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中华人民共和国出入境检验检疫行业标准

SN/T 2325—2009

进出口食品中四唑嘧磺隆、甲基苯苏呋安、醚磺隆等45种农药残留量的检测方法 高效液相色谱-质谱/质谱法

Determination of 45 pesticides residues including azimsulfron, bensulfron-methyl, cinosulfron et al in foods for import and export—HPLC-MS/MS method

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前　言

本标准的附录A、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：中华人民共和国河北出入境检验检疫局、中华人民共和国天津出入境检验检疫局。

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本标准系首次发布的出入境检验检疫行业标准。

进出口食品中四唑嘧磺隆、甲基苯苏呋安、醚磺隆等45种农药残留量的检测方法 高效液相色谱-质谱/质谱法

1 范围

本标准规定了食品中四唑嘧磺隆、甲基苯苏呋安、醚磺隆等45种农药残留量的高效液相色谱-质谱/质谱检测方法及样品的制备和保存方法。

本标准适用于糙米、大米、玉米、大麦和小麦中氟唑嘧磺草胺、醚磺隆、咪草酸、甲基噻吩磺隆、烟嘧磺隆、灭草喹、萘草胺、甲氧磺草胺、氯酯磺草胺、丙苯磺隆、甲磺草胺、甲酰胺磺隆、甲基胺苯磺隆、玉嘧磺隆、苯磺隆、三氟啶磺隆、四唑嘧磺隆、苄嘧磺隆、嘧啶磺隆、乙磺隆、氯嘧磺隆、咪唑磺隆、苯并双环酮、乙氧嘧磺隆、环丙嘧磺隆、吡嘧磺隆、恶草酸、双氟磺草胺、醚苯磺隆、甲磺隆、氯磺隆、五氟磺草胺、双氯磺草胺、甲基碘磺隆、烯草酮砜、甲磺胺磺隆、氟磺隆、杀鼠灵、2-甲-4-氯丙酸、氟嘧磺隆、氟磺胺草醚、氟胺磺隆、氯吡嘧磺隆、达诺杀和特乐酚45种农药残留量的检测。

2 方法提要

试样用水-丙酮提取，提取液经二氯甲烷液液萃取后，用凝胶渗透色谱净化，用高效液相色谱-质谱/质谱测定，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，水为去离子水。

3.1 甲醇，色谱纯。

3.2 甲酸，色谱纯。

3.3 环己烷。

3.4 乙酸乙酯。

3.5 丙酮。

3.6 二氯甲烷。

3.7 氯化钠。

3.8 无水硫酸钠：经650 ℃灼烧4 h，置于干燥器内备用。

3.9 15%氯化钠水溶液：准确称确150 g氯化钠，用水溶解并定容到1 L容量瓶中，混合均匀。

3.10 乙酸乙酯-环己烷(50+50，体积比)：等体积的乙酸乙酯和环己烷互溶。

3.11 甲醇+水(50+50，体积比)：等体积的甲醇和水互溶。

3.12 45种农药标准品(具体农药名称、英文名称及CAS号参见附录A中的表A.1和表A.2)：纯度大于等于98%。

3.13 标准储备液：准确称取适量的农药标准品，用少量的丙酮溶解，并以丙酮配制成浓度为100 μg/mL的标准储备液，−18 ℃避光保存6个月。

3.14 混合标准工作液：吸取适量标准储备溶液(3.13)，用甲醇稀释成杀鼠灵为0.2 μg/mL，其余44种农药为1 μg/mL的混合标准工作溶液，−18 ℃避光保存3个月。

3.15 基质混合标准工作液：根据需要，吸取一定量的混合标准工作液(3.14)，用基质空白液稀释至所需浓度，临用前配制。

3.16 硅藻土，cellite 545。

3.17 0.22 μm 有机滤膜。

4 仪器和设备

4.1 液相色谱-质谱/质谱仪:配有电喷雾离子源(ESI)。
4.2 凝胶渗透色谱。
4.3 振荡器。
4.4 旋转蒸发器。
4.5 氮吹仪。

5 试样的制备和保存

取代表性样品约 1 kg,用磨碎机全部磨碎并通过 20 目筛。混匀,均分成两份作为试样,分装入洁浮的盛样瓶内,密闭,标明标记。将试样于 0 ℃～4 ℃避光保存。

在制样的操作过程中,应防止样品受到污染及发生残留物含量的变化。

6 测定步骤

6.1 提取

称取试样 5 g(精确到 0.01 g)于 150 mL 具塞锥形瓶中,加入 0.5 g 硅藻土(3.16)和 15 mL 去离子水,浸泡 20 min 后加入 50 mL 丙酮,在振荡器上振荡提取 30 min,抽滤至浓缩瓶中。在 40 ℃水浴中将提取液浓缩至约 20 mL,转移至分液漏斗中,再用 30 mL 二氯甲烷分三次洗涤浓缩瓶,合并至同一分液漏斗中,然后加入 15 mL 氯化钠溶液(3.9),振摇萃取 2 min,静置分层。将二氯甲烷层经 5 g 无水硫酸钠过滤至浓缩瓶中。用 20 mL 二氯甲烷重复萃取一次,合并二氯甲烷于同一浓缩瓶中。将合并的二氯甲烷萃取液在 45 ℃下旋转蒸发至近干,用 10 mL 乙酸乙酯-环己烷(3.10)溶解残渣备净化。

6.2 净化

6.2.1 凝胶色谱条件

a) 净化柱:S-X3 Bio-Beads 填料,粒度 38 μm～75 μm,300 mm×25 mm(内径),或相当者;
b) 流动相:乙酸乙酯-环己烷(3.10),流速:5.0 mL/min;
c) 进样量:5 mL;
d) 净化程序:0 min～19 min 弃去淋洗液,19 min～30 min 收集淋洗液。

6.2.2 净化过程

5 mL 乙酸乙酯-环己烷溶解液进凝胶色谱系统,按 6.2.1 的条件净化。将收集的洗脱液 45 ℃水浴中浓缩至约 2 mL,然后用氮气吹干。准确加入 1.0 mL 甲醇＋水(3.11)溶解残渣,经 0.22 μm 有机滤膜(3.17)过滤备液相色谱-质谱/质谱测定。

6.3 测定

6.3.1 液相色谱条件

a) 色谱柱:C_{18} 150 mm×2.1 mm(内径),粒度 5 μm,或相当者;
b) 色谱柱温度:30 ℃;
c) 进样量:10 μL;
d) 流动相梯度及流速见表 1。

表 1 液相色谱梯度洗脱条件

时间/min	流速/(μL/min)	0.1%甲酸水溶液/%	甲醇/%
0.00	200	80	20
8.00	200	40	60
12.0	200	40	60
14.0	200	10	90

表 1（续）

时间/min	流速/(μL/min)	0.1%甲酸水溶液/%	甲醇/%
20.0	200	10	90
20.1	200	80	20
23.0	200	80	20

6.3.2 质谱条件

a) 离子化模式：45 种农药分为电喷雾正离子模式（ESI＋）和电喷雾负离子模式（ESI－）两组，两次进样；

b) 质谱扫描方式：多反应监测（MRM）；

c) 其他参考质谱条件参见附录 A 中的表 A.1 和表 A.2。

6.3.3 液相色谱-质谱/质谱测定

6.3.3.1 定量测定

根据样液中被测物的含量情况，选定响应值相近的基质混合标准工作液。基质标准工作溶液和样液中分析物的响应值均应在仪器的检测线性范围内。对标准工作溶液和样液等体积参差进样测定。在上述色谱条件下 45 种农药的标准多反应监测色谱图参见附录 B 中的图 B.1 和 B.2。

6.3.3.2 定性测定

如果样品谱图中各组分定性离子的相对丰度与浓度接近的混合基质标准校准溶液谱图中对应的定性离子的相对丰度进行比较，偏差不超过表 2 规定的范围，则可判定为样品中存在对应的待测物。

表 2 定性确证时相对离子丰度的最大允许误差

相对离子丰度（基峰）/%	＞50	＞20～50	＞10～20	≤10
允许的相对误差/%	±20	±25	±30	±50

6.4 空白实验

除不加试样外，均按上述操作步骤进行。

7 结果计算

试样中的残留含量，按式（1）计算，计算结果需扣除空白值：

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

式中：

X_i——试样中被测组分残留量，单位为微克每千克（μg/kg）；

c_i——标准工作溶液中被测组分浓度，单位为纳克每毫升（ng/mL）；

A_i——测定液中被测组分的峰面积；

A_{si}——标准液中被测组分的峰面积；

V——样品溶液最终定容体积，单位为毫升（mL）；

m——样品溶液所代表最终试样的质量，单位为克（g）。

8 方法的测定低限和回收率

8.1 测定低限

45 种农药除杀鼠灵为 1 μg/kg 外，其余均为 5 μg/kg。

8.2 回收率

45 种农药在大米、糙米、大麦、小麦、玉米 5 种基质三个不同添加水平的添加回收率范围见表 3。

表 3　45 种农药不同基质、三个水平添加回收率范围

分析物	添加水平/（μg/kg）	大米/%	小麦/%	大麦/%	糙米/%	玉米/%
氟唑嘧磺草胺	5	78.6～92.1	77.7～83.7	78.1～91.1	80.6～91.6	65.2～87.3
	10	76.5～86.6	80.2～90.9	80.0～93.7	85.3～93.9	70.9～92.1
	20	78.5～93.4	83.2～95.4	84.0～99.5	87.0～96.7	78.8～90.3
醚磺隆	5	85.2～97.8	79.4～88.7	84.2～95.6	82.2～96.8	73.3～90.7
	10	73.5～86.1	84.7～95.6	85.7～103	85.1～97.3	70.1～96.4
	20	85.5～99.3	87.5～100	89.8～106	86.7～102	76.8～95.0
咪草酸	5	87.8～94.6	82.8～89.5	88.4～93.9	82.6～96.8	80.3～94.8
	10	81.6～88.8	85.4～93.7	84.0～103	84.9～98.3	83.1～98.1
	20	90.6～98.0	83.8～98.4	92.3～113	87.2～99.7	84.1～99.3
甲基噻吩磺隆	5	83.3～92.4	82.7～87.7	83.8～91.3	86.4～95.4	68.7～91.4
	10	66.0～83.2	86.7～94.0	81.8～97.6	84.9～98.7	70.6～93.4
	20	83.5～94.0	84.4～97.7	88.8～105	96.2～105	73.4～95.8
烟嘧磺隆	5	68.8～78.2	68.4～77.7	68.1～77.3	66.8～83.6	72.7～83.4
	10	68.8～76.1	72.9～83.1	64.9～81.2	74.4～89.7	71.0～89.7
	20	69.5～80.5	72.8～87.2	71.4～79.5	75.8～89.5	77.0～85.9
灭草喹	5	74.9～81.3	68.9～77.5	73.2～80.4	73.0～87.8	65.6～77.4
	10	69.1～84.2	69.8～82.6	69.6～87.6	74.9～82.6	71.8～84.0
	20	75.9～84.0	72.6～86.8	76.1～96.4	79.2～97.7	69.4～80.3
萘草胺	5	60.1～71.4	60.8～71.4	60.8～80.4	60.0～79.2	60.3～72.8
	10	63.8～80.5	60.1～68.3	60.0～72.1	60.3～69.7	63.0～72.9
	20	60.5～72.5	60.6～78.2	56.8～74.9	60.4～72.2	61.3～70.7
甲氧磺草胺	5	82.5～96.3	80.5～89.0	82.7～95.2	82.6～93.8	72.0～86.1
	10	69.5～83.3	82.8～95.9	80.5～100	88.8～97.1	68.8～92.8
	20	82.5～97.6	83.8～98.6	88.4～105	91.9～102	77.9～90.3
氯酯磺草胺	5	81.8～99.0	78.9～88.6	84.8～96.7	83.6～93.6	71.1～91.9
	10	73.3～86.2	87.3～97.3	83.7～100	84.7～96.9	70.3～93.9
	20	82.0～100	86.8～102	86.5～107	88.2～103	77.7～90.0
丙苯磺隆	5	78.8～99.5	67.7～82.4	79.7～98.4	85.4～105	64.2～82.4
	10	60.0～69.9	79.3～90.9	76.5～97.1	89.3～106	70.3～101
	20	79.0～100	72.7～95.4	84.2～104	90.1～103	72.2～96.1
甲磺草胺	5	83.0～99.9	79.0～90.7	87.9～98.8	67.4～78.4	71.7～91.8
	10	76.2～89.6	85.1～104	85.4～102	70.4～89.9	73.9～94.6
	20	83.0～101	88.1～103	92.0～110	75.0～84.0	82.9～96.9

