INTERNATIONAL STANDARD

ISO 15373

First edition
2001-08-15

Plastics — Polymer dispersions — Determination of free formaldehyde

Plastiques — Dispersions de polymères — Dosage du formaldéhyde libre

Reference number
ISO 15373:2001(E)

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Printed in Switzerland

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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

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 International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 15373 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 9, *Thermoplastic materials*.

Plastics — Polymer dispersions — Determination of free formaldehyde

WARNING — This International Standard may involve hazardous chemicals, materials and operations. This International Standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user of this International Standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

1 Scope

This International Standard describes two methods for the determination of free formaldehyde (HCHO) in polymer dispersions. The procedure has been evaluated using acrylic, acrylonitrile butadiene, carboxylated styrene-butadiene and vinyl acetate polymer dispersions. Both test methods may also be applicable to polymer dispersions of other compositions.

Method A is the preferred method for polymer dispersions with a free-formaldehyde content higher than 10 mg/kg. Method B is recommended if lower formaldehyde contents have to be determined or arbitration analyses have to be carried out.

Both methods minimize changes in free-formaldehyde concentration that can result from changes in the physical or chemical properties of polymer dispersions.

There are no known limitations to these methods when used in the manner described.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 2227, *Formaldehyde solutions for industrial use — Determination of formaldehyde content*.

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

3 Principle

The polymers dispersed in a polymer dispersion are separated from the aqueous phase by filtration, centrifugation or coagulation. The resulting aqueous sample solution may be used to determine formaldehyde directly using method A by addition of 2,4-pentanedione reagent (Nash reagent) and subsequent measurement of the extinction coefficient at 410 nm. The concentration of formaldehyde is determined using a calibration plot obtained by plotting the extinction coefficients of formaldehyde standards against the corresponding formaldehyde concentrations.

If method B is applicable to the resulting aqueous sample solution, formaldehyde is separated from other species by liquid chromatography on an octadecyldimethylsilyl (C_{18}) reversed-phase column using an aqueous mobile phase.

The detection system includes a post-column reactor which produces a lutidine derivative by reaction of formaldehyde with 2,4-pentanedione reagent (Nash reagent) and a UV/visible detector operating at 410 nm.

The concentration of free formaldehyde in the aqueous solution is determined using peak areas from the standard and sample chromatograms (calibration by external standard). This method is specific for formaldehyde.

NOTE To determine free-formaldehyde levels in polymer dispersions, it is necessary to carry out the determination without upsetting any equilibria between the liquid phase and the polymer phase that might generate or deplete formaldehyde. Both test methods provide means for determining low levels of free formaldehyde in polymer dispersions without upsetting existing equilibria.

4 Interference

4.1 Method A

The following species have been identified as possible interferants in the method: acetaldehyde and glyoxylic acid. However, interference by acetaldehyde and glyoxylic acid is to be expected only when the species concerned is present in excess amounts (100-fold and more) compared with the formaldehyde concentration.

4.2 Method B

This method is very selective for formaldehyde because potential interferants such as acetaldehyde, acetone, benzaldehyde, formamide, formic acid, glyoxylic acid and propionaldehyde are either chromatographically separated from formaldehyde or do not react with the post-column reagent.

Because polymer dispersions vary in composition, the method run time may need to be extended to allow for late-eluting compounds. Compounds which remain on the column after an analysis may interfere with the formaldehyde peak in subsequent runs.

5 Reagents (methods A and B)

Unless otherwise stated, use only reagents of recognized analytical grade and only grade 1 water as defined in ISO 3696.

5.1 Acetic acid (CH_3CO_2H), glacial.

5.2 Ammonium acetate ($CH_3CO_2NH_4$).

5.3 Formaldehyde (HCHO), 37 % solution in water.

5.4 2,4-Pentanedione (acetyl acetone) ($CH_3COCH_2COCH_3$).

