INTERNATIONAL STANDARD

ISO 14184-2

Second edition
2011-08-15

Textiles — Determination of formaldehyde —

Part 2: Released formaldehyde (vapour absorption method)

Textiles — Dosage du formaldéhyde —

Partie 2: Formaldéhyde dégagé (méthode par absorption de vapeur)

Reference number
ISO 14184-2:2011(E)

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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 14184-2 was prepared by Technical Committee ISO/TC 38, *Textiles*.

This second edition cancels and replaces the first edition (ISO 14184-2:1998), of which it constitutes a minor revision.

ISO 14184 consists of the following parts, under the general title *Textiles — Determination of formaldehyde*:

— *Part 1: Free and hydrolysed formaldehyde (water extraction method)*

— *Part 2: Released formaldehyde (vapour absorption method)*

Textiles — Determination of formaldehyde —

Part 2: Released formaldehyde (vapour absorption method)

WARNING — This part of ISO 14184 calls for the use of substances and/or procedures that may be injurious to health if adequate precautions are not taken. It refers only to technical suitability and does not absolve the user from legal obligations relating to health and safety at any stage. It has been assumed in the drafting of this part of ISO 14184 that the execution of its provisions is entrusted to appropriately qualified and experienced people.

1 Scope

This part of ISO 14184 specifies a method for determining the amount of formaldehyde released under the conditions of accelerated storage from textiles in any form by means of a vapour absorption method.

The procedure is intended for use in the range of releasable formaldehyde on the fabric between 20 mg/kg and 3 500 mg/kg when determined by this method. The lower limit is 20 mg/kg. Below this limit, the result is reported as “not detectable”.

A method for determination of free formaldehyde and formaldehyde extracted partly through hydrolysis in aqueous solution is given in ISO 14184-1.

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 139:2005, *Textiles — Standard atmospheres for conditioning and testing*

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

3 Principle

A weighed fabric specimen is suspended over water in a sealed jar. The jar is placed in an incubator at a controlled temperature for a specified length of time. The amount of formaldehyde absorbed by the water is then determined colorimetrically.

4 Reagents

All reagents shall be of analytical reagent quality.

4.1 **Distilled water** or **grade 3 water** complying with ISO 3696.

4.2 Acetylacetone reagent (Nash reagent).

Dissolve 150 g of ammonium acetate in about 800 ml of water (4.1), add 3 ml of glacial acetic acid and 2 ml of acetylacetone, transfer into a 1 000 ml volumetric flask and make up to the mark with water (4.1). Store in a brown bottle.

The reagent darkens in colour slightly on standing over the first 12 h. For this reason, the reagent should be held for 12 h before use. Otherwise, the reagent is usable over a considerable period of time, at least 6 weeks. However, since the sensitivity may change slightly over a long period of time, it is good practice to run a calibration curve weekly to correct for slight changes in the standard curve. As an alternative, the chromotropic acid method described in Annex B may be used.

4.3 Formaldehyde solution, approximately 37 % (M/V or M/m).

5 Apparatus

5.1 Glass preserving jars, 0,95 l to 1,0 l with gas-tight sealing caps (see Figure 1).

5.2 Small wire-mesh baskets (or other suitable means for suspending the test specimen above the water level inside the jars. As an alternative to the wire-mesh baskets, a double strand of sewing thread may be used to make a loop in the test specimen that has been folded in half twice, suspended above the water level. The two double-thread ends are draped over the top of the jar and held securely by the jar cap.

NOTE A simple support for insertion in the preserving jars can be constructed as follows. A piece of aluminium wire screening 15,2 cm $\times$ 14,0 cm is bent around a length of wood 3,8 cm square and fastened together to form a rectangular, open-ended cage. One side is cut at the corners about halfway up the side and the cut section is folded inward and fastened. This folded piece forms the bottom of the wire basket while the other three sides form the support legs. Fastening can be accomplished by twisting short lengths of wire through or around the appropriate part.

5.3 Incubator, thermostatically controlled at (49 $\pm$ 2) °C.

5.4 Stoppered volumetric flasks, 50 ml, 250 ml, 500 ml and 1 000 ml.

5.5 Pipettes, 1 ml, 5 ml, 10 ml, 15 ml, 20 ml, 25 ml, 30 ml and 50 ml and graduated at intervals of 5 ml.

NOTE An automatic pipette system of the same accuracy as manual pipettes can be used.

