SLOVENSKI STANDARD
oSIST prEN 17844:2022

01-junij-2022

Gradbeni proizvodi - Ocenjevanje sproščanja nevarnih snovi - Določevanje policikličnih aromatskih ogljikovodikov (PAH), benzena, toluena, etilbenzena in ksilena (BTEX) - Plinska kromatografska metoda z masno spektrometrijsko detekcijo

Construction products: Assessment of release of dangerous substances - Determination of the content of polycyclic aromatic hydrocarbons (PAH) and of benzene, toluene, ethylbenzene and xylenes (BTEX) - Gas chromatographic method with mass spectrometric detection

Bauprodukte: Bewertung der Freisetzung von gefährlichen Stoffen - Bestimmung des Gehalts an polyzyklischen aromatischen Kohlenwasserstoffen (PAK) und an Benzol, Toluol, Ethylbenzol und Xylol (BTEX) - Gas-chromatographisches Verfahren mit massenspektrometrischer Detektion

Produits de construction - Évaluation de l'émission de substances dangereuses - Détermination de la teneur en hydrocarbures aromatiques polycycliques (HAP) et en benzène, toluène, éthylbenzène et xylènes (BTEX) - Chromatographie en phase gazeuse avec détection par spectrométrie de masse

Ta slovenski standard je istoveten z: **prEN 17844**

ICS:

13.020.99	Drugi standardi v zvezi z varstvom okolja	Other standards related to environmental protection
91.100.01	Gradbeni materiali na splošno	Construction materials in general

oSIST prEN 17844:2022 **en,fr,de**

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

DRAFT
prEN 17844

May 2022

ICS 91.100.01

English Version

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Recipients of this draft are invited to submit, with their comments, notification of any relevant patent rights of which they are aware and to provide supporting documentation.

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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 17844:2022) 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 polycyclic aromatic hydrocarbons (PAH) and of benzene, toluene, ethylbenzene and xylenes (BTEX) with gas chromatography with mass spectrometric detection (GC-MS). NEN 7331 has been used as basis [1].

This document is intended to be used for construction products and is suitable for determining:

— the full suite PAH, including the EPA-PAH series [2];

— six BTEX.

In some cases, additional analysis with high performance liquid chromatography (HPLC) can be necessary to determine a number of compounds.

The methods described have been subjected to robustness validation [3]. The detectability limit of the methods for individual compounds in construction products for PAH is 0,5 mg/kg to 1,5 mg/kg and for BTEX 0,1 mg/kg.

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 two methods for determining the content of polycyclic aromatic hydrocarbons (PAH) and one method for determining the content of benzene, toluene, ethylbenzene and xylenes (BTEX) with gas chromatography with mass spectrometric detection (GC-MS).

See Annex A for a list of PAH and BTEX that can be determined with this document.

This document is intended to be used for construction products.

In a number of cases additional analysis with high performance liquid chromatography (HPLC) can be necessary to determine a number of compounds. To determine PAH multiple liquid-liquid extraction is used to remove disturbing compounds. The tests that led to this document were carried out on different types of roofing material, asphalt and one tar containing asphalt, [3] and [5].

The detectability limit of the methods for individual compounds in roofing material, asphalt and tar containing asphalt for PAH is 0,5 mg/kg to 1,5 mg/kg and for BTEX 0,1 mg/kg.

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.

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*

EN ISO 15009, *Soil quality — Gas chromatographic determination of the content of volatile aromatic hydrocarbons, naphthalene and volatile halogenated hydrocarbons — Purge-and-trap method with thermal desorption (ISO 15009)*

ISO 20595, *Water quality — Determination of selected highly volatile organic compounds in water — Method using gas chromatography and mass spectrometry by static headspace technique (HS-GC-MS)*

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
Soxhlet extract
solution that is obtained after extraction of a solid subsample by the Soxhlet technique for determining organic compounds

3.14
final extract
solution that is obtained after clean-up the Soxhlet extract through a purification stage

3.15
injection standard
known quantity of a substance (where applicable deuterated) not present in the sample, that after clean-up is added to the analysis extract in order to check the analysis

3.16
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

3.17
surrogate 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.

BTEX	Alkylated benzenes: sum of benzene, toluene, ethylbenzene and xylenes
EOTA	European Organisation of Technical Assessment
GC	Gas chromatography
HPLC	High performance liquid chromatography NOTE High pressure liquid chromatography is an (outdated) synonym.
HRGC	High-resolution gas chromatography
LLE	Liquid-liquid extraction, also known as solvent extraction and partitioning
MS	Mass spectrometry; Mass selective detection
PAH	Polycyclic aromatic hydrocarbon(s)
PLE	Pressurized liquid extraction
SLE	Solid-liquid extraction
TR	Technical Report (ISO, CEN or EOTA)
TS	Technical Specification (ISO, CEN or EOTA)

5 Sample preparation

To obtain test samples for extraction (and analysis) guidance on sample preparation as specified in EN 17087 shall be applied. The sample shall be analysed for the total content of substances of interest.

