SLOVENSKI STANDARD
oSIST prEN 17845:2022

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Gradbeni proizvodi - Ocenjevanje sproščanja nevarnih snovi - Določevanje ostankov biocidov s tekočinsko kromatografijo in tandemsko masno spektrometrijo (LC-MS/MS)

Construction products: Assessment of release of dangerous substances - Determination of biocide residues using LC-MS/MS

Bauprodukte: Bewertung der Freisetzung von gefährlichen Stoffen - Bestimmung von Biozid-Rückständen mittels LC-MS/MS

Produits de construction - Évaluation des émissions de substances dangereuses - Détermination de la teneur en biocides par LC-MS/MS

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

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European foreword

This document (prEN 17845:2022) has been prepared by Technical Committee CEN/TC 351 “Construction products - Assessment of release of dangerous substances”, the secretariat of which is held by NEN.

This document is currently submitted to the CEN Enquiry.

This document has been prepared under a Standardization Request given to CEN by the European Commission and the European Free Trade Association.

Introduction

This document deals with the determination of the content of biocides in construction products and eluates using liquid chromatography and tandem mass spectrometric detection (LC-MS/MS).

Following an extended evaluation of available methods for content and eluate analysis in construction products (CEN/TR 16045 [1]) and subsequent method evaluation in the robustness validation [2] it was concluded that eluate analysis and content analysis for biocides can be based on EN 15637 [3] after some modifications.

This document is part of a modular horizontal approach and belongs to the analytical step. An overview of all modules which belong to a chain of measurement and the manner how modules are selected is given in CEN/TR 16220 [4].

In the growing amount of product and sector-oriented test methods it was recognized that many steps in test procedures are or could be used in test procedures for many products, materials and sectors. It was supposed that, by careful determination of these steps and selection of specific questions within these steps, elements of the test procedure could be described in a way that can be used for all materials and products or for all materials and products with certain specifications.

In this context a horizontal modular approach is adopted in CEN/TC 351. “Horizontal” means that the methods can be used for a wide range of materials and products with certain properties. “Modular” means that a test standard developed in this approach concerns a specific step in assessing a property and not the whole “chain of measurement” (from sampling to analyses). A beneficial feature of this approach is that “modules” can be replaced by better ones without jeopardizing the standard “chain”.

The use of modular horizontal standards implies the drawing of test schemes as well. Before executing a test on a certain material or product to determine certain characteristics, it is necessary to draw up a protocol in which the adequate modules are selected and together form the basis for the entire test procedure.

1 Scope

This document describes a method for the determination of the content of biocides in construction products, (either finished (dried) or in a ready-to-use state) and in eluates thereof, using liquid chromatography and tandem mass spectrometric detection (LC-MS/MS).

For content analysis liquid chromatography with UV-detection can also be used, if sufficient sensitivity and selectivity is ensured (see Annex A).

The method in this document is validated for the product types listed in Annex D. For eluate analysis quantification limits of 0,1 µg/l can be achieved.

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.

prEN 16637-2, *Construction products: Assessment of release of dangerous substances — Part 2: Horizontal dynamic surface leaching test*

prEN 16637-3, *Construction products: Assessment of release of dangerous substances — Part 3: Horizontal up-flow percolation test*

EN 16687:2015, *Construction products — Assessment of release of dangerous substances — Terminology*

EN 17087, *Construction products: Assessment of release of dangerous substances — Preparation of test portions from the laboratory sample for testing of release and analysis of content*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in EN 16687:2015 and the following 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
blank value
test result obtained by carrying out the test procedure in the absence of a test portion

Note 1 to entry: The blank value is expressed in the same units as for presenting the test results as usual for that test.

[SOURCE: EN 16687:2015, 4.1.10]

3.2
extract
solution resulting from extraction of a sample with a solvent

[SOURCE: CEN/TR 16045:2010, 2.2.4]

3.3
extraction
dissolution of substances in a solvent for subsequent chemical analysis

Note 1 to entry: Extraction is usually done with an organic solvent to extract organic substances for chemical analysis or for special analysis of inorganic substances.

[SOURCE: CEN/TR 16045:2010, 2.2.5]

3.4
laboratory sample
sample or subsample(s) sent to or received by the laboratory

[SOURCE: EN 16687:2015, 3.2.1]

3.5
method detection limit
MDL
smallest analyte concentration that can be detected with a specified analytical method including sample preparation with a defined statistical probability

[SOURCE: EN ISO 17294-1:2006, 3.12, modified – "including sample preparation" added, symbol replaced by abbreviation]

3.6
product matrix
main composition of the product dictating the manner of sample preparation and the type of digestion or extraction for later chemical analysis

Note 1 to entry: For construction products for example the following product matrices can be distinguished:

— bituminous products;
— metals;
— plastics/rubbers;
— silica-based products;
— wood-based products.

[SOURCE: CEN/TR 16045:2010, 2.2.6; edited]

3.7
sample
portion of material selected from a larger quantity of material

[SOURCE: EN 16687:2015, 3.1.5]

3.8
test portion
analytical portion
amount of the test sample taken for testing/analysis purposes, usually of known weight or volume

[SOURCE: EN 16687:2015, 3.2.3]

3.9
test sample
sample, prepared from the laboratory sample, from which test portions are removed for testing or analysis

[SOURCE: EN 16687:2015, 3.2.2]

3.10
bitumen
very viscous liquid or solid, mainly consisting of hydrocarbons or their derivatives, that is virtually fully soluble in carbon disulphide

3.11
asphalt
natural or artificial mixture of bitumen and mineral materials

3.12
Soxhlet extraction
chemical pre-treatment of a solid subsample, where the organic compounds to be determined are dissolved by the Soxhlet technique

3.13
final extract
solution that is obtained after reprocessing the Soxhlet extract through a purification stage

3.14
external standard
known quantity of the target analytes that is measured in the same series as the solution to be measured and is used for identification and quantification

3.15
internal standard
known quantity of a substance (where applicable deuterated) not present in the sample, which is added to the analysis sample in order to determine the recovery

4 Abbreviations

For the purposes of this document, the following abbreviations apply.

