Determination of Volatile Aromatic Compounds in Soil by Manual SPME and Agilent 5975T LTM GC/MSD

Application Note

Environmental

Author

Suli Zhao, Andy Zhai

Agilent Technologies Co., Ltd.

412 Yinglun Road

Shanghai 200131

China

Abstract

This application note describes an onsite solution for detecting 13 volatile aromatic compounds in soil with the transportable Agilent 5975T LTM GC/MSD. The solution uses a manual SPME method for sample pretreatment. The transportability of the Agilent 5975T LTM GC/MSD makes onsite detection possible while saving soil sampling time and storage. The testing results proved that this solution is practical and effective for detection of volatile organic compounds in soil in the field. The lowest detection amount of this method is 1.0 µg/kg in soil.

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Introduction

Volatile organic compounds (VOCs) contamination of soil is a serious issue. Volatile aromatic compounds are important species of VOCs. Because of their toxicity, analyzing for their presence is important in environmental studies. Currently the usual process for soil analysis consists of sampling from the site, sending the sample to the lab, storing soil in controlled conditions and extracting the targets from the soil before running samples on the GC or GC/MS. It takes a relatively long time to analyze one soil sample in a fixed lab. However, in emergency situations, the sampling sites are remote and need continuous data monitoring. The transportable Agilent 5975T LTM GC/MSD resolves these problems because it can bring the lab onsite.

Soil matrix is complex and its pretreatment is difficult. There are several methods for VOC analyses in labs, such as headspace, purge and trap (P&T) and classical solvent extraction. The EPA has issued soil VOC sampling and analysis methodology [SW 846 Method 5035]; ASTM has also adopted a standard for low VOC loss sampling [ASTM Standard D4547-98]. The headspace and P&T systems take more space and power than a limited movable lab. Classical extraction is labor intensive and high in solvent cost. Therefore these methods are not very suitable for field detection. A modern extraction and concentration technique, solid phase microextraction (SPME), facilitates the extraction of volatile aromatic compounds from soil despite matrix interference[1]. SPME requires no solvents, is simpler than other extraction techniques, and requires no power. Therefore, it is more suitable for transportable applications.

Highlights

- Fast, effective, robust SPME sample pretreatment

- Aromatic volatile compounds in soils

- Fast and good separation of compounds

- Transportable Agilent 5975T LTM GC/MSD

Experimental

Reagents and Chemicals

Reagents: Water (from a MilliQ system (Milford, Mass, USA) and free of organic volatile compounds; Methanol (HPLC grade; NaCl (SCRC, China); Phosphoric acid (H3PO4, Ashland).
The VOCs standards were purchased from Supecol.

Table 1.   Thirteen Aromatic Compounds and Two Internal Standards

Name	Name
Fluorobenzene(ISTD)	1,2-dichlorobenzene-D4(ISTD)
Benzene	1,3,5-Trimethylbenzene
Toluene	1,2,4-Trimethylbenzene
Ethyl benzene	pp-Isopropyltoluene
m-Benzene	n-Butylbenzene
Styrene	1,2,4-Trichlorobenzene
Bromobenzene	Naphthalene
	1,2,3-Trichlorobenzene

Equipment and Material

The analysis was performed on an Agilent 5975T LTM GC/MSD with manual injection mode. Separation of the compounds was achieved on an Agilent HP-5ms UI LTM (20 m × 0.18 mm, 0.18 µm). SPME kits for sample pretreatment are purchased from Supecol (57342-u:SPME fiber, PDMS, 100 µm, 23 ga, 57330-u manual fiber holder; 2637505: SPME inlet liner. SPME heat stand [57357-u, recommended].

Instrument Conditions

Table 2.   Instrumentation and Conditions of Analysis

Instrumentation

GCMS system	5975T LTM GC/MSD
Inlet	Split/splitless
Injection mode	Manual, SPME Fiber
Column	HP-5ms UI LTM 20 m × 0.18 mm, 0.18 µm
Guard column	1m deactivated column with no solid phase, connected to the injector

Experimental Conditions

Inlet temperature	220 ºC
Injection mode	Splitless for 3 min; 50 mL/min purge after 3 min
Carrier gas	Helium
Constant flow	1.5 ml/min
LTM oven temperature	45 °C (2min), 8 °C/min, 120 °C (0min), 20 °C/min, 150 °C (0.125min);
Transfer line temperature	220 °C
MSD interface	250 °C
Ion source	230 °C
Quad. temperature	150 °C
Ionization mode	EI
Scan mode	Full scan, 45–250 u
EMV mode	Gain Factor
Gain factor	5.00
Resulting EM voltage	1134 V
Solvent delay	0

Sample Preparation

Samples Origins

The soil samples were obtained from two different garden districts.

