

ENSURING COMPLIANCE WITH VDA 278 REGULATIONS





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INTRODUCTION

The well-recognized and coveted “new car smell” present in many new automobiles has long been viewed as an indicator of vehicle age and cleanliness. Less commonly known is the origin of the smell - a result of off-gassing of volatile organic compounds (VOC) found in leather, plastics and other textiles in the vehicle.

To ensure the levels of VOCs present in vehicles are not having a detrimental impact on air quality, vehicle manufacturers throughout Europe have adopted the testing recommendations outlined in the Verband der Automobilindustrie (VDA), or German Association of the Automotive Industry, guidance document. The guidance, VDA 278, is a gas chromatography/mass spectrometry (GC/MS) thermal desorption method for the quantification of levels of VOC emissions from interior components of vehicles.

DEFINITIONS

Thermal Desorption Analysis

For thermal desorption spectrometry analysis (TDS), small amounts of material are heated in a desorption tube under predetermined conditions, and the emitting volatile substances are cryo-focused using an inert gas stream into the condensation trap of a temperature-programmable evaporator.

After the heating phase is completed, the condensation trap is rapidly heated to 280 °C, resulting in the evaporation of the focused substances. These are then separated in the gas chromatographic separation column, and then detected by mass spectrometry.

Performing calibration with reference substances, a semi-quantitative estimation of the emission, indicated in $\mu\text{g/g}$,¹ is possible.

As quantitative reference substances, toluene for the VOC value,² and n-hexadecane for the Fogging value are used. Based on their mass spectra and retention indices, signal peaks can be assigned to substances.

VOC Value

The VOC value according to VDA 278 is the total of substances that are readily to moderately volatile. It is calculated as a toluene equivalent. With the method described herein, substances in the boiling or elution range up to n-pentacosane (C25) are recorded and evaluated.

It can be assumed that these substances are detectable in an analysis of the vehicle interior air. For the analysis, the



sample is heated at 90 °C for 30 minutes. The VOC value is determined in duplicates. The higher value of the duplicates is used as the result.

Fogging Value

To determine the Fogging value, the second sample is left in the desorption tube after the VOC analysis, and is heated again at 120 °C for 60 minutes.

The Fogging value represents the sum of the low volatile substances that elute starting from, and including, the retention time of n-tetradecane. It is calculated as a hexadecane equivalent. Substances in the boiling range of the C14 to C32 n-alkanes are detected and evaluated.

These substances can easily condense at room temperature and contribute to fogging on the windshield.

SAMPLING AND STORAGE

The age of the sample to be analyzed must be known. Usually, the material to be examined will be packaged airtight within eight hours after its production. The sample must be delivered to the laboratory immediately. When transporting and unpacking the sample, a temperature of 23 °C should not be exceeded. Immediately prior to the analysis, the samples will be stored open for seven days at room temperature (maximum 23 °C). Deviations from this procedure must be documented.

For the analysis, a representative sample is taken. No contamination must occur. Each sample shall be sealed airtight in an aluminum composite foil. Optionally, the sample should be wrapped twice completely and airtight in thick aluminum foil (30 μm), and the edges are to be folded several times. Additionally, the sample is sealed in a polyethylene bag to be sent to the laboratory.

Examples of suppliers of aluminum composite foil include Flöter, 71701 Schwieberdingen, Germany; Hermann Nawrot, 51688 Wipperführt, Germany.

1. μg substance per weighted gram that can be emitted and detected under these measuring conditions. This value does not reflect the actual content.
2. VOC value = Volatile Organic Compounds. This VOC value only applies to the here described procedure. It cannot be compared with VOC values obtained with other procedures.

ANALYSIS AND INSTRUMENT PARAMETERS

Minimum Requirements for Basically Suitable Device Systems

- Directly coupled TD/GC system
- Gas Chromatograph (electronic pneumatics regulation is recommended) with FID
- Cryo-focusing with split temperature programming
- Mass spectrometry detector, mass spectrum library
- Desorber tubes with inert surface, interior diameter 4-5 mm
- Silica capillary separation column for chromatography: stationary phase: 5% Phenylmethylsiloxane
- Software for instrument control and evaluation of chromatograms
- The recovery rates of the individual substances (calculated as toluene equivalent) in the control mixture described below must be between 60% and 140% under VOC conditions, with a toluene recovery of at least 80% and maximum 120%.
- It must be possible to remain below the following detection limits (DIN32645, confidence interval: CI=95%):
 - ▶ VOC run: toluene <0.04 µg, and eicosane (C20) <0.06 µg
 - ▶ Fogging run: N-alkane C32 <0.2 µg

To determine detection limits, various contents of the test substances dissolved in methanol (VOC run) or N-pentane (fogging) are injected into TENAX®-filled desorber tubes and desorbed at 280 °C. Split ratios and GC conditions correspond with the VOC or Fogging method.

