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**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

(ISO 15373:2001, Plastics - Polymer dispersions - Determination of free
formaldehyde, MOD)

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

WARNING -- This document may involve hazardous chemicals, materials and operations. This document does not identify all possible security issues. Users are responsible for taking appropriate safety and health measures and ensuring compliance with relevant national regulations.

1 Scope

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 (H_3PO_4) 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 [$\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$] 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 ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) 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 Mobile phase and standard diluent

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.

6.6.2 Post-column reactor (PCR)

It consists of an infusion pump providing a flow rate of 0.5 mL/min, a sample derivation tube that can be heated to 95°C, and a matching static mixing tee.

6.6.3 Chromatographic column

It is a C₁₈ pH reversed phase column with a particle size of 5 μm . The length is 250 mm. The inner diameter is 4.6 mm. When applicable, other suitable chromatographic columns can also be used (such as a special column for acid analysis, with a length of 100 mm and an inner diameter of 7.8 mm).

6.6.4 Guard column

It is a C₁₈ pH reversed phase guard column with a particle size of 5 μm . The length is 10 mm. The inner diameter is 4.6 mm. When applicable, other guard columns can also

Keys:

- 1 - Mobile phase;
- 2 - Pump;
- 3 - Straight-through one-way valve;
- 4 - Injector;
- 5 - Chromatographic column;
- 6 - Nash reagent;
- 7 - Post-column derivatization pump;
- 8 - Pulse damper;
- 9 - Straight-through one-way valve;
- 10 - Mixing tee;
- 11 - Derivative tube;
- 12 - Oven (temperature 95°C);
- 13 - Water bath (room temperature);
- 14 - UV/visible light detector;
- 15 - Data system;
- 16 - Waste liquid.

Figure 1 -- Schematic diagram of liquid chromatograph and post-column reaction system

7 Test steps

7.1 Preparation of specimens

7.1.1 Dilution of specimens

According to the characteristics and measurement range of the polymer dispersion, weigh 0.1 g~1.0 g (accurate to 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.

7.1.2 Filtration

Dilute the solution prepared in 7.1.1 to the mark with sample diluent (5.12) (Method B) or water (Method A) (with given volume). Use the 0.1 μm filter (6.2) to filter the solution.

If necessary, the filtrate can be further diluted with sample diluent.

7.1.3 Centrifugation

Dilute the solution prepared in 7.1.1 to the mark with sample diluent (5.12) (Method B)

7.4.1.2 Standard curve

Determine the absorbance of the standard solution. Draw a standard curve of formaldehyde mass fraction and absorbance in the standard solution (5.13.2). The standard curve shall appear linear.

7.4.2 Method B

7.4.2.1 Test conditions

Adjust the liquid chromatography according to the manufacturer's instructions and the following parameters:

- Column temperature: room temperature;
- Mobile phase: 6.3 mmol/L Na_2HPO_4 (pH = 7) or water;
- Flow rate: 0.6 mL/min;
- Injection volume: 50 μL ;
- Post-column reaction temperature: 95°C;
- Post-column reaction flow rate: 0.5 mL/min;
- Detector: UV/visible light (410±5) nm.

Equilibrate the instrument until a stable baseline is obtained in the data system.

7.4.2.2 Standard solution testing and standard curve

Before testing, ensure that the entire chromatography system is operating normally and that the formaldehyde concentration in the test solution does not exceed the linear response range of any component of the system (such as the chromatographic column, detector, integrator, and other components).

According to the conditions of 7.4.2.1, inject 50 μL of each standard solution (5.13.2) and blank reagent (standard diluent) (5.11) into the liquid chromatograph for testing.

Measure the formaldehyde peak area. Draw a standard curve with the formaldehyde peak area as the ordinate and the mass fraction of formaldehyde (mg/kg) as the abscissa, as shown in Figure 3. The standard curve shall appear linear.

Calculate the formaldehyde mass fraction in the sample according to formula (1):

$$\omega_{f,o} = (\omega_{f,d} - \omega_0) \times k \quad \dots\dots\dots (1)$$

Where,

$\omega_{f,o}$ - The mass fraction of formaldehyde in the sample, in milligrams per kilogram (mg/kg);

$\omega_{f,d}$ - The mass fraction of formaldehyde in the diluted polymer dispersion, in milligrams per kilogram (mg/kg);

ω_0 - The mass fraction of formaldehyde in the blank solution, in milligrams per kilogram (mg/kg);

k - The dilution coefficient of diluted polymer dispersion.

The arithmetic mean of the two measurements is used as the test result, in mg/kg.

NOTE: The dilution factor depends on the method of preparation of the test solution (7.1.2, 7.1.3 or 7.1.4).

9 Precision

Domestic interlaboratory precision data are not yet available. Annex B provides precision data given in ISO 15373:2001.

10 Test report

The test report shall include at least the following information:

- a) Reference to this document;
- b) All information necessary to characterize the performance of the test material;
- c) Details of the specimen;
- d) Test temperature and other test condition information;
- e) Free formaldehyde content (rounded to one decimal place);
- f) Any abnormal phenomena observed during the test;
- g) Any details that deviate from the standard methods specified in this document, and indicate the reasons;

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