Detection of Volatile Organic Compounds in polluted air by an Agilent mini Thermal Desorber and an Agilent 5975T LTM GC/MS

Application Note

Environmental

Author

Xiaohua Li

Agilent Technologies (Shanghai) Co., Ltd.

412 Ying Lun Road Waigaoqiao

Free Trade Zone

Shanghai 200131 P.R.China

Abstract

A fast responding mobile solution from sampler to detector with small size and low power consumption is highly desirable for on-site air pollutant analysis. The results of an air pollutants analysis demonstrated that an Agilent 7667A mini Thermal Desorber and an Agilent 5975T LTM GC/MS have the required mobility and superior chemical performance. Over 60 Volatile organic compounds (VOCs) including chlorofluorocarbons (C1~C6), aromatics (C6~C10), ethers, and esters were tested. Separations of all of these species were completed in less than 10 minutes on an Agilent DB-624 LTM 20 m × 0.18 mm, 1.0 µm column. The quantitative method ranging from 10 ng to 1,000 ng with excellent linearity was built for each compound. The total cycle time, which is important for emergency responding, was less than 15 minutes, including desorption and system cooling.

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Introduction

One of the most important environmental mobile lab tasks is to identify and quantify the wide range of VOCs in air pollutants. In general, most of these pollutants come from stationary or organized emission such as petrochemical plant, vehicle exhaust, and accidental or unorganized emission, for example, solvent leakage during transport. On-site air pollutants monitoring requires an automated sample preparation such as thermal desorption and a fast GCMS system which can quickly provide both qualitative and quantitative information.

Sample preparation is critical in the field analysis process, with an impact to data quality, test accuracy, and analysis speed. The most important criteria for field environmental measurements are ease of use, fast cycle time, bench space, and data quality. The Agilent 7667A mini Thermal Desorber fulfills those requirements. The 7667A mini Thermal Desorber provides truly mobile features including a much smaller size, lower power consumption, ease of installation, and so forth. This application note presents a total solution of on-site air pollutants analysis including air sampling, desorption and detection.

Experimental

Method parameters

Optimizing injection parameters and selection of sorbents are very important for thermal desorption. To develop a valid, repeatable, and low carryover method, a Tenax tube was selected as the sampling and desorbing tube. Split ratio is one of the most important factors to impact desorption performance. Experiments proved that high responses and good peaks are obtained when the total flow through the tube during injection is approximately 60 mL/min.

The optimized instrument conditions for TD and GC/MS System for VOCs analysis are listed in Table 1.

Table 1. TD+GC/MS Instruments Conditions

Instrument and accessories	Agilent 7667A mini Thermal Desorber (Enhanced)
	Agilent 5975T LTM/GC-MS
	Calibration Standard Loading Rig
TD injection mode	desorb mode
Leak detection	Yes
Dry purge	No
Tube	Tenax
Injection start time	1 minute
Tube low temperature	40 °C
Tube heating rate	500 °C/min
Tube high temperature	300 °C
Valve box temperature	150 °C
Transfer line temperature	150 °C
Desorption time	1 minute
Cleaning flow	100 mL/min
Cleaning time	5 minutes
Injector temperature	200 °C
Carrier gas	He
TD carrier flow	60 mL/min
Column flow	0.8 mL/min (constant flow)
Split ratio	80:1
Column	LTM DB-624 20 m × 0.18 mm, 1.0 µm
LTM program	50 °C (1 minute) > 120 °C (0 minutes) at 20 °C/min > 220 °C (1.5 minutes) at 50 °C/min
GC total run time	10 minutes
Isothermal oven	250 °C
Transfer line	250 °C
Solvent delay	1.5 minutes
Data aquiring mode	SCAN
Scan mass range	35–280 amu
Source temperature	230 °C
Quad. temperature	150 °C

Results and Discussion

Chromatograms

The biggest challenge of a traditional tube-only one-stage Thermal Desorber is getting sharp peak shapes and good sensitivities for volatile compounds. The 7667A mini TD is designed with an innovative flow diagram, using a normal six-port valve to significantly improve the peak shapes and sensitivities for high volatile compounds. The chromatogram in Figure 1 demonstrates the good desorption performance of the 7667A mini TD. Sixty four species from diethyl ether to 1,2,3-trichlorobenzene were analyzed in one injection. Table 2 presents detailed information of all the compounds.

