SLOVENSKI STANDARD
oSIST prEN ISO 7012-3:2024

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Barve in laki - Določanje konzervansov v premazih, topnih v vodi - 3. del: Določanje izotiazolinonov v pločevinki/posodi s tekočinsko kromatografijo LC/UV in LC-MS-MS (ISO/DIS 7012-3:2024)

Paints and varnishes - Determination of preservatives in water-dilutable coating materials - Part 3: Determination of in-can isothiazolinones with LC/UV and LC-MS-MS (ISO/DIS 7012-3:2024)

Beschichtungsstoffe - Bestimmung von Konservierungsmitteln in wasserverdünnbaren Beschichtungsstoffen - Teil 3: Bestimmung von Isothiazolinonen im Gebinde mit LC-UV und LC□MS□MS (ISO/DIS 7012-3:2024)

Peintures et vernis - Dosage des agents de préservation dans les produits de peinture diluables à l'eau - Partie 3: Dosage des isothiazolinones en pot par CL-UV et CL-SM (ISO/DIS 7012-3:2024)

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ICS:

87.040	Barve in laki	Paints and varnishes

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ISO/DIS 7012-3

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

Part 3: Determination of in-can isothiazolinones with LC-UV and LC-MS

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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.

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 documents 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).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 35, *Paints and varnishes*, Subcommittee SC 16, *Chemical analysis*.

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

Part 3: Determination of in-can isothiazolinones with LC-UV and LC-MS

1 Scope

This document specifies the apparatus and the analytical method for determining the content of in-can isothiazolinone preservatives in water-dilutable coating materials or related products.

NOTE 1 The document is also applicable for polymer dispersions.

NOTE 2 The document is in general applicable for OIT and DCOIT. However, the standard was not validated for these compounds in the round robin test. There are national standards covering these compounds.

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 4618, *Paints and varnishes — Vocabulary*

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

ISO 7012-1, *Paints and varnishes — Determination of preservatives in water-dilutable coating materials — Part 1: Determination of in-can free formaldehyde*

ISO 7012-2, *Paints and varnishes — Determination of preservatives in water-dilutable coating materials — Part 2: Determination of in-can total formaldehyde*

3 Terms and definitions

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

ISO and IEC maintain terminological 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, term 3.7]

3.2
water-thinnable coating material
water-dilutable coating material
water-reducible coating material
water-based coating material
water-borne coating material
DEPRECATED: water paint
coating material whose viscosity is reduced by the addition of water

[SOURCE: ISO 4618:2023, term 3.272]

3.3
detection limit of instrument
three times the standard deviation of the result obtained in the blank test using a specific instrument

[SOURCE: ISO 8124-5: 2015, term 3.5]

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

[SOURCE: ISO 4618:2023, term 3.141]

4 Principle

The sample is extracted with suitable dilution solvent using an appropriate homogenization such as ultrasonic water bath. The extract is purified by centrifugation, after which the isothiazolinones are identified and quantified by liquid chromatography (LC) in combination with UV/VIS detection or different mass spectrometry detectors. This includes liquid chromatography-tandem mass spectrometry (LC-MS/MS) and liquid chromatography-single quad mass spectrometry (LC-MS).

For the purposes of this document, LC also designates high-performance liquid chromatography (HPLC) or ultra-performance liquid chromatography (e.g., UPLC or UHPLC).

Atmospheric pressure chemical ionisation (APCI) and electrospray ionisation (ESI) have been found suitable. Other ionization techniques and mass analysers with sufficient performance can also be used.

NOTE The difference of the results is expected to be smaller than the reproducibility limits of the methods for a standard water-borne coating sample. In the round robin test according to Annex E, the determination by the LC-UV method and the LC-MS or LC-MS/MS method turned out to deliver comparable results within the reproducibility limits of the methods, validating the above statement.

5 Apparatus

5.1 Equipment for extraction and sample preparation

5.1.1 High speed centrifuge, with an acceleration at a suitable speed (typically 50 000 ×g).

5.1.2 Ultrasonic water bath, with a frequency from 35 kHz to 45 kHz.

5.1.3 Analytical balance, capable of weighing to an accuracy of 0.1mg.

5.1.4 One-mark volumetric flask, of 10 ml, 25 ml, 50 ml and 100 ml nominal capacity.

5.1.5 Pipettes, suitable single-volume pipettes, graduated pipettes and Pasteur pipettes.

5.1.6 Centrifuge tubes, with a suitable snap /screw cap.

5.1.7 Glass autosampler vials, with a suitable snap /screw pre-slit cap, 2 ml.

5.1.8 Syringe, minimum volume 2 ml.

5.1.9 Filtration membrane, about 0.22 µm pore size.

5.2 LC-UV/VIS system

5.2.1 LC system, equipped with a sample injection system, a solvent pumping system capable of mixing solvents, a sample compartment capable of maintaining required temperature and a temperature-controlled column compartment, a degassing system and data processing software. An LC system that is capable of performing at the flows, pressures, controlled temperatures, sample volumes and other requirements of the document shall be used.

