

Thermodesorption Analysis of Organic Emissions for the Characterization of Non-metallic Automobile Interior Materials VDA278

Purpose

The analysis procedure serves for the determination of emissions from non-metallic materials, which are used for interior parts in motor vehicles, for example: Textiles, carpets, adhesives, sealing compounds, foam materials, leathers, plastic parts, foils, lacquers or combinations of different materials. It determines the quality and quantity of released organic substances from them. In addition, two half-quantitative values is determined, which make an estimation of volatile organic compounds (VOC-value) as well as the portion of condensable substances (Fog-value) for the emission possible. Furthermore it can also find out single substances emission. During the analysis the emission of samples are thermally extracted, isolated and characterized spectroscopically by gaschromatography. The available testing methods are valid for the conditions described as here only. The results, which can be obtained with this method, however, are not applicable under some condition:

- To make estimations concerning a health evaluation by the emitted substances
- In any form as a basis for the estimation of concentrations as those in the complete vehicle interior, in driving or in a driving-similar condition

Terms

Emission, non-metallic materials, thermodesorption analysis (TDS), VOC-value, Fog-value.

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1. Definitions

1,1 Thermodesorption analysis

During the thermodesorption analysis (TDS), small quantities of sample is heated in a glass tube, the emitted volatile substances is cooled with the help of an inert gas stream in the cooling case by a temperature-programmable evaporator. After completion of the baking phase, those in the cooling case are rapidly heated to 280°C. The focused substances evaporate. They are then isolated in the gaschromatographic separating column and detected spectroscopically.

Appendix 7,3 shows the schematic construction of the thermodesorption analysis by calibration with reference substances expressed in "µg/g", making a half-quantitative estimation of the emission possible. Toluene is used as the quantitative reference substances for the VOC analysis while n-Hexadecane for the Fog value. Based on the mass spectra and retention indices of substance peaks, they can be assigned.

1,2 VOC value of VDA278

The VOC value of VDA278 is the sum of the light to medium volatile substances. It is computed as toluene equivalent. With the method described here substances in become boil respectively and the elution is evaluated by the sizes of n-Eicosane (C20).

For these substances, it is supposed that they are provable with the analysis of vehicle interior air. During the analysis the sample is heated up to 90°C for 30 minutes. The VOC value is determined by double method. In the result the higher value of the two-fold method is indicated.

1,3 Fog value of VDA278

Determination of the Fog value is by the second sample leaving in the desorption tube in connection of the VOC analysis and warmed up to 120°C for 60 minutes.

The Fog value is the sum of the less volatile substances, whose including the retention time of n-Hexadecane. It is computed as Hexadecane equivalent. Substances in the boiling range from the sizes of the n-alkanes "C16" to "C32".

These substances can condense at ambient temperature easily and contribute substantially to the fogging behaviour at the windshield.

2. Storage

The time for the analysis is to be selected in such a way the material age corresponds to that shortest possible delivered state of the special fitting in the final assembly work. Example: A foam material is delivered within of 2 to 12 days after the foaming in the automobile work. So the analysis of a foam sample is to be accomplished could ventilate a maximum of 2 days. It is always proceed according to the most unfavorable case (worst scenario). For the investigation a representative sample is taken without occurrence of contamination. Each sample is to be welded airtight into an aluminum sandwich foil. Alternatively, the sample is packed up doubly in thick aluminum foil (30µm) completely, airtight, with the edges folded several times. The sample is sealed additionally in a polyethylene bag and can be sent to the laboratory. There the sample can be stored at a maximum temperature of 18°C until the test actually carried out. Detail references of sample preparation and handling are described in appendices 7,1 and 7,2.

Appendix 7.1: Definition of the sample originally composed of different materials.

Appendix 7.2: Definitions of the production of varnish films

3. Analysis system, equipment parameter

3,1 Minimum requirements of suitable principle equipment systems

- Directly coupled thermodesorption system/ GC System
- Gaschromatograph (an electronic adjustment of pneumatics is urgently recommends).
- Temperature-programmable **Kryofokussierung** with split
- Mass-spectrometric detector, mass spectra database
- Desorber pipes with inert glass surface, inside diameter of 4-5 mm
- Chromatographic quartz capillary separating column: Stationary phase: 5%-Phenyl-Methyl-Siloxan
- Software for the device control
- Chromatographic software for the evaluation by the export of raw data files in the AIA- format
- The recovery rates of the single substances (computes as toluene equivalent) of the control mixture described in the chapter 4.2.1 must be between 60 and 140% in VOC conditions, while recovery of toluene may range from 80% to 120%
- The following collection borders (DIN32645, confidence interval: CI=95%) must be able to be maintained:

In the VOC run	Toluene < 0,04 µg, and	Eicosane (C20) < 0,06 µg
In the Fog run	n-Alkane C32 < 0,2 µg	

The determination of the collection borders: Different contents of test substances in methanol (for VOC run) and/or n-pentane (for Fog) is injected into Tenax filled desorber

pipes and desorbed at 280°C. Split ratio and GC conditions are corresponded to the VOC and/or Fog method parameter. See also chapter 5.2.

