

Method of Test for Banned Phthalate Esters in Cosmetics

1. Scope

This method is applicable to the determination of dibutyl phthalate (DBP), bis(2-methoxyethyl) phthalate (DMEP), di-*n*-pentyl phthalate (DnPP), diisopentyl phthalate (DiPP), benzyl butyl phthalate (BBP), bis(2-ethylhexyl) phthalate (DEHP) and di-*n*-octyl phthalate (DnOP) in cosmetics.

2. Method

After extraction, phthalate esters are determined by gas chromatography/mass spectrometry (GC-MS).

2.1. Equipment

2.1.1. Gas chromatograph/mass spectrometer

2.1.1.1. Ion source: electron ionization, EI.

2.1.1.2. Column: HP-5 MS, 0.25 μ m, 0.25 mm i.d. \times 30 m, or an equivalent product.

2.1.2. Centrifuge: \geq 3000 rpm.

2.1.3. Ultrasonicator.

2.2. Chemicals

Methanol, HPLC grade;

dibutyl phthalate, bis(2-methoxyethyl) phthalate, di-*n*-pentyl phthalate, diisopentyl phthalate, benzyl butyl phthalate, bis(2-ethylhexyl) phthalate, di-*n*-octyl phthalate, reference standards.

2.3. Apparatus^(note)

2.3.1. Volumetric flask: 10 mL.

2.3.2. Centrifuge tube: 10 mL, glass.

Note: The apparatus used in the test must be made of glass rather than made of plastic material. Rinse the apparatus with methanol, and then air-dry before use.

2.4. Standard solution preparation

Transfer about 10 mg of DBP, DMEP, DnPP, DiPP, BBP, DEHP and DnOP reference standards accurately weighed into each 10-mL volumetric flask, dissolve and dilute with methanol to volume as the standard stock solutions. Store in a refrigerator. When to use, mix appropriate amount of each standard stock solutions, and dilute with methanol to 0.5 ~ 40 μ g/mL as the standard solutions.

2.5. Sample solution preparation

Transfer about 1 g of homogenized sample accurately weighed into a 10-mL volumetric flask. Add 8 mL of methanol, ultrasonicate for 20 min, and then dilute to volume with methanol. Centrifuge at 3000 rpm for 10 min, and take the supernatant as the sample solution.

2.6. Identification and quantification

Accurately inject 1 μ L of the sample solution and the standard solutions into GC-MS separately. Identify each phthalate ester based on the retention time and the relative ion intensities^(note). Calculate the amount of each phthalate esters in the sample by the following formula:

$$\text{The amount of each phthalate ester in the sample (ppm)} = \frac{C \times V}{M}$$

Where,

C: the concentration of each phthalate ester in the sample solution calculated by the standard curve (μ g/mL)

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

M: the weight of the sample (g)

GC-MS operating conditions:

Column: HP-5 MS, 0.25 μ m, 0.25 mm i.d. \times 30 m.

Oven temperature program:

initial temperature: 100°C;

temperature gradient rate: 20°C/min;

final temperature: 280°C, hold for 9 min.

Carrier gas and flow rate: helium, 1.2 mL/min.

Injector temperature: 300°C.

Injection mode: splitless.

Injection volume: 1 μ L.

Interface temperature: 300°C.

Ion source temperature: 280°C.

Ionization mode: EI, 70 eV.

Detection mode: full scan, m/z 40 ~ 500; detection ions are as follows:

Analyte	Quantitative ion (m/z)	Qualitative ions (m/z)
DBP	149	223, 205
DMEP	59	149, 207
DnPP	149	237, 219
DiPP	149	237, 219

BBP	149	91, 206
DEHP	149	167, 279
DnOP	149	279, 261

Notes: 1. Relative ion intensities are calculated by peak areas of quantitative ions divided by peak areas of qualitative ions ($\leq 100\%$). Maximum permitted tolerances of relative ion intensities are as follows:

Relative ion intensity (%)	Tolerance (%)
> 50	± 10
> 20 ~ 50	± 15
> 10 ~ 20	± 20
≤ 10	± 50

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

Remark

1. The limit of quantification (LOQ) for each banned phthalate ester is 5 ppm.
2. Further validation should be performed when interference compounds appear in samples.

