Application Note
Environmental

Determination of Volatile Organic Compounds in the Cabins of Vehicles by Agilent 8890 GC/5977B MSD and Thermal Desorption Sampler

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Abstract

HJ/T 400-2007[1] was used to determine the concentration of volatile organic compounds (VOCs) in the cabins of vehicles. This Application Note presents a method for their analysis using an Agilent 8890 GC/5977B MSD and a Markes' TD 100-xr automated thermal desorption (TD) system.

Introduction

Increased awareness of the long-term exposure effects of VOCs in vehicle cabin air has resulted in tightened legislation over the last 20 years. There has also been pressure to ensure below-limit VOC concentration levels. VOC testing methods for vehicles include whole vehicle testing and parts and materials testing. ISO 12219-1:2012[2] was released by the International Organization for Standardization. This standard describes and specifies the vehicle test chamber, the vapor sampling assembly, and the operating conditions for the determination of VOC and carbonyl compounds in vehicle cabin air. HJ/T 400-2007, released by China's Ministry of Environmental Protection, focuses on testing the whole vehicle. The detection of VOC emission of parts and materials has different sampling methods such as using microscale test chambers, tubes, small chambers, and bags. ISO 12219-3[3] specifies a fast, qualitative, and semiquantitative screening method for vapor-phase VOCs released from vehicle trim materials under simulated real-use conditions using micro-scale test chambers. The German Association of the Automotive Industry (VDA) has released a series of methods for assessing VOC emissions from car trim components. VDA method 278[4] specifies a direct TD/GCMSD method for VOC analysis using sampling tubes. ISO 12219-4[5] specifies a method for the determination of VOC emissions from vehicle interior parts and materials using the small chamber method. ISO 12219-2[6] specifies a sampling bag test method for measuring VOCs, formaldehyde, and other carbonyl compounds that may diffuse from vehicle interior parts into the air inside the vehicles.

Regulations or voluntary standards regarding permissible concentration levels of VOCs in new vehicles have been implemented or adopted in a handful of countries. China's voluntary national standard GB/T 27630-2011,[7] *Guideline for Air Quality Assessment of Passenger Car*, was released in 2011 by China's Ministry of Environmental Protection and State Administration of Quarantine. This standard was revised to become a mandatory national standard, and more strict requirements were put forward for the standard limits of the benzene series.

TD is a powerful and versatile GC sample introduction technique for monitoring the vapor phase fraction of organic compounds in air. Compared to solvent extraction, TD is capable of transferring 95% or more of the retained analytes to the analytical system. It is also less labor-intensive than solvent extraction, requiring little manual sample preparation. This study demonstrates that the 8890 GC/5977B MSD system with the TD sampler can easily achieve the performance specification for VOCs using the HJ/T 400-2007 method.

Experimental

This study was performed on an Agilent 8890 GC coupled with an Agilent 5977B single quadrupole GC/MS with an electron ionization (EI) source. TD was involved for the extraction of VOCs from a sorbent or material by heating the sample in a flow of inert gas. The extracted analytes were then transferred in the flow of carrier gas to the GC/MSD system.

Tables 1 and 2 describe the TD/GC/MSD systems used for the experiment.

Table 1. TD 100-xr Sampler conditions.

TD	
Cold Trap	General-purpose carbon (p/n MKI-U-T11GPC-2S)
Tubes	Tenax TA (p/n C-TBP1TC)
Parameter	Value
General	
Standby Split On	20 mL/min
Flowpath Temperature	150 °C
GC Cycle Time	30 minutes
Minimum Carrier Pressure	5 psi
Pre-Desorb	
Prepurge Time	1 minute
Trap Flow (Trap in Line)	50 mL/min
Tube Desorption	
Desorption Time	10 minutes
Desorption Temperature	250 °C
Trap Flow	50 mL/min
Split Flow	50 mL/min
Trap Setting	
Trap Purge Time	1 minute
Trap Purge Flow	50 mL/min
Trap Low Temperature	25 °C
Trap Heat Rate	MAX
Trap High Temperature	300 °C
Trap Desorbtion Time	5 minutes
Split Flow	50 mL/min

Chemicals, standards, and samples

Standards for nine VOCs were made from aliquots of neat solvents (>98% purity, ANPEL) in methanol (99.9% purity, J&K). Five calibration levels were made by adding different volumes of stock standard to methanol. One microliter of the five levels solution were introduced to a Tenax TA tube in a stream of carrier gas using the Calibration Standard Loading Rig (CSLR, Markes International) separately. The sample amounts on the tubes were 10, 40, 100, 400, and 1,000 ng.

