

Analysis of VOCs in automotive trim components using TD-GC-MS

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Goal

To demonstrate a simple and effective analytical solution for the direct analysis of volatile organic compounds (VOC) and semi volatile condensable compounds (FOG) emitted from car interior trim material referencing base parameters in the VDA 278 method, utilizing the thermal desorption sampling technique coupled to GC-MS and Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software for data acquisition, processing, and intelligent reporting against hazardous chemical lists.



Introduction

The typical, distinct “new car” smell, liked by many, originates from a mixture of volatile organic compounds (VOC) present in automotive interior cabins, released from such material as carpets, adhesives, sealants, foams, plastic components, films, leather, interior paints, and composite materials.^{1,2} It is critical to investigate VOCs emissions from car trim components. Their presence can negatively affect vehicle interior air quality (VIAQ), resulting in drivers and passengers inhaling polluted air.

There are various standard test methods, as stated in regulations and original equipment manufacturer (OEM) specifications, that describe the VOC limits for newly manufactured cars, as well as emission tests to be performed and analytical procedures.³⁻⁶ Analysis of non-metallic automotive material typically focuses on semi-quantitative analysis of VOC emissions, or compounds with a high to medium volatility. The method also describes procedures for quantitation of condensable substances (FOG) compounds of low volatility such as semi-volatile organics (SVOCs), calculated as hexadecane equivalents. Current methods, for example VDA 278,⁶ use thermal desorption (TD) analysis, where thermally extracted substances are focused on a focusing trap and subsequently analyzed using gas chromatography (GC) coupled to single quadrupole mass spectrometry (MS).

This application demonstrates the analytical performance of a thermal desorption, gas chromatograph with MS detection (TD-GC-MS), for the direct desorption of car trim material for VOCs and FOG/SVOC.

Experimental

Sample preparation

A sample of specific mass is placed into the middle of an empty sample tube, then capped. If analysis is to be carried out immediately, DiffLok™ caps are recommended, otherwise brass storage caps are used. The capped tube is loaded on to the sample tray and placed in the Markes TD100-xr™ automated thermal desorber for TD-GC-MS analysis.

Specific sampling requirements may apply depending on the material being analyzed. As an example, thermoplastic polyurethane and polyurethane foam samples require $10 \text{ mg} \pm 5 \text{ mg}$ for TD analysis.

Standard preparation

Calibration standard

To determine VOCs and SVOC (FOG) values, which are calculated as toluene and hexadecane equivalents, respectively, single point toluene and hexadecane calibration standards (0.5 g/L) were prepared in methanol (HPLC grade) from individual stock standards (available from Merck UK).

Also, to ascertain the retention time limits for VOC and SVOC (FOG) group integration, a standard including *n*-C25 (*n*-pentacosane) was prepared in methanol (HPLC grade) and analyzed under VOC method conditions. A standard including *n*-C14 (*n*-tetradecane) and *n*-C32 (*n*-dotriacontane) was also prepared in methanol (HPLC grade) and analyzed under SVOC (FOG) method conditions.

Control standard

To assess the performance of the analytical configuration (TD-GC-MS) a control standard mix containing compounds (Table 1) at 0.112 g/L within the VOC and SVOC (FOG) ranges was prepared in methanol (HPLC grade) from individual stock standards (available from Merck UK).

