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中华人民共和国出入境检验检疫行业标准

SN/T 2320—2009

进出口食品中百菌清、苯氟磺胺、甲抑菌 灵、克菌丹、灭菌丹、敌菌丹和四溴菊 酯残留量检测方法 气相色谱-质谱法

Determination of chlorthalonil, dichlofluanid, tolylfluanid,
captan, folpet, captafol and deltamethrin residues in
food for import and export—GC/MS method

2009-07-07 发布

2010-01-16 实施

中 华 人 民 共 和 国 发 布
国家质量监督检验检疫总局

前 言

本标准的附录 A 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、中华人民共和国江苏出入境检验检疫局。

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本标准系首次发布的出入境检验检疫行业标准。

进出口食品中百菌清、苯氟磺胺、甲抑菌 灵、克菌丹、灭菌丹、敌菌丹和四溴菊 酯残留量检测方法 气相色谱-质谱法

1 范围

本标准规定了食品中百菌清、苯氟磺胺、甲抑菌灵、克菌丹、灭菌丹、敌菌丹和四溴菊酯残留量的检测方法(GC/MS)。

本标准适用于大米、糙米、大麦、小麦、玉米及大白菜中百菌清、苯氟磺胺、甲抑菌灵、克菌丹、灭菌丹、敌菌丹和四溴菊酯残留量的检测和确证。

2 方法提要

样品用乙腈提取,提取液经盐析萃取、活性炭小柱串联氨基小柱固相萃取净化后,再用 GPC 进行净化,GC/MS 进行检测,外标法定量。

3 试剂和材料

除另有规定外,所用试剂均为分析纯,水为二次超纯水。

- 3.1 乙腈:色谱纯。
- 3.2 甲苯:色谱纯。
- 3.3 丙酮:色谱纯。
- 3.4 环己烷:色谱纯。
- 3.5 盐酸。
- 3.6 氯化钠。
- 3.7 磷酸氢二钾。
- 3.8 磷酸二氢钾。
- 3.9 氢氧化钠。
- 3.10 无水硫酸钠:经 650 °C 灼烧 4 h,置于干燥器内备用。
- 3.11 1.0 mol/L 氢氧化钠:称取 40 g 氢氧化钠溶于适量水,并用水稀释至 1 000 mL。
- 3.12 1.0 mol/L 盐酸溶液:量取 90 mL 盐酸,加适量水并稀释至 1 000 mL。
- 3.13 0.5 mol/L 磷酸缓冲溶液:称取 52.70 g 磷酸氢二钾和 30.20 g 磷酸二氢钾,加入 500 mL 蒸馏水,混匀使得固体充分溶解,用 1.0 mol/L 氢氧化钠溶液或者 1.0 mol/L 盐酸溶液调至 pH7.0,加水至 1 000 mL。
- 3.14 乙腈-甲苯(3+1,体积比)溶液:量取 600 mL 乙腈和 200 mL 甲苯至 1 000 mL 试剂瓶中。
- 3.15 流动相,丙酮-环己烷(3+7,体积比)溶液:量取 300 mL 丙酮和 700 mL 环己烷至 1 000 mL 试剂瓶中。
- 3.16 标准物质:克菌丹(Captan,CAS 号:133-06-2,分子式: $C_9H_8Cl_3NO_2S$) $\geq 99\%$ 。敌菌丹(Captafol,CAS 号:2425-06-1,分子式: $C_{10}H_9Cl_4NO_2S$) $\geq 96\%$ 。灭菌丹(Folpet,CAS 号:133-07-3,分子式: $C_9H_4Cl_3NO_2S$) $\geq 99\%$ 。百菌清(Chlorothalonil,CAS 号:1897-45-6,分子式: $C_8Cl_4N_2$) $\geq 99\%$ 。苯氟磺胺(Dichlofluanid,CAS 号:1085-98-9,分子式: $C_9H_{11}Cl_2FN_2O_2S_2$) $\geq 98\%$ 。甲抑菌灵(Tolyfluanid,CAS 号:731-27-1,分子式: $C_{10}H_{13}Cl_2FN_2O_2S_2$) $\geq 98\%$ 。四溴菊酯(Tralomethrin,CAS 号:66841-25-6,分子

式： $C_{22}H_{19}Br_4NO_3 \geq 87\%$ 。

3.17 标准储备溶液(1 000 $\mu\text{g}/\text{mL}$):分别称取约 0.01 g(精确至 0.000 1 g)的克菌丹、敌菌丹、灭菌丹、百菌清、苯氟磺胺、甲抑菌灵和四溴菊酯的标准品于 10 mL 的容量瓶中,用丙酮配制成约 1 000 $\mu\text{g}/\text{mL}$ 的标准储备溶液,低于 5 $^{\circ}\text{C}$ 避光保存,保存期为 1 年。

3.18 混合标准中间溶液(10.0 $\mu\text{g}/\text{mL}$):各移取上述的标准储备液 1.00 mL~100 mL 容量瓶中,用丙酮稀释至刻度,低于 5 $^{\circ}\text{C}$ 避光保存,保存期为 3 个月。

3.19 混合标准工作溶液:根据需要将混合标准中间溶液用丙酮稀释成适当浓度的标准工作液,现用现配。

3.20 活性炭小柱:(ENVI-Carb;3 mL,250 mg)或相当者。

3.21 氨基柱:(LC-NH₂;3 mL,250 mg)或相当者。

3.22 滤膜:有机系 0.45 μm 。

4 仪器和设备

4.1 气相色谱-质谱联用仪:配有(ED)离子源。

4.2 凝胶色谱。

4.3 旋转蒸发器。

4.4 振荡器。

4.5 均质器。

4.6 固相萃取装置。

4.7 离心机:转速不低于 4 000 r/min。

4.8 氮吹仪。

5 试样制备与保存

5.1 试样制备

5.1.1 大麦、小麦、大米、玉米、糙米

取代表性样品约 200 g,粉碎,过筛(孔径为 2.0 mm),装入洁净的容器内,密封,标明标记。

5.1.2 蔬菜(大白菜)

白菜:取可食部分(不可水洗)约 200 g,捣碎均匀,装入洁净容器内,密封,标明标记。

5.2 试样保存

粮谷类试样于 0 $^{\circ}\text{C}$ ~4 $^{\circ}\text{C}$ 保存;蔬菜试样于-18 $^{\circ}\text{C}$ 以下冷冻保存。在抽样及制样的操作过程中,应防止样品受到污染或发生残留物含量的变化。

6 测定步骤

6.1 提取

6.1.1 大麦、小麦、大米、玉米、糙米样品

称取约 5 g 样品(精确至 0.01 g),于 50 mL 离心管中,加入 15.0 mL 去离子水,浸泡 20 min。

在离心管中加入 15.0 mL 乙腈,用均质器于 20 000 r/min 下均质 2 min。将离心管在 3 000 r/min 下离心 10 min。取出上清液于另一 50 mL 离心管中。样品再用 10.0 mL 乙腈,同上操作。合并上清液。在提取液中加入 3.5 g 氯化钠。

