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中华人民共和国出入境检验检疫行业标准

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进出口食品中31种酸性除草剂残留量的检测方法 气相色谱-质谱法

Determination of 31 acid pesticide residues in foods for import and export—GC-MS method

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前　言

本标准的附录A和附录B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：中华人民共和国湖南出入境检验检疫局。

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本标准系首次发布的出入境检验检疫行业标准。

进出口食品中31种酸性除草剂残留量的检测方法 气相色谱-质谱法

1 范围

本标准规定了食品中31种酸性除草剂残留量的气相色谱-质谱测定方法。

本标准适用于大米、糙米、大麦、小麦和玉米中二氯皮考啉酸、对氯苯氧乙酸、2-苯基苯酚、麦草畏、2甲4氯、2,4-滴丙酸、溴苯腈、2,4-滴、三氯吡氧乙酸、1-萘乙酸/NAA、5-氯苯酚、2,4,5滴丙酸、草灭平、2甲4氯丁酸、2,4,5-涕、氟草烟、2,4-滴丁酸、苯达松、碘苯腈、毒莠定、二氯喹啉酸、吡氟禾草灵、吡氟氯禾灵、麦草氟、三氟羧草醚、水杨菌胺、嘧草硫醚、环酰菌胺、氯甲酰草胺、喹禾灵、双草醚等31种酸性除草剂残留量的测定。

2 方法提要

试样用丙酮酸性水溶液提取，挥去提取液中丙酮后，经乙酸乙酯液液分配、凝胶渗透色谱仪(GPC)净化后，用三甲基硅烷化重氮甲烷衍生化，衍生化产物过弗罗里硅土固相萃取柱进一步净化，用气相色谱-质谱仪(GC-MS)选择离子监测方式(SIM)测定，外标法定量。

3 试剂和材料

除另有规定外，所有试剂均为分析纯，水为二次蒸馏水。

3.1 丙酮：优级纯。

3.2 正己烷：优级纯。

3.3 环己烷：色谱纯。

3.4 甲醇：色谱纯。

3.5 苯：色谱纯。

3.6 乙酸乙酯：色谱纯。

3.7 氯化钠。

3.8 氯化钠溶液(15%)：称取150 g氯化钠(3.7)溶于水中，定容至1 000 mL。

3.9 浓盐酸：优级纯。

3.10 盐酸溶液(0.1 mol/L)：准确移取9 mL(3.9)溶于水中，定容至1 000 mL。

3.11 盐酸溶液(4.0 mol/L)：准确移取360 mL(3.9)溶于水中，定容至1 000 mL。

3.12 三甲基硅烷化重氮甲烷正己烷溶液(2.0 mol/L)。

3.13 丙酮-环己烷提取液(2+8，体积比)：准确移取20 mL丙酮(3.1)和80 mL环己烷(3.3)混合均匀。

3.14 丙酮-正己烷提取液(2+8，体积比)：准确移取20 mL丙酮(3.1)和80 mL正己烷(3.2)混合均匀。

3.15 甲醇-苯提取液(2+8，体积比)：准确移取20 mL甲醇(3.4)和80 mL苯(3.5)混合均匀。

3.16 农药标准品：二氯皮考啉酸、对氯苯氧乙酸、2-苯基苯酚、麦草畏、2甲4氯、2,4-滴丙酸、溴苯腈、2,4-滴、三氯吡氧乙酸、1-萘乙酸/NAA、5-氯苯酚、2,4,5滴丙酸、草灭平、2甲4氯丁酸、2,4,5-涕、氟草烟、2,4-滴丁酸、苯达松、碘苯腈、毒莠定、二氯喹啉酸、吡氟禾草灵、吡氟氯禾灵、麦草氟、三氟羧草醚、水

杨菌胺、嘧草硫醚、环酰菌胺、氯甲酰草胺、喹禾灵、双草醚标准品(英文名、分子式和CAS登记号见附录A表A.1):纯度大于等于97%。

3.17 农药标准储备液:准确称取适量(精确至0.1 mg)各农药标准品,用丙酮溶解于50 mL棕色容量瓶,溶解定容,配制浓度为500 μg/mL单标储备液。此储备液在0 ℃～4 ℃避光保存,有效期为90 d。

3.18 混合标准中间溶液:准确吸取2.0 mL单个农药的标准储备溶液于100 mL棕色容量瓶中,用丙酮溶解定容,配制浓度为10 μg/mL混合标准中间溶液,标准中间液在0 ℃～4 ℃避光保存,有效期为30 d。

3.19 混合标准工作溶液:根据检测需要移取一定体积的混合标准中间溶液逐级稀释成适当浓度的混合标准工作溶液,现配现用。

3.20 弗罗里硅土固相萃取柱:250 mg,3 mL,或相当者。

4 仪器和设备

4.1 气相色谱-质谱仪:配有电子轰击源(EI)。

4.2 凝胶渗透净化系统。

4.3 固相萃取装置。

4.4 离心机:3 000 r/min。

4.5 涡旋混匀器。

4.6 旋转蒸发仪。

4.7 氮气吹干仪。

4.8 离心管:50 mL。

4.9 鸡心瓶:200 mL。

4.10 微量注射器:10 μL。

5 试样制备与保存

5.1 试样制备

取有代表性样品500 g,用粉碎机粉碎并通过40目筛,混匀,均分成两份作为试样,分装入洁净的盛样容器内,密封并标明标记。

5.2 试样保存

将试样于0 ℃～4 ℃保存。

在制样的操作过程中,应防止样品受到污染或发生残留物含量的变化。

6 测定步骤

6.1 提取

称取10 g(精确至0.01 g)试样于50 mL具塞磨口离心试管中,加入10 mL丙酮(3.1)和10 mL盐酸溶液(3.10),放置30 min,然后加入20 mL丙酮(3.1)置于旋转振荡器上振荡15 min,离心2 min(3 000 r/min),吸取上层清液,残渣再用2×20 mL丙酮(3.1)提取2次,合并全部提取液,将提取液转入200 mL鸡心瓶中,在45 ℃水浴下用平缓氮气流挥去提取液中的丙酮。然后加入10 mL氯化钠水溶液(3.8)和2.5 mL盐酸溶液(3.11),加入20 mL乙酸乙酯(3.6),剧烈振摇5 min,静置,待分层完全后,收集有机相,水相再用2×20 mL乙酸乙酯(3.6)重复提取两次,合并全部乙酸乙酯层于200 mL鸡心瓶中,于45℃水浴下旋转浓缩至近干,准确加入4.0 mL丙酮-环己烷(3.13)溶解残渣,过0.45 μm滤膜,待净化。

6.2 凝胶色谱净化

凝胶色谱条件

a) 凝胶柱:CLN pak EV 22000柱(300 mm×20 mm);

b) 流动相:丙酮-环己烷(3.13);

c) 流速:5.0 mL/min;

d) 进样量:2.0 mL;

e) 收集方式:时间模式,收集 12.0 min～30.0 min 洗脱流出液。

6.3 衍生化

将收集的凝胶色谱洗脱液在 45 ℃下,旋转浓缩近干,用 3×2 mL 丙酮(3.1)洗涤,然后转移至 10 mL 具塞刻度试管中,在 40 ℃下用平缓氮气流吹至近干,用 2 mL 苯-甲醇(3.15)溶液溶解残渣,加入 0.2 mL 三甲基硅烷化重氮甲烷正己烷溶液(3.12),盖塞,混匀,30℃下放置 30 min;然后用平缓氮气流吹至近干,用 5 mL 正己烷(3.2)溶解残渣。

6.4 固相萃取柱净化

先用 3 mL 丙酮(3.1),6 mL 正己烷(3.2)依次预淋洗弗罗里硅土固相萃取柱(3.20),弃去淋洗液,将 6.3 得到的试样正己烷溶解液过弗罗里硅土固相萃取柱(3.20),弃去流出液;然后用 6 mL 丙酮-正己烷(3.14)洗脱,收集全部洗脱液于 10 mL 具塞刻度试管中,45 ℃下用平缓氮气流吹至近干,用丙酮(3.1)溶解定容至 0.5 mL,供 GC-MS 测定。