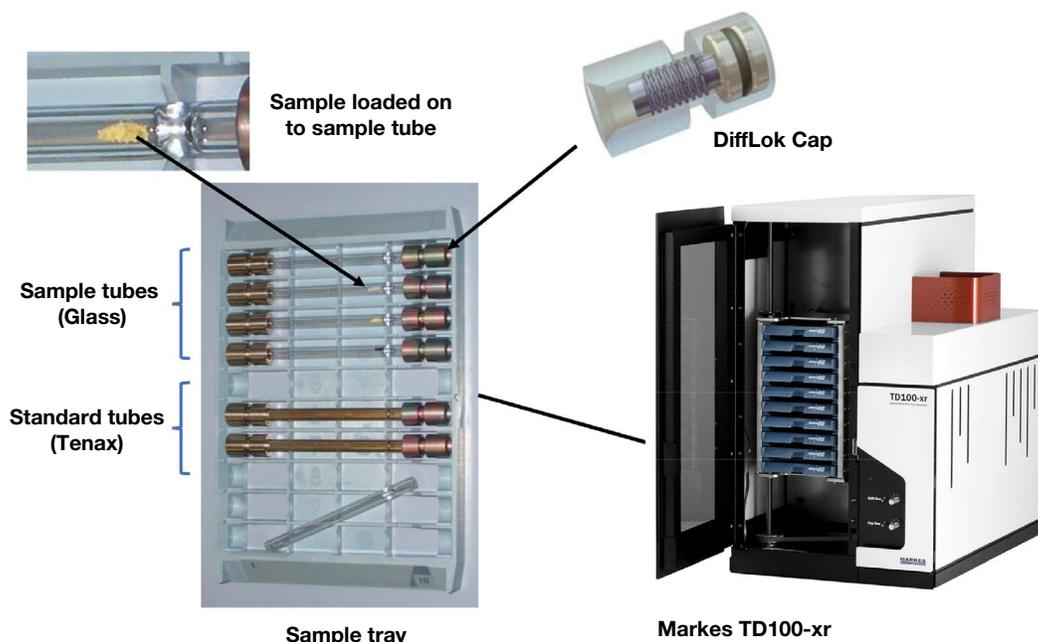


Figure 1. Markes TD instrument setup for thermal desorption analysis

Table 1. Control mixture used to assess TD-GC-MS instrument performance

No	Compound	CAS number
1	<i>n</i> -Heptane	142-82-5
2	Toluene	108-88-3
3	<i>n</i> -Octane	111-65-9
4	Benzene, 1,3-dimethyl-	108-83-3
5	<i>n</i> -Decane	124-18-5
6	<i>n</i> -Undecane	1120-21-4
7	<i>n</i> -Dodecane	112-40-3
8	<i>n</i> -Tetradecane	629-59-4
9	Dicyclohexylamine	101-83-7
10	<i>n</i> -Pentadecane	629-62-9
11	<i>n</i> -Hexadecane	544-76-3

It is important that both loading and analysis of calibration standards replicates as close as possible the analysis of samples themselves. This can be achieved using a Calibration Solution Loading Rig[®] (CSLR™ available from Markes International), where 4 µL of calibration or control standards are loaded on to Tenax™ standard tubes, in a stream of nitrogen (as shown in Figure 2).

Instrument and method setup

An analytical system comprised of Markes TD100-xr thermal desorption instrument connected to the Thermo Scientific™ TRACE™ 1310 Gas Chromatograph and the Thermo Scientific™ ISQ™ 7000 GC-MS was used (Figure 3).



Figure 3. Markes TD100-xr thermal desorption instrument connected to the Thermo Scientific TRACE 1310 Gas Chromatograph and the Thermo Scientific ISQ 7000 GC-MS used for VOC and FOG/SVOC analysis

The sample is placed into an empty glass sample tube, which is then heated in a flow of carrier gas to release the compounds of interest. The compounds are then collected on an electrically cooled focusing trap (kept at -30 °C). This sampling process is graphically represented in Figure 4A. The focusing trap is then rapidly heated with the carrier gas flow reversed to release and concentrate the compounds into a narrow band, before injection into the GC-MS, as shown in Figure 4B. This efficient re-focusing and fast desorption results in concentrated analytes, with improved sensitivity.

The Markes TD100-xr is an automated thermal desorption system, which offers unattended analysis of up to 100 samples. Samples can also be split and re-collected onto a clean sorbent tube at either the sample tube desorption and/or focusing trap desorption stages (Figure 4).

