SN

中华人民共和国出入境检验检疫行业标准

SN/T 1737.1—2006

除草剂残留量检测方法 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

Determination of herbicide residues—
Part 1: Multiple acetanilide herbicide residues in cereals and oil seeds determined by gas chromatography-mass spectrometry method

2006-01-26 发布　　2006-08-16 实施

中华人民共和国
国家质量监督检验检疫总局　发布

前　言

SN/T 1737《除草剂残留量检测方法》计划分为两个部分：

——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：大豆及粮谷中二苯醚类除草剂多残留的检测方法。

本部分为SN/T 1737的第1部分。

本部分附录A、附录B和附录C均为资料性附录。

本部分由国家认证认可监督管理委员会提出并归口。

本部分起草单位：中华人民共和国深圳出入境检验检疫局。

本部分主要起草人：谢丽琪、蓝芳、林黎、蔡伊娜、吴卫东。

本部分系首次发布的出入境检验检疫行业标准。

除草剂残留量检测方法 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

1 范围

SN/T 1737的本部分规定了进出口粮谷及油籽中酰胺除草剂残留量检验的抽样、制样和气相色谱-质谱测定方法。

本部分适用于进出口大米、大豆中酰胺除草剂残留量的检验。

2 抽样和制样

2.1 检验批

以不超过4 000袋(200 t)为一检验批。

同一检验批的商品应具有相同特征，如：包装、标记、产地、规格和等级等。

2.2 抽样数量

按式(1)计算抽样袋数：

$$a = \sqrt{N} \qquad \cdots\cdots(1)$$

式中：

N——全批袋数；

a——抽样袋数。a值取整数，小数部分向前进位为整数。

2.3 抽样工具

2.3.1 金属单管取样器：全长55 cm(包括手柄)，直径1.5 cm～2.0 cm，沟槽长度应超过袋对角长度的一半。

2.3.2 取样铲。

2.3.3 分样板。

2.3.4 样品筒(袋)：可密封。

2.3.5 分样布或适用铺垫物。

2.4 抽样方法

2.4.1 倒包抽样

从堆垛的各部位随机抽取2.2规定的应抽样件数的10%(每批一般不少于3袋)，将袋口缝线全部拆开，平置于分样布或其他洁净的铺垫物上，双手紧握袋底两角，提起约呈45°，倒拖1 m以上，使袋内货物全部倒出。查看袋内和袋间品质是否均匀。确认情况后，用取样铲随机在各部位抽取样品，立即将样品倒入盛样容器内。每袋抽取样品数量应基本一致。

2.4.2 袋内抽样

按2.2规定的应抽样袋数的90%，在堆垛四周的上、中、下各层以曲线形走向随机抽取。将取样器(2.3.1)管槽朝下，从每袋一角依斜对角方向插入袋内，然后将管槽旋转朝上，抽出取样器，立即将样品倒入盛样容器内。每袋抽取样品数量应与2.4.1基本一致。

每批样品总量应不少于4 kg。

2.4.3 大样缩分

集中袋内和倒包抽样所取全部样品，倒于分样布上，用分样板按四分法缩分出样品不少于2 kg，加

封后标明标记并及时送交实验室。

2.5 试样制备

将样品按四分法缩分至1 kg，全部磨碎并通过40目筛，混匀，均分成两份，装入洁净的容器内，密封，标明标记。

2.6 试样保存

将试样于−5℃以下避光保存。在抽样和制样过程中，应防止样品受到污染或发生残留物含量的变化。

3 测定方法

3.1 方法提要

试样中除草剂用丙酮和水提取，把提取液中丙酮减压去除后，加入氯化钠溶液，用正己烷反萃取，浓缩正己烷提取液，然后用乙腈提取，弗罗里硅土固相萃取柱净化，样液供气相色谱-质谱测试，外标法定量。

3.2 试剂和材料

除特殊规定外，所有试剂均为分析纯，水为超纯水。

3.2.1 正己烷、乙腈、丙酮、乙醚：色谱纯。

3.2.2 毒草胺、莠去津、乙草胺、二甲吩草胺、甲草胺、嗪草酮、异丙甲草胺、敌稗、丁草胺、丙草胺、草萘胺标准品：纯度大于98%。

3.2.3 标准溶液：分别准确称取25 mg±0.1 mg标准品(3.2.2)于50 mL容量瓶中，用丙酮溶解并定容，得到浓度为500 μg/mL单标储备液，此溶液在0℃～4℃中可保存3个月。根据需要再用丙酮稀释储备液，配制成适当浓度的混合标准工作液，此溶液在0℃～4℃中可保存1个月。

3.2.4 无水硫酸钠：经650℃灼烧4 h，冷却后置于干燥器中备用。

3.2.5 氯化钠。

3.2.6 氯化钠溶液：10%(质量浓度)，将100 g氯化钠溶于水中，并稀释至1 000 mL。

3.2.7 提取剂Ⅰ：乙腈加入少量正己烷饱和，摇匀。

3.2.8 提取剂Ⅱ：正己烷加入少量乙腈饱和，摇匀。

3.2.9 正己烷+乙醚(85+15)：取85 mL正己烷和15 mL乙醚，混匀。

3.2.10 弗罗里硅土固相萃取柱：125 mg，3 mL，或相当者。使用前依次用5 mL正己烷+乙醚溶液(3.2.9)和5 mL正己烷预淋洗柱子，流速1 d/s。

3.3 仪器和设备

3.3.1 气相色谱-质谱仪。

3.3.2 旋转蒸发仪。

3.3.3 固相萃取装置。

3.3.4 吹氮浓缩仪。

3.3.5 旋涡混合器。

3.3.6 均质机。

3.3.7 离心机。

3.3.8 茄形瓶：100 mL、250 mL。

3.3.9 离心管：15 mL、50 mL。

3.3.10 微量注射器：10 μL。

3.4 测定步骤

3.4.1 提取

称取约10 g(精确至0.01 g)样品于50 mL离心管中，加入10 mL水和20 mL丙酮，均质3 min，于

4 000 r/min 离心 4 min，将提取液移入 250 mL 茄形瓶中，离心管中残渣再用 2×30 mL 丙酮提取，提取液并入茄形瓶中。在 38℃下，减压蒸发去除丙酮，残液（约 10 mL）转移至另一 50 mL 离心管中。依次用 10 mL 10%氯化钠溶液和 15 mL 正己烷洗涤茄形瓶，洗涤液一并移入离心管中，振荡 3 min，于 2 500 r/min离心 3 min，收集正己烷相。离心管中的水相中再用 2×15 mL 正己烷提取，合并正己烷相。

3.4.2 液-液分配净化

正己烷相中加入适量无水硫酸钠脱水，将正己烷相完全转移至另一 250 mL 茄形瓶中，于 50℃，减压蒸发至干。残余物用 2×5 mL 提取液Ⅱ(3.2.8)溶解，一并转移至 50 mL 离心管中。加入 3×10 mL 提取液Ⅰ(3.2.7)，混匀、分层，乙腈相转移至另一 50 mL 离心管中。加入 10 mL 提取液Ⅱ(3.2.8)，混匀、分层后弃去正己烷相，乙腈相转移至 100 mL 茄形瓶中，在 50℃下，减压蒸发至干，残余物用 5 mL 正己烷溶解。

3.4.3 固相萃取净化

将上述正己烷溶液移入弗罗里硅土固相萃取柱中，液体过柱流速保持 0.5 d/s，用 15 mL 正己烷＋乙醚溶液(3.2.9)润洗茄形瓶并转移至柱中进行洗脱，流速为 1 d/s，收集全部洗脱液于定量试管中，于 40℃，在氮气流下吹至近干，加入正己烷溶解残渣并定容至 1.0 mL，供 GC-MS 测定。

