SN

中华人民共和国出入境检验检疫行业标准

SN/T 1737.4—2010

除草剂残留量检验方法
第4部分：气相色谱-质谱/质谱法测定进出口食品中芳氧苯氧丙酸酯类除草剂残留量

Determination of herbicide residues—Part 4: Determination of aryloxyphenoxypropionate herbicide residues in foodstuff for import and export by GC-MS/MS method

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前　言

SN/T 1737《除草剂残留量检验方法》共分为五部分：

——第 1 部分：气相色谱串联质谱法测定粮谷及油籽中酰胺类除草剂残留量；

——第 2 部分：气相色谱/质谱法测定粮谷及油籽中二苯醚类除草剂残留量；

——第 3 部分：液相色谱-质谱/质谱法测定进出口食品中环己烯酮类除草剂残留量；

——第 4 部分：液相色谱-质谱/质谱法测定进出口食品中芳氧苯氧丙酸酯类除草剂残留量；

——第 5 部分：液相色谱-质谱/质谱法测定进出口食品中硫代氨基甲酸酯类除草剂残留量。

本部分为 SN/T 1737 的第 4 部分。

本部分的附录 A、附录 B 和附录 C 均为资料性附录。

本部分由国家认证认可监督管理委员会提出并归口。

本部分起草单位：中华人民共和国江苏出入境检验检疫局。

本部分主要起草人：赵增运、柳菡、沈伟健、余可垚、沈崇钰、桂茜雯、龚玉霞、蒋原、陶宏锦。

本部分系首次发布的出入境检验检疫行业标准。

除草剂残留量检验方法
第4部分：气相色谱-质谱/质谱法测定
进出口食品中芳氧苯氧丙酸酯类除草剂残留量

1 范围

SN/T 1737的本部分规定了食品中2,4-滴丁酯、吡氟氯禾灵、吡氟禾草灵、炔草酯、禾草灵、氰氟草酯、噁唑禾草灵、精喹禾灵等芳氧苯氧丙酸酯类除草剂残留量的气相色谱-质谱/质谱检测方法。

本部分适用于大豆、大麦茶、粳米、胡萝卜、菠菜、青刀豆、蒜苗、草莓、蜂蜜、猪肉、鱼、禽蛋中2,4-滴丁酯、吡氟氯禾灵、吡氟禾草灵、炔草酯、禾草灵、氰氟草酯、噁唑禾草灵、精喹禾灵残留量的测定和确证。

2 方法提要

试样中残留的芳氧苯氧丙酸酯类除草剂经正己烷饱和过的乙腈(含1%冰乙酸)提取，基质分散固相萃取净化，用气相色谱-质谱/质谱仪测定，外标法定量。

3 试剂和材料

除另有规定外，所用试剂均为分析纯，水为去离子水。

3.1 乙腈：色谱纯。

3.2 正己烷：色谱纯。

3.3 丙酮：色谱纯。

3.4 冰乙酸。

3.5 无水乙酸钠。

3.6 无水硫酸镁：650 ℃下灼烧4 h，保存在干燥器中。

3.7 提取溶剂(含1%冰乙酸的经正己烷饱和过的乙腈溶液)：加10 mL冰乙酸到990 mL的乙腈(事先用正己烷饱和过)。

3.8 芳氧苯氧丙酸酯类除草剂标准品：2,4-滴丁酯(2,4-D butylate，CAS号：94-80-4，分子式：$C_{12}H_{14}C_{12}O_3$，纯度大于等于97.1%)；吡氟氯禾灵(Haloxyfop，CAS号：69806-34-4，分子式：$C_{15}H_{11}ClF_3NO_4$，纯度大于等于99%)；吡氟禾草灵(Fluazifop-butyl，CAS号：79241-46-6，分子式：$C_{19}H_{20}F_3NO_4$，纯度大于等于99%)；炔草酯(Clodinafop-propargyl，CAS号：105512-06-9，分子式：$C_{17}H_{13}ClFNO_4$，纯度大于等于99.0%)；禾草灵(Diclofop，CAS号：51338-27-3，分子式：$C_{16}H_{14}Cl_2O_4$，纯度大于等于96.5%)；氰氟草酯(Cyhalofop-butyl，CAS号：122008-85-9，分子式：$C_{20}H_{20}FNO_4$，纯度大于等于99.0%)；噁唑禾草灵(Fenoxaprop，CAS号：95617-09-7，分子式：$C_{16}H_{12}ClNO_5$，纯度大于等于99%)；精喹禾灵(Quizalofop-P-ethyl，CAS号：100646-51-3，分子式：$C_{19}H_{17}ClN_2O_4$，纯度大于等于99.5%)。

3.9 芳氧苯氧丙酸酯类除草剂标准储备溶液：准确称取适量芳氧苯氧丙酸酯类除草剂的标准品，经丙酮溶解、稀释和定容后，分别配制成100 μg/mL的单种标准储备溶液，此溶液可在0 ℃～4 ℃条件下避光储存6个月。

3.10 混合标准中间溶液：准确吸取每种芳氧苯氧丙酸酯类的标准储备溶液各5.0 mL于50 mL棕色容量瓶中，用丙酮稀释至刻度线后配制成浓度为10.0 μg/mL的混合标准中间溶液，此溶液可在0 ℃～4 ℃条件下避光储存3个月。

3.11 混合标准工作溶液：根据需要再用丙酮稀释成适用浓度的混合标准工作溶液，现用现配。

3.12 乙二胺-N-丙基甲硅烷(PSA)填料：40 μm～60 μm。

3.13 石墨化碳黑填料：120 μm～400 μm。

3.14 十八烷基硅烷(ODS)填料：60 μm～100 μm。

3.15 滤膜：0.45 μm，有机相。

4 仪器和设备

4.1 气相色谱-质谱/质谱联用仪。

4.2 振荡器。

4.3 电子天平(感量为 0.1 mg 和 0.01 g)。

4.4 涡旋混合器。

4.5 组织捣碎机。

4.6 粉碎机。

4.7 旋转蒸发仪。

4.8 氮气吹干仪。

4.9 具塞锥形瓶：250 mL。

4.10 试管：10 mL。

4.11 浓缩瓶：150 mL。

5 试样制备与保存

5.1 试样制备

5.1.1 胡萝卜、青刀豆、蒜苗、草莓、菠菜

取有代表性样品约 500 g(不可用水洗涤)，将其可食部分切碎后，用组织捣碎机将样品加工成浆状，装入洁净容器，密封并标明标记。

5.1.2 大豆、大麦茶、粳米

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

5.1.3 猪肉、鱼肉、禽蛋

取有代表性样品约 500 g，将其可食部分切碎后，用组织捣碎机将充分捣碎均匀，装入洁净容器，密封并标明标记。

5.1.4 蜂蜜

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

5.2 试样保存

在制样的操作过程中，应防止样品污染或发生残留物含量的变化。大豆、大麦茶、粳米、蜂蜜和禽蛋等试样于 4 ℃以下保存；胡萝卜、青刀豆、蒜苗、草莓、菠菜、猪肉、鱼肉、龙虾等试样于－18 ℃以下保存。

6 测定步骤

6.1 提取

6.1.1 胡萝卜、青刀豆、蒜苗、草莓和菠菜

称取 10 g 试样(精确至 0.01 g)于 250 mL 具塞锥形瓶中，加入 15 g 无水硫酸镁、6 g 无水乙酸钠和 50 mL 提取溶剂(3.7)，于振荡器上振荡 30 min，静置 10 min，过滤于 150 mL 浓缩瓶中。残渣再加入20 mL 提取溶剂(3.7)提取一次，合并两次滤液，40 ℃下旋转浓缩至干。用 2 mL 乙腈溶解残渣，待净化。

