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中华人民共和国出入境检验检疫行业标准

SN/T 1737.5—2010

除草剂残留量检验方法 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

Determination of herbicide residues—Part 5: Determination of thiocarbmate herbicide residues in foodstuffs for import and export—by LC-MS/MS

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前　言

SN/T 1737《除草剂残留量检验方法》共分为5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5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：深圳市检验检疫科学研究院、中华人民共和国深圳出入境检验检疫局。

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除草剂残留量检验方法 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

1 范围

SN/T 1737的本部分规定了进出口食品中禾草敌、克草敌、灭草敌、野麦畏、燕麦敌、禾草丹、环草敌、茵草敌和丁草敌的液相色谱-质谱/质谱测定方法。

本部分适用于大米、大豆、白萝卜、小白菜、椰菜、生姜、茶叶、花生、橙子、葡萄、鸡肉、鸡肝和鱼肉中禾草敌、克草敌、灭草敌、野麦畏、燕麦敌、禾草丹、环草敌、茵草敌和丁草敌残留量的检测与确证。

2 方法提要

采用乙腈提取试样中残留的硫代氨基甲酸酯除草剂，提取液经HLB和Envi-Carb固相萃取柱净化，液相色谱-质谱/质谱检测和确证，内标法定量。

3 试剂和材料

除另有说明外，所用试剂均为分析纯，水为去离子水。

3.1 乙腈：高效液相色谱纯。

3.2 正己烷。

3.3 丙酮。

3.4 乙酸：高效液相色谱纯。

3.5 氯化钠。

3.6 正己烷-丙酮溶液(7+3，体积比)。

3.7 乙腈-水溶液(1+1，体积比)。

3.8 标准物质：参见附录A表A.1，纯度均大于99%。

3.9 内标标准物质：D_3-甲萘威，100 μg/mL。

3.10 标准储备溶液：100 μg/mL。准确称取适量的各种硫代氨基甲酸酯标准物质(3.8)，用乙腈(3.1)配制成浓度为100 mg/L的标准储备溶液，避光－18 ℃保存。

3.11 混合标准中间溶液：1.0 μg/mL。吸取每种适量标准储备溶液(3.10)，用乙腈稀释成1.0 mg/L的混合标准工作溶液，避光－18 ℃保存。

3.12 内标中间溶液：1.0 μg/mL。准确吸取适量的内标标准物质(3.9)，用乙腈配制成浓度为1.0 mg/L内标工作溶液，避光－18 ℃保存。

3.13 基质混合标准工作溶液：吸取适量的混合标准中间溶液(3.11)和内标中间溶液(3.12)，用空白样品提取液配成浓度为0 μg/L、1.0 μg/L、5.0 μg/L、10.0 μg/L、20.0 μg/L、40.0 μg/L、100 μg/L的基质混合标准工作溶液，内标浓度均为20.0 μg/L。当天配制。

3.14 HLB固相萃取柱或相当者：200 mg，6 mL。用前用5 mL乙腈处理，保持柱体湿润。

3.15 Envi-Carb固相萃取柱或相当者：200 mg，3 mL。用前用5 mL正己烷-丙酮溶液(3.6)处理，保持柱体湿润。

3.16 微孔滤膜：0.22 μm，有机相型。

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 固相萃取装置。
4.3 吹氮浓缩仪。
4.4 均质器。
4.5 旋涡混匀器。
4.6 分析天平：感量 0.1 mg 和 0.01 g。
4.7 移液器：10 μL～100 μL 和 100 μL～1 000 μL。
4.8 聚丙烯离心管：50 mL 或 15 mL，具塞。
4.9 容量瓶：25 mL。
4.10 离心机：转速不低于 5 000 r/min。

5 试样制备与保存

5.1 试样制备

5.1.1 大米、大豆、花生和茶叶

取代表性样品约 500 g，用粉碎机充分粉碎，混匀。试样均分为两份，装入洁净容器，密封，并标明标记。常温下保存。

5.1.2 白萝卜、小白菜、椰菜、生姜、橙子、葡萄、鸡肉、鸡肝和鱼肉

取代表性样品约 500 g，将其可食用部分(不可用水洗)切碎后，用捣碎机将样品加工成浆状，混匀。试样均分为两份，装入洁净容器，密封，并标明标记。于－18 ℃以下冷冻存放。

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。

6 分析步骤

6.1 提取

6.1.1 大米、大豆、茶叶和花生

称取 5 g(精确至 0.01 g)样品于 50 mL 具塞离心管中，茶叶称取 2.5 g，加入 100 μL 内标中间溶液，加入 10 mL 水，混匀后放置 1 h，然后加入 4.0 g 氯化钠(3.3)，再加入 15 mL 乙腈高速均质提取 3 min，振荡提取 15 min，于 5 000 r/min 离心 5 min，将乙腈层转移至 25 mL 容量瓶(4.9)中。残渣再用 10 mL 乙腈重复提取一次，合并提取液，并用乙腈定容至 25 mL。

6.1.2 白萝卜、小白菜、椰菜、生姜、橙子、葡萄、鸡肉、鸡肝和鱼肉

称取 5 g(精确至 0.01 g)样品于 50 mL 具塞离心管中，加入 100 μL 内标中间溶液和 4.0 g 氯化钠，以下操作与 6.1.1 相同。

6.2 净化

6.2.1 大米、白萝卜、小白菜、椰菜、生姜、橙子、葡萄、鸡肉和鱼肉

取 5.0 mL 提取液于 15 mL 离心管中，40 ℃下用 N_2 吹至近干。残渣用 2.0 mL 正己烷-丙酮溶液溶解，将溶解液加入处理过的 Envi-Carb 固相萃取柱(3.15)中，以约 1.5 mL/min 的流速使样液全部通过固相萃取柱，再用 5 mL 正己烷-丙酮溶液润洗样品管，并将润洗液一并加入 Envi-Carb 固相萃取柱，收集全部流出液于 15 mL 离心管中，40 ℃吹氮至近干。残渣用乙腈-水溶液(3.7)定容至 1.0 mL，旋涡混匀后，过微孔滤膜(3.16)，供液相色谱-质谱/质谱仪测定。

6.2.2 大豆、茶叶、花生和鸡肝

取 5.0 mL 提取液于 15 mL 离心管中，茶叶提取液取 10.0 mL，40 ℃下用 N_2 吹至 2.0 mL 左右。

将浓缩液转入处理过的 HLB 固相萃取柱(3.14)中，以约 1.5 mL/min 的流速使样液全部通过固相萃取柱，再用 3 mL 乙腈淋洗并抽干固相萃取柱，收集全部流出液于 15 mL 离心管中，40 ℃下用 N_2 吹至近干。残渣用 2.0 mL 正己烷-丙酮溶液溶解，将溶解液加入处理过的 Envi-Carb 固相萃取柱中，以约 1.5 mL/min 的流速使样液全部通过固相萃取柱，再用 5 mL 正己烷-丙酮溶液润洗样品管，并将润洗液一并加入 Envi-Carb 固相萃取柱，收集全部流出液于 15 mL 离心管中，40 ℃吹氮至近干。残渣用乙腈-水溶液定容至 1.0 mL，旋涡混匀后，过微孔滤膜，供液相色谱-质谱/质谱仪测定。

6.3 测定

6.3.1 液相色谱条件

a) 色谱柱：Acquity BEH C_{18}色谱柱，50 mm×2.1 mm(内径)，1.7 μm，或相当者；

b) 柱温：40 ℃；

c) 进样量：10 μL；

d) 流动相、流速及梯度洗脱条件见表 1。

表 1 流动相、流速及梯度洗脱条件

时间/min	流速/(mL/min)	0.1%乙酸水溶液/%	甲醇/%
0	0.25	70	30
15.0	0.25	0	100
15.1	0.25	70	30
18.0	0.25	70	30

