GB

NATIONAL STANDARD OF THE
PEOPLE'S REPUBLIC OF CHINA

HJ/T 400-2007

Determination of Volatile Organic Compounds and Carbonyl Compounds in Cabin of Vehicles

车内挥发性有机物和醛酮类物质采样测定方法

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Announcement

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In order to implement "Environmental Protection Law of the People's Republic of China", protect the environment, safeguard human health, improve environment management level, normalize environmental monitoring, "Technical specifications for emission monitoring of stationary source" and other 3 standards have been approved and issued as national environment protection standards.

The names and serial numbers of the four standards are as follows:

1 Technical specifications for emission monitoring of stationary source (HJ/T 397-2007)

2 Stationary source emission-Determination of blackness of smoke plumes - Ringelmann smoke chart (HJ/T 398-2007)

3 Water quality - Determination of the chemical oxygen demand - Fast digestion-Spectrophotometric method (HJ/T 399-2007)

4 Determination of volatile organic compounds and carbonyl compounds in cabin of vehicles (/HJ/T 400-2007)

The aforesaid standards are guiding standards, implemented from March 1, 2008, published by China Environmental Science Press. The details may be searched on the website of the State Environmental Protection Administration (www.sepa.gov.cn/teeh/hjbz/bzwb).

Hereby it is announced.

December 7, 2007

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Foreword

In order to implement "Environmental Protection Law of the People's Republic of China", prevent and control air pollution in cabin of vehicles, and improve environmental quality in cabin of vehicles, this Standard is formulated.

This Standard specifies the arrangement of the sampling points for measuring the volatile organic compounds and carbonyl compounds in crew cabin of motor vehicles, technical requirements of sampling environment condition, sampling method and equipment, corresponding measurement method and equipment, data processing, and quality assurance etc.

This Standard is formulated for the first time.

This Standard is a guiding standard.

This Standard was proposed by the Department of Science, Technology and Standards of Ministry Environmental Protection of the People's Republic of China.

Main Drafting Organizations of this Standard: China Ordnance Equipment Group Corporation, Beijing Municipal Institute of Labor Protection, Beijing Municipal Environmental Monitoring Center, Environment Science and Technology Development Center of China North Industries Group Corporation, China National Institute of Standardization, Volkswagen (China) Investment Company Ltd., Nissan (China) Investment Co., Ltd., and GM (China) Investment Co., Ltd. etc.

The following organizations provide technical support in the preparation of this Standard: Dongfeng Nissan Passenger Vehicle Company of Dongfeng Motor Co., Ltd., Changan Ford Mazda Automobile Co., Ltd., Toyota Motor Technical Center(China) Co., Ltd., Zhengzhou Yutong Bus Co., Ltd., Honda Motor (China) Investment Co., Ltd., Shanghai Volkswagen Co. Ltd, Pan Asia Technical Automotive Center Co., Ltd., Chang'an Automobile Co., Ltd., National Institute of Metrology P.R. China, Centre Testing Co., Ltd. (Shenzhen), China Automotive Technology & Research Center, Beijing Institute of Technology, Chongqing Environmental Monitoring Center, Jiangsu Environmental Monitoring Center, Henan Environmental Monitoring Central Station, Hubei Environmental Monitoring Central Station, and Guangzhou Environmental Monitoring Central Station.

This Standard was approved by the General Administration of State Environmental Protection on December 7, 2007.

This Standard was implemented from March 1, 2008.

This Standard shall be interpreted by the General Administration of State Environmental Protection.

Determination of Volatile Organic Compounds and Carbonyl Compounds in Cabin of Vehicles

1 Application Scope

This Standard specifies the arrangement of the sampling points for measuring the volatile organic compounds and carbonyl compounds in crew cabin of motor vehicles, sampling environment condition and technical requirements, sampling method and equipment, corresponding measurement method and equipment, data processing, quality assurance etc.