6.5 测定

6.5.1 气相色谱-质谱条件

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

b) 色谱柱温度:50 ℃保持 1 min,以 5 ℃/min 的速率上升至 160 ℃保持 3 min,再以 10 ℃/min 的速率上升至 300 ℃,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%,1.0 mL/min;

f) 进样量:2 μL;

g) 进样方式:无分流进样,1 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(SIM),根据 31 种农药的保留时间分组,每种农药选择一个定量离子,1 个～2 个定性离子,每种农药的保留时间、定量离子、定性离子及定量离子与定性离子的丰度比值,参见附录 A 中表 A.1 和表 A.2;

k) 溶剂延迟时间:9 min。

6.5.2 气相色谱-质谱测定

6.5.2.1 定性测定

对标准溶液及样液均按 6.5.1 规定的条件进行测定,如果样液中的色谱峰的保留时间与标准样品相同,则对其进行质谱确证。当待测农药选择的监测离子在扣除背景后的样品质谱图中均出现,而且所选择的离子丰度比与标准品的离子丰度比相一致,其值在允许范围内(允许范围见表 1),则可判断样品中存在此待测农药。如果不能确证,则应重新进样,改变确证离子方式或采用其他灵敏度更高的检测方法来确证。在上述气相色谱-质谱条件下,各农药的保留时间和选择离子丰度比参见附录 A 中表 A.1。

表 1 使用气相色谱-质谱定性时相对离子丰度最大允许偏差

相对丰度(基峰)/%	>50	>20～50	>10～20	≤10
相对离子丰度最大允许偏差/%	±10	±15	±20	±50

6.5.2.2 定量测定

根据样液中农药的含量情况,选定峰面积相近的标准工作溶液。标准工作溶液和样液中农药的响

应值均应在仪器检测的线性范围内。对混合标准工作液和样液等体积交替进样测定，在上述色谱条件下，各农药的保留时间参见附录 A 中表 A.1，混合标准品 SIM 色谱图参见附录 B 中图 B.1。

6.6 空白试验

除不加试样外，均按上述测定步骤进行。

6.7 结果计算和表示表达

用色谱工作站或按式(1)计算试样中各农药的含量。

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

式中：

X——试样中各农药的残留量，单位为毫克每千克(mg/kg)；

A——样液中各农药的峰面积；

c_s——标准工作液中各农药的浓度，单位为微克每毫升(μg/mL)；

A_s——标准工作液中各农药的峰面积，单位为平方毫米(mm^2)；

V——样液最终定容体积，单位为毫升(mL)；

m——最终样液所代表的试样量，单位为克(g)。

注：计算结果须扣除空白值。

7 测定低限和回收率

7.1 测定低限

本方法在大米、糙米、大麦、小麦和玉米中各农药残留量的测定低限均为 0.01 mg/kg。

7.2 回收率

在大米、糙米、大麦、小麦和玉米中 31 种农药添加回收率的实验数据见表 2。

表 2 样品中添加浓度和回收率数据

序号	农药中文名称	添加浓度/(mg/kg)	回收率/%				
			大米	糙米	大麦	小麦	玉米
1	二氯皮考啉酸	0.1	94.6～108.6	90.0～103.2	83.1～95.2	77.6～92.3	88.0～96.6
		0.05	92.6～108.8	83.6～97.6	91.8～106.0	80.2～89.4	91.2～106.2
		0.01	103.3～114.6	87.9～107.2	80.1～93.8	83.3～94.2	77.3～90.6
2	对氯苯氧乙酸	0.1	93.7～104.6	87.6～102.5	87.0～105.1	89.8～103.9	92.7～104.8
		0.05	84.0～96.0	85.2～102.6	91.4～98.2	85.8～97.2	81.2～92.0
		0.01	83.0～97.5	85.8～109.1	78.6～92.4	81.2～105.1	82.2～102.8
3	2-苯基苯酚	0.1	69.3～81.2	87.4～100.5	75.9～83.5	74.4～89.1	86.1～96.9
		0.05	69.6～84.4	80.8～96.0	60.2～71.4	66.4～80.0	87.8～99.6
		0.01	69.6～84.0	79.4～92.8	63.0～75.8	72.8～90.9	80.7～93.1
4	麦草畏	0.1	77.1～91.2	71.6～86.9	79.0～92.2	76.6～92.0	68.1～76.0
		0.05	83.0～90.6	79.0～93.4	82.6～89.2	81.4～90.6	64.8～76.6
		0.01	84.9～92.9	69.8～82.5	75.5～81.0	73.2～83.9	78.5～92.5
5	2甲4氯	0.1	92.6～108.1	80.6～88.9	82.0～92.2	79.1～92.9	82.9～93.3
		0.05	89.2～95.2	80.2～92.4	82.8～92.0	82.4～97.2	86.0～98.4
		0.01	94.2～102.3	77.7～92.3	82.7～91.6	77.4～92.3	78.4～94.4

表 2(续)

序号	农药中文名称	添加浓度/(mg/kg)	回收率/%				
			大米	糙米	大麦	小麦	玉米
6	2,4-滴丙酸	0.1	84.0～93.3	77.5～88.9	80.5～90.6	77.60～85.9	73.5～83.0
		0.05	83.8～95.0	80.2～92.4	81.6～86.4	81.6～90.4	78.4～92.8
		0.01	82.6～93.0	71.3～86.1	83.1～88.8	75.8～86.7	80.7～101.0
7	溴苯腈	0.1	90.5～105.3	75.6～88.4	87.7～98.3	78.7～86.5	82.8～93.2
		0.05	88.2～97.8	74.6～88.4	87.8～93.6	79.8～95.4	75.8～86.4
		0.01	95.8～107.0	72.4～86.8	84.2～91.4	73.4～86.8	84.3～105.4
8	2,4-滴	0.1	92.9～105.8	82.4～92.7	88.1～102.6	78.9～90.5	83.4～93.2
		0.05	90.6～97.2	70.4～83.8	84.8～96.4	72.8～91.0	78.8～91.4
		0.01	86.0～102.4	64.2～78.8	72.5～89.8	72.5～89.8	78.6～95.5
9	三氯吡氧乙酸	0.1	81.1～91.1	81.4～92.0	89.0～95.1	74.7～85.4	75.9～85.6
		0.05	82.4～92.6	87.8～95.2	78.6～91.6	80.4～89.4	70.2～79.8
		0.01	74.4～92.7	68.7～85.2	78.5～90.2	74.2～90.9	74.7～88.6
10	1-萘乙酸	0.1	82.9～92.1	80.9～94.3	89.3～98.8	78.5～93.9	74.9～81.9
		0.05	84.8～91.2	98.2～103.0	93.6～98.6	83.8～94.8	79.6～90.8
		0.01	81.2～91.9	78.3～90.6	84.9～90.5	81.0～94.6	90.0～113.3
11	5-氯苯酚	0.1	63.2～73.6	65.6～77.3	63.8～74.0	61.0～74.0	60.4～82.2
		0.05	70.6～83.8	69.4～80.0	62.6～71.0	67.6～76.2	64.2～77.0
		0.01	75.5～89.6	65.0～75.3	62.3～70.7	62.3～78.3	63.4～82.2
12	2,4,5 滴丙酸	0.1	80.6～90.2	79.5～88.8	82.3～89.3	64.7～75.6	70.6～78.8
		0.05	79.8～93.2	85.8～107.4	71.0～76.4	61.8～76.6	65.4～77.6
		0.01	85.5～96.7	70.5～85.5	74.1～90.0	76.1～86.3	77.8～92.2
13	草灭平	0.1	63.7～78.5	61.2～68.1	63.8～74.0	64.5～77.7	61.1～72.3
		0.05	74.0～85.6	67.0～75.6	64.4～71.6	71.0～80.0	63.8～77.8
		0.01	67.6～79.7	60.1～77.6	65.0～78.1	63.2～74.4	62.1～84.1
14	2 甲 4 氯丁酸	0.1	72.5～84.1	85.3～92.2	90.0～98.4	75.8～89.7	76.3～85.1
		0.05	78.0～91.2	89.4～98.6	75.8～84.2	87.0～93.2	81.6～96.1
		0.01	79.3～88.3	84.5～91.2	83.4～94.1	81.3～98.1	74.6～88.3
15	2,4,5-涕	0.1	87.6～100.2	75.2～89.2	83.4～93.4	70.9～85.5	73.3～86.2
		0.05	80.8～91.6	71.4～84.6	77.2～82.0	80.8～92.0	73.5～82.1
		0.01	88.6～97.1	73.0～87.5	82.1～91.5	70.5～87.1	71.5～87.8
16	氟草烟	0.1	86.6～96.4	89.0～95.6	91.1～101.0	83.2～95.0	69.5～80.2
		0.05	84.4～96.2	91.6～103.6	85.2～92.2	90.2～102.2	78.2～90.8
		0.01	89.1～100.81	72.6～92.4	81.5～91.9	92.1～108.4	77.3～92.0

