



中华人民共和国出入境检验检疫行业标准

SN/T 4441—2016

进出口化妆品中甲醇的测定 多维气相色谱-质谱联用法

Determination of methanol in cosmetics for import and export—
MDGC-MS method

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中 华 人 民 共 和 国
国家质量监督检验检疫总局 发 布

前 言

本标准按照 GB/T 1.1—2009 给出的规则起草。

请注意本文件的某些内容可能涉及专利,本文件的发布机构不承担识别这些专利的责任。

本标准由国家认证认可监督管理委员会提出并归口。

本标准起草单位:中华人民共和国上海出入境检验检疫局、中华人民共和国厦门出入境检验检疫局。

本标准主要起草人:伊雄海、周瑶、柯志成、赵善贞、曲栗、时逸吟、邓晓军、徐敦明。

进出口化妆品中甲醇的测定

多维气相色谱-质谱联用法

1 范围

本标准规定了化妆品中甲醇含量的多维气相色谱-质谱测定方法。

本标准适用于香水、指甲油、洗甲水、沐浴露、洗发水、洗面奶、卸妆露、润肤露、爽肤水、摩丝中甲醇的测定和确证。

2 规范性引用文件

下列文件对于本文件的应用是必不可少的。凡是注日期的引用文件,仅注日期的版本适用于本文件。凡是不注日期的引用文件,其最新版本(包括所有的修改单)适用于本文件。

GB/T 6682 分析实验室用水规格和试验方法

3 方法提要

试样于密封的顶空进样瓶中,在一定的温度和时间平衡下,使试样中的甲醇在气液两相中达到动态平衡,以多维气相色谱-质谱联用法进行测定,外标法定量。

4 试剂材料

除非另有说明,所用试剂均为分析纯,水为 GB/T 6682—2008 规定的一级水。

4.1 无甲醇乙醇:乙醇:纯度 $\geq 99.99\%$ 。

4.2 75%乙醇溶液:取无甲醇乙醇 75 mL,用水稀释至 100 mL。

4.3 甲醇标准物质:甲醇(methonal, CAS:67-56-1, 分子式:CH₃O)纯度 $\geq 99.9\%$ 。

4.4 标准储备液的配制:准确量取适量的甲醇标准品,用 75%乙醇配制成浓度为 100 g/L, 10 g/L 的标准溶液。于 -18℃ 避光密封保存,有效期 6 个月。

4.5 标准工作溶液的配制:根据需要,临时时吸取一定量的标准储备溶液,用 75%乙醇配置成适当浓度的标准工作溶液。于 4℃ 避光保存,现用现配。

5 仪器与设备

5.1 电子天平:感量分别为 0.01 g, 0.000 1 g。

5.2 顶空进样瓶:10 mL。

5.3 多维气相色谱-质谱仪:配有 CTC 自动顶空进样器。1D 系统配有氢火焰离子化检测器(FID)和 Deans switch 切换阀。2D 系统配有四级杆质谱仪(EI 源)。

6 分析步骤

6.1 取样

香水、指甲油、洗甲水、沐浴露、洗发水、洗面奶、卸妆露、润肤露和爽肤水直接取样。摩丝等含推进剂的样品,取一定量 75%乙醇于顶空瓶中,在摩丝的喷嘴装上注射器针头,连接聚四氟乙烯细管,将此管另一端插入到乙醇液面下,缓缓按压喷嘴,使发胶从针头流出经聚四氟乙烯细管流入到乙醇溶液中,用减法计算取样量。如样品中甲醇浓度过高,应先将样品用 75%乙醇稀释。

6.2 预处理

称取 2.0 g 样品(准确至 0.01 g)于顶空进样瓶中,加入 75%乙醇溶液 2.0 mL,密封后于自动顶空进样器中 70 °C 恒温、500 r/min 振荡 10 min,取气液平衡后的液上气体供多维气相色谱-质谱联用仪测定。

6.3 测定

6.3.1 第一维气相色谱测定条件

第一维气相色谱测定条件如下:

