori-xr water removal device and UNITY-xr thermal desorber, coupled to an Agilent 8890B GC and 5977B single quadrupole GC/MSD system with a HydroInert EI source and 6 mm lens (part number G3870-20448).

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

Standard preparation

A 1 part per million (ppm) standard containing 65 "air toxics" compounds at 1 ppm was diluted in 6 L canisters with nitrogen balance gas to 10 parts per billion by volume (ppbv), unless otherwise stated. RH of 100% was achieved by injecting an appropriate volume of water into the canister.

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 100% RH, and Figure 2 shows extracted ion chromatograms (EICs) for 16 components spanning the volatility range. Note the excellent peak shape, especially for lighter VOCs, which demonstrates the effectiveness of the Kori-xr module at removing water before analyte trapping at 100% RH.

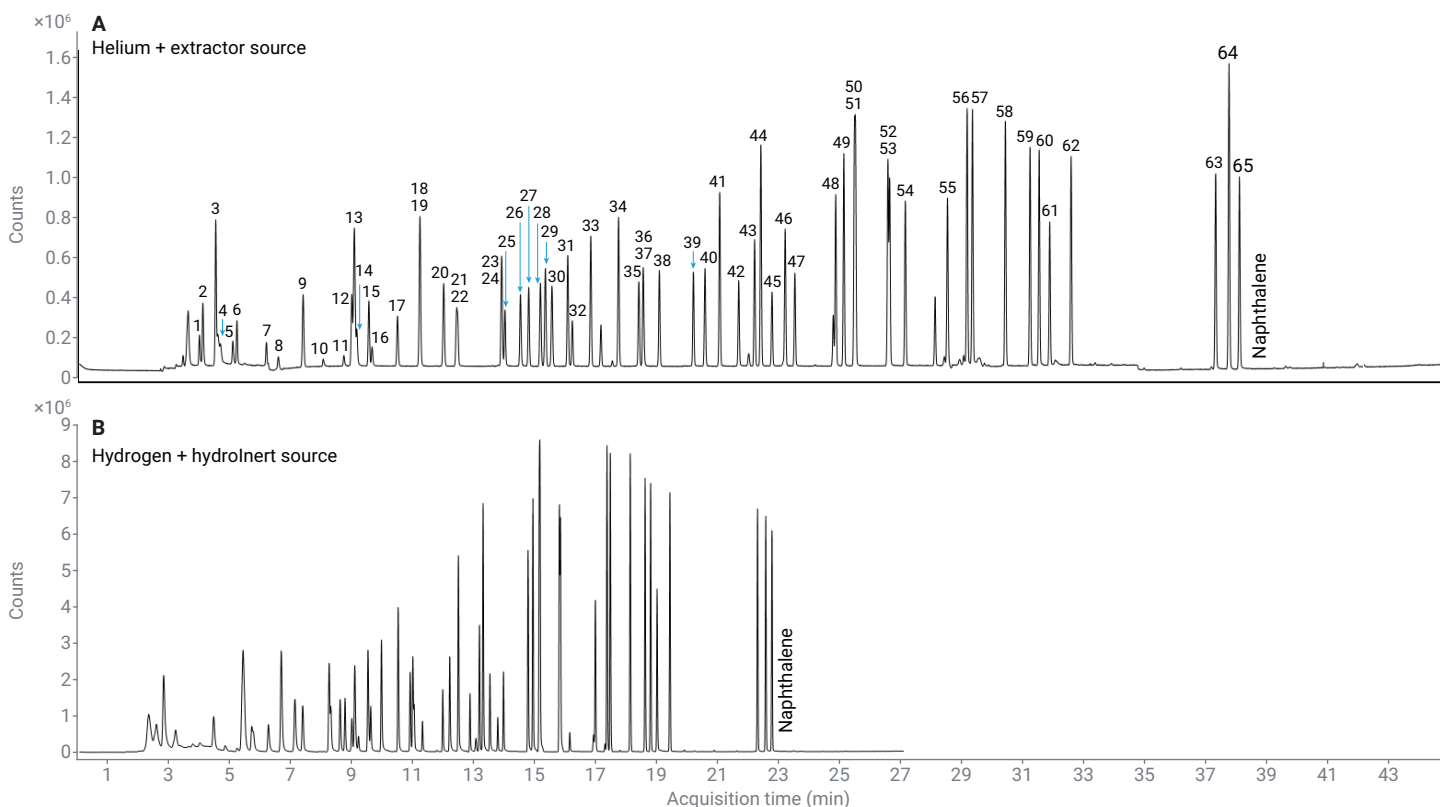
Another noteworthy aspect is that hydrogen carrier gas decreases the GC cycle time by 40% (45 to 27 minutes), as indicated by the shift in naphthalene from 38 to 23 minutes, while maintaining retention time order for all compounds. Faster chromatography can significantly increase sample throughput.