表 3（续）

分析物	添加水平/（μg/kg）	大米/%	小麦/%	大麦/%	糙米/%	玉米/%
甲酰胺磺隆	5	79.3～91.3	73.8～82.7	80.4～90.3	77.2～95.4	63.5～89.4
	10	69.6～79.3	82.1～89.6	76.5～94.8	84.6～101	68.9～87.3
	20	79.5～92.5	81.3～90.1	83.6～99.7	81.5～101	76.2～87.0
甲基胺苯磺隆	5	86.7～99.0	76.5～86.1	88.2～98.0	81.0～97.8	76.1～91.6
	10	74.6～89.4	90.3～107	84.5～99.5	83.7～101	76.7～98.3
	20	88.0～100	82.5～104	91.5～101	85.5～99.4	79.8～95.9
玉嘧磺隆	5	86.0～106	73.6～87.7	88.2～105	70.2～84.0	78.8～91.5
	10	60.7～81.9	85.7～104	83.8～101	72.7～90.3	71.0～96.3
	20	88.5～108	79.4～110	90.7～102	82.7～93.5	78.8～92.4
苯磺隆	5	65.9～98.9	59.7～78.5	70.9～87.9	66.4～87.4	66.1～93.0
	10	71.0～102	82.9～90.5	67.4～88.0	76.1～90.6	71.8～95.8
	20	71.0～100	75.4～95.0	72.6～92.5	70.1～92.2	66.0～98.6
三氟啶磺隆	5	81.6～100	78.8～91.5	84.0～99.3	74.4～99.0	64.1～87.4
	10	68.7～97.5	87.3～98.2	80.0～99.3	80.1～98.9	69.8～98.4
	20	81.5～102	86.7～103	86.0～105	82.9～98.1	77.4～93.5
四唑嘧磺隆	5	85.8～98.3	80.0～89.9	83.3～97.3	75.2～93.0	66.3～89.1
	10	66.6～88.0	87.2～99.3	81.3～102	77.7～96.3	74.7～106
	20	86.0～99.2	89.6～104	85.6～99.8	82.5～96.1	80.9～101
苄嘧磺隆	5	80.2～103	76.3～93.0	79.4～106	80.6～97.0	77.2～93.6
	10	72.0～89.0	84.1～97.3	81.8～105	80.7～104	75.9～97.5
	20	83.4～106	86.5～102	90.0～109	85.1～106	78.2～96.8
嘧啶磺隆	5	84.4～102	78.5～89.1	86.2～101	81.2～92.8	66.2～92.0
	10	67.3～88.5	90.5～99.5	81.9～99.9	80.5～98.9	72.3～95.6
	20	84.5～103	89.2～105	92.1～103	85.7～103	82.0～92.9
乙磺隆	5	82.3～97.0	80.2～89.5	85.4～96.0	81.8～95.0	71.5～87.9
	10	69.1～82.5	89.9～99.8	81.1～97.6	82.5～98.6	71.2～94.9
	20	82.5～98.4	88.8～103	89.4～98.6	86.3～96.9	77.3～90.1
氯嘧磺隆	5	82.4～98.9	76.9～86.9	85.6～97.8	76.6～93.8	65.9～90.6
	10	73.7～89.2	84.2～95.1	84.8～103	79.6～97.0	73.9～97.1
	20	82.5～99.7	82.6～99.9	86.9～100	80.8～103	77.1～92.4
咪唑磺隆	5	75.4～98.6	81.5～94.8	84.2～95.8	78.4～96.8	73.7～90.8
	10	67.3～82.0	81.6～92.7	84.4～99.1	81.7～100	64.8～90.6
	20	77.0～100	85.7～101	89.4～102	82.7～102	73.9～90.4
苯并双环酮	5	82.1～96.8	72.4～95.8	74.5～97.5	70.4～83.0	68.4～87.1
	10	64.7～90.0	71.4～94.4	79.3～90.6	75.7～85.8	68.1～106
	20	82.0～99.1	77.9～93.3	80.1～100	78.4～88.2	79.3～97.0

表 3（续）

分析物	添加水平/（μg/kg）	大米/%	小麦/%	大麦/%	糙米/%	玉米/%
乙氧嘧磺隆	5	87.0～101	76.2～89.9	86.1～99.4	68.8～98.0	76.5～93.8
	10	70.5～89.1	87.0～97.6	81.8～105	79.7～96.0	70.1～94.0
	20	87.0～102	87.6～102	90.0～102	72.6～99.7	76.4～93.5
环丙嘧磺隆	5	70.9～103	60.4～84.8	82.6～102	78.6～93.8	68.4～93.8
	10	69.1～88.9	75.4～94.2	80.2～104	79.2～97.1	69.8～96.4
	20	73.7～105	79.6～102	88.2～105	87.5～97.9	75.6～94.8
吡嘧磺隆	5	82.0～102	74.2～87.6	81.1～100	82.2～98.0	66.4～90.5
	10	77.3～86.8	86.3～98.4	77.0～96.0	84.0～101	73.8～96.7
	20	85.2～103	83.1～103	91.1～104	86.7～94.7	80.2～91.9
恶草酸	5	71.8～92.0	64.0～73.3	75.4～90.9	74.6～88.6	67.4～86.7
	10	75.2～104	67.5～77.8	73.8～95.5	82.6～91.8	63.7～92.7
	20	72.5～93.2	61.1～81.7	80.7～94.1	78.7～93.5	75.4～88.1
双氟磺草胺	5	80.4～119	74.2～90.2	85.6～104	76.4～87.2	68.3～94.0
	10	76.0～90.3	76.6～99.7	71.2～95.1	82.0～97.6	77.0～95.3
	20	76.9～99.6	80.0～97.4	75.5～95.1	86.3～95.4	81.9～99.2
醚苯磺隆	5	98.5～109	78.6～93.3	86.6～95.2	76.2～93.6	72.1～91.6
	10	82.8～95.4	75.8～93.2	82.2～101	77.3～93.8	77.6～90.3
	20	94.1～107	84.7～99.2	87.2～101	80.5～94.3	81.8～95.9
甲磺隆	5	62.5～94.5	75.1～96.4	82.8～95.8	74.2～85.6	67.1～82.3
	10	68.0～83.0	73.3～87.4	66.8～87.4	79.4～90.4	69.9～83.5
	20	64.2～83.5	81.4～95.8	71.7～87.4	78.4～91.9	73.4～85.8
氯磺隆	5	68.3～85.0	69.7～83.9	84.8～97.2	76.4～92.4	72.4～86.5
	10	68.7～79.9	73.4～87.8	64.7～80.7	80.3～97.8	73.1～84.4
	20	67.9～91.9	80.7～96.6	68.0～84.2	84.5～92.2	76.8～91.3
五氟磺草胺	5	86.3～112	75.8～94.0	75.8～94.0	76.0～89.2	75.8～94.0
	10	78.2～94.3	81.4～101	77.6～96.4	79.8～94.1	81.4～96.0
	20	83.8～107	81.7～106	82.3～99.3	84.0～99.0	85.9～101
双氯磺草胺	5	93.3～110	74.9～93.8	88.0～102	86.4～98.4	68.0～88.2
	10	85.5～99.9	71.1～86.5	84.9～105	90.8～99.6	74.8～88.5
	20	89.7～106	80.0～98.5	90.1～105	93.2～100	78.6～93.1
甲基碘磺隆	5	87.1～108	72.6～98.5	84.2～97.8	71.8～87.8	68.6～86.6
	10	88.6～101	70.1～88.5	88.0～106	78.2～92.9	76.9～91.0
	20	90.7～107	81.8～97.8	93.3～102	75.9～95.3	75.5～91.4
烯草酮砜	5	75.6～111	67.8～87.4	67.8～87.4	67.8～86.8	67.8～87.4
	10	65.1～89.9	71.8～92.6	64.7～83.5	71.2～91.8	74.0～95.4
	20	76.5～103	73.1～91.9	68.6～83.5	74.9～88.9	78.4～92.2

表 3（续）

分析物	添加水平/（μg/kg）	大米/%	小麦/%	大麦/%	糙米/%	玉米/%
甲磺胺磺隆	5	94.3～101	74.7～98.2	84.2～96.6	76.6～98.0	63.4～81.8
	10	68.9～98.1	69.7～86.9	81.8～98.1	80.4～97.9	72.0～84.4
	20	90.8～101	79.6～103	72.6～98.1	84.6～103	75.1～86.0
氟磺隆	5	81.3～109	63.9～78.2	78.0～108	82.8～92.4	60.1～79.1
	10	74.9～99.0	75.9～95.0	73.8～96.3	85.4～97.0	74.6～89.2
	20	78.2～107	79.2～94.5	81.0～96.1	87.5～99.9	72.5～89.3
杀鼠灵	1	88.5～114	71.8～93.8	90.4～98.6	86.2～95.0	67.8～90.7
	2	80.0～92.4	70.9～83.2	79.5～91.4	90.7～101	68.6～91.1
	4	85.2～115	81.6～91.5	84.3～97.3	91.1～101	81.9～94.3
2-甲-4-氯丙酸	5	61.6～74.0	63.5～74.5	65.4～80.2	60.8～74.0	60.4～74.1
	10	62.9～71.5	60.5～71.3	61.6～75.3	60.3～73.9	68.5～83.7
	20	60.3～72.1	67.7～86.4	65.4～75.4	62.3～78.9	70.5～83.1
氟嘧磺隆	5	80.7～101	60.2～72.4	60.2～80.0	61.8～72.0	61.0～76.0
	10	66.4～84.1	61.4～68.6	65.0～77.2	60.7～77.7	60.1～73.7
	20	77.6～99.8	60.9～75.5	70.4～88.6	61.5～75.7	62.0～80.2
氟磺胺草醚	5	76.8～104	60.0～75.5	60.0～73.6	64.4～87.0	62.0～79.6
	10	63.8～72.2	60.0～69.1	65.6～73.0	68.2～91.1	61.1～70.1
	20	73.9～91.8	60.7～78.3	67.2～76.1	78.6～95.9	60.4～76.6
氟胺磺隆	5	83.0～98.3	60.9～82.6	75.0～98.0	83.0～97.8	64.0～86.8
	10	74.0～101	63.9～86.1	74.1～100	87.9～100	68.2～86.1
	20	82.9～97.7	72.1～94.8	78.7～99.2	91.9～99.1	71.6～89.0
氯吡嘧磺隆	5	81.0～108	73.8～90.2	80.4～106	70.8～92.6	77.6～94.8
	10	66.6～88.2	70.1～87.5	65.4～80.6	74.4～98.0	67.0～84.3
	20	76.6～105	80.1～96.2	70.8～87.2	78.3～97.9	75.2～100
达诺杀	5	94.4～114	74.1～93.4	80.6～98.6	80.8～96.8	61.5～88.7
	10	79.2～92.0	73.7～90.2	78.7～95.6	85.2～96.9	70.9～89.9
	20	89.3～102	81.1～98.0	83.5～97.0	85.9～102	77.1～93.6
特乐酚	5	94.5～114	70.7～90.1	84.8～99.0	77.0～93.8	73.6～89.1
	10	71.2～87.2	71.3～89.5	75.0～89.3	81.6～98.0	75.0～86.3
	20	91.2～102	78.4～96.9	75.0～91.9	84.5～99.4	78.8～93.8