- a) 色谱柱:DB-5 ms,长 30 m,内径 0.25 mm,膜厚 0.25 μ m,或相当者;
- b) 升温程序:45 °C 保持 4 min,以 30 °C/min 升至 250 °C(保持 2.5 min);
- c) 载气:氦气,纯度 \geq 99.999%,恒压模式:142.1 kPa;
- d) 进样方式:分流进样,分流比:50 : 1;
- e) 进样量:500 μ L;
- f) 进样口温度:240 °C;
- g) 检测器:FID;
- h) 检测器温度:260 °C;
- i) 切割压力(APC):88.3 kPa;
- j) 中心切割窗口:3.45 min~3.65 min(此窗口只包含甲醇标准品所在位置,切勿包含乙醇或异丙醇)。

6.3.2 第二维气相色谱-质谱测定条件

第二维气相色谱-质谱测定条件如下:

- a) 色谱柱:HP-INNOWAX,长 30 m,内径 0.32 mm,膜厚 0.25 μ m,或相当者;
- b) 升温程序:50 °C 保持 6 min,以 30 °C/min 升至 180 °C(保持 3 min);
- c) 载气:氦气,纯度 \geq 99.999%,流速:1.5 mL/min;
- d) 电离方式:EI,70 eV;
- e) 接口温度:250 °C;
- f) 离子源温度:200 °C;
- g) 溶剂延迟:3 min;
- h) 测定方式:选择离子监测模式(SIM)。

监测离子:31.0*, 32.0, 29.0, 30.0, “*”为定量离子。

7 色谱测定

7.1 定性测定

按照多维气相色谱-质谱条件测定样品和标准工作溶液,样品的质量色谱峰保留时间与标准品中对应的保留时间一致;且样品中目标组分定性离子的相对丰度与接近浓度的标准工作溶液中相应的定性离子的相对丰度进行比较,偏差不超过表 1 规定的范围,则可判定样品中存在对应的被测物。

表 1 定性确证时相对离子丰度的最大允许偏差

相对离子丰度	>50 %	>20 %~50 %	>10 %~20 %	≤10 %
允许的相对偏差	±10 %	±15 %	±20 %	±50 %

7.2 定量测定

在仪器最佳工作条件下,对标准工作溶液进样。用标准工作曲线按外标法定量,样品溶液中被测物的响应值均应在仪器测定的线性范围内。根据试样中被测样液的含量情况,选取响应值相近的标准工作液进行色谱分析。标准工作液和样液中待测物的响应值均应在仪器线性响应范围内。在上述色谱条件下甲醇的参考保留时间约为 5.56 min,甲醇标准品的选择离子监测色谱图(SIM)和质谱图参见附录 A。如样品中甲醇含量超过本方法线性范围,应将样品用 75 %乙醇稀释后再行分析。

7.3 空白试验

除不加试样外,均按上述操作步骤进行。

8 结果计算和表达

结果用色谱数据处理机或按式(1)计算试样中甲醇的含量,计算结果需扣除空白值:

$$X_i = \frac{A_i \times C_i}{A_{si} \times m} \dots\dots\dots (1)$$

式中:

- X_i ——试样中甲醇含量,单位为毫克每千克(mg/kg);
- A_i ——样液中甲醇的峰面积;
- C_i ——标准工作溶液中甲醇的浓度,单位为毫克每升(mg/L);
- A_{si} ——标准工作溶液中甲醇的峰面积;
- m ——最终样液代表的试样量,单位为克(g)。

注: 计算结果应扣除空白值。

9 测定低限和回收率

9.1 测定低限

本方法对进出口香水、指甲油、洗甲水、沐浴露、洗发水、洗面奶、卸妆露、润肤露、爽肤水、摩丝中甲醇含量的测定低限均为 100 mg/kg。

9.2 回收率

不同添加浓度范围内回收率的试验数据,见表2。

表2 标准添加浓度及回收率的试验数据($n=6$)

