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GC-MS TD-30R/GCMS-QP2050

Application News

Analysis of VOC and SVOC Emissions from Automotive Interior Materials Using GCMS-QP2050 in Accordance with ISO 12219-11

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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 ISO 12219-11.
- The TVOC Calculation Tool can calculate in a simple manner quantitative emissions (toluene and hexadecane equivalents) in accordance with ISO 12219-11.

■ Introduction

In recent years, measures to reduce the use of organic compounds in automotive interiors have progressed, the ISO 12219-11 standard is being developed for the analysis of volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) that are emitted from automotive interior materials. The ISO 12219-11 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 (Fig. 2) 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.

TD-30R and GCMS-QP2020 NX will be listed as examples for suitable test equipment on ISO 12219-11. This Application News describes analyzing VOC and SVOC emissions from the materials of vehicle interiors in compliance with ISO 12219-11 using the GCMS-QP2050 together with the Nexis™ GC-2030 and the TD-30R thermal desorption system.

Fig. 1 GCMS-QP2050, Nexis™ GC2030, and TD-30R

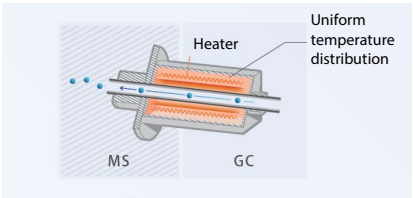

Fig. 2. Illustration of GCMS-QP2050's New Interface

■ 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 20 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 (20 min)
: SVOC	: 90 °C (30 min)
	: 120 °C (60 min)
Tube Desorb Flow	: 82 mL/min
Trap Cooling Temp.	: –20 °C
Dry purge	: -20 °C, 82 mL/min, 1min
Trap Desorb Temp.	: 280 °C (10 min)
Joint Temp.	: 280 °C
Valve Temp.	: 280 °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 (25 min)
[MS]	
TMP Evacuation Rate	: 60 L/sec
Ion Source Temp.	: 240 °C
Interface Temp.	: 280 °C
Acquisition Mode	: Scan
Event Time	: 0.5 sec
m/z Range	: 29 – 450
Tuning mode	: High Concentration

■ 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. 3 and 4, respectively.

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

Formula 1: Formula for calculating response factor (R_f)

Table 2 Control Sample Recovery Rates

Compound	Area	Recovery rate [%]
Benzene	835,986	77
n-Heptane	803,763	74
Toluene	1,082,965	100
n-Octane	907,774	84
p-Xylene	1,401,103	129
o-Xylene	1,382,117	127
n-Nonane	1,029,124	95
n-Decane	1,102,664	101
2-Ethylhexanol-1	1,014,840	93
n-Undecane	1,155,508	106
2,6-dimethylphenol	986,858	91
n-Dodecane	1,175,536	108
n-Tridecane	1,181,226	109
n-Tetradecane	1,156,078	106
Dicyclohexylamine	1,264,779	116
n-Pentadecane	1,104,602	102
n-Hexadecane	1,099,363	101
Di-(2-ethylhexl)-adipate	945,870	87

