SN

中华人民共和国出入境检验检疫行业标准

SN/T 0519—2010
代替 SN 0519—1996

进出口食品中丙环唑残留量的检测方法

Determination of propiconazole residue in food for import and export

2010-11-01 发布　　2011-05-01 实施

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。

本标准代替 SN 0519—1996《出口粮谷中丙环唑残留量检验方法》。

本标准与 SN 0519—1996 相比，主要技术变化如下：

——标准名称修改为“进出口食品中丙环唑残留量的检测方法”；

——取消了“抽样和制样”，增加了“试样制备与保存”；

——扩大了样品基质的适用范围；

——气相色谱检测器由氮磷检测器改为电子捕获检测器；

——增加了气相色谱-质谱检测方法。

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：中华人民共和国陕西出入境检验检疫局、中华人民共和国上海出入境检验检疫局、中华人民共和国江苏出入境检验检疫局、中华人民共和国天津出入境检验检疫局、中华人民共和国吉林出入境检验检疫局。

本标准主要起草人：李建华、何强、孔祥虹、乐爱山、朱坚、沈崇钰、沈伟建、葛宝坤、王云凤、王明泰。

本标准所代替标准的历次版本发布情况为：

——SN 0519—1996。

进出口食品中丙环唑残留量的检测方法

1 范围

本标准规定了食品中丙环唑残留量的气相色谱检测方法和气相色谱-质谱检测与确证方法。

本标准适用于大米、荞麦、绿豆、苹果、草莓、香蕉、柑橘、韭菜、西兰花、蘑菇、枸杞子、茶叶、板栗、蜂蜜、猪肾、牛肉、鸡肉、鱼肉等食品中丙环唑残留量的测定和确证。

2 方法提要

试样用乙酸乙酯或乙腈提取，经 C_{18} 和石墨化炭黑固相萃取柱净化，用配备电子捕获检测器的气相色谱仪和气相色谱-质谱仪进行检测和确证，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，水为二次蒸馏水。

3.1 乙酸乙酯。

3.2 乙腈。

3.3 甲醇：液相色谱级。

3.4 氯化钠。

3.5 无水硫酸钠：经 650 ℃灼烧 4 h，置于密闭容器中备用。

3.6 甲醇-水溶液(60+40，体积比)：量取 60 mL 甲醇(3.3)与 40 mL 水混合。

3.7 丙环唑标准物质(Propiconazole，$C_{15}H_{17}Cl_2N_3O_2$，CAS 编号：60207-90-7)：纯度大于等于 99%。

3.8 丙环唑标准储备溶液：准确称取适量的丙环唑标准物质，用乙酸乙酯配制成 1 000 μg/mL 的标准储备溶液，于 0 ℃～4 ℃储存。

3.9 丙环唑标准工作溶液 A：根据需要用乙酸乙酯将储备液稀释配制成适当浓度的标准工作溶液，供气相色谱测定，此溶液于 0 ℃～4 ℃储存。

3.10 丙环唑标准工作溶液 B：根据需要用空白基质提取液将储备液稀释配制成适当浓度的标准工作溶液，供气相色谱-质谱测定使用，现用现配。

3.11 C_{18} 固相萃取柱：500 mg，3 mL；使用前分别用 5 mL 甲醇和 5 mL 水预淋洗柱子，流速 1 mL/min。

3.12 石墨化炭黑固相萃取柱：250 mg，3 mL；使用前用 5 mL 甲醇预淋洗柱子，流速 1 mL/min。

4 仪器和设备

4.1 气相色谱仪：配电子捕获检测器(ECD)。

4.2 气相色谱-质谱联用仪：配电子轰击离子源(EI 源)。

4.3 组织捣碎机。

4.4 粉碎机。

4.5 电子天平：感量分别为 0.01 mg 和 0.01 g。

4.6 涡旋混合器。
4.7 均质器:10 000 r/min。
4.8 具塞离心管:聚丙烯,50 mL。
4.9 旋转蒸发器。
4.10 氮吹仪。
4.11 离心机:5 000 r/min。
4.12 固相萃取装置。

5 试样制备与保存

5.1 试样制备

5.1.1 苹果、草莓、香蕉、柑橘、枸杞子、韭菜、西兰花、蘑菇

取代表性样品约500 g,将其可食用部分切碎(不可水洗),用组织捣碎机加工成浆状,混匀,装入洁净的容器内,密闭并标明标记。

5.1.2 大米、荞麦、绿豆、茶叶、板栗

取代表性样品约500 g,用粉碎机粉碎并通过2.0 mm圆孔筛,混匀,装入洁净的容器内,密闭并标明标记。

5.1.3 猪肾、牛肉、鸡肉、鱼肉

取代表性样品约500 g,将其可食用部分切碎后,用组织捣碎机充分捣碎,混匀,装入洁净的容器内,密闭并标明标记。

5.1.4 蜂蜜

取代表性样品约500 g,对无结晶蜂蜜样品将其搅拌均匀;对有结晶析出的蜂蜜样品,在密闭情况下,将样品瓶置于不超过60 ℃的水浴中温热,振荡,待样品全部融化后搅匀,迅速冷却至室温。在融化时应注意防止水分挥发。装入洁净的容器内,密闭并标明标记。

5.2 试样保存

大米、荞麦、绿豆、茶叶、板栗、蜂蜜等试样于0 ℃～4 ℃保存;苹果、草莓、香蕉、柑橘、韭菜、西兰花、蘑菇、枸杞子、猪肾、牛肉、鸡肉、鱼肉等试样于－18 ℃以下冷冻保存。