3.4.4 测定

3.4.4.1 色谱条件

a) 色谱柱：HP-1701 MS，30 m×0.25 mm(内径)×0.25 μm(膜厚)，或相当者；

b) 载气：氦气(纯度大于 99.999%)，流量：1.0 mL/min；

c) 色谱柱程序升温条件：初始温度：70℃(保持 1 min)；15℃/min，升温至 160℃(保持 1 min)；2℃/min 的速度，升温至 200℃(保持 2 min)；20℃/min，升温至 280℃(保持 8 min)；

d) 进样口温度：270℃；

e) 进样方式：不分流进样，1 min 后打开分流阀，分流比 100∶1；

f) 进样量：1 μL。

3.4.4.2 质谱条件

a) 离子源温度：230℃；

b) 传输线温度：280℃；

c) 离子化模式：EI；

d) 扫描范围：50～400 amu；

e) 电子倍增管电压：自动调谐电压 200 V；

f) 测试方式：选择离子监测。

3.4.4.3 气相色谱-质谱测定

3.4.4.3.1 定量测定

根据样液中除草剂含量情况，选定峰面积相近的标准工作溶液，标准工作溶液和样液中除草剂的响应值均应在仪器检测的线性范围内。以单点或多点外标法定量，标准工作液和样液应等体积参插进样测定。

3.4.4.3.2 定性测定

定性测定的两个依据为：(1)被测样品峰与标准样品峰的色谱保留时间相同；(2)被测样品与标准样品的质谱图相似，被测样品的监测离子的相对丰度应与标准样品一致，两者之差不大于±10%(EI 模式)。各除草剂的监测离子及定量离子参见附录 A。

在上述色谱、质谱条件下，毒草胺、莠去津、乙草胺、二甲吩草胺、甲草胺、嗪草酮、异丙甲草胺、敌稗、丁草胺、丙草胺、草萘胺的保留时间分别为 11.2 min、13.2 min、13.8 min、14.9 min、15.3 min、15.7 min、15.9 min、16.9 min、19.3 min、20.6 min、21.9 min。选择离子色谱图参见附录 B，质谱图参见附录 C 中图 C.1～图 C.4。

3.4.5 空白试验

除不加试样外，均按上述测定步骤进行。

3.4.6 结果计算和表述

用色谱工作站或按式(2)计算试样中除草剂的含量，计算结果须扣除空白值。

$$X = \frac{A \times c \times V}{A_S \times m} \quad \cdots\cdots(2)$$

式中：

X——试样中除草剂含量，单位为毫克每千克(mg/kg)；

A——试样中除草剂峰面积；

A_S——标准溶液中除草剂峰面积；

c——标准溶液浓度，单位为毫克每升(mg/L)；

V——样品溶液最终定容体积，单位为毫升(mL)；

m——样品质量，单位为克(g)。

4 方法的测定低限和回收率

4.1 测定低限

毒草胺、莠去津、乙草胺、异丙甲草胺、丙草胺、草萘胺、二甲吩草胺、嗪草酮、敌稗：0.02 mg/kg；甲草胺、丁草胺：0.05 mg/kg。

4.2 回收率

大米中除草剂添加浓度及其回收率：

——毒草胺添加浓度为0.02 mg/kg～2.0 mg/kg范围内，回收率为90.3%～94.5%；

——莠去津添加浓度为0.02 mg/kg～2.0 mg/kg范围内，回收率为89.8%～95.5%；

——乙草胺添加浓度为0.02 mg/kg～2.0 mg/kg范围内，回收率为84.5%～93.5%；

——二甲吩草胺添加浓度为0.02 mg/kg～2.0 mg/kg范围内，回收率为84.5%～93.8%；

——甲草胺添加浓度为0.05 mg/kg～2.0 mg/kg范围内，回收率为83.7%～93.9%；

——嗪草酮添加浓度为0.02 mg/kg～2.0 mg/kg范围内，回收率为88.3%～95.6%；

——异丙甲草胺添加浓度为0.02 mg/kg～2.0 mg/kg范围内，回收率为88.1%～93.8%；

——敌稗添加浓度为0.02 mg/kg～2.0 mg/kg范围内，回收率为83.7%～95.8%；

——丁草胺添加浓度为0.05 mg/kg～2.0 mg/kg范围内，回收率为76.8%～89.5%；

——丙草胺添加浓度为0.02 mg/kg～2.0 mg/kg范围内，回收率为86.9%～97.5%；

——草萘胺添加浓度为0.02 mg/kg～2.0 mg/kg范围内，回收率为94.2%～101.9%。

大豆中除草剂添加浓度及其回收率：

——毒草胺添加浓度为0.02 mg/kg～2.0 mg/kg范围内，回收率为78.1%～92.0%；

——莠去津添加浓度为0.02 mg/kg～2.0mg/kg范围内，回收率为80.8%～92.8%；

——乙草胺添加浓度为0.02 mg/kg～2.0 mg/kg范围内，回收率为80.8%～88.6%；

——二甲吩草胺添加浓度为0.02 mg/kg～2.0 mg/kg范围内，回收率为78.7%～90.9%；

——甲草胺添加浓度为0.05 mg/kg～2.0 mg/kg范围内，回收率为76.1%～86.4%；

——嗪草酮添加浓度为0.02 mg/kg～2.0 mg/kg范围内，回收率为81.7%～91.5%；

——异丙甲草胺添加浓度为0.02 mg/kg～2.0mg/kg范围内，回收率为81.6%～90.3%；

——敌稗添加浓度为0.02 mg/kg～2.0 mg/kg范围内，回收率为82.9%～92.5%；

——丁草胺添加浓度为0.05 mg/kg～2.0mg/kg范围内，回收率为72.8%～83.6%；

——丙草胺添加浓度为0.02 mg/kg～2.0 mg/kg范围内，回收率为86.4%～92.7%；

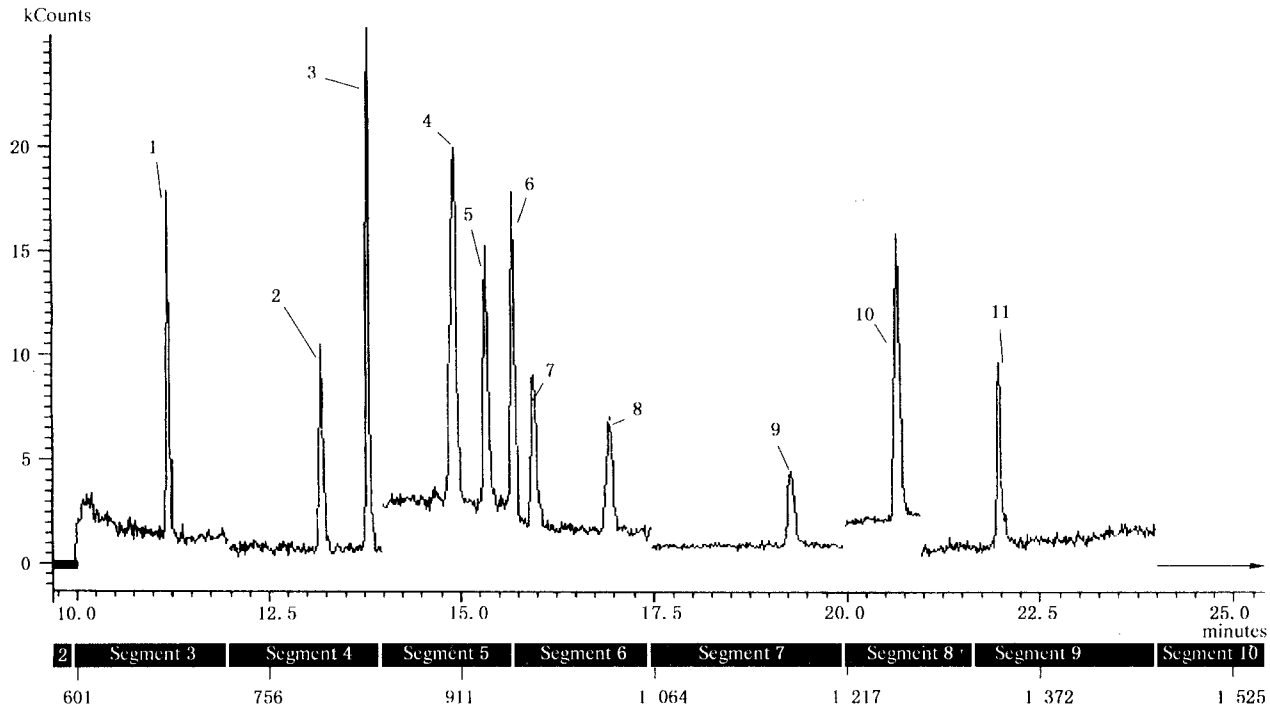
——草萘胺添加浓度为0.02 mg/kg～2.0 mg/kg范围内，回收率为88.4%～96.0%。

