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Determination of trace trimethylamine in methanol for industrial use - Gas chromatography-mass spectrometry

工业用甲醇中痕量三甲胺含量的测定 气相色谱质谱联用法

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Warning – This document is not intended to explain all safety issues related to its use; the user is responsible for taking appropriate safety and health measures, which shall also comply with the relevant national regulations.

1 Scope

This document specifies a method for the determination of trace trimethylamine in methanol for industrial use by gas chromatography-mass spectrometry.

This document applies to the determination of trimethylamine in methanol for industrial use, where the lower limit of determination is 14 μg/L.

2 Normative references

The following documents are normatively referenced in this document and are indispensable for its application. For dated references, only the version corresponding to that date is applicable to this document; for undated references, the latest version (including all amendments) is applicable to this document.

GB/T 3723, Sampling of chemical products for industrial use - Safety in sampling

GB/T 6680, General rules for sampling liquid chemical products

GB/T 6682, Water for analytical laboratory use - Specification and test methods

GB/T 8170, Rules of rounding off for numerical values & expression and judgment of limiting values

3 Terms and definitions

No terms and definitions need to be defined in this document.

4 Method summary

By adding hydrochloric acid to the methanol sample, convert trimethylamine, which is volatile at room temperature, into trimethylamine hydrochloride; before sample injection, add sodium hydroxide to convert it into trimethylamine. Adopt headspace injection and use gas chromatography-mass spectrometry for determination. Use the

trimethylamine retention time (RT) and mass-to-charge ratios (m/z), which are 42, 58, and 59, respectively, to double-qualify the qualitative ion; use the quantitative ion working curve method with a mass-to-charge ratio (m/z) of 58 for quantification.

5 Reagents and materials

Unless otherwise stated, use only guaranteed reagents in the analysis.

5.1 Water: in accordance with the stipulation for Grade-II water in GB/T 6682.

5.2 Methanol: chromatographic pure.

5.3 Helium: volume fraction not less than 99.999%, used as carrier gas.

5.4 Nitrogen: volume fraction not less than 99.999%, used as purge gas.

5.5 Trimethylamine standard solution: 0.1 mg/mL, methanol as solvent, certified reference material.

5.6 Sulfuric acid solution: 1.0 mol/L.

5.7 Hydrochloric acid solution: 0.1 mol/L.

5.8 Trimethylamine-free methanol reagent: Take 2 L of methanol (see 5.2); add 15 mL of sulfuric acid solution (see 5.6); distill; discard 100 mL of distillate before and after; take the middle distillate as a trimethylamine-free methanol reagent.

5.9 Trimethylamine-free methanol-hydrochloric acid solution: 0.05 mol/L. Mix the hydrochloric acid solution (see 5.7) with the trimethylamine-free methanol reagent (see 5.8) in a 1+1 volume ratio.

5.10 Saturated sodium hydroxide solution.

5.11 Trimethylamine standard stock solution: 4 000 μg/L. Pipette 4.00 mL of trimethylamine standard solution (see 5.5); use trimethylamine-free methanol-hydrochloric acid solution (see 5.9) to dilute it to 100 mL. It should be stored at 0 °C ~ 4 °C in a sealed place away from light, and the validity period is 1 week.

5.12 Trimethylamine standard working solution: Respectively pipette 0.50 mL, 1.00 mL, 2.00 mL, 3.00 mL, 4.00 mL, 5.00 mL to 100 mL of trimethylamine standard stock solution (see 5.11) to volumetric flasks; use 0.05 mol/L trimethylamine-free methanol-hydrochloric acid solution (see 5.9) to dilute to constant volume, to obtain trimethylamine standard working solutions with concentrations of 20 μg/L, 40 μg/L, 80 μg/L, 120 μg/L, 160 μg/L, and 200 μg/L, respectively.

6 Instruments and equipment

6.1 Gas chromatography-mass spectrometer: a gas chromatography-mass spectrometer (GC-MS) provided with temperature-programmed function, equipped with a split/splitless injection port, an electron bombardment ionization source (EI source), and a quadrupole mass detector; a data processing workstation.

6.2 Sampling device: headspace sampling device.

6.3 Chromatographic column: a quartz capillary column with basic deactivated polyethylene glycol as the matrix, 30 m in length, 0.25 mm in inner diameter, 0.25 μm in film thickness; or other equivalent chromatographic columns.

6.4 Headspace bottle: 20 mL, equipped with polytetrafluoroethylene silicone rubber gasket and sealing cap.

6.5 Sampling bottle: 1 000 mL, ground-glass stoppered flask.

6.6 Volumetric flask: 100 mL, brown glass bottle.

6.7 Pipettes: 0.5 mL, 1 mL, 2 mL, 5 mL.

7 Sample

7.1 Sampling

Sampling shall comply with the provisions of GB/T 6680; sampling safety shall comply with the provisions of GB/T 3723.

7.2 Sample pretreatment

7.2.1 Before sampling, add 1 mL ~ 2 mL of concentrated hydrochloric acid to a clean 1 000 mL sampling bottle (see 6.5).

7.2.2 Before analysis, add 100 mL of hydrochloric acid solution (see 5.7) to 100 mL of sample (see 7.2.1); pipette 5.00 mL into the headspace bottle (see 6.4); add 5 mL of saturated sodium hydroxide solution (see 5.10); gland seal to be tested.

8 Analysis steps

8.1 Drawing of the standard working curve

8.1.1 Set the instrument parameters with reference to Table A.1 - Reference gas chromatography-mass spectrometry working conditions for the determination of trace trimethylamine in methanol for industrial use - in Appendix A.

8.1.2 Pipette 5.0 mL of the series trimethylamine standard working solutions (see 5.12) into the headspace bottle in turn; add 5 mL of saturated sodium hydroxide solution; then, inject them into the gas chromatography-mass spectrometer through the headspace sampling device in turn for measurement. Take the mass concentration of trimethylamine as the abscissa and the peak height or peak area of the quantitative ion with a mass-to-charge ratio (m/z) of 58 as the ordinate, to draw the standard working curve, as shown in Formula (1).

$$A_i = a \times \rho_i + b \qquad \cdots\cdots(1)$$

Where:

A_i – the peak area of trimethylamine in the standard solution i;

a – slope of the linear equation;

ρ_i – trimethylamine content in the standard solution i, in micrograms per liter (μg/L);

b – intercept of the linear equation.

8.2 Sample determination

8.2.1 Qualitative analysis

Under the same gas chromatography-mass spectrometry working conditions as drawing the standard working curve (see 8.1.1), scan the trimethylamine standard solution (see 5.12) and the sample to be tested (see 7.2.2) in the selected ion mode (SIM) respectively. See Appendix B for a reference gas chromatograph mass spectrum.

Use the retention time (RT) of trimethylamine in the sample, the relative abundance of the auxiliary qualifier ions with the mass-to-charge ratios (m/z) of 42, 58, 59 to double-qualify. The deviation BETWEEN the relative abundance of the auxiliary qualifier ions of trimethylamine in the sample AND the relative abundance of the auxiliary qualifier ions of trimethylamine in the standard solution shall be controlled within 20%.

8.2.2 Quantitative analysis

Under the same gas chromatography-mass spectrometry working conditions as drawing the standard working curve (see 8.1.1), inject the sample to be tested (see 7.2.2) into the gas chromatography-mass spectrometer for determination through the headspace sampling device. Measure the samples to be tested twice in parallel.

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