
**Footwear — Critical substances
potentially present in footwear
and footwear components —
Determination of phenol in footwear
materials**

*Chaussures — Substances critiques potentiellement présentes dans
les chaussures et les composants de chaussure — Détermination du
phénol dans les matériaux de chaussure*

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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).

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For an explanation on 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 the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 216, *Footwear*.

Footwear — Critical substances potentially present in footwear and footwear components — Determination of phenol in footwear materials

WARNING — The user of this document should have work experience in a formal laboratory. This document does not indicate all possible safety issues. Users are responsible for taking appropriate safety and health practices.

1 Scope

This document specifies a method to determine the amount of phenol in footwear and footwear components. It is applicable to all parts of footwear except for metal parts.

NOTE ISO/TR 16178:2012, Table 1 defines which materials are included in this determination.

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 4787, *Laboratory glassware — Volumetric instruments — Methods for testing of capacity and for use*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at <http://www.electropedia.org/>
- ISO Online browsing platform: available at <http://www.iso.org/obp>

4 Principle

The sample is cut in small pieces and extracted with a mixture of toluene/acetone (80/20) percent by volume, in a sealed vial at 60 °C in an ultrasonic bath for 1 h.

The extract is analysed by gas chromatography/mass spectrometry (GC-MS).

The method uses an extraction surrogate (Phenol-D6), added just before the extraction step and quantified similar to a target compound. It is required to check the extraction efficiency and to calculate a recovery rate.

Anthracene-D10 is used as the internal standard and is added to the vial (sample and calibration) just before the chromatographic analysis. It is also used to make the calibration curve.

5 Reagents and materials

5.1 Chemicals

The substances mentioned in this document shall be used in a defined purity:

- above 95 % for the pure product used for the standard;
- analytical grade for the solvents.

5.1.1 Phenol CAS: 108-95-2 (target compound).

5.1.2 Phenol-D6 CAS: 13127-88-3 (extraction surrogate).

5.1.3 Anthracene-D10 CAS: 1719-06-8 (internal standard).

5.1.4 Toluene CAS: 108-88-3 (solvent).

5.1.5 Acetone CAS: 67-64-1 (solvent).

5.1.6 Mixture toluene/acetone (80/20) percent by volume (extraction mixture).

The composition of the mixture is based on the volume. For example, to make 100 ml of the mixture, mix 80 ml of toluene with 20 ml of acetone.

5.1.7 Methanol CAS: 67-56-1 (solvent).

5.2 Stock solutions

5.2.1 Internal standard – Anthracene-D10 – stock solution (1 000 mg/l).

Weigh 10 mg of Anthracene-D10 in a 10 ml volumetric flask and fill to the mark with acetone. Transfer the content to an amber 10 ml vial with a polytetrafluoroethylene (PTFE) stopper and store at 4 °C.

5.2.2 Internal standard – Anthracene-D10 – working solution (10 mg/l).

Prepare a 1:100 dilution of the stock solution (5.2.1). For example, take 100 µl of the stock solution in a 10 ml volumetric flask and fill to the mark with acetone.

5.2.3 Extraction surrogate – Phenol-D6 – stock solution (1 000 mg/l).

Weigh 10 mg of Phenol-D6 in a 10 ml volumetric flask and fill to the mark with acetone. Transfer the content to an amber 10 ml vial with PTFE stopper and store at 4 °C.

5.2.4 Extraction surrogate – Phenol-D6 – working solution (10 mg/l).

Prepare a 1:100 dilution of the stock solution (5.2.3). For example, take 100 µl of the stock solution in a 10 ml volumetric flask and fill to the mark with acetone.

5.2.5 Target compound – phenol – stock solution (1 000 mg/l).

Weigh 10 mg of phenol in a 10 ml volumetric flask and fill to the mark with acetone. Transfer the content to an amber 10 ml vial with PTFE stopper and store at 4 °C.