附 录 A
（资料性附录）

表 A.1 除草剂的定量离子和监测离子

除草剂	定量离子，m/z	监测离子，m/z 及其相对丰度
毒草胺	120	120(100)，176(37)，196(10)，211(8)
莠去津	200	200(100)，215(62)，172(15)，173(35)
乙草胺	146	146(100)，223(53)，174(48)，162(83)
二甲吩草胺	154	154(100)，203(42)，230(58)，232(20)
甲草胺	160	160(100)，188(93)，237(24)，269(6)
嗪草酮	198	198(100)，199(19)，144(14)，214(4)
异丙甲草胺	162	162(100)，238(47)，240(15)，211(7)
敌稗	161	161(100)，163(71)，217(18)，219(12)
丁草胺	176	176(100)，160(86)，188(49)，237(27)
丙草胺	238	162(100)，202(38)，238(69)，262(27)
草萘胺	128	72(100)，100(39)，128(63)，271(26)

附 录 B
（资料性附录）
标准品色谱图



1——毒草胺：11.2 min；
2——莠去津：13.2 min；
3——乙草胺：13.8 min；
4——二甲吩草胺：14.9 min；
5——甲草胺：15.3 min；
6——嗪草酮：15.7 min；
7——异丙甲草胺：15.9 min；
8——敌稗：16.9 min；
9——丁草胺：19.3 min；
10——丙草胺：20.6 min；
11——草萘胺：21.9 min。