5.5 Phosphoric acid solution, 33 mM.

Dissolve 2,3 ml of 85 % phosphoric acid (H_3PO_4) in water and dilute to 1 l with water.

5.6 Potassium ferrocyanide trihydrate solution, 36 g/l (Carrez solution I).

Dissolve 36 g of potassium ferrocyanide trihydrate ($K_4Fe(CN)_6 \cdot 3H_2O$) in water and dilute to 1 l with water.

5.7 Zinc sulfate heptahydrate solution, 72 g/l (Carrez solution II).

Dissolve 72 g of zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$) in water and dilute to 1 l with water.

5.8 Sodium hydroxide, 0,1 M.

Dissolve 4 g of sodium hydroxide in water and dilute to 1 l with water.

5.9 Sodium phosphate, dibasic (Na_2HPO_4).

5.10 Nash reagent, post-column reagent, prepared as follows:

5.10.1 Transfer 62,5 g of ammonium acetate (5.2) to a 1 l amber bottle (6.1) that contains a stir bar. Add 600 ml of water to the bottle and mix on a stir plate until the ammonium acetate has completely dissolved.

5.10.2 Pipette 7,5 ml glacial acetic acid (5.1) into the bottle. Pipette 5 ml of 2,4-pentanedione (5.4) into the bottle. Add 387,5 ml of water to the bottle and mix thoroughly (45 min of mixing is suggested).

NOTE If necessary, other concentrations of ammonium acetate, glacial acetic acid and 2,4-pentanedione in the Nash reagents are also possible.

2,4-Pentanedione is light-sensitive. Protect it from light during use.

Prepare fresh Nash reagent solution weekly.

5.10.3 Transfer the Nash reagent to the post-column reactor reservoir (see 6.6.1.2). The reservoir shall be protected from light.

5.10.4 Degas the Nash reagent with a helium sparge.

5.11 Mobile phase and standard diluent, prepared as follows:

5.11.1 Transfer 1,78 g of dibasic sodium phosphate (5.9) to a 2 l mobile-phase reservoir that contains a stir bar. Add 2 l of water and mix on a stir plate until the sodium phosphate has completely dissolved.

5.11.2 Adjust the pH of the solution to 7,0 with 33 mM phosphoric acid (5.5).

5.11.3 Prepare the standard diluent in the same manner.

5.11.4 Degas the mobile phase with a helium sparge.

Water may also be used as the mobile phase without the addition of a buffer. A water mobile phase shall be used, however, when the Carrez reagents are used in the sample preparation (see 7.1.4).

5.12 Sample diluent (method B), prepared as follows:

5.12.1 The sample diluent is prepared in the same way as the mobile phase described in 5.11.1.

5.12.2 The final step of the diluent preparation requires a pH adjustment. Before this step, measure the pH of the polymer dispersion to $\pm$ 0,1 pH units. Dilute the polymer dispersion to 1 l with a buffer that is within $\pm$ 0,1 pH units of the polymer dispersion. Adjust the pH of the diluent to within $\pm$ 0,1 pH units of the polymer dispersion using either NaOH (5.8) or H_3PO_4 (5.5).

5.13 Standard reference solution (methods A and B).

5.13.1 Stock standard reference solution

Prepare 25 ml of 1,18 % (11 840 mg/kg) stock formaldehyde solution by adding 0,8 g of 37 % formaldehyde solution (5.3) to 24,2 g of standard diluent.

Assay this formaldehyde solution in accordance with ISO 2227.

Calculate the mass fraction of the formaldehyde in the stock solution in mg/kg.

5.13.2 Series of standard reference solutions

Prepare a series of standard reference solutions ranging from 1 mg/kg to 15 mg/kg of formaldehyde in standard diluent.

5.13.3 Frequency of preparation

Stock and standard reference solutions shall be stored in a refrigerator when not in use. Fresh stock and standard reference solutions shall be prepared weekly.

