

Method of Test for Sunscreen Agents in Cosmetics (3)

1. Scope

This method is applicable to the determination of benzophenone-4, benzylidene camphor sulfonic acid, camphor benzalkonium methosulfate, and phenylbenzimidazole sulfonic acid in cosmetics.

2. Method

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

2.1. Equipment

2.1.1. High performance liquid chromatograph.

2.1.1.1. Detector: photodiode array detector.

2.1.1.2. Column: CAPCELL CORE AQ, 2.7 μm , 4.6 mm i.d. \times 15 cm, or an equivalent product.

2.1.2. Ultrasonicator.

2.2. Chemicals

Methanol, HPLC grade;

Acetonitrile, HPLC grade;

Ammonium formate, GR grade;

Formic acid, GR grade;

Ammonium solution (25%), GR grade;

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

Benzophenone-4 (BP-4), benzylidene camphor sulfonic acid (BCSA), camphor benzalkonium methosulfate (CBM), and phenylbenzimidazole sulfonic acid (PBSA), reference standards.

2.3. Apparatus

2.3.1. Volumetric flask: 10 mL.

2.3.2. Membrane filter: 0.45 μm , PTFE.

2.4. 0.25% ammonium solution in methanol:

Dilute 1 mL ammonium solution with methanol to 100 mL.

2.5. Mobile phase

2.5.1. Solvent A:

Dissolve and dilute 0.63 g of ammonium formate and 1 mL of formic acid with deionized water to 1000 mL, then filter with a membrane filter.

2.5.2. Solvent B: Methanol.

2.6. Standard solution preparation

Transfer about 10 mg of BP-4, BCSA, and CBM 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 PBSA reference standard accurately weighed into a 10-mL volumetric flask, dissolve and dilute with 0.25% ammonium solution in methanol to volume as the standard stock solution. Store in a refrigerator and in dark. When to use, mix appropriate volume of each standard stock solution, and dilute with methanol to 1-50 µg/mL as the standard solutions.

2.7. Sample solution preparation

Transfer about 1 g of the well-mixed sample accurately weighed into a 10-mL volumetric flask. Add 5 mL of methanol, and sonicate for 30 min. Add methanol to volume. Filter with a membrane filter, and take the filtrate as the sample solution.

2.8. Identification and quantification

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 sample (g)

HPLC operating conditions^(note) :

Photodiode array detector: the quantitative wavelength 290 nm.

Column: CAPCELL CORE AQ, 2.7 µm, 4.6 mm i.d. × 15 cm.

Column oven temperature: 40C

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

Time (min)	A (%)	B (%)
0 → 3	70 → 45	30 → 55
3 → 6	45 → 45	55 → 55
6 → 7	45 → 5	55 → 95

7 → 13	5 → 5	95 → 95
13 → 14	5 → 70	95 → 30
14 → 15	70 → 70	30 → 30

Flow rate: 0.7 mL/min.

Injection volume: 5 µL.

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

Remark

1. Limits of quantification (LOQs) are 0.001% for benzophenone-4, benzylidene camphor sulfonic acid, camphor benzalkonium methosulfate, and phenylbenzimidazole sulfonic acid.
2. Further validation should be performed when interference compounds appear in samples.

Reference

1. Wharton, M., Geary, M., O'Connor, N., Curtin, L. and Ketcher, K. 2015. Simultaneous liquid chromatographic determination of 10 ultra-violet filters in sunscreens. J. Chromatogr. Sci. 53: 1289-1295.
2. Kim, D., Kim, S., Kim, S. A., Choi, M., Kwon, K. J., Kim, M., Kim, D. S., Kim, S. H. and Choi, B. K. 2012. Simultaneous analysis and monitoring of 16 UV filters in cosmetics by high-performance liquid chromatography. J. Cosmet. Sci. 63: 103-117.

Reference chromatogram

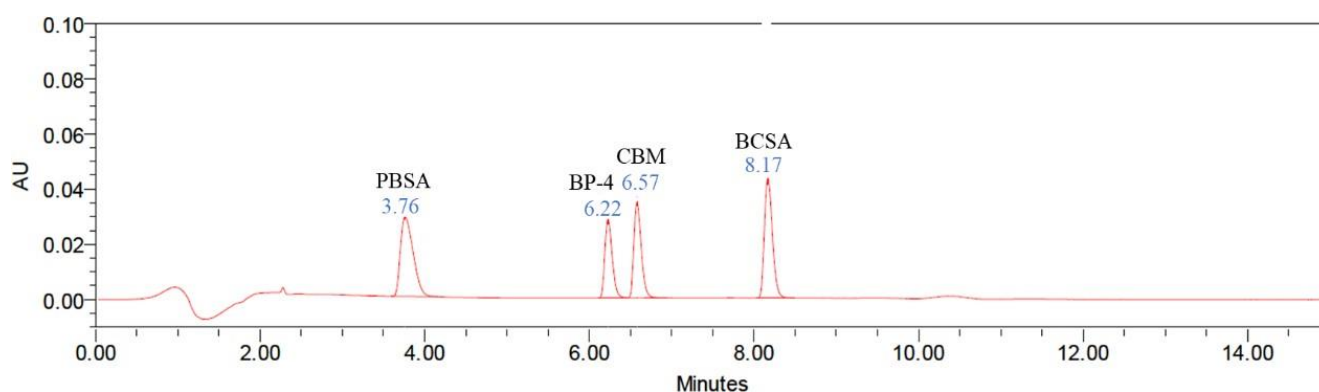


Figure. HPLC chromatogram of standards of 4 sunscreen agents.