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中华人民共和国出入境检验检疫行业标准

SN/T 2324—2009

进出口食品中抑草磷、毒死蜱、甲基毒死蜱等 33 种有机磷农药残留量的检测方法

Determination of 33 organophosphorous pesticides residues
(butamifos, chlorpyrifos, chlorpyrifos-methyl et al)
in foodstuffs for import and export

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前 言

本标准的附录 A 为规范性附录,附录 B、附录 C、附录 D 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:中华人民共和国江西出入境检验检疫局、中华人民共和国山西出入境检验检疫局、中华人民共和国厦门出入境检验检疫局。

本标准主要起草人:温志海、占春瑞、薛平、左海根、郭平、张志刚。

本标准系首次发布的出入境检验检疫行业标准。

进出口食品中抑草磷、毒死蜱、甲基毒死蜱等 33种有机磷农药残留量的检测方法

1 范围

本标准规定了粮谷类食品中33种有机磷农药残留量[抑草磷、毒死蜱、甲基毒死蜱、敌敌畏、敌瘟磷、杀螟硫磷、倍硫磷、地虫硫磷、异柳磷、氧异柳磷、甲基立枯磷、三唑磷、毒虫畏(E)、毒虫畏(Z)、丙线磷、特丁磷、二嗪磷、甲基毒虫畏(E)、甲基毒虫畏(Z)、苯硫磷、乙嘧啶磷、丰索磷、马拉硫磷、治螟磷、对硫磷、甲基对硫磷、稻丰散、甲基嘧啶磷、啶硫磷、杀虫畏、甲基乙拌磷、完灭硫磷、完灭硫磷砒]的气相色谱检测方法及气相色谱-质谱确证方法。

本标准适用于进出口大米、糙米、玉米、大麦、小麦中33种有机磷农药残留量的测定和确证。

2 方法提要

试样中农药残留经水-丙酮涡旋提取,经二氯甲烷液-液分配,二氯甲烷层浓缩并溶解定容,经凝胶色谱柱去除油脂,玉米样品再经石墨化碳黑固相萃取柱去除色素后,供气相色谱测定及气相色谱-质谱确证。

3 试剂和材料

除非另有规定,均使用分析纯试剂,水为超纯水。

- 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 氯化钠溶液:15%(质量浓度),将15g氯化钠溶于水中,并稀释到100 mL。
- 3.6 无水硫酸钠:取无水硫酸钠于650℃灼烧4 h,贮于密封容器中备用。
- 3.7 石墨化碳黑固相萃取柱:0.25 g,ENVI-Carb,或相当者。
- 3.8 33种有机磷农药标准品:见附录A。
- 3.9 标准储备液的配制:准确称取适量的每种农药标准品(精确至0.1 mg),用丙酮分别配制成浓度为100 $\mu\text{g}/\text{mL}$ ~1 000 $\mu\text{g}/\text{mL}$ 的标准储备溶液,5℃以下避光保存。
- 3.10 混合标准工作溶液:根据需要用丙酮稀释成适合浓度的系列混合标准工作溶液。
- 3.11 有机相滤膜:0.2 μm 。

4 仪器和设备

- 4.1 气相色谱仪:配有火焰光度检测器(FPD)。
- 4.2 气相色谱-质谱仪:配有质量选择检测器(MSD)。
- 4.3 离心机。
- 4.4 涡旋振荡器。
- 4.5 旋转蒸发器。
- 4.6 吹氮浓缩装置。
- 4.7 浓缩瓶:150 mL。

4.8 粉碎机。

4.9 筛子:2 mm。

5 试样制备与保存

5.1 试样制备

将样品按四分法缩分至1 kg,用粉碎机全部粉碎并通过2 mm圆孔筛。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。

5.2 试样保存

将试样于0℃~4℃密闭保存。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

称取试样约5 g(精确至0.01 g)于50 mL离心管中,加5 mL水混匀后放置30 min,然后加入15 mL丙酮,在涡旋振荡器上涡旋5 min。以4 000 r/min离心5 min,将上清液转移至浓缩瓶中。残渣中再加入15 mL丙酮重复提取一次,合并上清液后,于40℃水浴中旋转浓缩至约5 mL,待净化。

6.2 净化

6.2.1 液-液分配净化

将提取浓缩液倒入50 mL离心管中,并用2×5 mL二氯甲烷分二次洗涤浓缩瓶后合并到50 mL离心管中,加入10 mL氯化钠溶液(3.5)和10 mL二氯甲烷,在涡旋振荡器上振摇5 min,以4 000 r/min离心5 min,收集二氯甲烷层,经无水硫酸钠柱脱水后,收集于150 mL浓缩瓶中。水相再用2×10 mL二氯甲烷重复提取两次,合并二氯甲烷相。于40℃水浴中旋转浓缩至近干,加入10 mL环己烷-乙酸乙酯(1+1体积比)涡旋溶解残渣。

6.2.2 凝胶色谱(GPC)净化

6.2.2.1 凝胶色谱条件

- a) 净化柱:700 mm×25 mm,Bio Beads S-X3,或相当者;
- b) 流动相:环己烷-乙酸乙酯(1+1体积比);
- c) 流速:5.0 mL/min;
- d) 进样量:5.0 mL;
- e) 预淋洗时间:0 min~20 min;
- f) 收集时间:20 min~40 min。

6.2.2.2 凝胶色谱净化步骤

将5 mL待净化液按6.2.2.1规定的条件进行净化,合并馏分收集器中的收集液于150 mL浓缩瓶中,于40℃水浴中旋转浓缩至近干。对于大米、糙米、小麦、大麦样品,加入1 mL丙酮以溶解残渣,过0.2 μm滤膜后供气相色谱测定和气相色谱-质谱确证。对于玉米样品,加入2 mL乙酸乙酯溶解残渣,待净化。

6.2.3 固相萃取(SPE)净化

用6 mL乙酸乙酯预淋洗石墨化碳黑固相萃取柱(3.7),将上述的样液倾入柱中,用2 mL乙酸乙酯洗涤活性炭柱,然后用6 mL乙酸乙酯进行洗脱。收集全部洗脱液于15 mL刻度管中,于40℃水浴中氮吹至干,用丙酮溶解并定容至1 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:30 m×0.53 mm(内径),膜厚1.0 μm,DB-1701石英毛细管柱,或相当者;

- b) 色谱柱温度:50℃(1 min) $\xrightarrow{30\text{℃/min}}$ 170℃ $\xrightarrow{1.2\text{℃/min}}$ 210℃ $\xrightarrow{30\text{℃/min}}$ 260℃(20 min);
- c) 进样口温度:230℃;
- d) 进样方式:不分流进样;
- e) 进样量:2 μL;
- f) 载气:氮气,纯度≥99.999%,流速5.0 mL/min;
- g) FPD检测器:温度250℃;气体流量:氢气:75 mL/min;空气:100 mL/min;尾吹气:氮气60 mL/min。

6.3.2 气相色谱-质谱条件

- a) 色谱柱:30 m×0.25 mm(内径),膜厚0.25 μm,HP-5MS石英毛细管柱,或相当者;
- b) 色谱柱温度:50℃(1 min) $\xrightarrow{30\text{℃/min}}$ 170℃(25 min) $\xrightarrow{30\text{℃/min}}$ 280℃(10 min);
- c) 进样口温度:250℃;
- d) 色谱-质谱接口温度:280℃;
- 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:不分流进样,1.5 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):参见附录B;
- l) 溶剂延迟:5 min。

6.3.3 定量测定与确证

根据样液中被测物含量情况,选定浓度相近的标准工作溶液,标准工作溶液和待测样液中每种有机磷农药的响应值均应在仪器检测的线性范围内。

如果样液与标准工作溶液的选择离子色谱图中,在相同保留时间有色谱峰出现,则根据附录B中每种有机磷农药选择离子的种类及其丰度比确证,波动范围符合表1最大允许偏差之内。在上述气相色谱-质谱条件下,33种有机磷农药标准物的参考保留时间和气相色谱-质谱选择离子色谱图参见附录B、附录C和附录D。

表1 质谱相对离子丰度最大容许偏差

相对丰度(基峰)/%	EI-GC-MS(相对)/%
>50	±10
>20~50	±15
>10~20	±20
≤10	±50

6.4 空白试验

除不加试样外,均按上述操作步骤进行。

7 结果计算和表述

试样中每种有机磷农药残留量按式(1)计算:

$$X_i = \frac{A_i \times c_i \times V}{A_{is} \times m} \dots\dots\dots (1)$$

式中:

X_i ——试样中每种有机磷农药残留量,单位为毫克每千克(mg/kg);

- A_i ——样液中每种有机磷农药的峰面积(或峰高);
 A_{is} ——标准工作液中每种有机磷农药的峰面积(或峰高);
 c_i ——标准工作液中每种有机磷农药的浓度,单位为毫克每升(mg/L);
 V ——样液最终定容体积,单位为毫升(mL);
 m ——最终样液代表的试样质量,单位为克(g)。

8 测定低限、回收率

8.1 测定低限

本方法丙线磷、三唑磷、对硫磷在大米、糙米、玉米、大麦、小麦中的测定低限为 0.005 mg/kg,其余 30 种有机磷农药在大米、糙米、玉米、大麦、小麦中的测定低限均为 0.01 mg/kg。

8.2 回收率

33 种有机磷农药在大米、玉米、糙米、大麦、小麦中的添加回收率数据见表 2。

表 2 33 种有机磷农药在五种样品中的添加回收率范围(GC-FPD)

序号	农药名	添加/ (mg/kg)	添加回收率/%				
			大米	玉米	糙米	大麦	小麦
1	敌敌畏	0.01	76.4~80.3	73.0~84.3	71.1~86.3	79.6~89.9	78.4~85.8
		0.02	73.5~87.7	72.1~89.7	73.2~81.9	75.8~89.5	78.8~95.1
		0.04	75.3~86.2	74.0~83.5	73.1~89.4	71.5~87.4	75.2~97.6
		0.10	75.8~88.3	70.8~90.6	70.4~84.3	76.1~87.4	70.4~95.7
2	丙线磷	0.01	72.9~86.4	78.4~83.3	74.9~87.4	74.9~84.4	73.5~82.1
		0.02	75.4~89.1	78.1~91.2	72.1~94.2	73.2~82.1	73.1~97.5
		0.04	85.5~91.2	90.1~97.1	83.1~90.2	80.3~90.1	85.2~95.4
		0.10	81.2~92.7	87.6~93.6	81.2~103.4	87.6~100.7	82.5~93.1
3	特丁磷	0.01	80.0~95.3	79.3~89.5	74.7~82.3	75.8~94.4	68.4~96.8
		0.02	70.3~85.6	72.9~92.4	74.6~87.5	78.3~92.0	72.2~96.4
		0.04	74.8~82.0	72.5~93.6	75.4~89.8	79.4~91.3	75.5~94.1
		0.10	74.3~84.1	78.1~91.6	76.7~89.6	83.2~102.5	74.5~96.0
4	地虫硫磷	0.01	72.4~80.6	68.4~88.5	64.4~87.6	69.0~84.3	72.6~89.2
		0.02	75.2~96.8	79.1~95.4	76.2~89.7	76.1~90.8	73.5~95.1
		0.04	73.1~90.1	72.5~92.7	69.8~93.2	78.2~94.5	78.1~91.4
		0.10	77.9~95.6	79.5~93.7	74.4~92.9	86.9~96.5	83.1~89.5
5	甲基毒死蜱	0.01	70.6~89.1	73.5~87.9	73.4~84.4	68.7~83.8	70.9~90.4
		0.02	72.8~91.3	77.6~98.2	68.6~85.4	78.5~94.2	79.1~95.6
		0.04	84.3~90.3	83.4~93.1	73.2~81.3	81.5~93.0	76.5~94.7
		0.10	85.4~88.0	85.4~101.2	73.7~79.1	80.1~97.5	80.4~101.8
6	甲基立枯磷	0.01	75.0~93.6	77.7~95.1	70.0~92.6	79.9~87.7	70.4~82.3
		0.02	77.1~90.3	79.1~91.3	75.3~89.9	64.3~87.9	76.5~91.7
		0.04	77.3~84.3	72.1~92.1	80.2~89.3	69.9~86.5	85.2~96.3
		0.10	75.3~86.2	76.7~93.1	78.0~89.6	65.9~97.7	88.6~97.4