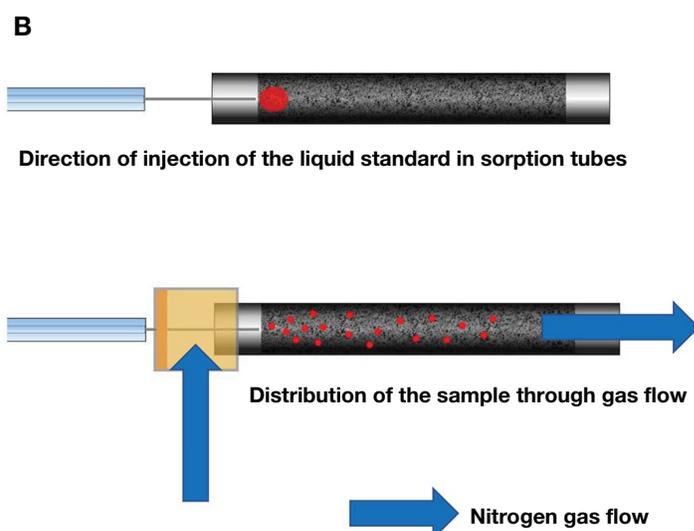
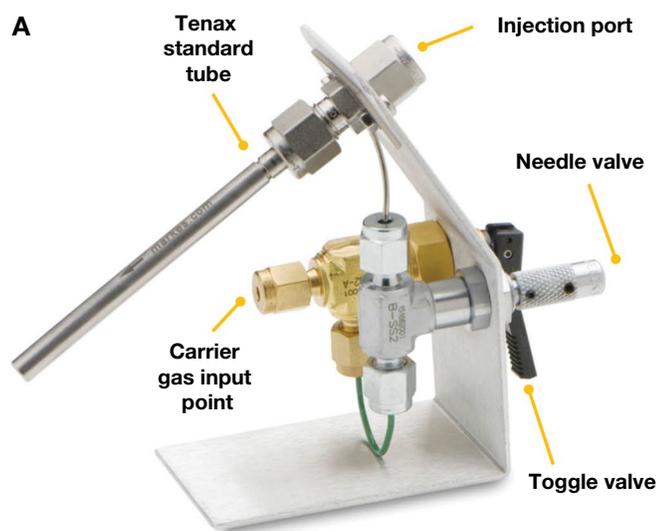
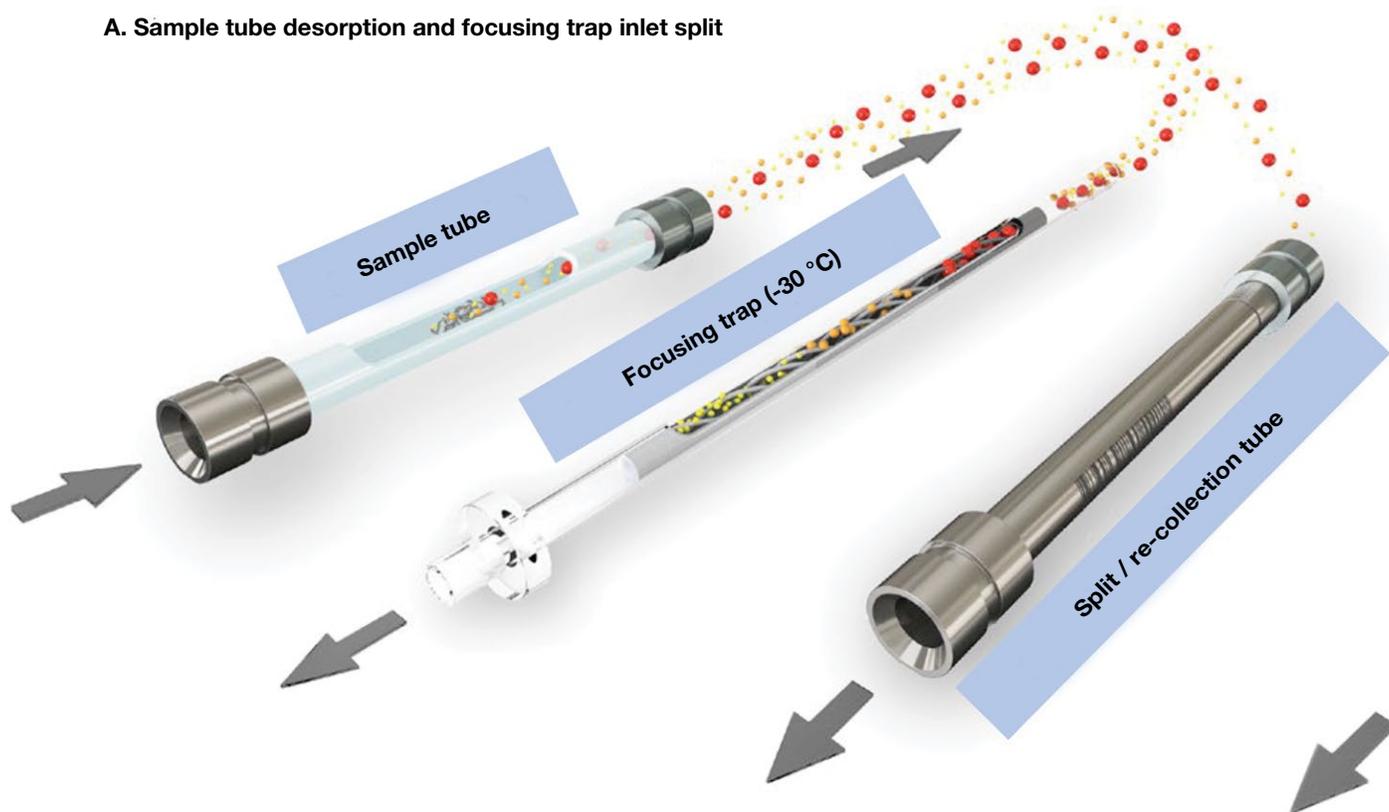


Figure 2. The calibration and control standard are loaded on to the Tenax standard tubes using a Calibration Solution Loading Rig (CSLR): [A] CSLR and connections; [B] illustration of standard injection and the distribution of the standard solution when using the CSLR standard loading rig

