Application Note 116

Monitoring VOCs in Ambient Air Using Sorbent Tubes with Analysis by TD-GC/MS in Accordance with Chinese EPA Method HJ 644-2013

Application Note

Abstract

This application note demonstrates the excellent performance offered by Markes International's automated cryogen-free thermal desorption (TD) system for the analysis of volatile organic compounds (VOCs) in ambient air, sampled using sorbent tubes. The system used is compliant with Chinese EPA Method HJ 644-2013, and features automated quantitative re-collection of split flows, which allows repeat analysis, method development, and results verification.

Introduction

Volatile organic compounds (VOCs) are important precursors for atmospheric photochemical reactions, including those that generate low-level ozone and particulate matter that give rise to poor air quality. In addition, some of these VOCs are harmful to health in their own right, and these air toxics or hazardous air pollutants (HAPs) are therefore monitored in many industrial and urban environments. They range in volatility from chloromethane (methyl chloride) and acetone to hexachlorobutadiene and dodecene, and include polar as well as nonpolar compounds. Several national and international standard methods have been developed for air toxics and related applications, including US EPA Methods TO-15 (canisters) and TO-17 (sorbent tubes).

In China, the Twelfth Five-Year Plan (2012) emphasises the need to "deepen the prevention and control of particulate matter pollution, and strengthen the control of volatile organic pollutants and toxic emissions". Control of VOCs has therefore become a priority in recent years, as reflected by the 2013 Atmospheric Pollution Control Act and standard method HJ 644-2013, released by the Chinese Ministry of Environmental Protection (MEP), and titled *Ambient air – Determination of volatile organic compounds – Sorbent adsorption and thermal desorption gas chromatography mass spectrometry method*.

Agilent Technologies

In response to demand for measurement of air toxics, analytical technologies have been developed that offer an automated platform compliant with sorbent-tube-based methods. In this application note, we describe the sampling of VOCs in ambient air using sorbent tubes, followed by HJ 644-compliant analysis using an automated, cryogen-free thermal desorption-gas chromatography-mass spectrometry (TD-GC/MS) system.

Background of thermal desorption

Thermal desorption (TD) is a versatile GC preconcentration technology used to analyze volatile and semivolatile organic compounds (VOCs and SVOCs) in a wide range of sample types. By concentrating organic vapors from a sample into a very small volume of carrier gas (Figure 1), TD maximizes sensitivity for trace-level target compounds, helps minimize interferences, and routinely allows analyte detection at the ppb level or below. It also greatly improves sample throughput by allowing full automation of sample preparation, desorption/extraction, preconcentration, and GC injection.

A   **Tube desorption and inlet split:**
Sample tube heated in a flow of carrier gas and analytes swept into an electrically cooled focusing trap, typically held between ambient and −30 °C.

Sample tubes and traps can contain multiple sorbents, for analysis of an extended range of analytes.

During either stage, the flow of analytes can be split and re-collected onto a clean sorbent tube.
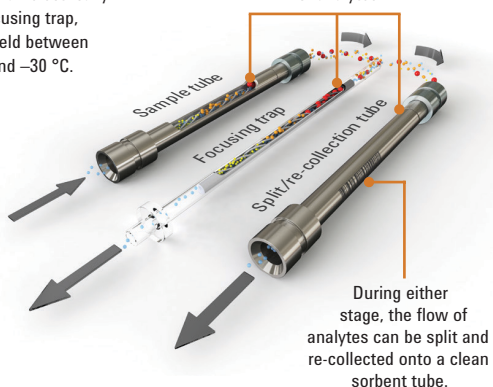
B   **Trap desorption and outlet split:**
Focusing trap rapidly heated (up to 100 °C/s) in a reverse flow of carrier gas (backflush operation), to transfer the analytes to the GC column.

Figure 1. How two-stage thermal desorption works.

The 'xr' range of TD instruments from Markes International enhances these capabilities, offering a wide analyte range (C_2-C_{44} including reactive species), automated re-collection and reanalysis of split portions for method validation and compliance with standard methods, optional internal standard addition for improved confidence in results, and electronic/manual options for control of carrier gas. In this study, we use the TD100-xr for fully automated analysis of up to 100 sorbent tube samples.

