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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Goal

This document provides a guide for carrying out the quantitation of volatile and condensable emissions in car trim in accordance with VDA 278, using the combined Thermo Scientific™ / Markes International TD-GC-MS system (Figure 1). In addition to describing the entire TD–GC–MS analytical process, advice on targeted aspects of sample preparation and the analytical procedure are included.

Introduction

VDA 278 describes procedures for the determination of volatile organic compounds (VOCs) and semi-volatile "fogging" (FOG) compounds in car-trim materials, along with associated standards to ensure instrument performance and allow semi-quantitation.[1]

Sampling is carried out using direct desorption, which involves placing a specified mass of the material directly into an empty 3½″ × ¼″ glass thermal desorption tube, followed by heating in a flow of gas to release the analytes.

The analytes are then collected on a narrower focusing trap, which is rapidly heated in a flow of gas to transfer the analytes to the GC instrument (Figure 2).

Figure 1. The combined Thermo Scientific / Markes International TD-GC-MS system

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VDA 278 requires that two separate tests be carried out, on different (but equivalent) portions of the same sample:

- VOC analysis: this involves desorbing the sample at 90 °C for 30 minutes to quantify volatile compounds up to *n*-C_{25}. Each compound is quantified as micrograms of toluene equivalents per gram of sample.
- FOG analysis: this involves first carrying out a VOC run by desorbing the sample at 90 °C for 30 minutes, as described above (for each compound, the higher of the two VOC values is the one reported). FOG compounds (those with volatility range from *n*-C_{14} to *n*-C_{32}) are then determined by leaving the sample in the desorption tube and raising the temperature to 120 °C for 60 minutes. Each compound is quantified as micrograms of *n*-hexadecane equivalents per gram of sample.

The large number of samples required by VDA 278 makes an automated system essential, and Markes International's TD100-xr™ instrument offers sequential unattended analysis of up to 100 samples and elimination of the cost of liquid cryogen through the use of electrical cooling. Markes' systems also allow samples to be split and re-collected onto a clean sorbent tube at the tube desorption and/or trap desorption stages (Figure 2), providing "insurance" against failed runs and simplifying demonstration of complete analyte transfer and absence of analytical bias.

