



Determination of Volatile and Semi-Volatile Organic Compounds from Vehicle Interior Materials

1 Introduction

Note: Nothing in this standard supercedes applicable laws and regulations.

Note: In the event of conflict between the English and domestic language, the English language shall take precedence.

1.1 Purpose. This test procedure is used for the qualitative and semi-quantitative determination of Volatile Organic Compound (VOC) and Semi-Volatile Organic Compound (SVOC/FOG) emissions in vehicle Interior Materials (IM) utilizing Thermal Desorption - Gas Chromatography/Mass Selective Detection (TD-GC/MSD).

1.1.1 Individual VOC and SVOC emissions in different vehicle interior materials can be identified, semi-quantified, and compared.

1.1.2 VOC emissions in the boiling point range ≤ 345 °C or chromatographic elution range from n-pentane (n-C5) to n-pentacosane (n-C25) (VOC value) can be detected by this method. It is assumed that these substances can be detected from an analysis of the vehicle interior air.

1.1.3 Emissions that condense on a vehicle surface, e.g., glass, plastic lens, etc., at ambient temperature, are classified as SVOC or FOG emissions. SVOC emissions are in the boiling point range ≥ 280 °C or chromatographic elution range from n-tetradecane (n-C14) to n-dotriacontane (n-C32) (SVOC/FOG value) and can be detected by this method.

1.2 Applicability. All materials that can contribute to emissions in the vehicle interior cabin interior have to be tested. Examples include emissions from textiles, carpets, adhesives, sealants, foams, plastic components, films, leather, interior paints, and composite materials.

1.2.1 In relation to emissions, the relevant vehicle interior area comprises all areas that are linked to the passenger compartment either directly or by air contact. Therefore, it includes the luggage compartment, the Heating, Ventilation, and Air Conditioning (HVAC) system, etc.

1.2.2 The results of this test procedure will provide additional information to interpret findings in GMW3059, GMW3205, and GMW3235. The analytical instruments described in Appendix A, Table A1, can be used in GMW15634 to determine the VOCs and SVOCs in vehicle cabin air.

1.2.3 Suppliers must submit the TD-GC/MSD analysis results together with a material sample.

1.2.4 This test procedure complements Verband der Automobilindustrie (VDA) 278 and results may be compared to the American Industrial Hygiene Association (AIHA) health standards.

1.3 Remarks. Determination of VOCs and SVOCs in vehicle interior air, is essential to meet customer requirements and regulatory requirements in some global markets. Emissions from the vehicle interior materials can be the source of the emissions in the vehicle interior air. Concentrations are in the Parts per Million (ppm) range, which warrants accurate analytical measurements.

2 References

Note: Only the latest approved standards are applicable unless otherwise specified.

2.1 External Standards/Specifications.

ISO 9001

ISO/IEC 17025

2.2 GM Standards/Specifications.

GMW3059

GMW3235

GMW15654

GMW16853

GMW3205

2.3 Additional References.

- Odor thresholds for chemicals with established occupational health standards, American Industrial Hygiene Association
- VDA 278 Thermal Desorption Analysis of Organic Emissions for the Characterization of Non-Metallic Materials for Automobiles English Translation, Verband der Automobilindustrie. Uniform Resource Locator (URL): http://www.vda.de/en/publikationen/publikationen_downloads/detail.php?id=1027

3 Resources

3.1 Facilities. All tests per this standard shall be performed by a laboratory that conforms to ISO/IEC 17025 or ISO 9001 or other third party accreditation that is acceptable to the GM Materials Engineer. The supplier shall submit documentation showing proof of accreditation. A list of laboratories certified to this standard can be obtained by the regional GM contact persons.

Note: Some of the laboratories on the GM list may not be formally recognized by third party accreditations.

3.1.1 Calibration. The test facilities and equipment shall be in good working order and shall have a valid calibration label.

