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Plastics — Polymer dispersions — Determination of free formaldehyde

Plastiques — Dispersions de polymères — Dosage du formaldéhyde libre

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO document should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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This document was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 9, *Thermoplastic materials*.

This second edition cancels and replaces the first edition (ISO 15373:2001), which has been technically revised.

The main changes are as follows:

— text is revised according to the latest ISO Directive, Part 2.

— added Figure 1, as illustration of the principle of this method.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Plastics — Polymer dispersions — Determination of free formaldehyde

1 Scope

This document specifies two methods for the determination of free formaldehyde (HCHO) in polymer dispersions.

This document is applicable to acrylic, acrylonitrile butadiene, carboxylated styrene-butadiene and vinyl acetate polymer dispersions. It is also applicable to polymer dispersions of other compositions.

Method A (UV/Vis spectrometer method) is applicable to polymer dispersions with a free-formaldehyde content higher than 10 mg/kg.

Method B (HPLC method) is applicable for determining lower formaldehyde contents or carrying out arbitration analyses.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 2227, *Formaldehyde solutions for industrial use — Determination of formaldehyde content*

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

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

4 Principle

The polymers dispersed in a polymer dispersion are separated from the aqueous phase by filtration, centrifuge or coagulation. The resulting aqueous sample solution containing formaldehyde reacts with 2,4-pentanedione to yield a lutidine derivative (see Figure 1), which can be analysed by UV detector at 410 nm.

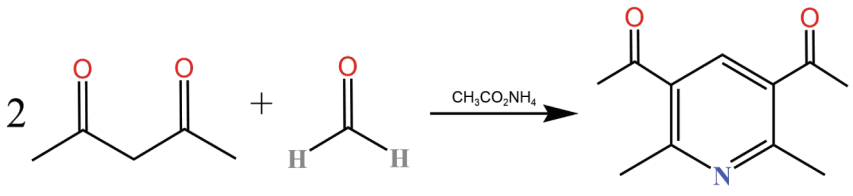


Figure 1 — Reaction of formaldehyde with 2,4-pentanedione

In method A, 2,4-pentanedione is added directly to the resulting aqueous solution. Absorption at 410 nm is measured with a UV/Vis spectrometer. The concentration of formaldehyde is determined using a calibration plot obtained by plotting the absorption at 410 nm of formaldehyde standards against the corresponding formaldehyde concentrations.

In method B, formaldehyde in the resulting aqueous solution 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 and a UV/Vis detector operating at 410 nm. The concentration of free formaldehyde in the resulting aqueous solution is determined using peak areas from the standard and sample chromatograms (calibration by external standard).

5 Interference

5.1 Method A

The following species have been identified as possible interferants in the method:

— acetaldehyde;

— 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.

5.2 Method B

This method is specific 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.

However, to adapt for various composition in different polymer dispersions, extended chromatography run time is recommended to allow for late-eluting compounds in Method B. Compounds which remain on the column after an analysis have potential interference with the formaldehyde peak in subsequent runs.

6 Reagents (method A and B)

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

6.1 Acetic acid (CH_3CO_2H), glacial.

6.2 Ammonium acetate ($CH_3CO_2NH_4$).

6.3 Formaldehyde (HCHO), mass fraction 37 % solution in water.

6.4 2,4-Pentanedione (acetyl acetone) ($CH_3COCH_2COCH_3$).

6.5 Phosphoric acid solution, 33 mmol/l**.**

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

6.6 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.

6.7 Zinc sulfate heptahydrate solution ($ZnSO_4 \cdot 7H_2O$), 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.

6.8 Sodium hydroxide (NaOH), 0,1 mol/l.

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

6.9 Sodium phosphate, dibasic (Na_2HPO_4).

6.10 Nash reagent, post-column reagent, prepared as follows.

6.10.1 Transfer 62,5 g of ammonium acetate (6.2) to a 1 l amber bottle (7.1) 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.