6.1.2 大豆、粳米、猪肉、鱼肉和禽蛋

称取 5 g 试样(精确至 0.01 g)于 250 mL 具塞锥形瓶中,加入 15 g 无水硫酸镁、6 g 无水乙酸钠和 50 mL 提取溶剂(3.7),于振荡器上振荡 30 min(猪肉、鱼肉、蜂蜜、禽蛋等肉制品应均质提取 5 min),静置 10 min,过滤于 150 mL 浓缩瓶中。残渣再加入 20 mL 提取溶剂(3.7)提取一次,合并两次滤液,40 ℃下旋转浓缩至干。用 2 mL 乙腈溶解残渣,待净化。

6.1.3 大麦茶

称取 5 g 试样(精确至 0.01 g)于 250 mL 具塞锥形瓶中,加入 5 mL 水浸泡过夜后,再加入 15 g 无水硫酸镁、6 g 无水乙酸钠和 50 mL 提取溶剂(3.7),于振荡器上振荡 30 min,静置 10 min,过滤于 150 mL浓缩瓶中。残渣再加入 20 mL 提取溶剂(3.7)提取一次,合并两次滤液,40 ℃下旋转浓缩至干。用 2 mL 乙腈溶解残渣,待净化。

6.1.4 蜂蜜

称取 5 g 试样(精确至 0.01 g)于 250 mL 具塞锥形瓶中,加入 5 mL 水溶解后再加入 15 g 无水硫酸镁、6 g 无水乙酸钠和 50 mL 提取溶剂(3.7),于振荡器上振荡 30 min,静置 10 min,过滤于 150 mL 浓缩瓶中。残渣再加入 20 mL 提取溶剂(3.7)提取一次,合并两次滤液,40 ℃下旋转浓缩至干。用 2 mL 乙腈溶解残渣,待净化。

6.2 净化

6.2.1 胡萝卜、青刀豆、蒜苗、草莓、菠菜和大麦茶提取液

将 6.1 相应样品提取液转移到事先装有 200 mg PSA 填料和 250 mg 石墨化碳黑填料的小试管中,充分涡旋 1 min,待色素完全消除后,过滤膜,供气相色谱-质谱测定和确证。

6.2.2 大豆、粳米、猪肉、鱼肉、蜂蜜和禽蛋提取液

将 6.1 相应样品提取液转移到事先装有 200 mg PSA 填料,150 mg 石墨化碳黑填料和 100 mg C_{18} 填料的小试管中,充分涡旋 1 min,过滤膜,供气相色谱-质谱测定和确证。

6.3 测定

6.3.1 气相色谱-质谱条件

a) 色谱柱:DB-5 ms 弹性石英毛细管柱,30 m×0.25 mm(内径)×0.25 μm,或相当者;

b) 柱温:初始温度 50 ℃(2 min),以 30 ℃/min 升至 180 ℃,再以 5 ℃/min 升至 280 ℃(保持 10 min);

c) 进样口温度:250 ℃;

d) 色谱-质谱接口温度:280 ℃;

e) 载气:氦气,纯度大于等于 99.999%;载气流速:1 mL/min;

f) 进样量:1 μL;

g) 进样方式:不分流进样,1.2 min 后开阀;

h) 离子源:电子轰击离子源(EI 源);

i) 离子源温度:230 ℃;

j) 电子能量:70 eV;

k) 溶剂延迟时间:9.0 min;

l) 扫描方式:反应离子监测模式(SRM);母离子和子离子见表 1。

表 1 选择离子及保留时间

中文名称	保留时间/min	母离子(m/z)	子离子(m/z)	碰撞能量/V
2,4-滴丁酯	12.07	175.9	111.0	15
		277.1	185.0[a]	5
		185.6	155.0	15

表 1（续）

中文名称	保留时间/min	母离子(m/z)	子离子(m/z)	碰撞能量/V
吡氟氯禾灵	15.31	288.9	180.0	30
		316.7	91.0[a]	15
吡氟禾草灵	17.32	254.5	146.0	25
		282.3	91.0[a]	20
		383.4	282.0	10
炔草酯	19.20	238.8	130.0	15
		349.8	266.0[a]	10
禾草灵	19.68	254.2	162.0[a]	15
		341.1	253.0	10
氯氟草酯	22.49	256.3	120.0[a]	10
		357.4	256.0	10
噁唑禾草灵	23.74	288.8	91.0	20
			119.0	10
		361.8	288.0[a]	10
精喹禾灵	26.23	299.8	91.0	20
		372.9	299.0[a]	10
[a] 定量离子。				

6.3.2 气相色谱-质谱检测及确证

根据样液中被测物的含量情况，选定浓度相近的标准工作溶液。标准工作溶液和样液中芳氧苯氧丙酸酯类的响应值均应在仪器检测线性范围内。对标准工作溶液和样液等体积参插进样测定。如果样液与标准工作溶液的选择离子色谱图中，在相同保留时间处有色谱峰出现，并且在扣除背景后的样品质量色谱图中，所选离子均出现，所选择离子的丰度比与标准品对应离子的丰度比，其值在允许范围内（允许范围见表 2）。在上述色谱条件下，芳氧苯氧丙酸酯类的保留时间分别见表 1。芳氧苯氧丙酸酯类标准物的气相色谱-质谱/质谱总离子流色谱图和全扫描质谱图参见附录 A 中图 A.1 和附录 B 中图 B.1。