Experimental

Standard

A 62-component gas standard in nitrogen (which includes the 34 target compounds in HJ 644), carried in pure helium, was loaded onto the sorbent tubes using a Calibration Solution Loading Rig (Markes International).
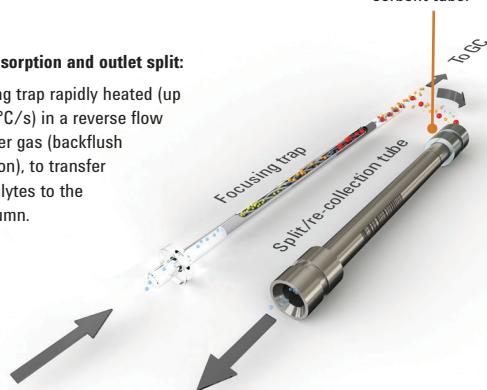
Table 1. Instrumental parameters.

Parameter	Value
Real air sample	
Pumped sampling:	ACTI-VOC (Markes International)
Flow rate:	50 mL/min for 20 minutes (total volume 1 L)
TD	
Instrument:	TD100-xr (Markes International)
Tube:	Universal (Markes International part no. C3-AXXX-5266)
Trap:	Air toxics (Markes International part no. U-T15ATA-2S)
Tube dry-purge:	1.0 minutes
Tube desorb:	220 °C (4 minutes)
Trap low:	25 °C
Trap heating rate:	40 °C/s
Trap high:	220 °C for 3 minutes
TD flow path:	120 °C
GC	
Carrier gas:	Helium
GC column:	Agilent J&W DB-624, 20 m × 0.18 mm, 1.0 µm
Mode:	Constant-flow, 1.2 mL/min
Oven ramp:	35 °C (3 minutes), then 15 °C/min to 190 °C (0 minutes)
MS	
Ion source:	250 °C
Quadrupole:	150 °C
Transfer line:	200 °C
Full scan range:	*m/z* 35-300

Results and Discussion

Chromatography

Figure 2 shows the chromatogram obtained for a sample equivalent to 2 L of a 1 ppbv standard. Excellent peak shape was obtained for all analytes, as illustrated for the challenging polar compound trichloromethane (expanded peak). These sharp peaks resulted from the rapid desorption of the focusing trap in the TD instrument, and are maintained even with splitless analysis, ensuring optimum sensitivity for trace-level analytes.

