

# SN

## 中华人民共和国出入境检验检疫行业标准

SN/T 2290—2009

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### 进出口化妆品中乙酰水杨酸的检测方法

Determination of acetylsalicylic acid in cosmetics for import and export

2009-02-20 发布

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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

本标准的附录 A、附录 B 和附录 C 均为资料性附录。

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：中华人民共和国广东出入境检验检疫局。

本标准主要起草人：陈捷、奚星林、焦红、吴映璇、李荀。

本标准系首次发布的出入境检验检疫行业标准。

# 进出口化妆品中乙酰水杨酸的检测方法

## 1 范围

本标准规定了进出口化妆品中乙酰水杨酸高效液相色谱测定方法和液相色谱-质谱/质谱确证方法。

本标准适用于美白、保湿等用途的面部使用的膏剂、乳霜和化妆水类化妆品中乙酰水杨酸的测定和确证。

## 2 原理

用甲醇提取化妆品中的乙酰水杨酸,提取液经离心过滤后,用高效液相色谱法进行测定。外标法定量,液相色谱-质谱/质谱法确证。

## 3 试剂和材料

除非另有说明,水为二次去离子水或重蒸馏。

- 3.1 甲醇:色谱级。
- 3.2 乙酸铵:分析醇。
- 3.3 乙酸铵溶液(0.02 mol/L):准确称取乙酸铵 1.544 g,用水溶解定容到 1 L。
- 3.4 乙酰水杨酸标准物质:纯度大于等于 99%。
- 3.5 乙酰水杨酸标准储备溶液:准确称取适量乙酰水杨酸标准物质(精确到 0.1 mg),以甲醇配制成浓度为 1 000 mg/L 的标准储备溶液。根据需要用甲醇稀释成适用浓度的标准工作溶液。
- 3.6 乙酰水杨酸标准工作溶液:吸取一定量的标准储备液,用甲醇稀释成适当浓度的标准工作液,临用时现配。

## 4 仪器与设备

- 4.1 高效液相色谱仪:配有紫外检测器。
- 4.2 液相色谱-质谱/质谱仪。
- 4.3 分析天平:感量 0.1 mg。
- 4.4 振荡器。
- 4.5 超声波清洗器。
- 4.6 低温离心机:10 000 r/min。
- 4.7 聚丙烯塑料刻度离心管:50 mL,具塞。
- 4.8 滤膜:0.45  $\mu\text{m}$ ,有机系。

## 5 测定步骤

### 5.1 试样处理

称取化妆品试样约 1 g(精确到 0.01 g),置于 50 mL 刻度离心管中,加入甲醇至 10 mL,在振荡机上振荡 1 min,超声波清洗器超声提取 10 min,在冰浴中放置 10 min,在 5  $^{\circ}\text{C}$  下,10 000 r/min 离心 10 min,上清液经滤膜过滤,供高效液相色谱测定。

### 5.2 测定

#### 5.2.1 色谱条件

- a) 紫外检测器:波长 230 nm;

- b) 色谱柱: C<sub>18</sub>柱, 250 mm×4.6 mm(内径), 5 μm, 或相当者;  
c) 流动相: 甲醇-0.02 mol/L 乙酸铵溶液(3.3), 按表 1 程序进行梯度洗脱;

表 1 梯度洗脱程序

时间/min	甲醇比例/%
0	20
5	40
10	60
18	90
19	20
30	20

- d) 流速: 1.0 mL/min;  
e) 柱温: 30 °C;  
f) 进样量: 10 μL。

### 5.2.2 高效液相色谱测定

根据样液中乙酰水杨酸含量, 选定峰面积相近的标准工作溶液。标准工作溶液和样液中乙酰水杨酸响应值均应在仪器检测线性范围内。标准工作溶液和样液等体积参插进样测定。以乙酰水杨酸色谱峰的峰面积为纵坐标, 与其对应的浓度为横坐标作图, 绘制标准工作曲线。在上述色谱条件(5.2.1)下乙酰水杨酸的保留时间约为 14.1 min。标准品的色谱图参见附录 A 中图 A.1。