表 2 使用定性气相色谱-质谱时相对离子丰度最大容许误差

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

6.4 空白试验

除不称取样品外，均按上述测定条件和步骤进行。

6.5 结果计算和表述

用色谱数据处理机或按式(1)计算试样中芳氧苯氧丙酸酯类残留含量，计算结果需扣除空白值。

$$X_i = \frac{A_i \times c_i \times V}{As_i \times m} \qquad \cdots\cdots(1)$$

式中：

X_i——试样中芳氧苯氧丙酸酯类残留量，单位为微克每千克(μg/kg)；

A_i——样液中芳氧苯氧丙酸酯类的峰面积；

c_i——标准工作液中芳氧苯氧丙酸酯类的浓度，单位为纳克每毫升(ng/mL)；

V——样液最终定容体积，单位为毫升(mL)；

As_i——标准工作液中芳氧苯氧丙酸酯类的峰面积；

m——最终样液所代表的试样质量，单位为克(g)。

7 测定低限与回收率

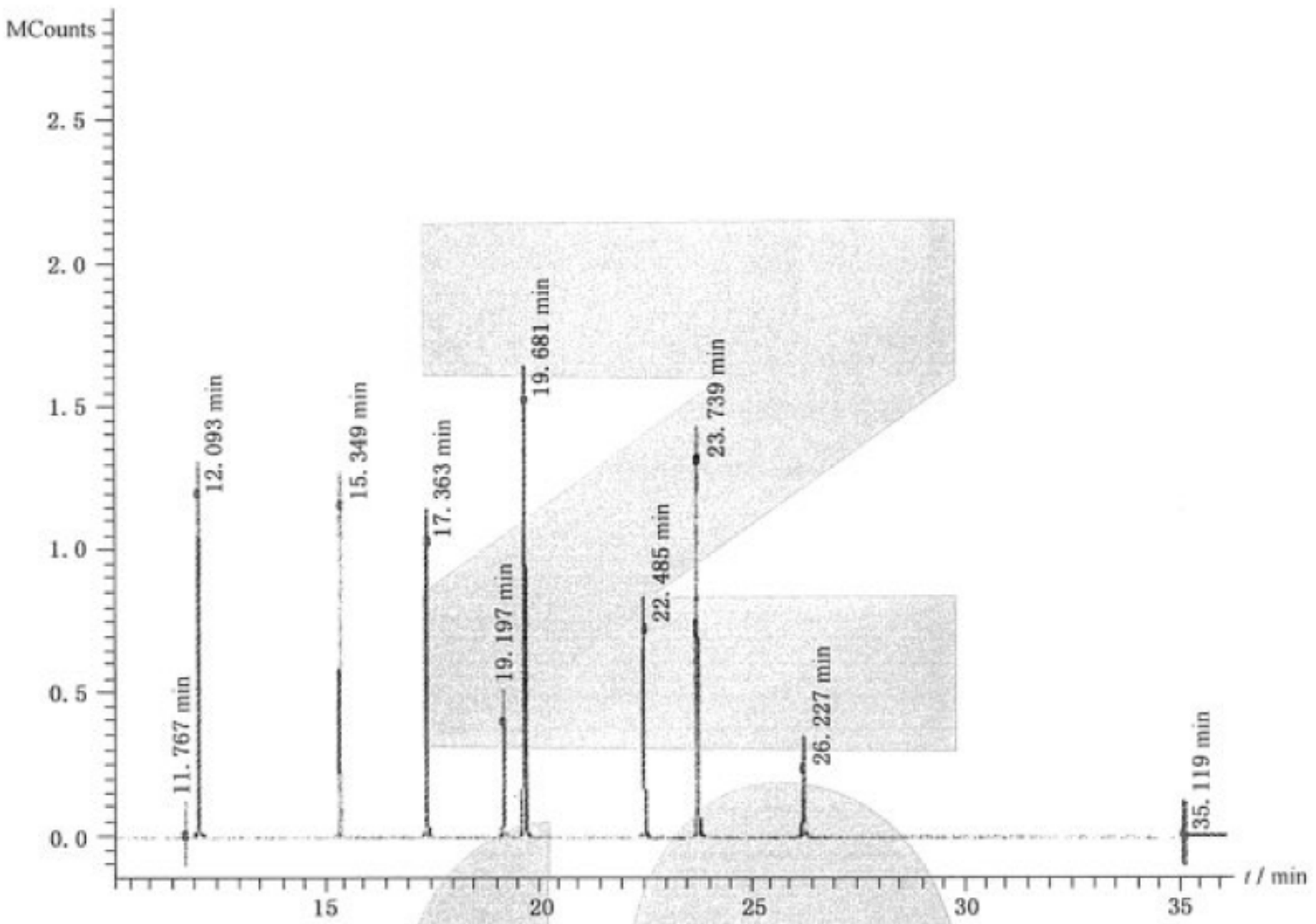
7.1 测定低限

本方法的测定低限为 0.005 mg/kg。

7.2 回收率

不同基质中添加浓度水平下的回收率范围参见附录 C。

附 录 A
（资料性附录）
芳氧苯氧丙酸酯类标准物质总离子流色谱图



2,4-滴丁酯(12.093 min)；吡氟氯禾灵(15.349 min)；吡氟禾草灵(17.363 min)；炔草酯(19.197 min)；禾草灵(19.681 min)；氰氟草酯(22.485 min)；噁唑禾草灵(23.739 min)；精喹禾灵(26.227 min)。