Table 1. GC and TD parameters.

Parameter	Value
Gas Chromatograph	Agilent 8890B GC
Column	Agilent J&W DB-624, 60 m × 0.25 mm, 1.40 μm (p/n 123-1364)
Inlet	Splitless
Inlet Temperature	120 °C
Oven Temperature Program	30 °C (3 min) 8.3 °C/min to 230 °C (0 min)
Total Run Time	27 min
MS Transfer Line Temperature	230 °C
Injection Volume	NA
Carrier Gas	Hydrogen, 2.0 mL/min constant flow
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	120 °C
Standby Split	10 mL/min
Sample Flow	50 mL/min
Trap Purge	1.0 min at 50 mL/min
Trap Desorption	2.0 min at 4 mL/min split flow
Cold Trap	Focusing trap: Air Toxics Analyzer (p/n U-T15ATA-2S)

Table 2. MS parameters.

Parameter	Value
Source	HydroInert source
Mode	Electron ionization, 70 eV
Source Temperature	300 °C
Quadrupole Temperature	200 °C
Scan Range	<i>m/z</i> 30 to 300



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

Figure 1. Analysis of 400 mL of a 10 ppbv 65-component TO-15 standard at 100% RH using helium (A) and hydrogen (B) gas. Naphthalene's retention time shifts from 38 to 23 minutes, indicating a 40% reduction in GC cycle time.