For the sample collection, as described in the HJ/T 400-2007 method, 3 L of air from the inside of vehicles was pumped at a rate of 50 mL/min onto sorbent tubes packed with Tenax TA. After sample collection, the tubes were sealed and sent to the laboratory for TD/GC/MSD analysis by following the conditions in Tables 1 and 2.

Results and discussion

The MSD data were collected in SCAN mode and analyzed by Agilent MassHunter 10.0 software. Figure 1 shows a typical chromatogram of nine target compounds at a concentration of 400 ng on tube. Most compounds were well separated on the HP-5 ms column except for styrene and *o*-xylene, which have similar boiling points. Different quantitative ions can be selected for the two compounds by the MSD, thus the quantitative analysis is not affected by the absence of baseline separation. The two compounds, *m*-xylene and *p*-xylene, eluted together and were quantified as one peak. If baseline separation of styrene and xylene is required, a polar column such as a DB-WAX column can be used.

Table 2. Instrument conditions.

Agilent 8890 GC	
Inlet	Splitless, purge flow to split vent at 999.99 minutes
Column	Agilent HP-5 ms, 30 m × 0.25 mm, 0.25 µm (p/n 19091S-433)
Carrier	Helium, 1.5 mL/min, constant flow
Oven	40 °C (5 minutes), then 10 °C/min to 200 °C
Transfer Line Temperature	250 °C
Agilent 5977B MSD	
Ionization Type	EI
Source Temperature	230 °C
Quad Temperature	150 °C
Drawout Plate	3 mm
Tune File	Atune.u
Acquisition Type	SCAN
Solvent Delay	0 minutes
Gain Factor	1

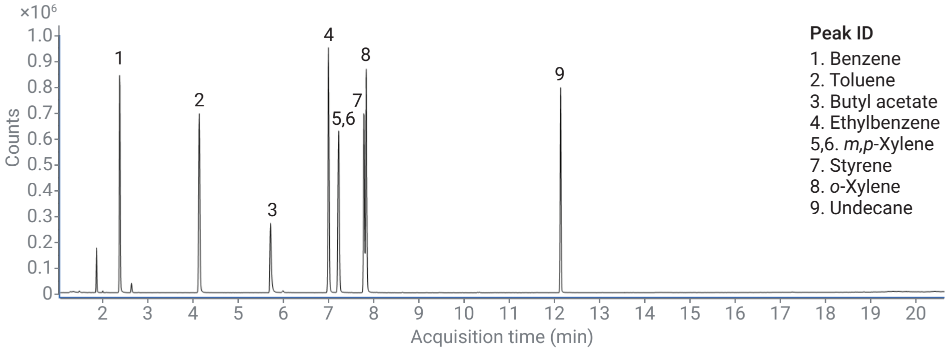

Figure 1. Total ion chromatogram of the target compounds (400 ng on tube).

Figure 2 demonstrates the overlaid chromatograms of the five calibration levels, showing excellent calibration linearity and chromatographic consistency. Table 3 shows the detailed repeatability and linearity results.

Calibration curves for nine compounds showed excellent linearity for concentrations ranging from 10 to 1,000 ng on tube. Table 3 shows calibration coefficients (R^2) for each component. The R^2 value for all compounds was above 0.9996. Figures 3A and 3B show the calibration curves of toluene and undecane.

Table 3 also shows eight consecutive injections of each standard sample at the concentration levels of 10 ng and 40 ng on tube, respectively. The area %RSD for all the compounds were below 4%, with the retention time %RSD less than 0.05%.

The limit of detection (LOD) calculations follow the EPA model, which is approached with replicates using a t-value at 99% confidence.[8] In this study, eight repetitive injections of VOCs with a low concentration level of 10 ng on tube were analyzed to calculate LOD. The HJ/T 400-2007 method shows that the volume of air pumped through the tube needs to be integrated into the MDL determination. Considering that the air volume pumped is 3 L, a sample of 10 ng on tube is equivalent to 3.3 μg/m.[3] Table 3 shows the results.

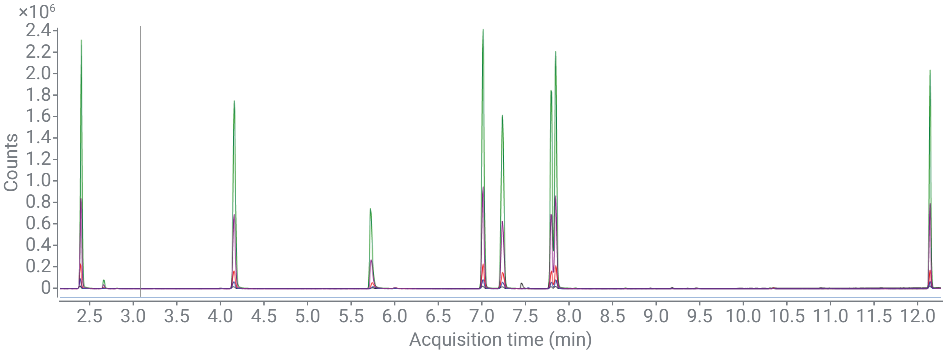

Figure 2. The overlaid chromatogram of the five calibration levels.

