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Methods of Detecting Polycyclic Aromatic Hydrocarbons in Automotive Materials

汽车材料中多环芳烃的检测方法

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Warning: The personnel using this Document shall have practical experience in formal laboratory work. This Document does not point out all possible security issues. The user is responsible for taking appropriate safety and health measures and ensuring compliance with the conditions stipulated by relevant national laws and regulations.

1 Scope

This Document specifies the terms and definitions of the methods of detecting polycyclic aromatic hydrocarbons in automotive materials, as well as the detection methods of gas chromatography-mass spectrometry, high performance liquid chromatography, proton nuclear magnetic resonance spectroscopy, and the like contents.

This Document is applicable to the qualitative and quantitative testing of 18 polycyclic aromatic hydrocarbons in automotive materials. Among them, gas chromatography-mass spectrometry is suitable for testing polycyclic aromatic hydrocarbons in textiles, plastics, thermoplastic elastomers, rubber and leather materials; high performance liquid chromatography is suitable for testing polycyclic aromatic hydrocarbons in plastics and rubber materials; proton nuclear magnetic resonance spectroscopy is suitable for testing polycyclic aromatic hydrocarbons in rubber materials.

2 Normative References

The following documents are essential to the application of this document. For the dated documents, only the versions with the dates indicated are applicable to this document; for the undated documents, only the latest version (including all the amendments) is applicable to this document.

GB/T 3516 Rubber - Determination of Solvent Extract

GB/T 6682 Water for Analytical Laboratory Use - Specification and Test Methods

GB/T 29614-2013 Determination the Content of Polycyclic Aromatic Hydrocarbons in Vulcanized Rubber Compounds

4 Method-I: Gas Chromatography-Mass Spectrometry

4.1 Method summary

After crushing, the specimen is added with organic solvent; extracted by ultrasonic or microwave; if necessary, the extract is purified, concentrated, made constant volume, and determined by gas chromatography-mass spectrometer (GC-MS), and qualitative analysis is performed by retention time; use internal standard method or external standard method to quantify.

4.2 Applicable material types

This method is suitable for the detection of polycyclic aromatic hydrocarbons in materials such as textiles, plastics, thermoplastic elastomers, rubber and leather, etc.

4.3 Reagents and materials

4.3.1 n-hexane: chromatographically pure.

4.3.2 Toluene: chromatographically pure.

4.3.3 Acetone: chromatographically pure.

4.3.4 Dichloromethane: chromatographically pure.

4.3.5 Cyclohexane: chromatographically pure.

4.3.6 Sodium chloride: analytically pure.

4.3.7 Class-I water: comply with the provisions of GB/T 6682.

4.3.8 Helium gas: purity≥99.999%.

4.3.9 n-hexane + acetone (volume ratio 1: 1).

4.3.10 n-hexane + dichloromethane (volume ratio 3: 2).

4.3.11 Dimethyl sulfoxide: analytically pure, saturated by cyclohexane (see 4.3.5).

4.3.12 4% sodium chloride solution: 4g of sodium chloride (see 4.3.6) is dissolved in 100mL of Class-I water (see 4.3.7).

4.3.13 Silica gel solid phase extraction column: 500mg/3mL or equivalent; activate with n-hexane (see 4.3.1) before use to keep it moist.

4.3.14 Standard solutions of 18 polycyclic aromatic hydrocarbons: purity≥95%.

4.4.7 Airtight microwave extractor.

4.4.8 Test tube with stopper.

4.4.9 Solid phase extraction device.

4.4.10 Rotary evaporator.

4.4.11 Thermometer: an accuracy of at least 1°C.

4.4.12 250mL separatory funnel.

4.4.13 Heating device: used to heat sodium chloride solution (see 4.3.12).

4.4.14 5mL volumetric flask.

4.4.15 Filter membrane: made of polytetrafluoroethylene, used to filter organic solvents, with a pore size of 0.45μm or equivalent.

4.5 Preparation of specimen

Use scissors (or similar tools) to crush representative specimens into particles with a particle size of less than 1mm and mix them. If necessary, use a liquid nitrogen crusher (see 4.4.2) for crushing.