表 2 (续)

序号	农药名	添加/ (mg/kg)	添加回收率/%				
			大米	玉米	糙米	大麦	小麦
7	杀螟硫磷	0.01	74.5~89.5	76.6~89.5	79.9~89.2	74.9~83.7	76.0~90.3
		0.02	78.2~96.5	76.2~91.4	68.5~91.7	70.3~89.4	74.2~92.2
		0.04	77.6~85.4	74.3~90.6	70.5~93.6	77.6~84.9	83.0~100.9
		0.10	78.9~91.9	70.6~94.5	75.9~99.9	67.9~93.6	89.0~99.8
8	倍硫磷	0.01	67.7~99.3	63.0~90.7	67.7~93.1	65.0~90.9	69.7~89.8
		0.02	79.3~85.7	77.1~95.2	77.2~93.4	75.4~89.5	75.4~92.9
		0.04	75.4~80.7	73.6~90.4	76.8~93.8	70.3~79.5	79.9~93.9
		0.10	76.5~97.9	81.0~98.7	80.8~100.7	74.4~94.9	83.7~104.1
9	毒死蜱	0.01	78.4~89.5	80.2~90.4	78.4~92.8	77.7~96.1	75.9~89.7
		0.02	80.3~94.5	80.8~96.7	79.1~93.5	76.3~93.4	87.9~95.2
		0.04	79.1~90.2	78.5~94.3	77.5~81.8	77.3~85.3	85.4~96.2
		0.10	84.9~96.8	87.2~103.1	80.6~102.9	73.3~102.5	74.8~90.7
10	氧异柳磷	0.01	83.5~90.1	80.4~95.1	80.5~94.1	78.4~89.8	78.9~93.7
		0.02	87.4~96.8	87.1~98.2	85.6~93.7	86.3~99.8	89.7~95.4
		0.04	85.4~94.3	79.0~99.2	84.3~91.5	82.6~92.6	81.3~97.3
		0.10	84.0~95.9	79.4~98.3	82.1~93.5	86.4~97.8	84.9~96.2
11	毒虫畏(E)	0.01	78.4~83.8	73.2~80.0	73.4~89.8	72.5~90.1	79.1~92.2
		0.02	76.1~101.3	68.5~98.1	75.6~96.1	73.2~95.6	76.4~95.3
		0.04	77.8~95.4	74.8~100.1	76.8~97.8	75.8~96.5	73.4~99.7
		0.10	79.2~89.7	78.4~97.9	83.2~103.8	80.8~99.9	79.8~107.9
12	毒虫畏(Z)	0.01	73.6~92.9	75.9~94.3	73.6~95.9	72.4~101.8	81.8~96.8
		0.02	82.1~94.5	80.1~91.4	84.6~99.6	84.1~92.9	75.4~88.5
		0.04	83.5~90.2	79.5~90.3	80.1~94.1	85.0~94.2	80.1~99.3
		0.10	85.0~98.2	85.9~101.3	79.2~102.3	77.4~98.0	86.5~92.4
13	异柳磷	0.01	77.9~84.4	79.1~90.0	69.9~94.4	73.6~89.9	69.4~98.9
		0.02	77.5~89.2	63.2~95.9	70.7~91.2	71.3~90.4	69.5~95.2
		0.04	72.5~84.3	72.9~97.4	75.8~89.6	71.8~94.6	73.8~95.2
		0.10	83.9~92.4	81.2~90.5	89.6~98.3	84.6~97.9	69.8~90.4
14	抑草磷	0.01	85.8~94.4	71.6~86.9	83.2~96.5	80.9~94.4	73.0~89.2
		0.02	87.3~96.5	85.1~108.3	87.5~92.3	74.7~86.5	79.4~96.8
		0.04	80.4~90.3	84.2~100.5	79.5~96.7	70.4~80.2	77.1~99.3
		0.1	84.1~93.2	79.2~96.9	75.4~99.1	79.2~99.5	75.7~90.4
15	三唑磷	0.01	79.0~87.3	69.6~90.2	77.3~92.3	75.9~84.4	70.2~93.7
		0.02	85.4~102.8	83.1~94.3	87.2~99.4	88.7~99.1	79.2~90.5

表 2 (续)

序号	农药名	添加/ (mg/kg)	添加回收率/%				
			大米	玉米	糙米	大麦	小麦
15	三唑磷	0.04	84.1~95.1	80.2~95.2	80.3~89.9	85.3~96.0	80.4~93.2
		0.10	86.5~96.1	89.6~98.2	84.0~102.3	85.8~102.4	79.2~95.7
16	敌瘟磷	0.01	68.7~77.8	60.1~78.9	65.6~77.2	66.0~90.3	76.0~80.3
		0.02	68.1~85.4	75.9~95.3	70.1~80.6	68.4~94.6	78.1~90.8
		0.04	73.4~80.5	78.7~96.4	73.1~85.1	70.2~90.4	79.1~98.2
		0.10	74.7~89.9	77.2~93.5	83.4~95.1	80.9~98.3	80.0~94.9
17	治螟磷	0.01	77.2~90.7	74.5~78.3	60.9~78.7	68.7~87.2	76.0~86.9
		0.02	71.3~81.5	75.3~95.2	70.8~83.4	74.1~88.5	72.2~97.9
		0.04	73.5~87.8	75.4~96.4	76.9~80.2	75.2~84.1	80.4~99.2
		0.10	83.4~95.1	75.3~92.6	82.9~96.1	88.6~101.9	82.7~95.5
18	甲基乙拌磷	0.01	71.1~93.4	70.1~89.6	64.9~83.2	65.9~73.7	75.5~84.9
		0.02	70.9~87.2	73.3~99.5	67.4~89.9	74.1~92.6	80.3~91.7
		0.04	73.4~85.6	72.7~98.0	73.4~85.2	70.2~93.6	78.4~97.6
		0.10	80.6~93.7	78.4~94.7	72.5~95.7	77.1~96.2	80.9~96.1
19	二嗪磷	0.01	71.3~93.6	76.3~88.4	77.1~95.2	69.9~93.2	83.9~96.9
		0.02	79.0~96.2	74.4~97.6	79.9~89.0	83.1~95.2	78.9~107.9
		0.04	74.2~87.5	70.3~99.4	72.1~80.4	79.4~84.2	78.9~94.9
		0.10	84.1~104.2	71.9~100.2	78.6~99.6	81.2~99.4	77.9~95.5
20	乙嘧硫磷	0.01	67.0~79.3	75.4~83.2	71.8~87.8	73.0~84.3	71.6~90.6
		0.02	76.6~91.8	77.0~97.3	84.1~91.4	72.4~89.2	73.8~97.8
		0.04	80.3~84.2	84.1~99.3	83.5~92.4	76.2~83.2	75.9~97.6
		0.10	88.8~103.9	80.6~102.6	78.4~102.2	69.8~88.0	85.8~96.8
21	甲基对硫磷	0.01	62.0~78.9	62.3~70.3	72.0~98.3	73.4~93.3	69.4~98.9
		0.02	80.3~96.8	83.4~92.9	72.8~92.5	80.4~98.9	76.8~98.0
		0.04	83.1~89.3	79.4~99.3	75.9~89.5	82.3~96.2	72.1~95.7
		0.10	90.0~101.5	72.3~96.3	88.3~104.3	89.4~100.3	81.4~103.3
22	甲基嘧啶磷	0.01	73.0~80.2	75.5~85.1	69.0~88.2	69.3~88.5	73.0~88.2
		0.02	81.4~103.9	72.3~95.5	80.0~92.3	70.5~89.1	79.6~89.9
		0.04	85.3~99.4	76.8~94.5	78.4~95.3	73.6~83.9	79.0~98.4
		0.10	90.0~105.2	79.8~101.1	80.3~98.2	89.0~104.2	85.3~99.5
23	甲基毒虫畏(E)	0.01	65.4~80.1	66.7~72.9	70.2~86.7	75.4~88.5	70.1~82.7
		0.02	78.3~88.7	82.1~95.1	74.2~95.1	79.3~92.1	85.2~97.4
		0.04	75.8~83.7	80.3~92.1	76.5~90.3	82.1~94.2	87.3~99.3
		0.10	89.2~102.3	84.4~97.3	89.0~94.2	80.8~98.7	90.6~102.1

表 2 (续)