## 5.3 定性确证

### 5.3.1 液相色谱-质谱/质谱仪质谱条件

#### 5.3.1.1 高效液相色谱参考条件

- a) 色谱柱: Ultimate™ XB C<sub>18</sub>柱, 150 mm×2.1 mm(内径), 3 μm, 或相当者;  
b) 流动相: 甲醇-水(40+60, 体积比);  
c) 流速: 0.2 mL/min;  
d) 柱温: 40 °C;  
e) 进样量: 10 μL。

#### 5.3.1.2 质谱条件

质谱条件参见附录 B。

#### 5.3.2 定性测定

当进行高效液相色谱样品测定, 检出试样中乙酰水杨酸的含量大于方法检测限时, 应以液相色谱-质谱/质谱法确证。被测组分选择 1 个母离子, 2 个以上子离子, 在相同实验条件下, 如果样品中待检测物质与标准溶液中对应的保留时间偏差在±2.5%之内; 样品定性时样品与浓度接近的标准溶液相对丰度一致, 相对丰度允许偏差不超过表 2 规定的范围, 则可判断样品中存在乙酰水杨酸。标准品的质谱图参见附录 C 中图 C.1 和图 C.2。

表 2 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/%	±20	±25	±30	±50

## 5.4 空白试验

除不称取试样外, 均按上述操作步骤进行。

## 6 结果计算

用色谱数据处理机或按(1)式计算试样中乙酰水杨酸的含量,计算结果需扣除空白值。

$$X = \frac{c \times V}{m} \dots\dots\dots (1)$$

式中:

$X$ ——试样中乙酰水杨酸含量,单位为毫克每千克(mg/kg);

$c$ ——从标准工作曲线得到被测样液中乙酰水杨酸的浓度,单位为微克每毫升( $\mu\text{g}/\text{mL}$ );

$V$ ——最终样液的定容体积,单位为毫升(mL);

$m$ ——最终样液所代表试样质量,单位为克(g)。

注:计算结果应表示到小数点后两位。

## 7 测定低限和回收率

### 7.1 测定低限

本方法对乙酰水杨酸的测定低限为 50 mg/kg。

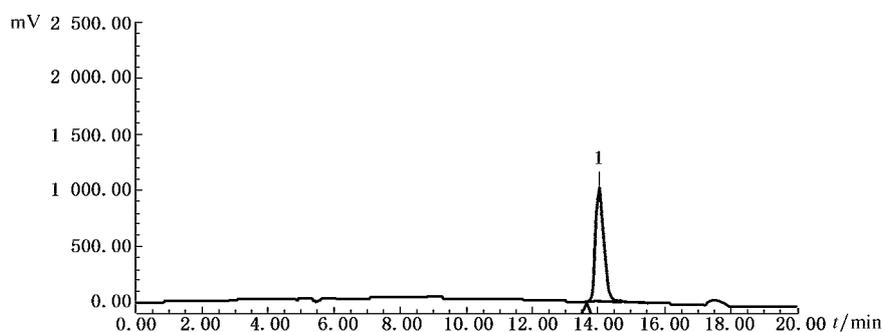
### 7.2 回收率

乙酰水杨酸添加浓度范围及回收率的数据见表 3。

表 3 乙酰水杨酸添加浓度范围及回收率数据

样品名称	添加浓度/(mg/kg)	回收率范围/%
乳霜	50	95.4~100
	100	95.8~101
	1 000	98.6~102
爽肤水	50	97.2~104
	100	94.6~102
	1 000	98.5~102
润肤膏	50	95.9~102
	100	98.5~103
	1 000	97.9~101

附 录 A  
(资料性附录)  
乙酰水杨酸标准品色谱图



1——乙酰水杨酸。

图 A.1 乙酸水杨酸标准品(5 µg/mL)色谱图

附 录 B  
(资料性附录)  
参考质谱参数<sup>1)</sup>

表 B.1 参考质谱参数

质谱参数	参数值
雾化气	9
气帘气	10
辅助加热气/(L/min)	7
碰撞气	10
辅助加热气温度/°C	400
喷雾电压/V	-4 500
去簇电压/V	-32
碰撞能/V	-11(m/z 179.1/136.8), -33(m/z 179.1/93.2)
采集时间/ms	100

