SHIMADZU
Excellence in Science

GC-MS TD-30R/GCMS-QP™2050

Application News

Analysis of VOC and SVOC Emissions from Automotive Interior Materials Using GCMS-QP2050 in Accordance with VDA 278

Yui Higashi, Kei Usui, and Masato Takakura

User Benefits

- The GCMS-QP2050 features a new interface that enables good peak shape and sensitivity even when analyzing compounds with high boiling points.
- When used with the TD-30R thermal desorption system, it can analyze compounds in accordance with VDA 278.
- The TVOC Calculation Tool can calculate in a simple manner quantitative emissions (toluene and hexadecane equivalents) in accordance with VDA 278..

■ Introduction

In recent years, measures to reduce the use of organic compounds in automotive interiors have progressed, the VDA 278 standard was developed in Germany for the analysis of volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) that are emitted from automotive interior materials. The VDA 278 analytical procedure involves filling a thermal desorption (TD) glass tube with a sample of materials, heating the tube using TD, and loading the VOCs (up to C25) and SVOCs (C14 to C32) that were emitted from the sample into a GC-MS system for analysis. Although this standardized procedure enables simple and quick analysis of VOC and SVOC emissions from these materials, contamination of the MS system caused by the simultaneous loading of compounds with high boiling points is a problem.

As shown in Fig. 1, the GCMS-QP2050 is equipped with a new contamination-resistant ion optical system that effectively minimizes contamination of the MS. Featuring a new interface that enables good peak shape and sensitivity even for compounds that are typically prone to adsorption, it is optimally suited to analyzing SVOCs, including those with high boiling points.

This edition of Application News describes analyzing VOC and SVOC emissions from the materials of vehicle interiors in compliance with VDA 278 using the GCMS-QP2050 together with the Nexis™ GC-2030 and the TD-30R thermal desorption system.

■ Optimal Analysis of High Boiling Point Compounds with GCMS-QP2050

As shown in Fig. 2, the GCMS-QP2050 is capable of realizing good peak shape and sensitivity even for compounds that are prone to adsorption because it is equipped with a new interface that inhibits the formation of cold spots. While this study necessitated analysis of SVOCs with a retention time up to that of dotriacontane (C32), as shown in Fig. 3, good peak shape was obtained not only for this compound but also for tritriacontane (C33), which has a high boiling point.

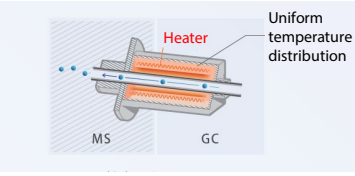

Fig. 2. Illustration of GCMS-QP2050's New Interface

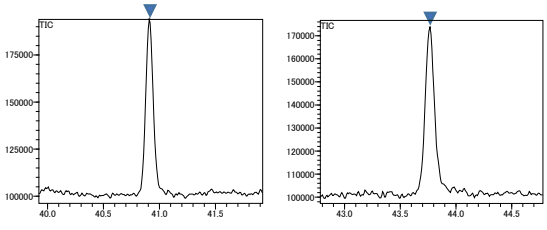

Fig. 3 TIC Chromatograms of High Boiling Point Compounds

Fig. 1 GCMS-QP™2050, Nexis™ GC2030, and TD-30R

■ Equipment Configuration and Analytical Conditions

The analytical conditions used in this analysis are described in Table 1. The tube heating temperature was set at 280 °C for 5 minutes when measuring the calibration curve and control standard samples, and it was set at 90 °C for 30 minutes (VOC) and 120 °C for 60 minutes (SVOC), respectively, when measuring the emissions of test samples.