Blank Soil Sample Preparation

Twenty grams of soil sample were weighed and 20 mL of water were added to clean the leaves and other small floaters. The sample was centrifuged 5 min, and the water poured out. Twenty milliliters of ACN were added to remove organic interference. The sample was centrifuged 5 min and the ACN layer discarded The soil was heated to 200 °C for 1h, and the soil blank collected.

Soil blank was prepared in the lab and used to test recoveries.

Matrix Modifying Solution

Oily material and organic sludge waste in soil inhibit the partitioning of the volatile target analytes into the headspace. Therefore recoveries will be low. This is called the matrix effect. Modifying the solution can effectively decrease the matrix effect and alter the recovery of the targets.

Using a pH meter, concentrated phosphoric acid was added dropwise to 100 mL of organic-free reagent water until the pH was 2.0. A 36-g amount of NaCl was added. All components were mixed well until dissolved. A 3.0-mL portion from each batch was analyzed to verify that the solution is free of contaminants [2].

Calibration Standards

An internal standard (ISTD) solution was prepared at 1.0 µg/mL in methanol. The final concentration in the soil was 20 µg/kg. Standard VOC calibrations were prepared with the concentrations: 1.0 µg/mL; 2.0 µg/mL; 4.0 µg/mL; 8.0 µg/mL; and 10.0 µg/mL in methanol. A series of 20-mL headspace vials were prepared for the calibration curve and recovery test. A 2.0 g soil blank was weighed to each 20-mL headspace vial for the recovery test. Three milliliters of matrix modifying solution were added to each soil vial. Three milliliters of matrix modifying solution were added to the series of blank vials for the calibration curve test. Forty microliters ISTD and 10 µL of different calibration standards were added to archive different levels in the soil and calibration vials: 0.0 µg/kg; 5 µg/kg; 10 µg/kg; 20 µg/kg; 40 µg/kg; 50 µg/kg. Soil at 0.0 µg/kg was used as the soil blank.

Sample Treatment

A fresh top soil layer from a different district was collected and 2.0 g weighed into 20 mL headspace vials. A 3.0-mL amount of matrix modifying solution was added to each vial.

SPME Conditions

Using the SPME holder stand as the stirring and heating equipment, the heat temperature was set to 60 ºC. The vials were equilibrated for 5 min before the SPME fiber inserted into the air space of the vials. Absorption time was set to 10 min for calibrations and samples. Desorption time was 1 min in the injector.

