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Investigation of Shortcomings/Limitations of Industrial Standard 278 of the Verband der Automobilindustrie for Measuring Volatile Organic Compounds

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Abstract

The Verband der Automobilindustrie (VDA) 278 is an industry method widely used to measure volatile organic compounds (VOCs). It is most commonly used in the automobile industry to measure and regulate VOC and FOG levels in automotive parts as a safety regulation. The current VDA 278 method has issues from poor accuracy, precision, and reproducibility. There is variability in data due to differences in sample type and handling as well as instrument model. There is little understanding on the reproducibility of measurements of different sample types analyzed on different makes of instruments using VDA 278 analysis. In this work, a round-robin study is performed on diverse sample types, using different makes of instruments in laboratories across the world. It uses improved method conditions developed internally, for better reproducibility, that reduce sources of error. The round-robin study shows good statistical agreement across variable sample types as well as across different makes of instruments. The study also helps qualify new instruments to perform this VDA 278 method to increase capacity for this high-demand analysis.

Keywords

VOC, Automotive industry, Car interior, Volatiles, Volatile organic compounds, VDA 278, Thermal desorption, Adhesive tape

Introduction

The "Verband der Automobilindustrie" (VDA) is the association of the automotive industry in Germany. The content of volatile organic compounds (VOCs) is the total of the readily volatile to medium volatile substances [1]. Substances that condense easily at room temperature and contribute to the fogging of the windscreen of an automobile are defined as FOG [1, 2]. Most commonly, these measurements of VOC and FOG are done to analyze the air of the vehicle interior of automobiles. VDA has several recommendations on how to measure VOC and FOG in car interiors.

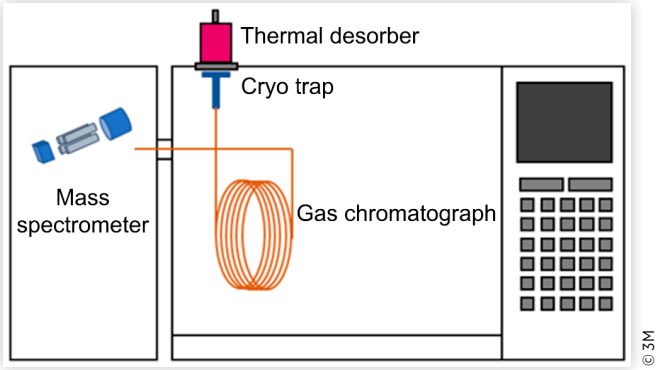
The current VDA 278 method has issues from poor accuracy, precision, and reproducibility. There is variability in data due to differences in sample type and handling as well as instrument model [3].

Exposure to VOCs can cause a range of health problems in humans as well as cause pollution in the atmosphere. The off-gassing of VOC and FOG is increased by heat, a common factor found in automobile cabins, making the automotive interior environment one of the highest in VOC and FOG concentrations that a person is exposed to [4, 5]. Due to these harmful effects caused by VOC and FOG, there is a lot of regulation surrounding levels of VOC and FOG allowed in products for human use.

TD-GC-MS Measurements

VDA 278 uses a thermal desorption–gas chromatography–mass spectroscopy (TD-GC-MS) to measure VOC and FOG [1].

FIGURE 1 Illustration of the TD-GC-MS setup.

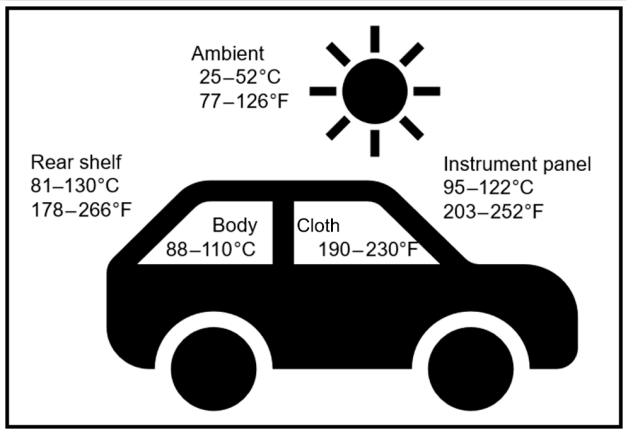


Thermal desorption (TD) often involves the collection of analytes onto solid sorbents and then release by heat and a flow of inert gas. In the case of VDA 278, the release of volatiles is done by directly heating the sample material. These analytes are then focused on a cold trap and then followed by heating again which releases the analytes rapidly. The analytes come off the cold trap and enter the analytical column of the gas chromatograph (GC). The GC is interfaced with a mass spectrometer (MS) as a detector to identify and measure the analytes (Figure 1). TD-GC-MS can be used to analyze a wide variety of samples including adhesives, powders, films, liquids, fibers, resins, and other types of materials.

VDA 278 is known to have limitations in precision. Poor reproducibility is observed across multiple users, instruments, and with variation in sample types. This study examines and explores in detail the many sources of error that cause limitations in VDA 278, using adhesive tapes as samples. Recommendations are made to help manage these sources of error to achieve the best possible outcomes with the VDA 278 test. The current variance between instruments can be 100% and between replicates in the same instrument 25–30% from published information on VDA 278 [3].

The prepared sample is placed into a sample tube and inserted into the thermal desorption device. A constant flow of inert gas is streaming by the sample at 80 mL/min. It is heated to 90°C for 30 min to measure the VOC content (Figure 2). A temperature of 90°C or more can easily be reached inside a car when placed in full sun in warm climates (Figure 3).

FIGURE 3 Illustration of temperatures in an automobile in warm summer.



For FOG analysis the same sample is subsequently heated to 120°C over a period of 60 min. The analytes volatilizing under these conditions are more likely to condensate on surfaces of the car like windows, dashboard, and panels [6] (Figure 2).

It should be noted that after this measurement with heating in Step 1 at 90°C for 30 min and followed by heating in Step 2 at 120°C for 60 min only, a fraction of the total sum of VOCs and FOG material inside the sample has been volatilized. VDA 278 accepts this fact as a matter of practicality to get a result within a reasonable time frame. It is agreed that as long as the overall conditions of this test method are consistently executed, results will be comparable [1].