6.1.2 白菜

称取约 10 g 样品(精确至 0.01 g),于 50 mL 离心管中。然后按 6.1.1 中的第二段操作。

6.2 盐析、液液萃取净化

在离心管中加入 2.0 mL 磷酸缓冲溶液。用往复式振荡器振摇 5 min 后,在 3 000 r/min 下离心 5 min。

分取上层乙腈相并经无水硫酸钠柱脱水,收集于 100 mL 梨形烧瓶中;无水硫酸钠柱用少许乙腈洗涤。将合并的溶液在旋转蒸发仪中于 40 °C 下浓缩近干。用 2.0 mL 乙腈-甲苯混合溶液溶解残渣。

6.3 SPE 净化

在活性炭小柱上加 0.5 cm 无水硫酸钠,下端串联 LC-NH₂ 氨基柱。用 10 mL 乙腈-甲苯混合溶液活化。将上述的溶解液转移至小柱中。用 10 mL 乙腈-甲苯混合溶液洗脱(在整个活化、上样和洗脱过程中应避免 SPE 柱干涸)。收集洗脱液于 15 mL 试管中并于氮吹仪上吹至近干,定量加入 0.5 mL GPC 流动相,供凝胶色谱串联气相色谱质谱检测。

6.4 测定

6.4.1 凝胶色谱条件

- 凝胶色谱柱:Shodex CLNpak EV-200 长 150 mm,内径 2.1 mm;或相当者;
- 流动相:丙酮-环己烷混合溶液(3+7,体积比);
- 流速:0.1 mL/min;
- 柱温:40 °C;
- 进样量:10 μL;
- GPC 的淋出液收集时间为 4.29 min~6.29 min。

6.4.2 气相色谱质谱条件

- 色谱柱:惰性石英管,5 m×0.53 mm(内径),空柱,中间没有涂层,或相当者;
预柱:DB-5MS 石英毛细管柱,5 m×0.25 mm(内径)×0.25 μm(膜厚),或相当者;
分析柱:DB-5MS 石英毛细管柱,30 m×0.25 mm(内径)×0.25 μm(膜厚);或相当者;
- 进样模式:大体积(PTV)进样;
- 进样口温度程序:120 °C 保持 5 min,然后以 100 °C/min 升温至 250 °C,保持 31.7 min;
- 色谱柱温度程序:82 °C 保持 5 min,然后以 8 °C/min 升温至 310 °C,保持 5 min;
- 载气:氦气,纯度大于等于 99.999%;1.7 mL/min;
- 电子轰击源(EI):70 eV;
- 离子源温度:200 °C;
- 接口温度:300 °C;
- 测定方式:选择离子监测模式(SIM);
- 监测离子:见表 1。

表 1 克菌丹、敌菌丹、灭菌丹、百菌清、苯氟磺胺、甲抑菌灵和四溴菊酯的监测离子及其丰度比

名称	监测离子(m/z)	监测离子丰度比/%
百菌清	266(定量离子)、109、231、194	100 : 25 : 15 : 9
苯氟磺胺	123(定量离子)、167、224、332	100 : 45 : 30 : 6
对-甲抑菌灵	137(定量离子)、238、181、355	100 : 40 : 25 : 5
克菌丹	149(定量离子)、107、264、182	100 : 70 : 25 : 15
灭菌丹	104(定量离子)、260、297、178	100 : 80 : 25 : 20
敌菌丹	183(定量离子)、149、313、236	100 : 80 : 60 : 20
四溴菊酯	181(定量离子)、253、174、209	100 : 85 : 25 : 9

6.4.3 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。其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,以色谱峰面积按外标法定量。在上述色谱条件下,百菌清、苯氟磺胺、甲抑菌灵、克菌丹、灭菌丹、敌菌丹和四溴菊酯的参考保留时间分别为 20.27 min、

22.13 min、23.12 min、23.42 min、23.71 min、27.30 min、33.56 min,标准溶液的选择离子色谱图参见附录 A 中图 A.1。

在相同实验条件下,试样中待测物质的保留时间与标准工作溶液中对应的保留时间偏差在±2.5%之内;并且被测样品与标准品的质谱图相似,所选择的全部监测离子均出现且丰度比也相一致,其允许偏差不超过表 2 规定的范围时,则可确定为样品中存在这种药物残留。

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
允许的相对偏差/%	±10	±15	±20	±50

6.5 空白试验

除不加试样外,均按上述操作步骤进行。

7 结果计算和表述

用色谱数据处理机或按式(1)计算样品中农药残留量。计算结果需扣除空白值。

$$X = \frac{A \cdot c \cdot V}{A_s \cdot m} \dots\dots\dots(1)$$

式中:

X——样品中待测组分残留量,单位为微克每克(μg/g);

A——样液中农药残留的峰面积;

A_s——标准工作溶液中农药残留的峰面积;

c——标准工作溶液中农药残留的浓度,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——最终样液所代表的试样量,单位为克(g)。

8 测定低限、回收率

8.1 测定低限

本方法对所测定的农药的测定低限均为 0.01 mg/kg。

8.2 回收率

回收率详见表 3。

表 3 添加浓度及回收率试验数据

样品名称	农药名称	添加浓度/(mg/kg)	回收率/%
大米	百菌清	0.01	72.0~119.0
		0.05	75.5~95.6
		0.10	71.2~94.3
	苯氟磺胺	0.01	76.0~114.0
		0.05	86.3~130.6
		0.10	69.4~104.4
	对-甲抑菌灵	0.01	60.0~89.0
		0.05	98.5~130.7
		0.10	75.4~101.5
	克菌丹	0.01	70.0~91.0
		0.05	89.8~125.8
		0.10	81.4~112.5

表 3 (续)

样品名称	农药名称	添加浓度/(mg/kg)	回收率/%	
大米	灭菌丹	0.01	62.0~85.0	
		0.05	66.1~83.1	
		0.10	88.5~122.7	
	敌菌丹	0.01	82.0~120.0	
		0.05	77.4~110.4	
		0.10	70.7~96.2	
	四溴菊酯	0.01	70.0~115.0	
		0.05	107.5~120.0	
		0.10	89.1~127.3	
糙米	百菌清	0.01	84.0~130.0	
		0.05	67.2~89.3	
		0.10	68.3~88.4	
	苯氟磺胺	0.01	65.0~91.0	
		0.05	71.3~96.4	
		0.10	71.5~95.6	
	对-甲抑菌灵	0.01	65.0~120.0	
		0.05	75.4~91.7	
		0.10	67.6~93.7	
	克菌丹	0.01	70.0~88.0	
		0.05	66.6~90.5	
		0.10	68.5~91.5	
	灭菌丹	0.01	65.0~82.0	
		0.05	76.2~95.5	
		0.10	65.3~91.4	
	敌菌丹	0.01	79.0~120.0	
		0.05	70.5~89.7	
		0.10	70.5~89.3	
	四溴菊酯	0.01	71.0~122.0	
		0.05	69.8~88.6	
		0.10	72.6~101.6	
	大麦	百菌清	0.01	67.0~90.0
			0.05	64.4~85.4
			0.10	78.4~95.4
苯氟磺胺		0.01	89.0~109.0	
		0.05	70.4~90.4	
		0.10	75.4~99.1	

表 3 (续)

