SN

中华人民共和国出入境检验检疫行业标准

SN/T 1606—2005

进出口植物性产品中苯氧羧酸类除草剂残留量检验方法　气相色谱法

Inspection of phenoxy acid herbicides residues in products of plant origin for import and export—GC

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前　言

本标准的附录A、附录B和附录C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：中华人民共和国上海出入境检验检疫局。

本标准主要起草人：李波、郭德华、俞秋蓉、韩丽、王敏、王传现、王东辉、魏玉璞。

本标准系首次发布的出入境检验检疫行业标准。

进出口植物性产品中苯氧羧酸类除草剂残留量检验方法　气相色谱法

1　范围

本标准规定了进出口粮谷中麦草畏、2,4-滴丙酸、2,4-滴、2,4,5-三氯苯氧基丙酸、2,4,5-三氯苯氧基乙酸、2,4-滴丁酸残留量的抽样、制样和气相色谱-质谱测定方法。

本标准适用于进出口小麦、大麦、大豆、油菜籽和大米中麦草畏、2,4-滴丙酸、2,4-滴、2,4,5-三氯苯氧基丙酸、2,4,5-三氯苯氧基乙酸、2,4-滴丁酸残留量的检验。

2　抽样和制样

2.1　检验批

以不超过 4 000 袋为一检验批。

同一检验批的商品应具有相同的特征，如包装、标记、产地、规格和等级等。

2.2　抽样数量

按式(1)确定抽样数量。

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

式中：

N——全批袋数；

a——抽样袋数。

注：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：不锈钢管，全长 55 cm(包括手柄)，直径 1.5 cm，沟槽长度应超过袋对角线长度的一半。

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，提起约成 45°倾角，倒拖约 1 m，使袋内货物全部倒出。查看袋内和袋间品质是否均匀。确认情况正常后，用取样铲随机在各部位抽取样品，立即将样品倒入盛样器内。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器内。每袋抽取样品数量应与 2.4.1 基本一致。

2.4.3　大样缩分

集中倒包抽样和袋内抽样所取全部样品，倒于分样布上，用分样板按四分法缩分出样品不少于

2 kg，盛于样品筒内，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出约 1 kg，全部磨碎并通过 20 目筛，混匀，均分成两份试样，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。

3 测定方法

3.1 方法提要

试样中的苯氧羧酸类除草剂用丙酮-乙醚在 pH 值为 2 的酸性条件下提取，提取液经氢氧化钾溶液净化除去脂溶性杂质后，再调 pH 值至小于 2 后，用乙醚提取，浓缩，重氮甲烷衍生化，用配有多级质量选择检测器的气相色谱仪测定，外标法定量。

3.2 试剂和材料

除另有规定外，所用试剂均为分析纯，水为蒸馏水。

3.2.1 丙酮。

3.2.2 无水乙醚。

3.2.3 正己烷。

3.2.4 异辛烷。

3.2.5 甲醇。

3.2.6 浓盐酸。

3.2.7 浓硫酸。

3.2.8 浓磷酸。

3.2.9 酸化的无水硫酸钠：650℃灼烧 4 h，在干燥器中冷却至室温。用无水乙醚浸没 100 g 无水硫酸钠固体表面，加 0.1 mL 浓硫酸并充分混合。通风橱中挥去乙醚。酸化测试：将 1 g 硫酸钠与 5 mL 蒸馏水混合，pH 小于 4。使用前 130℃活化 4 h。

3.2.10 磷酸缓冲溶液(0.1 mol/L)：称取 12 g 磷酸二氢钠溶解于 1 L 蒸馏水中，用磷酸调节溶液 pH 到 2.5。

3.2.11 三甲硅基重氮甲烷溶液：2 mol/L，市售。

3.2.12 37%氢氧化钾水溶液：称取 37 g 氢氧化钾溶解于 100 mL 蒸馏水中。

3.2.13 碱水溶液：37%氢氧化钾与蒸馏水的体积比(1+2)。

3.2.14 硫酸水溶液：硫酸-水(1+3)，储存于 4℃冰箱中。

3.2.15 麦草畏标准品：纯度≥99%。

3.2.16 2,4-滴丙酸标准品：纯度≥99%。

3.2.17 2,4-滴标准品：纯度≥99%。

3.2.18 2,4,5-三氯苯氧基乙酸标准品：纯度≥99%。

3.2.19 2,4-滴丁酸标准品：纯度≥99%。

3.2.20 2,4,5-三氯苯氧基丙酸标准品：纯度≥97%。

3.2.21 麦草畏、2,4-滴丙酸、2,4-滴、2,4,5-三氯苯氧基丙酸、2,4,5-三氯苯氧基乙酸、2,4-滴丁酸标准储备液：各准确称取 0.010 0 g 标准品，分别用甲醇溶解定容至 100 mL，溶液浓度为 100 μg/mL，存放于 4℃冰箱中。

3.2.22 麦草畏、2,4-滴丙酸、2,4-滴、2,4,5-三氯苯氧基丙酸、2,4,5-三氯苯氧基乙酸、2,4-滴丁酸标准混合溶液：根据需要用甲醇稀释成适用浓度的标准混合溶液。

3.3 仪器和设备

3.3.1 气相色谱仪:配有多级质量选择检测器(MSMS)。

3.3.2 振荡器。

3.3.3 涡旋器。

3.3.4 离心机:5 000 r/min。

3.3.5 旋转蒸发器。

3.3.6 氮吹仪。

3.3.7 塑料离心瓶:150 mL。

3.3.8 分液漏斗:125 mL、500 mL。

3.3.9 容量瓶:50 mL、100 mL。

3.3.10 离心管:50 mL、100 mL。

3.3.11 衍生瓶:4 mL。

3.3.12 浓缩瓶:150 mL。

3.3.13 酸化的无水硫酸钠干燥柱:80 mm×20 mm(内径)筒形漏斗,底部垫少许脱脂棉,再装入50 mm高的酸化无水硫酸钠。

3.3.14 锥形瓶:500 mL,具塞。

3.3.15 微量注射器:10 μL。

3.4 测定步骤

3.4.1 提取

准确称取 10.0 g 磨碎的均匀试样于 150 mL 塑料离心瓶中,加入 30 mL 磷酸缓冲溶液,混匀,用浓盐酸调节 pH 至 2,加入 10 mL 丙酮,振荡 20 min,再加入 40 mL 无水乙醚,振荡 20 min,于 3 500r/min 离心 5 min。将上层溶液转移至装有 200 mL 蒸馏水的 500 mL 分液漏斗中,残渣再分别用 10 mL 丙酮和 40 mL 无水乙醚重复提取两次,合并上层溶液于上述分液漏斗中,轻缓振摇 1 min,静置分层,收集乙醚层,水层再用 25 mL 无水乙醚重复提取一次,合并乙醚层,于 30℃水浴下减压浓缩至约 10 mL。

3.4.2 净化

将试样溶液移入 50 mL 离心管中,加入 15 mL 碱水溶液,充分混匀 2 min,于 1 500 r/min 离心 10 min,移取水相,乙醚相再用 15 mL 碱水溶液重复提取两次,合并水相,若试样含油脂量高(如大豆、油菜籽等),附加 10 mL 无水乙醚于水相中,充分混匀 2 min,于 1 500 r/min 离心 10 min,弃醚层。水相转移至 125 mL 分液漏斗中,小心用硫酸水溶液调节 pH 小于 2,冷却后,加入 40 mL 无水乙醚,振摇 2 min,静置分层,收集乙醚层。水层再用 20 mL 无水乙醚重复提取两次,合并乙醚层。经酸化的无水硫酸钠干燥柱脱水,收集于含 10 g 酸化的无水硫酸钠的锥形瓶中,不时振摇,2 h 后,倾出乙醚相于 30℃水浴下减压浓缩至近干。

3.4.3 衍生化

将残渣用无水乙醚溶解并转移至 4 mL 衍生瓶中,在 30℃水浴下用平缓氮气流吹干,加入 200 μL 异辛烷、200 μL 甲醇、400 μL 三甲硅基重氮甲烷溶液,涡旋混匀,70℃下保持 10 min。冷至室温后,用平缓氮气流吹干,用正己烷定容至 1 mL,过 0.45 μm 微孔滤膜,滤液供气相色谱-质谱测定。

标准工作溶液同步进行衍生测定。

3.4.4 测定

3.4.4.1 气相色谱-质谱条件

a) 色谱柱:CP-SIL8 LOW BLEED/MS 型毛细管柱,60 m×0.25 mm(内径)×0.25 μm(膜厚),或相当者;

b) 载气:氦气,纯度≥99.999%,流速 1.2 mL/min;

c) 柱温:70℃,保持 1 min,以 10℃/min 的速度升温到 190℃,保持 2 min,再以 5℃/min 的速度升

温到 250℃,保持 10 min;

d) 进样口温度:260℃;

e) 进样方式:无分流进样,0.75 min 后开阀;

f) 进样量:1 μL;

g) 离子阱温度:150℃;

h) 传输线温度:200℃;

i) 灯丝电流:80 μA;

j) 溶剂延迟:14.20 min;

k) MS/MS 监测:六种苯氧羧酸类除草剂根据保留时间分为六个时段检测,每种化合物的分析时段、保留时间、母离子、定性子离子、定量子离子、质量扫描范围、碰撞电压值等参数,参见附录 A。

3.4.4.2 气相色谱-质谱测定

根据样液中被测组分含量,选定浓度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。对标准工作溶液与样液等体积参插进样测定。在上述色谱条件下,除草剂标准品对应的衍生物选择离子色谱图参见附录 B。

定性测定,样液如果检出的色谱峰的保留时间与标准溶液中某种除草剂相一致,并且所选择的子离子均出现,而且之间的丰度比也相一致,则可判定试样中含有该种除草剂。除草剂标准品对应的衍生物的质谱图参见附录 C 。

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

用色谱数据处理机或按式(2)计算样品中各种苯氧羧酸类除草剂残留含量,计算结果应将空白值扣除。

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

式中:

X——试样中各种苯氧羧酸类除草剂的残留含量,单位为毫克每千克(mg/kg);

A——样液中各种苯氧羧酸类除草剂的峰面积;

A_s——标准工作溶液中各种苯氧羧酸类除草剂的峰面积;

c——标准工作溶液中各种苯氧羧酸类除草剂的浓度,单位为微克每毫升(μg/mL);

V——样液最终定容体积,单位为毫升(mL);

m——试样量,单位为克(g)。

4 测定低限、回收率

4.1 测定低限

本方法对下列除草剂的测定低限为:麦草畏 0.025 mg/kg;2,4-滴丙酸 0.05 mg/kg;2,4-滴 0.05 mg/kg;2,4,5-三氯苯氧基丙酸 0.05 mg/kg;2,4,5-三氯苯氧基乙酸 0.05 mg/kg;2,4-滴丁酸 0.05 mg/kg。

4.2 回收率

在小麦、大麦、大豆、油菜籽、大米中麦草畏,2,4-滴、2,4-滴丙酸、2,4-滴丁酸、2,4,5-三氯苯氧基丙酸和 2,4,5-三氯苯氧基乙酸的添加浓度及其回收率实验数据见表 1。

表 1　实验数据表

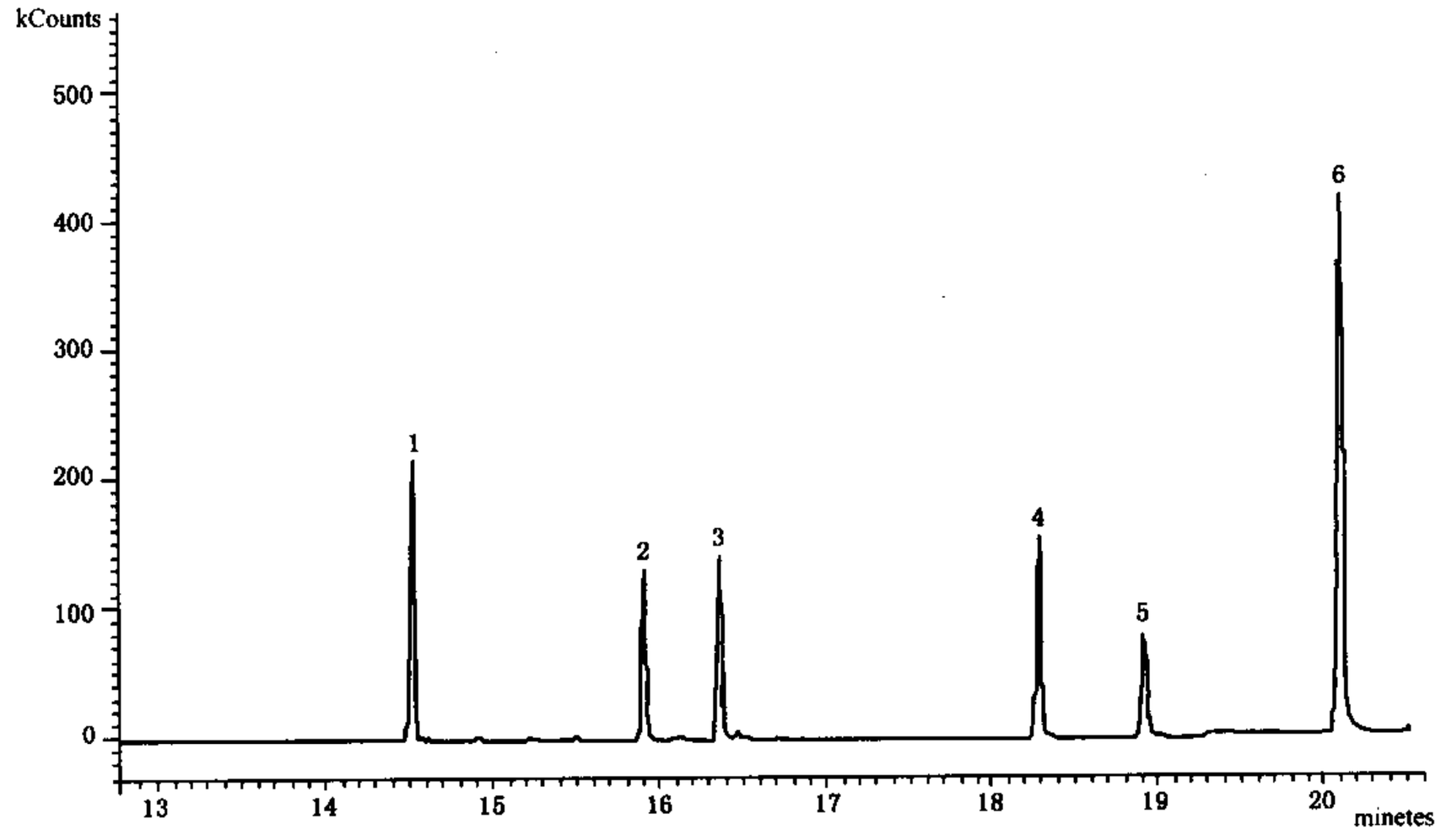
除草剂名称	添加浓度/(mg/kg)	回收率范围
麦草畏	0.025	90%～99%
	0.10	101%～103%
	0.25	96%～104%
2,4-滴丙酸	0.05	80%～90%
	0.20	85%～95%
	0.50	90%～100%
2,4-滴	0.05	78%～90%
	0.20	80%～95%
	0.50	88%～96%
2,4,5-三氯苯氧基丙酸	0.05	72%～84%
	0.20	75%～85%
	0.50	80%～92%
2,4,5-三氯苯氧基乙酸	0.05	82%～92%
	0.20	92%～102%
	0.50	90%～100%
2,4-滴丁酸	0.05	70%～80%
	0.20	70%～80%
	0.50	80%～84%

