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中华人民共和国出入境检验检疫行业标准

SN/T 1978—2007

进出口食品中狄氏剂和异狄氏剂残留量检测方法　气相色谱-质谱法

Determination of dieldrin and endrin residues in food for import and export—GC-MS method

2007-08-06 发布　　2008-03-01 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

本标准附录A、附录B均为资料性附录。

本标准由国家认证认可监督管理委员会提出并归口。

本标准起草单位：中华人民共和国广东出入境检验检疫局、中华人民共和国天津出入境检验检疫局、中华人民共和国吉林出入境检验检疫局、中华人民共和国河北出入境检验检疫局。

本标准主要起草人：陈捷、谢建军、王志元、王云凤、王明泰、葛宝坤、王凤池、朱柳明。

本标准系首次发布的出入境检验检疫行业标准。

进出口食品中狄氏剂和异狄氏剂残留量检测方法　气相色谱-质谱法

1　范围

本标准规定了食品中狄氏剂和异狄氏剂残留量检测的制样和气相色谱-质谱检测方法。

本标准适用于大米、绿豆、菠菜、青豆、柑橘、葡萄、板栗、醋、玫瑰花、茶叶、猪肉、鸡肉、猪肝、鳗鱼、蜂蜜中狄氏剂和异狄氏剂残留量的测定和确证。

2　方法提要

样品经乙腈-乙酸乙酯或正己烷-乙酸乙酯或乙酸乙酯提取后，通过中性氧化铝或弗罗里硅土或活性炭固相萃取小柱净化，采用气相色谱-质谱 NCI 模式选择离子测定，外标法定量。

3　试剂和材料

除另有规定外，试剂均为分析纯，水为去离子水。

3.1　丙酮。

3.2　乙酸乙酯。

3.3　正己烷。

3.4　乙腈：色谱纯

3.5　甲醇。

3.6　无水硫酸钠：650℃灼烧 4 h，在干燥器内冷却至室温，储于密封瓶中备用。

3.7　氯化钠。

3.8　乙腈＋乙酸乙酯(4＋1，体积比)：取乙腈 80 mL，加入 20 mL 乙酸乙酯，混匀。

3.9　乙腈＋乙酸乙酯(2＋3，体积比)：取乙腈 40 mL，加入 60 mL 乙酸乙酯，混匀。

3.10　正己烷＋乙酸乙酯(1＋1，体积比)：取正己烷 20 mL，加入 80 mL 乙酸乙酯，混匀。

3.11　正己烷＋丙酮(4＋1，体积比)：取正己烷 80 mL，加入 20 mL 丙酮，混匀。

3.12　标准物质及标准溶液：

a)　标准物质：狄氏剂：纯度大于等于 99.0%(CAS：60571)异狄氏剂：纯度大于等于 99.0%(CAS：72208)；

b)　狄氏剂和异狄氏剂标准储备液：准确称取适量狄氏剂、异狄氏剂，用乙酸乙酯配制成浓度为 1.00 mg/mL的标准储备液。该溶液于－18℃冰箱中保存；

c)　狄氏剂和异狄氏剂标准中间溶液：准确吸取适量标准储备液，用乙酸乙酯稀释至浓度为 10.0 μg/mL的标准中间溶液。该溶液在－18℃冰箱中保存；

d)　狄氏剂和异狄氏剂标准工作液：根据需要将标准中间溶液用乙酸乙酯稀释成适当浓度的标准工作液。该溶液在－18℃冰箱中保存。

3.13　中性氧化铝固相萃取柱：2 500 mg，6 mL。

3.14　弗罗里硅土固相萃取柱：1 000 mg，3 mL。

3.15　活性碳固相萃取柱：200 mg，3 mL。

3.16　Strata SDB-L 固相萃取柱：Styrene-Divinylbenzene Polymer，200 mg，3 mL，或相当者。

4 仪器和设备

4.1 气相色谱-质谱联用仪，配有负离子化学源(NCI)。
4.2 高速均质机。
4.3 水浴超声波发生装置。
4.4 离心机：4 000 r/min，6 000 r/min。
4.5 旋转蒸发仪。
4.6 氮气吹干仪。
4.7 固相萃取装置。
4.8 旋涡振荡器。
4.9 玻璃刻度离心试管，5 mL，具塞。
4.10 聚四氟乙烯螺口离心瓶：50 mL。
4.11 砂芯漏斗。