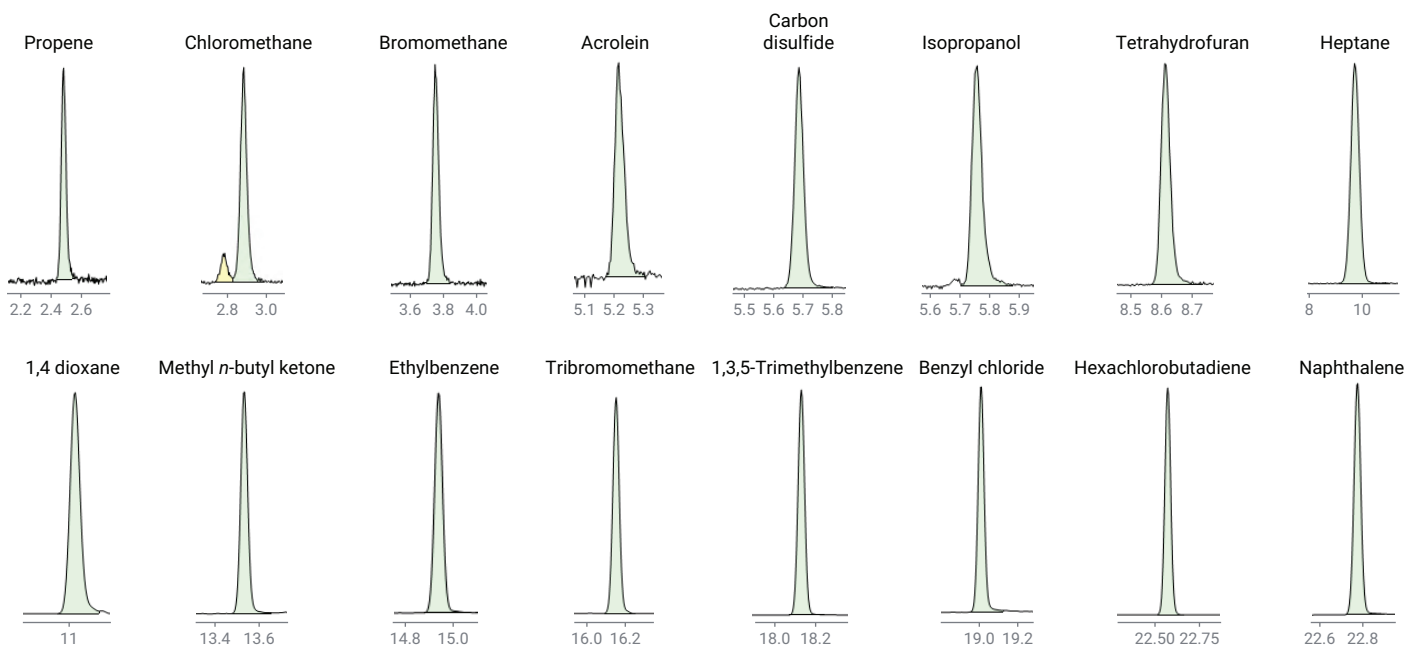


Figure 2. Excellent peak shape of EICs for 16 selected compounds at 2.5 ppbv analyzed using hydrogen gas.

Spectral fidelity

The HydroInert source maintains spectral fidelity by preventing hydrogenation and other reactions that can occur using hydrogen carrier gas. Library match scores (LMS) for all analytes in the 65-component mix were well above 90%, indicating that unwanted source reactions were prevented. Figure 3 shows two examples of high match scores to the National Institute of Standards and Technology helium library (NIST20).

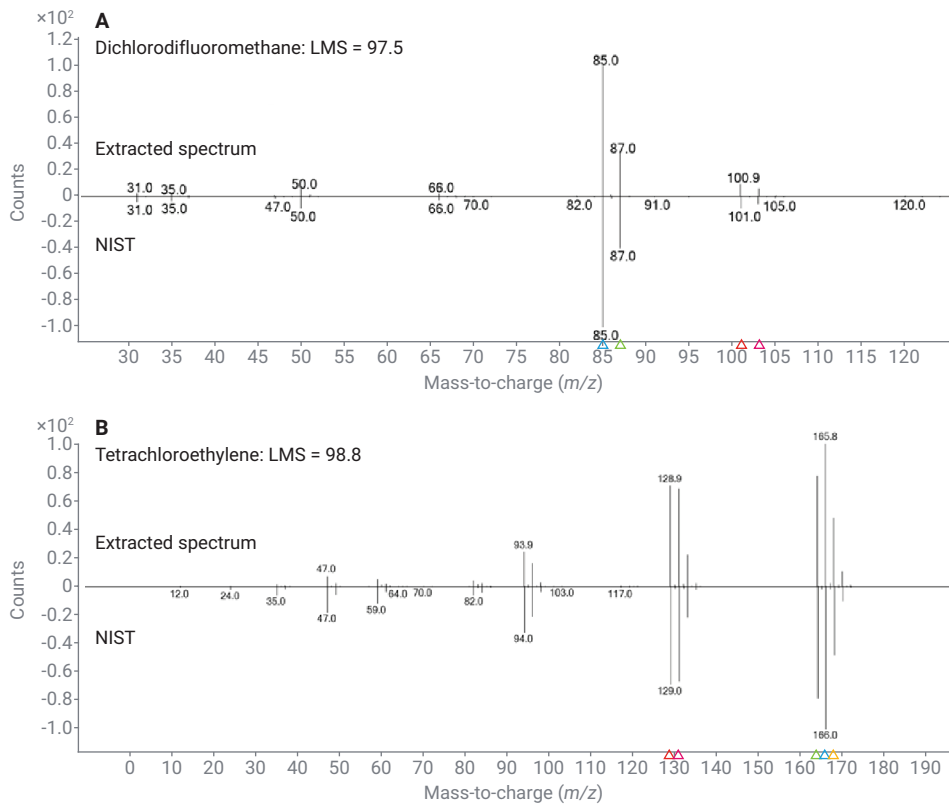


Figure 3. LMS and comparison of extracted versus NIST spectra for dichlorodifluoromethane (A) and tetrachloroethylene (B). Spectral fidelity is maintained.

Linearity

Linearities concerning concentration were calculated at 0.5, 1.25, 2.5, 5, 7.5, and 10 ppbv.

Excellent system linearities were obtained at 100% RH (Table A1), with a mean R^2 value of 0.999 from 0.50 to 10 ppbv. Figure 4 shows a linearity plot for the 100% RH sample, for the set of 14 compounds spanning the volatility range.

