TOYOTA ENGINEERING STANDARD

NO. : TSM0508G

TITLE : VOLATILE COMPONENT MEASUREMENT METHOD USING SAMPLING BAG

CLASS : C1

Established/Revised : Rev.2(Sep.2005)

This standard has been revised in consequence of the partial change of its contents for measurement accuracy improvement.

Engineering Information
Planning Dept.
Engineering Administration Div.
TOYOTA MOTOR CORPORATION

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TOYOTA ENGINEERING STANDARD TSM0508G

CLASS C1

VOLATILE COMPONENT MEASUREMENT METHOD USING SAMPLING BAG

1. Scope

This standard covers the method for measuring the following 9 components among those (VOC: volatile organic compounds) released from parts and materials used for the passenger compartments of vehicles.

Components to be measured:

Formaldehyde, acetaldehyde, toluene, xylene, ethyl benzene, styrene, tetradecane, di-n-butyl phthalate, and di-2-ethylhexyl phthalate

2. Test Environment

Unless otherwise specified, the measurement test shall be carried out in a room maintained at a temperature of 23±2 ℃ and a relative humidity of 50±5 %. Avoid testing in a laboratory where a solvent is used, in a newly built laboratory, or a recently refurbished laboratory, as much as possible. If it is difficult to follow the above requirement, report the actually used test environment. Before starting the test, measure and reduce the concentration of each volatile component contained in the laboratory.

3. Outline of Test

An outline of the test sequence is shown in Fig. 1. In this test, a test specimen is put in a 10 L bag together with 4 L of nitrogen gas. After the bag is maintained at 65 ℃ for 2 h, the volatile components are sampled and analyzed. Two analysis methods are used properly according to the component to be analyzed. Hydrocarbons are sampled in a Tenax tube and analyzed by a GC-MS (gas chromatograph mass spectrometer), while aldehydes are sampled in a DNPH (dinitrophenylhydrazine) cartridge and subjected to HPLC (high performance liquid chromatography). Since the test results are largely affected by the blanks including volatile components released from the bag itself, reduce the blank values according to Section 6 before starting the test.

Prepared and Written by:	Engineering Administration Div.
Organic Material Dept.	© TOYOTA MOTOR CORPORATION
Material Engineering Div.2	Established/ 2 Revised: Sep.2005

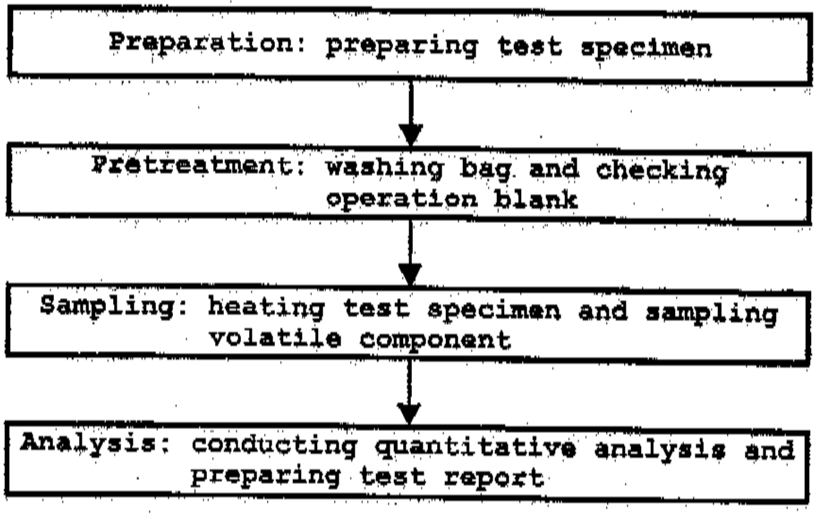


Fig. 1 Test Sequence

4. Items to Be Prepared

Examples of the instruments, devices, and reagents required for the test are shown in Table 1. Any one of these items may be substituted by a different one as long as the performance of the new item is confirmed to be equivalent to that of the originally specified item.

