Rapid Field Sampling of Airborne Compounds Using the Capillary Trap Sampler, Thermal Separation Probe, and an Agilent 5975T LTM GC/MS

Application Note

Author

Suli Zhao
Agilent Technologies, Inc.
Shanghai 200131
China

Abstract

Agilent has developed an innovative capillary-trap sampler (CTS) based on Snifprobe technology, enabling gas sampling to be performed in a few seconds to a few minutes in the field. After the gas sample is adsorbed onto capillary trapping columns, the thermal separation probe (TSP) is used to desorb the sample on the capillary column into the gas chromatography (GC) inlet. It is suitable for the analysis of both volatile (VOCs) and semivolatile (SVOCs) compounds.

Introduction

There is a continued and growing need to find better methods and easily transportable devices that enable fast sampling of airborne analytes in the field [1]. Airborne samples can originate from a variety of sources including air pollution, food and beverage aromas, cosmetics, chemical processes, off gases of processed materials, hidden explosives, drugs of abuse, and chemical warfare agents.

Agilent has developed an innovative CTS based on SnifProbe technology [1] which enables gas sampling in a few seconds to a few minutes in the field. The CTS uses a miniature pump to push air through a short capillary column that adsorbs airborne compounds, and it can be loaded with six 20 mm trapping columns simultaneously. Its handheld design and sampling speed make it ideal for field sampling and measurement.

The TSP is used to directly desorb the sample collected using the CTS. Each collection capillary is placed into a disposable micro-vial. The micro-vial is then placed in the TSP, which is inserted into a heated split/splitless inlet in the Agilent 5975T LTM GC/MS. The trapping column is then quickly and effectively desorbed into the GC injector. Use of the TSP eliminates time-consuming and expensive manual sample cleanup that could be difficult to perform at a remote site and could introduce error.

The 5975T LTM GC/MS is the only transportable GC/MS system to deliver lab quality results in the field. The CTS combined with the TSP and a 5975T LTM GC/MS solution is the best fit for broad field trace level airborne compound measurement. This application note demonstrates the utility of this system configuration for the airborne measurement of VOCs and SVOCs.

Experimental

Reagents and Standards

All of the standards and reagents used in this application note were obtained from Supelco, except for balm oil, which was purchased in China. The standards were diluted in air in 1-L glass bottles by adding 1 µL or 10 µL of the liquid sample and using a static dilution bottle technique. All of the trapping columns were cut from Agilent columns of the same type.

Instruments

This method was developed on the 5975T GC/MS system using a split/splitless inlet, the CTS (p/n G1181A) for airborne sample collection, and the TSP (p/n G4381A) installed on the split/splitless injector for sample desorption. Table 1 shows the instrument conditions used.

Sample preparation

The standards were prepared as described above. An adaptor cover was placed onto each standard bottle mouth for gas sampling. A 2-m^3 solvent cabinet was also used as a trace level gas supplier. The residual levels of solvent vapor were analyzed to determine the ability of the CTS to adsorb and release trace quantities of solvent vapor. The cabinet was assumed to have a constant concentration of solvent vapor that is not changed by CTS sampling. All of the sampling was performed at room temperature.

Table 1. CTS and GC/MS Run Conditions

CTS	
Sampling pump rate	60 mL/min for VOC and SVOC analysis
Sampling duration	1 minute for VOC and SVOC analysis
GC run conditions	
Guard column	0.5 m column with same phase as analytical column, connected to the injector
Analytical column	VOC analysis: DB-624 LTM module with a 20 m × 0.18 mm, 1.0 µm column (p/n G3900-63010) ordered as custom part number 100-2000LTM SVOC analysis: DB-5MS LTM module with a 10 m × 0.18 mm, 0.18 µm customized column
Injection volume	1 µL
Inlet temperature	Isothermal at 220 °C
Injection mode	Split, 10:1, using the TSP
LTM temperature gradient	Hold at 35 °C for 4 minutes, 35 °C to 240 °C at 15 °C/min, Hold at 240 °C for 0.33 minutes
Isothermal temperature	200 °C
Carrier gas	Helium, constant flow at 0.7 mL/min
Transfer line temp	230 °C
MS conditions	
Ion source temperature	230 °C
Quadrupole temperature	150 °C
Ionization	EI mode
Scan mode	Full scan, *m/z* 30–300
EMV mode	Gain factor
Gain factor	5.00
Resulting EM voltage	1,450 V
Solvent delay	0.2 minutes

Results and Discussion

Trapping Column Selection

The Agilent CTS uses wall coated open tubular (WCOT) or porous layer open tubular (PLOT) columns. As GC column theory dictates, the larger the column diameter and the thicker the column film, the higher the column capacity. A 0.32 mm id WCOT column with a 5-µm film thickness has a capacity of 5,000 ng, and it provides good quantitation and a predictable linear range. For optimal capacity, wide bore or megabore columns (such as 0.32 mm or 0.53 mm id) are recommended, with a film thickness greater than 3 µm for WCOT and more than 10 µm for PLOT columns.