3.1.2 Alternatives. Alternative test facilities and equipment may also be used. However, all measuring variables as specified in this standard shall be determined correctly with respect to their physical definition.

3.2 Equipment. This test procedure utilizes commonly available sampling equipment and analytical instrumentation. Specific instrumentation and test conditions are shown in Appendix A, Table A1.

3.2.1 Balance. Balance with a sensitivity of 0.01 mg.

3.2.2 Directly Coupled Thermal Desorption Gas Chromatography System with Cryofocusing and Split System.

3.2.3 Gas Chromatograph (GC) with Mass Selective Detector, Software, and Mass Spectra Library.

3.2.4 GC Capillary Column. GC Capillary Guard Column, to prevent thermal shock to increase capillary column longevity. Low-bleed Gas Chromatograph Mass Spectrometer (GC/MS) Capillary Column with Stationary Phase (5%-phenyl-methylpolysiloxane), e.g., Agilent Technologies 50 m × 0.32 mm × 0.50 µm Ultra 2 or comparable.

3.2.5 Sample Tubes. Sample tubes with deactivated glass surface or metal tubes.

3.2.5.1 Tenax TA (Glass) Thermal Desorption Tubes (TDT). Compatible with the specific corresponding thermal desorption system. See Appendix G, Figure G1.

3.2.5.2 Empty Glass Tubes/Metal tubes. Compatible with the specific corresponding thermal desorption system. Empty glass tubes with end-packed deactivated quartz wool or with glass frits at one (1) end of the tube can be used. These are designated as an Interior Material Thermal Desorption Tube (IM TDT). See Appendix G, Figure G1.

3.2.6 Tube Spiking Adapter. A tube spiking adapter is used for spiking liquid standards into Tenax TA TDTs and evaporating the solvent. See Appendix G, Figure G2 for details. **Note:** Other apparatus can also be used.

3.2.7 Carrier Gas. Grade ≥ 5.0 Helium (He) and a corresponding in-line purifier trap is used for the GC carrier gas, the Tenax TA TDT conditioning purge gas, and the tube spiking adapter gas.

3.2.8 Conditioning the Tenax TA Glass Thermal Desorption Tubes. Tenax TA filled tubes will be cleaned thermally with an apparatus designed for that purpose, e.g., a Dynatherm Model 9600 six-tube conditioner or equivalent. Set the helium purge gas flow rate to 30 mL/minute to 40 mL/minute for each port. Conditioning consists of heating Tenax TA Glass Thermal Desorption Tubes (GTDT) at 320 °C continuously for 3 h ± 10 minutes. Tenax TA TDTs must be conditioned before use.

3.2.8.1 For empty tubes, use an appropriate detergent for the cleaning of the empty glass tubes. After cleaning with the detergent, the tubes have to be cleaned with distilled water and then heated in a drying oven at 105 °C for 45 minutes.

3.2.8.2 After the cleaning, thermally and/or with detergent, the tubes should be packed airtight in aluminum foil or special Teflon tubes to prevent contamination.

3.2.9 Syringes. The required syringe sizes for spiking tubes is 10 µL.

3.2.10 Solvents for Standard Dilutions.

3.2.10.1 Methanol (MeOH), HPLC grade.

3.2.10.2 Methylene Chloride (MeCl₂), HPLC grade.

3.2.11 Standards and Dilutions. Standards of desired VOC and SVOC components at ≥ 98% purity or equivalent are required. All standards and dilutions are to be kept in sealed containers and refrigerated ≤ 8 °C when not in use.

3.2.11.1 Check standard containing a mixture of 18 individual components, 110 µg/mL ± 10 µg/mL each in methanol. See Appendix B, B1, Check Standard.

3.2.11.2 Calibration standards consisting of toluene and n-hexadecane, 500 µg/mL ± 50 µg/mL each in methanol. See Appendix B, B2 Calibration Standard.

3.2.11.3 n-Alkane standard containing n-C5 (n-Pentane) to n-C32 (n-dotriacontane) of 28 individual n-alkane components, 2000 µg/mL each in methylene chloride.

