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中华人民共和国出入境检验检疫行业标准

SN/T 2431—2010

进出口食品中苄螨醚残留量的检测方法

Determination of halfenprox residues in food for import and export

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前　言

本标准的附录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：中华人民共和国山西出入境检验检疫局。

本标准主要起草人：薛平、杜利军、苑利、吴海军、张晓峰、潘亚利。

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进出口食品中苄螨醚残留量的检测方法

1 范围

本标准规定了进出口食品中苄螨醚残留量检测的气相色谱测定和气相色谱-质谱确证的方法。

本标准适用于芦笋、土豆、葱、梨、桃、玉米、荞麦、茶叶、食醋、蜂蜜、核桃仁、兔肉、鸡肝、虾仁、鸡肉中苄螨醚残留量的检测。

2 方法提要

醋和蜂蜜用水溶解和稀释后，固相萃取净化；葱和茶叶用乙酸乙酯-环己烷提取固相萃取净化；动物源性食品和含油量高的食品用乙腈提取，其他食品用乙酸乙酯-环己烷混合溶剂提取，提取液用凝胶色谱仪(GPC)净化，供带有电子捕获检测器的气相色谱仪测定，外标法定量，阳性样品用气相色谱-质谱法确证。

3 试剂和材料

除非另有规定，所用试剂均为分析纯，水为二次蒸馏水。

3.1 乙酸乙酯：色谱纯。

3.2 环己烷：色谱纯。

3.3 乙腈：色谱纯。

3.4 正己烷：色谱纯。

3.5 丙酮：色谱纯。

3.6 无水硫酸钠：650 ℃灼烧 4 h，贮于密封容器中备用。

3.7 氯化钠。

3.8 乙酸乙酯-环己烷混合溶剂(1＋1，体积比)：量取 500 mL 乙酸乙酯和 500 mL 环己烷，混匀。

3.9 正己烷-丙酮混合溶剂(9＋1，体积比)：量取 90 mL 正己烷和 10 mL 丙酮，混匀。

3.10 环己烷-乙酸乙酯混合溶剂(6＋1，体积比)：量取 10 mL 乙酸乙酯和 60 mL 环己烷，混匀。

3.11 苄螨醚标准物质：(halfenprox；CAS 编号：111872-58-3；$C_{24}H_{23}BrF_2O_3$；相对分子质量：477.34)纯度大于等于 99%。

3.12 标准储备液(100 mg/L)：准确称取适量标准物质，用乙酸乙酯溶解，配制成浓度为 100 mg/L 的标准储备液，该溶液在 0 ℃～4 ℃冰箱中保存。

3.13 标准工作液：根据需要再用乙酸乙酯稀释成适用浓度的标准工作溶液。标准工作液应现用现配。

3.14 石墨化碳黑和 PSA 混合柱：1 mL，50 mg 石墨化碳黑＋50 mg PSA，用 3 mL 环己烷-乙酸乙酯混合溶剂(3.10)活化。

3.15 HLB 固相萃取柱：3 mL，60 mg，或相当者，依次用 2 mL 正己烷-丙酮混合溶液(3.9)，2 mL 丙酮，5 mL 蒸馏水预淋洗。

3.16 有机相滤膜：0.45 μm。

4 仪器和设备

4.1 气相色谱仪，配有电子捕获检测器。

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4.2 气相色谱-质谱仪，配有电子轰击源(EI)。

4.3 分析天平：感量为0.01 g。

4.4 分析天平：感量为0.1 mg。

4.5 凝胶色谱仪，配有单元泵，馏分收集器。

4.6 离心机：4 000 r/min。

4.7 旋转蒸发器。

4.8 无水硫酸钠柱：7.5 cm×1.5(内径)cm玻璃柱，内装5 cm高无水硫酸钠。

4.9 涡旋混合器。

4.10 均质器。

4.11 氮吹仪。

4.12 具塞离心管：50 mL聚四氟乙烯。

5 样品制备与保存

5.1 样品制备

5.1.1 粮谷及茶叶类

将样品按四分法缩分至500 g，用磨碎机全部磨碎。混匀，均分成两份作为试样，分装入洁净的盛样瓶内，密闭，标明标记。

5.1.2 水果及蔬菜类

抽取水果或蔬菜样品500 g，或去壳、去籽、去皮、去茎、去根、去冠(不可用水洗涤)，将其可食用部分切碎后，依次用食品捣碎机将样品加工成浆状。混匀，均分成两份作为试样，分装入洁净的盛样袋内，密闭，标明标记。

5.1.3 肉及肉制品类、坚果类

从所取全部样品中取出有代表性样品约1 kg，取可食部分经捣碎机充分捣碎均匀，均分成两份，分别装入洁净容器内作为试样。密封并标明标记。

5.2 试样保存

粮谷类、茶叶类、坚果类、蜂蜜及蜂蜜制品类试样于0 ℃～4 ℃保存；其他类试样于－18 ℃以下冷冻保存。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

6.1.1 蔬菜、水果、粮谷

蔬菜、水果、粮谷称取10 g(精确到0.01 g)均匀试样，置于50 mL具塞塑料离心管中，加入20 mL乙酸乙酯-环己烷混合溶剂(3.8)，10 000 r/min匀浆1 min，4 000 r/min离心3 min，收集上层有机相，残留物再用20 mL乙酸乙酯-环己烷混合溶剂重复提取一次，合并上层有机相，过无水硫酸钠柱(4.8)脱水，收集于150 mL浓缩瓶中，于40 ℃水浴中旋转浓缩至近干，准确加入10.0 mL乙酸乙酯-环己烷溶解残渣，并过0.45 μm滤膜，待凝胶色谱净化。