Linearity

System linearity was assessed by analyzing a variety of VOCs at 0.5, 1, 2, 5, and 9 ppbv (equivalent to a 2 L sampling volume, and consistent with ambient concentrations). All R^2 values were above 0.99 (Figure 3 and Table 2).
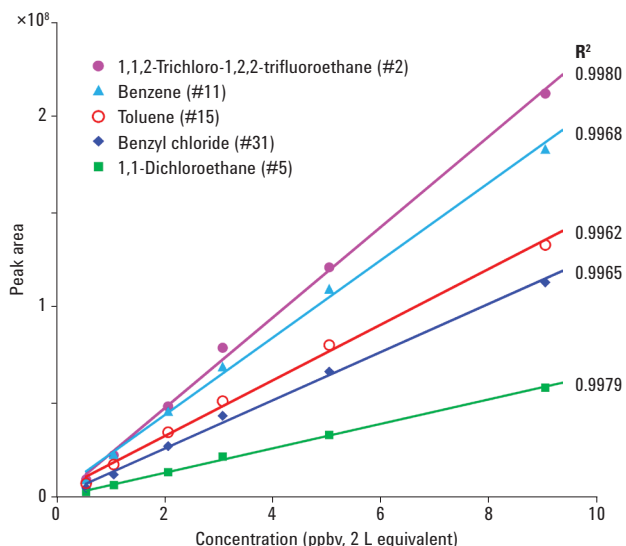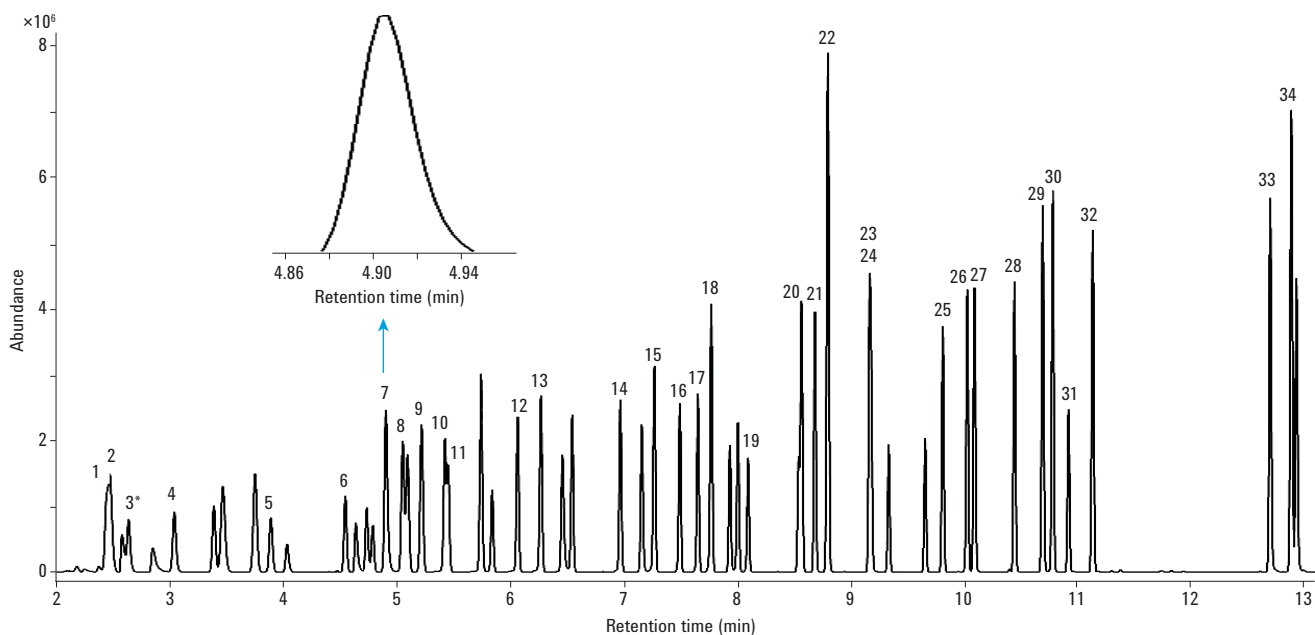

Figure 3. Linearities for five key compounds from the standard.

1. 1,1-Dichloroethene
2. 1,1,2-Trichloro-1,2,2-trifluoroethane
3. Chloropropene*
4. Dichloromethane
5. 1,1-Dichloroethane
6. cis-1,2-Dichloroethene
7. Trichloromethane
8. 1,1,1-Trichloroethane
9. Tetrachloromethane

10. 1,2-Dichloroethane
11. Benzene
12. Trichloroethene
13. 1,2-Dichloropropane
14. cis-1,3-Dichloropropene
15. Toluene
16. trans-1,3-Dichloropropene
17. 1,1,2-Trichloroethane
18. Tetrachloroethene

19. 1,2-Dibromoethane
20. Chlorobenzene
21. Ethylbenzene
22. m,p-Xylene
23. o-Xylene
24. Styrene
25. 1,1,2,2-Tetrachloroethane
26. 4-Ethyltoluene
27. 1,3,5-Trimethylbenzene

28. 1,2,4-Trimethylbenzene
29. 1,3-Dichlorobenzene
30. 1,4-Dichlorobenzene
31. Benzyl chloride
32. 1,2-Dichlorobenzene
33. 1,2,4-Trichlorobenzene
34. Hexachlorobutadiene

* Chloropropene was not present in the standard mix used; the label indicates where it would be expected to elute.

Figure 2. Chromatogram obtained for a sample equivalent to 2 L of a 1 ppbv standard, with the 34 target compounds listed in HJ 644 labeled. The trichloromethane peak is expanded, showing excellent peak shape.

Table 2. Linearity, detection limit, and repeatability data for the target VOCs. Note that chloropropene (#3) was not present in the standard mix used, and that chlorobenzene (#20) is obscured by the internal standard chlorobenzene-d$_5$, so quantitation was not possible.

