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Application Data Sheet

No.137

GC-MS
Gas Chromatograph Mass Spectrometer

Analysis of VOC and SVOC Emissions from Automotive Interior Materials in Accordance with VDA278 Using the Thermal Desorption Method

In recent years, measures to reduce the use of organic compounds in automotive interiors have progressed. In Germany, the VDA278 standards were created for the analysis of volatile organic compounds (VOC) and semi-volatile organic compounds (SVOC) produced from automotive interior materials. In the VDA278, measurement samples are added to a TD glass tube. The VOC (up to C20) and SVOC (up to C32) are heated at different temperatures, and the gases produced are loaded into a GC-MS. The VOC and SVOC from the automotive interior materials can be analyzed conveniently and quickly. However, since the gas is loaded directly, if the SVOC content is highly concentrated, caution is needed regarding carryover.
The TD-30 thermal desorption system features an inert sample line that is kept as short as possible, and samples are heated up to 300 °C, reducing SVOC carryover. In this investigation, an analysis of VOC and SVOC emissions from automotive interior materials was attempted in accordance with VDA278 using the TD-30.

Experiment

Automotive interior materials (rubber, plastic, and leather) were sliced thinly, and TD glass tubes (from Shimadzu) were filled with approximately 30 mg of these samples. Both ends were fastened with 5 mg of quartz wool. The VOC samples were heated at 60 °C for 30 minutes, the SVOC samples were heated at 90 °C for 60 minutes, and the gases produced were loaded into a GC-MS. The samples loaded were analyzed in GC-MS Scan mode. The analysis conditions are shown in Table 1, and the analysis samples are shown in Fig. 1.

Table 1: Analysis Conditions

[Instrument Configuration]	
GC-MS:	GCMS-QP™ 2020
Sample Loader:	TD-30R
Workstation (GCMS-QP™2020):	GCMSsolution™ Ver.4.45
Workstation (TD-30):	TD-30 Control Software
Column:	SH-Rxi™-5Sil MS (60 m x 0.25 mm I.D., df = 0.25 μm) (SHIMADZU)

[TD-30]	
Tube Desorption Temperature:	90 °C for 30 min (VOC) 120 °C for 60 min (SVOC)
Tube Desorption Flowrate:	60 mL/min
Trap Cooling Temperature:	-20 °C
Trap Desorption Temperature:	280 °C for 10 min
Joint Temperature:	280 °C
Valve Temperature:	250 °C
Transfer Line Temperature:	280 °C

[GC]	
Control Mode:	Pressure
Pressure:	200 kPa
Injection Mode:	Split 1:100 (Column Flowrate 1.99 mL/min)
Column Oven Temperature:	40 °C (3 min) – (10 °C/min) – 300 °C (13.5 min)

[MS]	
Ion Source Temperature:	200 °C
Interface Temperature:	250 °C
Measurement Mode:	Scan Measurement
Scan Mass Range:	*m/z* 35-400
Scan Event Time:	0.5 sec
Scan Speed:	769 u/sec

(1) Flat Sample Tray Capable of Heating the Sample Directly

When the sample is added directly in the glass tube, if the glass tube is not stored horizontally, contamination will occur due to dropping of the wool and the sample. With the TD-30 sample tray, the glass tubes can be stored horizontally, eliminating any concerns about contamination.

(2) Inert Sample Line as Short as Possible and Capable of Being Heated

The TD-30 sample line is designed to be as short as possible, and is not connected to the GC sample vaporization chamber or other unnecessary parts. In addition, all parts of the sample line can be heated to at least 300 °C, so carryover is not a concern, even for SVOC with high boiling points.

Fig. 1: Features of Analysis Samples and the TD-30 When Analyzing Automotive Interior Materials

Analysis Results

Evaluative Results for Calibration Curves and Recovery Rates

The standard samples for the calibration curves were prepared by diluting toluene and n-hexadecane with methanol to concentrations of 0.5 μg/μL. 4 uL of the sample was added to a Tenax® TA collection tube, and the response factor was calculated. The response factor was used in the calculation of the quantitative values of the compounds in the automotive interior materials. The formula is shown below.

