



中华人民共和国出入境检验检疫行业标准

SN/T 0148—2011

代替 SN 0148—1992、SN 0153—1992、SN 0154—1992、SN 0155—1992、SN 0161—1992 等

进出口水果蔬菜中有机磷农药残留量 检测方法 气相色谱和气相色谱-质谱法

Determination of organophosphorus residues in fruits and vegetables for
import and export—GC-FPD and GC-MS methods

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前 言

本标准按照 GB/T 1.1—2009 给出的规则起草。

本标准代替 SN 0148—1992《出口水果中甲基毒死蜱残留量检验方法》、SN 0153—1992《出口水果中马拉硫磷残留量检验方法》、SN 0154—1992《出口水果中甲基嘧啶磷残留量检验方法》、SN 0155—1992《出口水果中内吸磷残留量检验方法》、SN 0161—1992《出口水果中甲基对硫磷残留量检验方法》、SN 0189—1993《出口水果中三硫磷残留量检验方法》、SN 0196—1993《出口蔬菜中水胺硫磷残留量检验方法》、SN 0278—1993《出口蔬菜中甲胺磷残留量检验方法》、SN 0288—1993《出口水果中倍硫磷残留量检验方法》、SN 0291—1993《出口水果中乐果、甲基对硫磷残留量检验方法》、SN 0334—1995《出口水果蔬菜中 22 种有机磷农药多残留检验方法》、SN 0342—1995《出口水果中甲基谷硫磷、乙基谷硫磷残留量检验方法》、SN 0344—1995《出口水果中甲噻硫磷残留量检验方法》、SN 0354—1995《出口水果中伏杀硫磷残留量检验方法》、SN 0599—1996《出口水果中速灭磷残留量检验方法》。

本标准与 SN/T 0148—1992 等 15 项标准相比,主要技术变化如下:

- 检测项目由 15 个标准中的 30 项增至 70 项;
- 增加了确证部分内容;
- 删除了抽样部分内容。

请注意本文件的某些内容可能涉及专利,本文件的发布机构不承担识别这些专利的责任。

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:中华人民共和国厦门出入境检验检疫局、中华人民共和国广东出入境检验检疫局、中华人民共和国湖南出入境检验检疫局、中华人民共和国吉林出入境检验检疫局。

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本标准所代替标准的历次版本发布情况为:

- SN 0148—1992;
- SN 0153—1992;
- SN 0154—1992;
- SN 0155—1992;
- SN 0161—1992;
- SN 0189—1993;
- SN 0196—1993;
- SN 0278—1993;
- SN 0288—1993;
- SN 0291—1993;
- SN 0334—1995;
- SN 0342—1995;
- SN 0344—1995;
- SN 0354—1995;
- SN 0599—1996。

进出口水果蔬菜中有机磷农药残留量 检测方法 气相色谱和气相色谱-质谱法

1 范围

本标准规定了水果蔬菜中敌敌畏、乙酰甲胺磷、硫线磷、百治磷、乙拌磷、乐果、甲基对硫磷、毒死蜱、嘧啶磷、倍硫磷、丙虫硫磷、辛硫磷、灭茵磷、三硫磷、三唑磷、哒嗪硫磷、亚胺硫磷、敌百虫、灭线磷、甲拌磷、氧化乐果、内吸磷、二嗪磷、地虫硫磷、异稻瘟净、氯唑磷、甲基毒死蜱、对氧磷、杀螟硫磷、溴硫磷、乙基溴硫磷、噻唑磷、丙溴磷、乙硫磷、敌瘟磷、吡唑硫磷、蝇毒磷、甲胺磷、治螟磷、特丁硫磷、久效磷、除线磷、皮蝇磷、甲基嘧啶磷、对硫磷、甲基毒虫畏、异柳磷、稻丰散、杀扑磷、甲基硫环磷、伐杀磷、伏杀硫磷、甲基谷硫磷、二溴磷、速灭磷、甲基乙拌磷、巴胺磷、乙密硫磷、磷胺、地毒磷、马拉硫磷、甲基异柳磷、水胺硫磷、啶硫磷、杀虫畏、碘硫磷、硫环磷、威茵磷、苯硫磷、乙基谷硫磷 70 种有机磷类农药残留量的气相色谱及气相色谱-质谱检测方法。

本标准适用于菠萝、苹果、荔枝、胡萝卜、马铃薯、茄子、菠菜、荷兰豆、鲜木耳、鲜蘑菇、鲜牛蒡、鲜香菇、大葱中上述 70 种有机磷类农药残留量的检测。

2 方法提要

样品中有机磷农药残留经乙腈提取,过 Envi-Carb/PSA 小柱净化,浓缩、定容后,用气相色谱法(GC-FPD)和气相色谱-质谱法(GC-MS)测定,外标法定量。

3 试剂材料

除另有说明外,所用试剂均为分析纯,水为去离子水。

3.1 乙腈:液相色谱纯。

3.2 丙酮:液相色谱纯。

3.3 甲苯:液相色谱纯。

3.4 乙酸乙酯:液相色谱纯。

3.5 丙酮-甲苯(65+35,体积比):量取 65 mL 丙酮(3.2)和 35 mL 甲苯(3.3),混匀。

3.6 无水硫酸镁:550 °C 灼烧 4 h,在干燥器内冷却至室温,贮于密封瓶中备用。

3.7 氯化钠:140 °C 烘烤 4 h,在干燥器内冷却至室温,贮于密封瓶中备用。

3.8 Envi-Carb/PSA 复合小柱¹⁾:500 mg/500 mg/6 mL(本标准中是使用 Sigma-Aldrich/Supelco 公司产品完成的),或相当者。

3.9 70 种有机磷类农药标准物质:纯度均 $\geq 95\%$,详细见表 A.1。

3.10 标准溶液:

3.10.1 标准储备溶液:分别准确称取 10.0 mg(按其纯度折算为 100%)的农药各标准物质(3.9)于小烧杯中,用少量丙酮溶解,转移至 100 mL 容量瓶中,再用少量乙酸乙酯洗涤小烧杯数次,洗涤液倒入容

1) 非商业性声明:此处列出公司名字仅为工作方便提供参考,并不涉及商业目的,鼓励标准使用者尝试不同厂家的产品。

量瓶中并用乙酸乙酯定容至刻度,混匀,配成标准储备溶液浓度为 100 mg/mL。0℃~4℃冷藏保存,备用。

3.10.2 混合标准储备液:将 70 种有机磷农药分为 4 组,按照表 B.1 中的组别,根据各农药在仪器上的响应值,逐一准确吸取一定体积的同组别的单个农药储备液分别注入同一容量瓶中,用乙酸乙酯稀释至刻度,配制成 4 组农药混合标准储备溶液。气相色谱图参见图 C.1~图 C.4。

3.10.3 混合标准工作溶液:使用前用乙酸乙酯将混合标准储备液稀释成所需浓度的标准工作液。

4 仪器和设备

4.1 气相色谱仪:配火焰光度检测器(FPD-磷滤光片)。

4.2 气相色谱质谱仪:配有电子轰击电离源(EI)。

4.3 分析天平:感量 0.1 mg 和 0.01 g。

4.4 容量瓶:100 mL,10 mL。

4.5 移液器:20 μL~200 μL 和 100 μL~1 000 μL。

4.6 玻璃离心管:50 mL 和 15 mL 具塞。

4.7 10 mL 玻璃刻度试管。

4.8 旋涡混合器。

4.9 离心机(4 000 r/min)。

4.10 氮吹浓缩仪。

4.11 均质器。

4.12 捣碎机。

5 样品制备与保存

从所取全部样品中取出有代表性样品可食部分约 500 g,用捣碎机全部磨碎混合均匀,均分成两份,分别装入洁净容器中,密封,并标明标记,于-18℃以下冷冻存放。在样品制备操作过程中,应防止样品受到污染或发生残留物含量的变化。

6 提取及净化

6.1 提取

称取均质试样 10 g(精确到 0.01 g),置于 50 mL 玻璃离心管中,加入 10 mL 乙腈溶液,高速均质 2 min,再加入约 4 g 无水硫酸镁和 1 g 氯化钠,盖上塞子剧烈振荡 2 min 后,以 4 000 r/min 的转速离心 4 min,取出乙腈层装入另一 50 mL 离心管,用 10 mL 乙腈重复提取一次,合并提取液,并加入 1 g 无水硫酸镁,剧烈振荡后,以 4 000 r/min 的转速离心 1 min,移出上清液并浓缩至约 1 mL(45℃氮吹),待净化。

6.2 净化

将 ENVI-Carb/PSA 小柱(3.8)装在固相萃取装置上,先用 5 mL 丙酮-甲苯混合溶剂(3.5)预淋洗小柱,保持流速约为 1 mL/min。将 6.1 提取液通过小柱,再用 10 mL 丙酮-甲苯混合溶剂洗脱,收集全部洗脱液于 10 mL 玻璃刻度试管,置于 40℃下氮吹至近 0.5 mL,用乙酸乙酯定容至 1.0 mL,供 GC-FPD 或 GC-MS 分析。

6.3 测定

6.3.1 仪器条件

6.3.1.1 气相色谱仪器条件(GC-FPD):

- 色谱柱:DB-17(30 m×0.53 mm×0.25 μm)石英毛细管柱或相当者;
- 柱箱升温程序:100 ℃保持 0.5 min,然后以 15 ℃/min 升温至 250 ℃,保持 20 min;
- 载气:氮气,纯度≥99.999%,恒流模式,流量为 10 mL/min;
- 进样口温度:200 ℃;
- 进样量:2 μL;
- 进样方式:不分流进样;
- 检测器温度:250 ℃。

6.3.1.2 气相色谱-质谱仪器条件(GC-MS):

- 色谱柱:DB-5MS(30 m×0.25 mm×0.25 μm)石英毛细管柱或相当者;
- 柱箱升温程序:60 ℃保持 6 min,然后以 10 ℃/min 升温至 250 ℃,再以 15 ℃/min 升温至 280 ℃,保持 6 min;
- 载气:氦气,纯度≥99.999%,恒压模式,压力为 120 kPa;
- 进样口温度:220 ℃;
- 进样量:1 μL;
- 进样方式:不分流进样,1.0 min 后打开分流阀和隔垫吹扫阀;
- 电子轰击电离源(EI):70 eV;
- 离子源温度:200 ℃;
- GC-MS 接口温度 250 ℃;
- 选择离子监测:每个目标化合物选择 1 个定量离子和 2 个~3 个定性离子,详参见表 D.1,每组所有需要检测离子按照出峰顺序,分时段分别检测。每组检测离子的开始时间和驻留时间参见表 E.1。气相色谱-质谱选择离子色谱图参见图 F.1~图 F.4。

6.3.2 气相色谱法测定

在仪器最佳工作条件下,气相色谱采用外标法定量。根据样液中被测物残留的含量情况,选定峰面积相近的标准工作溶液。标准工作溶液和样液中被测物的响应值应在仪器的线性范围内,如果含量超过标准曲线范围,应稀释到合适浓度后分析。对标准工作溶液和样液等体积参差进样测定。在 6.3.1.1 色谱条件下,70 种有机磷农药在气相色谱仪上的保留时间、方法的检出限参见附录 B 中的表 B.1,气相色谱图参见图 C.1~图 C.4。如检测结果出现阳性,建议使用其他准确定量方法进行测定。

6.3.3 气相色谱-质谱法测定

按 6.3.1.2 色谱-质谱条件下进行样品测定,如果样液保留时间与标准溶液相一致(±0.5%),并且在扣除背景后的样品质谱图中,所选择的离子均出现,而且所选择的离子峰度比与标准样品的离子相一致,则可判断样品中存在这种被测物。使用气相色谱-质谱定性分析时相对离子丰度最大允许误差见表 1。

表 1 使用气相色谱-质谱定性确证时相对离子丰度最大允许误差

相对离子丰度/%	>50	>20~50	>10~20	≤10
允许的相对偏差/%	±10	±15	±20	±50

6.3.4 空白试验

除不加试样外,按上述测定步骤进行。

7 结果计算与表述

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,单位为微克每毫升($\mu\text{g/mL}$);

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 测定低限与回收率

8.1 测定低限

本方法中气相色谱法对菠萝、苹果、荔枝、胡萝卜、马铃薯、茄子、菠菜、荷兰豆、鲜木耳、鲜蘑菇、鲜牛蒡、鲜香菇、大葱中 70 种农药的测定低限参见表 B. 1,气相色谱质谱法的测定低限参见表 D. 1。

8.2 回收率

菠萝、苹果、荔枝、胡萝卜、马铃薯、茄子、菠菜、荷兰豆、鲜木耳、鲜蘑菇、鲜牛蒡、鲜香菇、大葱中 70 种农药不同添加水平的平均回收率数据参见表 G. 1。

附 录 A
(规范性附录)
70 种有机磷农药种类表

表 A.1 70 种有机磷农药种类表

序号	中文名称	英文名称	分子式	相对分子质量	CAS 号	纯度 $\geq$
1	敌敌畏	dichlorvos	$C_4H_7Cl_2O_4P$	220.98	62-73-7	97.0%
2	乙酰甲胺磷	acephate	$C_4H_{10}NO_3PS$	183.17	30560-19-1	97.5%
3	硫线磷	cadusafos	$C_{10}H_{23}O_2PS_2$	270.39	95465-99-9	99.0%
4	百治磷	dicrotophos	$C_8H_{16}NO_5P$	237.22	141-66-2	97.5%
5	乙拌磷	disulfoton	$C_8H_{19}O_2PS_3$	274.4	298-04-4	95.3%
6	乐果	dimethoate	$C_5H_{12}NO_3PS_2$	229.28	60-51-5	98.0%
7	甲基对硫磷	parathion-methyl	$C_8H_{10}NO_5PS$	263.21	298-00-0	98.5%
8	毒死蜱	chloropyrifos	$C_9H_{11}Cl_3NO_3PS$	350.59	2921-88-2	99.5%
9	噻啉磷	pirimiphos-ethyl	$C_{13}H_{24}N_3O_3PS$	333.39	23505-41-1	98.5%
10	倍硫磷	fenthion	$C_{10}H_{15}O_3PS_2$	278.33	55-38-9	97.0%
11	丙虫硫磷	propaphos	$C_{11}H_{15}Cl_2O_2PS_2$	345.25	34643-46-4	93.5%
12	辛硫磷	phoxim	$C_{12}H_{15}N_2O_3PS$	298.3	14816-18-3	98.5%
13	灭菌磷	ditalimfos	$C_{12}H_{14}NO_4PS$	299.28	5131-24-8	99.5%
14	三硫磷	carbofenothion	$C_{11}H_{16}ClO_2PS_3$	342.87	786-19-6	95.0%
15	三唑磷	triazophos	$C_{12}H_{16}N_3O_3PS$	313.31	24017-47-8	81.0%
16	吡啶硫磷	pyridaphenthion	$C_{14}H_{17}N_2O_4PS$	340.33	119-12-0	98.0%
17	亚胺硫磷	phosmet	$C_{11}H_{12}NO_4PS_2$	317.32	732-11-6	98.5%
18	敌百虫	trichlorphon	$C_4H_8Cl_3O_4P$	257.44	52-68-6	97.0%
19	灭线磷	ethoprophos	$C_8H_{19}O_2PS_2$	242.34	13194-48-4	93.0%
20	甲拌磷	phorate	$C_7H_{17}O_2PS_3$	260.38	298-02-2	94.5%
21	氧化乐果	omethoate	$C_5H_{12}NO_4PS$	213.19	1113-02-6	97.0%
22	内吸磷	demeton	$C_8H_{19}O_3PS_2$	258.34	8065-48-3	98.0%
23	二嗪磷	diazinon	$C_{12}H_{22}N_2O_3PS$	304	333-41-5	96.0%
24	地虫硫磷	dyfonate	$C_{10}H_{15}OPS_2$	246.33	994-22-9	95.0%
25	异稻瘟净	iprobenfos	$C_{13}H_{21}O_3PS$	288.34	26087-47-8	94.5%
26	氯唑磷	isazofos	$C_9H_{17}ClN_3O_3PS$	313.74	42509-80-8	95.0%
27	甲基毒死蜱	chlorpyrifos methyl	$C_7H_7Cl_3NO_3PS$	322.53	5598-13-0	98.5%
28	对氧磷	paraoxon	$C_{10}H_{14}NO_6P$	275.2	311-45-5	99.0%
29	杀螟硫磷	fenitrothion	$C_9H_{12}NO_5PS$	277.23	122-14-5	97.5%
30	溴硫磷	bromophos methyl	$C_8H_8BrCl_2O_3PS$	366	2104-96-3	99.5%

表 A.1 (续)

