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中华人民共和国出入境检验检疫行业标准

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进出口水果和蔬菜中嘧菌酯残留量检测方法　气相色谱法

Determination of azoxystrobin residues in fruit and vegetable for import and export—GC method

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前　言

本标准附录A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：中华人民共和国青海出入境检验检疫局，甘肃农业大学食品科学与工程学院，中华人民共和国辽宁出入境检验检疫局。

本标准主要起草人：薄海波、孙洁、毕阳、李连通、王宏伟。

本标准系首次发布的出入境检验检疫行业标准。

进出口水果和蔬菜中嘧菌酯残留量检测方法　气相色谱法

1　范围

本标准规定了水果和蔬菜中嘧菌酯残留量的气相色谱测定方法。

本标准适用于苹果、葡萄、柑橘、甘蓝、番茄、马铃薯、西兰花中嘧菌酯残留量的测定。

2　方法提要

试样用乙酸乙酯＋环己烷(1＋1)混合溶剂提取，用配有氮磷检测器的气相色谱仪测定，外标法定量。

3　试剂和材料

除另有规定外，所用试剂均为分析纯，有机溶剂使用前重蒸馏。

3.1　丙酮。

3.2　环己烷。

3.3　乙酸乙酯。

3.4　氯化钠。

3.5　无水硫酸钠。用前在650℃灼烧4 h，置于干燥器中备用。

3.6　嘧菌酯标准品：纯度大于或等于99%。

3.7　标准储备溶液：准确称取适量的嘧菌酯标准品(精确到0.1 mg)，用丙酮配制成浓度为1 mg/mL标准储备溶液。该溶液在－18℃冰箱中保存。

3.8　标准工作溶液：根据需要再用环己烷＋乙酸乙酯(1＋1)稀释成适用浓度的标准工作溶液，该溶液在0℃～4℃冰箱中保存。

4　仪器和设备

4.1　气相色谱仪，配有氮磷检测器。

4.2　组织捣碎机：转速不低于20 000 r/min。

4.3　旋转蒸发仪。

4.4　离心机：最大转速5 000 r/min。

4.5　鸡心瓶：100 mL。

4.6　具塞离心管：80 mL。

5　试样制备与保存

5.1　试样制备

取代表性样品约500 g，将其可食用部分(不可用水洗)切碎后，用捣碎机将样品加工成浆状，混匀，装入洁净容器，密封，标明标记。

5.2　试样保存

将试样于0℃～4℃保存。在抽样及制样的操作过程中，应防止样品受到污染或发生残留物含量的

变化。

6 测定步骤

6.1 提取

称取 20 g(精确至 0.01 g)试样于 80 mL 具塞离心管中,加入 40 mL 环己烷+乙酸乙酯溶液(1+1),在15 000 r/min匀浆 1 min,加入 5 g 氯化钠(3.4)再匀浆提取 1 min,在 3 000 r/min 离心 5 min,吸取出上清液,用 2 g 无水硫酸钠(3.5)脱水,分取 20 mL 于鸡心瓶中,经 50℃水浴旋转蒸发近干,然后用氮气流吹干。用环己烷+乙酸乙酯(1+1)溶解,定容至 1.0 mL,供气相色谱分析。

6.2 测定

6.2.1 气相色谱分析条件

a) 色谱柱:HP-5 石英毛细管柱,30 m×0.25 mm(内径),膜厚 0.25 μm,或相当者;
b) 色谱柱温度程序:180℃保持 2 min,以 30℃/min 上升至 280℃,保持 10 min;
c) 进样口温度:290℃;
d) 氮磷检测器温度:300℃;
e) 载气:高纯氮气,纯度≥99.999%,流速为 1.8 mL/min;
f) 尾吹气:高纯氮气,纯度≥99.999%,流速为 20 mL/min;
g) 氢气:纯度≥99.999%,4.0 mL/min,分析开始后 0 min~1.5 min 关闭氢气;
h) 空气:60 mL/min;
i) 进样方式:无分流进样,1.5 min 后打开分流阀;
j) 进样量:1.0 μL。

6.2.2 气相色谱测定

根据样液中嘧菌酯的含量情况,选取峰面积相近的标准工作溶液一起进行色谱分析。标准工作溶液和待测样液中嘧菌酯的响应值均应在检测的线性范围内。对标准工作溶液和待测样液等体积参插进样测定。上述色谱条件下,嘧菌酯的保留时间约为 6.7 min。标准品和样品的气相色谱图参见附录 A.1。

