HJ

NATIONAL ENVIRONMENTAL PROTECTION STANDARD

OF THE PEOPLE'S REPUBLIC OF CHINA

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Ambient air – Determination of volatile organic compounds – Collected by specially-prepared canisters and analyzed by gas chromatography/mass spectrometry

环境空气　挥发性有机物的测定

罐采样/气相色谱-质谱法

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Warning: The standard substances used in experiment are volatile toxic chemicals, which shall be used with adequate ventilation. Protective devices shall be worn to avoid inhalation or contact with skin and clothing.

1 Application Scope

This Standard specifies the method for the determination of volatile organic compounds in ambient air which are collected by specially-prepared canisters and analyzed by gas chromatography/mass spectrometry.

This Standard applies to the determination of 67 volatile organic compounds in ambient air such as propylene. If other volatile organic compounds pass the method suitability validation, they can also be determined using this Standard.

When the sampling quantity is 400 ml in the full-scan mode, the detection limit of this method is 0.2 μg/m^3 ~ 2 μg/m^3 and the lower limit of determination is 0.8 μg/m^3 ~ 8.0 μg/m^3. For details see Annex A.

2 Normative References

This Standard cites the following documents or clauses therein. For undated reference documents, their valid editions apply to this Standard.

HJ/T 194, *Manual methods for ambient air quality monitoring*

3 Method principle

Use stainless steel canisters with inner wall deactivated to collect ambient air samples; after cold trap condensing and thermal analysis, come to gas chromatographic separation; and use mass spectrometry detector for testing. Conduct qualitative analysis by comparing with the mass spectrum and retention time of standard substances; and use the internal standard method for quantitative analysis.

a 70 eV electron impact (EI) ion source and has the functions including full-scan/selective ion mode (SIM) scan, auto/manual tuning and spectrum library retrieval.

5.2 Capillary chromatographic column: 60 m × 0.25 mm, 1.4 μm film thickness (stationary liquid of 6% cyanopropylphenyl-94% dimethylpolysiloxane), or other equivalent capillary chromatographic columns.

5.3 Gas cold trap concentrator: having the functions including automatic quantitative sampling and automatic addition of standard gas and internal standard substance. It has at least two stages of cold trap: the first stage of cold trap is capable of cooling to -180°C and the second stage of cold trap is capable of cooling to - 50°C; and if it has the third stage of cold trap (capable of cooling to -180°C) with refrigeration focusing function, it will be more effective. The connecting lines between gas concentrator and gas chromatograph-mass spectrometer are made of inert materials and capable of being heated within the range 50°C ~ 150°C.

5.4 Concentrator automatic sample injector: it is capable of automatic sample injection of sample from sampling canisters.

5.5 Canister washing equipment: it is capable of vacuumizing sampling canisters (< 10 Pa) and has the functions including heating, humidification and pressurized purging.

5.6 Gas dilution equipment: the maximum dilution ratio is up to 1000.

5.7 Sampling canister: stainless steel sampling canister with inner wall deactivated, of volume 3.2 L, 6 L and other specifications. The pressure withstanding value > 241 kPa.

5.8 Liquid nitrogen canister: stainless steel material, volume 100 L ~ 200 L.

5.9 Flow controller: it is used along with sampling canisters and shall be calibrated before use using standard flow metres.

5.10 Calibration flow metre: accurately measuring flow within the range 0.5 mL/min ~ 10.0 mL/min or 10 mL/min ~ 500 mL/min.