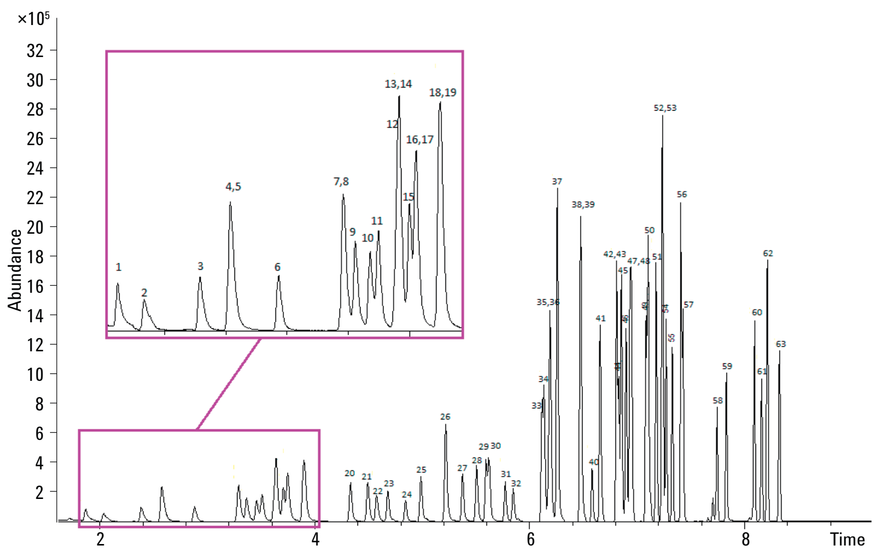

Figure 1. Chromatogram of 200-ng VOCs on a Tenax tube.

