



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

1 Scope

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 VOC emissions are in the boiling point range ≤ 345 °C or chromatographic elution range from n-pentane (n-C5) to n-eicosane (n-C20), and SVOC emissions are in the boiling range ≥ 280 °C or chromatographic elution range from n-hexadecane (n-C16) to n-dotriacontane (n-C32). This procedure can determine all of these components in vehicle interior air.

1.2 Foreword. 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.

1.3 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, GMW3059 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.

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

1.3.2 This test procedure complements GMW15600.

2 References

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

2.1 External Standards/Specifications.

EPA TO-17	ISO 12219-1	JASO Z125	MOLIT 2013-549
HJ/T400			

2.2 GM Standards/Specifications.

GMW3059	GMW15600	GMW15634	GMW16818
GMW3205			

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.

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 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 Trapping and Split System.

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

3.2.4 Gas Chromatograph Capillary Columns. GC Capillary Guard Column is used to prevent thermal shock to increase capillary column longevity. A low-Bleed Gas Chromatograph/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, Glass Thermal Desorption Tubes (GTDT). Compatible with the specific corresponding thermal desorption system. (See Appendix H, Figure H1.).

3.2.6 Tube-Spiking Adapter for loading liquid standards onto Tenax TA tubes and evaporating the solvent. See Appendix H, Figure H2 for details. Other tube-spiking apparatus can be used.

3.2.7 Carrier Gas. Grade ≥ 5.0 Helium and a corresponding in-line purifier trap is used for the GC carrier gas, the Tenax TA Glass Thermal Desorption Tubes conditioning purge gas, and the Tube-Spiking Adapter gas.

3.2.8 Conditioning Tenax TA Glass Thermal Desorption Tubes. Tenax TA tubes must be conditioned thermally with an apparatus designed for that purpose. Set the helium or nitrogen purge gas flow rate to 30 mL/minute to 40 mL/minute for each port. Conditioning consists of heating Tenax TA GTDTs at 320 °C continuously for 3 h ± 10 minutes. After thermal conditioning, the sorbent tubes should be packed airtight in aluminum foil or protective end caps to prevent contamination.

3.2.9 Syringes for Spiking Tubes. Ten (10) µL, 5 µL, and 1 µL syringes.

3.2.10 Solvents for Standard Dilutions.

- Methanol (MeOH), High Pressure Liquid Chromatography (HPLC) grade
- Dichloromethane (MeCl₂), HPLC grade

3.2.11 Standards and Dilutions. All standards and dilutions are to be kept in sealed containers and refrigerated at ≤ 8 °C when not in use.

3.2.11.1 Standards of desired VOC and SVOC components at ≥ 98% purity (or equivalent).

3.2.11.2 Check standard containing a mixture of 18 individual components, 110 µg/mL ± 10 µg/mL each in MeOH. (See Appendix B, Section B1.)

3.2.11.3 Calibration standard consisting of toluene, 500 µg/mL ± 50 µg/mL in MeOH. See Appendix B, Section B2.

3.2.11.4 Retention Time Lock Standard. The n-Alkane Standard containing n-C5 to n-C32 of 28 individual n-Alkane components, 2000 µg/mL each in MeCl₂.

3.2.11.5 Aromatic Performance Standard. Aromatic Standard containing aromatic hydrocarbons, e.g., 14 individual components, 2000 µg/mL each in MeOH.

3.2.11.6 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 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 less than 28 days after production as 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 above 30 °C, the sampling tube should be placed outside the vehicle to ensure quantitative collection of the VOC and SVOC species. Vehicles may be preconditioned as required, and details should 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 days

Test hours: 6 hours

Coordination hours: 4 hours

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 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. If necessary, the vehicle shall be prepared as it is mentioned in the respective test recommendations (2.1). For global testing, prepare the vehicle according to ISO 12219-1 and use HJ/T400 for vehicles exported to China, JASO Z125 for vehicles exported to Japan, and MOLIT 2013-549 for vehicles exported to South Korea. A known volume of vehicle interior air is drawn through preconditioned Tenax TA GTDT sampling tubes at a sampling rate of 100 mL/minute to 200 mL/minute for a period 30 minutes to 1 h. After sampling, the samples and field blanks are capped, labeled, and returned to the laboratory where they are analyzed by TD-GC/MSD to determine the identity and the quantitative amounts of substances in the vehicle interior air. If necessary, an air sample can be drawn 0.5 m outside of the vehicle for background VOC correction.