The best match between solute and phase polarity should provide maximum capacity. For that reason, VOCs were trapped using both HP-PLOTQ columns (0.53 mm id, 20-µm film), which should be best-suited for trapping highly volatile compounds, and HP-5 columns (0.53 mm id, 5-µm film), which should be best matched with SVOCs. The two column types were installed in the same CTS simultaneously, using a mixture of VOC and SVOC vapor with a pump rate of 24 mL/min for 1 minute. Ions with *m/z* 91 were used to measure high volatility aromatic compounds, and *m/z* 180 ions were used to measure lower volatility compounds, such as trichlorobezene. Figure 1 illustrates that the HP-5 column traps lower volatility compounds with higher efficiency, and the HP-PLOT Q column tends to trap higher volatility compounds with higher efficiency.

The trapping columns can be conditioned and desorbed in the GC injector before re-use, so all of the columns can be used repeatedly without carryover. New columns and those that have not been used for a long period of time should be conditioned in the GC injector for 1–2 minutes to reduce any background.

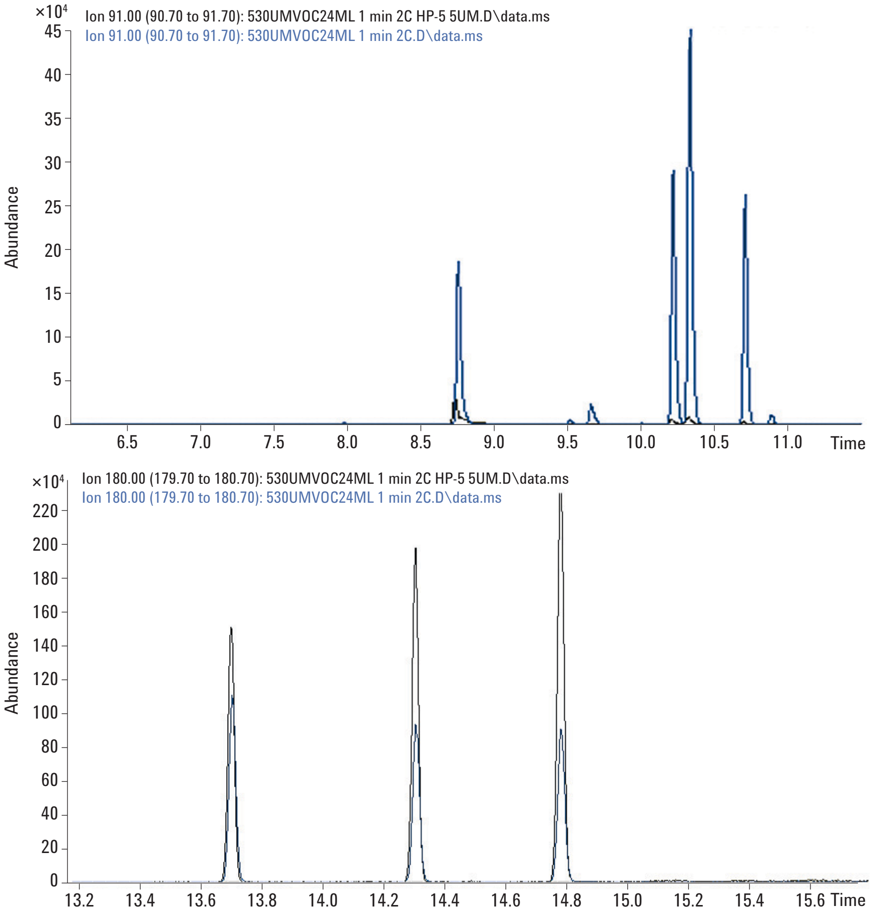

Figure 1. Upper Panel: Extracted ion chromatogram (EIC) of m/z 91 ion as a representative for high volatility compounds. Lower Panel: EIC of m/z 180 ion as a representative for low volatility compounds. The blue trace is the HP-PLOTQ column and the black trace is the HP-5 column.