For the preparation of tire samples, refer to Appendix B in GB/T 29614-2013.

NOTE: In case of hard specimens, it is recommended to use a liquid nitrogen crusher for crushing to prevent the loss of polycyclic aromatic hydrocarbons due to temperature rise during the crushing process.

4.6 Extraction and purification

4.6.1 Extraction

4.6.1.1 Ultrasonic extraction

Weigh 0.2g of the specimen after cutting, accurate to 0.1mg; put it into a sealable extraction container (see 4.4.4). Add 10mL (see Table 2) of extraction solvent with mass concentration of internal standard substance 1 (see 4.3.15), internal standard substance 2 (see 4.3.16) and internal standard substance 3 (see 4.3.17) of 50μg/L. Fully soak the specimen; then seal the extraction container; and place it in an ultrasonic water bath device (see 4.4.6); perform ultrasonic extraction at 60°C±2°C water temperature for 60min±2min. After the extraction is completed, take out the extraction container and cool to room temperature and mix well. If the extraction solution needs to be purified, follow procedures in 4.6.2 for purification; if no purification is required, place the extraction solution in a 35°C±2°C water bath and a vacuum of no less than

extraction column (see 4.3.13); and control the flow rate to 1 drop/2s. Then add 5mL of n-hexane to rinse; discard the washing liquid. Elute the specimen by 5 mL of n-hexane + dichloromethane (see 4.3.10) solution; and collect the eluate. Use a rotary evaporator to evaporate the eluate to near dryness in a water bath of 35°C±2°C and a vacuum of no less than 30kPa. Dissolve it by n-hexane + acetone and make constant volume to 5mL. After being filtered by a filter membrane, the filtrate is analysed by a gas chromatography-mass spectrometer. If necessary, analysis can be performed after dilution.

4.6.2.2 Purification of thermoplastic elastomer specimens

Use a rotary evaporator (heating temperature no higher than 40°C) to concentrate the extract prepared as per the procedures in 4.6.1 to about 1mL; add 10mL of cyclohexane (see 4.3.5) to dissolve the specimen; transfer the dissolved specimen to a separatory funnel (see 4.4.12) that has added 8 mL of dimethyl sulfoxide (see 4.3.11); shake vigorously for about 1 min; centrifuge or stand for stratification. Then transfer the lower layer of dimethyl sulfoxide phase to another separatory funnel. The residue liquid is extracted by 8 mL of dimethyl sulfoxide once more; combine the extracts; and discard the cyclohexane layer. Add 5mL of cyclohexane and 80mL of sodium chloride solution (see 4.3.12) to the dimethyl sulfoxide extract; shake vigorously for 2min; and let stand for stratification. Put the lower layer of aqueous phase into another separatory funnel; and then repeat the extraction of the lower layer of aqueous phase by 5 mL of cyclohexane once; combine the extracts; and discard the lower layer of aqueous phase obtained during the second time. The extract was washed twice by 5 mL of 70°C sodium chloride solution; and discard the aqueous layer. Combine the cyclohexane layers; use a rotary evaporator to evaporate to near dryness in a water bath of 35°C±2°C and a vacuum of no less than 30kPa; and use toluene (see 4.3.2) to make the constant volume to 5mL. After being filtered by a filter membrane, the filtrate is analysed by a gas chromatography-mass spectrometer. It can be analysed after dilution, if necessary.

4.6.2.3 Purification of rubber specimen

After cooling the extract prepared according to the procedures in 4.6.1 to room temperature, it is transferred to the solid phase extraction column; and the flow rate is controlled to 1 drop/2s. Then rinse by 5mL of n-hexane and discard the eluent. Elute the specimen by 5 mL of n-hexane + dichloromethane solution; and collect the eluate. In a water bath of 35°C±2°C and a vacuum of no less than 30kPa, use a rotary evaporator to evaporate the eluate to near dryness; and make constant volume to 5mL by toluene. After filtering through a filter membrane, the filtrate is analysed by a gas chromatography-mass spectrometer. It can be analysed after dilution, if necessary.

