HJ

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Stationary Source Emission -

Determination of Acrylonitrile - Gas Chromatography

固定污染源排气中丙烯腈的测定 气相色谱法

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1 Scope of Application

1.1 This standard is applicable to the determination of acrylonitrile for both intentional and fugitive emissions from stationary pollution sources.

1.2 When the sampling volume is 30L, the detection limit of the method is 0.2 mg/m^3. The quantitative measurement concentration range of the method is 0.26~33.0mg/m^3.

2 Method Principle

Acrylonitrile (CH_2=$CHCH_2CN$) is adsorbed and enriched by activated charcoal at room temperature; and then desorbed by carbon disulfide at room temperature. The components in the desorbed liquid are separated by the chromatographic column and then enter the hydrogen flame ionization detector (FID). From the measured acrylonitrile chromatogram peak height (or area), quantify the concentration of acrylonitrile in the desorption solution; and finally calculate the concentration of acrylonitrile in the gas sample from the volume, concentration, and sampling volume of the desorption solution.

3 Normative References

The provisions in following documents become the provisions of this Standard through reference in this Standard:

GB 16297-1996 Comprehensive Emission Standard of Air Pollutants

GB 16157-1996 The Determination of Particulates and Sampling Methods of Gaseous Pollutants Emitted from Exhaust Gas of Stationary Source

4 Reagents and Materials

4.1 Acrylonitrile: Chromatographically pure (or analytically pure, but there must be no chromatographic interference peaks for acrylonitrile).

and dilute to the mark with carbon disulfide.

5 Instruments

5.1 Gas chromatograph: Equipped with hydrogen flame ionization detector

5.2 Chromatographic column

5.2.1 Column material: Glass or PTFE.

5.2.2 Column length: 3m.

5.2.3 Column inner diameter: 3mm.

5.2.4 Column type: packed column.

5.2.5 In-column packing: GDX-502, 60~80mesh.

5.2.6 Preparation and aging of chromatographic column (see Appendix B).

5.3 Micro syringe: 1.0μL

5.4 Sampling instrument

Refer to 9.3 in GB 16157-1996 to configure the sampling instrument.

5.4.1 Sampling instrument for intentional emission monitoring

5.4.1.1 Sampling tube

It is made of stainless steel, hard glass or PTFE, with appropriate dimensions, and is equipped with an insulation jacket that can be heated to above 120°C.

5.4.1.2 Sample collecting device

Activated charcoal adsorption tube (4.7).

5.4.1.3 Flowrate measuring device

See 9.3.6 of GB 16157-1996.

5.4.1.4 Suction pump

See 9.3.7 of GB 16157-1996.

5.4.1.5 Connecting pipe

PTFE hose or silicone rubber tube lined with PTFE film.

1-flue; 2-heating sampler; 3-bypass adsorption tube; 4-thermometer; 5-pressure gauge; 6-adsorption tube; 7-three-way valve; 8-dryer; 9-flow meter; 10- suction pump.

Figure 2 – Flue Gas Sampling System

6.1.3 Sample collection

Plug an appropriate amount of glass wool into the port of the sampling tube; then extend it to the sampling point in the exhaust cylinder; start the suction pump; and first make the gas in the exhaust cylinder circulate flow through the bypass adsorption tube to fully wash the sampling pipeline. Then let the exhaust gas pass through the adsorption tube; and record the sampling time, temperature, and flow rate. After sampling, the adsorption tube shall be removed immediately; and its two ends shall be tightly covered by plastic caps; and then take back to the laboratory for analysis.

6.1.4 Heating temperature control of sampling tube

The heating temperature of the sampling tube shall be based on the principle that water vapor and the sample do not condense on the wall of the sampling tube; but the maximum heating temperature shall not exceed 160°C. If the exhaust gas temperature is close to room temperature, the sampling tube is exempted from being heated.

6.1.5 Sampling flowrate

The sampling flowrate shall generally be controlled between 0.3L/min and 1.0L/min. When the temperature is higher than 30°C, the sampling flow rate shall be reduced to no greater than 0.5L/min; so that ensure that the adsorption capacity of the activated charcoal in the Section-B is less than 2% of the total adsorption capacity.

6.1.6 Sampling amount

For each activated charcoal adsorption tube, the sampling amount shall be controlled to the concentration of acrylonitrile in the carbon disulfide desorption solution at 10~400μg/mL. The maximum sampling amount of each activated charcoal adsorption tube shall generally not exceed 1.6mg; and the acrylonitrile adsorbed by the activated charcoal in Section-B shall not exceed 2% of the total adsorbed amount of acrylonitrile.

6.2 Sample collection of fugitive emissions

6.2.1 Sampling location and sampling point

Determine the location of the fugitive emission monitoring point according to the provisions of Appendix C in GB 16297-1996; or determine the location of the sampling point according to other specific requirements.

6.2.2 Connection of sampling device

The solutions of each concentration are injected for three times; take the average value; and draw the calibration curve by the concentration c_i (μg/ml) and the corresponding peak height h_i (or area A_i); and calculate the linear regression equation of the calibration curve.