在制样的操作过程中,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

6.1.1 大米、荞麦、绿豆、板栗、猪肾、牛肉、鸡肉、鱼肉

称取5 g试样(精确至0.01 g)于50 mL离心管中,加入10 g无水硫酸钠,20 mL乙酸乙酯,10 000 r/min均质提取2 min,3000 r/min离心10 min,上清液倒入浓缩瓶中。残渣再用2×20 mL乙酸乙酯重复提取两次,合并提取液于浓缩瓶中,于45 ℃浓缩至近干,加5 mL甲醇-水溶液溶解残渣,待净化。

6.1.2 茶叶、苹果、草莓、香蕉、柑橘、韭菜、西兰花、蘑菇、枸杞子、蜂蜜

称取 5 g(精确至 0.01 g)试样于 50 mL 离心管中,加入 5 g 氯化钠,10 mL 水(对于茶叶,加水后静置 30 min),20 mL 乙腈,涡旋振荡提取 10 min,3 000 r/min 离心 10 min,上清液转移到浓缩瓶中。残渣再用 2×20 mL 乙腈重复提取两次,合并提取液于浓缩瓶中,于 45 ℃浓缩至近干,加 5 mL 甲醇-水溶液溶解残渣,待净化。

6.2 净化

将上述提取液(6.1)通过经活化过的 C_{18} 固相萃取柱(3.11),再用 5 mL 甲醇-水溶液淋洗 C_{18} 固相萃取柱,保持液滴流速约 1 mL/min,弃去流出液。将 C_{18} 固相萃取柱抽干后与石墨化炭黑固相萃取柱(3.12)(柱内填约 1 cm 高无水硫酸钠)依次串接,在 C_{18} 固相萃取柱中加入 3 mL 甲醇洗脱,待甲醇全部流过 C_{18} 固相萃取柱后,弃掉 C_{18} 固相萃取柱,再用 8 mL 甲醇洗脱石墨化炭黑固相萃取柱,收集全部洗脱液,于 40 ℃水浴中氮气吹干,用乙酸乙酯溶解定容至 1.0 mL,供气相色谱和气相色谱-质谱测定和确证。

6.3 测定

6.3.1 气相色谱条件

气相色谱条件如下:

a) 色谱柱:DB-35 弹性石英毛细管柱,0.25 mm(内径)×30 m,膜厚 0.25 μm,或相当者;

b) 色谱柱温度:80 ℃(1 min)$\xrightarrow{20\ ℃/min}$ 230 ℃(1 min)$\xrightarrow{4\ ℃/min}$ 250 ℃(8 min)$\xrightarrow{30\ ℃/min}$ 280 ℃(5 min);

c) 进样口温度:250 ℃;

d) 检测器温度:280 ℃;

e) 载气:氦气,纯度大于等于 99.999%,流量 1.0 mL/min;

f) 尾吹气:90 mL/min;

g) 进样方式:无分流进样,1 min 后开阀;

h) 进样量:1.0 μL。

6.3.2 气相色谱-质谱条件

气相色谱-质谱条件如下:

a) 色谱柱:石英毛细管柱 DB-1701,0.25 mm(内径)×30 m,膜厚 0.25 μm,或相当者;

b) 色谱柱温度:80 ℃(1 min)$\xrightarrow{15\ ℃/min}$230 ℃(1 min)$\xrightarrow{4\ ℃/min}$250 ℃(5 min)$\xrightarrow{20\ ℃/min}$270 ℃(5 min);

c) 进样口温度:250 ℃;

d) 色谱-质谱接口温度:270 ℃;

e) 载气:氦气,纯度≥99.999%,0.6 mL/min;

f) 进样量:1.0 μL;

g) 进样方式:不分流进样,1 min 后开阀;

h) 电离方式:EI;

i) 电离能量:70 eV;

j) 测定方式:选择离子监测方式(SIM);

k) 监测离子(m/z):259,173,191,261;定量离子(m/z):259;

l) 溶剂延迟：10 min。

6.3.3 气相色谱检测

根据样液中丙环唑含量情况，选定与样液浓度相近的标准工作溶液(3.9)，标准工作溶液和样液中丙环唑的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，以保留时间定性，测量峰面积与标准工作溶液比较进行定量。在 6.3.1 给定的色谱条件下，丙环唑及异构体的保留时间约为 19.2 min 和 19.4 min。丙环唑标准品的色谱图参见附录 A 中图 A.1。

6.3.4 气相色谱-质谱检测及确证

根据样液中丙环唑含量情况，选定与样液浓度相近的标准工作溶液(3.10)，标准工作溶液和样液中丙环唑的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。

在 6.3.2 规定的气相色谱-质谱条件下，样品中待测物质的保留时间与标准工作溶液中对应的保留时间的偏差在±2.5%以内，且样品中被测物质的相对离子丰度与浓度相当的标准工作溶液的相对离子丰度允许偏差不超过表 1 规定的范围，则可确定样品中存在对应的被测物。在上述气相色谱-质谱条件下，丙环唑及异构体的保留时间约为 18.5 min 和 18.7 min。丙环唑标准品的气相色谱-质谱总离子流图和全扫描质谱图参见附录 B 中图 B.1 和图 B.2。