3.2 suitability examination of thermodesorption systems

Manufacturer/Address	Product name
Company Gerstel D-45473 Muehlheim at the Ruhr, Aktienstr.232-234	TDSA with KAS-3, KAS-3+, KAS-4
Company Perkin Elmer D-63110 Rodgau Juegesheim, Ferdinand Porsche Ring 17	Turbo-matrix (A) TD

Example for test audit and device combination

Device	Device combination 1	Device combination 2
Thermodesorptions unit	TDSA, Company: Gerstel Glass-desorption tube: Diameter : Outside= 6mm Inside= 4mm	Turbomatrix ATD, Company: Perkin-Elmer Glass-Desorption tube, Diameter: Outside=6mm Inside= 4mm
Gaschromatograph	HP6890 with electronic pressure regulation (EPS) Company: Agilent (Ohne detector-Split)	Autosystem XL, Company: Perkin-Elmer Column-Split: MSD/FID=1.1 Inactivated capillary to MSD: 3.6m(l)/ 0.15µm(ID) FID:2m(l)/ 0.15µm(ID)
Carrier gas	Helium 5.0, postclean with megasorb-gas cleaner, Company: Messer Griesheim	Helium 5.0
Separating column	50 m x 0.32 mm, 0.52µm 5% Phenyl-Methyl-Siloxane HP Ultra 2 (19091B-115)	50 m x 0.32 mm, 0.52µm 5% Phenyl-Methyl-Siloxane HP Ultra 2 (19091B-115)
Chill trap	KAS 3, Company: Gerstel Glass liner: smooth execution, filled with inactivated quartz cotton (Kat. No. 842010)	In Turbomatrix integrate inactivated quartz-glass-liner (2.8mm inside diameter), filled with 0.5cm quartz-wool, 2cm Tenax TA and 1cm quartz-wool (in desorption tube)
Detector	Mass selective detector (MSD): HP5972A, Company: Agilent	Mass selective detector: Turbomass + Flame ionization detector (FID), Company: Perkin-Elmer
Evaluation software	Chemstation G1701BA, MS-Excel97, Wiley 7N/ NIST-MS-Spectra database	Turbomass 4.1.1, MS-Excel2000, Wiley 7N/NIST-MS-Spectra database

3.3.2 Device parameter for Fog Analysis

Unit	Device Combination 1	Device Combination 2
Thermodesorptions unit	TDSA Sample Mode Sample Remove Flow-Mode Splitless Initial Temp. 20°C Delay Time 1 minute 1 st Rate 60K/min 1 st Final Temp. 120°C 1 st Final-time 60 minutes Transferline 280°C GC-Run-Time 57 minutes	Turbomatrix Temp.: Valve/Tube : 280°C Tube: (Fog) 120°C 60 min (2 stage desorption) 1 min (purge) Flow: 14 psi (column form) 20 ml/min (desorb) 22 ml/min (inlet) 19 ml/min (outlet)
Parameter for chill trap	Flow Mode Split 1:30 Initial Temp. -150° C 1 st Rate 12K/sec 1 st Final Temp. 280°C	Trap: -30°C(low) 280°C (high) 20 min (hold) 40 K/s (rate)
Gaschromatography (GC)	Transferline to MSD Stove temperature program: (Whole term: approximate 48 min.)	280°C 50°C, 2 min. isotherm, 25 K/min. at 160°C 10 K/min. at 280°C, 30 min. isotherm
	Flow speed: 1.3ml/min. Pneumatic (EPS): Constant flow-mode	Prove from the flow of the Thermodesorption tube
Setting of mass-spectrometer (MSD)	Beginning data admission: ex. 12.5 minutes Mass calibration: Standard-Spectra-Autotune (at 100°C stove temp.) Scan-mode (low/high-mass): 29-370 amu, with 2.3 Scans/s MS-Threshold: 100	
Setting of FID		Temperature: 320°C O ₂ -Flow: 45ml/min H ₂ -Flow: 450ml/min Attenuation:- 6, range:1
Evaluation	Qualitative and quantitative from the Total-Ions-Chromatogram (TIC)	Qualitative evaluation from the Total-Ions-Chromatogram; Quantification from the FID-Chromatogram

3.3.3 Device parameter for calibration and control solution

Unit	Device Combination 1	Device Combination 2
Thermodesorptions unit	<u>TDSA</u> Sample Mode Sample Remove Flow-Mode Splitless Initial Temp. 20°C Delay Time 1 minute 1 st Rate 60K/min 1 st Final Temp. 280°C 1 st Final-time 5 minutes Transferline to KAS 280°C	<u>Turbomatrix</u> Temp.: Valve/Tube : 280°C Tube: 280°C 30 min (2 stage desorption) 1 min (purge) Flow: 14 psi (column form) 20 ml/min (desorb) 22 ml/min (inlet) 19 ml/min (outlet)
Parameter for chill trap	Flow Mode Split 1:30 (see chap.6.7) Initial Temp. -150° C 1 st Rate 12K/sec 1 st Final Temp. 280°C 1 st Final Time 5 minutes Equilibrium Time 1 minute	Trap: -30°C(low) 280°C (high) 20 min (hold) 40 K/s (rate)
Evaluation	Qualitative and quantitative from the Total-Ions-Chromatogram (TIC)	Qualitative evaluation from the Total-Ions-Chromatogram; Quantification from the FID-Chromatogram