5.2.2 Analytical column, reverse phase C18 particle columns were used to develop this test method. Any column that achieves adequate resolution may be used. The retention times and order of elution may change depending on the column used and need to be monitored.

5.2.3 UV/VIS detector, a UV/VIS detector or optionally a diode array detector (DAD).

5.3 LC-MS/MS or LC-MS system

5.3.1 LC system, equipped with a sample injection system, a solvent pumping system capable of mixing solvents, a sample compartment capable of maintaining required temperature and a temperature-controlled column compartment, a degassing system and data processing software. An LC system that is capable of performing at the flows, pressures, controlled temperatures, sample volumes, and other requirements of the document shall be used.

5.3.2 Analytical column, reverse phase C18 particle columns were used to develop this test method. Any column that achieves adequate resolution may be used. The retention times and order of elution may change depending on the column used and need to be monitored.

5.3.3 MS/MS or MS-system, equipped with APCI or ESI. Other ionization techniques and mass analysers with sufficient performance can also be used.

6 Reagents and materials

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of grade 1 in accordance with ISO 3696. Solvents shall be of a suitable quality for LC-UV/VIS and LC-MS, i.e. LC-MS grade for LC-MS analysis.

6.1 Reference substances: MIT(CAS no.: 2682-20-4), CMIT(CAS no.: 26172-55-4), BIT(CAS no.: 2634-33-5).

6.2 Methanol (CAS no. : 67-56-1).

6.3 Acetonitrile (CAS no.: 75-05-8).

6.4 Formic acid (CAS no.: 64-18-6).

6.5 Acetic acid, > 99% (CAS no.: 64-19-7) (optional for better recovery rates).

NOTE The acetic acid is found useful to improve the recovery rate by loosening up the structure of the emulsion paint.

6.6 Ammonium acetate (CAS no.: 631-61-8)**.**

6.7 Precipitating agent (optional for better precipitation when using LC-UV/VIS), e.g. aluminum sulphate > 98%, Carrez reagent.

A precipitating agent (e.g., aluminum sulphate, Carrez reagent) can be used to clean up the sample solution after the extration. In this case tests must be carried out to ensure that the use of the precipitating agent does not reduce the recovery rate as compared to the analysis without precipitation agent.

6.8 Dilution solvent

Use a solvent suitable for diluting the sample. It shall have a purity of at least 99% by mass or shall be of known purity, and it shall not contain any substances which interfere with the determination, e.g., causing overlapping peaks in the chromatogram. Methanol and mixture of water and methanol (1:1 by volume) has been found suitable.

Alternatively, other suitable solvents can also be used. However, it should be ensured that the sample does not agglomerate, which can lead to the inclusion of preservatives and thus to analytical errors.

6.9 Internal Standard (ISTD) for LC-MS method

If used, internal standard should be added at the extraction step and to standard working solutions.

Use as much as possible isotope labelled internal standards, if commercially available at a reasonable price.

6.10 Calibration standard solutions

6.10.1 General

The calibration standard solutions should be prepared in the same dilution solvent as the final sample solution. All standard solutions used in this method shall be prepared as described below.

Commercially available standard stock solutions with known content can also be used. If necessary the content of these solutions must be determined using certified/traceable standards (see 6.1 Reference substances).

NOTE If commercially available standard stock solution is used, standard working solutions are prepared in one-mark volumetric flask (5.1.4) by diluting the stock solution with dilution solvent (6.8).

6.10.2 Standard stock solutions

Weigh each of the target reference substances (6.1) into a 100 ml one-mark volumetric flask (5.1.4) at concentrations that are sufficiently high to allow the preparation of standard working solutions, fill up to the mark with dilution solvent (6.8), let them dissolve completely. Transfer the standard stock solutions to amber-glass flask and seal with glass cap or PTFE-coated cap, seal the bottle neck again with flexible laboratory sealing film. The preparation of standard stock solutions has to be repeated after a time period that needs to be specified in the laboratory, after which a degradation can occur.

NOTE Normally, a stock solution can be kept in the refrigerator at 2°C to 6°C in the dark for up to 1 month, when stability has been proven or according to the expire date of the producer.