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VDA 278 Method Transition from TDS 3 to TD 3.5+

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Abstract

Material emissions in automobiles are an important subject for the whole automotive sector. The VDA 278 method is widely used for analysis of emissions from interior materials. The original GERSTEL TDS was built specifically for this method. Currently the GERSTEL TDS 3 is also widely used and for many users the question arises if the GERSTEL TD 3.5+ is equally suitable. This AppNote addresses the transfer of method VDA 278 from TDS to TD 3.5+.

To verify the suitability of the TD 3.5+, the system performance test described in method VDA 278 was performed, including analysis of a control mixture, used to verify selectivity, recovery, and precision. A further criterion tested in this work is the limit of quantitation (LOQ), which was determined in accordance with DIN 32645 for the VOC and FOG runs. The final compatibility test performed was the analysis of material samples with TD 3.5+.

Introduction

The VDA 278 method is used and accepted world-wide for the estimation of emissions of automotive interior materials. GERSTEL is one of the manufacturers from thermal desorption systems mentioned in VDA 278; the method was developed on a GERSTEL TDS and later adapted to other formats. The Gerstel TDS 3 combined with the TDS A2 Autosampler has been used successfully by many routine and production laboratories for decades and is considered to be the reference instrument for this method. The TD 3.5+ is a more recent thermal desorption system developed by GERSTEL, which relies on the MultiPurpose Sampler (MPS) robotic for automation. The MPS allows greater flexibility in terms of performing other applications such as liquid injection or static headspace (the latter is discussed in VDA 277). In addition, the TD3.5+ is compatible with 3.5-inch tubes used for many other automotive standards such as the ISO 12219 series. Therefore, more and more TD 3.5+ customers are looking to use the TD 3.5+ for their VDA 278 analysis. This raises the question whether the TD 3.5+ is compatible with VDA 278.

This question is best answered by performing the suitability test, analyzing the VDA 278 control mixture to verify the analytical performance and by determining the limits of quantitation for the VOC and FOG runs.

Following the suitability test, real samples were analyzed using the TD 3.5+. Adjustments were made to the VDA 278 method to enable analysis based on GC 8890 and MSD 5977 B (both from Agilent Technologies), which are more recent and more sensitive instruments than those specified in the method.

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Experimental

Samples

The control mixture and calibration standards were diluted in accordance with VDA 278 [1]. The analytes and their respective concentrations are shown in Table 1.

Table 1: VDA 278 control mixture and calibration standards.

Compound	Mass Conc. [µg/µL]
Control mixture	
Benzene	0.115
Heptane	0.115
Toluene	0.115
Octane	0.115
p-Xylene	0.115
o-Xylene	0.115
Nonane	0.115
Decane	0.115
2-Ethyl-1-hexanol	0.115
Undecane	0.115
2,6-Dimethylphenol	0.115
Dodecane	0.115
Tridecane	0.115
Tetradecane	0.115
Dicyclohexylamine	0.115
Pentadecane	0.115
Hexadecane	0.115
Bis(2-ethylhexyl) adipate	0.115
Calibration Standard	
Toluene	0.55
Hexadecane	0.53

Three analytes are used for the determination of the limits of quantitation. These are toluene and hexadecane diluted in methanol for the VOC measurements, while triacontane (C32 alkane) diluted in pentane is used for the FOG measurements. The limit of quantitation is determined in accordance with DIN 32645 standard [2].

The dilution levels and concentrations used to determine the limits of quantitation are shown in Table 2.

Table 2: Dilution levels of toluene, eicosane and triacontane for the limits of quantitation.

Dilution level	Mass Conc. Toluene [ng/µL]	Mass Conc. Eicosane [ng/µL]	Mass Conc. Triacontane [ng/µL]
1	0.023	0.030	0.10
2	0.046	0.060	0.20
3	0.069	0.090	0.30
4	0.092	0.120	0.40
5	0.115	0.150	0.50
6	0.138	0.180	0.60
7	0.161	0.210	0.70
8	0.184	0.240	0.80
9	0.207	0.270	0.90
10	0.230	0.300	0.100

Representative real samples were provided by IMAT UVE, Mönchengladbach, Germany, enabling us to gain an overview of the suitability of the TD 3.5+ for the VDA 278 standard method. The sample types analyzed are listed in Table 3.