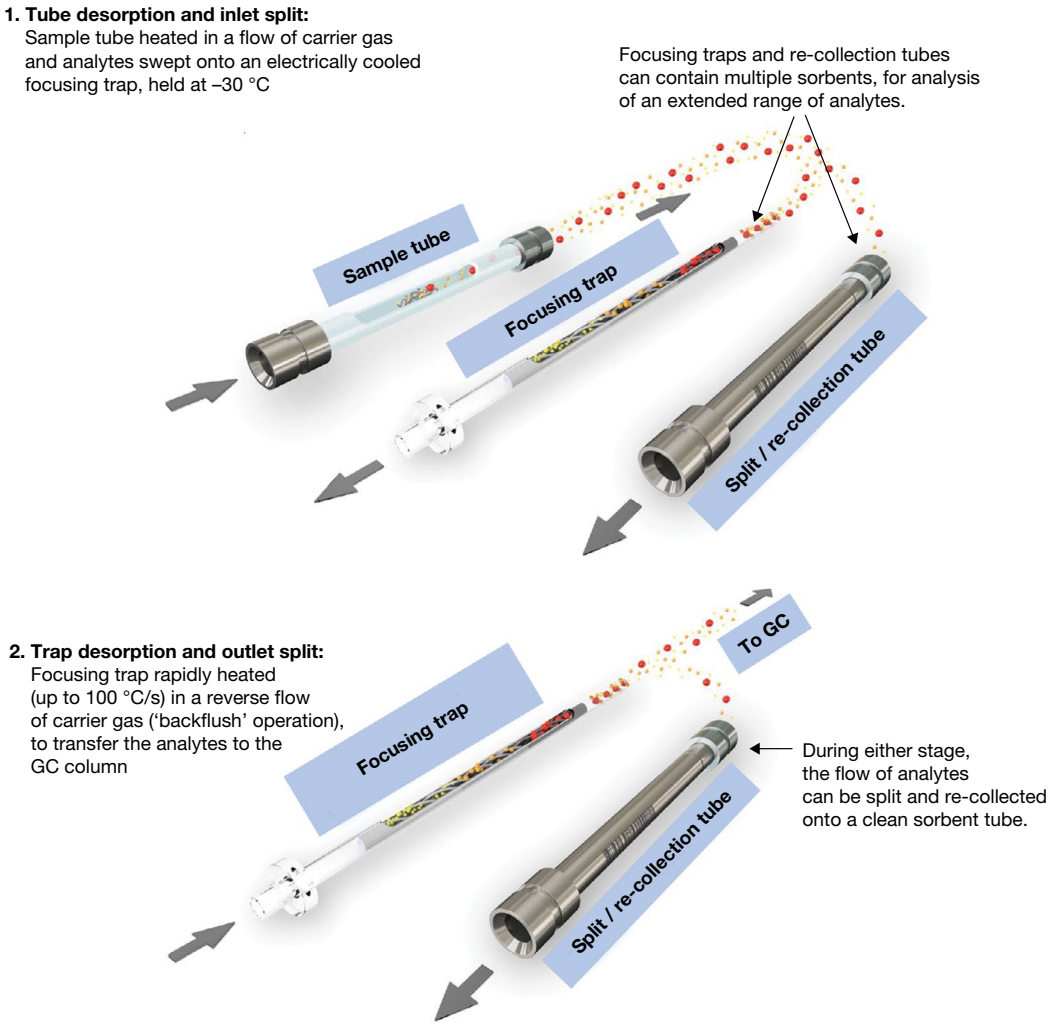


Figure 2. Schematic showing the two-stage operation of direct thermal desorption in accordance with VDA 278, as used in Markes' instruments

Experimental conditions

Tube conditioning

VDA 278 requires the use of two types of thermal desorption tubes:

- Stainless steel Tenax® TA tubes for calibration and system performance checks
- Empty glass tubes for sample desorption, with a restriction 15 mm from one end

Tubes must be completely free from contamination, and should be checked for cleanliness, and then capped as required before use.

The method does not specify conditions for routine tube conditioning, but we would recommend conditioning both the Tenax TA sorbent tubes and empty glass tubes for 2 hours at 320 °C in a 50 mL/min flow of inert gas (nitrogen or helium). Conditioning can either be carried out on the system or using a dedicated tube conditioner such as Markes International's TC-20™, which allows batches of 20 tubes to be conditioned simultaneously, saving instrument time.

If glass tubes become physically contaminated, they should be left to soak in an alkaline cleaning solution for several hours, and preferably overnight (most commercial washing-up liquids mixed with water will suffice). The tubes should be rinsed thoroughly, first with hot water for at least one minute and then with deionized water. The tubes should then be dried at 105 °C for 45 minutes, either in a drying oven or on a TC-20. Once conditioned, the tubes should be sealed at both ends using brass long-term storage caps fitted with PFTE ferrules. Caps should be finger-tightened, and then tightened by a further quarter-turn using a CapLok™ tool. Take particular care not to over-tighten caps on glass tubes, because damage to the tube (and injury) may result.

Samples

Sample storage

When choosing a sample, it is important to ensure that it is representative of the batch. The material should be sealed (air-tight) within 8 hours of production, making sure that no contamination occurs. The method suggests that to seal the sample it should either be welded inside aluminium foil or wrapped twice in thick (30 µm) aluminium foil, ensuring that the edges are folded several times. Samples should then be sealed in a polyethylene bag and sent to the laboratory.

Until the samples are analyzed they should be kept at temperatures below 23 °C. Prior to being analyzed, the samples should be stored uncovered for 7 days. If for any reason it is necessary to deviate from the conditions stated, this should be recorded and included in the report for the samples affected.

Minimizing contamination

The sample preparation stage is when contamination of the test material is most likely to occur. Steps to ensure minimal contamination include:

- Do not prepare samples in a room where solvents are present, or in areas where there are likely to be high quantities of VOCs/SVOCs in the atmosphere, such as wet labs or areas containing LC or HPLC equipment.
- When handling the sample, use clean metal tweezers or similar.
- When cutting the sample, use a clean scalpel.
- Weighing boats should be low- or non-emitting materials, such as glass, metal, or ceramic.
- If quartz wool is being used to keep the material in place, it should be conditioned prior to use and not re-used.
- Avoid touching the ends of the tube with bare hands, as this can result in contamination by squalene (which is naturally present on the skin).
- Ideally at least one tube out of a batch should be analyzed empty prior to use, to assess levels of cleanliness.

Sample preparation

Method stipulations

Before a sample is placed in a tube, its mass must be measured. The mass and preparation technique stipulated by VDA 278 vary according to the substance being analyzed and are summarized in Table 1.

Table 1. Stipulations of VDA 278 regarding sample size and preparation

Material type	Sample size	Remarks
Foam	15 ± 2 mg	The sample should be taken from the surface of the material (because of the influence of the release agent) and packed loosely in the tube.
Fiber-based materials*	60 ± 20 mg	Thicker sheets must be split parallel to the sheet surface.
Films	30 ± 5 mg	The material should be cut into strips.
Leather	10 ± 2 mg	Most of the reverse side of the leather sample should be removed, in order to focus on the effects of the treated side.
Paint	50 ± 5 µm film thickness	Paint should be applied to aluminum foil and dried in accordance with production conditions.
Adhesives or similar	30 ± 5 mg	The adhesive should be applied to aluminum foil at the typical thickness used for the application, and then cut to the appropriate dimensions.