6.1.2 核桃仁、兔肉、鸡肝、虾、鸡肉

称取10 g(精确到0.01 g)均匀试样，置于50 mL具塞塑料离心管中，加入20 mL乙腈，10 mL蒸馏水，3 g氯化钠，10 000 r/min匀浆1 min，4 000 r/min离心3 min，收集上层有机相，残留物再用20 mL乙腈重复提取一次，合并上层有机相，过无水硫酸钠柱脱水，收集于150 mL浓缩瓶中，于40 ℃水浴中旋转浓缩至近干，准确加入10.0 mL乙酸乙酯-环己烷溶解残渣，并过0.45 μm滤膜，待凝胶色谱净化。

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6.1.3 茶叶、葱

称取2.5 g(精确到0.01 g)均匀试样,置于50 mL具塞塑料离心管中,加入15 mL蒸馏水,静置1 h,加入20 mL乙酸乙酯-环己烷混合溶剂(3.8),10 000 r/min匀浆1 min,4 000 r/min离心3 min,收集上层有机相,残留物再用20 mL乙酸乙酯-环己烷混合溶剂重复提取一次,合并上层有机相,过无水硫酸钠脱水,收集于150 mL浓缩瓶中,于40 ℃水浴中旋转浓缩至近干,用乙酸乙酯-环己烷混合溶剂(3.10)准确定容到10.0 mL,过0.45 μm滤膜,待固相萃取净化。

6.2 净化

6.2.1 蔬菜、水果、粮谷、核桃仁、兔肉、鸡肝、虾、鸡肉凝胶色谱净化

6.2.1.1 凝胶色谱净化条件

a) 凝胶净化柱:300 mm×10 mm(内径),Bio Beads S-X3,或相当者;

b) 流动相:环己烷-乙酸乙酯(1+1);

c) 流速:4.7 mL/min;

d) 样品定量环:5 mL;

e) 收集时间:7.5 min~12.5 min。

6.2.1.2 凝胶色谱净化步骤

将10 mL待净化液按6.2.1.1条件净化,收集全部收集液于氮吹管中,于35 ℃水浴中氮吹至近干,用乙酸乙酯定容至1.0 mL,供气相色谱仪测定,阳性样品采用气相色谱-质谱法确证。

6.2.2 醋、蜂蜜固相萃取净化

称取2.5 g(精确到0.01 g)均匀试样,加入5 mL水旋涡振荡混匀30 s,将溶液全部过HLB固相萃取柱,流速控制在1 mL/min,再用2 mL蒸馏水淋洗柱子,弃去淋洗液,真空抽干2 min,再用4 mL正己烷-丙酮混合溶液(3.9)洗脱,收集洗脱液于离心管中,40 ℃下氮气吹干,0.5 mL乙酸乙酯定容,待测。

6.2.3 茶叶、葱固相萃取净化

取0.5 mL待净化液上石墨化碳黑和PSA混合柱(3.14),用1.5 mL乙酸乙酯-环己烷混合溶剂(3.10)洗脱,流速控制在1 mL/min,收集所有流出液于离心管中,40 ℃下氮气吹干,0.5 mL乙酸乙酯定容,待测。

6.3 气相色谱测定

6.3.1 气相色谱条件

a) 色谱柱:DB-1301石英毛细管柱,30 m×0.25 mm(内径)×0.25 μm,或性能相当者;

b) 色谱柱温度:50 ℃ $\xrightarrow{20\ ℃/min}$ 200 ℃ $\xrightarrow{5\ ℃/min}$ 260 ℃(10 min);

c) 进样口温度:260 ℃;

d) 检测器温度:300 ℃;

e) 载气:氮气,纯度大于等于99.999%,柱流量2 mL/min;

f) 进样方式:无分流,0.75 min后打开分流阀;

g) 进样量:1 μL。

6.3.2 气相色谱测定

根据样液中苄螨醚含量情况,选定峰面积相近的标准工作溶液,标准工作溶液和样液中苄螨醚相应值均应在仪器检测线性范围内。标准品的色谱图参见附录A中图A.1。标准溶液及样液均按6.3.1的条件进行测定,如果样液中与标准溶液相同的保留时间有峰出现,则对其进行气相色谱-质谱确证。

6.4 气相色谱-质谱确证

6.4.1 气相色谱-质谱条件

a) 色谱柱:HP-5MS石英毛细管柱,30 m×0.25 mm(内径)×0.25 μm,或性能相当者;

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b) 色谱柱温度：50 ℃(1 min)$\xrightarrow{10\ ℃/min}$280 ℃(10 min)；

c) 进样口温度：250 ℃；

d) 色谱-质谱接口温度：280 ℃；

e) 电离方式：EI；

f) 电离能量：70 eV；

g) 载气：氦气，纯度大于等于 99.999%，流速 1 mL/min；

h) 进样方式：无分流，0.75 min 后打开分流阀；

i) 进样量：1 μL；

j) 测定方式：选择离子监测；

k) 选择监测离子(m/z)：183、264、265(丰度比 25∶75∶100)；

l) 溶剂延迟：5.0 min。

6.4.2 气相色谱-质谱法确证

经确证分析被测物质量色谱峰保留时间与标准品相一致，并且在扣除背景后的样品谱图中，所选择的离子均出现；同时所选择离子的丰度比与标准样品相关离子的相对丰度一致，相似度在允许差之内(见表 1)，则可判定样品为苄螨醚阳性检出。苄螨醚标准物质的气相色谱-质谱选择离子色谱图和质谱图参见附录 A 中图 A.2 和图 A.3。