5.6 Burettes, 10 ml and 50 ml.

5.7 Spectrophotometer, capable of reading absorbance to a minimum of 3 decimal places at a wavelength of 412 nm.

5.8 Test tubes or **spectrophotometer tubes**.

5.9 Water bath, capable of maintaining a temperature of (40 $\pm$ 2) °C.

5.10 Balance, accurate to 0,2 mg.

6 Preparation of standard solution and calibration

6.1 Preparation

Prepare an approximately 1 500 mg/l stock solution of formaldehyde by diluting 3,8 ml of formaldehyde solution (4.3) to 1 litre with water (4.1). Determine the concentration of formaldehyde in the stock solution by the method given in Annex A.

Record the accurate concentration of this standardized stock solution. This stock solution will keep for up to 4 weeks and is used to prepare standard dilutions.

6.2 Dilution

The equivalent concentrations of the formaldehyde in the test specimen, based on a mass of 1 g of the test specimen and 50 ml of water, will be 50 times the accurate concentration of the standard solutions.

6.2.1 Preparation of the standard solution (S2)

Dilute 10 ml of the titrated standard solution (containing 1,5 mg/ml of formaldehyde), prepared in 6.1, with water (4.1) to 200 ml in a volumetric flask. This solution contains 75 mg/l of formaldehyde.

6.2.2 Preparation of the calibration solutions

Dilute calibration solutions from the standard solution (S2), by diluting with water (4.1) in 500 ml volumetric flasks, using a minimum of five solutions from the following:

— 1 ml of S2 to 500 ml, containing 0,15 µg CH_2O/ml = 7,5 mg/kg CH_2O on the fabric

— 2 ml of S2 to 500 ml, containing 0,30 µg CH_2O/ml = 15 mg/kg CH_2O on the fabric

— 5 ml of S2 to 500 ml, containing 0,75 µg CH_2O/ml = 37,5 mg/kg CH_2O on the fabric

— 10 ml of S2 to 500 ml, containing 1,50 µg CH_2O/ml = 75 mg/kg CH_2O on the fabric

— 15 ml of S2 to 500 ml, containing 2,25 µg CH_2O/ml = 112,5 mg/kg CH_2O on the fabric

— 20 ml of S2 to 500 ml, containing 3,00 µg CH_2O/ml = 150 mg/kg CH_2O on the fabric

— 30 ml of S2 to 500 ml, containing 4,50 µg CH_2O/ml = 225 mg/kg CH_2O on the fabric

— 40 ml of S2 to 500 ml, containing 6,00 µg CH_2O/ml = 300 mg/kg CH_2O on the fabric

Calculate the first-order regression curve of the type $y = a + bx$. This regression curve will be used for all measurements. If the test specimens contain a higher amount of formaldehyde than 500 mg/kg, dilute the sample solution.

NOTE This double-dilution is necessary to have the same formaldehyde concentrations in the calibration solutions as in the test solutions of the fabrics. If the fabric contains 20 mg/kg of formaldehyde, a 1,00 g specimen is extracted with 50 ml of water; the solution contains 20 µg of formaldehyde and from this it follows that 1 ml of the test solution contains 0,4 µg of formaldehyde.

7 Preparation and conditioning of test specimens

Do not condition the test specimen because the predrying and humidity in connection with the conditioning may cause changes in the formaldehyde content of the sample. Prior to testing, store the sample sealed in a container.

From the sample, cut at least two specimens into small pieces and weigh approximately 1 g of the pieces to an accuracy of 10 mg.

NOTE Storage can be in a polyethylene bag and wrapped in aluminium foil. The reason for the storage precaution is that formaldehyde might diffuse through the pores of the bag. In addition, catalysts, or other compounds present in a finished, unwashed fabric, can react with the foil if in direct contact.