Method detection limits

MDLs were calculated based on seven replicate samples at 0.1 ppbv.² To comply with Method TO-15, MDLs are required to be ≤ 0.5 ppbv.

Calculations using hydrogen carrier gas gave a mean MDL of 28 pptv for the 28 compounds analyzed (Table 3), which is well within method criteria confirming that method compliance can be achieved, and exceeded, for TO-15 using the HydroInert source. Values ranged from 11 pptv for 4-ethyltoluene, to 53 pptv for carbon disulfide, with a solitary outlier at 113 pptv for propene. These values are all much lower than the requirement of ≤ 0.5 ppbv.

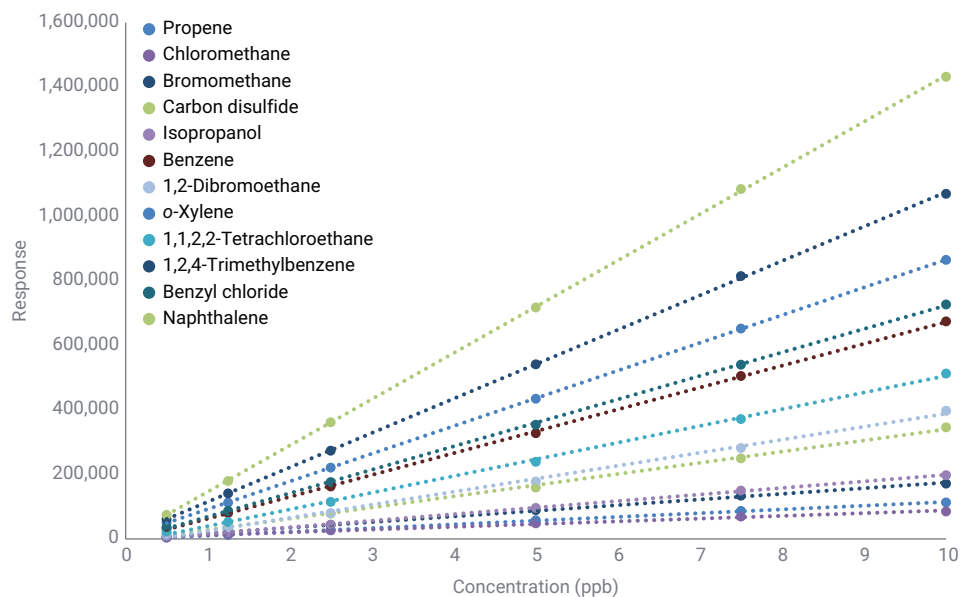


Figure 4. Linearities from 0.5 to 10 ppbv for 14 compounds spanning the range of volatilities, from the 100% RH sample.

Table 3. MDL values for 28 compounds at 0.1 ppbv from the 100% RH sample.

No.	Compound	Hydrogen MDL (pptv)	No.	Compound	Hydrogen MDL (pptv)
1	Propene	113	15	Methyl methacrylate	34
2	Dichlorodifluoromethane	38	16	Bromodichloromethane	34
3	Vinyl chloride	29	17	Toluene	14
4	Butadiene	33	18	Tetrachloroethene	13
5	1,1-Dichloroethene	24	19	1,2-Dibromoethane	28
6	1,1,2-Trichloro-1,2,2-trifluoroethane	25	20	Chlorobenzene	14
7	Carbon disulfide	53	21	Ethylbenzene	14
8	Dichloromethane	29	22	Styrene	23
9	tert-Butyl methyl ether	16	23	1,1,2,2-Tetrachloroethane	16
10	Vinyl acetate	23	24	4-Ethyltoluene	11
11	Methyl ethyl ketone	42	25	1,3,5-Trimethylbenzene	14
12	Tetrachloromethane	17	26	1,2-Dichlorobenzene	17
13	Benzene	19	27	Hexachlorobutadiene	23
14	Heptane	13	28	Naphthalene	50
				Average	28

Reproducibility

Method TO-15 requires that the calculated relative standard deviations (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 for 100% RH at 7.47% RSD. Further, for 10 replicates of 10 ppbv at 100% RH, average area RSD was 1.22%. For 50 injections of varying concentrations of 100% RH, average retention time

RSD was 0.09%, where criteria state <1% variation (Figure 5). Efficient water management using UNITY-Kori-CIA Advantage-xr enables stable retention times and highly reproducible peak area responses, even with hydrogen carrier gas.