No.	Compound	t$_R$ (min)	R^2	Quant ion (m/z)	Analyte concentration (ppbv)							Mean conc. (ppbv)	Std. dev. (ppbv)	Peak area RSD (%)	LOD (ppbv)
					Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7				
1	1,1-Dichloroethene	2.43	0.9965	61	0.446	0.438	0.495	0.493	0.468	0.467	0.452	0.466	0.022	4.8	0.070
2	1,1,2-Trichloro-1,2,2-trifluoroethane	2.46	0.9980	151	0.419	0.417	0.466	0.466	0.444	0.443	0.428	0.440	0.020	4.6	0.063
4	Dichloromethane	3.03	0.9981	49	0.363	0.377	0.454	0.418	0.413	0.413	0.392	0.404	0.030	7.5	0.095
5	1,1-Dichloroethane	3.88	0.9979	63	0.479	0.466	0.535	0.528	0.498	0.448	0.443	0.485	0.036	7.5	0.114
6	cis-1,2-Dichloroethene	4.54	0.9986	61	0.381	0.370	0.416	0.413	0.387	0.361	0.361	0.384	0.023	5.9	0.072
7	Trichloromethane	4.90	0.9848	85	0.466	0.463	0.529	0.523	0.513	0.481	0.472	0.492	0.028	5.7	0.088
8	1,1,1-Trichloroethane	5.05	0.9860	97	0.263	0.276	0.295	0.302	0.293	0.272	0.264	0.281	0.016	5.6	0.049
9	Tetrachloromethane	5.22	0.9864	117	0.321	0.322	0.359	0.354	0.342	0.329	0.312	0.334	0.018	5.4	0.056
10	1,2-Dichloroethane	5.43	0.9967	78	0.523	0.521	0.584	0.581	0.561	0.522	0.497	0.541	0.034	6.3	0.106
11	Benzene	5.46	0.9968	62	0.523	0.522	0.588	0.582	0.564	0.523	0.499	0.543	0.034	6.3	0.108
12	Trichloroethene	6.07	0.9962	130	0.526	0.518	0.578	0.572	0.563	0.519	0.503	0.540	0.030	5.6	0.095
13	1,2-Dichloropropane	6.27	0.9965	63	0.543	0.554	0.622	0.616	0.603	0.570	0.536	0.578	0.036	6.2	0.112
14	cis-1,3-Dichloropropene	6.97	0.9962	75	0.442	0.444	0.490	0.481	0.477	0.426	0.407	0.452	0.031	6.9	0.098
15	Toluene	7.27	0.9962	92	0.534	0.515	0.575	0.557	0.546	0.500	0.471	0.528	0.036	6.8	0.112
16	trans-1,3-Dichloropropene	7.50	0.9945	75	0.467	0.461	0.520	0.494	0.500	0.459	0.436	0.477	0.029	6.1	0.091
17	1,1,2-Trichloroethane	7.66	0.9959	97	0.532	0.530	0.583	0.578	0.567	0.535	0.514	0.548	0.027	4.9	0.085
18	Tetrachloroethene	7.77	0.9924	166	0.640	0.627	0.699	0.682	0.673	0.629	0.607	0.651	0.034	5.2	0.106
19	1,2-Dibromoethane	8.10	0.9980	107	0.428	0.423	0.477	0.467	0.463	0.448	0.432	0.448	0.021	4.8	0.067
21	Ethylbenzene	8.69	0.9926	106	0.537	0.530	0.581	0.562	0.552	0.510	0.487	0.537	0.032	6.0	0.101
22	m,p-Xylene	8.80	0.9709	106	0.695	0.691	0.761	0.735	0.716	0.658	0.619	0.696	0.048	6.8	0.150
23	o-Xylene	9.17	0.9868	106	0.490	0.495	0.544	0.531	0.514	0.483	0.454	0.501	0.030	6.1	0.096
24	Styrene	9.19	0.9868	104	0.489	0.495	0.543	0.532	0.514	0.481	0.452	0.501	0.031	6.2	0.098
25	1,1,2,2-Tetrachloroethane	9.82	0.9925	85	0.573	0.559	0.624	0.616	0.601	0.574	0.551	0.585	0.029	4.9	0.090
26	4-Ethyltoluene	10.03	0.9880	120	0.456	0.457	0.507	0.483	0.473	0.429	0.405	0.459	0.034	7.4	0.107
27	1,3,5-Trimethylbenzene	10.10	0.9799	120	0.456	0.468	0.511	0.492	0.475	0.431	0.405	0.463	0.036	7.8	0.113
28	1,2,4-Trimethylbenzene	10.45	0.9865	120	0.446	0.442	0.484	0.465	0.446	0.417	0.383	0.440	0.032	7.4	0.102
29	1,3-Dichlorobenzene	10.70	0.9809	146	0.667	0.655	0.739	0.698	0.694	0.656	0.616	0.675	0.039	5.8	0.124
30	1,4-Dichlorobenzene	10.78	0.9784	146	0.672	0.663	0.733	0.707	0.692	0.649	0.622	0.677	0.037	5.5	0.117
31	Benzyl chloride	10.93	0.9965	91	0.368	0.365	0.403	0.384	0.385	0.346	0.324	0.368	0.026	7.2	0.083
32	1,2-Dichlorobenzene	11.14	0.9814	146	0.631	0.635	0.694	0.672	0.659	0.620	0.586	0.643	0.036	5.6	0.112
33	1,2,4-Trichlorobenzene	12.70	0.9754	180	0.553	0.545	0.607	0.601	0.586	0.553	0.517	0.566	0.033	5.8	0.104
34	Hexachlorobutadiene	12.89	0.9590	225	0.401	0.424	0.457	0.447	0.437	0.429	0.402	0.428	0.021	4.9	0.066