8 Procedure

Pour 50 ml of water (4.1) into the bottom of each jar. Suspend one specimen above the water in each jar, using a wire-mesh basket or other means. Seal the jars and place them in the incubator (5.3) at (49 ± 2) °C for 20 h ± 15 min. Remove and cool the jars for (30 ± 5) min and remove the specimen and baskets, or other support, from the jars. Recap the jars and shake them to mix any condensation formed on the jar sides.

Pipette 5 ml of acetylacetone reagent (4.2) into a suitable number of tubes (5.8), and pipette 5 ml of the acetylacetone reagent into at least one additional tube for a reagent blank. Add 5 ml aliquots from each of the sample-preserving jars to the tubes and 5 ml of water (4.1) to the tube which is used as a reagent blank.

Mix and place the tubes in a water bath (5.9) at (40 ± 2) °C for (30 ± 5) min. Cool and read the absorbance in the colorimeter or spectrophotometer (5.7) against the reagent blank using a wavelength of 412 nm in a 10 mm absorption cell. Determine the formaldehyde concentration, in µg/ml, in the sample solutions using the prepared calibration curve.

If it is anticipated that the fabrics have formaldehyde release levels of more than 500 mg/kg, or if the calculated levels from the test using a 5:5 ratio are more than 500 mg/kg, dilute the extract to give an absorbance in the range of the calibration curve (the dilution factor shall be taken into account when calculating the results).

CAUTION — Exposure of the developed yellow colour to direct sunlight for a period of time will cause some fading. If there is appreciable delay (e.g. 1 h) in reading the tubes after colour development and strong sunlight is present, care should be exercised to protect the tubes, such as by covering them with a formaldehyde-free enclosure. Otherwise, the colour is stable for a considerable time (at least overnight) and reading may be delayed, if desired.

9 Calculation

Calculate the amount of formaldehyde released for each specimen (w_F), to the nearest mg/kg, using the following equation:

$$w_F = \frac{\rho \times 50}{m}$$

where

ρ is the concentration of formaldehyde in solution, in mg/l, as read from the calibration graph;

m is the mass of test specimen, in grams.

Calculate the arithmetic mean of the two values.

If the result is less than 20 mg/kg, report it as “not detectable”.

10 Test report

The test report shall include the following information:

a) a reference to this part of ISO 14184, i.e. ISO 14184-2:2011;

b) the date the sample was received, the means in which it was stored prior to testing and the date tested;

c) description of the sample tested and how packaged;

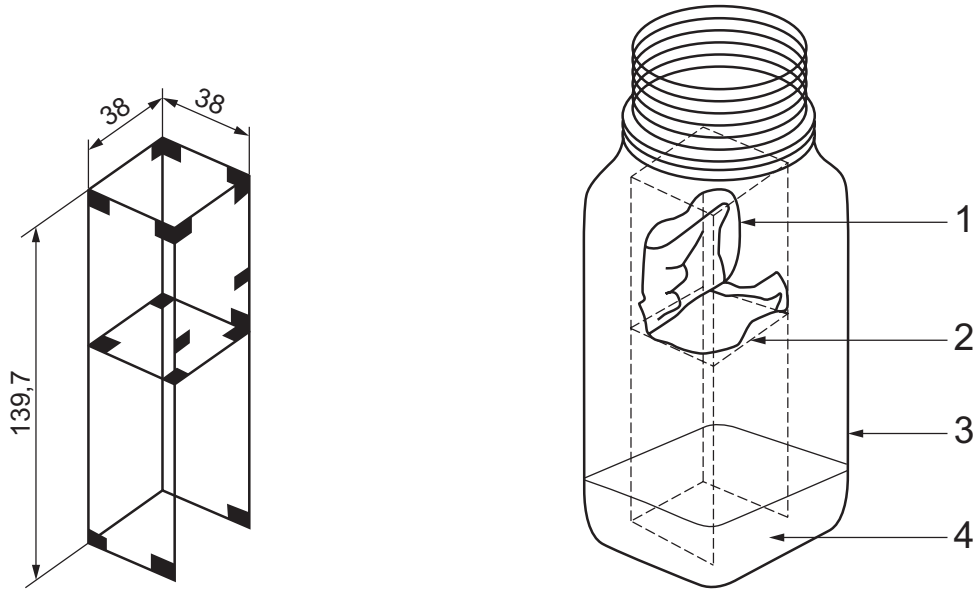
d) the mass of the test specimens;

e) the range of the calibration graph;

f) the amount of formaldehyde released from the sample, expressed as in Clause 9;

g) any deviation, by agreement or otherwise, from the procedure specified.