Sample Preparation

Based on VDA recommendations and keeping contamination levels in mind, the following in-house procedure was designed:

Samples are taken within 8 hours after the last production step and any deviation is reported. Disposable gloves must be worn while handling the sample to prevent contamination from handling. The sample is wrapped twice in 30 µm thick

FIGURE 2 Illustration of the VDA 278 method.

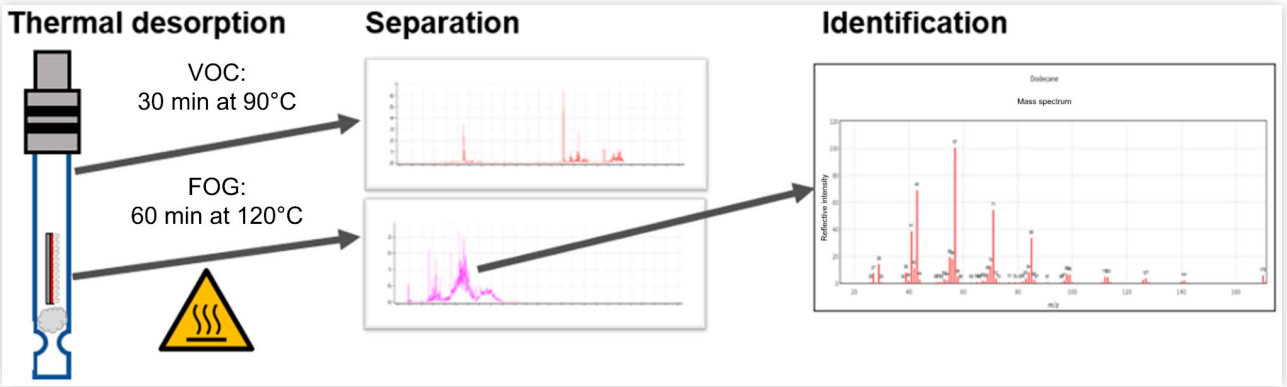
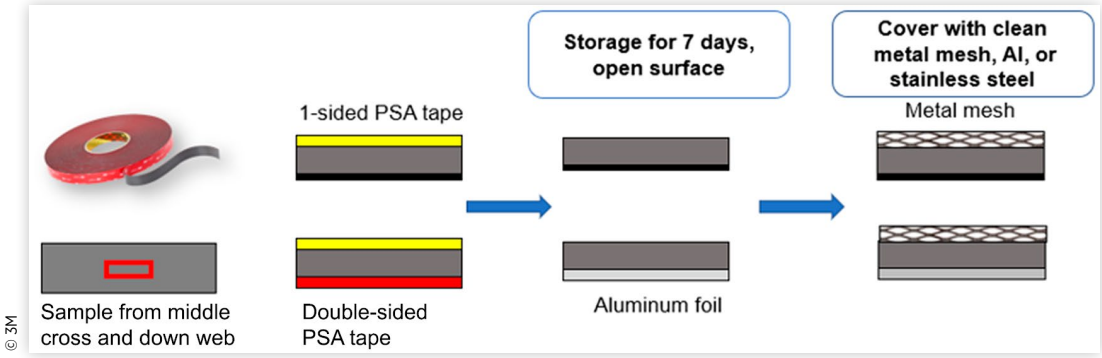


FIGURE 4 Illustration of the sample preparation procedure—proposed house method.



laboratory-type aluminum foil and preferably transported in a sealable freezer bag. It is recommended that liners that are part of the product must also be provided for testing.

It is known that liners can contribute to the VOC content of the final product.

For tape roll sampling in the laboratory for experiments, five windings are removed before sampling. A piece of 5 cm length is then cut from the roll. Specimens are taken from the middle of the tape or sheet (cross-web as well as down-web direction). The specimen weight is about 30 mg. The size of the sample is recommended to be approximately 3 mm × 20 mm. The adhesive side is covered with a clean metal mesh. If the adhesive tape is double sided, a clean aluminum foil should be used to cover the other adhesive side of the tape (Figure 4). The sample is stored in the open, away from variable airflow such as the door or a hood at room temperature for 7 days [7]

Cover Material

It is recommended to cover the adhesive layer of interest with a cover material that allows free diffusion of VOCs from the adhesive layer to the environment. It is important to use a clean cover material that has low background signal. If the cover material is not clean, it will have a substantial background signal which has to be subtracted from the samples.

Paper tissues are commonly used in laboratories as cover material. However, paper tissue contains recycled fibers which were found to have many contaminants (Figure 5), e.g., hydrocarbons that potentially come from mineral oil, which appear as a large background signal. This could introduce a significant error into the analysis, making such materials a poor choice for cover material.

FIGURE 5 GC-MS analysis of the cover material: red, commercial paper tissue; blue, metal mesh; green, glass wool; black, automotive tissue.