表 2(续)

序号	农药中文名称	添加浓度/(mg/kg)	回收率/%				
			大米	糙米	大麦	小麦	玉米
17	2,4-滴丁酸	0.1	80.3～90.8	83.7～93.8	93.4～100.5	74.5～87.2	78.3～85.1
		0.05	81.6～97.8	87.2～98.2	78.4～89.6	86.6～96.4	81.6～91.0
		0.01	84.1～93.1	88.9～105.6	79.6～90.8	78.5～91.5	78.9～95.8
18	苯达松	0.1	81.0～97.2	86.4～95.5	86.3～96.6	81.9～92.0	75.8～84.5
		0.05	81.9～91.6	92.4～102.4	83.8～88.6	85.0～98.2	73.6～87.0
		0.01	86.9～93.5	71.6～86.1	88.7～98.4	86.1～110.8	73.4～94.5
19	碘苯腈	0.1	91.7～104.3	79.7～85.2	92.4～103.6	80.0～95.1	89.2～100.5
		0.05	97.4～103.6	77.2～91.6	84.8～91.6	84.2～94.6	83.0～95.6
		0.01	96.4～109.8	75.0～86.0	87.4～95.7	86.2～94.7	78.4～94.7
20	毒莠定	0.1	91.0～101.9	81.4～89.8	92.9～105.1	85.4～97.3	85.9～96.4
		0.05	86.0～96.4	79.8～87.0	84.0～96.6	86.4～98.2	93.4～108.2
		0.01	86.9～91.7	93.5～111.2	84.7～102.0	76.2～93.3	83.8～101.2
21	二氯喹啉酸	0.1	85.2～96.9	85.8～95.0	84.7～92.2	81.2～92.5	75.7～86.0
		0.05	87.4～100.4	84.6～92.8	90.2～96.8	71.0～83.8	73.4～84.5
		0.01	85.8～96.7	80.8～94.8	79.0～86.7	77.8～88.9	66.0～88.2
22	吡氟禾草灵	0.1	90.7～105.8	72.9～83.2	81.9～90.5	79.4～90.5	81.0～92.7
		0.05	92.4～105.2	84.2～97.0	81.4～87.2	79.0～89.8	71.4～91.5
		0.01	89.9～100.9	67.3～81.7	80.2～90.4	75.2～88.6	71.1～88.6
23	吡氟氯禾灵	0.1	79.8～90.2	67.5～80.4	69.3～82.9	60.7～72.6	75.9～85.0
		0.05	80.0～91.2	70.0～79.8	76.0～81.4	65.2～85.2	72.0～81.1
		0.01	78.0～89.7	65.0～73.6	64.4～71.8	63.3～75.6	70.2～83.5
24	麦草氟	0.1	74.3～82.7	86.4～94.7	84.2～99.7	80.6～92.7	69.1～77.7
		0.05	75.0～85.0	89.2～100.2	80.4～91.6	85.0～91.8	80.0～89.0
		0.01	88.7～99.3	85.8～101.1	84.9～90.5	80.6～95.1	69.4～86.3
25	三氟羧草醚	0.1	87.6～95.8	72.2～80.5	82.9～94.5	91.3～100.1	76.3～86.6
		0.05	83.8～95.8	70.2～79.2	108.6～115.8	81.0～93.4	71.8～88.6
		0.01	84.8～94.6	82.6～94.3	84.4～111.4	86.5～97.2	74.8～85.5
26	水杨菌胺	0.1	79.8～88.4	92.0～102.6	62.2～76.5	63.7～71.8	64.7～73.6
		0.05	81.8～94.8	89.2～97.6	67.0～78.0	62.8～81.2	77.8～89.1
		0.01	67.3～80.9	87.4～96.3	72.4～84.0	78.7～90.6	78.1～92.9
27	嘧草硫醚	0.1	89.9～101.5	75.5～88.3	82.5～90.9	77.5～90.9	75.2～83.9
		0.05	85.8～95.0	85.6～97.6	78.6～85.8	77.2～85.6	78.0～90.6
		0.01	89.4～102.5	65.0～72.4	81.0～90.9	71.4～88.9	78.6～91.6

表 2(续)

序号	农药中文名称	添加浓度/(mg/kg)	回收率/%				
			大米	糙米	大麦	小麦	玉米
28	环酰菌胺	0.1	79.1～86.3	82.4～92.4	75.3～77.8	81.9～92.9	71.5～85.0
		0.05	83.2～97.2	83.0～92.4	61.2～72.2	76.0～93.2	80.6～87.4
		0.01	90.7～108.9	81.9～91.9	66.8～74.9	76.2～87.9	88.6～102.0
29	氯甲酰草胺	0.1	85.8～104.1	79.5～92.6	86.6～97.7	77.2～91.9	80.2～91.2
		0.05	90.6～111.8	77.6～88.8	85.8～97.6	71.6～84.8	75.8～88.2
		0.01	83.3～102.4	92.1～115.7	82.1～97.7	62.0～74.6	78.8～95.4
30	喹禾灵	0.1	83.0～97.9	100.2～114.0	90.8～105.7	93.0～110.7	81.6～92.1
		0.05	82.6～97.8	74.2～87.4	88.8～102.0	76.2～89.8	82.2～96.7
		0.01	86.8～94.4	87.1～103.4	89.7～100.6	92.1～103.9	91.0～111.4
31	双草醚	0.1	93.5～107.9	80.4～96.0	91.8～110.2	80.5～95.8	76.4～85.4
		0.05	85.0～98.0	78.4～88.0	88.8～98.2	76.6～90.4	80.6～91.8
		0.01	82.0～91.6	85.9～95.3	89.8～110.4	80.7～95.3	80.1～91.7