Dimensions in millimetres



a) Wire-mesh basket

b) Sealed jar containing one specimen and a basket

Key

1 fabric specimen
2 basket
3 jar
4 water

Figure 1 — Wire-mesh basket (aluminium) which is suspended in a sealed jar with one specimen

Annex A
(normative)

Standardization of formaldehyde stock solution

A.1 General

The stock solution containing approximately 1 500 µg/ml of formaldehyde shall be accurately standardized in order to prepare a precise calibration curve for use in colorimetric analysis.

A.2 Principle

An aliquot of the stock solution is reacted with an excess of sodium sulfite followed by a back-titration with acid solution in the presence of thymolphthalein as an indicator.

A.3 Apparatus

A.3.1 Volumetric pipette, 10 ml.

A.3.2 Volumetric pipette, 50 ml.

A.3.3 Burette, 50 ml.

A.3.4 Erlenmeyer flask, 150 ml.

A.4 Reagents

A.4.1 Sodium sulfite, $c(Na_2SO_3)$ = 1 mol/l, made by dissolving 126 g of anhydrous Na_2SO_3 per litre of water (4.1)

A.4.2 Thymolphthalein, 10 g/l in ethanol.

A.4.3 Sulfuric acid, $c(H_2SO_4)$ = 0,01 mol/l.

This reagent may be purchased in a standardized form or should be standardized using a standard sodium hydroxide solution.

A.5 Procedure

Pipette 50 ml of sodium sulfite (A.4.1) into the Erlenmeyer flask (A.3.4). Add two drops of thymolphthalein indicator (A.4.2). Add a few drops of sulfuric acid (A.4.3), if necessary, until the blue colour disappears.

Pipette 10 ml of the stock formaldehyde solution into the flask (the blue colour will reappear). Titrate the solution with sulfuric acid (A.4.3) until the blue colour is discharged. Record the volume of sulfuric acid solution used.

The volume of sulfuric acid should be approximately 25 ml.

NOTE A calibrated pH meter can be used in place of thymolphthalein indicator, in which case the end-point is reached at pH = 9,5.

Carry out the procedure in duplicate.

A.6 Calculations

1 ml of 0,01 mol/l sulfuric acid is equivalent to 0,6 mg of formaldehyde.

Calculate the formaldehyde concentration in the stock solution, in µg/ml, from the following formula:

$$\frac{V_A \times 0{,}6 \times 1\,000}{V}$$

where

V_A is the volume of sulfuric acid used, in ml;

V is the volume of sample used, in ml.

Calculate the average of the results and use the concentration determined above in preparing the calibration curve for the colorimetric analysis.

Annex B
(informative)

Alternative procedure using chromotropic acid

CAUTION — Since concentrated sulfuric acid is used with the chromotropic acid method, adequate care should be exercised to protect operating personnel and spectrometric equipment.

B.1 Reagents

B.1.1 Chromotropic acid, 50 g/l, aqueous solution freshly made using water (4.1) and, if necessary, filtered before use.

This reagent is supplied as a sodium salt for formaldehyde determination. Considerable variations are evident in its quality and a new calibration curve should be prepared for each new batch purchased. Solutions older than 12 h should be discarded.

B.1.2 Concentrated sulfuric acid (density 1,84 g/l), of analytical reagent quality.

B.1.3 Sulfuric acid, $c(H_2SO_4)$ = 7,5 mol/l. Concentrated sulfuric acid (B.1.2) (750 g, 405 ml) is added with care to water (4.1), allowed to cool and made up to 1 l with water (4.1) and allowed to cool before use.

B.2 Procedure

Transfer an aliquot of 1,0 ml of the liquor (from Clause 8) to a boiling tube. To this aliquot, add in turn 4,0 ml of 7,5 mol/l sulfuric acid (B.1.3), 1.0 ml of 50 g/l chromotropic acid solution (B.1.1) and 5,0 ml of concentrated sulfuric acid (B.1.2). Mix the contents of the boiling tube thoroughly after each addition, with a minimum wait of 2 min before adding the next reagent.

