INTERNATIONAL STANDARD

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Plastics — Phenolic resins — Determination of hexamethylenetetramine content — Kjeldahl method, perchloric acid method and hydrochloric acid method

Plastiques — Résines phénoliques — Détermination de la teneur en hexaméthylènetétramine — Méthode Kjeldahl, méthode à l'acide perchlorique et méthode à l'acide chlorhydrique

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ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 8988 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 12, *Thermosetting materials*.

This third edition cancels and replaces the second edition (ISO 8988:1995), which has been technically revised to include a hydrochloric acid method.

Plastics — Phenolic resins — Determination of hexamethylenetetramine content — Kjeldahl method, perchloric acid method and hydrochloric acid method

SAFETY STATEMENT — Persons using this document should be familiar with normal laboratory practice, if applicable. This document does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any regulatory requirements.

1 Scope

This International Standard specifies three methods for the determination of the hexamethylenetetramine ("hexa") content of phenolic resins. The three methods are equivalent. The Kjeldahl method described in Clause 3 is not applicable if there are other components containing nitrogen in the phenolic resin. The perchloric acid method and the hydrochloric acid method described in Clause 4 and Clause 5, respectively, are only applicable if there are no other basic or acidic additives in the resin. If the resin contains additives which can be oxidized by perchloric acid, only the hydrochloric acid method (Clause 5) is applicable.

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.

ISO 385, *Laboratory glassware — Burettes*

3 Kjeldahl method

WARNING — For safety reasons, the Kjeldahl determination must be carried out in a well ventilated fume cupboard.

3.1 General

This clause specifies a method for the determination of total nitrogen, expressed as hexamethylenetetramine, in phenolic resins. The method is applicable to hexamethylenetetramine contents of $\geqslant$ 0,5 % (by mass).

3.2 Principle

The hexamethylenetetramine in a test portion is converted to ammonium bisulfate by decomposition in hot concentrated sulfuric acid in the presence of a catalyst.

The ammonium bisulfate is converted to sodium sulfate and ammonia by reaction with sodium hydroxide.

The ammonia is distilled off and collected in hydrochloric acid.

The excess hydrochloric acid is titrated with a standard volumetric solution of sodium hydroxide using a colorimetric indicator.

3.3 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade, free of nitrogen, and only distilled water or water of equivalent purity.

3.3.1 Sulfuric acid, concentrated.

3.3.2 Kjeldahl catalytic mixture, consisting of 97 g of sodium sulfate decahydrate ($Na_2SO_4 \cdot 10H_2O$), 1,5 g of copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) and 1,5 g of selenium (Se).

3.3.3 Sodium hydroxide, 30 % (by mass) solution.

3.3.4 Hydrochloric acid, c(HCl) = 0,10 mol/l.

3.3.5 Sodium hydroxide, standard volumetric solution, c(NaOH) = 0,10 mol/l.

3.3.6 Mixed indicator, solution.

Dissolve 60 mg of methyl red and 40 mg of methylene blue in 100 ml of ethanol.

3.4 Apparatus

Ordinary laboratory apparatus, plus the following:

3.4.1 Kjeldahl flask, capacity 250 ml or 300 ml, for the digestion.

3.4.2 Distillation apparatus (various models are available commercially).

3.4.3 Burette, capacity 50 ml, graduated in 0,1 ml steps, conforming to ISO 385.

3.4.4 Analytical balance, accurate to 1 mg.

3.4.5 Silicon carbide crystals, for use as boiling chips.

3.5 Procedure

3.5.1 Digestion

Weigh 1 g to 2 g of phenolic resin to the nearest 1 mg into a Kjeldahl flask (3.4.1). Add 5 g of the catalytic mixture (3.3.2) and 25 ml of concentrated sulfuric acid (3.3.1). Heat carefully until the colour of the mixture changes from black or amber to clear. When the mixture is clear, increase the rate of heating and heat for 5 min beyond the time of the colour change; the mixture may possibly boil. Allow the digested liquid to cool almost to room temperature, just short of solidification. Add carefully 100 ml of water and transfer the solution quantitatively into the flask of the distillation apparatus, rinsing with water. Add a few silicon carbide crystals (3.4.5) to prevent bumping and two drops of mixed indicator solution (3.3.6). Add 30 % (by mass) NaOH solution (3.3.3) to this solution until it is basic. Then distill over the ammonia given off, together with water vapour, into a receiver containing 50 ml of hydrochloric acid (3.3.4). Continue the distillation until about 300 ml of water has been collected.

3.5.2 Titration

When the distillation is completed, add a few drops of mixed indicator solution (3.3.6) to the contents of the receiver and titrate the excess hydrochloric acid with sodium hydroxide solution (3.3.5), using the burette (3.4.3).

3.6 Expression of results

The hexamethylenetetramine content, expressed as a percentage by mass, is given by the formula:

$$\frac{0{,}35\,(V_0 - V_1)}{m_0}$$

where

V_0 is the volume, in millilitres, of hydrochloric acid (3.3.4) in the receiver of the distillation apparatus;

V_1 is the volume, in millilitres, of sodium hydroxide solution (3.3.5) used in the back-titration;

m_0 is the mass, in grams, of the test portion.

3.7 Reproducibility

The results are reproducible to within 0,30 % (by mass) hexamethylenetetramine.