This Standard is applicable to the sampling and measurement of volatile organic compounds and carbonyl compounds in cabin of vehicles in static state.

2 Normative References

This Standard cites the provisions of the following documents. For undated documents, the latest edition of the normative document referred to applies.

GB/T 15089 Classification of Power-driven Vehicles and Trailers

3 Terms and Definitions

For the purpose of this Standard, the following terms and definitions apply.

3.1 Vehicles of categories M_1, M_2, M_3 and N

Adopt the definitions in GB/T 15089:

M_1–category vehicle refer to the passenger motor vehicles having four wheels, and the seat number does not exceed nine, including the driver's seat.

M_2–category vehicle refer to the passenger motor vehicles having at least four wheels, and the seat number does not exceed nine, including the driver's seat, and the maximum design total weight does not exceed 5000 kg.

M_3–category vehicle refer to the passenger motor vehicles having at least four wheels, and the seat number does not exceed nine, including the driver's seat, and the maximum design total weight exceeds 5000 kg.

N–category vehicles refer to the cargo motor vehicles having four wheels.

3.2 Volatile organic constituent

4.4 Sampling procedure

4.4.1 Preparation stage of vehicles-to-be-tested

a) Place the vehicle-to-be-tested in sampling environmental chamber;

b) The covering (for example plastic film used to protect seats and carpet, etc.) on the internal component surfaces shall be removed, and the covering shall be moved out of the sampling environmental chamber.

c) Open the windows and doors (if they can be opened) of the vehicle-to-be-tested, and keep the vehicle stationary for at least 6h;

d) During process of the whole preparation stage, the environment condition of the sampling environmental chamber shall, at least in the last 4h, meet the requirements of sampling technical condition specified in 4.1.2 of this Standard; quality assurance measures meeting the requirements of 6.7 of this Standard shall be taken to monitor environment condition.

4.4.2 Closing stage of vehicles-to-be-tested

a) Enter closing stage after preparation stage is completed;

b) Install sampling devices in the vehicle-to-be-tested according to the requirements of 4.3.2 in this Standard; completely close the windows and doors of the vehicle-to-be-tested to ensure tightness of the complete vehicle.

c) Keep the vehicle-to-be-tested closed for 16h, and then start collecting samples;

d) During the whole closing stage, the environment condition of the sampling environmental chamber at where the vehicle-to-be-tested is located shall meet the requirements of sampling technical condition specified in 4.1.2 of this Standard; the environment condition shall be monitored according to the requirements of 6.7 in this Standard.

4.4.3 Sampling stage

In sampling stage, the sampling environment condition shall meet the requirements of 4.1.2 in this Standard.

Use the packed column sampling tube of solid-phase adsorbent specified in Appendix B of this Standard to collect volatile organic constituents; and use the packed column sampling tube of solid-phase adsorbent specified in Appendix C of this Standard to collect aldehyde ketone constituent. Respectively install packed column sampling tubes on sampling system; and collect samples with constant-flow gas sampler.

When collecting volatile organic constituents with packed column sampling tube, the sampling flow shall be 100 ml/min ~ 200 ml/min, and the sampling time shall be 30 min; when collecting aldehyde ketone constituent with packed column sampling tube, the sampling flow shall be 100 ml/min ~ 500 mL/min, and the sampling time shall be 30min.

6.5 On-site blank inspection

At least two sampling tubes shall be served as blank in each sampling, and shall be equally treated as other sampling tubes. As on-site blank during the sampling process, they shall be delivered to the laboratory together with other sampling tubes. On-site blank value shall be determined during sample analysis and compared with the zero concentration value of calibration curve. If it is abnormal, then this batch of samples shall not be used.

6.6 Parallel sample inspection

For parallel sampling (not less than two parallel samples), the relative deviation between measured value difference and the arithmetic mean value shall not exceed 20%.