Table 2. Target Volatile Organic Compounds (VOCs) List

No.	Name	R.T.	Calibration range	Linearity (R^2)
1	Diethyl ether	1.91	10–1,000 ng	0.999
2	1,1-Dichloroethylene	2.082	10–1,000 ng	0.999
3	Methylene chloride	2.421	10–1,000 ng	0.999
4	MTBE	2.602	10–500 ng	1.000
5	*trans*-1,2-Dichloroethylene	2.614	10–1,000 ng	1.000
6	1,1-Dichloroethane	2.911	10–1,000 ng	0.998
7	2,2-Dichloropropane	3.31	10–500 ng	0.998
8	*cis*-1,2-Dichloroethylene	3.313	10–1,000 ng	0.999
9	Methyl acrylate	3.388	10–1,000 ng	0.999
10	Bromochloromethane	3.481	10–1,000 ng	1.000
11	Chloroform	3.532	10–1,000 ng	0.999
12	1,1,1-Trichloroethane	3.64	10–1,000 ng	0.998
13	Dibromofluoromethane	3.643	10–1,000 ng	0.999
14	Pentafluorobenzene	3.66	10–1,000 ng	0.999
15	1-Chlorobutane	3.726	10–1,000 ng	0.999
16	1,1-Dichloropropene	3.766	10–1,000 ng	0.999
17	Carbon tetrachloride	3.766	10–1,000 ng	0.998
18	Benzene	3.913	10–1,000 ng	0.998
19	1,2-Dichloroethane	3.928	10–1,000 ng	0.998
20	Trichloroethylene	4.346	10–1,000 ng	0.999
21	1,2-Dichloropropane	4.505	10–1,000 ng	0.999
22	Dibromomethane	4.589	10–1,000 ng	0.999
23	Bromodichloromethane	4.691	10–1,000 ng	1.000
24	2-Nitropropane	4.855	10–1,000 ng	1.000
25	*cis*-1,3-Dichloropropene(z)	4.997	10–1,000 ng	0.999
26	Toluene	5.225	10–1,000 ng	0.999
27	*trans*-1,3-Dichloropropene(e)	5.381	10–1,000 ng	0.999
28	1,1,2-Trichloroethane	5.513	10–1,000 ng	0.999
29	Tetrachloroethene	5.604	10–1,000 ng	0.999
30	1,3-Dichloropropane	5.628	10–1,000 ng	0.999
31	Dibromochloromethane	5.778	10–1,000 ng	1.000
32	1,2-Dibromoethane	5.85	10–1,000 ng	1.000
33	1-Chlorohexane	6.119	10–1,000 ng	0.999
34	Chlorobenzene	6.138	10–1,000 ng	0.999
35	1,1,1,2-Tetrachloroethane	6.186	10–1,000 ng	1.000
36	Ethylbenzene	6.195	10–1,000 ng	0.999
37	*m/p*-Xylene	6.261	10–1,000 ng	0.997
38	*o*-Xylene	6.474	10–1,000 ng	0.999
39	Styrene	6.48	10–1,000 ng	0.999
40	Bromoform	6.582	10–1,000 ng	1.000
41	Cumene	6.66	10–1,000 ng	0.999
42	1,1,2,2-Tetrachloroethane	6.81	10–1,000 ng	0.999
43	Bromobenzene	6.81	10–1,000 ng	1.000
44	1,2,3-Trichloropropane	6.831	10–1,000 ng	1.000
45	*n*-Propylbenzene	6.855	10–1,000 ng	0.998
46	2-Chlorotoluene	6.9	10–1,000 ng	0.999
47	1,3,5-Trimethylbenzene	6.936	10–1,000 ng	0.999
48	4-Chlorotoluene	6.948	10–1,000 ng	0.999
49	*tert*-Butylbenzene	7.087	10–1,000 ng	1.000
50	1,2,4-Trimethylbenzene	7.105	10–1,000 ng	0.999
51	*sec*-Butylbenzene	7.18	10–1,000 ng	0.998
52	1,3-Dichlorobenzene	7.234	10–1,000 ng	0.999
53	*p*-Isopropyltoluene	7.24	10–1,000 ng	0.998
54	1,4-Dichlorobenzene	7.27	10–1,000 ng	1.000
55	Benzyl chloride	7.33	10–1,000 ng	1.000
56	*n*-Butylbenzene	7.411	10–1,000 ng	0.998
57	1,2-Dichlorobenzene	7.429	10–1,000 ng	1.000
58	1,2-Dibromo-3-chloropropane	7.747	10–1,000 ng	1.000
59	Nitrobenzene	7.834	10–1,000 ng	0.999
60	1,2,4-Trichlorobenzene	8.095	10–1,000 ng	1.000
61	Hexachlorobutadiene	8.161	10–1,000 ng	0.999
62	Naphthalene	8.215	10–1,000 ng	0.999
63	1,2,3-Trichlorobenzene	8.326	10–1,000 ng	1.000

Carryover evaluation

Carryover is always a big concern with sampler concentration technology. High quality items such as O-ring seals inside of the system help the 7667A mini Thermal Detector deliver very low carryover after injection of high concentration samples. The cleaning function of this system can also help to remove contaminants. The second desorption after injection of 1,000-ng VOCs standards in Figure 2 shows no carryover.

Linearity

Calibration curves are obtained by a liquid standards loading rig (MKICCSLR) at different concentration levels, namely 10 µg/mL, 20 µg/mL, 50 µg/mL, 200 µg/mL, and 1,000 µg/mL. A 1-µL solution of each level of liquid standards is injected into a Tenax tube by syringe and purged with nitrogen for 1 minute. The final calibration curves will be from 10 ng to 1,000 ng. Figure 3 shows that, for most of the compounds, for example, diethyl ether and 1,2,3-trichlorobenzene, the linearity in this range is excellent.