添加浓度 mg/kg	样品名称	回收率范围 %	添加浓度 mg/kg	样品名称	回收率范围 %
100.0	香水	81.38~96.79	100.0	洗面奶	100.89~109.67
1 000.0		82.35~103.54	1 000.0		94.04~103.38
2 000.0		93.17~107.04	2 000.0		83.09~101.31
5 000.0		95.01~103.14	5 000.0		86.51~106.37
100.0	指甲油	80.24~99.29	100.0	卸妆露	90.64~104.09
1 000.0		83.98~99.32	1 000.0		93.47~103.79
2 000.0		95.11~106.13	2 000.0		86.72~99.85
5 000.0		85.59~99.53	5 000.0		90.04~105.98
100.0	洗甲水	81.44~96.42	100.0	润肤露	86.53~107.25
1 000.0		80.72~86.69	1 000.0		90.74~102.96
2 000.0		89.62~107.04	2 000.0		96.81~107.57
5 000.0		84.29~97.83	5 000.0		95.05~108.33
100.0	沐浴露	95.67~102.61	100.0	爽肤水	81.19~94.76
1 000.0		93.35~109.61	1 000.0		93.81~106.18
2 000.0		89.38~95.84	2 000.0		83.99~98.61
5 000.0		98.49~105.42	5 000.0		80.51~94.19
100.0	洗发水	92.99~107.82	100.0	摩丝	96.54~107.99
1 000.0		88.43~108.53	1 000.0		96.49~106.21
2 000.0		89.49~98.99	2 000.0		92.77~98.29
5 000.0		100.39~107.16	5 000.0		99.09~109.85

附录 A
(资料性附录)

甲醇标准品选择离子色谱图及质谱图

甲醇标准品选择离子色谱图及质谱图见图 A.1 和图 A.2。

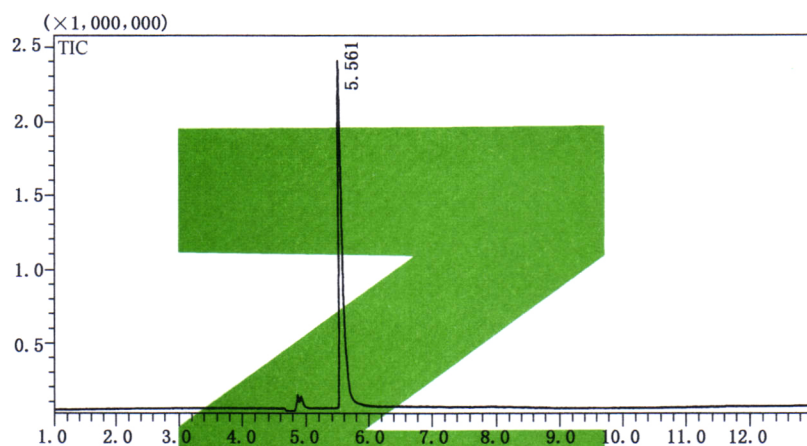


图 A.1 甲醇标准溶液的选择离子色谱图

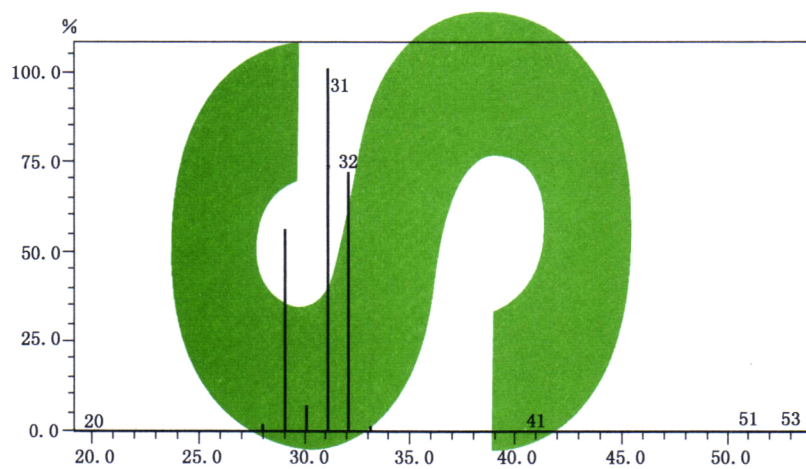


图 A.2 甲醇标准品的全扫描质谱图

Foreword

The standard is drafted in accordance with the rules given in the GB/T 1.1—2009 *Directives for standardization—Part 1: Structure and drafting of standards*.

Attention is drawn to the possibility that some of the elements of this standard may be the subject of patent rights. The issuing body of this document shall not be held responsible for identifying any or all such patent rights.

