
**Plastics — Polymer dispersions —
Determination of free formaldehyde**

Plastiques — Dispersions de polymères — Dosage du formaldéhyde libre

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ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.ch
Web www.iso.ch

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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 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*.

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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.

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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 (C₁₈) 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.

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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 (CH₃CO₂H), glacial.

5.2 Ammonium acetate (CH₃CO₂NH₄).

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

5.4 2,4-Pentanedione (acetyl acetone) (CH₃COCH₂COCH₃).

5.5 Phosphoric acid solution, 33 mM.

Dissolve 2,3 ml of 85 % phosphoric acid (H₃PO₄) 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 (K₄Fe(CN)₆·3H₂O) 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 (ZnSO₄·7H₂O) 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 \pm 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 \times 4,6 mm internal diameter, packed with reversed-phase pH-stable 5 μm C₁₈ particles.

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

6.6.1.4 Chromatographic guard column, 10 mm in length \times 4,6 mm internal diameter, packed with reversed-phase pH-stable 5 μm C₁₈ 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.

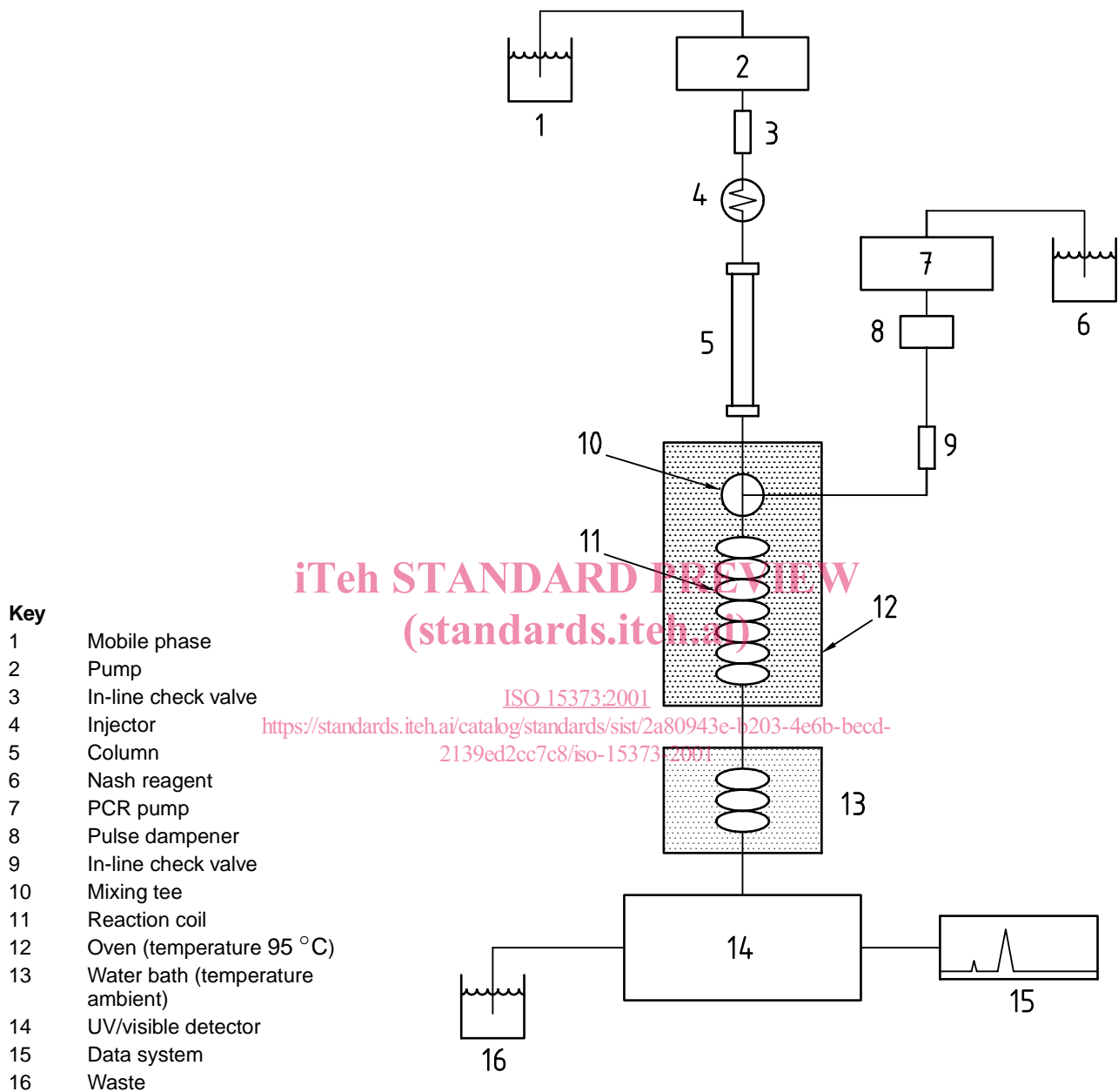


Figure 1 — Schematic diagram of liquid chromatograph and post-column reaction systems