6 Apparatus

Ordinary laboratory apparatus and glassware, together with the following:

6.1 Amber bottle, of 1 l capacity, capable of filtering out ultraviolet and visible light.

6.2 Sample filter, consisting of a 5 ml sample syringe and a 0,1 μm filter assembly to remove micro-particulate matter from the prepared sample solution.

6.3 High-speed centrifuge, capable of operating at 50 000 r/min (275g) or greater (see 7.1.3).

6.4 Low-speed centrifuge, capable of operating at 1 000 r/min (see 7.1.4).

6.5 Method A

6.5.1 Photoelectric colorimeter or **spectrophotometer** [wavelength (410 ± 5) nm].

6.5.2 Test tubes, **colorimeter tubes** or **photometric cells** (1 cm is suitable).

6.6 Method B

6.6.1 HPLC system, consisting of the following:

6.6.1.1 Liquid chromatograph, having an injection valve, a post-column reactor, a UV/visible detector operating at 410 nm and an isocratic solvent-delivery system capable of delivering a mobile-phase flow of 0,6 ml/min.

The UV/visible detector may incorporate either a tungsten lamp or a deuterium lamp with suitable filters.

6.6.1.2 Post-column reactor, with a reservoir capable of delivering a reagent flow of up to 0,5 ml/min and containing a knitted reaction coil that can be heated to 95 °C and a suitable static mixing tee.

6.6.1.3 Chromatographic column, 250 mm in length × 4,6 mm internal diameter, packed with reversed-phase pH-stable 5 μm C_{18} particles.

If necessary, other suitable columns may be used (e.g. fast acid, 100 mm × 7,8 mm).

6.6.1.4 Chromatographic guard column, 10 mm in length × 4,6 mm internal diameter, packed with reversed-phase pH-stable 5 μm C_{18} particles. If appropriate, other suitable columns may be used.

6.6.1.5 Data system, capable of collecting data at a rate of 1 point/s from a 1 V output detector.

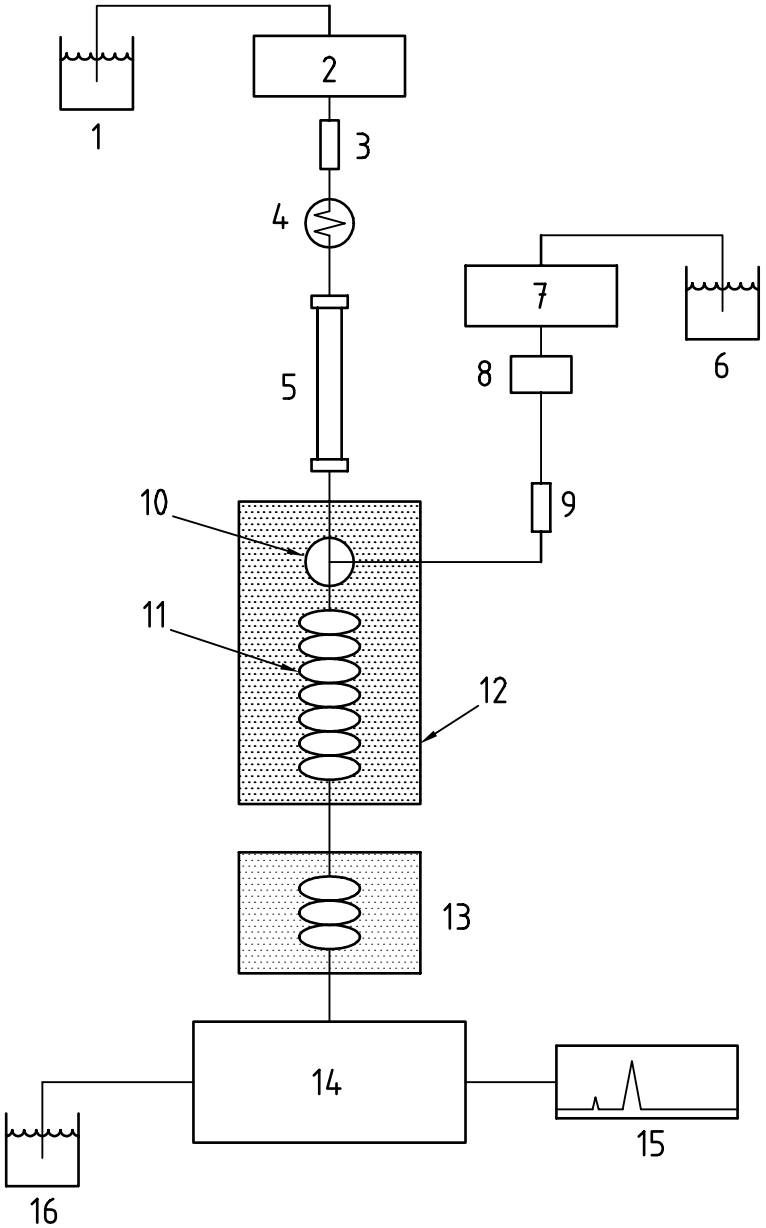
6.6.1.6 Configuration of liquid chromatograph

