Fast Continuous Online Analysis of VOCs in Ambient Air using Agilent 5975T LTM GC/MSD and Markes TD

Application Note

Environmental

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Abstract

The ability to monitor volatile organic compounds (VOCs) is one of the most important requirements for environmental mobile labs. A fast method integrating online sampling and analysis of toxic volatile organic compounds (VOCs) in ambient air was developed on the integrated transportable system, the Agilent 5975T LTM GC/MSD. The target quantitative compounds measured by this method include hydrocarbons (C4-C6), halohydrocarbons, benzene hydrocarbons (C6-C9), as well as many polar and active oxygenated volatile organic compounds (OVOCs). The method detection limits (MDL) ranged between 0.019~0.218 ppbv, depending on the VOCs species in 1L of air sample. Real air samples were tested by this method and a customized report template was created to show the continuous variation tendency profiles of target compounds.

Agilent Technologies

Introduction

Air quality is one of the most important worldwide concerns because it closely relates to human health. Toxic volatile organic compounds (VOCs) in ambient air (air toxics) are monitored in many industrial and residential environments as a measure of air quality. Several national and international standard methods such as US EPA method TO-15 and TO-17 have been developed for air toxics and related applications. This study developed a fast method for online measuring of 62 target air toxic components, covering most of the VOC species specified in EPA method TO-15 and many polar and active carbonyl compounds, based on the integrated transportable Agilent 5975T LTM GC/MSD system, which is designed for out-of-lab use in remote field locations.

The analytical challenge for a field-transportable GC/MS instrument is laboratory-level performance with fast screening analysis capability. Based on the experimental results in this paper, this method is demonstrated to be accurate, rapid, and sensitive for determining more than 60 VOC species in air, in concentrations ranging from low ppb to ppm level. The method is advantageous for both field emergency monitoring and routine tests because of its short cycle times, low detection limits, and compact physical footprint.

The Agilent 5975T LTM GC/MSD, combined with the cryogen-free and flow controlled online or canister sampling equipment UNITY-Air Server from Markes, Inc., is a complete automatic solution for air monitoring. This solution provides continuous online data monitoring that helps to associate emissions with local industries when correlating the data with local weather parameters such as wind direction, precipitation and temperature inversions. Low Thermal Mass (LTM) technology, achieves high time resolution for continuous monitoring. The total cycle run time for this solution is approximately 20 min. Systematic online sampling and analysis for 62 VOCs in ambient air, on a half-hour basis, produce an extremely large and complex data set. However, the customized report template in Agilent ChemStation software can display the continuous variation tendency profiles of target compounds easily.

Experimental

Standard Gas Preparation

A dynamic dilution system was built to make different con-centration levels of gas standards. The diagram of this system is shown in Fig 1. A gas standard mix including 71 target compounds at concentrations of around 1 ppmv each (TO15 customized gas standard mix @SPECTRA) stored in dry nitrogen was diluted by humid nitrogen to simulate the real air sample. A humidifier was connected into the adjustable mass flow controllers (MFC) in order to make calibration gas standards at different relative humidity levels. The maximum dilution factor of about 1: 2000 produced gas mixtures with mixing ratios close to the detection limits of target VOCs. By adjusting the flow rates of the two mass flow controller (MFC), the dilution factor of the calibration gas was set, and the diluted gas mix stored in a stainless steel canister. The gas standard flow path, shown as a dashed line in the diagram (Figure 1) was constructed of Teflon tubing and connectors to reduce the risk of adsorption of polar compounds in the dilution system.
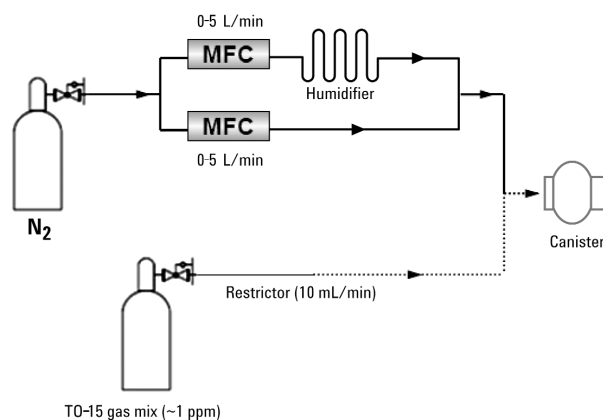

Figure 1.   Diagram of dynamic dilution system.