6.3.2 质谱条件

a) 离子化模式：电喷雾离子源；

b) 扫描方式：正离子扫描；

c) 检测方式：多反应监测(MRM)；

d) 分辨率：单位分辨率；

e) 其他参考质谱条件参见附录 B。

6.3.3 液相色谱-串联质谱测定

6.3.3.1 定性测定

每种被测组分选择 1 个母离子，2 个以上子离子，在上述实验条件下，样品中待测物质的保留时间，与基质标准溶液的保留时间偏差在±2.5%之内；且样品中各组分定性离子的相对丰度与浓度接近的基质混合标准工作溶液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偏差

相对离子丰度/%	>50	>20～50	>10～20	≤10
允许的最大偏差/%	±20	±25	±30	±50

6.3.3.2 定量测定

在仪器最佳工作条件下，对基质混合标准工作溶液进样，以待测物和内标物峰面积的比值为纵坐标，基质混合标准工作溶液浓度为横坐标绘制标准工作曲线，用标准工作曲线对样品进行定量，样品溶液中待测物的响应值均应在仪器测定的线性范围内；如果超出线性范围，应用空白基质溶液进行适当稀释后进样测定。9 种硫代氨基甲酸酯类除草剂标准物质的多反应监测(MRM)色谱图参见附录 C 中的图 C.1。

6.4 空白试验

除不加标样外，按上述测定步骤进行。

7 结果计算和表述

按式(1)计算试样中硫代氨基甲酸酯类除草剂的残留量。计算结果需扣除空白值。

$$X = \frac{c \times c_i \times A \times A_{si} \times V \times 1\,000}{c_{si} \times A_i \times A_s \times m \times 1\,000} \quad \cdots\cdots(1)$$

式中：

X——样品中待测组分残留量，单位为微克每千克(μg/kg)；

c——标准工作溶液中药物的浓度，单位为微克每升(μg/L)；

c_i——样液中内标物的浓度，单位为微克每升(μg/L)；

A——样液中药物的峰面积；

A_{si}——标准工作溶液中内标物的峰面积；

V——样品溶液最终定容体积，单位为毫升(mL)；

c_{si}——标准工作溶液中内标物的浓度，单位为微克每升(μg/L)；

A_i——样液中内标物的峰面积；

A_s——标准工作溶液中药物的峰面积；

m——最终样液代表的试样质量，单位为克(g)。

8 方法的测定低限和回收率

8.1 测定低限

本方法对9种硫代氨基甲酸酯类除草剂的测定低限均为5.0 μg/kg。

8.2 回收率

在5.0 μg/kg～200 μg/kg添加浓度范围内，大米、大豆、白萝卜、小白菜、椰菜、生姜、茶叶、花生、橙子、葡萄、鸡肉、鸡肝和鱼肉中9种硫代氨基甲酸酯类除草剂的回收率数据见表3。

表 3　不同食品中 9 种硫代氨基甲酸酯除草剂添加回收率数据

化合物名称	添加水平/(μg/kg)	回收率/%												
		大米	大豆	白萝卜	小白菜	椰菜	生姜	橙子	葡萄	花生	茶叶	鸡肉	鸡肝	鱼肉
禾草敌	5.0	83.3～99.1	73.6～95.6	61.5～79.7	76.1～92.7	66.0～84.0	66.1～80.1	73.4～86.6	80.4～95.4	75.1～97.5	75.9～93.2	80.9～91.1	69.8～88.5	77.1～90.4
	10.0	88.3～104	72.2～87.2	64.4～78.4	67.1～79.2	66.3～84.3	65.4～79.8	68.9～83.5	77.5～93.2	73.6～88.9	70.8～85.0	73.6～90.2	74.2～91.8	70.2～86.0
	20.0	81.7～91.5	70.3～85.5	65.8～83.6	77.6～97.5	79.5～93.5	68.5～82.6	74.2～82.8	80.0～85.8	71.7～87.2	68.5～83.4	70.4～85.3	74.7～92.4	67.1～81.3
	大米:100 大豆、白萝卜、小白菜、椰菜、生姜、橙子、葡萄、茶叶、花生、鸡肉、鸡肝、鱼:50.0	84.3～95.1	75.4～89.6	71.6～90.2	81.2～89.8	82.4～96.4	69.6～81.8	67.2～83.8	80.6～88.6	76.9～91.4	73.5～87.4	71.2～87.8	76.4～87.0	67.9～83.7
茵草敌	5.0	87.2～104	70.9～85.8	63.0～79.3	74.2～88.2	63.2～79.8	68.1～78.0	74.2～89.9	66.3～90.3	73.7～89.2	69.1～83.7	90.6～99.5	67.6～85.2	86.4～94.9
	10.0	82.3～94.4	69.1～86.1	67.8～81.9	77.4～94.6	65.5～77.8	68.3～86.3	78.5～96.6	76.7～89.3	71.9～89.5	67.4～83.9	71.5～92.7	62.2～77.9	68.2～88.4
	20.0	71.2～79.1	68.6～78.4	65.2～80.5	87.4～101	67.6～78.6	79.2～93.8	77.9～97.8	68.6～80.2	71.3～81.5	67.8～76.4	76.1～87.3	74.4～93.3	72.6～83.2
	大米、大豆、白萝卜、小白菜、椰菜、生姜、橙子、葡萄、茶叶、花生:100 鸡肉、鸡肝、鱼:50.0	68.5～76.9	68.5～76.9	68.5～85.1	88.2～99.8	68.5～80.5	78.5～90.8	80.9～92.1	69.1～82.1	71.2～80.0	66.8～75.0	77.8～88.2	71.6～86.2	74.2～84.1
克草敌	5.0	94.9～112	79.9～88.2	70.0～83.2	66.1～82.5	71.5～80.4	70.8～88.6	67.6～92.1	71.6～99.9	83.1～92.1	77.9～86.4	80.2～97.0	71.0～81.2	76.5～92.5
	10.0	87.3～107	72.8～86.6	64.1～82.0	67.3～80.1	63.2～79.7	70.4～79.6	68.9～89.5	70.4～92.2	75.7～90.1	71.0～84.4	71.2～88.4	68.2～86.4	67.9～84.3
	20.0	87.0～92.6	74.5～84.2	74.9～85.8	84.4～99.1	71.0～82.0	70.0～75.7	76.8～91.9	70.9～81.6	77.5～87.6	72.6～82.1	71.4～87.7	75.3～85.8	68.1～83.6
	100	73.9～82.6	73.9～82.6	76.2～88.4	88.3～98.2	72.5～81.9	74.6～82.1	83.1～95.4	74.2～84.3	76.9～85.9	72.1～80.5	73.4～86.1	77.3～86.1	70.0～82.1
灭草敌	5.0	96.8～112	74.6～93.3	72.2～89.9	71.8～94.0	72.2～81.9	68.1～83.1	67.4～92.8	80.5～98.7	77.2～96.6	72.7～91.0	78.4～89.6	71.7～89.8	74.7～85.4
	10.0	86.7～105	73.3～83.6	67.2～79.0	68.5～79.2	71.2～78.5	65.9～79.7	80.6～95.3	67.8～91.1	75.9～89.1	71.5～83.9	70.6～86.9	70.3～90.5	67.3～79.3
	20.0	82.0～90.6	70.0～81.5	72.4～85.1	79.4～92.5	69.0～82.9	70.3～78.9	75.4～90.1	69.4～90.6	72.5～84.4	68.3～79.5	70.9～84.4	75.9～92.4	67.6～80.5
	100	70.5～82.1	70.5～82.1	75.4～88.3	80.2～95.4	70.8～83.2	70.9～83.1	76.8～92.3	74.2～90.5	73.0～84.1	68.7～80.0	72.5～86.1	76.9～91.5	69.1～82.1
环草敌	5.0	106～119	67.0～87.6	70.4～88.2	68.1～89.1	68.3～85.6	72.0～80.2	62.2～81.7	81.1～103	75.7～91.2	65.3～85.4	77.0～92.8	78.7～94.5	73.4～88.5
	10.0	102～119	75.7～94.6	74.7～89.4	65.8～80.4	67.1～86.6	72.8～87.2	79.5～104	83.6～99.9	78.8～98.5	73.8～92.2	71.8～90.2	82.9～98.8	68.5～86.0