7 空白实验

除不称取试样外,均按上述步骤进行。

8 结果计算与表述

用色谱数据处理机或按式(1)计算样品中嘧菌酯残留量,计算结果应扣除空白值。

$$X = \frac{A \cdot c \cdot V}{A_S \cdot m} \qquad \cdots\cdots(1)$$

式中:

X——试样中嘧菌酯残留量,单位为毫克每千克(mg/kg);

A——样液中嘧菌酯的色谱峰面积;

A_S——标准溶液中嘧菌酯的色谱峰面积;

c——标准溶液中嘧菌酯的浓度,单位为微克每毫升(μg/mL);

V——样液最终定容体积,单位为毫升(mL);

m——最终样液所代表的样品质量,单位为克(g)。

9 测定低限和回收率

9.1 测定低限

本方法的测定低限为:0.01 mg/kg。

9.2 添加浓度及回收率

本方法添加浓度及回收率见表1。

表1 本方法添加浓度及回收率

样品名称	添加浓度范围/(mg/kg)	回收率范围/%
苹果	0.01～1.0	86.6～97.3
葡萄	0.01～1.0	86.8～104.2
柑橘	0.01～1.0	86.6～104.4
甘蓝	0.01～1.0	85.8～105.9
番茄	0.01～1.0	81.2～95.2
马铃薯	0.01～1.0	84.4～96.6
西兰花	0.01～1.0	79.2～102.6

附 录 A
（资料性附录）
嘧菌酯标准品的气相色谱图

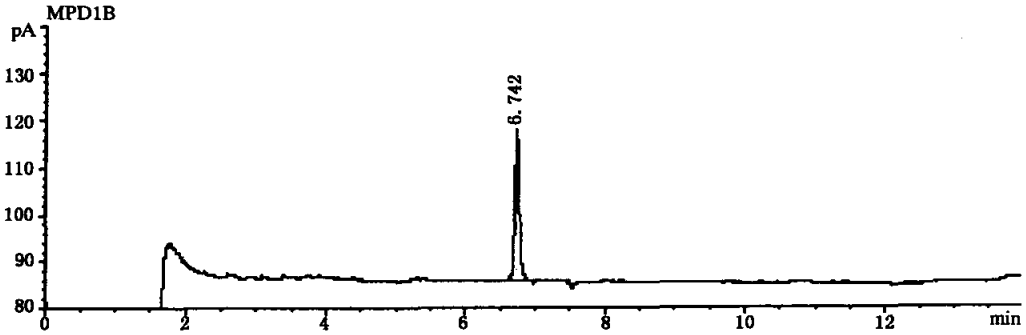

图 A.1 嘧菌酯标准品的气相色谱图

Foreword

The annex A of this standard is an informative annex.

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

This standard was drafted by Qinghai Entry-Exit Inspection and Quarantine Bureau of the People's Republic of China, Gansu Agricultural University, and Liaoning Entry-Exit Inspection and Quarantine Bureau of the People's Republic of China.

The main drafters of this standard are Bo Haibo, Sun Jie, Bi Yang, Li Liantong and Wang Hongwei.

This standard is a professional standard for entry-exit inspection and quarantine promulgated for the first time.

Determination of azoxystrobin residues in fruit and vegetable for import and export—GC method

1 Scope

This standard specifies the method for the determination of azoxystrobin residues in fruit and vegetable by gas chromatography (GC).

This standard is applicable to the determination of azoxystrobin residues in apple, citrus fruit, grape, cabbage, tomato, cauliflower and potato.

2 Principle of determination

Azoxystrobin residue in the test samples is extracted with ethyl acetate-cyclohexane (1 + 1). The extract is determined by means of GC with N/P detector, using external standard method.

3 Reagents and materials

Unless other specified, all reagents were of analytical-reagent grade. Water is the first grade water.

3.1 Acetone.

3.2 Cyclohexane.

3.3 Ethyl acetate.

3.4 Sodium chloride.

3.5 Anhydrous sodium sulfate: Ignited at 650℃ for 4 h, and kept in a desiccator.

3.6 Azoxystrobin standard: Purity≥99 %.

3.7 Stock standard solution: Accurately weigh (accurate to 0.000 1 g) azoxystrobin standard (3.6), dissolve with acetone to 1 mg/mL. The solution should be stored at −18℃.