Table 3: Emission samples provided by IMAT UVE.

Sample Identification	Material
Sample No. 1	Polypropylene
Sample No. 2	Polypropylene
Sample No. 3	Composit
Sample No. 4	Polyurethane foam
Sample No. 5	TPE-SEBS
Sample No. 6	Leather
Sample No. 7	Varnish
Sample No. 8	Rubber
Sample No. 9	Leather
Sample No. 10	Composit

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Instrumentation

GERSTEL TD Core System on Agilent 8890 GC and 5977B Inert Plus MSD.

Some adjustments were made to the analysis method, such as the mass axis calibration of the mass selective detector and transfer zone temperature of the TD 3.5+.

Analysis Conditions TD Core System

CIS 4

glas wool filled liner

other settings are described in VDA 278

TD 3.5+

splitless

30 °C (0 min); 60 °C/min; 90 °C (30 min) - VOC run

30 °C (0 min); 60 °C/min; 120 °C (60 min) - FOG run

transfer zone   100 °C - VOC run

                    130 °C - FOG run

Analysis Conditions Agilent 8890 GC

all settings are described in VDA 278

Analysis Conditions Agilent 5977B Inert Plus MSD

Begin data acquistion   3 min

Calibration mass axis   e-tune

Scan mode   29-450 amu, > 3 scans/s

MS threshold   50

Results and Discussion

Performance of the TD 3.5+

The control mixture consists of 18 compounds ranging from low boiling (C6) to high boiling (C 22). The performance of the analytical system was verified using this mixture. The selectivity of the system is accepted if all substances are base line separated. In Figure 1 the separation of o-xylene and nonane is shown.
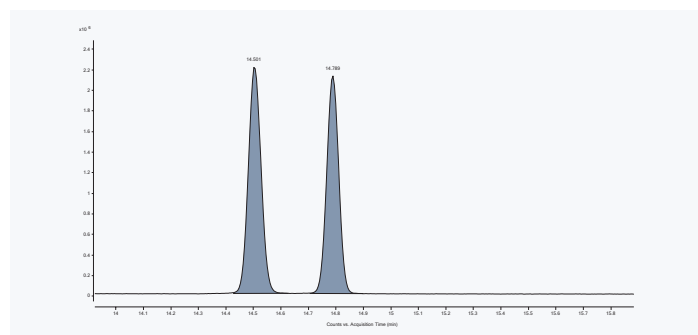

Figure 1: Selectivity test, o-xylene and C9 are base line separated.

Recovery rates for the control mixture compounds are another critical factor of system performance. For toluene the recovery rate must be in the range from 80 to 120 %, for other analytes the range is 60 to 140 %. The average recovery rates for the control mixture compounds are shown in Table 4.

Table 4: Average recovery rates and precisions achieved for the control mixture with TD 3.5+.

Compound	Average Recovery [%]	RSD [%]
Benzene	90.1	6.0
Heptane	79.0	5.7
Toluene	102.6	6.4
Octane	81.4	5.5
p-Xylene	105.4	6.9
o-Xylene	106.5	6.4
Nonane	92.6	4.5
Decane	86.4	5.4
2-Ethyl-1-hexanol	82.5	5.2
Undecane	100.8	5.6
2.6-Dimethylphenol	84.1	5.1
Dodecane	105.7	5.1
Tridecane	116.5	5.0
Tetradecane	119.3	4.9
Dicyclohexylamine	110.6	6.8
Pentadecane	118.9	5.0
Hexadecane	120.4	5.2
Bis(2-ethylhexyl) adipate	111.4	11.9

Results for all 18 substances were within the ranges specified in the VDA 278 method. Even critical compounds like benzene with its high volatility and the high boiling analyte bis(2-ethylhexyl) adipate are within the specifications listed in the method. The precision of the TD 3.5+ is also within method specifications. All but one substance show RSDs between 4.5% and 6.9%, which is a highly acceptable value for such an analysis.