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
允许相对偏差/%	±10	±15	±20	±50

6.5 空白试验

除不称取样品外，均按上述步骤进行。

7 结果计算和表述

用色谱数据处理机或按式(1)计算试样中苄螨醚残留量：

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

式中：

X——试样中苄螨醚残留量，单位为毫克每千克(mg/kg)；

A——样液中苄螨醚的峰面积；

c_s——标准工作液中苄螨醚的浓度，单位为微克每毫升(μg/mL)；

A_s——标准工作液中苄螨醚的峰面积；

V——样液最终定容体积，单位为毫升(mL)；

m——最终样液所代表的试样量，单位为克(g)。

注：计算结果应扣除空白值。

8 测定低限和回收率

8.1 测定低限

本标准对桃、梨、芦笋、土豆、玉米、荞麦、蜂蜜、食醋、核桃仁、虾仁、鸡肉、兔肉、大葱、茶叶和鸡肝的测定低限为 0.01 mg/kg。

8.2 回收率

本方法添加水平和回收率见表 2。

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表 2　回收率

样　　品	添加水平/(mg/kg)	回收率/%	确证低限/(mg/kg)
桃	0.01	80.2～98.4	0.01
	0.05	81.6～97.2	
	2.0	82.6～99.1	
梨	0.01	84.3～98.2	0.01
	0.05	85.2～98.2	
	2.0	87.6～99.5	
芦笋	0.01	82.3～101.3	0.01
	0.05	84.4～100.8	
	2.0	96.1～99.7	
大葱	0.01	73.7～99.2	0.01
	0.05	77.0～89.8	
	2.0	81.2～102.4	
土豆	0.01	85.5～99.4	0.01
	0.05	86.2～98.6	
	2.0	85.8～99.6	
蜂蜜	0.01	71.7～94.8	0.01
	0.05	71.8～91.4	
	2.0	81.3～98.1	
荞麦	0.01	79.7～96.5	0.01
	0.05	82.2～95.8	
	2.0	83.1～98.4	
茶叶	0.01	78.4～104.3	0.01
	0.05	82.2～97.8	
	2.0	83.2～102.1	
玉米	0.01	81.2～102.4	0.01
	0.05	83.0～101.0	
	2.0	83.6～99.8	
食醋	0.01	81.3～96.2	0.01
	0.05	81.6～95.0	
	2.0	83.4～98.7	
核桃仁	0.01	80.3～97.5	0.01
	0.05	80.0～98.2	
	2.0	83.8～99.1	

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表 2（续）

样　　品	添加水平/(mg/kg)	回收率/%	确证低限/(mg/kg)
兔肉	0.01	83.1～96.8	0.01
	0.05	86.2～95.6	
	2.0	85.7～98.3	
鸡肝	0.01	81.2～103.2	0.01
	0.05	85.0～96.5	
	2.0	81.2～90.0	
虾仁	0.01	77.6～104.1	0.01
	0.05	79.4～99.6	
	2.0	80.1～101.3	
鸡肉	0.01	83.1～97.8	0.01
	0.05	84.4～96.2	
	2.0	84.8～98.1	