图 B.1 酰胺除草剂标准混合液的 SIS 色谱图（浓度均为 0.1 mg/L）

附 录 C
（资料性附录）
标准品质谱图

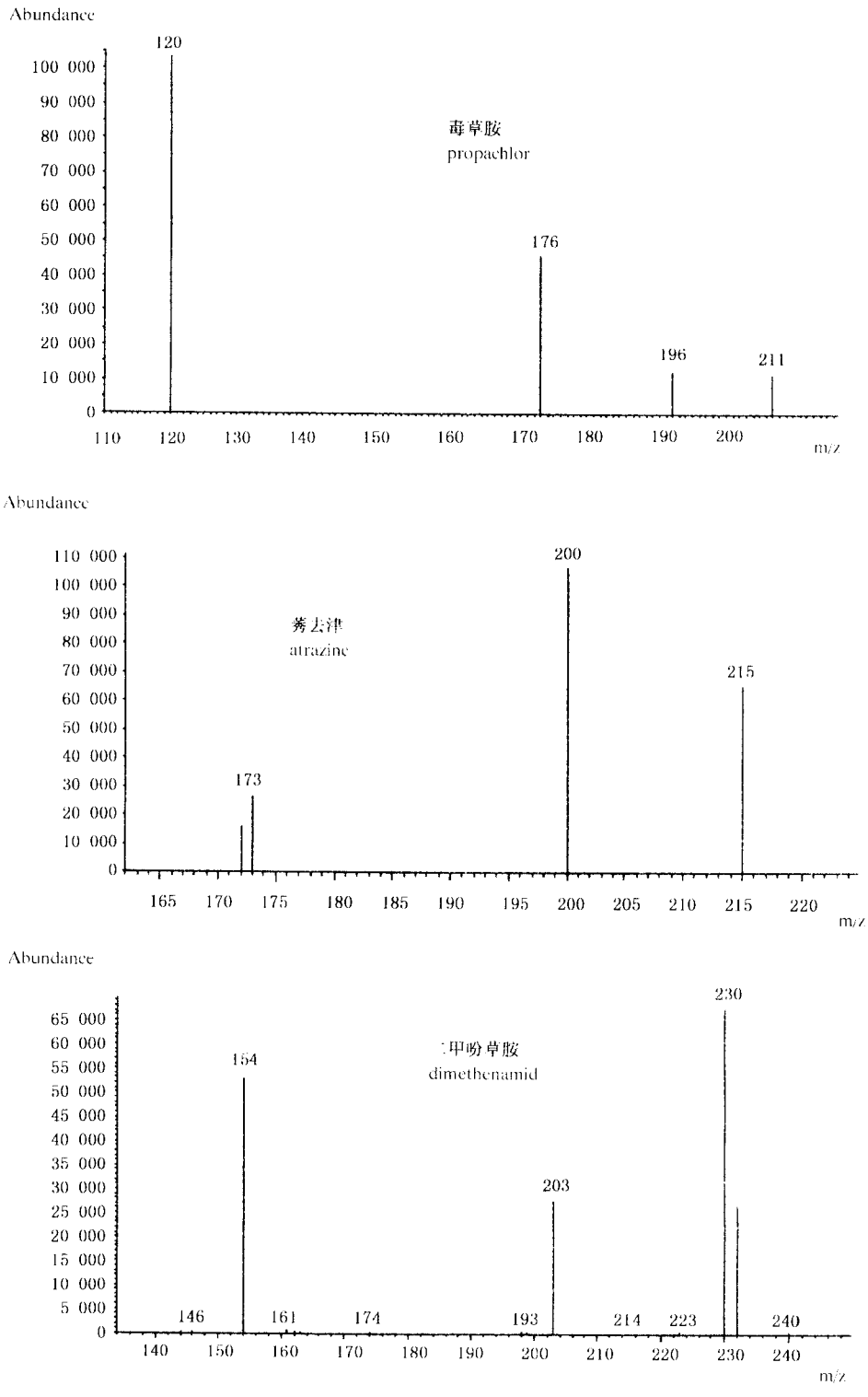


图 C.1 毒草胺、莠去津和二甲吩草胺的 SIM 质谱图

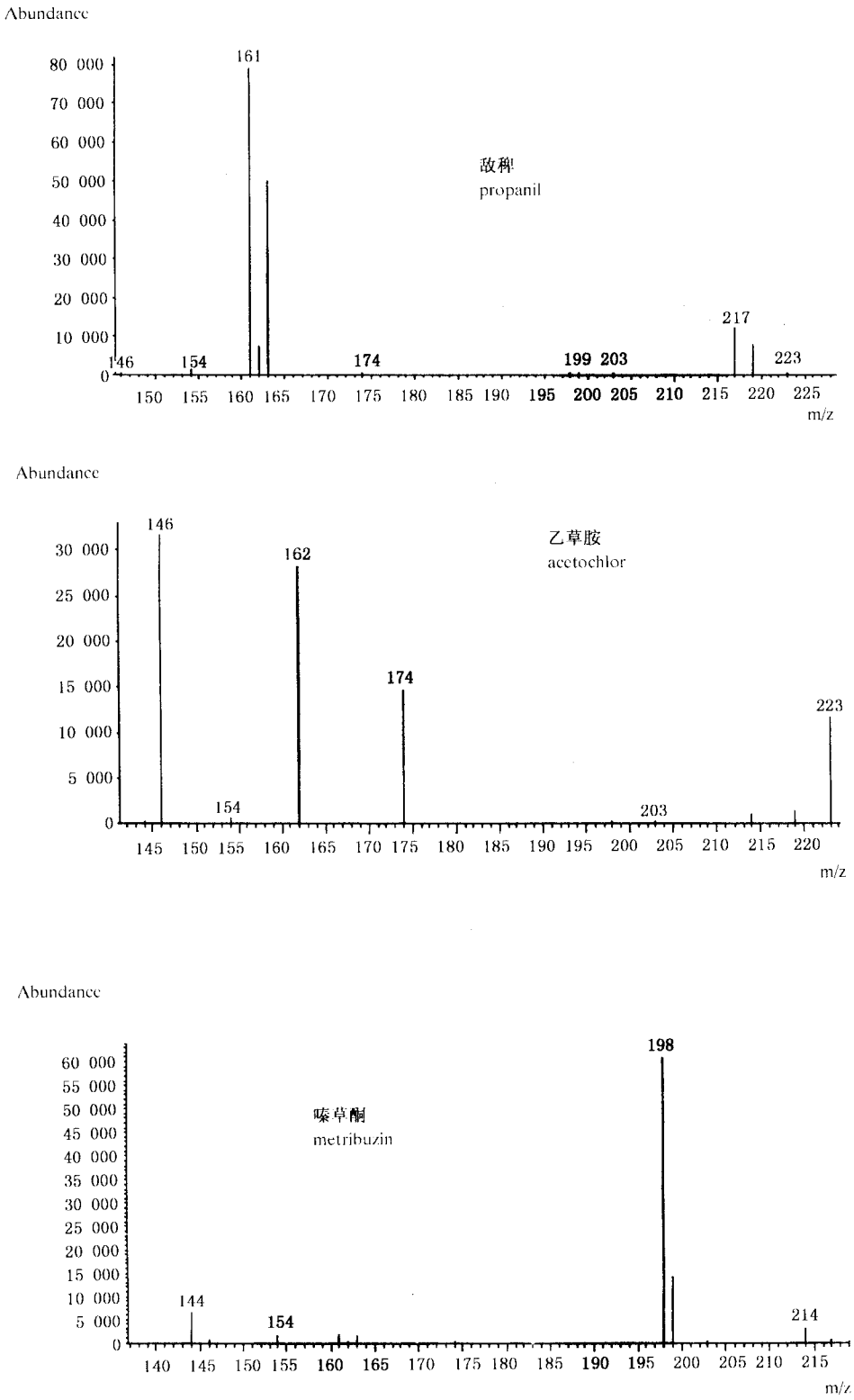


图 C.2 嗪草酮、敌稗、乙草胺的 SIM 质谱图

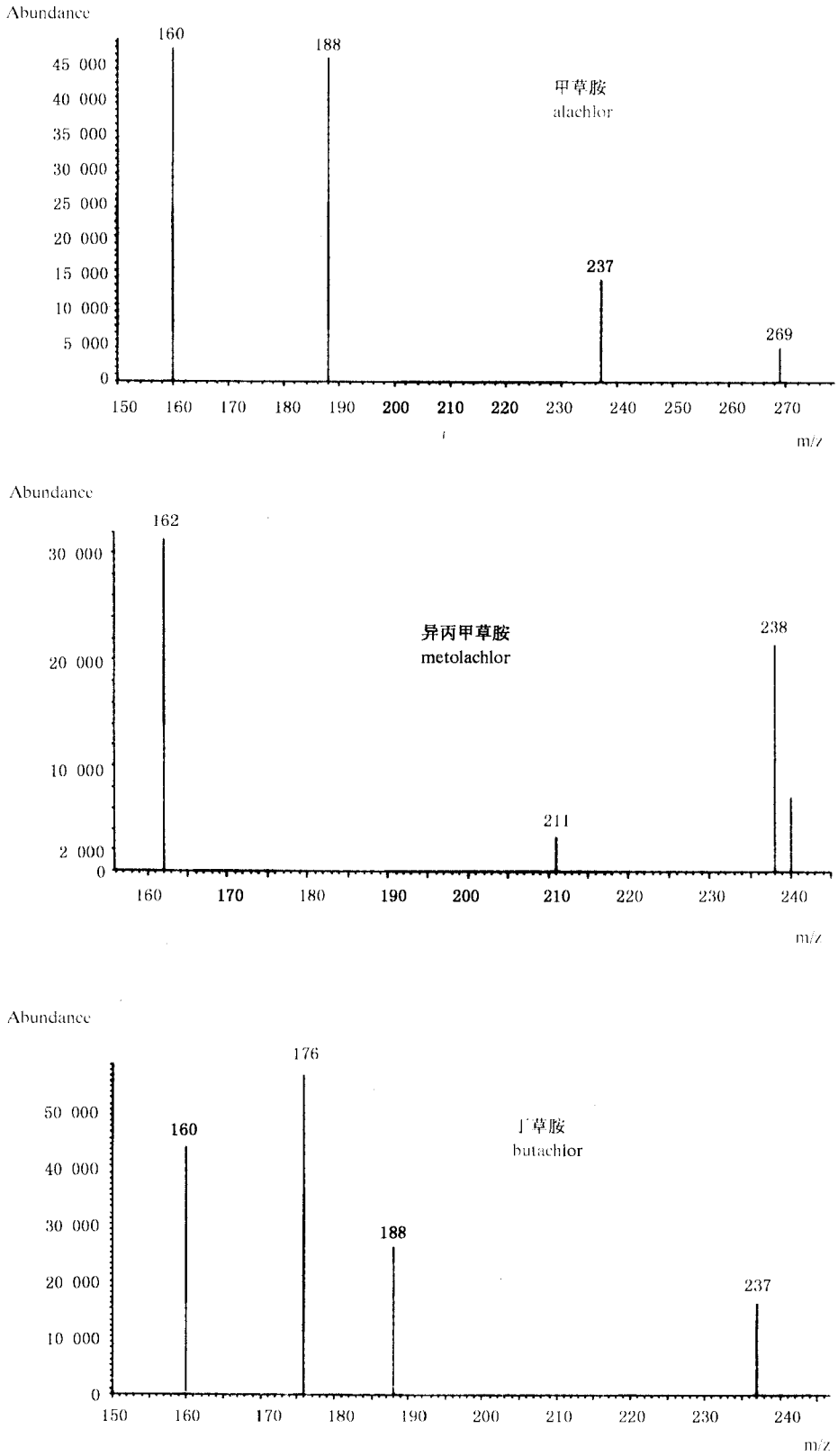


图 C.3　丁草胺、甲草胺、异丙甲草胺的 SIM 质谱图

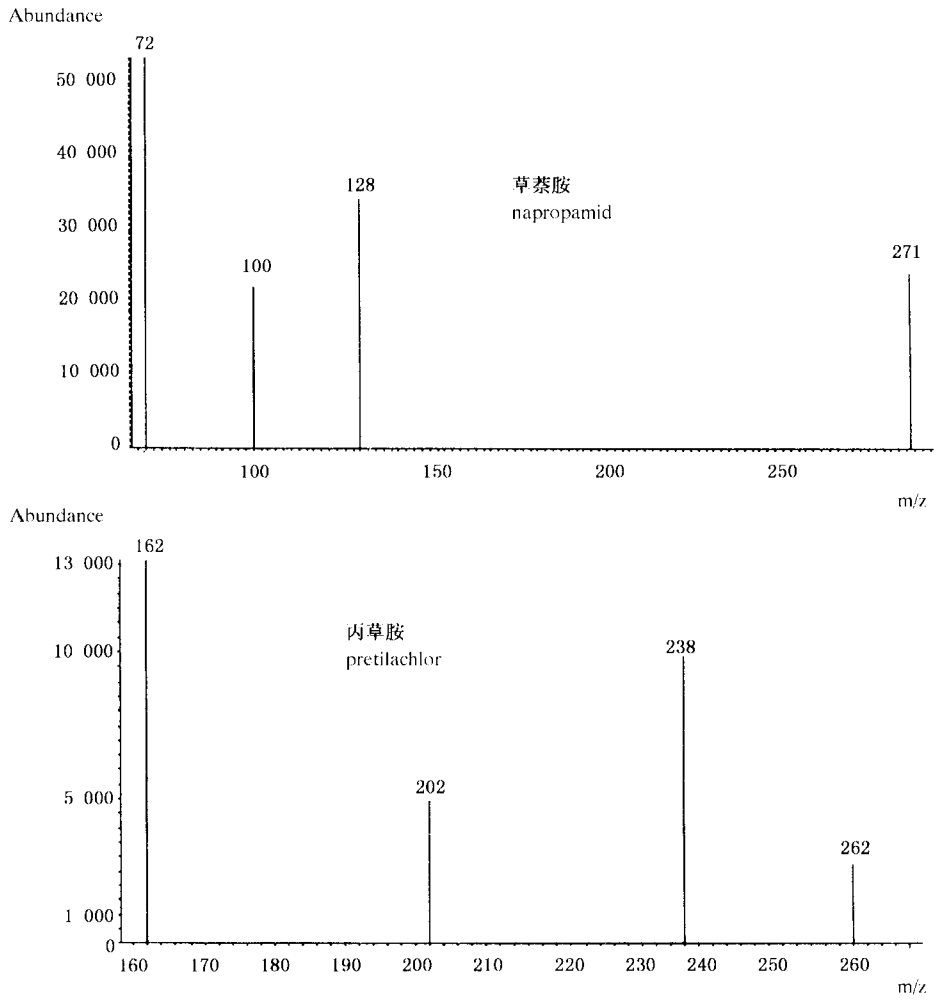


图 C.4　丙草胺、草萘胺的 SIM 质谱图

Foreword

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

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

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

The main drafters of this standard are Xie Liqi, Lan Fang, Lin li, Cai Yina and Wu Weidong.