Suitability-tested Thermal Desorption Systems According to VDA 278

Examples for Suitability-Tested Device Combinations

PerkinElmer LAS (Germany) GmbH; Ferdinand-Porsche-Ring 17; D-63110 Rodgau-Jügesheim

Thermal Desorption	TurboMatrix™ ATD, PerkinElmer Desorption tubes, diameter: External = 6 mm, internal = 4 mm
Condensation Trap	Integrated in TurboMatrix ATD, silanized quartz glass liner (2.8 mm internal diameter) filled with 0.5 cm silanized glass wool 2 cm TENAX®-TA and 1 cm silanized glass wool (in desorption direction)
Gas Chromatograph	Clarus® 690, PerkinElmer Column end-split: MSD/FID=1:1 deactivated capillary to MSD: 3.6 m (I)/0.15 µm (ID) FID: 2 m (I)/0.15 µm (ID)
Carrier Gas	Helium 5.0, recommended: additional gas filters (activated carbon Gas-Clean)
Separation Column	50 m x 0.32 mm, 0.52 µm, 5% phenyl-methyl-siloxane HP Ultra 2 (19091B-115)
Detector	Mass selective detector: Clarus MS/SQ8 + flame ionization detector (FID), Perkin-Elmer
Evaluation Software	TurboMass, MS-Excel, Wiley7N/ NIST-MS spectral library

Instrument Parameter Settings for the VOC Analysis Run

PerkinElmer LAS (Germany) GmbH; Ferdinand-Porsche-Ring 17; D-63110 Rodgau-Jügesheim

Thermal Desorption Unit	Temp: Valve: 280°C Tube: (VOC) 90°C 30 min (2 stage desorb) 1 min (purge) Flow: 14 psi (column inlet pressure) or const. flow 2.0 mL/min, if possible. (column and column/desorb) 40 mL/min (desorb) 44 mL/min (inlet) 19 mL/min (outlet)
Total Desorber Tube Flow	82 ± 2 mL/min (resulting from the flow settings at split 1:60)
Condensation Trap Parameters	Trap: -30 °C (low) 280 °C (high) 20 min (hold) 99 K/s (rate)
Instrument Parameters Gas Chromatograph	Transfer line to MSD 280 °C Oven temperature program: 40 °C, 2 min isothermal, 3 K/min to 92 °C, 5 K/min to 160 °C 10 K/min to 280 °C, 10 min isothermal For TurboMatrix models with PPC, it is preferable to work in constant-flow mode (flow = 2.0 mL/min)
Settings Mass Spectrometry Device (MSD)	Start data acquisition: 3.0 min Mass axis calibration: Standard spectra autotune (at 100 °C oven temp.) Scan mode (low/high-mass): 29-450 amu, >3 scans/sec MS threshold: 50
Settings FID	Temperature: 320 °C O2 flow: 45 mL/min H2 flow: 450 mL/min Attenuation: - 6 range: 1
Evaluation	Qualitatively over the total ion chromatogram; quantification over FID