6.10.2 Pipette 7,5 ml glacial acetic acid (6.1) into the bottle. Pipette 5 ml of 2,4-pentanedione (6.4) into the bottle. Add 387,5 ml of water to the bottle and mix thoroughly (45 min of mixing is suggested).

If necessary, other concentrations of ammonium acetate, glacial acetic acid and 2,4-pentanedione in the Nash reagents can be used.

2,4-Pentanedione is light-sensitive. Protect it from light during use. Prepare fresh Nash reagent solution weekly.

6.10.3 Transfer the Nash reagent to the post-column reactor reservoir (7.6.1.2). The reservoir shall be protected from light.

6.10.4 Degas the Nash reagent with a helium sparge.

6.11 Mobile phase and standard diluent, prepared as follows.

6.11.1 Transfer 1,78 g of dibasic sodium phosphate (6.9) 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.

6.11.2 Adjust the pH of the solution in 6.11.1 to 7,0 with 33 mmol/l phosphoric acid (6.5).

6.11.3 Prepare the standard diluent in the same manner described in 6.11.1. and 6.11.2.

6.11.4 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 8.1.4).

6.12 Sample diluent, prepared as follows.

6.12.1 Transfer 1,78 g of dibasic sodium phosphate (6.9) 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.

6.12.2 Measure the pH of the polymer dispersion to ±0,1 pH units, then adjust the pH of the diluent in 6.12.1 to within ±0,1 pH units of the polymer dispersion using either NaOH (6.8) or H_3PO_4 (6.5).

6.13 Standard reference solution, prepared as follows.

6.13.1 Stock standard reference solution

Prepare 25 ml of 1,18 % mass fraction (11,840 mg/kg) stock formaldehyde solution by adding 0,8 g of 37 % formaldehyde solution (6.3) 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.

6.13.2 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. At least 5 different standards shall be prepared for calibration.

6.13.3 Frequency of preparation

Stock and standard reference solutions shall be stored in 4 °C in a refrigerator when not in use. Fresh stock and standard reference solutions shall be prepared weekly.

7 Apparatus

Ordinary laboratory apparatus and glassware, together with the following.

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

7.2 Sample filter, consisting of a 5 ml sample syringe and a filter assembly to remove micro-particulate matter from the prepared sample solution. Filter pore size shall be 0,1 um or smaller.

7.3 High-speed centrifuge, capable of operating at 50,000 r/min (200,000 ×g) or greater (see 8.1.3).

7.4 Low-speed centrifuge, capable of operating at 1,000 r/min (see 8.1.4).

7.5 Method A.

7.5.1 Photoelectric colorimeter or spectrophotometer, with wavelength precision no larger than 0,1 nm at 410 nm.

7.5.2 Cuvette, quartz, path length 1 cm.

7.6 Method B.

7.6.1 HPLC system, consisting of the following.

7.6.1.1 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.

7.6.1.2 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.

7.6.1.3 Chromatographic column, 250 mm in length × 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 × 7,8 mm).

7.6.1.4 **Chromatographic guard column**, 10 mm in length × 4,6 mm internal diameter, packed with reversed-phase pH-stable 5 µm C18 particles. If appropriate, other suitable columns may be used.

7.6.1.5 **Data system**, capable of collecting data.