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.

6 Principle

6.1 Flow chart

The method for determination of PAH and BTEX is summarized schematically in Annex E.

6.2 Sample pre-treatment

The quantity of construction product that is processed is reduced prior to grinding by quartering according to EN 17087. This procedure is repeated until a suitable quantity of subsample is obtained. The construction product is reduced cryogenically prior to analysis according to EN 17087. For some samples such as for very open asphalt concrete (ZOAB), cryogenic pre-reduction with a jaw crusher may be performed.

If pure bitumen or bitumen containing materials are tested according to this document, a representative subsample shall be taken. Pre-treatment may be chosen here according to the methods described above, but for some materials direct sampling is also permitted. The latter is for example the case when pure bitumen is tested.

6.3 Extraction and sample pre-treatment

6.3.1 Determination of PAH

A known quantity of the homogenized sample is extracted with petroleum ether for about 16 h with a Soxhlet extraction set-up. Part of the extract is purified according to one of the two methods described and the final extract is then analysed for PAH with GC-MS.

6.3.2 Determination of BTEX

A known quantity of the homogenized sample is extracted with methanol for about 24 h. The final extract is analysed after dilution with water with the purge-and-trap method and GC-MS or headspace-GC-MS.

6.4 Gas chromatography determination

6.4.1 Determination of PAH

For the separation a column with a slightly polar immobile phase is used. Injection takes place via a non-discriminating technique, such as on-column injection or splitless injection. Detection takes place using mass spectrometry. Calibration and quantification take place by measurement of an external standard.

The hexane extract of purification method 1, that is reprocessed for the gas chromatographic determination with mass selective detection, may, after additional purification with aluminium oxide and conversion to acetonitrile, further be tested with HPLC for the determination of the chrysene content.

6.4.2 Determination of BTEX

A known quantity of the final extract is placed in the purge vessel after dilution with water. In the case of online systems, the sample is transferred into a suitable sample bottle and injected by the equipment into the purge vessel. A known quantity of the injection standard is then placed in the purge vessel. After injection via an injection technique such as purge-and-trap, the compounds to be measured are separated on a slightly polar or medium polar column and detected with mass spectrometry. Calibration and quantification take place by measurement of an external standard.

NOTE The method described here is fully in accordance with EN ISO 15009.

7 Reagents

Use only reagents of at least analysis quality. These substances shall be free of disturbing compounds. Check this beforehand by carrying out a blank determination (see 11.2.2 and 11.3.2).

WARNING — Working with chemicals can be harmful to your health. For this reason, consult the relevant Chemical Cards [5] and take the preventive action recommended in them.

7.1 BTEX.

The substances listed in Table A.2.

7.2 Methanol [CAS 67-56-1].

7.3 PAH.

The polycyclic aromatic hydrocarbons listed in Table A.1.

7.4 Hexane [CAS 110-54-3].

7.5 Surrogate standard.

Preferably choose deuterated compounds, of which the undeuterated form is looked for as a target analyte in the sample. The following may be used:

— ethylbenzene-d_{10} [CAS 25837-05-2] for determining BTEX;

— naphthalene-d_8 [CAS 1146-65-2] for determining PAH;

— anthracene-d_{10} [CAS 1719-06-8] for determining PAH;

— chrysene-d_{12} [CAS 1719-03-5] for determining PAH.

7.6 Injection standard.

Choose compounds for the injection standard that are physically and chemically similar to the compounds to be analysed, but not present in the sample. The following may be used:

— trifluorotoluene [CAS 98-08-8] for determining BTEX;

— mirex [CAS 2385-85-5] for determining PAH;

— 6-methylchrysene [CAS 1705-85-7] for determining chrysene with HPLC.

6-methylchrysene is used specifically for any HPLC analysis following the GC-MS analysis (11.6).

7.7 Stock solution for BTEX determination.

Prepare, where applicable starting from a commercial standard solution, a stock solution with a content of 5 mg/l of each individual compound (7.1) in methanol (7.2).

This solution has a shelf life of at least six months, provided it is stored in the dark and at −20 °C.

7.8 Surrogate standard solution for BTEX determination.

Dissolve 50 mg ethylbenzene-d_{10} (7.5) in 100 ml methanol (7.2). Pipette 5 ml of this solution into a 50 ml measuring flask and dilute with methanol to 50 ml. The content of ethylbenzene-d_{10} is 50 mg/l.

The surrogate standard solution has a shelf life of at least three months, provided it is stored in a cool (<4 °C) and dark place.

7.9 Stock solution for PAH determination.

Prepare, where applicable starting from a commercial standard solution, a stock solution with a content of 200 mg/l of each separate compound (7.3) in hexane (7.4).

This solution has a shelf life of at least two years, provided it is stored in the dark and at −20 °C.

NOTE Due to the hazards associated with working in particular with PAH in solid form, it is not recommended to make up standard solutions oneself. For this reason, preferably use commercially available standard solutions, for example an ampoule of 1 ml of 2 000 mg/l.