表 1 使用定性气相色谱-质谱时相对离子丰度最大允许偏差

相对丰度/%	>50	>20～50	>10～20	≤10
允许的相对偏差/%	±20	±25	±30	±50

6.4 空白试验

除不称取试样外，均按上述检测步骤进行。

6.5 结果计算和表述

用色谱数据处理软件或按式(1)计算试样中丙环唑残留量：

$$X = \frac{A \times c_s \times V}{A_s \times m} \quad \cdots\cdots(1)$$

式中：

X ——试样中丙环唑的残留量，单位为毫克每千克(mg/kg)；

A ——样液中丙环唑及异构体的色谱峰面积之和；

c_s ——标准工作液中丙环唑的浓度，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)；

A_s ——标准工作液中丙环唑及异构体的色谱峰面积之和；

m ——最终样液所代表的试样质量，单位为克(g)。

注：计算结果须扣除空白值。

7 测定低限和回收率

7.1 测定低限

本方法中气相色谱法和气相色谱-质谱法的测定低限均为 0.01 mg/kg。

7.2 回收率

本方法中气相色谱法和气相色谱-质谱法回收率的数据分别见表2和表3。

表2 样品的添加浓度及回收率的数据(GC)

样品名称	添加浓度 mg/kg	回收率范围 %	样品名称	添加浓度 mg/kg	回收率范围 %
大米	0.010	81.6～84.4	蘑菇	0.010	84.3～90.8
	0.020	76.7～79.7		0.020	85.1～93.8
	0.050	73.2～84.2		0.050	85.3～98.1
荞麦	0.010	70.9～83.1	枸杞子	0.010	76.9～86.1
	0.020	75.9～85.5		0.020	75.9～90.5
	0.050	71.8～86.7		0.050	77.8～92.7
绿豆	0.010	87.1～99.3	茶叶	0.010	76.5～90.3
	0.020	88.9～99.9		0.020	85.6～95.8
	0.050	83.9～103.8		0.050	92.1～98.7
苹果	0.010	92.9～100.9	板栗	0.010	79.5～91.7
	0.020	96.3～102.7		0.020	88.3～97.8
	0.050	94.6～102.2		0.050	89.7～100.5
草莓	0.010	95.2～101.1	蜂蜜	0.010	88.0～104.7
	0.020	94.4～107.6		0.020	79.1～105.1
	0.050	91.1～103.8		0.050	90.1～95.5
香蕉	0.010	75.5～98.2	猪肾	0.010	76.8～88.9
	0.020	88.3～92.8		0.020	78.5～89.6
	0.050	86.2～109.7		0.050	79.2～89.5
柑橘	0.010	98.4～105.5	牛肉	0.010	76.5～89.7
	0.020	95.6～112.4		0.020	78.7～89.2
	0.050	85.2～112.3		0.050	78.8～86.9
韭菜	0.010	88.7～94.8	鱼肉	0.010	78.2～88.1
	0.020	87.6～93.8		0.020	80.0～89.7
	0.050	89.3～98.2		0.050	82.9～90.8
西兰花	0.010	86.9～92.0	鸡肉	0.010	75.3～86.7
	0.020	86.5～94.3		0.020	81.3～87.9
	0.050	86.4～96.7		0.050	85.6～91.3

表 3　样品的添加浓度及回收率的数据(GC-MS)

样品名称	添加浓度 mg/kg	回收率范围 %	样品名称	添加浓度 mg/kg	回收率范围 %
大米	0.010	74.7～90.6	蘑菇	0.010	93.5～91.7
	0.020	76.0～81.1		0.020	86.3～94.8
	0.050	75.9～83.8		0.050	85.8～99.1
荞麦	0.010	72.2～79.8	枸杞子	0.010	74.4～83.3
	0.020	75.7～82.6		0.020	77.3～87.2
	0.050	74.6～85.4		0.050	78.3～90.8
绿豆	0.010	87.4～96.6	茶叶	0.010	76.2～92.2
	0.020	90.3～97.4		0.020	85.2～97.9
	0.050	90.3～103.4		0.050	88.3～99.9
苹果	0.010	88.6～101.8	板栗	0.010	84.0～93.9
	0.020	86.5～97.0		0.020	88.5～96.5
	0.050	93.4～98.1		0.050	88.6～99.6
草莓	0.010	93.9～102.2	蜂蜜	0.010	92.6～103.1
	0.020	92.1～102.9		0.020	85.2～102.2
	0.050	95.3～104.1		0.050	88.2～98.4
香蕉	0.010	96.0～93.6	猪肾	0.010	75.8～88.9
	0.020	84.4～94.3		0.020	79.9～90.8
	0.050	91.2～99.5		0.050	79.5～91.7
柑橘	0.010	94.5～103.6	牛肉	0.010	76.6～88.4
	0.020	96.8～103.4		0.020	77.9～85.7
	0.050	96.1～107.0		0.050	79.6～87.4
韭菜	0.010	87.3～95.6	鱼肉	0.010	77.0～86.2
	0.020	88.9～95.4		0.020	80.8～88.8
	0.050	90.2～99.8		0.050	83.2～90.6
西兰花	0.010	85.1～94.7	鸡肉	0.010	76.9～87.2
	0.020	88.2～93.3		0.020	80.3～88.3
	0.050	87.8～95.3		0.050	85.3～90.3