EOTA	European Organisation of Technical Assessment
LC	Liquid chromatography
MS	Mass spectrometry; Mass selective detection
TR	Technical Report (ISO, CEN or EOTA)
TS	Technical Specification (ISO, CEN or EOTA)

5 Principle

Quantification of biocides is performed by liquid chromatography with tandem mass spectrometric detection (LC-MS/MS), using electrospray ionization. Eluates are injected directly into the LC-MS system.

Solid and pasty samples are extracted with methanol or a methanol/water mixture. Clean up may be applied when necessary by solid phase supported liquid-liquid extraction.

To achieve the required selectivity the mass spectrometer is operated in the multiple reaction monitoring mode (MRM).

6 Sample preparation

To obtain test samples for extraction (and analysis) guidance on sample preparation as specified in EN 17087 shall be applied.

Precautions shall be taken before and during transport of the laboratory sample as well as during the time in which the samples are preserved in the laboratory before being analysed, to avoid alteration of the sample (see CEN/TR 16220).

Extracts are susceptible to change due to physical or chemical reactions which can take place between the time of extraction and the analysis.

It is therefore essential to take the necessary precautions to minimize these reactions and in the case of many parameters to analyse the extract with a minimum of delay. The maximum delay is given in the respective analytical standards.

7 Reagents

Use reagents of recognized analytical grade, unless otherwise specified. Take every precaution to avoid possible contamination of water, solvents, inorganic salts, etc.

7.1 Additive for LC-eluent depending on method used, e.g. ammonium formate, formic acid, acetic acid.

7.2 Water, HPLC quality.

7.3 Dichloromethane, for biocide analysis.

7.4 Methanol, HPLC quality.

7.5 Internal Standard (ISTD) solutions in methanol, mass concentration ρ = 10 µg/ml to 50 µg/ml[1].

Use as much as possible isotope labelled internal standards, if available and obtainable at reasonable price. The internal standard solution should be added at the extraction step and to standard solutions.

7.6 Biocide stock solutions.

Prepare individual stock solutions of analytical standards at concentrations that are sufficiently high to allow the preparation of complex biocide mixtures. The solvent used shall not negatively influence the stability of the biocides employed.

Usually, store stock solutions at ~ −18 °C. Check the stability of stock solutions during storage regularly. In some cases, the addition of acids or bases is helpful to enhance stability and extend the acceptable storage period.

7.7 Biocide mixtures.

Because of the broad applicability of this method and due to the partly divergent pH-stability of biocides, analyte mixtures of different composition might be needed. These are prepared by mixing together defined volumes of the required biocide stock solutions (7.6) and appropriately diluting them with methanol. The analyte concentrations in this mixture should be sufficient to allow the preparation of the required matrix matched standards (see 7.8.3) with moderate dilution of the blank sample extract (e.g. less than 20 %).

Usually, biocide mixtures are stored at approximately −18 °C. Since the stability of the biocides in the mixture can be lower than in stock solutions, stability has to be checked regularly. In some cases, the addition of acids or bases is helpful to enhance stability and extend acceptable storage times.

7.8 Standard solutions.

7.8.1 Standard solutions prepared in pure solvent (solvent-based standards).

Solvent-based standards are prepared by mixing a certain volume of methanol with known amounts of biocide mixtures (7.7). The preparation of multiple standards of different biocide concentration is useful to cover a broad concentration range.

NOTE The linear range of calibration depends on the sensitivity of the instrument and the MS signal response of the biocide. A calibration range of 0,1 µg/l to 100 µg/l correlates to a biocide content of 0,3 mg/kg to 300 mg/kg when a 10 g sample is employed (see 9.3.1).

7.8.2 Standard solutions with internal standard prepared in pure solvent.

Solvent-based standards with ISTD are prepared by mixing a certain volume of methanol with known amounts of biocide mixtures (7.7) and a fixed volume of internal standard solution (7.5).

The volume used shall result in that concentration of ISTD which is obtained in the final extracts after sample extraction and clean-up (see 9.2 and 9.3). The concentration of internal standard in the final extract ($c_{\mathrm{ISTD}}^{\mathrm{sample}}$) is calculated using Formula (1). The preparation of multiple standards of different biocide concentration but with constant ISTD concentration is useful to cover a broad concentration range.

$$c_{\mathrm{ISTD}}^{\mathrm{sample}} = \frac{V_{\mathrm{ISTD}} \times c_{\mathrm{ISTD}} \times V_1}{V_{\mathrm{ex}} \times V_{\mathrm{end}}} \quad (1)$$

where

$c_{\mathrm{ISTD}}^{\mathrm{sample}}$ is the concentration of internal standard in the final extract, in µg/ml;

V_{ISTD} is the volume of internal standard solution (7.5) added to the test portion, in ml;

c_{ISTD} is the concentration of internal standard solution (7.5), in µg/ml;

V_1 is the volume used for solid supported liquid/liquid extraction, in ml (here: 5 ml);

V_{ex} is the total volume of extraction solvents, in ml (here: 30 ml);

V_{end} is the final volume of extract obtained after clean-up, in ml (here: 0,5 ml).

In case no clean-up is applied Formula (1) simplifies to:

$$c_{\mathrm{ISTD}}^{\mathrm{sample}} = \frac{V_{\mathrm{ISTD}} \times c_{\mathrm{ISTD}}}{V_{\mathrm{ex}}} \quad (1')$$