5 样品制备与保存

5.1 样品制备

5.1.1 菠菜、青豆、柑橘、葡萄

取有代表性样品约 500 g，将其可食用部分切碎后，用捣碎机加工成浆状。混匀，装入洁净容器，密闭，标明标记。

5.1.2 大米、绿豆、板栗、玫瑰花、茶叶

取有代表性样品约 500 g，用粉碎机粉碎并通过孔径 2.0 mm 圆孔筛。混匀，装入洁净容器，密闭，标明标记。

5.1.3 猪肉、鸡肉、猪肝、鳗鱼

取有代表性样品约 500 g，剔骨去皮，用绞肉机绞碎，混匀，装入洁净容器，密闭，标明标记。

5.1.4 醋

取有代表性样品约 500 g，混匀，装入洁净容器，密闭，标明标记。

5.1.5 蜂蜜

取代表性样品约 500 g，对无结晶的蜂蜜样品将其搅拌均匀；对有结晶析出的蜂蜜样品，在密闭情况下，将样品瓶置于不超过 60℃的水浴中温热，振荡，待样品全部融化后搅匀，迅速冷却至室温，在融化时应注意防止水分挥发。装入洁净容器，密封，标明标记。

5.2 试样保存

茶叶、蜂蜜、醋、粮谷及坚果类等试样于 0℃～4℃保存；水果蔬菜类和动物源性食品等试样于－18℃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 大米、绿豆

称取 5.0 g(精确至 0.01 g)试样于 50 mL 离心管中，加 3 g 氯化钠，加 20 mL 乙腈＋乙酸乙酯(4＋1，体积比)(3.8)，加 3 g 无水硫酸钠，匀质提取 1 min，超声 10 min，4 000 r/min 离心 5 min，移取上清液于鸡心瓶中，再分别用 10 mL 乙腈＋乙酸乙酯(4＋1，体积比)洗涤残渣两次，合并提取液，在 45℃下减压浓缩至近干，用 1.0 mL 正己烷溶解残渣，待净化。

6.1.2 菠菜、青豆、柑橘、葡萄

准确称取 20.0 g(精确至 0.01 g)试样于 100 mL 具塞三角锥瓶，加入 6 g 氯化钠，搅匀，加入 20 mL

乙酸乙酯提取，振荡 1 min，再加 10 g 无水硫酸钠，涡动 1 min，超声 10 min。

取砂芯漏斗装入 40 g 的无水硫酸钠，将上述的样本及乙酸乙酯混合液过此无水硫酸钠柱。再用 15 mL×3 乙酸乙酯淋洗残渣 3 次，合并滤液其于 50 mL 比色管中，用乙酸乙酯定容至 50 mL，摇匀，移取 10 mL 于 20 mL 试管中，待净化。

6.1.3 猪肉、鸡肉、猪肝

称取 5.0 g(精确至 0.01 g)试样于 50 mL 离心管中，加 10 g 无水硫酸钠，25 mL 乙腈＋乙酸乙酯(2＋3，体积比)(3.9)，匀质提取 1 min，超声 10 min，6 000 r/min 离心 5 min，移取 10 mL 上清液于 20 mL试管中，待净化。

6.1.4 鳗鱼、板栗

称取 5.0 g(精确至 0.01 g)试样于 50 mL 离心管中，加 10 g 无水硫酸钠，25 mL 乙腈＋乙酸乙酯(4＋1，体积比)，匀质提取 1 min，超声 10 min，6 000 r/min 离心 5 min，移取 10 mL 上清液于20 mL试管中，待净化。

6.1.5 茶叶、玫瑰花

称取 0.5 g(精确至 0.001 g)试样于 10 mL 离心管中，加 1.5 mL 水，浸泡 20 min，加 0.2 g 氯化钠，0.2 g 无水硫酸钠，振荡混匀，加 3×2 mL 正己烷＋乙酸乙酯(4＋1，体积比)(3.10)提取 3 次，旋涡振荡提取，离心 4 000 r/min 离心 3 min，合并提取液，待净化。