样品名称	农药名称	添加浓度/(mg/kg)	回收率/%
大麦	对-甲抑菌灵	0.01	67.0~85.0
		0.05	65.5~86.7
		0.10	89.2~103.3
	克菌丹	0.01	63.0~82.0
		0.05	69.7~91.5
		0.10	82.3~101.4
	灭菌丹	0.01	78.0~101.0
		0.05	78.6~99.2
		0.10	75.4~99.3
	敌菌丹	0.01	61.0~75.0
		0.05	64.4~88.4
		0.10	68.5~90.4
四溴菊酯	0.01	74.0~98.0	
	0.05	81.5~98.2	
	0.10	75.5~102.2	
小麦	百菌清	0.01	66.0~95.0
		0.05	69.2~85.3
		0.10	80.8~98.3
	苯氟磺胺	0.01	72.0~91.0
		0.05	72.4~91.3
		0.10	73.5~89.5
	对-甲抑菌灵	0.01	62.0~85.0
		0.05	74.3~89.4
		0.10	63.5~85.2
	克菌丹	0.01	75.0~98.0
		0.05	69.4~91.4
		0.10	72.1~86.2
	灭菌丹	0.01	86.0~110.0
		0.05	68.5~93.6
		0.10	68.3~91.4
	敌菌丹	0.01	71.0~95.0
		0.05	65.1~94.1
		0.10	63.4~91.4
四溴菊酯	0.01	79.0~110.0	
	0.05	82.3~101.3	
	0.10	67.4~95.5	

表 3 (续)

样品名称	农药名称	添加浓度/(mg/kg)	回收率/%	
玉米	百菌清	0.01	68.0~91.0	
		0.05	75.3~101.4	
		0.10	62.8~85.7	
	苯氟磺胺	0.01	65.0~85.0	
		0.05	66.6~87.7	
		0.10	67.6~87.8	
	对-甲抑菌灵	0.01	71.0~94.0	
		0.05	64.6~94.6	
		0.10	62.8~91.9	
	克菌丹	0.01	70.0~86.0	
		0.05	63.5~90.7	
		0.10	74.5~94.4	
	灭菌丹	0.01	75.0~98.0	
		0.05	61.2~85.4	
		0.10	75.4~99.1	
	敌菌丹	0.01	65.0~81.0	
		0.05	62.4~80.5	
		0.10	69.4~91.8	
	四溴菊酯	0.01	67.0~89.0	
		0.05	81.4~98.5	
		0.10	79.3~97.4	
	大白菜	百菌清	0.01	66.0~91.0
			0.05	61.4~81.5
			0.10	71.6~98.1
苯氟磺胺		0.01	73.0~92.0	
		0.05	71.5~93.7	
		0.10	72.4~94.4	
对-甲抑菌灵		0.01	69.0~92.0	
		0.05	76.6~98.7	
		0.10	67.5~91.6	
克菌丹		0.01	65.0~95.0	
		0.05	75.5~102.1	
		0.10	67.4~93.5	

表 3 (续)

样品名称	农药名称	添加浓度/(mg/kg)	回收率/%
大白菜	灭菌丹	0.01	72.0~89.0
		0.05	74.4~102.5
		0.10	70.7~91.5
	敌菌丹	0.01	69.0~96.0
		0.05	69.5~94.5
		0.10	70.3~101.4
	四溴菊酯	0.01	85.0~105.0
		0.05	62.8~85.1
		0.10	76.4~103.1

附录 A

(资料性附录)

百菌清、苯氟磺胺、甲抑菌灵、克菌丹、灭菌丹、敌菌丹和四溴菊酯标准品的气相色谱-质谱选择离子色谱图

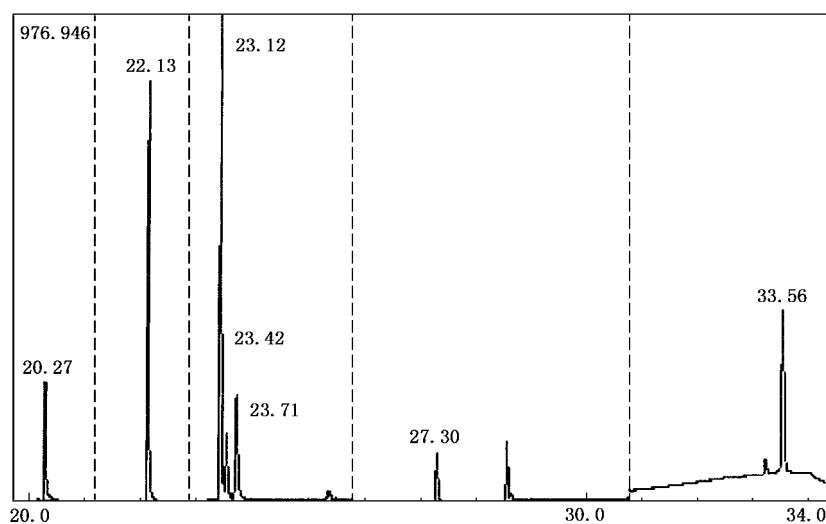
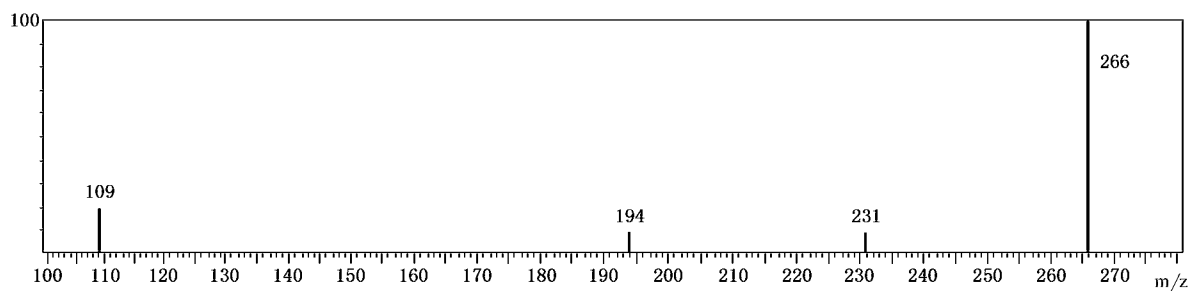
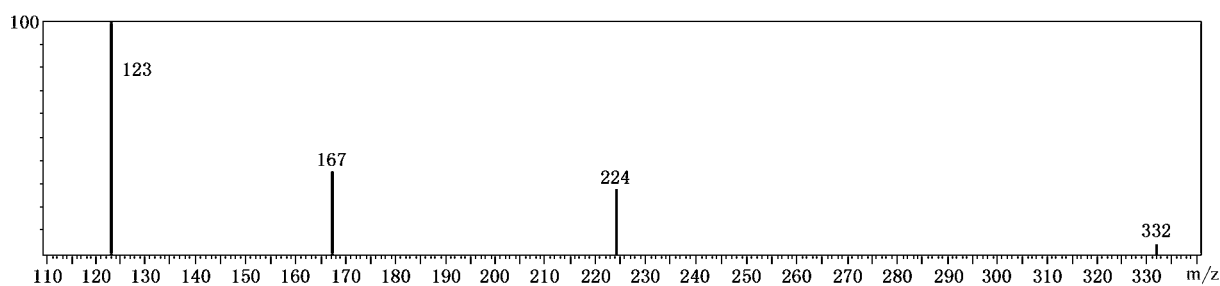