附 录 A
（资料性附录）
质谱条件[1)]

参考质谱条件：

a） 鞘气压力：30 unit；

b） 辅助气压力：8 unit；

c） 正离子模式电喷雾电压(IS)：4 000 V；

d） 负离子模式电喷雾电压(IS)：－3 200 V；

e） 毛细管温度：320 ℃；

f） 源内诱导解离电压：10 V；

g） Q1，Q3 分辨率：Q1 为 0.4，Q3 为 0.7；

h） 碰撞气：高纯氩气；

i） 碰撞气压力：1.5 mTorr。

j） 其他质谱参数见表 A.1 和 A.2。

表 A.1 正离子模式组 27 种被测物的英文名称、CAS 号、参考保留时间、监测离子对和碰撞能量

药物名称	英文名称	CAS 号	保留时间/min	监测离子对 (m/z)	碰撞能量/ev
氟唑嘧磺草胺	Flumetsulam	98967-40-9	6.52	325.9/129.0[a]	33
				325.9/109.0	47
醚磺隆	Cinosulfuron	94593-91-6	9.52	414.2/183.0[a]	19
				414.2/157.0	25
咪草酸	Imazamethabenz-methyl	81405-85-8	9.54	289.1/143.9[a]	34
				289.1/220.0	20
甲基噻吩磺隆	Thifensulfuron-methy	79277-27-3	10.02	388.2/167.0[a]	17
				388.2/205.0	25
烟嘧磺隆	Nicosulfuron	111991-09-4	10.17	411.1/182.0[a]	21
				411.1/213.0	17
灭草喹	Imazaquin	81335-37-7	10.37	312.1/267.0[a]	20
				312.1/180.9	37
萘草胺	Naptalam	132-66-1	10.52	292.2/144.1[a]	11
				292.2/149.0	24
甲氧磺草胺	Metonsulam	139528-85-1	10.62	418.0/175.0[a]	35
				418.0/140.0	46
氯酯磺草胺	Cloransulam-methyl	147150-35-4	10.85	430.1/397.9[a]	14
				430.1/370.0	22

1） 非商业性声明：附录 A 所列参考质谱条件是在 Thermo TSQ Quantum Ultra AM 型液质联用仪上完成的，此处列出试验用仪器型号仅为提供参考，并不涉及商业目的，鼓励标准使用者尝试不同厂家或型号的仪器。

表 A.1（续）

药物名称	英文名称	CAS 号	保留时间/min	监测离子对（m/z）	碰撞能量/ev
丙苯磺隆	Propoxycarbazone-sodium	181274-15-7	10.95	416.1/399.1[a]	8
				416.1/199.0	24
甲磺草胺	Sulfentrazone	122836-35-5	11.08	404.0/387.0[a]	12
				404.0/307.0	28
甲酰胺磺隆	Foramsulfuron	173159-57-4	11.09	452.9/182.0[a]	27
				452.9/255.0	23
甲基胺苯磺隆	Ethametsulfuron-methyl	97780-06-8	11.22	411.2/196.1[a]	17
				411.2/168.0	35
玉嘧磺隆	Rimusulfuron	122931-48-0	11.09	432.0/182.0[a]	20
				432.0/325.0	15
苯磺隆	Tribenuron-methyl	101200-48-0	11.83	396.2/155.1[a]	12
				396.2/181.0	16
三氟啶磺隆	Trifloxysulfuron-sodium	199119-58-9	12.33	438.0/182.0[a]	22
				438.0/139.0	40
四唑嘧磺隆	Azimsulfuron	120162-55-2	12.46	425.1/182.0[a]	16
				425.1/156.0	37
苄嘧磺隆	Bensulfuron-methyl	83055-99-6	13.64	411.1/149.0[a]	21
				411.1/182.0	19
嘧啶磺隆	Flazasulfuron	104040-78-0	13.89	408.2/182.0[a]	18
				408.2/139.1	38
乙磺隆	Sulfosulfuron	141776-32-1	14.45	471.1/211.1[a]	15
				471.1/218.0	25
氯嘧磺隆	Chlorimuron-ethyl	90982-32-4	15.74	415.1/186.0[a]	17
				415.1/184.7	29
咪唑磺隆	Imazosulfuron	122548-33-8	15.80	413.1/153.0[a]	13
				413.1/156.0	22
苯并双环酮	Benzobicyclon	156963-66-5	16.88	446.9/257.0[a]	24
				446.9/229.0	34
乙氧嘧磺隆	Ethoxysulfron	126801-58-9	16.00	399.1/261.0[a]	17
				399.1/218.0	26
环丙嘧磺隆	Cyclsulfamuron	136849-15-5	16.26	422.1/260.9[a]	18
				422.1/218.0	26
吡嘧磺隆	Pyrazosulfuron-ethyl	93697-74-6	16.35	415.2/182.1[a]	18
				415.2/139.1	42

表 A.1（续）

药物名称	英文名称	CAS 号	保留时间/min	监测离子对（m/z）	碰撞能量/ev
恶草酸	Propaquizafop	111479-05-1	17.97	444.1/100.0[a]	19
				444.1/371.0	18
[a] 为定量离子对，对于不同质谱仪器，仪器参数可能存在差异，测定前应将质谱参数优化到最佳。					

表 A.2　负离子模式组 18 种被测物的英文名称、CAS 号、参考保留时间、监测离子对和碰撞能量

药物名称	英文名称	CAS 号	保留时间/min	离子对（m/z）	碰撞能量/ev
双氟磺草胺	Florasulam	145701-23-1	8.48	358.0/167.1[a]	−16
				358.0/152.0	−31
醚苯磺隆	Triasulfuron	82097-50-5	9.82	400.1/139.2[a]	−23
				400.1/198.2	−12
甲磺隆	Metsulfuron-methyl	74223-64-6	10.27	380.2/139.1[a]	−16
				380.2/107.2	−44
氯磺隆	Chlorsulfuron	64902-72-3	11.02	356.0/139.0[a]	−20
				356.0/190.1	−13
五氟磺草胺	Penoxsulam	219714-96-2	11.05	482.0/307.1[a]	−28
				482.0/179.0	−17
双氯磺草胺	Diclosulam	145701-21-9	11.22	404.0/181.1[a]	−17
				404.0/153.1	−30
甲基碘磺隆	Iodosulfuron-methyl	185119-76-0	12.2	502.2/267.1[a]	−24
				502.2/347.1[a]	−18
烯草酮砜	Clethodim-sulfone	99129-21-2	13.34	390.1/298.2[a]	−18
				390.1/270.1	−23
甲磺胺磺隆	Mesosulfuron-methyl	208465-21-8	12.08	506.1/139.2[a]	−24
				506.1/308.0	−15
氟磺隆	Prosulfuron	94125-34-5	15.32	417.9/139.2[a]	−22
				417.9/252.0	−17
杀鼠灵	Warfarin	81-81-2	15.50	307.0/161.1[a]	−21
				307.0/250.1	−23
2-甲-4-氯丙酸	Mecoprop	93-65-2	15.59	212.9/141.1[a]	−21
				212.9/83.2	−37
氟嘧磺隆	Primisulfuron-methyl	86209-51-0	15.97	467.0/226.0[a]	−18
				467.0/176.1	−32
氟磺胺草醚	Fomesafen	72178-02-0	16.15	436.9/195.0[a]	−43
				436.9/286.0	−27

表 A.2（续）

药物名称	英文名称	CAS 号	保留时间/min	离子对（m/z）	碰撞能量/ev
氟胺磺隆	Triflusulfuron-methyl	126535-15-7	16.27	491.2/236.1[a]	−17
				491.2/196.1	−39
氯吡嘧磺隆	Halosulfuron-methyl	100784-20-1	16.53	432.9/252.1[a]	−18
				432.9/154.2	−32
达诺杀	Dinoseb	88-85-7	17.16	239.1/194.1[a]	−22
				239.1/193.1	−26
特乐酚	Dinoterb	1420-07-1	17.27	239.1/207.1[a]	−27
				239.1/177.2	−34
[a] 为定量离子对，对于不同质谱仪器，仪器参数可能存在差异，测定前应将质谱参数优化到最佳。					