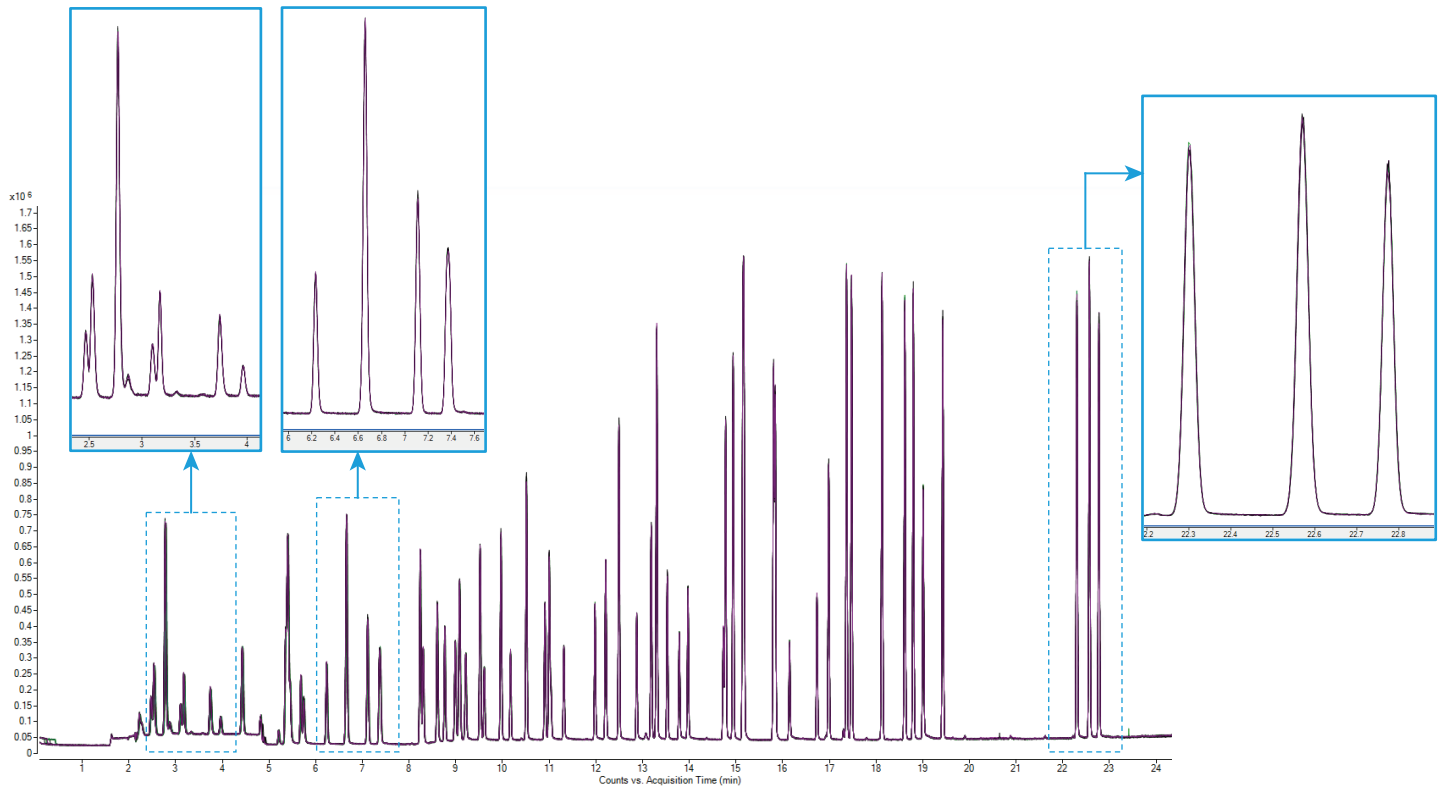


Figure 5. Overlay of 10 replicates at 10 ppbv concentration of 100% RH sample. Average retention time RSD is 0.09%.