This standard was proposed by and is under the charge of the Certification and Accreditation Administration of the People's Republic of China.

This standard was drafted by the Shanghai Entry-Exit Inspection and Quarantine Bureau of the People's Republic of China and Xiamen Entry-Exit Inspection and Quarantine Bureau of the People's Republic of China.

The main drafters of this standard are Yi xionghai, Zhou yao, Ke zhicheng, Zhao shanzhen, Qu li, Shi yiyin, Deng xiaojun, Xu dunming.

Note: This English version, a translation from the Chinese text, is solely for guidance.

Determination of methanol in cosmetics for import and export—MDGC-MS method

1 Scope

This standard specifies the MDGC-MS method for determination of methanol in cosmetics for export.

This standard is applicable to the determination and confirmation of content of methanol in perfume, nail polish, nail polish remover, bath cream, shampoo, mildy wash, make-up remover, body lotion, astringent lotion, mousse for export.

2 Normative reference

The following normative documents contain provisions which, through reference in this text, constitute provisions of this standard. For dated references, subsequent amendments to, or revisions of any of these publications do not apply. However parties to agreements based on this standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies.

GB/T 6682 analysis laboratory water specification and test method

3 Principle

The test samples are weighed into sealed vials. Under certain temperature and time, the methanol in samples reaches dynamic balance in the gas-liquid two-phase, then determined by Multidimensional Gas Chromatography with Mass Spectrometric Detection, and quantified by external standard method.

4 Reagents and materials

All the reagents used should be analytically pure unless otherwise specified. "Water" is first class water as GB/T 6682 specified.

4.1 Ethanol (contain no methanol): purity $\geq 99.99\%$.

4.2 75% ethanol: obtained by dissolving 75 mL ethanol in Milli-Q water, with a final volume of 100 mL.

4.3 Methonal standards: Methonal (CAS: 67-56-1, 分子式: CH_4O): Purity $\geq 99.0\%$.

4.4 Standard stock solution: accurately weigh certain amount of methanol standard and dissolve with 75% ethanol to make the standard stock solution of 100 g/L, 10 g/L. The solution is stored in a refrigerator at $-18\text{ }^{\circ}\text{C}$, assign a shelf life of 6 months.

4.5 Working standard solutions: according to the need, transfer adequate intermediate solution of standards to 75% ethanol for preparation of working standard solutions when it will be used, store refrigerated at $4\text{ }^{\circ}\text{C}$. Prepare the solutions when use.

5 Apparatus and equipment

5.1 Electronic balance: accurate to 0.01 g, 0.000 1 g.

5.2 Headspace vials: 10 mL.

5.3 Multidimensional Gas Chromatography-Mass Spectrometric Detection, equipped with CTC Analytics Combi PAL automatic headspace sampler. The 1D chromatograph, equipped with flame-ionization detection (FID) and Deans switching system. The 2D chromatograph, equipped with quadrupole mass spectrometer and electron impact ion source (EI).

6 Analysis Steps

6.1 Preparation of test sample

Perfume, nail polish, nail polish remover, bath cream, shampoo, mildly wash, make-up remover, body lotion, astringent lotion are weighted directly. Samples which contain propellant, such as mousse, sample in the following way: Transfer certain 75% ethanol to the crimp top vial, install a syringe needle on the nozzle of the mousse to connect a teflon tube, then insert the other end of teflon tube into the ethanol liquid level, press the nozzle gently, make the hair spray outflow from teflon tube into ethanol solution, and use the subtraction method to calculate the sample quantity. If concentration of methanol in the sample is too high, samples shall be diluted.

6.2 Pretreatment

Weigh 2.0 g (accurate to 0.01 g) of the test sample into headspace vials, inject 2.0 mL 75% ethanol. Samples are sealed and incubated at $70\text{ }^{\circ}\text{C}$ in the heating block for 10 min with 500 r/min vibration. Take the gas on the liquid after the balance of gas-liquid and determined by MGDC-MS.