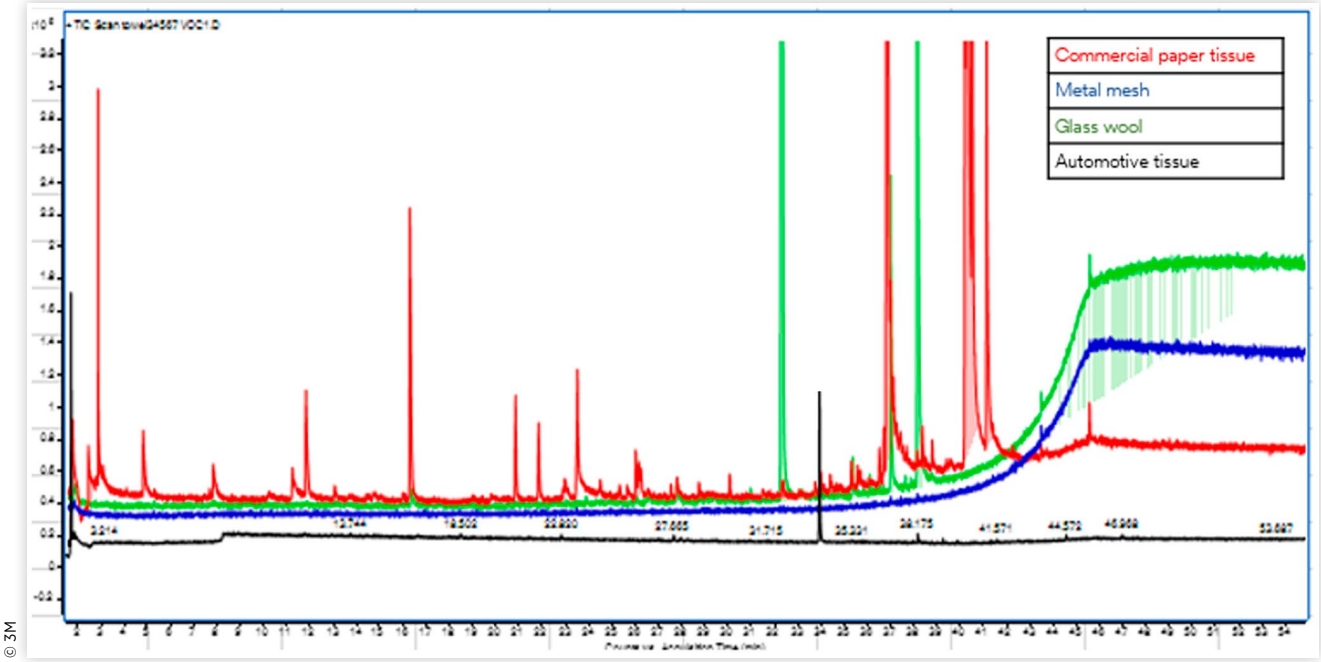
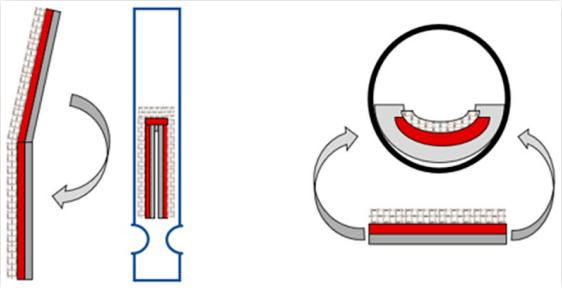


FIGURE 6 Illustration of sample placement in the TD tube.



Another popular cover material is glass beads. However, glass beads pose some practical challenges. They must be applied by pouring a surplus of beads over the surface. Beads that do not stick to the adhesive have to be discarded because cross-contamination from one sample to the next has to be avoided. The split beads pose a severe danger in the laboratory.

The preferred cover material was found to be a clean metal mesh. The mesh can be cleaned by two methods: First, it can be cleaned in an ultrasonic bath on full power in analysis-grade acetone for 15 min. Alternatively, the cut mesh pieces can be baked (conditioned) at 450°C in an oven for 8 hours. This renders the metal mesh contaminant free and additionally provides the sample construction stability. This makes handling easier when the sample is to be inserted into the narrow sample tube.

Glass wool was also observed to contain organic materials causing high background signals (Figure 5). The glass wool can also be baked at 450°C for 8 hours in an oven. This conditioning helps to remove impurities.

Influence of Sample Weight and Sample Dimensions

Samples should be weighed in the range of 30 ± 5 mg with an accuracy of 0.1 mg [1]. In cases of thin adhesive tapes, this might be difficult to fit within the sample holding tube of the instrument, especially the relatively small oven dimension of the Gerstel TDU 2. It is important that the sample size fits the sample tube dimension. Thus, when the sample tube is introduced into the TD oven, the entire sample experiences a uniform heating rate. If the sample size is too big, the heating will be nonuniform across the sample and cause errors in the analysis.

One option could be to double the length of the sample, folding the long sample stripe in half with the adhesive layer to the outside but without touching the glass walls. Another option is to place a wider stripe into the sample holder by cupping the strip into a semicircle with the adhesive layer facing inward (Figure 6).

In the case of high VOC, 30 mg of content materials might overload the MS detector. In such instances, lowering the sample weight is recommended to prevent overloading the detector.

VDA 278 only characterizes VOC and FOG by the weight of the sample and calculating the end results as milligrams per kilogram (mg/kg). It does not consider the thickness of materials which could contribute to the volatile emission [8]. By comparing samples of the same material with different thicknesses, it is observed that increasing thickness increases the volatile emissions.

The influence of the sidewalls of a thick adhesive tape was tested experimentally. The adhesive tape chosen was such that it was available in different thicknesses for the same type of tape. The same base area was cut, and the adhesive sides on the bottom and top were covered with aluminum foil. Only the sidewalls of the adhesive tape were kept open (Figure 7).

It was observed that the VOC content increases with increasing sample thickness (Figure 8 and Table 1). This is potentially due to the increase of open surface at the "sidewalls" with increasing thickness. For FOG values this dependence on the open surface area is not seen, at least not for the given adhesive material. FOG components are higher boiling substances (defined as the retention time of tetradecane and later), and a hypothesis is that these substances are not prone to migrate from the core material of the samples during thermal desorption as much as those substances detected for VOC. Therefore, the surface evaporation area for material migrating to the surface during thermal desorption is not as relevant for FOG substances as it is for VOC substances.

One recommendation could be to minimize the effect for VOC measurements by covering the sidewalls with aluminum foil as well, not only the backside.

Desorption Temperature

To examine the effect of desorption temperature on volatile emissions, an adhesive tape was analyzed at three TD temperatures. It was observed that with increase in desorption temperature, the VOC values increased (Figure 9). Emissions

FIGURE 7 Specimen construction: sandwich of aluminum foil and adhesive tape.

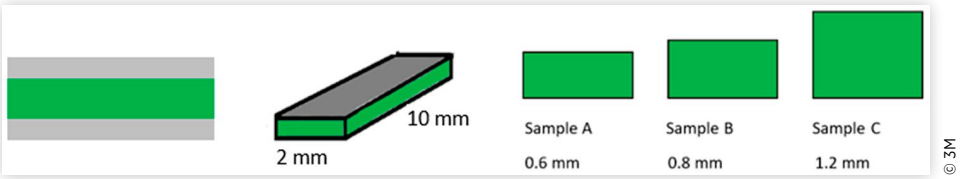


FIGURE 8 Graph of VOC and FOG by varying sample thicknesses measured by the TD GC-MS. *Data point omitted due to instrument malfunction.