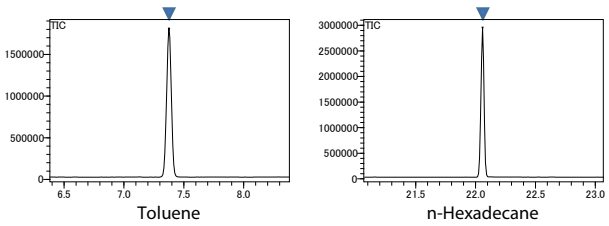

Fig. 3 TIC Chromatograms of Calibration Curve Sample

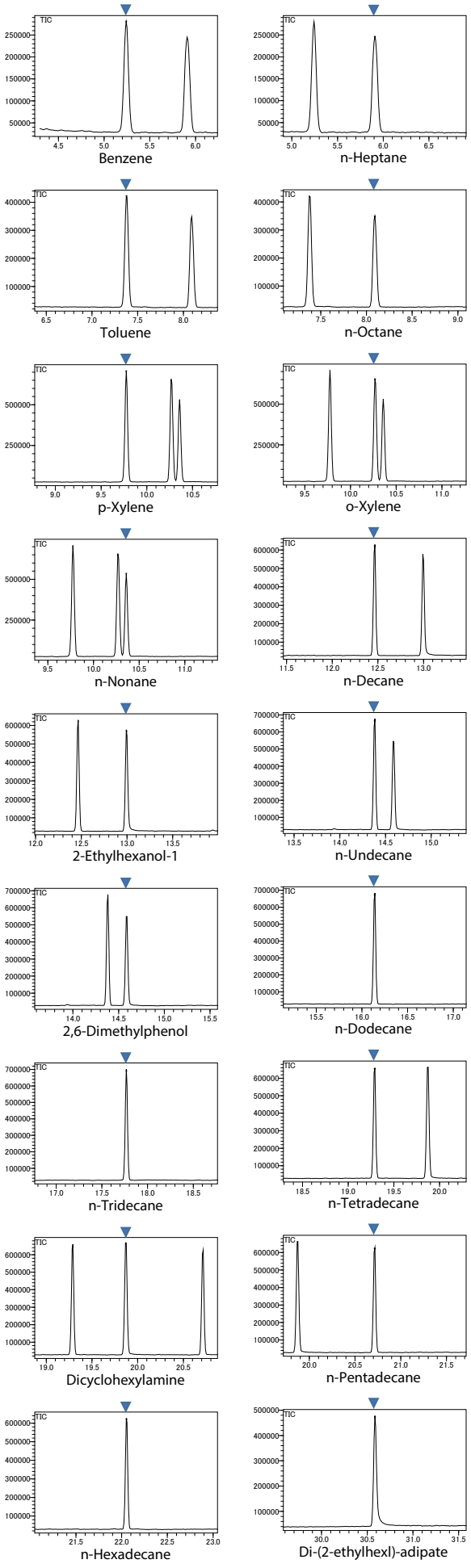

Fig. 4 Chromatograms of Control Sample

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

When analyzing samples according to ISO 12219-11, 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. 5, the steps for calculating these equivalent emission values and generating reports can be automated.

[ISO 12219-11 method for calculating emission values]

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

SVOCs (C14-C32): calculated in hexadecane equivalents

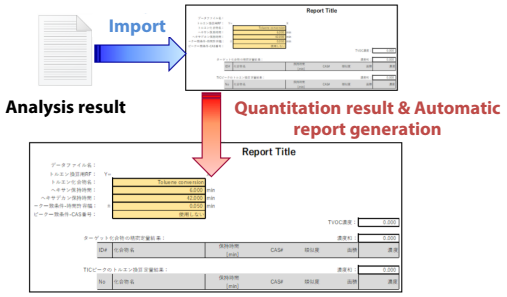

Fig. 5 TVOC Calculation Tool

■ Analysis of Automotive Interior Materials

A TD glass tube was filled with a sample of approximately 10 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. 6 and 7, 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. 8 and 9).

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.

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

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 1 in the "dilution factor" parameter setting in the LabSolutions™ GCMS batch file.