5.2.6 Phenol + Phenol-D6 – intermediate calibration solution (10 mg/l).

Take a volume of 100 µl of the stock solution of the extraction surrogate (5.2.3) and the target compound (5.2.5) in a 10 ml volumetric flask and fill to the mark with the mixture of toluene/acetone (80/20).

5.2.7 Phenol + Phenol-D6 – working calibration solution (1 mg/l).

Take a volume of 1 000 µl of the intermediate calibration solution (5.2.6) in a 10 ml volumetric flask and fill to the mark with the mixture of toluene/acetone (80/20).

6 Apparatus

Usual lab equipment and the following. Use laboratory glassware in accordance with ISO 4787.

6.1 **Analytical balance**, with an accuracy of at least 0,1 mg.

6.2 **Glass vial**, which can be tightly sealed, 40 ml.

6.3 **Ultrasonic bath**, with adjustable temperature.

6.4 **PTFE-membrane filter**, pore width 0,45 µm.

6.5 **2 ml sample vials**, PTFE-capped.

6.6 **20 ml sample vials**, PTFE-capped.

6.7 **Gas chromatograph with a mass selective detector (MSD)**. Other chromatographic technics may be used provided that they have been validated for this analysis.

7 Sampling

In the footwear, the upper and the complex lining plus the insock shall be tested.

The test piece consists of a single material (leather, textile or polymer). Homogenous textile, leather and polymer samples are cut into pieces with an edge length of up to 5 mm.

The sample should not be subjected to grinding as it results in the loss of volatile phenol.

8 Test method

8.1 Extraction

Weigh 1 g of the sample in a 20 ml glass vial (6.6). Then add 9,8 ml of the extraction mixture (5.1.6) and 200 µl of the extraction surrogate working solution (5.2.4).

The extraction is conducted with an ultrasonic device at 60 °C ± 5 °C during 60 min ± 2 min.

NOTE It has been proven that acetone is efficient as extraction solvent. However, its high polarity (compared to the extraction mixture) can conduct to a high amount of co-extracted compounds (such as dyes or other polar compounds like glycols) which could disturb the analysis.

Some polymeric materials can be dissolved in the extraction mixture and can cause problems during the quantification. In these cases, precipitation by methanol could be necessary. Precipitate the solution obtained by adding 20 ml of methanol (5.1.7) and allow the precipitate to settle for at least 5 min. Filtrate, if necessary, using a 0,45 µm PTFE filter.

8.2 Analysis

Take an aliquot of exactly 1 ml of the extract and add 50 µl of the internal standard working solution (5.2.2).

Analyse with GC-MS (6.7) according to Clause 9.

8.3 Calibration

For practical reasons the calibration is based on a solution containing the target compound and the extraction surrogate.

Within the linear range use at least five measurements at different concentrations. The calibration is conducted directly in 2 ml sample vials, see Table 1.

Table 1 — Calibration solutions

Standard	L1	L2	L3	L4	L5
Volume of the working calibration solution (µl) (5.2.7)	50	100	250	500	1 000
Volume of extracting mixture (µl) (5.1.6)	950	900	750	500	0
Concentration of phenol and Phenol-D6 (µg/l)	50	100	250	500	1 000
Volume of the internal standard working solution (µl) (5.2.2)	50				
Concentration of the internal standard (µg/l)	500				

9 Determination with GC-MS

9.1 Measuring method

Validated analysis methods other than the method described in Annex A are permitted, provided a comparable precision and quantification limit (9.3.1) can be reached.

The ions given in Table 2 shall be used.

Examples are given in Annex A.