6.3 Determination

6.3.1 1D chromatograph operating conditions

1D chromatograph operating conditions are as follows:

- a) Chromatograph column: DB-5 ms column, 30 m × 0.25 mm (i.d), 0.25 μm film thickness (or other equivalent ones);
- b) Oven temperature program: 45 °C for 4 min, then increased at a rate of 30 °C/min to 250 °C (maintain for 2.5 min);
- c) Carrier gas: He, Purity ≥ 99.999%. Constant voltage mode, 142.1 kPa;
- d) Injector mode: split mode; Split ratio: 50 : 1;
- e) Injector volume: 500 μL;
- f) Injector port temperature: 240 °C;
- g) Detector: FID;
- h) Detector temperature: 260 °C;
- i) Cutting pressure (APC): 88.3 kPa;
- j) Heart-Cutting window: 3.45 min~3.65 min(This window contains only the location of methanol standard, be sure not to contain ethanol or isopropanol).

6.3.2 2D chromatograph operating conditions

2D chromatograph operating conditions are as follows:

- a) Chromatograph column: HP-INNOWAX column, 30 m × 0.32 mm (i.d), 0.25 μm film thickness (or other equivalent ones);
- b) Oven temperature program: 50 °C for 6 min, then increased at a rate of 30 °C/min to 180 °C (maintain for 3 min);
- c) Carrier gas: He, Purity ≥ 99.999%. Flow rate: 1.5 mL/min;
- d) Ionization mode: EI, 70 eV;

- e) Interface temperature: 250 °C ;
- f) Ion source temperature: 200 °C ;
- g) Solvent Delay: 3 min;
- h) Determination mode: select ion monitor mode (SIM) ;

Monitoring ion: 31.0⁺, 32.0, 29.0, 30.0, " * " for the quantitative ion.

7 Chromatograph Determination

7.1 Confirmation of the method

Under the MGDC-MS operating conditions, the standard working solution and sample solution is injected. If the retention times of sample chromatogram peaks are consistent with that of standard solution, calibration curve method is used for quantitative measurement. The relative intensities of sample transitions shall correspond to those of standard solution transitions for confirmation. The concentration of standard solution should be same with those of sample solution. The permitted tolerances listed in Table 1, the corresponding analyte must be present in sample.

Table 1—Maximum permitted tolerances relative ion intensities while confirmation

relative intensity	>50%	>20% ~50%	>10% ~20%	≤10%
permitted tolerances	± 10%	± 15%	± 20%	± 50%

7.2 Quantitation of the method

According to the approximate concentration of analyte in sample solution, select the standard working solution with similar responses to that of sample solution. The responses of analyte in the standard working solution and the sample solution should be within the linear range of the instrument detection. Under the above MGDC-MS operating conditions, the retention time of methanol is about 5.56 min. SIM chromatogram of methanol standard working solution is listed in Annex A. If the content of methanol exceeds the method linearity, the sample should be diluted with 75% ethanol before analysis.

7.3 Blank test

Undergo according to the above procedures excluding the sample.

8 Calculation and expression of the result

Calculate the content of methanol residues in the test sample according to the followed formula(1), the calculation results need to deduct blank value.

$$X_i = \frac{A_i \times C_i}{A_{si} \times m} \dots\dots\dots (1)$$

where:

X_i —the residue content of methanol in the test sample,mg/kg;

A_i —the peak area of methanol in the sample solution;

C_i —the total concentration of methanol in the standard working solution, mg/L;

A_{si} —the total peak area of methanol in the standard working solution;

m —the corresponding mass of the test sample in the final sample solution, g.

Note: The result of calculation should be deducted with blank value.

9 Detection limit and recoveries

9.1 Determination Limits

The limit of quantitation for perfume, nail polish, nail polish remover, bath cream, shampoo, mildy wash,make-up remover, body lotion, astringent lotion, mousse, is 100 mg/kg.

9.2 Range of fortification and recoveries

The range of fortification and recovery of this method is shown in Table 2.