6.1.6 蜂蜜、醋

称取 1.0 g(精确至 0.01 g)试样于 10 mL 试管中，蜂蜜需加 5 mL 水，稀释混匀，过 SDB-L 固相萃取柱(3.16，依次用 2 mL 甲醇、2 mL 水活化小柱)，用 15 mL 水洗涤，流速控制为 3 mL/min，抽干 2 min，依次用 2 mL 丙酮、3 mL 乙酸乙酯洗脱，流速控制为 1 mL/min，收集洗脱液于鸡心瓶中，在 45℃下减压浓缩至约 0.5 mL，待净化。

6.2 净化

6.2.1 大米、绿豆、蜂蜜、醋

弗罗里硅土固相萃取柱(3.14)上端填装 0.5 g 无水硫酸钠。用 3 mL 正己烷＋丙酮(4＋1，体积比)(3.11)活化小柱。将待净化溶液过弗罗里硅土固相萃取柱，用 4×1.0 mL 正己烷＋丙酮(4＋1，体积比)洗脱 4 次。流速控制为 1 mL/min，收集洗脱液于 10 mL 玻璃试管中，在 45℃下吹氮浓缩至近干，用乙酸乙酯定容至 1.0 mL，待测。

6.2.2 菠菜、青豆、柑橘、葡萄

活性碳固相萃取柱(3.15)用 2×2 mL 乙酸乙酯活化柱两次，弃去流出液。将待净化溶液过活性炭固相萃取柱，再用 2×2 mL 乙酸乙酯洗脱两次，流速控制为 1 mL/min，收集洗脱液 10 mL 玻璃试管中，在 45℃下吹氮浓缩至近干，用乙酸乙酯定容至 1.0 mL，待测。

6.2.3 猪肉、鸡肉、猪肝、鳗鱼、板栗

中性氧化铝固相萃取柱(3.13)上填装 1 g 无水硫酸钠，用 4 mL 乙腈＋乙酸乙酯(4＋1，体积比)活化，弃去流出液。将待净化溶液过中性氧化铝固相萃取柱，用 2 mL 乙腈＋乙酸乙酯(4＋1，体积比)洗脱，控制流速为 1 mL/min，收集洗脱液于玻璃试管中，在 45℃下减压浓缩至近干，加入 1.0 mL 正己烷＋丙酮(4＋1，体积比)振摇溶解残渣，过弗罗里硅土固相萃取柱(柱上填装 0.5 g 无水硫酸钠)，用 4×1.0 mL正己烷＋丙酮(4＋1，体积比)洗脱4 次，流速控制为 1 mL/min，收集洗脱液，在 45℃下吹氮浓缩至近干，用乙酸乙酯定容至 1.0 mL，待测。

6.2.4 茶叶、玫瑰花

活性炭固相萃取柱用 2×2 mL 乙酸乙酯活化两次，弃去流出液。将待净化溶液过活性炭固相萃取柱，用1 mL乙酸乙酯洗脱，流速控制为 1 mL/min，收集洗脱液，在 45℃下吹氮浓缩至约 0.5 mL，过弗罗里硅土固相萃取柱(柱上端填装 0.5 g 无水硫酸钠)，用 4×1.0 mL 正己烷＋丙酮(4＋1，体积比)洗脱 4 次，流速控制为 1 mL/min，收集洗脱液 10 mL 玻璃试管中，在 45℃下吹氮浓缩至近干，用乙酸乙酯定

