ICS 61.060
CCS Y 78

NATIONAL STANDARD OF THE PEOPLE'S REPUBLIC OF CHINA

GB/T 44943-2024

Footwear - Chemical tests - Determination of the content of ortho-phenylphenol - HPLC-MS/MS

鞋类 化学试验方法 邻苯基苯酚含量的测定 高效液相色谱-串联质谱法

Issued on: November 28, 2024 **Implemented on: June 1, 2025**

Issued by: State Administration for Market Regulation;
Standardization Administration of the PRC

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1 Scope

WARNING - Persons using this document should have practical experience of work in a formal laboratory. This document does not point out all the possible safety problems; it is the responsibility of the user to take appropriate safety and health measures and to ensure that the conditions laid down in the relevant national regulations are met.

This document describes a method for the determination of ortho-phenylphenol in footwear and footwear components by high performance liquid chromatography with tandem mass spectrometry (HPLC-MS/MS).

This document applies to the determination of the content of ortho-phenylphenol in footwear products and footwear materials.

NOTE: GB/T 29292 gives the test materials that may contain ortho-phenylphenol.

2 Normative references

The contents of the following document constitute indispensable provisions of this document through the normative reference made to it in the text. For dated references, only

the version corresponding to that date applies to this document; for undated references, the latest version (including all amendments) applies to this document.

GB/T 6682 Water for analytical laboratory use - Specification and test methods

3 Terms and definitions

No terms and definitions need to be defined for this document.

4 Principle

The cut-up test specimen is fully wetted with an appropriate quantity of acetonitrile and extracted in an ultrasonic water bath; the extract is then cooled and filtered to give the solution to be tested. An appropriate quantity of that solution is analysed on a high performance liquid chromatograph with tandem mass spectrometer (HPLC-MS/MS) and quantified by the external standard method.

5 Reagents or materials

5.1 Acetonitrile, chromatographic grade.

5.2 Water. Water for HPLC testing shall meet the requirements for grade one water in GB/T 6682, or shall be water of equivalent purity.

5.3 Anhydrous sodium sulfate, analytical grade (dried at 400 degrees Celsius for 4 h before use and then kept in a closed desiccator).

5.4 Ortho-phenylphenol (OPP), CAS No. 90-43-7, purity not lower than 98.5%.

5.5 Standard stock solution. Weigh out an appropriate quantity of the OPP standard substance (5.4) and make it up with acetonitrile (5.1) into a standard stock solution with a mass concentration of 1 000 mg/L. Store it protected from light in a refrigerator at 0 degrees Celsius to 4 degrees Celsius; the shelf life is one year.

5.6 Standard working solutions. Dilute the standard stock solution (5.5) stepwise with acetonitrile (5.1) to prepare at least six standard working solutions of corresponding mass concentration, for example 0.005 mg/L, 0.01 mg/L, 0.05 mg/L, 0.1 mg/L, 0.5 mg/L and 1 mg/L. Store them protected from light in a refrigerator at 0 degrees Celsius to 4 degrees Celsius; the shelf life is one month.

6 Apparatus

6.1 Analytical balance, with an accuracy of 0.1 mg.

6.2 Glass screw-neck bottle, brown, 30 mL, with cap and sealing liner.

6.3 Pipettes, with ranges such as 100 µL, 1 mL and 10 mL.

6.4 Ultrasonic generator, with a temperature control device.

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

6.6 Sample vial with a polytetrafluoroethylene (PTFE) stopper, 2 mL.

6.7 High performance liquid chromatograph with tandem quadrupole mass spectrometer, fitted with an electrospray (ESI) ion source.

7 Test procedure

7.1 Preparation of the test specimen. The test specimen shall be taken from a single material of the footwear product or the footwear material, cut into small pieces with edges of 2 mm to 3 mm and mixed evenly ready for testing. Glue and adhering matter on the surface of the specimen shall be removed. NOTE: For footwear products carrying materials in several patterns and several colours, each material and each colour should as far as possible be sampled separately and tested separately, and this shall be stated in the test report.