* For example, fiberglass or carbon-fiber-reinforced polymer.

Cutting the sample

When cutting the two portions of the sample (for the VOC and FOG runs, respectively), the aim should be to achieve samples that are representative of the whole, rather than necessarily the largest possible surface area. A good way of doing this is to start by cutting the sample to a width of 3 mm (to ensure a comfortable fit within the glass tube, which has an internal diameter of 4 mm). The length can then be selected to achieve the correct mass, so long as it is not significantly longer than 4 cm (this allows for a little movement within the 6 cm heated zone of the thermal desorber).

Sample loading

Once the sample has been prepared and weighed, it needs to be placed carefully into the tube. The easiest way to do this is to use a pair of tweezers to hold the sample, and then use a long, thin piece of metal to guide it into place.

The glass tubes suggested by the method have a restriction 15 mm from the front end to keep the sample in place, and a plug of conditioned quartz wool should be placed on the other side of the sample for this reason. Retaining springs can be used to keep the glass wool in place. (Conditioning is carried out by inserting a large quantity of quartz wool, with springs, into an empty tube and conditioning it for 30 minutes at 300 °C.)

Samples that could be swept into the flow path during desorption (such as viscous liquids, gels, and powders) should also have conditioned quartz wool placed in front of them. Solid, single-piece samples will not require this precaution if they have been cut as described above.

However, issues can arise from the use of quartz wool for this process because it is able to trap semi-volatile analytes such as those often seen in the FOG runs (indeed, it is used as a TD sorbent for high-boiling compounds). Runs using quartz wool can therefore return FOG values lower than those that do not, giving misleading emission values. We therefore suggest only using quartz wool when the instrument flow path is at risk from becoming contaminated.

Once the sample has been securely placed inside the tube, a photograph should be taken that shows the sample in the tube, details of the sampling location, and the laboratory ID number. This photograph is then included in the laboratory test report.

Preparation of standards

Two standards are required for VDA 278 – a calibration standard and a control standard. Details of these are provided below.

Calibration standard

The calibration standard contains toluene and *n*-hexadecane in methanol. The suggested procedure for making a 0.5 µg/µL solution used for the system response calibration is to weigh toluene (25 ± 0.1 mg) and *n*-hexadecane (25 ± 0.1 mg) into a 50 mL measuring flask, which is then filled with methanol to just below the calibration mark. The flask should be sealed, shaken well, filled with methanol up to the calibration mark, and shaken again.

Control standard

The control standard (also called a control solution or mix) contains a range of compounds used to check the performance of the TD–GC–MS system on the column used, across a broad analyte range.

This standard is commonly purchased to ensure that the concentrations are correct. The method suggests a concentration of 0.112 µg/µL, with 4 µL of this solution being spiked onto a Tenax TA sorbent tube. However, we find that this gives rise to an unacceptably large amount of solvent on-tube, which if not dealt with can cause poor reproducibility and results that are skewed in favor of the heavier compounds in the mixture. Dry-purging prior to analysis resolves this issue, but it is still desirable to minimize the amount of solvent on-tube to reduce the dry-purge time.

Consequently, it is advisable to depart from the method slightly, by using a 0.45 µg/µL standard and spiking 1 µL of this onto the tube. This results in the same mass of compounds on-tube but reduces the amount of time required for dry-purging.

A typical chromatogram of the standard is shown in Figure 3.

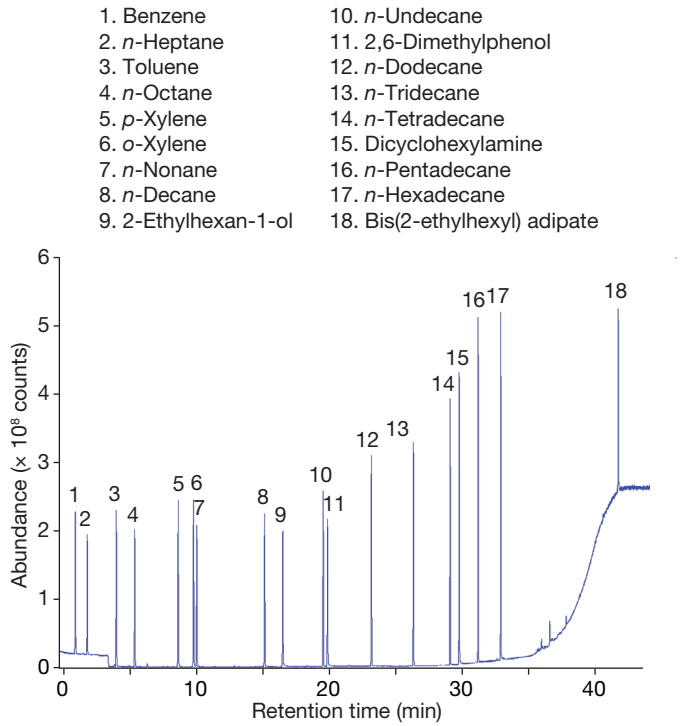


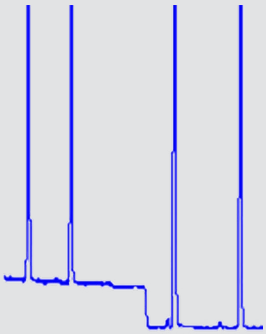
Figure 3. Typical chromatogram of the control standard

