

## Identification and Assay for Methyl Methacrylate in Cosmetics

### 1. Scope

This method is applicable to the determination of methyl methacrylate in cosmetics.

### 2. Method

After heating, the analytes in the headspace are analyzed by gas chromatography/mass spectrometry (GC/MS) with headspace sampler.

#### 2.1. Equipment

##### 2.1.1. Gas chromatograph/mass spectrometer

2.1.1.1. Ion source: electron ionization, EI.

2.1.1.2. Column: DB-624, 1.4  $\mu\text{m}$ , 0.25 mm i.d.  $\times$  60 m, or an equivalent product.

2.1.2. Headspace sampler: with heating and shaking function, temperature control  $\geq 90^\circ\text{C}$ .

2.1.3. Ultrasonicator.

#### 2.2. Chemicals

1,3-Dimethyl-2-imidazolidinone, DMI, GC grade;

Methyl methacrylate, reference standard;

Toluene- $\text{d}_8$ , internal standard.

#### 2.3. Apparatus

2.3.1. Headspace vial: 20 mL, glass, with screw cap and Teflon septa.

2.3.2. Volumetric flask: 20 mL and 50 mL.

#### 2.4. Internal standard solution preparation

Transfer about 20 mg of toluene- $\text{d}_8$  internal standard accurately weighed into a 20-mL volumetric flask, dissolve and dilute to volume with DMI, well-mixed, as the internal standard stock solution. When to use, dilute appropriate amount of internal standard stock solution to 100  $\mu\text{g}/\text{mL}$  with DMI as the internal standard solution.

#### 2.5. Standard solution preparation

Transfer about 160 mg of methyl methacrylate reference standard accurately weighed into a 50-mL volumetric flask, dissolve and dilute to volume with DMI, well-mixed, as the standard stock solution. When to use, mix appropriate volume of standard stock solution, and dilute with DMI to 40-640  $\mu\text{g}/\text{mL}$ , as the standard solutions.

#### 2.6. Sample solution preparation

Transfer about 0.1 g of the well-mixed sample accurately weighed into a headspace vial, add 25  $\mu$ L of internal standard solution and 25  $\mu$ L of DMI. Seal with a cap quickly, mix well, as the sample solution.

## 2.7. Calibration curve preparation

Transfer about 0.1 g of the blank sample accurately weighed into each headspace vial. Add 25  $\mu$ L of the standard solution with different concentrations separately and 25  $\mu$ L of internal standard solution. Seal with caps quickly and mix well as the calibration solutions. Operate GC/MS with headspace autosampler according to the following conditions. Establish the calibration curve of methyl methacrylate by the ratios of the peak area of methyl methacrylate to that of the internal standard vs. the added concentrations in the range of 1-16  $\mu$ g.

Headspace injection operating conditions:

Heating temperature: 90°C.

Injection syringe temperature: 100°C.

Heating time: 20 min.

Injection volume: 2.5 mL.

Filling rate of syringe: 100  $\mu$ L/s.

Injection rate: 500  $\mu$ L/s.

GC/MS operating conditions:

Column: DB-624 Capillary, 1.4  $\mu$ m, 0.25 mm i.d.  $\times$  60 m.

Column temperature:

Initial temperature: 40°C, 1 min;

Temperature rising rate: 8°C /min;

Middle temperature: 150°C;

Temperature rising rate: 50°C /min;

Final temperature: 250°C, 3 min.

Carrier gas and flow rate: helium, 1 mL/min.

Injector temperature: 140°C.

Interface temperature: 250°C.

Ion source temperature: 250°C.

Ionization mode: EI, 70 eV.

Injection mode: split, 20:1.

Detection mode: full scan.  $m/z$  33-250. Detection ions are shown as follows.

Analyte	Quantitative ion ( <i>m/z</i> )	Qualitative ion ( <i>m/z</i> )
Methyl methacrylate	69	100, 99
Toluene-d <sub>8</sub> (I.S.)	98	-

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

## 2.8. Identification and quantification

Place the headspace vials of the sample solution and the standard solutions on the headspace autosampler. Heat for 20 min at 90°C, and operate according to the conditions described in section 2.7. Identify methyl methacrylate based on the retention time and the relative ion intensities<sup>(note)</sup>. Calculate the amount of methyl methacrylate (ppm) in the sample by the following formula:

$$\text{The amount of methyl methacrylate in the sample (ppm)} = \frac{M}{W}$$

where,

M: the amount of methyl methacrylate in the sample calculated by the calibration curve (µg)

W: the weight of the sample (g)

Note: Relative ion intensities are calculated by peak areas of qualitative ions divided by peak areas of quantitative ion (≤100%). Maximum permitted tolerances for relative ion intensities by GC-MS are as follows.

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

### Remark

1. Limit of quantification (LOQ) for methyl methacrylate is 10 ppm.
2. Further validation should be performed when interfering compounds appear in samples.

## Reference

1. Deconinck, E., Canfyn, M., Sacré, P. Y., Baudewyns, S., Courselle, P. and de Beer, J. O. 2012. A validated GC-MS method for the determination and quantification of residual solvents in counterfeit tablets and capsules. *J. Pharm. Biomed. Anal.* 70: 64-70.
2. Wojciech, F., Andreas, S., Maria, M. B., Clemens, A., Anna, F., Helmut, W., Markus, N., Jakob, T. and Anton, A. 2012. Characterization of volatile metabolites taken up by or released from *Streptococcus pneumoniae* and *Haemophilus influenzae* by using GC-MS. *Microbiology* 158: 3044-3053.