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Paints and varnishes — Testing of formaldehyde-emitting coatings and melamine foams — Determination of the steady-state concentration of formaldehyde in a small test chamber

Peintures et vernis — Essais des revêtements et mousses mélamines qui émettent du formaldéhyde — Détermination de la concentration à l'équilibre du formaldéhyde dans une petite chambre d'essai

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Foreword

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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 15234 was prepared by Technical Committee ISO/TC 35, *Paints and varnishes,* Subcommittee SC 10, *Test methods for binders for paints and varnishes.*

Annexes A and B form an integral part of this International Standard. Annex C is for information only.

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Paints and varnishes — Testing of formaldehyde-emitting coatings and melamine foams — Determination of the steady-state concentration of formaldehyde in a small test chamber

1 Scope

This International Standard specifies a test method for determining the equilibrium concentration of formaldehyde from formaldehyde-emitting coatings and melamine foams in a small test chamber.

It describes the determination of the equilibrium concentration of formaldehyde that is established in air at 23 °C and 50 % relative humidity. The test closely simulates practical conditions and can be performed on a laboratory scale. Good correlation is obtained with values obtained on samples of the same material in a 40 m^3 test chamber. The method, which is simple to perform, is therefore suitable for the preliminary determination of limits that have to be adhered to.

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 3270:1984, *Paints and varnishes and their raw materials — Temperatures and humidities for conditioning and testing*.

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

3 Definitions

For the purposes of this International Standard, the following definitions apply.

3.1
equilibrium concentration

c_{eql}

the concentration of formaldehyde in the air in the test chamber that is reached when several successive values of the concentration determined at one-hour intervals differ by less than 0,02 mg/m^3

3.2
air-replacement rate

n

the number of air changes per hour in the test chamber, given by

$$n = \frac{V_t}{t \times V}$$

where

V_t is the volume, in cubic metres, of air passed through the test chamber during the test;

t is the duration, in hours, of the test;

V is the volume, in cubic metres, of the test chamber

3.3
relative specimen area

a

the area of formaldehyde-emitting surface per unit volume of the test chamber, given, in square metres per cubic metre (i.e. m^{-1}), by

$$a = \frac{A}{V}$$

where

A is the area of the specimen, in square metres (see annexes A and B);

V is the volume, in cubic metres, of the test chamber

3.4
steady-state ratio

n/a

the ratio of the air-replacement rate n to the relative specimen area a, given, in metres per hour, by

$$n/a = \frac{V_t}{t \times A}$$

where

V_t is the volume, in cubic metres, of air passed through the test chamber during the test;

t is the duration, in hours, of the test;

A is the area, in square metres, of the specimen

3.5
formaldehyde concentration

c

the concentration, in milligrams per cubic metre, of formaldehyde at a given steady-state ratio n/a over the period of time concerned, given by

$$c = \frac{m}{V_t}$$

where

m is the mass, in milligrams, of formaldehyde;

V_t is the volume, in cubic metres, of air passed through the test chamber during the test

NOTE The value determined for c can be converted into ppm by dividing by the density of formaldehyde, i.e. by 1,22 g/l at a temperature of 23 °C and an atmospheric pressure of 101,3 kPa.

4 Principle

Test specimens are conditioned at (23 ± 1) °C and (50 ± 3) % relative humidity and exposed under specified conditions in a small test chamber (desiccator).

The desiccator is set up in an air-conditioned room so that air from the room can be passed first through the desiccator and then into a water trap where formaldehyde (HCHO) is absorbed. The water in the water trap is changed at regular intervals, and the formaldehyde concentration c is determined photometrically by the acetylacetone method or another suitable method. The test is continued until the value measured for c no longer changes (see 3.1). The equilibrium concentration c_{eql} in the air in the test chamber is then considered to be attained.

5 Choice of method for determination of formaldehyde

The acetylacetone method has been chosen as the preferred method. Other methods of determination, e.g. a fluorimetric method, may be used instead of the photometric method with acetylacetone, provided they can be shown to give equivalent results. (See also annex C, clause C.7.)