4.1.1 Vehicle. The vehicle has to be conditioned according to the respective test procedure.

4.1.2 Tube Conditioning. The Tenax TA GTDTs are thermally conditioned before sampling (3.2.8).

4.1.3 Air Sampling. Calibrate the sampling pump, and record the sampling rate. The sampling has to be done on two (2) tubes in parallel. Place the sample pumps and Tenax TA GTDTs in the car with the pumps on the seat and the Tenax TA GTDTs at driver breath level (use the headrest to hold the Tenax TA GTDTs).

Assemble the Tenax TA GTDTs and sampling pumps so that the flow direction is that indicated by the labeled arrow on the tube. Use a sampling rate of 100 mL/minute to 200 mL/minute for a period 30 minutes to 1 h. Start the sampling pumps and record the time. Close the vehicle doors and windows. After an appropriate sampling time, open the vehicle doors and stop the sampling pumps, noting the elapsed sampling time. Remove the Tenax TA GTDT air sample(s), cap it and label it with the details VIN, sampling time, and flow rate, etc., of the test. Refrigerate the Tenax TA GTDT samples at ≤ 8 °C if a delay of > 24 h is expected before analysis.

4.2 Conditions.

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

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.

- 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 if a Markes Thermodesorption unit is used.

4.3.1 Spiked Standards. The known standard solutions ($\mu\text{g/mL}$) of sought compounds are spiked on separate preconditioned Tenax TA GTDT tubes. This is accomplished by using an apparatus as described in 3.2.6 and Appendix H, Figure H2. Use a $0.7 \text{ L/minute} \pm 0.3 \text{ L/minute}$ helium flow rate for 3 minutes to 4 minutes to achieve a 2.5 L to 3.0 L total helium volume. Other apparatus can also be used.

Create a quantitative calibration curve by spiking preconditioned Tenax TA GTDTs with, 200 ng, 400 ng, 800 ng, 1200 ng, and 1600 ng of sought VOC or SVOC standard(s) depending on the requirements. Record calibration concentrations.

4.3.1.1 Check Standard. Perform a TD-GC/MSD run on a Tenax TA GTDT spiked with 4 μL per 3.2.11.2, in 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 in this way 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.

4.3.1.1.1 From time to time, a calibration curve is prepared by spiking a number of Tenax TA GTDT with different volumes of the check standard solution (range $0.016 \mu\text{g}$ to $6 \mu\text{g}$ per substance per injection).

4.3.1.2 Calibration Standard. Perform a TD-GC/MSD run on a Tenax TA GTDT spiked with 4 μL of Calibration Standard (3.2.11.3) in SCAN mode to acquire toluene equivalent data for VOCs and SVOCs (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 GTDT spiked with 1 μL of n-Alkane Standard (3.2.11.4) or 1 μL of Aromatics Standard (3.2.11.5) in SCAN mode. The retention times of the components in these mixtures are suitable as reference points to determine the retention time indices of unknown substances (Appendix H, Figure H3 and Table H1), and in this way can be used for an additional check of Mass Selective Detector (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.

4.3.2.1 This 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.

4.3.2.2 The performance of the mass selective 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.

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

4.3.2.4 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. Prior to the analysis of vehicle interior air samples, a calibration has to be done and the following limits of detection have to be reached:

- Toluene $< 0.04 \mu\text{g}$
- n-Hexadecane (n-C16) $< 0.05 \mu\text{g}$
- n-Eicosane (n-C20) $< 0.06 \mu\text{g}$
- n-Dotriacontane (n-C32) $< 0.2 \mu\text{g}$

4.3.3.1 The recovery rate of the individual substances in the check standards should be between 60% to 140%, with the exception of toluene which should be 80% to 120%.

4.3.3.2 For a complete analytical run, the following measurements must be accomplished.

4.3.3.2.1 Blank sample (empty glass tube) under the same thermal desorption conditions as the sample to check the cleanliness of the TD-GC/MSD system.

4.3.3.2.2 The check standard mix is spiked on a Tenax TA tube for testing the TD-GC/MSD system.

4.3.3.2.3 Different volumes of the requested calibration standard for quantitative determination of the requested analytes. Optionally, a toluene calibration can be done.

4.3.3.2.4 Analysis of the background air sample.

4.3.3.2.5 Analysis of the vehicle interior air sample.

4.3.3.3 After every change of the TD-GC/MSD system, (e.g., cleaning, changing the column, etc.) the Grob Test Mix, n-Alkane standard, and aromatic standard, must be analyzed to determine the retention time of the analytes for quality assurance.

5 Data

5.1 Calculations. Not applicable.

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. (Appendix D, Table D1 for notation examples.)

5.1.2 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 $\geq 1 \mu\text{g}/\text{m}^3$ are still detected reliably. For the total amount of VOCs and SVOCs, all peaks in the corresponding chromatogram have to be integrated, including peaks beyond the retention time of the n-C32 alkane as well as peaks with a concentration lower than $1 \mu\text{g}/\text{m}^3$.