3.8 Working standard solution: According to the concentration required, dilute stock standard solution (3.7) with ethyl acetate-cyclohexane (1+1), The solution should be stored at 0℃～4℃.

4 Apparatus and equipment

4.1 Gas chromatography: Equipped with nitrogen/phosphorous detector.

4.2 Homogenizer: The max rotate speed is 20 000 r/min.

4.3 Rotary vacuum evaporator.

4.4 Centrifuge: the max rotate speed is 5 000 r/min.

4.5 Heart-shaped flask: 100 mL.

4.6 Centrifuge tube: 80 mL.

5 Sample preparation and storage

5.1 Preparation of test sample

Weigh ca 500.0 g of representative sample. The edible portions of the sample are minced with mincing knife, homogenized, sealed and labeled as the test sample.

5.2 Storage of test sample

The test sample should be stored at 0℃～4℃ until analysis.

6 Procedure

6.1 Extraction

Weigh ca 20 g (accurate to 0.01 g) of test sample into a 80 mL centrifuge tube (4.6). Add 40 mL of ethyl acetate-cyclohexane (1+1), and homogenize for 1 min. Add 5g sodium chloride (3.4), and homogenize for 1 min again and centrifuge for 5 min at 3 000 r/min. Transfer the supernatant into another centrifuge tube, add 2 g anhydrous sodium sulfate (3.5) to dehydrate. Take 20 mL of the dehydrated extract into a heart-shaped flask (4.5), evaporate to near dryness at 50℃ using rotary vacuum evaporator (4.3), and blow to dryness on the nitrogen evaporator (4.4). Reconstitute with 1 000 μL ethyl acetate-cyclohexane (1+1) for analysis.

6.2 Determination

6.2.1 GC conditions

a) Column: HP-5 capillary column, 30 m×0.25 mm(id)×0.25 μm, or the equivalent;

b) Column temperature: 180℃ for 2 min, ramp at 30℃/min to 280℃, hold for 10 min;

c) Injection port temperature: 290℃;

d) Detector temperature: 300℃;

e) Carrier gas: Nitrogen purity≥99.999%, 1.8 mL/min.

f) Trail blow: Nitrogen, purity≥99.999%, 20 mL/min;

g) Hydrogen: purity≥99.999%, 4.0 mL/min, (0～1.5) min after analysis starting hydrogen is turn off;

h) Air: 60 mL/min;

i) Injection mode: Splitless, purge after 1.5 min;

j) Injection volume: 1.0 μL.

6.2.2 Determination

According to the approximate concentration of azoxystrobin residues in sample, select the working standard solution with similar responses to that of sample solution. The responses of azoxystrobin in the working standard and the sample solution should be within the linear range of the instrument. The standard working solution and the sample solution should be injected alternatively. Under the above gas chromatographic operating conditions, the retention time of azoxystrobin is 6.74 min. Chromatogram of standard is shown as figure A.1 in Annex A.

7 Blank test

The operation of the blank test is the same as the described in the method of determination, but with the omission of sample addition.

8 Calculation and expression of result

Calculation the content of azoxystrobin residues in test sample with chromatographic data processor or with the formula(1), the blank value should be subtracted from the result of calculation.

$$X = \frac{A \cdot c \cdot V}{A_s \cdot m} \qquad \cdots\cdots(1)$$

where

X—the residue of azoxystrobin in test sample, mg/kg;

A—the peak area of azoxystrobin of the sample solution;

A_s—the peak area of azoxystrobin of the standard solution;

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

V—the final volume of the sample solution, mL;

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

9 Limit of determination and recovery

9.1 Limit of determination

The limit of determination of this method is 0.01 mg/kg.

9.2 Fortified concentration and recovery

The fortified concentration and recovery of this method are shown in table 1.

Table 1—The fortified concentration and recovery of this method

Sample	Fortified concentration/(mg/kg)	Recovery/%
apple	0.01～1.0	86.6～97.3
grape	0.01～1.0	86.8～104.2
citrus fruit	0.01～1.0	86.6～104.4
cabbage	0.01～1.0	85.8～105.9
tomato	0.01～1.0	81.2～95.2
potato	0.01～1.0	84.4～96.6
cauliflower	0.01～1.0	79.2～102.6

Annex A
(informative)
Chromatogram of azoxystrobin standard

Figure A.1—GC chromatagram of azoxystrobin standard