图 A.1 百菌清、苯氟磺胺、甲抑菌灵、克菌丹、灭菌丹、敌菌丹和四溴菊酯标准品的气相色谱-质谱选择离子色谱图(时间为 20.27 min、22.13 min、23.12 min、23.42 min、23.71 min、27.30 min、33.56 min)

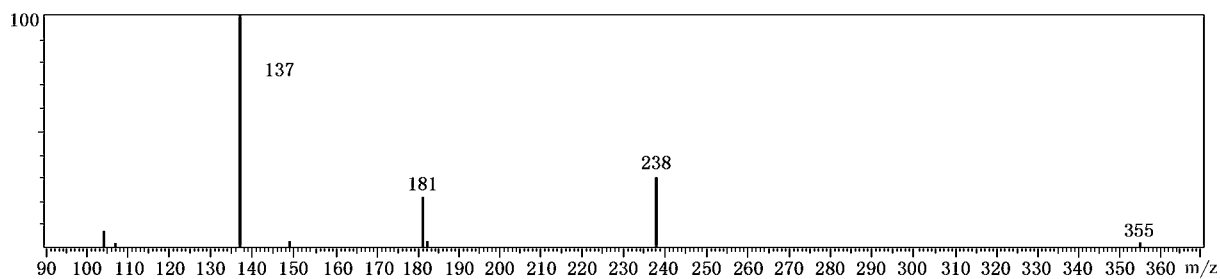


a) 百菌清质谱图

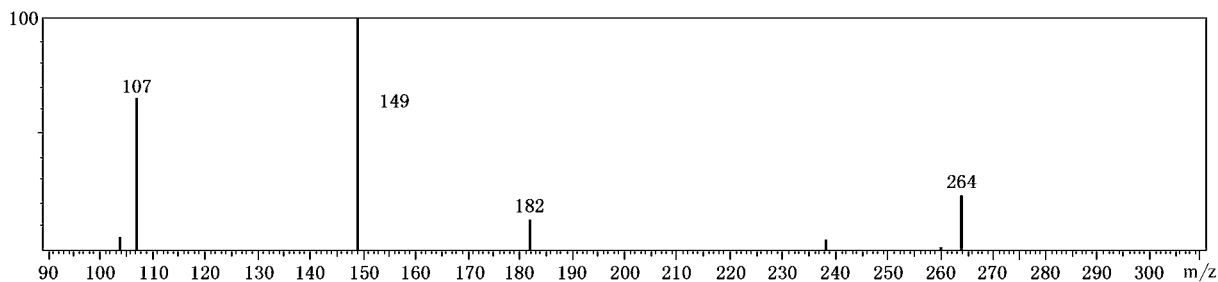


b) 苯氟磺胺质谱图

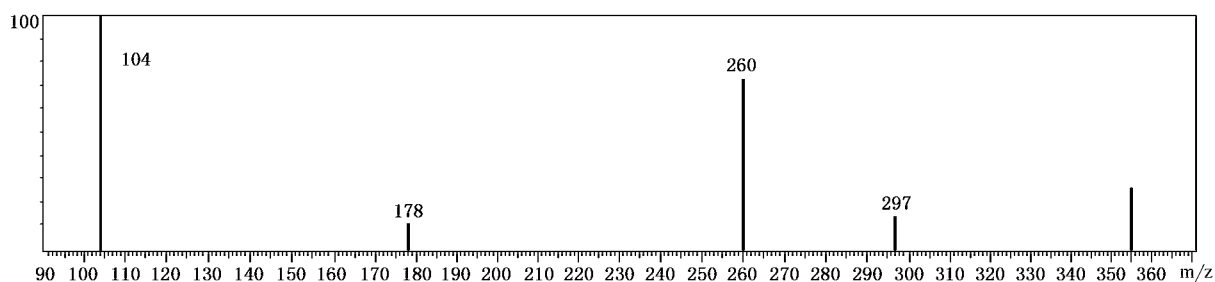
图 A.2 百菌清、苯氟磺胺、甲抑菌灵、克菌丹、灭菌丹、敌菌丹和四溴菊酯标准品的气相色谱-质谱图



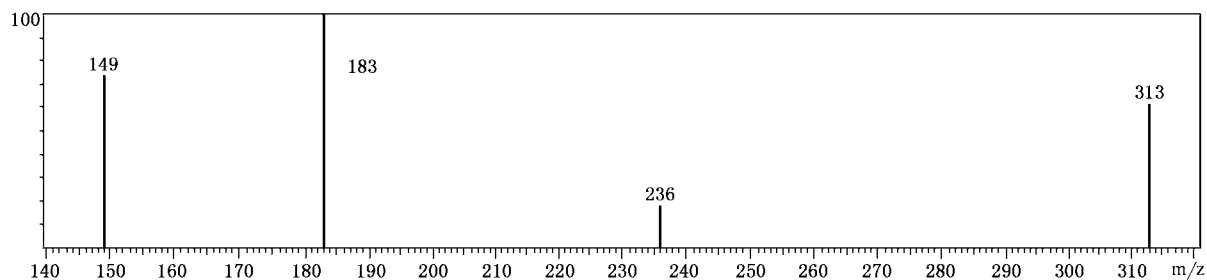
c) 甲抑菌灵质谱图



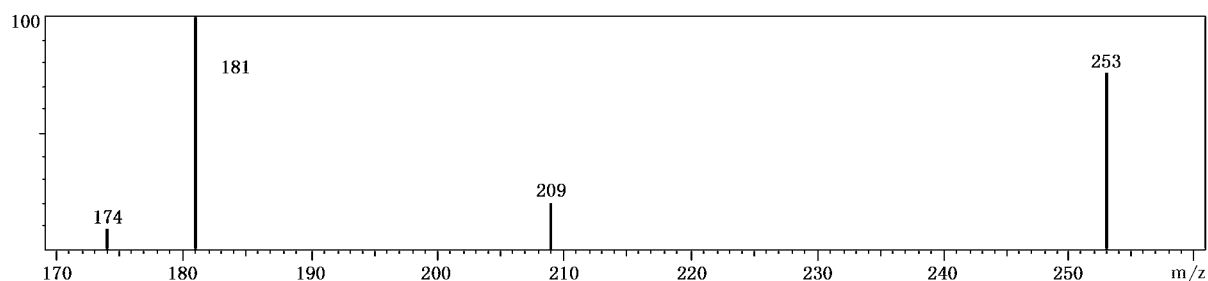
d) 克菌丹质谱图



e) 灭菌丹质谱图



f) 敌菌丹质谱图



g) 四溴菊酯质谱图

图 A.2 (续)

Foreword

Annex A is an informative annex.

This standard was proposed by and is under the charged of 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, Jiangshu Entry-Exit Inspection and Quarantine Bureau of the People's Republic of China.

The standard was mainly drafted by Yang huiqin, Guo dehua, Wang chuanxian, Libo, Zhu jian, Shen chongyu, Sheng yonggang, Chen huilan, Deng xiaojun, Wang min.