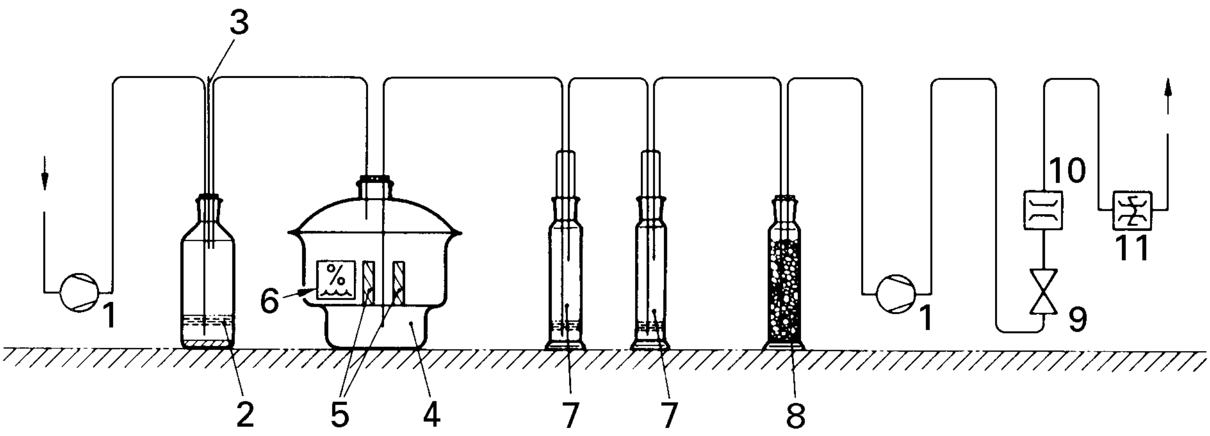
6 Apparatus

Ordinary laboratory apparatus and glassware, together with the following:

6.1 Air-conditioned room or similar facility, maintained at a temperature of (23 ± 1) °C and a relative humidity of (50 ± 3) %.

6.2 Apparatus (see figure 1) consisting of

- — two gas-metering pumps, rate of pumping at least 100 l/h, pressure head dependent on pressure requirements,
- — bubble counter;
- — 1 000 ml bottle with modified wash-bottle insert;
- — test chamber, volume 20 l, such as a desiccator, with lid containing a wire cage for the specimens;
- — hygrometer;
- — two 30 ml wash-bottles with Muenke fitting, or other suitable absorption vessels;
- — 500 ml wash-bottle filled with silica gel to act as a drying tower;
- — flowmeter, measuring range 0 l/h to 100 l/h; with fine-control valve;
- — integrating flowmeter, operating range 1 l/h to 220 l/h.



Key

1	Gas-metering pumps
2	Bottle containing saturated calcium nitrate solution to bring the air to (50 ± 2) % relative humidity
3	Vent tube with bubble counter
4	Test chamber
5	Specimens
6	Hygrometer
7	Wash-bottles/absorption vessels
8	Wash-bottle containing silica gel (drying tower)
9	Valve
10	Flowmeter
11	Integrating flowmeter

Figure 1 — Apparatus (schematic diagram)

If necessary, two bottles (2) may be connected in tandem. In this case, however, only the second bottle shall be fitted with a vent tube (3).

Checks shall be made to ensure that there are no leaks in the apparatus during the test.

Connecting tubing shall be as short as possible.

6.3 Spectrophotometer or **filter photometer with a 412 nm filter.**

6.4 50 mm spectrophotometer cell.

6.5 100 ml, 500 ml and 1 000 ml volumetric flasks.

6.6 10 ml microburette.

6.7 1 ml volumetric pipette.

6.8 Water bath, capable of being maintained at (60 ± 2) °C.

6.9 Analytical balance, capable of weighing to an accuracy of 0,1 mg.

7 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.

7.1 Colour-developer solution.

Weigh 75,0 g of ammonium acetate into a 500 ml volumetric flask and dissolve in water. Add 1,5 ml of concentrated acetic acid (96 % minimum) and 1,0 ml of acetylacetone. Make up to the mark with water and mix well.

The solution is not stable. It may not be kept for more than 14 days at room temperature (temperature no higher than 28 °C).

7.2 Formaldehyde, standard stock solution containing about 1 g/l of formaldehyde.

Weigh about 3 g of 30 % formaldehyde solution into a 100 ml beaker and dilute with water. Transfer the diluted solution into a 1 000 ml volumetric flask, make up to the mark with water and mix well.

