SLOVENSKI STANDARD
oSIST prEN 17937:2023

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Regulirane kemikalije v izdelkih - Določanje vsebnosti policikličnih aromatskih ogljikovodikov (PAH) z metodo plinske kromatografije z masno spektrometrijo v polimernih materialih in gumi v izdelkih, namenjenih širši javnosti, ki prihajajo v neposredni stik s človeško kožo in ustno votlino

Regulated chemicals in products - Determination of the content of polycyclic aromatic hydrocarbons (PAHs) by gas chromatography coupled to mass-spectrometry in plastic and rubber in articles supplied to the general public that come into direct contact with human skin and oral cavity

Reglementierte Chemikalien in Erzeugnissen - Bestimmung des Gehalts von polyzyklischen aromatischen Kohlenwasserstoffen (PAK) mittels Gaschromatographie in Kunststoff und Gummi in Gegenständen für die breite Öffentlichkeit, die in direkten Kontakt mit der menschlichen Haut und der Mundhöhle kommen

Substances chimiques règlementées dans les produits - Détermination de la teneur en hydrocarbures aromatiques polycycliques (HAP) par chromatographie en phase gazeuse couplée à la spectrométrie de masse dans les articles en plastique et en caoutchouc fournis au grand public entrant en contact direct avec la peau humaine et la cavité buccale

Ta slovenski standard je istoveten z: **prEN 17937**

ICS:

71.080.15	Aromatski ogljikovodiki	Aromatic hydrocarbons
83.140.01	Izdelki iz gume in polimernih materialov na splošno	Rubber and plastics products in general

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EUROPEAN STANDARD

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EUROPÄISCHE NORM

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ICS 71.080.15; 83.140.01

English Version

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This draft European Standard is submitted to CEN members for enquiry. It has been drawn up by the Technical Committee CEN/TC 462.

If this draft becomes a European Standard, CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration.

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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

CEN-CENELEC Management Centre: Rue de la Science 23, B-1040 Brussels

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European foreword

This document (prEN 17937:2023) has been prepared by Technical Committee CEN/TC 462 “Regulated chemicals in products”, the secretariat of which is held by AFNOR.

This document is currently submitted to the CEN Enquiry.

Introduction

In December 2013, based on a report established in 2010 by the German authorities, the European Commission amended the REACH Annex XVII through the Regulation (EU) No. 1272/2013, with amend entry 50, with the addition of paragraphs 5 and 6. This Regulation addresses and restricts the use of eight PAHs (Polycyclic Aromatic Hydrocarbons) in rubber and plastic articles supplied to the general public that come into direct as well as prolonged contact or short-term repetitive contact with human skin or the oral cavity, under normal or reasonably foreseeable conditions of use.

To support the enforcement of this restriction the European Commission requested the European Committee for Standardization (CEN) and the European Committee for Electrotechnical Standardization (CENELEC) to draft harmonized standards for the analytical determination of the individual concentrations of the 8 carcinogenic PAHs, listed in entry 50 of Annex XVII to Regulation (EC) No. 1907/2006 (REACH), in plastic and rubber components (see standardization request M/556).

A Technical Board Working Group 13 "PAHs" (CEN-CLC/BT/WG 13) established by CEN-CENELEC had to investigate that request through a scoping study which had to identify if any existing methods to determine the total content for PAHs in rubber and plastic articles exist but also if any spectroscopic methods could assist Market Surveillance Authorities in performing non-destructive screening tests.

The result of the scoping study based on an up to date literature review concluded the need to develop a harmonized standard to support (EU) No. 1272/2013 legislation, which is developed hereafter.

1 Scope

This document specifies a method to determine the total content of the 8 regulated polycyclic aromatic hydrocarbons (PAHs), see Table 1, in plastic and rubber articles by using GC-MS allowing detection at 0,1 mg PAHs/kg for plastic and 0,2 mg PAHs/kg for rubber material.