序号	中文名称	英文名称	分子式	相对分子质量	CAS 号	纯度 $\geq$
31	乙基溴硫磷	bromophos ethyl	$C_{10}H_{12}BrCl_2O_3PS$	394.05	4824-78-6	98.5%
32	噻唑磷	fosthiazate	$C_9H_{18}NO_3PS_2$	283.35	98886-44-3	96.5%
33	丙溴磷	profenofos	$C_{11}H_{15}BrClO_3PS$	373.63	41198-08-7	95.0%
34	乙硫磷	ethion	$C_9H_{22}O_4P_2S_4$	384.48	563-12-2	98.8%
35	敌瘟磷	edifenphos	$C_{14}H_{15}O_2PS_2$	310.37	17109-49-8	93.5%
36	吡唑硫磷	pyraclofos	$C_{14}H_{18}ClN_2O_3PS$	360.8	77458-01-6	97.0%
37	蝇毒磷	coumaphos	$C_{14}H_{16}ClO_5PS$	362.77	56-72-4	97.5%
38	甲胺磷	methamidophos	$C_5H_9NO_2PS$	141.13	10265-92-6	98.5%
39	治螟磷	sulfotep	$C_8H_{20}O_5P_2S_2$	322.32	3689-24-5	94.0%
40	特丁硫磷	terbufos	$C_9H_{21}O_4PS_3$	288.43	13071-79-9	93.0%
41	久效磷	monocrotophos	$C_8H_{14}NO_5P$	223.16	6923-22-4	97.5%
42	除线磷	dichlofenthion	$C_{10}H_{13}Cl_2O_5PS$	315.15	97-17-6	98.5%
43	皮蝇磷	fenchlorphos	$C_9H_9Cl_2O_5PS$	321.55	299-84-3	98.0%
44	甲基嘧啶磷	pirimiphos-methyl	$C_{11}H_{20}N_3O_3PS$	305.33	29232-93-7	99.0%
45	对硫磷	parathion	$C_{10}H_{14}NO_5PS$	291.26	56-38-2	99.0%
46	甲基毒虫畏	dimethylvinphos	$C_{10}H_{10}Cl_3O_4P$	331.52	71363-52-5	99.0%
47	异柳磷	isophenphos	$C_{15}H_{24}NO_4PS$	345.39	25311-71-1	91.0%
48	稻丰散	phenthoate	$C_{12}H_{17}O_4PS_4$	320.36	2597-03-7	96.6%
49	杀扑磷	methidathion	$C_8H_{11}N_2O_4PS_3$	302.33	950-37-8	98.5%
50	甲基硫环磷	phosfolan methyl	$C_5H_{10}NO_4PS_2$	227.25	14731-55-2	97.5%
51	伐灭磷	famphur	$C_{10}H_{16}NO_4PS_2$	325.34	52-85-7	99.0%
52	伏杀硫磷	phosalone	$C_{12}H_{15}ClNO_4PS_2$	357.81	2310-17-0	98.5%
53	甲基谷硫磷	azinphos methyl	$C_{10}H_{12}N_3O_3PS_2$	317.32	86-50-0	99.0%
54	二溴磷	dibrom	$C_8H_7Br_2Cl_2O_4P$	380.78	300-76-5	98.0%
55	速灭磷	phosdrin	$C_7H_{13}O_6P$	224.15	26718-65-0	92.0%
56	甲基乙拌磷	thiometon	$C_6H_{15}O_2PS_3$	246.35	640-15-3	92.0%
57	巴胺磷	propetamphos	$C_{10}H_{20}NO_4PS$	281.31	31218-83-4	94.0%
58	乙嘧硫磷	etrimfos	$C_{10}H_{17}N_2O_4PS$	292.29	38260-54-7	96.5%
59	磷胺	phosphamidon	$C_{10}H_{19}ClNO_5P$	299.69	13171-21-6	95.5%
60	壤虫磷	trichloronate	$C_{10}H_{12}Cl_3O_2PS$	333.6	327-98-0	96.0%
61	马拉硫磷	malathion	$C_{10}H_{19}O_6PS_2$	330.36	121-75-5	99.0%
62	甲基异柳磷	isofenphos-methyl	$C_{14}H_{22}NO_4PS$	331.37	99675-03-3	96.0%
63	水胺硫磷	isocarbophos	$C_{11}H_{16}NO_4PS$	289.29	24353-61-5	95.0%
64	喹硫磷	quinalphos	$C_{12}H_{15}N_2O_3PS$	298.3	13593-03-8	96.0%

表 A.1 (续)

序号	中文名称	英文名称	分子式	相对分子质量	CAS 号	纯度 $\geq$
65	杀虫畏	tetrachlorvinphose	$C_{10}H_9Cl_4O_4P$	365.96	22350-76-1	99.5%
66	碘硫磷	iodofenphos	$C_8H_8Cl_2IO_3PS$	413	18181-70-9	97.5%
67	硫环磷	phosfolan	$C_7H_{14}NO_3PS_2$	255.29	947-02-4	97.5%
68	威菌磷	triamiphos	$C_{12}H_{19}N_6OP$	294.29	1031-47-6	96.3%
69	苯硫磷	EPN	$C_{14}H_{14}NO_4PS$	323.3	2104-64-5	99.0%
70	乙基谷硫磷	azinphos ethyl	$C_{12}H_{16}N_3O_3PS_2$	345.38	2642-71-9	97.7%

附 录 B

(资料性附录)

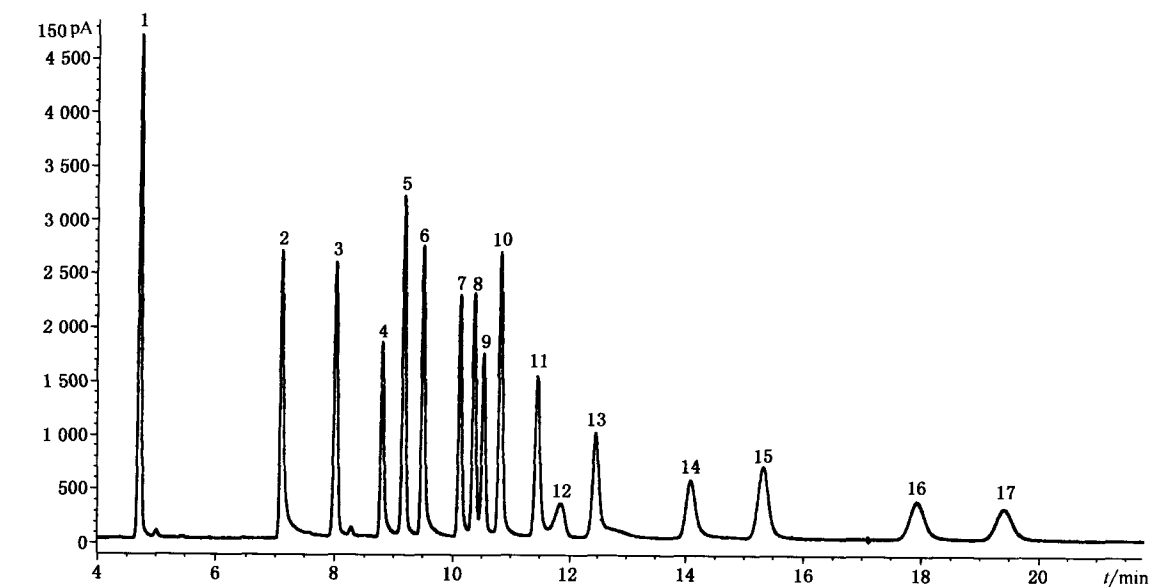
有机磷农药 GC-FPD 检测参考数据

表 B.1 有机磷农药 GC-FPD 检测参考数据

序号	中文名称	保留时间 min	测定低限 mg/kg	组别	序号	中文名称	保留时间 min	测定低限 mg/kg	组别
1	敌敌畏	4.733	0.01	I	36	吡唑硫磷	21.968	0.01	II
2	乙酰甲胺磷	7.139	0.01	I	37	蝇毒磷	25.171	0.01	II
3	硫线磷	8.043	0.01	I	38	甲胺磷	5.531	0.01	III
4	百治磷	8.821	0.01	I	39	治螟磷	8.288	0.01	III
5	乙拌磷	9.196	0.01	I	40	特丁硫磷	8.740	0.005	III
6	乐果	9.519	0.01	I	41	久效磷	9.095	0.01	III
7	甲基对硫磷	10.155	0.01	I	42	除线磷	9.481	0.01	III
8	毒死蜱	10.397	0.01	I	43	皮蝇磷	9.988	0.01	III
9	噻啉磷	10.533	0.01	I	44	甲基噻啉磷	10.204	0.01	III
10	倍硫磷	10.843	0.01	I	45	对硫磷	10.481	0.01	III
11	丙虫硫磷	11.483	0.01	I	46	甲基毒虫畏	10.817	0.01	III
12	辛硫磷	11.878	0.01	I	47	异柳磷	10.927	0.01	III
13	灭菌磷	12.493	0.01	I	48	稻丰散	11.614	0.01	III
14	三硫磷	14.126	0.01	I	49	杀扑磷	12.335	0.01	III
15	三唑磷	15.322	0.01	I	50	甲基硫环磷	12.876	0.01	III
16	哒嗪硫磷	17.938	0.01	I	51	伐杀磷	15.375	0.01	III
17	亚胺硫磷	19.424	0.01	I	52	伏杀硫磷	18.837	0.01	III
18	敌百虫	5.328	0.01	II	53	甲基谷硫磷	22.955	0.01	III
19	灭线磷	7.883	0.005	II	54	二溴磷	4.714	0.01	IV
20	甲拌磷	8.359	0.01	II	55	速灭磷	6.460	0.01	IV
21	氧化乐果	8.570	0.01	II	56	甲基乙拌磷	8.750	0.01	IV
22	内吸磷	7.595/8.732	0.01	II	57	巴胺磷	8.853	0.01	IV
23	二嗪磷	8.886	0.01	II	58	乙噻硫磷	9.228	0.01	IV
24	地虫硫磷	9.211	0.01	II	59	磷胺	9.483/10.006	0.01	IV
25	异稻瘟净	9.436	0.01	II	60	地毒磷	10.285	0.01	IV
26	氯唑磷	9.545	0.01	II	61	马拉硫磷	10.430	0.01	IV
27	甲基毒死蜱	9.980	0.01	II	62	甲基异柳磷	10.836	0.01	IV
28	对氧磷	10.157	0.01	II	63	水胺硫磷	11.096	0.01	IV
29	杀螟硫磷	10.475	0.01	II	64	嗪硫磷	11.364	0.01	IV
30	溴硫磷	10.824	0.01	II	65	杀虫畏	11.817	0.01	IV
31	乙基溴硫磷	10.142	0.01	II	66	碘硫磷	12.251	0.01	IV
32	噻唑磷	11.636	0.01	II	67	硫环磷	13.325	0.01	IV
33	丙溴磷	12.038	0.01	II	68	威菌磷	14.703	0.01	IV
34	乙硫磷	13.257	0.01	II	69	苯硫磷	16.978	0.01	IV
35	敌瘟磷	15.878	0.01	II	70	乙基谷硫磷	24.363	0.01	IV

附录 C
(资料性附录)

70 种有机磷农药标准物质的气相色谱图 (GC-FPD)



- 1 —— 敌敌畏；
- 2 —— 乙酰甲胺磷；
- 3 —— 硫线磷；
- 4 —— 百治磷；
- 5 —— 乙拌磷；
- 6 —— 乐果；
- 7 —— 甲基对硫磷；
- 8 —— 毒死蜱；
- 9 —— 嘧啶磷；
- 10 —— 倍硫磷；
- 11 —— 丙虫硫磷；
- 12 —— 辛硫磷；
- 13 —— 灭菌磷；
- 14 —— 三硫磷；
- 15 —— 三唑磷；
- 16 —— 哒嗪硫磷；
- 17 —— 亚胺硫磷。

图 C.1 第 I 组有机磷农药标准溶液的气相色谱图

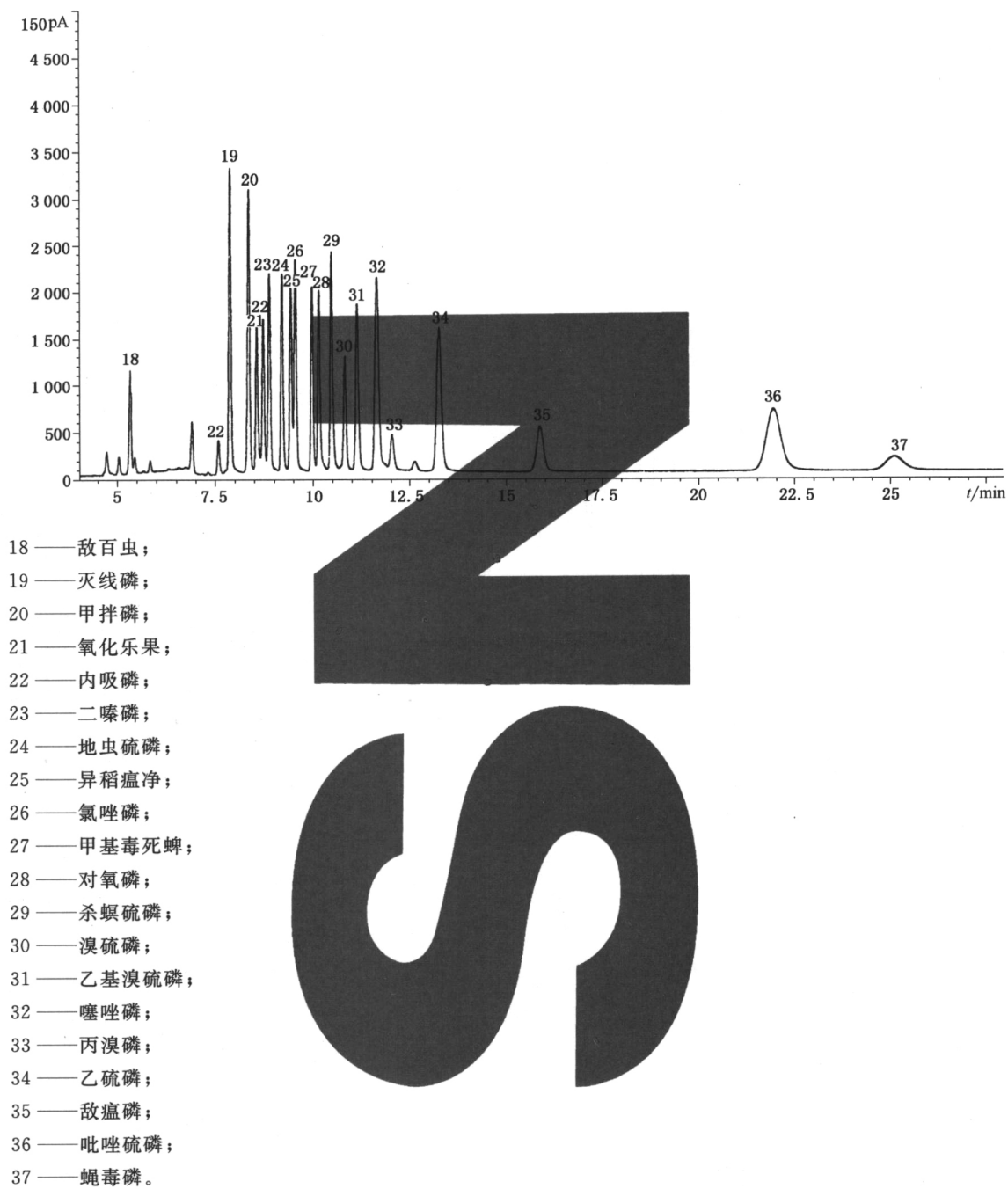
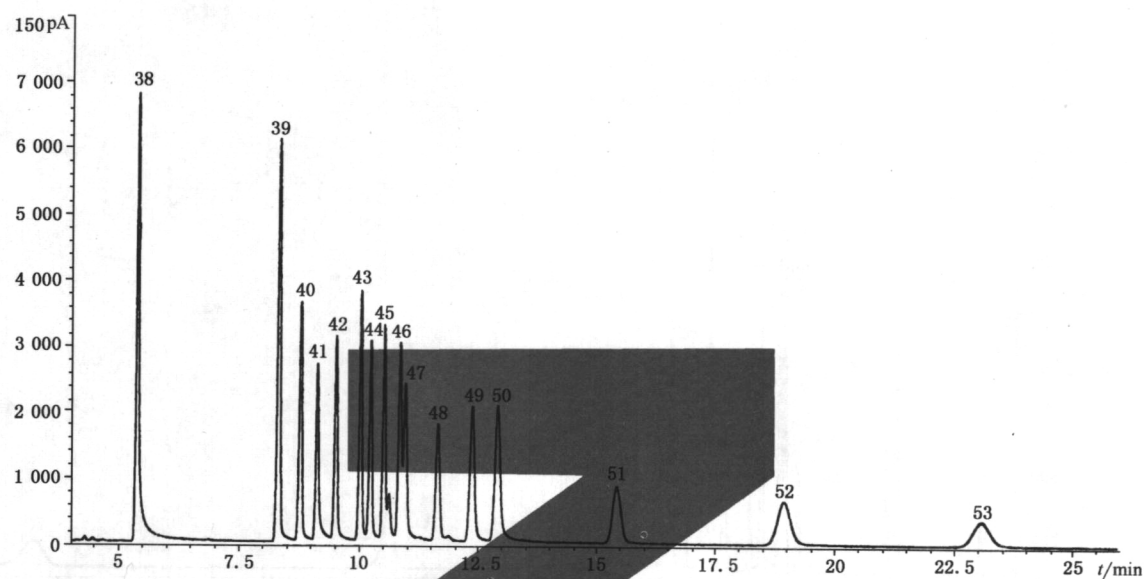
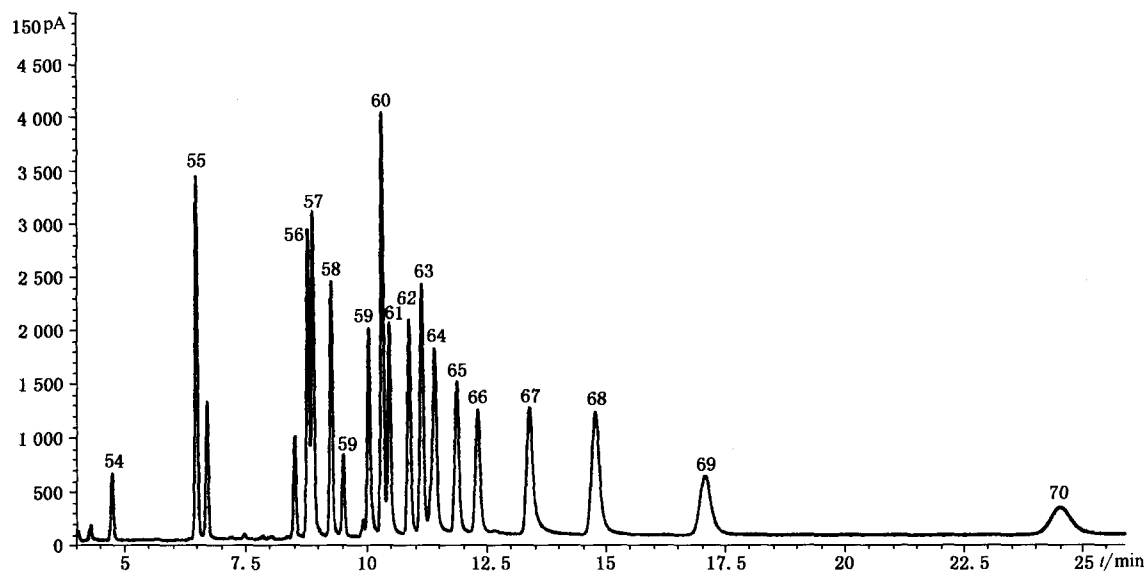