附 录 B
（资料性附录）
标准物质多反应监测色谱图

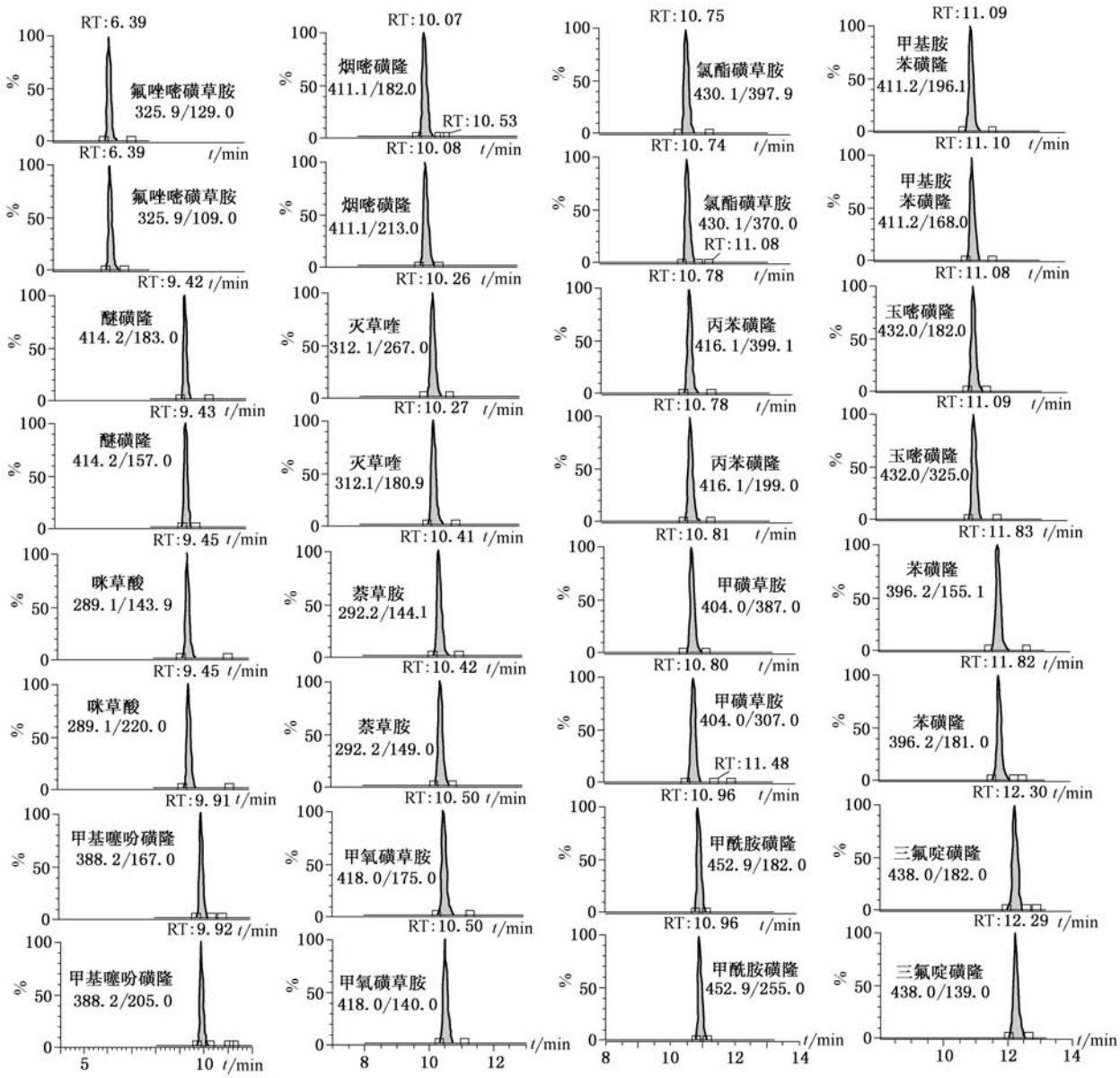

图 B.1 电喷雾正离子扫描模式下 27 种农药标准物质的多反应监测色谱图

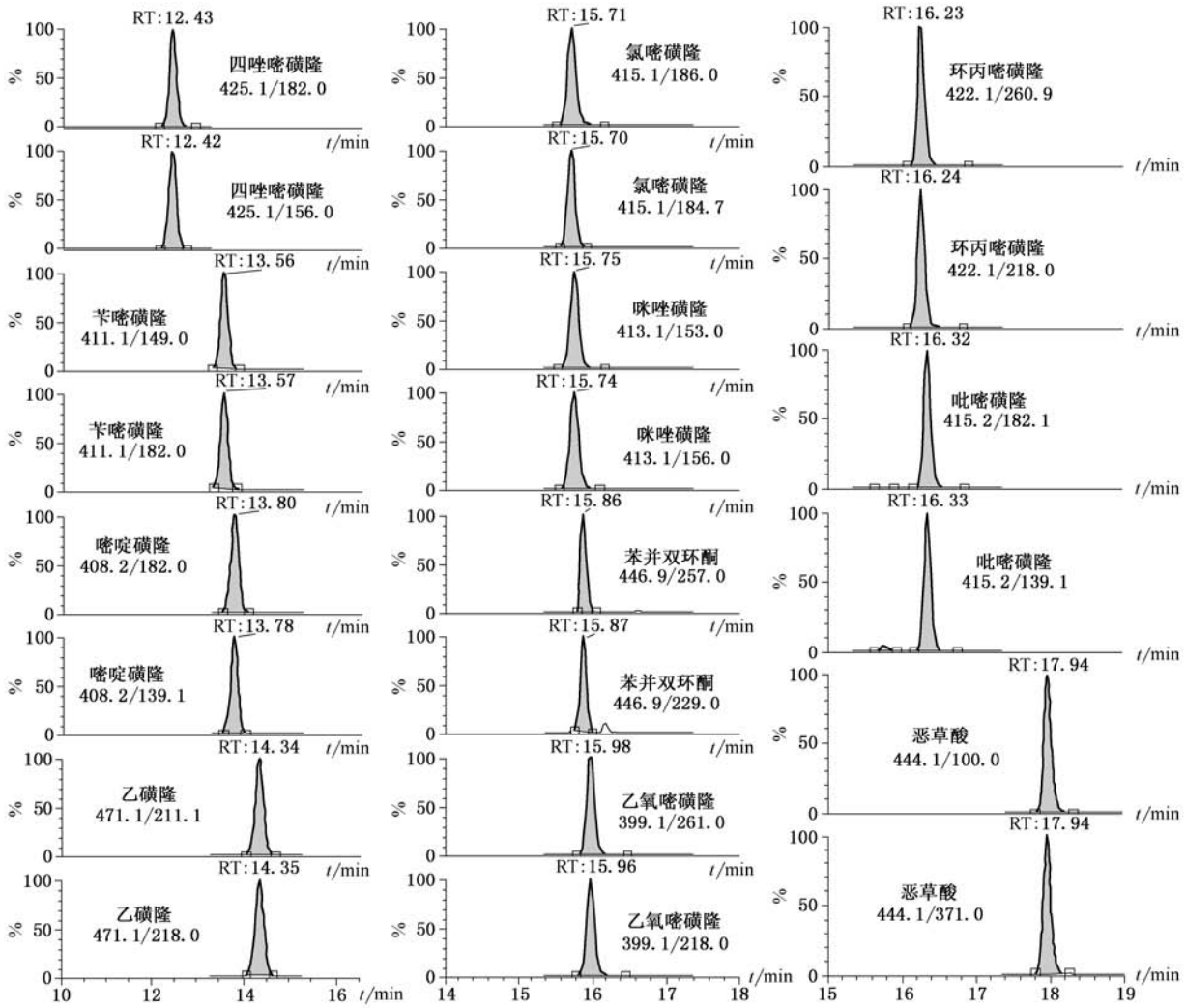

图 B.1（续）

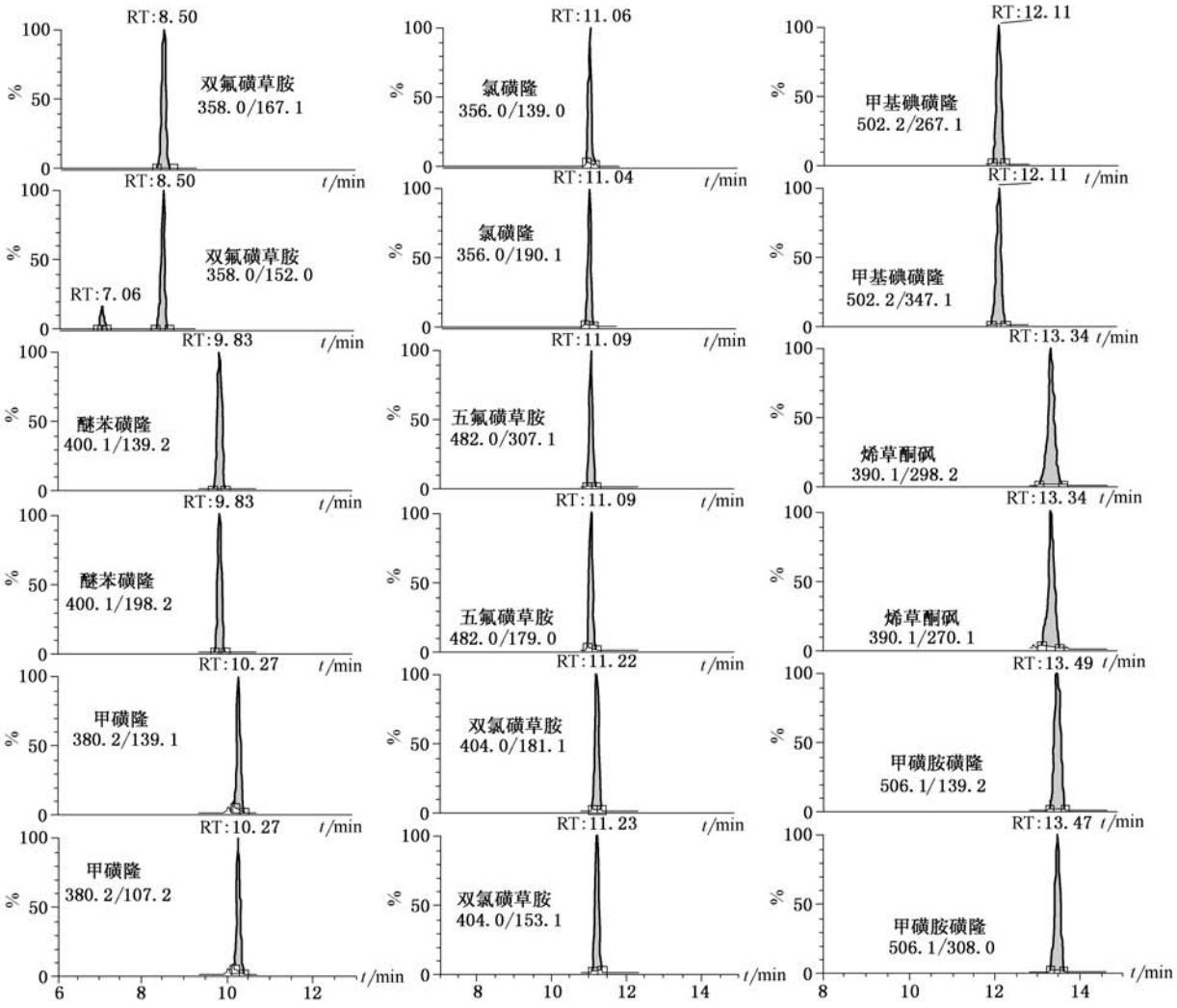

图 B.2　电喷雾负离子扫描模式下 18 种农药标准物质的多反应监测色谱图

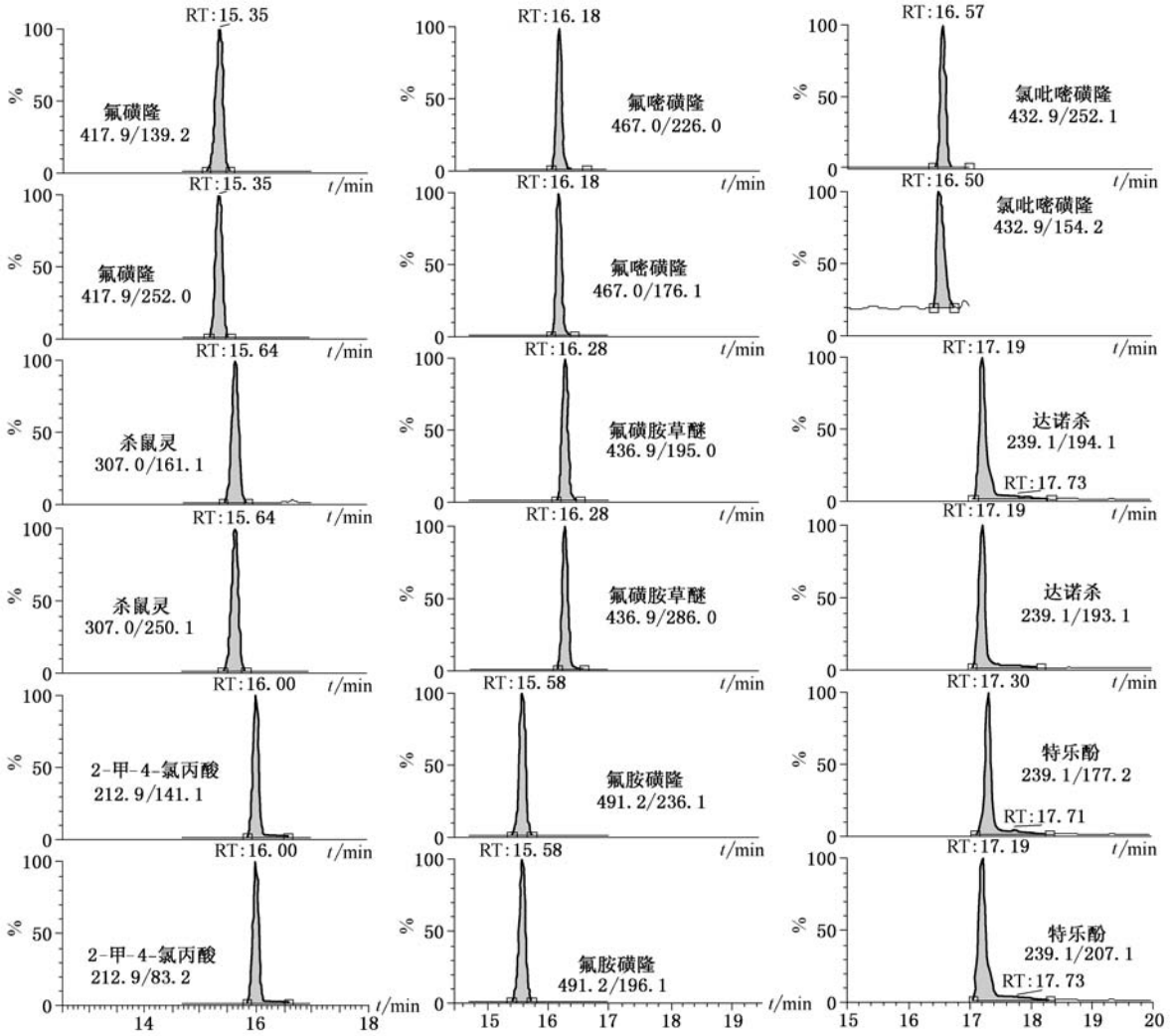

图 B.2(续)

Foreword

Annex A, Annex B of this standard are an informative one.

