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Footwear - Chemical tests - Determination of dimethyl fumarate (DMF)

鞋类 化学试验方法 富马酸二甲酯（DMF）的测定

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Footwear - Chemical tests - Determination of dimethyl fumarate (DMF)

1 Scope

This Standard specifies the test methods for dimethyl fumarate in footwear and footwear components - gas chromatography-mass spectrometry and gas chromatography-secondary mass spectrometry.

This Standard applies to the determination of dimethyl fumarate in footwear and footwear components.

2 Normative references

The following documents are indispensable for the application of this document. For the dated references, only the editions with the dates indicated are applicable to this document. For the undated references, the latest edition (including all the amendments) are applicable to this document.

GB/T 22049 Footwear - Standard atmospheres for conditioning and testing of footwear and components for footwear

3 Principle

Use dehydrated ethyl acetate to ultrasonically extract dimethyl fumarate in the specimen. After the extract is purified, use gas chromatography-mass spectrometry (GC-MS) or gas chromatography-secondary mass spectrometry (GC-MS-MS) to determine and confirm; use external standard method to quantify.

Note: When the matrix interference determined by GC-MS is serious, and the content of dimethyl fumarate is low, only GC-MS-MS can be used.

4 Reagents and materials

Unless otherwise specified, only use analytically-pure reagents or higher-purity reagents.

4.1 Ethyl acetate: It shall be dehydrated by 5A molecular sieve.

materials shall also be sampled and determined respectively. If the lining and the upper cannot be separated, the lining and the upper shall be sampled and determined together. The determination method shall also be in accordance with the lining material.

6.2 Specimen treatment

6.2.1 Textiles, artificial leather, synthetic leather and fillers

Weigh about 5.0 g (accurate to 0.001 g) from the cut small test pieces; place the specimen in a conical flask with stopper (5.8). Add 30 mL of ethyl acetate (4.1) dehydrated by 5A molecular sieve; close the conical flask and vigorously oscillate; so that all the specimens are immersed in the liquid (if the specimens are not completely submerged in the liquid, add an appropriate amount of dehydrated ethyl acetate until the specimens are completely submerged in liquid). Ultrasonically extract in an ultrasonic extractor (5.6) for 10 min; filter the extract into a round-bottom flask (5.10). Use 20 mL of dehydrated ethyl acetate to repeat the above steps once; combine the extracts. Finally, use 10 mL of dehydrated ethyl acetate to rinse the conical flask and the specimen; shake vigorously; combine the extracts. Concentrate the extract to about 3 mL on the rotary evaporator (5.4); transfer into a measuring cylinder with stopper (5.5); use a small amount of dehydrated ethyl acetate to rinse the round-bottom flask; incorporate the washing liquid into the measuring cylinder with stopper. Finally, use dehydrated ethyl acetate to dilute the volume to 5.0 mL to prepare a test solution. If the test solution is turbid or has precipitation, use a syringe (5.7) to suck a small amount of test solution into a centrifuge (5.12) with a 2 mL centrifuge tube (5.13) for centrifugation and layering for 5 min~10 min (speed is 8000 r/min). The supernatant after centrifugation is filtered by a syringe filter (5.14) and immediately analyzed by a gas chromatograph-mass spectrometer (5.2).

6.2.2 Leather samples

Weigh about 5.0 g (accurate to 0.001 g) from the cut small test pieces; place the specimen in a conical flask with stopper (5.8). Add 30 mL of ethyl acetate (4.1) dehydrated by 5A molecular sieve; close the conical flask and vigorously oscillate; so that all the specimens are immersed in the liquid (if the specimens are not completely submerged in the liquid, add an appropriate amount of dehydrated ethyl acetate until the specimens are completely submerged in liquid). Ultrasonically extract in an ultrasonic extractor (5.6) for 10 min; filter the extract into a round-bottom flask (5.10). Use 20 mL of dehydrated ethyl acetate to repeat the above steps once; combine the extracts. Finally, use 10 mL of dehydrated ethyl acetate to rinse the conical flask and the specimen; shake vigorously; combine the extracts. Concentrate the extract to about 1 mL on the rotary evaporator. Pour 5 mL of n-hexane into the neutral alumina cartridge (4.3)

to activate the cartridge; and then add 5 mL of dehydrated ethyl acetate to rinse the cartridge. Then, transfer the concentrated extract to the cartridge. After cartridge purification, the test solution is collected by a measuring cylinder with stopper. Use a small amount of dehydrated ethyl acetate to rinse the round-bottom flask several times; pour the washing liquid into the cartridge; combine the purification liquid and dilute to 5 mL. If the test solution is turbid or has precipitation, use a syringe to suck a small amount of test solution into a centrifuge with a 2 mL centrifuge tube for centrifugation and layering for 5 min (speed is 8000 r/min). The supernatant after centrifugation is filtered by a syringe filter and immediately analyzed by a gas chromatograph-mass spectrometer.