图 A.1 芳氧苯氧丙酸酯类混合标准溶液总离子流色谱图

附 录 B
（资料性附录）
芳氧苯氧丙酸酯类标准物质质量图

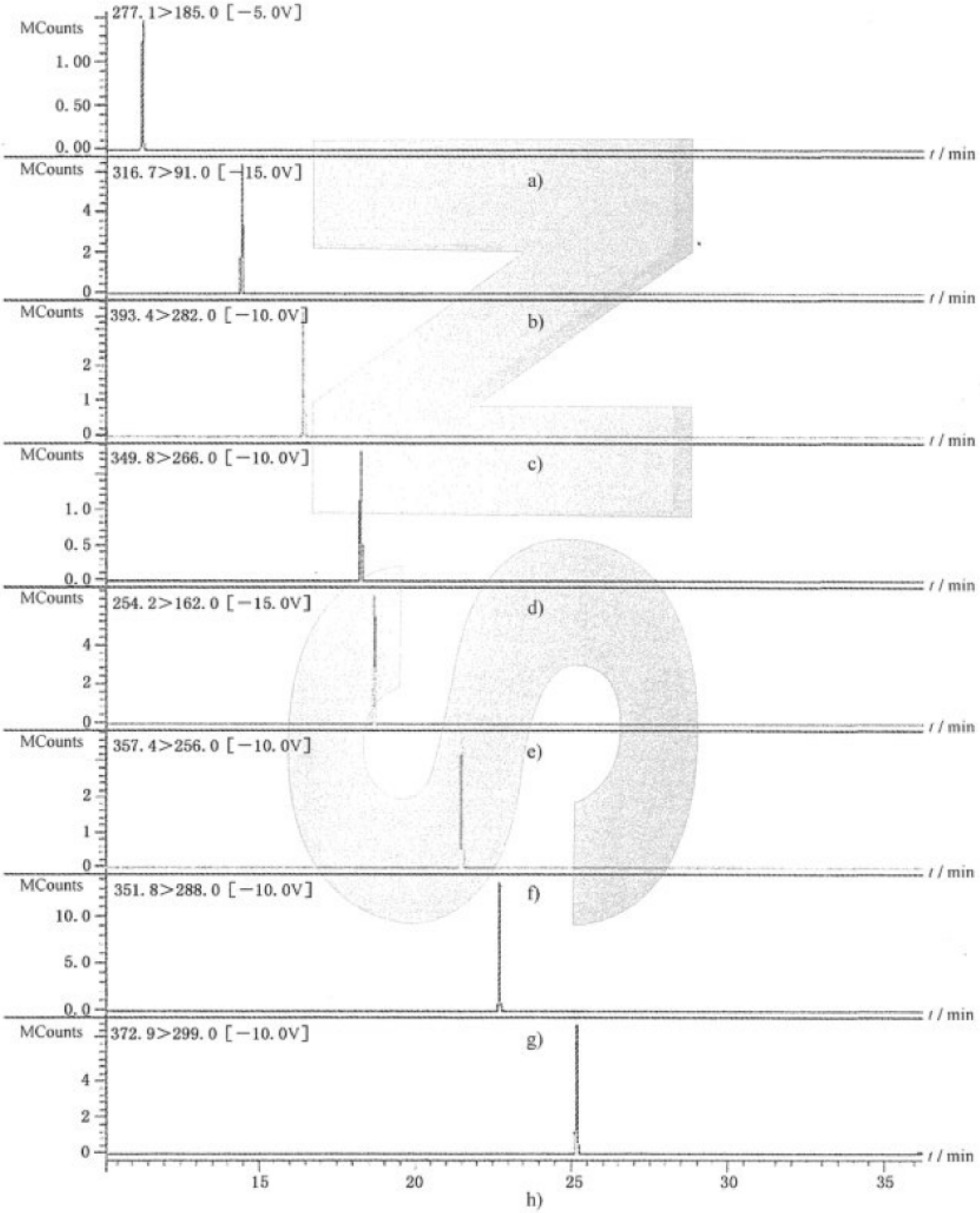


图 B.1 芳氧苯氧丙酸酯类混合标准溶液质谱图

附 录 C
（资料性附录）
不同基质中芳氧苯氧丙酸酯类农药添加浓度及回收率

表 C.1 不同基质中芳氧苯氧丙酸酯类农药添加浓度及回收率

样品名称	农药名称	添加浓度及回收率/%		
		0.005 mg/kg	0.010 mg/kg	0.020 mg/kg
大豆	2,4-滴丁酯	72.4～97.0	83.9～104.7	79.0～98.7
	吡氟氯禾灵	79.8～106.6	76.3～93.6	81.9～97.6
	吡氟禾草灵	75.2～101.1	79.4～100.6	77.4～93.1
	炔草酯	71.0～99.8	71.9～91.2	79.0～94.9
	禾草灵	88.6～114.4	72.9～102.8	79.8～94.1
	氯氟草酯	75.4～106.0	72.9～101.9	78.9～94.3
	噁唑禾草灵	85.0～115.6	70.9～91.9	77.7～92.6
	精喹禾灵	77.2～107.8	75.0～101.6	78.8～92.6
大麦茶	2,4-滴丁酯	70.8～99.4	93.3～116.0	81.0～96.8
	吡氟氯禾灵	68.4～98.4	79.2～103.5	79.1～94.4
	吡氟禾草灵	76.0～107.8	79.0～101.4	78.6～94.4
	炔草酯	86.6～99.0	78.5～91.5	82.8～91.2
	禾草灵	76.4～106.0	70.9～94.4	81.5～96.9
	氯氟草酯	78.2～113.0	72.7～94.3	79.8～94.14
	噁唑禾草灵	79.4～110.4	74.5～98.6	78.8～94.24
	精喹禾灵	83.2～119.2	72.6～94.6	77.7～92.6
粳米	2,4-滴丁酯	78.2～110.2	80.3～106.7	81.7～97.9
	吡氟氯禾灵	82.8～114.2	86.2～107.8	81.9～98.0
	吡氟禾草灵	90.8～118.8	78.9～101.7	83.8～98.9
	炔草酯	76.0～101.4	75.9～105.7	82.8～98.3
	禾草灵	79.8～110.6	76.4～104.7	83.0～99.1
	氯氟草酯	74.4～99.4	84.9～111.7	81.9～97.6
	噁唑禾草灵	78.8～111.2	80.1～110.1	81.9～97.6
	精喹禾灵	77.4～103.8	78.6～106.7	79.0～95.2
胡萝卜	2,4-滴丁酯	74.6～103.8	73.0～97.3	78.6～94.4
	吡氟氯禾灵	88.6～114.8	70.9～94.4	81.1～96.0
	吡氟禾草灵	79.0～112.8	78.9～101.7	81.0～96.8
	炔草酯	79.4～100.8	75.9～105.7	79.8～94.1
	禾草灵	81.6～116.2	76.4～104.7	80.3～96.4
	氯氟草酯	72.6～102.0	78.4～96.2	79.0～95.2

表 C.1（续）

样品名称	农药名称	添加浓度及回收率/%		
		0.005 mg/kg	0.010 mg/kg	0.020 mg/kg
胡萝卜	噁唑禾草灵	70.8～96.6	75.4～98.4	80.6～95.8
	精喹禾灵	84.4～101.4	78.6～100.7	81.1～96.0
菠菜	2,4-滴丁酯	75.4～98.0	81.2～105.6	79.1～98.8
	吡氟氯禾灵	77.6～105.3	74.7～98.2	77.9～96.5
	吡氟禾草灵	73.1～99.4	80.4～101.5	79.9～94.5
	炔草酯	78.0～98.9	77.6～90.8	80.0～97.8
	禾草灵	82.4～104.5	77.6～106.3	78.9～95.6
	氯氟草酯	78.5～101.2	78.2～100.2	77.6～99.6
	噁唑禾草灵	84.3～101.9	71.4～95.6	78.2～94.7
	精喹禾灵	78.3～99.8	77.6～104.2	88.1～95.7
青刀豆	2,4-滴丁酯	79.4～103.8	69.3～90.3	79.8～94.9
	吡氟氯禾灵	76.0～101.4	76.4～104.7	79.0～94.2
	吡氟禾草灵	79.8～110.6	78.9～101.7	82.8～98.0
	炔草酯	74.4～103.2	74.6～99.1	79.0～94.4
	禾草灵	81.6～107.8	76.0～99.3	79.0～95.2
	氯氟草酯	77.2～103.4	77.3～98.5	82.0～98.0
	噁唑禾草灵	88.6～115.4	76.0～95.7	79.0～95.3
	精喹禾灵	76.2～103.0	69.3～90.3	84.3～99.4
蒜苗	2,4-滴丁酯	71.2～96.8	72.3～93.3	85.5～101.6
	吡氟氯禾灵	70.8～94.6	76.0～99.3	84.1～99.0
	吡氟禾草灵	80.4～111.1	79.9～102.3	81.7～98.1
	炔草酯	77.4～103.8	76.0～95.7	83.2～98.2
	禾草灵	76.4～104.4	76.4～104.7	82.0～98.0
	氯氟草酯	79.0～108.0	84.9～106.2	79.6～94.4
	噁唑禾草灵	73.4～103.2	78.9～103.1	81.2～96.0
	精喹禾灵	80.6～112.2	82.8～107.4	83.3～96.1
草莓	2,4-滴丁酯	79.1～108.2	78.9～101.7	83.2～98.2
	吡氟氯禾灵	73.2～100.8	83.0～109.6	79.6～94.4
	吡氟禾草灵	81.0～113.4	76.0～99.0	84.3～99.4
	炔草酯	72.4～105.6	79.1～103.4	82.1～98.0
	禾草灵	77.8～105.2	76.0～99.3	82.2～98.2
	氯氟草酯	77.6～105.2	76.6～101.2	82.4～97.8
	噁唑禾草灵	80.4～111.0	78.9～99.9	83.4～99.4
	精喹禾灵	71.2～97.4	76.0～99.3	82.8～97.9

表 C.1（续）

样品名称	农药名称	添加浓度及回收率/%		
		0.005 mg/kg	0.010 mg/kg	0.020 mg/kg
蜂蜜	2,4-滴丁酯	74.6～103.8	78.9～101.7	84.3～99.4
	吡氟氯禾灵	80.4～111.0	76.0～99.3	83.2～98.2
	吡氟禾草灵	76.4～108.6	78.5～104.7	81.7～98.0
	炔草酯	71.2～97.4	69.3～90.3	81.9～97.6
	禾草灵	80.4～109.0	76.1～95.7	79.4～93.8
	氯氟草酯	80.6～112.2	79.0～102.9	82.1～98.0
	噁唑禾草灵	74.2～103.4	77.3～98.5	79.0～95.2
	精喹禾灵	77.4～103.8	70.3～90.3	81.0～96.0
猪肉	2,4-滴丁酯	71.3～97.6	78.9～101.7	80.3～95.7
	吡氟氯禾灵	77.4～103.8	76.1～98.9	79.8～94.9
	吡氟禾草灵	88.6～114.8	78.4～102.2	81.8～97.8
	炔草酯	80.4～101.2	75.9～109.2	84.3～99.8
	禾草灵	74.6～104.0	77.9～102.3	83.2～99.9
	氯氟草酯	76.4～102.9	76.7～100.7	83.0～98.6
	噁唑禾草灵	81.0～108.2	74.6～99.1	83.0～98.6
	精喹禾灵	82.2～105.8	75.9～100.0	83.3～99.7
鱼	2,4-滴丁酯	74.4～102.2	79.1～103.4	79.4～93.8
	吡氟氯禾灵	77.2～103.4	82.2～103.1	84.3～99.4
	吡氟禾草灵	82.0～111.4	80.1～107.8	79.6～94.4
	炔草酯	77.6～107.4	86.5～111.7	83.2～99.9
	禾草灵	84.4～112.8	83.0～109.6	84.1～99.0
	氯氟草酯	80.4～111.0	83.7～113.5	82.6～97.6
	噁唑禾草灵	70.8～94.6	77.9～100.8	81.2～97.2
	精喹禾灵	72.8～94.6	77.1～98.9	84.3～99.4
禽蛋	2,4-滴丁酯	79.1～108.5	78.9～102.5	83.1～99.9
	吡氟氯禾灵	88.6～113.6	80.1～100.8	80.4～96.6
	吡氟禾草灵	80.4～111.0	83.0～109.6	79.6～94.4
	炔草酯	76.4～108.6	76.7～98.9	80.4～95.2
	禾草灵	81.0～108.2	73.8～89.0	79.8～94.9
	氯氟草酯	77.2～103.4	75.8～97.3	81.8～97.8
	噁唑禾草灵	82.0～109.0	71.4～90.3	83.0～98.6
	精喹禾灵	76.0～101.4	81.9～106.7	86.3～99.8

Foreword

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

This standard was proposed by and is under the charge of Certification and Accreditation Administration.

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

This main drafters of this standard are Zhao Zengyun, Liu Han, Shen Weijian, Yu Keyao, Shen chongyu, Gui Qianwen, Gong Yuxia, Jiang Yuan and Tao Hongjin.

This standard is a professional standard for entry-exit inspection and quarantine promulgated for the first time.