附 录 A
（资料性附录）
31种农药化合物方法测定低限、保留时间、定量离子、定性离子及选择离子的丰度比值、选择监测离子分组表

表 A.1 31种农药化合物方法检出限、保留时间、定量离子、定性离子及选择离子的丰度比值表

序号	农药中文名称	农药英文名称	分子式	CAS号	保留时间/min	定量离子（丰度比）	定性离子1（丰度比）	定性离子2（丰度比）	测定低限/(mg/kg)
1	二氯皮考啉酸	Clopyralid	$C_6H_3Cl_2NO_2$	1702-17-6	20.42	147(100)	149(57)	146(65)	0.01
2	对氯苯氧乙酸	4-CPA	$C_8H_7ClO_3$	122-88-3	21.28	200(100)	141(96)	111(60)	0.01
3	2-苯基苯酚	D2-phenylphenol	$C_{12}H_{10}O$	90-43-7	21.92	170(100)	169(76)	141(34)	0.01
4	麦草畏	Dicamba	$C_8H_6O_3Cl_2$	1918-00-9	21.97	203(100)	205(64)	234(25)	0.01
5	2甲4氯	MCPA	$C_9H_9ClO_3$	94-74-6	23.15	214(100)	141(94)	155(65)	0.01
6	2,4-滴丙酸	Dichlorprop	$C_9H_8Cl_2O_3$	120-36-5	24.34	162(100)	189(54)	248(45)	0.01
7	溴苯腈	Bromoxynil	$C_7H_3Br_2NO$	1689-84-5	24.67	291(100)	276(51)	289(53)	0.01
8	2,4-滴	2,4-D	$C_9H_8C_{12}O_3$	120-36-5	25.01	199(100)	234(62)	175(37)	0.01
9	三氯吡氧乙酸	Triclopyr	$C_7H_4Cl_3NO_3$	64700-56-7	26.92	210(100)	269(31)	212(45)	0.01
10	1-萘乙酸	NAA	$C_{12}H_{10}O_2$	86-87-3	26.92	141(100)	200(40)	210(18)	0.01
11	5-氯苯酚	pentachlorphenol	C_6Cl_5OH	87-86-5	27.37	265(100)	280(95)	237(90)	0.01
12	2,4,5滴丙酸	Fenoprop	$C_9H_7Cl_3O_3$	93-72-1	28.28	196(100)	198(97)	223(38)	0.01
13	草灭平	Chloramben	$C_7H_5Cl_2NO_2$	133-90-4	28.44	188(100)	219(76)	160(40)	0.01
14	2甲4氯丁酸	MCPB	$C_9H_9ClO_3$	94-74-6	28.85	101(100)	59(68)		0.01
15	2,4,5-涕	2,4,5-T	$C_8H_5Cl_3O_3$	93-76-5	28.89	233(100)	235(66)	268(50)	0.01
16	氟草烟	Fluroxypyr	$C_7H_5Cl_2FN_2O_2$	69377-81-7	30.02	209(100)	211(65)	268(48)	0.01
17	2,4-滴丁酸	2,4-DB	$C_{10}H_{10}Cl_2O_3$	94-82-6	30.05	101(100)	59(60)	162(23)	0.01
18	苯达松	Bentazone	$C_{10}H_{12}N_2O_3S$	25057-89-0	30.58	212(100)	105(65)	254(27)	0.01

表 A.1（续）

序号	农药中文名称	农药英文名称	分子式	CAS 号	保留时间/min	定量离子（丰度比）	定性离子 1（丰度比）	定性离子 2（丰度比）	测定低限/(mg/kg)
19	碘苯腈	OH-Ioxynil	$C_7H_3I_2NO$	1689-83-4	30.65	385(100)	370(35)	243(38)	0.01
20	毒莠定	Picloram	$C_6H_3Cl_3N_2O_2$	1918-2-1	31.43	196(100)	198(95)		0.01
21	二氯喹啉酸	Quinclorac	$C_{10}H_5Cl_2NO_2$	84087-01-4	31.89	224(100)	226(65)	197(51)	0.01
22	吡氟禾草灵	Fluazifop	$C_{19}H_{20}F_3NO_4$	79241-46-6	32.36	341(100)	282(97)	254(90)	0.01
23	吡氟氯禾灵	Haloxyfop	$C_{15}H_{11}ClF_3NO_4$	69806-34-4	33.50	316(100)	288(94)	375(81)	0.01
24	麦草氟	Flamprop acid	$C_{16}H_{13}ClFNO_3$	58667-63-3	34.38	105(100)	77(36)		0.01
25	三氟羧草醚	Acifluorfen	$C_{14}H_7ClF_3NO_5$	50594-66-6	34.76	375(100)	344(55)	223(44)	0.01
26	水杨菌胺	Trichlamide	$C_{13}H_{16}Cl_3NO_3$	70193-21-4	34.95	135(100)	77(11)	246(11)	0.01
27	嘧草硫醚	Pyritiobacsodium	$C_{13}H_{10}ClN_2NaO_4S$	123343-16-8	35.25	281(100)	283(38)	282(15)	0.01
28	环酰菌胺	Fenhxamid	$C_{14}H_{17}Cl_2NO_2$	126833-17-8	36.62	97(100)	55(38)	191(27)	0.01
29	氯甲酰草胺	Clomeprop	$C_{16}H_{16}Cl_2NO_2$	84496-56-0	37.20	120(100)	288(46)		0.01
30	喹禾灵	Quizalofop	$C_{19}H_{17}ClN_2O_4$	76578-14-8	39.64	299(100)	243(87)	163(35)	0.01
31	双草醚	Bispyribacsodium	$C_{19}H_{18}N_4NaO_8$	125401-92-5	40.30	385(100)	386(22)		0.01

附　录　B
（资料性附录）
31 种农药标准品 SIM 色谱图

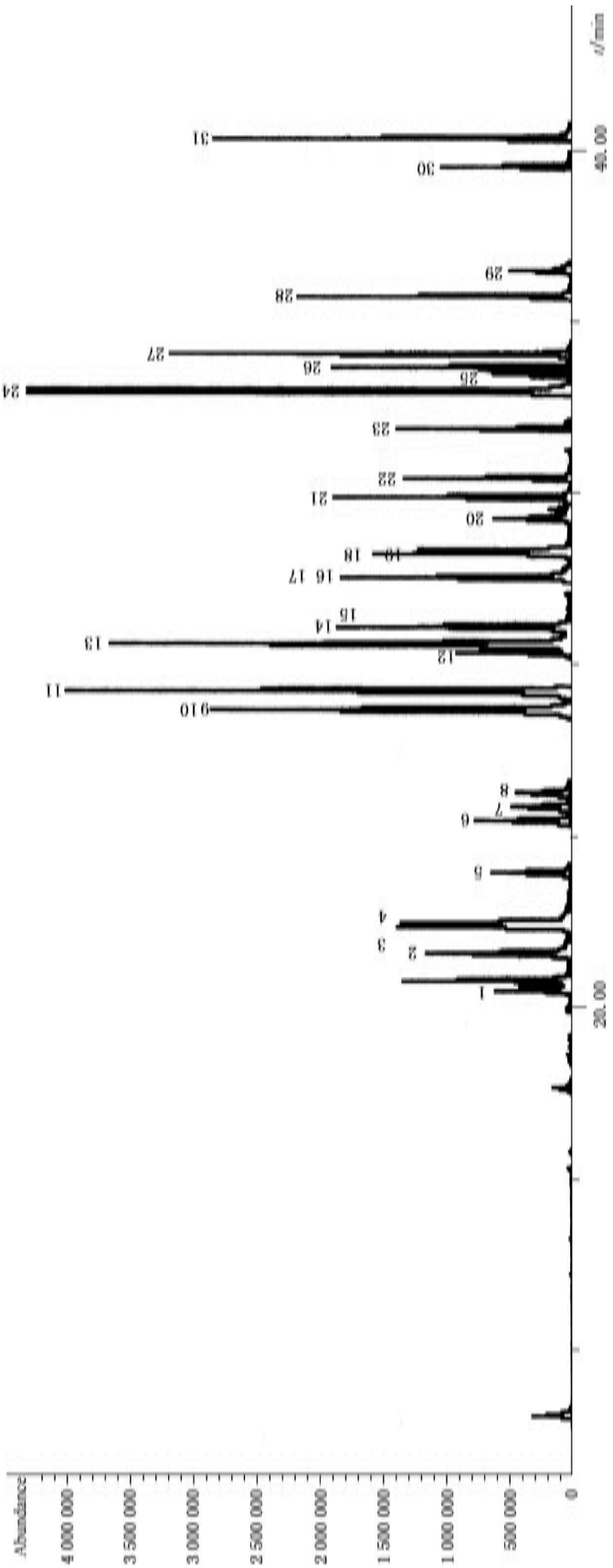

图 B.1　31 种农药标准品 SIM 色谱图（各农药的保留时间参见附录 A 中表 A.1）

Foreword

Annex A and B of this standard are informative annex.

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

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

The main drafters of this standard are Yan Hongfei, Zhang Ying, Huang Zhiqiang, Huang Ping, Li Yongjun, Wang Meiling.