Parameter for Gaschromatograph with calibrating and control analysis:

For the toluene calibration and the analysis of the control mix, the same parameters as for the VOC test. When the **Datenerfassung** begins more spatter, the methanol peak will fade out in approximate. 5,5 minutes. The hexadecane calibration is accomplished with the GC conditions of the Fog analysis. The GC run can be shortened in relation to the sample runs, by breaking off the stove temperature program after the elution of the calibration substances.

4 Execution of the analysis

4.1 Cleaning of the desorption tubes

Only perfectly contamination-free desorber pipes can be used. Procured desorption tubes must be cleaned carefully before the first use. For this Verfahren is suitable to be used.

For glass tubes the following proceeding is recommended: For best cleaning the pipes are store in an alkaline cleaning solution for several hours or over night. Afterwards they are rinsed thoroughly, first under flowing hot water at least one minute, then with demineralized water. Subsequently, the pipes are put in the drying furnace (approx. 45 minutes at 105°C) and kept up to be contamination-free (air tightly packed in aluminum foil).

4.2 Examination of the system

For the examination of the function of the equipment system a serial analysis with control standard solution is undertaken (see 4.2.1). The control standard solution contains nonpolar, polar basic and acidic components, whose unwanted adsorption will exhibit a noticeable peak tailing. Furthermore it can be detected that whether material losses are arise by leakages. Closely successive peaks, e.g. o-xylene and n-Nonan, indicate the separating power of the chromatograph. With the selected chromatographic conditions, these two substance peaks must show almost separate base line. All substances of this measure must be clearly identified in the mass-spectra-database.

The efficiency of the measure-spectroscopic detector is guaranteed by measurement and sensitivity Tuning, whereby the specifications demanded by the manufacturer must be achieved. Likewise an air wading check must be accomplished for the test to ensure the tightness of the overall system.

Furthermore the entire TDS/GC system has to be examined for possible memory effects, as before each sample series, at least a blind run empty desorption tube should be carried out.

If negative effects, as e.g. strong peak tailing, disturbing blind run peaks or significant material loss arise, the system must be cleaned. If necessary an exchange of GC column, glass liner or the seals is necessary.

It is advisable to document the results of the control runs to every test series within the context of quality control (rule map) as control dimensions offer e.g.

- Peak area conditions of the control substances
- Calculate the concentrations of the control substances as toluene equivalents
- The retention times.

4.2.1 Production of the control solution

The following substances dissolved in methanol proved to be suitable for system (listed in the elution under VOC conditions):

Table 1. Control mix

Retention index ⁷	Components	Retention index	Components
670	Benzene	1100	n-Undecan
700	n-Heptane	1110	2,6-Dimethylphenol
766	Toluene	1200	n-Dodecane
800	n-Octane	1300	n-Tridecane
870	p-Xylol	1400	n-Tetradecane
895	o-Xylol	1435	Dicyclohexylamine
900	n-Nonan	1500	n-Pentadecane
1000	n-Decane	1600	n-Hexadecane
1030	2-Ethylhexanol-1	2390	Di-(2-ethylhexyl)-adipat

Suggestion on the proceeding with the production:

For each component, 220 ± 20 mg are weighed and put into a glass container (e.g. 5ml roll edged glass) on 0.1 mg exactly. From this mix approx. 100mg (balance accuracy ± 0.1 mg). is weighed and transferred into a 50ml measuring flask. Subsequently, add additional methanol (Just underneath the calibration mark of the measuring flask), lock the piston and shake carefully until all solvent droplets completely dissolved in methanol. Then fill up to the calibration mark and shake again.

For the control 4 μ l of the solution is injected (in accordance with chapter 4.3.2) in a Tenaxdesorption tube, so that in the desorption tube, each component is approx. $0.45 \pm 0,1$ μ g. The retention times of the n-alkanes in this mixture are suitable as reference to determine the retention index of unknown quantity of substance peak and for additional MS identification of the sample.

4.2.2 Durability of the control solution

The control solution last for at least three months with adequate storage (cooled at max. 8°C).

4,3 calibration

The calibration is carried out according to the procedure of the external standard method. For this a desorption tube filled with Tenax TA is calibrated with the calibration solution.

4.3.1 Calibration solutions

Two calibration solutions are required:

1. For the VOC analysis approx. 0.5 μ g/ μ l toluene (p.a.) in methanol (p.a.)
2. For the Fog analysis approx. 0.5 μ g/ μ l n-Hexadecane (p.a.) in methanol (p.a.)