Spiking the standards onto tubes

The calibration and control standards should be spiked onto a sorbent tube in a stream of analytical-grade nitrogen, using a Calibration Solution Loading Rig (CSLR™, from Markes International) or similar apparatus that allows a known volume of gas to be purged through the

Why is the baseline elevated at the start of the run?

A section of elevated baseline, often called an "air step," can sometimes be seen at the start of the GC run. This panel answers some commonly asked questions about this phenomenon.



What is the cause of the elevated baseline?

The elevated baseline arises because of a small increase in the amount of air in the system, giving rise to ions from carbon dioxide, oxygen, and nitrogen. It is not associated with a system leak.

Do all TD systems show an elevated baseline?

Yes – to a greater or lesser extent.

Instruments from other TD manufacturers, which rely on modifications to the GC injection port to desorb samples, supply carrier gas to the GC column via this inlet, and so the flow path is always in-line with the column. Any extra air present as a result of the extra TD flow path is constantly directed to the GC column throughout the analysis. There is therefore no change of flow path, with the result that the baseline is consistently elevated.

On Markes' TD systems the valve operates to switch the carrier flow from the 'bypass' to feed the column via the TD focusing trap. This only happens during trap desorption, meaning that the elevated baseline is only present at the start of the analysis.

Does the air step affect quantitation?

No, the elevated baseline does not affect quantitation, and peaks can be integrated as normal. This is because the baseline is simply higher for this portion of the chromatogram.

Are there any benefits from having a reduced section of elevated baseline?

Yes – the main benefit is that the lifetimes of the column and detector are extended, because of the significant reduction in the amount of air reaching them.

There are also other advantages resulting from the way the valve operates in Markes' TD systems. One of these is the ability to operate in "overlap mode," in which one sample is desorbed onto the focusing trap while the previous GC analysis continues. The resulting improvement in sample throughput is especially valuable when running VDA 278.

tube during and after injection (typically 100 mL/min for ~3 minutes – see Markes Application Note 007). This ensures that all the compounds in the solution are adsorbed onto the sorbent and that any excess solvent is purged from the tube before it is analyzed.

Analytical conditions

TD

VDA 278 cites three TD methods – "VOC," "FOG," and "calibration," which differ only in the desorption temperature and the tube and trap desorption times. Conditions for use on Markes' TD systems are shown in Table 2. The VOC and FOG methods are used for the respective runs on the two portions of the test sample, and the "calibration" method is used for the system suitability check, the system response calibration, and the control run on Tenax TA.

Table 2. TD conditions for the VOC, FOG and calibration runs

	VOC	FOG	Calibration
Cold trap		General-purpose hydrophobic (P/N 76473-0931)	
Pre-purge		1 min, trap in line, no split	
Desorption temperature	90 °C	120 °C	300 °C
Desorption time	30 min	60 min	10 min
Desorption flow rate		42 mL/min	
Inlet split		42 mL/min	
Trap low		–30 °C	
Trap high		300 °C	
Trap hold time	3 min	5 min	10 min
Outlet split		42 mL/min	
Trap heating rate		Max.	
Flow path temperature		200 °C	
Split ratio		66.6:1	

Although the method cites a split ratio of 66.6:1, there is no indication whether this should be applied at the inlet (tube desorption) and/or the outlet (trap desorption) stages. However, our experience is that materials analyzed for the first time should always be analyzed with both an inlet and an outlet split. If an inlet split is not used, all the analytes will be transferred to the cold trap, which will often result in trap overload because of the exhaustive nature of VDA 278 and contamination of subsequent runs.

We always recommend running VDA 278 with an outlet split, because this results in increased linear velocity during trap desorption, which means that the analytes reach the column head in a narrower band, greatly improving the chromatography. The outlet split also reduces the risk of column overload (and its associated risk of poorer quantitation and peak shape).

GC–MS

VDA 278 uses two GC methods – "VOC" and "FOG." These differ only in the oven program and are used for the respective runs on the two portions of the test sample, and for the system suitability check and the system response calibration (with toluene and *n*-hexadecane). The "VOC" method is used for the control run. Conditions are shown in Table 3. The Markes TD100-xr is seamlessly connected to the Thermo Scientific™ TRACE™ 1300 series Gas Chromatograph via the modular inlet configuration. Data connection and instrument parameters are processed through the Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, allowing a single software for ease of adoption and unified instrument control.