Table 2—The range of fortification and recovery of this method ($n=6$)

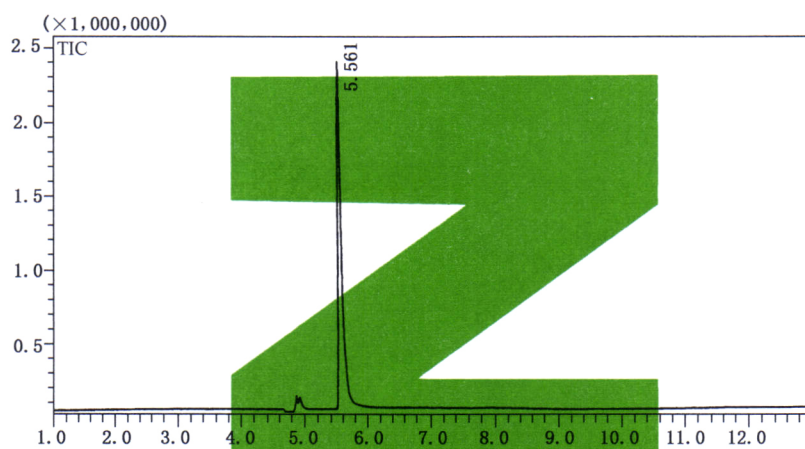
Fortified content mg/kg	Sample	Recovery range %	Fortified content mg/kg	Sample	Recovery range %
100.0	perfume	81.38~96.79	100.0	mildly wash	100.89~109.67
1 000.0		82.35~103.54	1 000.0		94.04~103.38
2 000.0		93.17~107.04	2 000.0		83.09~101.31
5 000.0		95.01~103.14	5 000.0		86.51~106.37
100.0	nail polish	80.24~99.29	100.0	make-up remover	90.64~104.09
1 000.0		83.98~99.32	1 000.0		93.47~103.79
2 000.0		95.11~106.13	2 000.0		86.72~99.85
5 000.0		85.59~99.53	5 000.0		90.04~105.98
100.0	nail polish remover	81.44~96.42	100.0	body lotion	86.53~107.25
1 000.0		80.72~86.69	1 000.0		90.74~102.96
2 000.0		89.62~107.04	2 000.0		96.81~107.57
5 000.0		84.29~97.83	5 000.0		95.05~108.33
100.0	bath cream	95.67~102.61	100.0	astringent lotion	81.19~94.76
1 000.0		93.35~109.61	1 000.0		93.81~106.18
2 000.0		89.38~95.84	2 000.0		83.99~98.61
5 000.0		98.49~105.42	5 000.0		80.51~94.19
100.0	shampoo	92.99~107.82	100.0	mousse	96.54~107.99
1 000.0		88.43~108.53	1 000.0		96.49~106.21
2 000.0		89.49~98.99	2 000.0		92.77~98.29
5 000.0		100.39~107.16	5 000.0		99.09~109.85

Annex A

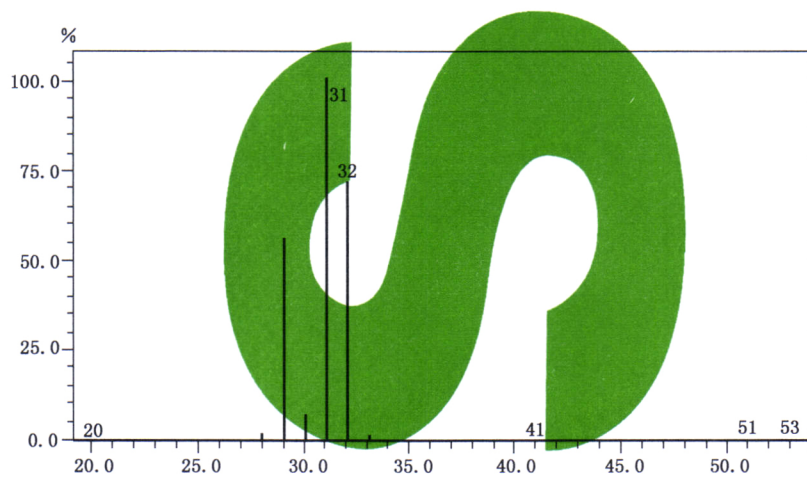
(informative)

SIM Chromatogram of the standard

SIM Chromatogram of the standard is shown in Fig.A.1 and Fig.A.2.



FigA.1—The SIM chromatogram of Methanol standards(1 000 mg/kg)



FigA.2—Full scan mass spectrogram of Methanol standard