This standard is promulgated for the first time.

Note: This English version, a translation from the Chinese text, is solely for guidance.

Determination of 31 acid pesticide residues in foods for import and export— GC-MS method

1 Scope

This standard specifies the gas chromtography-mass(GC-MS)method of determination of 31 acid herbicide residues in foods.

This standard is applicable for the determination of Clopyralid,4-CPA,D2-phenylphenol,Dicamba,MCPA,Dichlorprop,Bromoxynil,2,4-D,Triclopyr,NAA,Pentachlorphenol,Fenoprop,Chloramben,MCPB,2,4,5-T,Fluroxypyr,2,4-DB,Bentazone,OH-Ioxynil,Picloram,Quinclorac,Fluazifop,Haloxyfop,Flamprop acid, Acifluorfen, Trichlamide, Pyritiobac-sodium, Fenhxamid, Clomeprop, Quizalofop, Bispyribac-sodium 31 acid herbicide residues pesticide residues by gas chromatography-mass spectrometry in rice,brown rice,barley,wheat and corn.

2 Principle

The pesticides residues in the test sample are extracted with acetone and acid water solution then partitioned with ethyl acetate. The extration was cleaned up with gel permeation chromtography and methylation derivatization reaction with trimethylsilydiazomethane,then cleaned up through Florisil column. Determination is made by means of GC-MS with selected-ion monitoring(SIM)mode,using external standard method.

3 Reagents and materials

Unless otherwise specified ,the reagents should be analytically pure,"Water" is redistilled water.

3.1 Acetone:GR.

3.2 *n*-Hexane:GR.

3.3 Cyclohexane:HPLC.

3.4 Methanol:HPLC.

3.5 Benzene:HPLC.

3.6 Ethyl acetate:HPLC.

3.7 Sodium chloride(NaCl).

3.8 Sodium chloride(15%):Weigh 150 g Sodium chloride,disovled in 1 000 mL volume water.

3.9 Hydrochloric acid :GR.

3.10 Hydrochloric acid(0.1 mol/L):Weigh 9.0 mL hydrochloric acid(3.9)to 1 000 mL volumetric flask,mark up to the volume with water.

3.11 Hydrochloric acid(4.0 mol/L):Weigh 360 mL hydrochloric acid(3.9)to 1 000 mL volumetric flask,mark up to the volume with water.

3.12 Trimethylsilydiazomethane hexane solution(2.0 mol/L).

3.13 Acetone+Cyclohexane(2+8,*V*/*V*):Mixed 20 mL Acetone(3.1)with 80 mL Cyclohexane(3.3).

3.14 Acetone+hexane(2+8,*V*/*V*):Mixed 20 mL Acetone(3.1)with 80 mL hexane(3.2).

3.15 Methanol + Benzene(2+8,*V*/*V*):Mixed 20 mL methanol(3.1)with 80 mL benzene(3.3).

3.16 Pesticides standards:Clopyralid,4-CPA,D2-phenylphenol,Dicamba,MCPA,Dichlorprop,Bromoxynil,2,4-D,Triclopyr,NAA,pentachlorphenol,Fenoprop,hloramben,MCPB,2,4,5-T,Fluroxypyr,2,4-DB,Bentazone,OH-loxynil,Picloram,Quinclorac,Fluazifop,Haloxyfop,Flamprop acid,Acifluorfen,Trichlamide,Pyritiobac-sodium,Fenhxamid,Clomeprop,Quizalofop,Bispyribac-sodium(CAS NO and molecular formular seen in annex A table A.1):Purity≥97%.

3.17 Pesticides standard storage solution :Accurately weight an adequate amount of pesticides standard into 50 mL volumetric flask,dissolve in a small volume of acetone and mark up to the volume with acetone individually obtaining 500 μg/mL storage solution. Dilute with acetone to form a standard stock solution of 500 μg/mL in concentration. Then dilute the standard stock solution with *n*-hexane to the required concentration as the standard working solution. The standard solution should be stored below 0 ℃～4 ℃ and keep in dark place ,the storage is 90 days.

3.18 Multipesticides standard middle solution:Weigh 2.0 mL each pesticide storage solution to 100 mL volumetric flask individually,mark up to the volume with acetone obtaining 10 μg/mL middle multipesticides solution. The standard solution should be stored below 0 ℃～4 ℃ in dark place and the storage is 30 days.

3.19 Multipesticides standard working solution:Weigh amount of multipesticides standard middle solution ,then dilute the standard stock solution with acetone to the required concentration as the

standard working solution. The standard working solution should be made while it is using.

3.20 Florisil column:250 mg,3 mL,or equivalent.

4 Apparatus and equipment

4.1 Gas chromatograph,equipped with mass detector(EI).

4.2 Gel permeation chromatographyclean system.

4.3 Solid phase extraction device.

4.4 Centrifuge:3 000 r/min.

4.5 Vortex mixer.

4.6 Rotary vacuum evaporator.

4.7 Nitrogen concentrator.

4.8 Centrifuge tube:50 mL.

4.9 Heart-shaped glass flask:200 mL.

4.10 Micro-syringe:10 μL.

5 Preparation of test samples

5.1 Preparation and storage of test sample

The combined primary samples is reduced to ca 500 g,which is crushed with a grinder and let wholly pass through a 40 mesh sieve and then divided into two equal portions. Each portion is placed in a clean container as the test sample,which is sealed and labeled.

5.2 Storage of test samples

The test samples of tea,bee products,grains or cereals should be stored below 0 ℃～4 ℃. In the course of sampling and sample preparation,precaution must be taken to avoid contamination or any factors which may cause the change of residue content.

6 Procedure

6.1 Extraction

Weigh ca 10.0 g(accurate to 0. 01 g)of the test sample into a 50 mL centrifuge tube. Add 10 mL acetone(3.1)and 10 mL HCl solution(3.10),stand for 30 min . Add 20 mL acetone(3.1),blend for 15 min in vortex mixer,centrifuge for 2 min under 3 000 r/min,the acetone-water extraction was poured into 200 mL heart-shaped glass flask. The extration was repeated twice more with 20 mL acetone(3.1), combine the acetone-water extracts,Evaorate acetone with a rotary evaporator at 45 ℃. Then add 10 mL NaCl solution(3.8),2.5 mL HCl solution(3.11)and 20 mL ethyl acetate(3.6), vortex for 5 min,the ethyl acetate layer was poured into 200 mL heart-shaped glass flask. Repeat the extraction twice more with 2 × 20 mL ethyl acetate(3.6). The combined the ethyl acetate eorgnic phase was evaorated to near dryness on a rotary evaporator at 45 ℃. The residue ws transferred to a 5 mL volumetric centrifuge tube and made up to the mark using acetone-cyclohexane(3.13),then filted with 0.45 μm filter prior to GPC clean up.

6.2 GPC Clean up

6.2.1 GPC conditions

a) GPC gel column:CLN pak EV 22 000 column(300 mm × 20 mm).

b) Mobile phase:acetone-cyclohexane(3.13).

c) Flow speed:5.0 mL/min.

d) Injection volume:2.0 mL.

e) Collection mode:time mode,collect 12.0 min～30.0 min eluent.

6.3 Derivatization

The GPC collection eluent was concentrated and blowed to near dryness with nitrogen at 45 ℃,then the residue was transferred with 3 × 2 mL acetone to 10 mL centrifuge tube. The solution was blowed to dry with nitrogen purge at 45 ℃ and resolved with methanol-benzene(3.15),add 0.2 mL trimethylsilydiazomethane hexane solution(3.12),stand for 30 min at 30 ℃. Then blown dry with nitrogen purge,dissolved with 5 mL *n*-hexane(3.2).