Real air sample

To illustrate the performance of the system for a real air sample, 400 mL of lab air was analyzed under the same conditions as described previously. Seven components from the 65-member TO-15 list were found to be at quantifiable levels (Figure 6).

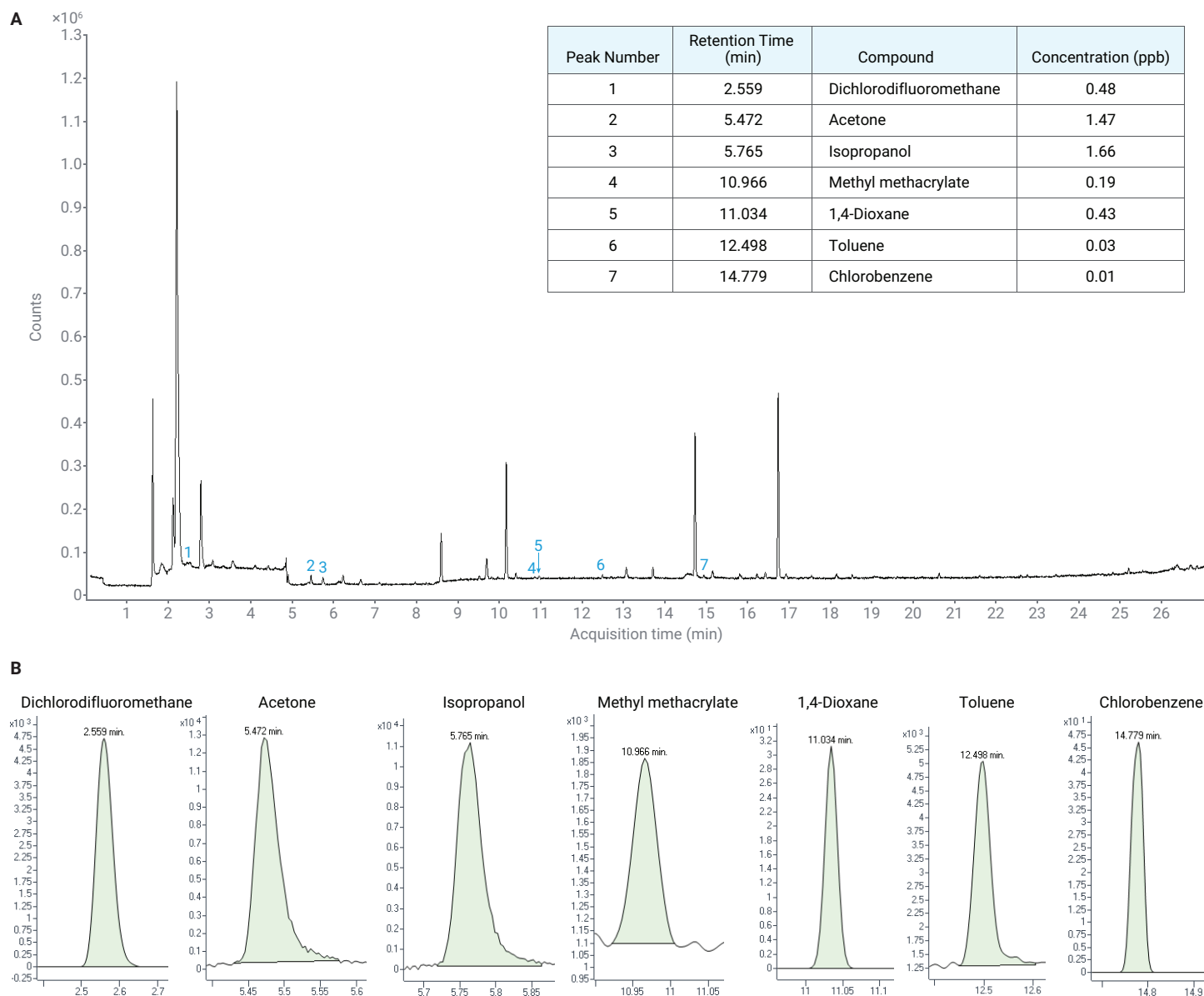


Figure 6. (A) Real sample chromatogram generated from analysis of 400 mL of rural air, using the conditions previously described. Compounds from the TO-15 listing are indicated. (B) Zoom of seven compounds detected from the TO-15 list.

