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中华人民共和国出入境检验检疫行业标准

SN/T 2158—2008

进出口食品中毒死蜱残留量检测方法

Determination of chlorpyrifos residue in foods for import and export

2008-09-04 发布　　2009-03-16 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：中华人民共和国吉林出入境检验检疫局、中华人民共和国湖南出入境检验检疫局、中华人民共和国深圳出入境检验检疫局。

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本标准系首次发布的出入境检验检疫行业标准。

进出口食品中毒死蜱残留量检测方法

1 范围

本标准规定了进出口食品中毒死蜱残留量的气相色谱检测和气相色谱-质谱确证方法。

本标准适用于玉米、糙米、大葱、菠菜、辣椒、柑桔、苹果、花生、松子仁、茶叶、鱼肉、蜂蜜、猪肉、鸡肾、鸡肝中毒死蜱残留量的检测和确证。

2 方法提要

试验用乙酸乙酯或水-丙酮提取，液液分配萃取，经固相萃取柱或凝胶色谱净化，用气相色谱仪火焰光度检测器检测，外标法定量；阳性样品用气相色谱-质谱仪确证。

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 丙酮：残留级。

3.2 二氯甲烷：残留级。

3.3 环己烷：残留级。

3.4 乙酸乙酯：残留级。

3.5 正己烷：残留级。

3.6 氯化钠。

3.7 无水硫酸钠：650 ℃灼烧 4 h，贮于密封容器中备用。

3.8 氯化钠水溶液(5%)：称取 5.0 g 氯化钠，用水溶解，并定容至 100 mL。

3.9 乙酸乙酯-正己烷(1+1，体积比)：量取 100 mL 乙酸乙酯和 100 mL 正己烷，混匀。

3.10 环己烷-乙酸乙酯：(1+1，体积比)：量取 100 mL 环己烷和 100 mL 正己烷，混匀。

3.11 毒死蜱标准品(Chlorpyrifos，$C_9H_{11}C_{13}NO_3PS$，CAS No. 2921-88-2)：纯度大于等于 98%。

3.12 毒死蜱标准储备溶液：准确称取适量的毒死蜱标准品，用乙酸乙酯配制成浓度为 100 μg/mL 的标准储备溶液。该溶液在 0 ℃～4 ℃冰箱中保存。

3.13 毒死蜱标准工作溶液：根据需要将毒死蜱标准储备溶液(3.12)用乙酸乙酯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。

3.14 氟罗里硅土固相萃取柱：Florisil，500 mg，6 mL，或相当者。

3.15 石墨化炭黑固相萃取柱：ENVI-Carb，250 mg，6 mL，或相当者。

3.16 微孔滤膜：0.45 μm。

3.17 石墨化炭黑：60 目～80 目。

4 仪器与设备

4.1 气相色谱仪：配有火焰光度检测器(FPD)，波长 526 nm。

4.2 气相色谱-质谱仪：配有电子轰击源(EI)。

4.3 电子天平：感量精确至 0.000 1 g。

4.4 凝胶色谱仪：配有单元泵、馏分收集器。

4.5 均质器。

4.6 旋转蒸发器。

4.7 具塞锥型瓶:250 mL。

4.8 分液漏斗:250 mL。

4.9 浓缩瓶:50 mL、250 mL。

4.10 离心机:4 000 r/min 以上。

4.11 具塞离心管:四氟乙烯,50 mL。

5 试样制备与保存

5.1 试样制备

5.1.1 玉米、糙米、茶叶、松子仁、花生、蜂蜜

取代表性样品约 500 g,用粉碎机粉碎,混匀,装入洁净容器,密封,标明标记。

5.1.2 柑桔、苹果、菠菜、大葱

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。

5.1.3 猪肉、鸡肝、鸡肾、鱼肉

取代表性样品约 1 kg,取可食部分,经捣碎机充分捣碎均匀,装入洁净容器,密封,标明标记。

5.1.4 辣椒

取代表性样品约 500 g,搅拌均匀,装入洁净容器,密封,标明标记。

5.2 试样保存

粮谷类、坚果类、茶叶、蜂蜜、辣椒试样于 0 ℃～4 ℃保存;其他类试样于－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 柑桔、苹果、玉米、糙米、菠菜、蜂蜜、大葱、辣椒

称取试样 10 g(精确到 0.01 g)于 50 mL 离心管中,加 6 g 无水硫酸钠(3.7)和 30 mL 乙酸乙酯(3.4),均质 2 min,在 5 000 r/min 离心 5 min,上清液过滤于 250 mL 浓缩瓶中,残渣加入 30 mL 乙酸乙酯再提取一次,过滤,合并滤液于 250 mL 浓缩瓶中,于 40 ℃下浓缩至近干,用 2 mL 乙酸乙酯-正己烷(3.9)溶液溶解残渣,待净化。

6.1.2 茶叶

称取试样 5 g(精确到 0.01 g)于 50 mL 离心管中,加 10 mL 水浸泡 10 min,加入 30 mL 乙酸乙酯,均质 2.0 min,5 000 r/min 离心 5 min,上清液经无水硫酸钠柱收集于 250 m 浓缩瓶中,残渣加入 30 mL 乙酸乙酯再提取一次,经无水硫酸钠柱脱水,合并提取液于 250 mL 浓缩瓶中,浓缩至近干,用乙酸乙酯-正己烷溶液并定容至 2 mL,待固相萃取(SPE)净化。