3.8 Number of determinations

Carry out the determination in duplicate. If the results differ by more than 5 %, repeat the determination, again in duplicate. If not, calculate the arithmetic mean of the two individual results.

4 Perchloric acid method

4.1 General

This clause specifies a method for the determination of hexamethylenetetramine in phenolic resins by direct titration. The results of the determination may be affected by the presence of acidic or basic additives. In such cases, the use of the Kjeldahl method is recommended. If additives oxidizable by perchloric acid are present, use the hydrochloric acid method.

The method is applicable to hexamethylenetetramine contents of $\geqslant$ 0,3 %.

4.2 Principle

One of the tertiary amine groups of the hexamethylenetetramine in a test portion is determined by titration with perchloric acid.

4.3 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade, free of nitrogen, and only distilled water or water of equivalent purity.

4.3.1 Hexamethylenetetramine, dry.

4.3.2 Acetone, analytical grade.

4.3.3 Perchloric acid, 70 % (by volume) solution.

WARNING — Perchloric acid is dangerous in the presence of organic matter since an explosion can occur if the perchloric acid is in excess.

4.4 Apparatus

Ordinary laboratory apparatus, plus the following:

4.4.1 Magnetic stirrer.

4.4.2 Automatic burette, nominal volume at least 15 ml, graduated in 0,1 ml steps, with a stopcock made of polytetrafluoroethylene.

4.4.3 Beakers, capacity 100 ml.

4.4.4 Graduated cylinder, capacity 1 000 ml.

4.4.5 Analytical balance, accurate to 0,1 mg.

4.4.6 pH-meter.

4.5 Procedure

4.5.1 Preparation and titration of a solution of perchloric acid in acetone

Into a 1 000 ml graduated cylinder (4.4.4), introduce 1 000 ml of acetone (4.3.2) then 8 ml of perchloric acid solution (4.3.3). Mix well.

Standardize the resulting solution with hexamethylenetetramine (4.3.1) as described below.

Weigh 150 mg to 170 mg of hexamethylenetetramine (4.3.1) to the nearest 0,1 mg into a 100 ml beaker (4.4.3).

Add 30 ml to 40 ml of acetone (4.3.2), and titrate as described in 4.5.2.

NOTE 1 Darkening of the solution will not affect the titration results.

The titre T, expressed in milligrams of hexamethylenetetramine per millilitre of solution, is given by the formula:

$$\frac{m_1}{V_2}$$

where

m_1 is the mass, in milligrams, of hexamethylenetetramine;

V_2 is the volume, in millilitres, of perchloric acid solution needed to reduce the apparent pH to just below zero.

4.5.2 Titration

Into a 100 ml beaker, weigh (to the nearest 1 mg) a quantity of phenolic resin equal to 100 times the titre determined as in 4.5.1, add 30 ml to 40 ml of acetone (4.3.2) and insert a magnetic stirrer bar. Place the beaker on the magnetic stirrer (4.4.1). Insert the glass electrode of the pH-meter (4.4.6) and switch on the stirrer and the pH-meter. When the resin has dissolved, add the perchloric acid solution prepared as in 4.5.1 dropwise until the pH-value drops suddenly below zero. As the resin dissolves in acetone more rapidly than hexamethylenetetramine, the pH-value may increase to above zero because residual hexamethylenetetramine may still be in the process of dissolving. Continue the titration until the pH-value remains constant, slightly below zero.

4.6 Expression of results

The hexamethylenetetramine content, expressed as a percentage by mass, is given by the formula:

$$\frac{V_2 \times T \times 100}{m_0}$$

where

V_2 is the volume, in millilitres, of perchloric acid solution used for the titration;

T is the titre, expressed in milligrams of hexamethylenetetramine per millilitre, of the perchloric acid solution, as determined in 4.5.1;

m_0 is the mass, in milligrams, of the test portion.

4.7 Number of determinations

Carry out the determination in duplicate. If the results differ by more than 5 %, repeat the determination, again in duplicate. If not, calculate the arithmetic mean of the two individual results.

5 Hydrochloric acid method

5.1 General

This clause specifies a method for the determination of hexamethylenetetramine in phenolic resins by direct titration with hydrochloric acid. The results of the determination may be affected by the presence of acidic or basic additives. In such cases, use of the Kjeldahl method is recommended.

The method is applicable to hexamethylenetetramine contents of $\geqslant$ 0,3 %.

5.2 Principle

Depending on the solubility of the resin system, there are two possible procedures:

Procedure A: The resin is dissolved in a mixture of butanol and ethylene glycol and the hexamethylenetetramine content is determined by potentiometric titration with hydrochloric acid, c(HCl) = 0,10 mol/l. If the resin contains modifiers which are not soluble in the solvent mixture, a cosolvent such as acetone may be added.

Procedure B: The resin is dissolved in a mixture of acetone and water and the hexamethylenetetramine content is determined with hydrochloric acid, c(HCl) = 0,2 mol/l.

5.3 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

5.3.1 Butanol-ethylene glycol solvent mixture, 7:3 (by volume) (procedure A), or **acetone-water**, 9:1 (by volume) (procedure B).

5.3.2 Hydrochloric acid, c(HCl) = 0,10 mol/l, prepared using butanol-ethylene glycol solvent mixture (see 5.3.1) (procedure A), or **hydrochloric acid**, c(HCl) = 0,20 mol/l, prepared using acetone-water solvent mixture (see 5.3.1) (procedure B).