Table 1 Instruments, Devices, and Reagents to Be Used for Test (Example)

-	No.	Item to be prepared	Performance (e.g. maker, grade)
Sampling device	1	Bag	Tedlar bag or fluorine resin bag Dimension: W450 mm, L340 mm; capacity: 10 L; sleeve outer diameter: 7 mm (AA-10 made by GL Science)
	2	Silicone tube	Inner dia. 5 mm × outer dia. 9 mm (φ5 × 9 mm made by Tigers Polymer)
	3	Teflon tube	Inner dia. 6 mm × outer dia. 8 mm (Tombo #9003 φ6 × 8 mm made by Nichias)
	4	Stop valve	Device for blocking up silicone tube (One-touch tube cock (medium size) made by As One)
	5	Aspirator	A water jet pump for vacuuming nitrogen gas from bag (A-3S made by Tokyo Rikakikai)
	6	Tape	Low VOC type polyester tape for closing the mouth of bag (51 mm wide protective tape for laboratory use made by As One)
	7	Pump	(1) Pump that can sample gas through Tenax tube at 0.1 to 0.5 L/min (2) Pump that can sample gas through DNPH cartridge at 0.5 to 2 L/min (MP-Σ100H made by Shibata Scientific Technology)
	8	Gas flowmeter	Meter that can integrate the quantity of gas from 1 to 5 L at a rate of 0.1 to 2 L/min (DC-1C made by Shinagawa). This gas flowmeter is unnecessary when the pump in item No. 7 is provided with a precision gas flow quantity integration function.
Sampling tube	9	Tenax tube	Glass tube of 3 to 4 mm in inner dia. filled with 100 to 500 mg of absorbent: Tenax-TA (2, 6-Diphenylene Oxide Polymer)
	10	DNPH cartridge	Commercially available DNPH (2.4-Dinitrophenyl hydrazine) cartridge (Presep-C DNPH made by Wako Pure Chemical Industries or Sep-Pak DNPH Xposure made by Waters)
Reagent	11	Standard solution and gas (Toluene, xylene, etc.)	(1) Standard solution containing 1000 µg/mL each of target components (standard stock solution mixed with VOCS made by Kanto Kagaku) (2) Standard gas containing 100 ppb each of target components (PAM958 100 ppb made by Takachiho Chemical Industrial)
	12	Standard solution (Aldehydes)	Standard solution containing 100 µg/mL each of target components (Solution containing aldehyde/ketone and DNPH derivative, made by GL Sciences)
	13	Acetonitrile	Reagent for high performance liquid chromatography
Gas	14	Inert gas	Nitrogen gas Purity: 99.999 % min. Helium gas Purity: 99.999 % min. except when GC-MS requires gas of different purity
Analyzer	15	Gas chromatograph mass spectrometer equipped with thermal desorption system (GC-MS)	Mass spectrometer that can perform thermal desorption required for analysis (TDTS-GC-MS made by Shimadzu)
	16	High performance liquid chromatography (HPLC)	Sensor: UV360 nm (HPLC VP made by Shimadzu)

Established/ 2 Revised:
Sep.2005

5. Test Specimen Preparation and Storage Methods

(1) Prepare parts or materials that were produced within 14 days before the test. If it is impossible to avoid performing the test later than 14 days after production of the parts or materials, attach to the test report a record of the number of days elapsed since the production date. Store the parts or materials until they are used for the test under the environment specified in Section 2.

(2) Prepare test specimens according to Table 2 with precautions given below.

Precautions:

(a) Do not reduce the thickness of the test specimens.

(b) Avoid welds when sampling test specimens from discrete plastic parts.

(c) Remove sharp edges from rigid plastic test specimens so that such edges do not break bags during sampling gases.

(d) If a power saw or the like is used to cut out test specimens, remove the 1 to 2 mm portion from each cut edge of the specimens with cutting pliers.

(e) Ensure that the cutting blades of the pliers are clean, by wiping with ethanol or by other proper means.

(f) When handling test specimens, use disposable polyethylene gloves to keep the specimens from contamination. Be sure not to touch the specimens with a bare hand.