Results and Discussion

Adsorption Times and Headspace Temperature Selection

A paper on volatile aromatic compounds in soil [1] describes optimized conditions for SPME technique. Considering this source's information about the target attributes, 60 ºC was selected for this application. The 10-min adsorption time requires a tradeoff between high efficiency results and the maximum adsorption with respect to field detection in the movable lab. Experiments showed that 10 min meets the detection limit requirements. Figure 1 is the chromatogram of 13 volatile aromatic by SPME extract.
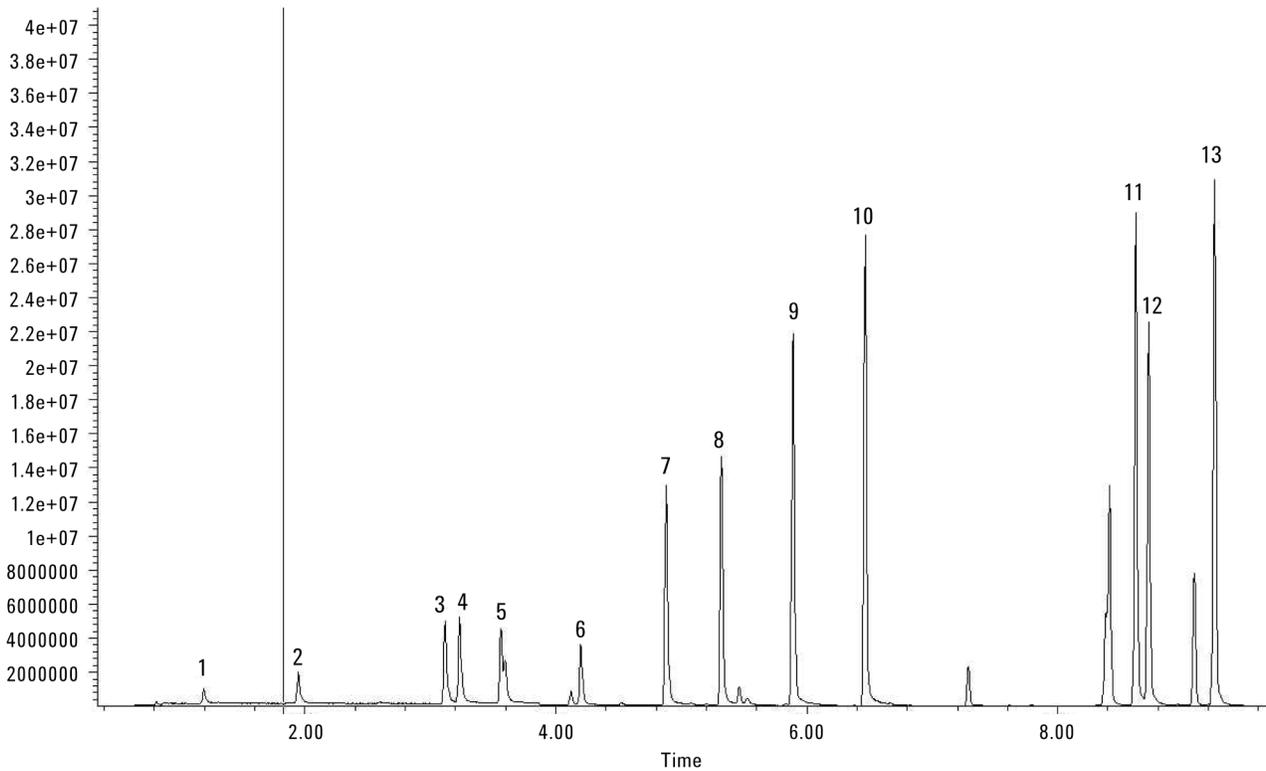
Figure 1.   TIC of 13 volatile aromatic compounds, 20 µg/kg in soil; peak number is concurrent with Table 1.

Linearity and Recovery Test for Targets in Soil

The recovery was evaluated on spiked samples at five different levels. The analysis was performed in replicates of two at each level to test the repeatability of the sample preparation. The RSD% between two replicates is less than 5.0%. The recovery of all the levels from 5.0 to 50.0 µg/kg are from 65.0 – 109%.

The linear calibration curves were generated by the calibration standards at a concentration range of 5.0– 50 µg/kg. All the linearity coefficients of the targets are better than 0.990. Figures 2 and 3 show the calibration curves of toluene and trichlorobenzene. Both have a good linearity coefficients of 0.997 and 0.998.
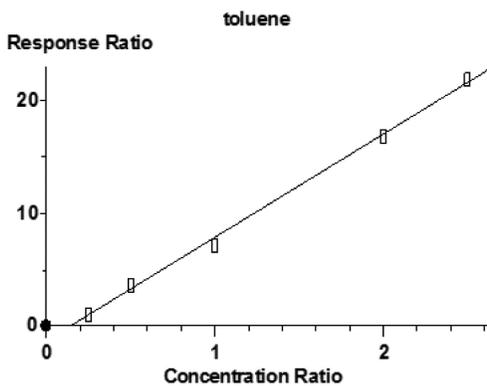
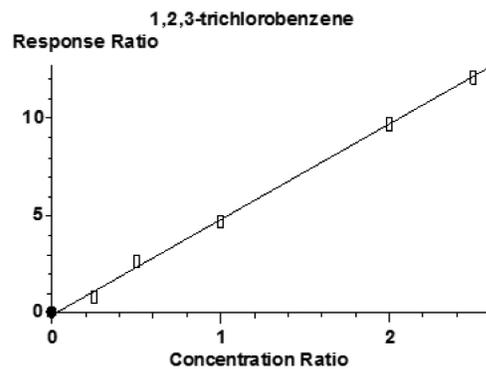

Figure 2.   The linearity curve of toluene.