5.11 Vacuum manometer: accuracy ≤ 7 kPa (1 psi); pressure range – 101 kPa ~ 202 kPa.

5.12 Filter: pore size ≤ 10 μm.

6 Sample

6.1 Preparation before sampling

Canister washing: use canister washing equipment (5.5) to wash sampling canisters; and the washing can be carried out in accordance with the instructions to canister washing equipment. Sampling canisters can be humidified during the washing process

173	Less than 2% of mass 174		

7.3 Calibration

7.3.1 Preparation of standard working gas

The concentration of standard working gas is 10 nmol/mol: connect standard gas (4.1) steel cylinders and high-purity nitrogen (4.8) steel cylinders to gas dilution equipment (5.6); set dilution ratio; open steel cylinder valves to adjust the flow speed of two gases; wait until the flow speed becomes stable before connecting sampling canisters (5.7) pre-washed and vacuumized to vacuo to gas dilution equipment (5.6); and open the valves of sampling canisters to start preparation. After the canister pressure achieves the preset value (generally 172 kPa), close the valves of sampling canisters and the valves of gas steel cylinders.

7.3.2 Preparation of internal standard working gas

The concentration of internal standard working gas is 100 nmol/mol. Prepare internal standard gas (4.3) in accordance with the procedures of 7.3.1.

7.3.3 Plotting calibration curve

Extract respectively 50.0 mL, 100 mL, 200 mL, 400 mL, 600 mL and 800 mL of standard working gas (4.2); add 50.0 mL of internal standard working gas (4.4) at the same time; prepare the standard series of the target substance concentrations 1.25 nmol/mol, 2.5 nmol/mol, 5.0 nmol/mol, 10.0 nmol/mol, 15.0 nmol/mol and 20.0 nmol/mol (they can be adjusted based on actual sample conditions) and the internal standard substance concentration 12.5 nmol/mol. In accordance with the instrument reference conditions, carry out determination from low concentrations to high concentrations. Calculate the relative response factor (RRF) of target substance in accordance with Equation (2) and calculate average relative response factor ($\overline{RRF}$) of all standard concentration points of target substance in accordance with Equation (3).

$$RRF = \frac{A_x}{A_{is}} \times \frac{\varphi_{is}}{\varphi_x} \qquad (2)$$

where,

RRF – relative response factor of target substance, dimensionless;

A_x – target compound quantitative ion peak area;

A_{is} – internal compound quantitative ion peak area;

φ_{is} – molar fraction of internal standard compound, nmol/mol;

φ_x – molar fraction of target compound, nmol/mol.

The concentration of target substance in transportation blanks and laboratory blanks shall be lower than the lower limit of determination of the method. Or else, find out the reason and take corresponding measures to eliminate interferences or pollutions.

10.1.1 Laboratory blanks

Inject high-purity nitrogen into clean sampling canisters as laboratory blanks; and laboratory blank test shall be carried out before the analysis of each batch of samples.

10.1.2 Transportation blanks

Analyze at least one transportation blank for each batch of samples. First inject high-purity nitrogen (4.8) or high-purity air (4.9) into clean, vacuum sampling canisters; and bring them to the sampling site. Pass through the same treatment process (including site exposure transportation, storage and laboratory analysis) and procedures as those of samples.

10.2 Determination of parallel samples

Analyze at least one parallel sample for each 10 samples or each batch (if less than 10 samples/batch). The relative deviation of target substance in parallel samples shall be less than or equal to 30%; or else, find out the reason and carry out re-analysis.

10.3 Internal standard substance

The deviation of the retention time of internal standard substance in samples from the retention time of internal standard substance in the calibration curve calibrated continuously on the same day or plotted lately, shall not exceed 20 s. The peak area change of quantitative ion shall be within 60% ~ 140%.

10.4 Calibration curve

Calibration curve requires at least 5 concentration points. The relative standard deviation (RSD) of relative response factor of target substance shall be less than or equal to 30%. Or else, find out the reason and plot standard curve once again.

10.5 Continuous calibration

Analyze the intermediate concentration point or the second-highest point of calibration curve every 24 h. The relative deviation of the determination result from the initial concentration value shall be less than or equal to 30%. Or else, find out the reason and plot standard curve once again.

11 Precautions

11.1 The experimental environment shall be kept away from organic solvents; and the background interferences of organic solvents and other volatile organic compounds shall be reduced and eliminated.

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