Determination of herbicide residues— Part 4: Determination of aryloxyphenoxypropionate herbicide residues in foodstuffs for import and export by GC-MS/MS method

1 Scope

The standard specifies the method of determination of 2,4-D butylate, Fluazifop-butyl, Fenoxaprop, Haloxyfop, Quizalofop-P-ethyl, Clodinafop-propargyl, Cyhalofop-butyl Diclofop residues in foodstuffs for import and export by GC-MS/MS.

The standard is applicable to the determination and the confirmation of 2,4-D butylate, Fluazifop-butyl, Fenoxaprop, Haloxyfop, Quizalofop-P-ethyl, Clodinafop-propargyl, Cyhalofop-butyl, Diclofop residues in soybean, barley-tea, rice, carrot, spinach, bean, garlic-stem, strawberry, honey, meat, crucian and egg.

2 Principle

The test samples are extracted with acetonitrile containing 1% acetic acid, and followed by dispersive solid-phase extraction (dispersive-SPE) using Primary secondary amine (PSA), Octadecylsilane (ODS) and graphitized carbon black. The residues is determined and confirmed by GC-MS/MS, using external standard method.

3 Reagents and Materials

All reagents used should be analytical pure unless otherwise specified.

3.1 Acetonitrile: LC grade.

3.2 *n*-Hexane: LC grade.

3.3 Acetone: LC grade.

3.4 Acetic acid.

3.5 Sodium Acetate Anhydrous.

3.6 Anhydrous sodium sulfate: Ignite at 650 ℃ for 4 h and stored in a desiccators.

3.7 Extraction solution (acetonitrile containing 1% acetic acid): Transfer 10 mL of acetic acid (3.4) into a 1 000 mL beaker, add approximately 990 mL of acetonitrile (3.1) and mix well.

3.8 Aryloxyphenoxy-propionate herbicide standard: 2,4-D butylate, CAS No: 94-80-4, $C_{12}H_{14}C_{12}O_3$, Purity≥97.1%; Fluazifop-butyl, CAS No: 79241-46-6, $C_{19}H_{20}F_3NO_4$, Purity≥99%; Fenoxaprop, CAS No: 95617-09-7, $C_{16}H_{12}ClNO_5$, Purity≥99%; Haloxyfop, CAS No: 69806-34-4, $C_{15}H_{11}ClF_3NO_4$, Purity≥99%; Quizalofop-P-ethyl, CAS No: 100646-51-3, $C_{19}H_{17}ClN_2O_4$, Purity≥99.5%; Clodinafop-propargyl, CAS No: 105512-06-9, $C_{17}H_{13}ClFNO_4$, Purity≥99.0%; Cyhalofop-butyl, CAS No: 122008-85-9, $C_{20}H_{20}FNO_4$, Purity≥99.0%; Diclofop, CAS No: 51338-27-3, $C_{16}H_{14}Cl_2O_4$, Purity≥96.5%.

3.9 Aryloxyphenoxypropionate herbicide stock standard solution: Accurately weigh an adequate amount of Aryloxyphenoxypropionate herbicide standard and dissolve with a little volume of acetone. Dilute with acetone to make final concentration of 100 μg/mL. The standard stock solution can be preserved by avoiding light in the refrigerator at range of 0 ℃～4 ℃ for 6 month.

3.10 Mixture standard solution: Accurately pipet 5.0 mL of Aryloxyphenoxypropionate herbicide stock standard solution into a 50 mL brown volumetric flask, dissolve and dilute to volume with acetone prepare a solution of 10.0 μg/mL as mixture intermediate standard solution. The standard stock solution can be preserved by avoiding light in the refrigerator at range of 0 ℃～4 ℃ for 3 month.

3.11 Mixture standard working solution: dilute a mixture standard solution with acetone to make required concentration just before use.

3.12 Primary secondary amine (PSA) sorbent: 40 μm～60 μm.

3.13 Agraphitized carbon black sorbent: 120 μm～400 μm.

3.14 Octadecylsilane (ODS) bonded phase: 60 μm～100 μm.

3.15 Teflon filter: 0.45 μm.

4 Apparatus and equipment

4.1 Gas chromatography-tandem mass spectrometry equipment.

4.2 Shaker.

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

4.4 Vortex mixer.

4.5 Tissue homogenizer.

4.6 Grinder.

4.7 Rotary evaporator.

4.8 Nitrogen evaporator.

4.9 Stoppered Erlenmeyer flask:250 mL.

4.10 Centrifuge tubes with ground stopper:10 mL.

4.11 Concentrate bottle:150 mL.

5 Preparation and storage of test sample

5.1 Preparation of test sample

5.1.1 Carrot, bean, garlic-stem, strawberry and spinach

Take approximately 500 g of representative sample (do not wash with water). Edible part is minced and crushed into pulp with a tissue homogenizer. The sample is placed in clean containers as the test sample, which is sealed and labeled.

5.1.2 Soybean, rice and barley-tea.

Take approximately 500 g of representative sample, grind with a grinder, and mix thoroughly. The sample is placed in clean containers as the test sample, which is sealed and labeled.

5.1.3 Meat, fish and egg.

Take approximately 500 g of representative sample. Edible part is blended thoroughly with a tissue homogenizer. The sample is placed in clean containers as the test sample, which is sealed and labeled.

5.1.4 Honey

Take about 500 g of representative sample. The non-crystallized sample should be stirred well to make homogeneous while the crystallized sample must be warmed under a water-bath at no more than 60 ℃ with the sample bottle covered tightly for prevention of loss of water, mix thoroughly

when all sample has melted, then cool immediately to room temperature. Take the prepared sample into two sample bottles, seal and label them.

5.2 Storage of test sample

In the course of sampling and sample preparation, precautions should be taken to avoid contamination or any factors which may cause the change of residue content.

The test samples of soybean, barley-tea, rice, honey and egg should be stored at 4 ℃ refrigerator. The test samples of carrot, bean, garlic-stem, strawberry, spinach, meat, crucian should be stored below −18 ℃.

6 Procedure

6.1 Extraction

6.1.1 Carrot, spinach, bean, garlic-stem and strawberry.

Weigh approximately 10 g (accurate to 0.01 g) of the test sample into a 250 mL stopperde Erlenmeyer flask. Add 15 g of anhydrous magnesium sulfate, 6 g of acetic acid sodium and 50 mL of extraction solution (3.7) into the flask and shake on the shaker for 30 min, stand for 10 min. Then filter the extract into a 150 mL concentrate bottle . The extraction is repeated with 20 mL extraction solution (3.7). Combine the filtrates into the same concentrate bottle, condense to nearly dryness by a rotary evaporator in a water bath under 40 ℃. Add 2 mL acetonitrile to dissolve the residue for cleanup procedure.

6.1.2 Soybean, rice, meat, fish and egg.

Weigh approximately 5 g (accurate to 0.01 g) of the test sample into a 250 mL stopperde Erlenmeyer flask. Add 15 g of anhydrous magnesium sulfate, 6 g of acetic acid sodium and 50 mL of extraction solution (3.7) into the flask. The sample of meat, fish and egg should be homogenized for 5 min. Then shake the flask on the shaker for 30 min, stand for 10 min. Then filter the extract into a 150 mL concentrate bottle . The extraction is repeated with 20 mL extraction solution (3.7). Combine the filtrates into the same concentrate bottle, condense to nearly dryness by a rotary evaporator in a water bath under 40 ℃. Add 2 mL acetonitrile to dissolve the residue for cleanup procedure.

6.1.3 Barley-tea.

Weigh approximately 5 g (accurate to 0.01 g) of the test sample into a 250 mL stopperde Erlenmeyer flask. Add 5 mL water and stand over night. Add 15 g of anhydrous magnesium sulfate, 6 g of acetic acid sodium and 50 mL of extraction solution (3.7) into the flask and shake on the shaker for 30 min, stand for 10 min. Then filter the extract into a 150 mL concentrate bottle . The extraction is repeated

with 20 mL extraction solution (3.7). Combine the filtrates into the same concentrate bottle, condense to nearly dryness by a rotary evaporator in a water bath under 40 ℃. Add 2 mL acetonitrile to dissolve the residue for cleanup procedure.