Conclusion

The Agilent 8890 GC coupled to the Agilent 5977B single quadrupole MS and CIA Advantage–Kori-xr–UNITY-xr preconcentration system with hydrogen carrier gas allows confident analysis of "air toxics" in humid environments, in accordance with U.S. 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 100% relative humidity. Performance was well within the requirements of method TO-15, with method detection limits as low as 11 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 VOCs or polar species. In addition, the system uses electrical trap cooling, eliminating the cost and inconvenience associated with liquid cryogen. The Agilent HydroInert source with hydrogen carrier gas retained mass spectral fidelity, allowing users to continue the use of existing helium-based mass spectral libraries and quantitative methods. The robustness and reliability of the GC/MSD allows long-term operation of the system while generating data in compliance with U.S. 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. Chinese EPA Method HJ 759, Ambient Air – Determination of Volatile Organic Compounds – Collected by Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry, *Chinese Ministry of Environmental Protection 2015*. http://kjs.mep.gov.cn/hjbhzb/bzwb/dqhjbh/jcgfffbz/201510/t20151030_315940.htm

Appendix

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

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.

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

Table A1. Data comparison of helium and hydrogen carrier gas results obtained for TO-15 standards at 100% RH. Linearity (R^2) values were generated for the concentration range 0.22 to 10 ppbv for analysis with helium carrier gas, and 0.5 to 10 ppv for hydrogen carrier gas.

No.	Compound	Helium Carrier (100% RH)			Hydrogen Carrier (100% RH)		
		RT (min)	RRF RSD (%)	RRF RSD (%)	RT (min)	RRF RSD (%)	RRF RSD (%)
1	Propene	4.894	0.9997	6.3	2.47	0.9994	12.4%
2	Dichlorodifluoromethane	5.032	0.9998	5.6	2.53	1.0000	8.4%
3	Dichlorotetrafluoroethane	5.500	0.9997	7.7	2.77	0.9999	4.2%
4	Chloromethane	5.686	0.9808	11.0	2.88	0.9929	9.3%
5	Vinyl chloride	6.122	0.9994	4.6	3.10	0.9997	10.1%
6	Butadiene	6.276	0.9998	2.0	3.17	0.9999	12.4%
7	Bromomethane	7.346	0.9988	14.4	3.74	0.9988	10.3%
8	Chloroethane	7.723	0.9870	9.1	3.95	0.9999	5.2%
9	Trichlorofluoromethane	8.646	0.9999	6.2	4.42	0.9996	5.6%
10	Ethanol	9.299	0.9997	24.4	4.80	0.9990	20.9%
11	Acrolein	9.925	0.9993	9.3	5.20	0.9988	18.9%
12	1,1-Dichloroethene	10.258	0.9998	1.2	5.35	0.9999	13.2%
13	1,1,2-Trichloro-1,2,2-trifluoroethane	10.337	1.0000	4.8	5.40	0.9998	2.2%
14	Acetone	10.401	1.0000	2.7	5.45	0.9999	5.1%
15	Isopropanol	10.868	0.9981	18.8	5.74	0.9996	14.2%
16	Carbon disulfide	10.884	0.9999	0.9	5.67	0.9984	5.6%
17	Dichloromethane	11.657	0.9998	2.0	6.23	0.9995	8.7%
18	1,2-Dichloroethene	12.461	0.9999	1.6	6.65	0.9997	11.8%
19	<i>tert</i> -Butyl methyl ether	12.513	0.9997	4.2	6.65	0.9999	3.4%
20	Hexane	13.285	0.9956	13.6	7.11	0.9999	2.3%
21	1,1-Dichloroethane	13.578	1.0000	5.5	7.36	0.9996	10.1%
22	Vinyl acetate	13.737	0.9998	1.5	7.39	0.9981	12.5%
23	<i>trans</i> -1,2-Dichloroethene	15.112	0.9998	3.6	8.24	0.9997	11.4%
24	Methyl ethyl ketone	15.127	0.9998	9.2	8.23	0.9998	6.9%
25	Ethyl acetate	15.314	0.9999	5.5	8.30	1.0000	4.7%
26	Chloroform	15.904	0.9999	5.5	8.76	0.9984	8.6%
27	Tetrahydrofuran	15.912	0.9998	9.2	8.60	0.9997	6.8%
28	1,1,1-Trichloroethane	16.447	0.9999	8.2	8.99	0.9969	7.9%
29	Cyclohexane	16.637	0.9999	8.8	9.08	0.9997	2.6%
30	Tetrachloromethane	16.902	1.0000	7.4	9.21	0.9942	11.1%
31	1,2-Dichloroethane	17.378	1.0000	3.5	9.61	0.9999	5.6%
32	Benzene	17.390	0.9999	6.1	9.52	0.9998	2.0%
33	Heptane	18.075	0.9995	19.0	9.97	0.9998	2.8%
34	Trichloroethene	19.022	0.9999	5.1	10.51	0.9990	10.0%
35	1,2-Dichloropropane	19.557	0.9999	7.1	10.91	0.9990	4.9%
36	Methyl methacrylate	19.822	0.9989	2.9	11.00	0.9997	2.8%
37	<i>p</i> -Dioxane	19.914	0.9998	12.6	11.01	0.9981	15.6%
38	Bromodichloromethane	20.227	0.9999	6.2	11.32	0.9953	11.9%
39	<i>cis</i> -1,3-Dichloropropene	21.399	1.0000	4.5	11.98	0.9961	12.9%
40	4-Methylpentan-2-one	21.760	0.9999	2.8	12.21	0.9996	5.6%
41	Toluene	22.326	0.9999	16.3	12.50	1.0000	4.1%
42	<i>trans</i> -1,3-Dichloropropene	22.810	0.9997	2.9	12.88	0.9973	13.1%
43	1,1,2-Trichloroethane	23.305	1.0000	7.9	13.19	0.9990	6.3%