序号	农药名	添加/ (mg/kg)	添加回收率/%				
			大米	玉米	糙米	大麦	小麦
24	马拉硫磷	0.01	71.5~89.5	71.7~82.0	77.3~86.0	73.8~84.9	76.8~83.9
		0.02	77.8~102.3	78.8~96.9	77.0~90.3	74.5~93.5	75.8~94.3
		0.04	85.1~99.4	80.4~98.0	78.2~86.4	77.3~91.5	78.0~97.2
		0.10	90.0~103.3	77.5~99.5	83.0~92.9	82.8~91.9	80.5~101.3
25	甲基毒虫畏(Z)	0.01	61.9~89.4	61.3~83.2	66.7~79.6	70.7~76.1	74.1~91.2
		0.02	83.2~106.3	82.1~99.5	77.1~99.2	89.4~101.5	87.7~95.6
		0.04	81.2~94.1	79.4~92.8	79.7~92.1	85.9~94.1	82.4~90.3
		0.10	93.7~101.6	80.3~92.2	75.8~97.1	82.3~88.7	78.3~90.1
26	对硫磷	0.01	68.0~89.2	69.3~80.1	70.5~84.9	81.6~93.5	71.8~84.8
		0.02	72.2~97.8	72.3~97.1	81.2~90.2	89.4~93.7	77.3~91.7
		0.04	71.0~90.3	75.1~98.2	78.3~95.4	84.2~89.7	79.4~94.2
		0.10	90.5~104.9	84.3~99.7	76.1~91.0	81.3~98.5	76.4~93.0
27	啶硫磷	0.01	70.6~79.9	60.8~72.1	72.9~86.9	73.0~90.7	69.8~78.0
		0.02	78.6~101.4	67.5~94.2	72.3~89.8	79.8~94.2	71.5~94.3
		0.04	75.3~95.4	70.4~96.1	76.3~90.7	76.8~95.8	75.3~97.6
		0.10	94.0~108.9	90.5~102.1	71.9~90.9	72.1~95.7	84.8~99.0
28	稻丰散	0.01	61.2~75.3	68.4~78.1	75.4~81.6	74.2~80.5	69.3~73.2
		0.02	78.3~101.5	72.1~95.3	76.2~92.5	87.3~99.1	70.3~95.7
		0.04	82.1~92.4	80.6~99.4	85.6~89.9	90.7~97.7	75.2~101.8
		0.10	92.2~105.6	87.2~96.2	80.1~94.9	83.0~90.6	89.6~95.0
29	完灭硫磷 (完灭硫磷砒)	0.01	58.8~76.9	70.3~83.4	66.4~70.7	74.4~82.3	70.2~81.7
		0.02	76.7~97.9	75.7~97.2	72.3~78.9	77.3~92.7	73.3~99.8
		0.04	80.3~93.8	74.3~99.5	78.9~84.2	79.6~95.2	76.4~98.8
		0.10	82.6~101.7	85.6~99.1	82.9~97.3	71.5~100.8	75.5~94.9
30	杀虫畏	0.01	69.7~96.5	67.2~84.8	71.7~86.5	73.4~90.0	66.0~78.3
		0.02	82.3~91.9	72.3~95.2	78.9~89.9	75.9~93.8	72.6~94.8
		0.04	80.4~93.9	80.2~94.7	77.3~80.5	79.0~95.7	79.4~98.4
		0.10	92.6~105.4	89.4~93.7	87.2~97.9	80.4~99.0	89.0~100.3
31	丰索磷	0.01	63.0~75.6	65.8~86.2	75.2~83.8	70.8~92.3	67.7~86.6
		0.02	71.2~99.7	70.2~91.4	82.3~95.7	83.8~95.1	71.3~89.5
		0.04	74.5~90.4	75.4~98.8	80.3~89.4	85.1~90.6	80.6~92.1
		0.10	93.2~103.8	83.2~97.5	87.3~93.7	87.9~96.2	86.1~92.0
32	苯硫磷	0.01	83.6~107.1	85.2~100.3	79.0~87.2	75.1~85.6	71.0~92.5
		0.02	87.0~99.9	87.3~99.6	88.7~102.4	78.0~102.6	86.3~97.8
		0.04	89.4~98.5	80.4~96.3	85.1~94.4	80.4~96.6	80.6~90.6
		0.10	91.9~100.6	89.4~94.1	87.5~95.9	82.5~99.8	86.3~99.7

附 录 A
(规范性附录)

33 种有机磷农药的化学结构式等信息

表 A.1 33 种有机磷农药的化学结构式等信息

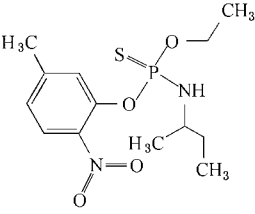
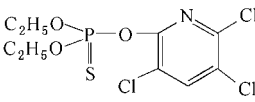
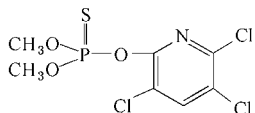
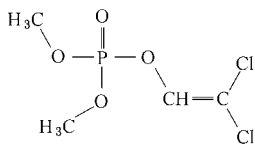
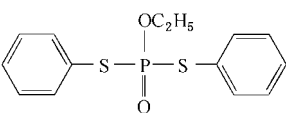
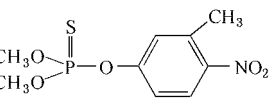
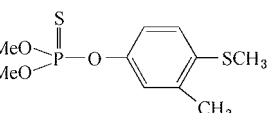
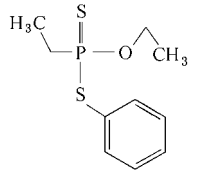
序号	英文名	中文名	结 构 式	分子式	CAS 号	相对分子质量
1	Butamifos	抑草磷		$C_{13}H_{21}N_2O_4PS$	36335-67-8	332.4
2	Chlorpyrifos	毒死蜱		$C_9H_{11}Cl_3NO_3PS$	2921-88-2	350.6
3	Chlorpyrifos-methyl	甲基毒死蜱		$C_7H_7Cl_3NO_3PS$	5598-13-0	322.5
4	Dichlorvos	敌敌畏		$C_4H_7Cl_2O_4P$	62-73-7	221.0
5	Edifenphos	敌瘟磷		$C_{14}H_{15}O_2PS_2$	17109-49-8	310.4
6	Fenitrothion	杀螟硫磷		$C_9H_{12}NO_5PS$	122-14-5	277.2
7	Fenthion	倍硫磷		$C_{10}H_{15}O_3PS_2$	55-38-9	278.3
8	Fonofos	地虫硫磷		$C_{10}H_{15}OPS_2$	944-22-9	246.3

表 A.1 (续)

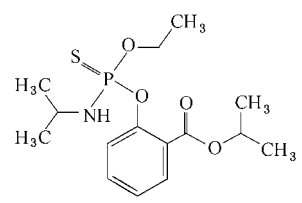
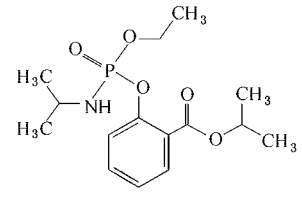
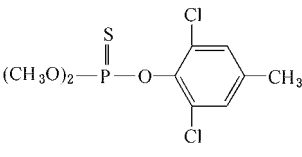
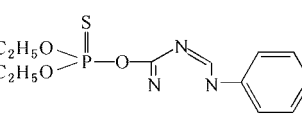
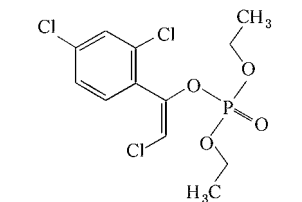
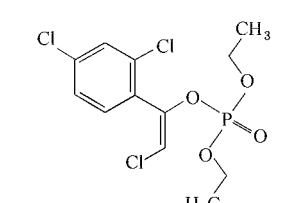
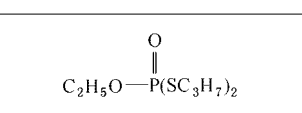
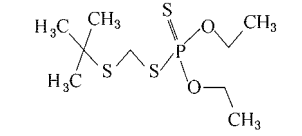
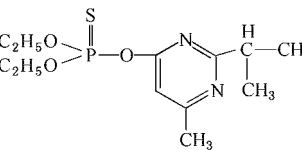
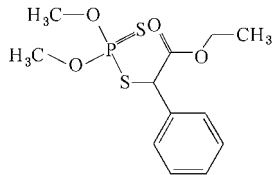
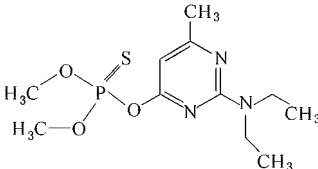
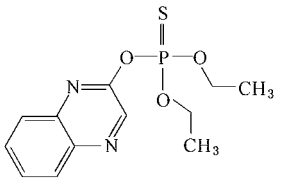
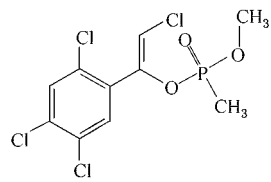
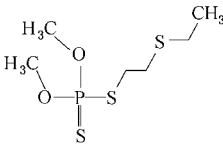
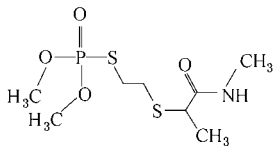
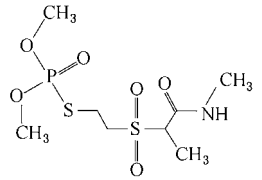
序号	英文名	中文名	结构式	分子式	CAS号	相对分子质量
9	Isofenphos	异柳磷		$C_{15}H_{24}NO_4PS$	25311-71-1	345.4
10	Isofenphos-oxon	氧异柳磷		$C_{15}H_{24}NO_5PS$	31120-85-1	329.3
11	Tolclofos-methyl	甲基立枯磷		$C_9H_{11}Cl_2O_3PS$	57018-04-9	301.1
12	Triazophos	三唑磷		$C_{12}H_{16}N_3O_3PS$	24017-47-8	313.3
13	Chlorfenvinphos(E)	毒虫畏(E)		$C_{12}H_{24}NO_4P$	18708-87-7	359.6
14	Chlorfenvinphos(Z)	毒虫畏(Z)		$C_{12}H_{24}NO_4P$	18708-87-7	359.6
15	Ethoprophos	丙线磷		$C_8H_{19}O_2PS_2$	13194-48-4	242.3
16	Terbufos	特丁磷		$C_9H_{21}O_2PS_3$	13071-79-9	288.4
17	Diazinon	二嗪磷		$C_{12}H_{21}N_2O_3PS$	333-41-5	304.4

表 A.1 (续)

序号	英文名	中文名	结构式	分子式	CAS号	相对分子质量
18	Dimethylvinphos (E)	甲基毒虫畏 (E)		$C_{10}H_{10}Cl_3O_4P$	71363-52-5	331.5
19	Dimethylvinphos(Z)	甲基毒虫畏 (Z)		$C_{10}H_{10}Cl_3O_4P$	71363-52-5	331.5
20	EPN	苯硫磷		$C_{14}H_{14}NO_4PS$	2104-64-5	323.3
21	Etrimfos	乙嘧啶磷		$C_{10}H_{17}N_2O_4PS$	38260-54-7	292.3
22	Fensulfothion	丰索磷		$C_{11}H_{17}O_4PS_2$	115-90-2	308.4
23	Malathion	马拉硫磷		$C_{10}H_{19}O_6PS_2$	121-75-5	330.4
24	Methacrifos	治螟磷		$C_8H_{20}O_5P_2S_2$	3689-24-5	322.3
25	Parathion	对硫磷		$C_{10}H_{14}NO_5PS$	56-38-2	291.3
26	Parathion-methyl	甲基对硫磷		$C_8H_{10}NO_5PS$	298-00-0	263.2

表 A.1 (续)

序号	英文名	中文名	结构式	分子式	CAS号	相对分子质量
27	Phenthoate	稻丰散		$C_{12}H_{17}O_4PS_2$	2597-03-7	320.3
28	Pirimiphos-methyl	甲基嘧啶磷		$C_{11}H_{20}N_3O_3PS$	29232-93-7	305.3
29	Quinalphos	喹硫磷		$C_{12}H_{15}N_2O_3PS$	13593-03-8	298.3
30	Tetrachlorvinphos	杀虫畏		$C_{10}H_9Cl_4O_4P$	22248-79-9	366.0
31	Thiometon	甲基乙拌磷		$C_6H_{15}O_2PS_3$	640-15-3	246.3
32	Vamidothion	完灭硫磷		$C_8H_{18}NO_4PS_2$	2275-23-2	287.4
33	Vamidothion-sulfone	完灭硫磷砒		$C_8H_{18}NO_6PS_2$	70898-34-9	319.3

附 录 B
(资料性附录)

