



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

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 quantitative determination of Volatile Organic Compound (VOC) and Semi-Volatile Organic Compound (SVOC) emissions in vehicle interior air utilizing Tenax TA adsorbent media and Thermal Desorption - Gas Chromatography/Mass Selective Detection (TD-GC/MSD).

1.1.1 Individual VOC and SVOC emissions in different vehicle interior air samples can be identified, quantified, and compared.

1.1.2 In combination with GMW15634 the sources of VOCs and SVOCs in vehicle air can be identified.

1.1.3 "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). Note that if the Total Volatile Organic Compound (TVOC) definition is different per a regional protocol then this TVOC definition must be used if required. "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. This test procedure can be used for all air samples for the determination of VOC and SVOC emissions including cabin air inside vehicles in a stationary or dynamic mode. The results will provide complementary information to interpret findings in GMW3205, GMW16853, CG5025 and GMW15634. The test procedure can be used to pursue customer complaints regarding odor. The analytical instrumentation described herein is also applicable for GMW15634 to determine the sources of VOCs and SVOCs in interior materials.

1.2.1 This test procedure was modified from EPA TO-17.

1.2.2 This test procedure complements GMW15600.

1.3 Remarks. The determination of VOCs and SVOCs in vehicle interior air is essential to meet customer and regulatory requirements in global markets. Concentrations are in the micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) range which warrants accurate analytical measurements.

Note: There is no direct correlation between the limits on material, component and vehicle level due to the high complexity of chemical interactions, unpredictable influence of different part sizes and addition, interaction and elimination of their emissions.

2 References

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

2.1 External Standards/Specifications.

EPA TO-17	ISO 12219-1	ISO 17034	MOLIT 2019-144
HJ/T400	ISO 17025	JASO Z125	

2.2 GM Standards/Specifications.

GMW3205	GMW15634	GMW16853
GMW15600	GMW16818	

2.3 Additional References.

- CG5025 VIAQ Regulated Volatile
- Flow Calibrator(s) (e.g., BIOS DC-1) available at www.atecorp.com/products/bios-international/DC-1.

3 Resources

3.1 Facilities. The air samples shall be collected inside a vehicle in a garage or in a stable environment with low background levels. If data is acquired for regulatory purposes, the use of a vehicle sampling chamber is required. The test chamber requirements and sampling protocol may differ for different government regulations.

All laboratory tests per this standard shall be performed by a laboratory that conforms to ISO 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 laboratory calibration is to be valid to ISO 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 equipment and instrumentation. Equivalent instrumentation and test conditions are suggested in Appendix A, Table A1.

3.2.1 Balance with a sensitivity of 0.01 mg.

3.2.2 Directly Coupled Thermodesorption 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 libraries.

3.2.4 GC Capillary Columns. GC Capillary Guard Column is used to prevent thermal shock to increase capillary column longevity. A low-Bleed GC/Mass Spectrometer (GC/MS) Capillary Column, Stationary Phase: 5% phenyl - methylpolysiloxane is used (e.g., 50 m × 0.52 mm × 0.32 µm Ultra 2 capillary column).

3.2.5 Tenax TA or equivalent. Compatible with the specific corresponding thermal desorption system, see Appendix G, Figure G1.

3.2.6 Tube-Spiking Adapter for loading liquid standards onto Tenax TA tubes and evaporating the solvent, see Appendix G, Figure G2 for details. Other tube-spiking apparatus can be used.

3.2.7 Carrier Gas. Gases. Grade ≥ 5.0 helium 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 Conditioning 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 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.

3.2.9 Syringes for Spiking Tubes. 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.

- Methanol (MeOH), High Pressure Liquid Chromatography (HPLC) grade, pesticide residue grade, or purge and trap grade.
- Dichloromethane (CH₂Cl₂), HPLC grade. or pesticide residue grade.

3.2.11 Initial Calibration Standards. Initial Calibration Standards consisting of at least five (5) concentration levels prepared from standard(s) obtained from an ISO 17034 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 shall 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. Standard containing, at least, a mixture of benzene, toluene, ethylbenzene, *m*-xylene, *p*-xylene, *o*-xylene and styrene purchased from a different, ISO 17034 certified vendor than the initial calibration standard, spiked on a Tenax TA tube. The solvent for liquid standards shall 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 and G (Figure G3 and Table G1) for further guidance.