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

Determination of chlorthalonil, dichlofluanid, tolylfluanid, captan, folpet, captafol and deltamethrin residues in food for import and export—GC /MS method

1 Scope

The standard specifies the method of sample preparation and determination of chlorthalonil, dichlofluanid, tolylfluanid, captan, folpet, captafol and deltamethrin residues in foods by GC /MS.

This standard is applicable to the determination and confirmation of chlorthalonil, dichlofluanid, tolylfluanid, captan, folpet, captafol and deltamethrin residues in foodstuff of plant origin (wheat, barley, corn, rice, brown rice, vegetable etc).

2 Principle

Chlorthalonil, dichlofluanid, tolylfluanid, captan, folpet, captafol and deltamethrin residues are extracted from the sample with acetonitrile and liquid-liquid extraction, then cleaned up with ENVI-Crab, LC-NH₂ column and GPC. The residual content is determined by GC/MS, and quantified by external standard method.

3 Reagents and materials

Unless otherwise specified, all the reagents used should be analytical grade, “water” is HPLC-grade water.

3.1 Acetonitrile: HPLC grade.

3.2 Toluene: HPLC grade.

3.3 Acetone: HPLC grade.

3.4 Cyclohexane: HPLC grade.

3.5 Hydrochloric acid.

3.6 Sodium chloride.

- 3.7 Dibasic potassium phosphate.
- 3.8 Potassium phosphate.
- 3.9 Sodium hydrate.
- 3.10 Anhydrous sodium sulfate: Ignite at 650 °C for 4 h then put it into the drier.
- 3.11 1.0 mol/L sodium hydrate: Dissolve 40 g of Sodium hydrate to final volume of 1 000 mL with water.
- 3.12 1.0 mol/L hydrochloric acid: Dissolve 90 mL of hydrochloric acid to final volume of 1 000 mL with water.
- 3.13 0.5 mol/L phosphate buffered solution: Weigh 52.70 g dibasic potassium phosphate and 30.20 g potassium phosphate, add 500 mL distilled water, dissolve completely change pH value to 7.0 with 1.0 mol/L sodium hydrate or 1.0 mol/L hydrochloric acid, dissolve to final volume of 1 000 mL.
- 3.14 Acetonitrile-toluene (3 + 1, V/V): Combine 600 mL acetonitrile and 200 mL toluene.
- 3.15 Mobile phase: Acetone-cyclohexane (3 + 7, V/V): Combine 300 mL acetone and 700 mL cyclohexane.
- 3.16 Standard substance: Captan; CAS code 133-06-02, formula: $C_9H_8Cl_3NO_2S$, purity $\geq 99\%$. Captafol; CAS code 2425-06-1, formula: $C_{10}H_9Cl_{14}NO_2S$, purity $\geq 96\%$. Folpet; CAS code 133-07-3, formula: $C_9H_4Cl_3NO_2S$, purity $\geq 99\%$. Chlorothalonil; CAS code 1897-45-6, formula: $C_8Cl_4N_2$, purity $\geq 99\%$. Dichlofluanid; CAS code 1085-98-9, formula: $C_9H_{11}Cl_2FN_2O_2S_2$, purity $\geq 98\%$. Tolyfluanid; CAS code 731-27-1, formula: $C_{10}H_{13}Cl_2FN_2O_2S_2$, purity $\geq 98\%$. Tralomethrin; CAS code 66841-25-6, formula: $C_{22}H_{19}Br_4NO_3$, purity $\geq 87\%$.
- 3.17 Stock standard solution (1 000 $\mu\text{g}/\text{mL}$): Accurately weigh 0.01 ± 0.0001 g of captafol, folpet, captan, chlorthalonil, dichlofluanid, tolyfluanid and tralomethrin standard into a 10 mL volumetric flask and dilute to volume with acetone. Mix well. This solution is a stock solution of 1 000 $\mu\text{g}/\text{mL}$ captafol, folpet, captan, chlorthalonil, dichlofluanid, tolyfluanid and tralomethrin in acetone, these solutions can be used one year when stored at < 5 °C.
- 3.18 Intermediate standard solution (10.0 $\mu\text{g}/\text{mL}$): Dilute the stock standard solution with acetone to 10.0 $\mu\text{g}/\text{mL}$, these solutions can be used three months when stored at < 5 °C.
- 3.19 Working standard solution: pipette adequate amount of intermediate standard solution, dilute with acetone to prepare appropriate concentration standard working solution.

3.20 ENVI-Carb column (3 mL, 250 mg), equivalent.

3.21 LC-NH₂ column (3 mL, 250 mg), equivalent.

3.22 Organic phase 0.45 μm film.

4 Apparatus and equipment

4.1 GC/MS with EI.

4.2 GPC.

4.3 Rotary vacuum evaporator.

4.4 Vibrator.

4.5 Vortex mixer.

4.6 Apparatus of SPE.

4.7 Centrifuge: 4 000 r/min equipped.

4.8 Nitrogen evaporator.

5 Preparation and storage of test sample

5.1 Preparation of sample

5.1.1 wheat, barley, rice, corn, brown rice

Take about 200 g of representative sample, pass through a 2.0 mm sieve, mix thoroughly and place into a clean container as test sample, seal and label.

5.1.2 Vegetable (Chinese cabbage)

Chinese cabbage: Take the eatable portions from the whole primary sample. It is about 200 g, and homogenize and place into a clean container as the test sample, seal and label.

5.2 Storage of test sample

The test samples of cereals should be stored at the range of 0 °C ~4 °C. The test sample of vegetable should be stored below -18 °C. During sampling and sample preparation, precaution should be taken to avoid contamination or any factor which may cause the change of residue content.

6 Procedure

6.1 Extraction

6.1.1 wheat, barley, corn, rice, brown rice

Weigh 5 ± 0.01 g of the test sample into a 50 mL polypropylene bottle, add 15.0 mL of HPLC-grade water, stand for 20 min.

Add 15.0 mL acetonitrile into the polypropylene bottles, blend for 2 min with vortex mixer in 20 000 r/min, centrifuge for 10 min under 3 000 r/min, transfer the above solution, extract the residue with 15.0 mL acetonitrile once more, filter and combine the washings in another 50 mL, polypropylene bottle with adding 3.5 g sodium chloride.

6.1.2 Vegetable

Weigh 10 ± 0.01 g of the test sample into a 50 mL polypropylene bottle, then according to 6.1.1 the second section.

6.2 Liquid-liquid extraction

Add 2.0 mL Phosphate buffered solution into the polypropylene bottles, shake for 5 min, centrifuge for 5 min under 3 000 r/min, combined the acetonitrile phase, and let pass through anhydrous sodium sulfate to remove the water. Collect the effluent in a 100 mL concentrate bottle and evaporate to near dryness in a rotary evaporator with a bath temperature below 40 °C, dilute exactly to 2.0 mL with acetonitrile-toluene.