Repeatability and limits of detection

Seven repeat analyses of a 0.5 ppbv gas standard (2 L equivalent) were conducted, and showed excellent consistency of retention times (Figure 4). Relative standard deviations (RSDs) of repsonses for all target compounds were below 8% (Table 2), and limits of detection (LODs) were below 0.15 ppbv.

Quantitative re-collection of split flows

Markes' TD instruments have the ability to re-collect samples by directing the split flow (which would otherwise carry excess sample to vent) onto a sorbent tube. This process of re-collection can either be onto the tube from which the sample was originally desorbed, or onto a clean tube. This process can be fully automated, and offers a significant advantage over solvent extraction, because it allows a single sample to be analyzed multiple times. Sample splitting and re-collection makes method validation easier, and more importantly, avoids the need to collect another sample should the analysis unexpectedly fail to proceed correctly.
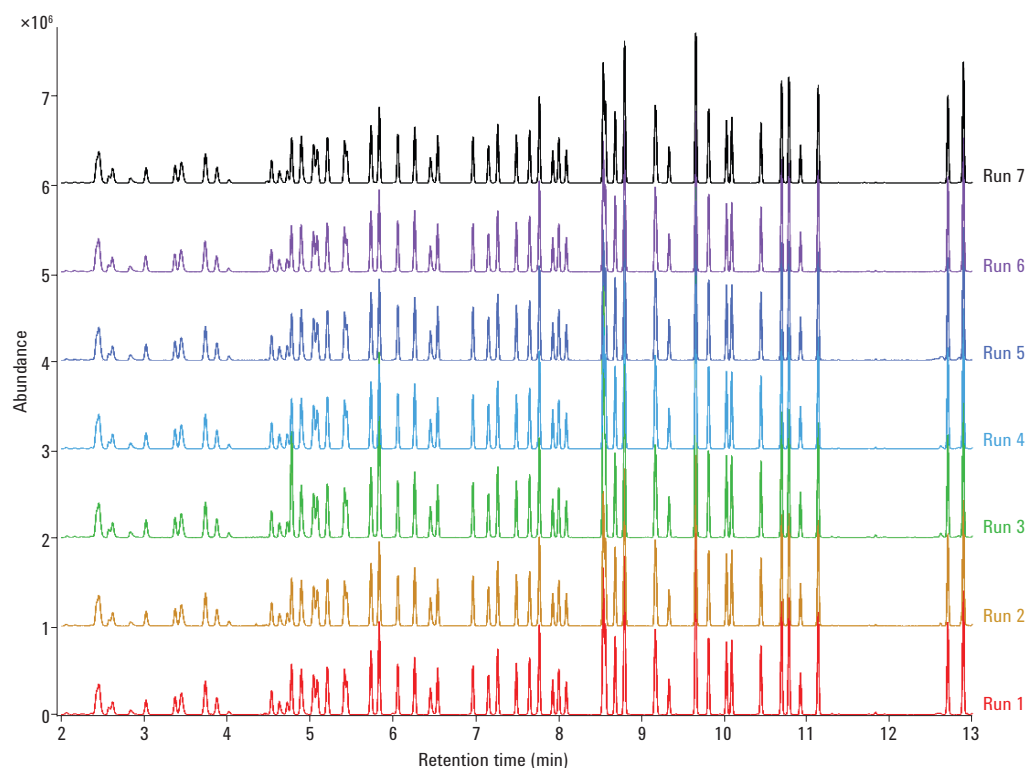