1) 非商业性声明,质谱条件是在 API 3000 液相色谱-质谱/质谱联用仪上完成,此处列出试验用仪器型号仅为提供参考,并不涉及商业目的,鼓励标准使用者尝试不同厂家或型号的仪器。

附录 C  
(资料性附录)

乙酰水杨酸标准物质 LC/MS/MS 质谱图和色谱图

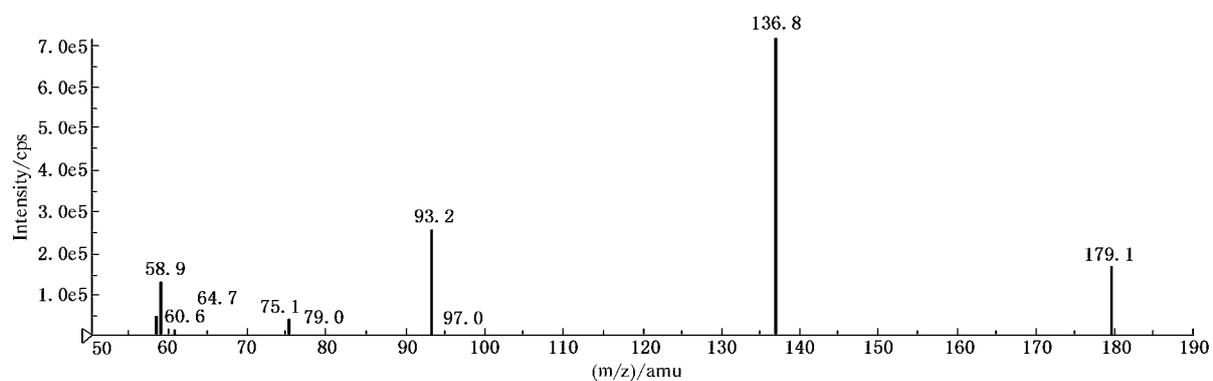


图 C.1 乙酰水杨酸标准品离子全扫描质谱图

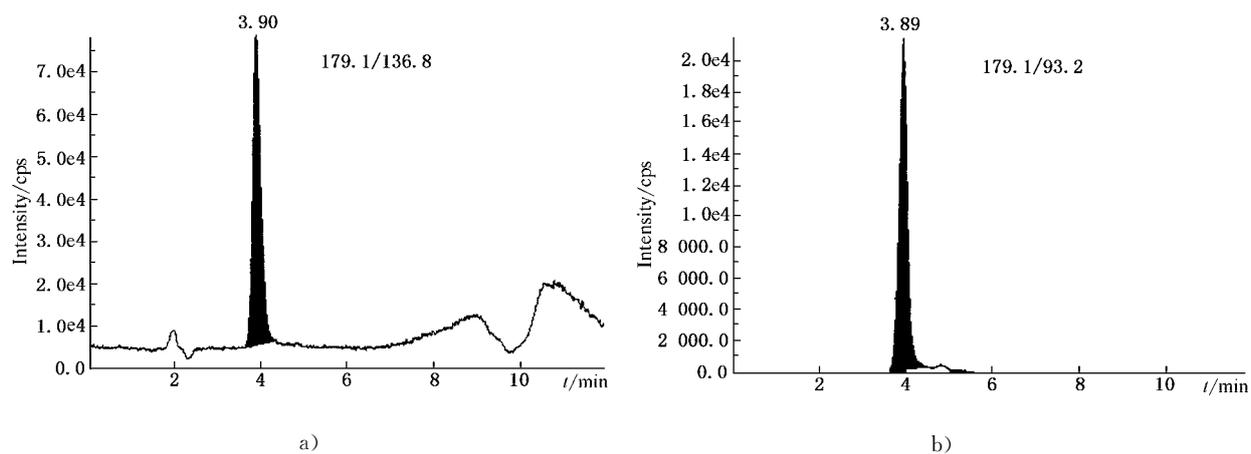


图 C.2 乙酰水杨酸标准品多反应监测(MRM)色谱图

## Foreword

Annex A and Annex B and Annex C of this standard are an informative annexes.

