



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). For material approvals total VOC/SVOC, and restricted compounds (benzene, toluene, ethylbenzene, xylene (BTEX) and styrene) with a concentration > 1 ppm must be measured using method A. Method B can be used to identify compounds not on the restricted substances list if required for problem solving purposes.

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

1.1.2 "Total VOC" emissions are defined as compounds in the chromatographic elution range from the beginning of the chromatogram to the end of *n*-eicosane (*n*-C20).

1.1.3 "Total SVOC" or "FOG" are emissions that condense on a vehicle surface, e.g., glass, plastic lens, etc., at ambient temperature, and are defined as compounds in the chromatographic elution range from the beginning of *n*-hexadecane (*n*-C16) to the end of *n*-dotriacontane (*n*-C32).

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 Methods A and B will provide additional information to interpret findings in GMW16853, GMW3205, and GMW3235. The analytical instruments described in Appendix A, Table A1, can be used in GMW15654 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 These test procedures complement 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 Guide 34 ISO/IEC 17025

2.2 GM Standards/Specifications.

GMW3205 GMW3235 GMW15654 GMW16853

2.3 Additional References.

- CG5025 VIAQ Regulated Volatile
- 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 for Methods A and B

3.1 Facilities. All tests per this standard shall be performed by a laboratory that conforms to ISO/IEC 17025 and is accredited to these standards by a third-party body that is acceptable to General Motors. The supplier shall submit documentation showing proof of accreditation.

3.1.1 Calibration. The test facilities and equipment shall be in good working order and shall have a valid calibration label. The calibration is to be valid to ISO/IEC 17025.

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 with a sensitivity of 0.01 mg.

3.2.2 Directly Coupled Thermal Desorption Gas Chromatography System with trap focusing and split system. (Gerstel uses Cryotrap and Markes uses Peltier trap.)

3.2.3 Gas Chromatograph (GC) with mass selective detector, software, and mass spectra library.

3.2.4 GC Capillary Column (with GC capillary guard column), low-bleed gas chromatograph mass spectrometer (GC/MS) capillary column with stationary phase (5%-phenyl-methylpolysiloxane), e.g., Agilent Technologies 60 m × 0.32 mm × 0.50 µm or comparable.

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

3.2.5.1 Tenax TA (Glass) Thermal Desorption Tubes (TDT) compatible with the thermal desorption system being used. See Appendix G, Figure G1.

3.2.5.2 Empty and Conditioned Glass Tubes/Metal tubes compatible with the thermal desorption system being used. Empty glass tubes with end-packed deactivated quartz wool or with glass frits at one end of the tube can be used. Cleaned tubes should be stored in a way that prevents contamination, such as by wrapping in aluminum foil. 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 Gases. Grade ≥ 5.0 helium (He) and a corresponding (optional) *in-line* purifier trap is used for the GC carrier gas, the Tenax TA TDT. Nitrogen can be used as the conditioning purge gas and the tube spiking adapter gas.

3.2.8 Conditioned Tenax TA Glass Thermal Desorption Tubes. Tenax TA filled tubes will be cleaned thermally with an apparatus designed for that purpose.

3.2.9 Syringes. Syringes of varying sizes are used as needed. Syringes are most accurate when used to measure volumes closer to the middle of the total volume.

3.2.10 Solvents for standard dilutions.

3.2.10.1 Methanol (MeOH), HPLC grade, pesticide residue grade, or purge and trap grade.

3.2.10.2 Methylene chloride (CH₂Cl₂, MeCl₂), HPLC or pesticide residue grade.

3.2.11 Initial Calibration Standards consisting of at least 5 concentration levels prepared from standard(s) obtained from an ISO Guide 34 certified vendor. The stock standard will consist of at least the following compounds: benzene, toluene, ethylbenzene, *m*-xylene, *p*-xylene, *o*-xylene, styrene, spiked onto a Tenax TA tube. Standards may be made from liquid or gas based cylinder standards. The solvent for liquid standards

should be one that is compatible with Tenax TA, such as methanol. A single point standard of toluene-*d*8 and hexadecane-*d*34 is used to determine total VOCs and total SVOCs. See Appendix B for further guidance.

3.2.11.1 Check Standard containing, at least, a mixture of benzene, toluene, ethylbenzene, *m*-xylene, *p*-xylene, *o*-xylene and styrene purchased from a different, ISO Guide 34 certified vendor than the initial calibration standard, spiked on a Tenax TA tube. The solvent for liquid standards should be one that is compatible with Tenax TA, such as methanol. See Appendix B for further guidance.

3.2.11.2 Retention Time Standard: *n*-Alkane standard containing *n*-C5 (*n*-pentane) to *n*-C32 (*n*-dotriacontane) of 28 individual *n*-alkane components, 2000 µg/mL each. This standard is used to establish the retention times used to integrate the total VOC and total SVOCs. See Appendix B for further guidance.