6.3 SPE clean up

With the ENVI-Carb column and the LC-NH₂ column, above is ENVI-Carb column, under is LC-NH₂ column, add anhydrous sodium sulfate about 0.5 cm into the ENVI-Carb column, rinse the ENVI-Carb column and LC-NH₂ column with 10 mL of acetonitrile-toluene before use, transfer the above solution into the ENVI-Carb column and the LC-NH₂ column. Then elute with 10 mL of acetonitrile-toluene, collect all the elutes in a 15 mL clean tube and operate to nearly dryness with gentle nitrogen in 40 °C water bath. Dissolve the residue and dilute exactly to 0.5 mL with mobile phase for GPC-GC/MS de-

termination and confirmation.

6.4 Determination

6.4.1 GPC operating condition

- a) GPC column: Shodex CLNpak EV-200 150 mm × 2.1 mm (i. d.);
- b) Mobile phase: Acetone-cyclohexane (3+7, V/V);
- c) Flow rate: 0.1 mL/min;
- d) Column temperature: 40 °C;
- e) Injection volume: 10 μL;
- f) Collect the time: 4.29 min~6.29 min.

6.4.2 GC/MS condition

- a) Column(uncoated): Deactivated silica tubing 5 m × 0.53 mm(i. d.); equivalent;
Column(pre-column): DB-5MS 5 m × 0.25 mm(i. d.) × 0.25 μm(film thickness); equivalent;
Column(analysis): DB-5MS 30 m × 0.25 mm(i. d.) × 0.25 μm(film thickness); equivalent;
- b) PTV injection mode;
- c) Injection temperature: 120 °C (5 min) → 100 °C/min → 250 °C (31.7 min);
- d) Column temperature: 82 °C (5 min) → 8 °C/min → 310 °C (5 min);
- e) Carrier gas: Helium, purity ≥ 99.999%, 1.7 mL/min;
- f) Ionization mode: (EI): 70 eV;
- g) Ionization temperature: 200 °C;
- h) Transfer line temperature: 300 °C;
- i) Determination mode: SIM mode;

j) Selected monitoring ion (m/z): table 1.

Table 1—Monitor ion and relative intensity for chlorthalonil, dichlofluanid, tolylfluanid, captan, folpet, captafol and deltamethrin

Pesticides	Monitor ion(m/z)	Relative intensity/%
Chlorothalonil	266 (Quantitattion ion), 109, 231, 194	100 : 25 : 15 : 9
Dichlofluanid	123 (Quantitattion ion), 167, 224, 332	100 : 45 : 30 : 6
Tolyfluanid	137 (Quantitattion ion), 238, 181, 355	100 : 40 : 25 : 5
Captan	149 (Quantitattion ion), 107, 264, 182	100 : 70 : 25 : 15
Folpet	104 (Quantitattion ion), 260, 178, 297	100 : 80 : 25 : 20
Captafol	183 (Quantitattion ion), 149, 313, 236	100 : 80 : 60 : 20
Tralomethrin	181 (Quantitattion ion), 253, 174, 209	100 : 85 : 25 : 9

6.4.3 Determination and confirmation by GC/MS

According to operating parameters of GC/MS above, sample solution and the standard working solution are determined simultaneously. The responses of the analyte in the standard working solution and the sample solution all should be within the linear range of the instrument detection and quantified by internal standard. The reference retention time of chlorthalonil, dichlofluanid, tolylfluanid, captan, folpet, captafol and deltamethrin is about 20.27 min, 22.13 min, 23.12 min, 23.42 min, 23.71 min, 27.30 min and 33.56 min respectively. MRM chromatograms of the standards are listed as figure A.1 in annex A.

Use the established GC/MS parameters above for determination, and calculate the abundance ratio of two selected ion pairs of the sample solution and the standard working solution. If the retention times of sample chromatogram peaks are consistent with that of working solution, and relative abundance ratio tolerance is listed in table 2, it is positive to conclude that this pesticide do exist in the sample.

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

Relative intensity/%	>50	>20~50	>10~20	≤10
Permitted tolerances/%	±10	±15	±20	±50

6.5 Blank test

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

7 Calculation and expression of result

Calculate the content of pesticide residue in the test sample by GC/MS data processor or according to the formula (1). The blank value should be subtracted from result of calculation above.

$$X = \frac{A \cdot c \cdot V}{A_s \cdot m} \dots\dots\dots (1)$$

where

X —the residue content of pesticides in the test sample, $\mu\text{g/g}$;

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

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

c —the concentration of pesticides in the standard working solution, $\mu\text{g/mL}$;

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

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

8 Limit of quantitation(LOQ)and recovery

8.1 Limit of quantitation

The limit of quantitation (LOQ) of the method for tea is 0.01 mg/kg.

8.2 Recovery

Listed in table 3.

Table 3—Recovery range of chlorothalonil, dichlofluanid, tolyfluanid, captan, folpot, captafol and tralomethrin

Sample	Pesticides	Spike/(mg/kg)	Recovery/%
Rice	Chlorothalonil	0.01	72.0~119.0
		0.05	75.5~95.6
		0.10	71.2~94.3
	Dichlofluanid	0.01	76.0~114.0
		0.05	86.3~130.6
		0.10	69.4~104.4
	Tolyfluanid	0.01	60.0~89.0
		0.05	98.5~130.7
		0.10	75.4~101.5
	Captan	0.01	70.0~91.0
		0.05	89.8~125.8
		0.10	81.4~112.5
	Folpot	0.01	62.0~85.0
		0.05	66.1~83.1
		0.10	88.5~122.7
	Captafol	0.01	82.0~120.0
		0.05	77.4~110.4
		0.10	70.7~92.2
Tralomethrin	0.01	70.0~115.0	
	0.05	107.5~120.0	
	0.10	89.1~127.3	

Table 3 (continued)

Sample	Pesticides	Spike/(mg/kg)	Recovery/%
Brown rice	Chlorothalonil	0.01	84.0~130.0
		0.05	67.2~89.3
		0.10	68.3~88.4
	Dichlofluanid	0.01	65.0~91.0
		0.05	71.3~96.4
		0.10	71.5~95.6
	Tolyfluanid	0.01	65.0~120.0
		0.05	75.4~91.7
		0.10	67.6~93.7
	Captan	0.01	70.0~88.0
		0.05	66.6~90.5
		0.10	68.5~91.5
	Folpot	0.01	65.0~82.0
		0.05	76.2~95.5
		0.10	65.3~91.4
	Captafol	0.01	79.0~120.0
		0.05	70.5~89.7
		0.10	70.5~89.3
	Tralomethrin	0.01	71.0~122.0
		0.05	69.8~88.6
		0.10	72.6~101.6
Barley	Chlorothalonil	0.01	67.0~90.0
		0.05	64.4~85.4
		0.10	78.4~95.4
	Dichlofluanid	0.01	89.0~109.0
		0.05	70.4~90.4
		0.10	75.4~99.1
	Tolyfluanid	0.01	67.0~85.0
		0.05	65.5~86.7
		0.10	89.2~103.3

Table 3 (continued)