6.1.3 猪肉、鸡肝、鸡肾、鱼肉、松子仁、花生

称取 20 g 试样(松子仁、花生称取 5.0 g,精确到 0.01 g)于 250 mL 具塞锥形瓶中,加入 20 mL 水和 100 mL 丙酮(3.1),均质提取 3 min。将提取液过滤于 250 mL 浓缩瓶中,残渣再用 50 mL 丙酮重复提取一次,合并滤液,于 40 ℃水浴中浓缩至约 20 mL。

将浓缩提取液转移至 250 mL 分液漏斗中,加入 100 mL 氯化钠水溶液(3.8)和 100 mL 二氯甲烷(3.2),振摇 3 min,静置分层,收集二氯甲烷相。水相再用 50 mL 二氯甲烷重复提取两次,合并二氯甲烷相。经无水硫酸钠脱水,收集于 250 mL 浓缩瓶中,于 40 ℃水浴中浓缩至近干。加入 10 mL 环己烷-乙酸乙酯(3.10)溶解残渣,用 0.45 μm 滤膜过滤,待凝胶色谱(GPC)净化。

6.2 净化

6.2.1 凝胶色谱(GPC)净化

6.2.1.1 凝胶色谱条件

a) 凝胶净化柱:Bio Beads S-X3,700 mm×25 mm(内径),或相当者;

b) 流动相:乙酸乙酯-环己烷(1+1,体积比);

c) 流速:4.7 mL/min;

d) 样品定量环:10 mL;

e) 预淋洗时间:10 min;

f) 凝胶色谱平衡时间:5 min;

g) 收集时间:22 min～31 min。

6.2.1.2 凝胶色谱净化步骤

将10 mL待净化液(6.1.3)按6.2.1.1规定的条件进行净化,收集组分于40 ℃下浓缩至近干,并用2 mL乙酸乙酯-正己烷溶解残渣,待固相萃取净化(松子仁、花生样品应按6.2.1.1规定的条件重复进行一次凝胶净化)。

6.2.2 固相萃取(SPE)净化

将石墨化炭黑固相萃取柱和氟罗里硅土固相萃取柱按照从上到下依次连接(对于菠菜、茶叶、辣椒试样,在石墨化炭黑固相萃取柱上加1.5 cm高的石墨化炭黑(3.17),使用前用6 mL乙酸乙酯-正己烷预淋洗,弃去淋洗液;将6.1.1、6.1.2和6.1.3全部(2 mL)待净化液倾入上述连接柱中,并用3 mL乙酸乙酯-正己烷分3次洗涤浓缩瓶,将洗涤液倾入连接柱中,再用12 mL乙酸乙酯-正己烷洗脱,收集上述洗脱液至浓缩瓶中,于40 ℃水浴中旋转蒸发至近干,用乙酸乙酯溶解并定容至1.0 mL,供气相色谱测定和气相色谱-质谱确证。

6.3 测定

6.3.1 气相色谱条件:

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:50 ℃(1 min)$\xrightarrow{30\ ℃/min}$180 ℃(1 min)$\xrightarrow{10\ ℃/min}$250 ℃(10 min);

c) 进样口温度:250 ℃;

d) 检测器温度:250 ℃;

e) 载气:氮气,纯度≥99.999%,流速1.0 mL/min;

f) 进样量:1 μL;

g) 进样方式:无分流进样(1.2 min后开阀)。

6.3.2 气相色谱-质谱条件:

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:50 ℃(2 min)$\xrightarrow{20\ ℃/min}$200 ℃(1 min)$\xrightarrow{5\ ℃/min}$270 ℃(18 min);

c) 进样口温度:280 ℃;

d) 色谱-质谱接口温度:280 ℃;

e) 载气:氦气,纯度≥99.999%,流速1.0 mL/min;

f) 进样量:1 μL;

g) 进样方式:无分流进样,1.2 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;

k) 选择监测离子(m/z):定量离子197,定性离子258、286、314;

l) 溶剂延迟：9.0 min。

6.3.3 气相色谱检测

根据样液中毒死蜱含量情况，选定于样液浓度相近的标准工作液。毒死蜱标准工作液和样液中毒死蜱响应值均应在检测线性范围内，试样峰面积与工作液峰面积比较进行定量。在上述色谱条件下，毒死蜱的保留时间约为 14.24 min 毒死蜱标准物质的气相色谱图见附录 A 中图 A.1。

6.3.4 气相色谱-质谱确证

标准溶液及样液均按在上述色谱条件进行测定，如果样液中与标准溶液相同的保留时间有峰出现，则对其进行确证，在上述气相色谱-质谱条件下，毒死蜱的保留时间约为 12.64 min。经确证分析被测物色谱峰保留时间与标准物质相一致，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物质相关离子的相对丰度一致，相似度在允差之内(见表 1)，被确证的样品可判定为毒死蜱阳性检出。在 6.3.1 规定的条件下，可根据待测阳性检出物中碎片离子 197、258、286、314 amu(丰度比 100∶25∶58∶40)的种类和丰度比作为其阳性判别的依据。

