INTERNATIONAL STANDARD

ISO 11402

Second edition
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Phenolic, amino and condensation resins — Determination of free-formaldehyde content

Résines phénoliques, aminiques et de condensation — Dosage du formaldéhyde libre

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Contents

Page

iTeh STANDARD PREVIEW
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ISO 11402:2004
https://standards.iteh.ai/catalog/standards/sist/1e528953-4ccd-416c-b380-02818ce688da/iso-11402-2004

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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 11402 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 12, *Thermosetting materials*.

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This second edition cancels and replaces the first edition (ISO 11402:1993), as well as ISO 9020:1994 and ISO 9397:1995. The three standards have been combined into one, the sulfite procedure being taken from ISO 9020 and the hydroxylamine hydrochloride procedure from ISO 9397.

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Phenolic, amino and condensation resins — Determination of free-formaldehyde content

1 Scope

This International Standard specifies three methods for determining the free-formaldehyde content in the following:

a) **Phenolic resins,** by potentiometric titration in aqueous or organic solution (hydroxylamine hydrochloride procedure). The method is applicable to resins with free-formaldehyde contents up to and including 15 % by mass. For free-formaldehyde contents between 15 % by mass and 30 % by mass, it may be necessary to adjust the concentrations of the standard volumetric solutions used accordingly.

b) **Amino resins and furan resins** (sulfite procedure). The method is applicable to resins resulting from the polycondensation of urea and melamine with formaldehyde and to furan resins resulting from the polycondensation of furfuryl alcohol with formaldehyde without further modification.

c) **Condensation resins** (KCN procedure), including urea resins, furan resins, melamine resins and phenolic resins, as well as combinations and modifications of these resins.

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The purpose of this International Standard is to establish recognized and useful determination procedures (for instance in order to check whether official regulations on the handling of hazardous workplace materials are observed). As far as possible, all formaldehyde-containing resins are to be included in this connection.

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The free-formaldehyde content determined in formaldehyde condensation resins using this International Standard represents the actual content at the time of the determination. The value bears no quantitative relationship to the free-formaldehyde content during or after processing.

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 385-1, *Laboratory glassware — Burettes — Part 1: General requirements*

ISO 648, *Laboratory glassware — One-mark pipettes*

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 15528, *Paints, varnishes and raw materials for paints and varnishes — Sampling*

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3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
free formaldehyde
formaldehyde that is present in unbound form as formaldehyde, formaldehyde dihydrate (dihydroxymethylene) or polyoxymethylene in a condensation resin

4 Test procedures

4.1 General

The choice of test procedure for the determination of free formaldehyde in condensation resins is made in accordance with Table 1.

Table 1 — Selection of procedure

Procedure	Suitable for testing of
Hydroxylamine hydrochloride procedure	Phenolic resins, furan resins[a] (unmodified with urea or melamine resin)
Sulfite procedure	Urea resins, melamine resins, furan resins[a], urea-melamine resins, furan-urea resins
KCN procedure[b]	Melamine-phenolic resins, urea-phenolic resins, urea-melamine-phenolic resins
[a] See Annex A, Clause A.2.	
[b] See Annex A, Clause A.3.	

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4.2 Hydroxylamine hydrochloride procedure

4.2.1 Principle

The formaldehyde is converted to the oxime with hydroxylamine hydrochloride. The hydrochloric acid formed during this reaction is determined by potentiometric back-titration, using sodium hydroxide solution.

Oximation reaction: $CH_2O + NH_2OH \cdot HCl \rightarrow CH_2NOH + HCl + H_2O$

4.2.2 Reagents

During the analysis, use only reagents of recognized analytical grade and only water of at least grade 3 purity as defined in ISO 3696.

4.2.2.1 **Hydroxylamine hydrochloride**, 10 % by mass solution, the pH of which has been adjusted to 3,5 by the addition of sodium hydroxide solution.

4.2.2.2 **Sodium hydroxide**, standard volumetric solutions, c(NaOH) = 1 mol/l and c(NaOH) = 0,1 mol/l.

4.2.2.3 **Hydrochloric acid**, standard volumetric solutions, c(HCl) = 1 mol/l and c(HCl) = 0,1 mol/l.

4.2.2.4 **Methanol**, free of aldehydes and ketones.

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4.2.2.5 **Propan-2-ol**, free of aldehydes and ketones.

4.2.3 Apparatus

Ordinary laboratory apparatus and glassware, together with the following:

4.2.3.1 **Balance**, accurate to 0,1 mg.

4.2.3.2 **pH-meter**, sensitive to 0,1 pH-units, equipped with a glass indicating electrode and a standard calomel reference electrode.

4.2.3.3 **Magnetic stirrer**.

4.2.3.4 **Graduated burettes**, of capacity 10 ml and 25 ml, the latter being for use if the formaldehyde content is likely to be greater than 5 % by mass.

4.2.4 Sampling

Take a representative sample of the product to be tested, as described in ISO 15528.

4.2.5 Procedure

4.2.5.1 Test temperature

Carry out the test at (23 ± 1) °C.

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4.2.5.2 Test portion

Weigh, to the nearest 0,1 mg, into a 250 ml beaker, a test portion of mass from 1 g to 5 g, depending on the assumed formaldehyde content (see Table 2).

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Table 2 — Mass of test portion

Assumed formaldehyde content % by mass	Mass of test portion g
< 2	5,0 ± 0,2
2 to 4	3,0 ± 0,2
> 4	1 to 2

4.2.5.3 Determination

Add 50 ml of methanol (4.2.2.4), or 50 ml of a mixture of 3 volumes of propan-2-ol (4.2.2.5) and 1 volume of water, to the contents of the beaker, switch on the magnetic stirrer (4.2.3.3) and stir until the resin has dissolved and the temperature has stabilized at (23 ± 1) °C.

