Measurement of VOCs in Vehicle Interiors Using Thermal Desorption GC-MS with Nitrogen as the Carrier Gas

Waldemar Weber, Shimadzu Europa GmbH

The amount of toxic volatile organic compounds (VOC) in the air is one index of the extent of air pollution and is used for environmental monitoring in factories, urban areas, and indoor environments. VOCs can be measured efficiently using TD-GC/MS, which does not require solvent extraction.

Helium is the most frequently used carrier gas in GCMS analysis. Due to its inertness it allows high sensitivity analysis combined with very good chromatographic separation. As the worldwide production of Helium is decreasing while the demand is permanently growing, Helium prices have doubled in the last 12 months. As the gap between supply and demand is expected to persist for longer times, further price increases are likely.

In this article, analysis was performed using nitrogen rather than helium as the carrier gas. Nitrogen gas can be less sensitive than helium gas, but it is inexpensive and readily available.

An analysis was performed of VOCs typically analysed in voluntary assessments of vehicle interiors and vehicle interior materials, using thermal desorption GC/MS with nitrogen as the carrier gas. The calibration curve, repeatability and efficiency of retrapping were also tested.

Analysis System

In the TD-30R thermal desorption instrument, the sample gas collected within a sample tube is thermally desorbed and then concentrated in a cold trap before injection into the GC-MS. In theTD-30R, there is a retrapping function that collects the split sample gas again in a tube, and a function that automatically adds the internal standard. Using this retrapping function reduces the risk of analysis failure. In addition, the value calculated by the retrapping function can be corrected by using this function together with the internal standard auto addition.

Figure 1. TD-30R + GCMS-QP2020 NX.

Measurement

The standard mixture of toluene, benzene, ethylbenzene, *m,p,o*-xylene, styrene, 1,4-dichlorobenzene, and tetradecane diluted with methanol were prepared with concentrations of 10ppm, 40ppm, 100ppm, 400ppm, and 1000 ppm. These standard mixtures were added 1µL to each TENAX-TA sample tube and then analysed. The analytical conditions are shown in *Table 1*. During the analysis, toluene-*d8* was added by theTD-30R's internal standard automatic addition function.

Table 1. Analytical Conditions.

Analytical Conditions	
Model	GCMS-QP 2020 NX
Autosampler	TD-30R
[TD-30R]	
Tube Desorption Temperature	280°C (10 min)
Tube Desorption Flow	60 mL/min
Trap Cooling Temperature	-20°C
Trap Desorption Temperature	280°C (10 min)
Valve Temperature	250°C
Transfer Line Temperature	250°C
[GC]	
Injection Mode	Split
Split Ratio	1:50
Carrier Gas	Nitrogen
Carrier Gas Control	Linear Velocity (40 cm/sec)
Column	SH-5MS (P/N 221-758555-30), Shimadzu (30 m ×0.25 mm I.D., 0.25 µm)
Column Temp	40 °C(1 min) with 10 °C/min to 100 °C, 40 °C/min to 200 °C, 20 °C/min to 300 °C (5 min)
[MS]	
Ion Source Temperature	230°C
Interface Temperature	280°C
Acquisition Mode	SCAN
Event Time	0.3 sec
m/z Range	m/z = 45-600

The Calibration Curve, Repeatability, and Retrapping Results

The standard mixture of benzene, toluene, ethylbenzene, *m*,*p*-xylene, *o*-xylene, styrene, 1,4-dichlorobenzene, and tetradecane were measured. The TIC chromatogram is shown in *Figure 2*, and the calibration curve linearity, repeatability, and retrapping results are shown in *Table 2*. The range of the calibration curve created was 10 ng to 1000 ng, and for all compounds, a good result was obtained, with R>0.999. As an example, the calibration curve for toluene is shown in *Figure 3*. In addition, when the repeatability was checked at 10 ng, the minimum concentration in the calibration curve, the % RSD (n=5) for all compounds was found to be 5% or less. Furthermore, when the measurement repeatability was checked by retrapping at 10 ng using the TD-30R retrapping (Restore) function, the % RSD (n=5) for all compounds was 6% or less.