6.1.4 Honey.

Weigh approximately 5 g(accurate to 0.01 g) of the test sample into a 250 mL stopperde Erlenmeyer flask. Add 5 mL water to dissolve the sample. Then add 15 g of anhydrous magnesium sulfate, 6 g of acetic acid sodium and 50 mL of extraction solution (3.7) into the flask and shake on the shaker for 30 min, stand for 10 min. Then filter the extract into a 150 mL concentrate bottle. The extraction is repeated with 20 mL extraction solution (3.7). Combine the filtrates into the same concentrate bottle, condense to nearly dryness by a rotary evaporator in a water bath under 40 ℃. Add 2 mL acetonitrile to dissolve the residue for cleanup procedure.

6.2 Clean-up

6.2.1 The extraction of carrot, bean, garlic-stem, strawberry, spinach and barley tea.

Take the extraction of sample from 6.1 above into 10 mL Centrifuge tube. Add 200 mg of PSA (3.12) and 200 mg graphitized carbon black sorbent (3.13) into the tube. Mix for 1 min. The solution is filtered through the 0.45 μm filter (3.15) for GC-MS/MS determination.

6.2.2 The extraction of soybean, rice, meat, fish, egg and honey.

Take the extraction of sample from 6.1 above into 10 mL Centrifuge tube. Add 200 mg of PSA (3.12), 200 mg graphitized carbon black sorbent (3.13) and 100 mg of ODS (3.14) into the tube. Mix for 1 min. The solution is filtered through the 0.45 μm filter (3.15) for GC-MS/MS determination.

6.3 Determination

6.3.1 GC-MS/MS conditions

a) Column: DB-5 ms fused quartz capillary column, 30 m × 0.25 mm (i.d.), film thickness 0.25 μm, or the equivalent;

b) Column temperature:

$$50\ ℃\ (2\ \text{min}) \xrightarrow{30\ ℃/\text{min}} 80\ ℃ \xrightarrow{5\ ℃/\text{min}} 80\ ℃\ (10\ \text{min})$$

c) Inlet temperature: 250 ℃;

d) Interface temperature: 280 ℃;

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

f) Injection volumn:1 μL;

g) Injection mode:splitless,purge after 1.2 min;

h) Ion source:EI,positive ionisation mode.

i) Ionization source temperature:230 ℃;

j) Ionization energe:70 eV;

k) Solvent protection delay:9.0 min;

l) Scan mode:selected reaction monitoring (SRM);the parent ions and daughter ions were listed in table 1.

Table 1—Selected reaction monitoring (SRM) condition

Compound	Retention time/min	Parent ion(m/z)	Daughter ion(m/z)	Collision Energy/V
2,4-D butylate	12.065	175.9	111.0	15
		277.1	185.0[a]	5
		185.6	155.0	15
Haloxyfop	15.313	288.9	180.0	30
		316.7	91.0[a]	15
Fluazifop-butyl	17.316	254.5	146.0	25
		282.3	91.0[a]	20
		383.4	282.0	10
Clodinafop-propargyl	19.197	238.8	130.0	15
		349.8	266.0[a]	10
Diclofop	19.681	254.2	162.0[a]	15
		341.1	253.0	10
Cyhalofop-butyl	22.485	256.3	120.0[a]	10
		357.4	256.0	10
Fenoxaprop	23.739	288.8	91.0	20
			119.0	10
		361.8	288.0[a]	10
Quizalofop-P-ethyl	26.227	299.8	91	20
		372.9	299.0[a]	10
[a] ion for quantification.				

6.3.2 GC-MS/MS determination and confirmation

According to the approximate concentration of the pesticide in the sample solution, select the standard working solution with similar concentration of the sample solution. The standard working solution should be injected in-between the injections of the sample solution with one common volume. The response of Aryloxyphenoxypropionate herbicide in the standard working solution and sample solution should be within the linear range of the instrument detection. If there is a peak appeared at the same retention time for both of sample solution and standard working solution, and the qualification ions for every compound must be found, and for the same analysis batch and the same compound, the variation range of the ion ratio between the two daughter ions for the unknown sample and the standard working solution at the similar concentration cannot be out of range of table 2.

Under the above GC-MS/MS operating conditions, the retention time of Aryloxyphenoxypropionate herbicide peaks are listed in table 1. The GC-MS/MS total ion chromatogram and its mass spectrum of standard solution are shown respectively by figure A.1 in annex A and figure B.1 in annex B.

Table 2—Maximum permitted tolerances for relative ion intensities while confirmation

Relative intensity/%	>50	>20~50	>10~20	≤10
Permitted tolerances/%	±20	±25	±30	±50

6.4 Blank test

The operation of the blank test is the same as the described in the method of determination, without sample addition.

6.5 Calculation and expression of the result

Calculate the content of Aryloxyphenoxypropionate herbicide residue in the test sample by GC-MS/MS data processor or using the followed formula (1).

$$X_i = \frac{A_i \times c_i \times V}{As_i \times m} \quad \cdots\cdots(1)$$

Where:

X_i—the residue content of Aryloxyphenoxypropionate herbicide in the test samples, μg/kg;

A_i—the peak area of Aryloxyphenoxypropionate herbicide in the test sample solution;

c_i—the concentration of Aryloxyphenoxypropionate herbicide in the standard working solution, ng/mL;

V—the final volume of sample solution, mL;

As_i—the peak area of Aryloxyphenoxypropionate herbicide in the standard working solution;