Table 3. Thermo Scientific™ ISQ™ 7000 GC–MS system conditions for VOC and FOG methods

	VOC	FOG
GC Column		
Column	J&W™ Ultra™ 2	
Length	50 m	
Internal diameter	0.32 mm	
Film thickness	0.52 µm	
Column flow	1.3 mL/min	
GC oven program		
Start temperature	40 °C	50 °C
Hold	2 min	2 min
Ramp 1	3 °C/min	25 °C/min
Temperature 2	92 °C	160 °C
Ramp 2	5 °C/min	10 °C/min
Temperature 3	160 °C	—
Ramp 3	10 °C/min	—
Final temperature	280 °C	280 °C
Final hold	10 min	30 min
MS		
Scan rate	>3 scans/s	
Mass range	*m/z* 29–450	
Transfer line	280 °C	
Ion source	ExtractaBrite™ ion source	
Ionization mode	Electron ionization	
Source temperature	280 °C	
Electron energy	70 eV	
Emission current	50 µA	
Acquisition mode	Full Scan	

Analytical procedure

The sections below describe the individual parts of the analytical procedure, in the order that they should be conducted.

Pre-run system checks

The system to be used should be clean and fit for purpose. If it has not been used for an extended period, or if it has just been used for a different method or type of analysis, then the following process should be carried out.

1. Tube blank: an empty, clean sorbent tube should be run. If the chromatogram is acceptable, then proceed with the system suitability check (next section). If contamination is detected, then proceed to step 2.

2. Trap fire blank: carrying out a trap fire shows any interferences in the analytical path between the trap and the heated valve. If the interference disappears, then the source must be between the tube and the valve. If not, then proceed to step 3.

3. Column blank: running the GC on its own with no injected sample enables assessment of whether there is any carryover on the column. This also gives a reference point for the background and can be used for troubleshooting at a later stage. If the interferences are being generated by the column, then the column should be "baked out" for 1 hour and then re-tested. If the interference is not on the column, then the trap should be conditioned.

For each of these troubleshooting steps, the method employing the highest temperatures should be used (Table 4).

Table 4. Suggested conditions for the pre-run system checks

Step	Check	TD method	GC method
1	Tube blank	Calibration	VOC
2	Trap fire blank	Calibration	VOC
3	Column blank	—	VOC and FOG

The performance of the Thermo Scientific™ ISQ™ 7000 mass spectrometric detector should be periodically checked by means of mass and sensitivity tuning. An air/water check must also be performed periodically to test the integrity of the entire system.

System suitability check

Before any sample analysis takes place, the suitability of the system should first be checked by ensuring a linear response from the toluene and *n*-hexadecane calibration standard. The method does not specify an exact calibration range, but the standards should be within the range expected for the test material, and we would suggest that at least five points are used – for example, 0.01, 0.05, 0.1, 0.5, and 1 µg/µL. If this is followed, then the 0.5 µg/µL standards can also be used for the system response calibration. Two tubes should be spiked at each concentration so that the responses can be assessed under VOC and FOG conditions (Table 5).

Table 5. Run order for the system suitability check

Run no.	Sample	TD method	GC method	Conc. (µg/µL)
1	Toluene calibration	Calibration	VOC	0.01
2	Toluene calibration	Calibration	VOC	0.05
3	Toluene calibration	Calibration	VOC	0.1
4	Toluene calibration	Calibration	VOC	0.5
5	Toluene calibration	Calibration	VOC	1
6	*n*-Hexadecane calibration	Calibration	FOG	0.01
7	*n*-Hexadecane calibration	Calibration	FOG	0.05
8	*n*-Hexadecane calibration	Calibration	FOG	0.1
9	*n*-Hexadecane calibration	Calibration	FOG	0.5
10	*n*-Hexadecane calibration	Calibration	FOG	1

When good linearity has been achieved, the sample sequences can be carried out. We recommend that R^2 values should be ≥0.990.

Sample analysis

Setup in Chromeleon CDS software, the sequence for analyzing samples has ten runs and requires nine separate tubes (Table 6), six of which are packed with Tenax TA. The remaining three tubes are glass, of which two contain the two portions of the test sample, and the other functions as a blank (the same tube is used in runs 1 and 5). The following sections provide notes for each of the runs.

Blank run (runs 1 and 5)

This involves performing a "dummy run" with an empty glass tube, both before the system response calibration and before the test samples, in order to check for any memory (carryover) effects. The tubes should be identical to those containing the sample, so if quartz wool is being used in the test sample tubes, then it should also be in the blank tube.