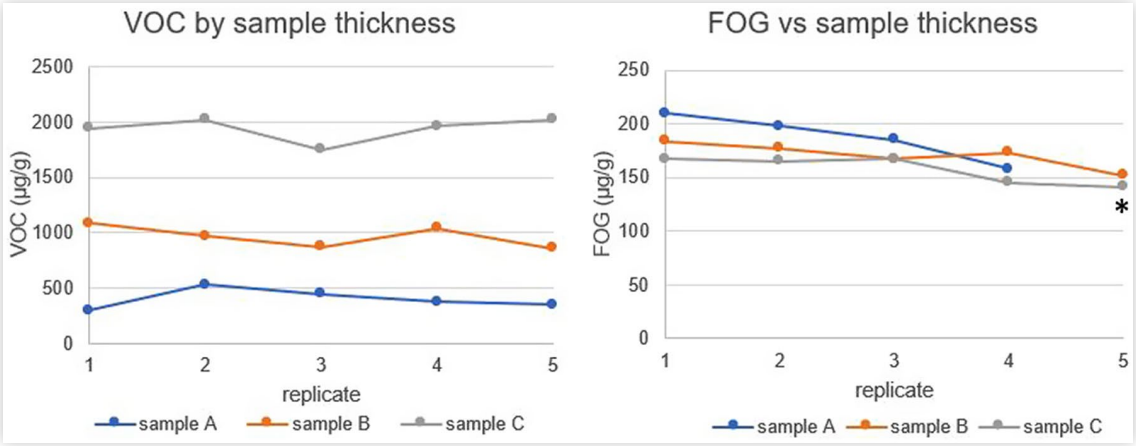


TABLE 1 Results of VOC and FOG values with growing thickness measured by the TD-GC-MS.

VOC (µg/g)	VOC1	VOC2	VOC3	VOC4	VOC5
Sample A	298	529	446	374	350
Sample B	1087	967	875	1041	860
Sample C	1945	2017	1752	1963	2020
FOG (µg/g)	**FOG1**	**FOG2**	**FOG3**	**FOG4**	**FOG5**
Sample A	210	198	185	158	*
Sample B	184	177	167	173	152
Sample C	167	165	167	145	141

* Data point omitted due to instrument malfunction.

are directly related to the boiling point of the substances, so with increases in the temperature of desorption, more substances become volatile enough to undergo emission from the sample. This leads to higher VOC values being observed. This has been reported previously [9], and it shows the importance of having the correct desorption temperature and sample dimensions inside the oven for reliable results.

Influence of the Cryo Trap and Cryo Trap Liner

Instrument manufacturers have carried out extensive research on what the optimal flow rate is for desorption in their individual instruments. However, there is little data on how cold trap liners affect the accuracy or precision of the measurements. Liners are usually glass liners with inert surface treatment and can be modified in their shape to reduce the gas flow, e.g., diameter restrictions or with baffles. It is also possible to insert inert glass wool, glass frits, or adsorbent materials like Tenax® TA or special types of carbon black (Figure 10). Figure 10 shows some general use cold trap liners from Gerstel. They vary in packing material and minimum

FIGURE 9 VOC values with increasing TD temperatures measured by the TD-GC-MS.

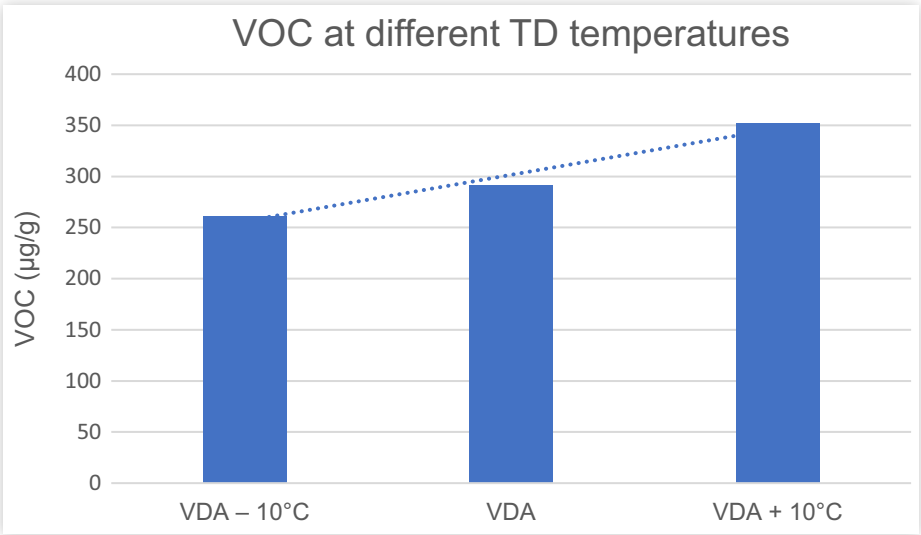


FIGURE 10 Illustration of cryo trap liners (from Gerstel CIS4) filled with glass wool, baffled empty, filled with glass beads, and filled with Tenax® TA (top to bottom).

temperature at which they can be operated. Carbotrap liners were not tested as they have a high retention of VOC and FOG components.

From the desorption tube, the carrier gas containing the volatiles passes through the liner which is placed inside the cryo trap and is filled with liner material onto which the volatile components are collected by condensation. Based on the nature of the material inside the liner, the amount of VOC/FOG retained varies. Once volatile components are condensed on the liner material or glass surfaces, they will be released all at once when the cryo trap is heated up after the desorption step.

Liners should be chosen based on application to ensure maximum volatiles are retained. If the liner is not retentive enough, some low-boiling analytes may pass through the cryo trap. If the liner is too retentive, high-boiling point molecules may not elute off from the liner during the heating step and will not be analyzed. In addition, if during heating, some of the condensed compounds remain on the liner, it could carry forward causing contamination and errors in future measurements [10].

In the example of a very high bond (VHB) tape, it can be shown that FOG is not much affected by differently packed liners while the VOC value decreases the greater the surface area available in the liner (Figure 11). In our experience, glass wool works best for adhesive tapes to maximize adsorption while preventing the overloading of the detector at the same time.