表 3（续）

化合物名称	添加水平/(μg/kg)	回收率/%												
		大米	大豆	白萝卜	小白菜	椰菜	生姜	橙子	葡萄	花生	茶叶	鸡肉	鸡肝	鱼肉
环草敌	20.0	96.1～103	80.8～91.6	83.2～99.0	80.6～94.3	68.8～74.4	70.6～78.7	70.9～88.4	78.9～91.8	84.1～95.4	78.8～89.3	75.5～91.1	78.2～93.9	72.0～86.9
	50.0	82.4～96.6	82.4～96.6	86.6～98.2	79.8～94.6	69.8～82.4	72.2～85.8	73.0～89.2	76.4～90.6	85.8～101	80.3～94.2	78.2～93.8	84.0～97.2	74.6～87.9
禾草丹	5.0	101～113	78.7～97.0	85.6～99.4	76.8～92.0	74.5～85.1	76.0～81.6	69.6～91.8	83.8～105	81.5～100	76.7～94.6	77.7～94.3	102～113	74.1～89.9
	10.0	103～113	79.7～92.0	95.2～99.0	79.7～87.6	75.7～87.8	79.4～84.0	85.6～100	89.4～96.7	82.6～95.3	77.7～89.7	72.3～92.0	93.3～106	68.9～87.7
	20.0	95.1～102	80.1～93.0	82.2～101	80.1～100	93.5～99.6	82.5～88.6	82.2～98.5	85.8～94.7	83.0～96.3	78.1～90.7	81.9～101	98.3～114	78.1～96.2
	200	81.4～92.0	81.4～92.0	90.5～100	81.0～96.0	90.5～99.5	81.5～91.0	82.0～96.5	89.5～97.0	84.3～95.3	79.4～89.7	82.0～98.0	97.5～109	78.2～93.4
燕麦敌	5.0	102～111	66.5～83.6	73.1～87.7	68.9～82.8	70.5～82.4	64.6～78.8	63.4～81.6	85.4～110	68.4～85.9	64.8～81.5	72.2～90.2	90.3～98.4	68.8～86.0
	10.0	83.6～98.96	73.3～86.9	89.6～80.3	68.8～80.9	65.3～78.7	75.7～86.9	73.7～95.0	85.5～100	75.4～89.3	71.5～84.7	77.9～93.2	83.3～94.5	74.3～88.9
	20.0	87.7～104	77.1～93.2	84.5～101	83.7～97.4	71.2～82.4	75.2～83.6	74.8～91.5	82.2～93.5	79.3～95.8	75.2～90.9	75.4～88.5	80.7～91.6	71.9～84.4
	大米、大豆、白萝卜、小白菜、椰菜、生姜、橙子、葡萄、花生、鸡肉、鱼：50.0 茶叶：100、鸡肝：200	79.2～93.8	79.2～93.8	88.6～100	82.6～95.6	71.6～89.2	77.4～90.0	72.2～91.2	82.4～92.6	81.4～96.4	77.2～91.5	76.8～90.2	81.0～91.5	73.2～86.0
野麦畏	5.0	89.6～109	67.6～86.6	69.9～86.1	84.4～99.67	67.2～80.2	68.2～88.7	72.0～87.8	77.6～102	69.4～88.9	65.9～84.4	70.4～86.0	69.1～86.6	67.1～84.5
	10.0	95.4～116	76.9～89.6	65.0～78.2	73.3～81.66	68.1～76.3	75.9～88.8	71.0～87.3	83.5～96.9	79.0～92.0	75.0～87.4	70.8～82.8	86.4～106	67.5～78.9
	20.0	95.5～109	70.1～88.6	80.1～95.6	77.8～93.7	84.1～89.0	79.3～88.4	77.0～93.6	83.2～90.0	72.0～88.6	73.2～86.4	77.9～99.4	81.0～91.3	74.3～94.8
	大米、大豆、花生：50.0 白萝卜、小白菜、椰菜、生姜、橙子、茶叶、葡萄、鸡肉、鱼：100 鸡肝：200	74.2～88.6	73.6～88.6	82.4～96.1	79.2～93.5	85.1～91.3	80.6～89.1	81.0～92.1	81.7～91.3	76.2～91.0	71.8～86.4	81.9～94.5	81.5～92.0	78.1～90.1
丁草敌	5.0	90.0～109	70.6～84.6	69.7～85.1	70.0～89.7	66.5～80.5	66.3～79.3	67.8～86.4	79.5～101	72.7～81.0	70.1～82.5	72.2～94.1	65.0～75.0	68.8～88.2
	10.0	88.8～103	68.6～81.7	70.9～79.6	68.5～88.0	72.0～84.8	68.7～83.3	78.2～97.1	78.8～89.1	70.7～84.2	66.9～79.7	70.8～87.4	68.4～77.9	67.5～83.3
	20.0	84.1～91.7	70.3～85.8	69.6～85.0	81.8～96.1	68.4～80.5	66.0～80.7	75.9～86.9	72.5～87.2	72.4～88.4	68.5～83.7	75.1～80.6	71.0～86.8	70.6～76.8
	100	73.4～82.4	73.4～82.4	71.2～86.1	82.1～96.4	71.2～84.2	69.3～82.1	76.9～86.1	73.1～85.4	75.6～84.9	71.6～80.3	73.2～85.4	74.5～86.1	69.8～81.4