6.7 Sampling environmental monitoring

6.7.1 Monitoring objects

The data of the sampling environment condition at where the tested vehicle is located include: environmental temperature, relative environmental humidity, environmental air flow rate, atmospheric pressure, and single pollutant concentration (only methanal and toluene shall be monitored at present) specified in environmental air.

6.7.2 Monitoring frequency

In the last 4h of the whole preparation stage process, data in the chamber shall be collected at least once in the intermediate phase OR the environment condition in the chamber shall be continuously monitored by online monitoring facilities.

During the whole closing stage process, data in the chamber shall be collected at least once in the intermediate phase OR the environment condition in the chamber shall be continuously monitored by online monitoring facilities.

6.7.3 Positions of the monitoring points

The number of monitoring points for environmental temperature, relative humidity, pollutant background mass concentration shall be one as a minimum; the positions shall be within 0.5m from the outer surface of the vehicle-to-be-tested and at the same height as that of the positions of the sampling points in the vehicle cabin.

At least 5 monitoring points for environmental air flow rate shall be arranged prior to the test; at least one shall be arranged after the environmental air flow rate is stable. They shall be arranged on the front, top, back, left side, right side within 0.5m from the outer surface of the vehicle-to-be-tested.

6.8 Calibration of sampling volume

When calculating the concentration, the sampling volume shall be converted to the volume in the normal state according to the following formula:

Appendix A

(Normative)

Sampling Environmental Chamber

A.1 Technical requirements

A.1.1 The sampling environmental chamber shall be able to meet the sampling environment condition requirements specified in 4.1.2 of this Standard, within 0.5m from the outer surface of the vehicle-to-be-tested; and keep it throughout the sampling process.

A.1.2 Sampling environmental chamber shall have complete envelop enclosure; the internal surface of chamber body shall be low-release, low-permeability and low-adsorption material; material and facilities volatilizing pollutants which affect the background concentration value of environmental pollutant shall not be placed in the chamber. The chamber shall be large enough to contain the vehicle-to-be-tested and convenient for testing and sampling by the person(s).

A.1.3 Technical measures shall be taken for the sampling environmental chamber to reduce the influence of air flow on the air interchange inside and outside the vehicle-to-be-tested.

A.1.4 The main cabin shall be arranged with main door and auxiliary door; the main door shall guarantee normal access of the vehicle-to-be-tested and cannot be opened during the whole sampling process; the auxiliary door shall allow the safe access of personnel. During the whole sampling process, it shall be guaranteed that the auxiliary door meets the sampling environment condition requirements specified in 4.1.2 of this Standard, within 0.5m from the outer surface of the vehicle-to-be-tested when it is opened.

A.1.5 The control accuracy of air conditioning system at 25°C shall be less than or equal to ±1.0°C, and less than or equal to ±10% when the relative humidity is 50%. At least 2 temperature and humidity monitoring points shall be arranged in the chamber; at least one of them shall be within 0.5m from the outer surface of the vehicle-to-be-tested.

A.1.6 For sampling environmental chamber, online monitoring facilities should be adopted to continuously monitor the environment condition in the chamber specified in 4.1.2 of this Standard. Online monitoring facilities shall have data storage function. Environmental pollutant monitoring instrument may monitor the volatile organic constituents by using online mass spectrum, gas chromatography of hydrogen flame ionization detector, etc. The positions of the monitoring point shall be within 0.5m from the outer surface of the vehicle-to-be-tested and at the same height as that of the positions of sampling points in the vehicle cabin.

A.2 Composition

Appendix B

(Normative)

Determination Method for Volatile Organic Constituents

(Thermal Desorption/Capillary Gas Chromatography/Mass Spectrometry)

B.1 Application scope

This Appendix specifies the determination method for volatile organic constituents.

Solid-phase adsorbent shall be used to determine volatile organic constituents. When the sampling volume is 3L, the method detection lower limit of single volatile organic constituent is 1.5μg/m^3.