图 C.2 第Ⅱ组有机磷农药标准溶液气相色谱图



- 38 —— 甲胺磷；
- 39 —— 治螟磷；
- 40 —— 特丁硫磷；
- 41 —— 久效磷；
- 42 —— 除线磷；
- 43 —— 皮蝇磷；
- 44 —— 甲基嘧啶磷；
- 45 —— 对硫磷；
- 46 —— 甲基毒虫畏；
- 47 —— 异柳磷；
- 48 —— 稻丰散；
- 49 —— 杀扑磷；
- 50 —— 甲基硫环磷；
- 51 —— 伐杀磷；
- 52 —— 伏杀硫磷；
- 53 —— 甲基谷硫磷。

图 C.3 第Ⅲ组有机磷农药标准溶液气相色谱图



- 54 —— 二溴磷；
- 55 —— 速灭磷；
- 56 —— 甲基乙拌磷；
- 57 —— 巴胺磷；
- 58 —— 乙嘧硫磷；
- 59 —— 磷胺；
- 60 —— 地毒磷；
- 61 —— 马拉硫磷；
- 62 —— 甲基异柳磷；
- 63 —— 水胺硫磷；
- 64 —— 啶硫磷；
- 65 —— 杀虫畏；
- 66 —— 碘硫磷；
- 67 —— 硫环磷；
- 68 —— 威菌磷；
- 69 —— 苯硫磷；
- 70 —— 乙基谷硫磷。

图 C. 4 第Ⅳ组有机磷农药标准溶液气相色谱图

附 录 D
(资料性附录)

70 种有机磷农药的保留时间、定量和定性选择离子及测定低限

表 D.1 70 种有机磷农药的保留时间、定量和定性选择离子及测定低限表

序号	农药名称	保留时间 min	特征碎片离子 amu				测定低限 mg/kg
			定性			丰度比	
1	敌敌畏	9.63	109 *	185	220	100 : 19 : 4	0.01
2	乙酰甲胺磷	12.64	136 *	94	142	100 : 45 : 10	0.01
3	硫线磷	15.36	159 *	127	270	100 : 65 : 9	0.01
4	百治磷	15.15	127 *	193	237	100 : 10 : 7	0.01
5	乙拌磷	16.77	88 *	89	142	100 : 35 : 8	0.01
6	乐果	16.05	87 *	93	125	100 : 65 : 50	0.01
7	甲基对硫磷	17.75	109 *	125	263	100 : 82 : 30	0.01
8	毒死蜱	18.51	97 *	199	314	100 : 45 : 20	0.01
9	噻啉磷	18.88	168 *	318	333	100 : 40 : 35	0.01
10	倍硫磷	18.63	125 *	109	278	100 : 95 : 70	0.01
11	丙虫硫磷	19.83	220 *	304	262	100 : 70 : 35	0.01
12	辛硫磷	8.67	103 *	130	77	100 : 50 : 42	0.01
13	灭菌磷	20.19	130 *	148	299	100 : 40 : 18	0.01
14	三硫磷	21.48	157 *	342	199	100 : 49 : 28	0.01
15	三唑磷	22.08	161 *	162	172	100 : 55 : 40	0.01
16	哒嗪硫磷	24.11	97 *	199	340	100 : 38 : 25	0.01
17	亚胺硫磷	24.17	160 *	161	—	100 : 18	0.01
18	敌百虫	13.15	79 *	109	145	100 : 80 : 25	0.01
19	灭线磷	14.81	158 *	139	200	100 : 55 : 40	0.01
20	甲拌磷	15.52	75 *	121	260	100 : 25 : 5	0.01
21	氧化乐果	14.47	110 *	156	79	100 : 80 : 79	0.01
22	内吸磷	14.52/15.91	88 *	89	171	100 : 70 : 30	0.01
23	二嗪磷	16.52	137 *	179	304	100 : 95 : 30	0.01
24	地虫硫磷	16.56	109 *	137	246	100 : 75 : 50	0.01
25	异稻瘟净	17.13	91 *	204	288	100 : 45 : 7	0.01
26	氯唑磷	16.83	161 *	119	257	100 : 87 : 25	0.01
27	甲基毒死蜱	17.62	125 *	286	288	100 : 86 : 75	0.01
28	对氧磷	18.04	109 *	81	275	100 : 63 : 22	0.01
29	杀螟硫磷	18.29	125 *	109	277	100 : 87 : 55	0.01

表 D.1 (续)

序号	农药名称	保留时间 min	特征碎片离子 amu				测定低限 mg/kg
			定性		丰度比		
30	溴硫磷	19.04	125 *	329	331	100 : 67 : 90	0.01
31	乙基溴硫磷	19.85	97 *	302	358	100 : 98 : 66	0.01
32	噻唑磷	19.09	195 *	97	283	100 : 80 : 25	0.01
33	丙溴磷	10.66	156 *	97	208	100 : 95 : 15	0.01
34	乙硫磷	21.62	231 *	97	153	100 : 99 : 92	0.01
35	敌瘟磷	22.37	109 *	172	309	100 : 85 : 75	0.01
36	吡啶硫磷	27.92	138 *	194	360	100 : 80 : 55	0.01
37	蝇毒磷	28.73	109 *	226	362	100 : 60 : 45	0.01
38	甲胺磷	9.95	94 *	95	141	100 : 68 : 58	0.01
39	治螟磷	15.19	97 *	202	322	100 : 90 : 80	0.01
40	特丁硫磷	16.40	57 *	231	—	100 : 40	0.01
41	久效磷	15.61	127 *	67	192	100 : 23 : 13	0.01
42	除线磷	17.42	223 *	279	97	100 : 88 : 87	0.01
43	皮蝇磷	17.93	285 *	125	287	100 : 60 : 50	0.01
44	甲基嘧啶磷	18.08	276 *	305	290	100 : 64 : 53	0.01
45	对硫磷	18.72	97 *	109	291	100 : 80 : 30	0.01
46	甲基毒虫畏	18.57	109 *	295	297	100 : 55 : 35	0.01
47	异柳磷	19.34	58 *	121	213	100 : 35 : 35	0.01
48	稻丰散	19.47	121 *	125	274	100 : 92 : 70	0.01
49	杀扑磷	19.86	145 *	85	—	100 : 98	0.01
50	甲基硫环磷	19.55	196 *	140	106	100 : 85 : 69	0.01
51	伐杀磷	22.28	218 *	125	93	100 : 45 : 39	0.01
52	伏杀硫磷	26.17	182 *	121	367	100 : 54 : 12	0.01
53	甲基谷硫磷	26.72	77 *	132	160	100 : 82 : 78	0.01
54	二溴磷	15.07	109 *	145	301	100 : 55 : 10	0.01
55	速灭磷	12.20	127 *	109	192	100 : 30 : 30	0.01
56	甲基乙拌磷	15.78	88 *	125	93	100 : 35 : 20	0.01
57	巴胺磷	16.85	138 *	194	236	100 : 45 : 25	0.01
58	乙噻硫磷	16.88	181 *	153	292	100 : 92 : 63	0.01
59	磷胺	16.55/17.35	127 *	72	264	100 : 55 : 25	0.01
60	地毒磷	18.88	109 *	268	296	100 : 75 : 55	0.01
61	马拉硫磷	18.34	125 *	173	93	100 : 98 : 81	0.01
62	甲基异柳磷	19.07	58 *	199	121	100 : 45 : 35	0.01

表 D.1 (续)

序号	农药名称	保留时间 min	特征碎片离子				测定低限 mg/kg
			amu			丰度比	
			定性				
63	水胺硫磷	18.86	136 *	121	230	100 : 75 : 15	0.01
64	啉硫磷	19.56	146 *	157	298	100 : 87 : 13	0.01
65	杀虫畏	19.92	109 *	329	331	100 : 35 : 30	0.01
66	碘硫磷	20.37	376 *	125	378	100 : 55 : 35	0.01
67	硫环磷	19.54	92 *	140	196	100 : 75 : 45	0.01
68	威菌磷	21.72	160 *	135	294	100 : 35 : 15	0.01
69	苯硫磷	24.57	167 *	169	185	100 : 50 : 30	0.01
70	乙基谷硫磷	27.56	132 *	160	77	100 : 78 : 50	0.01
注：标“*”的离子为定量离子。							

附 录 E
(资料性附录)
选择离子监测分组表

表 E.1 选择离子监测分组表

组别	序号	时间 min	离子 amu	驻留时间 s
第 I 组	1	7.00	77,103,130	0.36
	2	9.00	109,185,220	0.36
	3	10.00	94,136,142	0.36
	4	13.00	127,159,193,237,270	0.59
	5	15.80	87,88,89,93,237,270	0.70
	6	17.00	109,125,263	0.36
	7	18.00	97,109,125,168,199,278,314,318,333	1.05
	8	19.30	130,148,220,262,299,304	0.70
	9	21.00	77,97,125,161,162,172,293	0.82
	10	23.00	97,160,161,199,340	0.59
第 II 组	1	9.00	79,97,109,145,156,208	0.70
	2	13.50	79,88,89,109,110,139,156,158,170,200	1.16
	3	15.10	75,88,89,121,170,260	0.70
	4	16.20	109,119,137,152,161,179,246,257,304	1.05
	5	16.95	91,125,204,286,288	0.59
	6	17.85	81,109,125,275,277	0.59
	7	18.60	97,125,195,283,302,329,331,358	0.93
	8	20.00	109,172,309	0.36
	9	21.00	97,153,231	0.36
	10	22.00	109,138,194,226,360,362	0.70
第 III 组	1	8.00	94,95,141	0.24
	2	11.00	67,97,127,192,202,322	0.70
	3	16.00	57,231	0.24
	4	17.00	97,125,223,276,279,285,287,290,305	1.05
	5	18.30	97,109,291,295,297	0.59
	6	19.00	58,85,106,121,125,140,145,196,213,274	1.16
	7	21.00	93,125,128	0.36
	8	23.00	77,121,132,160,182,367	0.70

表 E. 1 (续)

组别	序号	时间 min	离子 amu	驻留时间 s
第Ⅳ组	1	11.00	109,127,192	0.36
	2	13.00	88,93,109,125,145,301	0.70
	3	16.00	72,127,138,153,181,194,236,264,292	1.05
	4	18.00	93,125,173,109,268,296,136,121,230	0.70
	5	18.95	58,92,109,121,140,146,157,196,199,298,329,331	1.05
	6	20.00	125,376,378	0.36
	7	21.00	135,160,294	0.36
	8	23.00	157,169,185	0.36
	9	25.00	77,132,160	0.36

附录 F

(资料性附录)

70 种有机磷农药标准物质的气相色谱-质谱图(GC-MSD)