A. Sample tube desorption and focusing trap inlet split



B. Focusing trap analyte release and focusing trap outlet split

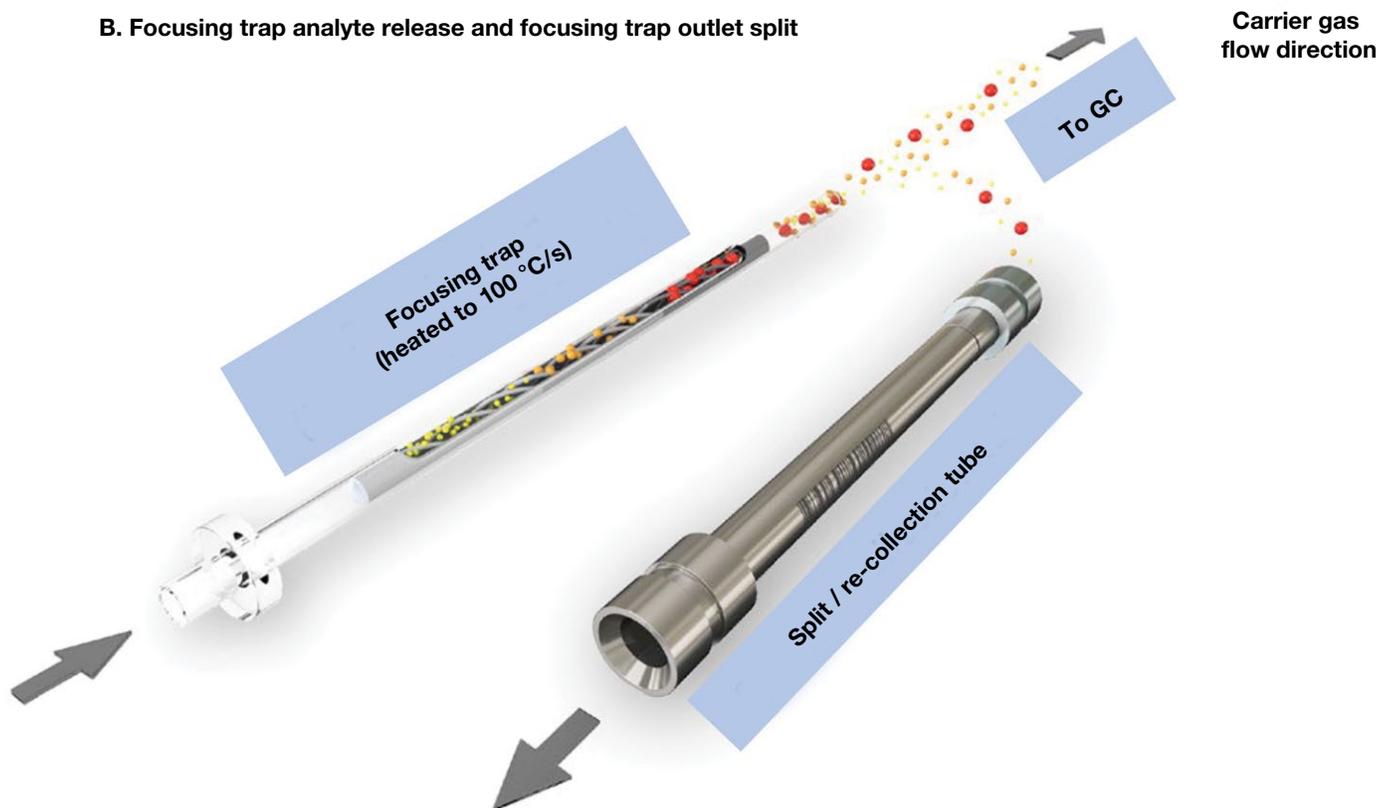


Figure 4. Schematic showing the thermal desorption operation, using a Markes TD100-xr automated thermal desorption system.⁷ [A] sample desorption in a flow of carrier gas where analytes are swept from the sample tube onto an electrically cooled focusing trap held at -30 °C. Samples can also be split and re-collected onto a clean sorbent tube at this stage; [B] focusing trap analyte release, with rapid heating (up to 100 °C/s), with a reverse carrier gas flow to transfer the concentrated analytes from the focusing trap to the GC column. Samples can also be split and re-collected onto a clean sorbent tube at this stage.

Compound separation was achieved using a Thermo Scientific™ TRACE™ TR-5MS GC 30 m × 0.25 mm i.d. × 0.25 µm film capillary column (P/N 260F142P).

Additional instrument parameters are listed in Tables 2, 3, and 4.

Table 2. Thermal desorption conditions

TD 100 system parameters	
Focusing trap	General-purpose hydrophobic (Markes P/N U-T2GPH-2S, containing Tenax TA – graphitized carbon black)
Flow path temperature	200 °C
Desorption time and temperature	30 min at 90 °C (VOC) 60 min at 120 °C (FOG/SVOC)
Trap low temperature	-30 °C
Trap high temperature	300 °C
Split ratio (high)	Desorption: 4.2:1 Injection: 27:1 Total: 113:1
Split ratio (low)	Desorption: 2.1:1 Injection: 15.6:1 Total: 32.8:1

Table 3. GC conditions

TRACE 1310 GC system parameters			
Inlet type/temperature	SSL/200 °C		
Carrier gas, flow rate, mode	He, 1.2 mL/min, constant flow		
Purge flow	5 mL/min		
Column	TRACE TR-5MS 30 m x 0.25 mm i.d. x 0.25 µm		
Oven temperature program - VOC			
	Rate (°C/min)	Target temp. (°C)	Hold time (min)
Initial	-	40	2.0
Stage 1	3	92	0.0
Stage 2	5	160	0.0
Final	10	280	10.0
Oven temperature program - FOG			
	Rate (°C/min)	Target temp. (°C)	Hold time (min)
Initial	-	50	2.0
Stage 1	25	160	0.0
Final	10	200	30.0

Table 4. Mass spectrometer conditions

ISQ 7000 MS conditions	
Transfer line temperature	280 °C
Ionization mode	EI (Thermo Scientific™ ExtractaBrite™)
Ion source temperature	280 °C
Electron energy	70 eV
Emission current	50 µA
Scan time	0.2 s
Acquisition mode	Full scan (m/z 29–450)

Data processing results and discussion

Customization of data collection parameters, processing methods, and reports for the VOC and FOG methodologies was made possible using Chromeleon CDS software, version 7.2

Compound identification was accomplished using comparative spectral evaluation against the NIST library, with additional classification against hazard lists such as REACH, CLP, and GADSL (Global Automotive Declarable Substance List).⁹

Tailoring of processing methods and reports to individual methods using Chromeleon software ensures accuracy from run to run and simplifies adoption of new analytical techniques for all skill levels.

Control standard

To assess the performance of the TD-GC-MS system, the control standard mix was prepared, loaded on to a Tenax standard tube and analyzed as detailed. A typical total ion current (TIC) full scan chromatogram is shown in Figure 5 with excellent chromatographic separation and narrow peak widths for all compounds, confirming a sample transfer capable of preserving the column efficiency.