附 录 A
（资料性附录）
丙环唑标准品气相色谱图

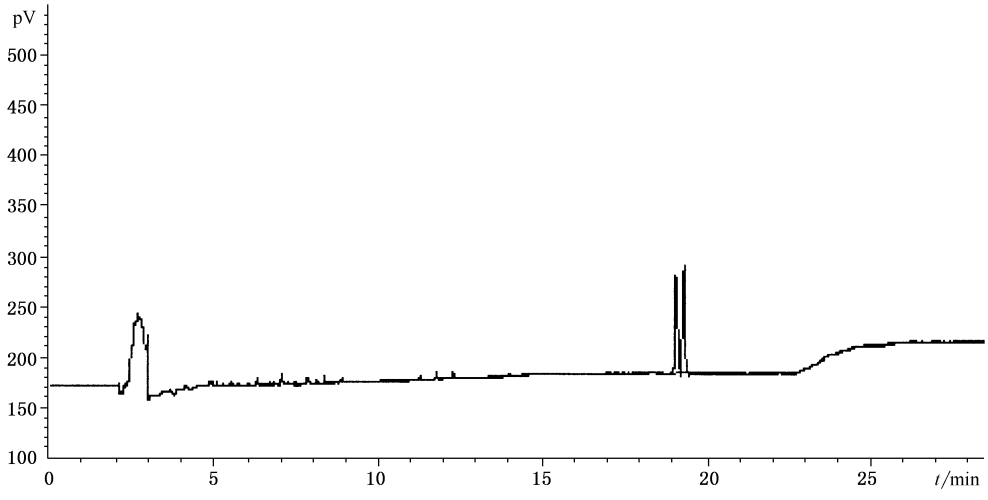

图 A.1 丙环唑标准品气相色谱图

附 录 B
（资料性附录）
丙环唑标准品总离子流色谱图和质谱图

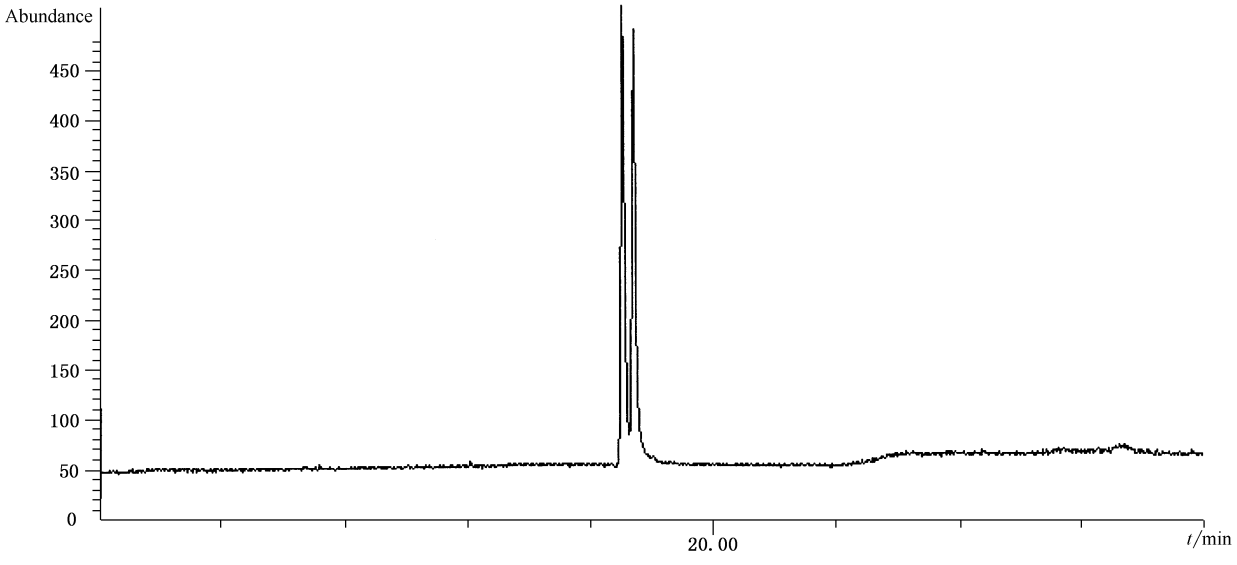

图 B.1 丙环唑标准品总离子流色谱图

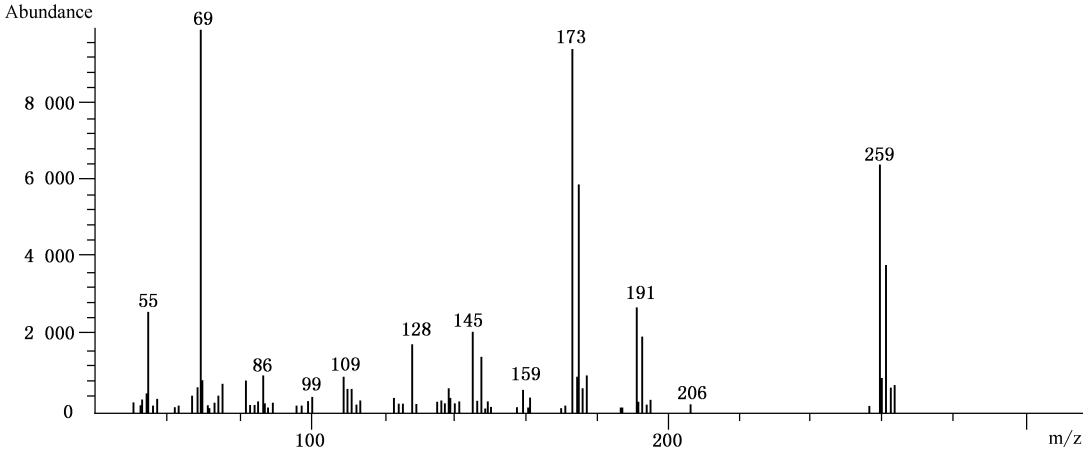

图 B.2 丙环唑质谱图

Foreword

This standard substituted SN 0519—1996:Method for the determination of propiconazole residues in cereals for export.

The differences between this standard and SN 0519—1996 is as follows:

—Modified the title as "Determination of propiconazole residue in food for import and export";

—Removed "sampling and sample preparation",added "preparation and storage of test sample";

—Added sample category tested;

—The NPD detector of GC replaced by ECD detector;

—Added gas chromatography-mass spectrometry method of determination.