Reference

1. Thomas, C., Siong, D. and Pirnay, S. 2014. Evaluation of the content-containing interaction in cosmetic products using gas chromatography-mass spectrometry. *Int. J. Cosmet. Sci.* 36: 327-335.
2. Cheng, S. C., Chang, C. W., Huang, S. C., Chou, H. K. and Cheng, H. F. 2016. Survey on methanol, benzene and phthalate esters in marketed nail polishes in Taiwan. *Ann. Rep. Food Drug Res.* 7: 216-221.

Reference chromatogram

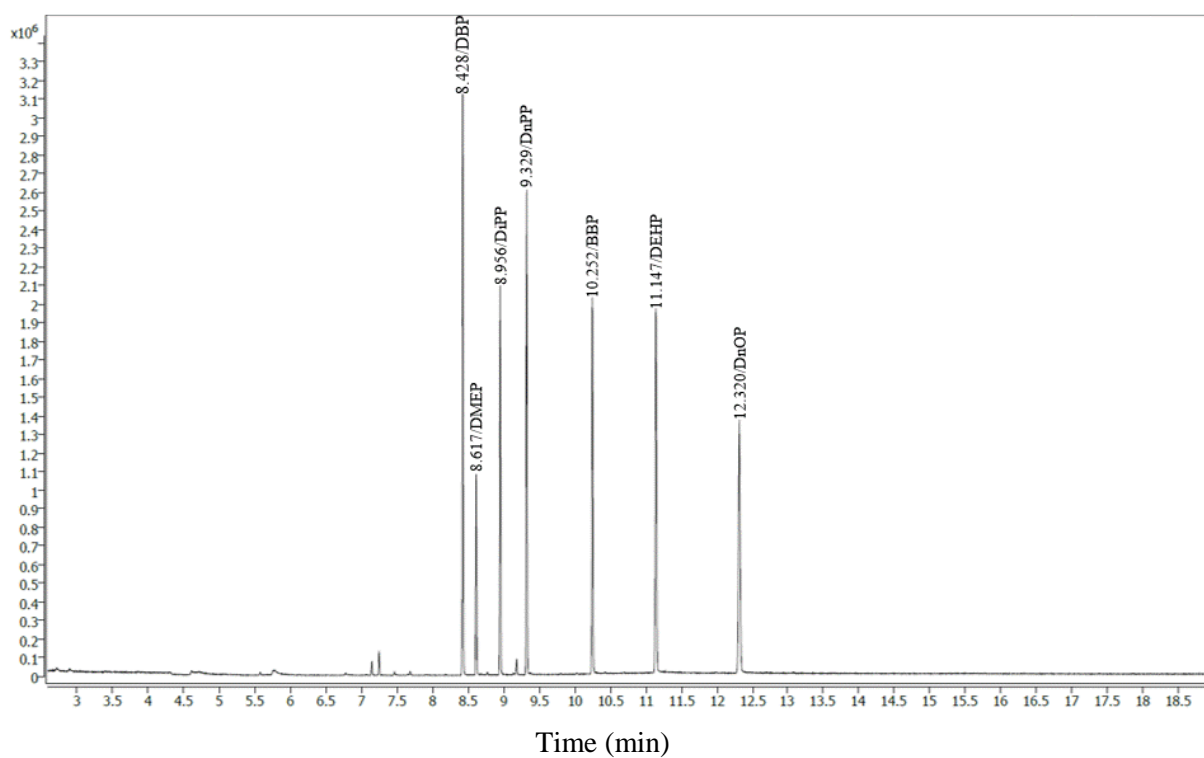


Figure. TIC chromatogram of 7 phthalate ester standards analyzed by GC-MS.