Sampling

A Markes International Series 2 ULTRA-UNITY Thermal Desorber (TD) configured with Air Server was used as the sample source in this study. Air Server modules were added to a Series 2 (ULTRA-)UNITY system to allow a controlled flow of whole air from a canister or ambient air. The whole system was introduced directly into the electrically-cooled focusing trap of the desorber. The combined systems were operated under cryogen-free conditions to minimize operating and maintenance costs and to offer an optimal analytical sensitivity. Figure 2 shows the schematic for this integrated sampling and analysis system.
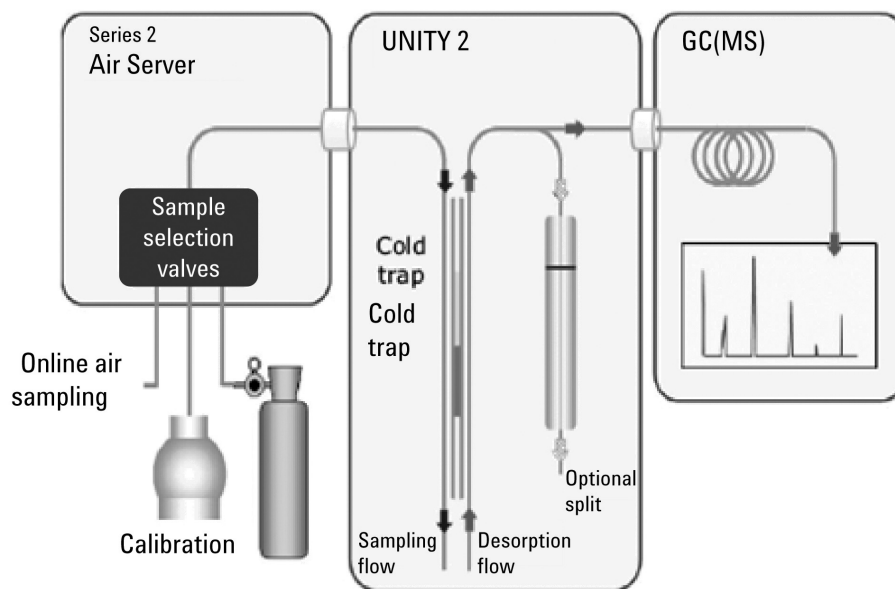
Figure 2.   Schematic of sampling operation by Air Server.

Instrument Conditions

The recommended instrument conditions for the thermal desorption and GC/MS system are listed in Tables 1 and 2. These operating parameters can be used as a reference for other instrument systems and may have to be optimized.

Table 1.   TD Instrument Conditions for VOC Analysis

Thermal Desorption System	
Instrument	Markes Series 2 ULTRA-UNITY
Sampling device	Air Server
Sampling time	20 min
Sampling flow	50 mL/min
Trap desorb split flow	20 mL/min
HV temperature	150 °C
Transfer line	150 °C
Cold trap	Air Toxic trap
Trap low temperature	−10 °C
Trap high temperature	300 °C
Heating rate(°C/s)	40 °C/min
Trap hold time	5 min

Table 2.   GC/MS Instrument Conditions for VOC Analysis

Transportable GC/MSD system	
Instrument	Agilent 5975T LTM GC/MSD
LTM program	35 °C (3 min) >150 °C (0 min) at 10 °C/min > 200 °C (1 min) at 50 °C/min
GC total run time	16.5 min
Injector temperature	200 °C
Column	Agilent LTM DB-624 20 m × 0.18 mm, 1.0 µm
Column flow	0.9 mL/min
Small oven	220 °C
Transfer Line	220 °C
Solvent delay	0.8 min
Data aquaire mode	Scan and SIM
Scan mass range	35–200 amu
Source temperature	230 °C
Quad temperature	150 °C