The glass bead liner was found to clog up for samples with high VOC content, and samples with a high water content had ice form on the beads. Tenax was found to degrade with the samples used. The baffled liner did not retain toluene. This gave an artificially high (×3) VOC due to the fact that the toluene calibration standard was reduced and the VOC peaks remained about the same. As hexadecane has a lower vapor pressure and moderate freezing point, FOG was less affected. Glass wool as liner material was found to be robust to a range of adhesive materials.

Split Rate—The Lower the Rate the More VOCs Are Detected

The split ratio is the amount of gas flow going to the capillary column versus the amount discarded to waste through the split valve (Figure 12). This is necessary to prevent overloading the MS detector and to improve the overall chromatography of analyte peaks. Depending on the adhesive tape, it might be necessary to change the split ratio because some tapes might emit a large quantity of VOCs. In such cases, increasing the split ratio will reduce the concentration of analytes passing through the TD system and the detector, thereby preventing overloading. A split rate of 1:60 works best as a default. It is not possible to make a correlation between the results at different split rates (Figure 13) because the change is also related to the sample.

Nature of Sample

Several physical properties of a tape can influence the desorption step of the analysis.

FIGURE 11 Effect of a cryo trap liner on VOC and FOG values.

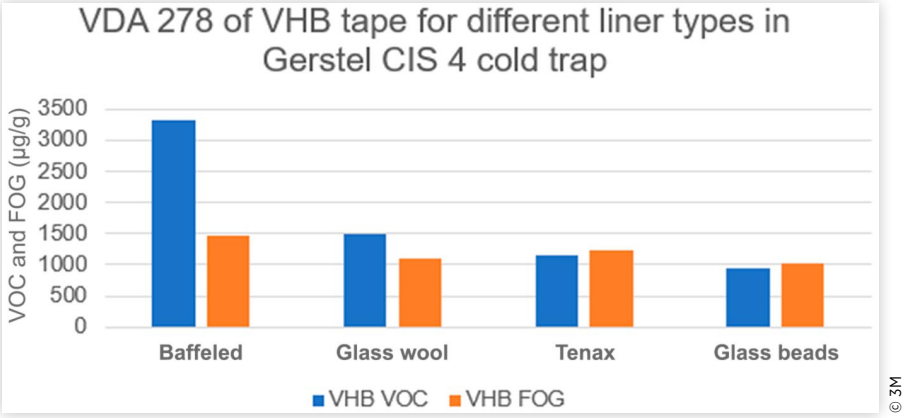


FIGURE 12 Schematic illustration of the recommended split rate of 1:60.

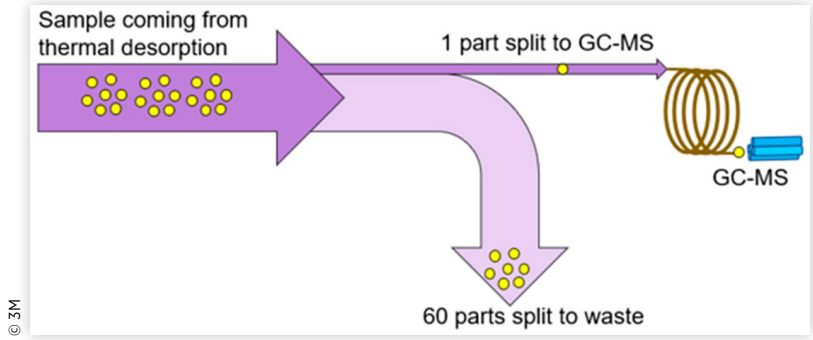
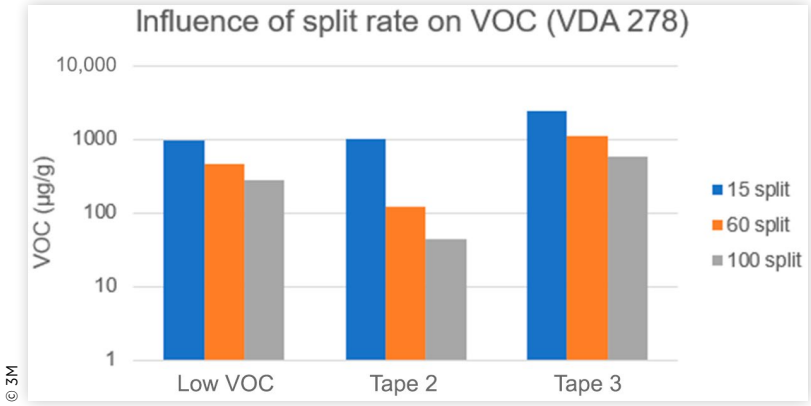


FIGURE 13 Influence of split rate on VOC values.



Foam tapes have different thicknesses of the foam core and therefore a different evaporation surface area. Trims or single-layer adhesive on the other side will have almost no such effect. Adhesives of different types are used (acrylic, silicone, rubber, water based, or solvent based) that behave differently during storage time prior to analysis. The liner material is known to contribute to the VOC content and, therefore, should be supplied to the laboratory as well. But not every liner and not each combination or liner and tape adhesive behaves the same. The VOC content for most tapes will decrease as time goes by. It is important to keep this in mind when "mature" samples are sent to the laboratory, and the results are then compared to results from factory-fresh samples as the VDA 278 recommends (sample taken within 8 hours of the last production step).

Aeration of Sample

VDA 278 recommends a waiting time of 7 days before the analysis measurement is conducted. The sample is uncovered from any liner and kept at normal laboratory atmosphere. It is best to store the samples away from variable airflow areas such as doors and safety hoods. This aeration time is meant to represent real-life conditions where supply chains, transport, and storage beside production lines will cause a delay between production and usage at the customer. In reality, this time can differ significantly for products, suppliers, or original equipment manufacturers (OEMs). VDA 278 gives a framework to make results comparable [11].

A decrease in VOC value is observed after 7 days of aeration time. The extent of the decrease measured varies greatly for different materials (as shown in Figure 14). That makes it quite unpredictable for analysts. Known low VOC tapes have been observed to have higher VOC without the 7-day aeration period, making this a key observation in this study.