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附　录　A
（资料性附录）
苄螨醚标准品色谱图

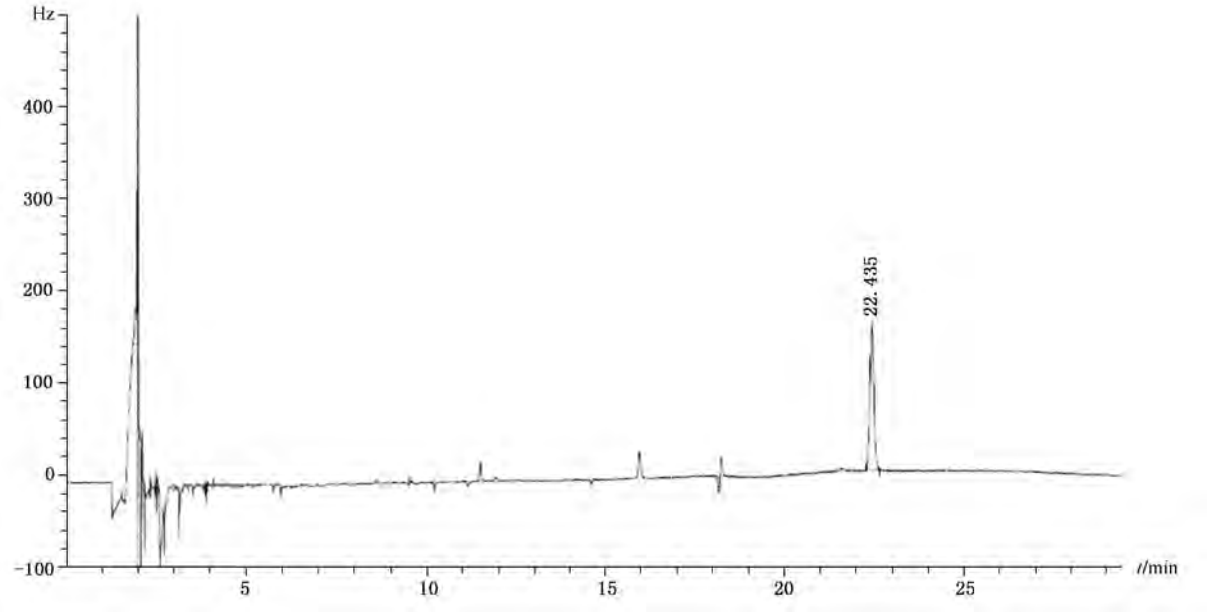


图 A.1　苄螨醚标准品气相色谱图

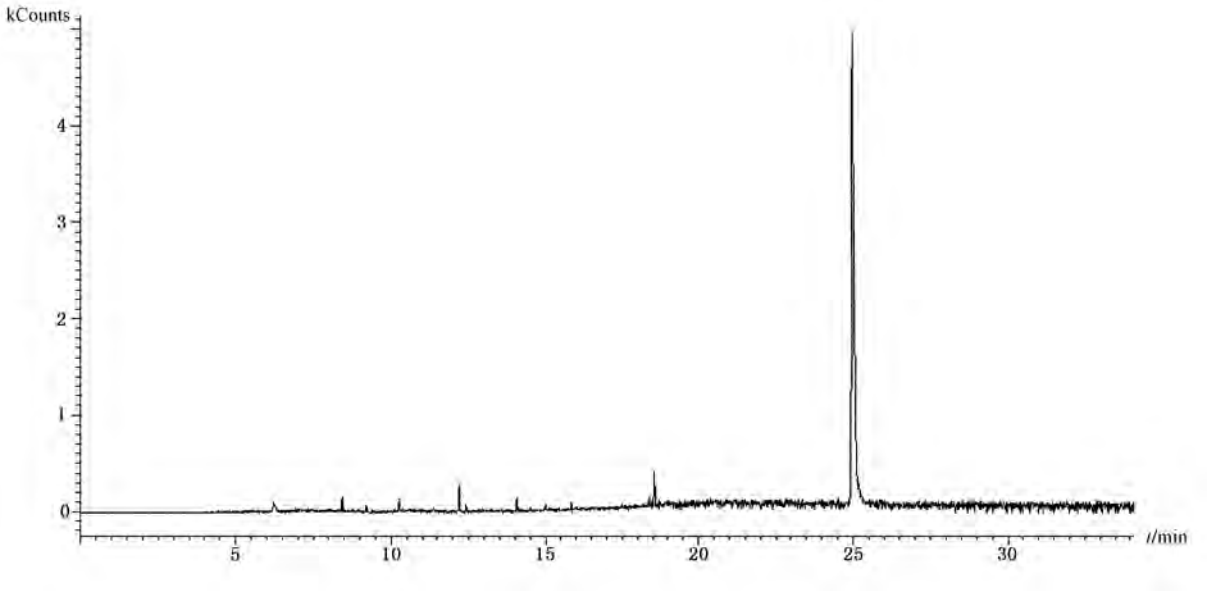


图 A.2　苄螨醚气相色谱-质谱选择离子色谱图

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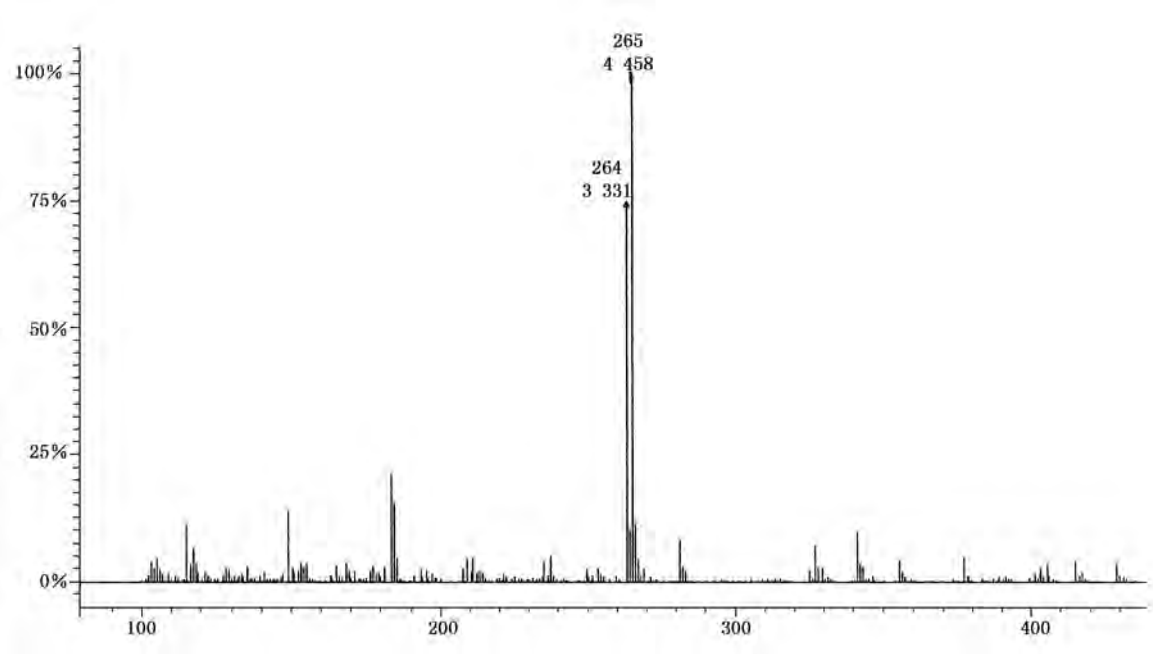


图 A.3　苄螨醚标准物质质谱图

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Foreword

Annex A of this standard is informative annexes.

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

This standard was drafted by Shanxi Entry-Exit Inspection and Quarantine Bureau.

This main drafters of this standard are：XuePing，DuLijun，YuanLi，WuHaijun，ZhangXiaofeng，PanYali.