Results

Chromatograph Separation

A narrow bore LTM column (Agilent LTM DB-624 20 m × 0.18 mm, 1.0 µm) was used in this study to get fast chromatographic separation. Figure 3 shows the total ion chromatogram (TIC) in selected ion mode (SIM) for analysis of gas calibration standards mixture (equivalent to 1 ppbv in 1L humidified nitrogen).
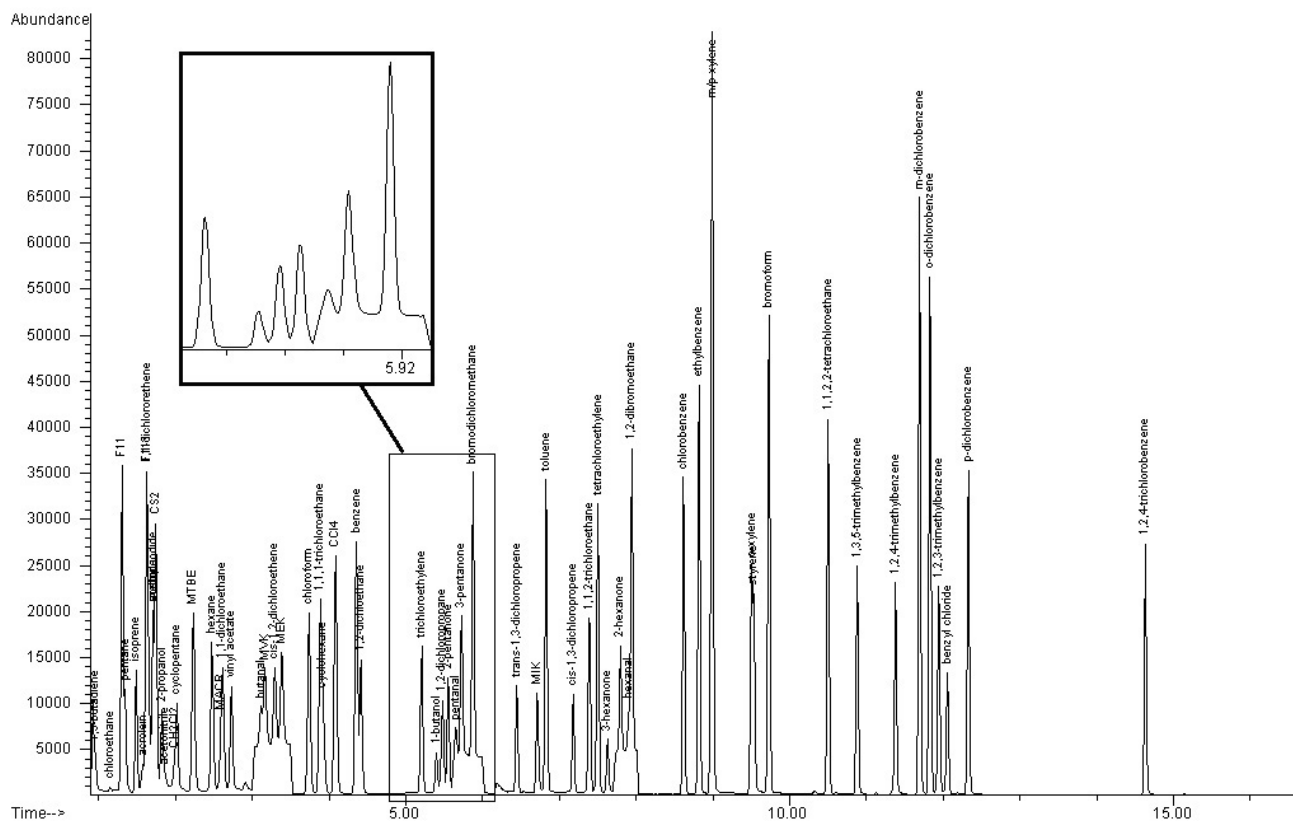
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Figure 3.   SIM chromatogram for analysis of 1 ppbv calibration standards mix.

Method Performance (Linearity, Method Detection Limit Repeatability)

Several different concentration levels of gas standards were prepared and collected in canisters for calibration, MDL determination, and repeatability study. The calibration curves of various VOCs species were measured at concentrations ranging from 0.26 ppbv to 6.5 ppbv (equivalent to 1L sampling volume), as the normal range of ambient concentrations of these species. Five-point calibration curves (0.26 ppbv, 0.65 ppbv, 1.3 ppbv, 2.6 ppbv, and 6.5 ppbv) were generated by analyzing each cal level standard. A response factor (RF) was calculated for each concentration level using formulas in Compendium Method TO-15. The percent Relative Standard Deviation (%RSD) for all 62 target compounds in the study ranged from 4 to 29.8% (Table 3), and all within the acceptance criteria of 30% specified in Method TO-15. Figure 4 shows example calibration curves for 1,3-butadiene and 1,2,4-trichlorobenzene.