Support the tube vertically in a boiling water bath, the level of which shall be above that of the solution in the tube, for (30 ± 1) min. After cooling, transfer the solution to a 50 ml volumetric flask, make up to the mark with water (4.1) and shake. Allow the flask and contents to cool to ambient temperature for a minimum period of 1 h. If necessary, add more water (4.1) to make up to the mark.

Using a spectrometer or colorimeter, measure the absorbance, at 570 nm, of the diluted solution in a 10 mm cell against a blank made from 1,0 ml of water (4.1), 4,0 ml of 7,5 mol/l sulfuric acid (B.1.3), 1,0 ml of 50 g/l chromotropic acid (B.1.1) and 5,0 ml of concentrated sulfuric acid (B.1.2).

If the absorbance exceeds 1,0, repeat the colorimetric determination using a 0,5 ml aliquot of the original liquor, adding 0,5 ml of water (4.1).

At high formaldehyde concentrations, the relationship between absorbance and concentration is non-linear and other coloured species are thought to be present. Therefore, at measured absorbances greater than 1,0, the procedure should be repeated with a smaller aliquot of the test solution from the jar. The total volume of the test solution and water (4.1) should be made up to 1,0 ml using water (4.1).

NOTE 1 No changes in absorbance values have been observed for periods up to 4 h after colour development.

NOTE 2 If absorbances lower than 0,1 are recorded, the sensitivity of the procedure can be increased by measuring the absorbance before the solution is diluted to 50 ml, provided the solution is allowed to cool for a minimum period of 1 h to reach room temperature and the appropriate low formaldehyde calibration graph is used.

During dilution of the coloured solution, the contents of the volumetric flask should be mixed thoroughly, otherwise layering of the solutions will occur, giving erroneous results.

When using this method, a change may be necessary in the size of both the aliquots taken from the sample jars and the standard formaldehyde solutions used in preparing the calibration curve.

Annex C
(informative)

Information on accuracy of the test

C.1 Precision

Interlaboratory studies (ILS) of the AATCC method 112 on which this method is based were conducted with a 20 h incubation at 49 °C and a 5/5 ratio of sample to Nash solution. Single operators in each participating laboratory ran triplicate determinations on each fabric. In the first ILS, results from nine laboratories testing one fabric each at three low formaldehyde levels in the range of 100 µg/g to 400 µg/g were analysed by analysis of variance. In the second ILS, results from eight laboratories testing ten fabrics of nominal level 0 µg/g were analysed.

Critical differences were calculated for zero-formaldehyde fabrics, shown in Table C.1, and for low-level-formaldehyde fabrics, shown in Table C.2.

When two or more laboratories wish to compare test results, it is recommended that laboratory levels be established between them prior to beginning test comparisons.

If comparisons are made between laboratories on a single fabric level of formaldehyde release, the critical differences in the third column in Table C.2 should be used.

If comparisons are made between laboratories on a series of fabrics of a range of formaldehyde levels, the critical differences in the fourth column in Table C.2 should be used.

The number of determinations per laboratory average (det/avg) also determines the critical difference.

Table C.1 — Critical differences for zero formaldehyde

Critical differences for averages 95 % probability, µg/g			
Det/avg	**Within laboratory**	**Single fabric between laboratories**	**Multiple fabric between laboratories**
1	7,7	12,0	13,8
2	5,5	10.6	12,7
3	4,5	10,2	12,3

Table C.2 — Critical differences for low level formaldehyde

Critical differences for averages 95 % probability, µg/g			
Det/avg	**Within laboratory**	**Single fabric between laboratories**	**Multiple fabric between laboratories**
1	21,6	80,3	116,0
2	15,2	78,9	115,0
3	12,4	78,4	114,7

C.2 Bias

The formaldehyde release of a fabric can be defined only in terms of a test method. There is no independent method for determining the true value. As a means of estimating formaldehyde released from a fabric under the conditions of accelerated storage, this method has no known bias.

Bibliography

[1] AATCC Test Method 112-2008, *Formaldehyde Release from Fabric, Determination of: Sealed Jar Method*

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