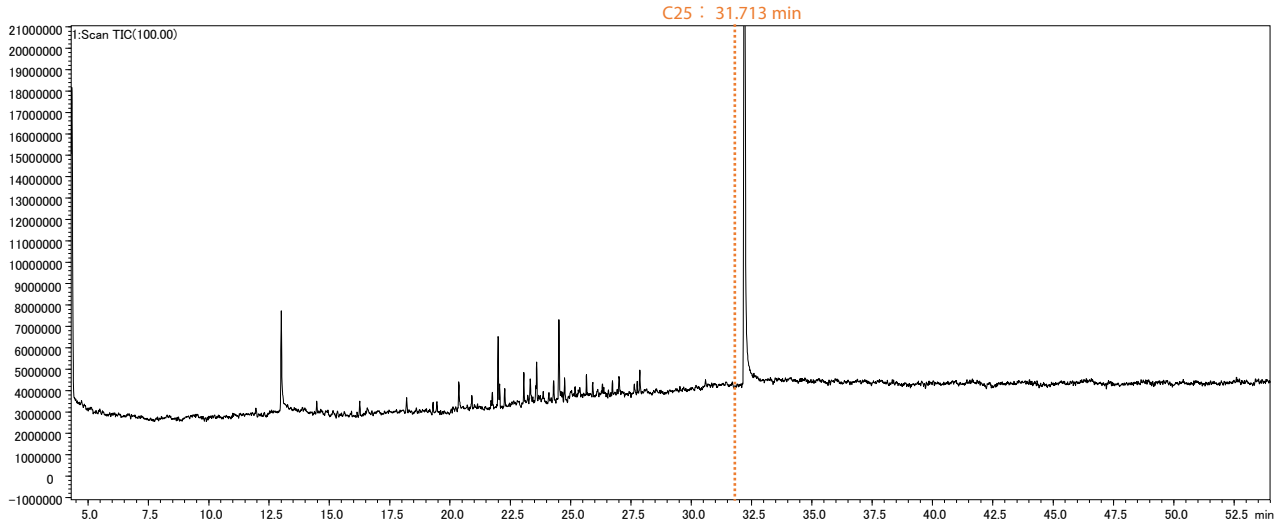

Fig. 6 TIC Chromatograms for VOCs

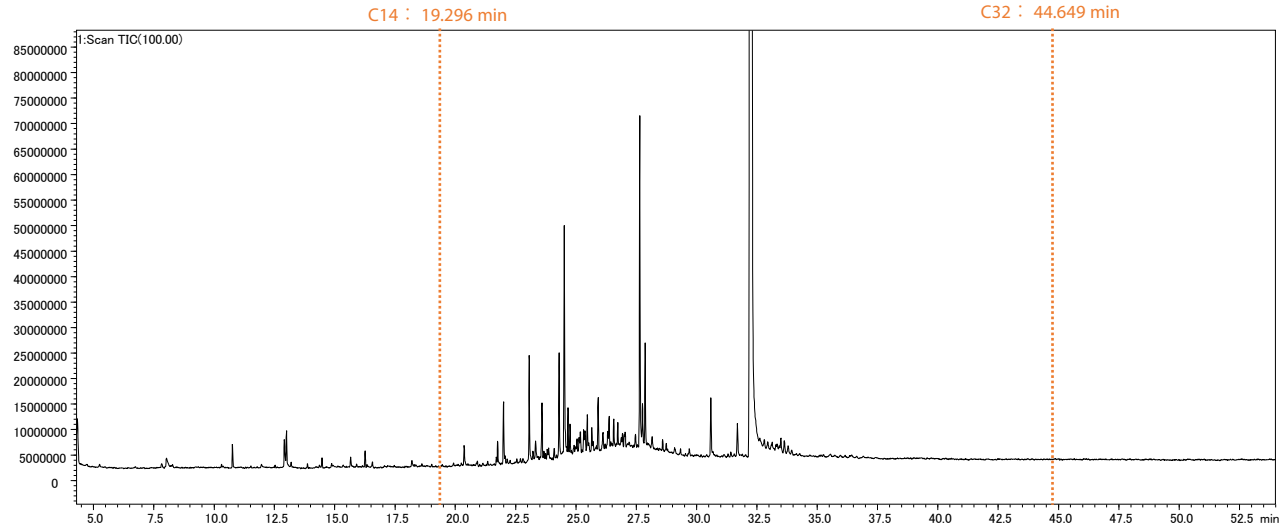

Fig. 7 TIC Chromatograms for SVOCs

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

Data File Name:
RF for equiv.: Y= 2470.7535 X
equiv. Comp. Name: Toluene_Conv
Start R.T.: 0.000 min
End R.T.: 31.713 min
Ident Peak by RT allowance: ± 0.050 min
Ident Peak by CAS Number: 使用しない