A suitable in-line check valve is placed between the pump and the injector. The guard and analytical columns are connected to the injector. The outlet of the analytical column is connected to the mixing tee as described in 6.6.1.7.

6.6.1.7 Configuration of post-column reactor (PCR)

The post-column reagent passes through a pulse dampener and an in-line check valve prior to entering one side of the mixing tee. The outlet of the analytical column is connected to the other side of the mixing tee. The reaction coil is connected to the outlet of the mixing tee. Stainless-steel tubing with 0,25 mm inside diameter is used to make the connections. Tubing lengths shall be kept to a minimum. The mixing tee and reaction coil are placed in an oven at 95 °C.

A 40 cm length of 0,25 mm stainless-steel tubing is connected to the outlet of the reaction coil and placed in a stirred ambient-temperature water bath (this configuration acts as a heat exchanger). The outlet end of the stainless-steel tubing is connected to the UV/visible detector. Figure 1 shows a schematic diagram of the system.



Key

1	Mobile phase
2	Pump
3	In-line check valve
4	Injector
5	Column
6	Nash reagent
7	PCR pump
8	Pulse dampener
9	In-line check valve
10	Mixing tee
11	Reaction coil
12	Oven (temperature 95 °C)
13	Water bath (temperature ambient)
14	UV/visible detector
15	Data system
16	Waste

Figure 1 — Schematic diagram of liquid chromatograph and post-column reaction systems

6.6.1.8 Operating conditions

Adjust the liquid chromatograph in accordance with the manufacturer's directions and the following parameters:

— Column temperature: ambient

— Mobile phase: 6,3 mM Na_2HPO_4 (pH = 7) or water

— Flow rate: 0,6 ml/min

— Injection volume: 50 µl

— PCR temperature: 95 °C

— PCR flow rate: 0,5 ml/min

— Detector: UV/visible (410 ± 5) nm

Allow the instrument to equilibrate until a stable baseline is obtained in the data system.

6.6.2 Syringe, of 100 µl capacity.

7 Procedure

7.1 Preparation of test solution

7.1.1 Dilution of test sample

The amount of sample used for the analysis depends on the particular polymer dispersion and on the determination limit necessary.

Weigh, to the nearest 0,1 g, approximately 0,1 g to 1,0 g of sample into a 25 ml volumetric flask. Dilute by addition of approximately 10 ml of standard diluent (5.11) (method B) or water (method A) and shake thoroughly for at least 30 min. The analysis requires a clear, particulate-free, aqueous solution of the diluted polymer dispersion. Three procedures are described (see 7.1.2 to 7.1.4) in order to generate a suitable solution for analysis.

7.1.2 Filtration

Dilute the solution prepared in 7.1.1 to the mark with sample diluent (5.12) (method B) or water (method A) (defined volume). Filter the solution using for example a 0,1 µm filter (6.2). The filtrate is used for the analysis.