Table 2 Test specimen preparation method

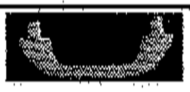
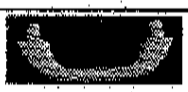
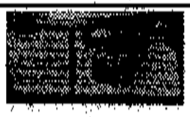
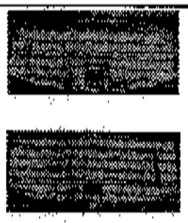
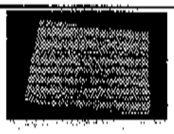
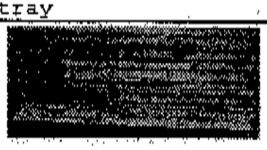
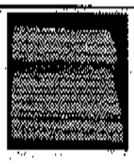
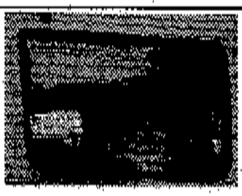
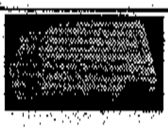
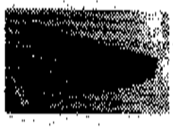
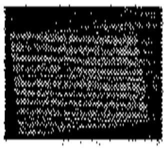
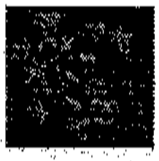
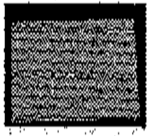
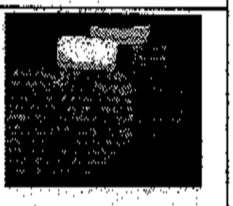
Part			Preparation method	Designation of preparation method	Example	
Size	Structure	Shape			Part	Test specimen
Smaller than bag	---	---	Entire part	Part ALL	 Example: assist grip	
Can be put in a bag when split into smaller pieces	---	---	Whole of split piece	Split ALL	 Example: sun visor	
Larger than bag	Homogeneous	Flat plate	Cutting to 8 cm × 10 cm (by remaining plate thickness unchanged)	Cutout (8 × 10)	 Example: package tray	
		Complex	Cutting to a size equivalent to 8 cm × 10 cm (by remaining plate thickness unchanged)	Cutout (portion)	 Example: scuff plate	

Table 2 (Continued)

Part			Preparation method	Designation of preparation method	Example	
Size	Structure	Shape			Part	Test specimen
Larger than bag	Inhomogeneous	Flat plate/ complex	① Group parts according to portions where they are installed. ② Prepare test specimen for each portion according to this table. ③ Test each specimen.	Cutout (split)	 Example: door trim	    
					  Example: carpet	

6. Pretreatment of Tenax Tube, Bag, and Tubes

The quantitative values of test results are affected by the pollutants (blanks) released from Tenax tube, bag, tubes, and other devices. Before using them for the test, remove the blanks as much as possible according to the pretreatment procedures given below.

6.1 Aging Tenax Tube

Before the test, age the Tenax tube according to the following procedures:

(1) While flowing inert gas through the Tenax tube at a rate of approximately 50 mL/min, maintain (age) the tube for 2 h or more at a temperature 10 to 15 ℃ higher than the thermal desorption temperature specified in Section 8.1.1, Table 4.

(2) When the aging the Tenax tube, plug its both ends with septum caps supplied as an accessory or with a Teflon tape. Wrap the tube in aluminum foil for light proofing and further wrap it in a plastic film (e.g. Saran Wrap) so that it will not be contaminated.

(3) Use the aged Tenax tube for the test as earlier as possible.

6.2 Washing Tubes

Tubes that have been stored for a long time may have been contaminated. When using them for the test, cut off their both ends by approximately 5 cm. Before starting the test, wash the tubes by purging with nitrogen gas.

6.3 Washing Bag

Before starting the test, wash the bag by either one of the following methods:

(1) Hot washing method

After filling the bag with approximately 8 L of nitrogen gas, place the bag for 30 min in a thermostatic oven maintained at 80 ℃. Then completely remove the nitrogen gas from the sampling bag, using an aspirator. Repeat this process three times as a rule. If the washed bag is stored for a long period of time, it may be contaminated again. Use the washed bag for the test as earlier as possible.

(2) Hot humidification washing method

Place the bag in a thermostatic oven. Through a small tube fitted to the sleeve of the bag, feed air or nitrogen gas into the bag at a rate of approximately 0.5 L/min. Before entering into the bag, the air or nitrogen gas shall be passed through an activated charcoal filter and bubbler for purification. With the thermostatic oven maintained at 80 ℃ or 100 ℃, wash the bag (for 4 h at 80 ℃ or for 1 h at 100 ℃). (See Fig. 2.) Then dry the inside of the bag by feeding clean air or nitrogen gas for 30 min at a rate of 0.5 L/min. If the washed bag is stored for a long period of time, it may be contaminated again. Use the washed bag for the test as earlier as possible.

Remark:

Tedlar bags shall always be disposed of after being used once. Fluorine resin bags shall be washed according to method (1) or (2) above immediately after every use, and stored in a manner in which they will not be contaminated. Limit the re-use of each bag to 5 times.