33 种有机磷农药的保留时间、定量和定性选择离子

表 B.1 33 种有机磷农药的保留时间、定量和定性选择离子

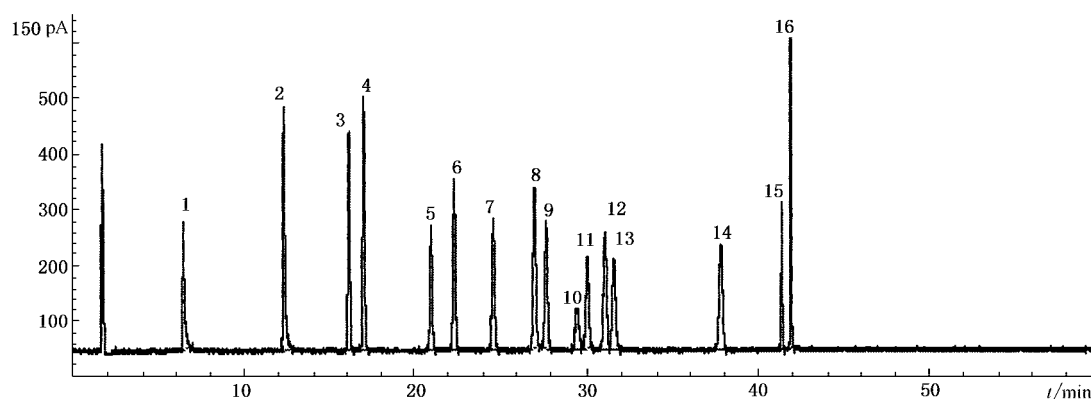
序号	农药名称	保留时间/min	特征碎片离子(amu)		
			定量	定性	丰度比
1	敌敌畏	5.62	185	109,187	29 : 100 : 10
2	丙线磷	9.59	242	158,200	23 : 100 : 39
3	特丁磷	13.03	231	186,203	100 : 15 : 8
4	地虫硫磷	13.20	246	109,137	50 : 100 : 50
5	甲基毒死蜱	17.46	286	288,125	100 : 70 : 50
6	甲基立枯磷	17.86	265	125,267	100 : 18 : 37
7	杀螟硫磷	20.48	277	247,260	100 : 42 : 56
8	倍硫磷	22.97	278	169,245	100 : 19 : 5
9	毒死蜱	23.27	314	197,258	84 : 100 : 44
10	氧异柳磷	24.78	229	201,314	100 : 68 : 11
11	毒虫畏(E)	28.53	323	267,269	63 : 100 : 64
12	毒虫畏(Z)	30.36	323	267,269	63 : 100 : 64
13	异柳磷	30.47	213	255,185	100 : 43 : 42
14	抑草磷	32.31	286	200,258	100 : 36 : 23
15	三唑磷	33.78	313	161,257	13 : 100 : 34
16	敌瘟磷	33.90	310	173,201	71 : 100 : 35
17	治螟磷	10.63	322	202,238	100 : 38 : 23
18	甲基乙拌磷	11.33	158	125,246	15 : 100 : 19
19	二嗪磷	13.92	304	276,248	100 : 47 : 42
20	乙嘧硫磷	14.99	292	181,277	100 : 71 : 32
21	甲基对硫磷	17.48	263	233,125	100 : 12 : 87
22	甲基嘧啶磷	21.08	290	276,305	100 : 81 : 74
23	甲基毒虫畏(E)	21.35	295	297,206	100 : 65 : 10
24	马拉硫磷	22.34	285	173,256	5 : 100 : 8
25	甲基毒虫畏(Z)	23.08	295	297,206	100 : 65 : 9
26	对硫磷	23.41	291	235,263	100 : 17 : 12
27	啶硫磷	30.46	146	298,157	100 : 25 : 66

表 B.1 (续)

序号	农药名称	保留时间/min	特征碎片离子(amu)		
			定量	定性	丰度比
28	稻丰散	30.64	274	246,320	100 : 27 : 5
29	完灭硫磷	31.72	145	109,169	100 : 56 : 20
30	完灭硫磷砒				
31	杀虫畏	31.92	328	330,332	80 : 100 : 46
32	丰索磷	33.38	236	308,293	12 : 36 : 100
33	苯硫磷	34.83	323	293,278	100 : 47 : 21

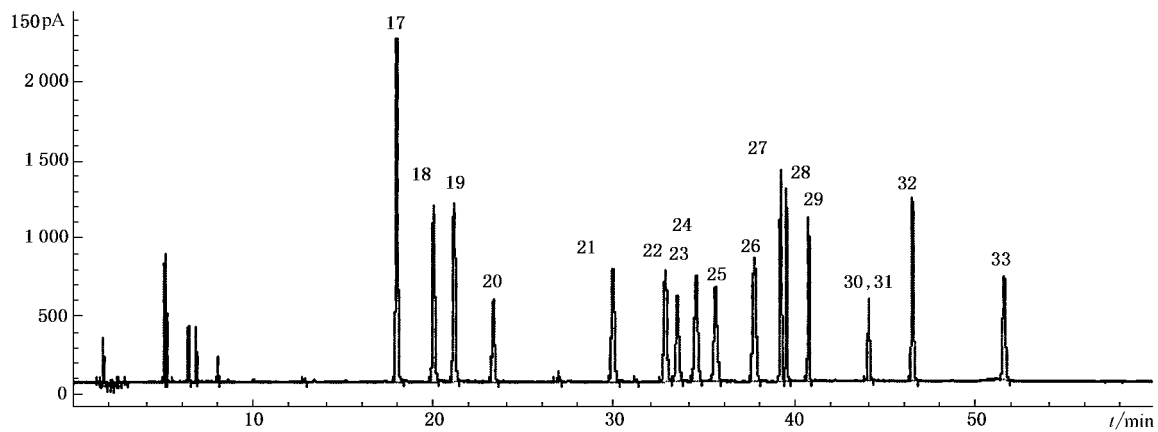
附录 C
(资料性附录)

33 种有机磷农药标准物气相色谱色谱图(GC-FPD)



- 1——敌敌畏；
- 2——丙线磷；
- 3——特丁磷；
- 4——地虫硫磷；
- 5——甲基毒死蜱；
- 6——甲基立枯磷；
- 7——毒死蜱；
- 8——倍硫磷；
- 9——杀螟硫磷；
- 10——氧异柳磷；
- 11——毒虫畏(E)；
- 12——异柳磷；
- 13——毒虫畏(Z)；
- 14——抑草磷；
- 15——敌瘟磷；
- 16——三唑磷。

图 C.1 33 种有机磷农药标准物的气相色谱图(组 1)

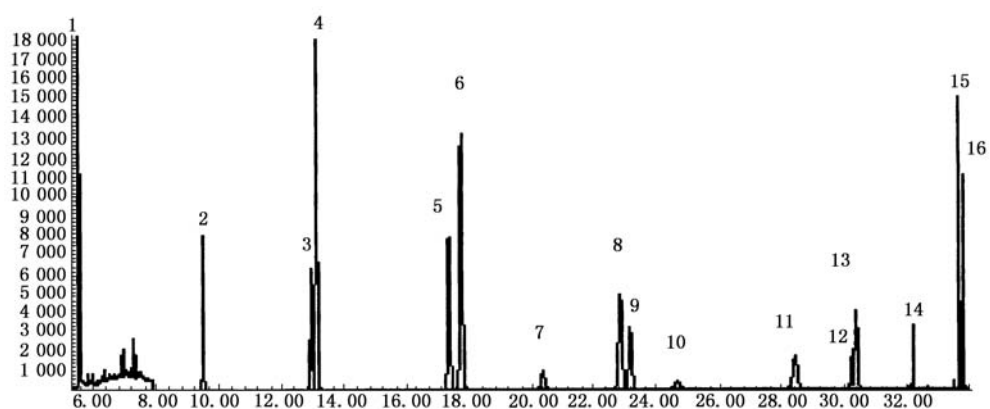


- 17——治螟磷；
- 18——甲基乙拌磷；
- 19——二嗪磷；
- 20——乙嘧啶磷；
- 21——甲基嘧啶磷；
- 22——甲基对硫磷；
- 23——甲基毒虫畏(E)；
- 24——马拉硫磷；
- 25——甲基毒虫畏(Z)；
- 26——对硫磷；
- 27——啶硫磷；
- 28——稻丰散；
- 29——杀虫畏；
- 30——完灭硫磷；
- 31——完灭硫磷砒；
- 32——丰索磷；
- 33——苯硫磷。

图 C.2 33 种有机磷农药标准物的气相色谱图(组 2)

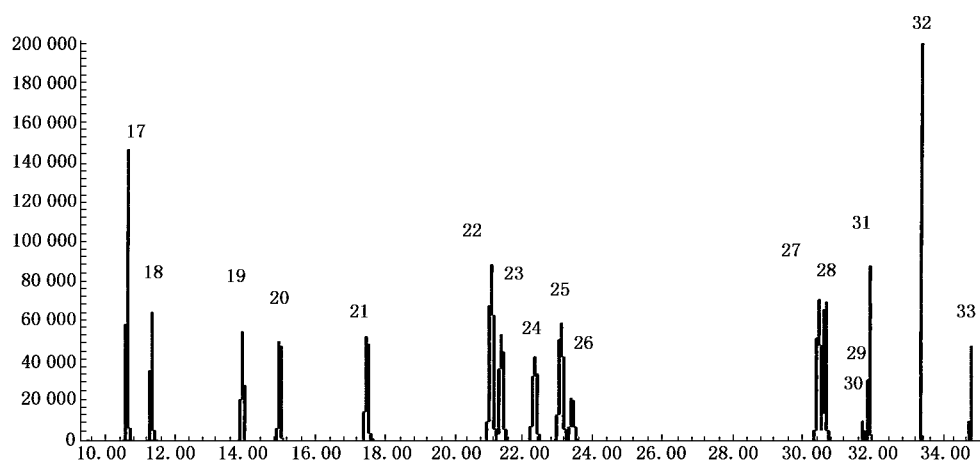
附录 D
(资料性附录)

33 种有机磷农药标准物气相色谱-质谱选择离子色谱图(GC-MS)



- 1——敌敌畏；
- 2——丙线磷；
- 3——特丁磷；
- 4——地虫硫磷；
- 5——甲基毒死蜱；
- 6——甲基立枯磷；
- 7——杀螟硫磷；
- 8——倍硫磷；
- 9——毒死蜱；
- 10——氧异柳磷；
- 11——毒虫畏(E)；
- 12——毒虫畏(Z)；
- 13——异柳磷；
- 14——抑草磷；
- 15——三唑磷；
- 16——敌瘟磷。

图 D.1 33 种有机磷农药标准物的气相色谱-质谱选择离子色谱图(组 1)



- 17——治螟磷；
 18——甲基乙拌磷；
 19——二嗪磷；
 20——乙嘧啶磷；
 21——甲基对硫磷；
 22——甲基嘧啶磷；
 23——甲基毒虫畏(E)；
 24——马拉硫磷；
 25——甲基毒虫畏(Z)；
 26——对硫磷；
 27——啶硫磷；
 28——稻丰散；
 29——完灭硫磷；
 30——完灭硫磷砒；
 31——杀虫畏；
 32——丰索磷；
 33——苯硫磷。

图 D.2 33 种有机磷农药标准物的气相色谱-质谱选择离子色谱图(组 2)

Foreword

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

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

This standard was drafted by the JiangXi Entry-Exit Inspection and Quarantine Bureau of the People's Republic of China, the ShanXi Entry-Exit Inspection and Quarantine Bureau of the People's Republic of China, the XiaMen Entry-Exit Inspection and Quarantine Bureau of the People's Republic of China.

This main drafters of this standard are Wen Zhihai, Zhan Chunrui, Xue Ping, Zuo Haigen, Guo Ping, Zhang Zhigang.