Other key points in system performance tests are the limits of quantitation (LOQs) achieved for the VOC and FOG methods. VOC system performance is tested with toluene and hexadecane,

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for the FOG analysis performance, n-triacontane (C32) is used. The LOQ is determined by using the calibration line method described in DIN 32645. The results of the LOQ tests are shown in Table 5.

Table 5: Calibration line method in accordance with DIN 32645 for TD 3.5+.

Compound	Correlation R²	Limit of quantitation [µg]
Toluene	0.9985	0.021
Eicosane	0.9995	0.016
Triacontane	0.9934	0.192

The required system performance specified in VDA 278 was achieved for all analytes, demonstrating the suitability of the TD 3.5+ for the analysis of material emissions in accordance with the method.

Analyzing Material Emission Samples with the TD 3.5+
The final suitability test for the TD 3.5+ was the analysis of real emission samples. All analyses were performed in duplicate. The sample weight used was 30 mg for all samples as specified in the VDA 278 method, except for foam (15 mg) and leather (10 mg). Analysis results for the emission samples are shown in Table 6.

Table 6: VOC and FOG values of emission samples determined with the TD 3.5+.

Sample Identification	Material	Analysis	VOC 1 [µg/g]	VOC 2 [µg/g]	FOG [µg/g]	RSD VOC [%]	RSD FOG [%]
Sample No. 1	Polypropylene	A	143.80	264.00	469.90	27.59	2.61
		B	237.50	293.40	487.60		
Sample No. 2	Polypropylene	A	80.40	79.90	265.30	2.60	6.67
		B	83.40	78.40	241.40		
Sample No. 3	Composit	A	39.00	49.30	101.50	10.60	9.04
		B	47.50	49.20	89.30		
Sample No. 4	Polyurethane foam	A	514.00	574.30	223.00	12.75	1.22
		B	638.70	691.40	219.20		
Sample No. 5	TPE-SEBS	A	83.80	115.50	174.10	16.69	15.30
		B	84.10	86.30	140.10		
Sample No. 6	Leather	A	201.50	181.50	235.20	10.11	10.65
		B	228.70	220.40	273.50		
Sample No. 7	Varnish	A	16.60	22.20	2072.30	36.64	14.47
		B	16.60	8.10	1687.70		
Sample No. 8	Rubber	A	847.30	910.60	2511.20	6.31	10.50
		B	964.80	973.90	2164.00		
Sample No. 9	Leather	A	24.60	29.70	287.80	27.53	31.37
		B	15.00	20.80	183.30		
Sample No. 10	Composit	A	94.70	42.30	107.50	33.75	9.51
		B	57.70	66.00	123.00		

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The VOC and FOG values are comparable in their respective analysis series. Deviations are within expectations for emission samples. As the VDA 278 committee [1] demonstrated in a round-robin test in 2002, precision depends heavily on the sample matrix. The results of the interlaboratory test are shown in Table 7. The data shown here are an extract of the data presented by VDA 278.

Table 7: Results of the round-robin test, extract from VDA 278 [1].

Sample	PES film				TPO film			
	VOC value	FOG value	Selected single peaks		VOC value	FOG value	Selected single peaks	
Statistical value			n-Butyl acetate	Tinuvin P			Main peak (isoalkane)	Hexadecanoic acid
Mean value [µg/g]	584	22	19	1	134	505	28	95
Standard deviation [µg/g]	184	12	6	1	48	265	11	43
Variation [%]	31	53	34	70	36	52	40	45

Usually, an emission sample should be within 15% relative standard deviation, but in borderline cases some matrices reduce the precision. In such cases the deviation can be up to 50%. Often those matrices are composite, foam or leather samples. Even the sample preparation has an influence on the emission value.