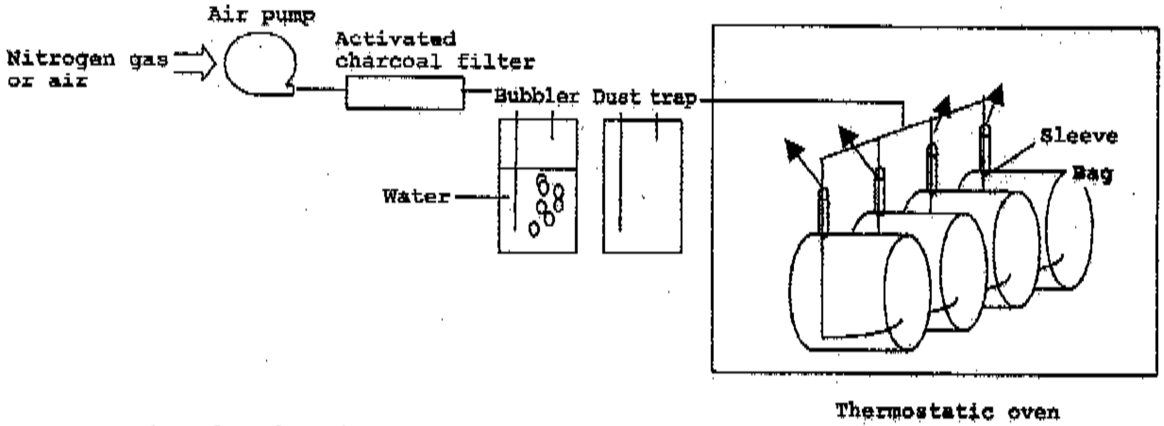


Fig. 2 Cleaning Bag by Hot Humidification Washing Method

6.4 Checking Blank

Using the Tenax tube, bag, and tubes that have been treated in accordance with Sections 6.1 through 6.3, and DNPH cartridges (no pretreatment necessary), check the blanks. For the check, determine the blank value of each volatile component according to the procedures specified in Sections 7 and 8 which are the same as those to be applied for the test specimens. However, neglect Section 7.1 (5) (putting test specimen in bag).

Precautions:

(1) Follow Section 7.1 (4) (cutting bag) and Section 7.1 (6) (sealing bag).

(2) Use a DNPH cartridge belonging to the same treatment lot as that to be used for the test specimens. The laboratory, instruments, devices, and reagents shall also be the same as those used for the test specimens.

(3) Remove a DNPH cartridge and Tenax tube from the refrigerator 30 minutes before use and let them stand until they reach room temperature.

Use three bags for checking the blanks, and make sure that the three blank values are not greater than the allowable upper limit specified in Table 3. If any one of the three blank values exceeds the upper limit, review the pretreatment conditions specified in Section 6 and modify them as needed.

Table 3 Upper Limits of Blank Values

Component	Bag blank value (μg/bag)
Formaldehyde	<0.08
Acetaldehyde	<0.038
Toluene	<0.21
Xylene	<0.70
Ethyl benzene	<3.04
Styrene	<0.176
Tetradecane	<0.264
Di-n-butyl phthalate	<0.176
Di-2-ethylhexyl phthalate	<0.096

7. Sampling

7.1 Heating Test Specimen

The test specimen heating system is schematically illustrated in Fig. 3.

(1) After connecting silicone tubes and a Teflon tube to the bag that has been washed in Section 6.3, attach stop valves to the tubes. (Fig. 3)

(2) Fill the bag with nitrogen gas (approx. 8 L).

(3) Remove the nitrogen gas from the bag with an aspirator. If the aspirator is not available, use a pump or remove the gas manually. Make sure that the nitrogen gas has been completely removed. A particular sound is heard if nitrogen gas leaks from the bag. Pay close attention to a change in sound. Leakage often occurs from the base of the sleeve. If a leaking sound is heard, check the bag and tubes and repeat steps (2) and (3). If leakage from the sampling bag continues, replace the bag with a new one.

(4) Cut off one edge of the bag with scissors while taking care not to cut the edge too largely as compared with the size of the test specimen to be put in the bag.

(5) After weighing the test specimen prepared in Section 5, put it in the bag.

(6) According to one of the following methods, tightly seal the cut edge of the bag.

(a) Sealing method A (See Fig. 4)

(i) Fold once the sampling bag at a point approximately 3 cm apart from the cut. Closely overlap the folded area.

(ii) Fold the folded area into half in the direction opposite to that in (i). Press nails against the folded area to put a crease firmly.

(iii) Ensure that the folded area is closely overlapped, and fasten the area with a tape allowing no wrinkles in the sampling bag. Also ensure that no air is entrapped between the sampling bag and tape to remove a cause of leakage.

(b) Sealing method B

Thermo-compression bond the cut edge of the bag using a heat sealer.

(7) Fill the bag with nitrogen gas.