7.3 Sample determination

7.3.1 Desorption of the sample

Open the caps at both ends of the activated charcoal adsorption tube after collecting the sample; use a hooked iron wire to take out the V-shaped spring hook pressed on the activated charcoal particles in Section-A; and respectively transfer the activated charcoal in Section-A (including the upper end of glass wool) and the activated charcoal in Section-B (including sponge) to two dry test tubes with grinding mouths; and immediately used a pipette to pipette 2.00mL and 1.00mL of carbon disulfide; and respectively put them into the test tubes containing Section-A and Section-B activated charcoal. Quickly close the test tube stopper; and continue to gently shake the test tube; so that the carbon disulfide can be fully contacted and mixed with the activated charcoal. After 30min, perform gas chromatographic determination.

7.3.2 Gas chromatographic determination

Adjust the instrument according to the same gas chromatographic working conditions for drawing the calibration curve; and perform gas chromatographic determinations on the carbon disulfide desorbed liquids that obtain the activated carbon in Section-A and Section-B in 7.3.1. Take the supernatant of the desorbed solution and inject the sample; each injection volume is 1.0μL; repeat the injection for three times; and take the average value of the acrylonitrile chromatographic peak height (or area) for quantification.

8 Calculation and Representation of Result

8.1 Qualitative analysis

Be Qualitative based on the retention time of the chromatographic peak of the acrylonitrile standard sample.

For standard chromatogram, refer to Figure 3.

c_b – concentration of acrylonitrile in the activated charcoal desorption solution in Section-B, in μg/mL;

V_a – volume of carbon disulfide desorption solution of activated charcoal in Section-A, in mL;

V_b – volume of carbon disulfide desorption solution of activated charcoal in Section-B, in mL;

V_{nd} – dry gas sampling volume converted into the standard state, in L (calculate according to 10.1 or 10.2 in GB 16157-1996).

8.3 Calculation of the "emission concentration" of acrylonitrile intentional emission

Calculate the "emission concentration" of acrylonitrile according to 11.1.2 in GB16157-1996.

8.4 Calculation of the "emission rate (kg/h)" of acrylonitrile intentional emission

Calculate the "emission rate" of acrylonitrile according to 11.4 in GB 16157-1996.

8.5 Calculation of "fugitive emission monitoring concentration value" of acrylonitrile

8.5.1 Calculation of the average concentration of acrylonitrile at a monitoring point

Calculate the average concentration of acrylonitrile at a monitoring point for fugitive emission by the following formula.

$$c = \frac{\sum_{i=1}^{n} c_i}{n}$$

Where:

c – average concentration of acrylonitrile at a monitoring point for fugitive emission;

c_i – acrylonitrile concentration of a sample;

n – the number of samples taken at a monitoring point for fugitive emission.

8.5.2 Calculation of "fugitive emission monitoring concentration value"

According to C2.3 in Appendix C of GB 16297-1996, calculate the “fugitive emission monitoring concentration value” of acrylonitrile.

Appendix A

(Standard)

Acrylonitrile-Assisted Qualitative Chromatographic Column Conditions

A1 Stationary phase

β, β-Oxydipropionitrile: 6201 (60~80 mesh glazing) = 20:80

A2 Chromatographic column characteristics

A2.1 Length of column: 2m.

A2.2 Inner diameter of column: 4mm.

A2.3 Materials of column: Stainless steel.

A2.4 Detector: Hydrogen flame ionization (FID).

A3 Chromatographic conditions

A3.1 Column temperature: 80±0.5°C.

A3.2 Nitrogen flowrate: 80mL/min.

A3.3 Hydrogen flowrate: 50mL/min.

A3.4 Air flowrate: 500mL/min.

A4 Standard chromatogram

Appendix B

(Standard)

Preparation and Aging of Chromatographic Column

B1 Treatment of filling

Use appropriate amount of cyclohexane (analytically pure) as extractant; elute GDX-502 in a Soxhlet extractor for several hours; and then dry it at 30~40°C. After the cyclohexane is basically volatilized, place GDX-502 in a vacuum drying oven (or in a nitrogen atmosphere) and dry it under vacuum at 130°C for 2~3h. After the temperature drops to room temperature, take it out and pack the column.

B2 Packing of chromatographic column

One end of the glass column is plugged with glass wool; a buffer bottle and a control piston are connected; and then a vacuum pump is connected. A funnel is connected to the other end of the column. While the vacuum pump is turned on for suction, slowly add the treated dry filler GDX-502 into the funnel and put it into the glass column. Use a piston to control the pumping speed; pump and fill at the same time. And gently vibrate the glass column at the same time (a small electric massager can be used to continuously massage and vibrate the glass column for about 20min) until the filling is tightly and evenly packed in the column. After filling, plug the other end of the column with glass wool.

B3 Aging of chromatographic column

Place the packed chromatographic column to the injection port of the chromatograph, without a detector at the outlet; pass N_2 gas at a flow rate of 30mL/min; gradually increase the column temperature to 150°C; and age for 7~10h until the baseline is stable.

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