The method detection limit (MDL) is defined for each system by making seven repeated measurements of the compound of interest at a concentration near the expected detection limit, calculating the standard deviation for the seven concentrations, and multiplying this value by the confidence coefficient 3.14 [1]. By employing this approach, seven replicates of the cal level 1 (0.26 ppbv) standards were measured and the concentration of each compound was calculated using the initial calibration curve. The calculated method detection limits of the VOCs species are given in Table 3.

Repeatability was evaluated by calculating the relative standard deviations (RSD) of the responses of the seven replicated measurements. The RSD (%) results of all the target compounds were below 20% (Table 3). Figure 5 shows the overlapped chromatograms for these seven replicated analysis of the calibration level 1 standards.
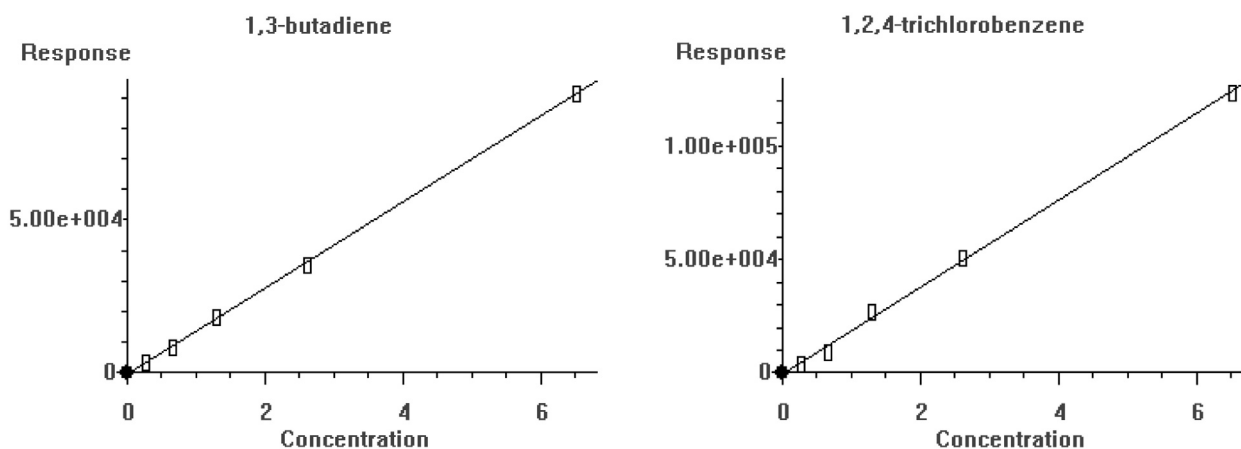
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Figure 4.   Calibration curves for 1,3-butadiene and 1,2,4-trichlorobenzene (0.26~6.5 ppbv).

Table 3.   Linearity, MDL and Repeatability of Target Volatile Organic Compounds (VOCs)