Figure 4. Seven repeated analyses of the same 0.5 ppbv standard. The baseline of each chromatogram is offset by 10^6 for clarity.

Figure 5 shows a repeat analysis of a gas standard equivalent to 2 L at 1 ppbv with a 60:1 split flow, illustrating quantitative re-collection over a wide range of volatilities. Note the consistency of peak position and shape.
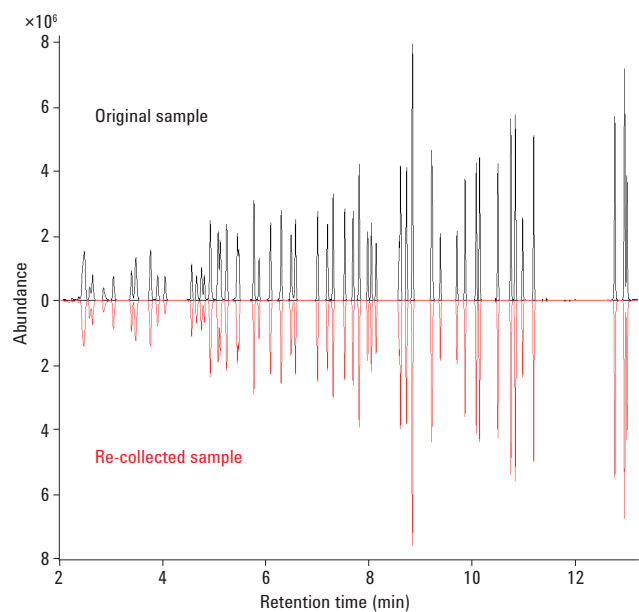
The accuracy of the analysis was also validated by loading a sorbent tube with 20 ng benzene and 40 ng toluene, and performing 10 re-collection/analysis cycles with a split ratio of 6.5:1 after the initial analysis. This showed excellent consistency with the theoretical values (Figure 6).
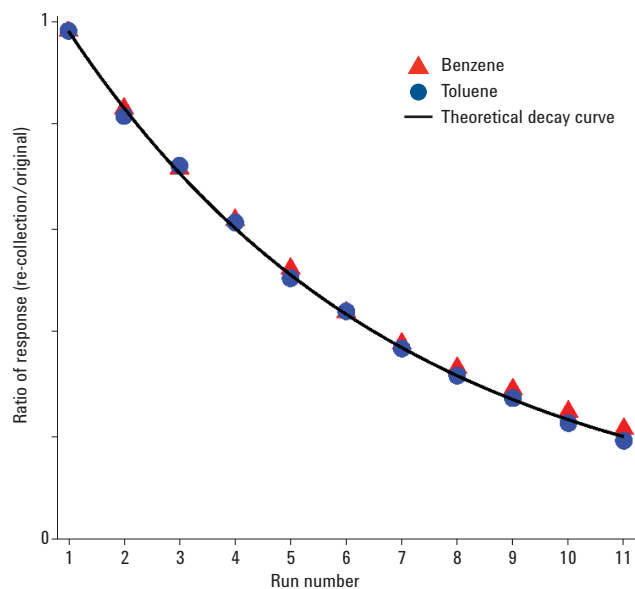

Figure 5. Original analysis (black) and repeat analysis (red) of tubes containing analytes equivalent to 2 L of a 1 ppbv standard with a 60:1 outlet split.

Figure 6. Evaluation of the decay in response for benzene and toluene from a tube repeatedly analyzed with a 6.5:1 outlet split.

Real air samples

To evaluate the performance of the system for a real-world scenario, 1 L of ambient air was collected onto a sorbent tube in an office, a laboratory, and semirural outside air, followed by analysis under the conditions described earlier. The results clearly show raised levels of VOCs in the office air (Figure 7).