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

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

The main drafters of this standard are Wang Fengchi, Ai Lianfeng, Guo Chunhai, Chen Ruichun, Li Chengcheng and Lin Anqing.

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

Determination of 45 pesticides residues including azimsulfron, bensulfron-methyl, cinosulfron et al in foods for import and export—HPLC-MS/MS method

1 Scope

This standard specifies the methods for qualified and determination 45 pesticide residues in foods by liquid chromatography-tandem mass spectrometry and sample preparation.

This standard is applicable to the determination 45 pesticide residues of Flumetsulam, Cinosulfron, Imazamethabenz-methyl, Thifensulfuron-methy, Nicosulfuron, Imazaquin, Naptalam, Metonsulam, Clornsulam-methyl, Propoxycarbazone-sodium, Sulfentrazone, Foramsulfuron, Ethametsulfuron-methyl, Rimusulfuron, Tribenuron-methyl, Trifloxysulfuron-sodium, Azimsulfron, Bensulfron-methyl, Flazasulfuron, Sulfosulfuron, Chlorimuron-ethyl, Imazosulfuron, Benzobicyclon, Ethoxysulfron, Cyclsulfamuron, Pyrazosulfron-ethyl, Propaquizafop, Florasulam, Triasulfuron, Metsulfuron-methyl, Chlorsulfuron, Penoxsulam, Diclosulam, Iodosulfuron-methyl, Clethodim-sulfone, Mesosulfuron-methyl, Prosulfuron, Warfarin, Mecoprop, Primisulfuron-methyl, Fomesafen, Triflusulfuron-methyl, Halosufuron-methyl, Dinoseb, and Dinoterb in rice, brown rice, wtheat, barley and maize.

2 Abstract of this method

The 45 pesticide residues in the test sample are extracted with acetone-water. The extract is partitioned with dichloromethane, and cleaned up with gel penetration chromatography. Determination is made by LC-MS /MS using the external standard method.

3 Reagents and materials

Unless specifically noted, all reagents used should be of analytical grade; "water" is deionized water.

3.1 Methanol, HPLC grade.

3.2 Formic acid, HPLC grade.

3.3 Cyclohexane.

3.4 Ethyl acetate.

3.5 Actone.

3.6 Dichloromethane.

3.7 Sodium chloride.

3.8 Anhydrous sodium sulfate: Ignite at 650 ℃ for 4 h, and keep in a tightly closed container after cool.

3.9 15% sodium chloride solution: Accurately weigh 150 g sodium chloride, dissolved and diluted with water to 1 L, and mix to homogeneteity.

3.10 Ethyl acetate-cyclohexane(50 + 50, V/V): Mix the same volume ethyl acetate and cyclohexane.

3.11 Methanol-warter(50 + 50, V/V): Mix the same volume Methanol and warter.

3.12 Standards of 45 pesticide(the all coumpounds and their CAS # were listed in table A.1 and A.2 of Annex A): Purity ≥98.0%.

3.13 Stock standard solution: Accurately weigh 10 mg (accurate to 0.1 mg) standard, dissolve in 100 mL acetone and mix to homogeneity. The concentration of the solutions is 100 μg/mL. The solutions should be stored below −18 ℃ in dark for more than 6 months.

3.14 Mixed standard solution: Accurately measure 1.00 mL stock standard solution(3.13) (warfarin 0.2 mL) respectively into a 100 mL umber volumetric flask, dilute with methanol to 100 mL and mix to homogeneity.

The concentration of the solution is 1 μg/mL(warfarin 0.2 μg/mL). The solutions should be stored at −18 ℃ in dark for more than 3 months.

3.15 Standard working solution: According to the requirement, accurately measure an adequate volume of mixed standard solution, dilute with blank matrix extract solution just before use.

3.16 Diatomite, cellite545.

3.17 0.22 μm filter.

4 Apparatus and equipment

4.1 High performance liquid chromatography tandem mass spectrograph.

4.2 Gel permeation chromatography.

4.3 Mechanical Shaker.

4.4 Rotary vacuum evaporator.

4.5 Nitrogen evaporator.

5 Sample preparation

About 1 kg representative samples should be taken from all samples, then grinded with a grinder to let all pass through a 20-mesh sieve. Mix thoroughly and divide into two equal portions as the samples. Place in clean sample containers, seal and label. The test Samples should be stored 0 ℃ ～4 ℃ and kept away from light. In the course of sample preparation, precautions must be taken to avoid contamination or any factors that may cause the change of residue content.

6 Procedure of determination

6.1 Extraction

Weigh 5 g of the test sample into 150 mL conical flask, add 0.5 g cellite545(3.16)and 15 mL water, and stand for 20 min. Add 50 mL acetone and shake for 30 min with a shaker. Filter the extract into 200 mL evaporated flask under reduced pressure. Concentrate the filtrate solution at 40 ℃ until approx. 20 mL. Transfer the solution into a separator funnel, wash the flask thrice using 30 mL dichloromethane and transfern the washing solution to the same separator funnel. Add 15 mL sodium chloride solution(3.9), then shake violently for 2 min and let stand to sepatate clearly. Filter the dichloromethane layer through an anhydrous sodium dulfate layer into a evaporated flask. then use 20 mL dichloromethane to liquid-liquid extract again and mix the dichloromethane into the flask. Evaporate the dehydrate dichlromethane to dryness with rotary evaporator in a water-bath below 45 ℃. Dissovle the residues with 10 mL cyclohexane-ethyl acetate(3.10). The solution is ready cleanup by GPC.

6.2 Clean up

6.2.1 Conditions of GPC

a) Column: Packed with S-X3 Bio-Breads, 300 mm × 25 mm(i.d), or equivalent;

b) Mobile phase: Cyclohexane-ethyl acetate(3.10), flow rate: 5.0 mL/min;

c) Injection volume: 5 mL;

d) Clean-up procedure: The first fraction of 0 min～19 min was discarded; the second fraction of 19 min～30 min was collected.

6.2.2 Clean up procedure

Inject 5 mL of the solution into GPC to clean up. Evaporate the collection to near dryness, then blow to dryness under a nitrogen flow. Dissolve the residues with 1.0 mL methanol-water(3.11)and vortex to homogeneity. After being filtrated with 0.22 μm filter(3.17), the final solution is ready analysis by HPLC-MS/MS.

6.3 Determination

6.3.1 HPLC operating conditions

a) Column: C_{18} 150 mm × 2.1 mm(i.d.), 5 μm particle size, or equivalent;

b) Column temperature: 30 ℃;

c) Injection volume: 10 μL;

d) Mobile phase: The elution gradient and flow rate are listed in table 1.

Table 1—Elution gradient of LC

Time/min	Flow rate/(μL/min)	0.1% formic acid solution/%	Methanol/%
0.00	200	80	20
8.00	200	40	60
12.0	200	40	60
14.0	200	10	90
20.0	200	10	90
20.1	200	80	20
23.0	200	80	20

6.3.2 MS conditions

a) Ionization mode: the 45 analytes were divided two groups, one adopts ESI+, the other adopts ESI−;

b) scan mode: MRM;

c) other reference mass operating conditions are listed in Table A.1 and A.2 of Annex A.

6.3.3 LC-MS/MS determination

6.3.3.1 Quantitative analysis

According to the approximate concentration of analyte in the test sample solution, select the standard working solution with)similar responses to that of sample solution. The responses of the analyte

in the standard working solution and the sample solution should be within the linear range of the instrument detection. The mixed standard working solution should be injected randomly in between the injuections of the sample solution of equal volume. Under the above operating condition, The chromatogram of the standard can be foud in annex B.

6.3.3.2 Qualitative analysis

Under above determination, for the same analysis batch and the same compoud, the variation of the ion tation between the two daughter ions fo the unkown sample and the standard working solution at the similar concentration can not be out of range of table 2, then the corresponding analyte must be present in the sample.

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

Relative intensity/%	>50	>20～50	>10～20	≤10
Permitted tolerance/%	±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, but with the omission of sample addition.

7 Calculation an expression of result

Calculation the content of residues in test sample by data processor or according to formula (1), the blank value should be subtracted from the result of calculation.

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

where:

X_i —the residue content of analyte in test sample, μg/kg;

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

A_i —the peak area of analyte in the sample solution;

A_{si} —the peak area of analyte in the standard working solution;

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

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

8 Limit of determination and recovery

8.1 Limit of determination

The limit of quantification for warfarin is 1 μg/kg; the other 44 pesticides are all 5 μg/kg.

8.2 Recovery

The recovery range of 45 pesticides in rice, brown rice, wtheat, barley and maize at three level was

showd in Table3.

Table 3—The recovery range of 45 pesticides in deferent matrice at three fortify levels

Compound	Levels/（μg/kg）	Rice/%	Wheat/%	Barley/%	Brown rice/%	Maize/%
Flumetsulam	5	78.6～92.1	77.7～83.7	78.1～91.1	80.6～91.6	65.2～87.3
	10	76.5～86.6	80.2～90.9	80.0～93.7	85.3～93.9	70.9～92.1
	20	78.5～93.4	83.2～95.4	84.0～99.5	87.0～96.7	78.8～90.3
Cinosulfuron	5	85.2～97.8	79.4～88.7	84.2～95.6	82.2～96.8	73.3～90.7
	10	73.5～86.1	84.7～95.6	85.7～103	85.1～97.3	70.1～96.4
	20	85.5～99.3	87.5～100	89.8～106	86.7～102	76.8～95.0
Imazamethabenz-methyl	5	87.8～94.6	82.8～89.5	88.4～93.9	82.6～96.8	80.3～94.8
	10	81.6～88.8	85.4～93.7	84.0～103	84.9～98.3	83.1～98.1
	20	90.6～98.0	83.8～98.4	92.3～113	87.2～99.7	84.1～99.3
Thifensulfuron-methy	5	83.3～92.4	82.7～87.7	83.8～91.3	86.4～95.4	68.7～91.4
	10	66.0～83.2	86.7～94.0	81.8～97.6	84.9～98.7	70.6～93.4
	20	83.5～94.0	84.4～97.7	88.8～105	96.2～105	73.4～95.8
Nicosulfuron	5	68.8～78.2	68.4～77.7	68.1～77.3	66.8～83.6	72.7～83.4
	10	68.8～76.1	72.9～83.1	64.9～81.2	74.4～89.7	71.0～89.7
	20	69.5～80.5	72.8～87.2	71.4～79.5	75.8～89.5	77.0～85.9
Imazaquin	5	74.9～81.3	68.9～77.5	73.2～80.4	73.0～87.8	65.6～77.4
	10	69.1～84.2	69.8～82.6	69.6～87.6	74.9～82.6	71.8～84.0
	20	75.9～84.0	72.6～86.8	76.1～96.4	79.2～97.7	69.4～80.3
Naptalam	5	60.1～71.4	60.8～71.4	60.8～80.4	60.0～79.2	60.3～72.8
	10	63.8～80.5	60.1～68.3	60.0～72.1	60.3～69.7	63.0～72.9
	20	60.5～72.5	60.6～78.2	56.8～74.9	60.4～72.2	61.3～70.7
Metonsulam	5	82.5～96.3	80.5～89.0	82.7～95.2	82.6～93.8	72.0～86.1
	10	69.5～83.3	82.8～95.9	80.5～100	88.8～97.1	68.8～92.8
	20	82.5～97.6	83.8～98.6	88.4～105	91.9～102	77.9～90.3
Cloransulam-methyl	5	81.8～99.0	78.9～88.6	84.8～96.7	83.6～93.6	71.1～91.9
	10	73.3～86.2	87.3～97.3	83.7～100	84.7～96.9	70.3～93.9
	20	82.0～100	86.8～102	86.5～107	88.2～103	77.7～90.0
Propoxycarbazone-sodium	5	78.8～99.5	67.7～82.4	79.7～98.4	85.4～105	64.2～82.4
	10	60.0～69.9	79.3～90.9	76.5～97.1	89.3～106	70.3～101
	20	79.0～100	72.7～95.4	84.2～104	90.1～103	72.2～96.1
Sulfentrazone	5	83.0～99.9	79.0～90.7	87.9～98.8	67.4～78.4	71.7～91.8
	10	76.2～89.6	85.1～104	85.4～102	70.4～89.9	73.9～94.6
	20	83.0～101	88.1～103	92.0～110	75.0～84.0	82.9～96.9