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

This standard is drafted by Chinese Academy of Inspection and Quarantine.

Main drafters of this standard are: Cheng Jie, Xi Xinglin, Jiao Hong, Wu Yingxuan, Li Xun.

This standard is an inspection and quarantine professional standard of the People's Republic of China promulgated for the first time.

# Determination of acetylsalicylic acid in cosmetics for import and export

## 1 Scope

This standard specifies the method of determination of acetylsalicylic acid in cosmetics for import and export by HPLC and HPLC-MS/MS.

This standard is applicable to the determination of acetylsalicylic acid in cosmetics for cream and pleasium refreshing toner and lotion.

## 2 Principle

Acetylsalicylic acid is extracted from sample with methanol. After centrifugation of extraction solvents, acetylsalicylic acid is determined by HPLC and quantified by external standard method. Acetylsalicylic acid is confirmed by HPLC-MS/MS.

## 3 Reagents and materials

Unless otherwise specified, all reagents used are A. R., and pure “water” is redistilled water.

3.1 Methanol: HPLC grade.

3.2 ammonium acetate: A. R.

3.3 0.02 mol/L ammonium acetate: Dilute 1.544 g ammonium acetate(3.2) in 1 L water.

3.4 Standard: Acetylsalicylic acid, purity  $\geq 99\%$ .

3.5 Standard stock solution: Accurately weigh an adequate amount of each standard (accurate to 0.1 mg), dissolve in methanol and prepare a solution of 1 000 mg/L as the standard stock solution.

3.6 Standard working solution: According to the requirement, dilute the standard solution to appropriate concentration with methanol just before use.

## 4 Apparatus and equipment

4.1 Liquid chromatography equipped with UV detector.

4.2 Liquid Chromatograph-Mass Spectrometry.

4.3 Balance: Accuracy:0.1 mg.

4.4 Vortex mixer.

4.5 Ultrasonic water bath.

4.6 Low temperature centrifuge: 10 000 r/min.

4.7 Centrifuge tube: polytetrafluoroethylene,50 mL.

4.8 filter membrane: 0.45 μm,organic system.

## 5 Procedure

### 5.1 Preparation of test samples

Weigh about 1 g(accurate to 0.01 g)of the test sample into a 50 mL polytetrafluoroethylene centrifuge tube,add 10 mL of methanol to the tube. Shake the tube for 1 min by vortex mixer,extract in ultrasonic water bath for 10 min,then place the tube in ice bath for 10 min . Centrifuge at 10 000 r/min for 10 min. Filter the solution into a HPLC vial through a 0.45 μm syringe filter.

### 5.2 Determination

#### 5.2.1 HPLC operating conditions

a) UV detector: wave 230 nm;

b) Column: C<sub>18</sub>,250 mm × 4.6 mm(i. d. ),5 μm,or equivalent;

c) Mobile phase:methanol-0.02 mol/L ammonium acetate,gradient see table 1;

Table 1—The mobile phase wash gradient of HPLC

Time/min	Methanol/%
0	20
5	40
10	60
18	90
19	20
30	20

- d) Flow rate: 1.0 mL/min;
- e) Column thermostat: 30 °C ;
- f) Injection volume: 10  $\mu$ L.

### 5.2.2 HPLC determination

According to the estimated approximate concentration of acetylsalicylic acid in the sample solution, select the standard working solution of similar concentration to that of sample solution. The responses of acetylsalicylic acid in the sample solution should be in the linear range of the instrumental detection. The standard working solution should be injected randomly in between the injections of the sample of equal volume. Under the above instrumental condition, the retention time of acetylsalicylic acid is 14.1 min, For the chromatogram of acetylsalicylic acid standard, see annex A, Figure A. 1.