Determine the formaldehyde content of this solution as follows:

To 20 ml of the formaldehyde stock solution add 25 ml of iodine solution [$c(I_2) = 0{,}05$ mol/l, corresponding to 12,69 g/l of I_2] and 10 ml of sodium hydroxide solution [$c(\mathrm{NaOH}) = 1$ mol/l, corresponding to 40,00 g/l of NaOH].

After five minutes, add 11 ml of hydrochloric acid [$c(\mathrm{HCl}) = 1$ mol/l, corresponding to 36,46 g/l of HCl] and a few drops of starch solution (1 % soluble, Zulkovsky). Titrate the excess iodine solution with sodium thiosulfate solution [$c(Na_2S_2O_3) = 0{,}1$ mol/l, corresponding to 15,81 g/l of $Na_2S_2O_3$].

Calculate the formaldehyde content using the following equation:

$$w(CH_2O) = \frac{0{,}001\,5\,(25 - V) \times 1\,000}{20}$$

where

$w(CH_2O)$ is the formaldehyde content, in grams per litre, of the standard stock solution;

V is the volume, in millilitres, of sodium thiosulfate solution used.

7.3 Standard formaldehyde solution (8 mg/l formaldehyde).

Run from the microburette (6.6) a volume of standard stock solution (7.2) containing 8 mg of formaldehyde into a 1 000 ml volumetric flask, make up to the mark with water and mix well.

1 ml of this standard solution contains 8 µg of formaldehyde.

7.4 Saturated calcium nitrate solution, prepared by dissolving calcium nitrate tetrahydrate, $Ca(NO_3)_2 \cdot 4H_2O$, (reagent grade) in water.

8 Preparation of specimens

The required area A of the specimens can be calculated from the air-replacement rate n and the volume V of the test chamber. For instance, if the number of air changes per hour is three ($n = 3\ \mathrm{h}^{-1}$) and the volume of the test chamber is 20 l, the specimen area required is 600 cm^2. This corresponds to a steady-state ratio n/a of 1, which has proved to be suitable for tests performed in accordance with this standard. For further details of the preparation of specimens:

- see annex A for paint coatings;
- see annex B for melamine foams.

Details of the preparation of specimens made of other materials shall be the subject of agreement (see annex C).

Condition the specimens at (23 ± 1) °C and (50 ± 3) % relative humidity for 28 days (or as otherwise agreed) before use (see annexes A and B).

9 Procedure

9.1 Number of determinations

Carry out at least three determinations — in each case on fresh specimens of the same material.

9.2 Treatment of specimens

9.2.1 Method A (for formaldehyde concentrations $\leqslant$ 0,15 mg/m^3)

Set up the apparatus (6.2) in the air-conditioned room (6.1) and place the conditioned specimens in the desiccator. Introduce 10 ml of water into the first formaldehyde-absorbing wash-bottle and 5 ml of water into the second. Start up the pumps. Adjust the pump that passes air into the bottle containing the calcium nitrate solution so that, during the entire test, more air is passed into the bottle than is withdrawn from it. This can be checked by means of the bubble counter. With the lid on the desiccator, pass air at (23 ± 1) °C from the air-conditioned room at a steady rate through the wash-bottle containing the calcium nitrate solution [to bring the relative humidity to (50 ± 2) %], then over the specimens in the desiccator, through the wash-bottles containing water and, finally, through the drying tower and back into the air-conditioned room. Check the relative humidity in the desiccator with a hygrometer. Set the required airflow rate, e.g. (60 ± 3) l/h for A = 600 cm^2, by means of the flowmeter. At intervals of 1 h during the test, read off and note the exact reading of the integrating flowmeter and determine the formaldehyde concentration c in the combined contents of the water-filled wash-bottles, preferably by the method described in 9.3. Continue the test until several successive values of c (at least three) are obtained which do not differ by more than 0,02 mg/m^3.

9.2.2 Method B (for formaldehyde concentrations > 0,15 mg/m^3) 1)

The procedure in this case is the same as that described in 9.2.1, except that the formaldehyde-absorbing wash-bottles are filled with 15 ml (wash-bottle No. 1) and 10 ml (wash-bottle No. 2) of water.

9.3 Determination of formaldehyde

9.3.1 Principle

Formaldehyde in aqueous solution reacts with ammonium ions and acetylacetone to yield diacetyldihydrolutidine (DDL) (Hantzsch reaction). The DDL thus formed has an absorption maximum at 412 nm.

