ICS 83.080.01
CCS G31

NATIONAL STANDARD OF THE PEOPLE'S REPUBLIC OF CHINA

GB/T 43085-2023

Plastics - Polymer dispersions - Determination of the content of free formaldehyde

塑料 聚合物分散体 游离甲醛含量的测定

Issued on: September 7, 2023 **Implemented on: April 1, 2024**

Issued by: State Administration for Market Regulation;
Standardization Administration of the PRC

Table of Contents

0.1

g) of sample into a 25 mL volumetric flask. Add approximately 10 mL of standard diluent (5.11) (Method B) or water (Method A) to dilute. Mix thoroughly for at least 30 min. The diluted polymer dispersion shall be a clear, particle-free aqueous solution. Depending on the difficulty of filtering the sample, use one of the three methods in 7.1.2~

7.1.4 to prepare a test solution suitable for analysis.

1 Scope

GB/T 43085-2023 gives the determination of free formaldehyde in polymer dispersions. The dispersions concerned - acrylic, styrene-butadiene, vinyl acetate and nitrile latexes - are the binders of paints, adhesives, coated papers and textile finishes, and formaldehyde reaches them both as a residue of the monomers and from the formaldehyde-releasing

preservatives used to keep a water-based latex from spoiling in the drum. Since the dispersion carries the formaldehyde into the finished article, this is where indoor emission limits are enforced upstream. The standard describes two methods, a spectrophotometric method and a high performance liquid chromatographic method, with the general rules, the reagents, the instruments and equipment, the test steps, the calculation and presentation of results, the precision and the test report, and annexes giving a comparison of structural numbers and the precision data for the second method. It took effect on 1 April 2024.

This document describes a spectrophotometric method (Method A) and a high-performance liquid chromatographic method (Method B) for the determination of free formaldehyde (HCHO) content in polymer dispersions. This document applies to polymer dispersions such as acrylic, acrylonitrile butadiene, carboxylated styrene butadiene and vinyl acetate.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

GB/T 6682, Water for analytical laboratory use -- Specification and test methods (GB/T 6682-2008, ISO 3696:1987, MOD)

ISO 2227, Formaldehyde solutions for industrial use - Determination of formaldehyde content

3 Terms and definitions

There are no terms or definitions to be defined in this document.

4 General rules

This document contains two methods (Method A and Method B). Method A is more suitable for polymer dispersions with free formaldehyde content above 10 mg/kg. Method B shall be used when the free formaldehyde content is less than or equal to 10 mg/kg. Both methods minimize changes in free formaldehyde concentration caused by changes in the physical or chemical properties of the polymer dispersion. NOTE: When measuring free formaldehyde content in polymer dispersions, disruption of the equilibrium between the aqueous and polymer phases can produce or consume formaldehyde. Both methods provide steps for detecting low levels of free formaldehyde in polymer dispersions without disturbing the existing equilibrium. The polymer phase in the polymer dispersion is separated from the aqueous phase by filtration, centrifugation or coagulation to obtain a sample aqueous solution. Add Nash reagent to the sample aqueous solution. Use spectrophotometry directly (Method A). Test the sample absorbance at 410 nm. Calculate the formaldehyde

concentration to be measured through the standard curve. Acetaldehyde and glyoxylic acid may interfere with formaldehyde testing when using Method A. But interference will only occur when the concentration of acetaldehyde and glyoxylic acid exceeds the concentration of formaldehyde by 100 times. NOTE: For dispersions with smaller particle sizes, particles that cannot be completely filtered will interfere with the detection of the spectrophotometer, thus affecting the detection accuracy. If high performance liquid chromatography (Method B) is used, use water as the mobile phase. Formaldehyde and other substances can be separated by a liquid chromatograph equipped with an octadecyldimethylsilane (C18) reversed-phase column. The concentration of free formaldehyde in the aqueous solution was obtained by measuring the peak areas of the standard and sample chromatographic peaks (using external standard calibration method). Because potential interfering substances (such as acetaldehyde, acetone, benzaldehyde, formamide, formic acid, glyoxylic acid and propionaldehyde) can be separated from formaldehyde by chromatography or do not react with post-column reagents, this method is specific for the determination of formaldehyde. The detection system for Method B consists of a post-column reactor that reacts formaldehyde with Nash reagent to form pyridine derivatives and a UV/visible detector that operates at 410 nm. Due to the different compositions of the polymer dispersions, compounds remaining on the column after analysis may interfere with the formaldehyde peak in subsequent samples. It may be necessary to extend the method run time to elute compounds with longer retention times.