(8) Remove the nitrogen gas with an aspirator. Pay attention to a change in sound in the same manner as in step (3) to check for possible leakage. When removing the nitrogen gas, bring the test specimen close to the sleeve. Keep the bag from wrinkling by patting it with hands. Also take care not to rip the bag. If leakage occurs or the bag is ripped, replace the bag with a new one and repeat the procedures from step (1).

(9) Fill the bag again with 4 L of nitrogen gas by correctly measuring the quantity with a gas flowmeter. Close the stop valves attached to the silicone tubes.

(10) Place the bag in a thermostatic oven that has been maintained at 65 ℃, and bring the Teflon tube outside the oven through a hole on the oven wall. The thermostatic oven shall be of a forced circulation type equipped with a fan or other proper device to ensure a uniform temperature distribution throughout the oven. Nonuniform temperature distribution may affect the accuracy of quantitative determination of volatile components.

(11) Under this condition, hold the bag at 65 ℃ for 2 h.

Remark:
It is advisable to use at least three test specimens and to report the average value, since the measured value differs according to test specimen. However, neglect this if the reproducibility of test specimens has already been confirmed.

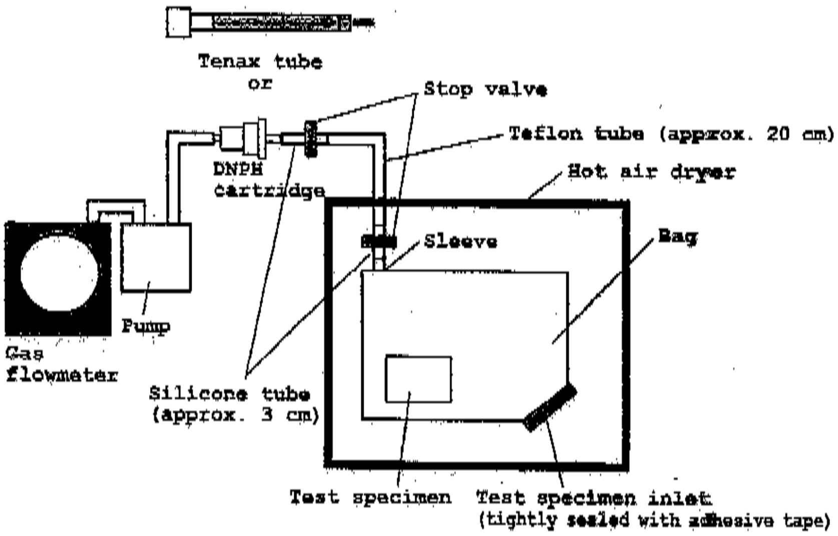


Fig. 3 Schematic Illustration of Test Specimen Heating System

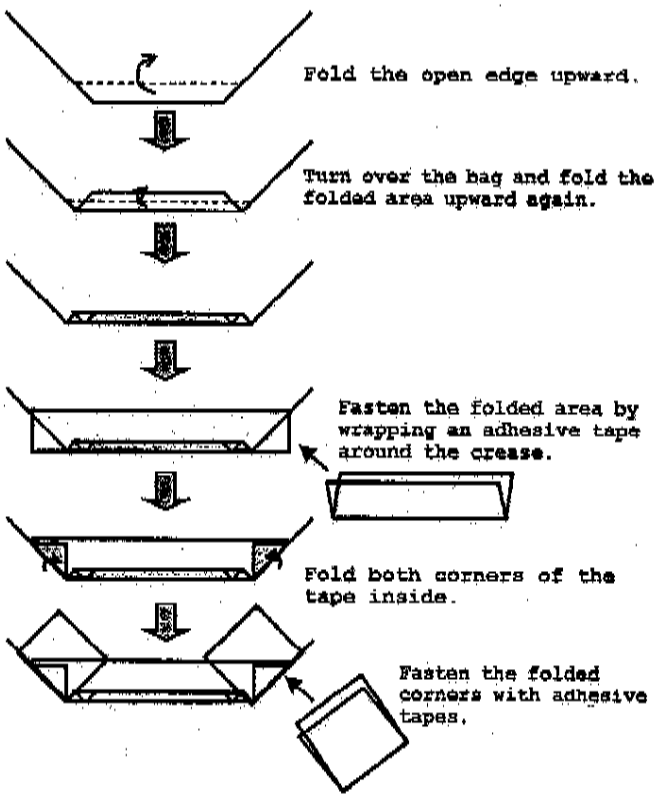


Fig. 4 Bag Sealing Method

7.2 Volatile Component Sampling Method

Immediately after heating the test specimen (to 65 ℃ for 2 h) according to Section 7.1, sample the volatile components in accordance with the following procedures while maintaining the bag at the same temperature.