Annex A and annex B of this standard are informative.

This standard was proposed by and is under the charge of China National Regulatory Commission for Certification and Accreditation.

This standard was drafted by Shanxi Entry-Exit Inspection and Quarantine Bureau of the People's Republic of China,Shanghai Entry-Exit Inspection and Quarantine Bureau,Jiangsu Entry-Exit Inspection and Quarantine Bureau,Tianjin Entry-Exit Inspection and Quarantine Bureau,and Jilin Entry-Exit Inspection and Quarantine Bureau,of the People's Republic of China.

The main drafters of this standard are Li Jianhua,He Qiang,Kong Xianghong,Yue Aishan,Zhu Jian,Shen Chongyu,Shen Weijian,Ge Baokun,Wang Yunfeng and Wang Mingtai.

The previous standard was issued in 1996,and modified at the first time.

Determination of propiconazole residue in food for import and export

1 Scope

This standard specifies the method of determination by gas chromatography and gas chromatography-mass spectrometry of propiconazole residues in food.

This method is applicable to determine and confirm propiconazole residues in rice, buckwheat, mung bean, apple, strawberry, banana, orange, leek, cauliflower, mushroom, *Lycium*, tea, Chinese chestnut, honey, hog kidney, beef, chicken, and fish for import and export.

2 Principle

The propiconazole residues in the test sample are extracted with acetonitrile or ethyl acetate, the extract is cleaned up by passing through a C_{18} and an ENVI Carb solid phase cartridges after concentrated. Then add a certain quantity of organic solvent to the concentrated elute and determined by gas chromatography and gas chromatography-mass spectrometry, using external standard method for quantitative analysis.

3 Reagents and Materials

Unless otherwise specified, all reagents should be of analytical grade or higher one, "water" is distilled water.

3.1 Ethyl acetate.

3.2 Acetonitrile.

3.3 Methanol.

3.4 Sodium chloride.

3.5 Anhydrous sodium sulfate, ignite at 650 ℃ for 4 h, and keep in a tight closed container.

3.6 Methanol-water solution (60+40 *V*/*V*).

3.7 Propiconazole standard ($C_{15}H_{17}Cl_2N_3O_2$, CAS No.: 60207-90-7), purity ≥99%.

3.8 Standard stock solution: Accurately weigh an adequate amount of propiconazole standard dissolve in a small volume ethyl acetate. Dilute with ethyl acetate to form a standard stock solution of 1 000 μg/mL in concentration. Store at 0 ℃～4 ℃.

3.9 Standard working solution A: GC determination, dilute the standard stock solution with ethyl acetate to the required concentration as the standard working solution. Store at 0 ℃～4 ℃.

3.10 Standard working solution B: Matrix calibration solution for GC-MS determination, dilute the standard stock solution with blank sample extract to the required concentration as the standard working solution. The matrix calibration solution should be prepared just before using.

3.11 C_{18} solid phase cartridge: 500 mg, 3 mL. Rinse the cartridge with 5 mL acetonitrile and 5 mL water, keeps the flow speed at 1 drop/second.

3.12 Supelclean™ ENVI™-Carb solid phase cartridge: 250 mg, 3 mL. Rinse the cartridge with 5 mL acetonitrile, keeps the flow speed at 1 mL/min.

4 Apparatus

4.1 Gas chromatograph equipped with electron capture detector (ECD).

4.2 Gas chromatograph equipped with mass detector, including EI.

4.3 Grinder.

4.4 Solid phase extraction equipment.

4.5 Tissue blender: 0.01 mg、0.01 g.

4.6 Vortex mixer.

4.7 Homogenizer: 10 000 r/min.

4.8 Polypropylene centrifuge tube, 50 mL.

4.9 Rotary vacuum evaporator.

4.10 Nitrogen evaporator.

4.11 Centrifuge:5 000 r/min.

4.12 Evaporating bottle.

5 Sample preparation and storage

5.1 Preparation of test samples

5.1.1 Apple,strawberry,banana,orange,leek,cauliflower,mushroom,and ***Lycium***

The combined primary samples are reduced to the ca 500 g,which has been removed shell,seed,peel,stem,root,coronal (do not wash by water). The edible portions are cut and homogenized thoroughly in a high speed blender. Keep the prepared sample into a clean container,sealed and labeled.

5.1.2 Rice,buckwheat,mung bean,Tea and Chinese chestnut

The combined primary samples are reduced to the ca 500 g,which is crushed with a grinder and let wholly pass through a 20 mesh sieve. Keep the prepared sample into a clean container,sealed and labeled.

5.1.3 Hog kidney,beef,chicken,and fish

The combined primary samples is reduced to ca 500 g,the edible potions are thoroughly ground and homogenized in a meat grinder. Keep the prepared sample into a clean container,sealed and labeled.

5.1.4 Honey

Take about 500 g of representative sample. The sample that is not crystallized shall be stirred well to produce a homogenous sample. If the sample is crystallized,it should be warmed in a water bath at below 60 ℃ with the sample bottle covered tightly. Mix thoroughly when all sample has melted,then cool immediately to room temperature. In the course of melting the sample,precautious measures must be taken to avoid evaporation of water from the sample. Keep the prepared sample into a clean container,sealed and labeled.

5.2 Storage of test samples

The test samples of tea,bee products,grains or cereals shall be stored at 0 ℃～4 ℃. The test samples of fresh fruits,vegetables,meat and meat products shall be stored below －18 ℃. In the course

of sampling and sample preparation, precaution shall be taken to avoid contamination or any factors which may cause the change of residue content.