Table 3（continued）

Compound	Levels/（μg/kg）	Rice/%	Wheat/%	Barley/%	Brown rice/%	Maize/%
Foramsulfuron	5	79.3～91.3	73.8～82.7	80.4～90.3	77.2～95.4	63.5～89.4
	10	69.6～79.3	82.1～89.6	76.5～94.8	84.6～101	68.9～87.3
	20	79.5～92.5	81.3～90.1	83.6～99.7	81.5～101	76.2～87.0
Ethametsulfuron-methyl	5	86.7～99.0	76.5～86.1	88.2～98.0	81.0～97.8	76.1～91.6
	10	74.6～89.4	90.3～107	84.5～99.5	83.7～101	76.7～98.3
	20	88.0～100	82.5～104	91.5～101	85.5～99.4	79.8～95.9
Rimusulfuron	5	86.0～106	73.6～87.7	88.2～105	70.2～84.0	78.8～91.5
	10	60.7～81.9	85.7～104	83.8～101	72.7～90.3	71.0～96.3
	20	88.5～108	79.4～110	90.7～102	82.7～93.5	78.8～92.4
Tribenuron-methyl	5	65.9～98.9	59.7～78.5	70.9～87.9	66.4～87.4	66.1～93.0
	10	71.0～102	82.9～90.5	67.4～88.0	76.1～90.6	71.8～95.8
	20	71.0～100	75.4～95.0	72.6～92.5	70.1～92.2	66.0～98.6
Trifloxysulfuron-sodium	5	81.6～100	78.8～91.5	84.0～99.3	74.4～99.0	64.1～87.4
	10	68.7～97.5	87.3～98.2	80.0～99.3	80.1～98.9	69.8～98.4
	20	81.5～102	86.7～103	86.0～105	82.9～98.1	77.4～93.5
Azimsulfuron	5	85.8～98.3	80.0～89.9	83.3～97.3	75.2～93.0	66.3～89.1
	10	66.6～88.0	87.2～99.3	81.3～102	77.7～96.3	74.7～106
	20	86.0～99.2	89.6～104	85.6～99.8	82.5～96.1	80.9～101
Bensulfuron-methyl	5	80.2～103	76.3～93.0	79.4～106	80.6～97.0	77.2～93.6
	10	72.0～89.0	84.1～97.3	81.8～105	80.7～104	75.9～97.5
	20	83.4～106	86.5～102	90.0～109	85.1～106	78.2～96.8
Flazasulfuron	5	84.4～102	78.5～89.1	86.2～101	81.2～92.8	66.2～92.0
	10	67.3～88.5	90.5～99.5	81.9～99.9	80.5～98.9	72.3～95.6
	20	84.5～103	89.2～105	92.1～103	85.7～103	82.0～92.9
Sulfosulfuron	5	82.3～97.0	80.2～89.5	85.4～96.0	81.8～95.0	71.5～87.9
	10	69.1～82.5	89.9～99.8	81.1～97.6	82.5～98.6	71.2～94.9
	20	82.5～98.4	88.8～103	89.4～98.6	86.3～96.9	77.3～90.1
Chlorimuron-ethyl	5	82.4～98.9	76.9～86.9	85.6～97.8	76.6～93.8	65.9～90.6
	10	73.7～89.2	84.2～95.1	84.8～103	79.6～97.0	73.9～97.1
	20	82.5～99.7	82.6～99.9	86.9～100	80.8～103	77.1～92.4
Imazosulfuron	5	75.4～98.6	81.5～94.8	84.2～95.8	78.4～96.8	73.7～90.8
	10	67.3～82.0	81.6～92.7	84.4～99.1	81.7～100	64.8～90.6
	20	77.0～100	85.7～101	89.4～102	82.7～102	73.9～90.4
Benzobicyclon	5	82.1～96.8	72.4～95.8	74.5～97.5	70.4～83.0	68.4～87.1
	10	64.7～90.0	71.4～94.4	79.3～90.6	75.7～85.8	68.1～106
	20	82.0～99.1	77.9～93.3	80.1～100	78.4～88.2	79.3～97.0

Table 3（continued）

Compound	Levels/（μg/kg）	Rice/%	Wheat/%	Barley/%	Brown rice/%	Maize/%
Ethoxysulfron	5	87.0～101	76.2～89.9	86.1～99.4	68.8～98.0	76.5～93.8
	10	70.5～89.1	87.0～97.6	81.8～105	79.7～96.0	70.1～94.0
	20	87.0～102	87.6～102	90.0～102	72.6～99.7	76.4～93.5
Cyclsulfamuron	5	70.9～103	60.4～84.8	82.6～102	78.6～93.8	68.4～93.8
	10	69.1～88.9	75.4～94.2	80.2～104	79.2～97.1	69.8～96.4
	20	73.7～105	79.6～102	88.2～105	87.5～97.9	75.6～94.8
Pyrazosulfuron-ethyl	5	82.0～102	74.2～87.6	81.1～100	82.2～98.0	66.4～90.5
	10	77.3～86.8	86.3～98.4	77.0～96.0	84.0～101	73.8～96.7
	20	85.2～103	83.1～103	91.1～104	86.7～94.7	80.2～91.9
Propaquizafop	5	71.8～92.0	64.0～73.3	75.4～90.9	74.6～88.6	67.4～86.7
	10	75.2～104	67.5～77.8	73.8～95.5	82.6～91.8	63.7～92.7
	20	72.5～93.2	61.1～81.7	80.7～94.1	78.7～93.5	75.4～88.1
Florasulam	5	80.4～119	74.2～90.2	85.6～104	76.4～87.2	68.3～94.0
	10	76.0～90.3	76.6～99.7	71.2～95.1	82.0～97.6	77.0～95.3
	20	76.9～99.6	80.0～97.4	75.5～95.1	86.3～95.4	81.9～99.2
Triasulfuron	5	98.5～109	78.6～93.3	86.6～95.2	76.2～93.6	72.1～91.6
	10	82.8～95.4	75.8～93.2	82.2～101	77.3～93.8	77.6～90.3
	20	94.1～107	84.7～99.2	87.2～101	80.5～94.3	81.8～95.9
Metsulfuron-methyl	5	62.5～94.5	75.1～96.4	82.8～95.8	74.2～85.6	67.1～82.3
	10	68.0～83.0	73.3～87.4	66.8～87.4	79.4～90.4	69.9～83.5
	20	64.2～83.5	81.4～95.8	71.7～87.4	78.4～91.9	73.4～85.8
Chlorsulfuron	5	68.3～85.0	69.7～83.9	84.8～97.2	76.4～92.4	72.4～86.5
	10	68.7～79.9	73.4～87.8	64.7～80.7	80.3～97.8	73.1～84.4
	20	67.9～91.9	80.7～96.6	68.0～84.2	84.5～92.2	76.8～91.3
Penoxsulam	5	86.3～112	75.8～94.0	75.8～94.0	76.0～89.2	75.8～94.0
	10	78.2～94.3	81.4～101	77.6～96.4	79.8～94.1	81.4～96.0
	20	83.8～107	81.7～106	82.3～99.3	84.0～99.0	85.9～101
Diclosulam	5	93.3～110	74.9～93.8	88.0～102	86.4～98.4	68.0～88.2
	10	85.5～99.9	71.1～86.5	84.9～105	90.8～99.6	74.8～88.5
	20	89.7～106	80.0～98.5	90.1～105	93.2～100	78.6～93.1
Iodosulfuron-methyl	5	87.1～108	72.6～98.5	84.2～97.8	71.8～87.8	68.6～86.6
	10	88.6～101	70.1～88.5	88.0～106	78.2～92.9	76.9～91.0
	20	90.7～107	81.8～97.8	93.3～102	75.9～95.3	75.5～91.4
Clethodim-sulfone	5	75.6～111	67.8～87.4	67.8～87.4	67.8～86.8	67.8～87.4
	10	65.1～89.9	71.8～92.6	64.7～83.5	71.2～91.8	74.0～95.4
	20	76.5～103	73.1～91.9	68.6～83.5	74.9～88.9	78.4～92.2

Table 3（continued）

Compound	Levels/（μg/kg）	Rice/%	Wheat/%	Barley/%	Brown rice/%	Maize/%
Mesosulfuron-methyl	5	94.3～101	74.7～98.2	84.2～96.6	76.6～98.0	63.4～81.8
	10	68.9～98.1	69.7～86.9	81.8～98.1	80.4～97.9	72.0～84.4
	20	90.8～101	79.6～103	72.6～98.1	84.6～103	75.1～86.0
Prosulfuron	5	81.3～109	63.9～78.2	78.0～108	82.8～92.4	60.1～79.1
	10	74.9～99.0	75.9～95.0	73.8～96.3	85.4～97.0	74.6～89.2
	20	78.2～107	79.2～94.5	81.0～96.1	87.5～99.9	72.5～89.3
Warfarin	1	88.5～114	71.8～93.8	90.4～98.6	86.2～95.0	67.8～90.7
	2	80.0～92.4	70.9～83.2	79.5～91.4	90.7～101	68.6～91.1
	4	85.2～115	81.6～91.5	84.3～97.3	91.1～101	81.9～94.3
Mecoprop	5	61.6～74.0	63.5～74.5	65.4～80.2	60.8～74.0	60.4～74.1
	10	62.9～71.5	60.5～71.3	61.6～75.3	60.3～73.9	68.5～83.7
	20	60.3～72.1	67.7～86.4	65.4～75.4	62.3～78.9	70.5～83.1
Primisulfuron-methyl	5	80.7～101	60.2～72.4	60.2～80.0	61.8～72.0	61.0～76.0
	10	66.4～84.1	61.4～68.6	65.0～77.2	60.7～77.7	60.1～73.7
	20	77.6～99.8	60.9～75.5	70.4～88.6	61.5～75.7	62.0～80.2
Fomesafen	5	76.8～104	60.0～75.5	60.0～73.6	64.4～87.0	62.0～79.6
	10	63.8～72.2	60.0～69.1	65.6～73.0	68.2～91.1	61.1～70.1
	20	73.9～91.8	60.7～78.3	67.2～76.1	78.6～95.9	60.4～76.6
Triflusulfuron-methyl	5	83.0～98.3	60.9～82.6	75.0～98.0	83.0～97.8	64.0～86.8
	10	74.0～101	63.9～86.1	74.1～100	87.9～100	68.2～86.1
	20	82.9～97.7	72.1～94.8	78.7～99.2	91.9～99.1	71.6～89.0
Halosulfuron-methyl	5	81.0～108	73.8～90.2	80.4～106	70.8～92.6	77.6～94.8
	10	66.6～88.2	70.1～87.5	65.4～80.6	74.4～98.0	67.0～84.3
	20	76.6～105	80.1～96.2	70.8～87.2	78.3～97.9	75.2～100
Dinoseb	5	94.4～114	74.1～93.4	80.6～98.6	80.8～96.8	61.5～88.7
	10	79.2～92.0	73.7～90.2	78.7～95.6	85.2～96.9	70.9～89.9
	20	89.3～102	81.1～98.0	83.5～97.0	85.9～102	77.1～93.6
Dinoterb	5	94.5～114	70.7～90.1	84.8～99.0	77.0～93.8	73.6～89.1
	10	71.2～87.2	71.3～89.5	75.0～89.3	81.6～98.0	75.0～86.3
	20	91.2～102	78.4～96.9	75.0～91.9	84.5～99.4	78.8～93.8

Annex A
（Informative）
Mass conditions[1)]

Reference mass conditions

a） Sheath gas:30 unit;

b） Auxilliar gas:8 unit;

c） Ion spay voltage in ESI+mode:4 000 V;

d） Ion spay voltage in ESI−mode:−3 200 V;

e） Capillary tempreture:320 ℃;

f） Source CID:10 V;

g） Width of Q1 and Q3:0.4 and 0.7;

h） Collision gas:Argon;

i） Collision gas pressure:1.5 m Torr. Other mass operating conditions are list in table A.1 and table A.2.

