Identification and Assay for Methanol, Acetonitrile, Methylene Chloride, Chloroform, Benzene, 1,4-Dioxane and Toluene in Cosmetics

1. Scope

This method is applicable to the identification and determination of methanol, acetonitrile, methylene chloride, chloroform, benzene, 1,4-dioxane and toluene in cosmetics

2. Method

Analytes are determined directly by gas chromatography/mass spectrometry (GC-MS) with a headspace sampler.

2.1. Equipments

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 μm, 0.25 mm i.d. × 60 m, or an equivalent product.

2.1.2. Headspace sampler: with a shaking heater, capable of controlling temperature ≥ 90°C

2.1.3. Ultrasonicator.

2.2. Chemicals

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

Methanol, acetonitrile, methylene chloride, chloroform, benzene, 1,4-dioxane and toluene, reference standards;

Toluene-d_8, isotope-labeled internal standard.

2.3. Apparatus

2.3.1. Headspace vial: 20 mL, glass, with an aluminum cap and a Teflon gasket.

2.3.2. Volumetric flask: 20 mL and 100 mL.

2.4. Internal standard solution preparation

Transfer about 100 mg of toluene-d_8 isotope-labeled internal standard accurately weighed into a 100-mL volumetric flask, dissolve and dilute with DMI to volume as the internal standard stock solution. When to use, dilute appropriate amount of the stock solution to 100 μg/mL with DMI as the internal standard solution.

2.5. Standard solution preparation

Transfer about 80 mg of methanol, acetonitrile, methylene chloride, chloroform, benzene, 1,4-dioxane and toluene reference standards accurately weighed into each 20-mL volumetric flask, dissolve and dilute with DMI to volume as the standard stock solutions. When to use, mix appropriate amount of each standard stock solution, and dilute with DMI to 40 ~ 800 μg/mL for methanol, and 8 ~ 160 μg/mL for acetonitrile, methylene chloride, chloroform, benzene, 1,4-dioxane and toluene 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 µL of the internal standard solution and 25 µL of DMI, and then screw a cap immediately as the sample solution.

2.7. Calibration standard curve preparation

Take about 0.1 g of a blank sample into each headspace vial, add 25 µL of the standard solutions and 25 µL of the internal standard solution separately, and screw caps immediately. The amounts of the standards are 1 ~ 20 µg for methanol, and 0.2 ~ 4 µg for acetonitrile, methylene chloride, chloroform, benzene, 1,4-dioxane and toluene. Mix well, and analyze the headspace of each vial by a headspace sampler coupled with a GC-MS operated according to the following conditions. Establish the calibration standard curve of each analyte by the ratios of the peak area of each analyte to that of the internal standard vs. the added amounts.

Headspace sampler operating conditions (note) :

Heating temperature: 90°C.

Syringe temperature: 100°C.

Vial heating time: 20 min.

Inject volume: 2.5 mL.

GC-MS operating parameters(note) :

Column: DB-624, 1.4 µm, 0.25 mm i.d. × 60 m

Oven temperature program:

initial temperature: 40°C, hold for 1 min;
temperature gradient rate: 8°C /min;
middle temperature: 150°C;
temperature gradient rate: 50°C /min;
final temperature: 250°C, hold for 3 min

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

Injector temperature: 140°C.

Interface temperature: 250°C.

Ion source temperature: 200°C.

Ionization mode: EI, 70 eV.

Inlet mode and ratio: split, 20:1.

Detection mode: full scan, *m/z* 29 ~ 250. Detection ions are as follows.

Analyte	Quantitative ion (*m/z*)	Qualitative ions (*m/z*)
Methanol	31	33, 30

Acetonitrile	41	40, 39
Methylene chloride	84	49, 86
Chloroform	83	85, 47
Benzene	78	77, 51
1,4-Dioxane	88	58, 43
Toluene	91	92, 65
Toluene-d_8 (IS)	98	-

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

2.8. Identification and quantification

Place the headspace vials of the sample solution and the standard solutions on the headspace sampler, and operate according to the conditions described in section 2.7. Identify each analyte based on the retention time and the relative ion intensities(note). Calculate the amount of methanol, acetonitrile, methylene chloride, chloroform, benzene, 1,4-dioxane or toluene in the sample by the following formula:

The amount of methanol, acetonitrile, methylene chloride, chloroform, benzene, 1,4-dioxane or toluene in the sample (ppm) = $\frac{M}{W}$

Where,

M: the amount of methanol, acetonitrile, methylene chloride, chloroform, benzene, 1,4-dioxane and toluene in the sample solution calculated by the calibration standard 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 ions (≤100%). Maximum permitted tolerances for relative ion intensities by GC-MS are as the following:

Relative ion intersity (%)	Tolerance (%)
> 50	± 10
> 20～50	± 15
> 10～20	± 20
≦ 10	± 50

Remark

1. Limits of quantification (LOQs) are 10 ppm for methanol, and 2 ppm for acetonitrile, methylene chloride, chloroform, benzene, 1,4-dioxane and toluene.
2. Further validation shall be done when interference compounds appear in samples.

References

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. Vinci, R. M., Canfyn, M., De Meulenaer, B., de Schaetzen, T. van Overmeire, I., de Beer, J. and van Loco, J. 2010. Determination of benzene in different food matrices by distillation and isotope dilution HS-GC/MS. Anal. Chim. Acta 672: 124-129.