3.2.11.4 Aromatics standard containing aromatic hydrocarbons, 14 individual components, 2000 µg/mL each in methanol.

3.2.11.5 Grob test mix for testing the GC column performance.

3.3 Test Vehicle/Test Piece. This test procedure is used to test vehicle interior materials that are contributing emissions. Test pieces should be obtained from suppliers as soon as possible after production. Unless otherwise specified in GMW16853, no pre or post treatment of the test samples beside the production process and the test sample preparation, e.g., drying, if necessary, is allowed. Manufacturing date and sampling date should be documented. Care should be taken to prevent material out-gassing before analysis, i.e., package, refrigerate. See GMW16853 for test sample preparation.

3.3.1 Materials. For the analysis, a representative sample of the material is taken. For larger parts, smaller samples are cut into an approximate sample size of 25 cm × 20 cm. The sample should not be touched with bare fingers. The cutting has to be done with an oil-free tool. For packing requirements see GMW16853, Packaging of Test Pieces.

Note: Samples without identification labels will not be analyzed until clarification is received.

3.3.2 Parts/Samples. The delivered Parts/Samples shall be unpacked and then stored for 16 h ± 4 h at +23 °C ± 2 °C and 50% ± 10% Relative Humidity (RH) in a room with a controlled atmosphere free of dust and air drafts. If a sample has not been directly packed after production, this pre-storage time has to be subtracted from the above mentioned time. After storage the test samples can be prepared.

3.4 Test Time.

Calendar time: 1 day

Test hours: 8 hours

Coordination hours: 4 hours

3.5 Test Required Information. For test required information see GMW16853.

3.6 Personnel/Skills. Proper training is required to operate the instrumentation in this procedure. Professional degrees in chemistry, chemical engineering, or the health sciences are preferred.

4 Procedure

4.1 Preparation.

4.1.1 IM TDT. For each material sample, two (2) tubes are loaded with the weighed amount specified for the material. See Appendix C, Table C1.

4.1.1.1 Tube A. First VOC analysis run.

4.1.1.2 Tube B. Second analysis run for VOC, followed by SVOC/FOG analysis run.

4.1.2 Material Samples.

4.1.2.1 Two (2) samples should be taken from the material. For each sample, one (1) small strip is cut off with a scalpel and weighed into one (1) IM TDT. Weight of sample should range from 10 mg to 30 mg.

4.1.2.2 In order to insert a sample as large as possible, maximum use should first be made of the width of the sample tube when cutting the sample to size. The maximum sample width is generally 3 mm. The dimensions of the cut sample should be documented in the report.

4.1.2.3 Some suggested interior material masses are given in Appendix C, Table C1. The required accuracy for weighing is ± 0.01 mg.

4.1.2.4 A photograph shall be taken from the sampling point as well as from the packed glass tubes.

4.1.3 Thick Samples. For samples with a height of more than 3 mm, or multi-layered samples, cores of 3 mm diameter are stamped out. These cores are cut into halves. For analysis, two (2) different halves are weighed into one (1) tube.

4.1.4 Multi-Layer Sandwich Samples. With relatively thick individual layers, i.e., more than 0.5 cm, the material in each layer should be analyzed separately. This helps to allocate the emitted substances accordingly, and to target problem materials.

4.1.5 Paint Films. Two (2) samples, 30 mm $\times$ 3 mm, are weighed into a glass tube. The weight of the aluminum foil must be subtracted.

4.1.6 Samples with a High Water Content. In order to produce accurate test results, reduce the weight of high water content samples. For example, leather could lead to a freezing of the cold trap. This leads to lower values or the run is aborted. To prevent this, reduce the weight of these samples to 10 mg $\pm$ 2 mg.

4.2 Conditions.

4.2.1 Environmental Conditions. Not applicable.

4.2.2 Test Conditions. Deviations from the requirements of this standard shall have been agreed upon. Such requirements shall be specified on component drawings, test certificates, reports, etc.

