GM	WORLDWIDE ENGINEERING STANDARDS	Test Procedure	GMW15600

Determination of Aldehyde and Ketone Emissions in Vehicle Interior Cabin 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 quantitative determination of aldehyde and ketone emissions in vehicle interior cabin air, utilizing a coated solid adsorbent followed by High Performance Liquid Chromatography (HPLC) with ultraviolet (UV) detection.

1.2 Applicability. This test procedure can be used for all air samples for the determination of aldehyde and ketone emissions, including cabin air inside vehicles in a stationary or dynamic mode. The results will provide complementary information to interpret findings in GMW16818 and GMW15635.

1.3 Remarks. The determination of aldehydes and ketones in vehicle cabin air is essential to meet customer and regulatory requirements in global automotive markets. Concentrations are in the parts per million (ppm) ranges, which warrant accurate, analytical measurements. This test procedure is based on test method EPA T0-11A. It has been updated to reflect updated technology in air sampling and analytical instrumentation.

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 T0-11A	ISO 12219-1	JASO Z125	MOLIT 2013-549
HJ/T400			

2.2 GM Standards/Specifications.

GMW15635	GMW16818

2.3 Additional References.

- Mine Safety Appliances (e.g., Number 49772 and DC-1 flow calibrator) available at http://us.msasafety.com
- Sigma Aldrich products available at www.sigmaaldrich.com/catalog/product/supelco
- SKC AirCheck pumps and equipment available at www.skcinc.com/catalog/index.php
- Waters brand cartridges available at www.waters.com/waters/partDetail.htm?partNumber=WAT047205&locale=en_US

3 Resources

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

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

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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. Specific instrumentation and test conditions are noted in all the tables and figures in Appendix A thru Appendix C. Other equipment can also be used when compatibility has been shown.

3.2.1 Test Apparatus.

3.2.1.1 High performance liquid chromatograph with (binary) pump, solvent degasser, heated column compartment, auto sampler (optional), variable wavelength, or diode array detector, and computer based controller and data evaluation. System must be capable of gradient operation to 3.5 mL/minute and 350 bar (maximum), and UV detection at 360 Nm to 365 Nm.

3.2.1.2 HPLC column capable of separating the 2, 4-Dinitrophenylhydrazine (DNPH) derivatives of the specified aldehydes/ketones using gradient elution conditions. The column is critical for this procedure.

3.2.2 Sample Pump. Portable sampling pump with a minimum flow range between 50 mL/minute to 1000 mL/minute (e.g., Mine Safety Appliance Number 49772 or SKC AirCheck 2000).

3.2.3 Flow Calibrator. Appropriate flow calibrator (e.g., DC-1 flow calibrator) should be used to calibrate the sampling pumps prior to sampling.

3.2.4 Sample cartridges filled with 2, 4-DNPH on silica gel. Cartridges should have a capacity of 70 µg of formaldehyde and blank values of formaldehyde < 0.15 µg/tube, acetaldehyde < 0.10 µg/tube, other substances < 0.10 µg/tube. Cartridges are:

- Waters Sep-Pak WPoSure carbonyl sampling cartridge Number WAT047205.
- Sigma Aldrich LpDNPH S10, 21014, Supelco

3.2.5 Reagents.

3.2.5.1 Acetonitrile, HPLC grade.

3.2.5.2 Tetrahydrofuran, HPLC grade, no antioxidants.

3.2.5.3 Water, HPLC grade.

3.2.5.4 Calibration standards containing the components of interest already derivatized in appropriate concentration range, typically 0.1 µg/mL to 15 µg/mL in acetonitrile.

3.2.6 Volumetric Flasks: 5 mL, glass, Class A.

3.2.7 Syringes: (Polyethylene) syringes 10 mL to 20 mL.

3.3 Test Vehicle/Test Piece. The vehicle to be tested is determined by the test director. This method is used to test the air inside a vehicle cabin. It is applicable to vehicles from -20 °C to +65 °C. However, at temperatures > 40 °C, the sampling cartridge should be placed outside the vehicle to ensure quantitative collection of the carbonyl species. Vehicles may be preconditioned as required, but details should be documented.

3.4 Test Time.

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

3.5 Test Required Information. The Vehicle Identification Number (VIN) number and the odometer reading shall be recorded, including remarks on the condition of the vehicle with a brief history of the vehicle in question, per sample Appendix D, Data Sheet D1.