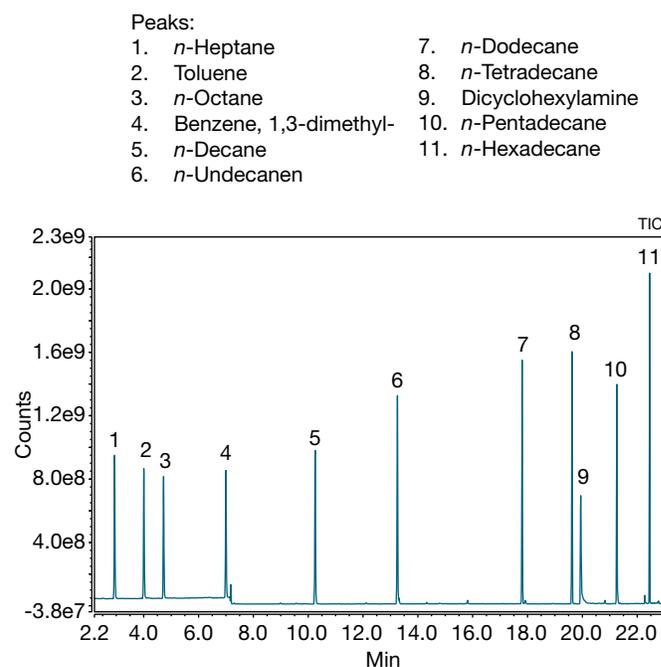


Figure 5. Control standard full scan EI TIC (m/z 29–370), with excellent chromatographic separation and narrow peak widths

Semi-quantification of VOC and FOG/SVOC in automotive interior material

VOC testing

For VOC analysis, the sample is desorbed at 90 °C for 30 minutes. The total VOC value is determined by the total area of all chromatographic peaks integrated from the start of the chromatogram to the retention time of pentacosane (*n*-C25). Each compound is quantitated as micrograms of toluene equivalents per gram of sample. The toluene standard TIC chromatogram is shown in Figure 6.

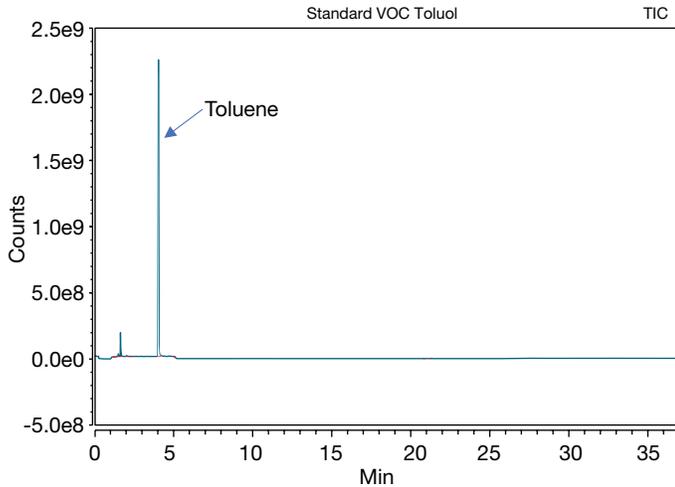


Figure 6. Standard TIC chromatogram for toluene (2 µg injected)

The VOC concentration of the sample is then calculated using the response factor for toluene using formula [1], with VOC emission levels calculated according to equation [2].

$$R_f = \frac{\mu\text{g toluene}}{A_T} \times 10^6 \quad [1]$$

$$C_{\text{VOC}} = \frac{R_f \times A}{1000 \times M_s} \quad [2]$$

A = Sample, chromatographic total peak area integration from start of the chromatogram to *n*-C25 (area counts)

A_T = Toluene reference chromatographic peak area (area counts)

M_s = Weighted sample mass (mg)

C_{VOC} = VOC concentration in the sample (µg/g)

R_f = Response factor of the toluene reference

SVOC (FOG) testing

After first carrying out a VOC run as described, the sample is left in the desorption tube to cool down to ambient temperature, immediately following the FOG run is carried out as described, starting with the temperature raised to 120 °C for 60 min. The total SVOC (FOG) value of a sample is determined by the total area of all chromatographic peaks integrated between *n*-tetradecane (*n*-C14) and *n*-dotriacontane (*n*-C32). Each compound is quantified as micrograms of *n*-hexadecane equivalents per gram of sample. The hexadecane standard TIC chromatogram is shown in Figure 7.

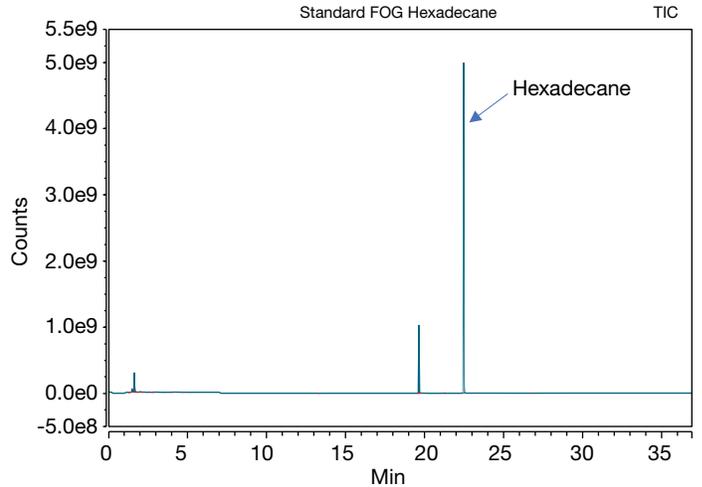


Figure 7. Standard TIC chromatogram for *n*-hexadecane (2 µg injected)