Figure 4 shows that, because of breakthrough, linearity ranges for two compounds will be different.

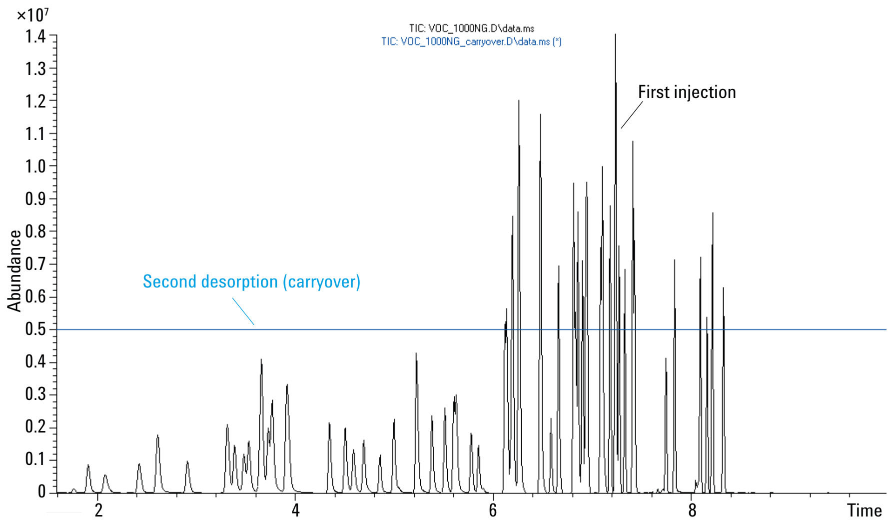

Figure 2. Overlapped chromatograms of 1,000 ng VOCs standards and second desorption as carryover.

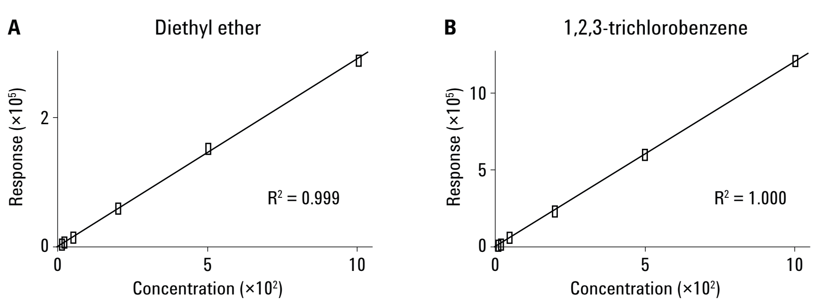

Figure 3. Calibration curves and linearity results for diethyl ether and 1,2,3-trichlorobenzene.

Real air sample analysis

Air pollutants can be sampled using a built-in on-line sampling pump or an off-line personal pump. To get accurate gas volume, calibrate the personal pump before sampling.
Five liters of air, close to the solvent waste bottle was sampled into a conditioned Tenax tube through a personal pump. The chromatogram in Figure 5 shows that solvents, such as acetonitrile, hexane, BTEX and so forth, which were frequently used in the sampling, were identified.

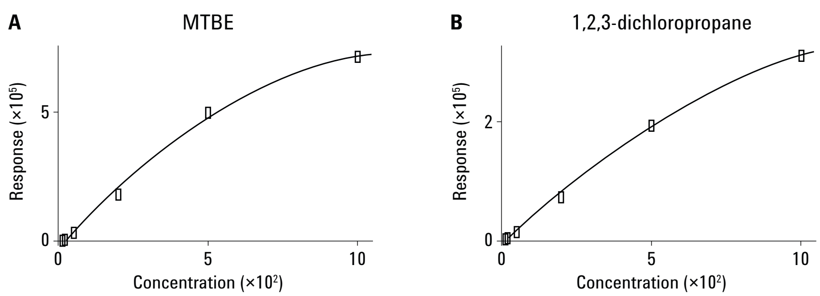

Figure 4. Calibration curves and linearity results for MTBE and 2,2-dichloropropane.