3.6 Personnel/Skills. Proper training is required to collect the air samples and operate the HPLC instrument. Individuals with experience in air sampling and an analytical chemist familiar with the use of HPLC equipment is required. 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 outlined in the test specifications listed in 2.1 and as follows. For global testing, prepare the vehicle according to ISO 12219-1 and use HJ/T400 for vehicles

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exported in China, JASO Z125 for vehicles exported to Japan and MOLIT 2013-549 for vehicles exported to South Korea. A known volume of vehicle cabin interior air is drawn through a sampling cartridge packed with acidified 2, 4-DNPH on silica gel at a sampling rate of 100 mL/minute to 1000 mL/minute for a period 0.5 h to 2 h. If the air in the sample vehicle enclosure has not been scrubbed of ozone, an ozone scrubber cartridge should be placed on the front of the DNPH sampling cartridge (this may be the case if the cabin air sampling is conducted while the vehicle is in motion).

If necessary, a blank sample can be obtained by drawing a known volume of air from outside the vehicle cabin through a DNPH cartridge in a similar manner to the sample cartridge. After sampling, the sample cartridges and blanks are capped, labeled, and returned to the laboratory for analysis. Cartridges are eluted with 5 mL of acetonitrile. The acetonitrile elute is analyzed by HPLC using gradient elution and UV detection at 365 Nm. Individual aldehydes and ketones are identified and quantitated by comparison of the retention times and peak areas respectively of their DNPH derivatives to known standard solutions.

4.1.1 Air Sampling. Calibrate the sampling pump, and record the sampling rate. Use a sampling rate of 400 mL/minute for a period 30 minutes respectively to acquire 12 L air samples. The sampling must be done on two tubes in parallel.

- Position and affix a stainless-steel rod between steering wheel and headrest to hold the DNPH cartridges near the breathing zone of driver.

  Note: Use a non-emissive tubing, such as Poly Tetra Fluoro Ethylene (PTFE) or silicone, to attach to the DNPH cartridges. There is no specific direction of air flow for DNPH cartridges so tubing can be attached to either side of cartridge. Tubing to go to outside of vehicle to where the pump shall be located.
- Attach tubing to pump.
- Close vehicle doors and windows insuring that tubing is not crushed to the extent to inhibit sufficient air flow for air sampling.
- Allow vehicle to equilibrate for 2 h.
- Record air temperature and humidity.
- At the end of 2 h, start the sampling pumps and record the time.
- After a 30 minute sampling time, stop sampling pumps and open the vehicle doors.
- Immediately remove the DNPH cartridge with air sample(s), cap the cartridges and replace DNPH cartridges in aluminum zip-lock bags and label with the date, VIN, sampling time, and flow rate, etc., of the test.
- Refrigerate the DNPH samples at ≤ 8 °C as soon as possible after removing from vehicle until analysis can be initiated.

4.1.2 HPLC Determination of the Concentration of Aldehydes and Ketones.

4.1.2.1 Calibration Standards and Chromatograms. Calibration standard solutions of the aldehydes and ketones must be prepared in concentrations of 0.1 µg/mL to 15 µg/mL (related to the corresponding carbonyl compound) in acetonitrile.

4.1.2.1.1 Calibration curves are created by measuring the calibration solutions by HPLC according to the test conditions in the tables and figures in Appendix A thru Appendix C. For example:

- If using a Restek Ultra C18 column (see 3.2.1.2), use the HPLC instrument and solvent conditions in Appendix A, Table A1 and Table A2. See Appendix A, Figure A1 for chromatogram example.
- If using a Restek Allure AK 5 column (see 3.2.1.2), use the HPLC instrument and solvent conditions in Appendix B, Table B1 and Table B2. See example of chromatogram in Appendix B, Figure B1.
- If using a Phenomenex Synergi 4 µm maximum column (see 3.2.1.2), use the HPLC instrument and solvent conditions in Appendix C, Table C1 and Table C2. See example of chromatogram in Appendix C, Figure C1.

4.1.2.1.2 Each measuring sequence using diode array detectors should start with pure solvent. Afterward, calibration standards are measured with carbonyl content 1.0 µg/mL and 3.0 µg/mL. Annually, a linearity and limit of detection study is done on the HPLCs with the 0.01, 0.02, 0.05, 0.1, 0.5, 1.0, 3.0 and 15 µg/mL standards. The maximum allowable limit of detection (LOD) is 0.0075 µg/mL for each carbonyl derivative. The instruments must pass the “LOD” and “linearity” criteria. From the regression analysis, the correlation coefficient (r) is determined. The instrument is considered linear for one-point calibrations when the value of (r) is > 0.995.

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