Table 1 Analytical Conditions

GC Model:	Nexis GC-2030
MS Model:	GCMS-QP2050 Entry
Autosampler:	TD-30R
[TD-30R]	
Tube Desorb Temp.	
Standard:VOC:	280 °C (5 min)
SVOC:	90 °C (30 min)
	120 °C (60 min)
Tube Desorb Flow:	60 mL/min
Trap Cooling Temp.:	–20 °C
Trap Desorb Temp.:	280 °C (10 min)
Joint Temp.:	280 °C
Valve Temp.:	250 °C
Transfer Line Temp.:	280 °C
[GC]	
Injection Mode:	Split
Split Ratio (0 min – 3 min):	100
Carrier Gas Save Mode:	ON (Split ratio of 20 from 3 min after starting analysis)
Carrier Gas:	He
Carrier Gas Control:	Pressure (200 kPa)
Column:	SH-I-5Sil MS (P/N 227-36036-02) (60 m × 0.25 mm I.D., 0.25 µm)
Column Temp.:	40 °C (3 min) – 10 °C/min – 300 °C (13.5 min)
[MS]	
TMP Evacuation Rate:	60 L/sec
Ion Source Temp.:	230 °C
Interface Temp.:	300 °C
Acquisition Mode:	Scan
Event Time:	0.3 sec
m/z Range	35 – 400

■ Analysis of Calibration Curve and Control Samples

The calibration curve standard samples were prepared by diluting toluene and n-hexadecane with methanol to concentrations of 0.5 µg/µL and then adding 4 µL of these respective samples to a Tenax TA collection tube. The analytical system's recovery rates were evaluated by preparing control standard samples of typical VOCs (a concentration of approximately 0.11 µg/µL) and adding 4 µL of each control sample to a Tenax TA collection tube for analysis. The response factors (R_f) for toluene and n-hexadecane were calculated based on the measurement results for each calibration curve standard sample and Formula 1, which is shown below. As shown in Table 2, the calculation of control sample recovery rates that are based on toluene R_f indicated good recovery rates of 60 % to 140 % for each compound, including 80 % to 120 % for toluene. The total ion chromatograms (TIC Chromatograms) for the calibration curve samples and the control samples are shown in Fig. 4 and 5, respectively.

$$R_f = \frac{\text{µg (Toluene, C16)}}{\text{Peak area}} \times 1{,}000{,}000$$

Formula 1: Formula for calculating response factor (R_f)

Table 2 Control Sample Recovery Rates

Compound	Area	Recovery rate (%)
Benzene	1,046,011	93%
n-Heptane	818,314	73%
Toluene	1,315,440	117%
n-Octane	1,006,139	90%
p-Xylene	861,971	77%
o-Xylene	865,129	77%
n-Nonane	709,422	63%
n-Decane	783,710	70%
2-Ethylhexanol-1	1,134,868	101%
n-Undecane	842,626	75%
2,6-Dimethylphenol	1,180,647	105%
n-Dodecane	907,103	81%
n-Tridecane	897,343	80%
n-Tetradecane	913,958	81%
Dicyclohexylamine	882,875	79%
n-Pentadecane	980,758	87%
n-Hexadecane	1,056,643	94%
Di-(2-ethylhexl)-adipate	1,534,123	137%