## 5.3 Confirmation

### 5.3.1 MS/MS operating conditions

#### 5.3.1.1 HPLC operating conditions

- a) LC column: Ultimate™ XB C<sub>18</sub> , 150 mm × 2.1 mm(i. d. ) ,3  $\mu$ m or equivalent;
- b) Mobile phase: methanol-water(40 + 60, V / V);
- c) Flow rate: 0.2 mL/min;
- d) Column thermostat: 40 °C ;
- e) Injection volume: 10  $\mu$ L.

#### 5.3.1.2 Ms/Ms operating conditions

Ms/Ms operating conditions see annex B.

### 5.3.2 Confirmation procedure

When the content of acetylsalicylic acid in test sample determined by HPLC is greater than limit of method, confirmation should be carried out by MS/MS. A Precursor ion and two daughter ions are chosen. Under above determination condition, the variation range of the retention time for the peak of analyte in unknown sample and in the standard working solution can not be out of range of  $\pm 2.5\%$ . For the same analysis batch and the same compound, the variation range of the ion ratio between the two daughter ions for the unknown sample and the standard working solution at the similar

concentration can not be out of range of table 2, and then the corresponding analyte must be present in the sample. MRM Chromatogram of the standard see annex C, Figure C. 1 and Figure C. 2.

Table 2—Maximum permitted tolerances for relative ion intensities while confirmation

Relative intensity/%	>50	>20~50	>10~20	≤10
Permitted tolerances/%	± 20	± 25	± 30	± 50

5.4 Blank test

The operation of blank test is the same as above, except without sample.

6 Calculation and expression of result

The content of acetylsalicylic acid is calculated by computer processor or by the following formula (1). The blank value should be subtracted from the result of calculation.

$$X = \frac{c \times V}{m} \dots\dots\dots ( 1 )$$

Where

X—the content of acetylsalicylic acid in test sample, mg/kg;

c—the concentration in the standard working solution, μg/mL;

V—the final volume of sample solution, mL;

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

Note: show two decimal places in expression of result.

7 Limit of determination and recovery

7.1 Limit of determination

The limit of determination of this method is 50 mg/kg.

7.2 Recovery

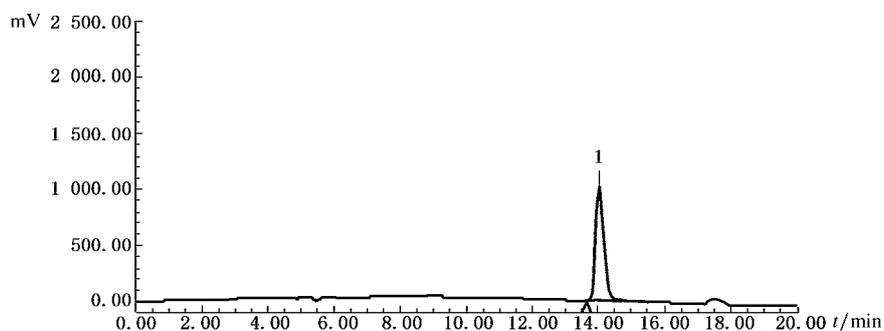
Recovery of acetylsalicylic acid see table 3.

Table 3—Recovery of acetylsalicylic acid

Compound	Fortifying concentration/(mg/kg)	Recovery/%
cream	50	95.4~100
	100	95.8~101
	1 000	98.6~102
Pleasium refreshing toner	50	97.2~104
	100	94.6~102
	1 000	98.5~102
lotion	50	95.9~102
	100	98.5~103
	1 000	97.9~101

Annex A  
(informative)

The chromatogram of acetylsalicylic acid standard



1—acetylsalicylic acid standard.

Figure A. 1—The chromatogram of acetylsalicylic acid standard (5  $\mu\text{g/mL}$ )

Annex B  
(informative)  
MS/MS condition<sup>1)</sup>

Table B. 1—MS/MS condition

MS/MS condition	Values
Nebulizer Gas	9
Curtain Gas	10
Auxiliary Heating Gas/(L/min)	7
Collision Gas	10
Temperature/ $^{\circ}\text{C}$	400
Ion Spray Voltage/V	- 4 500
Declustering Potential/V	- 32
Collision energy/V	- 11( $m/z$ 179. 1/136. 8) , - 33( $m/z$ 179. 1/93. 2)
Dwell time/ms	100

1) The non-commercial character stated that the mass spectrum condition is in API 3 000 liquid chromatography-mass spectrum/mass spectrum unites, here lists the experiment is only provides the reference with the instrument model, does not involve the business objective, encourages the standard user to attempt the different factory or the model instrument.