Table 2 — Monitoring ions

Compounds	Ions
Phenol	94
	66
Phenol-D6	99
	71
Anthracene-D10	188

9.2 Quantification

9.2.1 Calibration curve

Set up the linear regression function by using the following ratio (A_e/A_{is}) and (C_e/C_{is}) with the help of [Formula \(1\)](#):

$$\frac{A_e}{A_{is}} = a \times \left(\frac{C_e}{C_{is}} \right) + b \quad (1)$$

where

A_e is the area of the target of phenol based on the monitoring ions;

A_{is} is the area of the peak of Anthracene-D10 based on the monitoring ions;

C_e is the concentration of phenol in the calibration standard, in $\mu\text{g/l}$;

C_{is} is the concentration of Anthracene-D10 in the calibration standard, in $\mu\text{g/l}$;

a is the slope of the linear function;

b is the ordinate intercept of the calibration curve. The units depend on the evaluation.

The same calculation shall be conducted for Phenol-D6.

9.2.2 Recovery rate

The use of an extraction surrogate permits the calculation of an extraction yield using [Formula \(2\)](#):

$$R(\%) = \frac{C_{\text{calculated}}}{C_{\text{theoretical}}} \times 100 \quad (2)$$

where

$C_{\text{calculated}}$ is the concentration of Phenol-D6 analysed in the sample after the extraction;

$C_{\text{theoretical}}$ is the concentration of Phenol-D6 initially introduced before the extraction (200 μl of a 10 mg/l solution into 10 ml of extraction mixture; in this case $C_{\text{theoretical}}$ is 200 $\mu\text{g/l}$).

If the extraction is below 75 % or above 125 %, the sample shall be reanalysed.

9.2.3 Determination of the phenol content

The content of phenol is calculated according to [Formula \(3\)](#) as a mass fraction W in mg/kg :

$$W = (V/m) \times \left(\frac{A_{\text{ech}} - b}{A_{\text{is}}} \right) \times C_{\text{is}} \quad (3)$$

where

W is the content of the phenol in the specimen, in mg/kg ;

V is the volume of extraction mixture used for the extraction, in ml (in most cases this value will be equal to 10 ml);

m is the mass of the test specimen, in kg;

- A_{ech} is the area of the peak of phenol in the sample;
- A_{is} is the area of the peak of Anthracene-D10 in the sample;
- C_{is} is concentration of Anthracene-D10 in the sample, in $\mu\text{g/l}$;
- a is the slope of the linear function determined in (9.2.1);
- b is the ordinate intercept of the calibration curve determined in (9.2.1).

9.3 Performances of the test method

9.3.1 Quantification limit of the GC-MS method

The quantification limit of the method should be 0,5 mg/kg considering a mass of sample of 1 g and an extraction volume of 10 ml.

It can be lowered by concentrating the sample solution. This is done by reducing the extraction volume to 1 ml under a gentle stream of nitrogen.

9.3.2 Interlaboratory tests

The results of the interlaboratory tests are given in [Annex B](#).

10 Test report

The test report shall contain the following information:

- a) a reference to this document, i.e. ISO 20536;
- b) the date of the test;
- c) all the details necessary for complete identification of the sample tested;
- d) the different material types (see [Clause 7](#)) that have been tested;
- e) the condition of storage before the test, if available;
- f) a determination of the extracted phenol as calculated in [9.2.3](#);
- g) deviations from the method specified in this document.

Annex A (informative)

Example of an instrumental method

A.1 General

The phenol and Phenol-D6 are analysed by gas chromatography/mass spectrometry on a single quad/MS use in a simultaneous SIM/SCAN mode.

A.2 Chromatographic conditions

Column: DB-5MS (or equivalent-5 %phenyl-95 %dimethylpolysiloxane).

Dimension: 30 m × 0,25 mm × 0,25 µm.

Carrier gas: Helium with a linear velocity of 36 cm/s.

Oven:

50 °C during 1 min.

245 °C at 15 °C/min.

300 °C at 25 °C/min during 4 min.

Injector: 265 °C in pulse splitless mode with an injection volume of 1 µl.

Pulse pressure: 120 kPa during 1,5 min.

Split flow: 60 ml/min at 1,5 min.