In addition, in order to evaluate the recovery rate for the analysis system, a standard sample of typical VOCs (with a concentration of approximately 0.11 ug/uL) was prepared. 4 uL of this was added to a Tenax® TA collection tube and then analyzed. When the recovery rate was calculated from the response factor, values between 60 % and 140 % were obtained regardless of the compound, which is a favorable recovery rate.

$$R_f = \frac{\mu g \text{ Toluene (C16)}}{\text{Peak area}} \times 1000000$$

Formula 1: Formula for the Response Factor (Rf)

$$\text{Emission } [\mu g/g] = R_f \text{ (Toluene, C16)} \times \frac{\text{Peak area [count]}}{1000 \times \text{sample weight [mg]}}$$

Formula 2: Formula for the Quantitative Values (Emission[μg/g]) of Compounds Produced by Automotive Interior Materials

Table 2: Recovery Rate for Typical VOCs

Name of Compound	Recovery Ratio (%)
Benzene	106.53
Toluene	93.49
p-Xylene	99.91
o-Xylene	75.38
2-Ethyl-1-hexanol	101.26
2,6-Dimethylphenol	94.19
Dicyclohexylamine	89.15

Analysis Results for Automotive Interior Materials

The quantitative values (μg/g) for compounds produced by rubber, plastic, and leather samples are shown in Table 3. A high concentration of Bis(2-ethylhexyl) phthalate (at a concentration of 333.28 μg/g) was detected from the leather sample. When a blank sample was analyzed immediately after analyzing the leather sample, the carryover was less than 0.05 %, which is a favorable result.

Table 3: List of Quantitative Values of Compounds Produced by Automotive Interior Materials

Name of Compound	VOC			SVOC		
	Rubber	Plastic	Leather	Rubber	Plastic	Leather
C8	0.00	0.00	0.00	0.00	0.00	0.11
Toluene	0.35	0.54	0.53	0.31	0.44	0.24
C9	0.00	0.00	0.00	0.00	0.00	0.13
C11	0.00	0.00	0.00	0.00	0.00	0.31
Benzene, 1,3-dichloro-	0.00	0.00	0.00	0.00	0.00	0.08
2-Propyl-1-pentanol	0.36	0.52	0.73	0.11	0.18	0.78
C12	0.00	0.00	0.17	0.00	0.03	0.06
Nonanal	0.00	0.00	0.43	0.09	0.06	0.87
C13	0.20	0.14	0.26	0.09	0.13	0.13
C15	0.14	0.12	0.36	0.13	0.16	0.14
C16	0.31	0.00	0.60	0.42	0.16	0.86
C18	0.14	0.00	0.73	0.39	0.00	2.02
C19	0.00	0.00	0.30	0.39	0.00	1.37
Dibutyl phthalate	0.00	0.00	2.92	0.00	0.00	17.53
C20	0.00	0.00	0.18	0.14	0.00	1.28
C22	0.00	1.09	0.17	0.00	0.00	0.82
C23	0.00	0.00	0.15	0.00	0.00	0.82
C25	0.00	0.00	0.00	0.00	0.00	1.78
Bis(2-ethylhexyl) phthalate	0.41	1.60	33.67	0.00	0.00	333.28

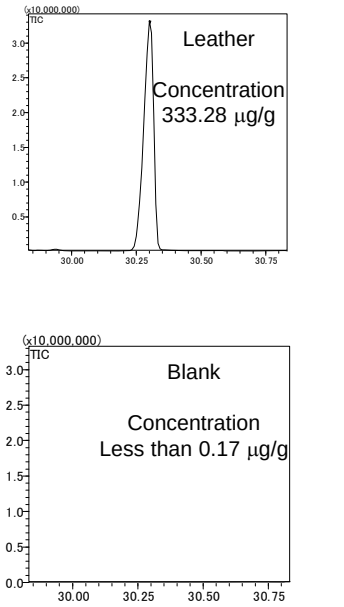

Fig. 2: Chromatograms for Bis(2-ethylhexyl) Phthalate in the Leather and Blank Samples

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