In a 50 ml measuring flasks approx. 25 mg ($\pm 0,1$ mg exactly) of toluene and/or n-Hexadecane is weighed, then measuring flask is filled with methanol just briefly below the calibration mark, locked and well shaken. Subsequently, the piston is unlocked and the calibration mark is filled up with methanol and shakes again. The calibration solutions can be stored for at least 3 months under cooled condition. The guaranteed of correctness of the concentration is a requirement of the quality control of the laboratory.

4.3.2 Calibration with control solution

A desorption tube filled with Tenax TA is connected to an injection device, which ensure self-possessed inert gas flow (helium 5,0) via the tube during the calibration with the calibration solution.

Constructions from septum screw connections of retired GC injectors or pure septum-free head of cold task provided with adapter (company Gerstel) work satisfactorily. The latter has the advantage that the dead volumes are relatively small and thus fewer losses can occur.

As a check of the helium flow a simple adjustable flow meter should be installed.

To the desorption tube, a gasmeter/ gas clock should be connected at the outlet side as a control of the whole volume flowed through and for the examination on tightness.

The flow rate is approx. 0.7 ± 0.3 l/min. The total flow rate is adjusted to approx. 2.5 to 3 litres. The applied methanol matrix is removed as far as possible thereby against the toluene and/or Hexadecane on the Tenax remains.

Illustration 1 shows the arrangement of an appropriate equipment for the test sample.

Illustration 1 Apparatus for the assignment of calibration solution

(ref. to the original standard p.13)

Using a 10ul-GC-Spritze, 4µl of calibration solution, which is free of bubbles, is drawn up and injected slowly at ambient temperature (approx. 5-10 seconds) into the glass cotton ball. The inert gas current is switched on thereby.

In order to avoid losses, it is advisable to inject the calibration solution direct into the glass cotton ball inside. Otherwise the measured fluctuations value has to be taking into account.

4.3.3 Tenax Desorption tube:

For the component density and quantity, refer to the recommendations of the equipment manufacturers. It worth particular attention that the Tenaxpacking fills out the tube in such a way that it can be completely seized by the heating zone of the desorption stove.

a) Example of desorption tubes of the TDSA system of the company Gerstel

For the tubes of the Gerstel TDSA equipment, the Tenaxfilling should exhibit a total length of approx. 5-6 cm with a distance of approx. 3 cm away from the tube end. Half of the distance, which is approx. 1 cm in length is filled with inactivated wad of (silanized) glass cotton in which the calibration solution is injected.

Illustration 2. Tenaxfilling in desorption tube (Company Gerstel)

(ref. to original standard p.14)

b) Example of desorption tube in Turbomatrix-system (Company Perkin-Elmer)

Illustration 3. Filling in desorption tube (Company Perkin-Elmer)

(ref. to original standard p.14)

The thermodesorption tube is filled with 200mg Tenax TA. The lateral transferline is filled with approx. 50mg of inactivated fibre glass at both sides.

While for the Tenax filled tubes, noble valley tubes are used, it is advisable to use glass tube or Teflon lined high-grade steel tubes for the thermodesorption test of material samples.

The Tenaxfilling is conditioned according to the manufacturer data and must be in a qualitative perfect condition. Tenax can age depending on the time course. The quality of the Tenax small tube must be guaranteed with suitable measures (e.g. visual inspection + control test).

4.4 Sequence of the samples analyses

4.4.1 Cutting and handling of the samples in the desorption tube

For each test, 2 tubes are filled with the weighted samples.

Tube A: first VOC analysis

Tube B: second VOC analysis + following Fog test

Frozen samples must attain the ambient temperature before opening the package to avoid condensation from the aerial humidity.

The content of the tests depend on the kind of the material to be examined (see appendix 7,1).

Necessary accuracy: ± 0.1 mg

Sample weight: material-specific definitions are summarized in the appendix 7,1!

Because of the diversity of the possible sample materials no generally accepted method can be specified for the sample dimensioning.

When cutting the sample, a very coherent “flat/extensive” dimension should be aimed.

It is not the goal to cut up the greatest possible surface. As an orientation the following approach serves:

The inside diameter (4 mm) of desorption tubes can be not completely used because of the thickness of the sample. The zone kept at a moderate temperature of the tube and thus maximum length of the sample is about 4 cm. For a very large surface, the test sample should be first cut as far as possible before getting into the test tube. This is usually possible to make the sample width of approx. 3 mm. The length and thickness of the sample are variable, whereby the prescribed handling is relevant (appendix 7,1).

The sample should be cut rather long with accordingly decreased thickness. The sample dimension is indicated (e.g. L x B x H = approx. 15 x 2.8 x 0.7 mm). For lacquers and adhesives a separate proceeding applies, with dried films applied on aluminum foil (see appendix 7.1-7.2).

