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Binders for paints and varnishes — Determination of free-formaldehyde content of amino resins — Sodium sulfite titrimetric method

Liants pour peintures et vernis — Dosage du formaldéhyde libre dans les résines aminoplastes — Méthode titrimétrique au sulfite de sodium

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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.

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 9020 was prepared by Technical Committee ISO/TC 35, *Paints and varnishes*, Subcommittee SC 10, *Test methods for binders for paints and varnishes.*

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Binders for paints and varnishes — Determination of free-formaldehyde content of amino resins — Sodium sulfite titrimetric method

1 Scope

This International Standard specifies a titrimetric method for determining the free-formaldehyde content of amino resins. It 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.

The method is not applicable to furan resins modified with phenolic resins.

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 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements.*

ISO 648:1977, *Laboratory glassware — One-mark pipettes.*

ISO 842:1984, *Raw materials for paints and varnishes — Sampling.*

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

3 Principle

The method is based on the following reactions:

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

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

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

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

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

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

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

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 Reagents and materials

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

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

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

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

4.4 Buffer solution.

Dissolve 12,37 g of boric acid in water in a 1 000 ml one-mark 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.

4.5 Iodine, standard volumetric solution, $c(\frac{1}{2}I_2)$ = 0,1 mol/l, i.e. 12,690 g/l. If necessary, standardize the solution against standard volumetric sodium thiosulfate solution, $c(Na_2S_2O_3)$ = 0,1 mol/l.

4.6 Dichloromethane, neutral (pH = 7).

Before use, cool the dichloromethane to 0 °C.

4.7 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).

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

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

5 Apparatus

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

5.1 High-speed mixer.

5.2 Magnetic stirrer.

5.3 Ice bath.

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

5.5 Pipettes, of capacity 10 ml and 25 ml.

6 Sampling

Take a representative sample of the product to be tested, as described in ISO 842.

7 Procedure

Carry out the determination in duplicate.

7.1 Test portion

By reference to table 1, select the appropriate test-portion mass. If the free-formaldehyde content cannot be predicted, take a test portion of about 1 g and carry out a preliminary determination.

Weigh, to the nearest 0,001 g, the test portion into a 600 ml beaker.

Table 1 — Mass of test portion

Expected free-formaldehyde content % (*m/m*)	Approximate mass of test portion g
up to 0,5	3,0
from 0,5 to 1	1,5
from 1 to 2	1,0
from 2 to 3	0,5
from 3 to 5	0,25

7.2 Determination

Ensure that the temperature of the contents of the beaker is not higher than 0 °C during the whole determination. If necessary, add some finely divided ice (4.9) to the mixture.

In the case of water-soluble products, dissolve the test portion immediately in a mixture of 150 ml of water containing ice (4.8), about 10 g of finely divided ice (4.9) and 25 ml of the buffer solution (4.4). In the case of products that do not form clear solutions with water, dissolve the test portion immediately in 50 ml of dichloromethane (4.6). Then add a mixture of 150 ml of water containing ice (4.8), about 20 g of finely divided ice (4.9) and 25 ml of the buffer solution (4.4) and emulsify with the high-speed mixer (5.1) for 10 s. Withdraw the mixer and rinse it with a small volume of water containing ice (4.8) to remove adhering liquid. Collect the rinsings in the test solution.

Place the beaker in the ice bath (5.3) and stir the contents of the beaker, using the magnetic stirrer (5.2). Whilst continuously stirring, add, by means of a burette (5.4), 2 ml of sodium sulfite solution (4.1). Continue stirring for 15 min and add 10 ml of acetic acid (4.2) and either 50 mg of powdered starch or 3 or 4 drops of starch solution (4.7). Titrate with iodine solution (4.5) until a greyish-blue or violet coloration is obtained that is stable for at least 10 s. Then add 30 ml of sodium carbonate solution (4.3). Titrate the liberated sodium sulfite with iodine solution until a blue coloration is obtained that is stable for at least 1 min. Record the volume V of the iodine solution required for the titration of the liberated sodium sulfite.

8 Expression of results

8.1 Calculation

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

$$w(CH_2O, \text{free}) = \frac{V \times 1{,}5 \times 0{,}1}{m}$$

where

V is the volume, in millilitres, of iodine solution (4.5) used;

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

1,5 is the mass, in milligrams, of formaldehyde corresponding to 1,00 ml of the iodine solution, $c(\frac{1}{2}I_2) = 0{,}1$ mol/l;

0,1 is the conversion factor necessary to convert milligrams to grams and to express w as a percentage.

If the two results (duplicates) differ by more than the value indicated in 8.2.1, repeat the procedure described in clause 7.

Calculate the mean of two valid results (replicates) and report the result to the nearest 0,1 % (*m/m*).

8.2 Precision

8.2.1 Repeatability (r)

The value below which the absolute difference between two single test results, each the mean of duplicates, obtained on identical material by one operator in one laboratory within a short interval of time using the standardized test method, may be expected to lie with a 95 % probability is

0,06 % (*m/m*) (absolute) for products having free-formaldehyde contents up to 1 % (*m/m*);

6 % (relative) for products having free-formaldehyde contents above 1 % (*m/m*).

8.2.2 Reproducibility (R)

The value below which the absolute difference between two single test results, each the mean of duplicates, obtained on identical material by operators in different laboratories using the standardized test method, may be expected to lie with a 95 % probability is

0,1 % (*m/m*) (absolute) for products having free-formaldehyde contents up to 1 % (*m/m*);

10 % (relative) for products having free-formaldehyde contents above 1 % (*m/m*).

9 Test report

The test report shall contain at least the following information:

a) all details necessary to identify the product tested;

b) a reference to this International Standard (ISO 9020);

c) the result of the test (mean value) as indicated in clause 8;

d) any deviation from the test method specified;

e) the date of the test.

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Descriptors: paints, varnishes, binders (materials), thermosetting resins, aminoplasts, chemical analysis, determination of content, formaldehyde, volumetric analysis.

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