INTERNATIONAL STANDARD

ISO 11402

First edition
1993-11-15

Plastics — Condensation resins — Determination of free formaldehyde

Plastiques — Résines de condensation — Détermination du formaldéhyde libre

Reference number
ISO 11402:1993(E)

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.

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.

International Standard ISO 11402 was prepared by Technical Committee ISO/TC 61, *Plastics*, Sub-Committee SC 12, *Thermosetting materials*.

Annexes A and B of this International Standard are for information only.

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Printed in Switzerland

Plastics — Condensation resins — Determination of free formaldehyde

1 Scope

This International Standard specifies test methods for the determination of free formaldehyde in condensation resins, including urea resins, furan resins, melamine resins and phenolic resins, as well as combinations and modifications of these resins.

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. The free formaldehyde determined in formaldehyde condensation resins according to this International Standard establishes the actual condition at the time of the test. The value has no quantitative relationship to free formaldehyde that may arise during or after processing.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods.*

ISO 9020:—[1], *Binders for paints and varnishes — Determination of free-formaldehyde content of amino resins — Sodium sulfite titrimetric method.*

ISO 9397:1989, *Plastics — Phenolic resins — Determination of free formaldehyde content.*

3 Definition

For the purposes of this International Standard, the following definition applies.

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

1) To be published.

4 Test procedures

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
Hydroxylammonium chloride procedure	Phenolic resins, furan resins[1] (unmodified with urea or melamine resin)
Sulfite procedure	Urea resins, melamine resins, furan resins[1], urea-melamine resins, furan-urea resins
KCN procedure[2]	Melamine-phenolic resins, urea-phenolic resins, urea-melamine-phenolic resins
1) See annex A, A.2. 2) See annex A, A.3.	

4.1 Hydroxylammonium chloride procedure

The determination is carried out in accordance with ISO 9397.

4.2 Sulfite procedure

The determination is carried out in accordance with ISO 9020.

4.3 KCN procedure

WARNING — Potassium cyanide is a very toxic material. It must be handled very carefully. In contact with acids, the toxic gas HCN is evolved. Work in a hood. Avoid contact with skin, eyes and clothing.

4.3.1 Principle

A test portion of the resin to be tested is dissolved or dispersed in water (if appropriate with the aid of *N,N'*-dimethylformamide), and the free formaldehyde quantitatively converted to cyanohydrin with excess potassium cyanide. The excess of potassium cyanide is subsequently back-titrated with mercury(II) nitrate solution using diphenylcarbazone as an indicator.

4.3.2 Reactions

The analytical procedure is based on the following reactions:

a) $CH_2O + KCN\ (\text{excess}) \rightarrow NC{-}CH_2{-}OK$

b) $2KCN + Hg(NO_3)_2 \xrightarrow{\text{pH 7}} 2KNO_3 + Hg(CN)_2$

4.3.3 Reagents

During the analysis, use only reagents of recognized analytical grade and only distilled or de-ionized water of at least grade 3 as defined in ISO 3696.

4.3.3.1 ***N,N'*-dimethylformamide**.

4.3.3.2 Nitric acid, $c(HNO_3)$ = 2 mol/l.

4.3.3.3 Potassium cyanide solution, $c(KCN)$ = 0,1 mol/l.

The concentration of the potassium cyanide solution shall be checked weekly against a standard reference solution of mercury(II) nitrate (4.3.3.6).

4.3.3.4 Phosphate buffer solution.

Dissolve 348 g of K_2HPO_4 and 136 g of KH_2PO_4 in water and make up to 1 000 ml.

4.3.3.5 Borate buffer solution.

Dissolve 76,4 g of $K_2B_4O_7.4H_2O$ in water and make up to 1 000 ml.

4.3.3.6 Mercury(II) nitrate solution, $c[Hg(NO_3)_2]$ = 0,05 mol/l.

A dilute solution of formaldehyde of known concentration (e.g. 3,6 g/l) is used to determine the formaldehyde equivalent of the mercury(II) nitrate solution. Use 10 ml of this solution (corresponding to 36 mg of formaldehyde) for the determination. See annex A for information on disposal of the analytical residues.

4.3.3.7 Indicator solution: 1 % diphenylcarbazone in methanol.

4.3.4 Apparatus

Customary laboratory materials, plus the following:

4.3.4.1 Analytical balance, accurate to 0,1 mg.

4.3.4.2 Burettes, capacity 25 ml.

4.3.4.3 Graduated pipette, capacity 5 ml.

4.3.4.4 Transfer pipettes, capacity 10 ml and 20 ml.

CAUTION — Pipetting by mouth is prohibited.

4.3.4.5 Erlenmeyer flask, capacity 500 ml, with ground-glass neck and stopper.

4.3.4.6 Stopwatch.

4.3.5 Procedure

4.3.5.1 Determination

Weigh into the 500 ml Erlenmeyer flask (4.3.4.5), to the nearest 0,1 mg, a test portion of not more than 1 g containing 10 mg to 40 mg of free formaldehyde. Dissolve or disperse the test portion in 150 ml of water; dissolve test portions having poor miscibility with water in 10 ml of *N,N*-dimethylformamide (4.3.3.1) prior to addition of the water. Add 40 ml of borate buffer solution (4.3.3.5) with a graduated cylinder, and immediately thereafter 20 ml of the potassium cyanide solution (4.3.3.3) with a transfer pipette (4.3.4.4); then swirl the flask briefly. Close the flask and allow the mixture to react at room temperature for 2 min. Then add 5 ml of phosphate buffer solution (4.3.3.4) with the graduated pipette (4.3.4.3) and 8 drops of diphenylcarbazone solution (4.3.3.7). Adjust the pH to 7 by adding nitric acid (4.3.3.2) from a burette until the mixture becomes almost colourless, then immediately titrate the solution with mercury(II) nitrate solution (4.3.3.6) to a light violet coloration.