Target compounds	RSD(%) of RF	Measured conc (ppbv) of cal level 1 gas standards							RSD (n = 7) of Cal level 1 (%)	SD (n = 7)	MDL* (ppbv)
		Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7			
F-12	21.1	0.309	0.263	0.27	0.289	0.255	0.276	0.278	6.42	0.018	0.056
F-22	4	0.279	0.235	0.196	0.201	0.177	0.262	0.209	16.73	0.037	0.117
R114	4.7	0.32	0.252	0.265	0.269	0.256	0.267	0.279	8.33	0.023	0.071
Chloromethane	11.1	0.294	0.202	0.248	0.266	0.226	0.244	0.258	11.81	0.029	0.092
Isobutene	5.2	0.304	0.205	0.256	0.258	0.243	0.257	0.253	11.44	0.029	0.091
Vinyl chloride	7.8	0.269	0.181	0.197	0.212	0.192	0.204	0.215	13.58	0.029	0.090
1,3-butadiene	14.2	0.289	0.196	0.208	0.229	0.209	0.209	0.225	13.83	0.031	0.097
Acetaldehyde	14.2	0.352	0.307	0.35	0.338	0.322	0.349	0.338	4.95	0.017	0.052
Bromomethane	12.3	0.322	0.229	0.246	0.269	0.26	0.277	0.29	11.21	0.030	0.095
Chloroethane	3.9	0.288	0.33	0.212	0.236	0.33	0.216	0.234	19.57	0.052	0.162
F11	11	0.318	0.25	0.26	0.275	0.256	0.261	0.272	8.42	0.023	0.071
Pentane	14.3	0.37	0.218	0.234	0.261	0.238	0.238	0.25	19.73	0.051	0.160
Ethanol	14	0.317	0.193	0.215	0.238	0.214	0.202	0.221	18.16	0.042	0.130
Isoprene	14.7	0.248	0.17	0.165	0.185	0.169	0.171	0.177	15.88	0.029	0.092
F113	4.6	0.14	0.197	0.177	0.184	0.128	0.169	0.181	14.85	0.025	0.078
Methyl iodide	19.1	0.208	0.212	0.227	0.253	0.225	0.205	0.245	8.21	0.018	0.058
CS2	21	0.318	0.255	0.212	0.247	0.278	0.237	0.245	13.18	0.034	0.106
CH2Cl2	17.2	0.202	0.116	0.132	0.149	0.132	0.132	0.147	19.22	0.028	0.087
Cyclopentane	18.9	0.21	0.124	0.139	0.158	0.141	0.142	0.149	18.20	0.028	0.087
MTBE	8.6	0.265	0.179	0.192	0.213	0.196	0.198	0.203	13.44	0.028	0.087
Hexane	8.7	0.238	0.161	0.173	0.196	0.179	0.18	0.181	13.29	0.025	0.078
1,1-dichloroethane	15.2	0.276	0.208	0.194	0.224	0.179	0.213	0.227	14.18	0.031	0.097
Vinyl acetate	15.3	0.301	0.269	0.238	0.257	0.287	0.241	0.245	9.23	0.024	0.076
Butanal	15.8	0.255	0.178	0.19	0.213	0.195	0.193	0.2	12.32	0.025	0.079
MEK	5.5	0.284	0.183	0.205	0.218	0.233	0.214	0.216	14.12	0.031	0.098
Chloroform	10.8	0.295	0.21	0.219	0.235	0.219	0.224	0.234	12.16	0.028	0.089

Continued

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Table 3.   Linearity, MDL and Repeatability of Target Volatile Organic Compounds (VOCs) (Continued)