6.4 SPE clean up

Set up the solid phase extraction vaccum manifold and mechanical pump. Washing the Florisil column with 3 mL aceton(3.1)and 6mL *n*-hexane(3.2),waste the eluent. Transfer the extracts into the

column then discard the elution. Elute the Florisil column with 6 mL acetone-*n*-hexane solution (3.14), and collect the total eluent. The collected eluent was blown to near dryness with nitrogen purge at 45 ℃. Dissolve the residue and dilute exactly to 0.50 mL with acetone(3.1)for GC-MS.

6.5 Determination

6.5.1 GC-MS operating conditions

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

b) Column temperature:Initial temperature 50 ℃,hold for 1 min,ramp at 5 ℃/min to 160 ℃,hold for 3 min,ramp at 10 ℃/min to 300 ℃,hold for 10 min;

c) Injection port temperature:250 ℃;

d) GC/MS interface temperature:280 ℃;

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

f) Injection volume:2 μL;

g) Injection mode:Splitless,purge after 1 min;

h) Ionization mode:EI;

i) Ionization energy:70 ev;

j) Acquistion mode:SIM mode. The retention time,quantitative ion,qualifier ions,quantifier ions,qualifier/quantifier ions abundance ration of 31 pesticides and monitor ions groups Monitor ion seen in annex table A.1 and A.2;

k) Sovlent delay:9 min.

6.5.2 GC-MS determination

6.5.2.1 Qualitative determination

According to the GC-MS operating conditions desribed in 6.5.1,analyze the standard solution and sample solution. If the retention time of sample chromatogram peaks are consistent with the standards,the confirmation test should be conducted. The analyte can be confirmed when subtracted chromatogram from background compensation,selected ions are all present and the relative ion abundance of the selected ions according with that of the calibration standard at comparable concentra-

tions, within the tolerances (seen table 1). If the confirmation can not be made, repeat the injection , or change the qualifier ions, or choose other confirmation methods with higher sensitivity. Under the above GC-MS operating conditions, the retention time, quantitative ion, qualifier ions, quantifier ions, qualifier/quantifier ions abundance ration of 31 pesticides and monitor ions groups, monitor ion seen in annex table A. 1 and A. 2.

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

Relative abundance (base peak)/%	>50	>20～50	>10～20	≤10
Permitted tolerances/%	±10	±15	±20	±50

6.5.2.2 Quantitative determination

According to the approximate concentration of pesticide in the test sample solution, select the standard working solution with similar peak area to that of sample solution. The standard working solution should be injected randomly in between the injections of sample solution of equal volume. The responses of each pesticide standard working solution in and sample solution should be in the linear range of the instrumental detection. Under the above GC-MS operating conditions, the retention time of 31 pesticides standard seen in annex A table A. 1 and the SIM chromatogram seen in annex B figure B. 1.

6.6 Blank test

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

6.7 Calculation and expression of result

The calculation of pesticide content in the sample is carried out by GC-MS data processor or according to the following formula:

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

Where:

X —Pesticide content in the sample, mg/kg;

A —Peak area of pesticide in the sample solution, mm;

c_s —Peak area of pesticide in the standard working solution, mm;

A_s —Concentration of pesticide in the standard working solution, μg/mL;

V —Final volume of sample solution, mL;

m —Mass of test sample, g.

Note: The blank value should be subtracted from the above result of calculation.

7 Limit of determination and recovery

7.1 Limit of determination

The limit of determination of 31 pesticide in rice, brown rice , barley, wheat and corn of this method is 0.01 mg/kg.

7.2 Recovery

According to the experimental data, the fortifying concentrations of 31 pesticides in rice, brown rice, barley, wheat and corn and their corresponding recoveries are as follows:

Table 2—Fortified concentration and corresponding recoveries in sample

NO	Name	Fortified concentration/(mg/kg)	Recovery/%				
			Rice	Brown rice	Barley	Wheat	Corn
1	Clopyralid	0.1	94.6～108.6	90.0～103.2	83.1～95.2	77.6～92.3	88.0～96.6
		0.05	92.6～108.8	83.6～97.6	91.8～106.0	80.2～89.4	91.2～106.2
		0.01	103.3～114.6	87.9～107.2	80.1～93.8	83.3～94.2	77.3～90.6
2	4-CPA	0.1	93.7～104.6	87.6～102.5	87.0～105.1	89.8～103.9	92.7～104.8
		0.05	84.0～96.0	85.2～102.6	91.4～98.2	85.8～97.2	81.2～92.0
		0.01	83.0～97.5	85.8～109.1	78.6～92.4	81.2～105.1	82.2～102.8
3	D2-phenylphenol	0.1	69.3～81.2	87.4～100.5	75.9～83.5	74.4～89.1	86.1～96.9
		0.05	69.6～84.4	80.8～96.0	60.2～71.4	66.4～80.0	87.8～99.6
		0.01	69.6～84.0	79.4～92.8	63.0～75.8	72.8～90.9	80.7～93.1
4	Dicamba	0.1	77.1～91.2	71.6～86.9	79.0～92.2	76.6～92.0	68.1～76.0
		0.05	83.0～90.6	79.0～93.4	82.6～89.2	81.4～90.6	64.8～76.6
		0.01	84.9～92.9	69.8～82.5	75.5～81.0	73.2～83.9	78.5～92.5
5	MCPA	0.1	92.6～108.1	80.6～88.9	82.0～92.2	79.1～92.9	82.9～93.3
		0.05	89.2～95.2	80.2～92.4	82.8～92.0	82.4～97.2	86.0～98.4
		0.01	94.2～102.3	77.7～92.3	82.7～91.6	77.4～92.3	78.4～94.4
6	Dichlorprop	0.1	84.0～93.3	77.5～88.9	80.5～90.6	77.60～85.9	73.5～83.0
		0.05	83.8～95.0	80.2～92.4	81.6～86.4	81.6～90.4	78.4～92.8
		0.01	82.6～93.0	71.3～86.1	83.1～88.8	75.8～86.7	80.7～101.0
7	Bromoxynil	0.1	90.5～105.3	75.6～88.4	87.7～98.3	78.7～86.5	82.8～93.2
		0.05	88.2～97.8	74.6～88.4	87.8～93.6	79.8～95.4	75.8～86.4
		0.01	95.8～107.0	72.4～86.8	84.2～91.4	73.4～86.8	84.3～105.4

Table 2(continue)