4.2.2.1 The IM TDT is analyzed using two (2) initial thermal desorption stages. In the first thermal desorption stage, an IM TDT is heated to 90 °C for 30 minutes. The evolved VOC emissions are trapped on a silanized glass wool liner at -150 °C. The tube is removed after the first thermal desorption stage is complete. The trapped VOC emissions are then thermally desorbed off the silanized wool at 280 °C into the TD-GC/MSD system for qualitative and semi-quantitative analysis. This VOC value is measured from Tube A and Tube B.

4.2.2.2 The second thermal desorption stage is performed immediately after VOC analysis of the second tube is complete. The same IM TDT is heated to 120 °C for 60 minutes. The evolved SVOC/FOG emissions are trapped on a silanized glass wool liner at -150 °C. The IM TDT remains in place until the entire SVOC analysis is complete. The trapped SVOC/FOG emissions are then thermally desorbed off the silanized wool at 280 °C into the TD-GC/MSD system for qualitative and semi-quantitative analysis. The SVOC/FOG value is measured only from Tube B.

4.2.2.3 A semi-quantitative determination of the emissions expressed as mass parts per million can be obtained by calibration with reference substances. Toluene is used as a reference substance for VOC and n-hexadecane as reference substance for the SVOC/FOG value. Unknown substances can be identified from the mass spectra and the retention time.

4.3 Instructions.

Note: The instrument conditions for the VOC and SVOC/FOG analysis are given in Table D1 thru Table D4 of Appendix D.

4.3.1 Spiked Standard(s). The known standard solutions (microgram (μ g)/microliter (μ L)) of sought compounds are spiked on separate preconditioned Tenax TA tubes. This is accomplished by using an apparatus as described in 3.2.6 and Appendix G, Figure G2. Use a 0.7 L/minute $\pm$ 0.3 L/minute helium flow rate for 3 minutes to 4 minutes to achieve a 2.5 L to 3.0 L total helium volume.

4.3.1.1 Check Standard. Perform a TD-GC/MSD run on a Tenax TA TDT spiked with 4 μL of check standard (3.2.11.1) in the scan over specified mass range (SCAN) mode to acquire standard VOC and SVOC compounds. The retention times of the components in this mixture are suitable as reference points to determine the retention time indices of unknown substances, and can be used as an additional check of MSD identification during test runs. Keep a running record of the individual components response and retention times as a method monitor.

4.3.1.2 Calibration Standard. Perform a TD-GC/MSD run on a Tenax TA TDT spiked with 4 μL of calibration standard (3.2.11.2) in SCAN mode to acquire toluene equivalent data for VOCs and hexadecane equivalent data for SVOCs.

Note: This calibration is used for compounds beyond the specific sought substances.

4.3.1.3 n-Alkane and Aromatics Standards. Perform a TD-GC/MSD run on a Tenax TA TDT spiked with 1 μL of n-alkane standard (3.2.11.3) or 1 μL aromatics standard (3.2.11.4) in SCAN mode with VOC and SVOC conditions. The retention times of the components in these mixtures are suitable as reference points to determine the retention time indices of unknown substances (Appendix G, Figure G3 and Figure G4, and corresponding chromatogram retention times, compound names, and chemical abstracts service numbers in Table G1 and Table G2), and can be used for an additional check of MSD identification during test runs. Keep a running record of the individual components response and retention times as a method monitor.

4.3.2 Testing the TD-GC/MSD System. The function of the instrument system is tested by analyzing a check standard during the analysis sequence. A calibration curve is prepared by spiking a number of Tenax TA TDTs with different volumes of the check standard solution (range 0.01 μg to 6 μg per substance per injection). The calibration will be performed regularly. Only the check standard and calibration standard shall be implemented for each test series. Other standards listed in 3.2.11 may also be used to evaluate system performance and retention time locking studies.