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Determination of halfenprox residues in food for import and export

1 Scope

This standard specifies the methods of determination and confirmation of halfenprox residues in foods for import and export by GC and GC-MS.

This standard is applicable to the determination of halfenprox residues in asparagus, murphy, scallion, apple, peach, corn, buckwheat, tea leaf, vinegar, honey, walnut, chicken liver, chicken, rabbit meat and shrimp.

2 Principle

The halfenprox residues were extracted with ethyl acetate-cyclohexane or acetonitrile, purified by a gel permeation chromatography(GPC) or SPE, determinated by GC-ECD and confirmation by GC-MS, using external standard method.

3 Reagents and materials

All the reagents used should be analytically pure unless otherwise specified. "Water" is distilled water.

3.1 Ethyl acetate: HPLC grade.

3.2 Cyclohexane: HPLC grade.

3.3 Acetonitrile: HPLC grade.

3.4 Hexane: HPLC grade.

3.5 Trichloromethane: HPLC grade.

3.6 Anhydrous sodium sulfate: Ignited at 650 ℃ for 4 h and kept in a tightly closed container.

3.7 Sodium chloride.

3.8 Ethyl acetate + cyclohexane(1 + 1, V/V).

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3.9 Hexane + trichloromethane (9 + 1, V/V).

3.10 Cyclohexane + ethyl acetate(6 + 1, V/V).

3.11 Halfenprox standard (Halfenprox; CAS No.: 111872-58-3; molecular formula: $C_{24}H_{23}BrF_2O_3$; molecular weight: 477.34) pure: 99%。

3.12 Standard stock solution: Accurately weigh a certain amount of halfenprox standard and dissolve it in a small volume of ethyl acetate. Dilute with ethyl acetate to make the standard stock solution of 100 mg/L. It should be stored in a refrigerator at 0 ℃～4 ℃.

3.13 Standard working solution: Then dilute the standard stock solution with ethyl acetate to the required concentration as the standard working solution. These solutions should be prepared before use.

3.14 Carbon-PSA tube: 1 mL, 50 mg, active with 3 mL acetonitrile + ethyl acetate(3.10).

3.15 HLB SPE tubes: 3 mL, 60 mg, or equivalent. Rinse with 2 mL of hexane + trichloromethane (3.9), 2 mL of trichloromethane and 5 mL of distilled water before starting.

3.16 Film: 0.45 μm.

4 Apparatus and equipment

4.1 Gas chromatography: Equipped with ECD.

4.2 Gas chromatography: Equipped with electron ionization mass spectrometry.

4.3 Analytical balance: Sense of 0.01 g.

4.4 Analytical balance: Sense of 0.1 mg.

4.5 Gel permeation chromatograph equipped with isocratic pump and fraction collector.

4.6 Centrifuge: 4 000 r/min.

4.7 Rotary vacuum evaporator.

4.8 Anhydrous sodium sulfate column: 7.5 cm × 1.5 cm (i.d.) fuel, filled anhydrous sodium sulfate upon 5 cm absorbent cotton. Rotary vacuum evaporator.

4.9 Vortex mixer.

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4.10 Ultrasonic machine.

4.11 Homogenizer.

4.12 50 mL stoppered plastic centrifuge tube.

5 Preparation and storage of test sample

5.1 Preparation of test sample

5.1.1 Cereals and tea

Quarter the sample to ca. 500 g, grind thoroughly in a high speed blender. Mix thoroughly and divide into two equal portions as test sample. Place in clean containers, seal and label them.

5.1.2 Fruits and vegetables

The combined primary sample is reduced to ca. 500 g, from which shell, seed, peel, stem, root, and coronal has been removed (do not wash by water). Collect the edible parts, and blend and mix thoroughly in a high speed blender. Divide into two equal portions. Each portion is placed in a clean container, which is sealed and labeled, as the test sample.

5.1.3 Meat and meat products, nuts

Take representative approximately 1 kg of sample. The edible parts are collected, blended and homogenized. Divide into two equal portions. Each portion is placed in a clean container, which is sealed and labeled, as the test sample.

5.2 Storage of test samples

The test samples of cereals, tea, nuts, vinegar, honey and honey products should be stored between 0 ℃～4 ℃. The test samples of other one should be stored below －18 ℃. While sampling and sample preparation, precaution must be taken to avoid contamination or any factors that may cause the change of residue content.

6 Procedure

6.1 Extraction

6.1.1 Vegetables, fruits, cereals

Weight 10 g(accurate to 0.01 g) of the test sample into a 50 mL stoppered plastic centrifuge tube,

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then add 20 mL ethyl acetate + cyclohexane(3.8), extracted with homogenizer at 10 000 r/min for 1 min, then centrifuge at 4 000 r/min for 3 min, transfer the supernatant to another clean tube, and repeat the extraction procedure with 20 mL ethyl acetate + cyclohexane again. The supernatants are passed through a column of anhydrous sodium sulfate(4.8) to remove the water, collect the effluent into a 150 mL concentrate bottle and condense to nearly dry by a rotary evaporator with a 40 ℃ water bath. Dissolve the residue with 10.0 mL of ethyl acetate + cyclohexane, filter through 0.45 μm membrane filter and wait for purification.