SN

附 录 A
（资料性附录）
硫代氨基甲酸酯除草剂信息

表 A.1 9种硫代氨基甲酸酯除草剂相关信息

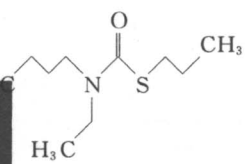
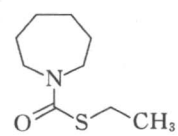
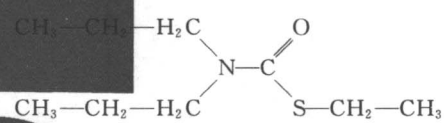
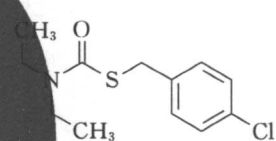
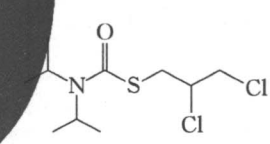
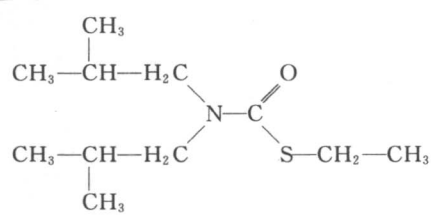
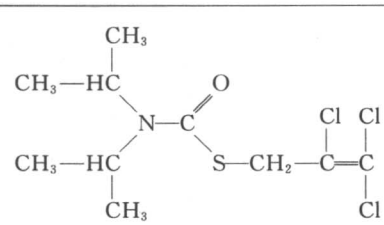
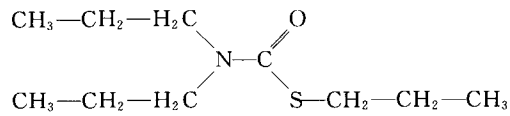
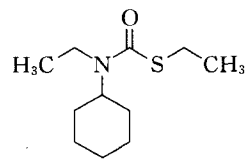
化合物	英文名	CAS编号	分子式	结构式
克草敌	pebulate	1114-71-2	$C_{10}H_{21}NOS$	
禾草敌	molinate	2212-67-1	$C_9H_{17}NOS$	
茵草敌	EPTC	759-94-4	$C_9H_{19}NOS$	
禾草丹	thiobencarb	28249-77-6	$C_{12}H_{16}ClNOS$	
燕麦敌	diallate	2303-16-4	$C_{10}H_{17}Cl_2NOS$	
丁草敌	butylate	2008-41-5	$C_{11}H_{23}NOS$	
野麦畏	triallate	2303-17-5	$C_{10}H_{16}Cl_3NOS$	

表 A.1（续）

化合物	英文名	CAS 编号	分子式	结构式
灭草敌	vernolate	1929-77-7	$C_{10}H_{21}NOS$	
环草敌	cycloate	1134-23-2	$C_{11}H_{21}NOS$	

附 录 B
（资料性附录）
参考质谱条件[1)]

质谱条件

a） 电喷雾电压：3 000 V；

b） 辅助气流速：700 L/h；

c） 碰撞气：氩气；

d） 幕帘气流速：50 L/h；

e） 离子源温度：105 ℃；

f） 辅助气温度：350 ℃；

g） 定性离子对、定量离子对，采集时间、提取电压及碰撞能量见表 B.1。

表 B.1 9种硫代氨基甲酸酯除草剂测定的质谱参数

分析物	参考保留时间/min	母离子	子离子	采集时间/s	提取电压/V	碰撞能量/eV
禾草敌	7.20	188	126[a]	0.10	32	14
			83			18
茵草敌	8.57	190	128[a]	0.05	28	11
			86			13
丁草敌	10.56	218	57[a]	0.05	32	17
			156			11
灭草敌	9.79	204	86[a]	0.05	30	15
			128			13
克草敌	9.84	204	57[a]	0.05	28	19
			72			13
野麦畏	11.62	306	86[a]	0.05	30	14
			145			26
禾草丹	9.77	258	100[a]	0.05	28	12
			125			22
环草敌	9.89	216	154[a]	0.05	24	11
			134			14
燕麦敌	10.30	270	86[a]	0.05	34	16
			109			28
D_3-甲萘威	4.22	205	145[a]	0.05	20	10
[a] 定量离子，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。						

1） 非商业性声明：附录 A 所列参考质谱条件是在 Waters Quattro Premier 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。

附 录 C
（资料性附录）
标准的多反应监测(MRM)色谱图

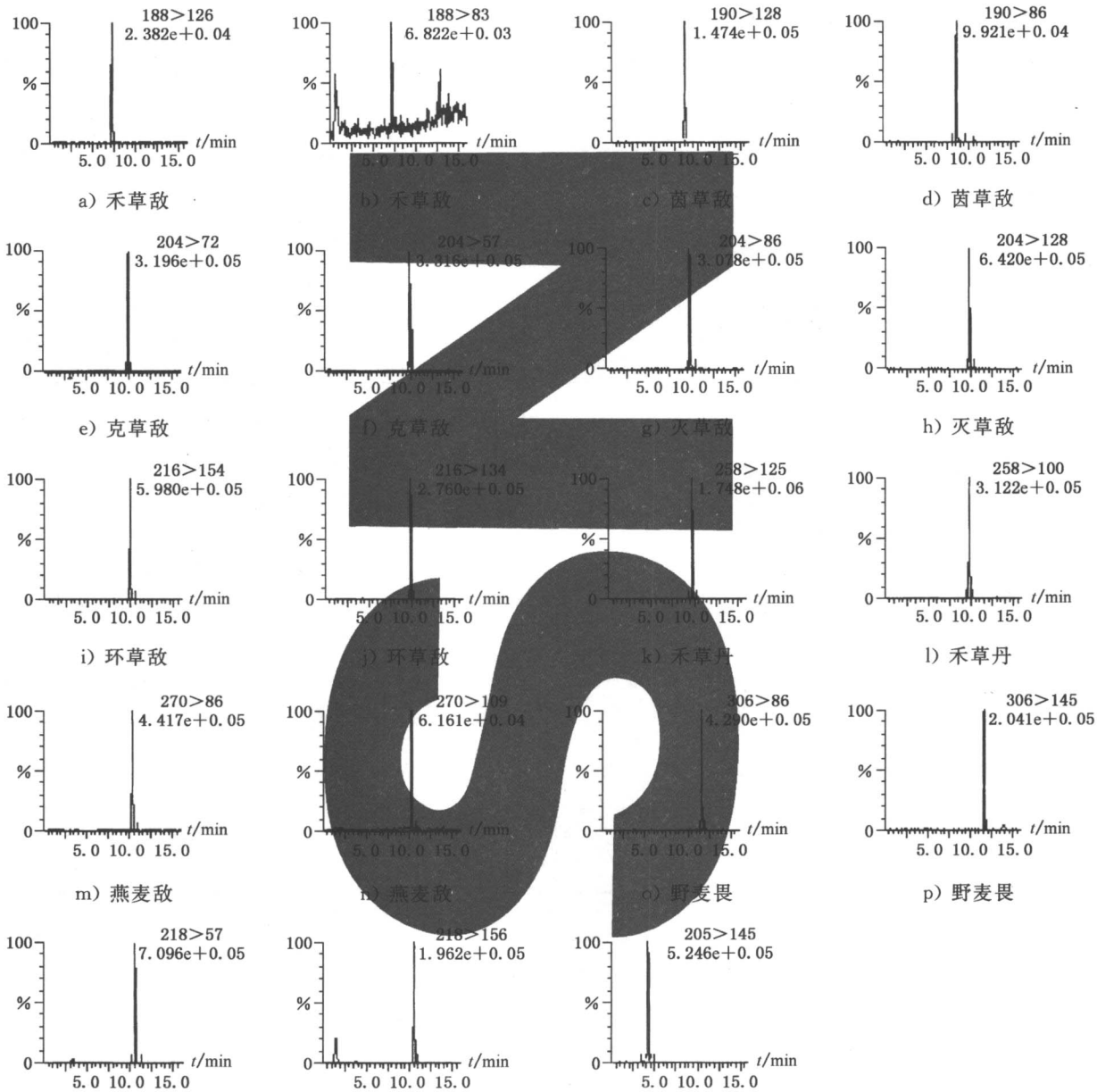


图 C.1 5.0 μg/L 9 种硫代氨基甲酸酯类除草剂标准溶液多反应监测(MRM)色谱图

Foreword

Annex A, B and C of this standard is an informative annex.

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

The standard was drafted by Shenzhen Academy of Inspection and Quarantine of the People's Republic of China and Shenzhen Entry-Exit Inspection and Quarantine Bureau of the People's Republic of China.

The main drafters of this standard are: Shen Jincan, Ge liya, Lu Jingzhang, Xiao Lailong, Xiong Bebe, Chen Bo.