5 Reagents

Unless otherwise specified, all reagents used are analytically pure, and the experimental water shall meet the requirements for grade one water specified in GB/T 6682.

5.1 Glacial acetic acid.

5.2 Ammonium acetate.

5.3 Formaldehyde solution. 37% formaldehyde aqueous solution. 5.4 2,4-Pentanedione (acetylacetone).

5.5 Phosphoric acid solution: Dissolve

2.3 mL of 85% phosphoric acid (H3PO4) in water. Use water to dilute to 1 L. Prepare an aqueous solution with a concentration of 33 mmol/L.

5.6 Potassium ferrocyanide trihydrate solution (Carrez solution I): Dissolve 36 g of potassium ferrocyanide trihydrate [K4Fe(CN)6 · 3H2O] in water. Use water to dilute to 1 L. Prepare a solution with a concentration of 36 g/L.

5.7 Zinc sulfate heptahydrate solution (Carrez solution II): Dissolve 72 g of zinc sulfate heptahydrate (ZnSO4 · 7H2O) in water. Use water to dilute to 1 L. Prepare a solution with a concentration of 72 g/L.

5.8 Sodium hydroxide solution: Dissolve 4 g of sodium hydroxide (NaOH) in water. Use water to dilute to 1 L. Prepare an aqueous solution with a concentration of

0.1 mol/L.

5.9 Disodium hydrogen phosphate.

5.10 Nash reagent Transfer

62.5 g of ammonium acetate (5.2) into a 1 L brown reagent bottle (6.1) equipped with stirring. Add 600 mL of water. Stir to dissolve. After the ammonium acetate is dissolved, add

7.5 mL of glacial acetic acid (5.1), 5 mL of 2,4-pentanedione (5.4) and 387.5 mL of water to the bottle. Mix thoroughly (recommended 45 min). NOTE: If necessary, use Nash reagent containing varying concentrations of ammonium acetate, glacial acetic acid, and acetylacetone. Since 2,4-pentanedione is photosensitive, Nash reagent shall be stored protected from light. Fresh Nash reagent needs to be prepared weekly. Degas the Nash reagent with helium before use. When using Method B, transfer the Nash reagent to the post-column reactor (6.6.2). The reactor shall be protected from light.

5.11.1 Preparation of mobile phase Transfer

1.78 g of disodium hydrogen phosphate (5.9) to a 2 L mobile phase reservoir equipped with stirring. Add 2 L of water and mix until disodium hydrogen phosphate is completely dissolved.

6 Instruments and equipment

6.1 Brown bottle The capacity is 1 L and it can filter out ultraviolet and visible light.

6.2 Sample filter It consists of a 5 mL sample syringe and a 0.1 μm filter head, which can remove particulate matter in the sample solution to be tested.

6.3 High speed centrifuge It can operate at speeds of 50000 r/min or higher (see 7.1.3).

6.4 Low speed centrifuge It can run at a speed of 1000 r/min (see 7.1.4).

6.5 Photoelectric colorimeter or spectrophotometer (Method A) It is equipped with 1 cm colorimetric tube or photometer test tube. Detection wavelength is (410±5) nm.

6.6 High performance liquid chromatography system (Method B)

6.6.1 Liquid chromatograph It is equipped with an injection valve, a post-column reactor, a tungsten lamp or deuterium lamp detector capable of providing a wavelength of 410 nm, and an infusion pump capable of providing a flow rate of

0.6 mL/min.