Table A.1—The mass operating conditions and compound message for the 27 pesticides under ESI+mode

Compound	CAS#	Retention time/min	Ion pairs(m/z)	Collision energy/eV
Flumetsulam	98967-40-9	6.52	325.9/129.0[a]	33
			325.9/109.0	47
Cinosulfuron	94593-91-6	9.52	414.2/183.0[a]	19
			414.2/157.0	25
Imazamethabenz-methyl	81405-85-8	9.54	289.1/143.9[a]	34
			289.1/220.0	20

1） Non-commercial statement:the reference mass parameters in Annex A are accomplished by Thermo TSQ Quantum Ultra AM LC-MS/MS,the 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 equipment of different corporation or different type.

Table A.1（continued）

Compound	CAS#	Retention time/ min	Ion pairs(m/z)	Collision energy/ eV
Thifensulfuron-methy	79277-27-3	10.02	388.2/167.0[a]	17
			388.2/205.0	25
Nicosulfuron	111991-09-4	10.17	411.1/182.0[a]	21
			411.1/213.0	17
Imazaquin	81335-37-7	10.37	312.1/267.0[a]	20
			312.1/180.9	37
Naptalam	132-66-1	10.52	292.2/144.1[a]	11
			292.2/149.0	24
Metonsulam	139528-85-1	10.62	418.0/175.0[a]	35
			418.0/140.0	46
Cloransulam-methyl	147150-35-4	10.85	430.1/397.9[a]	14
			430.1/370.0	22
Propoxycarbazone-sodium	181274-15-7	10.95	416.1/399.1[a]	8
			416.1/199.0	24
Sulfentrazone	122836-35-5	11.08	404.0/387.0[a]	12
			404.0/307.0	28
Foramsulfuron	173159-57-4	11.09	452.9/182.0[a]	27
			452.9/255.0	23
Ethametsulfuron-methyl	97780-06-8	11.22	411.2/196.1[a]	17
			411.2/168.0	35
Rimusulfuron	122931-48-0	11.09	432.0/182.0[a]	20
			432.0/325.0	15
Tribenuron-methyl	101200-48-0	11.83	396.2/155.1[a]	12
			396.2/181.0	16
Trifloxysulfuron-sodium	199119-58-9	12.33	438.0/182.0[a]	22
			438.0/139.0	40
Azimsulfuron	120162-55-2	12.46	425.1/182.0[a]	16
			425.1/156.0	37
Bensulfuron-methyl	83055-99-6	13.64	411.1/149.0[a]	21
			411.1/182.0	19
Flazasulfuron	104040-78-0	13.89	408.2/182.0[a]	18
			408.2/139.1	38
Sulfosulfuron	141776-32-1	14.45	471.1/211.1[a]	15
			471.1/218.0	25

Table A.1（continued）

Compound	CAS#	Retention time/min	Ion pairs(m/z)	Collision energy/eV
Chlorimuron-ethyl	90982-32-4	15.74	415.1/186.0[a]	17
			415.1/184.7	29
Imazosulfuron	122548-33-8	15.80	413.1/153.0[a]	13
			413.1/156.0	22
Benzobicyclon	156963-66-5	16.88	446.9/257.0[a]	24
			446.9/229.0	34
Ethoxysulfron	126801-58-9	16.00	399.1/261.0[a]	17
			399.1/218.0	26
Cyclsulfamuron	136849-15-5	16.26	422.1/260.9[a]	18
			422.1/218.0	26
Pyrazosulfuron-ethyl	93697-74-6	16.35	415.2/182.1[a]	18
			415.2/139.1	42
Propaquizafop	111479-05-1	17.97	444.1/100.0[a]	19
			444.1/371.0	18
[a] Quantitative Ion pair. For the different MS equipment, the parameters may be different, and the MS parameters should be optimiazed to the best before analysis.				

Table A.2—The mass operating conditions and compound message for the 18 pesticides under ESI-mode

Compound	CAS#	Retention time/min	Ion pairs(m/z)	Collision energy/ev
Florasulam	145701-23-1	8.48	358.0/167.1[a]	−16
			358.0/152.0	−31
Triasulfuron	82097-50-5	9.82	400.1/139.2[a]	−23
			400.1/198.2[a]	−12
Metsulfuron-methyl	74223-64-6	10.27	380.2/139.1	−16
			380.2/107.2[a]	−44
Chlorsulfuron	64902-72-3	11.02	356.0/139.0[a]	−20
			356.0/190.1	−13
Penoxsulam	219714-96-2	11.05	482.0/307.1[a]	−28
			482.0/179.0	−17
Diclosulam	145701-21-9	11.22	404.0/181.1[a]	−17
			404.0/153.1	−30
Iodosulfuron-methyl	185119-76-0	12.2	502.2/267.1[a]	−24
			502.2/347.1[a]	−18

Table A.2（continued）

Compound	CAS#	Retention time/ min	Ion pairs(m/z)	Collision energy/ ev
Clethodim-sulfone		13.34	390.1/298.2[a]	−18
			390.1/270.1	−23
Mesosulfuron-methyl	208465-21-8	12.08	506.1/139.2[a]	−24
			506.1/308.0	−15
Prosulfuron	94125-34-5	15.32	417.9/139.2[a]	−22
			417.9/252.0	−17
Warfarin	81-81-2	15.50	307.0/161.1[a]	−21
			307.0/250.1	−23
Mecoprop	93-65-2	15.59	212.9/141.1[a]	−21
			212.9/83.2	−37
Primisulfuron-methyl	86209-51-0	15.97	467.0/226.0[a]	−18
			467.0/176.1	−32
Fomesafen	72178-02-0	16.15	436.9/195.0[a]	−43
			436.9/286.0	−27
Triflusulfuron-methyl	126535-15-7	16.27	491.2/236.1[a]	−17
			491.2/196.1	−39
Halosulfuron-methyl	100784-20-1	16.53	432.9/252.1[a]	−18
			432.9/154.2	−32
Dinoseb	88-85-7	17.16	239.1/194.1[a]	−22
			239.1/193.1	−26
Dinoterb	1420-07-1	17.27	239.1/207.1[a]	−27
			239.1/177.2	−34

[a] Quantitative Ion pair. For the different MS equipment，the parameters may be different，and the MS parameters should be optimiazed to the best before analysis.

Annex B
（Informative）
MRM chromatogram of standard

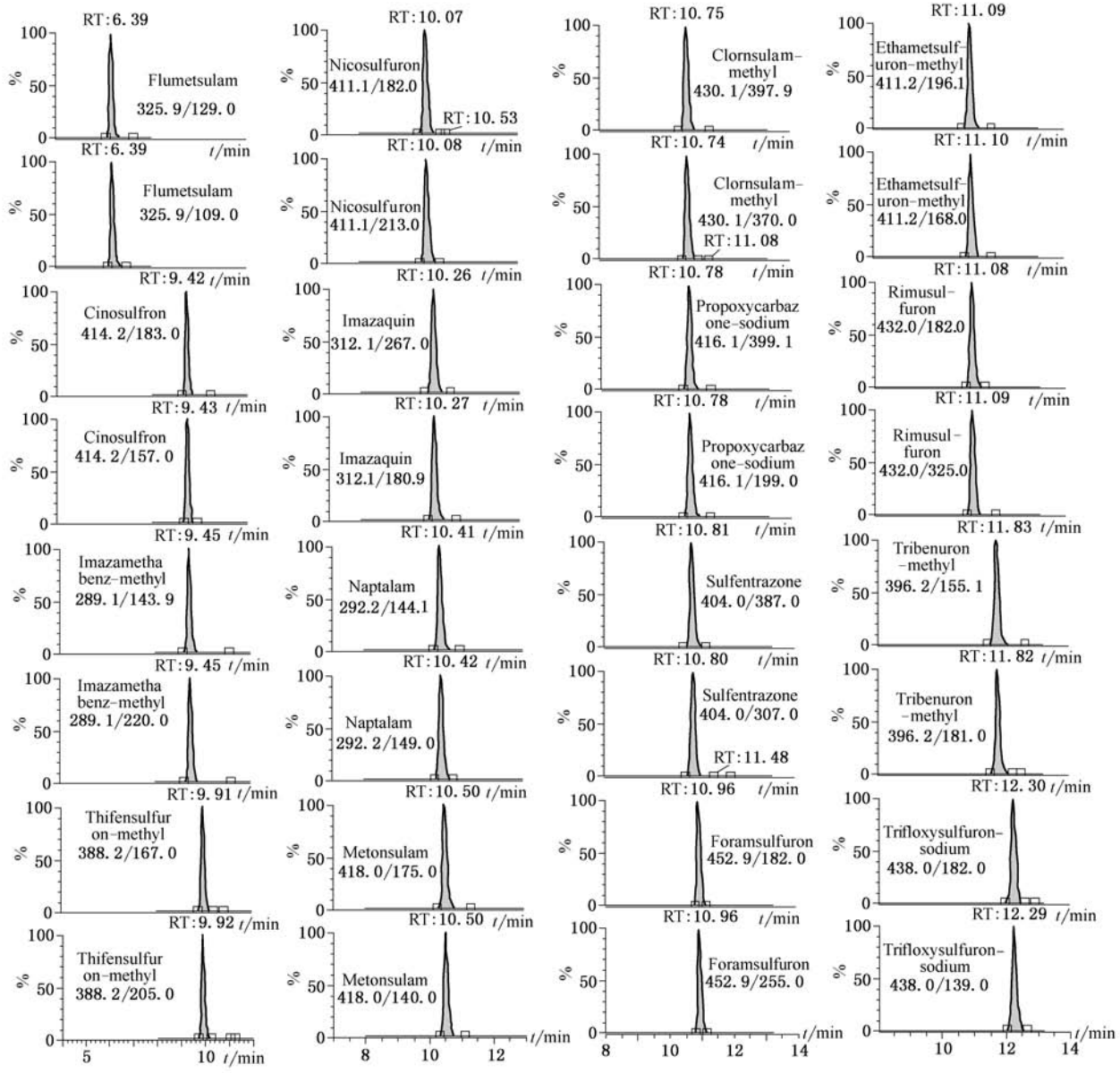

Figure B.1—**The MRM chromatogram of standard working solution for 27 pesticides under ESI + mode**