The SVOC (FOG) concentration of the sample is calculated using the response factor for hexadecane using formula [3], with SVOC (FOG) emission levels calculated according to equation [4].

$$R_f = \frac{\mu\text{g hexadecane}}{A_H} \times 10^6 \quad [3]$$

$$C_{\text{SVOC (FOG)}} = \frac{R_f \times A}{1000 \times M_s} \quad [4]$$

A = Sample chromatographic total peak area, integrated from *n*-C14 to *n*-C32 (area counts)

A_H = Hexadecane reference chromatographic peak area, (area counts)

M_s = Weighted sample mass (mg)

$C_{\text{SVOC (FOG)}}$ = SVOC (FOG) concentration in the sample (µg/g)

R_f = Response factor of the *n*-hexadecane reference

Samples of automotive interior material were prepared and analyzed for VOC and FOG/SVOC as detailed. Examples for chromatograms achieved for samples of thermoplastic polyurethane and polyurethane foam samples are shown in Figure 8.

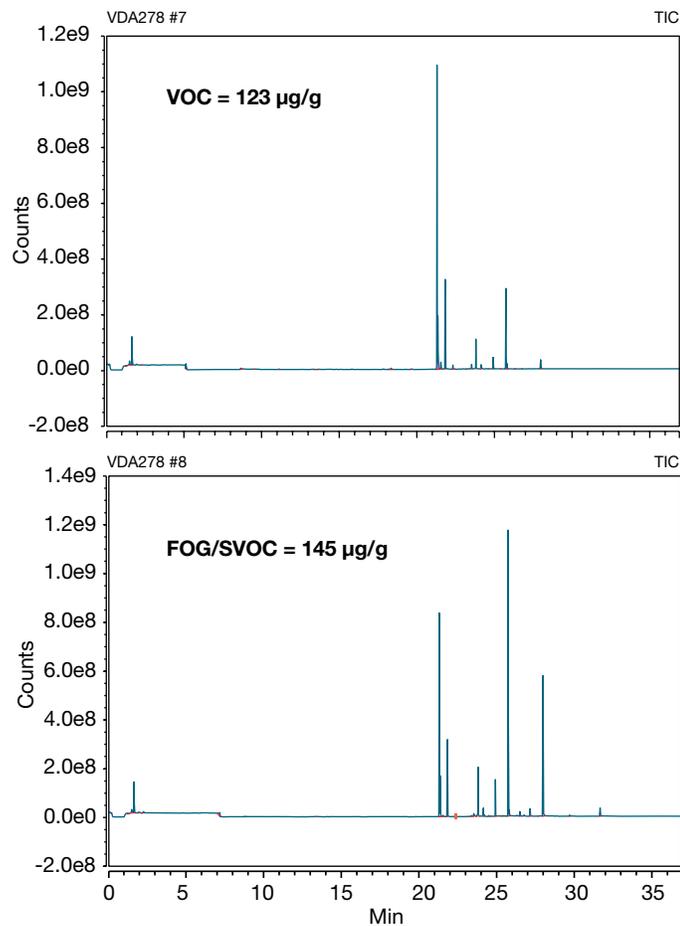
NIST library search report

The VDA278 method requires that all substances identified at levels $\geq 1 \mu\text{g/g}$ should be identified, which can be achieved using Chromeleon CDS report designer. An example of a generated report is shown in Figure 9, where the table is filtered by custom conditions to show only peaks $\geq 1 \mu\text{g/g}$, names and CAS numbers are identified and imported against a NIST library search, and matched

components are automatically compared against the Global Automotive Declarable Substance List (GADSL)⁹ including additional classification and reason code.

Declarable substance classifications are reportable substances identified in the sample that are present in the GADSL with a classification of "P" (prohibited or regulated in at least one region/market) and/or "D" (declarable). Reason codes are used to explain why a substance is included in the GADSL, and each declarable substance identified is listed with the appropriate reason code, "LR" (legally regulated), "FA" (for assessment) and "FI" (for information).