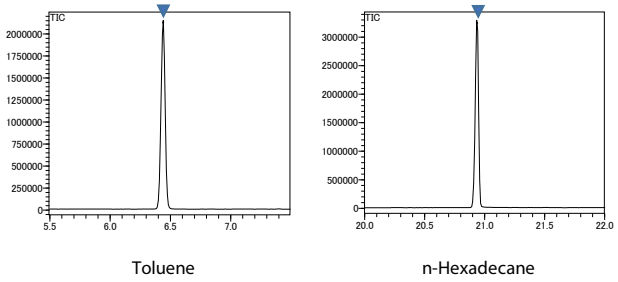

Fig. 4 TIC Chromatograms of Calibration Curve Sample

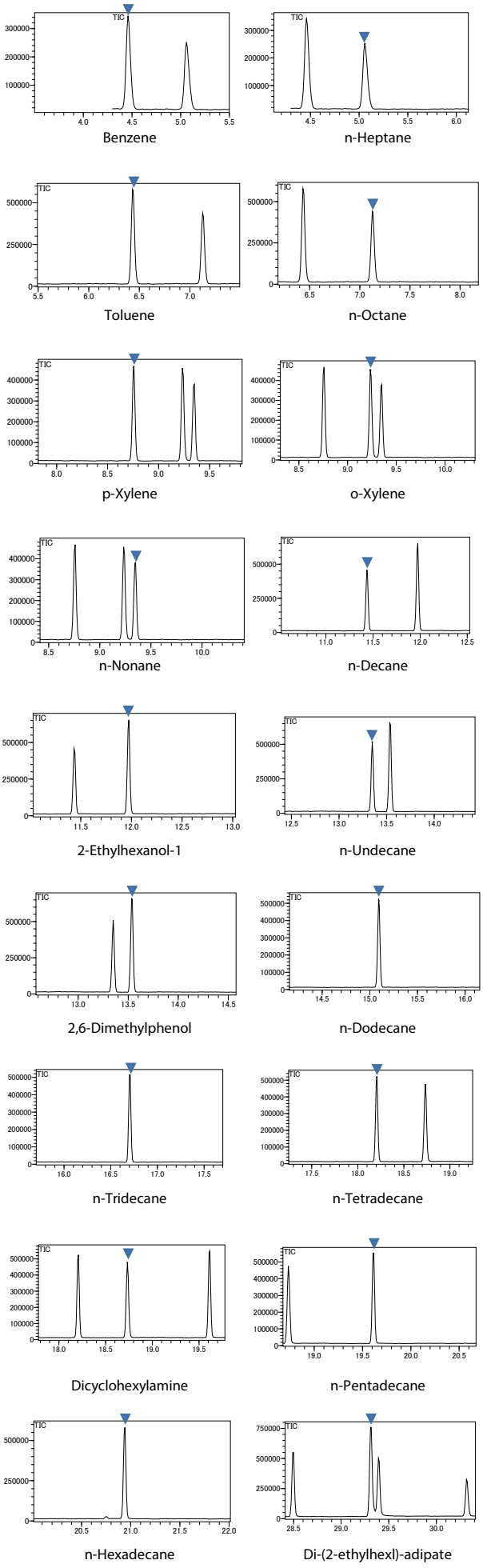

Fig. 5 Chromatograms of Control Sample

■ Tool for Calculating Toluene and Hexadecane Equivalents (TVOC Calculation Tool)

When analyzing samples according to VDA 278, emission values for VOCs (up to C25) are calculated in toluene equivalents, and emission values for SVOCs (C14–C32) are calculated in hexadecane equivalents.

By simply importing the detected compound data and using the TVOC Calculation Tool, as shown in Fig. 6, the steps for calculating these equivalent emission values and generating reports can be automated.

[VDA 278 method for calculating emission values]

VOCs (from initial retention time to C25): calculated in toluene equivalents

SVOCs (C14-C32): calculated in hexadecane equivalents

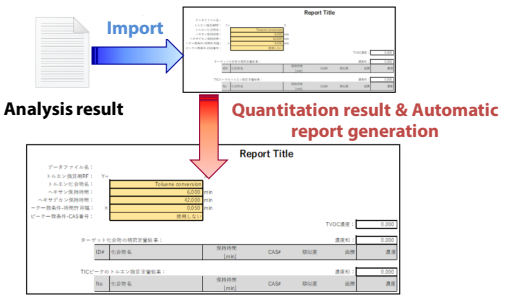

Fig. 6 TVOC Calculation Tool

■ Analysis of Automotive Interior Materials

A TD glass tube was filled with a sample of approximately 11 mg of thinly sliced leather materials taken from the interior of a vehicle. The sample was held in place by 5 mg of quartz wool inserted in both ends of the glass tube. Analyses of VOC and SVOC emissions were performed by heating the tube to 90 °C for 30 minutes and at 120 °C for 60 minutes, respectively, and measuring the emitted gases using the scan mode of the GCMS-QP2050. The TIC Chromatograms of VOCs and SVOCs that were emitted from the leather sample are shown in Figs. 7 and 8, respectively. The detected compound data were then imported into the TVOC Calculation Tool, and the VOC and SVOC emission values (µg/g) were automatically calculated (Figs. 9 and 10).