4.4.2 Calibration run, determination of the calibration factors (Response factor)

For each sample, at least two Tenaxdesorption tube, each with toluene and/or Hexadecane calibration solution are used (see chapter 4.2) and the surface values of the calibration peaks is determined from the run response factor existed as a quotient from the absolute mass (in μg) of toluene and/or Hexadecane, which were injected into the tube resulting in the peak areas in each case.

Equation 1

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

4.5 Chromatographic evaluation

4.5.1 Peak integration for the

The sum parameters (VOC and Fog value) from the total area of all substance peaks, which lie over the base line, originating from the sample, are determined. Peaks with a signal-to-noise ratio < 5 , are negligible. The process of the base line must admit to suitable control analyses.

The total concentration of VOC calculated as toluene equivalent in the VOC value. The total concentration of Fog computed as Hexadecane equivalent in the Fog value. If the VOC results show a more than 20% variation to the average value, repeating analysis

including Fog run is necessary. Both the VOC values are documented in the test report. For the evaluation of the analysis, the highest value is consulted.

All substances with a concentration > 1 µg/g must be listed in the result report, i.e. the chromatographic integration conditions are selected for the determination of the single substances in such a way that 1 µg/g - peak are always seized.

The chromatogram is so-called "oil mountains", consisting of chemically relevant and homogeneous isomer mixtures, are summarily integrated with the base line as the foot of the "mountain". If larger clearly definable peaks of other substance classes arise within this range, then they are separated and listed. Such peaks are quantified as bouncing peaks, i.e. they are not integrated to the basic base line, but stand out from the "oil mountain".

Sketch : Integration of “bouncing peaks” on “Oil mountain”-peaks
(ref. to original standard p.16)

4.5.2 Computation of the emission:

For the half-quantitative computation of the concentration the peak areas are multiplied by the response factor (see chapter 4.4.2) by toluene for the VOC analysis or by Hexadecane for the Fog analysis and divided by the sample weight respectively.

Equation 2

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

4.5.3 Qualitative analysis

The individual peaks (> 1 µg/g) is assigned based on their mass spectra and their retention indices (from the literature or based on a comparison analysis with n-alkanes). Each MS browsing result is examined before assuming the result table for plausibility.

If a substance cannot be identified clearly or the naming of a supposition marked with a question mark, a tip to the substance class (e.g. typical mass fragments) permit appropriate conclusions.

For the representation of the different security of the substance identification, the following conventions are considered:

Example for name	Explanation
Toluene, Methylbenzene	Mass spectrum and retention of the reference substance agree practically (very surely identified)
? 1,1-Bis(p-tolyl) ethane 210 195 179 104	Placed in question mark: On the basis of mass spectra and/or retention no clear allocation possible, but this substance is considered possible (very similarly). Significant mass fragments are as indicated
? Alcohol, 31 57 85	=> <u>Question mark + Substance class name:</u> typical fragments or well-known fragment pattern give tips to substance class
? 54 76 99 109	No conclusions on the connection possible

Paraffin fraction Isomer, boiling range "C16-C26"	With "oil mountains" the substance class and the approximate boiling range is indicated to relate to n-alkanes as substance name. In the column "retention time" is registered as the time of the mountain maximum.
Cyclohexane + ?	An identified peak is overlaid of one or more unknown substances
Artifact	Peak, which can not develop from the sample or in the system

4.5.4 Presentation of the analysis result

Following satisfactory work, the kind and range of result should be present:

The chromatograph result is transferred into an Excel table, which contains at least the following data concerning the examined sample:

Head	Result
Precise name of the examined material (material, load)	Retention time
Name of construction unit	Substance name
Manufacturer/ supplier's name	CAS No.
Date of the material production	Percentage share of the peaks
Date of the analysis	Concentration [$\mu\text{g/g}$]
Sample weight [mg]	Remark to peak
Approx. sample dimension [mm x mm x mm]	VOC (Fog) value
Part No.	VOC runner-up value
	Remark to the analysis

Note to the substance name:

There are different ways of writing a substance, how they are often offered by MS database. In case of substance cannot be undertaken directly, to avoid overloading of naming, it is sufficient to indicate a maximal 1-3 "more common" designations in addition to the CAS No.

With the transfer of the chromatographic results to the Excel data format the observance of conventions is compellingly necessary, in order to make an electronic data exchange possible. Therefore certain contents must stand in defined Excel cells. As a model, the Excel expression serves in the attached result (appendix 7,6).

The ordered laboratory provides a written report on findings, which contains the VOC and Fog value as well as the list (Excel table) of the quantified substances.

Furthermore the chromatogram expression of the VOC/Fog analyses must be added. In addition, the complete analysis raw data on a CD-ROM is provided. This CD-ROM contains the following files:

- 2 Chromatogram raw data file of the VOC method
- 1 Chromatogram raw data file of the Fog method
- Chromatogram raw data files of the blank test
- Chromatogram raw data files of the calibrating and control tests

- Excel files with the single results of the VOC/Fog analysis

The data format of the Chromatogram file must be compatible with the principle. With different chromatographic evaluation software, it is possible to exchange data by import/export function in AIA format.