Target compounds	RSD(%) of RF	Measured conc (ppbv) of cal level 1 gas standards							RSD (n=7) of Cal level 1 (%)	SD (n = 7)	MDL* (ppbv)
		Rep1	Rep2	Rep3	Rep4	Rep5	Rep6	Rep7			
1,1,1-trichloroethane	13.6	0.184	0.125	0.101	0.169	0.133	0.138	0.163	19.85	0.029	0.090
Cyclohexane	11.8	0.281	0.213	0.223	0.242	0.267	0.229	0.234	10.12	0.024	0.077
CCl4	10.6	0.299	0.209	0.221	0.234	0.218	0.224	0.234	12.78	0.030	0.094
Benzene	7.8	0.115	0.075	0.092	0.115	0.102	0.099	0.131	17.46	0.018	0.057
1,2-dichloethane	13.6	0.201	0.119	0.134	0.143	0.13	0.133	0.139	18.77	0.027	0.084
Trichloroethylene	6.4	0.265	0.175	0.188	0.211	0.198	0.201	0.204	13.85	0.029	0.090
1-butanol	19.8	0.312	0.196	0.204	0.255	0.204	0.208	0.21	18.58	0.042	0.132
1,2-dichloropropane	17.2	0.267	0.19	0.2	0.215	0.199	0.203	0.21	12.05	0.026	0.080
2-pentanone	18.9	0.296	0.191	0.194	0.212	0.204	0.206	0.207	16.77	0.036	0.114
1,4-dioxane	27.6	0.28	0.197	0.203	0.214	0.209	0.208	0.206	13.10	0.028	0.089
3-pentanone	16.1	0.235	0.143	0.146	0.175	0.174	0.164	0.177	17.57	0.030	0.096
Bromodichloromethane	7.7	0.345	0.263	0.27	0.284	0.279	0.275	0.281	9.56	0.027	0.086
trans-1,3-dichloropropene	17.5	0.195	0.111	0.121	0.145	0.133	0.131	0.136	19.48	0.027	0.085
MIK	20.8	0.277	0.181	0.185	0.197	0.195	0.192	0.198	16.20	0.033	0.104
Toluene	16	0.26	0.194	0.204	0.222	0.212	0.211	0.214	9.68	0.021	0.066
cis-1,3-dichloropropene	21.6	0.284	0.223	0.227	0.242	0.232	0.235	0.238	8.48	0.020	0.064
1,1,2-trichloroethane	4	0.279	0.185	0.196	0.214	0.199	0.204	0.211	14.51	0.031	0.097
Tetrachloroethylene	8.5	0.293	0.212	0.221	0.241	0.232	0.236	0.238	10.85	0.026	0.081
3-hexanone	24.3	0.26	0.178	0.182	0.195	0.19	0.194	0.194	13.91	0.028	0.087
2-hexanone	28.7	0.286	0.216	0.215	0.221	0.218	0.223	0.224	11.08	0.025	0.080
1,2-dibromoethane	13.9	0.365	0.279	0.292	0.311	0.285	0.305	0.306	9.31	0.028	0.089
Chlorobenzene	15.5	0.302	0.225	0.236	0.253	0.253	0.252	0.247	9.58	0.024	0.076
Ethylbenzene	29.7	0.286	0.215	0.224	0.242	0.237	0.236	0.235	9.42	0.023	0.071
m/p-xylene	29	0.282	0.228	0.231	0.246	0.24	0.239	0.242	7.33	0.018	0.056
o-xylene	27	0.319	0.263	0.267	0.282	0.278	0.278	0.278	6.49	0.018	0.057
Styrene	28.8	0.331	0.291	0.292	0.304	0.302	0.301	0.3	4.39	0.013	0.042
Bromoform	22.5	0.31	0.238	0.322	0.322	0.192	0.33	0.319	18.43	0.054	0.168
1,1,2,2-tetrachloroethane	7.6	0.3	0.209	0.212	0.233	0.221	0.228	0.226	13.27	0.031	0.097
1,3,5-trimethylbenzene	28.2	0.311	0.258	0.245	0.264	0.282	0.261	0.26	8.04	0.022	0.068
1,2,4-trimethylbenzene	23.7	0.349	0.291	0.295	0.307	0.306	0.308	0.307	6.11	0.019	0.059
m-dichlorobenzene	27	0.228	0.165	0.166	0.181	0.184	0.187	0.188	11.30	0.021	0.066
o-dichlorobenzene	29.8	0.231	0.176	0.176	0.19	0.193	0.197	0.193	9.53	0.018	0.058
1,2,3-trimethylbenzene	26.5	0.332	0.286	0.286	0.307	0.283	0.306	0.293	5.84	0.017	0.055
Benzyl chloride	28.5	0.312	0.277	0.277	0.287	0.288	0.289	0.289	4.05	0.012	0.037
p-dichlorobenzene	29.2	0.213	0.137	0.14	0.157	0.169	0.161	0.16	15.47	0.025	0.079
1,2,4-trichlorobenzene	26.6	0.242	0.228	0.228	0.233	0.239	0.241	0.238	2.51	0.006	0.019

*MDL is defined for each system by making seven repeated measurements of the compound of interest at a concentration near the expected detection limit, calculating the standard deviation for the seven concentrations, and multiplying this value by the confidence coefficient 3.14 (EPA TO-15).

