

Identification and Assay for Sunscreen Agents in Cosmetics (2)

1. Scope

This method is applicable to the determination of benzophenone-3, isoamyl *p*-methoxycinnamate, 4-methylbenzylidene camphor, octocrylene, ethylhexyl dimethyl PABA, ethylhexyl methoxycinnamate, ethylhexyl salicylate, homosalate, diethylhexyl butamido triazone, ethylhexyl triazone, diethylamino hydroxybenzoyl hexyl benzoate, butyl methoxydibenzoylmethane, drometrizole trisiloxane, terephthalylidene dicamphor sulfonic acid, methylene bis-benzotriazolyl tetramethylbutylphenol, and bis-ethylhexyloxyphenol methoxyphenyl triazine in cosmetics.

2. Method

After extraction, analytes are determined by high performance liquid chromatography (HPLC).

2.1. Equipment

2.1.1. High performance liquid chromatograph.

2.1.1.1. Detector: photodiode array detector.

2.1.1.2. Column: Acquity UPLC[®] BEH C18, 1.7 μm , 2.1 mm i.d. \times 10 cm, or an equivalent product.

2.1.2. Ultrasonicator.

2.2. Chemicals

Methanol, HPLC grade;

Tetrahydrofuran, HPLC grade;

Ammonium formate, GR grade;

Ammonia water (28%), GR grade;

Deionized water, resistivity $\geq 18 \text{ M}\Omega \cdot \text{cm}$ (at 25°C);

Benzophenone-3, isoamyl *p*-methoxycinnamate, 4-methylbenzylidene camphor, octocrylene, ethylhexyl dimethyl PABA, ethylhexyl methoxycinnamate, ethylhexyl salicylate, homosalate, diethylhexyl butamido triazone, ethylhexyl triazone, diethylamino hydroxybenzoyl hexyl benzoate, butyl methoxydibenzoylmethane, drometrizole trisiloxane, terephthalylidene dicamphor sulfonic acid, methylene bis-benzotriazolyl tetramethylbutylphenol, and bis-ethylhexyloxyphenol methoxyphenyl triazine, reference standards.

2.3. Apparatus

2.3.1. Volumetric flask: 10 mL, 25 mL, 50 mL, and 100 mL.

2.3.2. Membrane filter: 0.22 μm , PVDF.

2.4. Ammonia water: Methanol (1:99, v/v):

Mix ammonia water and methanol at the ratio of 1:99 (v/v).

2.5. Mobile phase

2.5.1. Solvent A: Methanol

2.5.2. Solvent B: Dissolve and dilute 3.15 g of ammonium formate with deionized water to 500 mL, mix well. Filter with a membrane filter as solvent B.

2.6. Standard solution preparation

Transfer about 10 mg of benzophenone-3, isoamyl *p*-methoxycinnamate, 4-methylbenzylidene camphor, octocrylene, ethylhexyl dimethyl PABA, ethylhexyl methoxycinnamate, ethylhexyl salicylate, homosalate, diethylhexyl butamido triazone, ethylhexyl triazone, diethylamino hydroxybenzoyl hexyl benzoate, butyl methoxydibenzoylmethane and drometrizole trisiloxane reference standards accurately weighed into each 10-mL volumetric flask, dissolve and dilute with methanol to volume as the standard stock solutions. Transfer about 10 mg of methylene bis-benzotriazolyl tetramethylbutylphenol, and bis-ethylhexyloxyphenol methoxyphenyl triazine reference standards accurately weighed into each 10-mL volumetric flask, dissolve and dilute with tetrahydrofuran to volume as standard stock solutions. Transfer about 10 mg of terephthalylidene dicamphor sulfonic acid reference standard accurately weighed into a 10-mL volumetric flask, dissolve and dilute with ammonia water : methanol (1:99, v/v) solution to volume as standard stock solution. When to use, mix appropriate amount of each standard stock solution, and dilute with methanol to 0.5-50 µg/mL as the standard solutions.

2.7. Sample solution preparation

Transfer about 0.5 g of the well-mixed sample accurately weighed into a 10-mL volumetric flask, add 5 mL of tetrahydrofuran, and ultrasonicate for 30 min. Dilute to volume with methanol, and filter with a membrane filter. Take the filtrate as the sample solution.

2.8. Identification and quantitation

Accurately inject 5 µL of the sample solution and the standard solutions into HPLC separately, and operate according to the following conditions. Identify each sunscreen agent based on the retention time and the UV absorption

spectrum. Calculate the amount of each sunscreen agent in the sample by the following formula:

$$\text{The amount of each sunscreen agent in the sample (\%)} = \frac{C \times V}{M} \times 10^{-4}$$

where,

C: the concentration of each sunscreen agent in the sample solution calculated by the standard curve (µg/mL)

V: the final make-up volume of sample (mL)

M: the weight of the sample (g)

HPLC operating conditions:

Photodiode array detector:

Analyte	Quantitative wavelength (nm)
benzophenone-3, isoamyl <i>p</i> -methoxycinnamate, 4-methylbenzylidene camphor, octocrylene, ethylhexyl dimethyl PABA, ethylhexyl methoxycinnamate, ethylhexyl salicylate, homosalate, diethylhexyl butamido triazone, and ethylhexyl triazone	310
diethylamino hydroxybenzoyl hexyl benzoate, butyl methoxydibenzoylmethane, drometrizole trisiloxane, terephthalylidene dicamphor sulfonic acid, methylene bis-benzotriazolyl tetramethylbutylphenol, and bis-ethylhexyloxyphenol methoxyphenyl triazine	350

Column: Acquity UPLC® BEH C18, 1.7 µm, 2.1 mm i.d. × 10 cm.

Mobile phase: a gradient program of solvent A and solvent B is as follows.

Time (min)	Solvent A (%)	Solvent B (%)
0.0 → 5.5	77 → 77	23 → 23
5.5 → 7.5	77 → 100	23 → 0
7.5 → 12.5	100 → 100	0 → 0
12.5 → 13.0	100 → 77	0 → 23
13.0 → 15.0	77 → 77	23 → 23

Flow rate: 0.5 mL/min.

Note: All the parameters can be adjusted depending on the instruments used if the above conditions are not applicable.

Remark

1. Limits of quantitation (LOQs) for benzophenone-3, isoamyl *p*-methoxycinnamate, 4-methylbenzylidene camphor, octocrylene, ethylhexyl dimethyl PABA, ethylhexyl methoxycinnamate, ethylhexyl salicylate 、homosalate 、ethylhexyl triazone, diethylhexyl butamido triazone, and diethylamino hydroxybenzoyl hexyl benzoate are 0.001%; LOQs for terephthalylidene dicamphor sulfonic acid, drometrizole trisiloxane, methylene bis-benzotriazolyl tetramethylbutylphenol, bis-ethylhexyloxyphenol methoxyphenyl triazine, and butyl methoxydibenzoylmethane are 0.002%.
2. Further validation should be performed when interference compounds appear in samples.