气相色谱-质谱选择离子色谱图和质谱图见附录 B 和附录 C。

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/%	±20	±25	±30	±50

6.4 空白试验

除不称取试样外，均按上述步骤进行。

6.5 结果计算和表述

用色谱数据处理机或按式(1)计算试样中毒死蜱残留量：

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

式中：

X——试样中毒死蜱残留量，单位为毫克每千克(mg/kg)；

A——样液中毒死蜱的色谱峰面积；

c——标准工作液中毒死蜱的浓度，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——标准工作液中毒死蜱的色谱峰面积；

m——最终样液所代表的试样质量，单位为克(g)。

注：计算结果应扣除空白值。

7 测定低限和回收率

7.1 测定低限和确证低限

本方法的测定低限和确证低限见表 2。

7.2 添加浓度及回收率范围

本方法添加浓度及回收率范围见表 2。

表 2 本方法添加浓度及回收率范围

样品名称	添加浓度/(mg/kg)	回收率范围/%	测定低限和确证低限/(mg/kg)
玉米	0.010	92.4～96.0	0.01
	0.020	88.0～92.0	
	0.200	92.4～93.5	

表 2（续）

样品名称	添加浓度/(mg/kg)	回收率范围/%	测定低限和确证低限/(mg/kg)
糙米	0.010	99.1～102.4	0.01
	0.020	92.5～94.6	
	0.200	81.8～87.2	
大葱	0.010	88.6～90.8	0.01
	0.020	89.5～93.0	
	0.200	93.3～98.1	
菠菜	0.010	90.0～94.2	0.01
	0.020	89.6～91.0	
	0.200	99.3～102.0	
柑桔	0.010	97.5～99.6	0.01
	0.020	97.5～102.5	
	0.200	89.9～92.3	
苹果	0.010	100.5～106.2	0.01
	0.020	84.8～87.0	
	0.200	96.3～99.3	
辣椒	0.010	96.2～98.6	0.01
	0.020	92.5～98.0	
	0.200	94.8～96.2	
蜂蜜	0.010	82.0～90.2	0.01
	0.020	81.2～83.6	
	0.200	80.7～89.5	
茶叶	0.020	80.0～83.1	0.02
	0.050	101.6～104.0	
	0.200	93.2～98.6	
花生	0.020	80.1～84.5	0.02
	0.050	93.0～96.0	
	0.200	93.4～93.8	
松子仁	0.020	101.6～105.1	0.02
	0.050	98.0～100.5	
	0.200	84.2～86.1	
猪肉	0.005	88.1～90.3	0.005
	0.020	89.3～90.8	
	0.200	80.2～80.6	

表 2（续）

样品名称	添加浓度/(mg/kg)	回收率范围/%	测定低限和确证低限/(mg/kg)
鸡肝	0.005	102.2～104.1	0.005
	0.020	93.0～97.0	
	0.200	80.9～81.8	
鸡肾	0.005	100.1～106.2	0.005
	0.020	89.5～93.0	
	0.200	94.0～96.2	
鱼肉	0.005	94.1～98.3	0.005
	0.020	92.5～97.5	
	0.200	80.4～84.5	