7.2.1 Hydrocarbons Sampling Method

Store a Tenax tube in a dark and cold place. Remove it from the storage place 30 minutes before use and let it stand until it reaches room temperature.

(1) Connect the Tenax tube that has been aged in accordance with Section 6.1 to the bag, pump, and gas flowmeter by using silicone tubes as shown in Fig. 5. In this procedure, position the Tenax tube so that its edge to be connected to the injection port of the GC-MS comes close to the bag.

(2) Before starting the sampling operation, shake the bag sufficiently so that the volatile components distribute uniformly in the bag.

(3) Open the two stop valves shown in Fig. 3 to sample 1 L of gas containing hydrocarbons from the bag at a rate of 0.5 L/min or less. Record the quantity of the sampled gas in L down to the second decimal place.

(4) Immediately after completion of the sampling, stop the pump and close the two stop valves. Disconnect the Tenax tube from the silicone tubes and keep it from contamination by tightly sealing both ends in the same manner as that in Section 6.1.

(5) After sampling the gas, conduct the analysis as soon as possible (within one week after sampling). Until the analysis, store the Tenax tube containing the hydrocarbons in a cool, dark place.

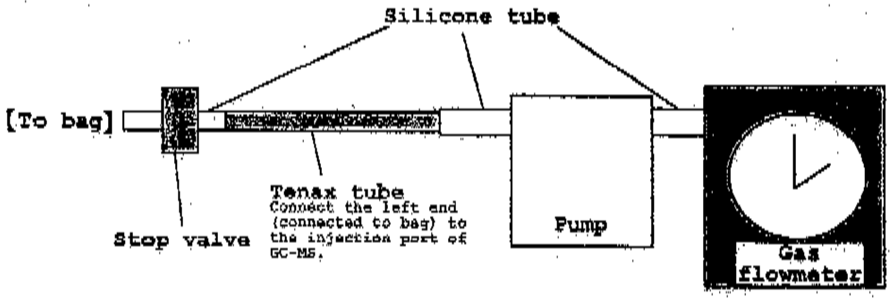


Fig. 5 Sampling Hydrocarbons

7.2.2 Aldehydes Sampling Method

Immediately after sampling hydrocarbons according to Section 7.2.1, sample aldehydes. For the sampling, use a DNPH cartridge that has been stored in a refrigerator and the performance is still guaranteed. Remove the cartridge from the refrigerator 30 minutes before use and let it stand until it reaches room temperature.

(1) Connect the DNPH cartridge to the bag, pump, and gas flowmeter with silicone tubes as shown in Fig. 6. In this procedure, position the cartridge as specified in its instruction manual.

(2) Open the two stop valves shown in Fig. 3 to sample the entire quantity of gas containing aldehydes (gas remaining after hydrocarbons have been sampled) in the bag at a rate of 2 L/min or less. For a bulky test specimen, do not press it firmly with hands but evacuate the gas with a pump. Record the quantity of sampled gas in L down to the second decimal place.

(3) Put the DNPH cartridge with sampled gas in an aluminum bag, seal it tightly, and store it in a refrigerator until analysis. Conduct analysis as soon as possible (within one week after the sampling).

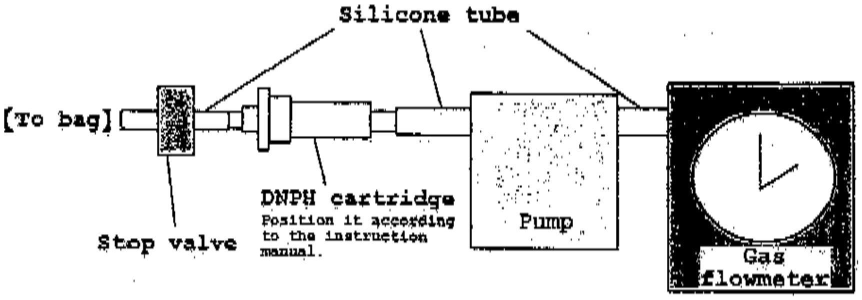


Fig. 6 Sampling Aldehydes

8. Analysis Method

8.1 Hydrocarbons Analysis Method

8.1.1 Drawing Calibration Curve

A standard solution or gas may be used to draw the calibration curve. The following is an example of calibration curve drawing procedures using a standard solution. (Concentration of each component in the standard solution is 1000 μg/mL.)