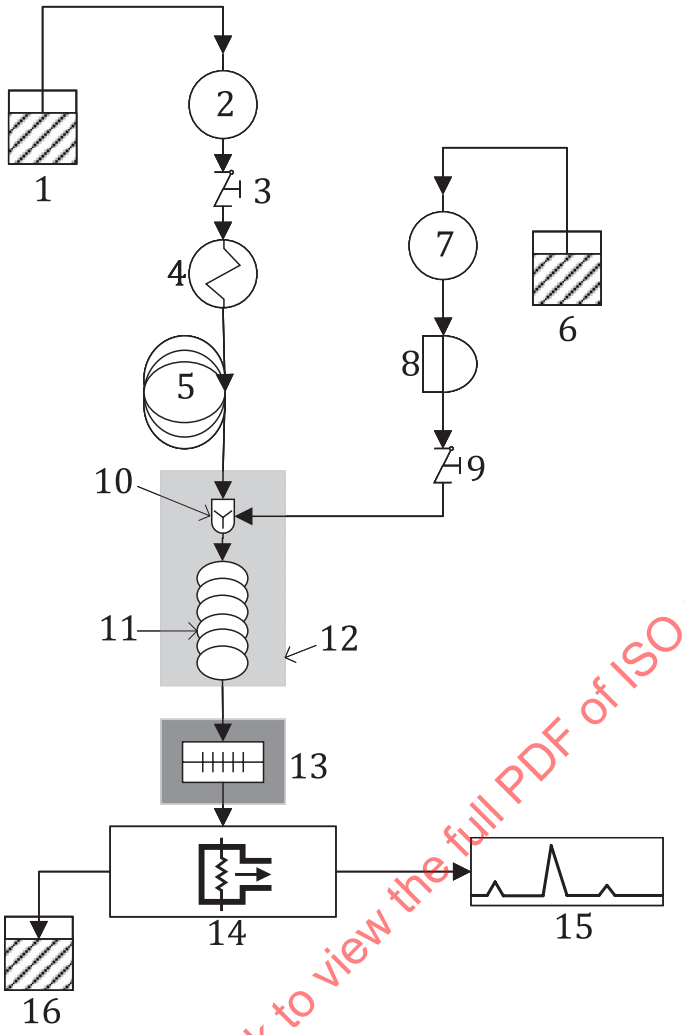
7.6.1.6 Configuration of liquid chromatograph.

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 7.6.1.7.

7.6.1.7 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. The outlet end of the stainless-steel tubing is connected to the UV/Vis detector. Figure 2 shows a schematic diagram of the PCR 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/Vis detector
15 data system
16 waste

Figure 2 — Schematic diagram of liquid chromatograph and post-column reaction systems

7.6.1.8 Operating conditions

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

— Column temperature: ambient

— Mobile phase: 6,3 mmol/l 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 wavelength: 410 nm

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

7.6.2 Syringe, of 100 µl capacity.

8 Procedure

8.1 Preparation of test solution

8.1.1 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 mg, 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 (6.11) (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. Choose one of three the procedures described in 8.1.2 to 8.1.4 to generate test solution for analysis.

8.1.2 Filtration

Dilute the solution prepared in 8.1.1 to the mark with sample diluent (6.12) (method B) or water (method A) (defined volume). Filter the solution using sample filter (7.2). The filtrate is used as test solution.

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

8.1.3 Centrifugation

Prior to centrifugation, dilute the solution prepared in 8.1.1 to the mark with sample diluent (6.12) (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 sample filter (7.2). The filtrate is used as test solution.

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

8.1.4 Coagulation

Add 2 ml of Carrez I reagent solution (6.6) and 2 ml of Carrez II reagent solution (6.7) to the solution prepared in 8.1.1 to cause coagulation. Dilute to the mark using sample diluent (6.12) (method B) or water (method A) and shake thoroughly for approximately 30 min. Afterwards, filter the supernatant liquid through a

sample filter (7.2). The filtrate is used as test solution. 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.

8.2 Blank solution

Repeat the steps in 8.1 with standard diluent and without sample addition to give a blank solution. Prepare one blank for each procedure used (see 8.1.2, 8.1.3, 8.1.4).

8.3 Check test (method B)

8.3.1 Determine whether the system is working properly by injecting 50 µl of a 10 mg/kg formaldehyde standard reference solution (6.13.2). A typical chromatogram of a 10 mg/kg formaldehyde standard obtained under the conditions outlined in 7.6.1.8 is shown in Figure 3. The peak asymmetry 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.