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

7 Detection limit and recovery

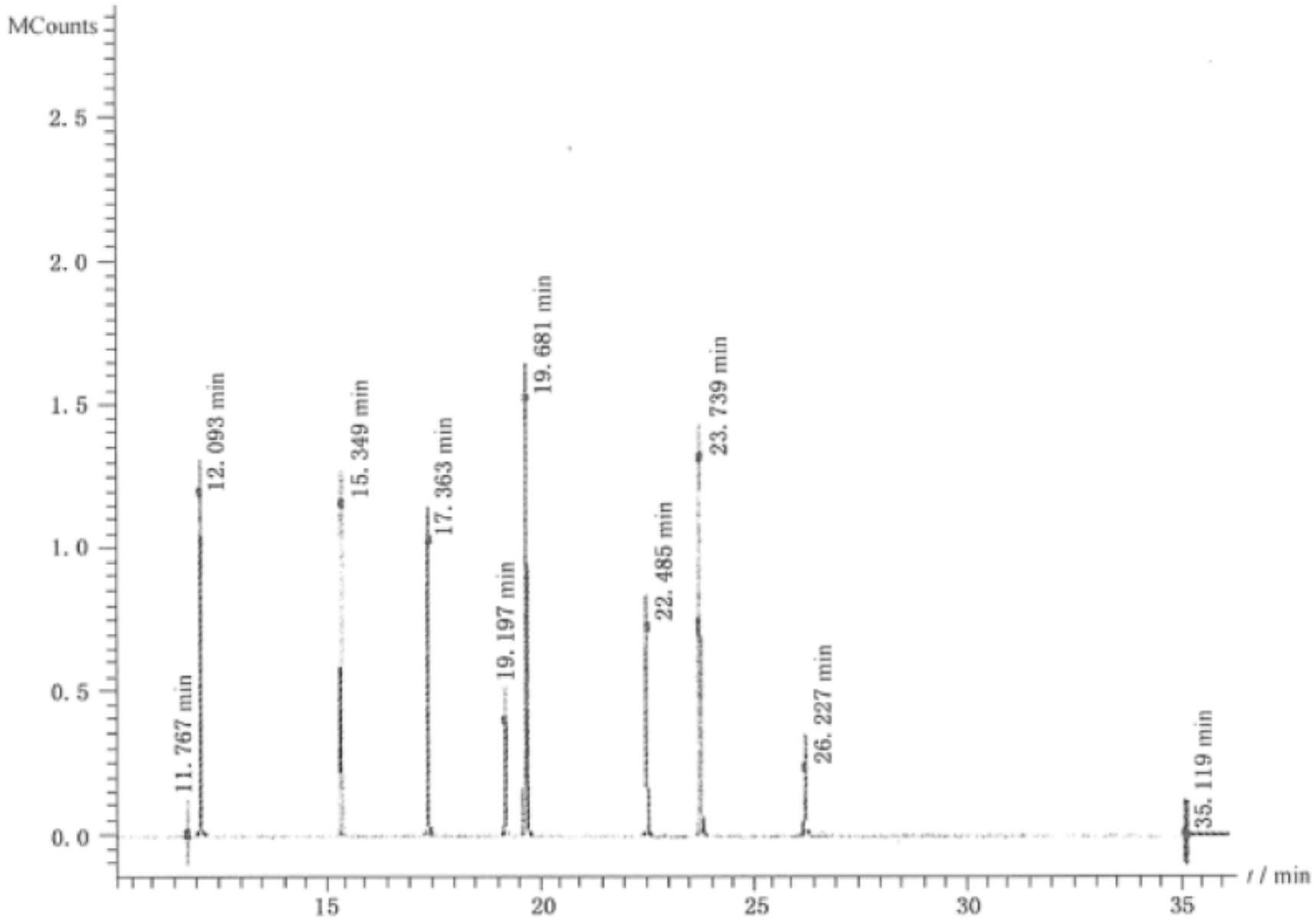
7.1 Limit of quantification

The limit of determination of this method is 0.005 mg/kg.

7.2 Recovery

The recovery and the fortifying concentration of aryloxyphenoxypropionate herbicide in different matrix is shown in annex C.

Annex A
(informative)
GC/MS/MS selected ion chromatogram of
the aryloxyphenoxypropionate herbicide standard



2,4-Dbutylate(12.093 min);Haloxyfop(15.349 min);Fluazifop-butyl(17.363 min);
Clodinafop-propargyl(19.197 min);Diclofop(19.681 min);Cyhalofop-butyl(22.485 min);
Fenoxaprop(23.739 min);Quizalofop-P-ethyl(26.227 min).

Figure A.1—GC/MS/MS selected ion chromatogram of
the aryloxyphenoxypropionate herbicide standard (1.0 μg/mL)

Annex B
(informative)
Chromatogram of the aryloxyphenoxypropionate herbicide standard

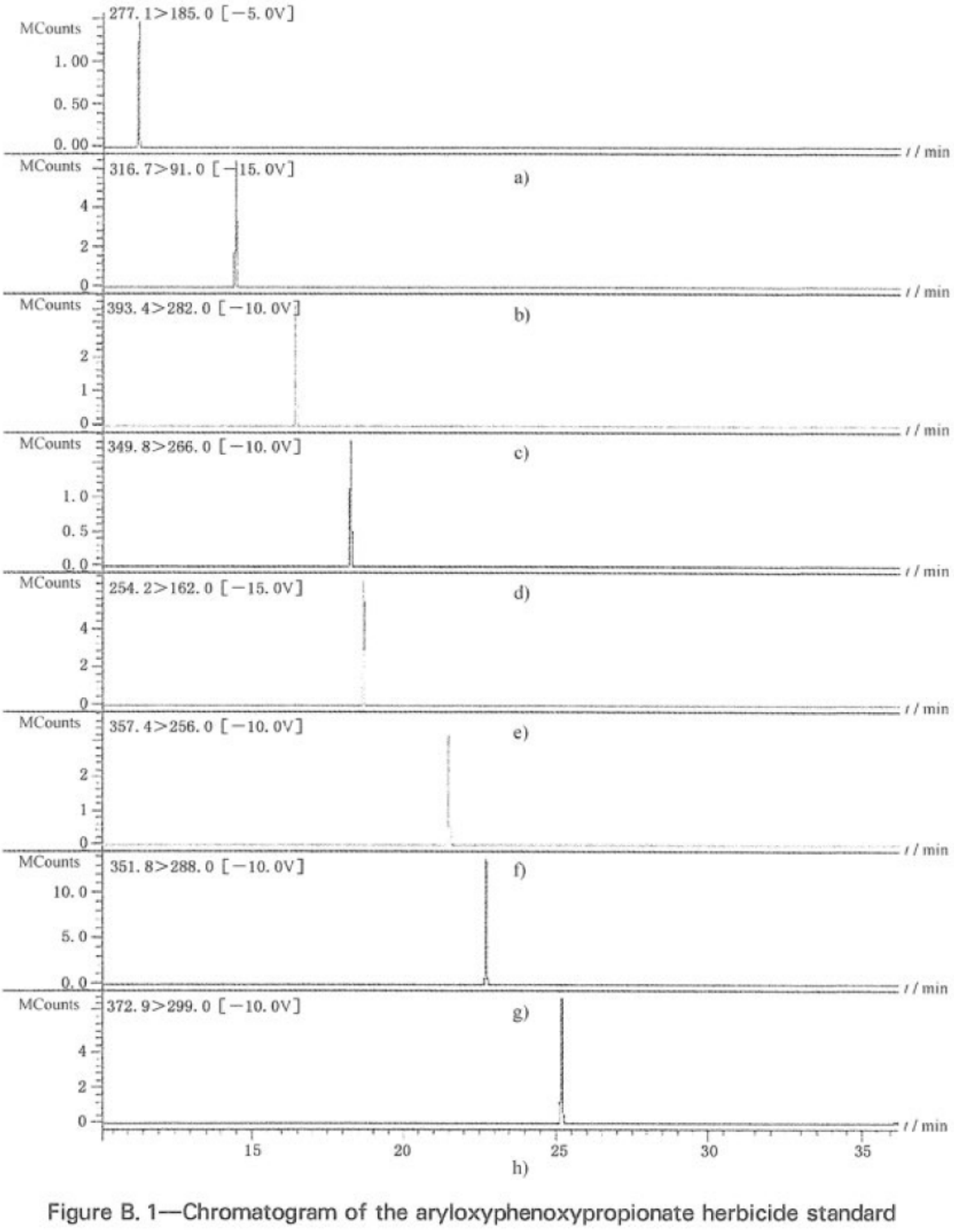


Figure B. 1—Chromatogram of the aryloxyphenoxypropionate herbicide standard

Annex C
(informative)
The recovery and the fortifying concentration of aryloxyphenoxypropionate herbicide in different matrix

Table C. 1—Recovery and the fortifying concentration of aryloxyphenoxypropionate herbicide in different matrix

Sample	Compound	Fortifying and recovery/%		
		0. 005 mg/kg	0. 010 mg/kg	0. 020 mg/kg
soybean	2,4-D butylate	72. 4～97. 0	83. 9～104. 7	79. 0～98. 7
	Haloxyfop	79. 8～106. 6	76. 3～93. 6	81. 9～97. 6
	Fluazifop-butyl	75. 2～101. 1	79. 4～100. 6	77. 4～93. 1
	Clodinafop-propargyl	71. 0～99. 8	71. 9～91. 2	79. 0～94. 9
	Diclofop	88. 6～114. 4	72. 9～102. 8	79. 8～94. 1
	Cyhalofop-butyl	75. 4～106. 0	72. 9～101. 9	78. 9～94. 3
	Fenoxaprop	85. 0～115. 6	70. 9～91. 9	77. 7～92. 6
	Quizalofop-P-ethyl	77. 2～107. 8	75. 0～101. 6	78. 8～92. 6
barley-tea	2,4-D butylate	70. 8～99. 4	93. 3～116. 0	81. 0～96. 8
	Haloxyfop	68. 4～98. 4	79. 2～103. 5	79. 1～94. 4
	Fluazifop-butyl	76. 0～107. 8	79. 0～101. 4	78. 6～94. 4
	Clodinafop-propargyl	86. 6～99. 0	78. 5～91. 5	82. 8～91. 2
	Diclofop	76. 4～106. 0	70. 9～94. 4	81. 5～96. 9
	Cyhalofop-butyl	78. 2～113. 0	72. 7～94. 3	79. 8～94. 14
	Fenoxaprop	79. 4～110. 4	74. 5～98. 6	78. 8～94. 24
	Quizalofop-P-ethyl	83. 2～119. 2	72. 6～94. 6	77. 7～92. 6
rice	2,4-D butylate	78. 2～110. 2	80. 3～106. 7	81. 7～97. 9
	Haloxyfop	82. 8～114. 2	86. 2～107. 8	81. 9～98. 0
	Fluazifop-butyl	90. 8～118. 8	78. 9～101. 7	83. 8～98. 9
	Clodinafop-propargyl	76. 0～101. 4	75. 9～105. 7	82. 8～98. 3
	Diclofop	79. 8～110. 6	76. 4～104. 7	83. 0～99. 1
	Cyhalofop-butyl	74. 4～99. 4	84. 9～111. 7	81. 9～97. 6
	Fenoxaprop	78. 8～111. 2	80. 1～110. 1	81. 9～97. 6
	Quizalofop-P-ethyl	77. 4～103. 8	78. 6～106. 7	79. 0～95. 2
carrot	2,4-D butylate	74. 6～103. 8	73. 0～97. 3	78. 6～94. 4
	Haloxyfop	88. 6～114. 8	70. 9～94. 4	81. 1～96. 0
	Fluazifop-butyl	79. 0～112. 8	78. 9～101. 7	81. 0～96. 8