Control run (runs 2 and 10)

This involves running the control standard, both before the first system response calibration and after the second system response calibration, as a check of performance and to flag up any chromatographic discrepancies, including analyte losses due to leaks.

Specific points are:

- All substances in the control standard must be clearly identified in the mass spectral library.
- The recovery rate of the individual substances in the check-standards under VOC conditions should be in the range 60–140%, with the exception of toluene, which should be 80–120%.
- It should be possible to see baseline separation between *o*-xylene and *n*-nonane.
- Severe peak tailing is an indication of activity in the flow path.
- If necessary, the retention times of the *n*-alkanes can be used to determine the retention indices of unknown substances, aiding identification.

If negative effects such as severe peak tailing, disruptive artefacts, or significant loss of substance occur, the system must be cleaned, and the GC column, focusing trap, transfer line or seals may need to be replaced. We recommend documenting the results of the control run for each sample series as part of quality control procedures. The peak area ratios, concentrations as toluene equivalents, and retention times can be used as control quantities.

System response calibration (runs 3, 4, 8, and 9)

This involves running toluene and *n*-hexadecane calibration standards (both at 0.50 µg/µL) on the instrument as part of the test run, before and after each set of test samples, to generate response factors used for quantitation.

If the peak areas of the calibration for either compound differ significantly between the start and end of the analysis, it can indicate that the system needs cleaning or re-tuning or that the results should be adjusted to account for the observed decrease in signal. We recommend a tolerance level of 20%.

Test samples (runs 5 and 6)

The two portions of the test sample are run in accordance with the VOC and FOG conditions, respectively, as described in Analytical conditions.

- The VOC analysis involves desorbing the sample at 90 °C for 30 minutes.
- The FOG analysis involves first carrying out a VOC run. The sample is then desorbed again at 120 °C for 60 minutes.

Because the FOG run has two desorption stages, two sets of VOC values are obtained. For each compound, the higher of the two VOC values is the one reported. Reproducibilities for the VOC value are generally below 15%.

Table 6. Run order for sample analysis.[a] If multiple analyses are required, then runs 5–7 can be repeated with multiple samples. However, we would recommend performing system response calibrations at least twice per day (once at the beginning of the day and once at the end of the day), to ensure accurate quantitation.

Run no.	Run name	Sample	Tube type	TD method	GC method	Conc. (µg/µL)
1	Blank run	—	Glass	Calibration	VOC	—
2	Control run	Control standard	Tenax TA	Calibration	VOC	0.45
3	System response calibration	Calibration standard (for toluene)	Tenax TA	Calibration	VOC	0.50
4		Calibration standard (for *n*-hexadecane)	Tenax TA	Calibration	FOG	0.50
5[a]	Blank run	—	Glass	VOC	VOC	—
6[a]	Test samples	Sample portion 1 (VOC)	Glass	VOC	VOC	—
7[a]		Sample portion 2 (FOG)	Glass	VOC + FOG	VOC + FOG	—
8	System response calibration	Calibration standard (for toluene)	Tenax TA	Calibration	VOC	0.50
9		Calibration standard (for *n*-hexadecane)	Tenax TA	Calibration	FOG	0.50
10	Control run	Control standard	Tenax TA	Calibration	VOC	0.45

Results and discussion

Once the sequence has been run, the results need to be quantified, to give total VOC (TVOC) and total FOG (TFOG) values.

VOC and FOG integration

The first step is to integrate the chromatograms within the limits given for each analysis, using toluene equivalents (to give TVOC values) or *n*-hexadecane equivalents (to give TFOG values):

- VOC: from the beginning of the chromatogram and the retention time for *n*-C_{25}
- FOG: between the retention times for *n*-C_{14} and *n*-C_{32}

To ascertain the limits for each run, a standard including *n*-C_{25} is run under VOC conditions, and a standard including *n*-C_{14} and *n*-C_{32} is run under FOG conditions. *n*-C_{14} (*n*-tetradecane) is included in the control standard, so if you already have this standard on hand then there is no need to make another one – it just needs to be run under FOG conditions. Once these values have been acquired, the chromatograms can be integrated.

Individual peak integration

The method requires that all substances at levels ≥1 µg/g should be listed separately, and the compound identity noted. The baseline should be known from blank runs carried out prior to sampling, and baseline compensation can be carried out manually or using software. If the sample is very complex, the method advises that individual peaks are ignored and the area above the baseline is integrated (Figure 4).