3.2.11.3 Grob-Test Mix for testing the GC column performance.

3.2.12 Sampling Pump. Portable sampling pumps with a flow calibrator and a minimum flow range between 50 mL/minute to 1000 mL/minute and an appropriate flow calibrator (e.g., type DC-1 flow calibrator BIOS International Number (No.) DC-MC-1).

3.3 Test Vehicle/Test Piece. The vehicle to be tested is determined by the test director. The actual age of the vehicle may vary according to the purpose of the test. It may be a used vehicle with a customer complaint or a new vehicle < 28 days after production or whatever is required by sampling protocols.

3.3.1 The nominal temperature in the test vehicle interior air can range from 10 °C to 65 °C. However, at temperatures > 30 °C, the sampling tube shall be placed outside the vehicle to ensure quantitative collection of the VOC and SVOC species unless the regional protocol states otherwise. Vehicles may be preconditioned as required, and details shall be documented.

3.4 Test Time. A preconditioning procedure (e.g., addressing time, temperature, humidity, etc.,) as specified within an individual government regulation must be followed.

Calendar time:	Up to 2 d
Test time:	6 h
Coordination time:	> 16 h

3.5 Test Required Information. The Vehicle Identification Number (VIN), vehicle build date and the odometer reading shall be recorded, including remarks on the condition of the vehicle and a brief vehicle history.

3.6 Personnel/Skills. Proper training is required to operate the instrumentation in this procedure. A professional degree in chemistry, chemical engineering, industrial hygiene or the health sciences is a prerequisite.

4 Procedure

4.1 Preparation. For regulatory testing the vehicle must be prepared according to relevant Government protocol. HJ/T400 is to be used for vehicles exported to China, JASO Z125 for vehicles exported to Japan, MOLIT 2019-144 for vehicles exported to South Korea and ISO 12219-1 for vehicles exported to Europe if testing for the region is mandatory.

4.1.1 Vehicle. The vehicle must be conditioned according to the respective test procedure, see preceding.

4.1.2 Tube Conditioning. The Tenax TA GTDTs are thermally conditioned before sampling, see 3.2.8.

4.1.3 Vehicle Air Sampling. Calibrate the sampling pump and record the sampling rate. For vehicle air sampling guidelines refer to appropriate regional procedures if regulatory testing is required. For problem solving purposes the air sampling procedure as described in MOLIT 2019-144 can be used.

4.2 Conditions.

4.2.1 Environmental Conditions. The environmental conditions are described in the respective method used for testing, see 4.1.

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. The operating parameters for the TD-GC/MCD instrumentation are given in Appendix C, Tables C1 thru C8;

- Table C1 includes the instrument conditions for the Gerstel Thermal Desorption System (TDS) system.
- Table C2 shows the conditions of the Gerstel Cooled Injection System (CIS) system.
- Table C3 describes the Agilent GC inlet conditions.

- Table C4 shows the split ratio.
- Table C5 includes the analytical column conditions.
- Table C6 shows the GC oven conditions and Table C7 the Agilent MSD conditions.
- Table C8 shows the conditions/parameters if a Markes Thermodesorption unit is used.

4.3.1 Spiking Tenax TA Tubes with Liquid Standards. A liquid spiking apparatus designed to spike the type of Tenax TA tubes used for analysis shall 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.

4.3.1.1 Initial Calibration. A curve consisting of at least five (5) points shall 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.

4.3.1.2 Initial Calibration Preparation. The lowest concentration level must be at the reporting limit of each compound. The highest concentration level shall be the highest level at which linearity can be maintained. An example initial calibration from a 2000 µg/mL liquid standard 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- <i>d8</i>	--	--	--	1000	--
Hexadecane- <i>d34</i>	--	--	--	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.

4.3.1.3 Calibration Check Standard Preparation. The concentration of the check standard can vary but shall be between the lowest concentration and mid-point concentration of the calibration curve constructed in 4.3.1.1. A check standard above the mid-point concentration shall 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 4.3.1.2, a mid-point calibration check standard of 1000 ng can be made by placing 0.5 µL of a 2000 µg/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.

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

4.3.1.5 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.

4.3.1.6 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.

4.3.2 Test Procedure. Prior to the analysis of vehicle interior air samples, a calibration must be done and the following limits of detection must be reached:

- Toluene: < 0.01 µg
- *n* Hexadecane (*n*-C16): < 0.05 µg.
- *n*-Eicosane (*n*-C20): < 0.06 µg.
- *n*-Dotriacontane (*n*-C32): < 0.2 µg.