[A] Thermoplastic polyurethane sample



[B] Polyurethane foam sample

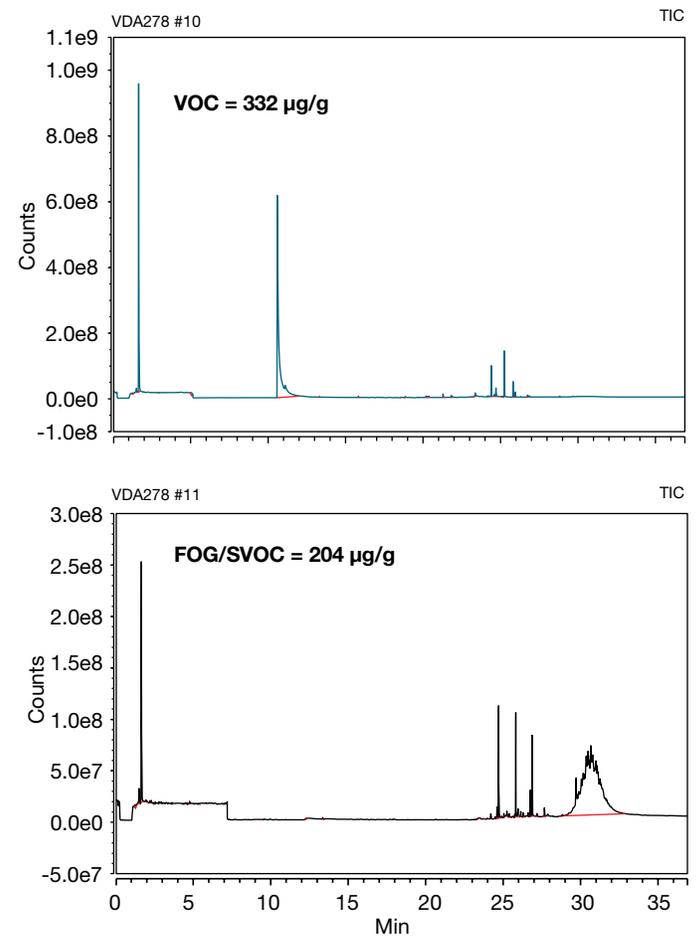
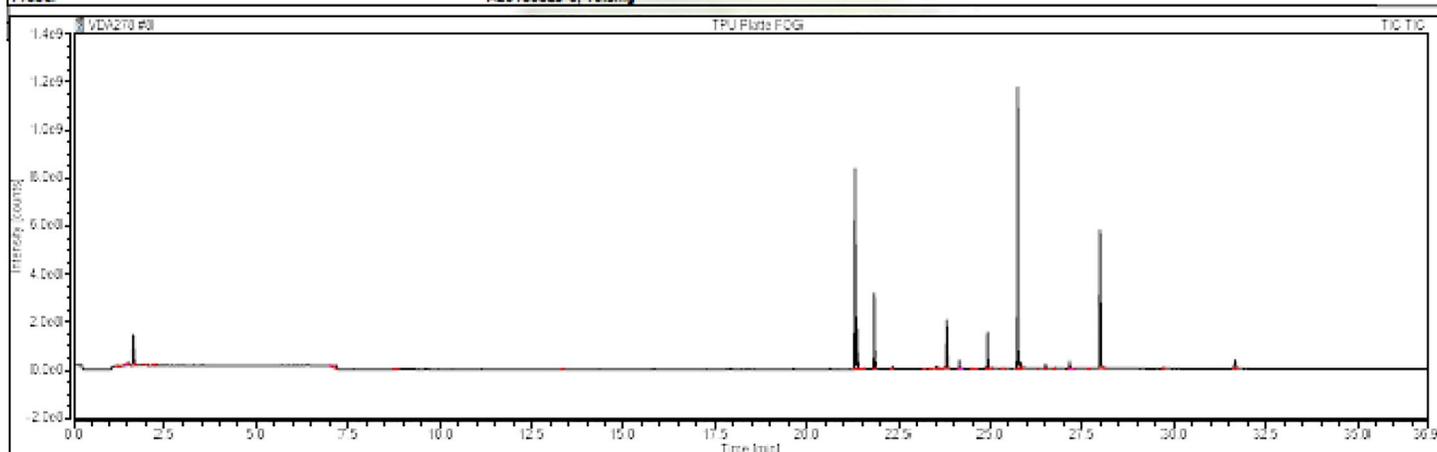


Figure 8. TIC chromatograms for [A] a thermoplastic polyurethane sample, and [B] a polyurethane foam sample, annotated with VOC and FOG/SVOC results ($\mu\text{g/g}$)

Emission investigation thermal desorption			
Injection Details			
Probe name:		Run time (min):	36.66
Val Number:	6	Injection volume (µL):	20.00
Type:	Unknown	Calibration level:	
Date /time:	16/Apr/16 21:48	Factor:	1.0000
Instrument method:	VD4275kurz	Weight (mg):	10.3
Processing method:	VD4275 FOG.pld	Cal. RF (C16):	6192
Probe:	A20160629-6, 10.3mg		