Determination of herbicide residues— Part 5: Determination of thiocarbmate herbicide residues in foodstuffs for import and export—by LC-MS/MS

1 Scope

This standard specifies the methods of determination by liquid chromatography-electrospray mass spectrometry of 9 kinds of thiocarbmate herbicide residues including molinate, pebulate vernolate, triallate, diallate, thiobencarb, cycloate, EPTC and butylate in foodstuffs for import and export.

This standard is applicable to the qualitative and quantitative determination of 9 kinds of thiocarbmate herbicide residues including molinate, pebulate vernolate, triallate, diallate, thiobencarb, cycloate, EPTC and butylate in rice, soybean, radish, baby bok choy, broccoli, ginger, orange, grape, peanut, tea, chicken and chicken liver.

2 Abstract

The residues of thiocarbmate herbicide in the test sample are extracted with acetonitrile. The extraction is cleaned by passing through a HLB and Envi-Carb cartridge. The residues are determined by LC-MS/MS, using internal standard method.

3 Reagents and materials

Unless otherwise specified, all reagents should be of analytical grade; "Water" is deionized water.

3.1 Acetonitrile: HPLC grade.

3.2 Hexane.

3.3 Acetone.

3.4 Acetic acid: HPLC grade.

3.5 Sodium chloride.

3.6 Hexane-Acetone (7+3, *V*/*V*).

3.7 Acetonitrile-Water (1+1, *V*/*V*).

3.8 Standards: See table A.1 in annex A, purity more than 99%.

3.9 Internal standard: D_3-carbary, 100 μg/mL.

3.10 Standard stock solution: Accurately weigh adequate thiocarbmate herbicide standard (3.8), dissolve in acetonitrile (3.2) to make a standard stock solution of 100 μg/mL in concentration. The solution can be preserved in the temperature below −18 ℃.

3.11 Intermediate standards mixed solution: Accurately draw an adequate volume standard stock solution (3.10), dilute with acetonitrile to make an intermediate standard mixed solution of 1.0 μg/mL in concentration. The solution can be preserved in the temperature below −18 ℃.

3.12 Intermediate internal standard solution: Accurately draw an adequate volume internal standard stock solution (3.9), dilute with acetonitrile to make an intermediate standard mixed solution of 1.0 μg/mL in concentration. The solution can be preserved in the temperature below −18 ℃.

3.13 Standard working solution: According to the requirement, accurately draw an adequate volume of intermediate internal standard solution (3.12) and intermediate standard mixed solution (3.11), dilute with blank sample extract solution and prepare a series of standard working solution of 0 μg/L、1.0 μg/L、5.0 μg/L、10.0 μg/L、20.0 μg/L、40.0 μg/L、100.0 μg/L. The concentration of internal standard in each preparation is 20.0 μg/L. The solution should be prepared daily.

3.14 HLB cartridge: 200 mg, 6 mL or equivalent. The column is activated with 5 mL acetonitrile before use. The column should be kept wet always.

3.15 Envi-Carb: 200 mg, 3 mL or equivalent. The column is activated with 5 mL Hexane + Acetone (3.6) before use. The column should be kept wet always.

3.16 Membrane filter: 0.22 μm, for organic phase.

4 Apparatus and equipment

4.1 Liquid chromatography tandem mass spectrometry, equipped with electrospray ion source.

4.2 Solid phase extraction.

4.3 Nitrogen evaporator.

4.4 Homogenizer.

4.5 Vortex mixer.

4.6 Analytical balance, sensitivity: 0.1 mg, 0.01 g.

4.7 Micropipettor, 10 μL～100 μL and 100 μL～1 000 μL.

4.8 Polypropylene centrifuge tube: 50 mL or 15 mL, with screw cap.

4.9 Volumetric flask, 25 mL.

4.10 Centrifuge ≥5 000 r/min.

5 Sample preparation and storage

5.1 Sample preparation

5.1.1 Soybean, rice, peanut and tea

Take approximately 500 g of representative sample, smash thoroughly by a pulverizer, mix thoroughly. The prepared sample would be devided into two part, and put into clean containers, seal and label them. The test sample could be stored under room temperature.

5.1.2 Radish, baby bok choy, broccoli, ginger, orange, grape, chicken, chicken liver and fish

Take approximately 500 g of representative sample, collect the edible parts (do not wash with water) and cut into minces. Crush with a crusher into pulp and mix thoroughly. The prepared sample would be devided into two part, and put into a clean containers. Seal and label them. The test sample should be stored at the temperature below −18 ℃.

5.2 Sample storage

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

6 Procedure

6.1 Extraction

6.1.1 Soybean, rice, tea and peanut

Weigh 5 g of the test sample (accurate to 0.01 g) in a 50 mL centrifuge tube, 2.5 g for tea, added

100 μL intermediate internal standard solution (3.12), and added 10 mL distilled water, mixed, placed for 1 h. Add 4.0 g sodium chloride (3.3) and 15 mL acetonitrile, homogenized for 3 min, extraction by surge for 15 min, then centrifuged at 5 000 r/min for 5 min. Transfer the supernate into a 25 mL volumetric flask (4.9). Repeat the above extract procedure with 10 mL acetonitrile, combined the supernates, dilute the extract to 25 mL with acetonitrile.

6.1.2 Radish, baby bok choy, broccoli, ginger, orange, grape, chicken, chicken liver and fish

Weigh 5 g of the test sample (accurate to 0.01 g) in a 50 mL centrifuge tube, Add 4.0 g sodium chloride (3.3). The following operate is as the same as 6.1.1.

6.2 Cleanup

6.2.1 Radish, baby bok choy, broccoli, ginger, orange, grape, chicken, chicken liver and fish

Accurately draw 5.0 mL extract into a 15 mL centrifuge tube, concentrate the extract to near dryness under nitrogen at 40 ℃ for further cleanup. Dissolve the residues with 2.0 mL hexane-acetone (3.6), Transfer the concentrated extract onto the activated Envi-Carb cartridge (3.15) and keep the flow speed at about 1.5 mL/min, collect the eluate into a 15 mL centrifuge tube. Rinse the centrifuge tube with 5 mL more hexane-acetone (3.6), add the rinse solution onto the cartridge and keep the flow speed at about 1.5 mL/min, combine the eluate and concentrate to dry under nitrogen at 40 ℃. Dissolve the residues with 1.0 mL actonitrile-water (3.7) and filter for further LC-MS/MS analysis.

6.2.2 Rice, soybean, tea and peanut

Accurately draw 5.0 mL extract into a 15 mL centrifuge tube, 10.0 mL for tea extraction, concentrate the extract to about 1.5 mL/min under nitrogen at 40 ℃ for further cleanup. Transfer the concentrated extract onto the activated HLB cartridge and keep the flow speed at about 1.5 mL/min, collect the eluate into a 15 mL centrifuge tube. Rinse the cartridge with 3 mL acetonitrile, combine the eluate and concentrate to dry under nitrogen at 40 ℃. Dissolve the residues with 2.0 mL hexane-acetone. Transfer the concentrated extract onto the activated Envi-Carb cartridge and keep the flow speed at about 1.5 mL/min, collect the eluate into a 15 mL centrifuge tube. Rinse the centrifuge tube with 5 mL more hexane-acetone (3.6), add the rinse solution onto the cartridge and keep the flow speed at about 1.5 mL/min, combine the eluate and concentrate to dry under nitrogen at 40 ℃. Dissolve the residues with 1.0 mL actonitrile-water and filter for further LC-MS/MS analysis.