No.	Compound	Helium Carrier (100% RH)			Hydrogen Carrier (100% RH)		
		RT (min)	RRF RSD (%)	RRF RSD (%)	RT (min)	RRF RSD (%)	RRF RSD (%)
44	Tetrachloroethene	23.828	1.0000	8.8	13.31	0.9996	2.9%
45	Methyl <i>n</i> -butyl ketone	23.959	0.9998	2.5	13.53	0.9942	17.0%
46	Chlorodibromomethane	24.398	0.9999	4.7	13.79	0.9973	12.6%
47	1,2-Dibromoethane	24.735	1.0000	4.4	13.98	0.9973	14.2%
48	Chlorobenzene	26.102	1.0000	11.9	14.78	0.9998	2.2%
49	Ethylbenzene	26.407	0.9999	20.2	14.94	1.0000	4.6%
50	<i>m</i> -Xylene	26.732	1.0000	20.8	15.16	0.9999	4.7%
51	<i>p</i> -Xylene	26.732	1.0000	20.8	15.16	0.9999	4.7%
52	<i>o</i> -Xylene	27.837	1.0000	25.2	15.81	1.0000	5.7%
53	Styrene	27.857	0.9999	10.3	15.84	1.0000	4.1%
54	Tribromomethane	28.376	0.9998	4.4	16.15	0.9976	6.8%
55	1,1,2,2-Tetrachloroethane	29.624	0.9999	6.8	16.99	0.9990	8.1%
56	4-Ethyltoluene	30.385	0.9999	6.3	17.37	1.0000	4.1%
57	1,3,5-Trimethylbenzene	30.551	1.0000	19.6	18.13	1.0000	4.5%
58	1,2,4-Trimethylbenzene	31.653	1.0000	10.4	17.48	0.9999	4.6%
59	1,2-Dichlorobenzene	32.485	0.9999	3.9	18.62	1.0000	1.0%
60	1,4-Dichlorobenzene	32.738	0.9999	3.3	18.80	0.9999	2.4%
61	Benzyl chloride	33.107	0.9998	2.3	19.01	0.9998	2.0%
62	1,3-Dichlorobenzene	33.840	0.9999	7.4	19.43	0.9999	3.8%
63	1,2,4-Trichlorobenzene	38.594	0.9965	18.9	22.30	0.9998	2.2%
64	Hexachlorobutadiene	39.121	0.9997	9.4	22.57	0.9988	7.5%
65	Naphthalene	39.315	0.9975	19.7	22.78	1.0000	1.6%
	Mean values		0.9992	8.5		0.9990	7.5%

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