Table 3. The results of linearity, RSD, and MDL for nine compounds.

No.	Name	RT	*m/z*	CF R^2	%RSD (n = 8)			LOD (ng)	MDL (μg/m³)
					RT	10 ng	40 ng		
1	Benzene	2.398	78.1	0.9998	0.014	3	1.8	1.9	0.6
2	Toluene	4.166	91.1	0.9999	0.05	2.1	1.8	1.4	0.5
3	Butyl acetate	5.733	43.1	0.9996	0.037	3.7	2.3	3	1
4	Ethylbenzene	7.025	91.1	0.9999	0.03	1.9	1.4	1.4	0.5
5,6	*m,p*-Xylene	7.251	91.1	0.9999	0.033	2.3	1.6	1.7	0.6
7	Styrene	7.806	104.1	0.9999	0.027	2.5	2.3	1.8	0.6
8	*o*-Xylene	7.86	91.1	0.9999	0.027	2.3	1.2	1.6	0.5
9	Undecane	12.152	57.1	0.9998	0.002	2.9	2	2.3	0.8

Conclusion

This Application Note demonstrates the capability of the Agilent 8890 GC/5977 MSD and the TD 100-xr sampler system to analyze VOCs in the cabins of vehicles following the HJ/T 400-2007 method. Excellent sensitivity, repeatability, and linearity are shown, which achieved the performance specifications of the HJ/T 400-2007 method. The inclusion of the automated thermal desorption system makes this system a useful tool for the analysis of VOCs in vehicles.

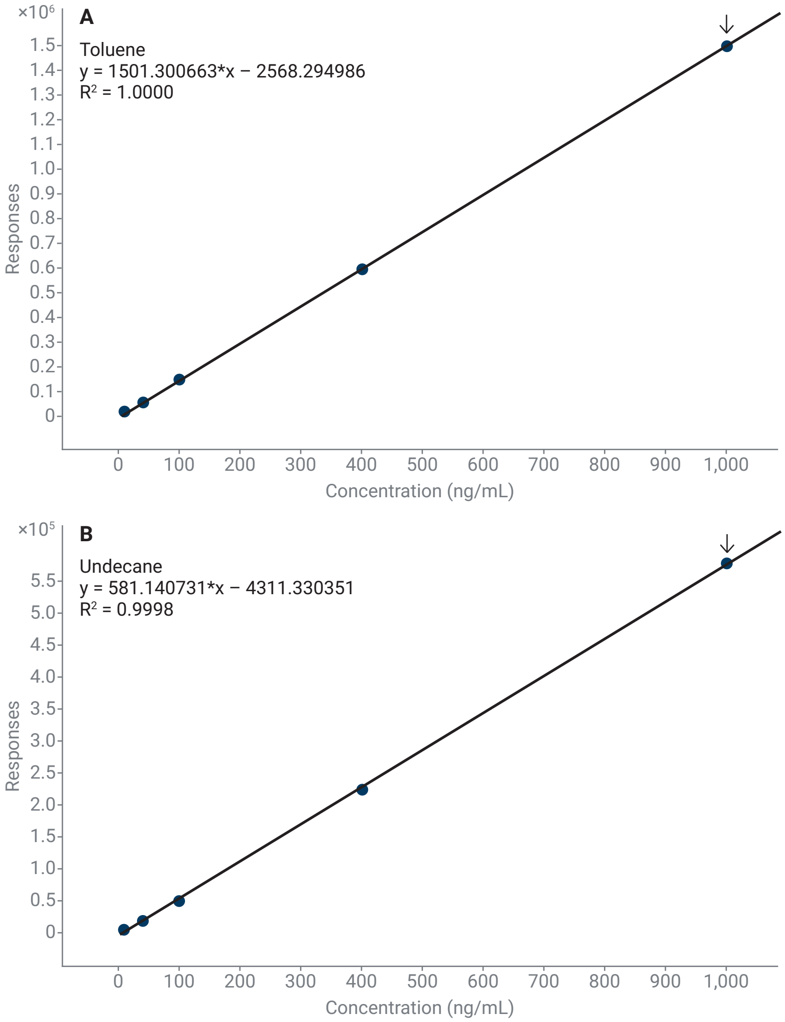

Figure 3A. (A) Calibration curve of toluene. (B) Calibration curve of undecane.

References

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Printed in the USA, December 5, 2019
5994-1463EN
DE.4873032407

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