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

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

Determination of herbicide residues—Part 1: multiple acetanilide herbicide residues in cereals and oil seeds determined by gas chromatography-mass spectrometry method

1 Scope

This Part specifies the method of sampling, sample preparation and determination by gas chromatography-mass spectrometry of acetanilide herbicide residues in cereals and oil seeds for import and export.

This Part is applicable to the determination of acetanilide herbicide residues in rice and soybean for import and export.

2 Sampling and Sample Preparation

2.1 Inspection lot

Each inspection lot should not exceed 4 000 bags (200 t).

The characteristics of the cargo within the same inspection lot, such as packing, mark, origin, specification and grade etc. should be the same.

2.2 Quantity of sample taken

The number of bags to be sampled shall be calculated according to the formula (1). If value a is with decimal, round off the decimal part, which is added as unity to the integral part of a.

$$a = \sqrt{N} \quad \cdots\cdots (1)$$

Where:

N——total number of bags in a lot;

a——number of bags to be sampled.

2.3 Sampling tools

2.3.1 Metallic sampler: Length (including handle): 55 cm; diameter 1.5 cm～2.0 cm; groove length: longer than half the diagonal length of the bag.

2.3.2 Sampling shovel.

2.3.3 Plate for quartering.

2.3.4 Sample can (bag), which can be sealed.

2.3.5 Cloth (or other suitable material)sheet: for sample dividing (quartering).

2.4 Sampling procedure

2.4.1 Sampling by emptying out

Draw 10 percent of the number of bags specified in 2.2(not less than 3 bags) at any part of the pile at random. Unseal and open the bag, and lay it on a clean cloth sheet (or other clean sheet). Grasp tight two corners of the bag bottom and raise up to an angle of 45°, tug backward for ca 1 m until all content of the bag is emptied out. Check the appearance, odor of the goods and whether the goods are moldy, rotten etc. Alsc check the quality of the goods is uniform within and between the bags. After confirming the goods is in normal condition, scoop up the sample from different parts of the out-poured content with a shovel, and place in a sample container promptly. The quantity of the sample drawn from each bag should be basically the same.

2.4.2 Sampling the cereals in the bag

According to the specified in 2.2, the number of sampling should be 90 percent of the total number of bags, draw the sample from the upper, middle and lower parts of the pile at random. Insert sampler (2.3.1), with its groove facing downward, diagonally into each bag, then turn the sampler upward, draw out the sampler, and promptly pour the sample into a container. The quantity of the sample drawn from each bag shall be basically the same as in 2.4.1.
The total weight of the sample drawn from each lot should not be less than 4 kg.

2.4.3 Reduction of gross sample

Pour all the samples (from both 2.4.1 and 2.4.2) on a clean sheet; reduce to not less than 2 kg with a plate by quartering. Place in a sample container, seal,label and send to the laboratory in time.

2.5 Preparation of test sample

Reduced the sample to ca 1 kg by quartering, grind thoroughly and let pass through a 40 mesh sieve, mix thoroughly and divide in two, place in clean containers, seal and label.

2.6 Storage of sample

The test sample should be stored below −5℃ and kept away from light. During sampling and prepa-

ration of sample, precautions must be taken to avoid contamination or any factors that may cause the change in residue content.

3 Method of Determination

3.1 Principle

Herbicides in a sample are extracted with acetone-water solution, the extract is concentrated with a rotary vacuum evaporator till acetone is removed, re-extracted with *n*-hexane, and acetonitrile. The acetonitrile extract is washed by *n*-hexane, and the acetonitrile phase is evaporated to dryness. The residue is dissolved with *n*-hexane, and cleaned up on a florisil solid-phase extraction cartridge. After eluate is evaporated to dryness, the residue is dissolved with *n*-hexane, and then determined by gas chromatography-mass spectrometry. External standard method is used for quantitative measurement.

3.2 Reagents and materials

Reagents were of analytical-reagent grade except for the specific reagents. The water used was doubly distilled or deionized water.

3.2.1 *n*-hexane, acetonitrile, acetone, diethyl ether: chromatographic grade.

3.2.2 Standard of propachlor, atrazine, acetochlor, dimethenamid, alachlor, metribuzin, metolachlor, propanil, butochlor, pretilachlor, napropamid: purity >98%.

3.2.3 Standard solutions: accurately weigh 25 mg ± 0.1 mg standard (3.2.2) into a 50 mL volumetric flask, dissolve the standard and mark up to the volume with acetone, individually, obtaining 500 μg/mL of the stock standard solution. Dilute the stock standard solutions with acetone to the required concentrations which being the mixed standard working solutions.

3.2.4 Anhydrous sodium sulfate: Ignite at 650℃ for 4 h, and keep in a tight closed container.

3.2.5 Sodium chloride.

3.2.6 Sodium chloride solution: 10 % (m/V), weigh 100 g of sodium chloride, dissolve and dilute to 1 000 mL with water.

3.2.7 Extract solution Ⅰ: acetonitrile is saturated with *n*-hexane, shaken and mixed.

3.2.8 Extract solution Ⅱ: *n*-hexane is saturated with acetonitrile, shaken and mixed.

3.2.9 *n*-hexane-diethyl ether (85 + 15) solution.

3.2.10 Florisil solid-extraction cartridge: 125 mg, 3 mL, or equivalent. Condition the florisil solid-extraction cartridge with 5 mL *n*-hexane-diethyl ether (3.2.9) and 5 mL *n*-hexane separately, keep the flow rate at 1 d/s.

3.3 Apparatus and equipment

3.3.1 Gas chromatography-mass spectrometry.

3.3.2 Rotary vacuum evaporator.

3.3.3 Solid-phase extraction device.

3.3.4 Nitrogen Concentrator.

3.3.5 Vortex mixer.

3.3.6 Homogeniser.

3.3.7 Centrifuge.

3.3.8 Round bottom flask: 100 mL, 250 mL.

3.3.9 Centrifuge tube: 15 mL, 50 mL.

3.3.10 Micro-syringe: 10 μL.

3.4 Procedure

3.4.1 Extraction

Weigh 10 g±0.01 g of a sample into a 50 mL centrifuge tube, add 10 mL of water and 20 mL of acetone, homogenize for 3 min, centrifuge for 4 min at 4 000 r/ min. Transfer the extract into a 250 mL round bottom flask. Add 2×30 mL of acetone to extract the residue in the centrifuge tube. Combine the extract into the round bottom flask. Evaporate acetone with a rotary vacuum evaporator at 38℃, transfer the residual solution (ca 10 mL) into another 50 mL centrifuge tube, Separately add 10 mL of 10 % sodium chloride solution and 15 mL of *n*-hexane to rinse the round bottom flask, transfer the solutions to the centrifuge tube, vortex for 3 min, centrifuge for 3 min at 2 500 r/ min, and collect the *n*-hexane extract. Add 2×15 mL of *n*-hexane to extract the water phase in the centrifuge tube, combine the total *n*-hexane extract.

3.4.2 Liquid-liquid cleanup

Add proper amount of anhydrous sodium sulfate to the *n*-hexane extract. Transfer the *n*-hexane phase to a 250 mL round bottom flask, and evaporate to dryness with a rotary vacuum evaporator at 50℃. Resuspend the residue with 2×5 mL of extract solution Ⅱ (3.2.8), and transfer into another 50 mL centrifuge tube. Add 3×10 mL of extract solution Ⅰ (3.2.7), vortex and partition. Transfer the acetonitrile phase into another 50 mL centrifuge tube, Add 10 mL of extract solution Ⅱ (3.2.8), mix well, then partition, discard the *n*-hexane phase. Transfer the acetonitrile phase into a 100 mL round bottom flask, and evaporate to dryness with a rotary vacuum evaporator at 50℃. Dissolve the residue with 5 mL *n*-hexane.

3.4.3 Solid-phase extraction cleanup

Load the hexane extract onto a florisil solid-extraction cartridge, keep the flow rate at 0.5d/s Rinse the round bottom flask with 15 mL of *n*-hexane-diethyl ether solution (3.2.9), and then load onto the cartridge (flow rate at 1 d/s), collect the eluate into a test tube with volume. Evaporate the eluate to dryness under nitrogen stream at 40℃. Resuspend the residue with 1.0 mL of *n*-hexane for GC-MS determination.