This standard is a professional standard for Entry-Exit Inspection and Quarantine Bureau of the People's Republic of China promulgated for the first time.

Determination of 33 organophosphorous pesticides residues (butamifos, chlorpyrifos, chlorpyrifos-methyl et al) in foodstuffs for import and export

1 Scope

This standard specifies the determination of 33 organophosphorous pesticides residues (Dichlorvos, Ethoprophos, Terbufos, Fonofos, Chlorpyrifos-methyl, Tolclofos-methyl, Chlorpyrifos, Fenthion, Fenitrothion, Isofenphos-oxon, Chlorfenvinphos (E), Isofenphos, Chlorfenvinphos (Z), Butamifos, Edifenphos, Triazophos, Methacrifos, Thiometon, Diazinon, Etrimfos, Pirimiphos-methyl, Parathion-methyl, Dimethylvinphos (E), Malathion, Dimethylvinphos (Z), Parathion, Quinalphos, Phenthoate, Vamidothion, Vamidothion-sulfone, Tetrachlorvinphos, Fensulfothion, EPN) by gas chromatography and confirmation by gas chromatography-mass spectrometry in foodstuffs for import and export.

This standard is applicable to the determination and confirmation of residue content of 33 organophosphorous pesticides in rice, unpolished rice, maize, barley and wheat for import and export.

2 Principle

The pesticides residues in the test samples are extracted with water-acetone, cleaned up by liquid liquid partition with dichloromethane. Then cleaned up by GPC. Moreover, maize need undergo SPE column cleaning-up. Determination is made by GC-FPD and confirmation by GC-MS.

3 Reagents and materials

Unless otherwise specified, all the reagents used should be analytical pure, "water" is distilled water.

3.1 Acetone: grade for residual analysis.

3.2 Dichloromethane: grade for residual analysis.

3.3 Cyclohexane: grade for residual analysis.

3.4 Ethyl acetate: grade for residual analysis.

- 3.5 Sodium chloride solution: 15% (m/V), weigh 15 g of sodium chloride, dissolve in 100 mL of water.
- 3.6 Anhydrous sodium sulfate: Ignite at 650 °C for 4 h, and keep in a tightly closed container.
- 3.7 SPE column: 0.25 g, ENVI-Carb, or equivalent.
- 3.8 Organophosphorous pesticides standard: refer to annex A.
- 3.9 Standard stock solution: Accurately weigh an adequate amount of Organophosphorous pesticides standard (accurate to 0.1 mg) and dissolve in a small volume of acetone. Dilute with acetone to prepare a standard stock solution of 100 $\mu\text{g/mL}$ ~ 1 000 $\mu\text{g/mL}$ in concentration. Keep in dark place below 5 °C.
- 3.10 Standard working solution: Then dilute the standard stock solution with acetone to the required concentration as the standard working solution.
- 3.11 Membrane filter for organic: 0.2 μm .

4 Apparatus and equipment

- 4.1 Gas chromatograph, equipped with flame photometric detector (FPD).
- 4.2 Gas chromatograph, equipped with mass selective detector (MSD).
- 4.3 Centrifuger.
- 4.4 Vortex shaker.
- 4.5 Rotary vacuum evaporator.
- 4.6 Nitrogen blowing device.
- 4.7 Concentrate bottle: 150 mL.
- 4.8 Pulverizer.
- 4.9 Sieve: 2 mm.

5 Preparation and storage of test sample

5.1 Preparation of test sample

All primary sample is reduce by quartering to 1 kg, crushed with Pulverizer to let all pass through a 2 mm round-hole sieve, mixed thoroughly and divided into two equal portions. Each portion is placed in clean sample containers as the test samples, which is sealed and labeled.

5.2 Storage of test sample

The test samples should be stored below 0 °C ~4 °C. In the course of sampling and sample preparation, precautions must be taken to avoid contamination or any factors that may cause the change of residue content.

6 Procedure

6.1 Extraction

Weigh about 5 g (accurate to 0.01 g) of the test sample into a 50 mL centrifuge tube, add 5 mL of water and mix well, then let stand for 30 min. Add 15 mL of acetone, vortex on a Vortex shaker for 5 min. Centrifuge for 5 min at 4 000 r/min. Transfer the upper layer to a 150 mL concentrate bottle. Repeat the above procedure twice. Evaporate the combined extract to 5 mL in a rotary evaporator with bath temperature below 40 °C.

6.2 Clean up

6.2.1 Partition Clean up

Transfer the concentrated solution into a 50 mL centrifuge tube, add 2 × 5 mL dichloromethane to wash the rotary evaporator and Transfer into the 50 mL centrifuge tube. add 10 mL of sodium chloride aqueous solution and 10 mL of dichloromethane, shake for 5 min on a Vortex shaker and centrifuge for 5 min at 4 000 r/min. Collect the dichloromethane phase and let pass through an Anhydrous sodium sulfate column to remove the water, collect the effluent in a 150 mL concentrate bottle. The water phase is extracted with 2 × 10 mL dichloromethane, Combine the dichloromethane phases and evaporate to near dryness in a rotary evaporator with a bath temperature below 40 °C. Dissolve the residue with 10 mL of cyclohexane-ethyl acetate(1 + 1 V/V).

6.2.2 GPC Clean up

6.2.2.1 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 V/V);
- c) Flow rate: 5.0 mL/min;
- d) Injection volume: 5.0 mL;
- e) Time for rinsing: 0 min~20 min;
- f) Time for collecting the eluate: 20 min~40 min.

6.2.2.2 GPC clean up operating

Transfer the above 5 mL solution into an GPC column, proceed as section 6.2.2.1. Combined the eluates in a 150 mL concentrate bottle, evaporate to dryness in a rotary evaporator with a bath temperature below 40 °C. For the sample of rice, unpolished rice, barley and wheat, dissolve the residue with 1 mL of acetone and filter through 0.2 μm membrane filter for determination and confirmation. For maize, dissolve the residue with 2 mL of ethyl acetate for furthermore cleanup.

6.2.3 SPE Clean up

Rinse the an ENVI-Carb column (3.7) with 6 mL ethyl acetate before use, Transfer the above solution into column. Wash the column with 2 mL ethyl acetate, Then elute with 6 mL of ethyl acetate, collect all the eluates in a 15 mL tube and Nitrogen blowing to dryness in Nitrogen blowing device with a bath temperature below 40 °C. Dissolve the residue and dilute exactly to 1 mL with acetone for GC-MS determination and confirmation.

6.3 Determination

6.3.1 GC-FPD operating condition

- a) Chromatographic column: 30 m × 0.53 mm (i. d.), 1.0 μm film thickness, DB-1701, silica capillary column or equivalent;
- b) Column temperature: 50 °C (1 min) $\xrightarrow{30\text{ °C/min}}$ 170 °C $\xrightarrow{1.2\text{ °C/min}}$ 210 °C $\xrightarrow{30\text{ °C/min}}$ 260 °C (20 min);
- c) Injection port temperature: 230 °C;
- d) Inject mode: Splitless;
- e) Injection volume: 2 μL;
- f) Carrier gas: Helium, purity $\geq 99.999\%$, flow rate 5.0 mL/min;

- g) FPD detector: Temperature: 250 °C ; Hydrogen: 75 mL/min; Air: 100 mL/min; Make-up gas: nitrogen 60 mL/min.

6.3.2 GC-MS operating condition

- a) Chromatographic column: 30 m × 0.25 mm (i. d.), 0.25 μm film thickness, HP-5 MS silica capillary column or equivalent;
- b) Column temperature: 50 °C (1 min) $\xrightarrow{30\text{ °C/min}}$ 170 °C (25 min) $\xrightarrow{30\text{ °C/min}}$; 280 °C (10 min);
- c) Injector port temperature: 250 °C ;
- d) Interface temperature: 280 °C ;
- e) Carrier gas: Helium, purity $\geq 99.999\%$, flow rate 1.0 mL/min;
- f) Injection volume: 1 μL;
- g) Injection mode: Splitless, purge on after 1.5 min;
- h) Ionization mode: EI;
- i) Ionization energy: 70 eV;
- j) Determination mode: SIM mode;
- k) Selected monitoring ion (m/z) : see annex B;
- l) Solvent delay: 5 min.

6.3.3 GC-MS determination and confirmation

According to the approximate concentration of the pesticide in the sample solution, select the standard working solution with similar peak height to that of the sample solution. The responses of per organophosphorous pesticides in the standard working solution and sample solution should be within the linear range of the instrumental detection.

If there is any peak of sample solution appeared at the same retention time as such peak of the standard solution, it must be confirmed by selected monitoring ions (m/z) of species and abundance ratio, see annex B. The tolerance for relative ion intensities meet with table 1. Under the above GC-MS condition, the retention time of 33 organophosphorous pesticides for GC-MS chromatogram (SIM) of the standard, see annex B and annex C and D.

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

Relative intensity/%	Permitted tolerances(EI-GC-MS)/%
>50	± 10
>20~50	± 15
>10~20	± 20
≤10	± 50

6.4 Blank

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

7 Calculation and expression of the result

Calculate the content of per organophosphorous pesticides residues in the test sample according to the followed formula (1).

$$X_i = \frac{A_i \times c_i \times V}{A_{is} \times m} \dots\dots\dots (1)$$

where

X_i —the residue content of per organophosphorous pesticides in the test sample,mg/kg;

A_i —the peak area (height) of per organophosphorous pesticides in the sample solution;

A_{is} —the peak area (height) of per organophosphorous pesticides in the standard working solution;

c_i —the concentration of per organophosphorous pesticides in the standard working solution,mg/L;

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

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

8 Limit of determination and recovery

8.1 Limit of determination

The limit of determination of this method for Ethoprophos, Triazophos, Parathion residues in rice, unpolished rice, maize, barley and wheat are 0.005 mg/kg, and the limit of determination of this method for the other thirty organophosphorous pesticides in rice, unpolished rice, maize, barley and wheat are 0.01 mg/kg.

8.2 Recovery

According to the experimental data, the recoveries of 33 organophosphorous pesticides are shown in table 2.