8.3.2 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.

8.4 Calibration

8.4.1 Method A

8.4.1.1 Two types of calibration are specified, depending on which test solution preparation procedure is used in 8.1.

If the test solution is to be prepared by filtration (see 8.1.2) or centrifugation (see 8.1.3), treat 5 ml of each prepared standard reference solution directly with 5 ml of Nash reagent as described in 8.5.1.

If the test solution is to be prepared by coagulation (see 8.1.4), 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 8.5.1.

8.4.1.2 Measure the absorption 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 (6.13.2). The calibration plot shall be linear.

8.4.2 Method B

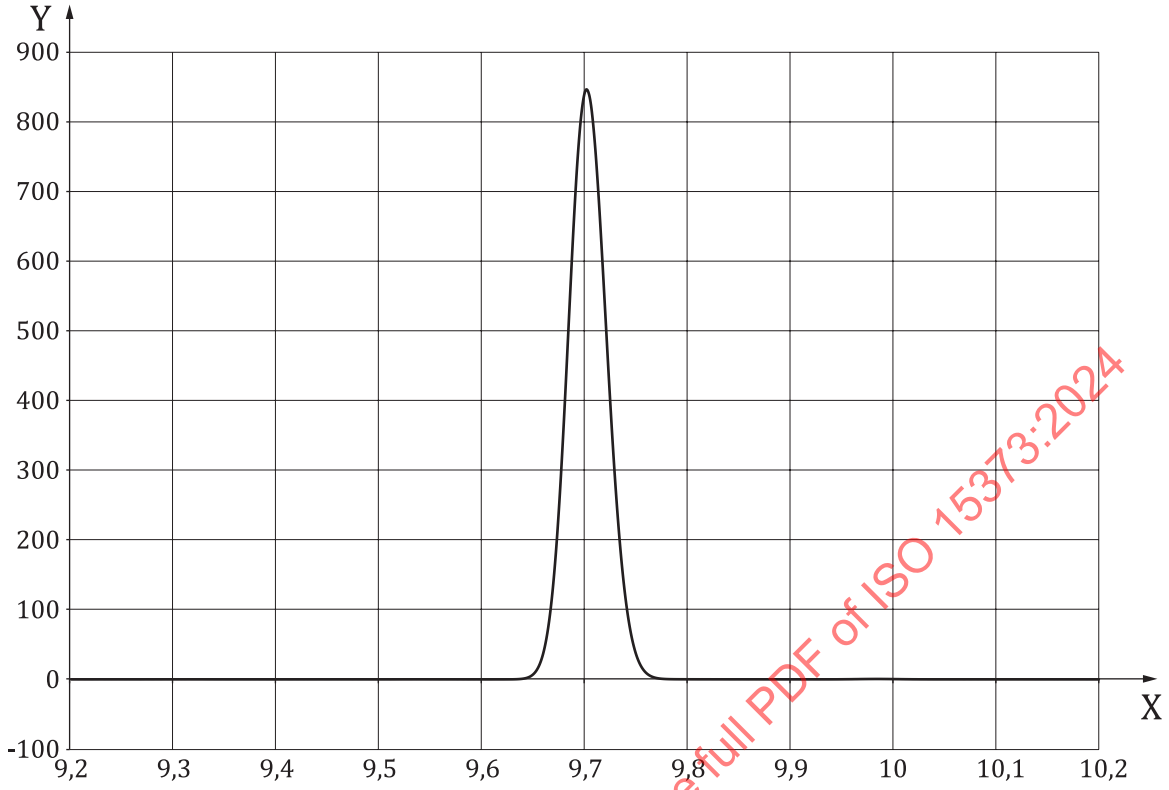
8.4.2.1 Inject 50 µl of each standard reference solution (6.13.2) and a reagent blank (standard diluent) (6.11) into the liquid chromatograph.