6 Method of Determination

6.1 Extraction

6.1.1 Rice, buckwheat, mung bean, Chinese chestnut, hog kidney, beef, chicken, and fish

Weigh 5 g (accurate to 0.01 g) of the test sample into a 50 mL centrifuge tube, add 10 g anhydrous sodium sulfate and 20 mL ethyl acetate. Homogenize for 2 min at 10 000 r/min and centrifuge for 5 min at 3 000 r/min. Transfer the upper extract into a 150 mL evaporating bottle.

Repeat above extract procedure with 20 mL of ethyl acetate twice, combine the upper extract into the same evaporating bottle. Evaporate to approach dryness in a rotary evaporator with a bath temperature below 45 ℃. Dissolve the residues with methanol-water solution 5 mL for next clean up.

6.1.2 Tea, apple, strawberry, banana, orange, leek, cauliflower, mushroom, ***Lycium***, and honey

Weigh 5.0 g (accurate to 0.01 g) of the test sample into a 50 mL centrifuge tube, add 5 g sodium chloride, 10 mL water and 20 mL acetonitrile. Vortex for 10 min and centrifuge at 3 000 r/min for 3 min. Transfer the upper extract into a 150 mL evaporating bottle. Repeat above extract procedure with 20 mL of acetonitrile twice, combine the upper extract into the same evaporating bottle. Evaporate to approach dryness in a rotary evaporator with a bath temperature below 45 ℃. Dissolve the residues with methanol-water solution (3.6) 5 mL for next clean up.

6.2 Clean up

Load above extract into C_{18} solid phase cartridge (3.11), wash the cartridge with 5 mL methanolwater solution (3.7) and discard the elute, keeps the flow speed at 1 mL/min during loading sample and washing. Pump the cartridge to dryness. Connect the C_{18} solid phase cartridge and Supelclean™ ENVI™-Carb solid phase cartridge (about 1 cm thickness anhydrous sodium sulfate was put into the cartridge) with C_{18} cartridge being upper. Elute the cartridges with 3 mL metanol. Discard the C_{18} cartridge after methanol pass through the C_{18} cartridge. Elute the ENVI™-Carb cartridge with another 8 mL methanol. Collect all the eluted solution in a 50 mL evaporating bottle and evaporate to approach dryness in a rotary evaporator with a bath temperature below 40 ℃ and blow dryness with nitrogen. Dissolve the residue and dilute exactly to 1.0 mL with ethyl acetate for GC-ECD or GC-MSD.

6.3 Determination conditions

6.3.1 GC operating conditions

a) Column: DB-35 ms, 30 m × 0.25 mm (i.d.) × 0.25 μm, or the equivalent;

b) Column temperature: 80 ℃ (1 min) —20 ℃/min→ 230 ℃ (1 min) —4 ℃/min→ 250 ℃ (8 min) —30 ℃/min→ 280 ℃ (5 min);

c) Injection port temperature: 250 ℃;

d) Detection temperature: 280 ℃;

e) Carrier gas: Nitrogen, purity > 99.999%; 1.0 mL/min;

f) Make-up gas: 90 mL/min;

g) Inject mode: Splitless, purge after 1 min;

h) Injection volume: 1 μL.

6.3.2 GC-MS operating conditions

a) Column: DB-1701, 30 m × 0.25 mm (i.d.) × 0.25 μm, or the equivalent;

b) Column temperature: 80 ℃ (1 min) —15 ℃/min→ 230 ℃ (1 min) —4 ℃/min→ 250 ℃ (5 min) —20 ℃/min→ 270 ℃ (5 min);

c) Injection port temperature: 250 ℃;

d) GC/MS interface temperature: 270 ℃;

e) Carrier gas: Helium, purity ≥ 99.999%, 0.6 mL/min;

f) Injection volume: 1.0 μL;

g) Inject mode: Splitless, purge after 1 min;

h) Ionization mode: EI;

i) Ionization energy:70 eV;

j) Acquisition mode:SIM;

k) Monitor ion (m/z):259,173,191,261;quantitative ion:259;

l) Solvent delay:10 min.

6.3.3 GC determination

According to the approximate concentration of propiconazole in the test sample solution, select the standard working solution with similar peak area to that of sample solution. The standard working solution should be injected randomly in between the injections of the sample solution of equal volume. The responses of propiconazole in the standard working solution and sample solution should be in the linear range of the instrumental detection. Identify by retention time and quantify with peak area. Under the above GC operating conditions (6.3.1), the reference retention time of propiconazole and isomer is 19.2 min and 19.4 min. Figure A.1 of annex A is the chromatogram of the propiconazole standard.

6.3.4 GC/MS determination and confirmation

According to the approximate concentration of propiconazole in the test sample solution, select the matrix calibration solutions with similar peak area to that of sample solution. The matrix calibration solution should be injected randomly in between the injections of sample solution of equal volume. The responses of propiconazole in the matrix calibration solution and sample solution should be in the linear range of the instrumental detection.

According to the GC-MSD operating conditions (6.3.2), if the retention time of sample chromatogram peaks are consistent with the standards, and subtracted from background compensation, selected ions are all present and the relative ion abundance of the selected ions according with that of the calibration standard, at comparable concentrations, within the tolerances (seen table 1). Under the above GC-MSD operating conditions, the retention time of propiconazole and isomer is 18.5 min and 18.7 min, and the ratio of the monitoring ions (m/z) is 173 ∶ 191 ∶ 259 ∶ 261 = 100 ∶ 40 ∶ 77 ∶ 55. For GC-MS chromatogram (TIC) and mass spectrum of the standard, see figure B.1 and B.2 in annex B.