3.2.11.3 Grob test mix, or another system evaluation standard, 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 (rinse and/or wipe cutting area of tool with a *non*-polar solvents such as hexane). 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 at least 168 h under ambient conditions that are considered reasonable for a workplace and away from sources of contamination, heat, sunshine and other conditions that may be destructive to the sample. If a sample has not been directly packed after production, this pre-storage time has to be subtracted from the preceding time. After storage the test samples can be prepared. See GMW16853.

3.4 Test Time.

Calendar time:	1 d
Test time:	8 h
Coordination time:	4 h

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. A professional degree in chemistry, chemical engineering, health science or equivalent, and familiarity with the operation of the instrumentation is required. Personnel without this background shall be trained carefully on the instrumentation before using it.

4 Procedure

4.1 Preparation.

4.1.1 Sample and Standard Tube Preparation Procedure for Methods A and B.

4.1.1.1 Conditioning Tenax TA 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 approximately 320 °C continuously for at least 3 h. Tenax TA TDTs must be conditioned before use and analyzed before use. All analytes must be less than the detection limit on each tube for the conditioning to be considered successful.

4.1.1.2 Conditioning Empty Glass Tubes. Use an appropriate detergent that will clean the sample out of the empty glass tubes. After cleaning with the detergent, like Alconox or soap, the tubes are rinsed with distilled water and then heated at approximately 105 °C until dry. After the cleaning, thermally and/or with detergent, the tubes should be packed airtight in aluminum foil or in special Teflon tubes to prevent contamination. The tubes should then be stored in an area free from possible contaminants, such as freezer or fridge.

4.1.1.3 Spiking Tenax TA Tubes with Liquid Standards. A liquid spiking apparatus designed to spike the type of Tenax TA tubes used for analysis should be used. This apparatus is generally connected to the tube conditioner and allows the liquid to be swept across the Tenax TA, where the analytes are absorbed onto the Tenax TA in a way similar to the samples. See Appendix G, Figure G2 for details.

Note: Other apparatus can also be used.

4.1.2 Sample Preparation Procedure for Methods A and B.

4.1.2.1 Preparation.

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

4.1.2.1.1.1 Tube A. First VOC analysis run.

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

4.1.2.1.2 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.

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

4.1.2.1.2.2 A photograph shall be taken from the sampling point as well as from the packed glass tubes, if requested.

4.1.2.1.3 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.

4.1.2.1.4 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.

4.1.2.1.5 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. Cut 2 pieces of 30 mm $\times$ 3 mm aluminum foil and record the weight. Apply the paint to the foil and allow to dry completely. Reweigh the foil + paint and subtract the weight of the foil to get the weight of the paint.

4.1.2.1.6 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.

4.1.3 Standard Preparation for Method A.

4.1.3.1. Initial Calibration. A curve consisting of at least 5 points should be analyzed for benzene, toluene, ethylbenzene, m-xylene, o-xylene, p-xylene and styrene is used to determine Table 1 (see CG5025) compounds. A single point standard of toluene-*d8* and hexadecane-*d34* is used to determine total VOCs and total SVOCs.

4.1.3.2 Initial Calibration Preparation. The lowest concentration level must be at the reporting limit of each compound. The highest concentration level should be the highest level at which linearity can be maintained. An example initial calibration from a 2000 $\mu\text{g/mL}$ liquid standards and using a 1 μL syringe is shown in Table 1.

Table 1: Example Initial Calibration Levels

ng on tube	10	100	500	1000	1500
Benzene	10	100	500	1000	1500
Ethylbenzene	10	100	500	1000	1500
m-Xylene	10	100	500	1000	1500
p-Xylene	10	100	500	1000	1500
o-Xylene	10	100	500	1000	1500
Styrene	10	100	500	1000	1500

Toluene	10	100	500	1000	1500
Toluene-d8	--	--	--	1000	--
Hexadecane-d34	--	--	--	1000	--

The initial calibration must have an $r^2 \geq 0.995$ if using a linear calibration or a %RSD $\leq 20\%$ using response/calibration factors to be considered valid. See Appendix B for additional guidance on calibrations.

4.1.3.3 Calibration Check Standard Preparation. The concentration of the check standard can vary but should be between the lowest concentration and mid-point concentration of the calibration curve constructed in 4.1.3.1. A check standard above the mid-point concentration should not be used because it does a poor job checking the lower concentration area of the curve, which is where most compounds will be detected and where the curve has the greatest instability. Checking the curve at a lower concentration results in the best chance of producing the most accurate data. In the example in 4.1.3.1, a mid-point calibration check standard of 1000 ng can be made by placing 0.5 μL of a 2000 $\mu\text{g/mL}$ liquid solution onto the tube spiking adapter. Each analyte must be $\leq 20\%$ RSD compared against the initial calibration before samples can be analyzed. A calibration check standard shall be analyzed at the beginning of the analytical sequence and every 24 h after.