NO	Name	Fortified concentration/(mg/kg)	Recovery/%				
			Rice	Brown rice	Barley	Wheat	Corn
8	2,4-D	0.1	92.9～105.8	82.4～92.7	88.1～102.6	78.9～90.5	83.4～93.2
		0.05	90.6～97.2	70.4～83.8	84.8～96.4	72.8～91.0	78.8～91.4
		0.01	86.0～102.4	64.2～78.8	72.5～89.8	72.5～89.8	78.6～95.5
9	Triclopyr	0.1	81.1～91.1	81.4～92.0	89.0～95.1	74.7～85.4	75.9～85.6
		0.05	82.4～92.6	87.8～95.2	78.6～91.6	80.4～89.4	70.2～79.8
		0.01	74.4～92.7	68.7～85.2	78.5～90.2	74.2～90.9	74.7～88.6
10	NAA	0.1	82.9～92.1	80.9～94.3	89.3～98.8	78.5～93.9	74.9～81.9
		0.05	84.8～91.2	98.2～103.0	93.6～98.6	83.8～94.8	79.6～90.8
		0.01	81.2～91.9	78.3～90.6	84.9～90.5	81.0～94.6	90.0～113.3
11	pentachlorphenol	0.1	63.2～73.6	65.6～77.3	63.8～74.0	61.0～74.0	60.4～82.2
		0.05	70.6～83.8	69.4～80.0	62.6～71.0	67.6～76.2	64.2～77.0
		0.01	75.5～89.6	65.0～75.3	62.3～70.7	62.3～78.3	63.4～82.2
12	Fenoprop	0.1	80.6～90.2	79.5～88.8	82.3～89.3	64.7～75.6	70.6～78.8
		0.05	79.8～93.2	85.8～107.4	71.0～76.4	61.8～76.6	65.4～77.6
		0.01	85.5～96.7	70.5～85.5	74.1～90.0	76.1～86.3	77.8～92.2
13	Chloramben	0.1	63.7～78.5	61.2～68.1	63.8～74.0	64.5～77.7	61.1～72.3
		0.05	74.0～85.6	67.0～75.6	64.4～71.6	71.0～80.0	63.8～77.8
		0.01	67.6～79.7	60.1～77.6	65.0～78.1	63.2～74.4	62.1～84.1
14	MCPB	0.1	72.5～84.1	85.3～92.2	90.0～98.4	75.8～89.7	76.3～85.1
		0.05	78.0～91.2	89.4～98.6	75.8～84.2	87.0～93.2	81.6～96.1
		0.01	79.3～88.3	84.5～91.2	83.4～94.1	81.3～98.1	74.6～88.3
15	2,4,5-T	0.1	87.6～100.2	75.2～89.2	83.4～93.4	70.9～85.5	73.3～86.2
		0.05	80.8～91.6	71.4～84.6	77.2～82.0	80.8～92.0	73.5～82.1
		0.01	88.6～97.1	73.0～87.5	82.1～91.5	70.5～87.1	71.5～87.8
16	Fluroxypyr	0.1	86.6～96.4	89.0～95.6	91.1～101.0	83.2～95.0	69.5～80.2
		0.05	84.4～96.2	91.6～103.6	85.2～92.2	90.2～102.2	78.2～90.8
		0.01	89.1～100.81	72.6～92.4	81.5～91.9	92.1～108.4	77.3～92.0
17	2,4-DB	0.1	80.3～90.8	83.7～93.8	93.4～100.5	74.5～87.2	78.3～85.1
		0.05	81.6～97.8	87.2～98.2	78.4～89.6	86.6～96.4	81.6～91.0
		0.01	84.1～93.1	88.9～105.6	79.6～90.8	78.5～91.5	78.9～95.8
18	Bentazone	0.1	81.0～97.2	86.4～95.5	86.3～96.6	81.9～92.0	75.8～84.5
		0.05	81.9～91.6	92.4～102.4	83.8～88.6	85.0～98.2	73.6～87.0
		0.01	86.9～93.5	71.6～86.1	88.7～98.4	86.1～110.8	73.4～94.5

Table 2(continue)

NO	Name	Fortified concentration/(mg/kg)	Recovery/%				
			Rice	Brown rice	Barley	Wheat	Corn
19	OH-loxynil	0.1	91.7～104.3	79.7～85.2	92.4～103.6	80.0～95.1	89.2～100.5
		0.05	97.4～103.6	77.2～91.6	84.8～91.6	84.2～94.6	83.0～95.6
		0.01	96.4～109.8	75.0～86.0	87.4～95.7	86.2～94.7	78.4～94.7
20	Picloram	0.1	91.0～101.9	81.4～89.8	92.9～105.1	85.4～97.3	85.9～96.4
		0.05	86.0～96.4	79.8～87.0	84.0～96.6	86.4～98.2	93.4～108.2
		0.01	86.9～91.7	93.5～111.2	84.7～102.0	76.2～93.3	83.8～101.2
21	Quinclorac	0.1	85.2～96.9	85.8～95.0	84.7～92.2	81.2～92.5	75.7～86.0
		0.05	87.4～100.4	84.6～92.8	90.2～96.8	71.0～83.8	73.4～84.5
		0.01	85.8～96.7	80.8～94.8	79.0～86.7	77.8～88.9	66.0～88.2
22	Fluazifop	0.1	90.7～105.8	72.9～83.2	81.9～90.5	79.4～90.5	81.0～92.7
		0.05	92.4～105.2	84.2～97.0	81.4～87.2	79.0～89.8	71.4～91.5
		0.01	89.9～100.9	67.3～81.7	80.2～90.4	75.2～88.6	71.1～88.6
23	Haloxyfop	0.1	79.8～90.2	67.5～80.4	69.3～82.9	60.7～72.6	75.9～85.0
		0.05	80.0～91.2	70.0～79.8	76.0～81.4	65.2～85.2	72.0～81.1
		0.01	78.0～89.7	65.0～73.6	64.4～71.8	63.3～75.6	70.2～83.5
24	Flamprop acid	0.1	74.3～82.7	86.4～94.7	84.2～99.7	80.6～92.7	69.1～77.7
		0.05	75.0～85.0	89.2～100.2	80.4～91.6	85.0～91.8	80.0～89.0
		0.01	88.7～99.3	85.8～101.1	84.9～90.5	80.6～95.1	69.4～86.3
25	Acifluorfen	0.1	87.6～95.8	72.2～80.5	82.9～94.5	91.3～100.1	76.3～86.6
		0.05	83.8～95.8	70.2～79.2	108.6～115.8	81.0～93.4	71.8～88.6
		0.01	84.8～94.6	82.6～94.3	84.4～111.4	86.5～97.2	74.8～85.5
26	Trichlamide	0.1	79.8～88.4	92.0～102.6	62.2～76.5	63.7～71.8	64.7～73.6
		0.05	81.8～94.8	89.2～97.6	67.0～78.0	62.8～81.2	77.8～89.1
		0.01	67.3～80.9	87.4～96.3	72.4～84.0	78.7～90.6	78.1～92.9
27	Pyritiobac-sodium	0.1	89.9～101.5	75.5～88.3	82.5～90.9	77.5～90.9	75.2～83.9
		0.05	85.8～95.0	85.6～97.6	78.6～85.8	77.2～85.6	78.0～90.6
		0.01	89.4～102.5	65.0～72.4	81.0～90.9	71.4～88.9	78.6～91.6
28	Fenhxamid	0.1	79.1～86.3	82.4～92.4	75.3～77.8	81.9～92.9	71.5～85.0
		0.05	83.2～97.2	83.0～92.4	61.2～72.2	76.0～93.2	80.6～87.4
		0.01	90.7～108.9	81.9～91.9	66.8～74.9	76.2～87.9	88.6～102.0
29	Clomeprop	0.1	85.8～104.1	79.5～92.6	86.6～97.7	77.2～91.9	80.2～91.2
		0.05	90.6～111.8	77.6～88.8	85.8～97.6	71.6～84.8	75.8～88.2
		0.01	83.3～102.4	92.1～115.7	82.1～97.7	62.0～74.6	78.8～95.4

Table 2(continue)

NO	Name	Fortified concentration/(mg/kg)	Recovery/%				
			Rice	Brown rice	Barley	Wheat	Corn
30	Quizalofop	0.1	83.0～97.9	100.2～114.0	90.8～105.7	93.0～110.7	81.6～92.1
		0.05	82.6～97.8	74.2～87.4	88.8～102.0	76.2～89.8	82.2～96.7
		0.01	86.8～94.4	87.1～103.4	89.7～100.6	92.1～103.9	91.0～111.4
31	Bispyribac-sodium	0.1	93.5～107.9	80.4～96.0	91.8～110.2	80.5～95.8	76.4～85.4
		0.05	85.0～98.0	78.4～88.0	88.8～98.2	76.6～90.4	80.6～91.8
		0.01	82.0～91.6	85.9～95.3	89.8～110.4	80.7～95.3	80.1～91.7

Annex A
(Imformation)
The limits, retention time, quantitative ion, qualifier ions, quantifier ions, qualifier/quantifier ions abundance ration of 31 pesticides and monitor ions groups

Table A. 1—The limits, retention time, quantitative ion, qualifier ions, quantifier ions, qualifier/quantifier ions abundance ration of 31 pesticides