附　录　A
（资料性附录）
毒死蜱标准品气相色谱图

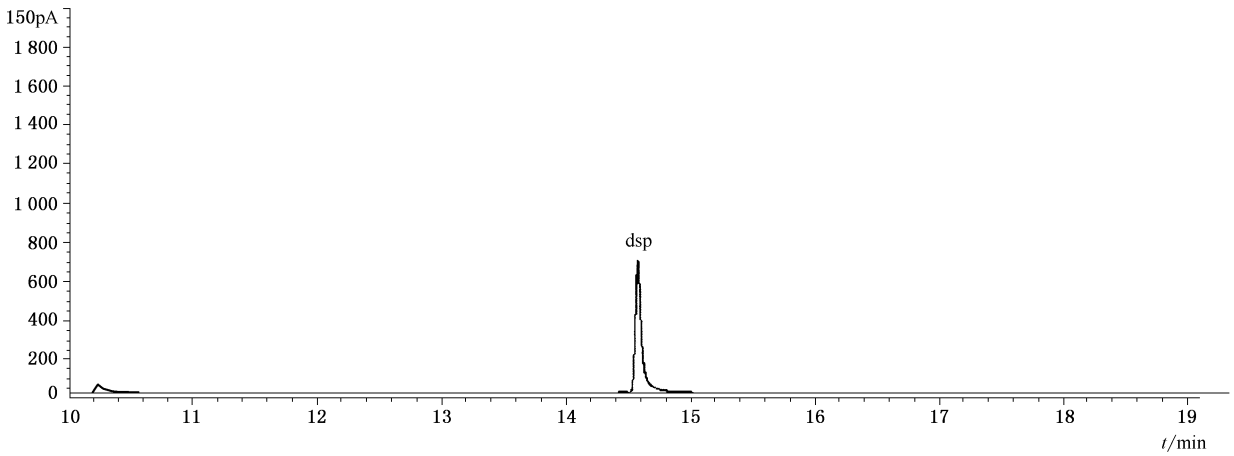

图 A.1　毒死蜱标准品气相色谱图

附　录　B
（资料性附录）
毒死蜱气相色谱-质谱选择离子色谱图

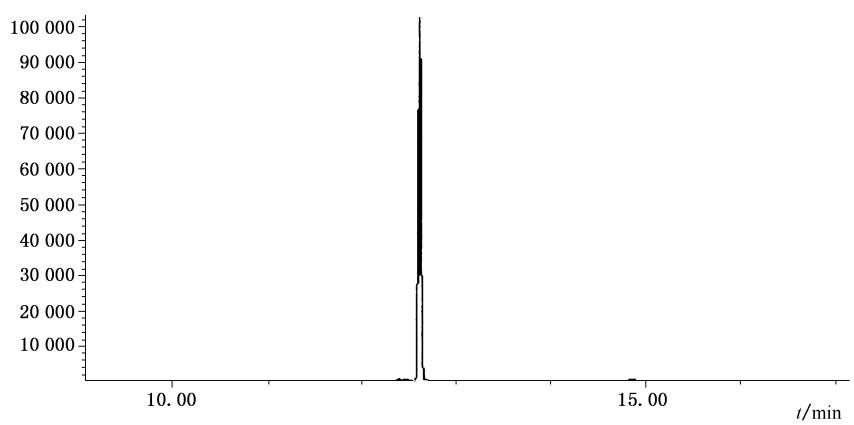

图 B.1　毒死蜱气相色谱-质谱选择离子色谱图

附 录 C
（资料性附录）
毒死蜱气相色谱-质谱图

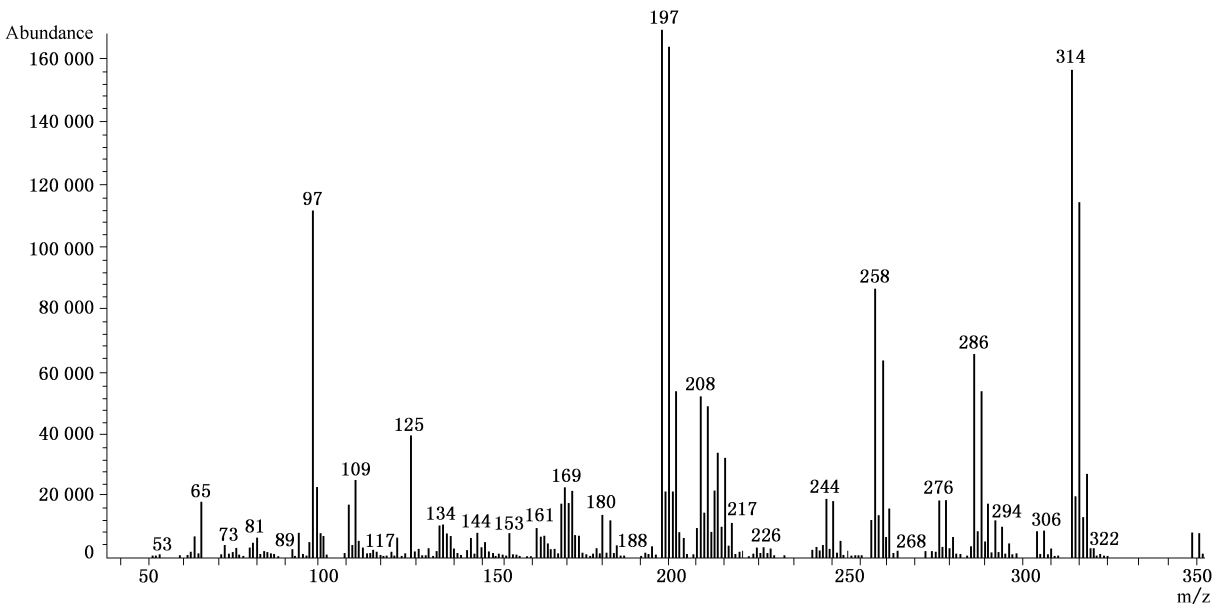

图 C.1 毒死蜱气相色谱-质谱图

Foreword

Annex A, Annex B and Annex C of this standard are informative.

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

This standard was drafted by the Jilin Entry-Exit Inspection and Quarantine Bureau, Hunan Entry-Exit Inspection and Quarantine Bureau, and Shenzhen Entry-Exit Inspection and Quarantine Bureau.

Main drafters of this standard are Li Aijun. , Wang Mingtai, Mu Jun, Hang Zhiqiang, Xie Liqi, Zhou Xiao.

This standard is an inspection and quarantine professional standard promulgated for the first time.

Determination of chlorpyrifos residue in foods for import and export

1 Scope

This standard specifies the method of testing Chlorpyrifos residue in foods for import and export by gas chromatography-flame photometric detector (GC-FPD) and gas chromatography-mass spectrometry(GC-MS).

This standard is applicable to the determination and confirmation of residue content of Chlorpyrifos in corn, brown-rice, scallion, spinach, chili, orange, apple, pine-nut kernel, tea, honey, fish, honey, pork, chicken kidney and chicken liver for import and export.