5. Validation

5.1 Measured value of real sample, interlaboratory test

The repeatability of the test depends on the condition of the sample matrix, their composition, the polarity and evaporability of the emitters. The result also depends substantially on whether the producible sample surface preparation. This can be more difficult e.g. with an open-porous foam than a compact plastic sample. Experiences with numerous measurements of different materials of intralaboratory measurement showed a value deviation from < 15%. Generally accepted precision of the thermodesorption analysis of the VDA278 have not been obtained. It must determine in the examined matrix separately on a case by case basis. With an interlaboratory test for the test in which 19 laboratories with different equipment participated, the precision of the procedure for VOC and Fog value during the two analyses on a polyester foil (PES) and a foil from thermoplastic polyolefin (TPO) are showed:

Table: Interlaboratory result of 01/2002

Test	PES-Film				TPO-Film			
	VOC Value	Fog Value	well chosen single peak		VOC Value	Fog Value	well chosen single peak	
			n-Butyl-acetate	Tinuvin-P			Major peak	Hexadecane acid
Average value [µg/g] (TA and HA respectively)	584	22	19	1	134	505	28	95
Standard deviation [µg/g] (TA and HA respectively)	184	12	6	1	48	265	11	43
Variation [%]	31	53	34	70	36	52	40	45

The precision for other test matrix can be much better since it concerned with the border lines values of the examined samples assignable with this method. The following reasons cause increased deviation in the interlaboratory test.

- The main component of the VOC value of the PES foil has several results of measurement outside the calibration range. Improvement in the future test is provided in the supplement (chapter 6,7 possibilities of error)

- The Fog value of the PES foil lay closely to the blank value range (sum of very small peaks)
- n-butyl acetate is an unstable component, which can decompose easily with inappropriate storage or with less inert surface during in the analysis system
- With the Tinuvin p - peak should be evaluated consciously within the range of the limit of determination, whereby higher relative deviation are resulted
- In the TPO film components, due to its high polarity, a strong tailing is showed and cause difficulty in uniform integration e.g. Hexadecane acid is a polar component with a weak reciprocal effect to the Methylsiloxanphase, which cause strong tailing in the chromatogram
- Several interlaboratory test participants had so far no or only few experiences with thermodesorption investigation of organic materials.

5,2 Detection limit of toluene on Tenax

The sample-independent performance of the overall system with the example of the linearity by toluene using unit combination 1 (chapter 3.3) defined toluene quantities were analyzed according to chapter 4.3 and the received peak areas was determined. Diagram 1 shows a linear response of the toluene up to a high concentration range. (5 µg from 30 mg sample which correspond to approx.150 ppm). Diagram 2 shows the linear process of the three lower measuring points.

Diagram 1 Linearity of Toluene about the whole measuring area

Diagram 2 Linearity of Toluene in the lower working environment
(ref. to original standard p.21)

$Y = a^1 X + a^0$	$a^1 = 6761000 + 48000$	$a^0 = 10300 + 98000$
Correlation coefficient: $r = 0.99998$		

For the lower working environment (confidence interval, CI=95%), arise from above measurement:

Proof border: 0.005 µg (Toluene on Tenax)

Detection limit: 0.02 µg (Toluene on Tenax)

The statistic values were computed according to DIN 32645. The method and the detection limit determined here only partly related with the real test measurement. They serve for reconstructing the minimum performance requirements of the analytic system. For the assessment/ evaluation of suitability of the system, refer to the minimum requirement described in chapter 3.1.

5,3 Deviation and recovery of toluene on Tenax

From the analyses of the control standards applied on Tenax the toluene content was computed. The following measured values resulted:

Number of measured values	N=20	
Number of time series	6	
Standard deviation		5.4%
Average value of recovery ([actual value/reference value] x 100)		102%
Highest recovery		117%

Smallest recovery

85%

The measuring series was accomplished in a period of approx. 6 weeks.

Note: The measurements for chap. 5.2 and 5.3 were accomplished with the unit combination No.1 (chapter 3.3).

6. Possibilities of error, troubleshooting

6.1 Sample preparation

For the sample preparation, it should pay attention that a contamination or an unnecessary heating up of the samples is avoided.

The samples may not work with temperature producing **Schneidtechniken** (e.g. high-speed rotation saws).

It is usually sufficient with the use of scalpel (with change blade), tweezers, cork borers, for shearing or pliering of harder samples.

Cutting and transferring of the sample in and out of the desorption tube must be taken place briskly. The filled desorption tubes must be placed into the autosampler immediately, in order to avoid emission losses. Also the specific sample surface has a great influence over the result and hence must be as reproducibly as possible. As a rule, higher sample surface usually result in a higher emission.

There the VOC /Fog value always related to the original sample weight but not to the surface and can behave differently with different matrixes, only cause linear effect.

6.2 Difficult samples with non-uniform surface

For some kinds of sample, it is difficult to prepare a defined surface finish reproducibly. Sometimes larger measured deviation (chapter 5.1) can occur e.g. with Vilese, foams with large pore or **zerbröselnden** SMC materials.