NOTE The filtrate can be further diluted with sample diluent if needed.

7.1.3 Centrifugation

Prior to centrifugation, dilute the test solution (7.1.1) to the mark with sample diluent (5.12) (method B) or water (method A). The speed shall be at least 50 000 r/min at 20 °C for 20 min. Filter the supernatant liquid through a 0,1 µm filter (6.2) prior to analysis.

NOTE The filtrate can be further diluted with sample diluent if needed.

7.1.4 Coagulation

Add 2 ml of Carrez I reagent solution (5.6) and 2 ml of Carrez II reagent solution (5.7) to the test solution (7.1.1) to cause coagulation. Dilute to the mark using sample diluent (5.12) (method B) or water (method A) and shake thoroughly for approximately 30 min. Afterwards, filter the supernatant liquid through a 0,1 µm filter. Prior to filtration, the solid may be separated by centrifugation at low speed (1 000 r/min).

NOTE The filtrate can be further diluted with sample diluent if needed.

7.2 Blank solution

Repeat the steps in 7.1 with standard diluent to give a blank solution. Prepare one blank for each procedure used (7.1.2, 7.1.3, 7.1.4).

7.3 Check test (method B)

7.3.1 Determine whether the system is working properly by injecting 50 µl of a 10 mg/kg formaldehyde standard reference solution (see 5.13.2). A typical chromatogram of a 10 mg/kg formaldehyde standard obtained under the conditions outlined in 6.6.1.8 is shown in Figure 2. The peak asymmetry A_s at 10 % peak height for formaldehyde shall be within the range 0,8 to 1,7. A typical retention time for formaldehyde is 6 min.

7.3.2 The run time for the analysis is 10 min. The run time may have to be extended by 20 min to 30 min if late-eluting compounds interfere with the formaldehyde peak in subsequent runs.

7.4 Calibration

7.4.1 Method A

7.4.1.1 Two types of calibration are specified, depending on which test solution preparation procedure is to be used (see 7.1).

If the test solution is to be prepared by filtration (see 7.1.2) or centrifugation (see 7.1.3), treat 5 ml of each prepared standard reference solution directly with 5 ml of Nash reagent as described in 7.5.1.

If the test solution is to be prepared by coagulation (see 7.1.4), pour 20 ml of each standard reference solution into a 25 ml volumetric flask together with 2 ml of Carrez I and 2 ml of Carrez II solution and fill up to the mark with water. Treat 5 ml of each of these resulting mixtures with 5 ml of Nash reagent as described in 7.5.1.

7.4.1.2 Measure the extinction coefficient of the standard solutions and prepare a calibration curve by plotting the extinction coefficient versus the mass fraction of formaldehyde in the standard reference solution (5.13.2). The calibration plot shall be linear.

7.4.2 Method B

7.4.2.1 Inject 50 µl of each standard reference solution (5.13.2) and a reagent blank (standard diluent) (5.11) into the liquid chromatograph.