Real Sample Measurements and Tendency Analysis

Twelve hours of unattended air monitoring at the lab were used to evaluate the analyzer performance. The analysis obtained 24 data files to generate a customized report for continuous variation tendency analysis. As illustrated, the aromatic hydrocarbons, specifically benzene, toluene, ethylbenzene and xylene, are the most abundant compounds in lab air (Figure 6). Figure 7 shows the profiles of toluene and ethylbenzene, running from before evening to dawn of the next day in a lab environment.
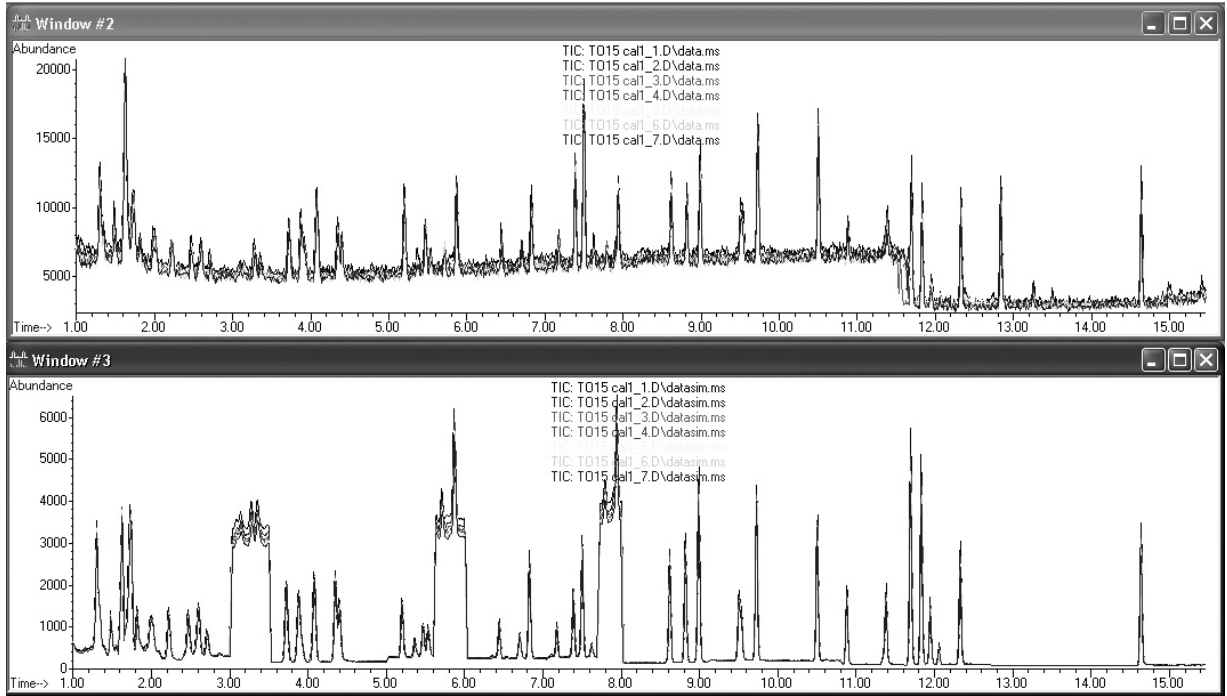
Figure 5.   Overlapped Scan and SIM chromatographs for analysis of level 1 calibration standards (n = 7).