B.2 Terms and Definitions

B.2.1 Grade 2 desorption

After the sampling tube is heated, the organic constituents are desorbed from the adsorbent; carrier gas carries the organic constituents into the collecting tube for adsorption again. And then the organic constituents are rapidly heated to be desorbed and carried into chromatographic column to separate for determination.

B.2.2 Sampling tube (adsorbent tube)

Generally, stainless steel, glass, lining glass stainless steel or fused silica stainless steel tubes that have the outer diameter of 6mm and contain with solid absorbing material of about 200 mg inside.

B.2.3 Collecting tube

The adsorbent tube or blank tube (inner diameter <3 mm) that is filled with a small amount of adsorbents; adsorb at normal or low temperature; rapidly heat up after organic constituents are enriched in this tube; after the organic constituents are rapidly desorbed, it shall be carried into chromatographic column for analysis.

B.2.4 Capillary gas chromatography column

Polarity index is less than 10, pillar length is 50 m ~ 60 m, inner diameter is 0.20 mm ~ 0.32 mm, film thickness is 0.2 μm ~ 1.8 μm.

B.2.5 Figure of total ion current (TIC)

The reconstructed ion spectrogram that is generated by mass spectrometric detector in full scan mode.

B.3 Method principle

before thermal desorption. Sample gas circuit shall be uniformly heated. Carrier gas purging system with the temperature close to the environmental temperature shall be used to remove oxygen.

B.5.2.1 Thermal desorption device

It is able to carry out Grade-2 thermal desorption for sampling tubes, and carry the desorbed gas to gas chromatography with carrier gas. The desorption temperature, desorption duration and the flow rate are adjustable; cold trap is able to achieve rapid temperature rise.

Grade-2 thermal desorption is used for high selective capillary gas chromatography. The analytes desorbed from sampling tube shall be enriched again before rapidly entering capillary gas chromatography column. Cold trap concentration equipment may be used.

B.5.2.2 Thermal desorption/capillary gas chromatography transmission line

Transmission line shall have heating function and directly connected, with capillary column through transmission line/interface.

B.5.3 Sampling tube activation equipment

If thermal desorption device has no sampling tube activation function, then sampling tube activation equipment shall be used.

Sampling tube activation equipment shall be able to prevent the entering of air; the temperature control accuracy is ± 5°C; the temperature control range shall at least be equivalent to the service temperature of the thermal desorption device. The flow rate of inert gas is 50~100ml/min.

B.6 Sample pre-treatment

Sampling tube shall be installed on the thermal desorption device prior to sample desorption, the airflow direction shall be opposite to that in sampling. All the parts of sample gas circuit shall be carried out with leak test. If any leakage is found in the sample gas circuit, the desorption of sampling tube shall be stopped.

After leak test, sampling tube, sample gas circuit and cold trap shall be purged at ambient temperature by using carrier gas.

During sample desorption, the sample is heated to make the volatile organic constituents to desorb from adsorbent and carry to cold trap by carrier gas for pre-concentration; then carry out with the second thermal desorption, and enter into gas chromatograph-mass spectrometer through transmission line. The temperature of transmission line shall be close to the desorption temperature to prevent the to-be-determined constituent from coagulation. See Table B.2 for the thermal desorption conditions.

Table B.2 Thermal Desorption Conditions for Samples

B.9.2 Linear range

10^3.

B.9.3 Precision

Respectively fill 0.5μg of standard gas of benzene, toluene, butyl acetate, ethylbenzene, m-xylene, styrene, o-xylene, hendecane, and dichlorobenzene respectively; the relative standard deviation range of the results of 6 times analysis using Tenax-TA solid-phase adsorbent is 0.5%~3.0%.

B.9.4 Accuracy

Fill 0.5μg of toluene into the Tenax-TA sampling tube at a temperature of 20°C and relative humidity of 50%; the relative error of analysis (average value of 5 measured results) is 5.0%.