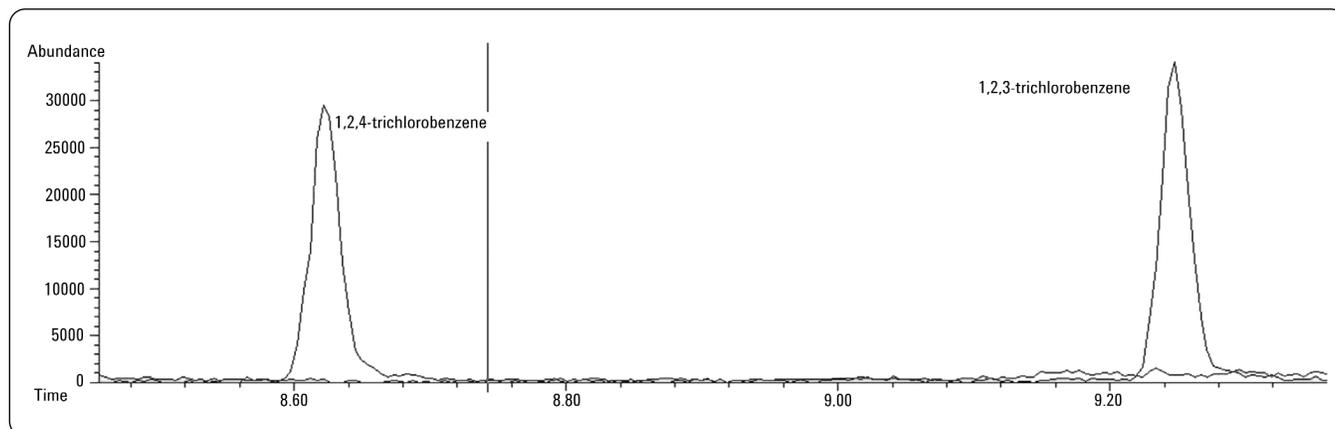Figure 3.   The linearity curve of 1,2,3-trichlorobenzene.

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Figure 4.   1.0 µg/kg 1,2,4- and 1,2,3-trichlorobenzene added into fresh soil and fresh soil blank comparison.

Real Soil Test

Fresh soil samples from two different gardens were collected and 1.0 µg/kg target added into the soil samples. Three milliliters of matrix modifying solution were added to each sample. Figure 4 shows a comparison of one fresh soil standard and one fresh soil blank. The results showed that the method detection limit in real samples is very good and SPME sample pretreatment has no matrix interference. Different soil sources produced similar results on the Agilent 5975T LTM GC/MSD with manual SPME fibers.

Customizing DRS Method Application

In order to quickly identify the targets in soils, Agilent's DRS software provides a good tool for quick screening. The dRS method can be customized according to needs. Table 2 shows the results of DRS report for identifying the targets added in to the sample.

Conclusion

This application showed that the manual SPME technique with an Agilent 5975T LTM GC/MS provides a practical method for detecting the volatile aromatic compounds in soils, especially for field monitoring. The solution is simple, requires no solvent, and is inexpensive; therefore it is more suitable for onsite testing. The Agilent 5975T LTM GC/MSD provides excellent performance for transportable applications. The combination of these two techniques provides a good solution for VOC tests in soil.

Table 2.   DRS Reports of 10 µg/kg Targets in Soils

| | | | Amount (ng) | | AMDIS | | NIST | |
| | | | Chem Station | AMDIS | Match | R.T. Diff sec | Reverse match | Hit number |
R.T.	Cas #	Compound name						
1.227	71432	Benzene	9.42		84	0.9	88	1
1.293	462066	Fluorobenzene	10		83	0.5	82	1
1.9768	108883	Toluene	10.48		85	0.7	87	2
3.1401	100414	Ethylbenzene	6.5		90	1.2	92	1
3.2564	108383	M-xylene	6.76		92	1.2	94	1
3.5814	100425	Styrene	6.51		89	0.6	95	1
4.213	108861	Bromobenzene	6.84		97	1.9	95	1
4.8898	108678	1,3,5-trimethyl benzene	6.83		96	1.0	94	2
5.329	95636	1,2,4-trimethyl benzene	6.96		96	1.5	94	2
5.8991	99876	P-isopropyl toluene	7.48		96	1.0	91	3
6.0173	2199691	1,2-dichlorobenzene-d4	10		92	1.0	91	2
6.4722	104518	N-butyl benzene	6.96		94	1.7	94	1
8.6161	120821	1,2,4-trichlorobenzene	7.29		99	0.2	95	1
8.7183	91203	Naphthalene	7.86		89	0.4	92	1
9.248	87616	1,2,3-trichlorobenzene	7.03		99	0.3	95	1

Reference

1. Ingrida Seduikiene, Vida V ichackaite etc. "Solid phase microextraction of volatile aromatic hydrocarbons from soil," ISSN 0235-7216. Chemija(Vilnius). 2001.T,12, Nr.2

2. EPA5021 Volatile organic compounds in soils and other solid matrices using equilibrium headspace analysis.

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