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Paints and varnishes — Determination of preservatives in water-dilutable coating materials —

Part 1: Determination of in-can free formaldehyde

Peintures et vernis — Dosage des agents de préservation dans les produits de peinture diluables à l'eau —

Partie 1: Dosage du formaldéhyde libre en pot

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Foreword

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This document was prepared by Technical Committee ISO/TC 35, *Paints and varnishes*, Subcommittee SC 16, *Chemical analysis*, in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 139, *Paints and varnishes,* in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

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Paints and varnishes — Determination of preservatives in water-dilutable coating materials —

Part 1:
Determination of in-can free formaldehyde

1 Scope

This document specifies the apparatus and analytical methods for determining the concentration of in-can free formaldehyde in water-dilutable coating materials.

This document can also be applied to polymer dispersions.

The determination method A for in-can free formaldehyde described in this document is only of limited suitability for pigmented systems, as the inherent coloration of the material can have an influence on the detection.

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 1513, *Paints and varnishes — Examination and preparation of test samples*

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

ISO 15528, *Paints, varnishes and raw materials for paints and varnishes — Sampling*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

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/

3.1
ready for use
state of a product when it is mixed in accordance with the manufacturer's instructions in the correct proportions and thinned if required using the correct thinners so that it is ready for application by the approved method

[SOURCE: ISO 11890-2:2020, 3.7]

3.2
in-can free formaldehyde content
concentration of formaldehyde which is available in the coating as an *in-can preservative* (3.9) as determined by:

— method A of this document, i.e. photometric detection after derivatization with acetylacetone;

— method B of this document, i.e. liquid chromatography detection after derivatization with DNPH (2,4-dinitrophenyl-hydrazine); or

— method C of this document i.e. liquid chromatography detection with post-column derivatization with acetylacetone; where water is used as an extraction solvent for all three methods

Note 1 to entry: In-can free formaldehyde content corresponds to the amount of formaldehyde in milligrams, based on 1 kg of *coating material* (3.4) or polymer dispersion, which is available unbound in the sample at the time of derivatization.

Note 2 to entry: Since the free formaldehyde is in equilibrium with bound formaldehyde and the equilibrium can be influenced by the solvent, the content of free formaldehyde in water can differ from that in another solvent. This definition for in-can free formaldehyde content is only valid with respect to water as the extraction solvent.

3.3
in-can total formaldehyde content
concentration of free and bound formaldehyde in the *coating material* (3.4)

3.4
coating material
DEPRECATED: coating
product, in liquid, paste or powder form, that, when applied to a substrate, forms a layer possessing protective, decorative and/or other specific properties

[SOURCE: ISO 4618:2023, 3.48]

3.5
water-dilutable coating material
water-reducible coating material
water-based coating material
water-borne coating material
water-thinnable coating material
DEPRECATED: water paint
coating material (3.4) whose viscosity is reduced by the addition of water

[SOURCE: ISO 4618:2023, 3.272]

3.6
formaldehyde depot substance
compound that releases formaldehyde over a long period of time

3.7
extinction
attenuation of a light beam traversing a medium through absorption and scattering

Note 1 to entry: Extinction depends on the wavelength of the radiation.

[SOURCE: ISO 13320:2020, 3.1.9]

3.8
preservative
substance that prevents the growth of undesirable microorganisms

[SOURCE: ISO 8124-7:2015, 3.6]

3.9
in-can preservative
biocide used to prevent growth of microorganisms during storage of a stock solution of a *coating material* (3.4) or *water-based coating material* (3.5)

[SOURCE: ISO 4618:2023, 3.141]

4 Principle

4.1 General

This document describes three methods for the determination of in-can free formaldehyde in coating materials which have been validated to show comparable results for selected samples with respect to their comparability limits statistically for methods A and B and with a single comparison for method C.

4.2 Equilibria of in-can free formaldehyde in the coating matrix

When a formaldehyde depot substance is added to a coating material, equilibrium is established between the formaldehyde bound to the formaldehyde depot substance and the in-can free formaldehyde. This equilibrium depends on the pH value, the coating matrix, the formaldehyde depot substance and the temperature. Furthermore, in water-dilutable coating materials, there is also equilibrium between the in-can free formaldehyde and the matrix itself. The in-can free formaldehyde can undergo a variety of equilibrium reactions, e.g. with water to form a hydrate or with other formaldehyde molecules to form trimers.