The check standard contains non-polar, polar, basic, and acid components that would display noticeable peak tailing even with low adsorption effects. Peaks occurring in close succession can be used to check the separation efficiency of the chromatographic column.

4.3.2.1 The performance of the mass spectrometric detector is verified by means of mass and sensitivity tuning and the specification required by the manufacturer must be achieved. An air/water check has to be done to check the integrity of the entire system.

4.3.2.2 All substances in the check standard must be clearly identified from the mass spectra library during the search run.

4.3.2.3 The thermal desorption system must also be checked for possible memory effects by performing a "blank" run with an empty desorption tube at least before every sample series.

4.3.3 Test Procedure.

4.3.3.1 Prior to the analysis of interior material samples, a calibration has to be done and the limits of detection shown in 4.3.3.1.1 through 4.3.3.1.4 must be reached at a Signal-to-Noise (S/N) ratio of 3:1.

4.3.3.1.1 Toluene < 0.04 μg .

4.3.3.1.2 n-Hexadecane (n-C16) < 0.05 μg .

4.3.3.1.3 n-Eicosane (n-C20) < 0.06 μg at VOC conditions.

4.3.3.1.4 n-Dotriacontane (n-C32) < 0.2 μg at SVOC conditions.

4.3.3.2 Recovery rate of the individual substances of the check standards under VOC conditions should be between 60% and 140%, with the exception of toluene which should be between 80% and 120%.

4.3.3.3 For a complete analytical run, the measurements described in 4.3.3.3.1 through 4.3.3.3.4 must be done.

4.3.3.3.1 Blank sample under VOC and SVOC conditions, to check the cleanliness of the TD-GC/MSD system.

4.3.3.3.2 Check standard mix spiked on a Tenax TA TDT for testing the TD-GC/MSD system.

4.3.3.3.3 Calibration standard (toluene and n-hexadecane), 4 μL of the standard solution spiked on a Tenax GTDT, as described in 4.3.1.2 for the semi-quantitative determination of the substances.

4.3.3.3.4 Analysis of the interior material, at VOC and SVOC conditions.

4.3.3.4 After every change of the TD-GC/MSD system, e.g., cleaning, changing the column, etc., the Grob test mix, n-alkane standard and aromatics standard must be analyzed to determine the retention time of the analytes for quality assurance.

5 Data

5.1 Calculations.

5.1.1 Qualitative Analysis. During this procedure, identification of individual VOC and SVOC components is accomplished by operating the mass filter in SCAN mode. Several sought compounds may be semi-quantitatively determined with an extracted ion chromatogram, e.g., when there are overlapping peaks, or an explicit determination is impossible. Usually the molecule's base ion (highest m/z abundance) or the molecule's parent ion (if available: $m/z = M^+$) serves as the target ion (quantitative m/z). A known corresponding fragment ion serves as a qualifier ion (m/z). With this information and the retention time of each analyte, an exact determination is possible. If a substance cannot be clearly identified, a possible identification (marked with a question mark) or a reference to the substance class can be given, provided that the appropriate reference points, e.g., typical mass fragments, permit such conclusions to be drawn. See Appendix E for notation examples.

5.1.2 Semi-Quantitative Analysis.

5.1.2.1 Total Amount of VOCs and SVOCs. The total area of all of the substance peaks occurring in the chromatogram (excluding artifacts) is determined first. The integration parameters for the chromatography software must be set so that peaks with a concentration of ≥ 1 ppm are detected reliably. For the total amount of VOCs, all peaks in the corresponding chromatogram have to be integrated, including peaks beyond the retention time of the n-C25 alkane, as well as peaks with a concentration lower than 1 ppm.

5.1.2.2 If the chromatogram includes so called "oil-mountains", consisting of unresolved species, these are integrated as one (1) peak in which the baseline is laid from the start to the end of the "oil-mountain". If clearly identified peaks of other substance occur in this zone, they must be integrated and specified separately.