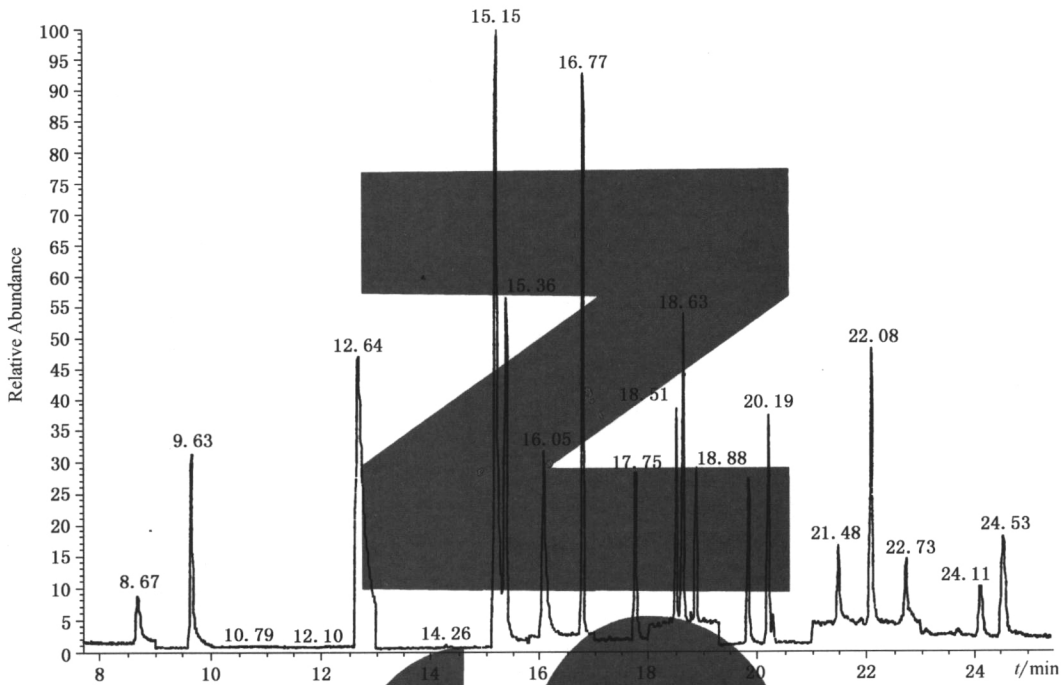


图 F.1 第 I 组 有机磷农药标准溶液气相色谱-质谱选择离子色谱图

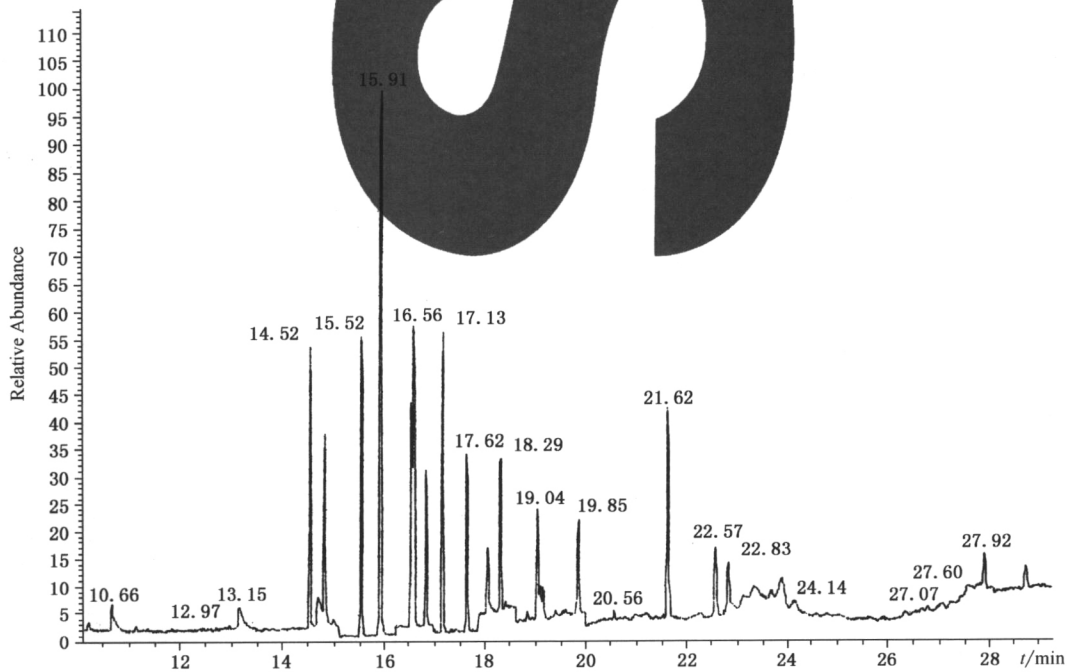


图 F.2 第 II 组 有机磷农药标准溶液气相色谱-质谱选择离子色谱图

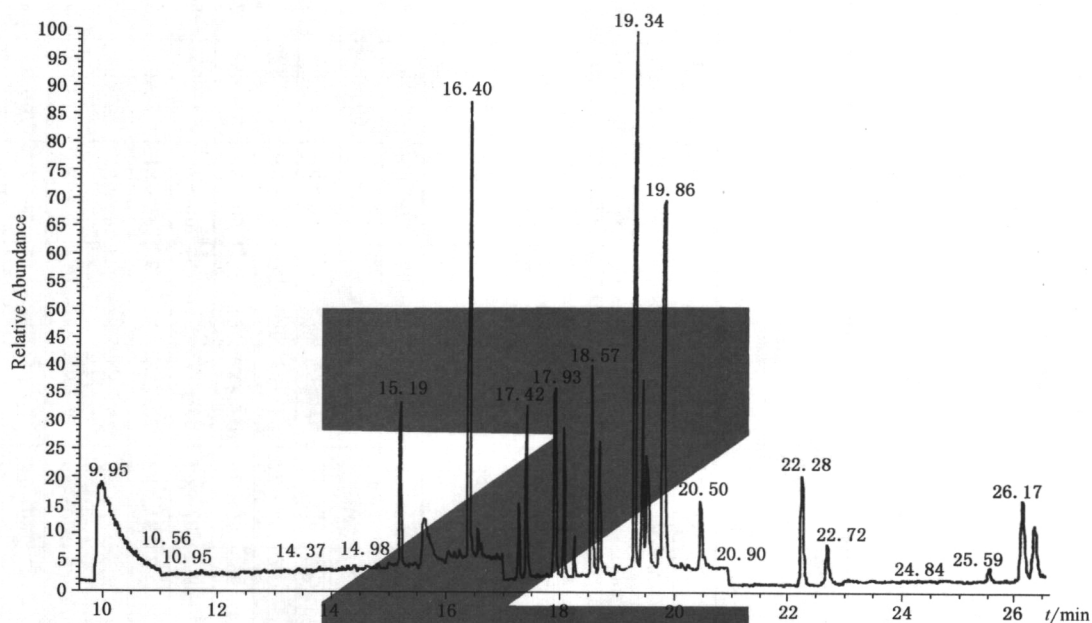


图 F.3 第Ⅲ组 有机磷农药标准溶液气相色谱-质谱选择离子色谱图

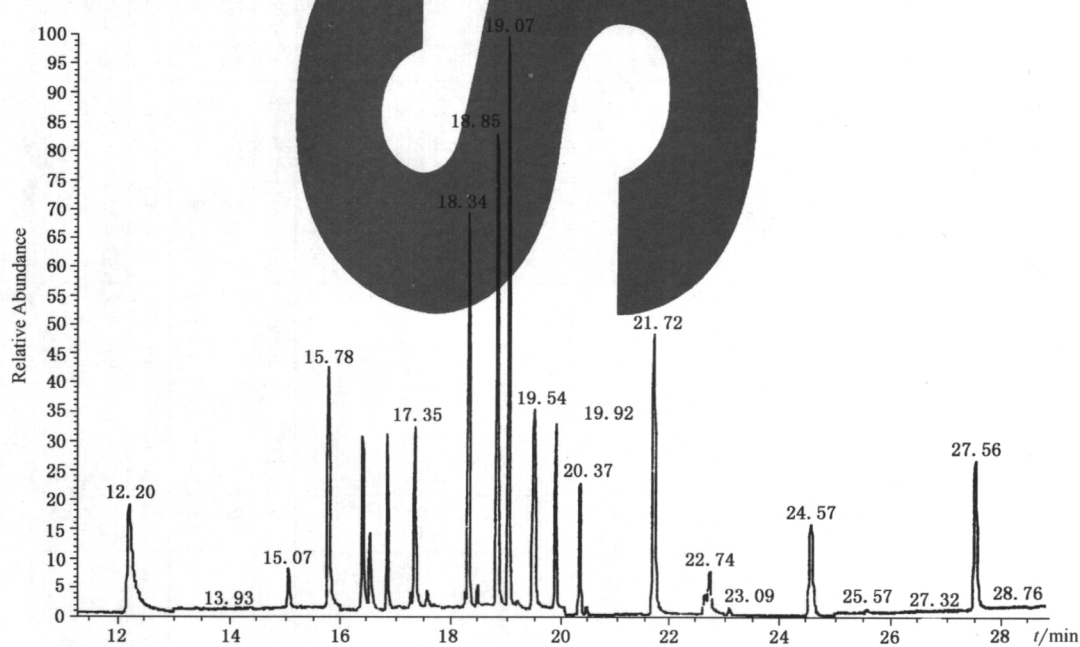


图 F.4 第Ⅳ组 有机磷农药标准溶液气相色谱-质谱选择离子色谱图

附录 G
(资料性附录)
70 种农药不同添加水平回收率数据

表 G.1 70 种农药不同添加水平回收率数据(n=10)

农药名称	添加水平 mg/kg	回收率范围 %												
		菠萝	苹果	荔枝	胡萝卜	马铃薯	茄子	菠菜	荷兰豆	鲜木耳	鲜蘑菇	鲜牛蒡	鲜香菇	大葱
敌敌畏	0.01~0.1	87~100	75~90	60~75	71~89	66~76	65~77	67~97	62~77	60~71	61~72	61~98	60~81	72~82
乙酰甲胺磷	0.01~0.1	78~95	81~89	67~80	83~97	70~81	67~81	84~108	64~85	68~77	66~73	60~87	67~78	68~83
硫线磷	0.01~0.1	81~97	80~92	64~77	66~85	73~78	69~91	85~99	65~79	63~75	71~88	61~78	60~86	70~76
百治磷	0.01~0.1	80~99	82~91	73~80	64~89	65~72	63~101	69~84	69~84	70~91	70~74	71~82	65~87	70~86
乙拌磷	0.01~0.1	79~90	85~96	68~75	76~112	65~78	65~79	69~94	60~87	60~111	71~76	63~77	75~92	78~83
乐果	0.01~0.1	82~104	83~98	73~80	64~88	69~78	66~84	69~95	65~84	66~120	78~87	70~83	60~89	80~85
甲基对硫磷	0.01~0.1	83~98	85~95	71~86	75~91	70~79	62~91	65~103	74~86	60~90	77~80	74~84	62~81	75~79
毒死蜱	0.01~0.1	80~97	88~99	70~82	73~90	72~81	71~98	75~88	68~81	63~80	87~92	70~83	63~82	88~99
啶啉磷	0.01~0.1	85~105	91~100	75~83	74~87	63~73	72~95	68~99	63~85	63~78	74~77	74~84	60~95	67~87
倍硫磷	0.01~0.1	87~97	80~91	72~84	72~94	65~78	75~92	64~108	65~78	61~74	79~87	70~81	65~84	76~88
丙虫硫磷	0.01~0.1	80~95	81~94	74~87	70~90	69~81	71~89	63~107	63~77	63~77	93~103	67~83	70~82	75~85
辛硫磷	0.01~0.1	90~107	65~82	60~89	78~96	68~80	61~82	64~95	65~76	102~120	61~69	60~77	64~96	76~87
灭菌磷	0.01~0.1	79~109	71~80	72~80	65~75	78~101	84~105	66~99	67~80	63~77	65~78	63~75	64~95	80~97
三硫磷	0.01~0.1	80~97	72~86	72~86	79~98	75~98	77~89	70~108	71~82	70~88	90~97	61~81	67~94	84~89
三唑磷	0.01~0.1	81~94	83~97	73~79	81~102	72~101	76~94	71~105	72~86	70~80	86~94	69~80	69~94	76~90
哒嗪硫磷	0.01~0.1	80~91	84~99	72~86	75~92	81~95	68~90	80~99	70~89	72~84	90~105	69~80	68~96	90~110
亚胺硫磷	0.01~0.1	84~112	70~97	72~87	85~115	88~98	62~84	79~103	69~83	73~87	86~93	68~78	70~85	67~89
敌百虫	0.01~0.1	77~82	90~105	60~75	63~98	65~73	61~99	64~75	63~74	61~83	61~102	60~71	80~96	77~90
灭线磷	0.005~0.1	75~85	88~104	60~77	71~83	63~78	64~108	66~89	65~79	60~75	87~104	60~80	60~84	78~97

表 G.1 (续)

农药名称	添加水平 mg/kg	回收率范围 %												
		菠萝	苹果	荔枝	胡萝卜	马铃薯	茄子	菠菜	荷兰豆	鲜木耳	鲜蘑菇	鲜牛蒡	鲜香菇	大葱
甲拌磷	0.01~0.1	74~84	84~97	60~75	62~74	65~74	63~97	63~85	63~75	61~74	80~87	65~79	65~87	69~98
氧化乐果	0.01~0.1	78~88	104~117	67~78	89~97	62~78	60~72	66~79	65~80	78~109	67~85	68~84	75~82	66~89
内吸磷	0.01~0.1	71~85	98~108	64~76	62~78	63~71	62~75	63~77	64~78	68~85	83~86	65~80	65~76	69~89
二嗪磷	0.01~0.1	94~109	62~77	68~95	71~88	65~78	65~77	64~78	63~79	69~86	85~93	69~89	65~86	78~89
地虫硫磷	0.01~0.1	77~89	82~97	67~77	74~86	66~82	66~88	63~75	64~76	72~96	86~94	63~81	60~74	79~87
异稻瘟净	0.01~0.1	74~91	84~90	65~77	71~82	70~85	64~89	60~79	76~84	71~99	89~103	69~93	83~90	70~75
氯唑磷	0.01~0.1	72~87	77~92	63~76	68~79	68~81	65~97	65~85	69~79	78~91	65~80	63~85	60~76	75~87
甲基毒死蜱	0.01~0.1	79~92	75~86	65~77	69~81	69~85	63~96	66~87	59~79	75~105	62~83	71~90	62~74	69~80
对氧磷	0.01~0.1	84~101	74~85	76~99	75~90	71~89	69~86	60~79	60~112	79~90	91~103	74~83	87~98	65~90
杀螟硫磷	0.01~0.1	97~102	71~84	75~84	80~98	66~81	69~92	63~78	60~115	69~85	76~87	71~81	78~90	74~89
溴硫磷	0.01~0.1	85~99	72~83	73~80	81~93	67~82	67~104	65~84	61~79	70~89	74~89	73~80	74~93	67~91
乙基溴硫磷	0.01~0.1	96~100	71~82	78~85	72~86	70~85	66~119	66~112	70~115	71~91	74~104	73~81	78~97	61~76
噻唑磷	0.01~0.1	98~108	75~87	77~85	76~89	71~90	73~112	63~82	70~92	70~93	94~102	74~85	94~106	80~90
丙溴磷	0.01~0.1	92~103	74~85	82~89	74~92	70~83	62~81	60~75	70~92	79~95	93~103	82~93	93~102	67~79
乙硫磷	0.01~0.1	79~92	75~88	76~85	71~89	68~79	63~99	61~84	80~108	71~93	94~105	72~81	97~108	67~90
敌瘟磷	0.01~0.1	90~105	77~89	77~81	73~88	69~85	60~76	60~75	77~111	73~94	100~104	76~83	95~108	78~90
吡啶硫磷	0.01~0.1	81~92	76~90	76~86	75~91	73~97	77~94	69~81	100~119	63~86	93~101	70~81	90~93	90~98
蝇毒磷	0.01~0.1	91~101	83~95	85~95	69~85	75~101	63~102	65~87	90~120	79~96	88~111	75~90	65~90	67~89
甲胺磷	0.01~0.1	77~88	73~81	70~88	63~77	72~93	74~97	63~79	63~89	60~73	64~85	74~87	73~82	67~90
治螟磷	0.01~0.1	79~93	80~87	60~73	61~78	80~92	88~104	70~84	60~79	61~75	84~104	70~80	63~80	77~80
特丁硫磷	0.005~0.1	65~80	85~91	64~79	62~99	66~78	84~118	70~105	101~120	66~77	70~82	70~88	60~81	85~90
久效磷	0.01~0.1	65~99	85~93	88~120	75~101	85~97	81~94	69~79	60~119	67~81	100~106	76~89	109~119	67~92
除线磷	0.01~0.1	85~99	83~90	84~107	70~81	71~88	88~101	79~87	75~97	63~78	61~82	66~84	70~74	68~89
皮蝇磷	0.01~0.1	83~92	88~93	79~110	72~98	73~89	82~89	69~88	64~75	68~79	69~75	73~86	72~76	65~78

表 G.1 (续)

农药名称	添加水平 mg/kg	回收率范围 %												
		菠萝	苹果	荔枝	胡萝卜	马铃薯	茄子	菠菜	荷兰豆	鲜木耳	鲜蘑菇	鲜牛蒡	鲜香菇	大葱
甲基嘧啶磷	0.01~0.1	89~97	81~95	77~98	87~110	75~98	76~109	70~102	63~78	74~91	82~93	75~89	70~79	78~90
对硫磷	0.01~0.1	87~94	82~99	75~85	78~96	78~101	81~103	63~89	60~78	67~79	89~104	74~88	80~89	65~78
甲基毒虫畏	0.01~0.1	92~103	90~100	85~90	91~108	82~95	77~98	64~79	63~83	65~80	100~104	70~87	87~112	80~98
异柳磷	0.01~0.1	75~84	80~89	70~80	65~81	75~93	71~92	75~83	60~75	64~81	101~106	70~82	86~95	77~87
稻丰散	0.01~0.1	81~91	81~92	69~81	63~82	85~110	72~106	73~86	60~82	64~76	74~94	74~89	71~83	67~90
杀扑磷	0.01~0.1	82~99	82~91	79~87	70~83	82~112	73~99	74~87	61~85	60~75	91~106	74~87	84~99	89~97
甲基硫环磷	0.01~0.1	80~90	80~87	80~87	71~86	82~101	71~92	70~89	67~95	63~77	104~118	61~73	90~102	70~90
伐灭磷	0.01~0.1	82~96	87~98	82~85	79~93	83~98	74~99	74~92	62~80	63~84	101~123	80~95	96~100	66~88
伏杀硫磷	0.01~0.1	83~95	82~94	83~97	78~104	79~95	73~95	70~90	60~105	64~78	93~111	78~86	101~111	69~97
甲基谷硫磷	0.01~0.1	79~84	70~81	78~87	74~85	78~98	97~107	71~99	61~120	71~88	91~98	61~74	96~107	87~98
二溴磷	0.01~0.1	104~120	83~96	68~79	63~86	75~93	70~92	63~85	80~88	97~120	101~107	88~112	87~97	78~94
速灭磷	0.01~0.1	64~70	85~99	60~77	62~69	82~98	76~92	64~90	65~105	60~71	64~74	79~87	81~86	78~89
甲基乙拌磷	0.01~0.1	65~75	75~90	92~104	61~83	83~77	77~82	60~75	60~89	60~70	61~89	60~83	70~85	68~88
巴胺磷	0.01~0.1	70~79	73~87	66~79	66~79	80~91	80~92	73~85	61~115	63~75	85~93	75~106	91~98	64~88
乙啶硫磷	0.01~0.1	65~80	78~90	99~109	62~76	88~93	72~93	64~86	69~107	63~74	77~97	75~87	73~85	65~78
磷胺	0.01~0.1	60~75	83~99	80~120	69~80	73~90	80~120	83~112	69~110	78~92	71~79	83~91	98~112	63~70
壤虫磷	0.01~0.1	69~78	80~89	80~93	75~86	88~101	90~110	85~98	83~111	71~80	86~91	80~90	83~96	79~100
马拉硫磷	0.01~0.1	71~86	79~94	80~93	74~86	80~99	82~94	79~89	66~120	75~84	71~80	79~93	93~103	69~89
甲基异柳磷	0.01~0.1	70~85	80~91	77~89	71~90	79~102	77~95	70~97	61~104	76~85	88~96	77~92	97~110	79~97
水胺硫磷	0.01~0.1	62~77	89~101	63~83	70~86	80~98	73~102	67~97	60~104	69~78	90~101	76~89	103~113	69~90
啶硫磷	0.01~0.1	64~80	80~93	75~85	73~90	86~103	75~110	70~108	61~96	68~78	87~90	76~88	91~99	75~87
杀虫畏	0.01~0.1	63~78	101~115	74~84	77~97	92~115	80~99	69~85	85~106	72~85	67~82	83~98	106~111	70~89
碘硫磷	0.01~0.1	79~85	65~79	76~92	76~91	84~103	79~100	68~88	70~101	76~80	70~84	81~95	103~113	67~89
硫环磷	0.01~0.1	65~78	60~75	82~91	77~93	83~98	82~104	74~100	60~112	77~85	101~103	60~74	91~98	90~98
威菌磷	0.01~0.1	80~95	63~78	72~81	65~78	81~95	69~94	60~75	60~103	70~80	96~102	60~71	106~122	80~85
苯硫磷	0.01~0.1	70~85	78~90	81~90	70~79	90~104	87~101	68~94	61~104	74~86	92~97	83~91	96~107	67~79
乙基谷硫磷	0.01~0.1	60~74	75~89	76~93	85~112	95~112	98~115	70~95	64~101	81~92	100~110	66~77	107~114	69~80

Foreword

This standard was drafted in accordance with the GB/T 1.1—2009.