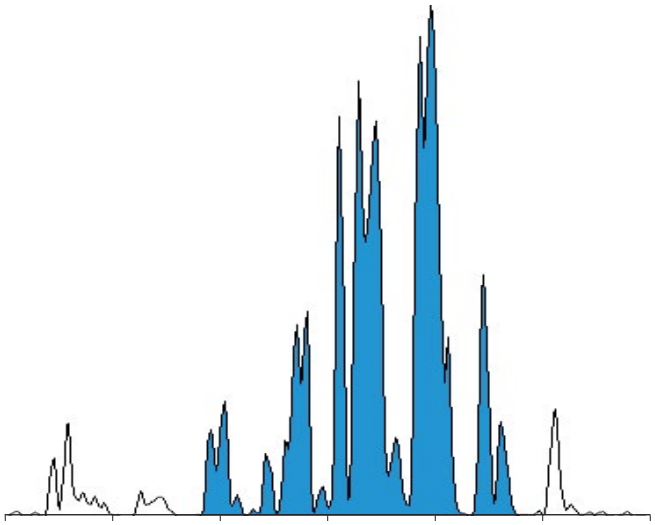


Figure 4. Integration of a portion of a complex chromatogram that has undergone dynamic baseline compensation (DBC) using Chromeleon software

- If the chromatogram contains "oil-humps" (accumulations of isomers that cannot be separated due to their chemical similarity), these should be treated as one peak and integrated from start to end (Figure 5, dark blue).
- Any "rider" peaks should be integrated separately (Figure 5, pale blue). The integration for these should not start at the baseline but rather from the point at which the peak protrudes from the "oil-hump."

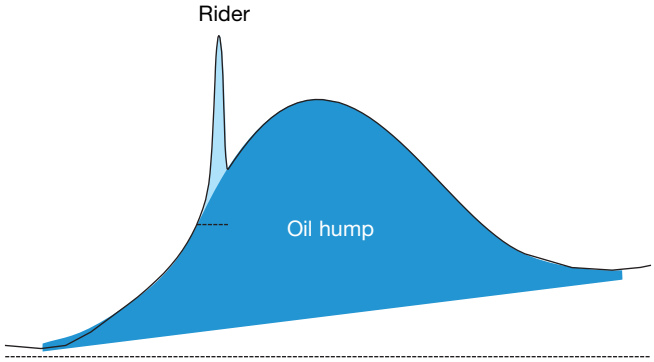


Figure 5. Integration of an oil-hump with a rider peak in Chromeleon CDS.

Quantitation

Once the chromatograms have been integrated, there are two methods to achieve quantitation – using response factors to give a semi-quantitative result (recommended by the method) and using a five-point calibration (not recommended). For completeness, both methods are explained below.

Using response factors

Although use of the response factor is only semi-quantitative, the resulting data is still meaningful even when the detector loses sensitivity (as might be expected when running samples for a long period without tuning).

To calculate emissions using the response factor:

- Calculate the total peak area for each of the runs.
- Calculate the response factor from the appropriate calibration compound (toluene for VOC and *n*-hexadecane for FOG), using Equation [1].

$$R_f = \frac{\text{Compound mass (µg)}}{\text{Peak area (counts)}} \times 10^6 \qquad [1]$$

- Insert the relevant values into Equation [2].

$$\text{Emmission (µg/g)} = R_f\,(\text{toluene, } n\text{-hexadecane}) \times \frac{\text{Peak area (counts)}}{\text{Compound mass µg} \times 10^3} \qquad [2]$$

Using a five-point calibration

Unlike quantitation using a response factor, the use of a five-point calibration graph is considered more rigorous because it allows accurate quantitation of results. However, ultimately it is still semi-quantitative, while being more time-consuming. In addition, the response (and therefore the values obtained) will fall over time, meaning that in order to maintain an accurate calibration, the instrument must be re-tuned and the five calibration standards must be run again, under both VOC and FOG conditions.

To calculate emissions using a calibration graph:

- Calculate the total peak area for each of the runs.
- From the calibration graph generate the trendline equation (Equation [3] and note the values for *m* (gradient) and *c* (intercept).

$$y = mx + c \qquad [3]$$

- Using the value for the total peak area (y_{total}), calculate the total mass of compounds in the analysis (x_{total}), according to Equation [4].

$$x_{total} = \frac{y_{total} - c}{m} \qquad [4]$$

- Now divide the total mass (µg) by the sample weight (g). This will give you the total TVOC or TFOG value in µg/g.

Qualitative analysis

Where possible, each peak representing a compound at ≥1 µg/g must be identified using the mass spectrum and confirmed by use of retention indices when possible. If a substance cannot be identified for certain, then it can be marked with "?" or reported as a compound type *(e.g.,* "tertiary alcohol") if the mass spectrum allows such a conclusion to be drawn. Examples of the use of these conventions are provided in Table 7.