Considering the preparative problems for the evaluation of the analysis, an appropriate remark must be documented in the report by the testing laboratory. In cases of Doubt, the sample preparation should be agreed upon the client.

6.3 Problems with the system of cold task (KAS 3, company Gerstel)

It was observed that with insufficient filling of the KAS liner with silanized glass wool a break-through of more volatile substances (including toluene) can take place.

This has not a directly recognizable influence on the calibration.

A strong indication for a break-through in the liner is present if during the control mix analysis, the semi-volatile substances exhibit small forepeaks (possibly from Decan).

=> Remedy: Additional glass wool is added loosely into the liner plug.

By increasing the glass wool portion, it can also increase the peak areas and achieve a better sensitivity. The liner change must be followed by a new calibration!

Note: with too strongly plugged liners the feed gas stream sometimes cannot be kept upright any longer (Pressure rises).

6.4 Problems with the thermal desorber (turbo-matrix ATD, company Perkin Elmer)

- Between valve and the cooling case a "Cold Spot" exists in the quartz liner, which can lead to lower value with the less volatile emissions. This problem can be solved by installation of turbo-matrix containing heat conducting tools.

- The quartz liner in the cooling case must be inactivated or may cause lower value in the control mix from 2-Ethylhexanol and Dicyclohexylamine.
- It should be made certain that in the cooling case, sufficient quartz wool (at least 0,5 cm laterally) is used or the less volatile substances can remain when heating the cooling case with Tenax.
- When using metal desorber tube substantial losses of strongly polar substances can occur.

6.5 Samples with high water content

If very large quantities of water can be emitted from the sample, it is not excluded that the -150°C cooled liners freeze completely during the desorption process.

=> Consequence: low values or the analysis completely breaks off (pressure increase is too highly). This effect sometimes appears with leather or natural fiber containing sample.

=> Remedy: reduce original sample weight.

6.6 Substance misidentification

In some cases misinterpretations may occur if substances with the selected analysis parameter that cannot or barely separated. In particular if substances eluted together with large concentration differences, the smaller peak can be easily ignored.

Example of substances with same or very similar retention time

Name	Significant mass fragments	Remark
Benzene/ Methyl-cyclopentane/ n-Butane	78/ 69/ 31	
1,3-Butadiene/ Acetaldehyde	39, 54/ 29, 44	
o-Xylol/ Cyclohexanon/ Butylacrylate	91/ 98/ 73	If one subtracts p/m-Xylol-MS of o-Xylol-MS, small quantities of cyclohexanon become recognized
p+m-Xylol/ Acetamide, N,N,-dimethyl/ Methoxypropylacetate	91/ 44 72 87/ 43 58 72 87	

6.7 Exceeding of the detection linearity at high emission values

Samples with very high emission values will receive "wrong-low" measured values, if the linearity of the detector is exceeded.

The sensitivity and the linearity range of detectors can be very different. While the more insensitive detector possibly is still in the linearity range of the calibration while a high measuring signal can to be already cut off with one in the lower calibrated but more sensitive detector.

This problem was observed with samples which showed very large single substance peaks e.g. with the MSD Agilent 5973 which measures about 10 times more sensitive than the predecessor model HP5972.

Measure: In case of an excess of the measurement linearity, the calibration must be repeated, whereby the split has to be increased in the cooling case suitably, e.g. instead of 30:1 to 60:1. Alternatively, the measured value is noted as “largely than being indicated” after consultation with the client.

7. Appendix

7.1 Material-specific original weight

The sample weight is not fixed and normally accepted to be 30 ± 5 mg. In the rule, **streifenförmige** samples are weighed, cut with a scalpel. For the following materials the original sample weight is fixed:

Materials	Weight (mg)	Remark
Foam	15 ± 2	Place material loosely and unrammed as possible in the tube. With foams the original weight can have great influence, therefore narrower border is necessary. Sampling place: in the foam surface (possibly influence by parting agents).
Fiber material group (SMC, coal fiber, etc.)	60 ± 20	To seize thicker plates usually split within the layer
Foil/ film sample	30 ± 5	If possible, separate to individual strips
Leather	10 ± 2	To mimic the reality use of the surface and taking the effect of final varnish into consideration, a part of the meat-sized fabric must be removed with thicker leather sample. Thus the danger of the freezing up of the cooling case existing with strongly aqueous leather samples is reduced. Those cooling case go after freezing over procedure should reduce the original sample weight into half.
Varnish/ lacquer	arises	Lacquers are applied on aluminum foil and dried according to the standard conditions. Film thickness: 50 ± 5 µm. Of the foil 30 mm x 3 mm - strips are cut out, weighed and analyzed (the aluminum weight per unit area should be deduced from the weight. Lacquer film production: see 7.2.
Adhesive material group	30 ± 5	If possible, film strips as in application thickness (order on aluminum foil)

Reasons for deviations from the given weight are to be taking into account.