Using the TVOC Calculation Tool eliminates the inconvenience of having to manually calculate emission values according to Formula 2, which is shown below. These results can also be obtained by simply generating a report. Please refer to the TVOC Calculation Tool Manual for details.

$$\text{Emission [µg/g]} = R_f(\text{Toluene, C16}) \times \frac{\text{Peak area [count]}}{1{,}000 \times \text{sample weight [mg]}}$$

Formula 2: Formula for calculating compound emissions (µg/g) from automotive interior materials

Note: Before running the analysis, be sure to input the sample weight (mg) in the "sample quantity" parameter setting and the value of 0.001 in the "dilution factor" parameter setting in the LabSolutions™ GCMS batch file.

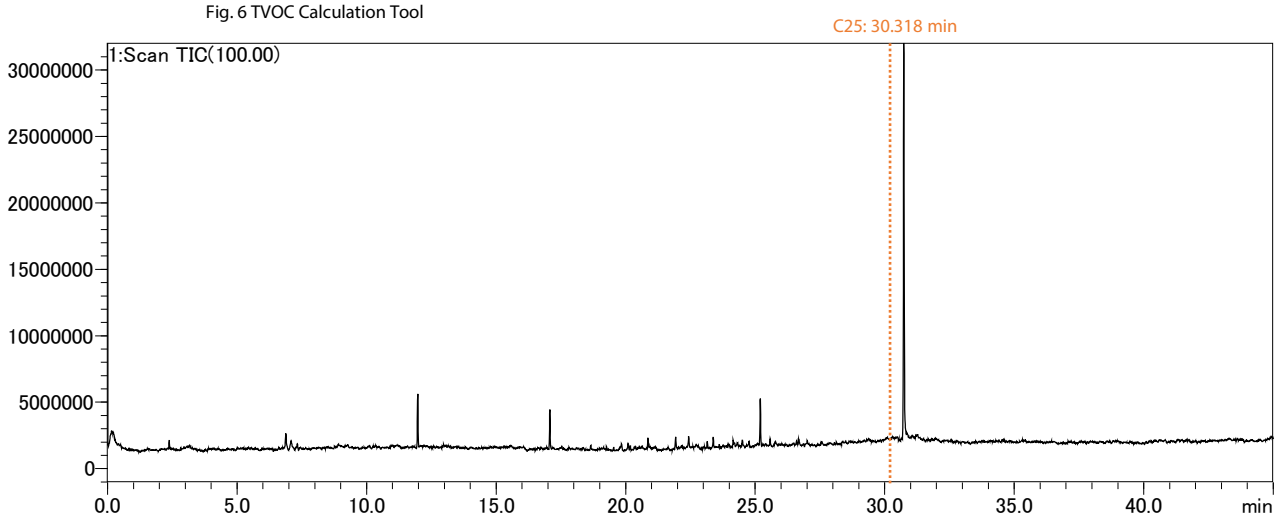

Fig. 7 TIC Chromatograms for VOCs

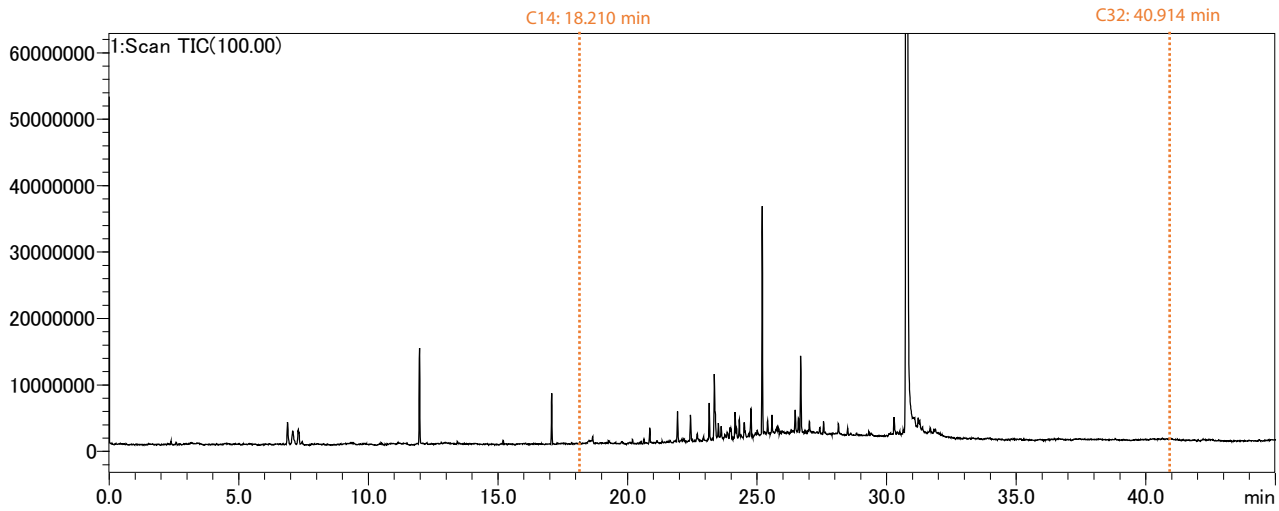

Fig. 8 TIC Chromatograms for SVOCs

Analysis Results of VOC Emissions from Leather Materials (μg/g)

Data File Name:
RF for equiv.: Y= 2.5488655 X
equiv. Comp. Name: Toluene conversion
Start R.T.: 0.000 min
End R.T.: 30.318 min
Ident Peak by RT allowance: ± 0.050 min
Ident Peak by CAS Number: Not use

Sample Amount : 11 mg

Total conc.: 10.319 μg/g

Quant Results of target Compounds: Sum of conc. 0.000 μg/g