3.4.4 Determination

3.4.4.1 GC operating conditions

a) Column: HP-1701 ms, 30 m ×0.25 mm (i.d.) × 0.25 μm (film thickness), or equivalent;

b) Carrier gas: helium, purity >99.999%, flow rate: 1 mL/ min.

c) Column temperature: 70℃ (1 min.) $\xrightarrow{15℃/min.}$ 160℃ (1 min.) $\xrightarrow{2℃/min.}$ 200℃ (2 min.) $\xrightarrow{20℃/min.}$ 280℃ (8 min.);

d) Injector temperature: 270℃;

e) Injection mode: splitless; 0.0 min, split valve off; 1.0 min, split valve on;

f) Injection volume: 1 μL.

3.4.4.2 MS operating conditions

a) Ion source temperature: 230℃;

b) Transfer line temperature: 280℃;

c) Ionization mode: EI;

d) Scan range: 50～400 amu;

e) Electron multiplier voltage: autotune voltage +200 V;

f) Selected ion monitoring mode.

3.4.4.3 GC-MS determination

3.4.4.3.1 Quantitative Determination

According to the concentration of herbicides in the sample solution, select the standard working solution with similar peak area to that of the sample solution. The responses of both the standard working solutions and the sample solution should be within the linear range of the instrumental detection. The standard working solutions should be randomly injected in between the injections of sample solution of equal volume.

3.4.4.3.2 Qualitative Determination

The presence of herbicides in a sample is confirmed by GC-MS data agree with the following criteria: (1) the peaks have the same retention time as the standards; (2) the selected monitoring ions are present in the same abundance ratio to one anther as seen in the standards, the difference should be within 10 %. The monitoring and quantitative ions of herbicides refer to Annex A.
Under the above GC-MS conditions, the retention times of propachlor, atrazine, acetochlor, dimethenamid, alachlor, metribuzin, metolachlor, propanil, butachlor, pretilachlor, and napropamid are ca 11.2 min, 13.2 min, 13.8 min, 14.9 min, 15.3 min, 15.7 min, 15.9 min, 16.9 min, 19.3 min, 20.6 min, and 21.9 min. The chromatogram of herbicides refers to Annex B. The mass spectra of herbicides refer to Annex Fig C.1～Fig C.4.

3.4.5 Blank test

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

3.4.6 Calculation and expression of result

The content of herbicide in the test sample is calculated with GC data processor or the following formula (2). The blank value should be subtracted from the result of calculation.

$$X = \frac{A \times c \times V}{A_S \times m} \quad \cdots\cdots (2)$$

Where:

X ——the content of herbicide in sample, mg/kg;

A ——the peak area of herbicide in sample solution;

A_S ——the peak area of herbicide in standard working solution;

c——the concentration of herbicide in standard working solution, μg/ mL;

V——final volume of sample solution, mL;

m——weight of the test sample, g.

4 Limit of Determination and Recovery

4.1 Limit of determination

The limit of determination of this method is: propachlor 0.02 mg/kg; atrazine 0.02 mg/kg; acetochlor 0.02 mg/kg; dimethenamid 0.02 mg/kg; alachlor 0.05 mg/kg; metribuzin 0.02 mg/kg; metolachlor 0.02 mg/kg; propanil 0.02 mg/kg; butachlor 0.05 mg/kg; pretilachlor 0.02 mg/kg; napropamid 0.02 mg/kg.

4.2 Recovery

The fortifying concentrations of herbicides in cereal and its corresponding recoveries are:

——propachlor 0.02 mg/kg~2.0 mg/kg, recovery 90.3%~94.5%;

——atrazine 0.02 mg/kg~2.0 mg/kg, recovery 89.8%~95.5%;

——acetochlor 0.02 mg/kg~2.0 mg/kg, recovery 84.5%~93.5%;

——dimethenamid 0.02 mg/kg~2.0 mg/kg, recovery 84.5%~93.8%;

——alachlor 0.02 mg/kg~2.0 mg/kg, recovery 83.7%~93.9%;

——metribuzin 0.02 mg/kg~2.0 mg/kg, recovery 88.3%~95.6%;

——metolachlor 0.02 mg/kg~2.0 mg/kg, recovery 88.1%~93.8%;

——propanil 0.02 mg/kg~2.0 mg/kg, recovery 83.7%~95.8%;

——butachlor 0.05 mg/kg~2.0 mg/kg, recovery 76.8%~89.5%;

——pretilachlor 0.02 mg/kg~2.0 mg/kg, recovery 86.9%~97.5%;

——napropamid 0.02 mg/kg~2.0 mg/kg, recovery 94.2%~101.9%.

The fortifying concentrations of herbicides in soybean and its corresponding recoveries are:

——propachlor 0.02 mg/kg~2.0 mg/kg, recovery 78.1%~92.0 %;

——atrazine 0.02 mg/kg~2.0 mg/kg, recovery 80.8%~92.8%;

——acetochlor 0.02 mg/kg~2.0 mg/kg, recovery 80.8%~88.6%;

——dimethenamid 0.02 mg/kg~2.0 mg/kg, recovery 78.7%~90.9%;

——alachlor 0.05 mg/kg~2.0 mg/kg, recovery 76.1%~86.4%;

——metribuzin 0.02 mg/kg~2.0 mg/kg, recovery 81.7%~91.5%;

——metolachlor 0.02 mg/kg~2.0 mg/kg, recovery 81.6%~90.3%;

——propanil 0.02 mg/kg~2.0 mg/kg, recovery 82.9%~92.5%;

——butachlor 0.02 mg/kg~2.0 mg/kg, recovery 72.8%~ 83.6%;

——pretilachlor 0.02 mg/kg~2.0 mg/kg, recovery 86.4%~92.7%;

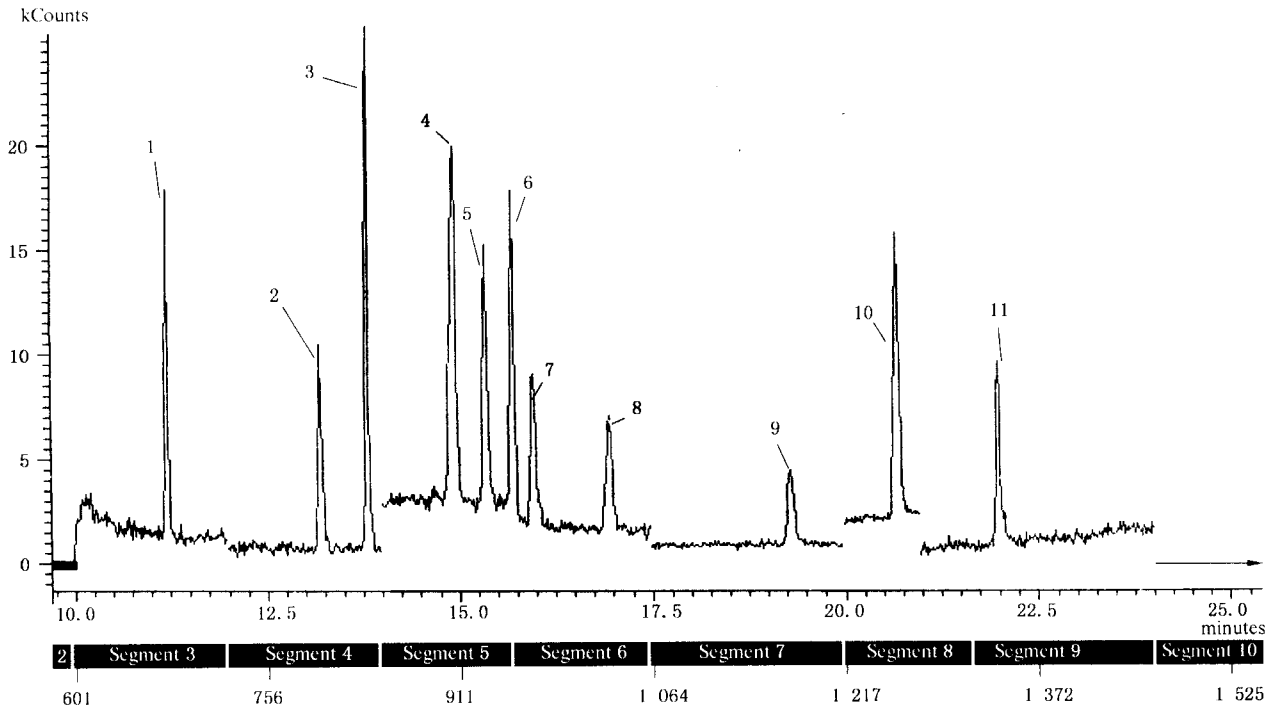
——napropamid 0.02 mg/kg~2.0 mg/kg, recovery 88.4%~96.0 %.