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

8.4.2.3 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 4. 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 10 was developed from results obtained using electronic integrators or on-line computers. The precision statement can be inaccurate if other methods of integration or peak area measurement are used.

NOTE 2 The precision statement in Clause 10 is based on a calibration plot obtained from at least five calibration standards (see Figure 4). The precision can be worse than the precision statement if fewer calibration standards are used.



Key

X retention time

Y detector response

Figure 3 — Chromatogram of a 10 mg/kg formaldehyde standard reference solution

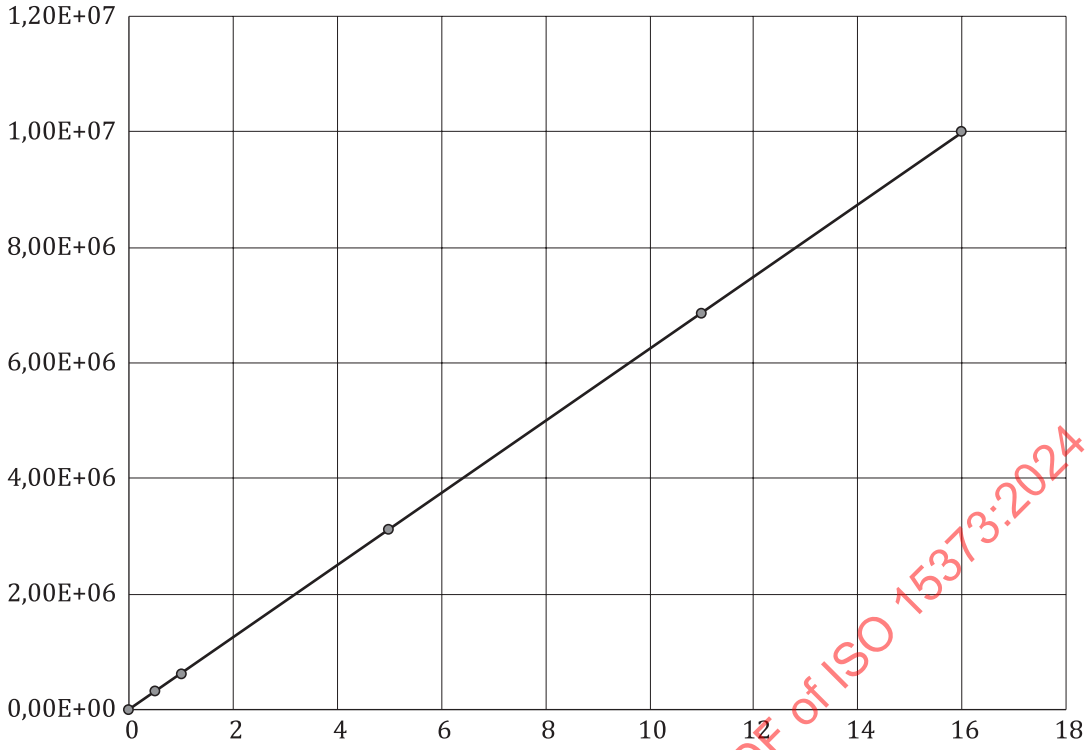


Figure 4 — Typical calibration curve

8.5 Determination of formaldehyde

8.5.1 Method A

Add 5 ml of the test solution prepared in 8.1.2, 8.1.3 or 8.1.4 to 5 ml of the Nash reagent (6.10). Keep this mixture for 10 min in a water bath regulated at 60 °C). After cooling to room temperature, measure the extinction coefficient of the solution by means of a spectrophotometer (7.5.1).

8.5.2 Method B

8.5.2.1 Analyse the test solution prepared in 8.1.2, 8.1.3 or 8.1.4 by injecting 50 µl into the liquid chromatograph.

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

8.5.2.3 Measure the formaldehyde peak area.

8.5.2.4 Analyse the reagent blank (standard diluent) (see 6.11) and the blank solution (see 8.2).

9 Calculation

9.1 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).