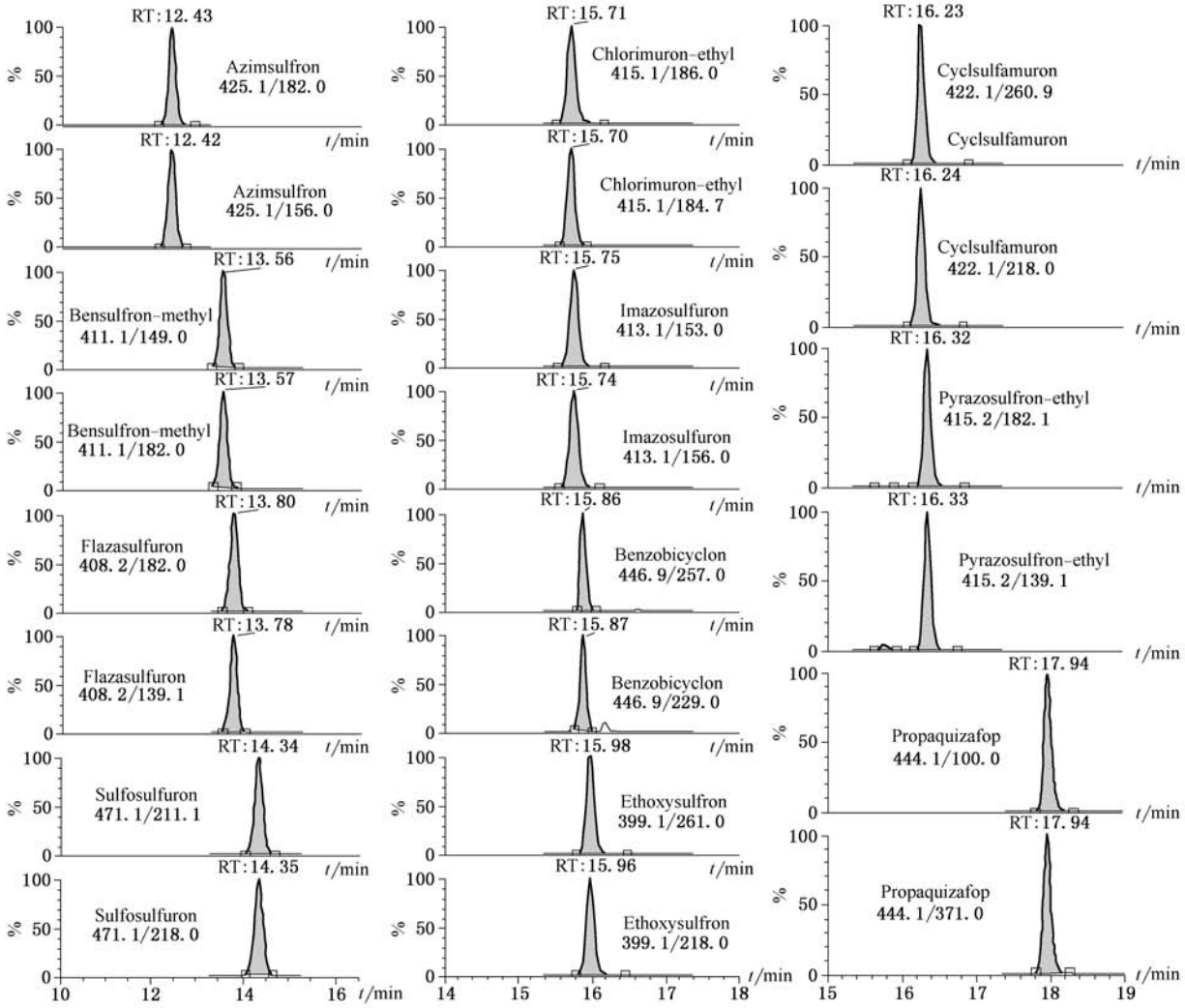

Figure B.1（continued）

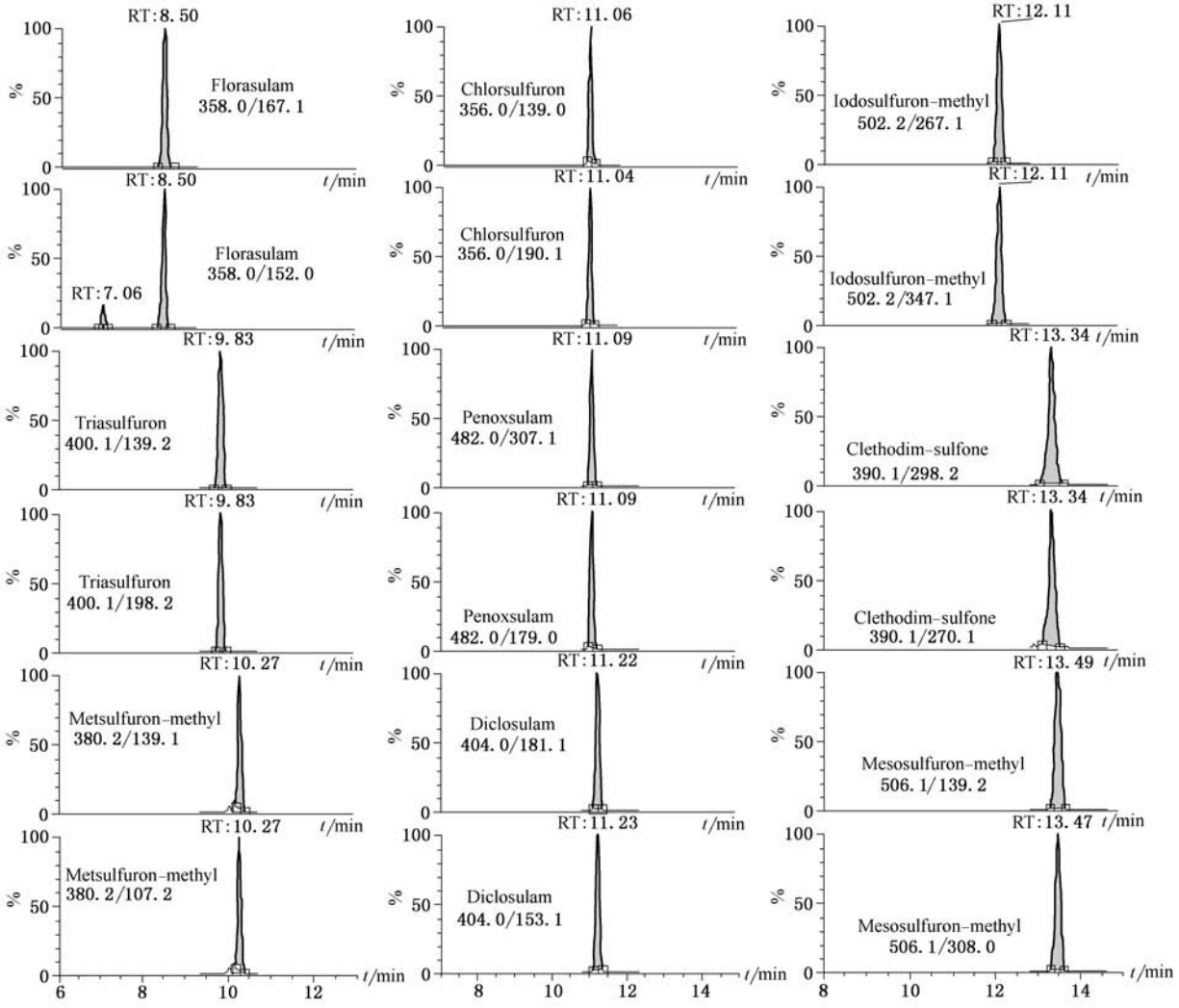

Figure B.2—The MRM chromatogram of standard working solution for 18 pesticides under ESI-mode

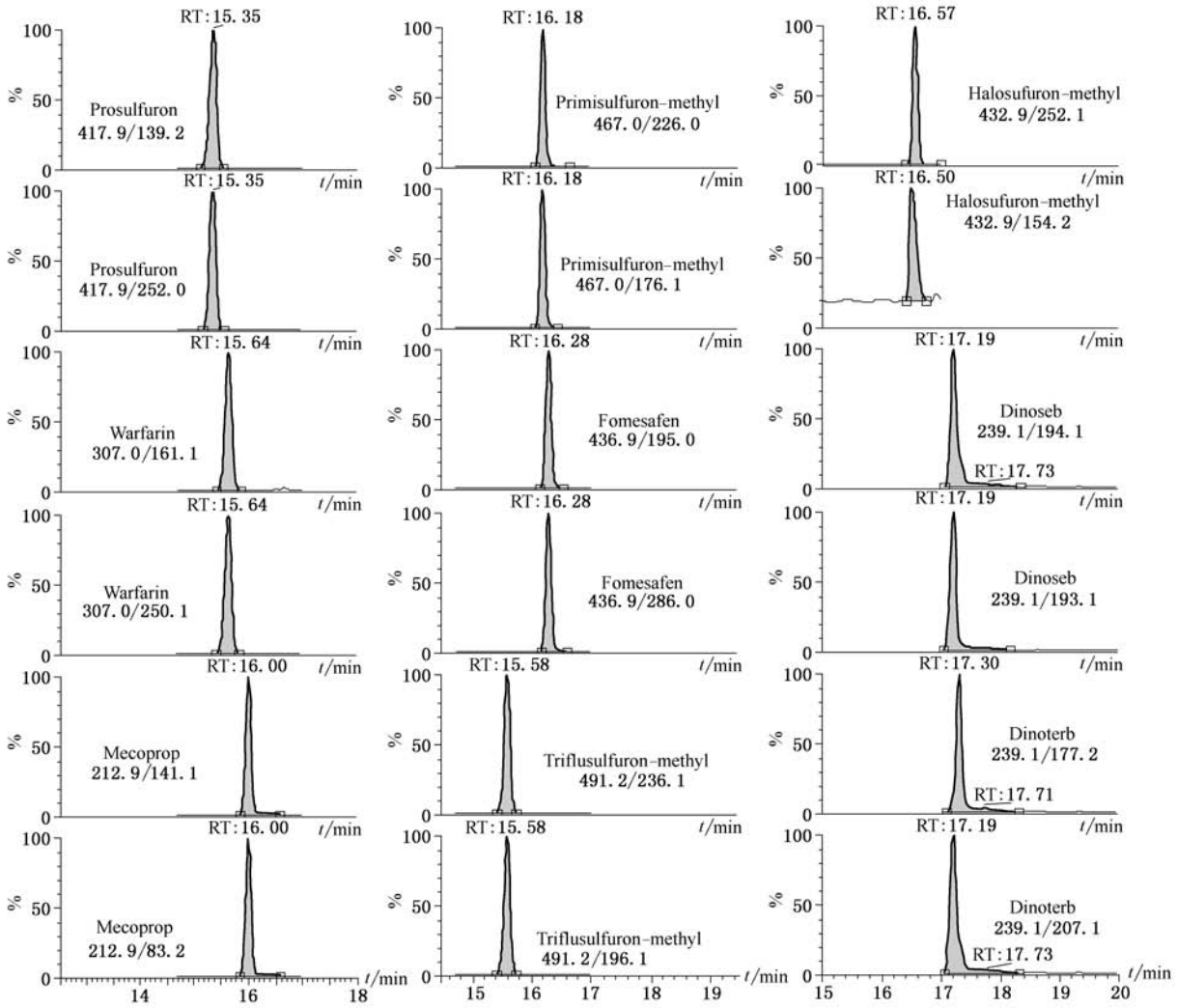

Figure B.2（continued）

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