This standard substitutes for the following standards as: SN/T 0148—1992《Method for determination of chlorpyrifos-methyl residues in fruit for export》、SN/T 0153—1992《Method for determination of malathion residue in fruit for export》、SN/T 0154—1992《Method for inspection of pirimiphos methyl residue in fruit for export》、SN/T 0155—1992《Method for determination of demeton residue in fruit for export》、SN/T 0161—1992《Method for determination of parathion methyl residue in fruit for export》、SN/T 0189—1992《Method for determination of carbophenothion residues in fruits for export》、SN 0196—1993《Method for determination of optunal residues in fresh vegetables for export》、SN 0278—1993《Method for determination of methamidophos residues in fresh vegetables for export》、SN 0288—1993《Method for the determination of fenthion residues in fruits for export》、SN 0291—1993《Method for the determination of dimethoate and parathion-methyl residues in fruits for export》、SN 0334—1995《Methods for the determination of 22 organophosphorus pesticide multi-residues in fruits and vegetables for export》、SN 0342—1995《Method for the determination of azinphos-methyl and azinphos-ethyl residues in cereals for export》、SN 0344—1995《Method for the determination of methidathion residues in fruits for export》、SN 0354—1995《Method for the determination of phosalone residues in fruits for export》 and SN 0599—1996《Method for the determination of mevinphos residues in fruits for export》.

The changes mainly include:

Testing items were increased to 70 pesticides;

To add method validation;

To delete the sampling part.

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 Xiamen Entry-Exit Inspection and Quarantine Bureau, Guangdong Entry-Exit Inspection and Quarantine Bureau, Hunan Entry-Exit Inspection and Quarantine Bureau and Jilin Entry-Exit Inspection and Quarantine Bureau of the People's Republic of China.

This main drafter of this standard is Zhou Yu, Xu Dunming, Zhang Zhigang, Liu Yanying, Du Fengjun, Cai Chun, Huang Zhiqiang, Mu Jun and Zhang Xianghua.

This standard replaced the previous version of the release of the standard as follows:

SN/T 0148—2011

—SN 0148—1992;

—SN 0153—1992;

—SN 0154—1992;

—SN 0155—1992;

—SN 0161—1992;

—SN 0189—1993;

—SN 0196—1993;

—SN 0278—1993;

—SN 0288—1993;

—SN 0291—1993;

—SN 0334—1995;

—SN 0342—1995;

—SN 0344—1995;

—SN 0354—1995;

—SN 0599—1996.

Determination of organophosphorus residues in fruits and vegetables for import and export— GC-FPD and GC-MS methods

1 Scope

This standard specifies the determination and confirmation of 70 organophosphorous pesticide residues by gas chromatography-FPD and gas chromatography-mass spectrometry in fruits and vegetables for import and export, respectively.

This standard is applicable to the determination and confirmation of residue content of 70 organophosphorous pesticides in pineapple, apple, lichee, carrot, potato, eggplant, spinach, pea, agaric, mushroom, burdock, Pasania fungus, scallion for import and export.

2 Principle

The test samples are extracted with acetonitrile. The extract is cleaned up by passing through on ENVI-Carb II /PSA SPE cartridge. The elutes solution is evaporated and made up to a definite volume. Determination and confirmation are made by GC-FPD and GC-MS, using external standard method.

3 Reagents and materials

Unless otherwise specified, all the reagents used should be analytically pure, “water” is distilled water.

3.1 Acetonitrile: Pesticide grade.

3.2 Acetone: Pesticide grade.

3.3 Toluene: Pesticide grade.

3.4 Ethyl acetate: Pesticide grade.

3.5 Acetone + Toluene (65 + 35, V + V): Volume 65 mL acetone into 35 mL toluene, and mix them.

3.6 Anhydrous magnesium sulfate: Ignite at 550 °C for 4 h, and keep in a tightly closed container.

3.7 Sodium chloride: Ignite at 140 °C for 4 h, and keep in a tightly closed container.

3.8 ENVI-Carb II /PSA SPE cartridge¹⁾: 500 mg/500 mg/6 mL (Sigma-Aldrich/Supelco).

3.9 Organophosphorous pesticides standard: Purity $\geq 95\%$ (Annex A).

3.10 Standard solution:

3.10.1 Standard stock solution: Accurately weigh an adequate amount of Organophosphorous pesticides standard (see annex A) and dissolve in a small volume of acetone. Dilute with ethyl acetate to form a standard stock solution of 100 mg/mL in concentration.

3.10.2 Mix standard stock solution: To mix 70 organophosphorous pesticides in 4 groups (annex B) to form a mix standard stock solution in ethyl acetate.

3.10.3 Standard working solution: To dilute the standard stock solution with ethyl acetate to the required concentration as the standard working solution.

4 Apparatus and equipment

4.1 GC; with FPD detector.

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

4.3 Electronic balance: accurate to 0.1 mg and 0.01 g.

4.4 Volumetric flask: 100 mL and 10 mL.

4.5 Pipette: 20 μ L~200 μ L and 100 μ L~1 000 μ L.

4.6 Concentrate bottle: 50 mL, 15 mL.

4.7 10 mL glass tube.

4.8 Whirlpool mixer.

4.9 Centrifuge: 4 000 r/min.

4.10 Termovap sample concentrator.

1) Non-commercial statement: Equipment and its type involved in the standard method is only for reference and not related to any commercial aim, and the analysts are encouraged to use equipments of corporation or different type.

4.11 Homogenizer.

4.12 Tissue blender.

5 Preparation and storage of test sample

Take approximately 500 g of representative sample. Collect the edible pieces. Crush with a crusher. Mix thoroughly. Put in clean containers. Seal and label them. The test samples should be frozen and stored below $-18\text{ }^{\circ}\text{C}$. While sampling and preparing sample, please avoid contamination or any factors that may change residue content.

6 Extraction and Clean up

6.1 Extraction and Clean up

Take 10 g of the processed sample in a 50 mL centrifuge tube, spike with pesticide standards. Add 10 mL acetonitrile and Homogenize for 2 min.

Add anhydrous magnesium sulfate (4 g) and sodium chloride (1 g) and vortex immediately. Shake for additional 2 min.

Centrifuge for 5 min at highest rotor speed 4 000 r/min.

Take the upper acetonitrile layer and mix with 1 g of anhydrous magnesium sulfate.

Centrifuge for 1 min at highest rotor speed 4 000 r/min.

Take an aliquot (5 mL) of the resulting extract and evaporate it down to 1 mL for SPE clean-up.

6.2 Clean up

Condition Supelclean ENVI-Carb II /PSA 500 mg/500 mg/6 mL SPE cartridge with 5 mL acetone; toluene. Load the sample extract.

Elute the sample 10 mL of acetone; toluene 65 : 35.

Evaporate the collection 0.5 mL and adjust the volume to 1.0 mL total volume with ethyl acetate for final analysis.

6.3 Determination

6.3.1 Instrument operating condition

6.3.1.1 GC operating condition:

- a) Chromatographic column: DB-17 (30 m × 0.53 mm × 0.25 μm) or equivalent;
- b) Column temperature: 100 °C keep 0.5 min, 15 °C/min to 250 °C, and keep 20 min;
- c) Carrier gas: N₂, purity ≥ 99.999%, flow rate: 10 mL/min;
- d) Injection port temperature: 200 °C;
- e) Injection volume: 2 μL;
- f) Injection mode: Splitless;
- g) Detector temperature: 250 °C.

6.3.1.2 GC-MS operating condition:

- a) Chromatographic column: 30 m × 0.25 mm (i. d.), 0.25 μm film thickness, DB-5 MS, silica capillary column or equivalent;
- b) Column temperature: 60 °C (6 min) $\xrightarrow{10\text{ }^{\circ}\text{C/min}}$ 250 °C $\xrightarrow{15\text{ }^{\circ}\text{C/min}}$ 280 °C (6 min);
- c) Carrier gas: Helium, purity ≥ 99.999%;
- d) Injection port temperature: 220 °C;
- e) Interface temperature: 270 °C;
- f) Injection volume: 1 μL;
- g) Injection mode: Splitless, purge on after 1.0 min;
- h) Electron ionization mode: EI, 70 eV;
- i) Ion source temperature: 200 °C;
- j) Transfer temperature: 250 °C;

k) Selected monitoring ion (m/z): see Annex D and Annex E.

6.3.2 GC determination

According to the approximate concentration of analyte in sample solution, select the standard working solution with similar responses to that of sample solution. The responses of analyte in the standard working solution and the sample solution should be within the linear range of the instrument detection. Under the above GC-FPD operating conditions, the retention time of analytes is listed in annex B and the chromatogram of standard working solution is listed in Annex C, quantified by external standard method.

6.3.3 GC-MS 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 standard working solution should be randomly injected in-between the injections of the sample solution of equal volume. 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 D. Under the above GC-MS condition, the retention time of 70 organophosphorous pesticides for GC-MS chromatogram (TIC) of the standard, see annex F.

Full scan and SIM: The relative intensities of the detected ions, expressed as a percentage of the intensity of the most intense ion or transition, shall correspond to those of the calibration standard, either from calibration standard solutions or from spiked samples, at comparable concentrations, measured under the same conditions, within the following tolerances:

Table 1—Maximum permitted tolerances for relative ion intensities using a range of mass spectrometric techniques

Relative intensity (base peak)/%	>50	>20~50	>10~20	≤10
Maximum permitted tolerances/%	± 10	± 15	± 20	± 50

6.3.4 Blank test

According to 6.1~6.2 to perform the blank testing.

7 Calculation and expression of the result

Calculate the content of per organophosphorous pesticides residues in the test sample by GC-MS data

processor or according to the 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, $\mu\text{g/mL}$;

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 determinations of this method for organophosphorous pesticides residues in foodstuffs for import and export see annex B for GC-FPD and annex D for GC-MSD.

8.2 Recovery

With spiked concentrations of 0.01 mg/kg~0.1 mg/kg in various matrixes, the recovery for organophosphorous pesticides residues in foodstuffs for import and export see annex G.

Annex A
(Normative)

Chemical information of 70 organophosphorous pesticides

Table A.1 Chemical information of 70 organophosphorous pesticides

Number	Compound	Molecular formula	Molecular weight	CAS No.	Purity $\geq$
1	dichlorvos	$C_4H_7Cl_2O_4P$	220.98	62-73-7	97.0%
2	acephate	$C_8H_{10}NO_3PS$	183.17	30560-19-1	97.5%
3	cadusafos	$C_{10}H_{23}O_3PS_2$	270.39	95465-99-9	99.0%
4	dicrotophos	$C_8H_{16}NO_6P$	237.22	141-66-2	97.5%
5	disulfoton	$C_8H_{19}O_2PS_3$	274.4	298-04-4	95.3%
6	dimethoate	$C_5H_{12}NO_4PS_2$	229.28	60-51-5	98.0%
7	parathion-methyl	$C_8H_{10}NO_3PS$	263.21	298-00-0	98.5%
8	chloropyrifos	$C_9H_{11}Cl_3NO_3PS$	350.59	2921-88-2	99.5%
9	pirimiphos-ethyl	$C_{13}H_{24}N_3O_3PS$	333.39	23505-41-1	98.5%
10	fenthion	$C_{10}H_{18}O_3PS_2$	278.33	55-38-9	97.0%
11	propaphos	$C_{11}H_{15}Cl_2O_2PS_2$	345.25	34643-46-4	93.5%
12	phoxim	$C_{12}H_{15}NO_3PS$	298.3	14816-18-3	98.5%
13	ditalimfos	$C_{12}H_{14}NO_4PS$	299.28	5131-24-8	99.5%
14	carbofenthion	$C_{11}H_{16}ClO_2PS_3$	342.87	786-19-6	95.0%
15	triazophos	$C_{12}H_{16}N_3O_3PS$	313.31	24017-47-8	81.0%
16	pyridaphenthion	$C_{14}H_{17}N_2O_4PS$	340.33	119-12-0	98.0%
17	phosmet	$C_{11}H_{12}NO_4PS_2$	317.32	732-11-6	98.5%
18	trichlorphon	$C_4H_6Cl_3O_3P$	257.44	52-68-6	97.0%
19	ethoprophos	$C_9H_{19}O_3PS_2$	242.34	13194-48-4	93.0%
20	phorate	$C_7H_{17}O_2PS_3$	260.38	298-02-2	94.5%
21	omethoate	$C_5H_{12}NO_4PS$	213.19	1113-02-6	97.0%
22	demeton	$C_8H_{19}O_3PS_2$	258.34	8065-48-3	98.0%
23	diazinon	$C_{12}H_{22}N_2O_3PS$	304	333-41-5	96.0%
24	dyfonate	$C_{10}H_{15}OPS_2$	246.33	994-22-9	95.0%
25	iprobefos	$C_{13}H_{21}O_3PS$	288.34	26087-47-8	94.5%
26	isazofos	$C_9H_{17}ClN_3O_3PS$	313.74	42509-80-8	95.0%
27	chlorpyrifos methyl	$C_7H_7Cl_3NO_3PS$	322.53	5598-13-0	98.5%
28	paraoxon	$C_{10}H_{14}NO_6P$	275.2	311-45-5	99.0%
29	fenitrothion	$C_9H_{12}NO_5PS$	277.23	122-14-5	97.5%
30	bromophos methyl	$C_8H_8BrCl_2O_3PS$	366	2104-96-3	99.5%

Table A.1 (continued)