ID#	Compund Name	R.T. [min]	CAS#	Similarity	Area	Conc.

Quant Results of TIC peaks (equiv.): Sum of conc. 10.319 μg/g

No	Compund Name	R.T. [min]	CAS#	Similarity	Area	Conc.
1	Heptane, 3-methylene-	6.882	1632-16-2	94	28145	1.004
2	1-Hexanol, 2-ethyl-	11.973	104-76-7	95	72914	2.601
3	Phthalic anhydride	17.073	85-44-9	97	53192	1.897
4	Sulfurous acid, pentadecyl 2-pentyl es	20.860	0-00-0	71	14195	0.506
5	Trichloroacetic acid, tetradecyl ester	21.927	74339-52-9	88	17948	0.640
6	Malonic acid, 2-butyl tetradecyl ester	22.434	0-00-0	73	11292	0.403
7	Octacosane	23.379	630-02-4	88	12558	0.448
8	Dibutyl phthalate	25.197	84-74-2	97	69347	2.473
9	Docosane, 1-iodo-	27.569	0-00-0	72	9731	0.347

Fig. 9 Analysis Results of VOC Emissions from Leather Materials
Note: To set the equivalent R_f, select "Manual setting" and then input the inverse of the toluene R_f that was calculated with Formula 1.

Analysis Results of SVOC Emissions from Leather Materials (μg/g)

Data File Name:
RF for equiv.: Y= 3.204301 X
equiv. Comp. Name: Toluene conversion
Start R.T.: 18.245 min
End R.T.: 40.914 min
Ident Peak by RT allowance: ± 0.050 min
Ident Peak by CAS Number: Not use

Sample Amount : 11 mg

Total conc.: 996.982 μg/g

Quant Results of target Compounds: Sum of conc. 0.000 μg/g

ID#	Compund Name	R.T. [min]	CAS#	Similarity	Area	Conc.