Annex A
(Informative)

Table A.1 Monitoring ions and quantitative ions of the herbicides

herbicides	Quantitative ions.m/z	monitoring ions.m/z and relative intensity
Propachlor	120	120(100),176(37),196(10),211(8)
Atrazine	200	200(100),215(62),172(15),173(35)
Acetochlor	146	146(100),223(53),174(48),162(83)
Dimethenamid	154	154(100),203(42),230(58),232(20)
Alachlor	160	160(100),188(93),237(24),269(6)
Metribuzin	198	198(100),199(19),144(14),214(4)
Metolachlor	162	162(100),238(47),240(15),211(7)
Propanil	161	161(100),163(71),217(18),219(12)
Butachlor	176	176(100),160(86),188(49),237(27)
Pretilachlor	238	162(100),202(38),238(69),262(27)
Napropamid	128	72(100),100(39),128(63),271(26)

Annex B
(Informative)
SIM chromatogram of the standards



1——propachlor:11. 2 min;
2——atrazine:13. 2 min;
3——acetochlor:13. 8 min;
4——dimethenamid:14. 9 min;
5——alachlor:15. 3 min;
6——metribuzin:15. 7 min;
7——metolachlor:15. 9 min;
8——propanil:16. 9 min;
9——butachlor:19. 3 min;
10——pretilachlor:20. 6 min;
11——napropamid:21. 9 min.

Fig B. 1 SIS chromatogram of mixed standard solution (concentration:0. 1 mg/L)