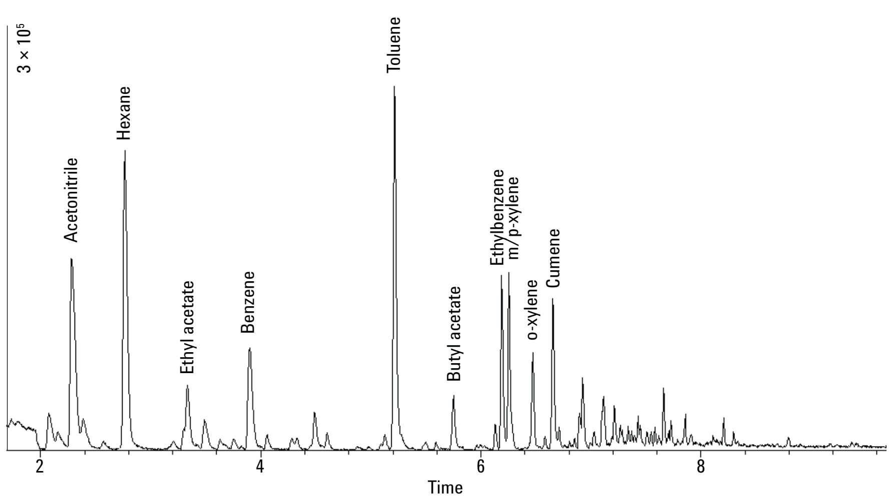

Figure 5. Chromatogram of 5 L air close to solvents waste bottle in sample preparation room.

Figure 6 shows a chromatogram of 1 L of tunnel air sampled by a personal pump. Analysis of tunnel air can provide key messages of detail VOC species from vehicle emission during the transportation. Some typical compounds such as toluene, benzene, and xylene are trapped in a Tenax tube and detected by GC/MS.

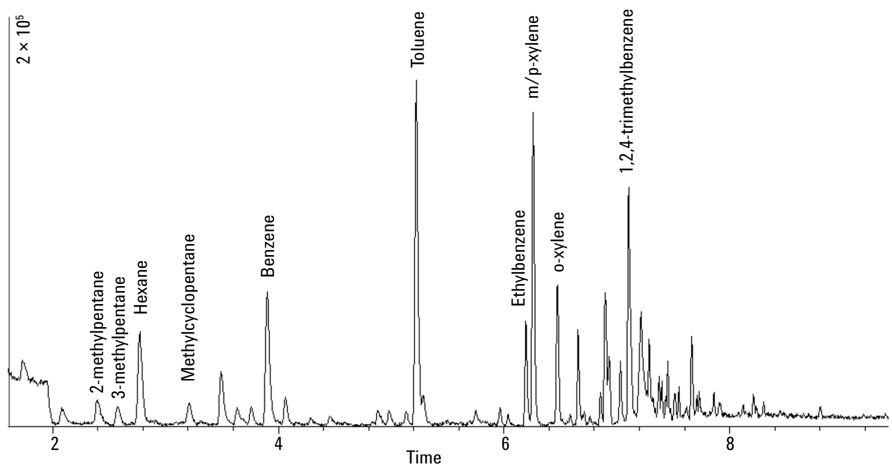

Figure 6. Chromatogram of 1 L of tunnel air sampled using a Tenax tube.

Conclusions

- This air pollutant analysis solution is suitable for mobile labs which require smaller size and lower consumption, with no sacrifice of performance.
- An Agilent 7667A mini Thermal Desorber can capture a wide range of gas phase compounds without a cooling function and desorb them well into a GC column.
- Good linearity of calibration curves can help mobile labs get accurate quantitative results.
- An air or gas phase sample with a wide range of concentration can be injected in this system.

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