The greater the surface area the higher the emission value will be during analysis. This effect is addressed by the VDA, and VDA recommendations should be followed.
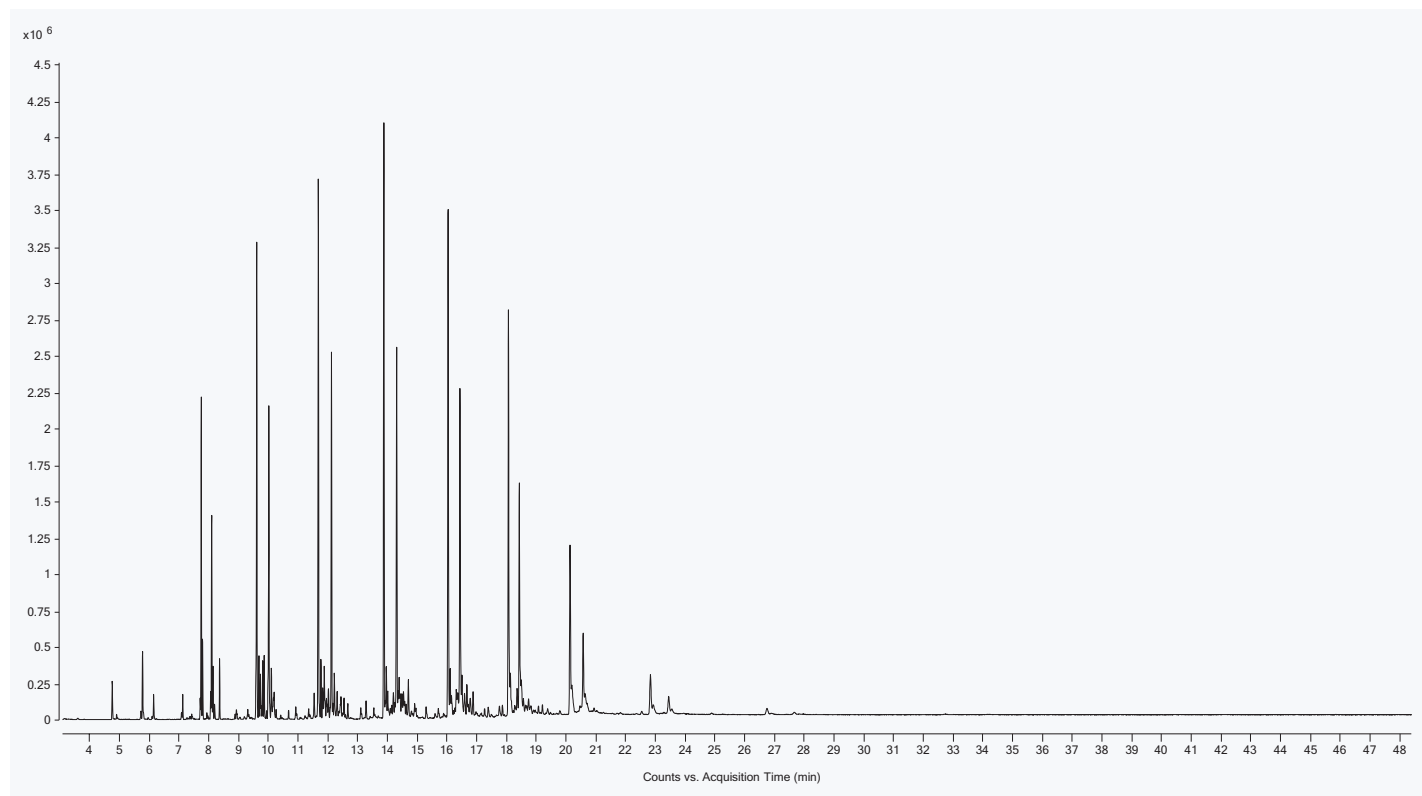
In Figure 2 the chromatogram of the VOC run of sample no. 1 is shown.
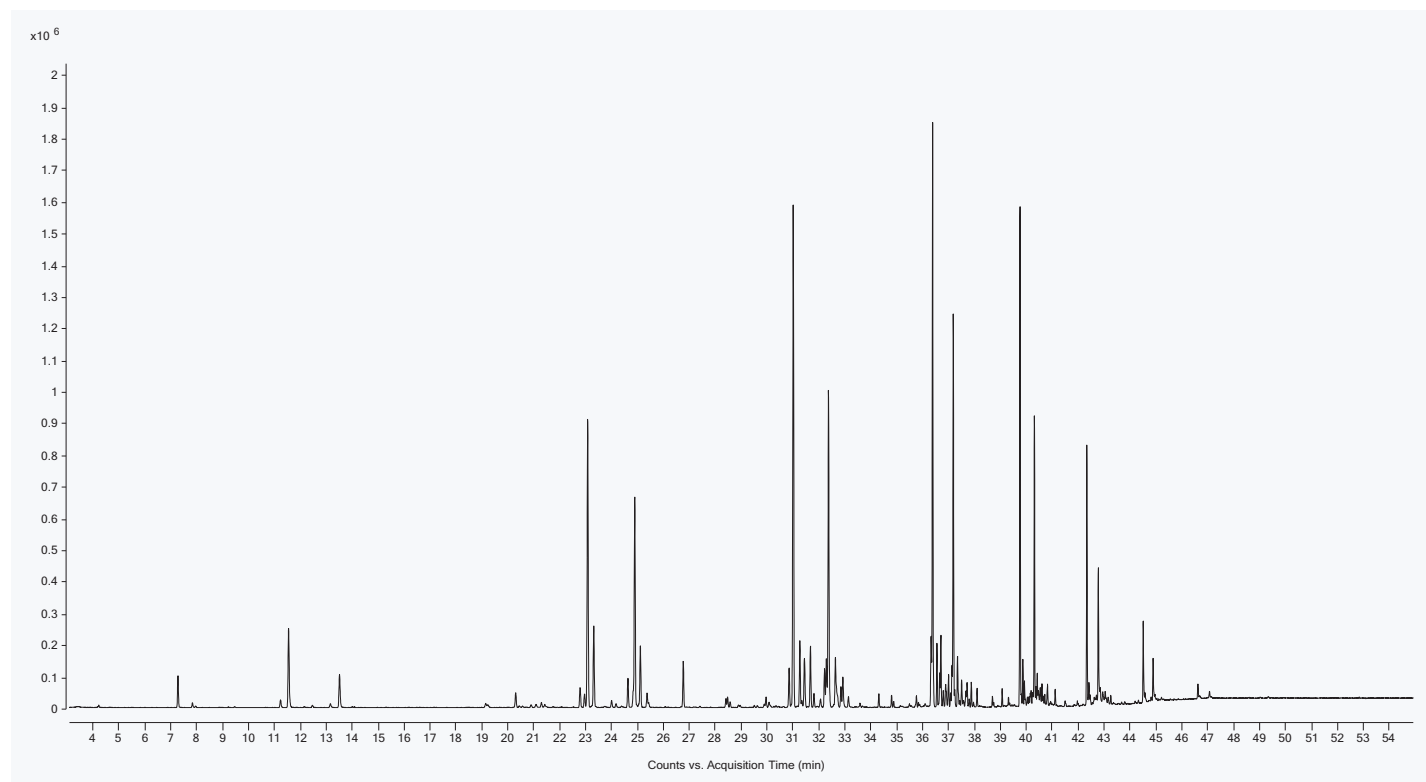
Figure 2: VOC-Run of sample no. 1 (polypropylene).

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The FOG -Run of sample no. 1 is shown in figure 3.

Figure 3: FOG-Run of sample no. 1 (polypropylene).

Conclusions

Using the proper set of method parameters, the TD 3.5⁺ is highly suitable for performing material emissions analysis following the VDA 278 method. Recovery and precision for the control mixture are within required specifications. Also, the limit of quantitation is within the required range demonstrating system suitability. The performed emission analyses of materials show that the TD 3.5⁺ meets the required precision for analysis following method VDA 278.

The TDS is still a highly suitable and rugged system for the analysis of materials and of air samples and remains the reference instrument for this method. For customers who want to gain flexibility and compatibility with 3.5-inch tubes without sacrificing the performance of the TDS, a TD 3.5⁺ is a perfectly suited thermal desorption instrument.

Acknowledgement

References

[1] Thermal Desorption Analysis of Organic Emissions for the Characterization of Non-Metallic Materials for Automobiles. VDA278. s.l. : Verband der Automobilindustrie, 2016

[2] Chemical analysis - Decision limit, detection limit and determination limit under repeatability conditions - Terms, methods, evaluation. DIN 32645:2008-11