Table 2—Recoveries of 33 organophosphorous pesticides in five types of samples (GC-FPD)

No.	Pesticides	Added/ (mg/kg)	Recoveries/%				
			Rice	Maize	Unpolished rice	Barley	Wheat
1	Dichlorvos	0.01	76.4~80.3	73.0~84.3	71.1~86.3	79.6~89.9	78.4~85.8
		0.02	73.5~87.7	72.1~89.7	73.2~81.9	75.8~89.5	78.8~95.1
		0.04	75.3~86.2	74.0~83.5	73.1~89.4	71.5~87.4	75.2~97.6
		0.10	75.8~88.3	70.8~90.6	70.4~84.3	76.1~87.4	70.4~95.7
2	Ethoprophos	0.01	72.9~86.4	78.4~83.3	74.9~87.4	74.9~84.4	73.5~82.1
		0.02	75.4~89.1	78.1~91.2	72.1~94.2	73.2~82.1	73.1~97.5
		0.04	85.5~91.2	90.1~97.1	83.1~90.2	80.3~90.1	85.2~95.4
		0.10	81.2~92.7	87.6~93.6	81.2~103.4	87.6~100.7	82.5~93.1
3	Terbufos	0.01	80.0~95.3	79.3~89.5	74.7~82.3	75.8~94.4	68.4~96.8
		0.02	70.3~85.6	72.9~92.4	74.6~87.5	78.3~92.0	72.2~96.4
		0.04	74.8~82.0	72.5~93.6	75.4~89.8	79.4~91.3	75.5~94.1
		0.10	74.3~84.1	78.1~91.6	76.7~89.6	83.2~102.5	74.5~96.0
4	Fonofos	0.01	72.4~80.6	68.4~88.5	64.4~87.6	69.0~84.3	72.6~89.2
		0.02	75.2~96.8	79.1~95.4	76.2~89.7	76.1~90.8	73.5~95.1
		0.04	73.1~90.1	72.5~92.7	69.8~93.2	78.2~94.5	78.1~91.44
		0.10	77.9~95.6	79.5~93.7	74.4~92.9	86.9~96.5	83.1~89.5
5	Chlorpyrifos-methyl	0.01	70.6~89.1	73.5~87.9	73.4~84.4	68.7~83.8	70.9~90.4
		0.02	72.8~91.3	77.6~98.2	68.6~85.4	78.5~94.2	79.1~95.6
		0.04	84.3~90.3	83.4~93.1	73.2~81.3	81.5~93.0	76.5~94.7
		0.10	85.4~88.0	85.4~101.2	73.7~79.1	80.1~97.5	80.4~101.8
6	Tolclofos-methyl	0.01	75.0~93.6	77.7~95.1	70.0~92.6	79.9~87.7	70.4~82.3
		0.02	77.1~90.3	79.1~91.3	75.3~89.9	64.3~87.9	76.5~91.7
		0.04	77.3~84.3	72.1~92.1	80.2~89.3	69.9~86.5	85.2~96.3
		0.10	75.3~86.2	76.7~93.1	78.0~89.6	65.9~97.7	88.6~97.4
7	Fenitrothion	0.01	74.5~89.5	76.6~89.5	79.9~89.2	74.9~83.7	76.0~90.3
		0.02	78.2~96.5	76.2~91.4	68.5~91.7	70.3~89.4	74.2~92.2
		0.04	77.6~85.4	74.3~90.6	70.5~93.6	77.6~84.9	83.0~100.9
		0.10	78.9~91.9	70.6~94.5	75.9~99.9	67.9~93.6	89.0~99.8
8	Fenthion	0.01	67.7~99.3	63.0~90.7	67.7~93.1	65.0~90.9	69.7~89.8
		0.02	79.3~85.7	77.1~95.2	77.2~93.4	75.4~89.5	75.4~92.9
		0.04	75.4~80.7	73.6~90.4	76.8~93.8	70.3~79.5	79.9~93.9
		0.10	76.5~97.9	81.0~98.7	80.8~100.7	74.4~94.9	83.7~104.1
9	Chlorpyrifos	0.01	78.4~89.5	80.2~90.4	78.4~92.8	77.7~96.1	75.9~89.7
		0.02	80.3~94.5	80.8~96.7	79.1~93.5	76.3~93.4	87.9~95.2

Table 2 (continued)

No.	Pesticides	Added/ (mg/kg)	Recoveries/%				
			Rice	Maize	Unpolished rice	Barley	Wheat
9	Chlorpyrifos	0.04	79.1~90.2	78.5~94.3	77.5~81.8	77.3~85.3	85.4~96.2
		0.10	84.9~96.8	87.2~103.1	80.6~102.9	73.3~102.5	74.8~90.7
10	Isofenphos-oxon	0.01	83.5~90.1	80.4~95.1	80.5~94.1	78.4~89.8	78.9~93.7
		0.02	87.4~96.8	87.1~98.2	85.6~93.7	86.3~99.8	89.7~95.4
		0.04	85.4~94.3	79.0~99.2	84.3~91.5	82.6~92.6	81.3~97.3
		0.10	84.0~95.9	79.4~98.3	82.1~93.5	86.4~97.8	84.9~96.2
11	Chlorfenvinphos (E)	0.01	78.4~83.8	73.2~80.0	73.4~89.8	72.5~90.1	79.1~92.2
		0.02	76.1~101.3	68.5~98.1	75.6~96.1	73.2~95.6	76.4~95.3
		0.04	77.8~95.4	74.8~100.1	76.8~97.8	75.8~96.5	73.4~99.7
		0.10	79.2~89.7	78.4~97.9	83.2~103.8	80.8~99.9	79.8~107.9
12	Chlorfenvinphos (Z)	0.01	73.6~92.9	75.9~94.3	73.6~95.9	72.4~101.8	81.8~96.8
		0.02	82.1~94.5	80.1~91.4	84.6~99.6	84.1~92.9	75.4~88.5
		0.04	83.5~90.2	79.5~90.3	80.1~94.1	85.0~94.2	80.1~99.3
		0.10	85.0~98.2	85.9~101.3	79.2~102.3	77.4~98.0	86.5~92.4
13	Isofenphos	0.01	77.9~84.4	79.1~90.0	69.9~94.4	73.6~89.9	69.4~98.9
		0.02	77.5~89.2	63.2~95.9	70.7~91.2	71.3~90.4	69.5~95.2
		0.04	72.5~84.3	72.9~97.4	75.8~89.6	71.8~94.6	73.8~95.2
		0.10	83.9~92.4	81.2~90.5	89.6~98.3	84.6~97.9	69.8~90.4
14	Butamifos	0.01	85.8~94.4	71.6~86.9	83.2~96.5	80.9~94.4	73.0~89.2
		0.02	87.3~96.5	85.1~108.3	87.5~92.3	74.7~86.5	79.4~96.8
		0.04	80.4~90.3	84.2~100.5	79.5~96.7	70.4~80.2	77.1~99.3
		0.1	84.1~93.2	79.2~96.9	75.4~99.1	79.2~99.5	75.7~90.4
15	Triazophos	0.01	79.0~87.3	69.6~90.2	77.3~92.3	75.9~84.4	70.2~93.7
		0.02	85.4~102.8	83.1~94.3	87.2~99.4	88.7~99.1	79.2~90.5
		0.04	84.1~95.1	80.2~95.2	80.3~89.9	85.3~96.0	80.4~93.2
		0.10	86.5~96.1	89.6~98.2	84.0~102.3	85.8~102.4	79.2~95.7
16	Edifenphos	0.01	68.7~77.8	60.1~78.9	65.6~77.2	66.0~90.3	76.0~80.3
		0.02	68.1~85.4	75.9~95.3	70.1~80.6	68.4~94.6	78.1~90.8
		0.04	73.4~80.5	78.7~96.4	73.1~85.1	70.2~90.4	79.1~98.2
		0.10	74.7~89.9	77.2~93.5	83.4~95.1	80.9~98.3	80.0~94.9
17	Methacrifos	0.01	77.2~90.7	74.5~78.3	60.9~78.7	68.7~87.2	76.0~86.9
		0.02	71.3~81.5	75.3~95.2	70.8~83.4	74.1~88.5	72.2~97.9
		0.04	73.5~87.8	75.4~96.4	76.9~80.2	75.2~84.1	80.4~99.2
		0.10	83.4~95.1	75.3~92.6	82.9~96.1	88.6~101.9	82.7~95.5

Table 2 (continued)

No.	Pesticides	Added/ (mg/kg)	Recoveries/%				
			Rice	Maize	Unpolished rice	Barley	Wheat
18	Thiometon	0.01	71.1~93.4	70.1~89.6	64.9~83.2	65.9~73.7	75.5~84.9
		0.02	70.9~87.2	73.3~99.5	67.4~89.9	74.1~92.6	80.3~91.7
		0.04	73.4~85.6	72.7~98.0	73.4~85.2	70.2~93.6	78.4~97.6
		0.10	80.6~93.7	78.4~94.7	72.5~95.7	77.1~96.2	80.9~96.1
19	Diazinon	0.01	71.3~93.6	76.3~88.4	77.1~95.2	69.9~93.2	83.9~96.9
		0.02	79.0~96.2	74.4~97.6	79.9~89.0	83.1~95.2	78.9~107.9
		0.04	74.2~87.5	70.3~99.4	72.1~80.4	79.4~84.2	78.9~94.9
		0.10	84.1~104.2	71.9~100.2	78.6~99.6	81.2~99.4	77.9~95.5
20	Etrifos	0.01	67.0~79.3	75.4~83.2	71.8~87.8	73.0~84.3	71.6~90.6
		0.02	76.6~91.8	77.0~97.3	84.1~91.4	72.4~89.2	73.8~97.8
		0.04	80.3~84.2	84.1~99.3	83.5~92.4	76.2~83.2	75.9~97.6
		0.10	88.8~103.9	80.6~102.6	78.4~102.2	69.8~88.0	85.8~96.8
21	Parathion-methyl	0.01	62.0~78.9	62.3~70.3	72.0~98.3	73.4~93.3	69.4~98.9
		0.02	80.3~96.8	83.4~92.9	72.8~92.5	80.4~98.9	76.8~98.0
		0.04	83.1~89.3	79.4~99.3	75.9~89.5	82.3~96.2	72.1~95.7
		0.10	90.0~101.5	72.3~96.3	88.3~104.3	89.4~100.3	81.4~103.3
22	Pirimiphos-methyl	0.01	73.0~80.2	75.5~85.1	69.0~88.2	69.3~88.5	73.0~88.2
		0.02	81.4~103.9	72.3~95.5	80.0~92.3	70.5~89.1	79.6~89.9
		0.04	85.3~99.4	76.8~94.5	78.4~95.3	73.6~83.9	79.0~98.4
		0.10	90.0~105.2	79.8~101.1	80.3~98.2	89.0~104.2	85.3~99.5
23	Dimethylvinphos (E)	0.01	65.4~80.1	66.7~72.9	70.2~86.7	75.4~88.5	70.1~82.7
		0.02	78.3~88.7	82.1~95.1	74.2~95.1	79.3~92.1	85.2~97.4
		0.04	75.8~83.7	80.3~92.1	76.5~90.3	82.1~94.2	87.3~99.3
		0.10	89.2~102.3	84.4~97.3	89.0~94.2	80.8~98.7	90.6~102.1
24	Malathion	0.01	71.5~89.5	71.7~82.0	77.3~86.0	73.8~84.9	76.8~83.9
		0.02	77.8~102.3	78.8~96.9	77.0~90.3	74.5~93.5	75.8~94.3
		0.04	85.1~99.4	80.4~98.0	78.2~86.4	77.3~91.5	78.0~97.2
		0.10	90.0~103.3	77.5~99.5	83.0~92.9	82.8~91.9	80.5~101.3
25	Dimethylvinphos (Z)	0.01	61.9~89.4	61.3~83.2	66.7~79.6	70.7~76.1	74.1~91.2
		0.02	83.2~106.3	82.1~99.5	77.1~99.2	89.4~101.5	87.7~95.6
		0.04	81.2~94.1	79.4~92.8	79.7~92.1	85.9~94.1	82.4~90.3
		0.10	93.7~101.6	80.3~92.2	75.8~97.1	82.3~88.7	78.3~90.1
26	Parathion	0.01	68.0~89.2	69.3~80.1	70.5~84.9	81.6~93.5	71.8~84.8
		0.02	72.2~97.8	72.3~97.1	81.2~90.2	89.4~93.7	77.3~91.7

Table 2 (continued)