6.3 Determination

6.3.1 LC operating conditions

a) Column: Acquity BEH C_{18} column, 50 mm × 2.1 mm(i.d.), 1.7 μm, or equivalent;

b) Column temperature: 40 ℃;

c) Injection volume:10 μL;

d) Mobile phase and the elution gradient are listed in table 1.

Table 1—Mobile phase and elution gradient

Time/min	Flow rate/(mL/min)	0.1% acetic acid solution/%	methanol/%
0	0.25	70	30
15.0	0.25	0	100
15.1	0.25	70	30
18.0	0.25	70	30

6.3.2 MS operating conditions

a) Ion source:ESI;

b) Scan mode:positive mode;

c) Detection mode:MRM;

d) Resolution:Unit resolution;

e) Other operating conditions are listed in annex B.

6.3.3 LC-MS/MS determination

6.3.3.1 Qualitative determination

Select one parent ion and two or more than two daughter ions for each analyte. If the deviation of retention time of analyte between test sample and standard solution is within ±2.5% under the same experiment conditions, and the difference of relative ion ratio of analyte between test sample and standard solution is also within the error allowed (the max deviation allowed for relative ion ratio are listed in table 2, corresponding analyte would be considered to be in the sample.

Table 2—Max deviation allowed for relative ion ratio in qualitative determination

Relative ion ratio/%	>50	>20~50	>10~20	≤10
Max deviation allowed/%	±20	±25	±30	±50

6.3.3.2 Quantitative determination

Under the optimized instrument working condition, different mixed matrix calibration solutions are injected into the instrument in a separate run. Using analyte peak area/internal peak area as y-axis,

and concentration as x-axis, the content of each thiocarbmate herbicide in sample is quantified by each standard calibration curve. The response of thiocarbmates herbicide in the standard working solution and sample solution should be in the linear range; if the concentration is over the linear range, the sample should be diluted by blank sample extract solution. The multiple reaction monitoring (MRM) chromatograms of thiocarbmate herbicides are shown as figure C. 1 in annex C.

6.4 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.

7 Calculation and expression of result

The calculation of thiocarbmates herbicides content in the sample is according to formula(1), the blank value should be subtracted from the result of calculation:

$$X = \frac{c \times c_i \times A \times A_{si} \times V \times 1\,000}{c_{si} \times A_i \times A_s \times m \times 1\,000} \qquad \cdots\cdots(1)$$

Where

X—the residue content of thiocarbmates in the test sample, μg/kg;

c—the concentration of thiocarbmates in the standard working solution, μg/L;

c_i—the concentration of internal standard in the sample solution, μg/L;

A—peak area of thiocarbmates in the sample solution;

A_s—peak area of thiocarbmates in the standard working solution;

V—the final volume of sample solution, mL;

c_{si}—the concentration of internal standard in the standard working solution, μg/L;

A_i—peak area of internal standard in the sample solution;

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

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

8 Limit of determination and recovery

8.1 Limit of determination

The limit of determination of each thiocarbmate herbicide is 5.0 μg/kg.

8.2 Recovery

According to the experimental data for rice, soybean, radish, baby bok choy, broccoli, ginger, peanut, tea, orange, grape, chicken, chicken liver and fish, when the concentration of thiocarbmates is in the range of 5.0 μg/kg～200 μg/kg, recovery is shown in table 3.

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Table 3—Range of recovery of 9 thiocarbmates herbiceds in foodstuffs for import and export

Com-pound	Added Level/ (μg/kg)	Recovery/%												
		Rice	Soybean	Radish	Baby bok choy	Broccoli	Genger	Orange	Grape	Peanut	Tea	Chicken	Chicken liver	Fish
Molinate	5.0	83.3~99.1	73.6~95.6	61.5~79.7	76.1~92.7	66.0~84.0	66.1~80.1	73.4~86.6	80.4~95.4	75.1~97.5	75.9~93.2	80.9~91.1	69.8~88.5	77.1~90.4
	10.0	88.3~104	72.2~87.2	64.4~78.4	67.1~79.2	66.3~84.3	65.4~79.8	68.9~83.5	77.5~93.2	73.6~88.9	70.8~85.0	73.6~90.2	74.2~91.8	70.2~86.0
	20.0	81.7~91.5	70.3~85.5	65.8~83.6	77.6~97.5	79.5~93.5	68.5~82.6	74.2~82.8	80.0~85.8	71.7~87.2	68.5~83.4	70.4~85.3	74.7~92.4	67.1~81.3
	rice:100 soybean, radish, baby bok choy, broccoli, ginger, orange, grape, tea, peanut, chicken, chicken liver and fish:50.0	84.3~95.1	75.4~89.6	71.6~90.2	81.2~89.8	82.4~96.4	69.6~81.8	67.2~83.8	80.6~88.6	76.9~91.4	73.5~87.4	71.2~87.8	76.4~87.0	67.9~83.7
EPTC	5.0	87.2~104	70.9~85.8	63.0~79.3	74.2~88.2	63.2~79.8	68.1~78.0	74.2~89.9	66.3~90.3	73.7~89.2	69.1~83.7	90.6~99.5	67.6~85.2	86.4~94.9
	10.0	82.3~94.4	69.1~86.1	67.8~81.9	77.4~94.6	65.5~77.8	68.3~86.3	78.5~96.6	76.7~89.3	71.9~89.5	67.4~83.9	71.5~92.7	62.2~77.9	68.2~88.4
	20.0	71.2~79.1	68.6~78.4	65.2~80.5	87.4~101	67.6~78.6	79.2~93.8	77.9~97.8	68.6~80.2	71.3~81.5	67.8~76.4	76.1~87.3	74.4~93.3	72.6~83.2
	rice, soybean, radish, baby bok choy, broccoli, ginger, orange, tea, peanut, grape:100 chicken, chicken liver and fish:50.0	68.5~76.9	68.5~76.9	68.5~85.1	88.2~99.8	68.5~80.5	78.5~90.8	80.9~92.1	69.1~82.1	71.2~80.0	66.8~75.0	77.8~88.2	71.6~86.2	74.2~84.1
Pebulate	5.0	94.9~112	79.9~88.2	70.0~83.2	66.1~82.5	71.5~80.4	70.8~88.6	67.6~92.1	71.6~99.9	83.1~92.1	77.9~86.4	80.2~97.0	71.0~81.2	76.5~92.5
	10.0	87.3~107	72.8~86.6	64.1~82.0	67.3~80.1	63.2~79.7	70.4~79.6	68.9~89.5	70.4~92.2	75.7~90.1	71.0~84.4	71.2~88.4	68.2~86.4	67.9~84.3
	20.0	87.0~92.6	74.5~84.2	74.9~85.8	84.4~99.1	71.0~82.0	70.0~75.7	76.8~91.9	70.9~81.6	77.5~87.6	72.6~82.1	71.4~87.7	75.3~85.8	68.1~83.6
	100	73.9~82.6	73.9~82.6	76.2~88.4	88.3~98.2	72.5~81.9	74.6~82.1	83.1~95.4	74.2~84.3	76.9~85.9	72.1~80.5	73.4~86.1	77.3~86.1	70.0~82.1

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Table 3 (continued)