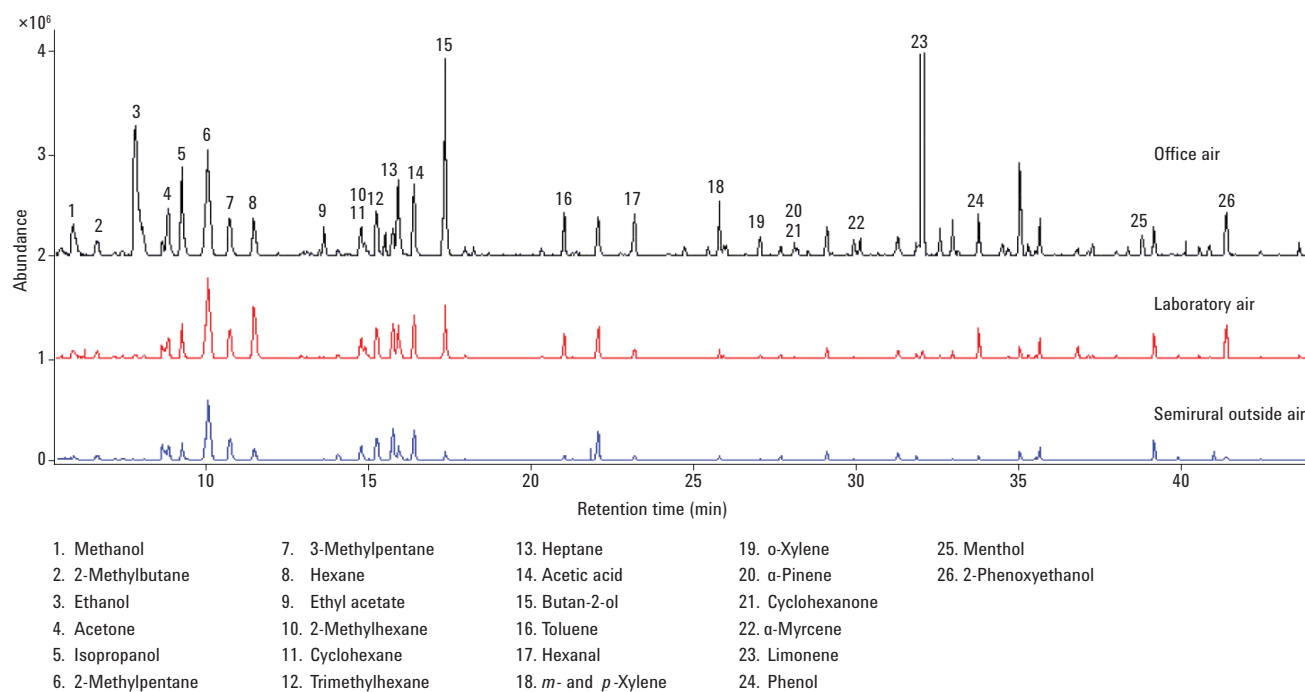|				
1. Methanol	7. 3-Methylpentane	13. Heptane	19. o-Xylene	25. Menthol
2. 2-Methylbutane	8. Hexane	14. Acetic acid	20. α-Pinene	26. 2-Phenoxyethanol
3. Ethanol	9. Ethyl acetate	15. Butan-2-ol	21. Cyclohexanone	
4. Acetone	10. 2-Methylhexane	16. Toluene	22. α-Myrcene	
5. Isopropanol	11. Cyclohexane	17. Hexanal	23. Limonene	
6. 2-Methylpentane	12. Trimethylhexane	18. *m*- and *p*-Xylene	24. Phenol	

Figure 7. Analysis of three 1 L air samples collected at three different locations using sorbent tubes, and analyzed by TD-GC/MS. Compounds listed in HJ 644 are marked in bold type.

Conclusions

This application note demonstrates that Markes International's automated, cryogen-free thermal desorption systems offer excellent results for monitoring air toxics in ambient air in accordance with Chinese EPA Method HJ 644. A particular feature of this method is the automated quantitative re-collection of split flows offered by the TD instrument, which makes method development and validation of results straightforward.

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