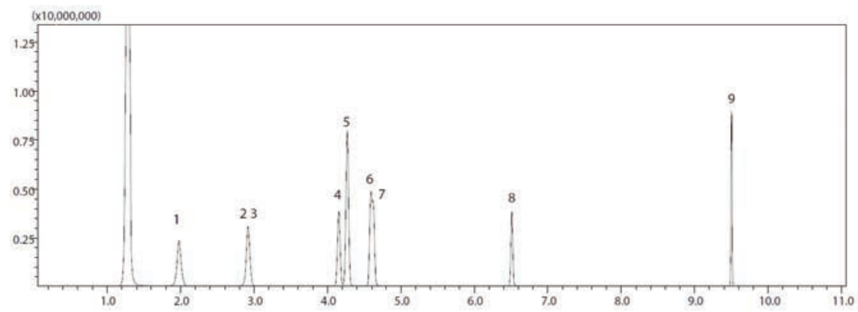

Figure 2. TIC Chromatogram for the 1000 ng Standard Sample.

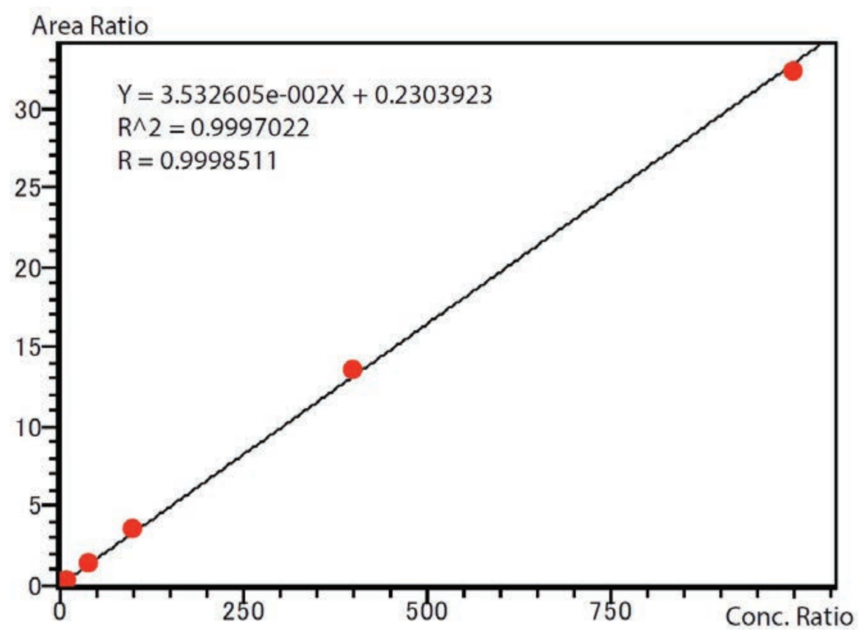

Figure 3. Toluene Calibration Curve Analysed with Nitrogen as the Carrier Gas (10 ng, 40 ng, 100 ng, 400 ng, 1000 ng).

Table 2. Results for Calibration Curve Linearity, Repeatability at 10 ng, and Retrapping Results.

ID	Compound	Retention Time	m/z	Linearity (R)	10 ng Average Concentration		10 ng Concentration %RSD (n=5)	
					1 time	Retrapping	1 time	Retrapping
1	Benzene	1.978	78	0.9997903	8.9	9.0	2.6	2.1
2	Toluene-*D8*	2.871	98	------------	-----------	------------	-----------	------------
3	Toluene	2.918	91	0.9998511	9.3	9.2	4.6	3.6
4	Ethylbenzene	4.154	91	0.9997918	8.4	8.4	3.9	1.7
5	*m*,*p*-Xylene	4.270	91	0.9998336	9.3	9.3	2.3	3.6
6	Styrene	4.587	104	0.999927	10.7	10.5	3.8	3.5
7	*o*-Xylene	4.624	91	0.9997498	9.4	9.3	3.7	5.9
8	1,4-Dichloro Benzene	6.510	146	0.999958	9.7	9.7	3.9	5.9
9	Tetradecane	9.502	57	0.9999466	11.1	10.8	2.1	2.3

Conclusion

This article described an analysis of VOCs frequently analysed in voluntary assessments of vehicle interiors and vehicle interior materials using the *TD-30R + GCMSQP-2020NX* with nitrogen as the carrier gas. Favourable values were obtained for the calibration curve, repeatability, and retrapping results. Using this method it was possible to measure nine VOCs (toluene, benzene, ethylbenzene, *m*,*p*,*o*-xylene, styrene, 1,4-dichlorobenzene, andtetradecane) within a vehicle interior using nitrogen as the carrier gas. Even when nitrogen is used, the mass spectrum is virtually the same as that when helium is used as the carrier gas. This means that existing mass spectral libraries can be used as is. For qualitative applications or quantitative analysis at a µg/mL (ppm) level, it is possible that a transition to nitrogen carrier gas can be made.