4.3.5.2 Blank test

Check the blank value of the potassium cyanide solution once a week using the same procedure and the same quantities of all reagents, but omitting the test portion.

4.3.5.3 Control

In the case of resins containing a complexing agent for mercury(II) ions (Hg^{2+}), determine also a control value by titration with mercury(II) nitrate solution (4.3.3.6) following the procedure described in 4.3.5.1 but without addition of potassium cyanide solution (4.3.3.3).

4.3.6 Expression of results

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

$$w(CH_2O,\ \text{free}) = \frac{(V_0 - V_1 + V_2)\cdot\rho(CH_2O)}{10m_0}$$

where

V_0 is the volume, in millilitres, of mercury(II) nitrate solution (4.3.3.6) required for titration of 20 ml of potassium cyanide solution (4.3.3.3) in the blank test (4.3.5.2);

V_1 is the volume, in millilitres, of mercury(II) nitrate solution (4.3.3.6) required for titration of the test portion;

V_2 is the volume, in millilitres, of mercury(II) nitrate solution (4.3.3.6) required for titration of the test portion in the control test (4.3.5.3), if one is carried out;

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

$\rho(CH_2O)$ is the formaldehyde equivalent, in milligrams per millilitre of the mercury(II) nitrate solution, calculated from the equation

$$\rho(CH_2O) = \frac{m_1}{V_0 - V_3}$$

m_1 being the mass, in milligrams, of formaldehyde used for the determination of the formaldehyde equivalent,

V_3 being the volume, in millilitres of mercury(II) nitrate solution required.

4.3.7 Precision

The precision of this procedure was determined in a round-robin test in which nine laboratories took part.

4.3.7.1 Repeatability (r)

At a free-formaldehyde content < 2 % (*m/m*), r = 0,08 % (*m/m*) absolute.

At a free-formaldehyde content ⩾ 2 % (*m/m*), r = 4 % (relative).

4.3.7.2 Reproducibility (R)

At a mass fraction of < 2 % of free formaldehyde, R = 0,16 % (absolute).

At a mass fraction of ⩾ 2 % of free formaldehyde, R = 8 % (relative).

5 Test report

The test report shall include the following information:

a) a reference to this International Standard;

b) the type, designation and date of manufacture of the condensation resin tested;

c) the sampling date;

d) the procedure used;

e) the free-formaldehyde content, $w(CH_2O, \text{free})$, (individual and average values);

f) the date of the test.

Annex A
(informative)

Suitability of the procedures for different types of resin

A.1 Carbonyl compounds

If a condensation resin contains aldehydes and/or ketones, adducts thereof (hemiacetals, hydrates) or dimers or oligomers thereof, these compounds may be partially or wholly determined in addition to formaldehyde.

A.2 Furan resins

Furan resins are condensation products of furfuryl alcohol and formaldehyde. They can be modified by chemical transformation or by physical distribution of the modification agent. They can contain up to 90 % of free furfuryl alcohol. If urea and melamine resins are used for modification, only the sulfite procedure is suitable (see also A.3). The hydroxylammonium chloride procedure can be used for phenolic-resin-modified furan resins.

A.3 KCN procedure

At present, this is the only procedure suitable for mixed resins containing both phenol and urea or melamine. Urea resins hydrolyse partially when the hydroxylamine hydrochloride procedure is used; phenolic resins give secondary reactions when the sulfite procedure is used. Straight-chain phenolic resins, furan resins and completely etherified urea and melamine resins may be analysed using this procedure, but because of the toxicity of KCN, the procedure should be limited to these resin types (UF/PF, MF/PF, UF/MF/PF) and only used when it is really necessary to obtain results with a high repeatability or reproducibility.

Annex B
(informative)

Removal of Hg^{2+} and CN^- from mercury and cyanide residues

B.1 Reaction

$Hg(CN)_2 + S_3^{2-} \rightarrow HgS + 2CNS^-$

B.2 Preparation of detoxification solution

Dissolve 30 g of $Na_2S.9H_2O$ in about 100 ml of water. Add 8 g of finely powdered sulfur, and bring the suspension to the boil in a covered vessel. The sulfur will dissolve after 30 min to 60 min. Cool, and dilute the solution to about 1 litre. The solution contains approximately 0,125 mol/l of Na_2S_3.

B.3 Treatment of titration solutions

Add approximately 10 ml of the detoxification solution to each titration solution — including those from the blank (4.3.5.2) and control (4.3.5.3) determinations — in a sealable collection vessel. The following day, the solution should be clear and it should not be possible to detect either Hg^{2+} or CN^- in the solution. Filter the solution or decant off the supernatant liquid, and discard into the sewage system.

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