Annex C
(Informative)
SIM mass spectra of the standards

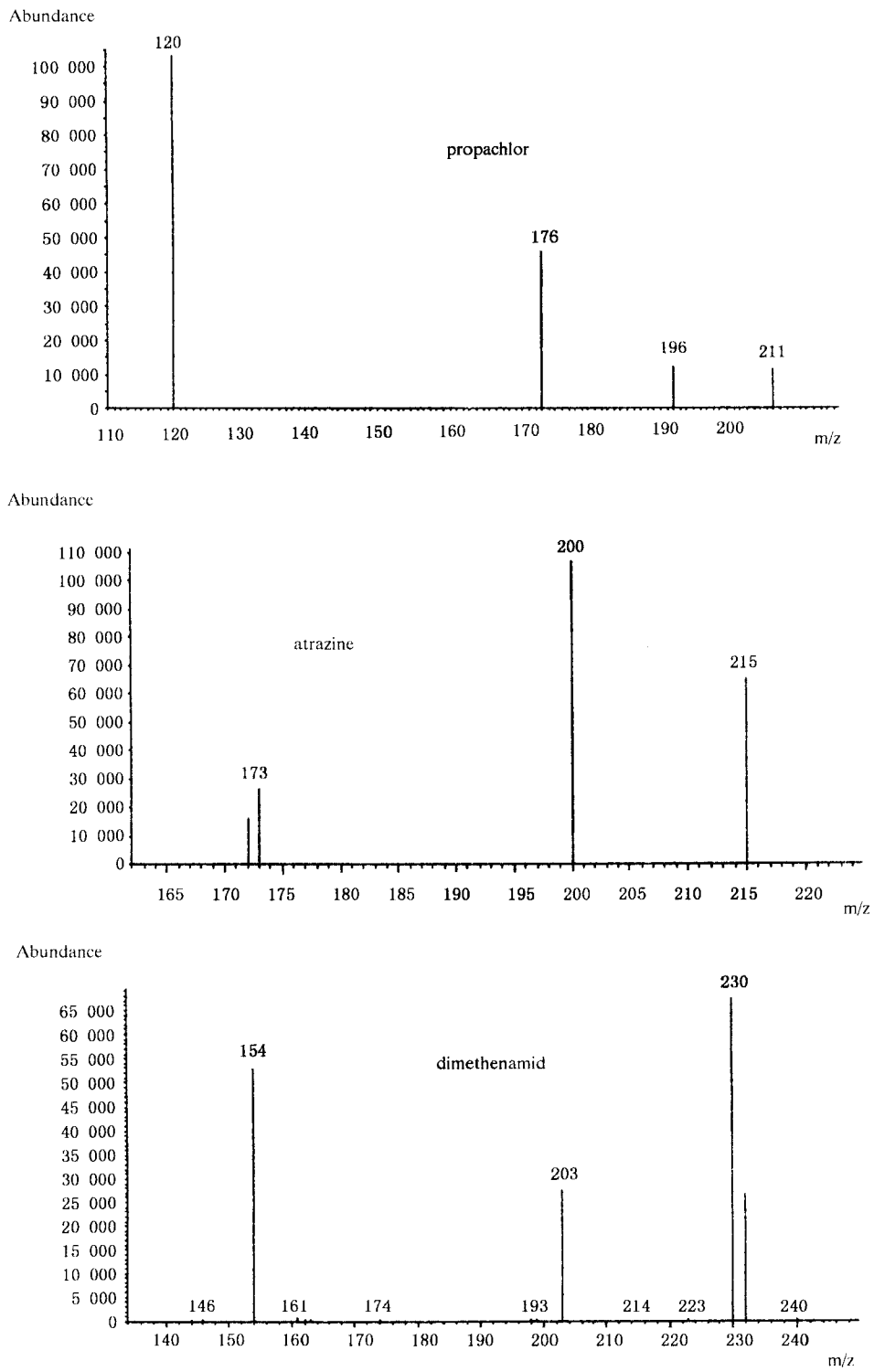


Fig C.1 SIM mass spectra of propachlor, atrazine, dimethenamid

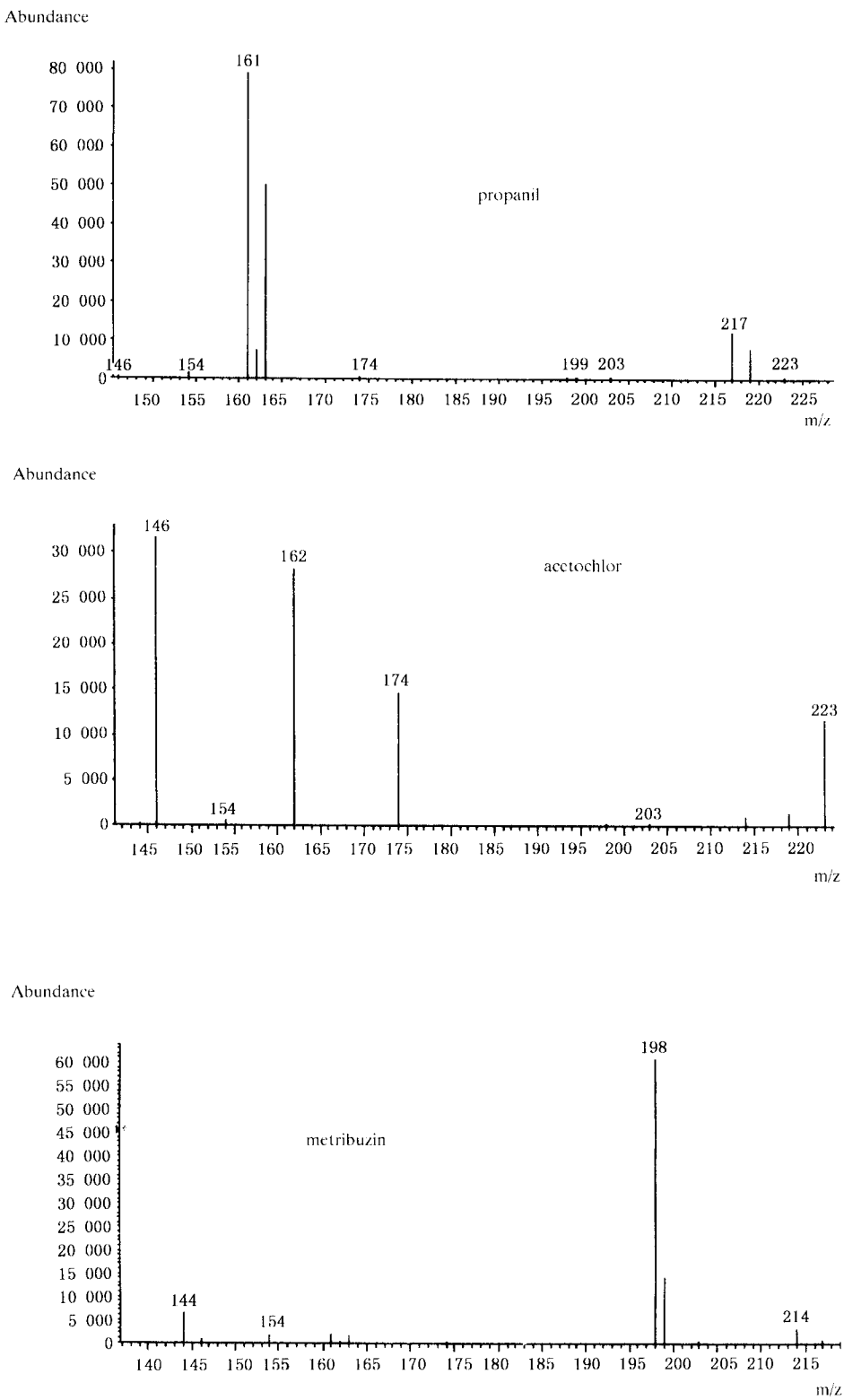


Fig C.2 SIM mass spectra of propanil, acetochlor, metribuzin

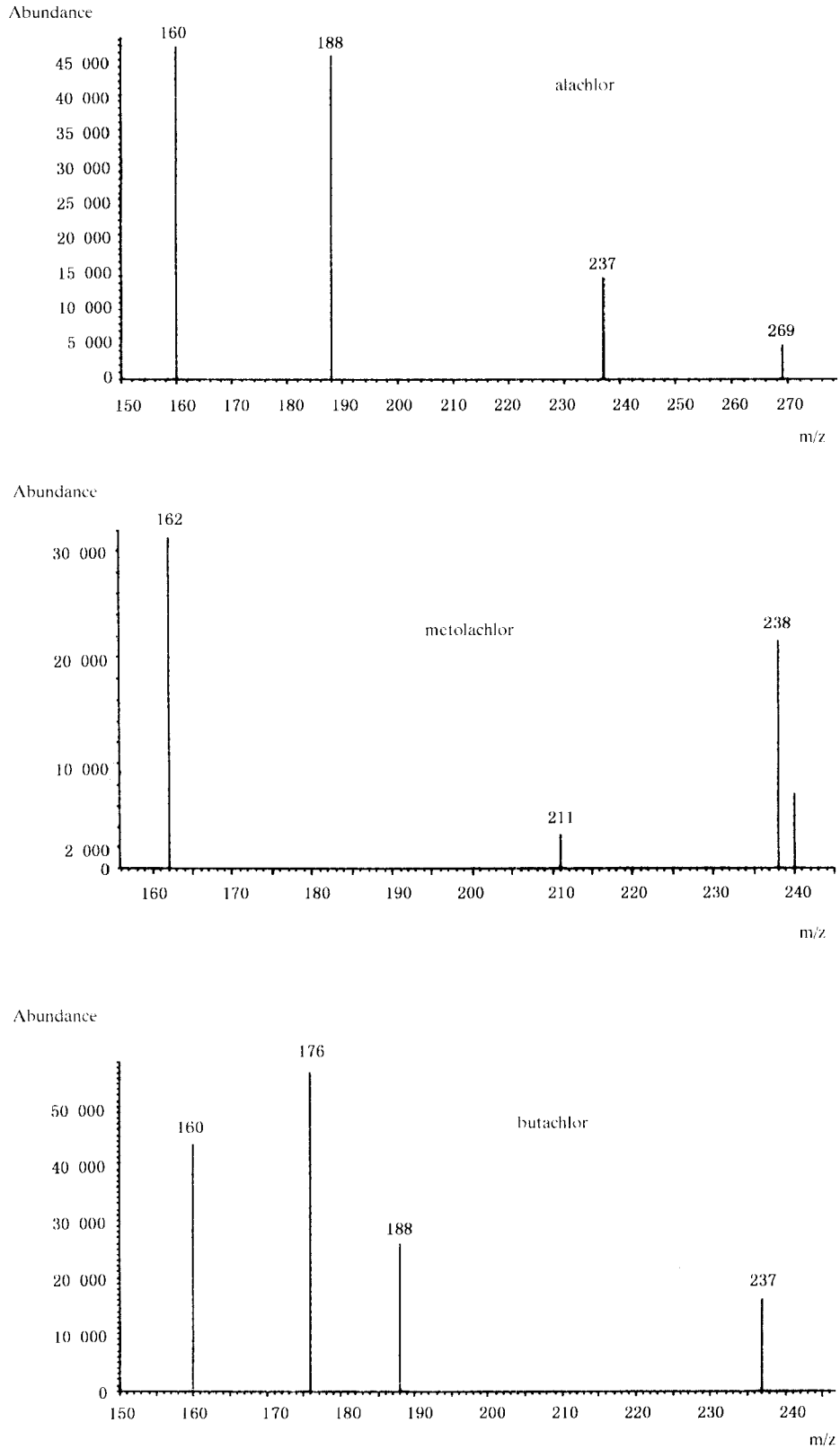


Fig C. 3 SIM mass spectra of alachlor, metolachlor, butachlor

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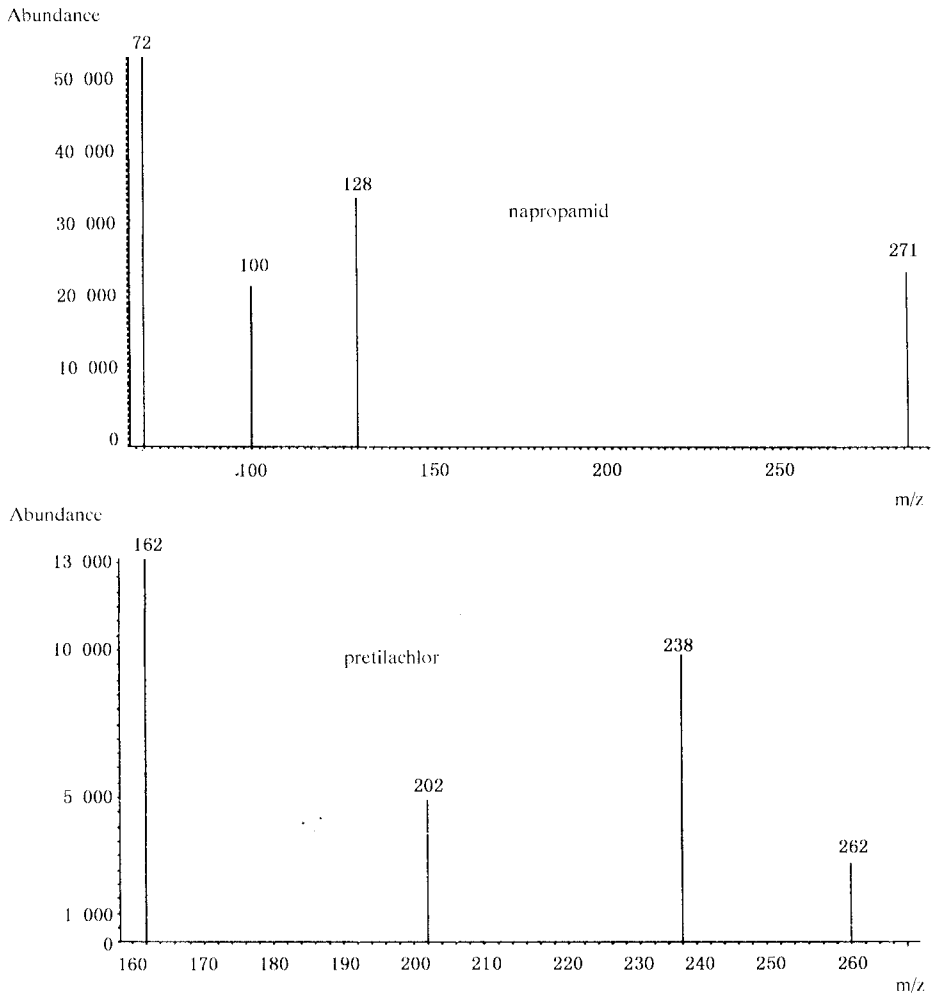

Fig C.4 SIM mass spectra of napropamid, pretilachlor

SN/T 1737.1-2006

书号:155066·2-16837
定价: 14.00 元