No.	Pesticides	Added/ (mg/kg)	Recoveries/%				
			Rice	Maize	Unpolished rice	Barley	Wheat
26	Parathion	0.04	71.0~90.3	75.1~98.2	78.3~95.4	84.2~89.7	79.4~94.2
		0.10	90.5~104.9	84.3~99.7	76.1~91.0	81.3~98.5	76.4~93.0
27	Quinalphos	0.01	70.6~79.9	60.8~72.1	72.9~86.9	73.0~90.7	69.8~78.0
		0.02	78.6~101.4	67.5~94.2	72.3~89.8	79.8~94.2	71.5~94.3
		0.04	75.3~95.4	70.4~96.1	76.3~90.7	76.8~95.8	75.3~97.6
		0.10	94.0~108.9	90.5~102.1	71.9~90.9	72.1~95.7	84.8~99.0
28	Phenthoate	0.01	61.2~75.3	68.4~78.1	75.4~81.6	74.2~80.5	69.3~73.2
		0.02	78.3~101.5	72.1~95.3	76.2~92.5	87.3~99.1	70.3~95.7
		0.04	82.1~92.4	80.6~99.4	85.6~89.9	90.7~97.7	75.2~101.8
		0.10	92.2~105.6	87.2~96.2	80.1~94.9	83.0~90.6	89.6~95.0
29	Vamidothion Vamidothion- sulfone	0.01	58.8~76.9	70.3~83.4	66.4~70.7	74.4~82.3	70.2~81.7
		0.02	76.7~97.9	75.7~97.2	72.3~78.9	77.3~92.7	73.3~99.8
		0.04	80.3~93.8	74.3~99.5	78.9~84.2	79.6~95.2	76.4~98.8
		0.10	82.6~101.7	85.6~99.1	82.9~97.3	71.5~100.8	75.5~94.9
30	Tetrachlorvin- phos	0.01	69.7~96.5	67.2~84.8	71.7~86.5	73.4~90.0	66.0~78.3
		0.02	82.3~91.9	72.3~95.2	78.9~89.9	75.9~93.8	72.6~94.8
		0.04	80.4~93.9	80.2~94.7	77.3~80.5	79.0~95.7	79.4~98.4
		0.10	92.6~105.4	89.4~93.7	87.2~97.9	80.4~99.0	89.0~100.3
31	Fensulfothion	0.01	63.0~75.6	65.8~86.2	75.2~83.8	70.8~92.3	67.7~86.6
		0.02	71.2~99.7	70.2~91.4	82.3~95.7	83.8~95.1	71.3~89.5
		0.04	74.5~90.4	75.4~98.8	80.3~89.4	85.1~90.6	80.6~92.1
		0.10	93.2~103.8	83.2~97.5	87.3~93.7	87.9~96.2	86.1~92.0
32	EPN	0.01	83.6~107.1	85.2~100.3	79.0~87.2	75.1~85.6	71.0~92.5
		0.02	87.0~99.9	87.3~99.6	88.7~102.4	78.0~102.6	86.3~97.8
		0.04	89.4~98.5	80.4~96.3	85.1~94.4	80.4~96.6	80.6~90.6
		0.10	91.9~100.6	89.4~94.1	87.5~95.9	82.5~99.8	86.3~99.7

Annex A
(Normative)

Some chemistry informations of 33 organophosphorous pesticides

Table A. 1 — Some chemistry informations of 33 organophosphorous pesticides

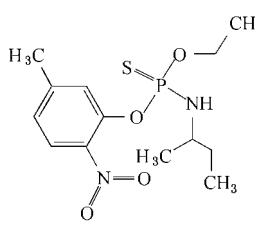
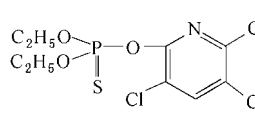
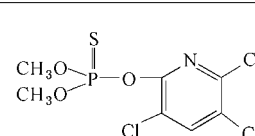
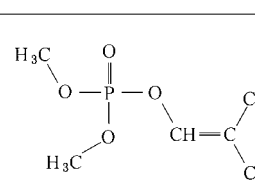
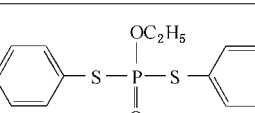
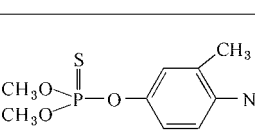
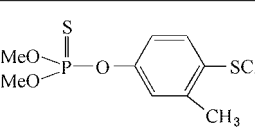
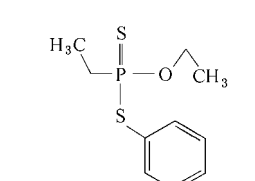
No.	Pesticides	Structure	Formula	CAS. No	M. W
1	Butamifos		$C_{13}H_{21}N_2O_4PS$	36335-67-8	332.4
2	Chlorpyrifos		$C_9H_{11}Cl_3NO_3PS$	2921-88-2	350.6
3	Chlorpyrifos-methyl		$C_7H_7Cl_3NO_3PS$	5598-13-0	322.5
4	Dichlorvos		$C_4H_7Cl_2O_4P$	62-73-7	221.0
5	Edifenphos		$C_{14}H_{15}O_2PS_2$	17109-49-8	310.4
6	Fenitrothion		$C_9H_{12}NO_5PS$	122-14-5	277.2
7	Fenthion		$C_{10}H_{15}O_3PS_2$	55-38-9	278.3
8	Fonofos		$C_{10}H_{15}OPS_2$	944-22-9	246.3

Table A. 1 (continued)

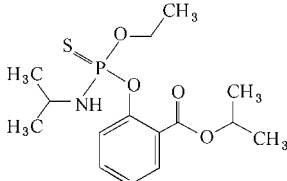
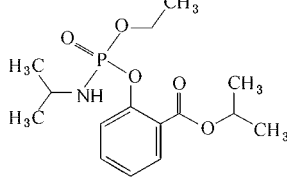
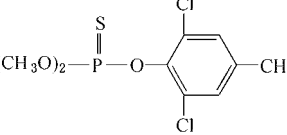
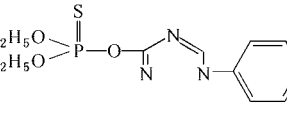
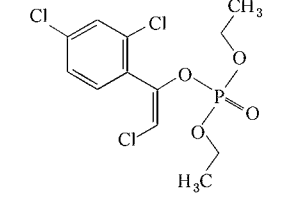
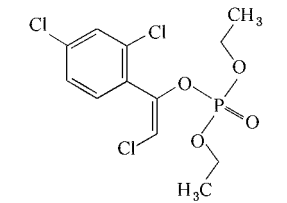
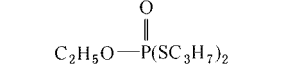
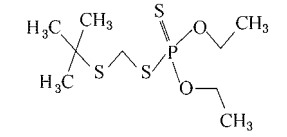
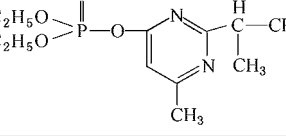
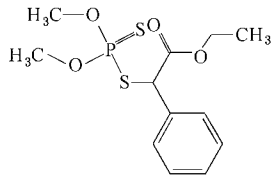
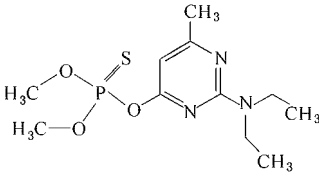
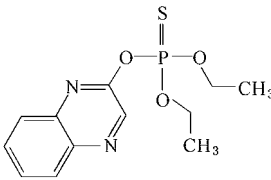
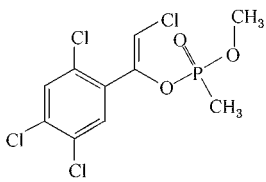
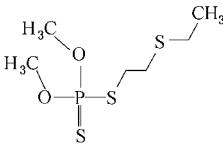
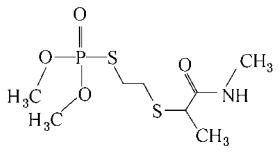
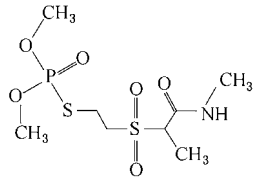
No.	Pesticides	Structure	Formula	CAS. No	M. W
9	Isofenphos		$C_{15}H_{24}NO_4PS$	25311-71-1	345. 4
10	Isofenphos-oxon		$C_{15}H_{24}NO_5PS$	31120-85-1	329. 3
11	Tolclofos-methyl		$C_9H_{11}Cl_2O_3PS$	57018-04-9	301. 1
12	Triazophos		$C_{12}H_{16}N_3O_3PS$	24017-47-8	313. 3
13	Chlorfenvinphosz(E)		$C_{12}H_{24}NO_4P$	18708-87-7	359. 6
14	Chlorfenvinphos (Z)		$C_{12}H_{24}NO_4P$	18708-87-7	359. 6
15	Ethoprofos		$C_8H_{19}O_2PS_2$	13194-48-4	242. 3
16	Terbufos		$C_9H_{21}O_2PS_3$	13071-79-9	288. 4
17	Diazinon		$C_{12}H_{21}N_2O_3PS$	333-41-5	304. 4

Table A. 1 (continued)

No.	Pesticides	Structure	Formula	CAS. No	M. W
18	Dimethylvinphos(E)		$C_{10}H_{10}Cl_3O_4P$	71363-52-5	331.5
19	Dimethylvinphos(Z)		$C_{10}H_{10}Cl_3O_4P$	71363-52-5	331.5
20	EPN		$C_{14}H_{14}NO_4PS$	2104-64-5	323.3
21	Etrimfos		$C_{10}H_{17}N_2O_4PS$	38260-54-7	292.3
22	Fensulfothion		$C_{11}H_{17}O_4PS_2$	115-90-2	308.4
23	Malathion		$C_{10}H_{19}O_6PS_2$	121-75-5	330.4
24	Methacrifos		$C_8H_{20}O_5P_2S_2$	3689-24-5	322.3
25	Parathion		$C_{10}H_{14}NO_5PS$	56-38-2	291.3
26	Parathion-methyl		$C_8H_{10}NO_5PS$	298-00-0	263.2

Table A. 1 (continued)

No.	Pesticides	Structure	Formula	CAS. No	M. W
27	Phenthoate		$C_{12}H_{17}O_4PS_2$	2597-03-7	320.3
28	Pirimiphos-methyl		$C_{11}H_{20}N_3O_3PS$	29232-93-7	305.3
29	Quinalphos		$C_{12}H_{15}N_2O_3PS$	13593-03-8	298.3
30	Tetrachlorvinphos		$C_{10}H_9Cl_4O_4P$	22248-79-9	366.0
31	Thiometon		$C_6H_{15}O_2PS_3$	640-15-3	246.3
32	Vamidotion		$C_8H_{18}NO_4PS_2$	2275-23-2	287.4
33	Vamidotion-sulfone		$C_8H_{18}NO_6PS_2$	70898-34-9	319.3

Annex B
(Informative)

The retention time, determination and confirmation selected monitoring ion
and limit of determination of 33 organophosphorous pesticides

Table B. 1—The retention time, determination and confirmation selected monitoring ion
and limit of determination of 33 organophosphorous pesticides