5.1.2.3 The calculation for the individual peaks can be found in Appendix F.

5.1.2.3.1 The total amount of VOCs is calculated as toluene equivalent, and the total amount of SVOCs as n-hexadecane (n-C16) equivalent by comparison of the peak areas to the peak area of the individual calibration standard. For the VOC, only the peak areas from the beginning of the chromatogram to n-pentacosane (n-C25) will be calculated. For the SVOC, only the peak areas from n-tetradecane (n-C14) to n-dotriacontane (n-C32) will be calculated.

5.1.2.3.2 If the VOC results deviate by more than 20% relative to the mean value, a repeat analysis, including a SVOC run, must be performed. Both VOC values must be stated in the test report, but the analysis with the higher value is used for evaluation.

5.1.3 Individual Amounts of VOCs and SVOCs.

5.1.3.1 Each analyte with a concentration > 1 ppm has to be identified and its concentration has to be calculated. At a minimum, the concentrations of the analytes that are mentioned in the individual regulation have to be calculated.

5.1.3.2 The individual VOCs and SVOCs are quantified by comparing the SCAN quantitative ion peak area amounts to those of known standard solutions (external standard calibration).

5.1.3.3 If there are individual peaks in the "oil-mountains", they have to be integrated manually at the height sticking out the "oil-mountains".

5.1.4 Calculated Result Disclaimer. The calculated semi-quantitative results obtained are from individual organic compounds thermally stripped and detected under these particular methods and corresponding sampling conditions. This semi-quantitative method should not be compared to other semi-quantitative or quantitative methods.

5.2 Interpretation of Results. Some VOCs and SVOCs are frequently cited as odorous compounds and may require additional testing in accordance with GMW3205. VOCs and SVOCs listed as restricted and reportable substances should meet the requirements specified under GMW3059. See Appendix C.

5.3 Test Documentation. The results are displayed in a report. See Appendix G, Data Form G1, for details. In addition, the chromatograms for the VOC/SVOC determination and associated substance lists must be attached to the results report. The full set of analytical data must be supplied electronically and should include the information described in 5.3.1 and 5.3.2.

5.3.1 Microsoft Excel files containing the detailed results of the VOC/SVOC analysis and the chromatogram of the appropriate sample.

5.3.2 Information on the TD-GC/MSD equipment used for the measurement.

5.3.3 The photograph of the sampling (see 4.1.2.4) shall be included in the test report.

5.3.4 Information about sample size and weight within the vehicle shall be included in the test report.

6 Safety

This standard may involve hazardous materials, operations, and equipment. This standard does not propose to address all the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

7 Notes

7.1 Glossary.

FOG: The thin coating that forms on the inside of a vehicle surface, e.g., glass, plastic lens, etc., at ambient temperature that can distort or reduce visibility. It is caused by the condensation of SVOC emissions, e.g., plasticizers, stabilizers, oils, greases, blowing agents, release agents, adhesives, etc., from trim materials.

7.2 Acronyms, Abbreviations, and Symbols.

%	Percent
AIHA	American Industrial Hygiene Association
AMU	Unified Atomic Mass Unit
CAS	Chemical Abstracts Service
CIS	Cooled Injection System
FOG	Same as SVOC
GC	Gas Chromatograph
GC/MS	Gas Chromatograph Mass Spectrometer
GTDT	Glass Thermal Desorption Tube
He	Helium
HVAC	Heating, Ventilation, and Air Conditioning
ID	Identification
IM	Interior Materials
Info.	Information
MSD	Mass Selective Detection
n-C5	n-Pentane
n-C14	n-Tetradecane
n-C16	n-Hexadecane
n-C20	n-Eicosane
n-C25	n-pentacosane/n-pentacontane
n-C32	n-Dotriacontane
No.	Number
ppm	Parts per Million
RH	Relative Humidity
RT	Retention Time
S/N	Signal-to-Noise
SCAN	Scan over specified mass range