附 录 A
（资料性附录）
GC-MS/MS 测定六种除草剂的检测参数

表 A.1

化合物	分析时段/min	CID 电压	质量扫描范围/amu	保留时间/min	二级质谱母离子(m/z)	二级质谱监测子离子(m/z)	定量离子(m/z)
麦草畏	14.20～15.50	0.96	45～250	14.518	203	188 175 147	188
2,4-滴丙酸	15.50～16.10	1.05	45～300	15.913	248	162 189 213	162
2,4-滴	16.10～17.00	0.65	45～250	16.377	199	156 125 141	156
2,4,5-三氯苯氧基丙酸	17.00～18.60	0.55	45～300	18.308	282	196 247 223	196
2,4,5-三氯苯氧基乙酸	18.60～19.30	1.05	45～300	18.932	233	190 159 218	190
2,4-滴丁酸	19.30～20.60	0.65	45～200	20.104	101	59 101	59

附 录 B
（资料性附录）
标准品衍生物选择离子色谱图



1——麦草畏 14.518 min；

2——2,4-滴丙酸 15.913 min；

3——2,4-滴 16.377 min；

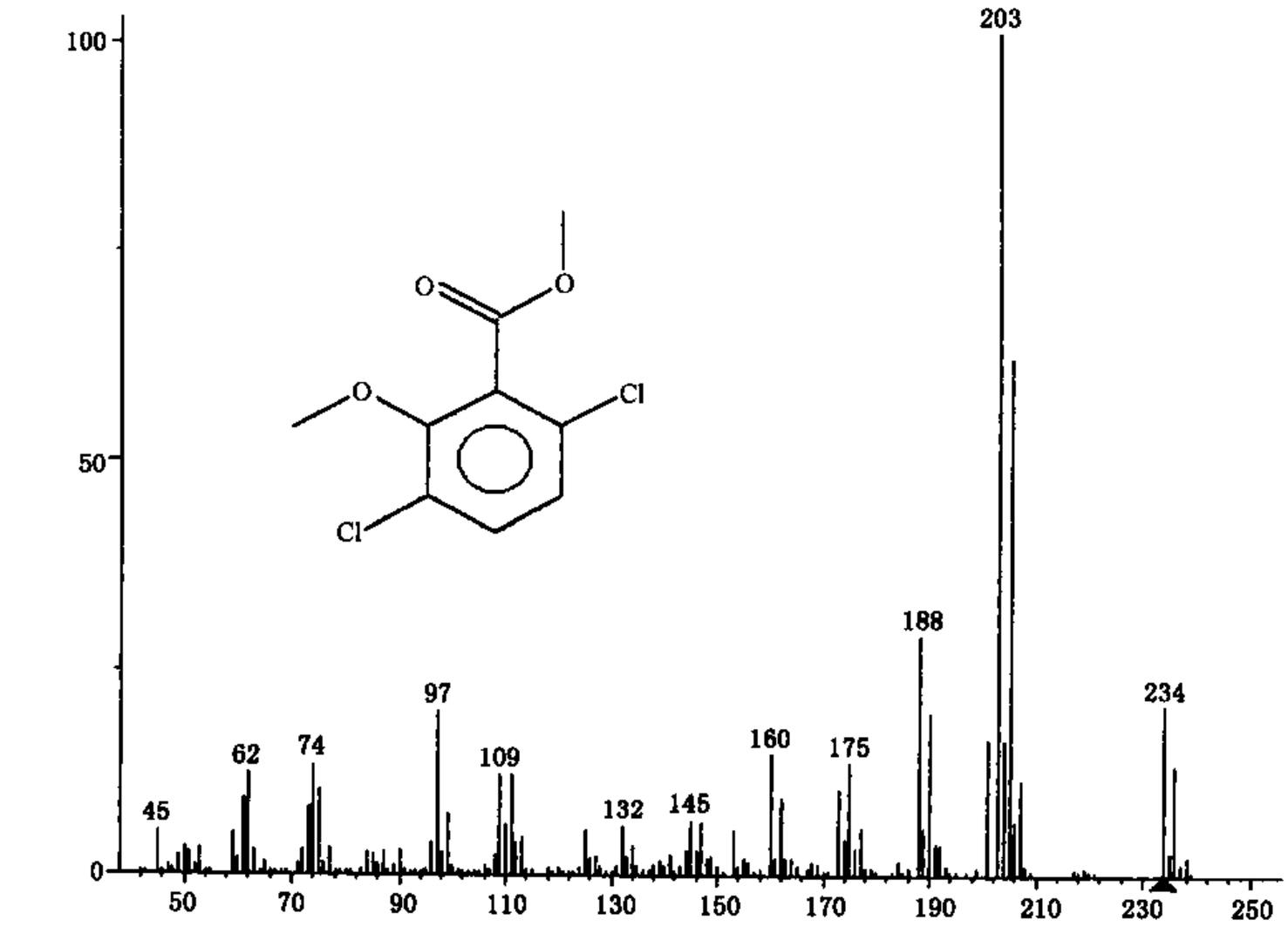
4——2,4,5-三氯苯氧基丙酸 18.308 min；

5——2,4,5-三氯苯氧基乙酸 18.932 min；

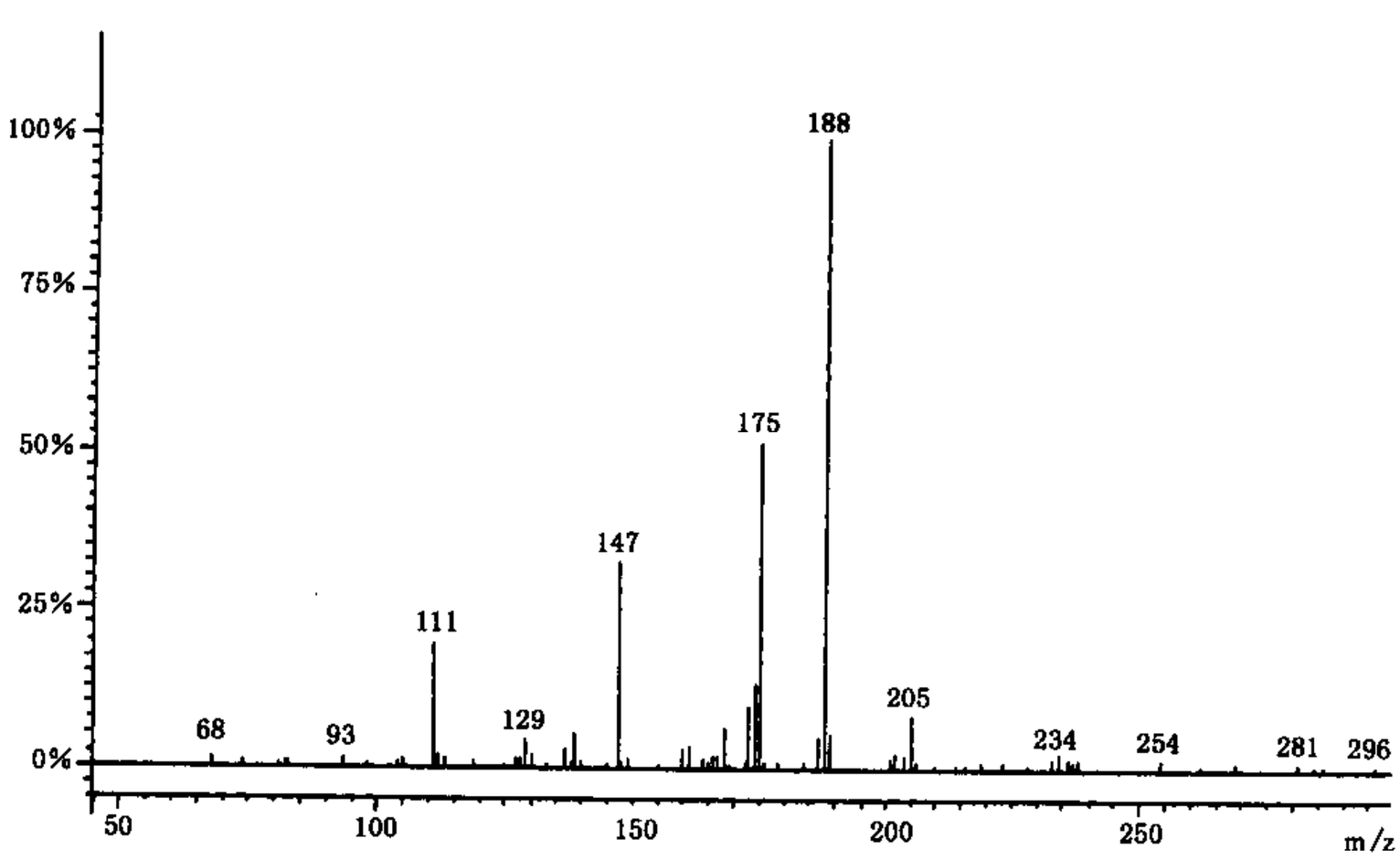
6——2,4-滴丁酸 20.104 min。

图 B.1 六种苯氧羧酸类除草剂标准品衍生物的选择离子色谱图

附 录 C
（资料性附录）
标准品质谱图

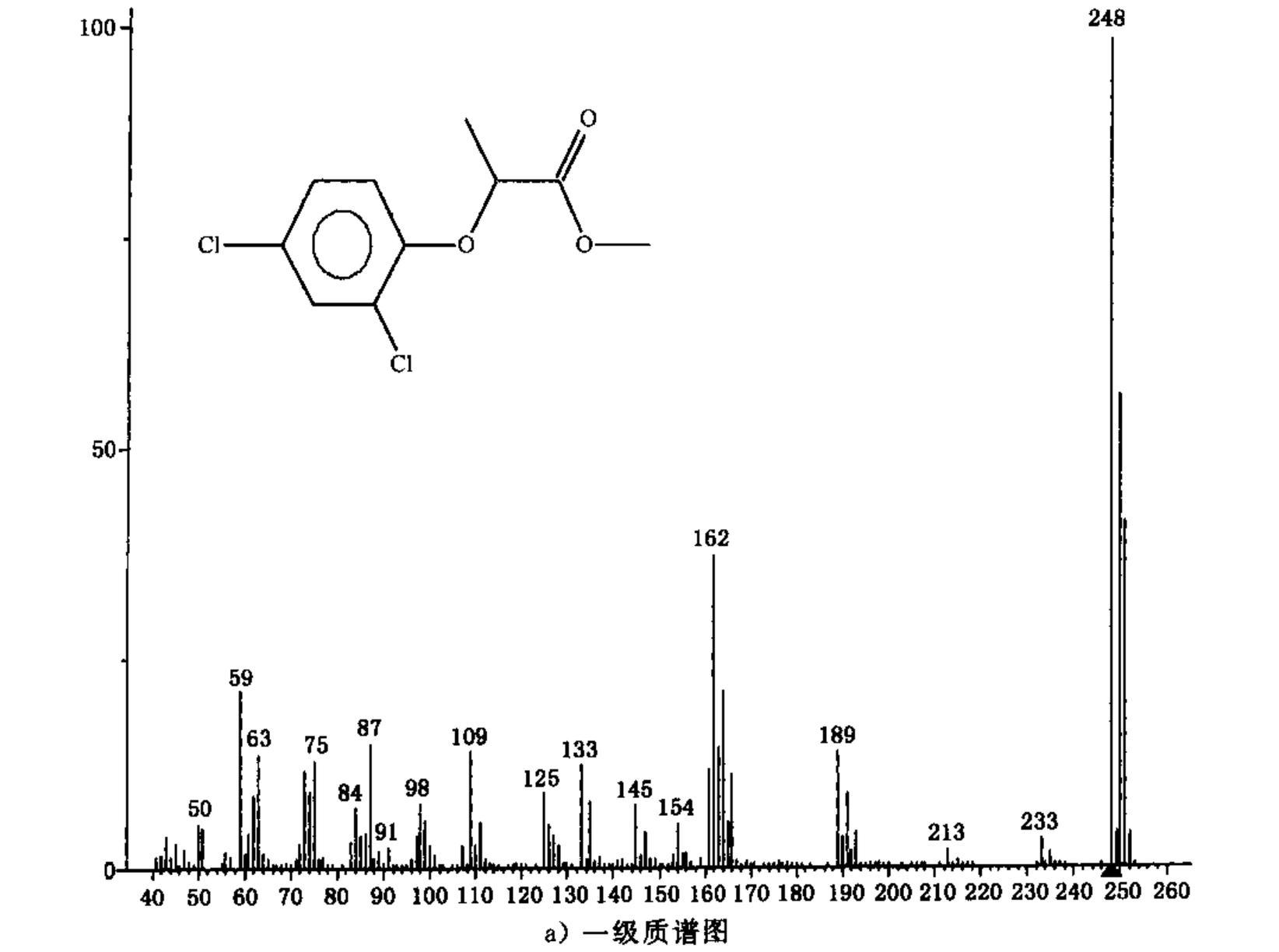


a）一级质谱图

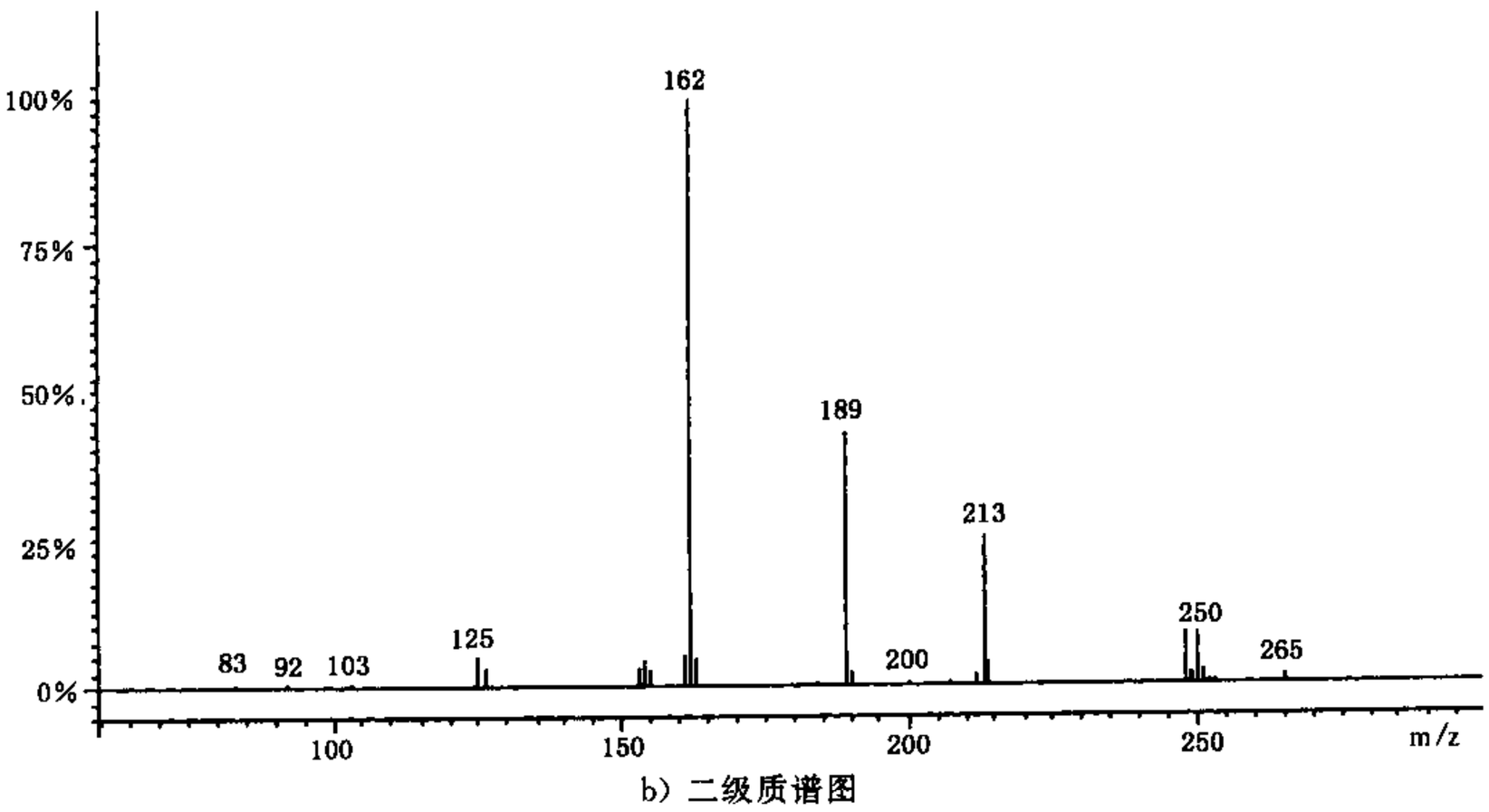


b）二级质谱图

图 C.1 麦草畏标准品衍生物的质谱图

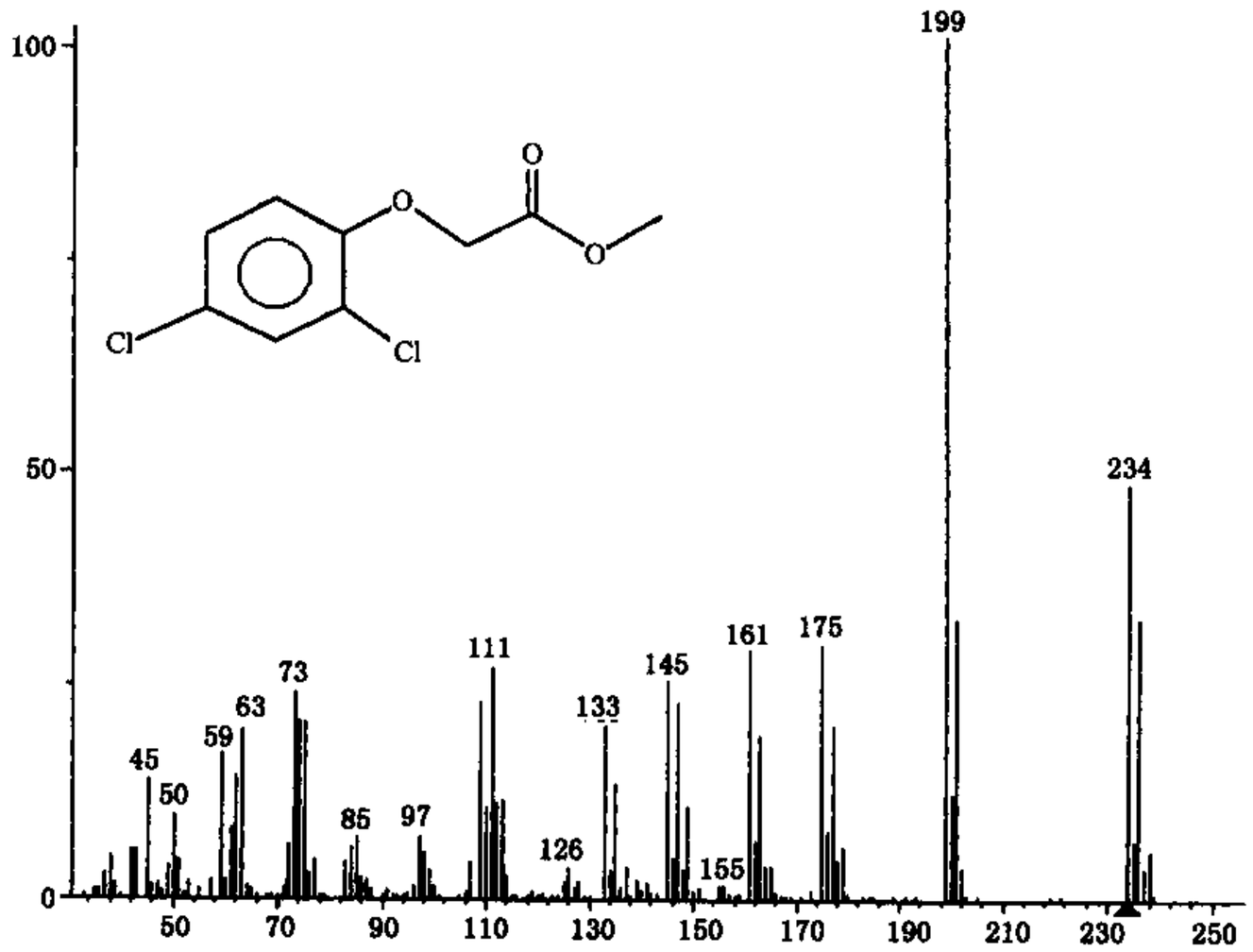


a) 一级质谱图

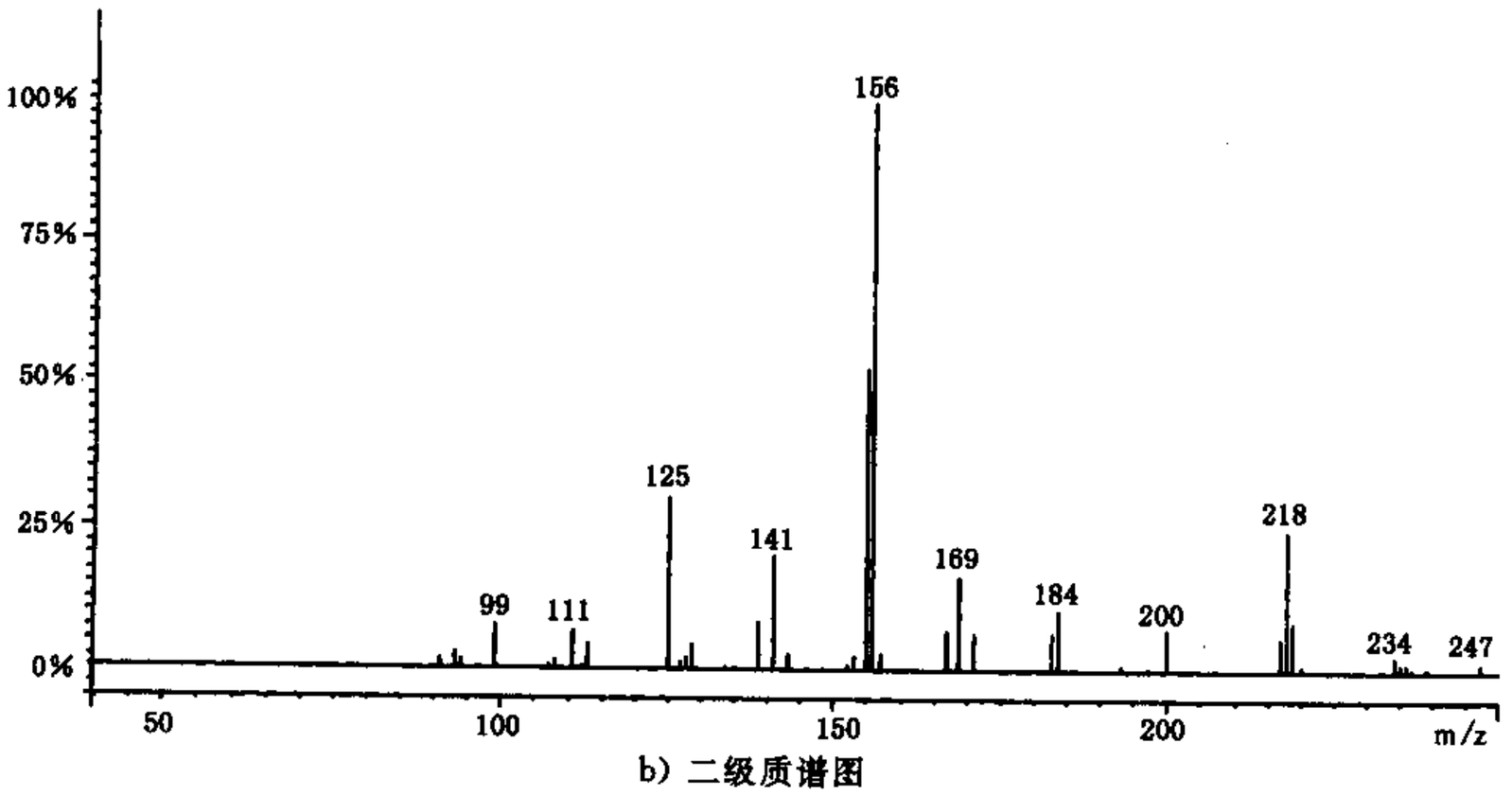


b) 二级质谱图

图 C.2　2,4-滴丙酸标准品衍生物的质谱图

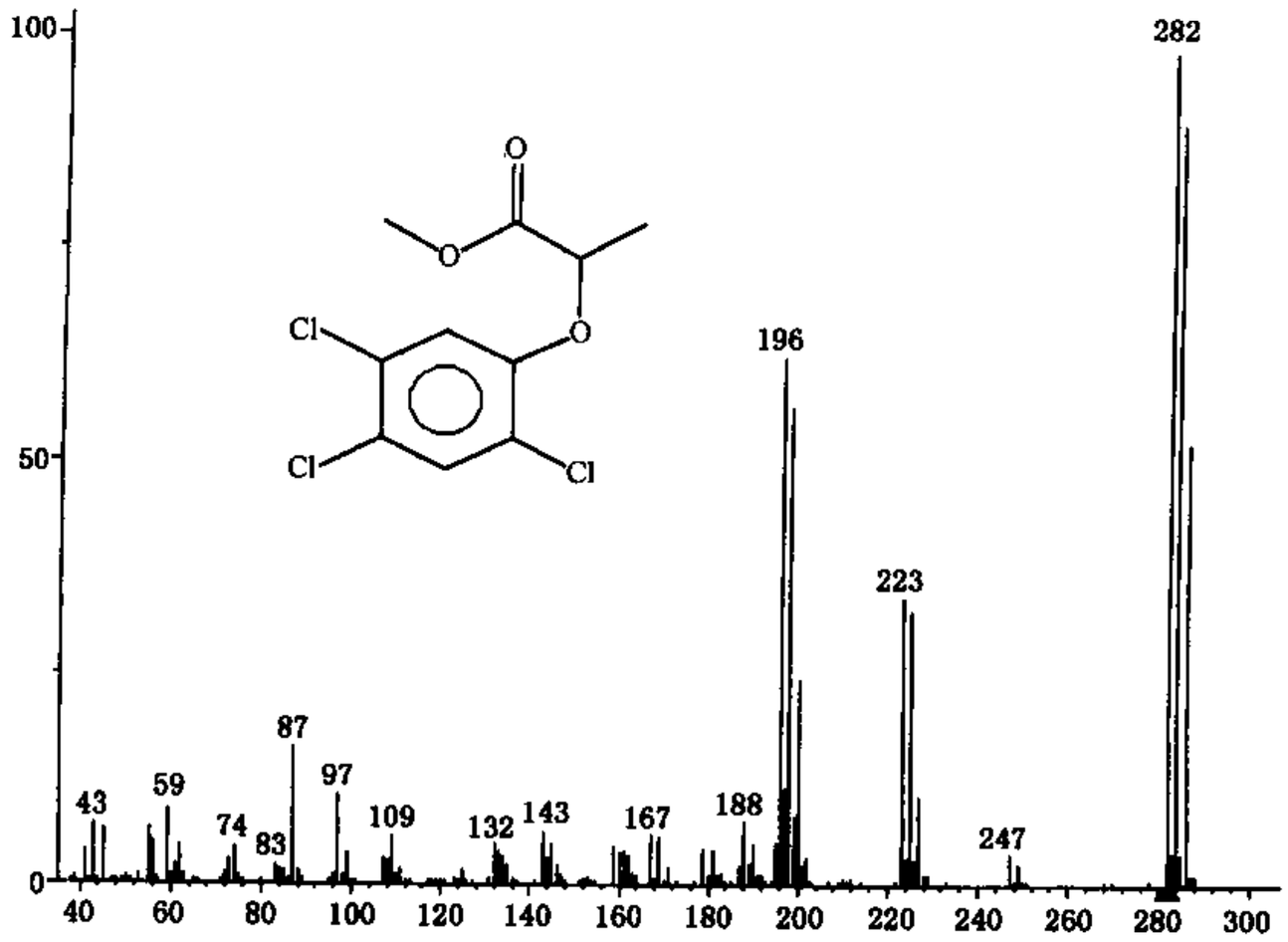


a) 一级质谱图

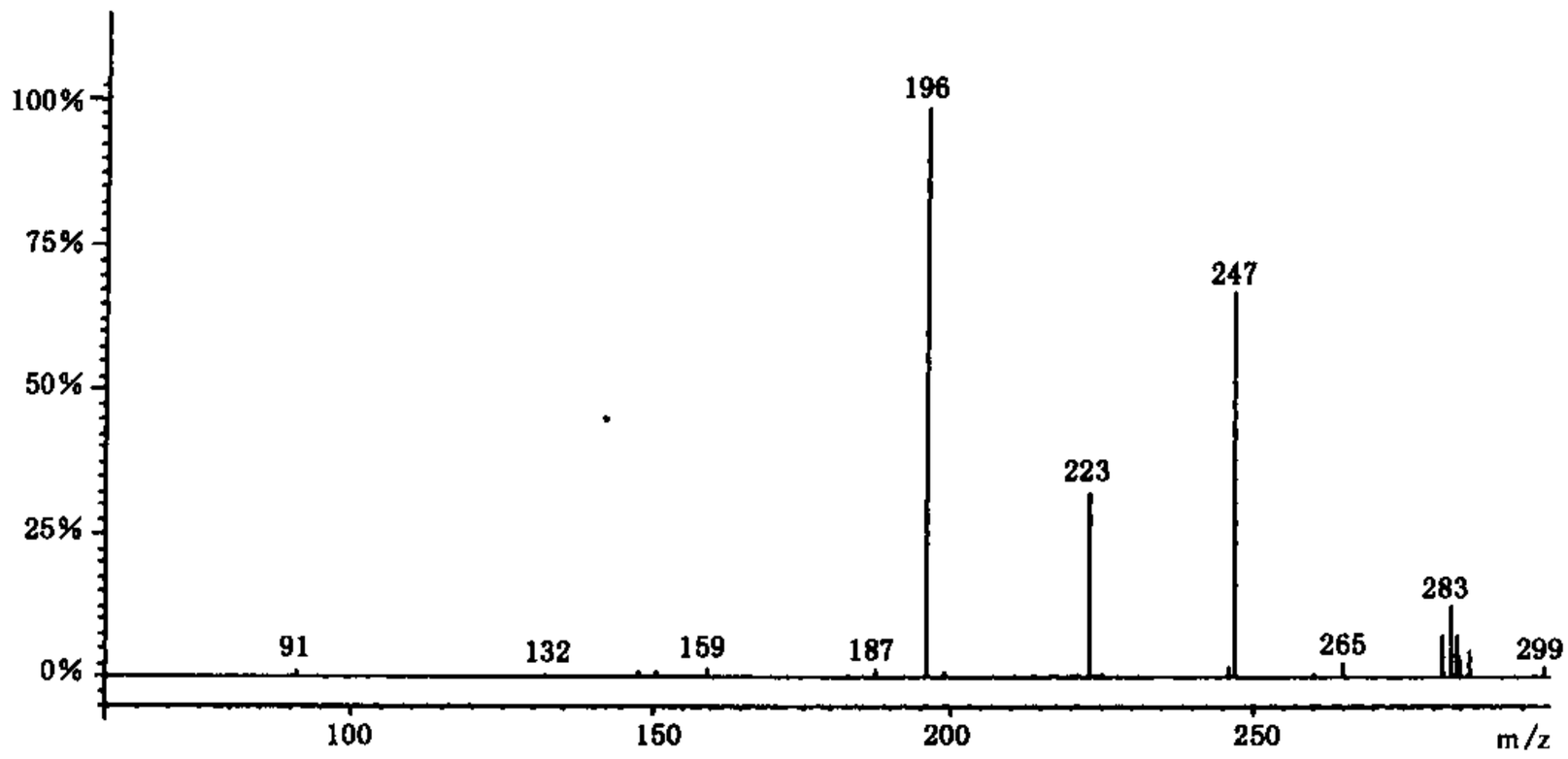