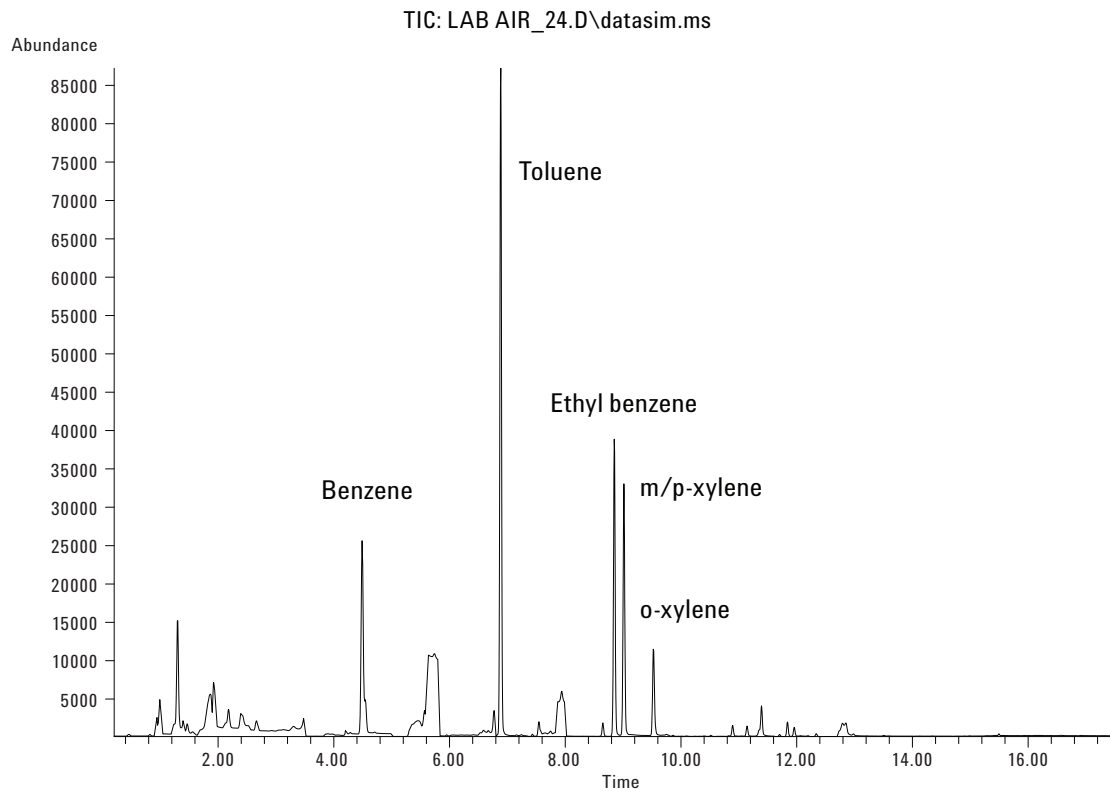TIC: LAB AIR_24.D\datasim.ms

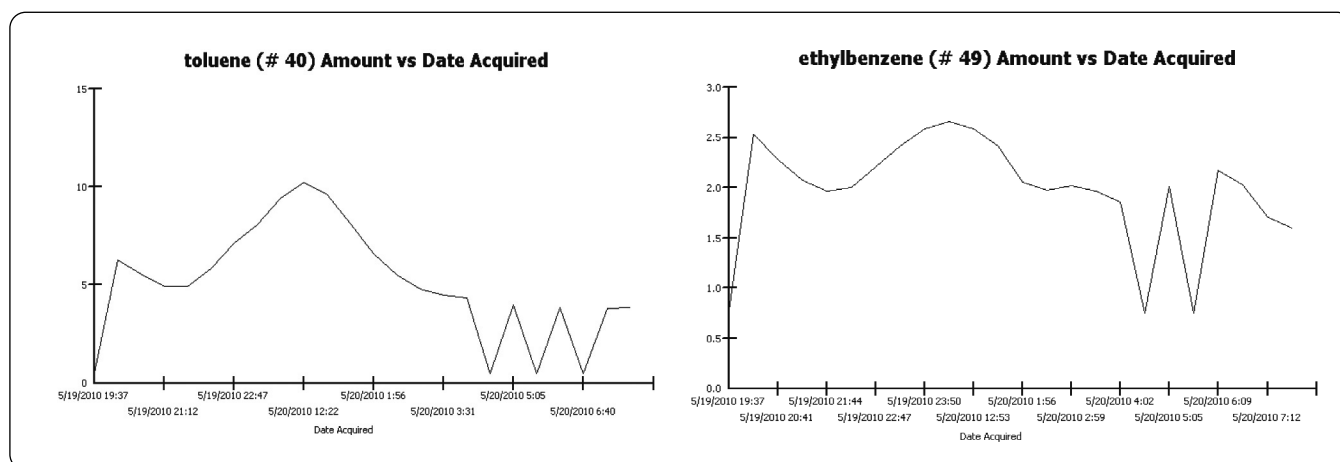Figure 6.   SIM chromatogram of lab air analysis using SIM/Scan method.

Figure 7.   Twelve hours continuous variation tendency profiles of toluene and ethylbenzene in lab air.

Summary and Conclusions

This application note provides an easy-to-operate solution for analysis of VOCs in air, using the vehicle transportable Agilent 5975T LTM GC/MSD. As a result of this study, the following conclusions can be made.

- Automated continuous online sampling technology make this solution easy to use and suitable for field environmental monitoring.

- This method achieves high sensitivity in determining most VOCs in air, at low ppb levels. Method performance also shows acceptable calibration linearity and good repeatability for most target compounds.

- LTM technology provides fast heating and cooling rates. Analysis of 62 VOC components can be accomplished in 16 min, while the total cycle time, including sampling and thermal desorption is approximately 20 min.

- A customized report provided by ChemStation software rapidly gives continuous variation profiles of target compounds.

References

1.   EPA Method TO15, Determination Of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/Mass Spectrometry (GC/MS).

2.   EPA Method TO17, Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes.

Acknowledgements

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