Sample Amount: 10 mg

Total conc.(equiv.): 24.362 μg/g

Quant Results of target Compounds (equiv.): 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. 24.362 μg/g

No	Compund Name	R.T. [min]	CAS#	Similarity	Area	Conc.
1	1-Hexanol, 2-ethyl-	13.006	104-76-7	96	125182	5.067
2	Decanal	16.259	112-31-2	89	10695	0.433
3	1-Dodecanol	20.367	112-53-8	92	25542	1.034
4	1-Dodecanol	21.755	112-53-8	85	10504	0.425
5	2,2,4-Trimethyl-1,3-pentanediol diisob	21.995	6846-50-0	91	69590	2.817
6	Hexadecane	22.059	544-76-3	90	21194	0.858
7	Tetradecanal	22.268	124-25-4	92	17678	0.715
8	n-Pentadecanol	23.061	629-76-5	93	26473	1.071
9	Pentadecane, 8-hexyl-	23.326	13475-75-7	69	13522	0.547
10	Pentadecanal-	23.553	2765-11-9	81	12585	0.509
11	Benzoic acid, 2-ethylhexyl ester	23.591	5444-75-7	93	35441	1.434

Fig. 8 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= 2655.834 X
equiv. Comp. Name: C16_Conv
Start R.T.: 19.296 min
End R.T.: 44.649 min
Ident Peak by RT allowance: ± 0.050 min
Ident Peak by CAS Number: 使用しない

Sample Amount: 10 mg

Total conc.(equiv.): 4327.196 μg/g

Quant Results of target Compounds (equiv.): 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. 4327.196 μg/g

No	Compund Name	R.T. [min]	CAS#	Similarity	Area	Conc.
18	1-Dodecanol	20.366	112-53-8	97	87792	3.306
19	Butylated Hydroxytoluene	20.914	128-37-0	87	12301	0.463
20	1,3-Dioxan-4-one, 2-(1,1-dimethyleth	21.339	119620-06-3	74	16517	0.622
21	1,6-Dioxacyclododecane-7,12-dione	21.700	777-95-7	88	31500	1.186
22	n-Tridecan-1-ol	21.753	112-70-9	96	104086	3.919
23	2,2,4-Trimethyl-1,3-pentanediol diisob	21.997	6846-50-0	80	283498	10.675
24	Hexadecane	22.060	544-76-3	91	33016	1.243
25	Ethanol, 2-[2-(2-methoxyethoxy)ethox	22.149	112-35-6	84	24209	0.912
26	2-Methyl-1-undecanol	22.546	10522-26-6	84	16586	0.625
27	Triethyl citrate	22.695	77-93-0	87	17595	0.663
28	Clidinium Bromide	22.798	3485-62-9	66	16614	0.626
29	n-Pentadecanol	23.062	629-76-5	96	451823	17.012
30	Dodecyl acrylate	23.217	2156-97-0	84	49859	1.877
31	Tritriacontane	23.325	630-05-7	69	118933	4.478
32	2,4,2',4'-Tetramethyl-biphenyl	23.435	0-00-0	77	23538	0.886
33	Benzoic acid, 2-ethylhexyl ester	23.590	5444-75-7	93	284431	10.710
34	2,4,2',4'-Tetramethyl-biphenyl	23.674	0-00-0	86	41169	1.550
35	1-Heptacosanol	23.738	2004-39-9	83	23544	0.887

Fig. 9 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 ISO 12219-11.

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.

01-00845-EN First Edition: Jan. 2025

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