b) 二级质谱图

图 C.3　2,4-滴标准品衍生物的质谱图

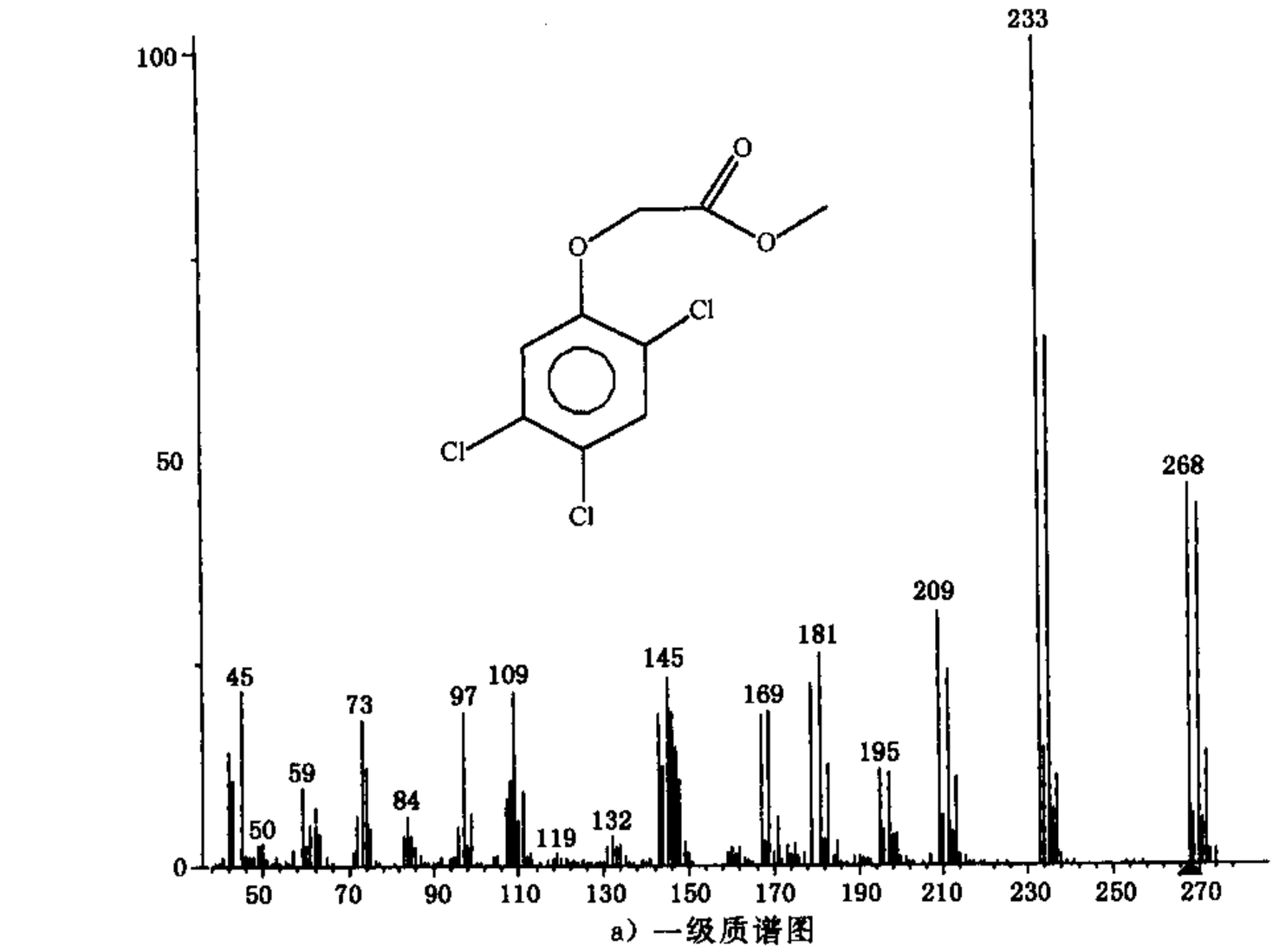


a) 一级质谱图

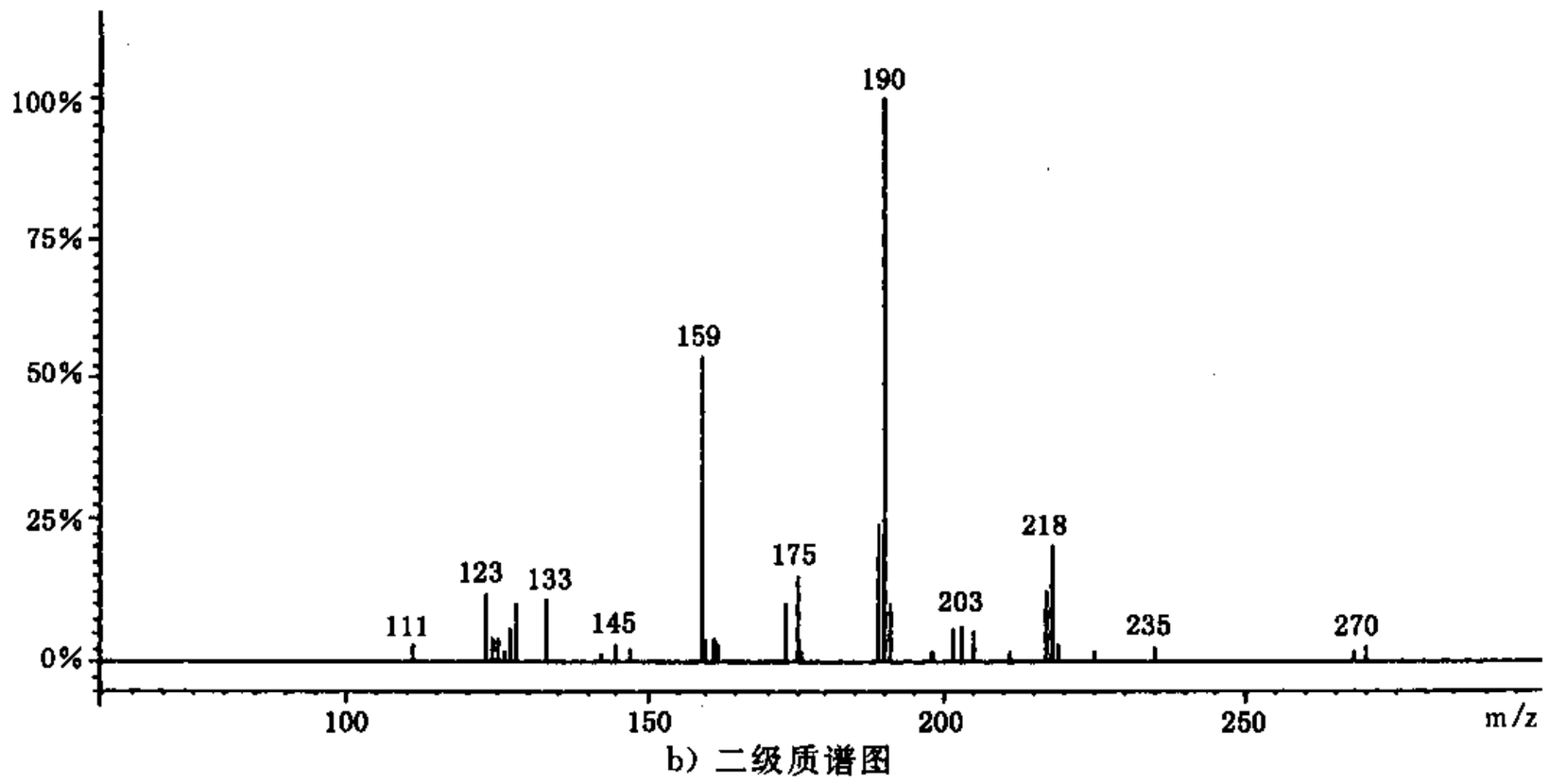


b) 二级质谱图

图 C.4　2,4,5-三氯苯氧基丙酸标准品衍生物的质谱图

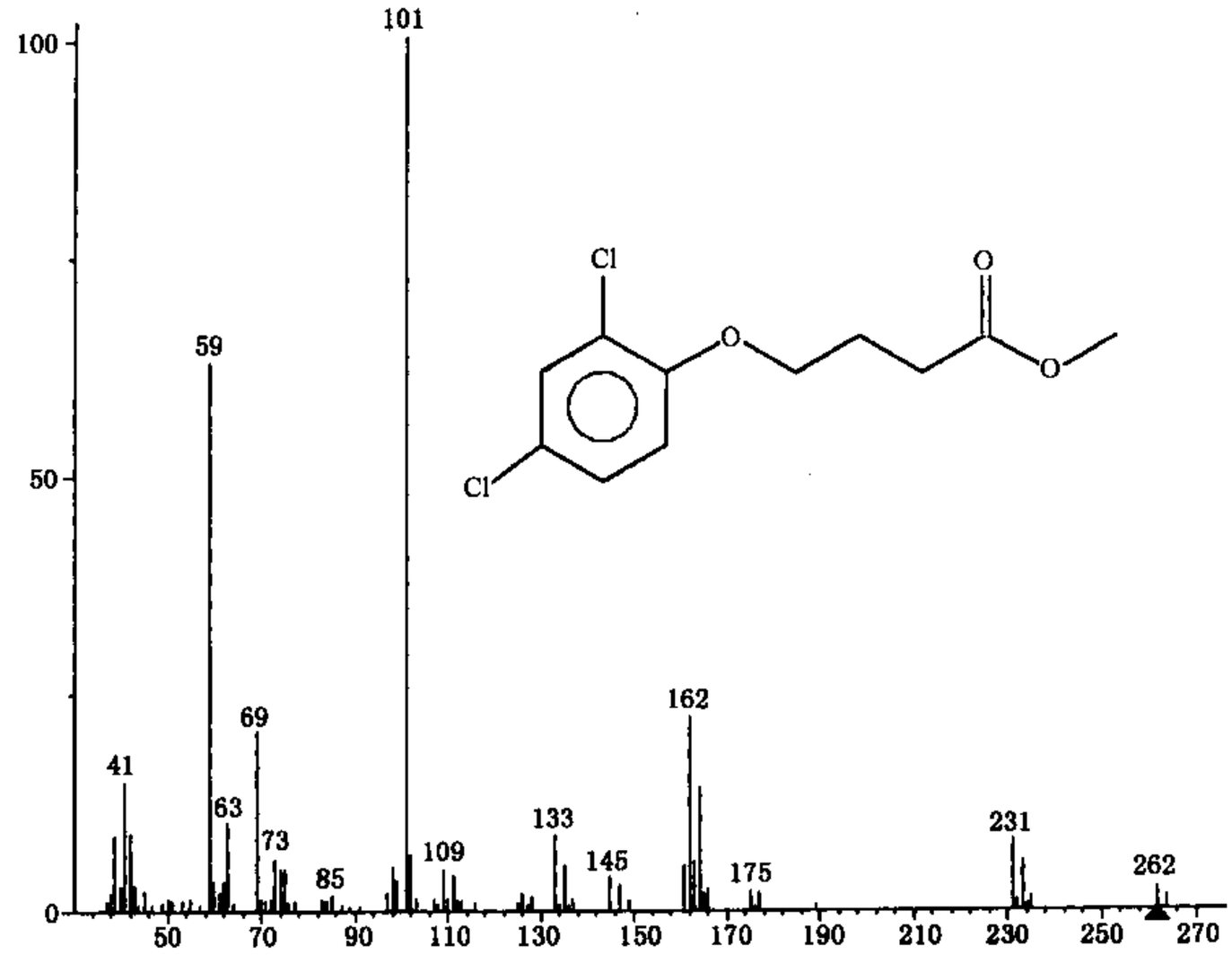


a) 一级质谱图

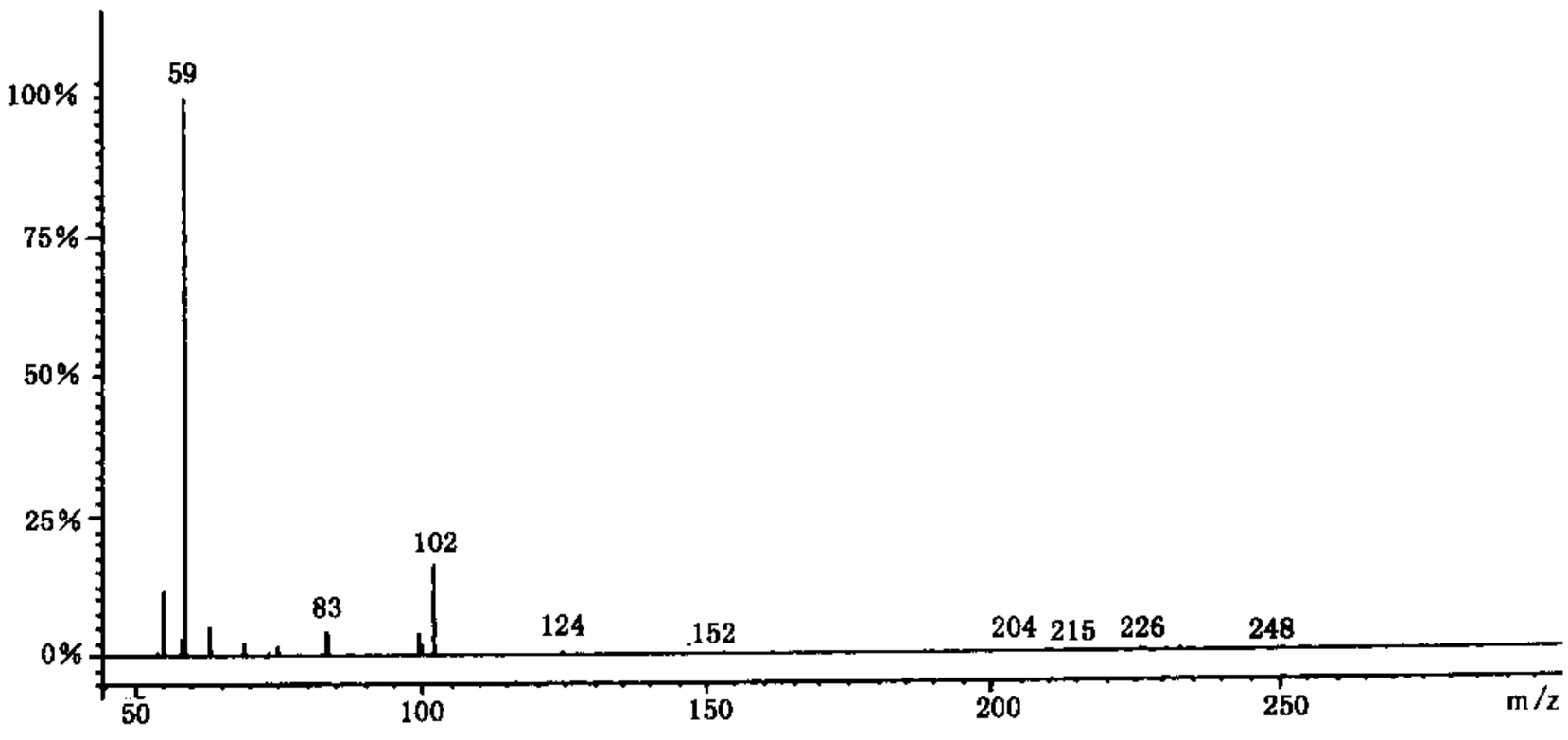


b) 二级质谱图

图 C.5　2,4,5-三氯苯氧基乙酸标准品衍生物的质谱图



a) 一级质谱图



b) 二级质谱图

图 C.6　2,4-滴丁酸标准品衍生物的质谱图

Foreword

Annex A, annex B and annex C of this standard is an 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 Shanghai Entry-Exit Inspection and Quarantine Bureau of the People's Republic of China.