Com-pound	Added Level/ (μg/kg)	Recovery/%												
		Rice	Soybean	Radish	Baby bok choy	Broccoli	Genger	Orange	Grape	Peanut	Tea	Chicken	Chicken liver	Fish
Vernolate	5.0	96.8～112	74.6～93.3	72.2～89.9	71.8～94.0	72.2～81.9	68.1～83.1	67.4～92.8	80.5～98.7	77.2～96.6	72.7～91.0	78.4～89.6	71.7～89.8	74.7～85.4
	10.0	86.7～105	73.3～83.6	67.2～79.0	68.5～79.2	71.2～78.5	65.9～79.7	80.6～95.3	67.8～91.1	75.9～89.1	71.5～83.9	70.6～86.9	70.3～90.5	67.3～79.3
	20.0	82.0～90.6	70.0～81.5	72.4～85.1	79.4～92.5	69.0～82.9	70.3～78.9	75.4～90.1	69.4～90.6	72.5～84.4	68.3～79.5	70.9～84.4	75.9～92.4	67.6～80.5
	100	70.5～82.1	70.5～82.1	75.4～88.3	80.2～95.4	70.8～83.2	70.9～83.1	76.8～92.3	74.2～90.5	73.0～84.1	68.7～80.0	72.5～86.1	76.9～91.5	69.1～82.1
Cycloate	5.0	106～119	67.0～87.6	70.4～88.2	68.1～89.1	68.3～85.6	72.0～80.2	62.2～81.7	81.1～103	75.7～91.2	65.3～85.4	77.0～92.8	78.7～94.5	73.4～88.5
	10.0	102～119	75.7～94.6	74.7～89.4	65.8～80.4	67.1～86.6	72.8～87.2	79.5～104	83.6～99.9	78.8～98.5	73.8～92.2	71.8～90.2	82.9～98.8	68.5～86.0
	20.0	96.1～103	80.8～91.6	83.2～99.0	80.6～94.3	68.8～74.4	70.6～78.7	70.9～88.4	78.9～91.8	84.1～95.4	78.8～89.3	75.5～91.1	78.2～93.9	72.0～86.9
	50.0	82.4～96.6	82.4～96.6	86.6～98.2	79.8～94.6	69.8～82.4	72.2～85.8	73.0～89.2	76.4～90.6	85.8～101	80.3～94.2	78.2～93.8	84.0～97.2	74.6～87.9
Thio-bencarb	5.0	101～113	78.7～97.0	85.6～99.4	76.8～92.0	74.5～85.1	76.0～81.6	69.6～91.8	83.8～105	81.5～100	76.7～94.6	77.7～94.3	102～113	74.1～89.9
	10.0	103～113	79.7～92.0	95.2～99.0	79.7～87.6	75.7～87.8	79.4～84.0	85.6～100	89.4～96.7	82.6～95.3	77.7～89.7	72.3～92.0	93.3～106	68.9～87.7
	20.0	95.1～102	80.1～93.0	82.2～101	80.1～100	93.5～99.6	82.5～88.6	82.2～98.5	85.8～94.7	83.0～96.3	78.1～90.7	81.9～101	98.3～114	78.1～96.2
	200	81.4～92.0	81.4～92.0	90.5～100	81.0～96.0	90.5～99.5	81.5～91.0	82.0～96.5	89.5～97.0	84.3～95.3	79.4～89.7	82.0～98.0	97.5～109	78.2～93.4
Diallate	5.0	102～111	66.5～83.6	73.1～87.7	68.9～82.8	70.5～82.4	64.6～78.8	63.4～81.6	85.4～110	68.4～85.9	64.8～81.5	72.2～90.2	90.3～98.4	68.8～86.0
	10.0	83.6～98.96	73.3～86.9	69.6～80.3	68.8～80.9	65.3～78.7	75.7～86.9	73.7～96.0	85.5～100	75.4～89.3	71.5～84.7	77.9～93.2	83.3～94.5	74.3～88.9
	20.0	87.7～104	77.1～93.2	84.5～101	83.7～97.4	71.2～82.4	75.2～83.6	74.8～91.5	82.2～93.5	79.3～95.8	75.2～90.9	75.4～88.5	80.7～91.6	71.9～84.4
	rice, soybean, radish, baby bok choy, broccoli, ginger, orange, grape, peanut chicken, and fish: 50.0 tea: 100 chicken liver: 200	79.2～93.8	79.2～93.8	88.6～100	82.6～95.6	71.6～89.2	77.4～90.0	72.2～91.2	82.4～92.6	81.4～96.4	77.2～91.5	76.8～90.2	81.0～91.5	73.2～86.0

Table 3 (continued)

Com-pound	Added Level/ (μg/kg)	Recovery/%												
		Rice	Soybean	Radish	Baby bok choy	Broccoli	Genger	Orange	Grape	Peanut	Tea	Chicken	Chicken liver	Fish
Triallate	5.0	89.6~109	67.6~86.6	69.9~86.1	84.4~99.67	67.2~80.2	68.2~88.7	72.0~87.8	77:6~102	69.4~88.9	65.9~84.4	70.4~86.0	69.1~86.6	67.1~84.5
	10.0	95.4~116	76.9~89.6	65.0~78.2	73.3~81.66	68.1~76.3	75.9~88.8	71.0~87.3	83.5~96.9	79.0~92.0	75.0~87.4	70.8~82.8	86.4~106	67.5~78.9
	20.0	95.5~109	70.1~88.6	80.1~95.6	77.8~93.7	84.1~89.0	79.3~88.4	77.0~93.6	83.2~90.0	72.0~88.6	73.2~86.4	77.9~99.4	81.0~91.3	74.3~94.8
	rice, soybean, peanut: 50.0 radish, baby bok choy, broccoli, ginger, orange, grape, tea, chicken, and fish: 100 chicken liver: 200	74.2~88.6	73.6~88.6	82.4~96.1	79.2~93.5	85.1~91.3	80.6~89.1	81.0~92.1	81.7~91.3	76.2~91.0	71.8~86.4	81.9~94.5	81.5~92.0	78.1~90.1
Butylate	5.0	90.0~109	70.6~84.6	69.7~85.1	70.0~89.7	66.5~80.5	66.3~79.3	67.8~86.4	79.5~101	72.7~81.0	70.1~82.5	72.2~94.1	65.0~75.0	68.8~88.2
	10.0	88.8~103	68.6~81.7	70.9~79.6	68.5~88.0	72.0~84.8	68.7~83.3	78.2~97.1	78.8~89.1	70.7~84.2	66.9~79.7	70.8~87.4	68.4~77.9	67.5~83.3
	20.0	84.1~91.7	70.3~85.8	69.6~85.0	81.8~96.1	68.4~80.5	66.0~80.7	75.9~86.9	72.5~87.2	72.4~88.4	68.5~83.7	75.1~80.6	71.0~86.8	70.6~76.8
	100	73.4~82.4	73.4~82.4	71.2~86.1	82.1~96.4	71.2~84.2	69.3~82.1	76.9~86.1	73.1~85.4	75.6~84.9	71.6~80.3	73.2~85.4	74.5~86.1	69.8~81.4