A distinction shall be made in a coating material between the in-can total formaldehyde content and the in-can free formaldehyde content. In this document, the in-can free formaldehyde content is understood to be the formaldehyde concentration determined by either:

— method A, i.e. derivatization with acetylacetone and subsequent photometric detection and quantification;

— method B, i.e. derivatization with DNPH and subsequent detection and quantification with liquid chromatography-ultraviolet/visible light detector (LC-UV/VIS) analysis; or

— method C, i.e. liquid chromatography (LC) separation followed by post-column derivatization with acetylacetone and subsequent quantification with ultraviolet/visible light detector (UV/VIS) detection.

4.3 Equilibria of in-can free formaldehyde during extraction

In addition to the equilibria in the coating matrix mentioned in 4.2, during extraction, the equilibrium of in-can free formaldehyde is also affected by the extraction solvent.

Depending on the nature of the extraction solvent, the sample/solvent ratio, extraction time and pH value, the equilibrium of bound and free in-can formaldehyde can be shifted to either side. Therefore, it is crucial to select the appropriate extraction solvent and extraction conditions.

4.4 Equilibria of in-can free formaldehyde during derivatization

The in-can free formaldehyde in the extract (or after chromatographic separation) is derivatized by chemical reaction with a derivatizing agent. The reaction is also an equilibrium reaction. To ensure complete derivatization, an excess of derivatization agent is added.

4.5 Principle of Method A: Derivatization with acetylacetone (ACAC) combined with photometric detection

4.5.1 Derivatization with ACAC

In order to enable photometric detection of formaldehyde, derivatization shall be carried out. Derivatization introduces a chromophore after reaction with formaldehyde, which has the property to absorb ultraviolet (UV) or visible (VIS) light.

The derivatization is performed prior to the photometric analysis (pre-column derivatization).

In-can free formaldehyde is derivatised to 3,5-diacetyl-1,4-dihydrolutidine by using ACAC and ammonium ions (Hantzsch reaction). The absorption maximum of the compound is at a wavelength of 412 nm.

4.5.2 Detection and quantification with a spectral photometer

A spectral photometer is applied to quantify the formaldehyde-ACAC reaction product, which, in turn, can be used to calculate the concentration of in-can free formaldehyde in the coating matrix.

4.6 Principle of Method B: Derivatization with dinitrophenylhydrazine (DNPH) combined with liquid chromatography (LC) separation and UV/VIS detection

4.6.1 Derivatization with DNPH

The in-can free formaldehyde can be derivatized with DNPH leading to the formation of a compound that can be separated by liquid chromatography and detected with a UV/VIS-detector at 360 nm.

4.6.2 Separation, detection and quantification with LC-UV/VIS

Liquid chromatography is applied to separate the different aldehyde-DNPH reaction products. Subsequent UV/VIS detection is used to identify and quantify the concentration of the formaldehyde-DNPH reaction product, which enables the calculation of the in-can free formaldehyde content in the coating sample.

If derivatization with DNPH is used, the determination of in-can free formaldehyde content shall be performed by LC-UV/VIS analysis, since the reaction with DNPH is also sensitive to other aldehydes, which can interfere when using a determination with a spectral photometer.

4.7 Principle of Method C: Liquid chromatography (LC) separation followed by post-column derivatization with ACAC and subsequent quantification with UV/VIS detection

4.7.1 Separation of free formaldehyde by liquid chromatography

Liquid chromatography is performed prior to derivatization. It is applied to separate free formaldehyde from all other components present in the water extract to avoid interferences in the detection.

4.7.2 Post-column derivatization with acetylacetone (ACAC) and quantification with UV/VIS detection

To enable detection of the separated formaldehyde, derivatization is performed as described in 4.5.1, in this case by mixing ACAC to the column outlet. Quantification is done in-line with UV/VIS detection at the maximum absorption of the formaldehyde ACAC reaction product, i.e. 412 nm.

5 Apparatus

5.1 General

The usual laboratory apparatus and, in particular, the following apparatus stated in 5.2 to 5.6 shall be used.

5.2 General apparatus

5.2.1 Precision scale, capable of weighing to an accuracy of 0,000 1 g.

5.2.2 Suitable volumetric flasks for calibration, with ground-glass stoppers.

5.2.3 Suitable pipettes.

5.3 Apparatus for extraction

5.3.1 Centrifuge, capable of producing a clear supernatant.