The main drafters of this standard are Li Bo, Guo Dehua, Yu Qiurong, Han Li, Wang Min, Wang Chuanxian, Wang Donghui and Wei Yupu.

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

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

Inspection of phenoxy acid herbicides residues in plant origin products for import and export—GC

1 Scope

This standard specifies the methods of sampling, sample preparation and determination of 2,4-D, 2,4-DP, 2,4-DB, 2,4,5-TP, 2,4,5-T and Dicamba residues by GC/MS in plant origin products.

This standard is applicable to the determination of 2,4-D,2,4-DP,2,4-DB, 2,4,5-TP, 2,4,5-T and Dicamba residues in wheat, barley, soybean, coleseed and rice for import and export.

2 Sampling and sample preparation

2.1 Inspection lot

The quantity of an inspection lot should not exceed 4 000 packages.

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

2.2 Quantity of sample taken

Sampling taken is according to the formula (1).

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

Where:

N——total number of bags in an inspection lot;

a——number of bags to be taken.

Note: If value a is with decimal, round off the decimal part, which is added as unity to the integral part of a.

2.3 Sampling tools

2.3.1 Metallic sampler: stainless steel; length (including handle) :55 cm; diameter: 1.5 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 container: Can or 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 empting out

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

2.4.2 Sampling from inside the bags

Draw the samples from 90 percent of the number of bags specified in 2.2 (by deducting the number of bags drawn in 2.4.1.1). Along the sine wave of the pile, draw the samples from the bags of the upper, middle and lower parts around the pile at random. Insert the sampler, with its groove facing downward, diagonally into each bag, then turn the sampler by 180 degree, draw out the sampler and promptly pour the sample into a container. The quantity of the sample drawn from each bag should be basically the same as in 2.4.1.

2.4.3 Reduction of gross sample

Pour all of samples on a clean sheet, reduce to not less than 2 kg with a plate by quartering. Place in a sample container, seal, label and sent to the laboratory in time.

2.5 Preparation of test sample

Reduce the sample to ca 1 kg by quartering, grind thoroughly and let pass through a 20 mesh sieve, mix thoroughly and divide into 2 equal portions. Each portion is placed in a clean container as the test sample, seal and label.

2.6 Storage of test sample

The test samples should be stored below −5 ℃ and kept away from light.

3 Method of determination

3.1 Principle

Phenoxy-acid Herbicides in the test sample are extracted with acetone-ether under the condition of acid with a pH = 2. After cleaned up to deprivate the liposolubility impurity through sodium hydroxide solution, adjust the pH to below 2, then extracted with ether, concentrated, and derivatizated by diazomethane. Determination made by means of gas chromatography equipped with multiple mass selective detector, using external standard method to quantitation.

3.2 Reagents and materials

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

3.2.1 Acetone.

3.2.2 Anhydrous ether.

3.2.3 Hexane.

3.2.4 Isooctane.

3.2.5 Methanol.

3.2.6 Concentrated hydrochloride acid.

3.2.7 Concentrated sulfuric acid.

3.2.8 Concentrated phosphoric acid.

3.2.9 Acidified anhydrous sodium sulfate: Heated at 650℃ for 4 hours, then cooled to room temperature. 100 g anhydrous sodium sulfate are covered the solid by anhydrous ether; then add 0.1 mL of concentrated sulfuric acid and mix thoroughly. Remove the ether in the fume hood. Acidify test: Mix lg of the resulting solid with 5 mL of distilled water and measure the pH of the mixture. The pH must be below 4. Activated 4 hours at 130℃ before using.

3.2.10 Phosphate buffer (0.1 mol/L): weight 12 g sodium phosphate (NaH_2PO_4) and dissolve in 1.0 L-distilled water. Add phosphoric acid to adjust the pH to 2.5.

3.2.11 Diazomethane: 2 mol/L, commercially.

3.2.12 37% potassium hydroxide solution: weight 37 g potassium hydroxide and dissolve in 100 mL-distilled water.

3.2.13 Alkaline (basic) solution: the volume ratio of 37% potassium hydroxide and distilled water is (1+2).

3.2.14 Sulfate acid solution: the volume ratio is sulfate acid -water(1+3), stored in refrigerator at 4℃.

3.2.15 Dicamba standard: Purity≥99%.

3.2.16 2,4-DP standard: Purity≥99%.

3.2.17 2,4-D standard: Purity≥99%.

3.2.18 2,4,5-T standard: Purity≥99%.

3.2.19 2,4-DB standard: Purity≥99%.

3.2.20 2,4,5-TP standard: Purity≥97%.

3.2.21 Dicamba; 2,4-DP; 2,4-D, 2,4,5-TP; 2,4,5-T; 2,4-DB standard stock solution: accurately weighing approximate 0.010 0 g standard and volume to 100 mL with methanol. The solution is 100 μg/mL in concentration and stored in the refrigerator at 4℃.

3.2.22 Dicamba; 2,4-DP; 2,4-D; 2,4,5-TP; 2,4,5-T; 2,4-DB standard mixture solution: Dilute the standard stock solution with methanol to the required concentration as the standard working solution.

3.3 Apparatus and equipment

3.3.1 Gas chromatograph: equipped with multiple select ion mass detector (MS/MS).

3.3.2 Wrist shaker.

3.3.3 High speed homogenizer.

3.3.4 Centrifuge: 5 000 r/min.

3.3.5 Rotary evaporator.

3.3.6 Nitrogen evaporator

3.3.7 Centrifuge bottle-Pasteur: 150 mL.

3.3.8 Separatory funnel: 125 mL, 500 mL.

3.3.9 Volumetric flasks: 50 mL, 100 mL.

3.3.10 Centrifuge tube: 50 mL, 100 mL.

3.3.11 Derivation bottle: 4 mL.

3.3.12 Concentration bottle: 150 mL.

3.3.13 Acidified anhydrous sodium sulfate drying column: 80 mm × 20 mm (internal diameter)

funnel. A little absorbent cotton cover the bottom and add acidified anhydrous sodium sulfate with 50 mm high.

3.3.14 Erlenmeyer flask: 500 mL, with stopcock.

3.3.15 Micro-syringe: 10 μL.

3.4 Procedure

3.4.1 Extraction

Accurately weigh 10.0 g test sample ground finely into a 150 mL plastic Centrifuge bottle, add 30 mL phosphate buffer, mixing uniformly, and adjust the pH to 2 with hydrochloric acid. Add 10 mL acetone and shock for 20 min, then add 40 mL ether again and shock for 20 min. Centrifuge for 5 min under 3 500 r/min. After transfer the upper solution to a 500 mL Separatory funnel contained 200 mL distilled water, residents are repeat extracted for 2 times with 10mL acetone and 40 mL anhydrous ether. Combine the upper layer solution to the same 500 mL Separatory funnel, gently mix for 1 min and set aside for separating. Collect the ether layer, and the aqueous fraction is re-extracted one time using 25 mL of anhydrous ether. Combine ether extract and concentrate to approximately 10 mL in decompression in a water bath at 30℃.

3.4.2 Cleanup

Transfer the above solution to a 50 mL Centrifuge tube. Add 15 mL alkaline water solution. Homogenate for 2 min with high speed, and centrifuge for 10 min at 1 500 r/min. Transferring water phase, ether layer is extracted to repeat 2 times with 15 mL alkaline water solution. Combine water phase. If the test sample containing high oil fat (such as bean and rapeseed), add 10 mL anhydrous ether again and homogenate for 2 min with high speed, then centrifuge for 10 min under 1 500 r/min. Discard the ether fraction. Transfer the aqueous layer to a 125 mL separatory funnel, add 40 mL anhydrous ether and shake for 2 min, stand to separate, collect the ether fraction. The aqueous layer is extracted 2 times again with 20 mL anhydrous ether, then combine the ether phase, and let pass through the column of acidified anhydrous sodium sulfate to remove the water. Collect the anhydrous ether in a Erlenmeyer flask which contain 10 g anhydrous sodium sulfate, mix well. After 2 h, evaporate to near dryness in a rotary evaporator with a bath temperature below 30℃.

3.4.3 Derivatization

The residue is transferred to derivatization bottle with ether and dried by a gentle stream of nitrogen in a water bath at 30℃. Add 200 μL isooctane, 200 μL methanol and 400 μL three methyl silica diazomethane. Vortex shake and hold 10 min at 70℃ and cool to room temperature. After evaperate to dryness under a gentle stream of nitrogen, dilute exactly to 1 mL with *n*-hexane and through 0.45 μm millipore filter. The filtrate is for GC/MSMS.

Standard sample is synchronous derivatization to determination.

3.4.4 Determination

3.4.4.1 GC/MSD operating conditions

a) Column: CP-SIL8 LOW BLEED/MS capillary column, 60 m × 0.25 mm(i.d.) × 0.25 μm (film thickness), or the equivalent;
b) Carrier gas: Helium, purity≥99.999%, 1.2 mL/min;
c) Column temperature: 70℃ for 1 min, ramp at 10℃ /min to 190℃, hold for 2 min, ramp at 5℃/min to 250℃, hold for 10 min;
d) Injection port temperature: 260℃;
e) Injection mode: Splitless, purge after 0.75 min;
f) Injection volume: 1 μL;
g) Ion trap temperature: 150℃;
h) GC/MS interface temperature: 200℃;
i) Filament electricity: 80 μA;
j) Solvent delay: 14.20 min;
k) MS/MS monitor: According the retention time of six kinds of phenoxy-acid herbicide, they are separated to six periods of time to determinate. Analytical period of time, retention time, mother ion, son ion, quantitative ion, mass scan scope, voltage value of collision and the other parameters of every compound, see annex A.

3.4.4.2 GC/MSD determination

According to the approximate concentration of component determination in the test sample solution, select the standard working solution with similar concentration. The responses of herbicides in the standard working solution and sample solution should be in the linear range of the instrumental detection. The standard working solution should be injected randomly in between the injections of sample solution of equal volume. Under the above GC/MS operating conditions, for the SIM chromatogram of the herbicide standards, See Figure B.1 in annex B.

Confirmation: If there is a peak appeared at the same retention time for both of the sample solution and standard working solution, and all selected ions appeared and the ratio of abundance is according, confirm the herbicide being in the test sample. For the mass chromatogram of the herbicide standards, see Figure C.1 to C.6 of annex C.

3.4.5 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.

3.4.6 Calculation and expression of the result

The calculation of phenoxy-acid herbicides contents in the sample are carried out by GC/MSMS data processor or according to the formula (2), The blank value should be subtracted from the above result of calculation.

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

Where:

X——Each phenoxy-acid herbicide content in the sample, mg/kg;

A——Peak area of each phenoxy-acid herbicide;

A_s——Peak area of each phenoxy-acid herbicide in the standard working solution;

C——Each phenoxy-acid herbicide concentration in the standard working solution, μg/mL;

V——Final volume of sample solution, mL;

m——Mass of test sample, g.

4 Limit of determination and recovery

4.1 The limit of determination

The limit of determination of this method is as follows:

Dicamba 0.025 mg/kg;2,4-DP 0.05 mg/kg;2,4-D 0.05 mg/kg;2,4,5-TP 0.05 mg/kg;2,4,5-T 0.05 mg/kg;2,4-DB 0.05 mg/kg.

4.2 Recovery

According to the experimental data, the fortifying concentrations of each herbicide in test sample and its corresponding recoveries in wheat, barley, soybean, coleseed, rice see Table 1.

Table 1 Experimental data table

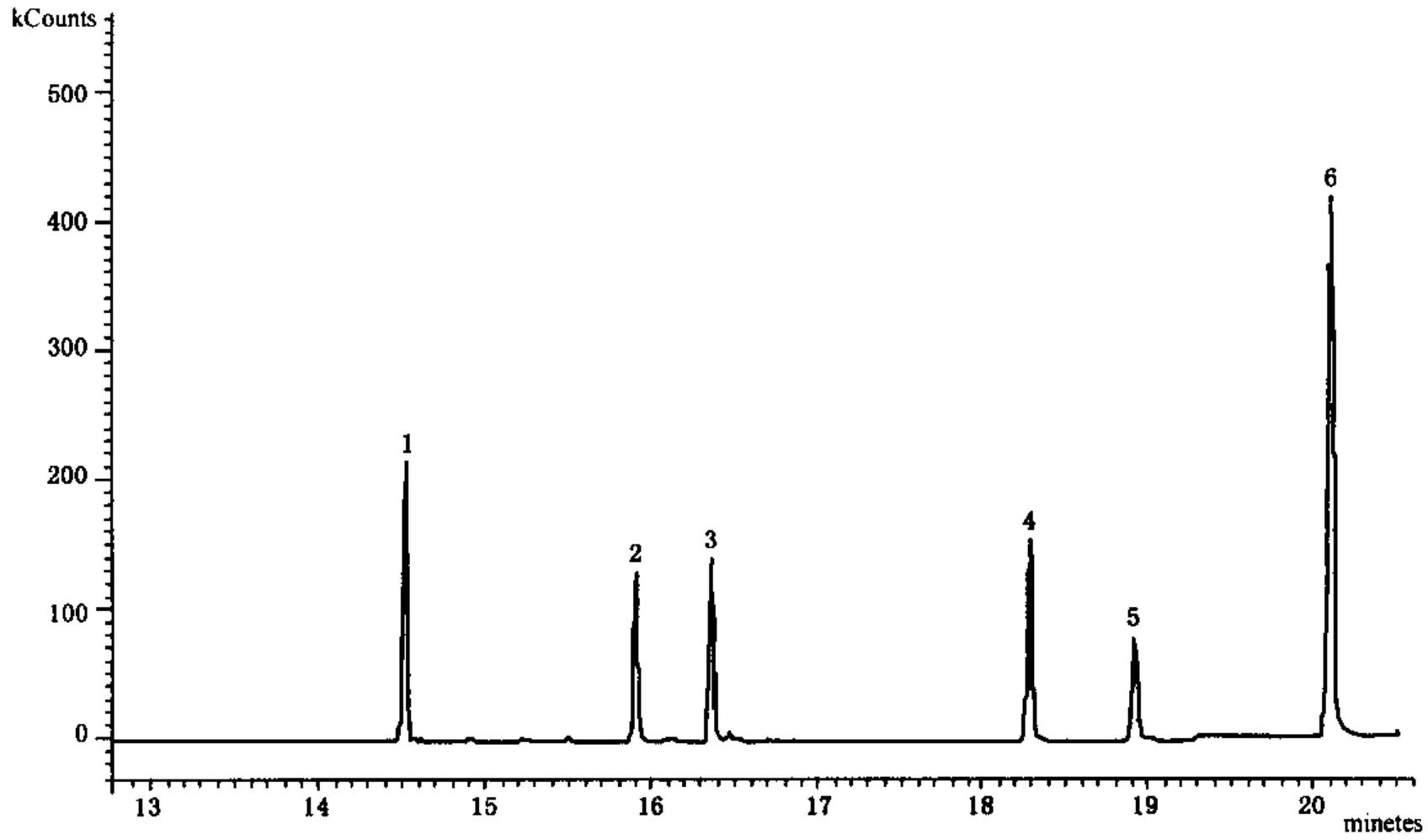
Herbicide	Fortifying concentrations/(mg/kg)	Recovery
Dicamba	0.025	90%～99%
	0.10	101%～103%
	0.25	96%～104%
2,4-DP	0.05	80%～90%
	0.20	85%～95%
	0.50	90%～100%
2,4-D	0.05	78%～90%
	0.20	80%～95%
	0.50	88%～96%
2,4,5-TP	0.05	72%～84%
	0.20	75%～85%
	0.50	80%～92%
2,4,5-T	0.05	82%～92%
	0.20	92%～102%
	0.50	90%～100%
2,4-DB	0.05	70%～80%
	0.20	70%～80%
	0.50	80%～84%

Annex A
(informative)
The parameters for determination of the six kinds of phenoxy-acid herbicides using GC-MS/MS