(1) Dilute the standard solution with a solvent to a proper concentration.

Remark:

When storing the diluted solution, place it in a sealable container and store it in a refrigerator. Use the diluted solution within one month after preparation.

(2) Add the diluted solution into a Tenax tube that has been aged in accordance to Section 6.1, while blowing inert gas toward the tube (Fig. 7). After this procedure, perform purging for 1 to 5 minutes.

Remark:

Prepare Tenax tubes for three or more levels of calibration curve within a range of 0 to 500 ng by adjusting the concentration of the diluted solution and the amount to be added.

(3) According to the analysis conditions specified in Table 4, analyze the diluted solution in the Tenax tube prepared in (2) above, using a GC-MS equipped with a thermal desorption system.

(4) Using the analysis results obtained in (3) above, draw a calibration curve (peak area or height vs. concentration). Check the correctness of the calibration curve once a day when sample gases are analyzed continuously under the same conditions using the same test set. Measure the peak area or height at an arbitrary concentration within the calibration range. If there is no difference between the conventional value and newly measured value, use the conventional calibration curve. If a problem is found or when using a different analyzer, drawing a new calibration curve is required.

Table 4 Analysis Conditions for GC-MS Equipped with Thermal Desorption System (Example)

Analyzer	TDTS-GC-MS made by Shimadzu
Thermal desorption temperature (°C)	280
Column	HP-1; length: 60 m; film thickness: 0.25 μm; dia.: 0.32 mm
Capillary column material	Pure dimethylpolysiloxane or equivalent (A low polarity material may also be used.)
He gas flow rate (mL/min)	1.0
Temperature increasing condition	40 °C (5 min) → 80 °C (10 min) → 280 °C (20 min) 4 °C /min 10 °C /min
Injection port temperature (°C)	280
Split ratio	1/30 in normal, excepting no split when volatilization rate is low. Split ratio may be changed as required.
MSD interface temperature (°C)	280
Measurement mode	SCAN mode
Uptake range (mass)	30 to 500
Number of masses to be measured	Toluene (91), xylene (91), ethyl benzene (91), styrene (104), tetradecane (57), DBP (149), DEHP (149)

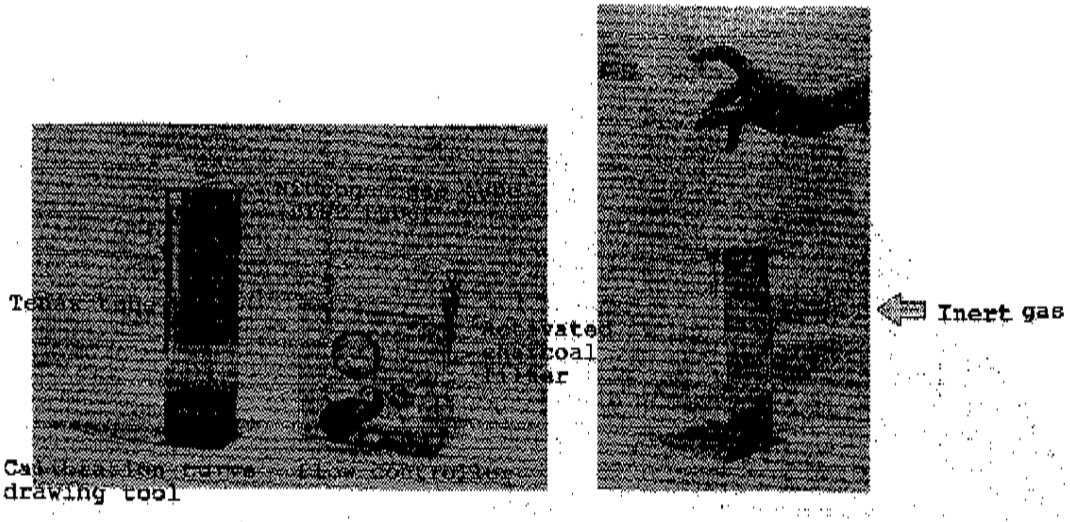


Fig. 7 Standard Solution Spiking Method

8.1.2 Analysis

Under the analysis conditions specified in Table 4, analyze the Tenax tube containing the gas sampled in accordance with Section 7.2.1 using a GC-MS equipped with a thermal desorption system. For the analysis, connect the Tenax tube to the thermal desorption system so that the gas flows in the direction opposite to that for gas sampling in Section 7.2.1. Using the applicable calibration curve, determine the weight W (μg) of each component from the analysis result (peak area or height) of each component.