Round-Robin

These overall improvements in practices and method conditions were incorporated into our 3M in-house test method. A round-robin experiment was conducted to observe the results in terms of accuracy and reproducibility across different instruments in several international laboratories. In this study, five types of TD-GC-MS instruments were compared (as listed in Table 2). A total of 2 out of 5 instruments are specifically approved for use by VDA 278. One of the goals of this study is to investigate the feasibility of qualifying additional instruments for VDA 278 use.

FIGURE 14 Effect of storage time of 7 days prior to measurement: individual reduction of VOC values.

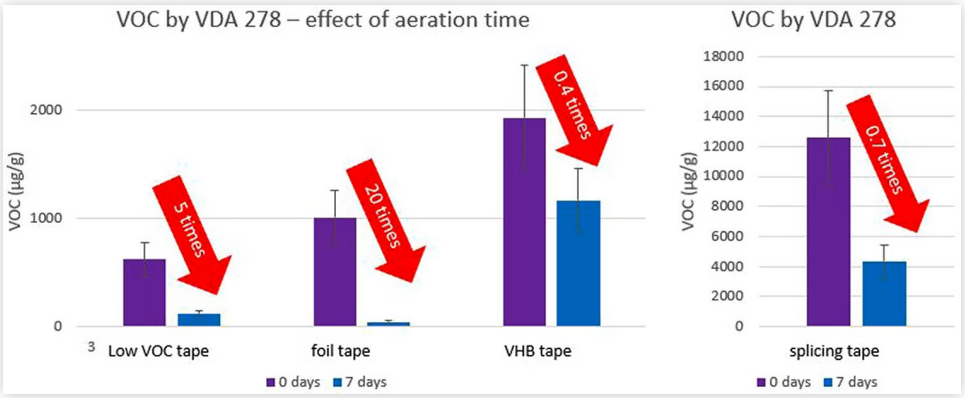


TABLE 2 Instruments used in the study.

Instrument	Manufacturer	Thermal desorption instrument	GC-MS instrumentation
1	Gerstel GmbH & Co.KG	TDU 3.5	Agilent GC 7890B & MS 5977B
2	Gerstel GmbH & Co.KG	TDS	Agilent GC 7890B & MS 5977A
3	Gerstel GmbH & Co.KG	TDU 2	Agilent GC 7890B & MS 5977B
4	PerkinElmer Inc	TurboMatrix	Agilent GC 7890B & MS 5977A
5	Gerstel GmbH & Co.KG	TDU 2	Agilent GC 7890B & MS 5977B
6	GL Sciences B.V.	Optic-4 multi-mode inlet	Agilent GC 7890B & MS 5977C

Reference Tapes for the Study

A special focus of this study was on adhesive tapes. Four different tapes were selected to represent low, medium, and high VOC/FOG materials. They also represent different characteristics such as thickness, backing, and liners to represent a large diversity of materials in the study.

1. Aluminum-backed tape: single-sided thin adhesive layer with thick metal sheet backing
2. Low VOC DCTT: double-sided thin adhesive layer with thin textile core
3. Double-coated foam tape: double-sided adhesive layer with thick foam core
4. Splicing tape: thick single-sided adhesive layer with polymer backing

Instruments in This Study

All four tapes were analyzed in replicates on each instrument. The number of replicates for the individual instrument is mentioned in Figure 15.

The arithmetic average of values for each instrument is summarized in Figure 15. None of the instruments is an outlier. There are differences between instruments, and it is more prominent with low values than with high values (Tapes 1 and 2 versus Tapes 3 and 4).

The same can be seen for the relative standard deviation (RSD) for each tape measured on each instrument (Figure 16). Again, instrument and user error are not separable because each instrument had only one analyst.

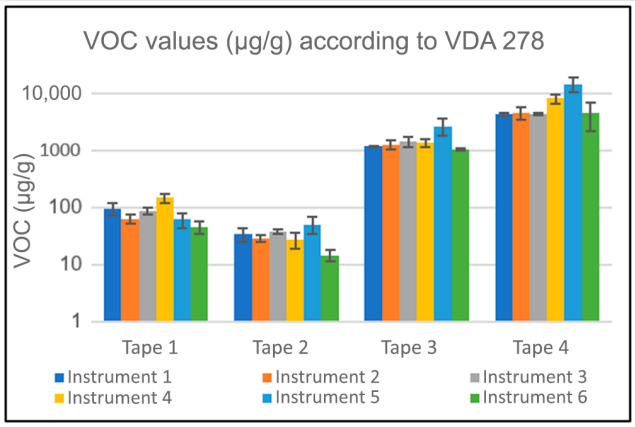
No instrument was performing exceptionally good or bad on all tapes and on both VOC and FOG measurements. No tape caused exceptional difficulties for all participating instruments.

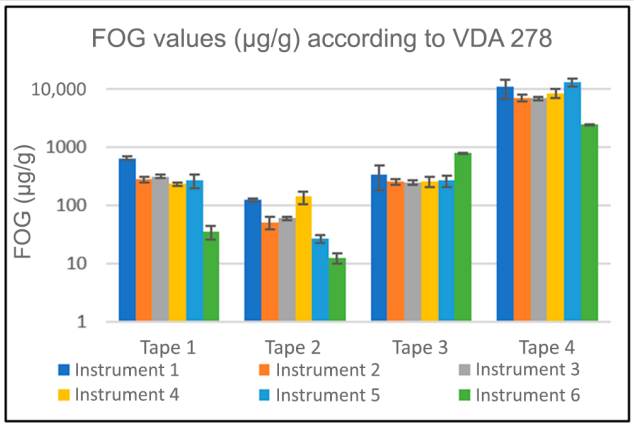
Conclusion

This work examined known sources of errors in the VDA 278 method and makes specific recommendations for best practices to minimize errors. The recommendations are

1. Sample handling: Aeration time of 7 days and consistent storage must be practiced for consistent results. The aeration time ensures that variability in sample sourcing and handling can be minimized.
2. Support material: Various popular diffusive materials were examined using GC-MS. A clean mesh is recommended as the best diffusive support layer as it contributes the lowest background signal compared to other support materials and the stability of the construction.
3. Cryo liner material: Glass wool is recommended as it is the most robust. Having assessed other cryo liner materials, each material encountered various issues. Glass wool showed the best absorption of volatiles and the most efficient release of volatiles upon heating

FIGURE 15 Average values for VOC and FOG results for each tape and instrument.