Table A. 1

Herbicides	periods of time/ min	voltage value of collision	Mass scan Scope/ amu	Retention time/ min	Parent ion (m/z)	product ions (m/z)	Quantitative ion (m/z)
Dicamba	14. 20～15. 50	0. 96	45～250	14. 518	203	188 175 147	188
2,4-DP	15. 50～16. 10	1. 05	45～300	15. 913	248	162 189 213	162
2,4-D	16. 10～17. 00	0. 65	45～250	16. 377	199	156 125 141	156
2,4,5-TP	17. 00～18. 60	0. 55	45～300	18. 308	282	196 247 223	196
2,4,5-T	18. 60～19. 30	1. 05	45～300	18. 932	233	190 159 218	190
2,4-DB	19. 30～20. 60	0. 65	45～200	20. 104	101	59 101	59

Annex B
(informative)
GC-MSMS chromatogram of the methylation standards



1——Dicamba 14.518 min;

2——2,4-DP 15.913 min;

3——2,4-D 16.377 min;

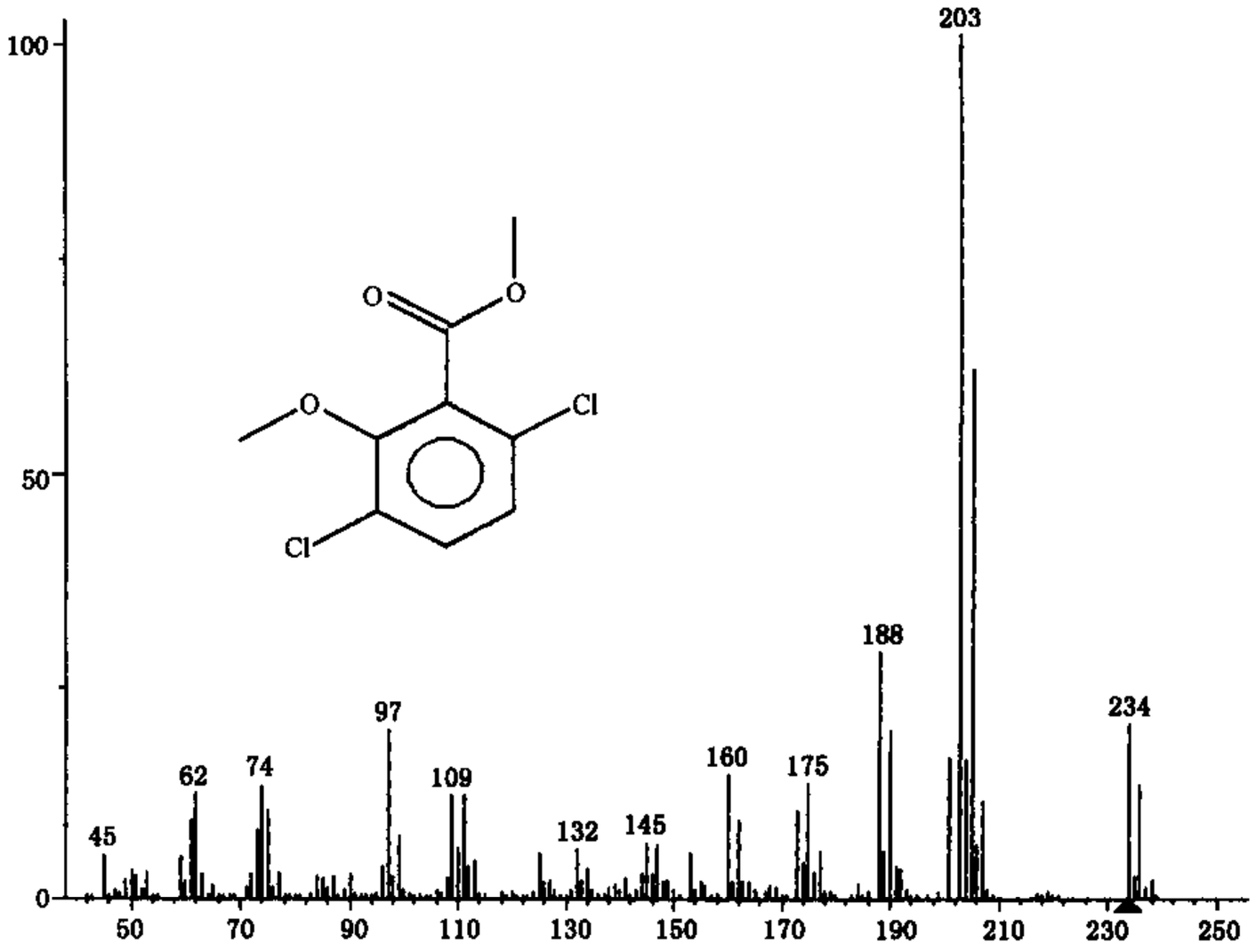
4——2,4,5-TP 18.308 min;

5——2,4,5-T 18.932 min;

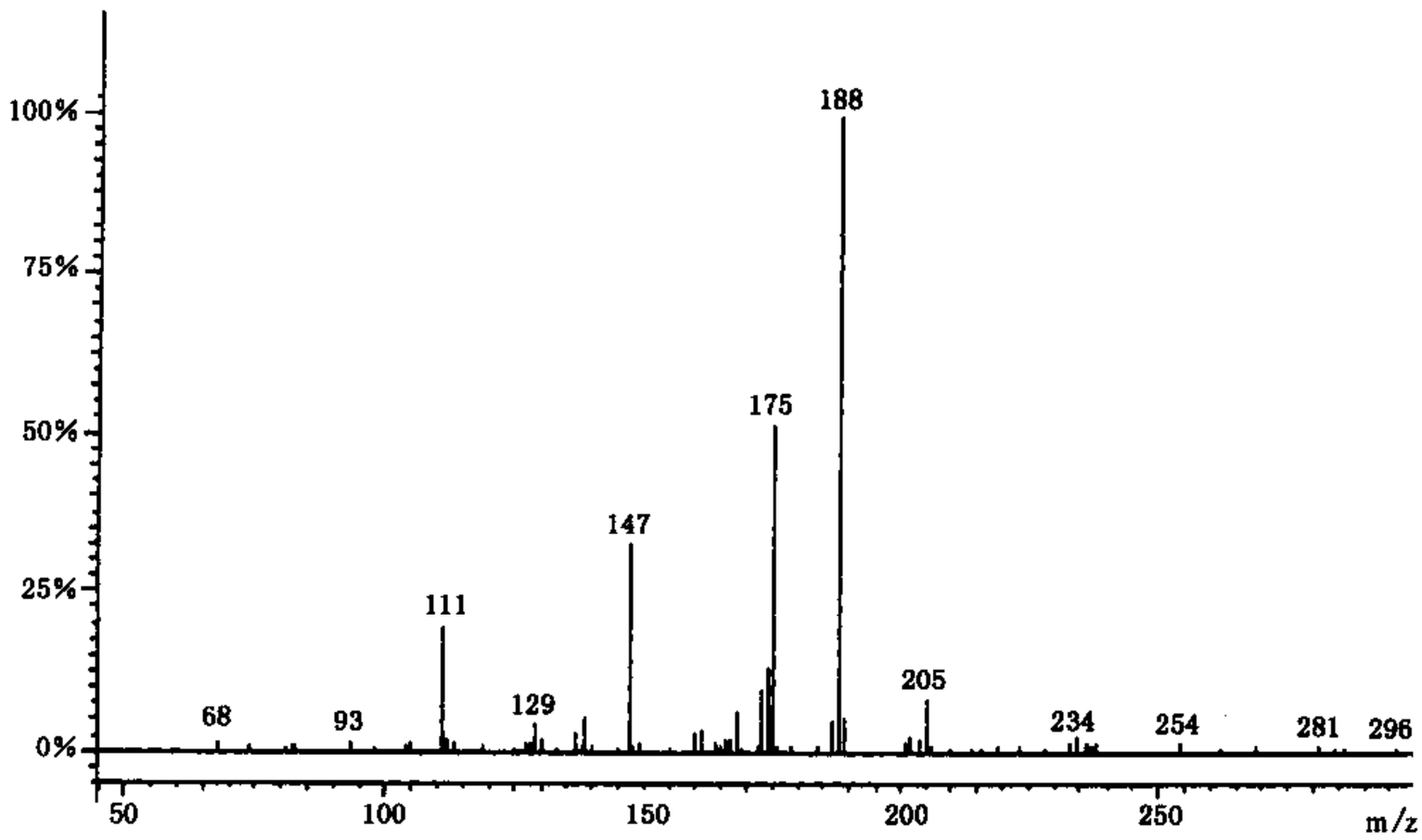
6——2,4-DB 20.104 min。

Fig. B.1 GC-MSMS chromatogram of the methylation standards of the six phenoxy-acid herbicides