Sample	Pesticides	Spike/(mg/kg)	Recovery/%
Barley	Captan	0.01	63.0~82.0
		0.05	69.7~91.5
		0.10	82.3~101.4
	Folpot	0.01	78.0~101.0
		0.05	78.6~99.2
		0.10	75.4~99.3
	Captafol	0.01	61.0~75.0
		0.05	64.4~88.4
		0.10	68.5~90.4
	Tralomethrin	0.01	74.0~98.0
		0.05	81.5~98.2
		0.10	75.5~102.2
Wheat	Chlorothalonil	0.01	66.0~95.0
		0.05	69.2~85.3
		0.10	80.8~98.3
	Dichlofluanid	0.01	72.0~91.0
		0.05	72.4~91.3
		0.10	73.5~89.5
	Tolyfluanid	0.01	62.0~85.0
		0.05	74.3~89.4
		0.10	63.5~85.2
	Captan	0.01	75.0~98.0
		0.05	69.4~91.4
		0.10	72.1~86.2
	Folpot	0.01	86.0~110.0
		0.05	68.5~93.6
		0.10	68.3~91.4
	Captafol	0.01	71.0~95.0
		0.05	65.1~94.1
		0.10	63.4~91.4
	Tralomethrin	0.01	79.0~110.0
		0.05	82.3~101.3
		0.10	67.4~95.5

Table 3 (continued)

Sample	Pesticides	Spike/(mg/kg)	Recovery/%
Corn	Chlorothalonil	0.01	68.0~91.0
		0.05	75.3~101.4
		0.10	62.8~85.7
	Dichlofluanid	0.01	65.0~85.0
		0.05	66.6~87.7
		0.10	67.6~87.8
	Tolyfluanid	0.01	71.0~94.0
		0.05	64.6~94.6
		0.10	62.8~91.9
	Captan	0.01	70.0~86.0
		0.05	63.5~90.7
		0.10	74.5~94.4
	Folpot	0.01	75.0~98.0
		0.05	61.2~85.4
		0.10	75.4~99.1
	Captafol	0.01	65.0~81.0
		0.05	62.4~80.5
		0.10	69.4~91.8
Tralomethrin	0.01	67.0~89.0	
	0.05	81.4~98.5	
	0.10	79.3~97.4	
Vegetable	Chlorothalonil	0.01	66.0~91.0
		0.05	61.4~81.5
		0.10	71.6~98.1
	Dichlofluanid	0.01	73.0~92.0
		0.05	71.5~93.7
		0.10	72.4~94.4
	Tolyfluanid	0.01	69.0~92.0
		0.05	76.6~98.7
		0.10	67.5~91.6
Captan	0.01	65.0~95.0	
	0.05	75.5~102.1	
	0.10	67.4~93.5	

Table 3 (continued)

Sample	Pesticides	Spike/(mg/kg)	Recovery/%
Vegetable	Folpot	0.01	72.0~89.0
		0.05	74.4~102.5
		0.10	70.7~91.5
	Captafol	0.01	69.0~96.0
		0.05	69.5~94.5
		0.10	70.3~101.4
	Tralomethrin	0.01	85.0~105.0
		0.05	62.8~85.1
		0.10	76.4~103.1

Annex A
(Informative annex)

GC-MS chromatogram (TIC) of the chlorothalonil, dichlofluanid, tolyfluanid, captan, folpot, captafol and tralomethrin standards

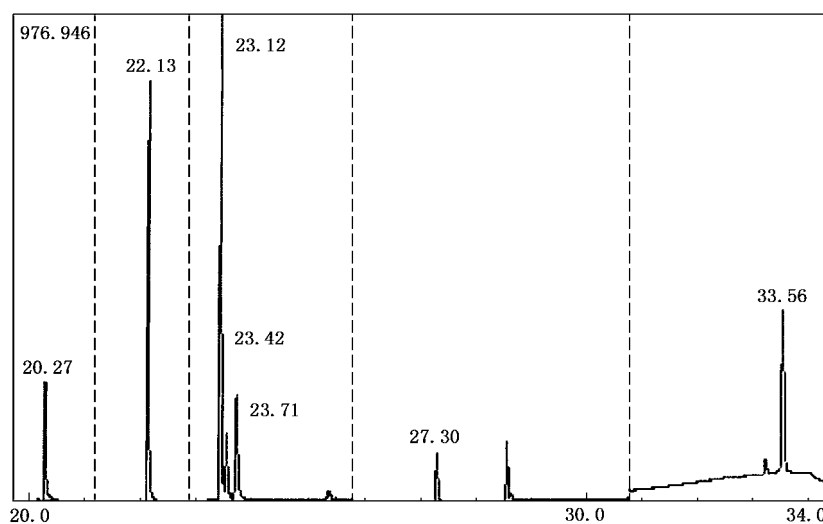
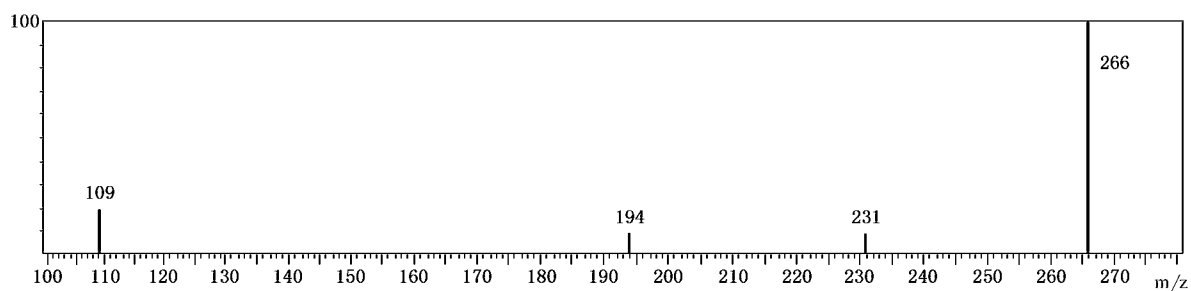
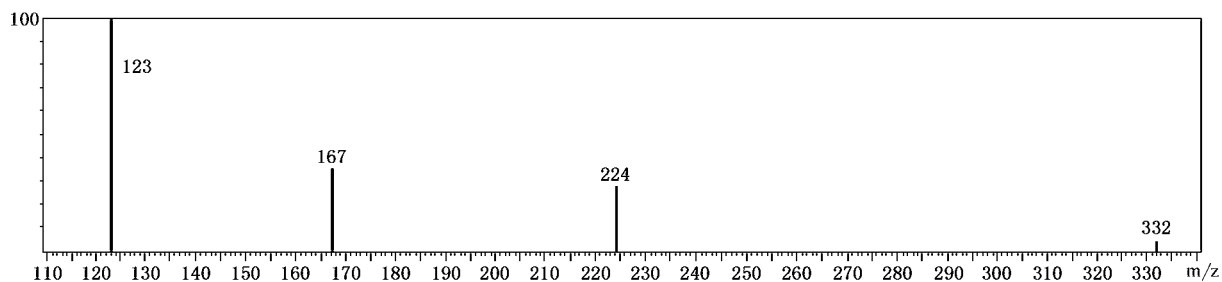