2 Principle

Orange or other vegetal sample is extracted with ethyl acetate, cleaned up by carbon ENVI-Carb column coupled with one florisil solid phase extraction (SPE) column, and determined by GC with external standard method. Pork or other animalized sample is extracted homogenously with water-acetone. The extract is partitioned with dichloromethane, is cleaned up by sequentially passing through gel permeation chromatography (GPC), and one active carbon ENVI-Carb column coupled with one florisil solid phase extraction (SPE) column, then the final solution is determined by GC with external standard method. The positive sample should be confirmed by GC-MS.

3 Reagents and materials

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

3.1 Acetone: residue grade.

3.2 Dichloromethane: residue grade.

3.3 Cyclohexane: residue grade.

3.4 Ethyl acetate: residue grade.

3.5 *n*-Hexane: residue grade.

3.6 Sodium chloride aqueous solution.

3.7 Anhydrous sodium sulfate: ignited at 650 ℃ for 4 h, and then stored in a tightly sealed container.

3.8 Sodium chloride aqueous solution. (5%): weigh sodium chloride 5.0 g. Dissolve with water and dilute to 100 mL in calibrated flask.

3.9 Ethyl acetate-*n*-Hexane(1+1 *V*/*V*): volume 100 mL Ethyl acetate into 250 mL erlenmeyer flask, then add 100 mL *n*-Hexane, mix them.

3.10 Ethyl acetate-Cyclohexane (1+1 *V*/*V*): volume 100 mL Ethyl acetate into 250 mL erlenmeyer flask, then add 100 mL Cyclohexane, mix them.

3.11 Chlorpyrifos standard($C_9H_{11}C_{13}NO_3PS$, CAS No. 2921-88-2): Purity≥98%.

3.12 Standard stock solution: accurately weigh certain amount of Chlorpyrifos standard and dissolve it with a small volume of ethyl acetate. Dilute with Ethyl acetate to make the standard stock solution of 100 μg/mL. The solution is stored in a refrigerator at 0 ℃～4 ℃. Expiry after one year.

3.13 Standard working solution: dilute the standard stock solution with ethyl acetate to the required concentration to make the standard working solution. The solution is stored in a refrigerator at 0 ℃～4 ℃. Expiry after six months.

3.14 Florisil SPE tube: Florisil, 500 mg, 6mL, or equivalent.

3.15 Active carbon SPE tube: ENVI-Carb, 250 mg, 6 mL, or equivalent.

3.16 Membrane filter: 0.45 μm.

3.17 Graphitic carbon: 60 mesh～80 mesh.

4 Apparatus and equipment

4.1 GC: gas chromatography equipped with FPD, 526 nm.

4.2 GC-MS: equipped with electro-Impact source (EI).

4.3 Centrifuge: 4 000 r/min.

4.4 GPC: equipped with isocratic pump and fraction collector.

4.5 Homogenizer.

4.6 Rotary vacuum evaporator.

4.7 Stoppered Erlenmeyer flask:250 mL.

4.8 Separatory funnel:250 mL.

4.9 Concentrate bottle:50 mL and 250 mL.

4.10 Electronic balance:accurate to 0.000 1 g.

4.11 Plastic centrifuge tube:50 mL.

5 Preparation and storage of test sample

5.1 Preparation of test sample

5.1.1 Corn,brown-rice,tea,pine-nut kernel,peanut and Honey

Take approximately 500 g of representative sample. Smash thoroughly by a breaker. Mix thoroughly. Put in clean containers. Seal and label them.

5.1.2 Orange,apple,spinach,and scallion

Take approximately 500 g of representative sample. Collect the edible parts (do not wash with water)and cut into minces. Crush with a crusher into pulp. Mix thoroughly. Put in clean containers. Seal and label them.

5.1.3 Pork,chicken liver,chicken kidney,and fish

Take approximately 1 kg of representative sample. Collect the edible pieces. Crush with a crusher. Mix thoroughly. Put in clean containers. Seal and label them.

5.1.4 Chilli

Take approximately 500 g of representative sample. Mix thoroughly. Put in clean containers. Seal and label them.

5.2 Storage of test sample

The test samples of cereals,nuts,tea,honey and chilli should be stored between 0 ℃～4 ℃. Other samples should be frozen and stored below －18 ℃. While sampling and preparing sample,please avoid contamination or any factors that may change residue content.

6 Procedure

6.1 Extraction

6.1.1 Orange, apple, spinach, scallion, corn, brown-rice, and chili

Weigh 10g (accurate to 0.01g) of the test sample into a 50 mL centrifuge tube (4.11). Add 6 g of anhydrous sodium sulfate and 30 mL ethyl acetate. Homogenize for 2 min. Centrifuge for 5 min at 5 000 r/min. Filter the supernatant into a 250 mL concentrate bottle. Extract the residue with 30 mL of Ethyl acetate once more and filter the second supernatant. Combine the filtrates. Condensed to nearly dry by a rotary evaporator in 40 ℃ water bath. Add 2 mL of ethyl acetate-*n*-Hexane (1+1) to dissolve the residue and then wait for cleaning-up.