Table 1—Maximum permitted tolerances for relative ion abundance while confirmation

Relative abundance (base peak)/%	>50	>20～50	>10～20	≤10
Permitted tolerances/%	±10	±15	±20	±50

6.4 Blank test

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

6.5 Calculation and expression of result

The calculation of propiconazole in the sample is carried out by GC or GC-MS data processor or according to the following formula (1).

$$X = \frac{A \times c_s \times V}{A_s \times m} \quad \cdots\cdots(1)$$

Where:

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

A —the sum of peak area of propiconazole and isomer in the sample solution;

c_s —the concentration of a propiconazole in the standard working solution, μg/mL;

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

A_s —the sum of peak area of propiconazole and isomer in the standard working solution;

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

Note: The blank value should be subtracted from the above result of calculation.

7 Limit of determination and recovery

7.1 Limit of determination

The limits of determination of GC and GC-MS method in this method are 0.010 mg/kg.

7.2 recovery

The recovery data of GC and GC-MS method in this method are list in table 2 and table 3.

Table 2—Fortifying concentrations in test samples and recovery data（GC）

Sample	Fortifying concentration mg/kg	Range of recovery %	Sample	Fortifying concentration mg/kg	Range of recovery %
rice	0.010	81.6～84.4	mushroom	0.010	84.3～90.8
	0.020	76.7～79.7		0.020	85.1～93.8
	0.050	73.2～84.2		0.050	85.3～98.1
buckwheat	0.010	70.9～83.1	*Lycium*	0.010	76.9～86.1
	0.020	75.9～85.5		0.020	75.9～90.5
	0.050	71.8～86.7		0.050	77.8～92.7
mung bean	0.010	87.1～99.3	tea	0.010	76.5～90.3
	0.020	88.9～99.9		0.020	85.6～95.8
	0.050	83.9～103.8		0.050	92.1～98.7
apple	0.010	92.9～100.9	chinese chestnut	0.010	79.5～91.7
	0.020	96.3～102.7		0.020	88.3～97.8
	0.050	94.6～102.2		0.050	89.7～100.5
strawberry	0.010	95.2～101.1	honey	0.010	88.0～104.7
	0.020	94.4～107.6		0.020	79.1～105.1
	0.050	91.1～103.8		0.050	90.1～95.5
banana	0.010	75.5～98.2	hog kidney	0.010	76.8～88.9
	0.020	88.3～92.8		0.020	78.5～89.6
	0.050	86.2～109.7		0.050	79.2～89.5
orange	0.010	98.4～105.5	beef	0.010	76.5～89.7
	0.020	95.6～112.4		0.020	78.7～89.2
	0.050	85.2～112.3		0.050	78.8～86.9
leek	0.010	88.7～94.8	fish	0.010	78.2～88.1
	0.020	87.6～93.8		0.020	80.0～89.7
	0.050	89.3～98.2		0.050	82.9～90.8
cauliflower	0.010	86.9～92.0	chicken	0.010	75.3～86.7
	0.020	86.5～94.3		0.020	81.3～87.9
	0.050	86.4～96.7		0.050	85.6～91.3

Table 3—Fortifying concentrations in test samples and recovery data（GC-MS）

Sample	Fortifying concentration mg/kg	Range of recovery %	Sample	Fortifying concentration mg/kg	Range of recovery %
rice	0.010	74.7～90.6	mushroom	0.010	93.5～91.7
	0.020	76.0～81.1		0.020	86.3～94.8
	0.050	75.9～83.8		0.050	85.8～99.1
buckwheat	0.010	72.2～79.8	*Lycium*	0.010	74.4～83.3
	0.020	75.7～82.6		0.020	77.3～87.2
	0.050	74.6～85.4		0.050	78.3～90.8
mung bean	0.010	87.4～96.6	tea	0.010	76.2～92.2
	0.020	90.3～97.4		0.020	85.2～97.9
	0.050	90.3～103.4		0.050	88.3～99.9
apple	0.010	88.6～101.8	chinese chestnut	0.010	84.0～93.9
	0.020	86.5～97.0		0.020	88.5～96.5
	0.050	93.4～98.1		0.050	88.6～99.6
strawberry	0.010	93.9～102.2	honey	0.010	92.6～103.1
	0.020	92.1～102.9		0.020	85.2～102.2
	0.050	95.3～104.1		0.050	88.2～98.4
banana	0.010	96.0～93.6	hog kidney	0.010	75.8～88.9
	0.020	84.4～94.3		0.020	79.9～90.8
	0.050	91.2～99.5		0.050	79.5～91.7
orange	0.010	94.5～103.6	beef	0.010	76.6～88.4
	0.020	96.8～103.4		0.020	77.9～85.7
	0.050	96.1～107.0		0.050	79.6～87.4
leek	0.010	87.3～95.6	fish	0.010	77.0～86.2
	0.020	88.9～95.4		0.020	80.8～88.8
	0.050	90.2～99.8		0.050	83.2～90.6
cauliflower	0.010	85.1～94.7	chicken	0.010	76.9～87.2
	0.020	88.2～93.3		0.020	80.3～88.3
	0.050	87.8～95.3		0.050	85.3～90.3