4.7 Analysis method

4.7.1 Measurement conditions

Perform gas chromatography-mass spectrometry analysis on a mixed standard working solution with no less than 5 concentration gradients; and take the ratio of the mass concentration of polycyclic aromatic hydrocarbons to the mass concentration of internal standard substances as the abscissa, and take the ratio of peak area of polycyclic aromatic hydrocarbons to the peak area of the corresponding internal standard substances as the ordinate to establish the internal standard curve. The linear correlation coefficient of the internal standard curve shall be no less than 0.995.

4.8.2 Drawing of external standard curve

Perform gas chromatography-mass spectrometry analysis on a mixed standard working solution with no less than 5 concentration gradients; and take the mass concentration of polycyclic aromatic hydrocarbons in the mixed standard working solution as the abscissa, and take the chromatographic peak area of the polycyclic aromatic hydrocarbons in the mixed standard working solution as the ordinate to establish an external standard curve. The linear correlation coefficient of the external standard curve shall be no less than 0.995.

4.9 Blank test

Perform blank test without adding a specimen according to the procedure requirements from 4.1 to 4.8.

4.10 Calculation of results

4.10.1 Quantitative calculation of internal standard method

Calculate the concentration of polycyclic aromatic hydrocarbons in the specimen solution according to Formula (1):

$$c_i = \left(\frac{A_i}{A_s} - b_i \right) \times \frac{c_s}{K_i} \qquad \cdots\cdots (1)$$

Where:

c_i – mass concentration of the i^{th} polycyclic aromatic hydrocarbon in the specimen solution, in μg/L;

K_i – slope of internal standard curve of the i^{th} polycyclic aromatic hydrocarbon;

A_i – peak area of the i^{th} polycyclic aromatic hydrocarbon in the specimen solution;

A_s – peak area of the internal standard substance corresponding to the i^{th} polycyclic aromatic hydrocarbon in the specimen solution;

b_i – intercept of internal standard curve of the i^{th} polycyclic aromatic hydrocarbon;

5 Method-II: High Performance Liquid Chromatography

5.1 Method summary

After crushing, the specimen is added with appropriate solvent and extracted by microwave. If necessary, the extract is purified by a silica gel solid phase extraction column, concentrated and made to constant volume; and then measured by high performance liquid chromatograph (HPLC) and quantified by external standard method.

5.2 Types of applicable material

This method is suitable for testing polycyclic aromatic hydrocarbons in materials such as plastics and rubber.

5.3 Reagents and materials

5.3.1 Acetonitrile: chromatographically pure.

5.3.2 n-hexane: chromatographically pure.

5.3.3 Acetone: chromatographically pure.

5.3.4 Dichloromethane: chromatographically pure.

5.3.5 Class-I water: meet the requirements of GB/T 6682.

5.3.6 n-hexane + acetone (volume ratio 1: 1).

5.3.7 n-hexane + dichloromethane (volume ratio 3: 2).

5.3.8 Silica gel solid phase extraction column: 500mg/3mL or equivalent, activate with n-hexane (see 5.3.2) before use to keep it moist.

5.3.9 Standard solutions of 18 polycyclic aromatic hydrocarbons: purity ≥95%.

5.3.10 Preparation of mixed standard working solution: Pipette an appropriate amount of 18 PAHs mixed standard solution (see 5.3.9); and dilute it by acetonitrile (see 5.3.1) into series of standard working solutions with mass concentration range of 2.5 μg/L~ 250μg/L.

5.4 Apparatus

5.4.1 High performance liquid chromatograph: equipped with suitable detectors such as ultraviolet-visible detector and diode array detector.

5.4.2 Liquid nitrogen crusher: equipped with a screen with an aperture of 1mm.

the supernatant. The precipitate is washed twice by 5mL of n-hexane; and the supernatants obtained from the two centrifugation operations are combined after centrifugation. The supernatant is concentrated to near dryness by a rotary evaporator; and add 2mL of n-hexane to shake and dissolve; and the resulting solution is transferred to a solid phase extraction column (see 5.3.8); and the flow rate is controlled to 1 drop/2s. Then rinse by 5mL of n-hexane and discard the eluent. Elute by 5mL of n-hexane + dichloromethane (see 5.3.7) solution; collect the eluate; use a rotary evaporator to concentrate to near dryness; dissolve by acetonitrile and make constant volume to 10mL. Filter through a filter membrane (see 5.4.11), then the filtrate is analysed by high performance liquid chromatograph (see 5.4.1), and it can be analysed after dilution, if necessary.