NO	Name	Molecular formular	CAS NO	RT/ min	Quantifier ions (abundance ration)	Qualifier ions1 (abundance ration)	Qualifier ions 2 (abundance ration)	LOQ/ (mg/kg)
1	Clopyralid	$C_6H_3Cl_2NO_2$	1702-17-6	20.42	147(100)	149(57)	146(65)	0.01
2	4-CPA	$C_8H_7ClO_3$	122-88-3	21.28	200(100)	141(96)	111(60)	0.01
3	D2-phenylphenol	$C_{12}H_{10}O$	90-43-7	21.92	170(100)	169(76)	141(34)	0.01
4	Dicamba	$C_8H_6O_3Cl_2$	1918-00-9	21.97	203(100)	205(64)	234(25)	0.01
5	MCPA	$C_9H_9ClO_3$	94-74-6	23.15	214(100)	141(94)	155(65)	0.01
6	Dichlorprop	$C_9H_8Cl_2O_3$	120-36-5	24.34	162(100)	189(54)	248(45)	0.01
7	Bromoxynil	$C_7H_3Br_2NO$	1689-84-5	24.67	291(100)	276(51)	289(53)	0.01
8	2,4-D	$C_9H_8C_{12}O_3$	120-36-5	25.01	199(100)	234(62)	175(37)	0.01
9	Triclopyr	$C_7H_4Cl_3NO_3$	64700-56-7	26.92	210(100)	269(31)	212(45)	0.01
10	NAA	$C_{12}H_{10}O_2$	86-87-3	26.92	141(100)	200(40)	210(18)	0.01
11	pentachlorphenol	C_6Cl_5OH	87-86-5	27.37	265(100)	280(95)	237(90)	0.01

Table A.1 (continue)

NO	Name	Molecular formular	CAS NO	RT/ min	Quantifier ions (abundance ration)	Qualifier ions1 (abundance ration)	Qualifier ions 2 (abundance ration)	LOQ/ (mg/kg)
12	Fenoprop	$C_9H_7Cl_3O_3$	93-72-1	28.28	196(100)	198(97)	223(38)	0.01
13	Chloramben	$C_7H_5Cl_2NO_2$	133-90-4	28.44	188(100)	219(76)	160(40)	0.01
14	MCPB	$C_9H_9ClO_3$	94-74-6	28.85	101(100)	59(68)		0.01
15	2,4,5-T	$C_8H_5Cl_3O_3$	93-76-5	28.89	233(100)	235(66)	268(50)	0.01
16	Fluroxypyr	$C_7H_5Cl_2FN_2O_2$	69377-81-7	30.02	209(100)	211(65)	268(48)	0.01
17	2,4-DB	$C_{10}H_{10}Cl_2O_3$	94-82-6	30.05	101(100)	59(60)	162(23)	0.01
18	Bentazone	$C_{10}H_{12}N_2O_3S$	25057-89-0	30.58	212(100)	105(65)	254(27)	0.01
19	OH-loxynil	$C_7H_3I_2NO$	1689-83-4	30.65	385(100)	370(35)	243(38)	0.01
20	Picloram	$C_6H_3Cl_3N_2O_2$	1918-2-1	31.43	196(100)	198(95)		0.01
21	Quinclorac	$C_{10}H_5Cl_2NO_2$	84087-01-4	31.89	224(100)	226(65)	197(51)	0.01
22	Fluazifop	$C_{19}H_{20}F_3NO_4$	79241-46-6	32.36	341(100)	282(97)	254(90)	0.01
23	Haloxyfop	$C_{15}H_{11}ClF_3NO_4$	69806-34-4	33.50	316(100)	288(94)	375(81)	0.01
24	Flamprop acid	$C_{16}H_{13}ClFNO_3$	58667-63-3	34.38	105(100)	77(36)		0.01
25	Acifluorfen	$C_{14}H_7ClF_3NO_5$	50594-66-6	34.76	375(100)	344(55)	223(44)	0.01
26	Trichlamide	$C_{13}H_{16}Cl_3NO_3$	70193-21-4	34.95	135(100)	77(11)	246(11)	0.01

Table A.1 (continue)

NO	Name	Molecular formular	CAS NO	RT/ min	Quantifier ions (abundance ration)	Qualifier ions1 (abundance ration)	Qualifier ions 2 (abundance ration)	LOQ/ (mg/kg)
27	Pyritiobac-sodium	$C_{13}H_{10}ClN_2NaO_4S$	123343-16-8	35.25	281(100)	283(38)	282(15)	0.01
28	Fenhxamid	$C_{14}H_{17}Cl_2NO_2$	126833-17-8	36.62	97(100)	55(38)	191(27)	0.01
29	Clomeprop	$C_{16}H_{16}Cl_2NO_2$	84496-56-0	37.20	120(100)	288(46)		0.01
30	Quizalofop	$C_{19}H_{17}ClN_2O_4$	76578-14-8	39.64	299(100)	243(87)	163(35)	0.01
31	Bispyribac-sodium	$C_{19}H_{18}N_4NaO_8$	125401-92-5	40.30	385(100)	386(22)		0.01

Annex B

(Imformation)

The SIM chromatogram of 31 pesticides standards

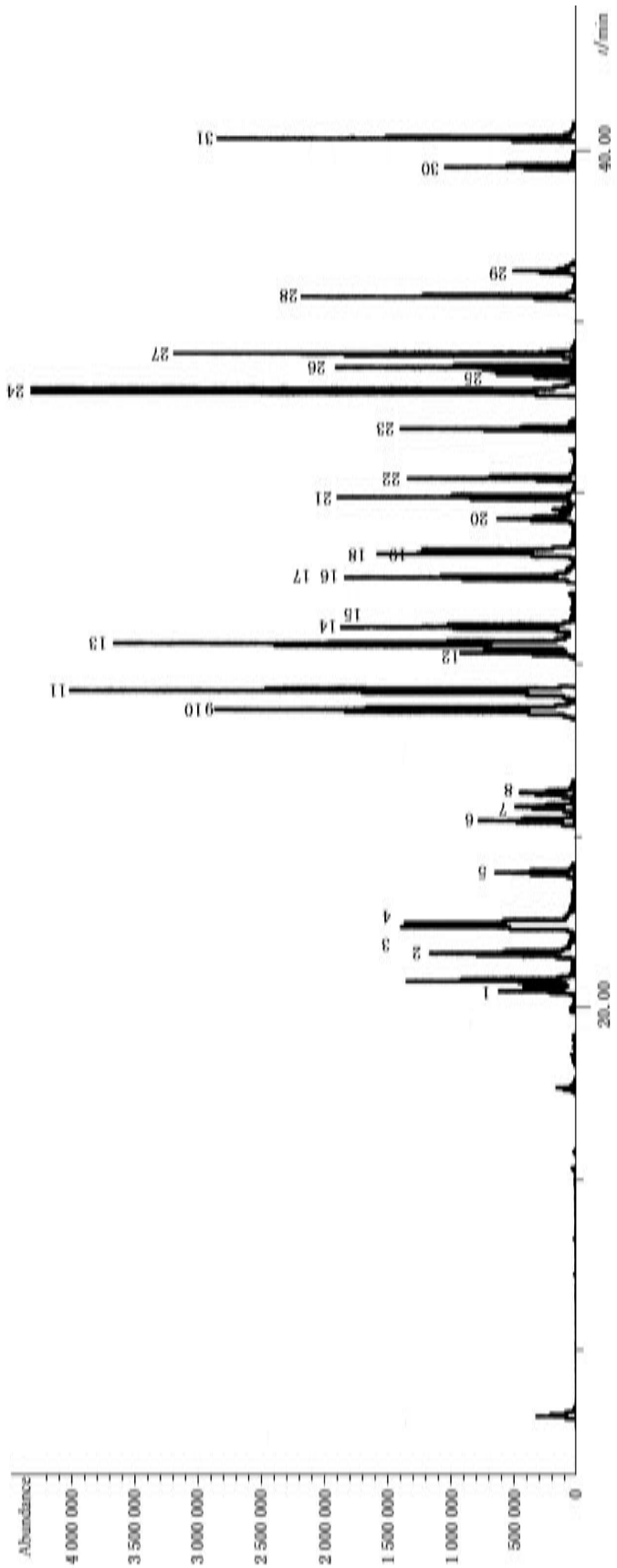

Figure B. 1—The SIM chromatogram of 31 pesticides standards(the retention time of pesticides shown in annex A table A. 1)