5.1.2.2 If the chromatogram includes so-called "oil-mountains" consisting of unresolved species, these are integrated as one peak in which the baseline is laid from the start to the end of the "oil-mountain". If clearly identified peaks of other substances 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 E.

5.1.2.3.1 The total amount of single VOCs and SVOCs is calculated as toluene equivalent by comparison of the peak areas to the peak area of the calibration standard. For the Total Volatile Organic Compound (TVOC) value the whole chromatogram has to be integrated and the total value has to be calculated as described before.

5.1.3 Individual Amounts of VOCs and SVOCs. Individual peaks in the samples are identified by their retention times and quantitated by comparison of their peak areas to the Selective Ion Monitoring (SIM) calibration curves constructed (see 5.1.4).

5.1.3.1 At a minimum, the concentrations of the analytes that are mentioned in a government regulation must be calculated.

5.1.3.2 If there are individual peaks in the "oil-mountains", they have to be integrated manually at the height above the "oil-mountain".

5.1.4 Quantitative Determination Using Selective Ion Monitoring (SIM).

5.1.4.1 Select SIM Ions for Sought Compounds. Quantitative determination of individual VOC components is accomplished by operating the quadrupole mass filter in SIM mode. In SIM, the mass filter is set during a particular retention time window +0.5 minutes to pass one (1) selected target ion (m/z) and at least one (1) selected corresponding qualifier ion (m/z). The analyst has prior knowledge from analyzing in SCAN mode of the sample matrix, retention times, and ions to expect for an individual sought compound. Several sought compounds may be quantitatively determined in a single SIM analysis. 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). At least one (1) and preferably two (2) qualifier ions (Q1, Q2, etc.) with an absolute uncertainty of $\pm 20\%$ should accompany one (1) target ion. The target ion and corresponding qualifier ions are collected using 100 ms dwell time. An example sample matrix using SIM is given in Appendix F, Table F1.

5.1.4.2 Construct SIM Calibration Curves. Separate spiked Tenax TA GTDTs are analyzed by TD-GC/MSD SIM. Next, utilizing data analysis software, the user measures peak areas of the quantitative ion (m/z) at specific retention times for the individual sought compounds. These peak areas are used to construct SIM calibration curves for the known standard solutions. Calibration curves should include at least three (3) level (points), not including a blank or a manually assigned origin.

5.1.4.3 Individual VOCs and SVOCs by SIM. The Tenax TA GTDT air sample of vehicle interior air is also analyzed by TD-GC/MSD SIM. Utilizing data analysis software, the user measures peak areas of the sought quantitative ions (m/z) at specific retention times from the SIM chromatographic data collected. These are the same quantitative ions (m/z) at specific retention times used to construct the calibration curves in 5.1.4.2. The Tenax TA GTDT air sample individual VOC components are quantified by comparing the SIM quantitative ion peak area amounts to those of known standard solutions.

5.1.5 Quantitate Air Sample. For the 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/m^3 to give final results in micrograms per cubic meter ($\mu\text{g/m}^3$). Total VOC and SVOC is a summation of all individual VOCs and SVOCs found within the chromatogram, respectively.

5.1.6 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 should 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 G, Data Form G1 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. It should include 5.3.1 through 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 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.

SCAN: Scan over specified mass range.

7.2 Acronyms, Abbreviations, and Symbols.

AMU	Atomic Mass Unit
CAS No.	Chemical Abstract Service Number
CIS	Cooled Injection System
CSLR	Calibration Standard Loading Rig
EPA	Environmental Protection Agency
GC	Gas Chromatograph
GC/MS	Gas Chromatograph/Mass Spectrometer
GTD	Glass Thermal Desorption Tube
He	Helium
HP	Hewlett Packard
HPLC	High Pressure Liquid Chromatography
ID	Internal Diameter
JASO	Japanese Automotive Standards Organization
MeCl₂	Dichloromethane
MeOH	Methanol
MOLIT	Ministry of Land, Infrastructure and Transport
m/z	Mass-to-charge ratio
MS	Mass Spectrometer
MSD	Mass Selective Detector
n-C5	n-pentane
n-C16	n-hexadecane
n-C20	n-eicosane
n-C32	n-dotriacontane
NIST	National Institute of Standards and Technology
No.	Number
OD	Outside Diameter
PC	Personal Computer
PN	Part Number
RT	Retention Time
SIM	Selective Ion Monitoring
SLH	Septumless Head
STBY	Standby
STD	Standard
SVOC	Semi-Volatile Organic Compounds
TD-GC/MSD	Thermal Desorption - Gas Chromatography/Mass Selective Detection
TDS	Thermal Desorption System
TIC	Total Ion Chromatogram