	Area FOG analysis	Emission FOG
		[µg/g] C14-C32
Total	73024729	145

Integration Results													
Name	Retention Time	CAS Number	M1	M2	M3	M4	M5	Rel.Area	Amount	SI	Listed?	Class.	Reason
	min							%	µg/g (C14-C32)				
Butylated Hydroxytoluene	21.313	128-37-0	205	57	220	41	145	23.90	37.747	957	Yes	D	FI
2-Butenoic acid, 2-methyl-, 4-methylpentyl ester, (E)-	21.368	94135-07-6	55	111	129	41	83	5.58	8.810	590	No	-	-
1,3-Dioxolane, 2-methyl-2-(4-methyl-3-methylenepentyl)-	21.562	66972-05-2	74	87	41	43	55	0.24	0.384	232	No	-	-
1,6-Dioxacyclododecane-7, 12-dione	21.838	777-95-7	55	54	41	84	100	8.74	13.814	916	No	-	-
1-Butanol, 4-(hexyloxy)-	22.333	4541-13-3	71	41	42	55	43	0.31	0.495	735	No	-	-
1-Tetradecene	23.163	1120-36-1	55	41	43	69	83	0.08	0.120	727	No	-	-
p-Anisic acid, 4-nitrophenyl ester	23.375	0	135	107	41	136	43	0.08	0.133	761	No	-	-
Tricyclo[3.3.1.1(3,7)]decanone, 4-iodo-, (1a,3b,4b,5a,7b)-	23.442	56781-86-3	107	135	149	121	55	0.10	0.163	402	No	-	-
Tridecanic acid, methyl ester	23.536	1731-88-0	74	87	43	41	55	0.35	0.552	802	No	-	-
Tricyclo[3.3.1.1(3,7)]decanone, 4-iodo-, (1a,3b,4b,5a,7b)-	23.667	56781-86-3	107	149	121	55	77	0.16	0.246	524	No	-	-
p-Anisic acid, 4-nitrophenyl ester	23.743	0	135	107	41	136	91	0.12	0.196	735	No	-	-
1-Azabicyclo[3.1.0]hexane	23.811	285-76-7	55	41	83	82	111	4.63	7.313	509	No	-	-
Benzene, 1,1'-[1,2-ethanedylbis(oxy)]bis-	24.150	104-66-5	77	65	121	120	91	0.76	1.197	888	No	-	-
Phenanthridine	24.213	229-87-8	179	178	89	180	151	0.15	0.240	893	No	-	-
Propane, 2-methyl-1-nitro-	24.488	625-74-1	149	57	41	76	104	0.07	0.118	445	No	-	-
1-Hexadecanol	24.615	36653-82-4	55	41	83	43	69	0.07	0.113	876	No	-	-
Hexadecanoic acid, methyl ester	24.874	112-39-0	74	87	43	55	41	0.11	0.180	900	No	-	-
4-(t-Butyl)benzaldehyde	24.920	939-97-9	277	57	147	41	219	2.97	4.691	329	No	-	-
Undecanoic acid	25.056	112-37-8	149	41	43	73	60	0.12	0.189	609	No	-	-
Heptadecane	25.306	629-78-7	57	43	71	41	85	0.09	0.139	609	No	-	-
1-Hexyl-2-nitrocyclohexane	25.416	118252-04-3	43	41	55	57	60	0.08	0.129	303	No	-	-
1,2-Pentadiene, 4-methoxy-4-methyl-	25.742	49833-91-2	71	42	41	73	55	22.83	36.060	319	No	-	-
Acetic acid, trifluoro-, 3,7-dimethyloctyl ester	25.818	28745-07-5	57	41	55	43	71	0.82	1.290	661	No	-	-
Heptadecane	26.309	629-78-7	57	43	71	85	41	0.07	0.112	826	No	-	-
Pyruvic acid, butyl ester	26.500	20279-44-1	43	41	185	129	57	0.45	0.705	413	No	-	-
Dodecane, 2,6,10-trimethyl-	26.762	3891-98-3	57	43	71	41	85	0.16	0.256	817	No	-	-
Hexanedioic acid, bis(2-ethylhexyl) ester	27.152	103-23-1	55	129	41	57	70	0.83	1.311	891	Yes	D	FI
Decane, 3,8-dimethyl-	27.203	17312-55-9	57	43	71	85	99	0.05	0.084	723	No	-	-
Pyroole, 1-(benzylideneamino)-	27.253	24046-22-8	77	65	39	51	94	0.07	0.103	366	No	-	-
Acetic acid, trifluoro-, 3,7-dimethyloctyl ester	27.673	28745-07-5	57	43	55	41	71	0.08	0.126	667	No	-	-
Tetrahydrofuran	27.982	109-99-9	71	42	41	72	43	15.45	24.405	653	No	-	-
2-Methyl-3-(3-methyl-but-2-enyl)-2-(4-methyl-pent-3-enyl)-oxetane	29.714	0	69	81	41	67	95	0.23	0.357	614	No	-	-
Tetrahydrofuran	31.662	109-99-9	42	71	41	72	43	2.05	3.241	744	No	-	-
Min									0.084	232			
Max									38	957			
Sum (C14-C32)									145				

Figure 9. Using Chromeleon software, users can automatically screen through large lists of samples to produce detailed reports. Here, the “emission investigation thermal desorption” report is shown for a thermoplastic polyurethane sample, including injection details, chromatogram, compound ID list, integration details, quantitative results, and for compounds identified present in the GADSL, classification “D” (declarable) and reason code “FI” (for information).

Conclusion

The results generated provide a representative profile of VOC content for the tested automotive material, referencing requirements in the VDA278 method, stating that all substances identified at levels ≥ 1 $\mu\text{g/g}$ should be identified. The Markes thermal desorption system combined with a TRACE 1310 GC and the ISQ 7000 single quadrupole MS deliver an ideal solution for the analysis of VOCs and SVOC (FOG) from automotive interior materials as demonstrated through the following:

- Ability to add internal standard to the focusing trap ensuring data quality
- An electrically-cooled focusing trap, which efficiently removes water and avoids the inconvenience and expense of liquid cryogen
- Full EPC control of carrier gas through the TD–GC–MS system that permits optimum retention time stability and improved qualitative identification of minor compounds
- Integration of Markes TD system via TRACE 1310 modularity providing efficient sample transfer, allowing highly sensitive determination of a wide range of VOC and SVOCs that is accurate and repeatable
- Consolidated control of both the TD and GC-MS along with fully customized data processing, easily automated data review and reporting using Chromeleon CDS software, allowing confident compound identification and data accuracy at any operator skill level

For further detail of the benefits of our combined TD-GC-MS solutions for automotive volatile emissions, please see [Thermo Fisher Scientific Technical Note 73565](#), Automotive Interior VOC and FOG emissions: A technical guide for analysis of interior materials by direct desorption TD-GC-MS in accordance with VDA 278.

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