B.10 Quality assurance and control

B.10.1 Interference of adsorbent

a) Strict condition treatment system and sampling tubes must be used, including temperature, air flow and duration, etc.; sampling tubes shall be sealed and stored well;

b) Some carbonous metals can accelerate the degradation of some organics during the process of high-temperature thermal desorption, therefore, cause error and low recovery rate

B.10.2 Humidity effect

a) Hydrophobic adsorbent shall be used to reduce water effect;

b) If the quantity of the samples collected is large, generally, analysis interference caused by water shall be eliminated by splitting samples;

c) Generally, dry inert gas shall be used to purge sampling tubes and cold trap prior to analysis, the purging temperature is close to the atmospheric temperature.

B.10.3 Interference of coexisting substances

Suitable chromatographic column and analytical condition shall be selected for the separation of various volatile organic constituents to solve the interference problem of coexisting substances.

B.10.4 Connection between thermal desorption instrument and gas chromatography device

Metal injector-type needle or long fused silicon tube that is not heated should not be inserted into gas chromatography injection port; such connection can generate cold spot and cause broadening of spectral band and air leakage.

B.10.5 Calibration of response

During the analysis process, as a calibration of system performance, it is recommended to carry out a single level correction (i.e. select the samples in medium concentration level) for every 10 samples. All the samples beyond the calibration range shall be attached with data quality qualification instructions in the analysis result.

B.10.6 Laboratory blank

For solid-phase adsorbents (for example Tenax, etc.), generally, the blank level of single compound in the laboratory is 0.01~0.1 ng. When the peak area or peak height of adsorbent background is larger than or equal to 10% of sample, the experimental results shall be marked.

B.10.7 Field blank

If the peak-shape of field blank is the same as that of sample, when the concentration level is greater than or equal to 5% of the sample concentration, the sealing and storage conditions of sample shall be inspected. When the concentration level is greater than or equal to 10% of the sample concentration, the sample collected is invalid.

B.11 Result report

It shall at least include the followings:

a) Analytical condition;

b) Calculation result, which shall cover the concentration values of 25 maximum air pollutants in cabin of vehicle, volatile organic constituents, measured value, background values of environmental pollutants and blank value;

c) Analytical spectra diagram.

B.12 Bibliography

ISO16000-6:2004(E); Determination of volatile organic compounds in indoor and test chamber air by active sampling on Tenax TA sorbent, thermal desorption and gas chromatography using MS/FID.

ISO16017-1; Indoor, ambient and workplace air-sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography-pumped sampling.

EPA/625/R-96/010b (TO-17); Determination of volatile organic compounds in ambient air using active sampling onto sorbent tubes.

R and R^1 are alkyls or aromatic groups (ketone) or hydrogen atom (aldehydes). Use the UV or diode array detector of High performance liquid chromatography for detection, the retention time is used for quality determination and peak area (peak height) is used for quantification.

C.4 Reagents and materials

C.4.1 DNPH sampling tube

The sampling tube filled with coated DNPH silica gel. Blank verification to ensure the quality of each batch of sampling tubes shall meet the following requirements:

- Methanal <0.15μg/tube;
- Acetaldehyde <0.10μg/tube;
- Acetone <0.30μg/tube;
- Other materials <0.10μg/tube.

C.4.2 Ultrapure acetonitrile (dedicated mobile phase of HPLC)

Grade-UV pure. The mass concentration of methanal shall be less than 1.5ng/ml.

C.4.3 Standard sample (standard substance)

Prepare the standard gas or liquid or solid into the standard gas of the required concentration, and collect it in certain quantity with constant-flow gas sampler to a DNPH sampling tube to form standard series. The concentration of the analyte of the prepared standard series shall be similar to that of the sample intended to be analyzed. During the collecting process, standard gas shall be collected at the same flow rate as that used for sampling.

It is feasible to buy dinitrophenyl hydrazine 2, 4-dinitro benzene hydrazone liquid standard samples (standard substances) of aldehyde ketone, or use solid standard samples (standard substances) to prepare standard series.