9.3.2 Plotting the calibration curve

9.3.2.1 Preparation of the calibration solutions

Run the volumes of standard formaldehyde solution (7.3) listed in table 1 from the microburette (6.6) into a series of six 100 ml volumetric flasks.

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1) See annex C.

Table 1 — Calibration solutions

Calibration solution No.	Volume of standard formaldehyde solution (7.3) ml	Formaldehyde concentration in the calibration solution µg/100 ml
0[1]	0	0
1	0,5	4
2	1	8
3	2	16
4	5	40
5	10	80

[1] Zero-concentration solution

Add to each volumetric flask 10 ml of colour-developer solution (7.1), make up to the mark with water and mix well.

9.3.2.2 Photometric measurements

Keep the measuring flasks with the calibration solutions for 20 min in a water bath (6.8) at 60 °C. Within 1 h, after they have cooled to room temperature, determine the extinction coefficients of the solutions at a wavelength of 412 nm by means of the spectrophotometer (6.3). Plot the extinction coefficients against the corresponding formaldehyde concentrations to give a straight line that passes through the origin, i.e.

$$E = b \times x$$

where

x is the formaldehyde concentration, in micrograms per 100 millilitres, in the calibration solutions;

E is the extinction coefficient of the calibration solution concerned.

Calculate the slope b, in 100 millilitres per microgram, by the method of least squares.

9.3.3 Determination

9.3.3.1 Method A (for formaldehyde concentrations $\leqslant$ 0,15 mg/m^3)

Transfer the contents of the two water-filled wash-bottles (see 9.2.1) to a 25 ml volumetric flask, rinsing the wash-bottles with 7,0 ml of water. Add 2,5 ml of colour-developer solution (7.1) and make up to the mark with water. Keep the flask for 20 min in a water bath regulated at (60 ± 2) °C. Within 1 h, after the flask and its contents have cooled to room temperature, measure the extinction coefficient of the solution as described in 9.3.2.

9.3.3.2 Method B (for formaldehyde concentrations > 0,15 mg/m^3)

Transfer the contents of the two water-filled wash-bottles (see 9.2.2) to a 50 ml volumetric flask, rinsing the wash-bottles with about 15 ml of water. Add 5 ml of colour-developer solution (7.1) and proceed as described in 9.3.3.1.

10 Expression of results

Calculate the formaldehyde concentration c, in milligrams per cubic metre, in the air in the desiccator from the following equation:

$$c = \frac{E \times f}{V_t \times b}$$

where

E is the extinction coefficient of the solution, measured as described in 9.3.3;

f is the dilution factor: $f_{\text{method A}} = 0{,}25$, $f_{\text{method B}} = 0{,}50$;

V_t is the volume, in litres, of the air passed through the test chamber in 1 h;

b is the slope of line plotted in 9.3.2.

11 Precision

Once the results of a further round-robin test are available, information on the precision of the method will be included in this standard. The results will be presented separately for the complete test and for the photometric determination of the formaldehyde concentration.

12 Test report

The test report shall contain at least the following information:

a) all details necessary to identify the product tested and, if applicable, the substrate;

b) a reference to this International Standard (ISO 15234);

c) the date of sampling;

d) all details of specimen preparation, e.g. for coating materials the date of preparation, the dry-film thickness of the coating and the contact area (see annex A);

e) the conditions under which the specimens were conditioned before the test and the conditioning time;

f) the number of air changes n per hour;

g) the relative specimen area a;

h) the method used for the determination of the formaldehyde;

i) the results of the test, as indicated in clause 10 (at least three single results);

j) any deviation from the test method specified;

k) the date of the test.