6.1.2 Tea

Weigh 5 g(accurate to 0.01 g)of the test sample into a 50 mL plastic centrifuge tube, Add 10 mL water and 30 mL ethyl acetate. Homogenize for 2 min. Centrifuge for 5 min at 5 000 r/min. Filter the supernatant into a 250 mL concentrate bottle. Extract the residue with 30 mL of Ethyl acetate once more and filter the second supernatant. Combine the filtrates. Condensed to nearly dry by a rotary evaporator in 40 ℃ water bath. Add 2 mL of ethyl acetate-*n*-Hexane (1+1) to dissolve the residue and then wait for cleaning-up.

6.1.3 Pork, chicken liver, chicken kidney, fish, pine-net kernel and peanut

Weigh 20 g (accurate to 0.01g) (5 g for pine-net kernel and peanut) of test sample into a 250 mL stoppered Erlenmeyer flask. Add 20 mL water and 100 mL acetone, and homogenize for 3 min. Filter the supernatant into a 250 mL concentrate bottle. Extract the residue with 50 mL of acetone once more and filter the second supernatant. Combine the filtrates. Condensed to about 20 mL by a rotary evaporator in 40 ℃ water bath.

Tranfer the extract into one 250 mL seperatory funnel. Add 100 mL sodium chloride aqueous solution and 100 mL dichloromethane. Shake 3 min. Stand still waiting for layering. Collect dichloromethane phase. Extract aqueous phase twice with 2×50 mL dichloromethane. Combine dichloromethane phases. Dehydrate with an anhydrous sodium sulfate tube. Collect eluates into one 250 mL concentrate bottle. Condensed to nearly dry by a rotary evaporator in 40 ℃ water bath. Add 10 mL of ethyl acetate-*n*-Hexane (1+1) to dissolve the residue, filter the solution with 0.45 μm membrane and then wait for cleaning-up.

6.2 Cleaning-up

6.2.1 GPC Cleaning-up

6.2.1.1 GPC operating condition

a) GPC column:700 mm×25 mm(i.d.), Bio Beads S-X3 or equivalent;

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

c) Flow rate:4.7 mL/min;

d) Injection volume at sample loop:10mL;

e) Time of pre-rinsing:10 min;

f) GPC balance time:5 min;

g) Time of collecting the eluates:22 min～31 min.

6.2.1.2 GPC cleaning-up procedure

Purify 10 mL of the solution which is waiting for cleaning-up (6.1.3) according to the condition described in the section 6.2.1.1. Condense the collected constituents to nearly dry at 40 ℃. Dissolve the residue with 3 mL of ethyl acetate-*n*-hexane (1+1) and wait for next SPE cleaning-up(pine-nut kernel and walnut kernel should repeat GPC cleaning-up step described in the section 6.2.1.1).

6.2.2 SPE Cleaning-up

Couple the active carbon SPE tube and florisil SPE tube up to down (for samples containing much colorants,such as spinach,tea etc.,add 1.5 cm high graphic carbon SPE tube (3.16) in the active carbon tube). Rinse the coupling columns with 6 mL of *n*-hexane-ethyl acetate (1+1) in advance. Discard the washings. Transfer 2 mL of the sample solution from 6.1.1、6.1.2 and 6.1.3 into the upper column. Elute with 3 mL of *n*-hexane-ethyl acetate (1+1). Collect eluates into a concentrate bottle. Evaporate to nearly dry in 40 ℃ water bath. Dissolve the residue and dilute exactly to 1.0 mL with ethyl acetate for determination by GC or confirmation by the GC-MS.

6.3 Determination

6.3.1 GC conditions

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

b) Column temperature:50 ℃ (1 min) $\xrightarrow{30\ ℃/min}$ 180 ℃ (1 min) $\xrightarrow{10\ ℃/min}$ 250 ℃ (10 min);

c) Injection port temperature:250 ℃;

d) Interface temperature:250 ℃;

e) Carrier gas: Nitrogen, purity≥99.999%, flow rate 1.0 mL/min;

f) Injection volume: 1 μL;

g) Injection mode: splitless.

6.3.2 GC-MS operating conditions

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

b) Column temperature: 50 ℃ (2 min) $\xrightarrow{20\ ℃/min}$ 200 ℃ (1 min) $\xrightarrow{5\ ℃/min}$ 270 ℃ (18 min);

c) Injection port temperature: 280 ℃;

d) Interface temperature: 280 ℃;

e) Carrier gas: Helium, purity≥99.999%, flow rate 1.0 mL/min;

f) Injection volume: 1 μL;

g) Injection mode: splitless. Open the valve after 1.2 min;

h) Electron ionization mode: EI;

i) Ionization energy: 70 eV;

j) Determination mode: SIM;

k) Selected monitoring ions (m/z): quantiation ion is 197 and confirmation ions are 258, 286, 314;

l) Solvent delay: 9.0 min.

6.3.3 GC determination

According to the approximate content of Chlorpyrifos, select one standard working solution which has a similar concentration of the sample solution. The responses of Chlorpyrifos in the standard working solution and in the sample solution should be within the linear range of the instrumental detection. Qualification is undergone by retention time; quantitation is undergone by the comparison peak areas between sample and standard work solution. Under the above-described condition, the chromatograph of Chlorpyrifos standard is shown in Annex A, Figure A.