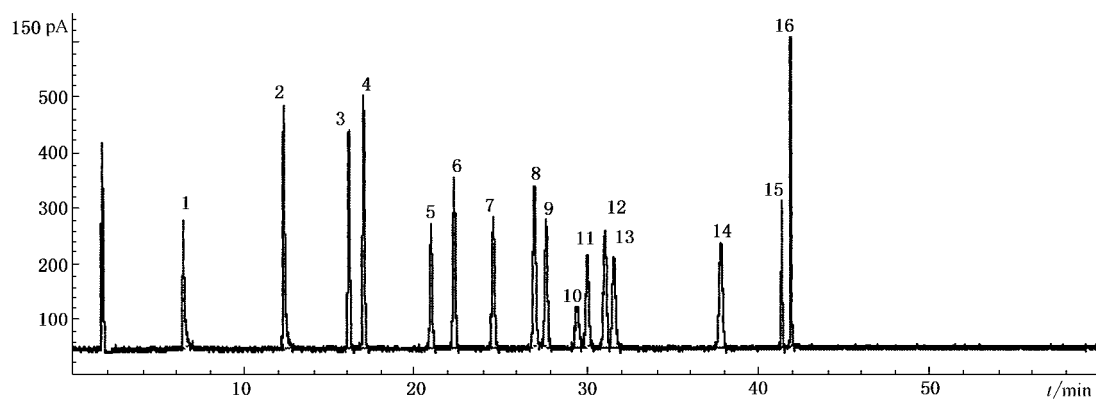
No.	Pesticides	t_R /min	Characteristic fragment ion (amu)		
			Qualnitification	Confirmation	Abundance ratio
1	Dichlorvos	5.62	185	109,187	29 : 100 : 10
2	Ethoprophos	9.59	242	158,200	23 : 100 : 39
3	Terbufos	13.03	231	186,203	100 : 15 : 8
4	Fonofos	13.20	246	109,137	50 : 100 : 50
5	Chlorpyrifos-methyl	17.46	286	288,125	100 : 70 : 50
6	Tolclofos-methyl	17.86	265	125,267	100 : 18 : 37
7	Fenitrothion	20.48	277	247,260	100 : 42 : 56
8	Fenthion	22.97	278	169,245	100 : 19 : 5
9	Chlorpyrifos	23.27	314	197,258	84 : 100 : 44
10	Isofenphos-oxon	24.78	229	201,314	100 : 68 : 11
11	Chlorfenvinphos(E)	28.53	323	267,269	63 : 100 : 64
12	Chlorfenvinphos(Z)	30.36	323	267,269	63 : 100 : 64
13	Isofenphos	30.47	213	255,185	100 : 43 : 42
14	Butamifos	32.31	286	200,258	100 : 36 : 23
15	Triazophos	33.78	313	161,257	13 : 100 : 34
16	Edifenphos	33.90	310	173,201	71 : 100 : 35
17	Methacrifos	10.63	322	202,238	100 : 38 : 23
18	Thiometon	11.33	158	125,246	15 : 100 : 19
19	Diazinon	13.92	304	276,248	100 : 47 : 42
20	Etrimfos	14.99	292	181,277	100 : 71 : 32
21	Parathion-methyl	17.48	263	233,125	100 : 12 : 87
22	Pirimiphos-methyl	21.08	290	276,305	100 : 81 : 74
23	Dimethylvinphos(E)	21.35	295	297,206	100 : 65 : 10
24	Malathion	22.34	285	173,256	5 : 100 : 8
25	Dimethylvinphos(Z)	23.08	295	297,206	100 : 65 : 9
26	Parathion	23.41	291	235,263	100 : 17 : 12

Table B. 1 (continued)

No.	Pesticides	t_R /min	Characteristic fragment ion(amu)		
			Qualnitification	Confirmation	Abundance ratio
27	Quinalphos	30.46	146	298,157	100 : 25 : 66
28	Phenthoate	30.64	274	246,320	100 : 27 : 5
29	Vamidothion	31.72	145	109,169	100 : 56 : 20
30	Vamidothion-sulfone				
31	Tetrachlorvinphos	31.92	328	330,332	80 : 100 : 46
32	Fensulfothion	33.38	236	308,293	12 : 36 : 100
33	EPN	34.83	323	293,278	100 : 47 : 21

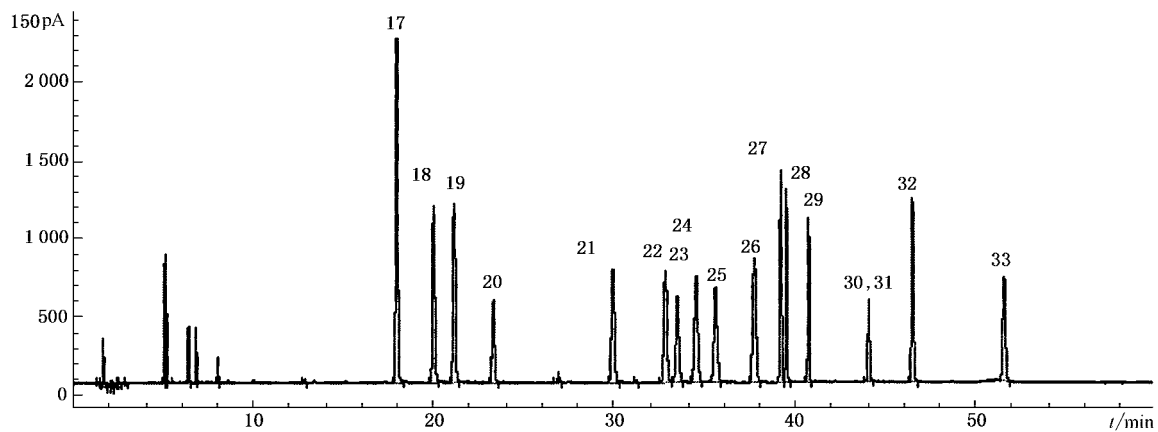
Annex C
(Informative)

GC chromatogram of the 33 organophosphorous pesticides standard



- 1—Dichlorvos;
- 2—Ethoprophos;
- 3—Terbufos;
- 4—Fonofos;
- 5—Chlorpyrifos-methyl;
- 6—Tolclofos-methyl;
- 7—Chlorpyrifos;
- 8—Fenthion;
- 9—Fenitrothion;
- 10—Isofenphos-oxon;
- 11—Chlorfenvinphos(E);
- 12—Isofenphos;
- 13—Chlorfenvinphos(Z);
- 14—Butamifos;
- 15—Edifenphos;
- 16—Triazophos.

Figure C. 1—GC chromatogram of the 33 organophosphorous pesticides standard(Group 1)

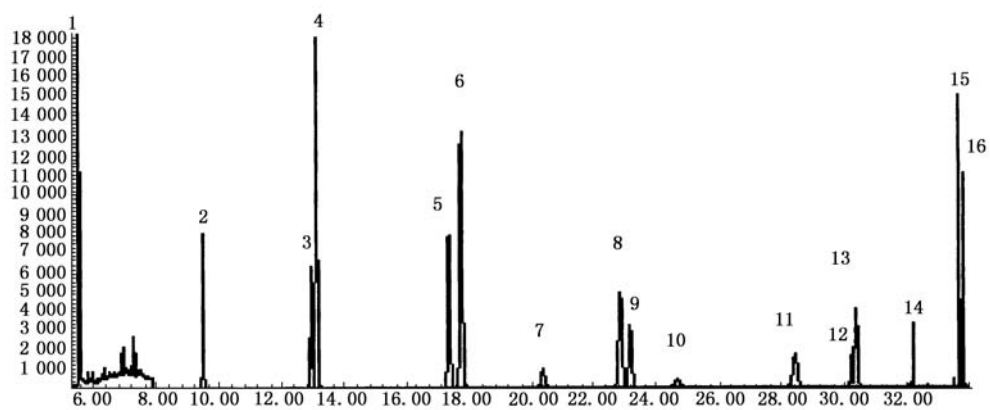


- 17—Methacrifos;
- 18—Thiometon;
- 19—Diazinon;
- 20—Etrimfos;
- 21—Pirimiphos-methyl;
- 22—Parathion-methyl;
- 23—Dimethylvinphos(E);
- 24—Malathion;
- 25—Dimethylvinphos(Z);
- 26—Parathion;
- 27—Quinalphos;
- 28—Phenthoate;
- 29—Tetrachlorvinphos;
- 30—Vamidothion;
- 31—Vamidothion-sulfone;
- 32—Fensulfothion;
- 33—EPN.

Figure C. 2—GC chromatogram of the 33 organophosphorus pesticides standard(Group 2)

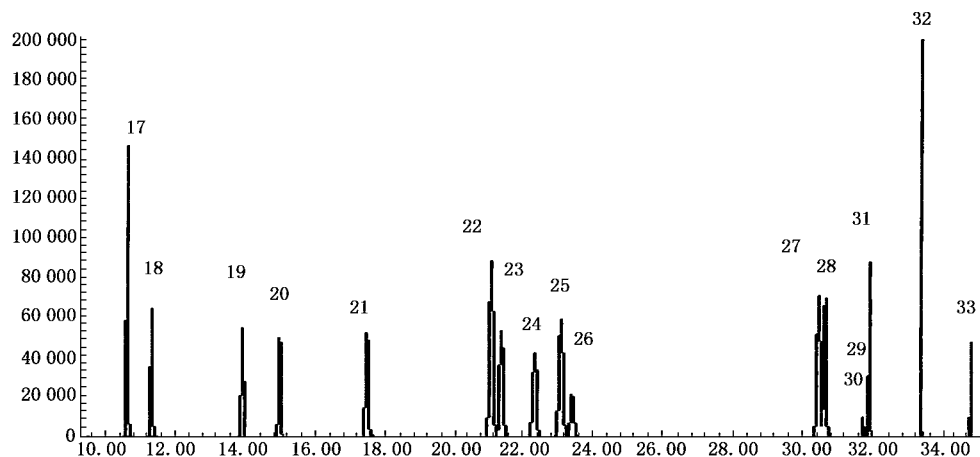
Annex D
(Informative)

GC-MS chromatogram of the 33 organophosphorous pesticides standard



- 1—Dichlorvos;
- 2—Ethoprophos;
- 3—Terbufos;
- 4—Fonofos;
- 5—Chlorpyrifos-methyl;
- 6—Tolclofos-methyl;
- 7—Fenitrothion;
- 8—Fenthion;
- 9—Chlorpyrifos;
- 10—Isofenphos-oxon;
- 11—Chlorfenvinphos(E);
- 12—Chlorfenvinphos(Z);
- 13—Isofenphos;
- 14—Butamifos;
- 15—Triazophos;
- 16—Edifenphos.

Figure D. 1—GC-MS chromatogram(SIM) of the 33 organophosphorous pesticides standard(Group 1)



- 17—Methacrifos;
- 18—Thiometon;
- 19—Diazinon;
- 20—Etrimfos;
- 21—Pirimiphos-methyl;
- 22—Parathion-methyl;
- 23—Dimethylvinphos(E) ;
- 24—Malathion;
- 25—Dimethylvinphos(Z) ;
- 26—Parathion;
- 27—Quinalphos;
- 28—Phenthoate;
- 29—Vamidothion;
- 30—Vamidothion-sulfone;
- 31—Tetrachlorvinphos;
- 32—Fensulfothion;
- 33—EPN.

Figure D. 2—GC-MS chromatogram(SIM) of the 33 organophosphorus pesticides standard(Group 2)

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