Annex A
(normative)

Preparation of specimens from paints, varnishes and similar coating materials

A method shall be chosen which produces uniform films, without defects, from paints, varnishes and similar coating materials. Unless otherwise agreed, apply a 600 cm^2 film to a pane of glass by means of a wire applicator. The wet thickness shall be such that a dry coat of (30 ± 3) µm thickness is obtained after drying under the following conditions: flash drying for 10 min at room temperature followed by stoving for 10 min each at 50 °C and 80 °C in a circulating-air oven (see note 1). After the drying period has finished, allow the pane of glass to cool to room temperature in a closed vessel, e.g. a desiccator without a desiccant. Immediately afterwards, bring the vessel into a room air-conditioned to (23 ± 1) °C and (50 ± 3) % relative humidity. Pronounced climatic differences during transport into the air-conditioned room shall be avoided, as the film may not return to its original state after even brief exposure to humid air, e.g. if it were produced from an acid-curing lacquer. Unless otherwise agreed, the duration of the period for conditioning the specimens in the air-conditioned room shall be 28 days. The specimens shall be kept uncovered and ready for testing under these conditions. The test shall follow subsequently without further treatment.

NOTE 1 The drying conditions have been selected so that fluctuations in atmospheric humidity do not exert any effect on the results of the measurements. This is the case at temperatures above 50 °C.

If paints or varnishes have to be tested on wood-based materials, the substrate shall be E1 particle board of 16 mm thickness, and the cut edges shall not be sealed.

NOTE 2 It is well known that properties may vary in different areas of a panel produced from wood-based materials. Consequently, if comparative tests are performed, it is recommended that several test specimens always be taken from different parts of the panel so that an average value can be obtained.

Unless otherwise agreed, condition these specimens for 28 days in the air-conditioned room at a temperature of (23 ± 1) °C and a relative humidity of (50 ± 3) %. They shall be cut to size and exposed uncovered in the air-conditioned room, and shall be subsequently tested without further treatment. As far as possible, interactions with other specimens that may emit formaldehyde shall be excluded during conditioning (control the formaldehyde concentration in the air in the room).

If specimens have to be transported, place them in a closed container, e.g. a desiccator without desiccant. Packing in plastics film or paper may lead to a change in the moisture content of the specimens. As soon as possible after they have been delivered to the air-conditioned room, remove the specimens from the container and condition them for 28 days. Subsequently, test the specimens without any further treatment.

NOTE 3 The interested parties may agree to seal the cut edges of a substrate, e.g. with three coats of polyurethane lacquer. However, not only does this entail an additonal operation but it also gives rise to defects, e.g. gas leakage from the coating or a change in the specimen brought about by a difference in moisture content.

Annex B
(normative)

Preparation of specimens from melamine foams

Take representative specimens from melamine foams and cut to the required size. The value taken for the area of the specimen panel shall include the area of the cut surfaces (the narrow sides). Unless agreed otherwise, the dimensions of the specimen panels shall be (20 ± 0,2) cm × (15 ± 0,2) cm × (2 ± 0,2) cm, and they shall be conditioned for 28 days in an air-conditioned room at a temperature of (23 ± 1) °C and a relative humidity of (50 ± 3) %. The specimens shall be cut to the required size and exposed, uncovered and ready for testing, to the conditions in the air-conditioned room. They shall be subsequently tested without further treatment. As far as possible, interactions with other specimens that may emit formaldehyde shall be excluded during conditioning (control the formaldehyde concentration in the air in the room).

If the specimens have to be transported, it shall be ensured that their moisture content does not change. Fluctuations in temperature shall also be restricted to a minimum. For this reason, a closed vessel, e.g. a desiccator without desiccant, shall be used for unavoidable transport. Immediately after they have been received, the specimens shall be laid out for conditioning in the air-conditioned room. Subsequently, the test shall be performed without further treatment.

Annex C
(informative)

Explanatory notes

C.1 The aim of the method described in this standard is to allow every user to perform formaldehyde emission measurements on materials. Accordingly, the layout of the apparatus has been kept deliberately simple. The complexity and duration of the test are considerably less than methods which use a full-size test chamber, which closely simulates practical conditions.

C.2 Any other test chamber may be used instead of the desiccator, provided that the other requirements laid down in this standard are adhered to. The design and nature of the test chamber do not have any influence on the results. The dimensions of the specimens will have to be calculated to conform to the volume of the chamber used.

C.3 The factors that govern formaldehyde emission include the material of the specimen, its age, the conditions of aging, and the moisture content. The method described in this standard yields values for the material that relate to equilibrium conditions for the temperature, relative humidity, air-replacement rate and relative specimen area. All test conditions should correspond closely to those encountered in practice.