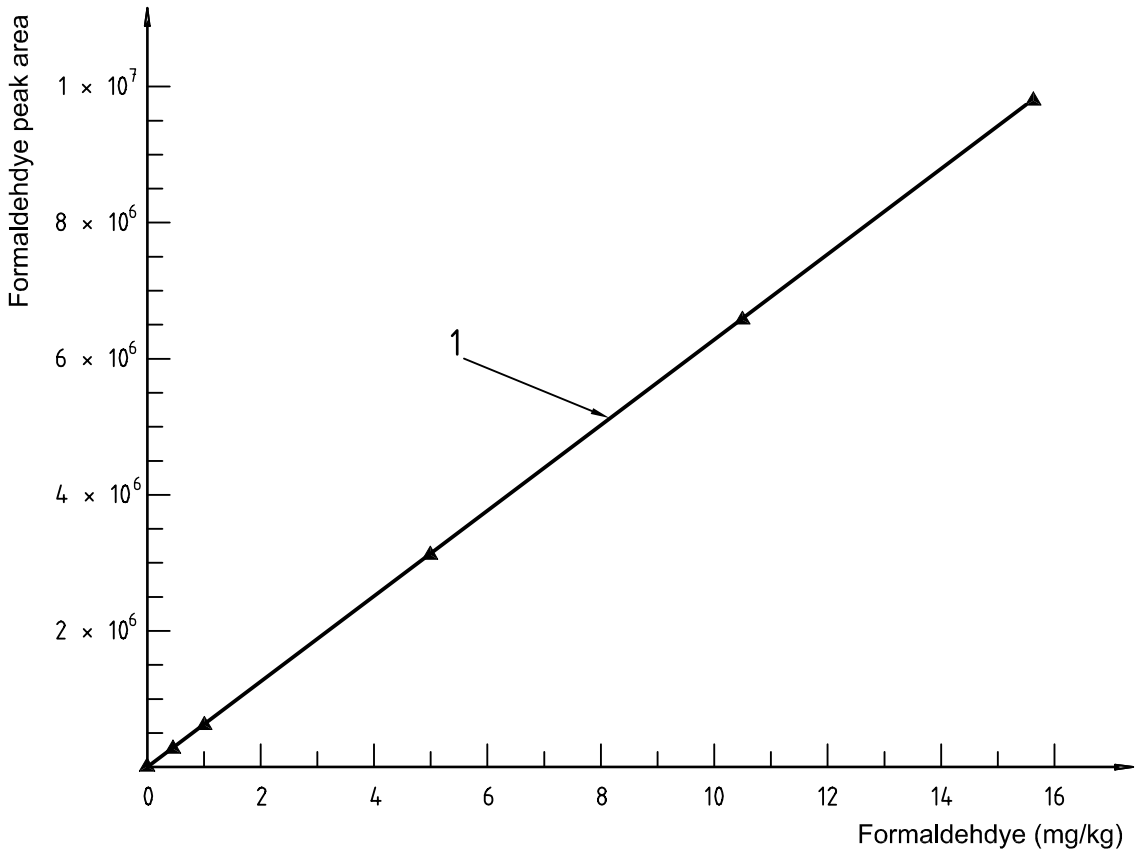
7.4.2.2 The area under the formaldehyde peak in the chromatogram is considered to be a quantitative measure of the amount of formaldehyde present.

7.4.2.3 Measure the area of the formaldehyde peak (see note 1). Prepare a calibration curve by plotting the peak area versus the mass fraction (mg/kg) of formaldehyde as shown in Figure 3. The calibration shall be done to ensure that the entire chromatographic system is operating properly and that the concentration of formaldehyde has not exceeded the linear response range of any part of the system, i.e. column, detector, integrator and other components. The calibration plot shall be linear (see note 2).

NOTE 1 The precision statement in clause 9 was developed from results obtained using electronic integrators or on-line computers. The precision statement may not apply if other methods of integration or peak area measurement are used.

NOTE 2 The precision statement in clause 9 is based on a calibration plot obtained from at least five calibration standards (see Figure 3). The precision statement may not apply (the precision may be worse) if fewer calibration standards are used.

Figure 2 — Chromatogram of a 10 mg/kg **formaldehyde standard reference solution**



Key

1 $y = 19\,093 + (6{,}428 \times 10^5)$
Correlation coefficient = 0,999 97

Figure 3 — Typical calibration curve

7.5 Determination of formaldehyde

7.5.1 Method A

Add 5 ml of the test solution prepared in 7.1.2, 7.1.3 or 7.1.4 to 5 ml of the Nash reagent (5.10). Keep this mixture for 10 min in a water bath regulated at 60 °C[1)]. After cooling to room temperature, measure the extinction coefficient of the solution by means of a spectrophotometer (6.5.1).