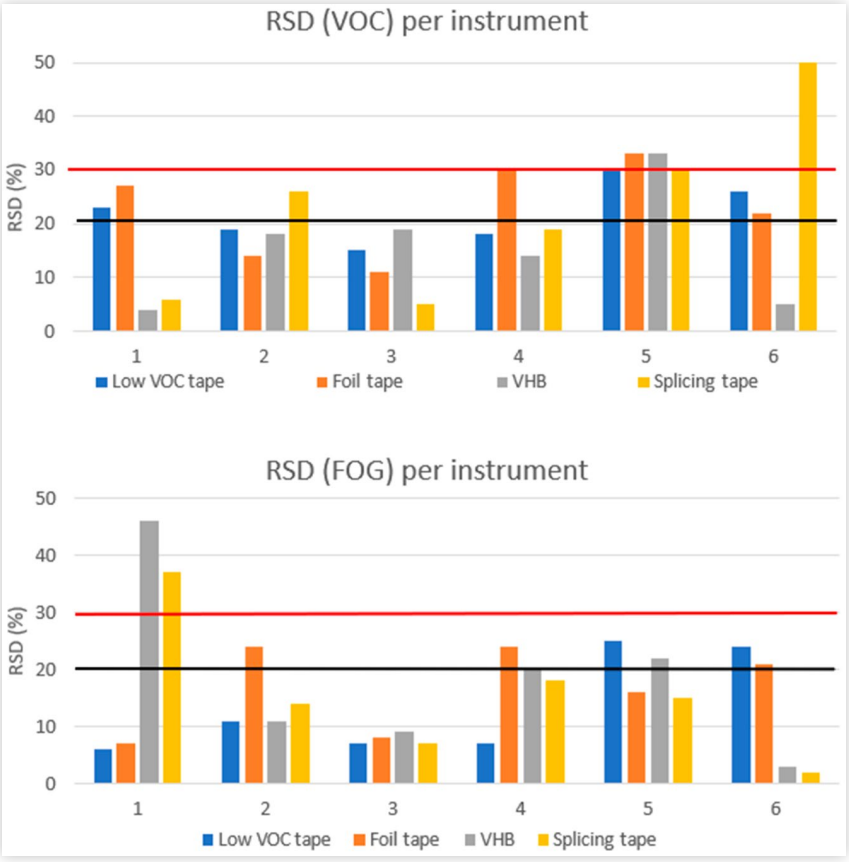




VOC values (µg/g) according to VDA 278						
Instrument	**1**	**2**	**3**	**4**	**5**	**6**
Low VOC tape	95	64	86	148	62	46
Foil tape	34	29	38	27	51	15
VHB	1172	1257	1423	1355	2662	1047
Splicing tape	4258	4535	4261	8109	14,539	4550
n =	3	9	9	9	9	3

FOG values (µg/g)						
Instrument	**1**	**2**	**3**	**4**	**5**	**6**
Low VOC tape	645	283	311	231	269	35
Foil tape	124	51	60	140	27	12
VHB	338	259	251	259	270	787
Splicing tape	10,826	7108	6979	8374	12,983	2468
n =	3	9	9	9	9	3

FIGURE 16 Summary of RSD for VOC and FOG results for each tape on each instrument.



for a wide range of adhesive tapes compared to other liner materials.

4. Sample thickness: Samples of variable thickness were investigated. Greater thickness contributes to higher VOCs. It is important to keep sample thickness in mind and not just sample weight while sampling materials. One possibility is to cover the sidewalls as well as the backside of the adhesive tape.
5. Split rates: For very high VOC samples, peak signal overloading introduces a lot of errors. Higher split rates can be used to prevent peak overloading, but any change shall be mentioned as exception from the default of 1:60.

A round-robin study was executed by incorporating all the above-recommended practices. Four different sample types were analyzed on six different instruments. Some of these instruments are of different manufacturers and different models. The round-robin results (Figure 15) showed the resulting RSDs are typically below 30% RSD, which is an acceptable industry value [3]. If the recommended practices are adopted to do VDA 278 measurements, it reduces errors, which leads to the lowering of variability, in terms of %RSD. Thus, the round-robin study results successfully validate the robustness of the practices recommended in this work. It suggests that if the recommendations are implemented, an analyst can get reliable results with minimized errors while using any of the listed instruments in this study.

VDA 278 recommends only three thermal desorption instruments to perform this method (Gerstel TDS, PerkinElmer TurboMatrix, and Markes TD100/Unity2). The results of this round-robin suggest that additional instruments could be used in the performance of the VDA 278 method, namely, Gerstel TDU 2, Gerstel TDU 3.5, and GL Sciences Optic-4-multi-mode inlet. Additional instruments for VDA 278 tests would greatly increase the capacity and flexibility to performing this test worldwide.

Acronyms

GC - Gas chromatography

MS - Mass spectroscopy

OEM - Original equipment manufacturer

PSA - Pressure sensitive adhesive

RSD - Relative standard deviation

TD - Thermal desorption

VDA - Verband der Automobilindustrie

VHB - Very high bond

VOC - Volatile organic compounds

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Appendix A

Instrument parameters and method parameters for each instrument in this study.

Instrument	Gerstel TDS	Gerstel TDU 2 and 3.5	GL Sciences B.V., Optic-4 multi-mode inlet	TurboMatrix ATD, PerkinElmer
Carrier/sweep gas	Helium, 99.999%	Helium, 99.999%	Helium, 99.999%	Helium, 99.999%
Desorb flow to trap	Splitless	Splitless	Cryo trap is after the split valve	Desorb 40 mL/min, inlet 44 mL/min, outlet 19 mL/min
Desorb flow	82 ± 2 mL/min—split ratio 1:60	82 ± 2 mL/min—split ratio 1:60	Split ratio 1:50	82 ± 2 mL/ min—split ratio 1:60

(*Continued*)