Table 1 — List of PAHs

PAHs	CAS number
Benzo[a]pyrene (BaP)	CAS No 50-32-8
Benzo[e]pyrene (BeP)	CAS No 192-97-2
Benzo[a]anthracene (BaA)	CAS No 56-55-3
Chrysene (CHR)	CAS No 218-01-9
Benzo[b]fluoranthene (BbFA)	CAS No 205-99-2
Benzo[j]fluoranthene (BjFA)	CAS No 205-82-3
Benzo[k]fluoranthene (BkFA)	CAS No 207-08-9
Dibenzo[a,h]anthracene (DBahA)	CAS No 53-70-3

NOTE Other PAHs compounds can also be analysed with this method, provided suitability has been proven.

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 ISO 22892:2011, *Soil quality — Guidelines for the identification of target compounds by gas chromatography and mass spectrometry (ISO 22892:2006)*

ISO 1407:2011, *Rubber — Determination of solvent extract*

ISO 21461:2012, *Rubber — Determination of the aromaticity of oil in vulcanized rubber compounds*

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:

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

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

4 Principle

The test specimen is extracted using toluene (or n-heptane) using a Soxhlet or Randall (automated Soxhlet) extraction or ultrasonic bath extraction method. The extract is concentrated and interfering compounds are removed by a clean-up method. An aliquot is then analysed using a gas chromatograph with mass selective detector (GC-MS).

PAHs are identified and quantified with GC-MS by comparison of relative retention times and relative peak heights (or peak areas) with respect to internal standards added.

5 Reagents

WARNING — Polycyclic Aromatic Hydrocarbons can cause cancer, are suspected of damaging an unborn child, can cause damage to organs through prolonged or repeated exposure, and can be fatal if swallowed and/or enter airways. Appropriate measures shall be taken to ensure safety.

All reagents shall be of recognized analytical grade unless specified in a different way.

— Toluene, CAS number: 108-88-3. or n-heptane, CAS number: 142-82-5

— Ethanol, CAS number: 64-17-5

— Cyclohexane, CAS number: 110-82-7

— PAHs standard solutions

The standards shall be chosen so that they behave in the same way as the corresponding analytes and that they can be readily quantified (see Table 2).

All purchased PAHs standard materials shall be 98 % pure or better and certified in respect of their purity, concentration level, and authenticity by the manufacturer. PAH standards diluted in cyclohexane can be accepted.

Standard solutions and extracts should be stored in a dark place (e.g. in amber glassware) at about (5+/- 3) °C. These standard solutions and extracts shall not be used after 1 year.

— Internal standards

At least 3 internal standards shall be used, using one of each ring system family as shown in Table 2. The internal standards given in Table 2 are examples. Others may be used, as long as they represent at least the 3+, the 4+ and the 5+ ring systems

Table 2 — Native (calibration standards) and deuterated (internal standards) PAHs compounds

Calibration standard	Ring system	Internal standard
benzo[a]anthracene	3+	benzo[a]anthracene-d12
chrysene	3+	benzo[a]anthracene-d12
benzo[k]fluoranthene	4+	benzo[b]fluoranthene-d12
benzo[b]fluoranthene	4+	benzo[b]fluoranthene-d12
benzo[j]fluoranthene	4+	benzo[b]fluoranthene-d12
benzo[a]pyrene	5+	benzo[a]pyrene-d12
benzo[e]pyrene	5+	benzo[a]pyrene-d12
dibenzo[a,h]anthracene	5+	benzo[a]pyrene-d12

6 Apparatus and materials

To prevent any interference, it is recommended to avoid plastic and other organic materials.

It is recommended to use the usual equipment and laboratory glassware according to EN ISO 4787:2021 and the following:

— Analytical balance, with a precision of at least 0,1 mg to weigh the samples;

  Analytical balance, with precision of at least 0,01 mg shall be used by labs which are preparing their stock solutions from pure chemicals.

— Micropipettes, 50 µl and 100 µl;

— Pipette, 0,5 ml to 5 ml capacity;

— Glass vials (amber);

— Gas chromatograph coupled to a mass-spectrometer (MS) with electron ionisation (EI) capability and single ion monitoring (SIM) mode or MS/MS with multiple reaction monitoring (MRM) mode.