Quant Results of TIC peaks (equiv.): Sum of conc. 996.982 μg/g

No	Compund Name	R.T. [min]	CAS#	Similarity	Area	Conc.
6	Pentanoic acid, 2,2,4-trimethyl-3-carb	20.860	0-00-0	78	40665	1.154
7	1-Tetradecanol	21.928	112-72-1	96	92182	2.615
8	Benzoic acid, 2-ethylhexyl ester	22.433	5444-75-7	90	77309	2.193
9	n-Pentadecanol	23.153	629-76-5	97	101960	2.893
10	Tris(2-chloropropyl) phosphate	23.350	6145-73-9	94	269764	7.653
11	Tris(2-chloropropyl) phosphate	23.507	6145-73-9	90	54800	1.555
12	Isopropyl myristate	23.614	110-27-0	91	44241	1.255
13	Benzoic acid, undecyl ester	23.955	6316-30-9	85	58701	1.665
14	1,2-Benzenedicarboxylic acid, bis(2-m	24.151	84-69-5	96	79482	2.255
15	Benzoic acid, undecyl ester	24.208	6316-30-9	87	32155	0.912
16	1-Octadecanol	24.314	112-92-5	96	50564	1.435
17	Nonadecane	24.504	629-92-5	89	29761	0.844
18	Hexadecanoic acid, methyl ester	24.763	112-39-0	96	86996	2.468
19	Dibutyl phthalate	25.198	84-74-2	98	634238	17.994
20	Butyl myristate	25.407	110-36-1	93	34528	0.980
21	Eicosane	25.574	112-95-8	94	47053	1.335
22	n-Nonadecanol-1	26.470	1454-84-8	97	74217	2.106
23	Heneicosane	26.595	629-94-7	89	51799	1.470
24	1,2-Benzenedicarboxylic acid isopropy	26.684	0-00-0	93	227298	6.449
25	Hexadecanoic acid, 2-methylpropyl es	27.020	110-34-9	93	27540	0.781
26	Docosane	27.567	629-97-0	95	31543	0.895
27	1,2-Benzenedicarboxylic acid, butyl 2-	28.136	85-69-8	95	27551	0.782
28	Tricosane	28.496	638-67-5	91	22030	0.625
29	Hexanedioic acid, bis(2-ethylhexyl) es	29.310	103-23-1	89	11517	0.327
30	Bis(2-ethylhexyl) phthalate	30.797	117-81-7	96	32933052	934.342

Fig. 10 Analysis Results of SVOC Emissions from Leather Materials
Note: To set the equivalent R_f, select "Manual setting" and then input the inverse of the hexadecane R_f that was calculated with Formula 1.

■ Conclusion

Using the new GCMS-QP2050, it was possible to consistently analyze SVOCs and other compounds with high boiling points. By combining this system with the TD-30R thermal desorption system and the TVOC Calculation Tool, even inexperienced users can rapidly analyze automotive interior materials and quantify emissions (i.e., calculate toluene and hexadecane equivalents) in compliance with VDA 278.

Note: The TVOC Calculation Tool is optional software that is compatible with the new GCMS system models. Please contact a Shimadzu sales representative for details.

01-00668-EN First Edition: Mar. 2024

Shimadzu Corporation
www.shimadzu.com/an/

Related Products Some products may be updated to newer models.

GCMS-QP2050

Gas Chromatograph Mass Spectrometer

SH Series

SH-I-5Sil MS

Related Solutions

- Automotive
- Engineering Materials
- Rubber
- Chemicals
- Plastics

- Price Inquiry
- Product Inquiry
- Technical Service / Support Inquiry
- Other Inquiry