Table C.1 (continued)

Sample	Compound	Fortifying and recovery/%		
		0.005 mg/kg	0.010 mg/kg	0.020 mg/kg
carrot	Clodinafop-propargyl	79.4～100.8	75.9～105.7	79.8～94.1
	Diclofop	81.6～116.2	76.4～104.7	80.3～96.4
	Cyhalofop-butyl	72.6～102.0	78.4～96.2	79.0～95.2
	Fenoxaprop	70.8～96.6	75.4～98.4	80.6～95.8
	Quizalofop-P-ethyl	84.4～101.4	78.6～100.7	81.1～96.0
spinach	2,4-D butylate	75.4～98.0	81.2～105.6	79.1～98.8
	Haloxyfop	77.6～105.3	74.7～98.2	77.9～96.5
	Fluazifop-butyl	73.1～99.4	80.4～101.5	79.9～94.5
	Clodinafop-propargyl	78.0～98.9	77.6～90.8	80.0～97.8
	Diclofop	82.4～104.5	77.6～106.3	78.9～95.6
	Cyhalofop-butyl	78.5～101.2	78.2～100.2	77.6～99.6
	Fenoxaprop	84.3～101.9	71.4～95.6	78.2～94.7
	Quizalofop-P-ethyl	78.3～99.8	77.6～104.2	88.1～95.7
bean	2,4-D butylate	79.4～103.8	69.3～90.3	79.8～94.9
	Haloxyfop	76.0～101.4	76.4～104.7	79.0～94.2
	Fluazifop-butyl	79.8～110.6	78.9～101.7	82.8～98.0
	Clodinafop-propargyl	74.4～103.2	74.6～99.1	79.0～94.4
	Diclofop	81.6～107.8	76.0～99.3	79.0～95.2
	Cyhalofop-butyl	77.2～103.4	77.3～98.5	82.0～98.0
	Fenoxaprop	88.6～115.4	76.0～95.7	79.0～95.3
	Quizalofop-P-ethyl	76.2～103.0	69.3～90.3	84.3～99.4
garlic-stem	2,4-D butylate	71.2～96.8	72.3～93.3	85.5～101.6
	Haloxyfop	70.8～94.6	76.0～99.3	84.1～99.0
	Fluazifop-butyl	80.4～111.1	79.9～102.3	81.7～98.1
	Clodinafop-propargyl	77.4～103.8	76.0～95.7	83.2～98.2
	Diclofop	76.4～104.4	76.4～104.7	82.0～98.0
	Cyhalofop-butyl	79.0～108.0	84.9～106.2	79.6～94.4
	Fenoxaprop	73.4～103.2	78.9～103.1	81.2～96.0
	Quizalofop-P-ethyl	80.6～112.2	82.8～107.4	83.3～96.1
strawberry	2,4-D butylate	79.1～108.2	78.9～101.7	83.2～98.2
	Haloxyfop	73.2～100.8	83.0～109.6	79.6～94.4
	Fluazifop-butyl	81.0～113.4	76.0～99.0	84.3～99.4
	Clodinafop-propargyl	72.4～105.6	79.1～103.4	82.1～98.0
	Diclofop	77.8～105.2	76.0～99.3	82.2～98.2

Table C. 1 (continued)

Sample	Compound	Fortifying and recovery/%		
		0.005 mg/kg	0.010 mg/kg	0.020 mg/kg
strawberry	Cyhalofop-butyl	77.6～105.2	76.6～101.2	82.4～97.8
	Fenoxaprop	80.4～111.0	78.9～99.9	83.4～99.4
	Quizalofop-P-ethyl	71.2～97.4	76.0～99.3	82.8～97.9
honey	2,4-D butylate	74.6～103.8	78.9～101.7	84.3～99.4
	Haloxyfop	80.4～111.0	76.0～99.3	83.2～98.2
	Fluazifop-butyl	76.4～108.6	78.5～104.7	81.7～98.0
	Clodinafop-propargyl	71.2～97.4	69.3～90.3	81.9～97.6
	Diclofop	80.4～109.0	76.1～95.7	79.4～93.8
	Cyhalofop-butyl	80.6～112.2	79.0～102.9	82.1～98.0
	Fenoxaprop	74.2～103.4	77.3～98.5	79.0～95.2
	Quizalofop-P-ethyl	77.4～103.8	70.3～90.3	81.0～96.0
meat	2,4-D butylate	71.3～97.6	78.9～101.7	80.3～95.7
	Haloxyfop	77.4～103.8	76.1～98.9	79.8～94.9
	Fluazifop-butyl	88.6～114.8	78.4～102.2	81.8～97.8
	Clodinafop-propargyl	80.4～101.2	75.9～109.2	84.3～99.8
	Diclofop	74.6～104.0	77.9～102.3	83.2～99.9
	Cyhalofop-butyl	76.4～102.9	76.7～100.7	83.0～98.6
	Fenoxaprop	81.0～108.2	74.6～99.1	83.0～98.6
	Quizalofop-P-ethyl	82.2～105.8	75.9～100.0	83.3～99.7
crucian	2,4-D butylate	74.4～102.2	79.1～103.4	79.4～93.8
	Haloxyfop	77.2～103.4	82.2～103.1	84.3～99.4
	Fluazifop-butyl	82.0～111.4	80.1～107.8	79.6～94.4
	Clodinafop-propargyl	77.6～107.4	86.5～111.7	83.2～99.9
	Diclofop	84.4～112.8	83.0～109.6	84.1～99.0
	Cyhalofop-butyl	80.4～111.0	83.7～113.5	82.6～97.6
	Fenoxaprop	70.8～94.6	77.9～100.8	81.2～97.2
	Quizalofop-P-ethyl	72.8～94.6	77.1～98.9	84.3～99.4
egg	2,4-D butylate	79.1～108.5	78.9～102.5	83.1～99.9
	Haloxyfop	88.6～113.6	80.1～100.8	80.4～96.6
	Fluazifop-butyl	80.4～111.0	83.0～109.6	79.6～94.4
	Clodinafop-propargyl	76.4～108.6	76.7～98.9	80.4～95.2
	Diclofop	81.0～108.2	73.8～89.0	79.8～94.9
	Cyhalofop-butyl	77.2～103.4	75.8～97.3	81.8～97.8

Table C. 1 (continued)

Sample	Compound	Fortifying and recovery/%		
		0. 005 mg/kg	0. 010 mg/kg	0. 020 mg/kg
egg	Fenoxaprop	82. 0～109. 0	71. 4～90. 3	83. 0～98. 6
	Quizalofop-P-ethyl	76. 0～101. 4	81. 9～106. 7	86. 3～99. 8

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