NOTE In order to get a suitable separation between toluene and phenol, another column with a more polar phase could be used, such as DB-35 (35 % phenyl), VF-17 (50 % phenyl) or DB-WAX (100 % polyethylene glycol).

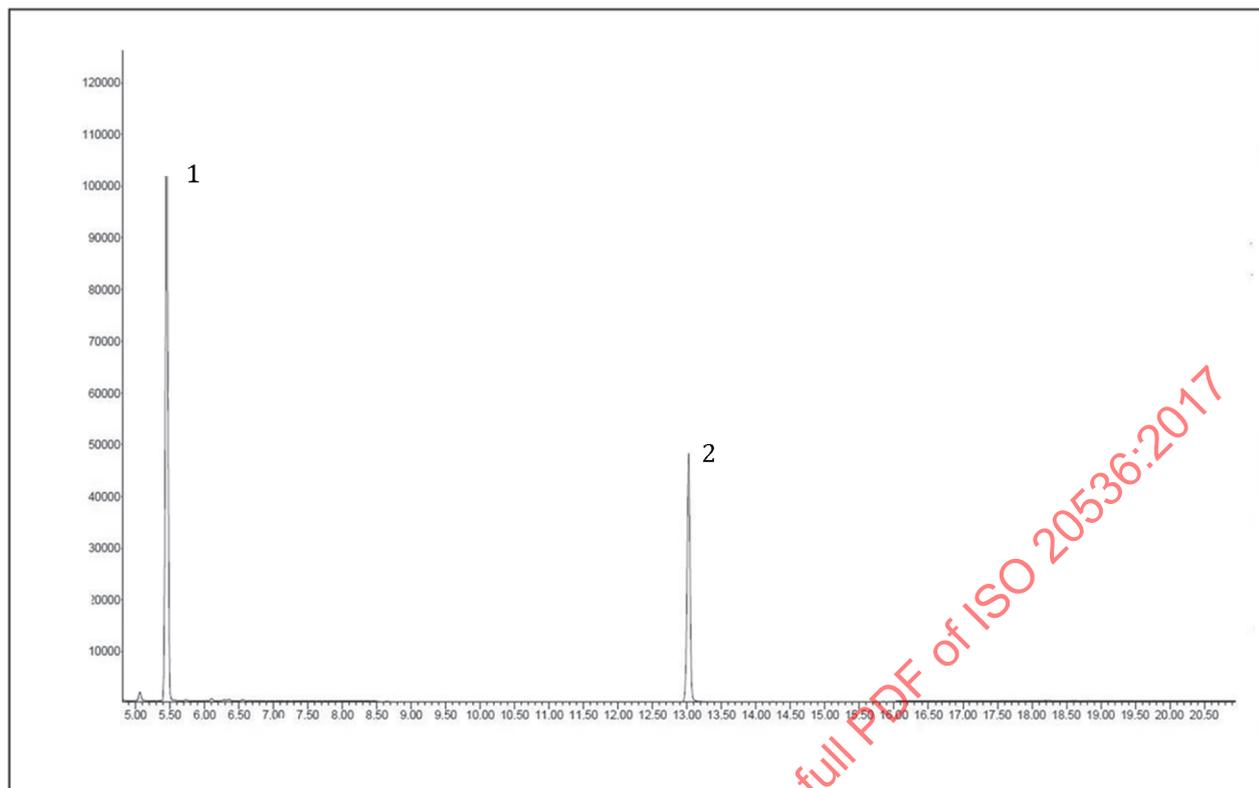
A.3 Detection conditions

Transfer line: 280 °C.

The single quad MS works in simultaneous SIM/SCAN mode.

The mass SCAN range is between 50 m/z and 300 m/z.

The SIM mode focus on the ions is given in [Table 2](#).



Key

- 1 phenol and Phenol-D6
- 2 Anthracene-D10

Figure A.1 — Total ion chromatogram (TIC) of a standard at 500 µg/l