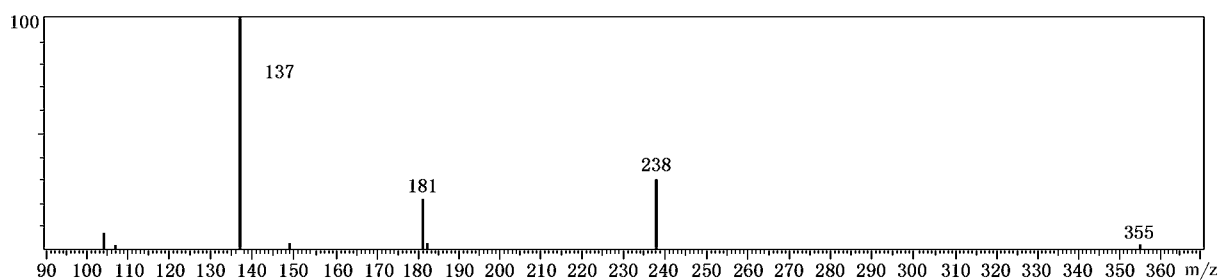
Figure A. 1—GC/MS chromatogram (TIC) of the chlorothalonil, dichlofluanid, tolyfluanid, captan, folpot, captafol and tralomethrin pesticides standards (Time is 20.27 min, 22.13 min, 23.12 min, 23.42 min, 23.71 min, 27.30 min and 33.56 min)



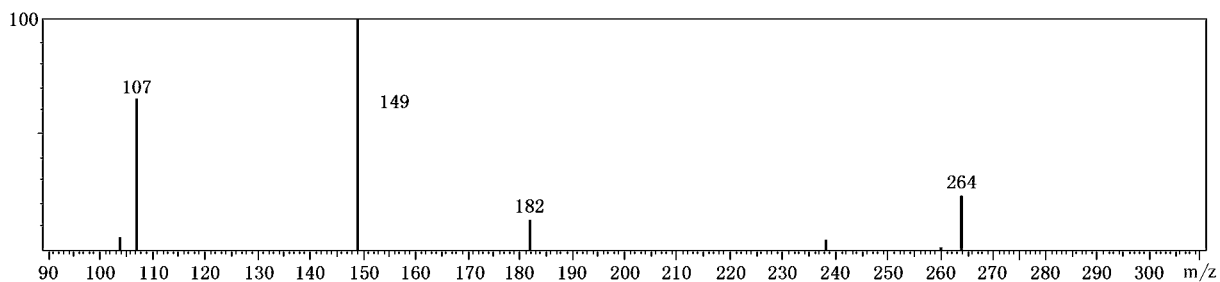
a) mass spectrum of chlorothalonil



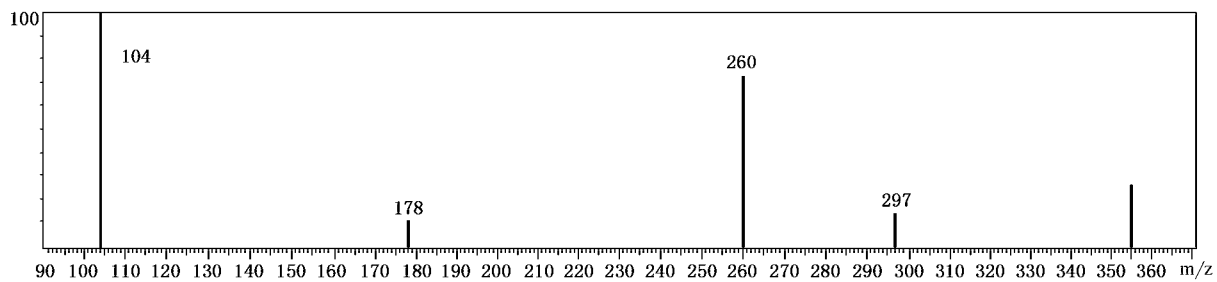
b) mass spectrum of dichlofluanid



c) mass spectrum of tolyfluanid



d) mass spectrum of captan



e) mass spectrum of folpot

Figure A. 2—Chromatogram and mass spectrum of chlorothalonil, dichlofluanid, tolyfluanid, captan, folpot, captafol and tralomethrin standards

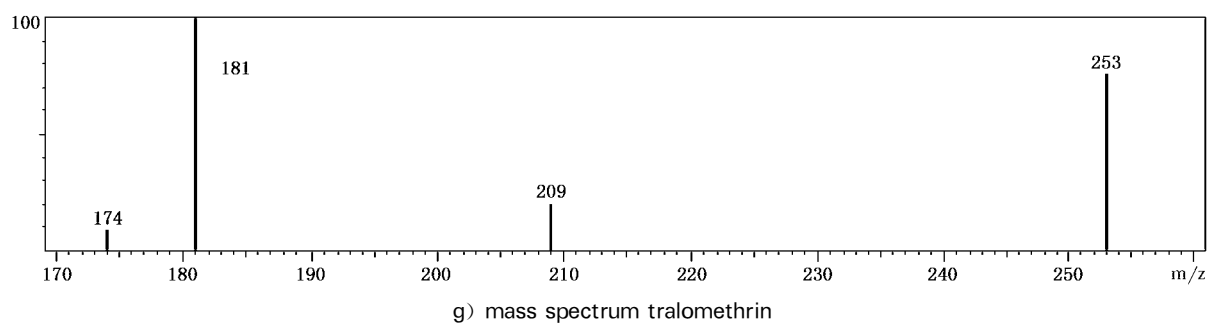
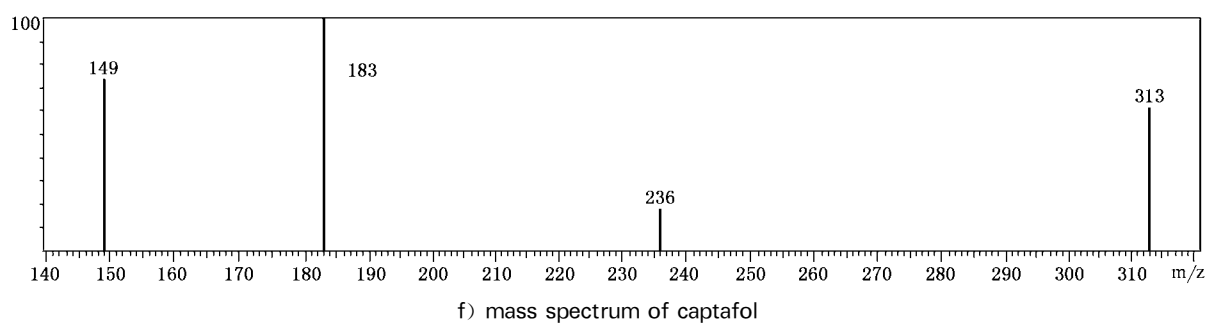


Figure A. 2 (continued)

中华人民共和国出入境检验检疫
行 业 标 准
进出口食品中百菌清、苯氟磺胺、甲抑菌
灵、克菌丹、灭菌丹、敌菌丹和四溴菊
酯残留量检测方法
气相色谱-质谱法
SN/T 2320—2009

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中国标准出版社出版
北京复兴门外三里河北街16号
邮政编码:100045

网址 www.spc.net.cn

电话:68523946 68517548

中国标准出版社秦皇岛印刷厂印刷

*

开本 880×1230 1/16 印张 2 字数 46 千字
2009年11月第一版 2009年11月第一次印刷
印数 1—2 000

*

书号: 155066·2-20015 定价 30.00 元



SN/T 2320—2009