Annex C
(informative)
Mass spectrogram of methyl ester standard

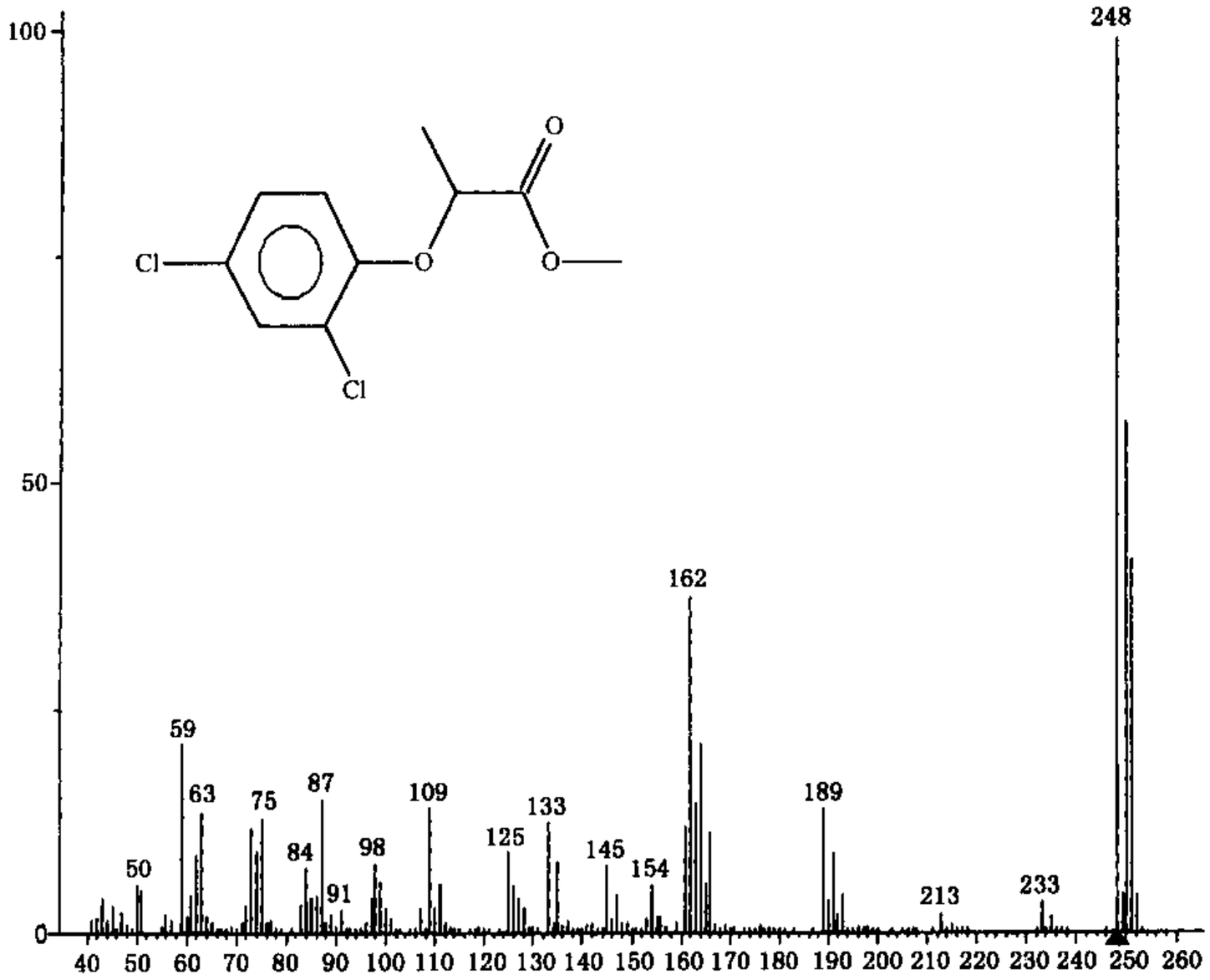


a) GC-MS(EI) spectrum of methyl ester standard

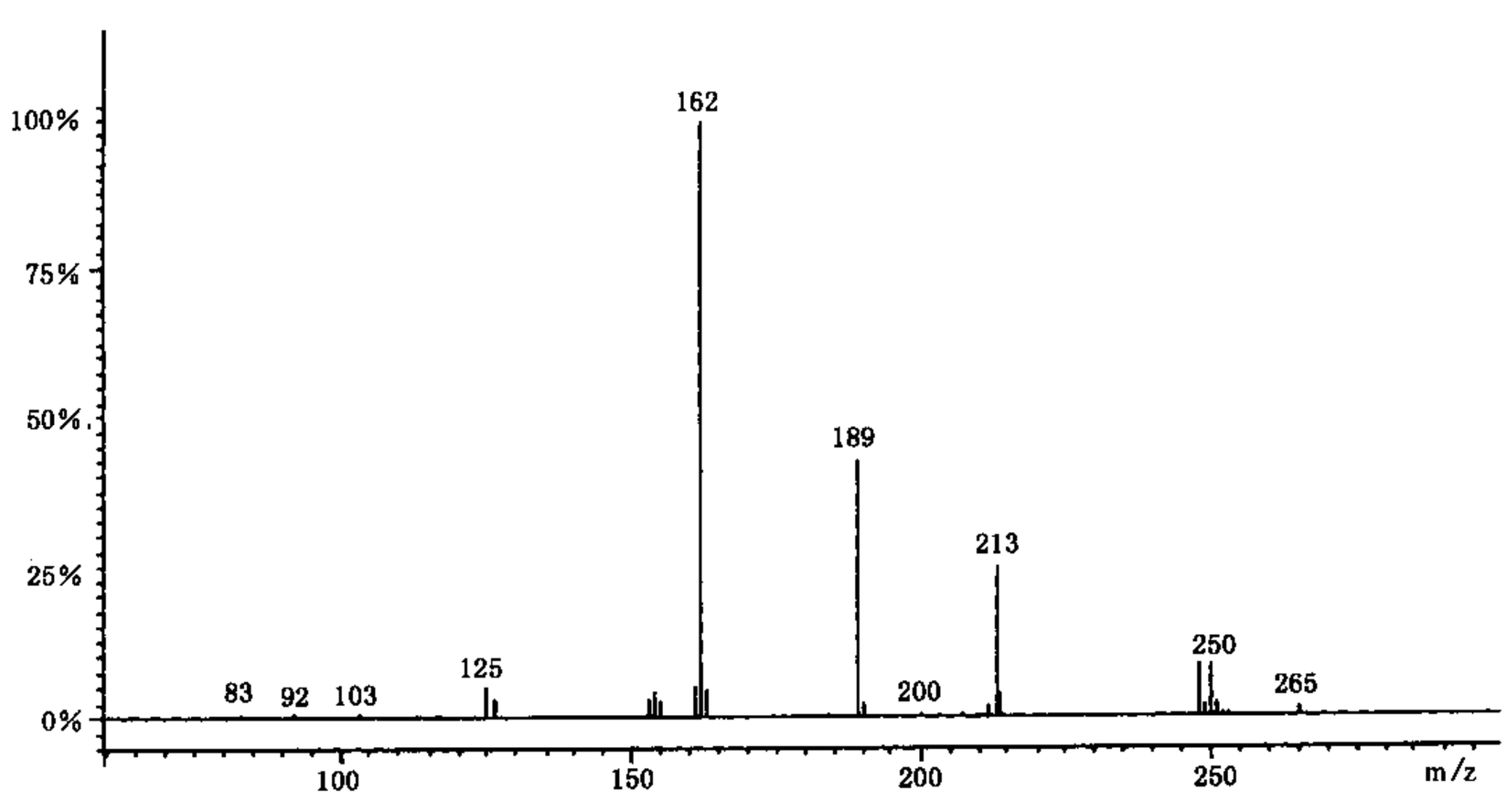


b) GC-MSMS spectrum of methyl ester standard

Fig. C. 1 Mass spectrum of the Dicamba methyl ester standard

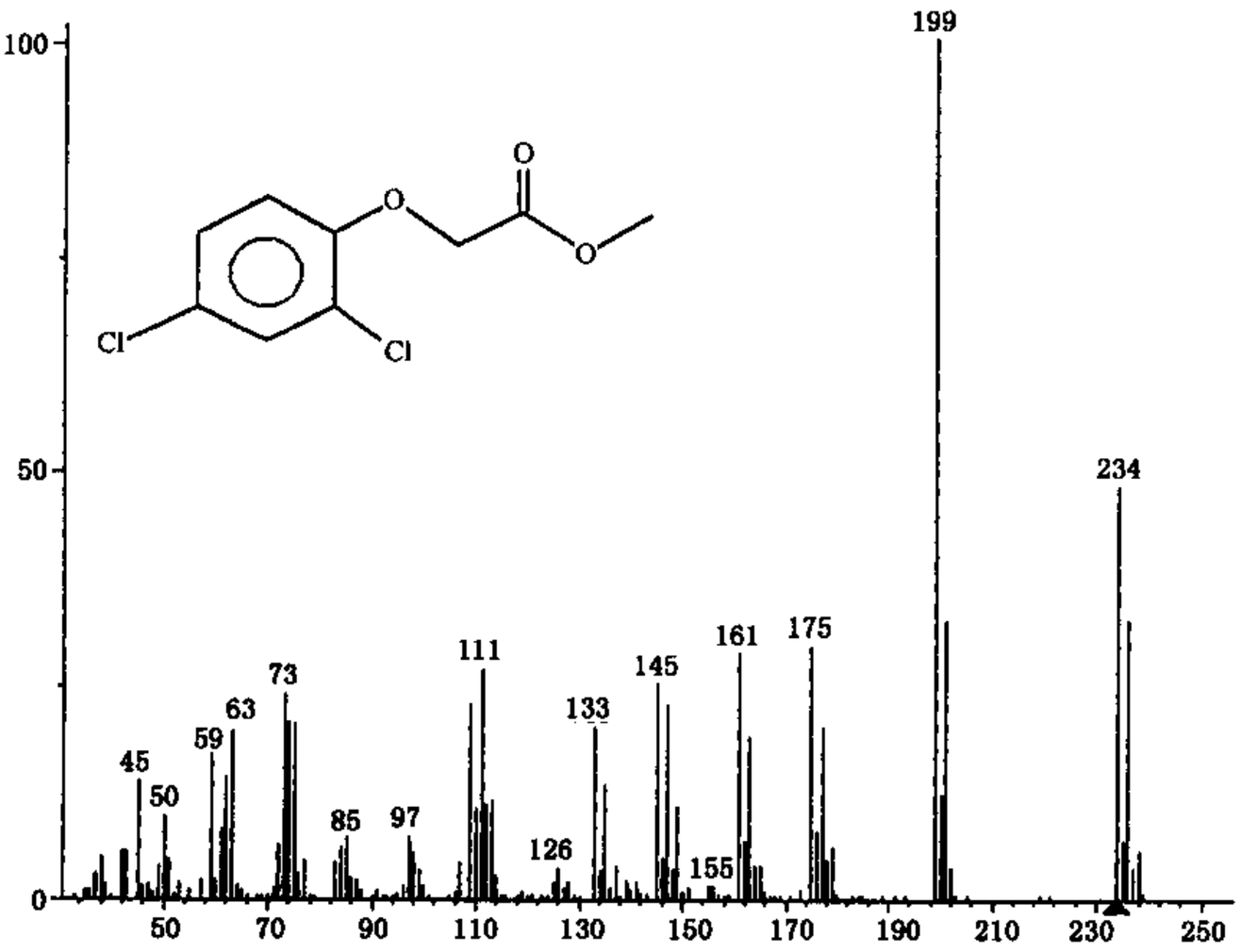


a) GC-MS(EI) spectrum of methyl ester standard

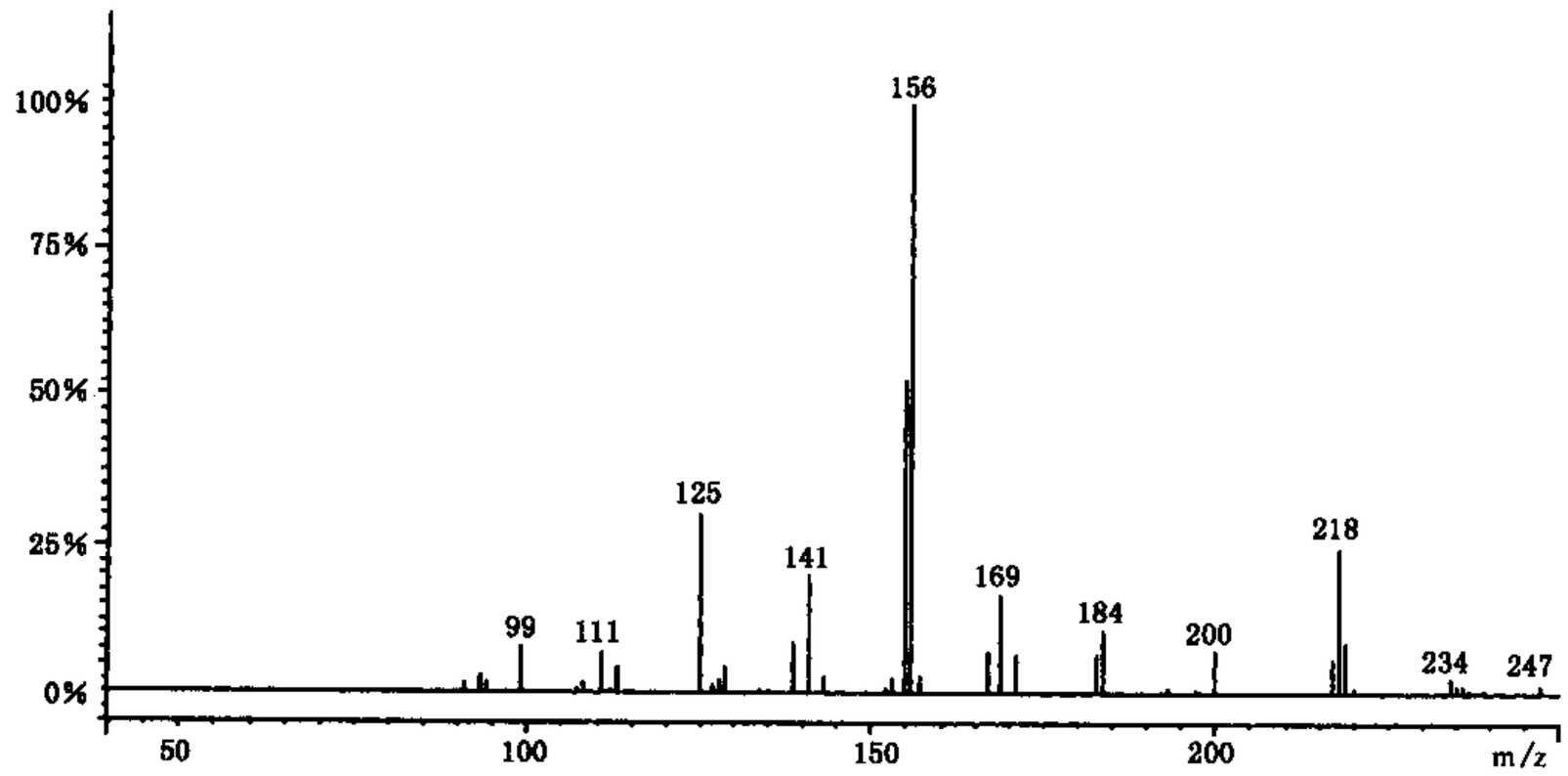


b) GC-MSMS spectrum of methyl ester standard

Fig. C. 2 Mass spectrum of the 2,4-DP methyl ester standard

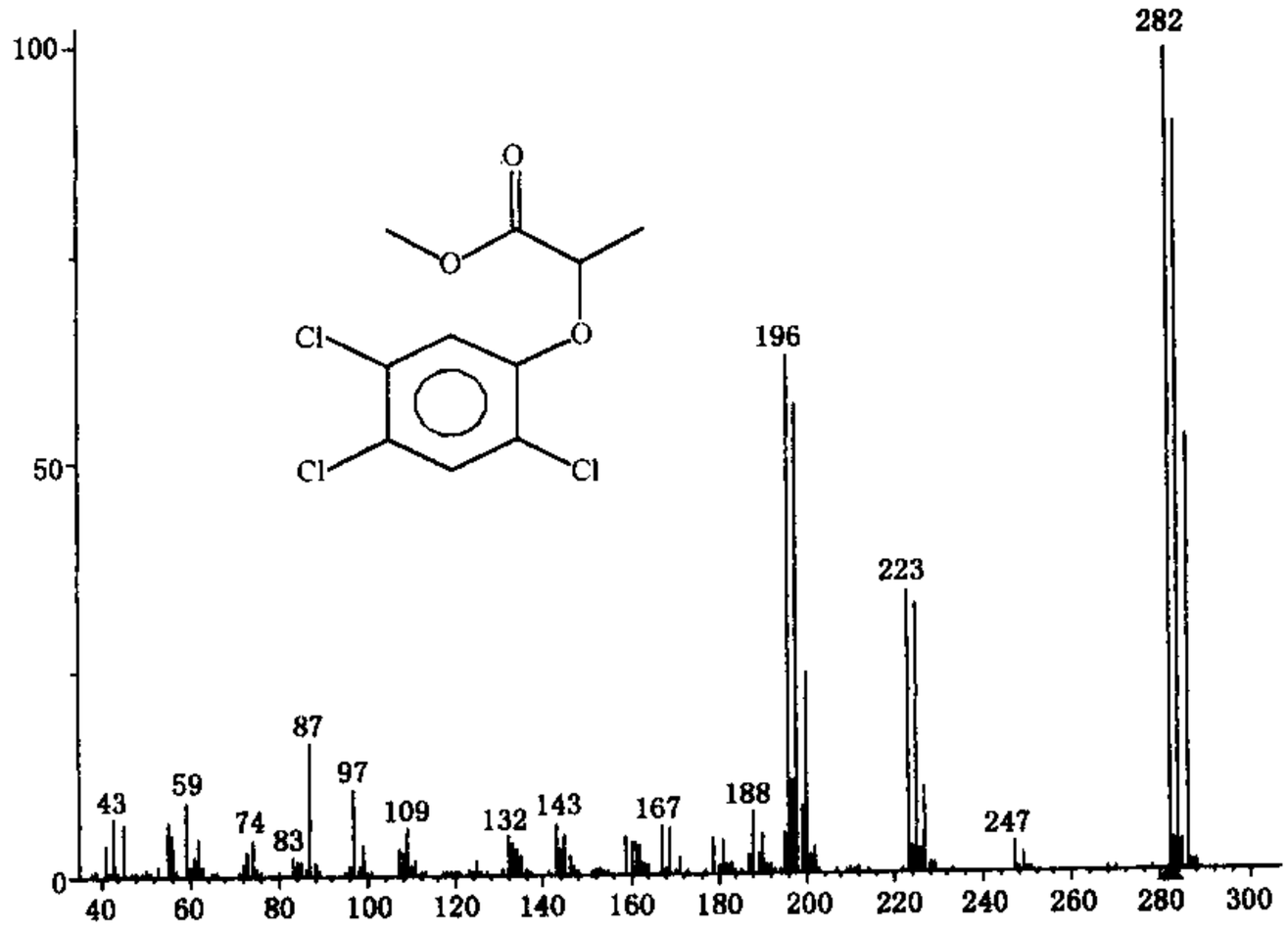


a) GC-MS(EI) spectrum of methyl ester standard

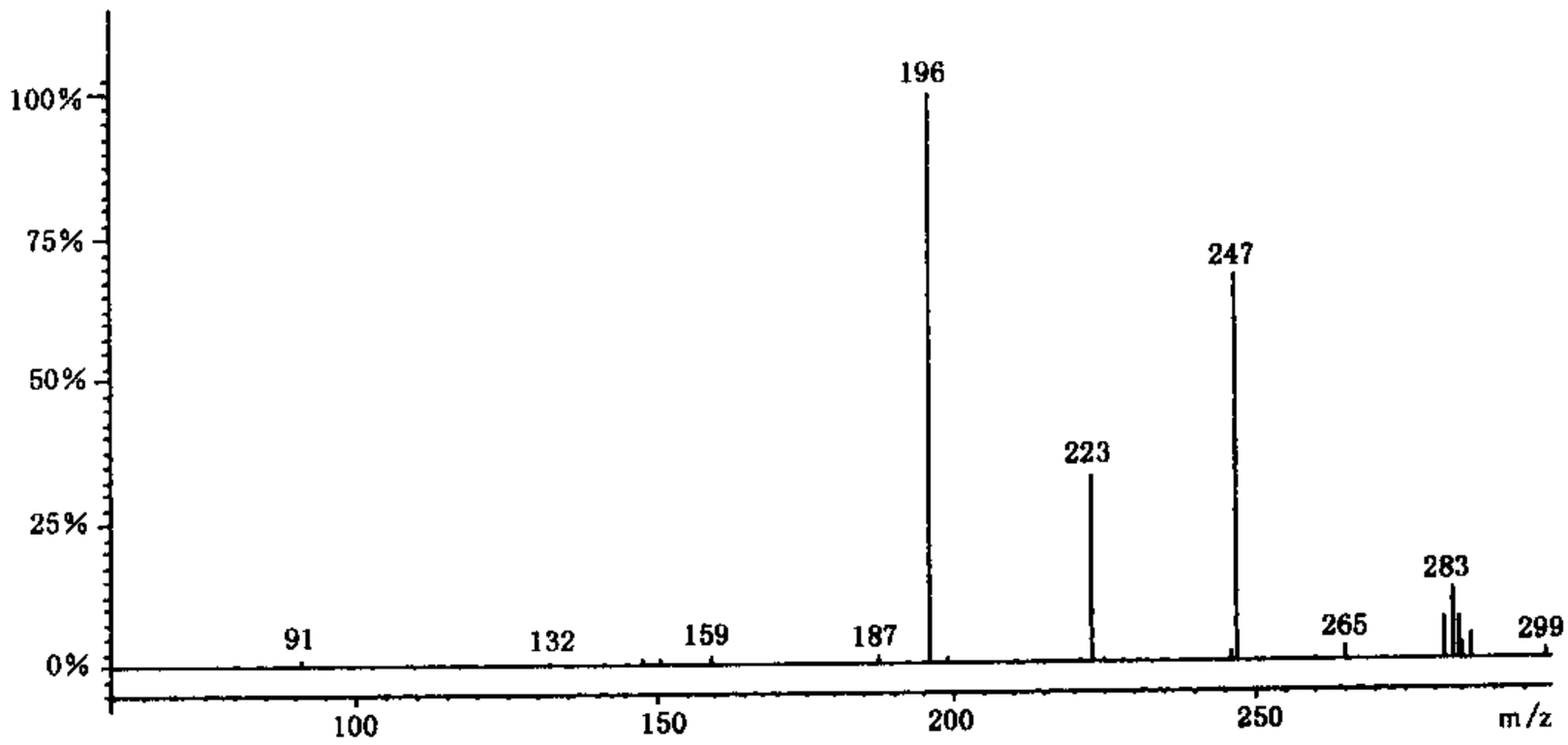


b) GC-MSMS spectrum of methyl ester standard

Fig. C. 3 Mass spectrum of the 2,4-D methyl ester standard