Effect of Film Thickness

In order to determine the effect of the trapping column film thickness, 20-µm and 40-µm film thickness PLOT columns were used in the analysis of a mixture of five VOCs. Similar trapping effciencies were obtained with both columns (Figure 2). The gas sample was taken from a 2-m^3 solvents cabinet used for storage of different solvents. Using liquid injection of toluene for the GC/MS calibration, the toluene gas concentration in the cabinet was approximately 10 ng/mL.

Analysis of a Mixture of VOCs

A mixture of 29 VOCs; EPA8260 was used to test the effectiveness of the CTS for VOC analysis. Table 2 lists the names of the VOCs analyzed, using Pora PlotQ (0.53 mm id, 20-µm film thickness) columns in the CTS. A gas sample of the 29 VOCs was prepared by injecting 10 µL of the VOC standard solution at a concentration of 1,000 µg/mL VOCs liquid into a 1-L bottle and equilibrating for 1 hour at room temperature, for a final gas concentration of 10 µg/L.

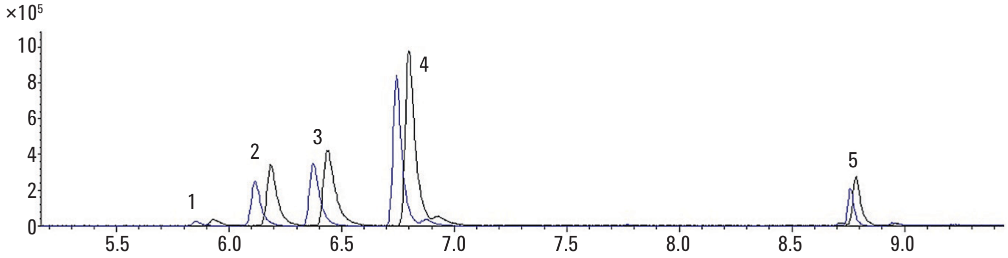

Figure 2. Separation of five VOCs using the CTS with a PLOT Q 0.53 mm I.D., 20 µm (blue trace) and 40 µm (black trace) film thickness. 1. Ethyl acetate; 2. Trichloromethane; 3. Cyclohexane; 4. Benzene; 5. Toluene.

Table 2. The 29 VOCs Analyzed in an Air Sample Using the CTS for Trapping

No.	Name	CAS	R.T (min)
1	Vinyl chloride	75-01-4	?
2	1,1-Dichloroethylene	75-35-4	3.1590
3	Methylene chloride	75-09-2	3.9107
4	*Trans*-1,2-Dichloroethylene	156-60-5	4.4108
5	*Cis*-1,2-Dichloroethylene	156-59-2	5.8366
6	Chloroform	67-66-3	6.2494
7	1,1,1-Trichloroethane	71-55-6	6.4341
8	Carbon tetrachloride	56-23-5	6.6204
9	Benzene	71-43-2	6.8522
10	1,2-Dichloroethane	107-06-2	6.8718
11	Trichloroethylene	79-01-6	7.5366
12	1,2-Dichloropropane	78-87-5	7.7579
13	Bromodichloromethane	75-27-4	8.0400
14	Toluene	108-88-3	8.7996
15	1,1,2-Trichloroethane	79-00-5	9.1850
16	Tetrachloroethene	127-18-4	9.3210
17	Dibromochloromethane	124-48-1	9.5576
18	Chlorobenzene	108-90-7	10.1414
19	Ethylbenzene	100-41-4	10.2509
20	M/P-Xylene	108-38-3	10.3588
21	O-Xylene	95-47-6	10.7412
22	Styrene	100-42-5	10.7474
23	Bromoform	75-25-2	10.9203
24	1,4-Dichlorobenzene	106-46-7	12.374
25	1,2-Dichlorobenzene	95-50-1	12.7285
26	1,2,4-Trichlorobenzene	120-82-1	13.695
27	1,3,5-Trichlorobenzene	108-70-3	14.296
28	Hexachlorobutadiene	87-68-3	14.473
29	1,2,3-Trichlorobenzene	87-61-6	14.770

The CTS captures all of the VOCs except vinyl chloride (Figure 3). CTS injection using TSP produces sharp peaks under these conditions. For example, the peak width at half height of benzene is 0.12 seconds. However, the CTS has a higher trapping efficiency for low volatility compounds, while compounds with higher volatility have a lower trapping efficiency because the adsorption rate is slow, and they are quickly desorbed after they are trapped. The TSP was used with a high inlet temperature (220 °C), and this could be the cause of the loss of very volatile compounds.