4.3.2.1 Analyze tune and/or tune evaluation.

4.3.2.2 Analyze air/water check.

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

4.3.2.4. Analyze initial calibration, initially and when the Calibration Check Standard fails.

4.3.2.5 Analyze Calibration Check Standard.

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

4.3.2.7 Analyze Method Blank.

4.3.2.8 Analyze background air sample.

4.3.2.9 Analyze vehicle interior air sample.

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 mass-to-charge ratio (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 D, Table D1 for notation examples.

5.1.2 Quantitative Analysis.

5.1.2.1 Total Amount of VOCs and SVOCs. 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 E. If a different TVOC range must be used according to a regional protocol then this range must be specified in the final report. 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 E.

5.1.2.2 If there is an "oil-mountain" at the termination of the defined total VOC/SVOC areas, a line shall be drawn from the curve to the baseline.

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

5.1.2.3.1 The total amount of single VOCs and SVOCs is calculated as toluene *d*8 equivalent for VOCs and Hexadecane *d*34 equivalent for SVOCs by comparison of the peak areas to the peak areas of the calibration standards.

5.1.3 Individual Amounts of VOCs and SVOCs.

5.1.3.1 Each analyte (BTEX and styrene) with a concentration $\geq 3.3 \mu\text{g}/\text{m}^3$ (10 ng on tube) must be identified and its concentration has to be calculated. See Appendix E for additional calculation information.

5.1.4 Quantitate Air Sample. Tenax TA GTDT air sample analysis calculations, the mass values obtained in micrograms (µg) are divided by the volume of vehicle interior air sampled in liters (L), and multiplied by 1000 L/m³

to give final results in $\mu\text{g}/\text{m}^3$. Total VOC and SVOC is a summation of all individual VOCs and SVOCs found within the chromatogram, respectively.

5.1.5 Calculated Result Disclaimer. The calculated quantitative results obtained are from individual organic compounds that were thermally stripped from Tenax TA polymer resin and detected under these particular methods and corresponding sampling conditions. This quantitative method shall not be compared to other quantitative methods.

5.2 Interpretation of Results. The qualitative and quantitative analyses of VOCs and SVOCs in vehicle interior air will be used to determine the sources of specific chemicals of interests to address customer satisfaction issues or meet voluntary and/or regulatory requirements in Vehicle Interior Air Quality (VIAQ).

5.2.1 Some VOCs and SVOCs are frequently cited as odorous compounds and may require additional testing in accordance with GMW16818.

5.3 Test Documentation. The results are displayed in a report form, see Appendix F, Data Sheet F1 for details. Additionally, the chromatograms for the VOC and SVOC determination and associated substance lists must be attached to the results report. The full set of analytical data must be supplied electronically. Analytical data shall include 5.3.1 thru 5.3.3.

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

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

5.3.3 Information about the calculation of the results.

6 Safety

This Engineering Standard may involve safety requirements for hazardous materials, the method of operations and equipment. This standard does not propose to address all the safety issues associated with its use. It is the responsibility of the user of this standard to ensure compliance with all appropriate safety and health practices. This would include any specific training that may be required. The safety and health standards include site specific rules and procedures, company rules and procedures, and Government Standards. Contact shall be made with the appropriate site Safety and Health personnel for further direction and guidance in these matters.

7 Notes

7.1 Glossary.

Glass Frit: Glass frit bonding, also referred to as glass soldering or seal glass bonding, describes a wafer bonding technique with an intermediate glass layer.

SCAN: Scan over specified mass range.

7.2 Acronyms, Abbreviations, and Symbols.

$^{\circ}\text{C}/\text{s}$	degrees Celsius per second
μg	microgram(s)
$\mu\text{g}/\text{m}^3$	micrograms per cubic meter
$\mu\text{g}/\text{mL}$	micrograms per milliliter
AMU	Atomic Mass Unit
CAS No.	Chemical Abstract Service Number
CIS	Cooled Injection System
CSLR	Calibration Standard Loading Rig
GC	Gas Chromatograph
GC/MS	Gas Chromatograph/Mass Spectrometer
GSSLT	Global Subsystem Leadership Team
GTD	Glass Thermal Desorption Tube
He	Helium
HP	Hewlett Packard
HPLC	High Pressure Liquid Chromatography

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June 2020

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Documents

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