Annex C  
(informative)

LC-MS/MS chromatogram of acetylsalicylic acid standard

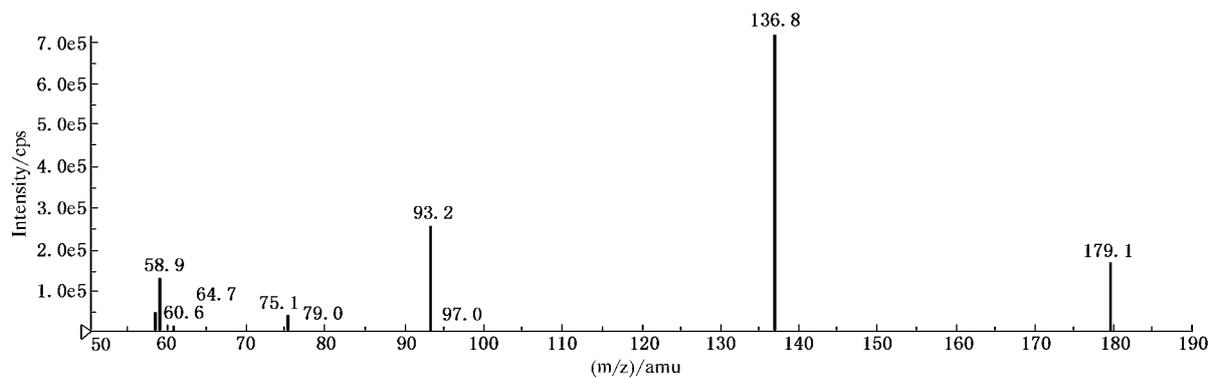


Figure C. 1—LC-MS/MS chromatogram of acetylsalicylic acid standard

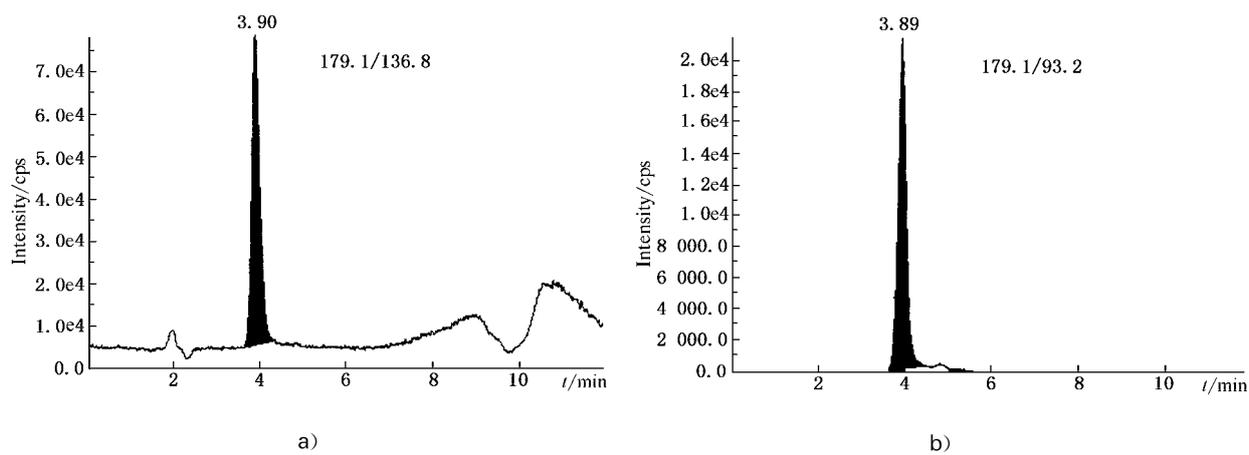


Figure C. 2—MRM chromatogram of acetylsalicylic acid standard

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