8.1.3 Quantitative Determination

Using the following equation, convert the weight W of each component obtained in Section 8.1.2 to the quantity (quantitative value) released from the test specimen.

$$\text{Quantitative value } (\mu\text{g/specimen}) = W \times (V_T + V_D)/V_T$$

where,

W: weight of component (μg)

V_T: quantity of gas sampled in Tenax tube (L)

V_D: quantity of gas sampled in DNPH cartridge (L)

8.2 Aldehides Analysis Method

8.2.1 Drawing Calibration Curve

An example of a calibration curve drawing method is shown below.

(1) Dilute the standard solution with a solvent (acetonitrile, for example) to a proper concentration. (It is advisable to adjust the standard solution to a concentration near that of the sampled gas.)

(2) According to the analysis conditions specified in Table 5, analyze each diluted solution prepared in (1) above using an HPLC.

(3) Using the analysis results obtained in (2) above, draw a calibration curve. Use peak height (not peak area) for the data.

Remark:

Conduct measurement on the standard solution once or more in each round of analysis.

Table 5 Analysis Conditions for HPLC (Example)

Analyzer	HPLC VP made by Shimadzu
Detector	UV360 nm
Column	INERTSIL ODS-80 made by GL Science
Developer	CH_3CN 55 % - H_2O 45 %
Column temperature (℃)	40

8.2.2 Analysis

According to the following procedures, analyze the gas that has been sampled in the DNPH cartridge in Section 7.2.2.

(1) Take a specified quantity (3 to 6 mL) of acetonitrile in a syringe and connect it to the DNPH cartridge to gradually extract the gas from the cartridge.

Remark 1:

Record the correct quantity of the extracted gas.

Remark 2:

For the extraction, ensure that the gas flows in the direction opposite to that used for sampling the gas in Section 7.2.2.

Remark 3:

Do not use a cation-exchange cartridge for the extraction, since it has an aldehyde retaining property.

(2) After the solvent has completely been removed from the DNPH cartridge, fill the syringe with a small quantity of air to entirely evacuate the solvent from the cartridge. Since acetonitrile is highly volatile, tightly seal the container immediately after the extraction. Even when the container needs to be stored in a refrigerator, the period of storage shall not exceed one week.

(3) According to the analysis conditions specified in Table 5, analyze the acetonitrile that has been extracted in (2) above using an HPLC. Using the calibration curve, determine the quantity C (μg/mL) of each component from the analysis result (peak height) of each component.

8.2.3 Quantitative Determination

From the following equation, convert the quantity C of each component obtained in Section 8.2.2 to the quantity (quantitative value) released from the test specimen.

$$\text{Quantitative value } (\mu\text{g/specimen}) = aC \times (V_T + V_D)/V_D$$

where,

C: quantity of component (μg/mL)
V_T: quantity of gas sampled in Tenax tube (L)
V_D: quantity of gas sampled in DNPH cartridge (L)
a: quantity of extracted acetonitrile (mL)

9. Reporting Measurement Results

Report the blanks determined in Section 6.4 and the analysis results obtained in Section 8 as shown in Table 6.

Table 6 Volatile Component Measurement Result

VOC Measurement Result Report

Vehicle model	Part number	Part name

Material standard		Portion where part was installed
Material manufacturer or brand		
Thickness/Weight		
Manufacturing plant		
Process	Actual process or Tentative process	
Test specimen shape	Part ALL or Split ALL cutout (5 × 10, portion, split) or T/P	
Test specimen size	[cm^2]or[g]	
Part size	[cm^2]or[g]	
Number of pieces per vehicle	pieces	
Conversion factor per vehicle		
Analysis company		
Bag	Tedlar or fluorine L	

Reporting manufacturer	Company name		
	Department name		
	Approved by	Confirmed by	Measured by

Test specimen storage	
Manufactured date of part	(D) (M) ,(Y)
Test date	(D) (M) ,(Y)
Storage environment	°C %RH

	Supplier	Component part	Material standard	Material manufacturer or brand		VOC generation (content) – Y/N Volume (µg/specimen)									Test specimen size A	Part size B	Unit	Number of pieces per vehicle C	Conversion factor per part D = B/A*C	Remarks
					Component to be measured	Formaldehyde	Acetaldehyde	Toluene	Xylene	Ethyl benzene	Styrene	Tetradecane	Di-n-butyl phthalate	Di-2-ethylhexyl phthalate						
					Target value															
1																				
2																				
3																				
Average a																				
Blank b																				
Average - Blank c = a - b																				
Generated amount per vehicle c × D																				