6.3.4 GC-MS determination and confirmation

The standard working solution and the sample solution are tested according to the condition described in section 6.3.1. If there is any peak of the sample solution appeared at the same retention time as the peak of the standard solution does, a confirmation will be followed. The retention time: 12.64 min. The accordance between the retention time of the measured sample solution and the time of the standard, the appearance of all selected ions in the chromatogram of the sample after background is deducted, the consistency between the abundance ratio of the selected ions from the sample and the ratio of ions from standard, and the similarity subject to the allowance (see table 1), can deliver the positive judgment of Chlorpyrifos detection. The chromatogram and mass spectrum of the Chlorpyrifos standard are shown in the figure B.1 in annex B, and Annex C.

Table 1—The maximum allowance of relative ionic abundance for the qualification and quantitation

Relative ionic abundance/%	>50	>20～50	>10～20	≤10
Allowed relative deviation/%	±20	±25	±30	±50

6.4 Blank test

Undergo according to the above procedures excluding the sample.

6.5 Calculation and expression of the result

Calculate the content of Chlorpyrifos residue in the test sample by GC-MS data processor or according to the followed formula.

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

where

X—the residue content of Chlorpyrifos in the test sample. Unit is milligram per kilogram, mg/kg.

A—the peak height of Chlorpyrifos in the sample solution.

A_s—the peak height of Chlorpyrifos in the standard working solution.

c—the concentration of Chlorpyrifos in the standard working solution. Unit is microgram per milliliter, μg/mL.

V—the final volume of the sample solution. Unit is milliliter, mL.

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

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

7 Detection limit and recovery

7.1 Limit of determination and confirmation

The method detection and confirmation limit is shown in Table 2.

7.2 Range of fortification and recovery

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

sample	Fortified content/ (mg/kg)	Recovery range/ %	Limit of determination and confirmation/(mg/kg)
corn	0.010	92.4～96.0	0.01
	0.020	88.0～92.0	0.01
	0.200	92.4～93.5	0.01
brown-rice	0.010	99.1～102.4	0.01
	0.020	92.5～94.6	0.01
	0.200	81.8～87.2	0.01
Scallion	0.010	88.6～90.8	0.01
	0.020	89.5～93.0	0.01
	0.200	93.3～98.1	0.01
Spinach	0.010	90.0～94.2	0.01
	0.020	89.6～91.0	0.01
	0.200	99.3～102.0	0.01
Orange	0.010	97.5～99.6	0.01
	0.020	97.5～102.5	0.01
	0.200	89.9～92.3	0.01
Apple	0.010	100.5～106.2	0.01
	0.020	84.8～87.0	0.01
	0.200	96.3～99.3	0.01
chili	0.010	96.2～98.6	0.01
	0.020	92.5～98.0	0.01
	0.200	94.8～96.2	0.01
honey	0.010	82.0～90.2	0.01
	0.020	81.2～83.6	0.01
	0.200	80.7～89.5	0.01

Table 2（continue）

sample	Fortified content/（mg/kg）	Recovery range/%	Limit of determination and confirmation/（mg/kg）
Tea	0.020	80.0～83.1	0.02
	0.050	101.6～104.0	0.02
	0.200	93.2～98.6	0.02
earth kernel	0.020	80.1～84.5	0.02
	0.050	93.0～96.0	0.02
	0.200	93.4～93.8	0.02
Pine-nut kernel	0.020	101.6～105.1	0.02
	0.050	98.0～100.5	0.02
	0.200	84.2～86.1	0.02
pork	0.005	88.1～90.3	0.005
	0.020	89.3～90.8	0.005
	0.200	80.2～80.6	0.005
chicken liver	0.005	102.2～104.1	0.005
	0.020	93.0～97.0	0.005
	0.200	80.9～81.8	0.005
chicken kidney	0.005	100.1～106.2	0.005
	0.020	89.5～93.0	0.005
	0.200	94.0～96.2	0.005
Fish	0.005	94.1～98.3	0.005
	0.020	92.5～97.5	0.005
	0.200	80.4～84.5	0.005