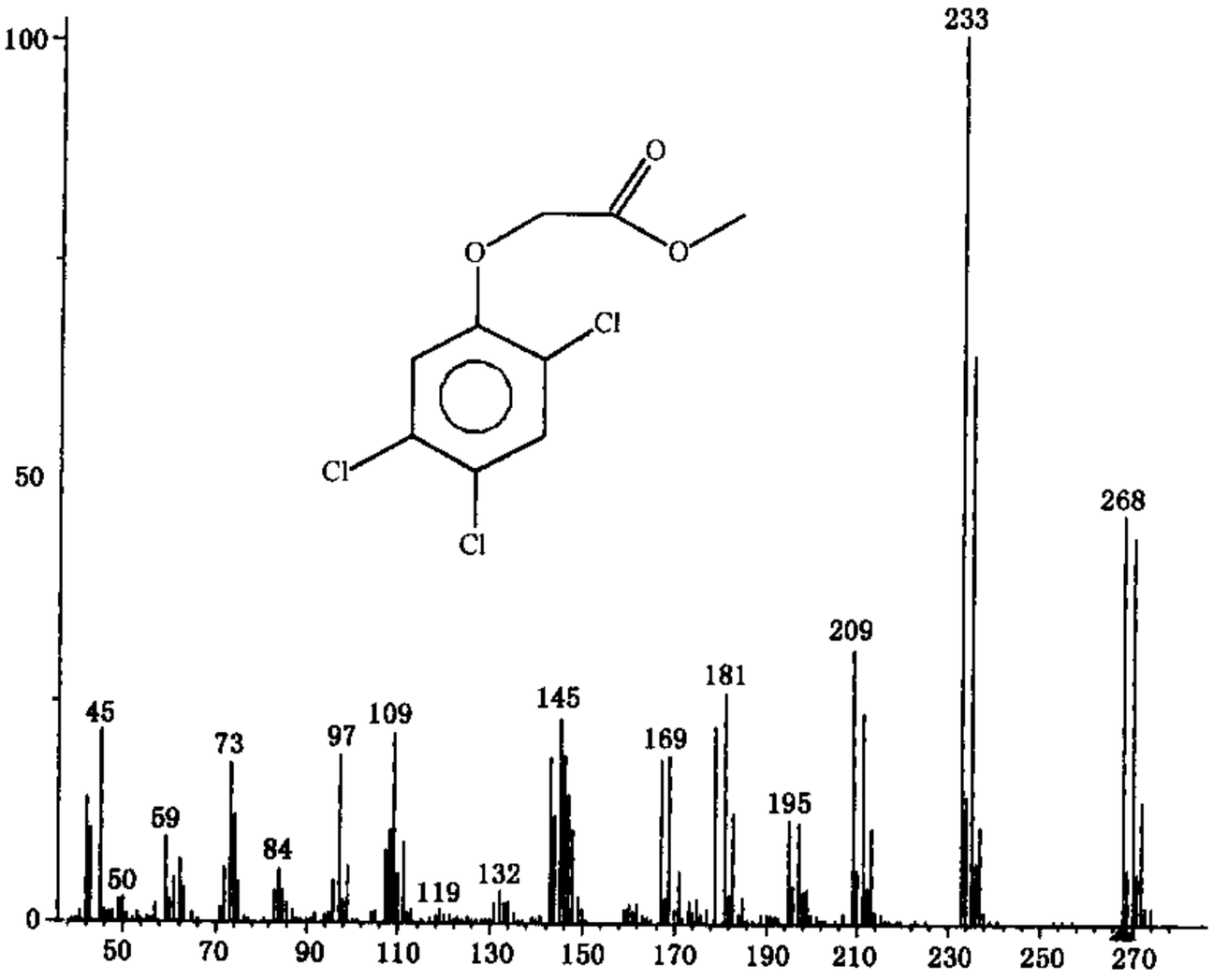


a) GC-MS(EI) spectrum of methyl ester standard

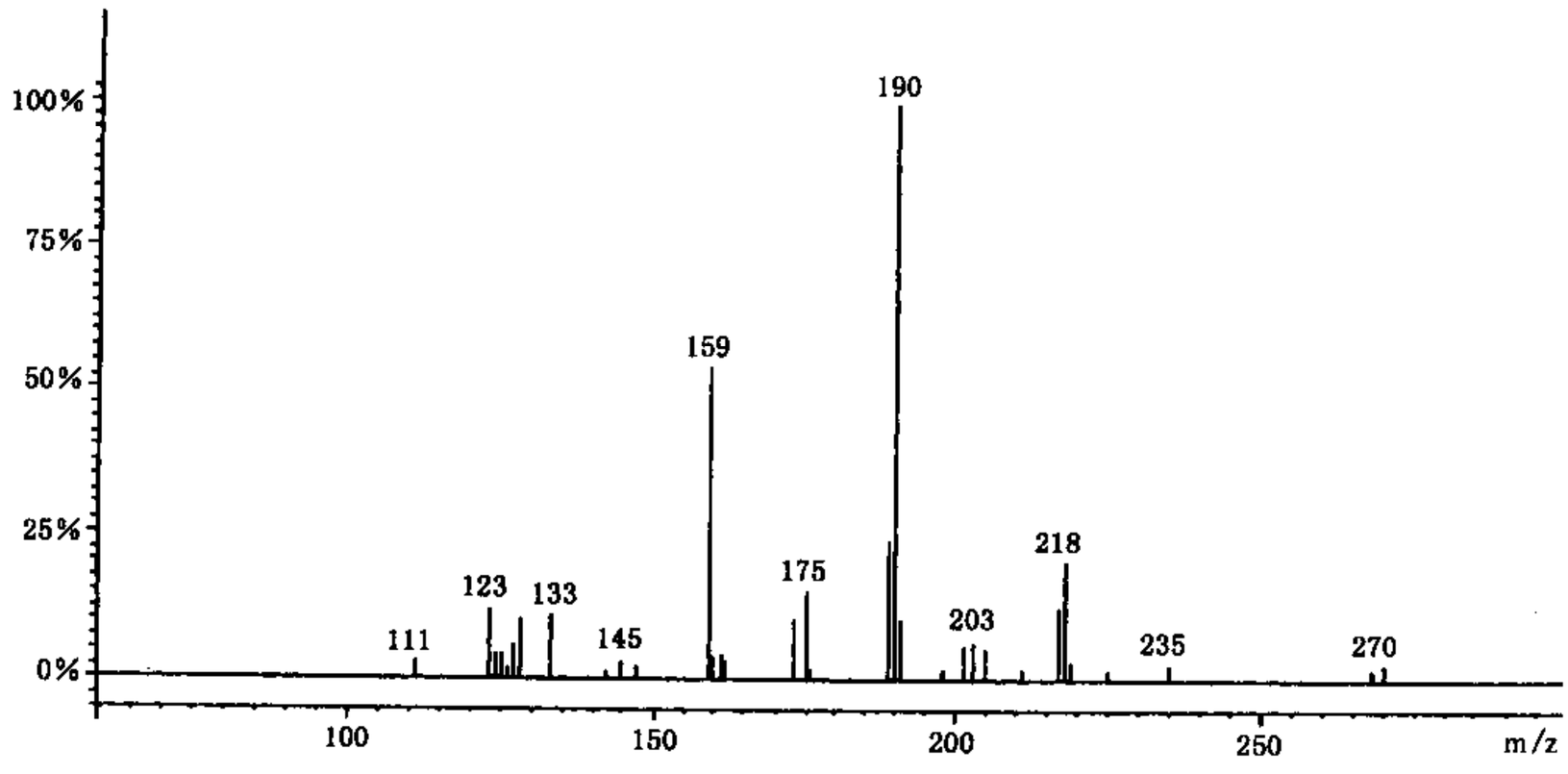


b) GC-MSMS spectrum of methyl ester standard

Fig. C. 4 Mass spectrum of the 2,4,5-TP methyl ester standard

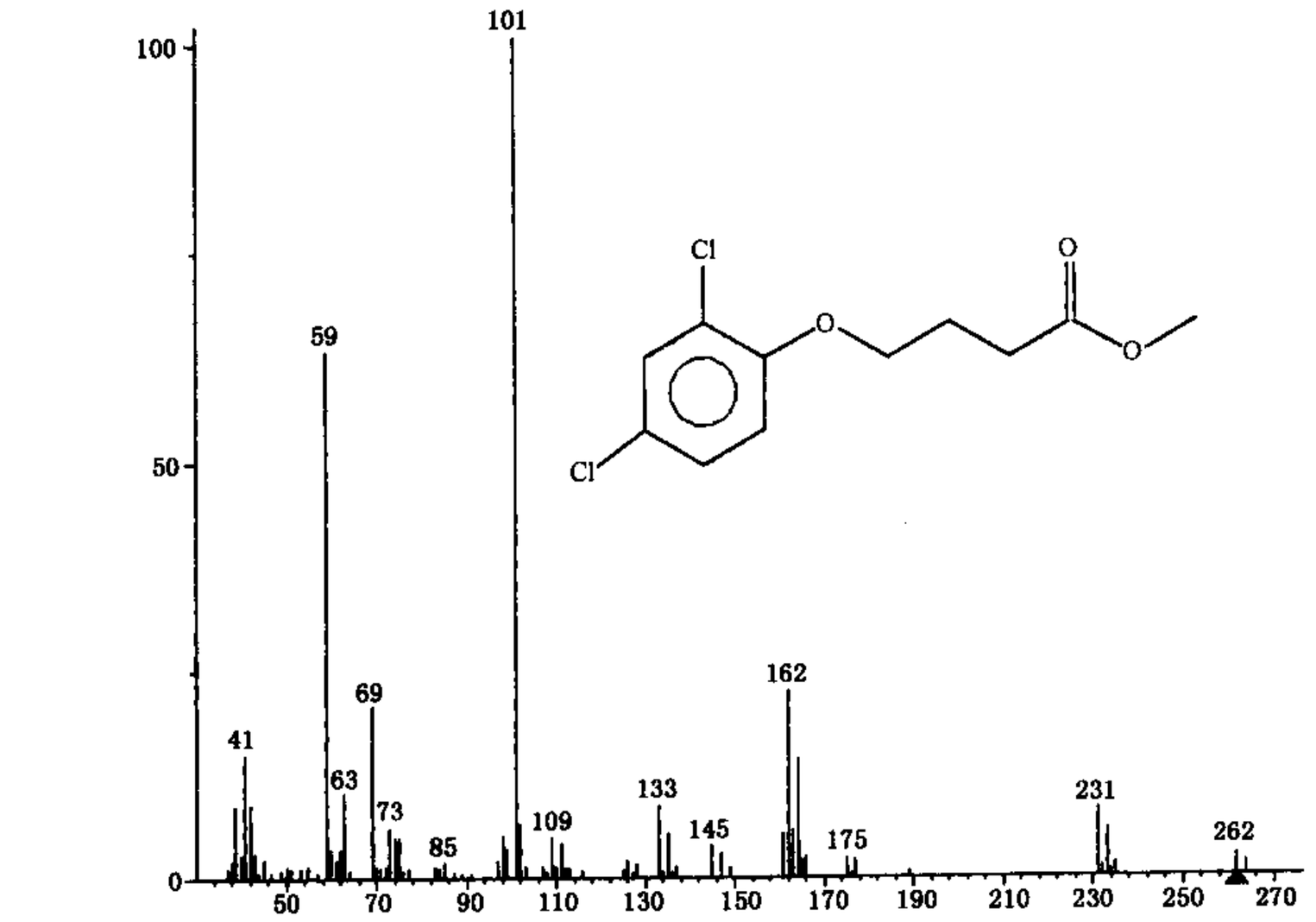


a) GC-MS(EI) spectrum of methyl ester standard

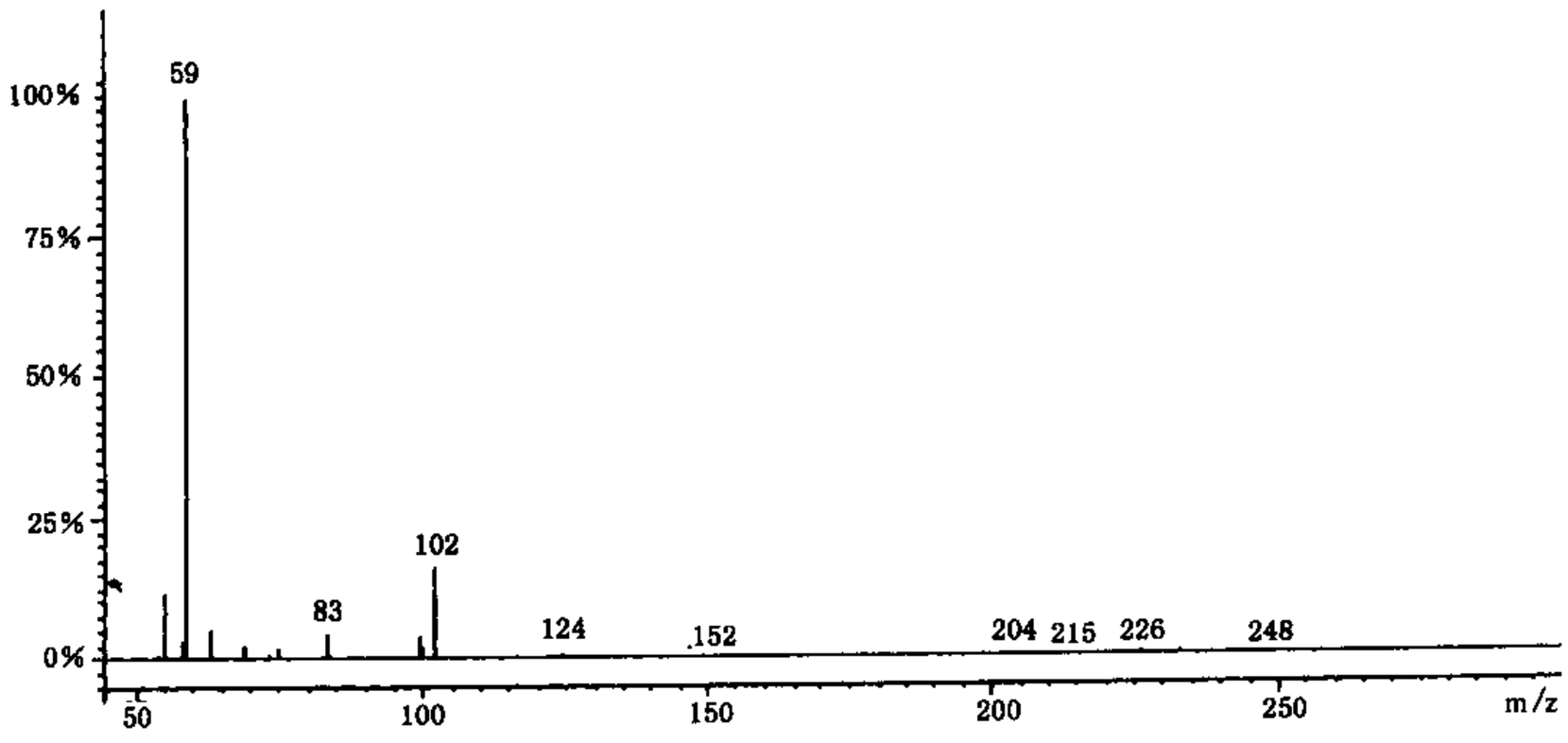


b) GC-MSMS spectrum of methyl ester standard

Fig. C. 5 Mass spectrum of the 2,4,5-T methyl ester standard



a) GC-MS(EI) spectrum of methyl ester standard



b) GC-MSMS spectrum of methyl ester standard

Fig. C. 6 Mass spectrum of the 2,4-DB methyl ester standard

中华人民共和国出入境检验检疫
行 业 标 准

进出口植物性产品中苯氧羧酸类除草剂残留量检验方法 气相色谱法

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