6.1.2 Walnut, chicken liver, chicken, rabbit meat and shrimp

Weight 10 g(accurate to 0.01 g) of the test sample into a 50 mL stoppered plastic centrifuge tube, then add 20 mL acetonitrile (3.3), 10 mL distilled water and 3 g sodium chloirde, extracted with homogenizer at 10 000 r/min for 1 min, then centrifuge at 4 000 r/min for 3 min, transfer the supernatant to another clean tube, and repeat the extraction procedure with 20 mL acetonitrile again. The supernatants are passed through a column of anhydrous sodium sulfate (4.8) to remove the water, collect the effluent into a 150 mL concentrate bottle and condense to nearly dry by a rotary evaporator with a 40 ℃ water bath. Dissolve the residue with 10.0 mL of ethyl acetate + cyclohexane, filter through 0.45 μm membrane filter and wait for purification.

6.1.3 Tea and onion

Weight 2.5 g (accurate to 0.01 g) of samples, into a 50 mL stoppered plastic centrifuge tube, add 15 mL distilled water, stand for 1 h. Then add 20 mL ethyl acetate + cyclohexane(3.8), stopper the tubes and vortex for 1 min, then centrifuge at 4 000 r/min for 3 min, transfer the supernatant to another clean tube, and repeat the extraction procedure with 20 mL ethyl acetate + cyclohexane again. The supernatants are passed through a column of anhydrous sodium sulfate (4.7) to remove the water, collect the effluent into a 150 mL concentrate bottle and condense to nearly dry by a rotary evaporator with a 40 ℃ water bath. Dissolve the residue with 10.0 mL of ethyl acetate + cyclohexane, filter through 0.45 μm membrane filter and wait for purification.

6.2 Cleaning-up

6.2.1 GPC cleaning-up for vegetables, fruits, cereals, walnut, chicken liver, chicken, rabbit meat and shrimp

6.2.1.1 GPC operating condition

a) GPC column: 300 mm × 10 mm (i.d.), Bio Beads S-X3 or equivalent;

b) Mobile phase: Cyclohexane-ethyl acetate (1 + 1);

c) Flow rate: 4.7 mL/min;

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d) Injection volume at sample loop: 5 mL;

e) Time of collecting the eluate: 7.5 min～12.5 min.

6.2.1.2 GPC cleaning-up step

Transfer the solution acquired at 6.1 into the column of GPC with the parameters of section 6.2.1. The elution are collected into a clean tube and evaporated to dryness at 35 ℃ under a stream of nitrogen, and redissolved in 1.0 mL ethyl acetate for determination and confirmation.

6.2.2 SPE cleaning-up for vinegar and honey

Weight 2.5 g of samples into a plastic centrifuge tube, add 5 mL of distilled water and vortex for 30 s. Transfer the above solution into SPE column, control the flow at 1 mL/min. Then elute with 2 mL of distilled water, discard the rinse liquid, make vacuum for 2 min, add 4 mL of hexane + trichloromethane, collect the eluates into a 10 mL centrifuge tube, then evaporated to dryness at 40 ℃ under a stream of nitrogen, and dissolved with 0.5 mL ethyl acetate for GC-ECD or GC-MS determination.

6.2.3 SPE cleaning-up for tea and onion

Transfer the solution acquired at 6.1.3 into carbon-PSA tube(3.14), rinse with 1.5 mL of cyclohexane + ethyl acetate(3.10), collect the eluates into a 10 mL centrifuge tube, control the flow at 1 mL/min, then evaporated to dryness at 40 ℃ under a stream of nitrogen, and dissolved with 0.5 mL ethyl acetate for GC-ECD or GC-MS determination.

6.3 GC determination

6.3.1 GC operation conditions

a) Column: DB-1301 30 m × 0.25 mm (i.d.) × 0.25 μm or equivalent;

b) Column temperature: 50 ℃ $\xrightarrow{20\ ℃/min}$ 200 ℃ $\xrightarrow{5\ ℃/min}$ 260 ℃ (10 min);

c) Injection port temperature: 260 ℃;

d) ECD temperature: 300 ℃;

e) Carrier gas: Nitrogen(purity≥99.999%, flow rate:2 mL/min);

f) Injection mode:Splitless, open the valve after 0.75 min;

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g) Injection volumn: 1 μL.

6.3.2 GC determination

According to the approximate concentration of halfenprox residues in sample solution, select the standard working solution with similar peak area to that of the sample solution. The standard working solution should be randomly injected in between the injection of sample solution of equal volumn. Under the above GC conditions, the retention time of halfenprox is about 22.4 min. The chromatogram of the halfenprox standard is shown by figure A.1 in annex A. Standard solution and sample solution were determined according the conditions of 6.3.1, if the sample solution with standard solution with the same retention time peaks, then confirmed by GC-MS.

6.4 GC-MS confirmation

6.4.1 GC-MS operation conditions

a) Chromatographic column: 30 m × 0.25 mm (i.d.), 0.25 μm film thickness, and HP-5MS silica capillary column or equivalent;

b) Column temperature: 50 ℃ (1 min) $\xrightarrow{10\ ℃/min}$ 280 ℃ (10 min);

c) Injection port temperature: 250 ℃;

d) Interface temperature: 280 ℃;

e) Electron ionization mode: EI;

f) Ionization energy: 70 eV;

g) Carrier gas: Helium, purity≥99.999%, flow rate 1 mL/min;

h) Injection mode: Splitless, open the valve after 0.75 min;

i) Injection volume: 1 μL;

j) Determination mode: SIM;

k) Selected monitoring ions (m/z): 183, 264, 265;

l) Solvent protection delay: 5.0 min.