Reporting of results

The structure of the report is described very thoroughly in the method. A complete report should contain:

- Sample information
- Two chromatogram data files of the VOC determination
- One chromatogram data file of the FOG determination
- Chromatogram data files of the blank runs
- Chromatogram data files of the calibration and control runs
- Spreadsheets with the individual VOC/FOG results
- Photographs of the samples in the tubes (see Sample loading)

Table 7. Examples of the substance classifications

Type of identification	Circumstances	Example text in report
Reliable identification	The mass spectrum of the compound matches the library spectrum, and the retention time agrees with the expected value.	Toluene
Reliable identification + unknown	An identified peak is overlaid by one or several unknown substances.	Cyclohexanone + ?
Uncertain identification	Reliable identification is not possible by mass spectra and retention time; however, the compound mentioned is considered to be possible. Significant mass fragments are indicated.	? 1,1-Bis(*p*-tolyl)ethane; 210 195 179 104
Class-type identification (single compound)	The mass fragments or fragment patterns indicate that the compound belongs to a known class of substances.	? Alcohol; 31 57 85
Class-type identification (multiple compounds)	For 'oil-humps' or accumulated isomers, the class of substances and the approximate boiling range should be indicated. In the 'retention time' column, the retention time of the maximum response should be entered.	Isomeric paraffin fractions, boiling range C_{16}–C_{26}
Unidentified	No conclusions on the possible substance are possible. Significant mass fragments are indicated.	? 54 76 99 109
Artefact	The peak belongs to a compound that does not originate from the sample, or has been generated in the system.	Artefact

Sample information

The information required is summarized below. Contract labs would typically also create a written report of the results using the Chromeleon 7.3 custom report editor.

Header section

- Precise designation of the material tested (material, batch)
- Component designation
- Name of manufacturer/supplier
- Date of material production
- Date of analysis
- Weight of sample (mg)
- Appropriate dimensions of sample (mm × mm × mm)
- Part number

Results section

- Retention time
- Compound name
- CAS number
- Peak area, as percentage of total identified peaks
- Concentration (µg/g)
- Comments on peak
- VOC (FOG) value
- Second VOC value
- Any remarks on analysis

Data files

Data files must be provided in their native format. It is important to ensure that you agree on a mutually acceptable data file format with any customer before sending the report.

Spreadsheet

Table 8 shows part of an example spreadsheet, set up to make the process of data input more efficient. The use of conditional formatting for values less than 1 µg/g (here shown in dark gray) allows results that can be removed from the report to be easily identified.

Table 8. Suggested spreadsheet layout

Peak name	Retention time (min)	Peak area (counts · min)	Sample mass (mg)	Emission (µg/g)
Cyclohexylamine	13.21	6639950	29.60	9.30
Cyclohexanone	14.81	233228	29.60	0.33
Phenol	19.06	972999	29.60	1.36
2-Ethylhexan-1-ol	21.47	1172726	29.60	1.64
4-Chloro-3-methylphenol	23.45	490557	29.60	0.69
2-Ethylhexanoic acid	25.08	796313	29.60	1.12
Naphthalene	27.89	3141923	29.60	4.40
2-Propylheptan-1-ol	28.62	404565	29.60	0.57
Benzothiazole	29.27	20913359	29.60	29.29
Isothiocyanato- cyclohexane	29.52	3974899	29.60	5.57
Quinoline	29.70	379830	29.60	0.53
2-Methylbenzothiazole	31.47	11282760	29.60	15.80
n-Tridecane	31.70	45899	29.60	0.06
1-Methylnaphthalene	32.03	1774039	29.60	2.48
2,4,8-Trimethyl-1,2,3,4-tetrahydroquinoline	34.76	8105772	29.60	11.35

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Conclusion

This guide demonstrates a stepwise process for carrying out the TD–GC–MS analysis of automotive interior materials using the combined Thermo Scientific / Markes International solution in accordance with VDA 278. The advice provided concerning aspects of sample preparation and the analytical procedures will ease the adoption of this method within automotive manufacturers and OEM part/assembly suppliers who are seeking guidance for VIAQ regulation compliance. The benefits of the combined system deliver a comprehensive solution more complete than each provider could individually, due to the following:

- Fully automated TD100-xr with 100 tube capacity, cryogen free trapping, and uniform trap heating.
- Effective sealing of all sample tubes loaded onto the autosampler (before and after analysis) to prevent contamination and loss of volatiles.
- Integration of Markes TD system via TRACE 1310 modularity providing efficient sample transfer and allowing highly sensitive determination of a wide range of VOC and SVOCs that is accurate and repeatable.
- Easily operated and maintained ISQ 7000 GC-MS system with removable ion source under vacuum and vent free column exchange reduces instrument downtime and allows technician level operation.
- Chromeleon CDS software that unifies control of the TD GC-MS solution, which includes automated easy-to-customize reports, eWorkflows™, and data analysis limiting errors and simplifying the path to compliance.

Reference

1. VDA 278: Thermal desorption analysis of organic emissions for the characterization of non-metallic materials for automobiles, Verband der Automobilindustrie, 2011, www.vda.de/en/services/Publications/vda-278-thermal- desorption-analysis-of-organic-emissions.html.

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