7.1.1 Approach with multilayer sandwich samples:

In order to minimize the test expenditure, it is permissible to analyze several connected/coherent layers together. If the individual layers are relative thick (more than approx. 0.5 mm), jades layer material should be analyzed for itself. This is sensibly to assign the emitted substances and to introduce purposeful remedy measures. Furthermore, one receives a better result certainty, since the emission values can be referred to the respective single material and the layer thickness relationship is no more taken into consideration during the sample preparation.(=> better comparability and improves material development).

If uncertainties are to be expected due to the structure of sample, each component must be analyzed (example: thin adhesive film on surface of foams with high layer thickness).

In some isolated cases an analysis of the entire sample in cross section can be meaningful and possible. On this occasion, the entire sample in cross section with a drill core ($\varnothing=3\text{mm}$) is punched out and lengthwise-halved. Drill core halves from different places are analyzed.

Even if necessarily another kind of sample preparation can be specified for special construction units. The selected sample preparation must be held in the result report.

7,2 Production of varnish/ lacquer film for the thermal desorption analysis

To ensure the comparability and measured value, the varnish/ lacquer drying conditions must be defined and adapted as far as possible. Furthermore, the standard test condition should correspond to the process specification provided by the lacquer supplier.

The production of the varnish/ lacquer film is specified as following:

- The lacquer sprayed on a DIN-A5 large, maximal 30 μm thick, clean aluminum foil. Dry film thickness with **Einschtsystemen**: $50\pm 5 \mu\text{m}$ (even if this deviates from the standard thickness). Dry film thickness with multi-layer systems: Whole structure according to the standard layer thickness.
- The wet lacquers are dried (**seriennahen**) in a laboratory drying accurate drying temperature must be determined with a thermometer attached as the same height of the sample and documented.
- The drying oven may not be equipped with different kinds of sample at the same time. To avoid contamination the oven must be baked for at least two hours at 200°C . Before the start of drying, the oven is warmed up about the target temperature ($\pm 1.5\text{K}$) and can be open only briefly for inserting the samples.
- Oven loading:
 - samples only on one module level (middle module height)
 - operation mode of oven: partial circulating air with maximum circulation ($>10[1/\text{min}]$)
 - Fresh air supply $10\pm 5\%$
 - Loading: $1\pm 0.2 [1/\text{m}]$
 - a. Oven volume = 0.13 m^3
 - b. Varnish area = 0.12 m^2 (correspond to 4 DIN-A5-area)
 - => c. Oven loading = $0.12 \text{ m}^2 / 0.13 \text{ m}^3 \sim 1 [1/\text{m}]$

With another furnace volume the sample surface must be adapted accordingly.

- Oven drying time and temperature:
The drying temperature and duration which can be used is provided as the average value from the upper and lower limit of the processing window indicated in the process specification by the lacquer manufacturer. The actual measured drying temperature and drying time must be logged and indicated during sampling. The samples for the regular production monitoring must be likewise manufactured at this temperature and duration.
- After withdrawal from the drying oven the lacquers are ventilate at ambient temperature (max. 23°C) for 24 hours. Subsequently, the paint must be covered and packed with aluminum foil, put in an airtight PE bag and sent to the analysis laboratory. Alternatively the samples can be stored after packing up to 14 at a maximum temperature of -18°C.
- The analysis laboratory cut two strips of 30 mm x 3 mm from the painted foil, weigh and transfer it directly into the thermodesorption tubes. For the determination of the actual original weight of lacquer, the respective weight per unit area of aluminum foil is taken off from the total weight. Therefore an empty sample of the used aluminum foil must be placed at disposal for the laboratory.

7.2.1 Remark to the standard lacquer finish

The quantity of solvent staying in the film of varnish depends substantially on the drying conditions (in particular the temperature), so the target temperature must be kept at all cost. Otherwise an increase in emission in the vehicle interior will be encounter.

7.2.2 Definition of the sample preparation for wood lacquers

Wood lacquers which are used in the vehicle interior, as a rule, have a very high layer thicknesses (approx. 800 µm). Therefore, this type of lacquer is not treated as "lacquer" (=> 50 µm-Film on aluminum) but treated similarly as a plastic sample. The wood lacquers are applied on aluminum foil and dried according to the standard conditions. Film thickness: 800±50 µm,

Strength of the aluminum foil: 30µm (smooth surface)

Surface: approx. DIN A4

Ventilating duration: with **Luftrocknenden** lacquer systems: 5 days, ambient temperature, so far not differently fixed. The samples for the analysis are then packed airtight to (in aluminum foil and in the PE bag). In laboratory, from the painted foil a 10 mm x 3 mm rectangular pieces (original weight: 30±5 mg) are cut out, weighed without aluminum foil and transfer directly into the thermal the tubes for the analysis.

7.3 Sketch of thermodesorption analysis

(ref. to original standard p.28)

7.4 Example of an control mix-chromatogram

(ref. to original standard p.29)

7.5 Excel report presentation, cell allocation: see Excel attached sheet A

7.6 Excel report presentation, sample Excel report: see Excel attached sheet B