INTERNATIONAL STANDARD

ISO 14184-1

Second edition
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Textiles — Determination of formaldehyde —

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

Textiles — Dosage du formaldéhyde —

Partie 1: Formaldéhyde libre et hydrolysé (méthode par extraction d'eau)

Reference number
ISO 14184-1:2011(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 14184-1 was prepared by Technical Committee ISO/TC 38, *Textiles*.

This second edition cancels and replaces the first edition (ISO 14184-1:1998), 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 1: Free and hydrolysed formaldehyde (water extraction 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 free formaldehyde and formaldehyde extracted partly through hydrolysis by means of a water extraction method. The method can be applied to the testing of textile samples in any form.

The procedure is intended for use in the range of free and hydrolysed formaldehyde on the fabric between 16 mg/kg and 3 500 mg/kg when determined by this method. The lower limit is 16 mg/kg. Below this limit, the result is reported as “not detectable”.

A method for determination of released formaldehyde is given in ISO 14184-2.

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*

ISO 4793:1980, *Laboratory sintered (fritted) filters — Porosity grading, classification and designation*

3 Principle

Formaldehyde is extracted from a textile sample with water at 40 °C. The amount of formaldehyde 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. 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.

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

4.4 Ethanolic solution of dimedone.

Prepare by dissolving 1 g of dimedone (dimethyl-dihydro resorcinol or 5,5-dimethyl-cyclohexanedione) in ethanol and by diluting the solution with ethanol to make 100 ml. Prepare immediately before use.

5 Apparatus

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

5.2 Flask, 250 ml, with a stopper.

5.3 Pipettes, 1 ml, 5 ml, 10 ml and 25 ml and graduated at intervals of 5 ml.

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

5.4 Burettes, 10 ml and 50 ml.

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

5.6 Test tubes or **spectrophotometer tubes**.

5.7 Water bath, capable of maintaining a temperature of (40 ± 2) °C.

5.8 Filters, made from heat-resistant glass having a pore size between 40 µm and 100 µm (pore symbol P100 in accordance with ISO 4793).

5.9 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 standard 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 100 ml of water, will be 100 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

Prepare 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 = 15 mg/kg CH_2O on the fabric

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

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

— 10 ml of S2 to 500 ml, containing 1,50 µg CH_2O/ml = 150 mg/kg CH_2O on the fabric

— 15 ml of S2 to 500 ml, containing 2,25 µg CH_2O/ml = 225 mg/kg CH_2O on the fabric

— 20 ml of S2 to 500 ml, containing 3,00 µg CH_2O/ml = 300 mg/kg CH_2O on the fabric

— 30 ml of S2 to 500 ml, containing 4,50 µg CH_2O/ml = 450 mg/kg CH_2O on the fabric

— 40 ml of S2 to 500 ml, containing 6,00 µg CH_2O/ml = 600 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 100 ml of water; the solution contains 20 µg of formaldehyde and from this it follows that 1 ml of the test solution contains 0,2 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 in a container.

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.

From the sample, cut two test specimens into small pieces, and weigh approximately 1 g of the pieces to an accuracy of 10 mg. If the formaldehyde content is low, increase the test specimen mass to 2,5 g in order to achieve a sufficient accuracy.

For each test specimen, put the weighed pieces into a 250 ml flask with a stopper (5.2) and add 100 ml of water (4.1). Stopper tightly and place in a water bath at (40 ± 2) °C for (60 ± 5) min. Shake the flask at least every 5 min, ensuring that the specimens are entirely wet. Then filter the solution into another flask through a filter (5.8).

If it is difficult to obtain completely wet specimens, a mechanical-shaking water bath should be used.

In cases of dispute, use a conditioned parallel specimen to calculate a correction coefficient to be used in correcting the mass of the test specimen to be used for the test.

Cut the test specimen from the sample, weigh it immediately and again after conditioning (in accordance with ISO 139). Use these values to calculate the correction coefficient to two integers and use the coefficient to calculate the conditioned mass of the test specimen used for the sample solution.

8 Procedure

8.1 Put 5 ml of the filtered test specimen solution in a tube (5.6) and 5 ml of the standard formaldehyde solutions in further tubes (5.6). Add 5 ml of acetylacetone reagent (4.2) into each tube and shake them.

8.2 Keep the test tubes first in a water bath at (40 ± 2) °C for (30 ± 5) min and then at ambient temperature for (30 ± 5) min. Take the solution of 5 ml of acetylacetone reagent solution in 5 ml of water having been treated in the same way as the blank reagent. Using a spectrophotometer (5.5), measure the absorbances in a 10 mm absorption cell at a wavelength of 412 nm against water (4.1).

8.3 If it is anticipated that the fabrics have formaldehyde extraction 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).

8.4 To account for the effect of any impurities or discoloration in the test specimen solution, put 5 ml of the sample solution in a separate test tube, add 5 ml of water (4.1) instead of acetylacetone and treat in the same way as above. Determine the absorbance of this solution, in the same way as above, but using water (4.1) as the control.

8.5 Make at least two parallel tests.

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.

8.6 If there is a doubt that the absorption may not be due to formaldehyde but, for example, to an extracted colouring agent, carry out a confirmation test with dimedone (see 8.7).

NOTE Dimedone reacts with formaldehyde, and thus no colour resulting from formaldehyde reaction will be observed.

8.7 For dimedone confirmation, put 5 ml of the sample solution in a test tube (diluted where necessary, see Clause 7), add 1 ml of ethanol solution of dimedone and shake.

Warm the solution in a water bath at (40 ± 2) °C for (10 ± 1) min, then add 5 ml of acetylacetone reagent, shake and continue to warm the solution in a water bath at (40 ± 2) °C for (30 ± 5) min. Leave the solution still at room temperature for (30 ± 5) min. Determine the absorbance of the solution using a control solution prepared in the same way as above, but with water instead of the sample solution. The absorbance from formaldehyde at 412 nm disappears.

9 Calculation and expression of the results

For each test specimen, correct the absorbance of the test specimen as follows:

$$A = A_s - A_b - (A_d)$$

where

A is the corrected absorbance;

A_s is the measured absorbance of the test specimen;

A_b is the measured absorbance of the blank reagent;

A_d is the measured absorbance of the blank specimen (only in the case of discoloration or other contamination).

Determine the amount of the formaldehyde, in µg/ml, from the calibration curve, using the value of the corrected absorbance.

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

$$w_F = \frac{\rho \times 100}{m}$$

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 16 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 14184-1:2011;

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 and, if required, the correction coefficient for the mass;

e) the range of the calibration graph;

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

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

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)

Information on accuracy of the method

This method is based on a Finnish method for which the accuracy of the test was found to depend on the formaldehyde content of the sample and to be as follows for uniform samples:

See Table B.1.

Table B.1

Formaldehyde content mg/kg	Approximate accuracy %
1 000	0,5
100	2,5
20	15
10	80

Note that the method in this part of ISO 14184 uses a different calibration graph from that used in the determination of the above-mentioned results.

Factors specific to the method result in the fact that contents below 16 mg/kg cannot be shown to be caused by formaldehyde.

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