

HJ

INDUSTRY STANDARD OF THE PEOPLE'S REPUBLIC OF CHINA

HJ 644-2013

**Ambient air - Determination of volatile organic compounds -
Sorbent adsorption and thermal desorption / gas
chromatography mass spectrometry method**

环境空气 挥发性有机物的测定

(English Translation)

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1 Scope of application

This Standard specifies the sorbent adsorption and thermal desorption / gas chromatography mass spectrometry method for the determination of volatile organic compounds (VOCs) in ambient air.

This Standard applies to the determination of 35 volatile organic compounds in ambient air. If verified, this Standard can also be applied to the determination of other non-polar or weakly polar volatile organic compounds.

When the sampling volume is 2 L, the detection limit of the method of this

Standard is 0.3~1.0 µg/m³; the lower limit of determination is 1.2~4.0 µg/m³.

See Appendix A for details.

2 Normative references

The contents of this Standard refer to the following documents or their provisions. For the undated references, the valid edition applies to this Standard.

HJ/T 194 Manual methods for ambient air quality monitoring

3 Method principle

USE a solid sorbent to enrich the volatile organic compounds in the ambient air;

PLACE the adsorption tube in a thermal desorption apparatus; USE gas chromatography to separate; USE mass spectrometry to detect. Compared with the standard mass spectrogram of the target to be determined and the retention time, carry out the qualitative analysis. USE the external standard method or internal standard method for quantitative analysis.

temperature.

Note 2: The gas chromatograph is equipped with a column oven cooling device, which can improve the peak type of the extremely volatile target and increase the sensitivity.

5.2 Mass spectrometer

Electron impact (EI) ionization source. It is capable of scanning from 35 amu to 270 amu in one second; has functions such as NIST mass spectrogram library, manual / automatic tuning, data acquisition, quantitative analysis and spectral library search.

5.3 Capillary column

30 m x 0.25 mm; 1.4 μ m in film thickness (6% nitrile propylbenzene, 94% dimethyl polysiloxane stationary liquid). Other equivalent capillary columns can also be used.

5.4 Thermal desorption device

The thermal desorption device shall have a secondary desorption function. The focusing tube part shall be able to heat up quickly (at least 40 °C/sec). The part connecting the thermal desorption device to the gas chromatograph and the gas pipeline in the instrument shall use silanized stainless steel tubes. They can be heated uniformly at least between 50~150 °C.

Note 3: The use of a thermal desorption device with cold focusing function can reduce the loss of extremely volatile targets and improve sensitivity.

5.5 Aging device

The maximum temperature of the aging device shall be above 400 °C. The maximum carrier gas flow can reach at least 100 ml/min. The flow can be adjusted.

5.6 Sampler

Dual-channel oil-free sampling pump. The dual-channel can independently adjust the flow rate and accurately maintain the flow rate within 10~500 ml/min.

The flow rate error shall be within $\pm 5\%$.

5.7 Calibration flowmeter

It can accurately measure the flow rate within 10~500 ml/min. The flow rate accuracy is 2%. Electronic mass flowmeters should be used.

5.8 Micro syringe

5.0, 25.0, 50.0, 100, 250 and 500 μL .

5.9

Commonly used instruments and equipment in laboratories.

least one on-site blank sample shall be taken for each sample collection.

Note 4: Temperature and wind speed will affect sample collection. When sampling, the ambient temperature shall be less than 40 °C. When the wind speed is greater than 5.6 m/s, during sampling, the adsorption tube shall be placed perpendicular to the wind direction; a bunker shall be placed upwind.

7.1.1 Reference conditions for thermal desorption apparatus

Transmission line temperature. 130 °C; initial temperature of adsorption tube.

35 °C; initial temperature of focusing tube. 35 °C; desorption temperature of adsorption tube. 325 °C; desorption time of adsorption tube. 3 min; desorption temperature of focusing tube. 325 °C; desorption time of focusing tube. 5 min;

primary desorption flow rate. 40 ml/min; focusing tube aging temperature.

350 °C; dry blowing flow rate. 40 ml/min; dry blowing time. 2 min.

7.1.2 Reference conditions for gas chromatograph

Inlet temperature. 200 °C; carrier gas. helium; split ratio. 5.1; column flow (constant flow mode). 1.2 ml/min. Temperature programming. Initial temperature is 30 °C, kept for 3.2 min; the temperature is increased to 200 °C at 11 °C/min for 3 min.

Note 5: In order to eliminate the interference of moisture and the overload of the detector, the split ratio can be set according to the situation. Some thermal desorption apparatus have a sample split function, which can be set according to the manufacturer's recommendations or specific conditions.

7.1.3 Reference conditions for mass spectrometry

Scan mode. full scan; scan range. 35~270 amu; ionization energy. 70 eV;

interface temperature. 280 °C. The remaining parameters are set according to the

instrument manual.

Note 6: In order to improve sensitivity, selective ion scanning can also be used for analysis.

Refer to Appendix B for characteristic ion selection.

7.2 Instrument performance check

USE a micro syringe to pipette 1.0 μL of BFB solution (4.3) and directly inject it into the gas chromatograph for analysis. The abundance of BFB key ions obtained by quadrupole mass spectrometry shall meet the standards specified adsorption tube shall be opposite to the direction the gas enters the adsorption tube during sampling. The target in the sample enters the chromatographic column with the desorption gas for determination. After the analysis is completed, remove the adsorption tube and age and store it according to step 4.7. If the sample concentration is low, the adsorption tube does not need to be aged.

7.4.2 Blank test

Analyze on-site blank sample in the same procedures as the sample determination.

8.1 Qualitative analysis

Qualitative analysis is performed by comparing retention time and mass spectrogram.

8.2 Quantitative analysis

Calculate according to the response value of the first characteristic ion of the target. When the first characteristic ion of the target in the sample has interference, the second characteristic ion can be used for quantification; see

Appendix B for details.

8.2.1.1 External standard method

When using the least square method to draw the calibration curve, the target mass m (ng) in the sample is calculated by the corresponding calibration curve.

8.2.1.2 Internal standard method

When the average relative response factor is used for calibration, the mass m (ng) of the target in the sample is calculated according to formula (5).

Where.

m - The mass of the target in the test portion, ng;

A_x - The response value of the quantitative ion of the target;

6 laboratories respectively measured the ambient air spiked samples with spiked amounts