Annex A
(Informative)
Relate information of thiocarbmate herbicide

Table A. 1—Relate information of 9 thiocarbmate herbicides

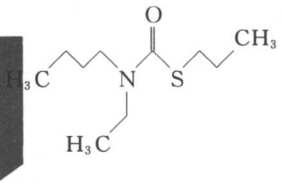
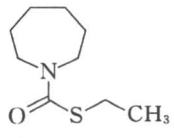
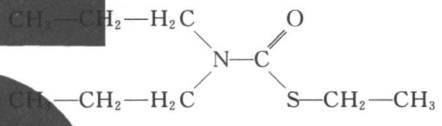
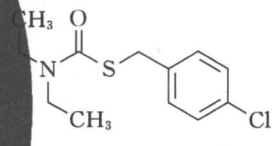
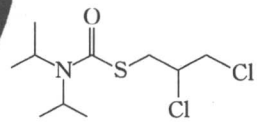
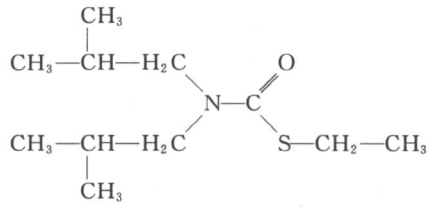
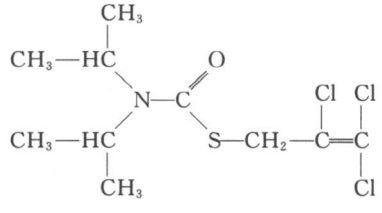
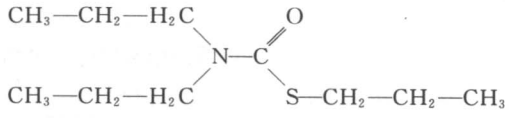
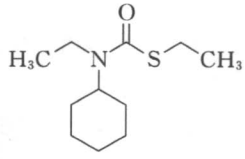
Compound	CAS No.	Formula	Structure
pebulate	1114-71-2	$C_{10}H_{21}NOS$	
molinate	2212-67-1	$C_9H_{17}NOS$	
EPTC	759-94-4	$C_9H_{19}NOS$	
thiobencarb	28249-77-6	$C_{12}H_{16}ClNOS$	
diallate	2303-16-4	$C_{10}H_{17}Cl_2NOS$	
butylate	2008-41-5	$C_{11}H_{23}NOS$	
triallate	2303-17-5	$C_{10}H_{16}Cl_3NOS$	

Table A. 1 (continued)

Compound	CAS No.	Formula	Structure
vernolate	1929-77-7	$C_{10}H_{21}NOS$	
cycloate	1134-23-2	$C_{11}H_{21}NOS$	

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Annex B
(Informative)
Operating conditions of mass spectrometer[1)]

Operating condition of mass spectrometer

a) Ion spray voltage:3 000 V;

b) Nebulizer gas flow rate:700 L/h;

c) Collision gas:argon;

d) Cone gas flow rate:50 L/h;

e) Source temperature:105 ℃;

f) Nebulizer gas temperature:350 ℃;

g) qualitative ions,quantitative ion,dwell time,cone and collision energy are listed in table B. 1.

Table B. 1—MS parameters for the detection of thiocarbmates herbicides

Compound	Reference retention time/min	Parent ion	Daughter ion	Dwell time/s	Cone voltage/V	Collision energy/eV
molinate	7. 20	188	126[a]	0. 10	32	14
			83			18
EPTC	8. 57	190	128[a]	0. 05	28	11
			86			13
butylate	10. 56	218	57[a]	0. 05	32	17
			156			11
vernolate	9. 79	204	86[a]	0. 05	30	15
			128			13
pebulate	9. 84	204	57[a]	0. 05	28	19
			72			13
triallate	11. 62	306	86[a]	0. 05	30	14
			145			26

1) Non-commercial statement: The reference mass parameters in Annex A are accomplished by Waters Quattro Premier 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 equipments of different corporation or different type.

Table B. 1 (continued)

Compound	Reference retention time/min	Parent ion	Daughter ion	Dwell time/s	Cone voltage/V	Collision energy/eV
thiobencarb	9. 77	258	100[a]	0. 05	28	12
			125			22
cycloate	9. 89	216	154[a]	0. 05	24	11
			134			14
diallate	10. 30	270	86[a]	0. 05	34	16
			109			28
D_3-carbary	4. 22	205	145[a]	0. 05	20	10
[a] ions for quantitative determination. For the different MS equipment, the parameters may be different, and the MS parameters should be optimized to the best before analysis.						

Annex C
(Informative)
MRM Chromatogram of thiocarbmate standard solution

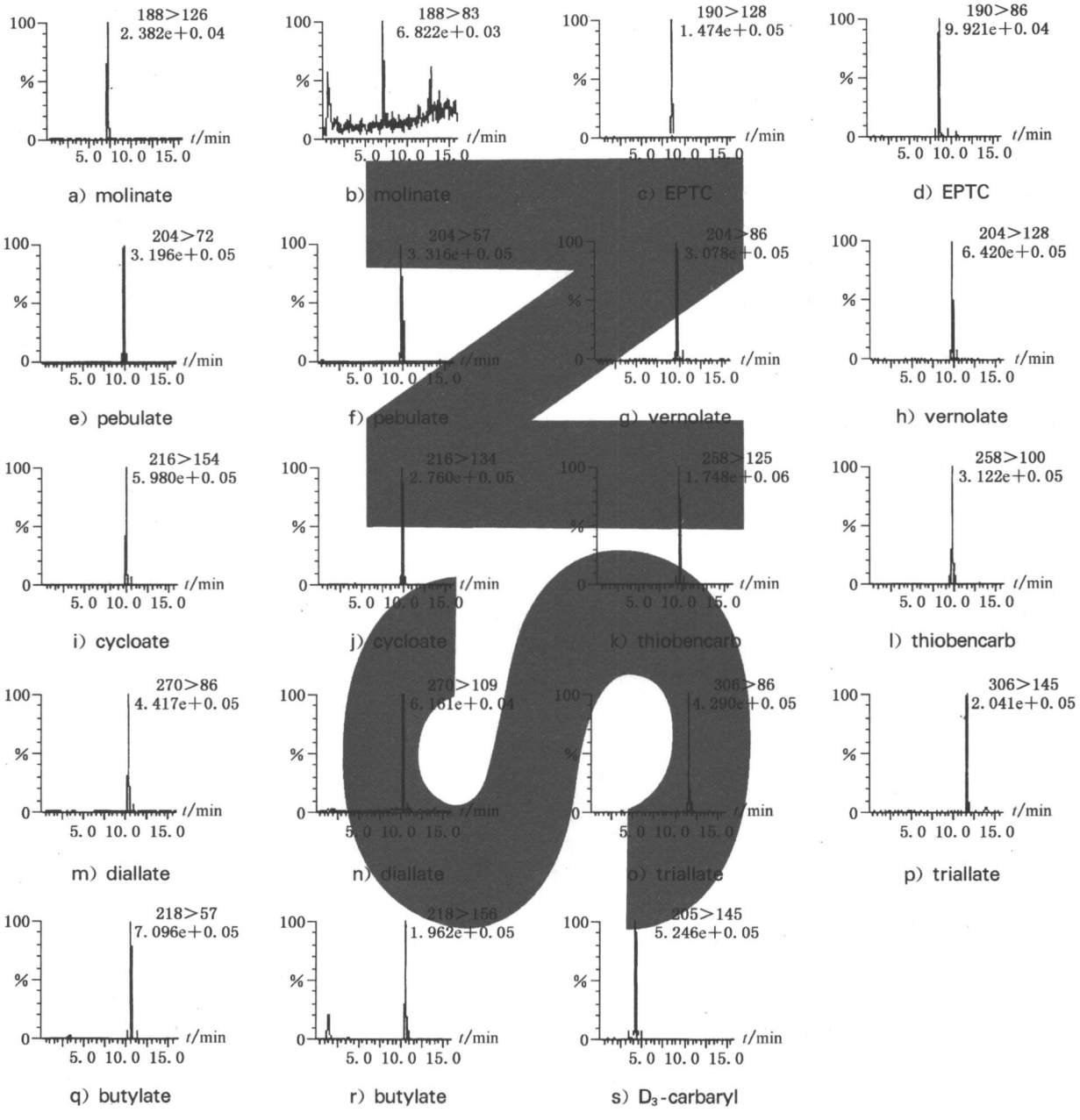


Figure C. 1—MRM chromatogram of 5. 0 μg/L thiocarbmate herbicide standard