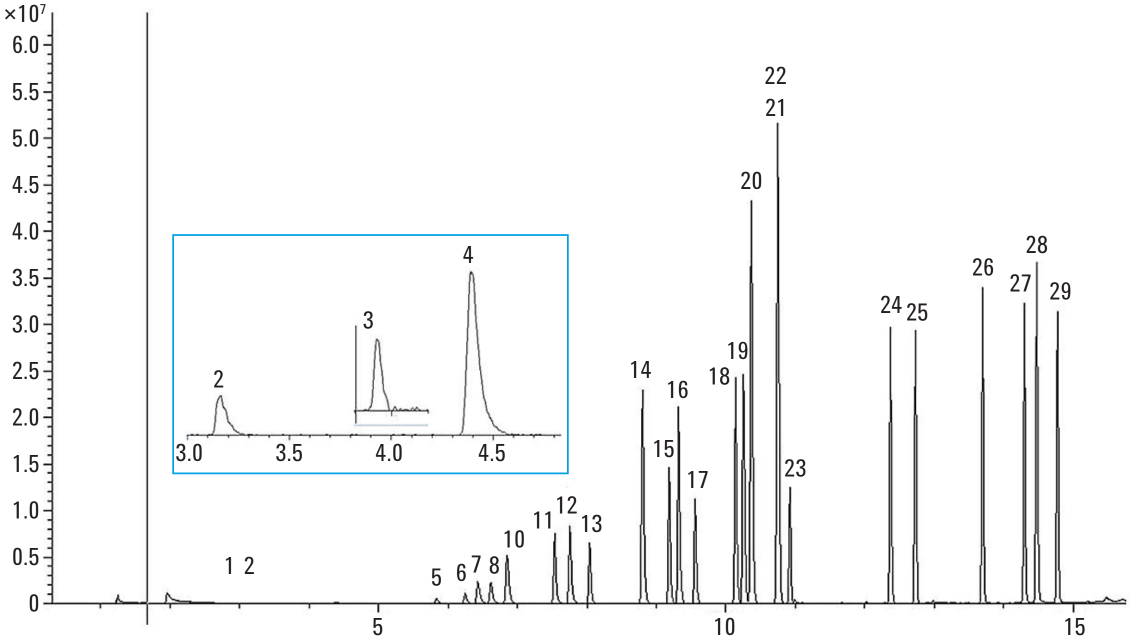

Figure 3. Total ion current (TIC) trace of the separation of a mixture of 29 VOCs, showing baseline separation. Only vinyl chloride was not adsorbed by the CTS and then detected. The inset is an expanded view of compounds 2,3,4 (1,1-dichloroethylene, methylene chloride, trans-1,2-dichloroethylene), as they are too small to see in the TIC. Note the low noise and baseline separation.

Analysis of Other Gas and Vapor Samples

The CTS can also be used to efficiently trap other types of compounds. Figure 4 illustrates the efficient trapping of four isomers of β-hexachlorocyclohexane (BHC) pesticides at 0.5 ng/L in air, using three HP-5 0.53 mm, 5-µm film thickness trapping columns. Balm oil vapor was trapped using three HP-PLOT Q 0.53 mm, 20-µm columns and analyzed to determine effectiveness of the CTS method for fragrance analysis (Figure 5). The sample was prepared by putting one drop of balm oil into a 1-L bottle, equilibrating for 1 hour, and sampling the headspace of the bottle using the CTS. Table 3 lists the main components that were detected using this method and identified by use of the AMDIS NIST EPA library.