It is feasible to buy the standard tubes of aldehyde ketone derivative standard substances and accompanied with the certificate approved by the national administrative departments. All the pre-assemble standard tubes shall be provided with the following information

Chromatogram of blank tube before filling standard substance and relevant analytical condition and date.

Date of filling standard substance.

Content and uncertainty of standard compounds.

Case analysis of standard substance (the same analytical condition as that of blank tube).

calibration curve to pass the zero point, then the curvilinear equation shall include intercept.

C.7.2.4 Each new calibration curve shall be analyzed and verified using standard substances of different sources. Standard substance shall be analyzed six times continuously; there shall be no significant difference between the analysis result and the nominal value of standard substance when the significant level α=5%, otherwise correct measures shall be taken to eliminate the error caused by the two standard substances with different sources.

C.7.2.5 Routine analysis quality control shall be conducted using quality control diagram. Within certain time interval, take two parallel control samples to repeat analysis 20 times and make mean control diagram (Figure x). In routine analysis, frequency shall be determined according to the sample. Two parallel control samples shall be determined together with the to-be-analyzed sample. Plot the analysis results of the control samples on the control diagram in sequence to judge whether they are in control state during the analysis process according to the following rules:

1) If this point is between the upper and lower warning lines, then the test process is in controlled state, the analysis result of the samples is effective;

2) If this point is off the upper and lower warning lines, but it is still within the upper and lower limit area, this indicates that the analyzed mass is becoming deteriorated and intended to be out of control, preliminary inspection shall be carried out and corresponding corrective measure shall be taken;

3) If this point is beyond the upper and lower control limits, the cause shall be immediately found out and the samples shall be re-determined;

4) Even though all the data are in the control range, when seven points continuously rise or drop, this indicates that the analysis process is inclined to be out of control, the cause shall be found out and the mistakes shall be corrected.

C.7.3 Sample analysis

Analyze sample according to the operation procedure of plotting calibration curve and the same analytical conditions (Figure C.3).

$\bar{h}$ - Average value of instrumental response peak height of single constituent standard substance, AU;

V - Sampling volume under standard condition, L.

C.9.2 Precision

The number of samples carried out with repetitive analysis shall be 10% of the field sample number, the samples carried out with the same repetitive analysis shall be analyzed 6 times and tested the precision by Grubbs method. There shall be no suspicious analysis data in 1% elimination level, otherwise corresponding measures shall be taken to correct.

C.9.3 Accuracy

The accuracy of analysis method shall be controlled using standard recovery rate quality control diagram. Determine the standard recovery rate of 20 standard substances covering the possible concentration range of actual samples (the added scalar cannot be larger than 3 times the contents of the to-be-determined substance), and make quality control diagram according to the standard recovery rate. The use of quality control chart may refer to C.7.2.5 of this Standard.

C.10 Quality assurance and control

C.10.1 Interference and elimination

a) Direct exposure of DNPH sampling tube to sunlight shall be avoided.

b) Because the methanal in acetonitrile may be converted into hydrazone in certain quantity, the determined concentration value of methanal in sample is relatively high, therefore, methanal in acetonitrile shall be inspected in the quality control procedure, and the concentration of methanal shall be less than 1.5 ng/ml.

c) If homemade sampling tube is used, DNPH must be purified to reach Grade UV standard through several times of recrystallization. Recrystallization is to acquire maximum crystal body by gradually evaporating solvent at 40~60°C. The purified DNPH shall be stored in Grade UV acetonitrile until use. Use HPLC to analyze the pollution level of aldehyde ketone constituent in DNPH, the blank value of each tube shall be less than 0.15 μg.

d) Methanal and acetone are common reagents used in laboratory and easily bring background interference.

e) Suitable chromatographic column and analytical condition shall be selected for the separation of various constituents to solve the interference problem of coexisting substances.

C.10.2 Liquid chromatography system performance

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