7.2 Extraction. Weigh 0.5 g of the specimen (to the nearest 1 mg) into a clean glass screw-neck bottle (6.2), add exactly 10.0 mL of acetonitrile (5.1), seal and shake so that the specimen is completely wetted (if the specimen cannot be fully immersed in the liquid, add further acetonitrile until it is completely wetted). Place the glass screw-neck bottle in the ultrasonic generator (6.4) and carry out ultrasonic extraction according to the material under the following conditions: a) for specimens of textile, leather or fur, or synthetic leather or artificial leather, ultrasonic extraction at (50+/-5) degrees Celsius for (40+/-2) min; b) for specimens of other materials, such as the sole materials polyurethane (PU), poly(vinyl chloride) (PVC), ethylene-vinyl acetate copolymer (EVA) and thermoplastic styrene-butadiene block copolymer (SBS), ultrasonic extraction at (70+/-5) degrees Celsius for (70+/-2) min. Once the extract has cooled to room temperature, take an appropriate quantity of the supernatant and filter it, through an organic microporous filter membrane (6.5) to which an appropriate quantity of anhydrous sodium sulfate (5.3) has been added, into a sample vial (6.6) as the solution to be tested; cap and seal it for HPLC-MS/MS analysis.

7.3 HPLC-MS/MS determination. Because the test result depends on the instrument used, it is not possible to give general parameters for the liquid chromatographic and mass spectrometric analysis; the parameters set shall ensure that the component to be determined can be effectively separated from the other components during the chromatographic run. The example given in Annex A has been shown to be workable.

7.4 Qualitative analysis. Determine the sample solution and the standard working solution under the same test conditions. If the retention time of the component to be determined in the sample solution agrees with the retention time of the corresponding component in the standard solution (with a deviation within +/-2.5%), and if the relative abundance of the

qualifier ions, compared with the relative abundance of the qualifier ions of the corresponding component in a standard solution of similar mass concentration, deviates by no more than the range specified in Table 1, then ortho-phenylphenol may be judged to be present in the sample.

Table 1 sets the maximum deviation permitted in the relative ion abundance for qualitative confirmation: where the relative ion abundance is greater than 50%, the maximum permitted deviation is +/-20%; where it is greater than 20% and not greater than 50%, +/-25%; where it is greater than 10% and not greater than 20%, +/-30%; and where it is 10% or less, +/-50%.

7.5 Quantitative analysis. Determine the sample solution and the OPP standard working solutions (5.6) under the same test conditions; plot the standard working curve with the concentration of the standard solutions on the horizontal axis and the peak area of the quantifier ion on the vertical axis, and quantify by the external standard method. The response value of the component to be determined in the sample solution shall lie within the linear range of the standard working curve. If the response value falls outside the range of the standard curve, dilute the solution with acetonitrile (5.1) until it is within the range of the standard working curve and determine it again.

8 Blank test

Except that no sample is added, carry out the procedure of 7.2 and 7.3.

9 Calculation of results

The content of OPP in the sample is calculated by Formula (1).

In the formula: W is the content of OPP in the test specimen, in milligrams per kilogram (mg/kg); Cs is the mass concentration corresponding to the peak area of OPP in the test specimen, in milligrams per litre (mg/L); Co is the mass concentration corresponding to the peak area of OPP in the blank, in milligrams per litre (mg/L); V is the volume of the extract, in millilitres (mL); K is the dilution factor of the extract; m is the mass of the test specimen, in grams (g).

Take the arithmetic mean of the results of two parallel determinations; the calculated result is retained to two decimal places.

10 Determination of recovery

Add to a blank test specimen an appropriate standard solution of known concentration, then carry out the determination in accordance with 7.2 and 7.3; the recovery shall be 85% to 115%.