Annex A
(informative)
Gas chromatogram of the Chlorpyrifos standard

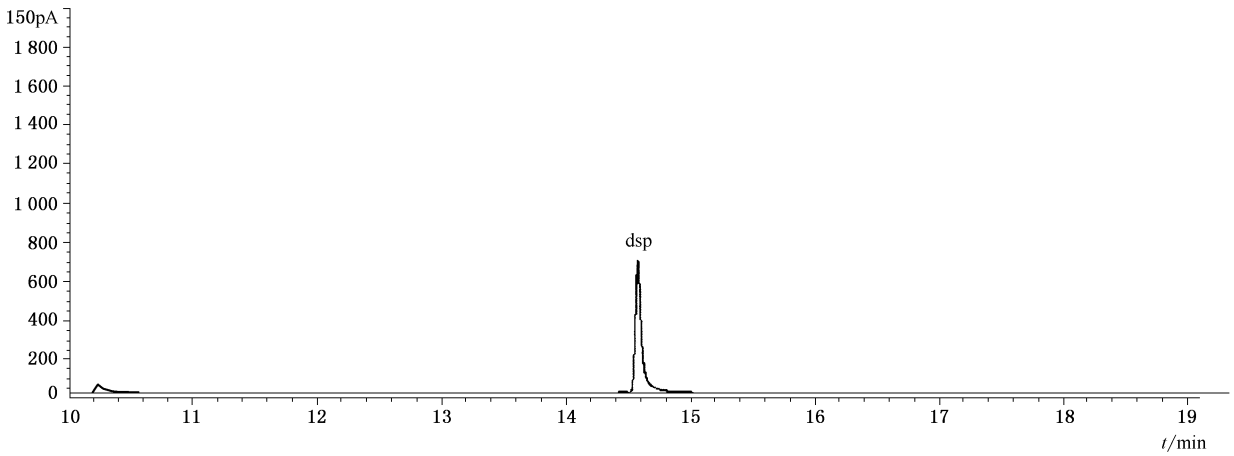

Figure A. 1—Gas chromatogram of the Chlorpyrifos standard at 1.0 μg/mL

Annex B
(informative)
GC-MS selected ion chromatogram of the Chlorpyrifos standard

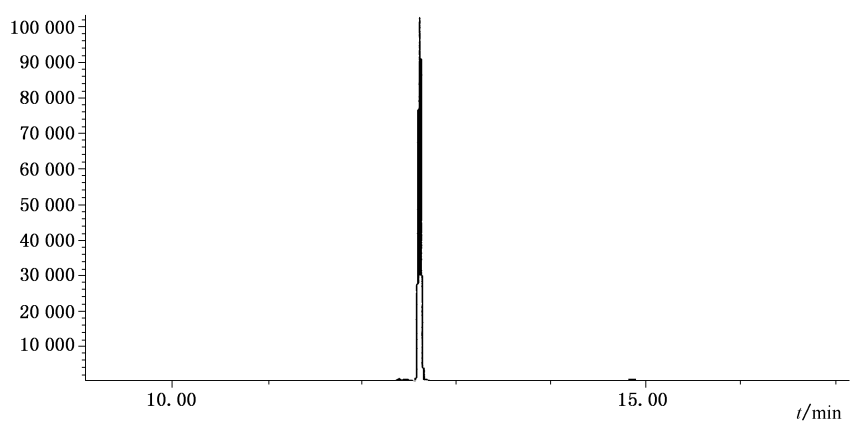

Figure B. 1—**GC-MS selected ion chromatogram of the Chlorpyrifos standard**(1.0 μg/mL)

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Annex C
（informative）
GC-MS spectrum of Chlorpyrifos standard

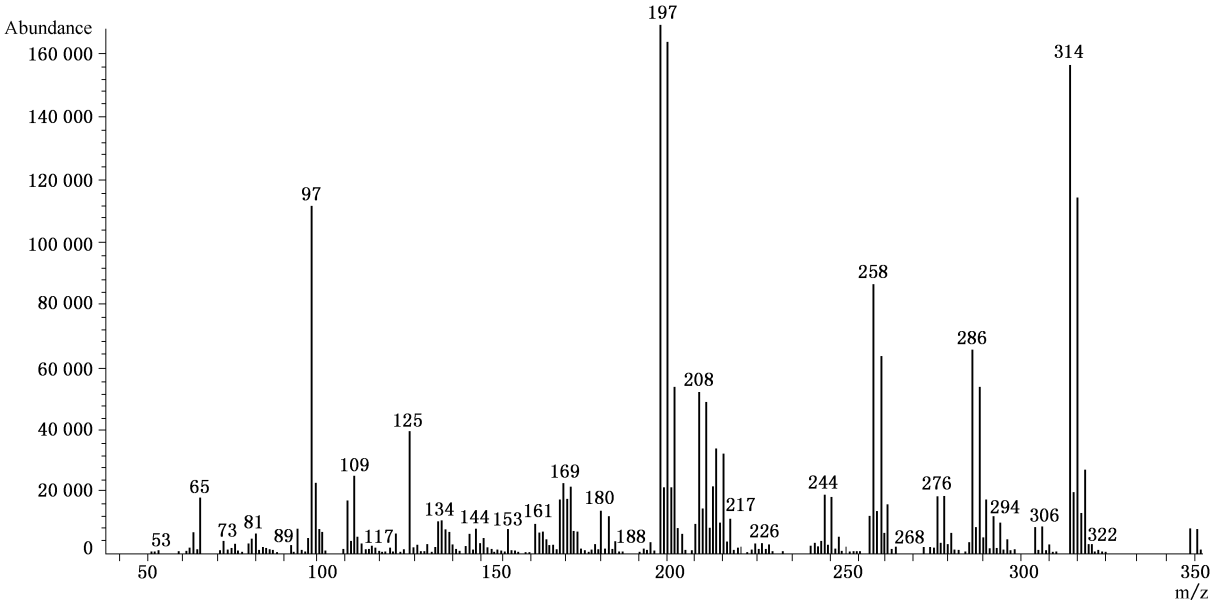

Figure C. 1—**GC-MS spectrum of Chlorpyrifos standard**