Analysis and Instrument Parameters, *continued*

Instrument Parameters for the Fog Analysis Run

Thermal Desorption Unit (TurboMatrix ATD)	<p>Temperature: Valve: 280 °C Tube: (Fog) 120 °C 60 min (2 stage desorb) 1 min (purge) Flow: 14 psi (column inlet pressure) or Const. flow 2.0 mL/min, if possible. (column and column/desorb 2) 40 mL/min (desorb) 44 mL/min (inlet) 19 mL/min (outlet)</p>
Total Desorber Tube Flow	82 ± 2 mL/min (resulting from flow settings at a total split 1:60)
Condensation Trap Parameters	<p>Trap: -30 °C (low) 280 °C (high) 20 min (hold) 99 K/s (rate)</p>
Instrument Parameters Gas Chromatograph	<p>Transfer line to MSD 280 °C Oven temperature program: 50 °C, 2 min isothermal, 25 K/min to 160 °C 10 K/min to 280 °C, 30 min isothermal For TurboMatrix models with PPC, it is preferable to work in constant-flow mode (flow = 2.0 mL/min)</p>
Settings Mass Spectrometry Device (MSD)	<p>Mass axis calibration: Standard spectra autotune (at 100 °C oven temp.)</p> <ul style="list-style-type: none"> • Scan mode (low/high-mass): 29-450 amu • MS threshold: 50
Settings FID	<p>Temperature: 320 °C O₂ flow: 45 mL/min O₂ flow: 45 mL/min H₂ flow: 450 mL/min Attenuation: - 6 range: 1</p>
Evaluation	Qualitatively over the total ion chromatogram; quantification over FID

Instrument Parameters for Calibration and Control Solution

Thermal Desorption Unit (TurboMatrix ATD)	<p>Temperature: Valve: 280 °C Tube: 280 °C 20 min (2 stage desorb) 1 min (purge) Flow: 14 psi (column inlet pressure) 40 mL/min (desorb) 44 mL/min (inlet) 19 mL/min (outlet)</p>
Condensation Trap Parameters	<p>Trap: -30 °C (low) 280 °C (high) 20 min (hold) 99 K/s (rate)</p>
Evaluation	Qualitatively over the total ion chromatogram; quantification over FID

IMPLEMENTATION OF THE ANALYSIS

Desorber Tube Cleaning

Only completely contamination-free desorber tubes may be used. New tubes must be carefully cleaned with suitable procedures before first-time use. For glass tubes, the following procedure is recommended: when cleaning, the tubes should be placed for several hours, preferably overnight, in an alkaline cleaning solution. Afterwards, they should be rinsed thoroughly, first under running hot water for at least one minute, then again with demineralized water. The tubes should then be dried in a drying cabinet for approximately 45 minutes at 105 °C, and should be stored free of contaminants (packed airtight in aluminum foil) until use.

System Verification

For functional verification of the device system, a control standard solution is analyzed in parallel to the sample series. The control standard solution contains nonpolar, polar basic and acidic components that would show a noticeable peak tailing in the case of undesirable adsorption effects. By this, it can also be determined whether substance losses have occurred as a result of leaks. Closely successive peaks, e.g. o-xylene and n-nonane, serve to check the separation efficiency of the chromatography column. Under the chosen chromatography conditions, these two substance peaks must be separated at near baseline levels. All substances of this control mixture must be clearly identified in the search run in the mass spectrum library.

The performance of the mass spectrometry detector is ensured by mass and sensitivity tuning, meeting the specifications required by the manufacturer. Also, to check the sealing of the entire system, an air/water check must be carried out.

Furthermore, the TDS/GC system should be checked for memory effects by performing a blank run at least before each sample run with an empty desorption tube. In the event negative effects are observed, e.g. considerable peak tailing, interfering peaks in the blank run or significant substance losses, the system must be cleaned. Replacement of the GC column, glass liner, transfer line or seals may also be required.

It is recommended to document the results of the control runs for each sample series as part of the quality control process (control chart). Control parameters are, for example:

- Peak area ratios of the control substances,
- Concentrations of the control substances, calculated as toluene equivalents,
- Retention times.

Preparation of the Control Solution

The following substances dissolved in methanol have proven suitable for system verification (listed in the order of elution under VOC conditions):

Retention Index*	Component	Retention Index	Component
670	benzene	1100	n-undecane
700	n-heptane	1110	2,6 dimethylphenole
766	toluene	1200	n-dodecane
800	n-octane	1300	n-tridecane
870	p-xylene	1400	n-tetradecane
895	o-xylene	1435	dicyclohexylamine
900	n-nonane	1500	n-pentadecane
895	n-decane	1600	n-hexadecane
900	2-ethylhexanol-1	2390	Di-(2-ethylhexyl)-adipate

*The indicated retention indices referring to n-alkanes are approximate.