7.5.2 Method B

7.5.2.1 Analyse the filtrate prepared in 7.1.2, 7.1.3 or 7.1.4 by injecting 50 µl into the liquid chromatograph.

7.5.2.2 Identify the formaldehyde peak on the chromatogram using the retention time.

7.5.2.3 Measure the formaldehyde peak area (see note 1 to 7.4.2.3).

7.5.2.4 Analyse the reagent blank (standard diluent) (see 5.11) and the blank solution (see 7.2).

1) The conditions used here (10 min/60 °C) differ from the conditions used in Japanese Law 112 (30 min/40 °C). However there is no significant difference between the results obtained by either method.

8 Calculation

8.1 Calculate the mass fraction of formaldehyde in the diluted polymer dispersion, $w_{f,d}$, by reading from the calibration curve the mass fraction of formaldehyde in mg/kg corresponding to the extinction coefficient determined (method A) or the peak area calculated (method B).

8.2 Determine the mass fraction of formaldehyde in the test sample, $w_{f,o}$, by correcting the mass fraction of formaldehyde found in the diluted polymer dispersion for the dilution according to the following equation:

$$w_{f,o} = w_{f,d} \times K_d$$

where

$w_{f,d}$ is the mass fraction of formaldehyde in the diluted polymer dispersion, in mg/kg;

K_d is the dilution factor of the diluted polymer dispersion.

Note that the dilution factor will depend on the particular procedure (7.1.2, 7.1.3 or 7.1.4) used to prepare the test solution.

9 Precision for method B

9.1 Precision estimates

The precision estimates are based on an interlaboratory study in which five different laboratories analysed in duplicate, on four days, four samples of polymer dispersion (see clause 1).

The intralaboratory coefficients of variation are given in Table 1.

Table 1 — Intralaboratory coefficients of variation

Average HCHO mg/kg	**Degrees of freedom**	**Coefficient of variation** %
900	15	4,40
300	15	7,07
10	15	13,34
1	15	25,77

The interlaboratory coefficients of variation are given in Table 2.

Table 2 — Interlaboratory coefficients of variation

Average HCHO mg/kg	**Degrees of freedom**	**Coefficient of variation** %
900	4	5,46
300	4	7,07
10	4	18,83
1	4	27,42

Based on these coefficients, the criteria given in 9.2 and 9.3 can be used for judging the acceptability of results at the 95 % confidence level.

9.2 Repeatability

Two results, each the mean of duplicate determinations, obtained by the same operator on different days should be considered suspect if they differ by more than the values given in Table 3.

Table 3 — Repeatability limits

Average HCHO mg/kg	**Degrees of freedom**	**Coefficient of variation** %	95 % **range** %
900	15	4,40	6,62
300	15	7,07	10,64
10	15	13,34	20,08
1	15	25,77	38,78

9.3 Reproducibility

Two results, each the mean of duplicate determinations, obtained by operators in different laboratories should be considered suspect if they differ by more than the values given in Table 4.

Table 4 — Reproducibility limits

Average HCHO mg/kg	**Degrees of freedom**	**Coefficient of variation** %	95 % **range** %
900	4	5,46	10,70
300	4	7,07	13,86
10	4	18,83	36,91
1	4	27,42	53,74

9.4 Bias

Since there is no accepted reference material suitable for determining the bias for the procedure in this test method, the bias cannot be determined.

10 Test report

The test report shall include at least the following information:

a) a reference to this International Standard;

b) all details necessary for complete identification of the sample analysed;

c) the average (arithmetic mean) of two determinations, in mg/kg, and the difference between the two determinations as an estimation of the precision;

d) the date of the analysis.

Bibliography

[1] ASTM D 1193, *Standard Specification for Reagent Water*.

[2] ASTM D 2194, *Standard Test Method for Concentration of Formaldehyde Solutions*.

[3] ASTM E 682, *Standard Practice for Liquid Chromatography Terms and Relationships*.

ICS 83.080.20

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