Instrument	Gerstel TDS	Gerstel TDU 2 and 3.5	GL Sciences B.V., Optic-4 multi-mode inlet	TurboMatrix ATD, PerkinElmer
Trap flow to split	Splitless	Splitless		14 psi (pre-column) or 2.0 mL/min constant flow
Initial temp.	20°C	20°C		
Valve temp.				280°C
Tube VOC				90°C
Delay time	0.2 min	0.2 min		30 min (2 stage desorption)
Initial time	0.0 min	0.0 min	Purge 1 min	
ramp	60 K/min	60 K/min	60 K/min	
End temp. VOC	90°C	90°C	90°C	90°C
Hold time. VOC	30 min	30 min	30 min	30 min
End temp. FOG	120°C	120°C	120°C	120°C
Hold time FOG	60 min	60 min	60 min	60 min
End temp. control/ calib	280°C	280°C		280°C
Hold time control/ calib	5 min	5 min		10 min
Sample mode	Sample remove	Sample remove		
Cold trap	**Gerstel CIS 4**	**Gerstel CIS 4**	**GL Sciences B.V., Optic-4**	**Integrated**
Cold trap	Liquid nitrogen	Liquid nitrogen	Liquid nitrogen	Liquid nitrogen
Cold trap liner	Glass wool	Glass wool	NA	Quartz liner with 1/2 cm silanized glass wool, Tenax TA, 1 cm silanized glass wool
Cold trap low temp.	–150°C	–150°C	–150°C	
Equil. time	0.5 min	0.5 min	2 min	
Initial time	0.1 min	0.1 min	0.5 min	–30°C
Cold trap heat ramp	12 K/sec	12 K/sec	12 K/sec	99 K/sec
Cold trap high temp.	280°C	280°C	280°C	280°C
Cold trap hold time VOC	10 min	10 min	33 min	20 min
Cold trap hold time FOG			63 min	
Cold trap hold time control/calib				
GC instrument	**Agilent 7890B GC**	**Agilent 7890B GC**	**Agilent 7890B GC**	**Clarus 600, Perkin Elmer**
Column	HP-Ultra 2, 50 m × 0.32 mm ID, 0.25 µm film	HP-5MS 30 m × 0.25 mm ID, 0.25 µm film	HP-Ultra 2, 50 m × 0.32 mm ID, 0.25 µm film	HP-Ultra 2, 50 m × 0.32 mm ID, 0.25 µm film
Carrier	Helium at 9.5 psi, constant pressure mode	Helium at 9.5 psi, constant pressure mode	Helium at 1 mL/min, constant flow mode	Helium at 9.5 psi, constant pressure mode
Column flow	1.3 mL/min	1.3 mL/min	1.0 mL/min	2.0 mL/min
Flow mode	Solvent vent	Solvent vent	Solvent vent	Constant flow
Vent time	0.1 min	0.1 min	0.1 min	
Vent flow	78 mL/min	78 mL/min		
Purge flow	3 mL/min	3 mL/min		
Purge time	0.02 min	0.02 min		
Pneumatic	Constant flow	Constant flow	Constant flow	

(*Continued*)

Instrument	Gerstel TDS	Gerstel TDU 2 and 3.5	GL Sciences B.V., Optic-4 multi-mode inlet	TurboMatrix ATD, PerkinElmer
Oven program VOC/ toluene calib/control	40°C (hold 2.0 min)	40°C (hold 2.0 min)	40°C (hold 0.0 min)	40°C (hold 2.0 min)
	3 K/min to 92°C (hold 0 min)	3 K/min to 92°C (hold 0 min)	10 K/min to 100°C (hold 0 min)	3 K/min to 92°C (hold 0 min)
	5 K/min to 160°C (hold 0 min)	5 K/min to 160°C (hold 0 min)	20 K/min to 320°C (hold 8 min)	5 K/min to 160°C (hold 0 min)
	10 K/min to 280°C (hold 10 min)/(0 min for calib)	10 K/min to 280°C (hold 10 min)/ (0 min for calib)		10 K/min to 280°C (hold 10 min)/(0 min for calib)
Oven program FOG/ hexadecane calib	50°C (hold 2.0 min)	50°C (hold 2.0 min)	50°C (hold 2.0 min)	50°C (hold 2.0 min)
	25 K/min to 160°C (hold 0 min)	25 K/min to 160°C (hold 0 min)	25 K/min to 160°C (hold 0 min)	25 K/min to 160°C (hold 0 min)
	10 K/min to 280°C (hold 30 min)/(0 min for calib)	10 K/min to 280°C (hold 30 min)/ (0 min for calib)	10 K/min to 280°C (hold 30 min)/(0 min for calib)	10 K/min to 280°C (hold 30 min)/(0 min for calib)
				1:1 deactivated capillary split
				MS—3.6 m/0.15 µm
				FID—2 m/0.15 µm
Transfer line temp.	280°C	280°C	280°C	280°C
Mass spectrometer	**Agilent 5977 MSD**	**Agilent 5977 MSD**	**Agilent 5977 MSD**	**Clarus 600C**
Detection	EI mass spectrometry at 70 eV	EI mass spectrometry at 70 eV	EI mass spectrometry at 70 eV	EI mass spectrometry at 70 eV
Range	Scan 29–450 Da	Scan 29–450 Da	Scan 29–550 Da	Scan 29–450 Da
Solvent delay	3.0 min (ca. 5.5 min for control/calib)	2.0 min (ca. 2.5 min for control/ calib)	3.0 min (ca. 5.5 min for control/calib)	3.0 min (ca. 5.5 min for control/calib)
MS threshold	50	50	100	50
Sample storage	7 days open to lab environment at max. 23°C	7 days open to lab environment at max. 23°C	7 days open to lab environment at max. 23°C	7 days open to lab environment at max. 23°C
Sample weight	30 mg ± 5 mg	30 mg ± 5 mg	30 mg ± 5 mg	30 mg ± 5 mg
Sample size	3 mm × 40 mm	3 mm × 20 mm	3 mm × 40 mm	3 mm × 40 mm
Sample tube	4 mm inner diameter	4 mm inner diameter	Inner diameter 4 mm	4 mm inner diameter
VOC integration range	2.5 min solvent delay till C25 retention time	2.5 min solvent delay till C25 retention time	2.5 min solvent delay till C25 retention time	2.5 min solvent delay till C25 retention time
FOG integration range	Retention time of C14 till retention time of C32	Retention time of C14 till retention time of C32	Retention time of C14 till retention time of C32	Retention time of C14 till retention time of C32

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