Suggested Preparation Procedure

Of each component, 220 ± 20 mg are weighed to within 0.1 mg into a glass jar (e.g. a 5 mL crimped glass jar). Approximately 100 mg of this mix are transferred to a 50 mL volumetric flask and weighed (balance accuracy ± 0.1 mg). Subsequently, methanol (p.a.) is added up to just below the calibration mark of the volumetric flask. The closed flask is shaken gently until all solvent droplets have completely dissolved in the methanol. The volumetric flask is then filled up to the calibration mark and shaken again.

For the control run, 4 μ L of this solution are injected into a TENAX®-TA filled desorption tube, as described above, in order to obtain an absolute amount of 0.45 ± 1 μ g of each component in the desorber tube. The retention times of the n-alkanes present in this mixture are suitable for determining the retention index of unknown substance peaks. They can be used for additional safeguarding of the MS identification during the sample runs.

Stability of the Control Solution

If properly stored (refrigerated at max. 8 °C), the control solution is stable for at least three months.

Implementation of the Analysis, *continued*

Calibration

The calibration is carried out according to the external standards method. For this purpose, a desorption tube filled with TENAX®-TA is subjected to a calibration solution.

Calibration Solutions

Two calibration solutions are required:

- for the VOC analysis approximately 0.5 µg/µL toluene (p.a.) in methanol (p.a.)
- for the Fogging analysis approximately 0.5 µg/µL toluene (p.a.) in methanol (p.a.)

Approximately 25 mg (± 0.1 mg) of toluene or n-hexadecane are weighed into a 50 mL volumetric flask, and the volumetric flask is then filled with methanol up to just below the calibration mark, closed and shaken well. The flask is then filled with methanol completely up to the calibration mark, and shaken again.

If stored refrigerated, the calibration solutions are stable for at least three months. Ensuring the accuracy of the concentration is part of the quality control of the laboratory.

Purpose of the Calibration or Control Solutions on TENAX®

A TENAX®-TA-filled desorption tube is connected to an injection device that allows a controlled inert gas flow

(helium 5.0) through the tube while the calibration solution is being applied.

For example, constructions of septum screw connections of used GC-injectors or a septum-free cold application head (Gerstel) provided with adapter, have proven to be useful, the latter having the advantage that dead volumes are relatively low and thus less losses occur. In order to control the helium flow, a simple controllable flow meter should be connected upstream.

Downstream of the desorption tube, a gas meter should be installed to control the total volume passing through, and to check for leaks.

The flow rate should be set to approximately 0.7 ± 0.3 L/min, and the total flow rate should be approximately 2.5 - 3 L. By this, the applied methanol matrix will be mostly removed, whereas toluene or hexadecane remain on the TENAX®.

From the calibration solution brought to room temperature, 4 µL are drawn bubble-free with a 10 µL GC syringe and injected slowly (within approximately 5-10 seconds) into the glass-wool pad. This is done with the inert gas flow being switched on.

In order to avoid losses, it is recommended to inject the calibration solution directly into the glass-wool pad.