6.4.2 GC-MS confirmation

According to the operating condition assigned in 6.3.1, analyze the standard solution and sample so-

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lution,if there is a peak appeared at the same retention time for both of the sample solution and standard working solution, the GC-MS confirmation test should be conducted. If the retention times of sample chromatogram peaks are consistent with the standard, and after subtracted background noise, the relative intensity ratios of each qualitative ions are also consistent with similar concentration standard, and the similarity degree of their relative abundance ratio in permitted tolerance(see table 1), we can confirm that there are corresponding analyte in the sample. The GC-MS selected ion chromatogram and mass spectrum of the halfenprox standard are shown respectively by figure A.2 and figure A.3 in annex A.

Table 1—Maximum permitted tolerance for relative ion intensities of confirmation

Relative intensity/%	>50	20～50	10～20	<10
Permitted relative tolerances/%	±10	±15	±20	±50

6.5 Blank test

Blank test will be conducted according to the procedures above without sample addition.

7 Calculation and expression of the result

Calculate the content of halfenprox residue in the test sample by GC processor or according to the followed formula (1):

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

Where:

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

A—the peak area of halfenprox in the sample solution;

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

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

A_s—the peak area of halfenprox in the standard working solution;

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

8 Limit of determination and recovery

8.1 Limit of determination

The limit of determination of peach, pear, aspraragus , corn buchwheat, honey, vinegar, walnut, rabbit meat, chicken, shrimp, tea leaf, scallion and chicken liver are 0.01 mg/kg.

8.2 Recovery

The confirmation limit and recovery of this method see table 2.

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Table 2—Limit of determination and recovery of this method

Name of test sample	The limit of determination/(mg/kg)	Recovery/%	The limit of confirmation/ (mg/kg)
Peach	0.01	80.2～98.4	0.01
	0.05	81.6～97.2	
	2.0	82.6～99.1	
Pear	0.01	84.3～98.2	0.01
	0.05	85.2～98.2	
	2.0	87.6～99.5	
Asparagus	0.01	82.3～101.3	0.01
	0.05	84.4～100.8	
	2.0	96.1～99.7	
Scallion	0.01	73.7～99.2	0.01
	0.05	77.0～89.8	
	2.0	81.2～102.4	
Potatoes	0.01	85.5～99.4	0.01
	0.05	86.2～98.6	
	2.0	85.8～99.6	
Corn	0.01	71.7～94.8	0.01
	0.05	71.8～91.4	
	2.0	81.3～98.1	
Buckwheat	0.01	79.7～96.5	0.01
	0.05	82.2～95.8	
	2.0	83.1～98.4	
Tea leaf	0.01	78.4～104.3	0.01
	0.05	82.2～97.8	
	2.0	83.2～102.1	
Honey	0.01	81.2～102.4	0.01
	0.05	83.0～101.0	
	2.0	83.6～99.8	
Vinegar	0.01	81.3～96.2	0.01
	0.05	81.6～95.0	
	2.0	83.4～98.7	
Walnut	0.01	80.3～97.5	0.01
	0.05	80.0～98.2	
	2.0	83.8～99.1	
Rabbit meat	0.01	83.1～96.8	0.01
	0.05	86.2～95.6	
	2.0	85.7～98.3	

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Table 2（continued）

Name of test sample	The limit of determination/（mg/kg）	Recovery/%	The limit of confirmation/（mg/kg）
Chicken liver	0.01	81.2～103.2	0.01
	0.05	85.0～96.5	
	2.0	81.2～90.0	
Shrimp	0.01	77.6～104.1	0.01
	0.05	79.4～99.6	
	2.0	80.1～101.3	
Chicken meat	0.01	83.1～97.8	0.01
	0.05	84.4～96.2	
	2.0	84.8～98.1	

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Annex A
（informative）
Chromatogram of the halfenprox standard