6.3 Preparation of standard solutions

Accurately weigh 0.02 g (accurate to 0.001 g) of standard dimethyl fumarate (4.2) in a 25 mL volumetric flask with stopper (5.11); use dehydrated ethyl acetate (4.1) to dissolve and dilute to the mark, shake well. Then, use dehydrated ethyl acetate to dilute step by step, to prepare standard working solutions with concentrations of 0.1 mg/L, 0.5 mg/L, 1.0 mg/L, 5.0 mg/L, 10.0 mg/L, 20.0 mg/L, and 50.0 mg/L respectively. Store in a refrigerator at 4 °C and protected from light for later use. The expiry date is 1 month.

6.4 Determination of gas chromatography-mass spectrometry (GC-MS)

6.4.1 Gas chromatography-mass spectrometry analysis conditions

Since the test results depend on the instrument used, it is impossible to give general parameters for gas chromatography-mass spectrometry. The set parameters shall ensure that the measured component and other components can be effectively separated during chromatographic determination. The following parameters are proved to be feasible:

a) Chromatographic column: DB-5MS column; 30 m×0.25 mm (inner diameter)×0.25 μm, or equivalent;

b) Inlet temperature: 250 °C;

c) Gas chromatography-mass spectrometry interface temperature: 280 °C;

d) Injection mode: Splitless injection; open the valve after 1 min;

e) Carrier gas: Helium; its purity is ≥99.999%. Control method: Constant flow rate is 1.0 mL/min;

f) Column temperature: Rise from 60 °C to 100 °C at a rate of 5 °C/min; then rise to 280 °C at a rate of 25 °C/min and keep it for 10 min;

parameters shall ensure that the measured component and other components can be effectively separated during chromatographic determination. The following parameters are proved to be feasible:

a) Chromatographic column: DB-5MS column; 30 m×0.25 mm (inner diameter)×0.25 μm, or equivalent;

b) Inlet temperature: 100 °C;

c) Gas chromatography-mass spectrometry interface temperature: 280 °C;

d) Injection mode: Splitless injection; open the valve after 1 min;

e) Carrier gas: Helium; its purity is ≥99.999%. Control method: Constant flow rate is 1.0 mL/min;

f) Column temperature: Rise from 60 °C to 100 °C at a rate of 5 °C/min; then rise to 280 °C at a rate of 25 °C/min and keep it for 10 min;

g) Injection volume: 1 μL;

h) Ion source: EI source;

i) Ionization energy: 70 eV;

j) Scan mode: Secondary mass spectrometry (MS-MS); qualitative ion m/z: 85, 53, 113; quantitative ion m/z: 85;

k) Pyrolysis method: Resonance;

l) Excitation storage level: 49.6 m/z;

m) Excitation pyrolysis voltage: 0.5 V;

n) Solvent delay time: 3 min.

6.5.2 Gas chromatography-secondary mass spectrometry analysis and confirmation of positive results

According to the content of dimethyl fumarate in the test solution, select standard working solutions with similar concentrations. The response values of dimethyl fumarate in the standard working solution and in the test solution shall be within the linear range of the instrument. Under the above-mentioned GC-MS-MS conditions, the retention time of dimethyl fumarate is about 6.5 min.

In the total ion chromatograms of the test solution and the standard working solution, if there are chromatographic peaks at the same retention time, it shall confirm it based on the characteristic ion fragments of dimethyl fumarate and

their abundance ratio.

Qualitative ion (m/z): 85, 53, 113 (the abundance ratio is 100:11:5);

Quantitative ion (m/z): 85.

Note: Refer to Appendix B for the GC-MS-MS standard spectrograms of dimethyl fumarate.

7 Blank test

Except that no specimen is added, proceed according to the above 6.2~6.5 determination steps, to prove that there is no dimethyl fumarate component in the reagents and materials used in the test process.

8 Result calculation

Calculate the content of dimethyl fumarate according to formula (1):

$$X = \frac{c \times V}{m} \qquad \cdots\cdots (1)$$

Where:

X - The content of dimethyl fumarate in the specimen, in milligrams per kilogram (mg/kg);

c - The mass concentration of dimethyl fumarate in the specimen solution obtained from the standard working curve, in milligrams per liter (mg/L);

V - The constant volume of the test solution, in milliliters (mL);

m - The mass of the specimen, in grams (g).

9 Determination of recovery rate

Add a standard solution with a content of dimethyl fumarate equal to that in the sample into a round-bottom flask containing 60 mL of ethyl acetate. Then follow the determination steps of 6.2~6.5. The recovery rate of dimethyl fumarate shall be greater than 80%.

10 Result representation

Take the average of the results of two parallel determinations. The result is rounded to two decimal places.

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