C.4 Although a free choice is theoretically permitted for the relative specimen area and the air-replacement rate, these two quantities depend on the time required for the equilibrium concentration to be attained. It has been demonstrated in practice that the equilibrium concentration c_{eql} at $a = 3$ m^2/m^3 and $n = 3$ h^{-1}, corresponding to a steady-state ratio of $n/a = 1$, is generally reached after a period of 2 h. In this case, the value measured after a period of 1 h can be rejected. The value measured after a period of 2 h and the further results should be constant and should lie within the limits given in 3.1. For instance, if $a = 1$ m^2/m^3 and $n = 1$ h^{-1}, the steady-state ratio is again 1 m $\cdot$ h^{-1}, but the equilibrium concentration c_{eql} is reached twice as slowly.

For comparative tests, it will be necessary for the interested parties to agree on the air-replacement rate n and relative specimen area a to be used.

C.5 The atmospheric humidity is a factor that greatly effects the determination of c_{eql}. Differences of 1 % in the moisture content of the air that flows through the chamber during the test can be detected in the results obtained for c_{eql}. Since many specimens are sensitive to hydrolysis, the conditions for conditioning the specimens must be exactly adhered to. The temperature of the bottle containing the calcium nitrate solution must be controlled at (23 ± 1) °C.

C.6 The shape, dimensions and age of the specimens and all the test conditions must be identical in comparative measurements. Any interruption in the air conditioning alters the rate of formaldehyde emission from the specimens. This can be explained by the fact that the properties of many materials, e.g. all amino resins, as well as wood-based materials and articles produced from them, tend towards an equilibrium state with the ambient humidity. For this reason, an attempt should be made to prepare the specimens, whenever possible, at the same location as that at which they will be tested. The fact that transportation is likely to affect unconditioned specimens throws doubt on the reliability of measured values for comparison purposes. There is no point in conditioning specimens intended for transport.

C.7 The acetylacetone method was given preference over the p-rosaniline method because it has given good results in practice for materials testing.

However, the precision of the determination also depends on the spectrophotometer and its precision, its zero stability and the error in the photometric correction. It must be ensured that the measurements are always performed within the range in which the spectrophotometer readings are reliable.

C.8 If only a 10 mm instead of a 50 mm cell can be used for the photometric method, it must be determined whether the extinction coefficient can still be determined to within sufficient accuracy or whether the test parameters must be altered to cope with very low formaldehyde contents. However, this will have to be the subject of agreement and noted in the test report. Examples of alterations that may be made are doubling the relative specimen area, the air-replacement rate or the duration of absorption.

C.9 It is recommended that the colour-developer solution be added immediately before the photometric measurements are carried out because the yellow coloration produced is sensitive to oxygen. The formaldehyde losses that have been observed on passing 60 l of air are 3 % or less. The loss in mass caused by entrainment of water by the air passing through the wash-bottles can be neglected in determining the value for c_{eql} provided it is not higher than 5 %. For this reason, the wash-bottles should be checked by weighing at regular intervals.

C.10 The test method can also be used for the determination of formaldehyde concentrations higher than those cited in this standard. In this case, 100 ml instead of 30 ml wash-bottles are recommended. These larger wash-bottles may contain up to 50 ml of water for the absorption of the formaldehyde. After 10 ml of colour-developer solution has been added, the contents of the wash-bottles can then be made up to 250 ml with water in a 250 ml volumetric flask. After the colour reaction, the solution can be measured photometrically as described.

C.11 The coefficient of determination r^2 should be calculated if information is required on the slope b of the linear relationship described in 9.3.2.2. It should be as close as possible to unity, and should not be less than 0,998 for five measured points. If $r^2 = 1$, all the measured points (total n) will lie in a straight line.

$$\mathrm{r}^2 = \frac{\left[\Sigma \mathrm{E_i x_i} - \dfrac{\Sigma \mathrm{E_i} \times \Sigma \mathrm{x_i}}{n}\right]^2}{\left[\Sigma \mathrm{E_i^2} - \dfrac{(\Sigma \mathrm{E_i})^2}{\mathrm{n}}\right]\left[\Sigma \mathrm{x_i^2} - \dfrac{(\Sigma \mathrm{x_i})^2}{\mathrm{n}}\right]}$$

C.12 It is planned to include in this standard at a later date additional annexes for the preparation of specimens from other materials.

C.13 Automatic instruments may be used to carry out this method provided it is certain that they give the same results.

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