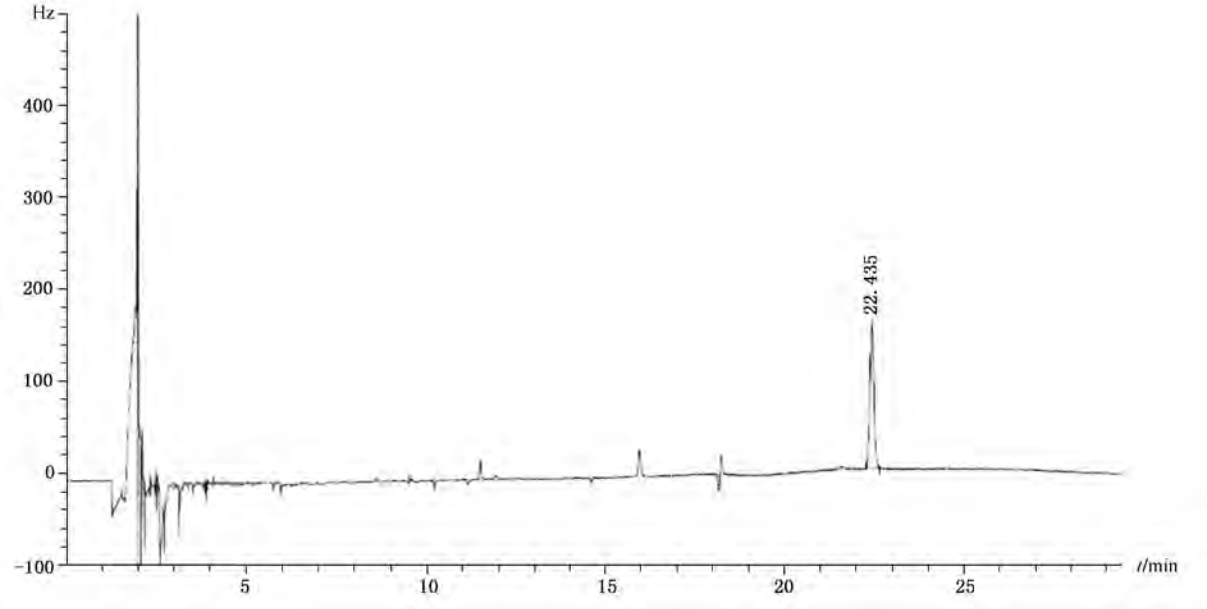


Figure A. 1—Chromatogram of the halfenprox standard

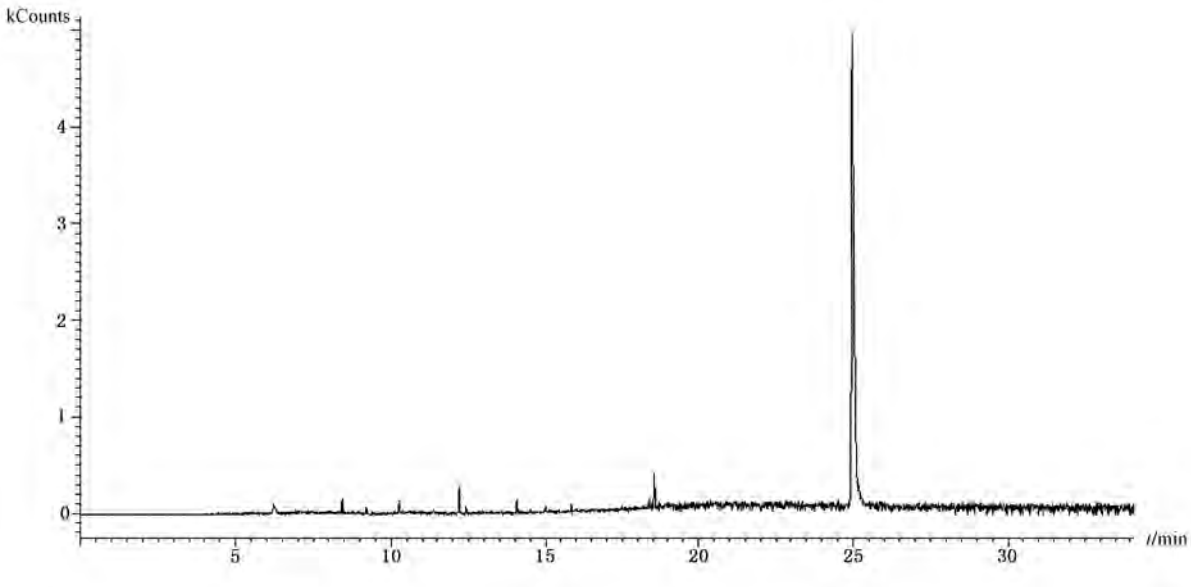


Figure A. 2—GC-MS selected ion chromatogram of the halfenprox standard derivative

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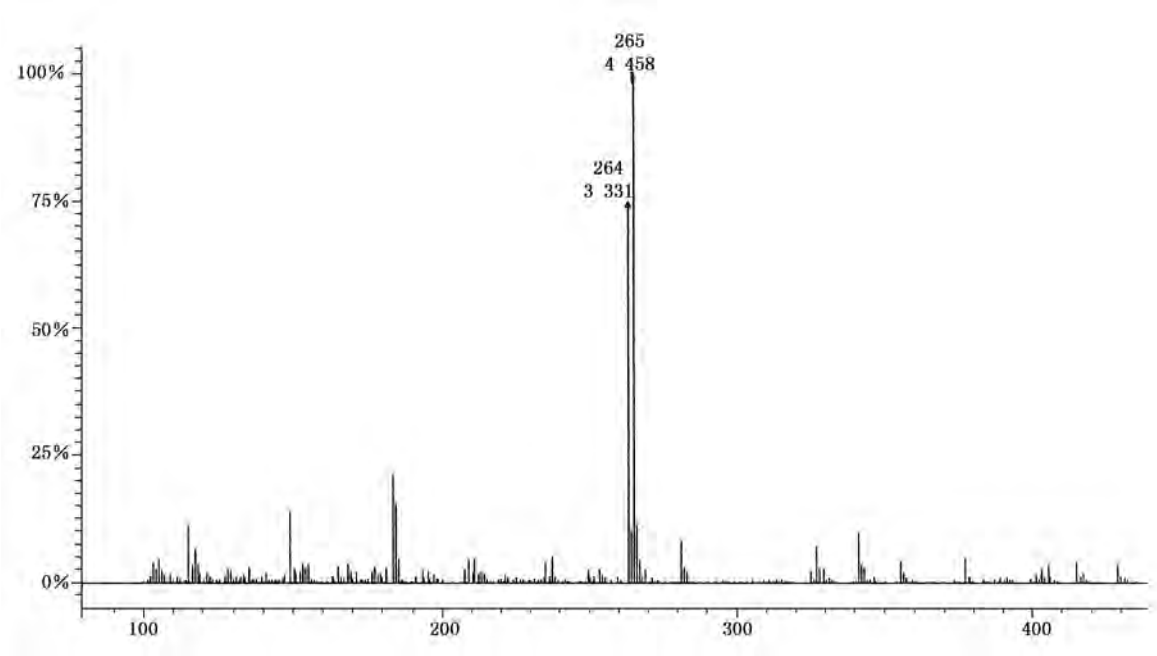


Figure A. 3—Gas chromatogram and mass spectrum of the halfenprox standard

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