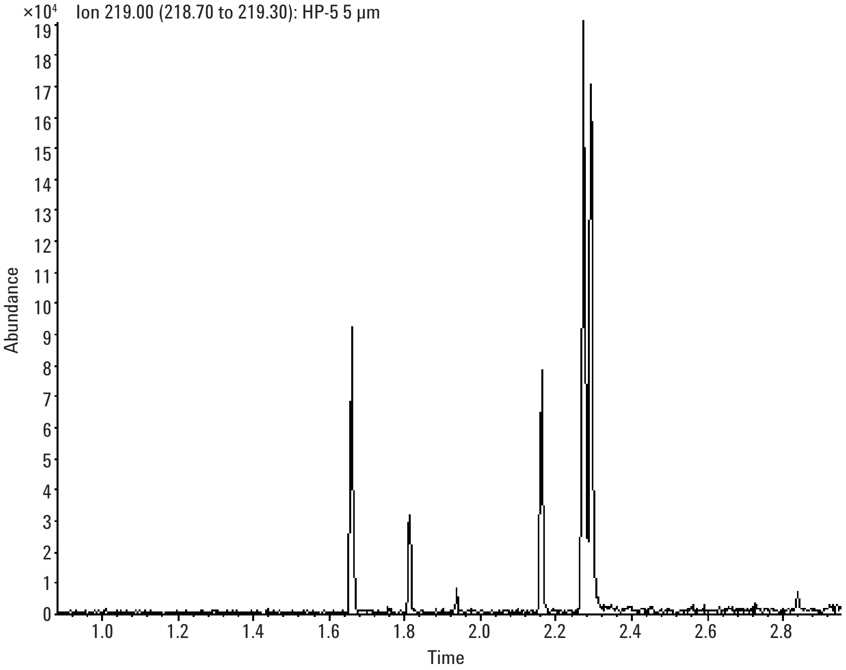

Figure 4. EIC of a 0.5 ng/L mixture of β-hexachlorocyclohexane (BHC) pesticide isomers in air, using HP-5 0.53 mm id, 5-µm film thickness trapping columns.

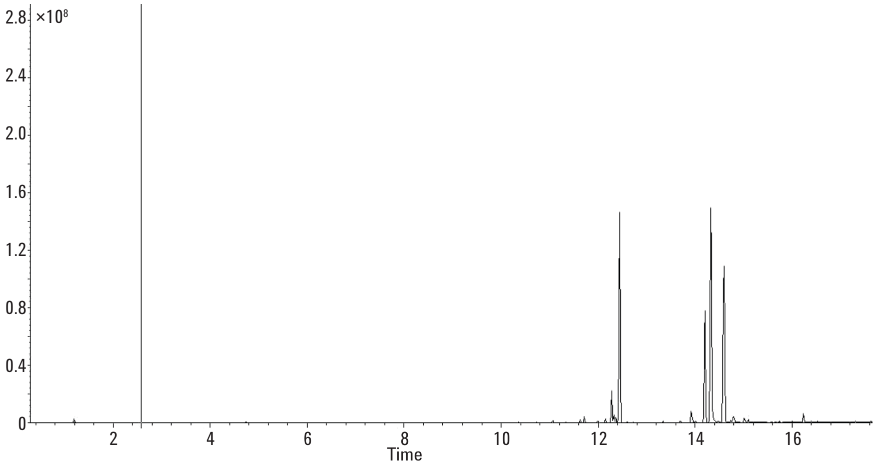

Figure 5. TIC of balm oil vapor trapped using the CTS.

Table 3. Main Components of Balm Oil

RT (min)	Components
11.0763	*alpha*-Pinene
11.106	Ethanol, 2-butoxy-
11.3381	Camphene
11.7192	Bicyclo[3.1.1]heptane, 6,6-dimethyl-2-methylene-, (1S)-
12.0134	Benzaldehyde
12.0461	3-Carene
12.1523	1,3-Cyclohexadiene, 1-methyl-4-(1-methylethyl)-
12.2814	Limonene
12.4517	Eucalyptol
12.6063	Cyclohexene, 1-methyl-4-(1-methylethylidene)-
13.4428	Bicyclo [2.2.1] heptan-2-one, 1,3,3-trimethyl-
13.9245	Phenylethyl alcohol
13.9471	Borneol
14.2096	Camphor
14.3403	Menthol
16.241	Eugenol

Conclusion

The capillary-trap sampler (CTS) can be used as a convenient, efficient, and easy-to-use gas sampler in field analysis. It has a broad application range for volatile compounds, using suitable trapping columns that are readily available. Matching the CTS with the thermal separation probe (TSP) and the transportable Agilent 5975T LTM GC/MS provides a sensitive analysis system for VOCs, SVOCs, and other compounds that is ideally suited for field analysis.

References

1. A. Gordin and A. Amirav, "SnifProbe: new method and device for vapor and gas sampling." *J. Chromatogr. A* 903, 155–172 (2000).

For More Information

These data represent typical results. For more information on our products and services, visit our Web site at www.agilent.com/chem.

www.agilent.com/chem

Printed in the USA
January 14, 2013
5991-1519EN

Agilent Technologies