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NATIONAL STANDARD OF THE PEOPLE'S REPUBLIC OF CHINA

GB/T 46183-2025

Footwear - Chemical tests - Determination of chlorinated phenols - GC-MS/MS

鞋类 化学试验方法 含氯苯酚的测定 气相色谱-串联质谱法

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Table of Contents

1 Scope

This document describes a method for the determination of chlorinated phenols in footwear and footwear components using gas chromatography-tandem mass spectrometry (GC-MS/MS).

This document is applicable to the determination of chlorinated phenols in textile, leather, fur, synthetic leather, and artificial leather materials used in footwear and footwear components. The determination of chlorinated phenols in other footwear materials shall be conducted by reference to this document, following validation.

2 Normative references

GB/T 6682

3 Terms and definitions

This document contains no terms or definitions requiring definition.

4 Principle

Chlorinated phenols are extracted from the specimen using a methanol-potassium hydroxide solution via ultrasonic extraction. Acetylation is performed using acetic anhydride. Following extraction with n-hexane, the analytes are determined using gas chromatography-tandem mass spectrometry (GC-MS/MS). Quantification is performed using the internal standard method.

5.1 General provisions. Unless otherwise specified, all reagents used shall be

analytically pure, and the water used for testing shall meet at least the requirements for Grade 3 water as specified in GB/T 6682.

5.2 Potassium hydroxide. purity >= 85.0%.

5.3 Aqueous potassium hydroxide solution. 2.0 mol/L.

5.4 Anhydrous sodium sulfate. purity >= 99.0%; dried at a temperature above 400 °C for not less than 4 h, then cooled and stored in a desiccator for use.

5.5 Acetic anhydride. purity >= 98.5%.

5.6 Methanol. analytically pure reagent shall be used for sample extraction, while

chromatographically pure reagent shall be used for the preparation of reference materials/standard samples.

5.7 n-Hexane. chromatographically pure.

5.8 Chlorinated phenols (CP) certified reference materials/reference samples. purity

>=95%. Specific information regarding the 19 CP species is provided in Annex A.

5.9 2-Chlorophenol-d4.CAS No. 93951-73-6, purity >=94%, internal standard.

5.10 2,4-Dichlorophenol-d3.CAS No. 93951-74-7, purity >=94%, internal standard.

5.11 2,3,4,6-Tetrachlorophenol-13C6. CAS No. 1246820-81-4, purity >=94%, internal standard.

5.12 Pentachlorophenol-13C6. CAS No. 85380-74-1, purity >=94%, internal standard.

5.13 CP stock solutions. prepare separate stock solutions of the CP reference

materials/standard samples listed in Table A.1, each with a mass concentration of 1000 mg/L, using methanol (5.6).

5.14 CP mixed working solution (10 mg/l). transfer an appropriate volume of the CP stock solution (5.13) and dilute with methanol (5.6) to prepare a mixed working solution with a mass concentration of 10 mg/L.

5.15 CP mixed working solution (1 mg/L). pipette an appropriate volume of the CP mixed working solution (10 mg/L) (5.14) and dilute with methanol (5.6) to prepare a mixed working solution with a mass concentration of 1 mg/L.

5.16 Internal standard stock solution (100 mg/L). prepare the internal standard

substances (5.9~5.12) individually into internal standard stock solutions with a mass concentration of 100 mg/L using methanol (5.6).

5.17 Internal standard mixed stock solution (10 mg/L). transfer an appropriate volume

of the internal standard stock solution (5.16) and dilute with methanol (5.6) to prepare an internal standard mixed stock solution with a mass concentration of 10 mg/L.

5.18 Methanol solution containing internal standard. pipette an appropriate volume of

the mixed internal standard stock solution (10 mg/L) (5.17), and dilute with methanol (5.6) to prepare a methanol solution containing the internal standard at a specific mass concentration (e.g., 0.05 mg/L).

6.1 Gas chromatograph-tandem mass spectrometer (GC-MS/MS). equipped with an

electron ionization (EI) source.

6.2 Analytical balance. with a readability of 0 0001 g.

6.3 Ultrasonic extractor. with adjustable temperature up to (70 ± 3)°C and an operating frequency of (40 ± 5) kHz. 6.4 Centrifuge.

6.5 Mechanical shaker. with a shaking frequency of >= 200 cycles/min, or other suitable shaking device.

6.6 Sealed container. capable of separating organic and aqueous phases (e.g., a 40 mL glass vial with a sealable screw cap). 6.7 Vortex mixer. 6.8 Sample vials. 6.9 Volumetric flasks.

6.10 Organic microporous membrane filter. with a pore size of 0.22 μm.

7.1 Specimen preparation

Test specimens are prepared from a single material taken from the shoe and formed into specimens with a diameter (or side length) not exceeding 4 mm.

7.2 Specimen extraction

Weigh 1.0 g (accurate to 1 mg) of the specimen into a sealed container (6.6). Add 10 mL of aqueous potassium hydroxide solution (5.3) and 10 mL of methanol solution containing the internal standard (5.18). After tightly closing the lid, place the container in an ultrasonic extractor (6.3) and perform ultrasonic extraction at (70 ± 3)°C for (120 ± 5) min. Upon completion of the extraction, allow the solution to cool to room temperature.

7.3 Acetylation

Add 2.5 mL of acetic anhydride (5.5) to the extract processed in accordance with Clause 7.2 Vortex-mix the solution on a vortex mixer (6.7) for approximately 1 min.

Accurately add 5.0 mL of n-hexane (5.7). Place the mixture on a mechanical shaker (6.5) and shake for (30 ± 3) min. After allowing the layers to separate by standing, transfer the upper layer through an organic microporous membrane (6.10) - to which an appropriate amount of anhydrous sodium sulfate (5.4) has been added - into a sample vial (6.8) for GC-MS/MS (6.1) analysis. If necessary, centrifuge the upper layer using a centrifuge (6.4) prior to filtration; then, proceed with the aforementioned steps using the n-hexane layer.

7.4 Preparation of standard working solution

Accurately pipette an appropriate volume of the CP mixed working solution into a sealed container (6.6). Add 10 mL of aqueous potassium hydroxide solution (5.3) and

10 ML of the methanol solution containing the internal standard (5.18). Proceed with

acetylation in accordance with Step 7.3.For example. accurately pipette 50 µL and 200 µL of the CP mixed working solution (1 mg/L) (5.15), and 50 µL, 100 µL, and 200 µL of the CP mixed working solution (10 mg/L) (5.14) for acetylation, thereby obtaining CP standard working solutions with mass concentrations of 10 µg/L, 40 µg/L, 100 µg/L, 200 µg/L, and 400 µg/L (with the internal standard concentration in all cases being 100 µg/L).

NOTE. Select appropriate concentration points to construct a standard curve. Adjust the concentration range of the standard working solutions based on the chlorophenol content levels in the actual samples.

7.5 Determination by gas chromatography-tandem mass spectrometry (GC-

MS/MS) Perform the determination using a gas chromatograph-tandem mass spectrometer (GC- MS/MS) (6.1). The instrumental conditions provided in Annex B have been proven to be feasible. An example of chromatographic analysis is presented in Annex C.