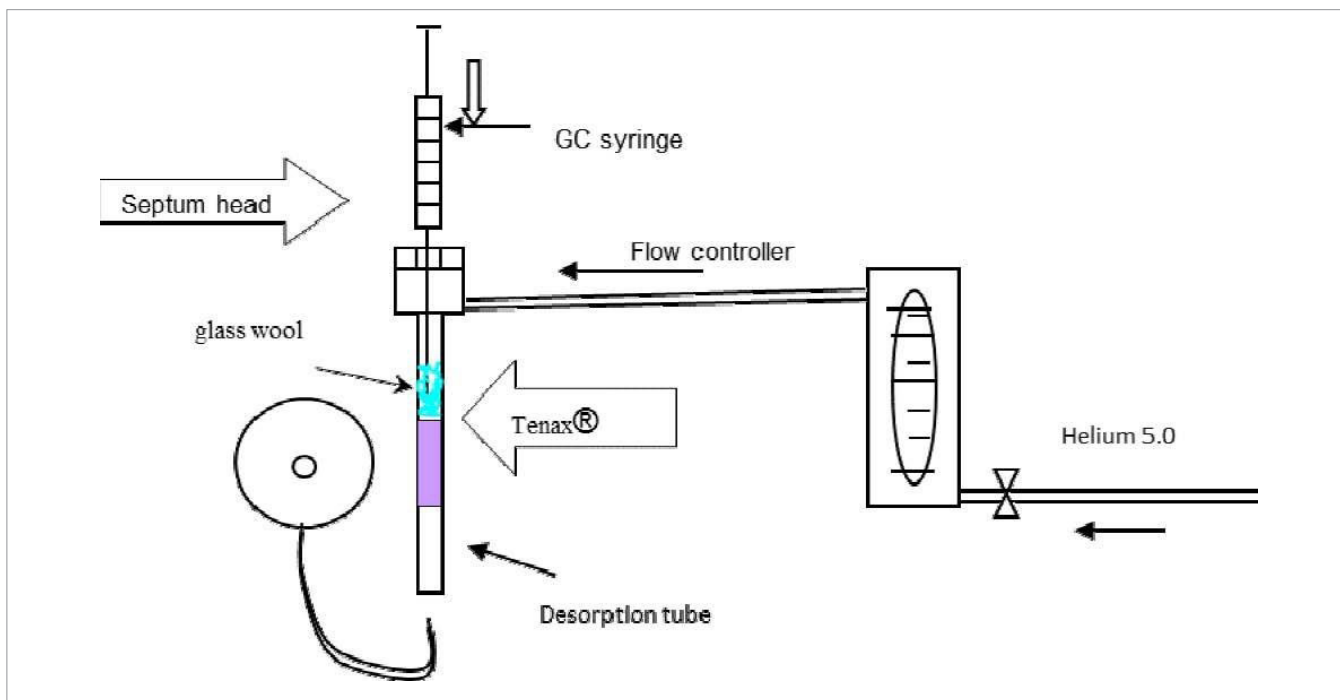


Figure 1. The design of a corresponding sample application apparatus.

Implementation of the Analysis, *continued*

TENAX® Desorption Tube

With regard to the packing density and quantity, the recommendations of the device manufacturer should be followed. In particular, make sure that the TENAX® pack fills the pipe so that it can be covered fully by the heating zone of the desorption oven.

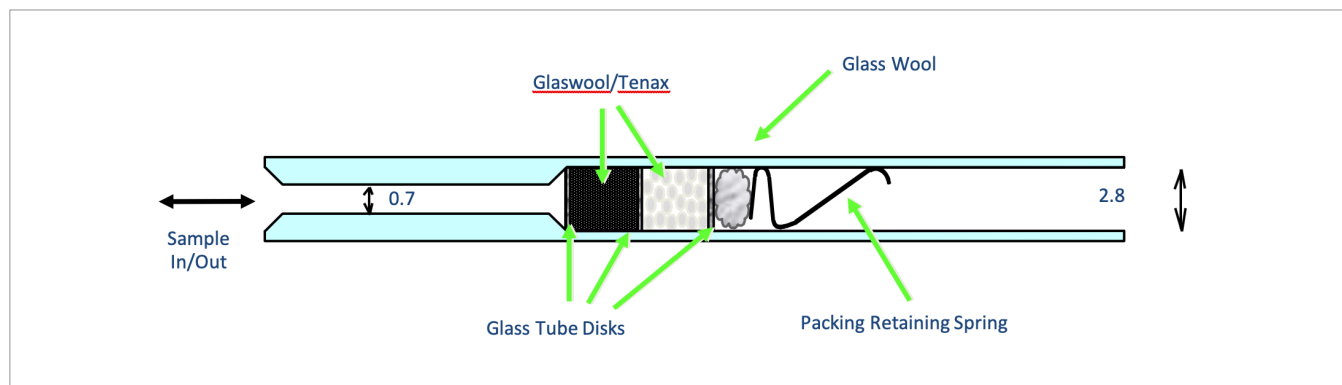


Figure 2. Cold Trap.

The thermal desorption tube is filled with 200 mg Tenax®-TA. Approximately 50 mg of silanized glass wool are filled in on the transfer-line side and sealed off on the carrier-gas side with approximately 50 mg glass wool. The TENAX® filling must be conditioned in accordance with the manufacturer's instructions, and must be in top-quality condition. Depending on frequency of use, TENAX® can age over time. The quality of the TENAX® tubes must be ensured suitably (by visual inspection, blank runs).



Claurs 690 SQ8 GC/MS with TurboMatrix 650 ATD