Introduce the electrodes of the pH-meter (4.2.3.2) into the solution and, using the 0,1 mol/l solution of hydrochloric acid (for neutralized resins) or the 1 mol/l solution (for highly alkaline resins) (see 4.2.2.3), adjust the pH to 3,5.

Pipette into the solution approximately 25 ml of hydroxylamine hydrochloride solution (4.2.2.1) at (23 ± 1) °C.

Stir for (10 ± 1) min.

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Titrate rapidly, using the 1 mol/l solution of sodium hydroxide (or the 0,1 mol/l solution for low formaldehyde contents) (see 4.2.2.2) contained in a suitable-capacity burette (4.2.3.4), until the pH is 3,5.

4.2.5.4 Blank test

Conduct a blank test in parallel with the determination, by the same procedure, using the same reagents as in the determination, but omitting the test portion.

4.2.6 Expression of results

Calculate the free-formaldehyde content $w(CH_2O, \text{free})$, expressed as a percentage by mass, using the equation:

$$w(CH_2O, \text{free}) = \frac{3c(V_1 - V_0)}{m}$$

where

c is the actual concentration, in moles per litre, of the solution of sodium hydroxide (4.2.2.2) utilized;

V_0 is the volume, in millilitres, of the solution of sodium hydroxide (4.2.2.2) utilized for the blank test (see 4.2.5.4);

V_1 is the volume, in millilitres, of the solution of sodium hydroxide (4.2.2.2) utilized for the determination (see 4.2.5.3);

m is the mass, in grams, of the test portion (see 4.2.5.2).

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4.2.7 Precision

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https://standards.iteh.ai/catalog/standards/sist/1e528953-4ccd-416c-b380-02818ce688da/iso-11402-2004

Repeatability: 0,2 % by mass formaldehyde;

Reproducibility: 0,4 % by mass formaldehyde.

4.3 Sulfite procedure

4.3.1 Principle

The method is based on the following reactions:

a) $CH_2O + Na_2SO_3 \text{ (excess)} + H_2O \xrightarrow[15\ \text{min}]{\text{pH} = 9,2 \text{ to } 9,4} HOCH_2{-}SO_3Na + NaOH$

b) $ROCH_2OH + Na_2SO_3 \text{ (excess)} + H_2O \xrightarrow[15\ \text{min}]{\text{pH} = 9,2 \text{ to } 9,4} HOCH_2{-}SO_3Na + ROH + NaOH$

c) $>N{-}CH_2OH + Na_2SO_3 \xrightarrow{0\ ^\circ C}$ no reaction under the test conditions

d) $\text{Excess } Na_2SO_3 + I_2 + H_2O \xrightarrow{\text{pH} \approx 4,5} Na_2SO_4 + 2HI$

e) $HOCH_2{-}SO_3Na + I_2 \xrightarrow{\text{pH} \approx 4,5}$ no reaction under the test conditions

f) $HOCH_2{-}SO_3Na + Na_2CO_3 \xrightarrow{\text{pH} = 9 \text{ to } 10} CH_2O + Na_2SO_3 + NaHCO_3$

g) $Na_2SO_3 + I_2 + H_2O \longrightarrow Na_2SO_4 + 2HI$

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Free formaldehyde and alcohol formaldehyde semiacetals in a test portion are reacted with excess sodium sulfite solution at a temperature of 0 °C to form hydroxymethane sulfonate. The excess sodium sulfite is titrated with iodine solution. The hydroxymethane sulfonate is decomposed with sodium carbonate solution and the sodium sulfite liberated is titrated with iodine solution.

4.3.2 Reagents

During the analysis, use only reagents of recognized analytical grade and only water of at least grade 3 purity as defined in ISO 3696.

4.3.2.1 **Sodium sulfite solution**, $c(Na_2SO_3)$ = 1 mol/l.

4.3.2.2 **Acetic acid**, $c(CH_3COOH)$ = 1 mol/l.

4.3.2.3 **Sodium carbonate solution**, $c(Na_2CO_3) \approx 100$ g/l.

4.3.2.4 **Buffer solution**.

Dissolve 12,37 g of boric acid in water in a 1 000 ml volumetric flask, add 100 ml of 1 mol/l sodium hydroxide solution, dilute to the mark with water and mix well.

Before use, cool the solution to 0 °C.

4.3.2.5 **Iodine**, standard volumetric solution, $c(I_2)$ = 0,05 mol/l, i.e. 12,690 g/l. If necessary, standardize the solution against sodium thiosulfate standard reference solution, $c(Na_2S_2O_3)$ = 0,1 mol/l.

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4.3.2.6 **Dichloromethane**, neutral (pH = 7).

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Before use, cool the dichloromethane to 0 °C.

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4.3.2.7 **Starch**, dissolved in hot water to give a 10 g/l solution, or **powdered starch,** soluble in cold water (so-called Zulkovsky starch is suitable).

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4.3.2.8 **Water containing ice**, prepared from water of at least grade 3 purity as defined in ISO 3696.

4.3.2.9 **Ice**, finely divided, prepared from water of at least grade 3 purity as defined in ISO 3696.

4.3.3 Apparatus

Ordinary laboratory apparatus and glassware complying with the requirements of ISO 385-1 (burettes) or ISO 648 (pipettes), together with the following:

4.3.3.1 **High-speed mixer**.

4.3.3.2 **Magnetic stirrer**.

4.3.3.3 **Ice bath**.

4.3.3.4 **Burettes** or, preferably, **microburettes**, of suitable capacity.

4.3.3.5 **Pipettes**, of capacity 10 ml and 25 ml.

4.3.4 Procedure

4.3.4.1 General

Carry out the determination in duplicate.

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