GC Capillary Column: it is strongly recommended to use a GC column specifically dedicated for PAHs analysis, with column length of at least 30 m, internal diameter 0,25 mm to 0,32 mm, film thickness 0,17 µm to 0,25 µm.

Deactivated straight borosilicate liner with small piece of deactivated glass wool - this liner may be used as long as peak resolution is satisfactory.

An alternative liner is a split/splitless not deactivated liner with glass wool (4-mm internal diameter, straight liner).

Liners shall be deactivated with a silanizing agent before use. Another alternative is a split/splitless liner with fluorocarbon liner seals. Such a liner will already contain conditioned silanized glass wool.

Other liners can be used if they produce acceptable results.

It is recommended to use a gold-plated seal for GC injector port or similar nonreactive seal.

GC/MS amber autosampler vials with polytetrafluoroethylene (PTFE)-coated caps.

Crimping tool.

— Extraction apparatus:

  — Ultrasonic bath: Minimum power 200W with a bath surface of 706 cm^2, corresponding to 0,28W/cm^2 without basket and with internal or external thermostat;

  — Soxhlet extractor equipped with Reflux Condenser of 50 ml or 100 ml capacity and Boiling Flasks having a volume capacity of 250 ml;

  — Randall extraction (automated Soxhlet);

— Material for sample clean-up:

  — Silica Solid-Phase Extractor Cartridges or MIP-SPE (Molecular Imprinted Polymer- SPE) cartridge, single-use application, having a volume capacity of approximately 5 ml or 2 cm to 3 cm length by 1 cm diameter;

— Drying Oven, gravity convection type, capable of maintaining 40 ± 10 °C, used for slowing down the cooling when the glassware is taken out of the muffle furnace;

— Furnace, capable of temperature regulation of 525 °C ± 75 °C, used to burn off organic contamination from glass surfaces (except volumetric glasses);

— Manometer, capable of pressure readings in the range of 5 ± 0,3 kPa.

7 Sample preparation and storage

7.1 Sample preparation

The sample shall be representative of the parts of the product expected to come into contact with skin or oral cavity.

The sample shall be reduced to small pieces of 2 mm to 3 mm in each dimension and shall be homogeneous. Thinner samples like sheets, coatings or paints need to be scraped off by means of a sharp blade and homogenized accordingly. Granulates (less than 3 mm) and powder samples are analysed in the original state.

NOTE Heterogeneous granulate samples are reduced to particle sizes below 2 mm in each dimension in order to ensure its representativeness.

The test pieces shall not be altered by their preparation; the composition shall remain unchanged.

The purification of the extract is obtained using molecularly imprinted polymers (MIPs), solid phase extraction (SPE) or other technique if the efficiency is proved by the laboratory. This removal of interfering compounds is not mandatory for GC-MS-MS analysis.

7.2 Preparation of standard solutions

Separate stock solutions of the three deuterated internal standards (IS) and of the non-deuterated (native) PAH calibration standards can be purchased or can be prepared from pure materials or individual solutions. A concentration range of 80 µg/ml to 100 µg/ml for both the native PAHs and IS is recommended. GC-MS stock solution can then be prepared according to the following example:

— Deuterated IS stock solution, of the following nature:

  — PI-1: 10 mg of each deuterated compound in 5 ml of toluene (2 000 µg/ml),

  — PI-2: 1,25 ml of PI-1 in a 25 ml flask, filled up with toluene (100 µg/ml)

  — PI-3: 5 ml of PI-2 in 25 ml flask, filled up with toluene (20 µg/ml).

— PAHs Standard solutions, of the following types:

  — PAH-1: 10 mg each PAHs in 100 ml of toluene (100 µg/ml),

  — PAH-2: 2,5 ml PAHs-1 in 25 ml flask, filled up with toluene (10 µg/ml).

— Injection Standard solutions, of the following nature:

  — INS-1: 10 mg of perylene-d12 in 5 ml of toluene (2 000 µg/ml),

  — INS-2: 1,25 ml INS-1 in 25 ml flask, filled up with toluene (100 µg/ml)

  — INS-3: 5 ml INS-2 in 25 ml flask, filled up with toluene (20 µg/ml).