Number	Compound	Molecular formula	Molecular weight	CAS No.	Purity $\geq$
31	bromophos ethyl	$C_{10}H_{12}BrCl_2O_3PS$	394.05	4824-78-6	98.5%
32	fosthiazate	$C_9H_{18}NO_3PS_2$	283.35	98886-44-3	96.5%
33	profenofos	$C_{11}H_{16}BrClO_3PS$	373.63	41198-08-7	95.0%
34	ethion	$C_9H_{22}O_4P_2S_4$	384.48	563-12-2	98.8%
35	edifenphos	$C_{14}H_{15}O_2PS_2$	310.37	17109-49-8	93.5%
36	pyraclofos	$C_{14}H_{18}ClN_2O_3PS$	360.8	77458-01-6	97.0%
37	coumaphos	$C_{14}H_{16}ClO_5PS$	362.77	56-72-4	97.5%
38	methamidophos	$C_2H_8NO_2PS$	141.13	10265-92-6	98.5%
39	sulfotep	$C_8H_{20}O_5P_2S_2$	322.32	3689-24-5	94.0%
40	terbufos	$C_9H_{21}O_2PS_3$	288.43	13071-79-9	93.0%
41	monocrotophos	$C_7H_{14}NO_5P$	223.16	6923-22-4	97.5%
42	dichlofenthion	$C_{10}H_{13}Cl_2O_3PS$	315.15	97-17-6	98.5%
43	fenchlorphos	$C_8H_8Cl_3O_3PS$	321.55	299-84-3	98.0%
44	pirimiphos-methyl	$C_{11}H_{20}N_3O_3PS$	305.33	29232-93-7	99.0%
45	parathion	$C_{10}H_{14}NO_5PS$	291.26	56-38-2	99.0%
46	dimethylvinphos	$C_{10}H_{10}Cl_3O_4P$	331.52	71363-52-5	99.0%
47	isophenphos	$C_{15}H_{24}NO_4PS$	345.39	25311-71-1	91.0%
48	phenthoate	$C_{12}H_{17}O_4PS_2$	320.36	2597-03-7	96.6%
49	methidathion	$C_6H_{11}N_2O_4PS_3$	302.33	950-37-8	98.5%
50	phosfolan methyl	$C_6H_{10}NO_8PS_2$	227.25	14731-55-2	97.5%
51	famphur	$C_{10}H_{16}NO_5PS_2$	325.34	52-85-7	99.0%
52	phosalone	$C_{12}H_{16}ClNO_4PS_2$	367.81	2310-17-0	98.5%
53	azinphos methyl	$C_{10}H_{12}N_3O_3PS_2$	317.32	86-50-0	99.0%
54	dibrom	$C_4H_7Br_2Cl_2O_4P$	380.78	300-76-5	98.0%
55	phosdrin	$C_7H_{13}O_6P$	224.15	26718-65-0	92.0%
56	thiometon	$C_6H_{15}O_2PS_3$	246.35	640-15-3	92.0%
57	propetamphos	$C_{10}H_{20}NO_4PS$	281.31	31218-83-4	94.0%
58	etrimfos	$C_{10}H_{17}N_2O_4PS$	292.29	38260-54-7	96.5%
59	phosphamidon	$C_{10}H_{19}ClNO_5P$	299.69	13171-21-6	95.5%
60	trichloronate	$C_{10}H_{12}Cl_3O_2PS$	333.6	327-98-0	96.0%
61	malathion	$C_{10}H_{19}O_6PS_2$	330.36	121-75-5	99.0%
62	isofenphos-methyl	$C_{14}H_{22}NO_4PS$	331.37	99675-03-3	96.0%
63	isocarbophos	$C_{11}H_{16}NO_4PS$	289.29	24353-61-5	95.0%
64	quinalphos	$C_{12}H_{15}N_2O_3PS$	298.3	13593-03-8	96.0%
65	tetrachlorvinphose	$C_{10}H_9Cl_4O_4P$	365.96	22350-76-1	99.5%

Table A. 1 (continued)

Number	Compound	Molecular formula	Molecular weight	CAS No.	Purity $\geq$
66	iodofenphos	$C_8H_8Cl_2IO_3PS$	413	18181-70-9	97.5%
67	phosfolan	$C_7H_{14}NO_3PS_2$	255.29	947-02-4	97.5%
68	triamiphos	$C_{12}H_{19}N_6OP$	294.29	1031-47-6	96.3%
69	EPN	$C_{14}H_{14}NO_4PS$	323.3	2104-64-5	99.0%
70	azinphos ethyl	$C_{12}H_{16}N_3O_3PS_2$	345.38	2642-71-9	97.7%

Annex B (Informative)

Reference data of 70 organophosphorous pesticides by GC-FPD

Table B. 1—Reference data of 70 organophosphorous pesticides by GC-FPD

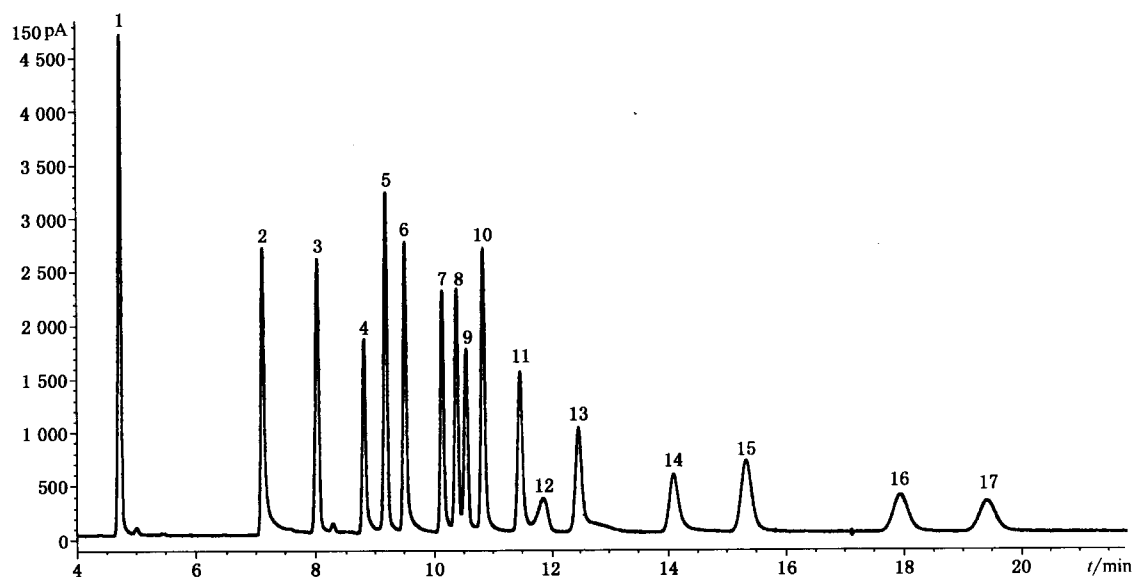
No	Compound	Time min	Limit mg/kg	Group	No	Compound	Time min	Limit mg/kg	Group
1	dichlorvos	4.733	0.01	I	26	isazofos	9.545	0.01	II
2	acephate	7.139	0.01	I	27	chlorpyrifos methyl	9.980	0.01	II
3	cadusafos	8.043	0.01	I	28	paraoxon	10.157	0.01	II
4	dicrotophos	8.821	0.01	I	29	fenitrothion	10.475	0.01	II
5	disulfoton	9.196	0.01	I	30	bromophos methyl	10.824	0.01	II
6	dimethoate	9.519	0.01	I	31	bromophos ethyl	10.142	0.01	II
7	parathion-methyl	10.155	0.01	I	32	fosthiazate	11.636	0.01	II
8	chloropyrifos	10.397	0.01	I	33	profenofos	12.038	0.01	II
9	pirimiphos-ethyl	10.533	0.01	I	34	ethion	13.257	0.01	II
10	fenthion	10.843	0.01	I	35	edifenphos	15.878	0.01	II
11	propaphos	11.483	0.01	I	36	pyraclofos	21.968	0.01	II
12	phoxim	11.878	0.01	I	37	coumaphos	25.171	0.01	II
13	ditalimfos	12.493	0.01	I	38	methamidophos	5.531	0.01	III
14	carbofenthion	14.126	0.01	I	39	sulfotep	8.288	0.01	III
15	triazophos	15.322	0.01	I	40	terbufos	8.740	0.005	III
16	pyridaphenthion	17.938	0.01	I	41	monocrotophos	9.095	0.01	III
17	phosmet	19.424	0.01	I	42	dichlofenthion	9.481	0.01	III
18	trichlorphon	5.328	0.01	II	43	fenchlorphos	9.988	0.01	III
19	ethoprophos	7.883	0.005	II	44	pirimiphos-methyl	10.204	0.01	III
20	phorate	8.359	0.01	II	45	parathion	10.481	0.01	III
21	omethoate	8.570	0.01	II	46	dimethylvinphos	10.817	0.01	III
22	demeton	7.595/8.732	0.01	II	47	isophenphos	10.927	0.01	III
23	diazinon	8.886	0.01	II	48	phenthoate	11.614	0.01	III
24	dyfonate	9.211	0.01	II	49	methidathion	12.335	0.01	III
25	iprobenfos	9.436	0.01	II	50	phosfolan methyl	12.876	0.01	III

Table B. 1 (continued)

No	Compound	Time min	Limit mg/kg	Group	No	Compound	Time min	Limit mg/kg	Group
51	famphur	15.375	0.01	Ⅲ	61	malathion	10.430	0.01	Ⅳ
52	phosalone	18.837	0.01	Ⅲ	62	isofenphos-methyl	10.836	0.01	Ⅳ
53	azinphos methyl	22.955	0.01	Ⅲ	63	isocarbophos	11.096	0.01	Ⅳ
54	dibrom	4.714	0.01	Ⅳ	64	quinalphos	11.364	0.01	Ⅳ
55	phosdrin	6.460	0.01	Ⅳ	65	tetrachlorvinphos	11.817	0.01	Ⅳ
56	thiomenton	8.750	0.01	Ⅳ	66	iodofenphos	12.251	0.01	Ⅳ
57	propetamphos	8.853	0.01	Ⅳ	67	phosfolan	13.325	0.01	Ⅳ
58	etrimfos	9.228	0.01	Ⅳ	68	triamphos	14.703	0.01	Ⅳ
59	phosphamidon	9.483/10.006	0.01	Ⅳ	69	EPN	16.978	0.01	Ⅳ
60	trichloronate	10.285	0.01	Ⅳ	70	azinphos ethyl	24.363	0.01	Ⅳ

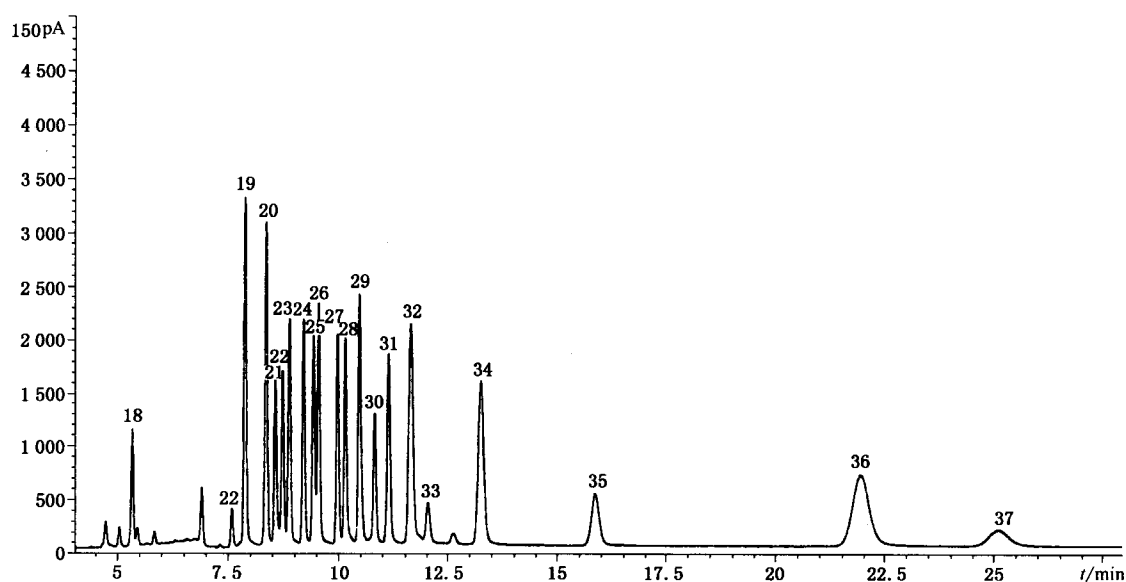
Annex C
(Informative)

Gas chromatogram of 70 organophosphorous pesticides by GC-FPD



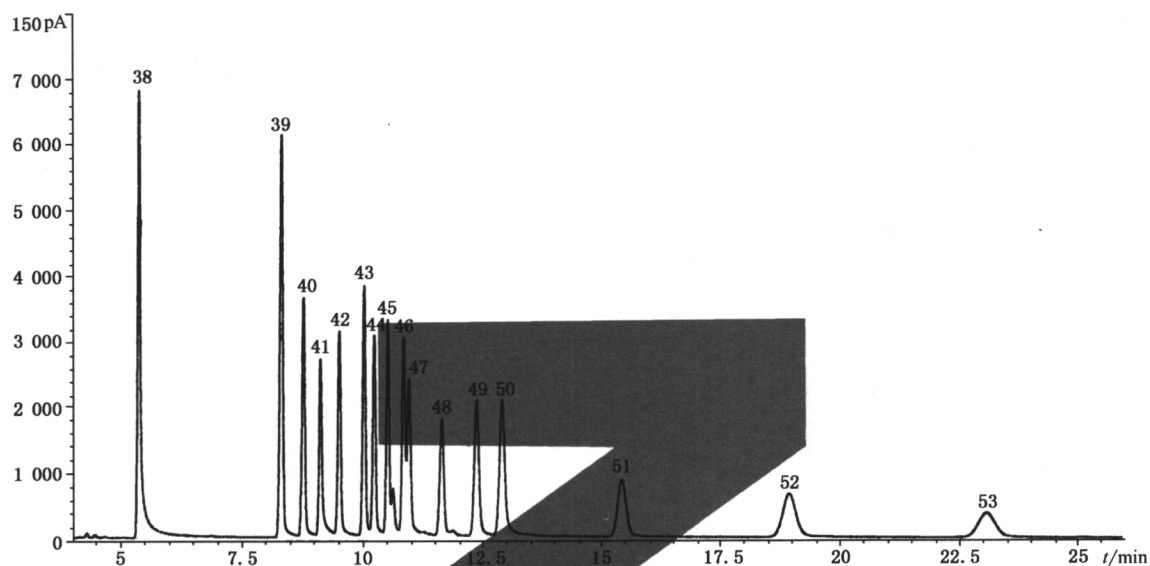
- 1 —Dichlorvos;
- 2 —Acephate;
- 3 —Cadusafos;
- 4 —Dicrotophos;
- 5 —Disulfoton;
- 6 —Dimethoate;
- 7 —Parathion-methyl;
- 8 —Dichlorvos;
- 9 —Pirimiphos-ethyl;
- 10 —Fenthion;
- 11 —Propaphos;
- 12 —Phoxim;
- 13 —Ditalimfos;
- 14 —Carbofenthion;
- 15 —Triazophos;
- 16 —Pyridaphenthion;
- 17 —Phosmet.

Figure C. 1—Gas chromatogram of Group I or ganophosphrous pesticides by GC-FPD



- 18 —Trichlorphon;
- 19 —Ethoprophos;
- 20 —Phorate;
- 21 —Omethoate;
- 22 —Demeton;
- 23 —Diazinon;
- 24 —Dyfonate;
- 25 —Iprobenfos;
- 26 —Isazofos;
- 27 —Chlorpyrifos methyl;
- 28 —Paraoxon;
- 29 —Fenitrothion;
- 30 —Bromophos methyl;
- 31 —Bromophos ethyl;
- 32 —Fosthiazate;
- 33 —Profenofos;
- 34 —Ethion;
- 35 —Edifenphos;
- 36 —Pyraclofos;
- 37 —Coumaphos.

Figure C. 2—Gas chromatogram of Group II or ganophosphrous pesticides by GC-FPD



- 38 — Methamidophos;
- 39 — Sulfotep;
- 40 — Terbufos;
- 41 — Monocrotophos;
- 42 — Dichlofenthion;
- 43 — Fenchlorphos;
- 44 — Pirimiphos-methyl;
- 45 — Parathion;
- 46 — dimethylvinphos;
- 47 — Isophenphos;
- 48 — Phenthoate;
- 49 — Methidathion;
- 50 — Phosfolan methyl;
- 51 — Famphur;
- 52 — Phosalone;
- 53 — Azinphos methyl.