4.1.3.4 System Check Standard. A Grob mixture or equivalent is used to evaluate the condition of the analytical system, following standard evaluation criteria.

4.1.3.5 Retention Time Standard. 2000 ng of the standard on a Tenax TA tube is analyzed and used to define the retention times for total VOCs and total SVOCs.

4.1.3.6 Method Blanks. A conditioned Tenax TA tube shall be analyzed at the beginning of the analytical sequence and every 24 h after. The analysis must show that all target analytes are below the detection limits before samples can be analyzed.

4.1.3.7 Analytical Procedure. The following must be performed and pass the appropriate criteria:

4.1.3.7.1 Prior to the analysis of interior material samples, a calibration of detection limits shown in the following must be reached at a Signal-to-Noise (S/N) ratio of 3:1:

- Toluene $< 0.01 \mu\text{g}$.
- *n*-Hexadecane (*n*-C16) $< 0.05 \mu\text{g}$.
- *n*-Eicosane (*n*-C20) $< 0.06 \mu\text{g}$ at VOC conditions.
- *n*-Dotriacontane (*n*-C32) $< 0.2 \mu\text{g}$ at SVOC conditions.

4.1.3.7.2 Tune and/or tune evaluation.

4.1.3.7.3 Air/water check.

4.1.3.7.4 Grob or other system evaluation check (initially and after major system changes; e.g., a new column).

4.1.3.7.5 Initial calibration, initially and when the Calibration Check Standard fails.

4.1.3.7.6 Calibration Check Standard.

4.1.3.7.7 Retention Time Standard (initially and after major system changes; e.g., a new column).

4.1.3.7.8 Method Blank.

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.

4.3 Instructions.

4.3.1 Sample and Data Analysis Procedure – Method A.

Note: The instrument conditions for the VOC and SVOC/FOG analysis are given in Table D1 thru Table D4 of Appendix D. Note that gas standards can also be used.

4.3.1.1 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.

4.3.1.2 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.

4.3.1.3 Individual Amounts of VOCs and SVOCs.

4.3.1.3.1 Each analyte (BTEX and styrene) with a concentration > 1 ppm must be identified and its concentration has to be calculated.

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

4.3.1.3.3 Total Amount of VOCs. To determine the total amount of VOCs, all area from the beginning of the chromatogram to the retention time corresponding to the end of a C-20 (*n*-eicosane) peak is integrated and compared against the area of the toluene-*d*8 standard (toluene-*d*8 equivalent). The calculations can be found in Appendix F.

4.3.1.3.4 Total Amount of SVOCs. To determine the total amount of SVOCs, all area from the retention time corresponding to the beginning of the C-16 (*n*-hexadecane) peak to the retention time corresponding to the end of the C-32 (*n*-dotriacontane) peak is integrated and compared against the area of the *n*-hexadecane-*d*34 standard (*n*-hexadecane-*d*34 equivalent). The calculations can be found in Appendix F.

4.3.1.3.5 If there is an “oil-mountain” at the termination of the defined total VOC/SVOC areas, a line should be drawn from the curve to the baseline.

4.3.1.3.6 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.

4.3.2 Sample and Data Analysis Procedure – Method B.

Note: The instrument conditions for the VOC and SVOC/FOG analysis are given in Table D1 thru Table D4 of Appendix D. Note that gas standards can also be an option for calibration.

4.3.2.1 The data produced from the SVOC analysis and second VOC analysis (see 4.3.1.1 and 4.3.1.2) can be used to perform a library search, when requested.

4.3.2.2 All library search compounds are reported. Compounds with a mass spectral quality match > 80% should be reported as the top match. Compounds with a mass spectral quality match < 80% should be reported as tentatively identified compounds. If a compound cannot be definitely identified, see Appendix E for guidance on reporting.

4.3.2.3 A semi-quantitative determination of the emissions expressed as mass parts per million can be obtained by calibration with reference substances. Toluene-*d*8 is used as a reference substance for VOC and *n*-hexadecane-*d*34 as reference substance for the SVOC/FOG value. Unknown substances can be identified from the mass spectra and the retention time.

5 Data

5.1 Calculations.

5.1.1 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. VOCs and SVOCs listed as restricted and reportable substances should meet the requirements specified under GMW16853, CG5025.

5.3 Test Documentation. The results are displayed in a report. See Appendix G, Data Sheet G1, for details. In addition, the chromatograms for the VOC/SVOC determination and BTEX and styrene list must be attached to the results report. The VOC/SVOC/Carbonyl Emissions Results Report in CG5025 must be completed showing that the requirements have been met.