Annex A
（Informative）
Chromatogram of propiconazole standard solution

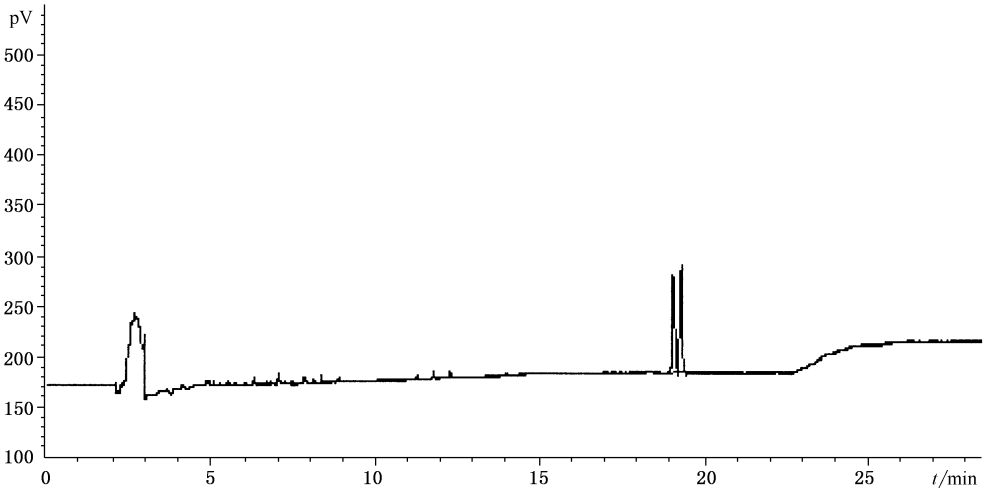

Figure A. 1—Chromatogram of propiconazole standard solution

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Annex B
（Informative）
GC-MSD selected ion chromatogram of the propiconazole standard solution

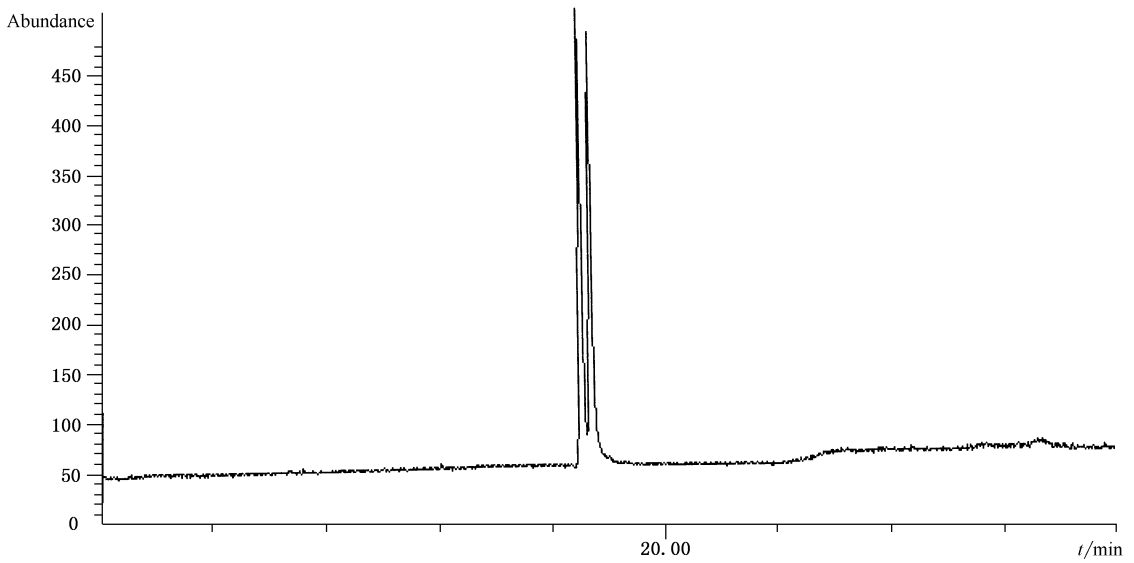

Figure B. 1—GC-MS selected ion chromatogram of the propiconazole standard solution

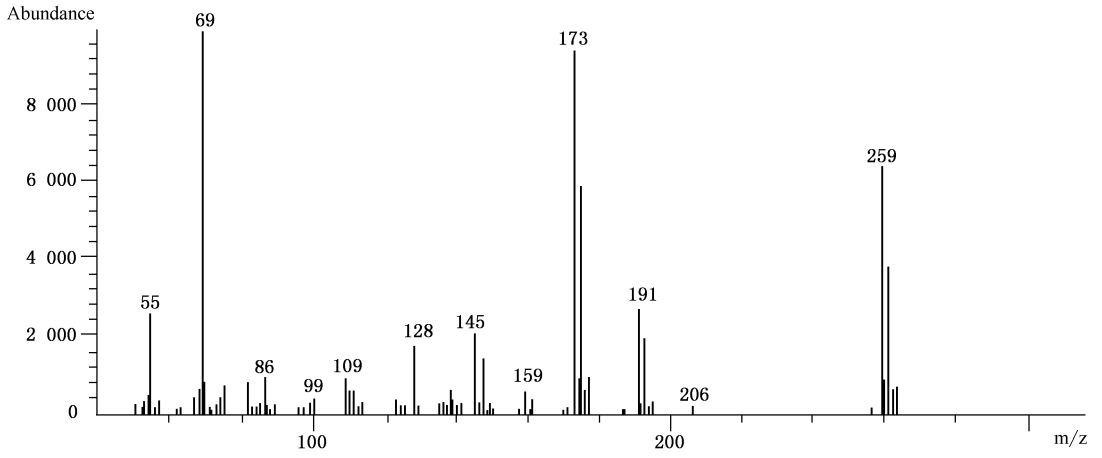

Figure B. 2—Mass spectrum of propiconazole gained from GC-MS