Figure C. 3—Gas chromatogram of Group III or ganophosphrous pesticides by GC-FPD

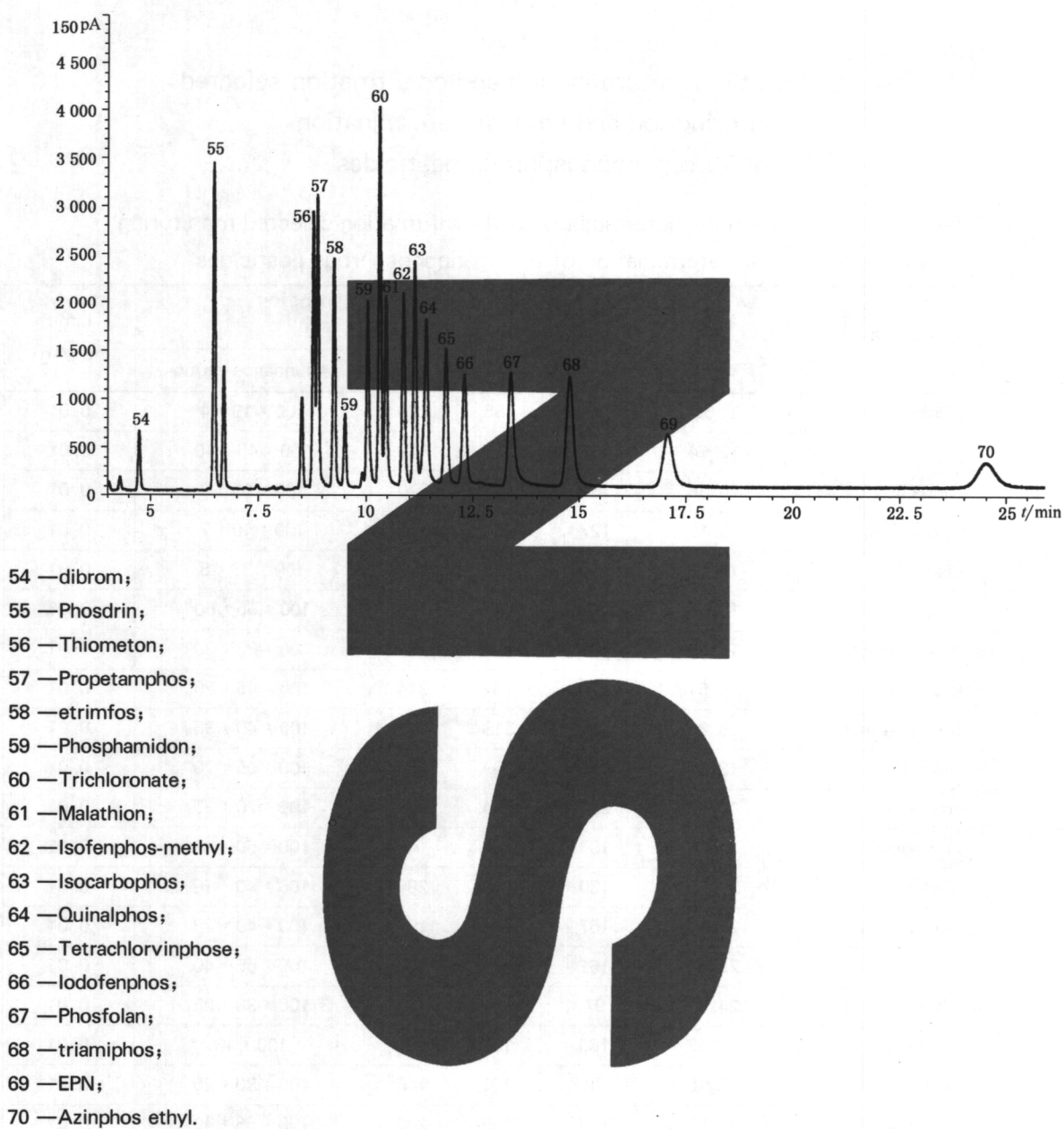


Figure C. 4—Gas chromatogram of Group IV or ganophosphrous pesticides by GC-FPD

Annex D

(Informative)

The retention time, determination and confirmation selected monitoring ion and limit of determination of 70 organophosphorous pesticides

Table D. 1—Retention time, determination and confirmation selected monitoring
ion and limit of determination of 70 organophosphorous pesticides

No	Compound	Time min	Characteristic fragment ion amu				Limit mg/kg
			Confirmation		Abundance ration		
1	dichlorvos	9. 63	109 *	185	220	100 : 19 : 4	0. 01
2	acephate	12. 64	136 *	94	142	100 : 45 : 10	0. 01
3	cadusafos	15. 36	159 *	127	270	100 : 65 : 9	0. 01
4	dicrotophos	15. 15	127 *	193	237	100 : 10 : 7	0. 01
5	disulfoton	16. 77	88 *	89	142	100 : 35 : 8	0. 01
6	dimethoate	16. 05	87 *	93	125	100 : 65 : 50	0. 01
7	parathion-methyl	17. 75	109 *	125	263	100 : 82 : 30	0. 01
8	chloropyriphos	18. 51	97 *	199	314	100 : 45 : 20	0. 01
9	pirimiphos-ethyl	18. 88	168 *	318	333	100 : 40 : 35	0. 01
10	fenthion	18. 63	125 *	109	278	100 : 95 : 70	0. 01
11	propaphos	19. 83	220 *	304	262	100 : 70 : 35	0. 01
12	phoxim	8. 67	103 *	130	77	100 : 50 : 42	0. 01
13	ditalimfos	20. 19	130 *	148	299	100 : 40 : 18	0. 01
14	carbofenothion	21. 48	157 *	342	199	100 : 49 : 28	0. 01
15	triazophos	22. 08	161 *	162	172	100 : 55 : 40	0. 01
16	pyridaphenthion	24. 11	97 *	199	340	100 : 38 : 25	0. 01
17	phosmet	24. 17	160 *	161	—	100 : 18	0. 01
18	trichlorphon	13. 15	79 *	109	145	100 : 80 : 25	0. 01
19	ethoprophos	14. 81	158 *	139	200	100 : 55 : 40	0. 01
20	phorate	15. 52	75 *	121	260	100 : 25 : 5	0. 01
21	omethoate	14. 47	110 *	156	79	100 : 80 : 79	0. 01
22	demeton	14. 52/15. 91	88 *	89	171	100 : 70 : 30	0. 01
23	diazinon	16. 52	137 *	179	304	100 : 95 : 30	0. 01
24	dyfonate	16. 56	109 *	137	246	100 : 75 : 50	0. 01
25	iprobefos	17. 13	91 *	204	288	100 : 45 : 7	0. 01
26	isazofos	16. 83	161 *	119	257	100 : 87 : 25	0. 01
27	chlorpyrifos methyl	17. 62	125 *	286	288	100 : 86 : 75	0. 01
28	paraoxon	18. 04	109 *	81	275	100 : 63 : 22	0. 01

Table D.1 (continued)

No	Compound	Time min	Characteristic fragment ion amu				Limit mg/kg
			Confirmation		Abundance ration		
29	fenitrothion	18. 29	125 *	109	277	100 : 87 : 55	0. 01
30	bromophos methyl	19. 04	125 *	329	331	100 : 67 : 90	0. 01
31	bromophos ethyl	19. 85	97 *	302	358	100 : 98 : 66	0. 01
32	fosthiazate	19. 09	195 *	97	283	100 : 80 : 25	0. 01
33	profenofos	10. 66	156 *	97	208	100 : 95 : 15	0. 01
34	ethion	21. 62	231 *	97	153	100 : 99 : 92	0. 01
35	edifenphos	22. 57	109 *	172	309	100 : 85 : 75	0. 01
36	pyraclofos	27. 92	138 *	194	360	100 : 80 : 55	0. 01
37	coumaphos	28. 73	109 *	226	362	100 : 60 : 45	0. 01
38	methamidophos	9. 95	94 *	95	141	100 : 68 : 58	0. 01
39	sulfotep	15. 19	97 *	202	322	100 : 90 : 80	0. 01
40	terbufos	16. 40	57 *	231	—	100 : 40	0. 01
41	monocrotophos	15. 61	127 *	67	192	100 : 23 : 13	0. 01
42	dichlofenthion	17. 42	223 *	279	97	100 : 88 : 87	0. 01
43	fenchlorphos	17. 93	285 *	125	287	100 : 60 : 50	0. 01
44	pirimiphos-methyl	18. 08	276 *	305	290	100 : 64 : 53	0. 01
45	parathion	18. 72	97 *	109	291	100 : 80 : 30	0. 01
46	dimethylvinphos	18. 57	109 *	295	297	100 : 55 : 35	0. 01
47	isophenphos	19. 34	58 *	121	213	100 : 35 : 35	0. 01
48	phenthoate	19. 47	121 *	125	274	100 : 92 : 70	0. 01
49	methidathion	19. 86	145 *	85	—	100 : 98	0. 01
50	phosfolan methyl	19. 55	196 *	140	106	100 : 85 : 69	0. 01
51	famphur	22. 28	218 *	125	93	100 : 45 : 39	0. 01
52	phosalone	26. 17	182 *	121	367	100 : 54 : 12	0. 01
53	azinphos methyl	26. 72	77 *	132	160	100 : 82 : 78	0. 01
54	dibrom	15. 07	109 *	145	301	100 : 55 : 10	0. 01
55	phosdrin	12. 20	127 *	109	192	100 : 30 : 30	0. 01
56	thiometon	15. 78	88 *	125	93	100 : 35 : 20	0. 01
57	propetamphos	16. 85	138 *	194	236	100 : 45 : 25	0. 01
58	etrimfos	16. 88	181 *	153	292	100 : 92 : 63	0. 01
59	phosphamidon	16. 55/17. 35	127 *	72	264	100 : 55 : 25	0. 01
60	trichloronate	18. 88	109 *	268	296	100 : 75 : 55	0. 01
61	malathion	18. 34	125 *	173	93	100 : 98 : 81	0. 01
62	isofenphos-methyl	19. 07	58 *	199	121	100 : 45 : 35	0. 01

Table D.1 (continued)

No	Compound	Time min	Characteristic fragment ion amu				Limit mg/kg
			Confirmation		Abundance ration		
63	isocarbophos	18. 86	136 *	121	230	100 : 75 : 15	0. 01
64	quinalphos	19. 56	146 *	157	298	100 : 87 : 13	0. 01
65	tetrachlorvinphose	19. 92	109 *	329	331	100 : 35 : 30	0. 01
66	iodofenphos	20. 37	376 *	125	378	100 : 55 : 35	0. 01
67	phosfolan	19. 54	92 *	140	196	100 : 75 : 45	0. 01
68	triamiphos	21. 72	160 *	135	294	100 : 35 : 15	0. 01
69	EPN	24. 57	157 *	169	185	100 : 50 : 30	0. 01
70	azinphos ethyl	27. 56	132 *	160	77	100 : 78 : 50	0. 01
Note; Those ions with “ * ” for determination.							

Annex E
(Informative)
Monitoring ion of the analytes

Table E. 1—Monitoring ion of 70 organophosphorous pesticides

Group	No	Time min	Ion amu	Dwell time s
Group I	1	7.00	77, 103, 130	0.36
	2	9.00	109, 185, 220	0.36
	3	10.00	94, 136, 142	0.36
	4	13.00	127, 159, 193, 237, 270	0.59
	5	15.80	87, 88, 89, 93, 237, 270	0.70
	6	17.00	109, 125, 263	0.36
	7	18.00	97, 109, 125, 168, 199, 278, 314, 318, 333	1.05
	8	19.30	130, 148, 220, 262, 299, 304	0.70
	9	21.00	77, 97, 125, 161, 162, 172, 293	0.82
	10	23.00	97, 160, 161, 199, 340	0.59
Group II	1	9.00	79, 97, 109, 145, 156, 208	0.70
	2	13.50	79, 88, 89, 109, 110, 139, 156, 158, 170, 200	1.16
	3	15.10	75, 88, 89, 121, 170, 260	0.70
	4	16.20	109, 119, 137, 152, 161, 179, 246, 257, 304	1.05
	5	16.95	91, 125, 204, 286, 288	0.59
	6	17.85	81, 109, 125, 275, 277	0.59
	7	18.60	97, 125, 195, 283, 302, 329, 331, 358	0.93
	8	20.00	109, 172, 309	0.36
	9	21.00	97, 153, 231	0.36
	10	22.00	109, 138, 194, 226, 360, 362	0.70
Group III	1	8.00	94, 95, 141	0.24
	2	11.00	67, 97, 127, 192, 202, 322	0.70
	3	16.00	57, 231	0.24
	4	17.00	97, 125, 223, 276, 279, 285, 287, 290, 305	1.05
	5	18.30	97, 109, 291, 295, 297	0.59
	6	19.00	58, 85, 106, 121, 125, 140, 145, 196, 213, 274	1.16
	7	21.00	93, 125, 128	0.36
	8	23.00	77, 121, 132, 160, 182, 367	0.70

Table E. 1 (continued)

Group	No	Time min	Ion amu	Dwell time s
Group IV	1	11.00	109, 127, 192	0.36
	2	13.00	88, 93, 109, 125, 145, 301	0.70
	3	16.00	72, 127, 138, 153, 181, 194, 236, 264, 292	1.05
	4	18.00	93, 125, 173, 109, 268, 296, 136, 121, 230	0.70
	5	18.95	58, 92, 109, 121, 140, 146, 157, 196, 199, 298, 329, 331	1.05
	6	20.00	125, 376, 378	0.36
	7	21.00	135, 160, 294	0.36
	8	23.00	157, 169, 185	0.36
	9	25.00	77, 132, 160	0.36

Annex F (Informative)

GC-MS chromatogram (TIC) of 70 organophosphorous pesticides by GC-MSD

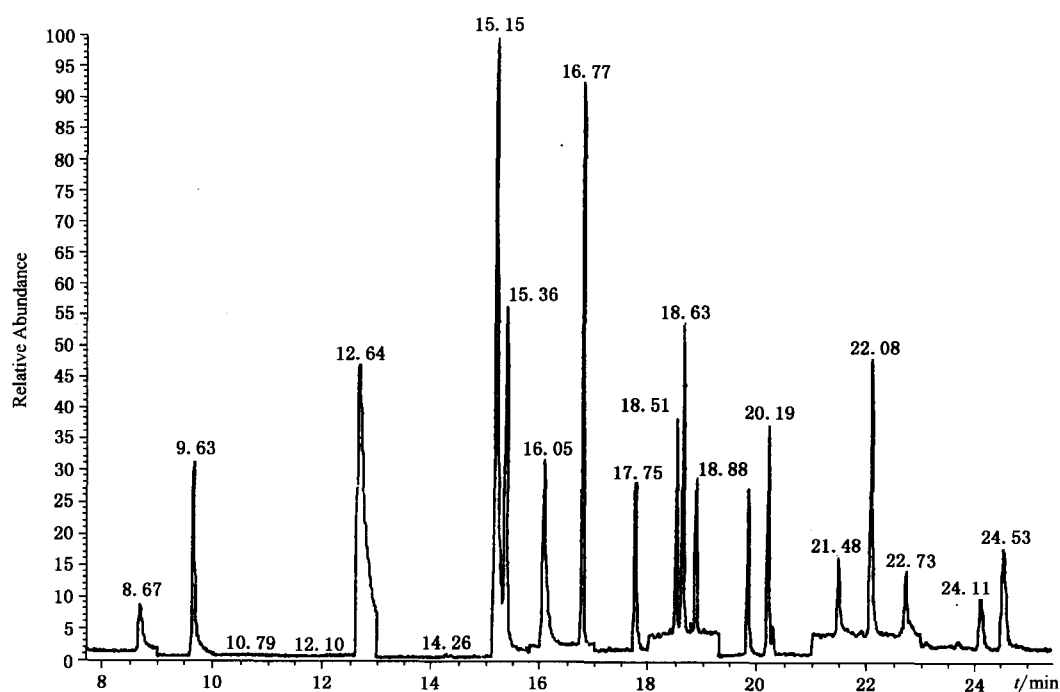


Figure F. 1—GC-MS chromatogram (TIC) of Group I organophosphorous pesticides by GC-MSD

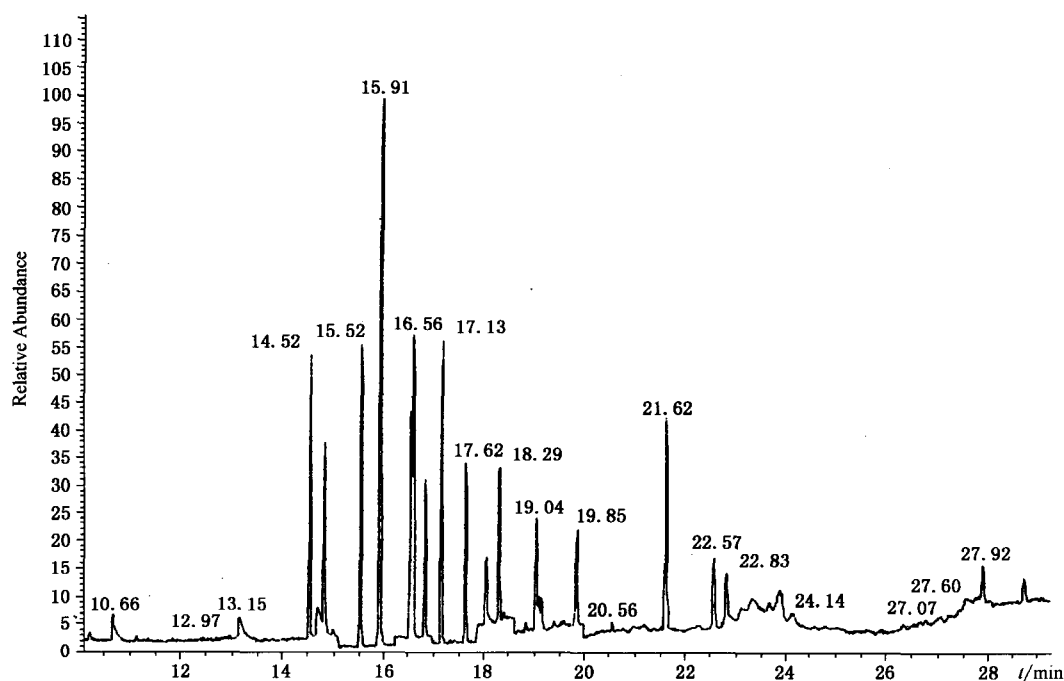


Figure F. 2—GC-MS chromatogram (TIC) of Group II organophosphorous pesticides by GC-MSD