If no precipitate occurs, the solution is concentrated to near dryness by a rotary evaporator; and add 2mL of n-hexane to shake and dissolve; and the solution is transferred to a silica solid phase extraction column; and the flow rate is controlled to 1 drop/2s. Then rinse by 5mL of n-hexane and discard the eluent. Elute by 5mL of n-hexane + dichloromethane solution; collect the eluate; concentrate it to near dryness by a rotary evaporator; dissolve it by acetonitrile and make constant volume to 10mL. After filtering through a filter membrane, the filtrate is analysed by high performance liquid chromatograph. It can be analysed after dilution, if necessary.

5.6.2.2 Purification of rubber specimens

Transfer the solution obtained after processing according to the method in 5.6.1 to the solid phase extraction column; and control the flow rate to 1 drop/2s. Then rinse by 5mL of n-hexane and discard the eluent. Elute by 5mL of n-hexane + dichloromethane solution; collect the eluate; concentrate it to dryness with a rotary evaporator; dissolve it by acetonitrile and make the constant volume to 10mL. After filtering through a filter membrane, analyse the filtrate by a high-performance liquid chromatograph. Analysis can be performed after dilution, if necessary.

5.7 Analysis method

5.7.1 Measurement conditions

The test conditions of high-performance liquid chromatography that can be referred to are as follows:

a) Chromatographic column: PAH chromatographic column, 250mm×4.6mm (inner diameter) × 5.0μm (particle size), or equivalent;

b) Column temperature: 25°C;

c) The mobile phase and flow rate are shown in Table 4;

d) Detection wavelength: 254nm;

evaporation residue is transferred to the SPE column.

6.6.4 After all the dichloromethane solution is adsorbed on the SPE column, start to elute the non-polar components by 25mL of n-hexane. During the elution process, maintain a steady flow rate; and the flow rate shall not exceed 5mL/min.

6.6.5 When all 25mL of n-hexane passes through the SPE column, stop collecting the purified components.

6.6.6 To avoid oxidation, use nitrogen (see 6.3.4) to dry the extract.

6.6.7 Weigh the dried residue (accurate to 0.1mg) and calculate the recovery percentage.

6.6.8 Repeat the extraction and purification process twice (see 6.6.1~6.6.7), using fresh purifying agent each time.

6.6.9 Calculate the average of the 3 recovery percentages. If the relative deviation between a single test value and the average value is within ±5%, proceed to the procedure in 6.7. Otherwise, continue extraction and purification until the relative deviation between the test value and the average value is within ±5%.

6.7 NMR test

6.7.1 The purified extract from the residue obtained in procedures of 6.6.7 is subjected to ^{1}H NMR spectrum measurement.

6.7.2 In a glass vial, use an appropriate amount (approximately 1mL) of deuterated chloroform (see 6.3.5) to dissolve the dried residue obtained from the operation of procedures in 6.6.7 and 6.6.8. If necessary, use a small magnetic stirrer or mechanical stirrer to accelerate the dissolution.

6.7.3 Perform nuclear magnetic resonance tests on the 3 purified extracts obtained in procedures of 6.6.7 and 6.6.8.

6.7.4 Add about 0.5mL of the specimen solution (see 6.7.1) to the NMR tube; and place the sample in the instrument to perform the NMR test under the conditions of 6.4.5.

6.7.5 After sampling, the Fourier transform is applied to obtain the free induction attenuation signal FID, which is amplified by the exponential function (LB=0.3Hz) to obtain the spectral frequency. Use TMS to calibrate from zero.

6.7.6 Carry out the blank test of the deuterated chloroform solvent at the same time.

6.8 Calculation of result

Integrate the hydrogen spectrum and record the following areas:

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