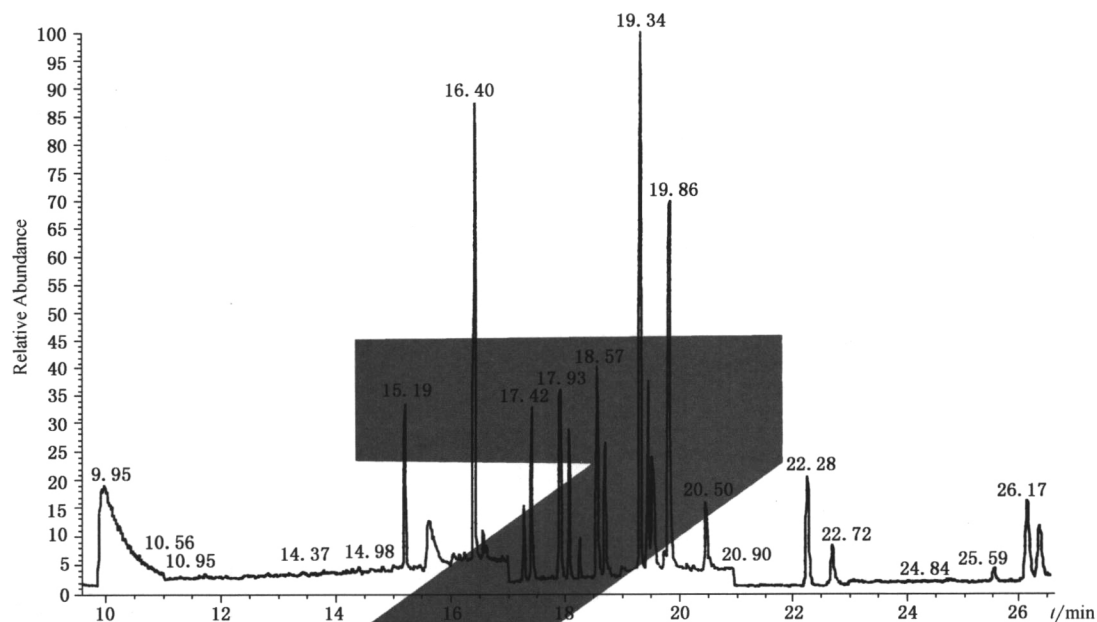


Figure F. 3—GC-MS chromatogram (TIC) of Group III organophosphorous pesticides by GC-MSD

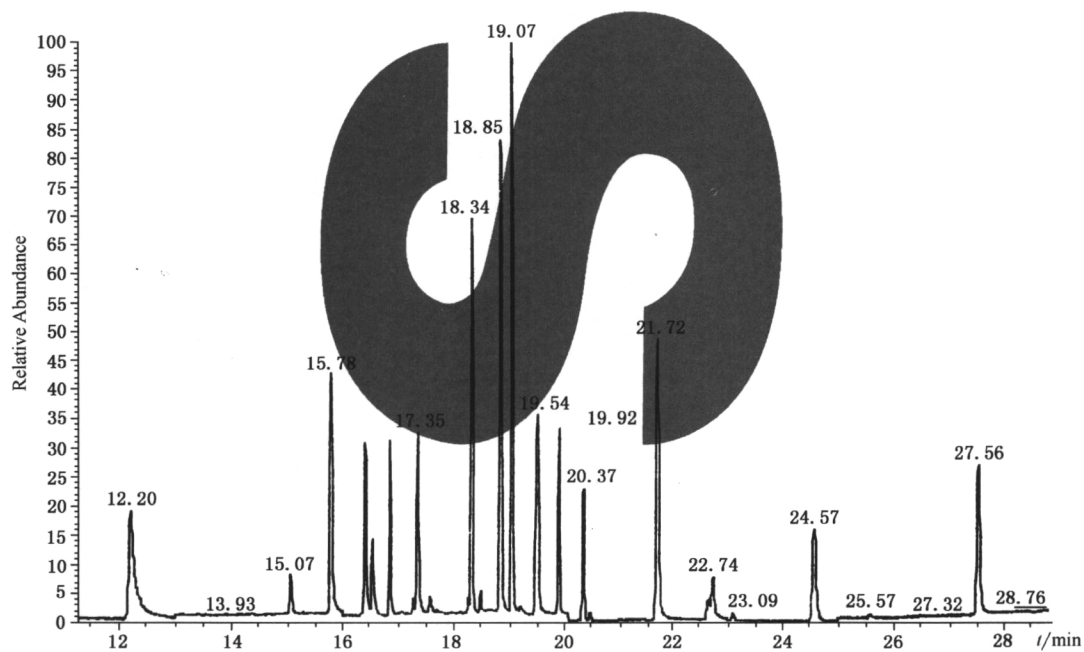


Figure F. 4—GC-MS chromatogram (TIC) of Group IV organophosphorous pesticides by GC-MSD

Annex G
(Informative)

Recovery of 70 organophosphorus pesticides in various fortified concentrations

Table G. 1—Recovery of 70 organophosphorus pesticides in various fortified concentrations ($n = 10$)

Compound	Spiked concentration mg/kg	Recovery %													
		pineapple	apple	lichee	carrot	potato	eggplant	spinach	pea	agaric	mushroom	burdock	Pasania Fungus	scallion	
dichlorvos	0.01~0.1	87~109	75~90	60~75	71~89	66~76	65~77	67~97	62~77	60~71	61~72	61~98	60~81	72~82	
acephate	0.01~0.1	78~95	81~89	67~80	83~97	70~81	67~81	84~108	64~85	68~77	66~73	60~87	67~78	68~83	
cadusafos	0.01~0.1	81~97	80~92	64~77	66~85	73~78	69~91	85~99	65~79	63~75	71~88	61~78	60~86	70~76	
dicrotophos	0.01~0.1	80~99	82~91	73~80	64~89	65~72	63~101	69~84	69~84	70~91	70~74	71~82	65~87	70~86	
disulfoton	0.01~0.1	79~90	85~96	68~75	76~112	65~78	65~79	69~94	60~87	60~111	71~76	63~77	75~92	78~83	
dimethoate	0.01~0.1	82~104	83~98	73~80	64~88	69~78	66~84	69~95	65~84	66~120	73~87	70~83	60~89	80~85	
parathion-methyl	0.01~0.1	83~98	85~95	71~86	75~91	70~79	62~91	65~103	74~86	60~90	77~80	74~84	62~81	75~79	
chlorpyrifos	0.01~0.1	80~97	88~99	70~82	73~90	72~81	71~98	75~88	68~81	63~80	87~92	70~83	63~82	88~99	
pirimiphos-ethyl	0.01~0.1	85~105	91~100	75~83	74~87	63~73	72~95	68~99	63~85	63~78	74~77	74~84	60~95	67~87	
fenthion	0.01~0.1	87~97	80~91	72~84	72~94	65~78	75~92	64~108	65~78	61~74	79~87	70~81	65~84	76~88	
propaphos	0.01~0.1	80~95	81~94	74~87	70~90	69~81	71~89	63~107	63~77	63~77	93~103	67~83	70~82	75~85	
phoxim	0.01~0.1	90~107	65~82	60~89	78~96	68~80	61~82	64~95	65~76	102~120	61~69	60~77	64~96	76~87	
ditalimfos	0.01~0.1	79~109	71~80	72~80	65~75	78~101	84~105	66~99	67~80	63~77	65~78	63~75	64~95	80~97	
carbofenothion	0.01~0.1	80~97	72~86	72~86	79~98	75~98	77~89	70~108	71~82	70~88	90~97	61~81	67~94	84~89	
triazophos	0.01~0.1	81~94	83~97	73~79	81~102	72~101	76~94	71~105	72~86	70~80	86~94	69~80	69~94	76~90	
pyridaphenthion	0.01~0.1	80~91	84~99	72~86	75~92	81~95	68~90	80~99	70~89	72~84	90~105	69~80	68~96	90~110	
phosmet	0.01~0.1	84~112	70~97	72~87	85~115	88~98	62~84	79~103	69~83	73~87	86~93	68~78	70~85	67~89	
trichlorphon	0.01~0.1	77~82	90~105	60~75	63~98	65~73	61~99	64~75	63~74	61~83	61~102	60~71	80~96	77~90	
ethoprophos	0.005~0.1	75~85	88~104	60~77	71~83	63~78	64~108	66~89	65~79	60~75	87~104	60~80	60~84	78~97	

Table G.1 (continued)

Compound	Spiked concentration mg/kg	Recovery %												
		pineapple	apple	lichee	carrot	potato	eggplant	spinach	pea	agaric	mushroom	burdock	Pasania Fungus	scallion
phorate	0.01~0.1	74~84	84~97	60~75	62~74	65~74	63~97	63~85	63~75	61~74	80~87	65~79	65~87	69~98
omethoate	0.01~0.1	78~88	104~117	67~78	89~97	62~78	60~72	66~79	65~80	78~109	67~85	68~84	75~82	66~89
demeton	0.01~0.1	71~85	98~108	64~76	62~78	63~71	62~75	63~77	64~78	68~85	83~86	65~80	65~76	69~89
diazinon	0.01~0.1	94~109	62~77	68~95	71~88	65~78	65~77	64~78	63~79	69~86	85~93	69~89	65~86	78~89
dyfonate	0.01~0.1	77~89	82~97	67~77	74~86	66~82	66~88	63~75	64~76	72~96	86~94	63~81	60~74	79~87
iprobenfos	0.01~0.1	74~91	84~90	65~77	71~82	70~85	64~89	60~79	76~84	71~99	89~103	69~93	83~90	70~75
isazofos	0.01~0.1	72~87	77~92	63~76	68~79	68~81	65~97	65~85	69~79	78~91	65~80	63~85	60~76	75~87
chlorpyrifos methyl	0.01~0.1	79~92	75~86	65~77	69~81	69~85	63~96	66~87	59~79	75~105	62~83	71~90	62~74	69~80
paraoxon	0.01~0.1	84~101	74~85	76~99	75~90	71~89	69~86	60~79	60~112	79~90	91~103	74~83	87~98	65~90
fenitrothion	0.01~0.1	97~102	71~84	75~84	80~98	66~81	69~92	63~78	60~115	69~85	76~87	71~81	78~90	74~89
bromophos methyl	0.01~0.1	85~99	72~83	73~80	81~93	67~82	67~104	65~84	61~79	70~89	74~89	73~80	74~93	67~91
bromophos ethyl	0.01~0.1	96~100	71~82	78~85	72~86	70~85	66~119	66~112	70~115	71~91	74~104	73~81	78~97	61~76
fosthiazate	0.01~0.1	98~108	75~87	77~85	76~89	71~90	73~112	63~82	70~92	70~93	94~102	74~85	94~106	80~90
profenofos	0.01~0.1	92~103	74~85	82~89	74~92	70~83	62~81	60~75	70~92	79~95	93~103	82~93	93~102	67~79
ethion	0.01~0.1	79~92	75~88	76~85	71~89	68~79	63~99	61~84	80~108	71~93	94~105	72~81	97~108	67~90
edifenphos	0.01~0.1	90~105	77~89	77~81	73~88	69~85	60~76	60~75	77~111	73~94	100~104	76~83	95~108	78~90
pyraclofos	0.01~0.1	81~92	76~90	76~86	75~91	73~97	77~94	69~81	100~119	63~86	93~101	70~81	90~93	90~98
counaphos	0.01~0.1	91~101	83~95	85~95	69~85	75~101	63~102	65~87	90~120	79~96	88~111	75~90	65~90	67~89
methamidophos	0.01~0.1	77~88	73~81	70~88	63~77	72~93	74~97	63~79	63~89	60~73	64~85	74~87	73~82	67~90
sulfotep	0.01~0.1	79~93	80~87	60~73	61~78	80~92	88~104	70~84	60~79	61~75	84~104	70~80	63~80	77~80
terbufos	0.005~0.1	65~80	85~91	64~79	62~99	66~78	84~118	70~105	101~120	66~77	70~82	70~88	60~81	85~90
monocrotophos	0.01~0.1	65~99	85~93	88~120	75~101	85~97	81~94	69~79	60~119	67~81	100~106	76~89	109~119	67~92
dichlofenthion	0.01~0.1	85~99	83~90	84~107	70~81	71~88	88~101	79~87	75~97	63~78	61~82	66~84	70~74	68~89
fenchlorphos	0.01~0.1	83~92	88~93	79~110	72~98	73~89	82~89	69~88	64~75	68~79	69~75	73~86	72~76	65~78

Table G.1 (continued)

Compound	Spiked concentration mg/kg	Recovery %												
		pineapple	apple	lichee	carrot	potato	eggplant	spinach	pea	agaric	mushroom	burdock	Pasania Fungus	scallion
pirimiphos-methyl	0.01~0.1	89~97	81~95	77~98	87~110	75~98	76~109	70~102	63~78	74~91	82~93	75~89	70~79	78~90
parathion	0.01~0.1	87~94	82~99	75~85	78~96	78~101	81~103	63~89	60~78	67~79	89~104	74~88	80~89	65~78
dimethylvinphos	0.01~0.1	92~103	90~100	85~90	91~108	82~95	77~98	64~79	63~83	65~80	100~104	70~87	87~112	80~98
isophenphos	0.01~0.1	75~84	80~89	70~80	65~81	75~93	71~92	75~83	60~75	64~81	101~106	70~82	86~95	77~87
phenthoate	0.01~0.1	81~91	81~92	69~81	63~82	85~110	72~106	73~86	60~82	64~76	74~94	74~89	71~83	67~90
methidathion	0.01~0.1	82~99	82~91	79~87	70~83	82~112	70~99	74~87	61~85	60~75	81~106	74~87	84~99	89~97
phosfolan methyl	0.01~0.1	80~90	80~87	80~87	71~86	82~101	71~92	70~89	67~95	63~77	104~118	61~73	90~102	70~90
famphur	0.01~0.1	82~96	87~98	82~85	79~93	83~98	71~93	74~92	62~80	63~84	101~123	80~95	96~100	66~88
phosalone	0.01~0.1	83~95	82~94	83~97	78~104	79~95	71~95	70~90	60~105	64~78	98~111	78~86	101~111	69~97
azinphos methyl	0.01~0.1	79~84	70~81	79~87	74~95	78~98	92~107	71~99	61~120	71~83	91~98	61~74	96~107	87~98
dibrom	0.01~0.1	104~120	83~96	68~79	63~86	75~93	71~92	63~85	60~88	97~120	101~107	88~112	87~97	78~94
phosdrin	0.01~0.1	64~79	85~93	60~77	62~69	82~98	71~92	64~90	65~105	60~71	64~74	79~87	81~86	78~89
thiometon	0.01~0.1	65~75	75~90	62~104	61~83	63~77	71~92	60~75	60~89	60~70	61~89	60~83	70~85	68~88
propetamphos	0.01~0.1	70~79	73~87	66~79	66~79	80~91	80~92	73~85	61~115	63~75	85~93	75~106	91~98	64~88
etrimfos	0.01~0.1	65~80	78~90	99~109	62~76	88~93	71~93	64~86	60~107	63~74	77~97	75~87	73~85	65~78
phosphamidon	0.01~0.1	60~75	83~99	80~120	69~80	73~90	80~120	88~112	69~110	78~92	71~79	83~91	98~112	63~70
trichloronate	0.01~0.1	69~78	80~89	80~93	75~86	88~101	90~110	85~98	89~111	71~80	86~91	80~90	83~96	79~100
malathion	0.01~0.1	71~86	79~94	80~93	74~86	80~99	82~94	79~89	66~120	75~84	71~80	79~93	93~103	69~89
isofenphos-methyl	0.01~0.1	70~85	80~91	77~89	71~89	79~102	71~95	70~97	61~104	76~85	88~96	77~92	97~110	79~97
isocabophos	0.01~0.1	62~77	89~101	63~83	70~86	80~98	73~102	67~97	60~104	69~78	90~101	76~89	103~113	69~90
quinalphos	0.01~0.1	64~80	80~93	75~85	73~90	86~103	75~110	70~108	61~96	68~78	87~90	76~88	91~99	75~87
tetrachlorvinphose	0.01~0.1	63~78	101~115	74~84	77~97	92~115	80~99	69~85	85~106	72~85	67~82	83~98	106~111	70~89
iodofenphos	0.01~0.1	79~85	65~79	76~92	76~91	84~103	79~100	68~88	70~101	76~80	70~84	81~95	103~113	67~89
phosfolan	0.01~0.1	65~78	60~75	82~91	77~93	83~98	82~104	74~100	60~112	77~85	101~103	60~74	91~98	90~98
triampinos	0.01~0.1	80~95	63~78	72~81	65~78	81~95	69~94	60~75	60~103	70~80	96~102	60~71	106~122	80~85
EPN	0.01~0.1	70~85	78~90	81~90	70~79	90~104	87~101	68~94	61~104	74~86	92~97	83~91	96~107	67~79
azinphos ethyl	0.01~0.1	60~74	75~89	76~93	85~112	95~112	98~115	70~95	64~101	81~92	100~110	66~77	107~114	69~80