容至 1.0 mL，待测。

6.3 测定

6.3.1 气相色谱-质谱条件

a) 色谱柱：DB-XLB 石英毛细管柱，30 m×0.25 mm(内径)×0.25 μm，或性能相当者；

b) 载气：氦气(纯度 99.999%)，流量 1.5 mL/min；压力：14.6 Psi；

c) 进样模式：无分流进样，1 min 后开阀；

d) 进样量：1 μL；

e) 进样口温度：270℃；

f) 接口温度：280℃；

g) 升温程序：80℃(1.5 min)$\xrightarrow{20℃/min}$220℃(3 min)$\xrightarrow{5℃/min}$255℃$\xrightarrow{20℃/min}$280℃(4 min)；

h) 电离方式：NCI；

i) 离子源温度(NCI)：150℃；

j) 四极杆温度：150℃；

k) 溶剂延迟：5 min；

l) 反应气：甲烷；流量：40%；

m) 检测方式：SIM；

n) 监测离子和定量离子：见表 1

表 1 监测离子和定量离子

目标物	时间/min	监测离子(m/z)	定量离子(m/z)
狄氏剂	16.1	237,380,239,346	346
异狄氏剂	16.9	380,70,308,315	380

6.3.2 气相色谱-质谱检测及确证

根据试样中被测物的含量情况，选取响应值相近的标准工作溶液，标准工作溶液和待测样液中被测物的响应值均应在仪器线性范围内。对标准工作溶液和样液等体积参插进样测定。

标准溶液及样液均按 6.3.1 规定的条件进行测定，如果样液中与标准溶液相同的保留时间有峰出现，则对其进行确证。经确证分析被测物质量色谱峰保留时间与标准物质相一致，并且在扣除背景后的样品谱图中，所选择的离子均出现；同时所选择离子的丰度比与标准样物质相关离子的相对丰度一致，相似度在允差之内(见表 2)，被确证的样品可判定为狄氏剂和异狄氏剂阳性检出。狄氏剂和异狄氏剂标准物质的气相色谱-质谱选择离子色谱图和质谱图参见附录 A 和附录 B。

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/%	±20	±25	±30	±50

6.4 空白试验

除不加试样外，按上述测定步骤进行。

7 结果计算和表述

用色谱数据处理机或按式(1)计算试样中狄氏剂和异狄氏剂的残留含量，计算结果需扣除空白值。

$$X = \frac{A \times c \times V}{A_s \times m} \quad \cdots\cdots(1)$$

式中：

X——试样中狄氏剂和异狄氏剂含量，微克每千克(μg/kg)；

A——样液中狄氏剂和异狄氏剂特征单离子的色谱峰面积；

A_S——标准工作溶液中狄氏剂和异狄氏剂特征单离子的色谱峰；

c——标准工作溶液中狄氏剂和异狄氏剂浓度，微克每升(μg/L)；

V——最终样液的定容体积，毫升(mL)；

m——最终样液所代表试样量，克(g)。

注：计算结果应扣除空白值。计算结果应表示到小数点后两位。

8 测定低限、回收率

8.1 测定低限

本方法鳗鱼和蜂蜜中狄氏剂的测定低限为2.5 μg/kg，其他样品中狄氏剂的测定低限均为5.0 μg/kg；异狄氏剂的测定低限均为5.0 μg/kg。

8.2 回收率

狄氏剂和异狄氏剂添加浓度及回收率的实验数据见表3。

表3 狄氏剂和异狄氏剂的回收率

样品名称	添加浓度/(μg/kg)	回收率/%	
		狄氏剂	异狄氏剂
大米	5.0	80.6～93.2	85.0～99.2
	10	84.5～98.6	86.5～97.4
	50	88.8～99.8	87.9～99.5
绿豆	5.0	82.8～93.6	88.6～98.4
	10	88.5～97.6	88.3～98.2
	50	90.4～98.2	87.6～98.4
菠菜	5.0	77.2～86.8	80.4～93.4
	10	87.6～95.4	83.2～94.7
	50	89.6～97.1	89.0～98.2
青豆	5.0	79.6～91.4	80.8～92.2
	10	88.7～94.1	89.0～94.1
	50	91.4～100.2	91.2～97.0
柑橘	5.0	76.2～87.2	76.8～84.0
	10	83.2～92.3	83.3～92.0
	50	85.2～95.6	89.4～96.4
葡萄	5.0	77.4～87.4	77.0～84.4
	10	86.5～94.0	83.2～95.7
	50	89.8～97.6	88.4～96.2
猪肉	5.0	80.4～88.4	87.0～100.6
	50	80.2～86.9	88.4～102.0
	100	85.9～93.2	90.5～94.7

表 3(续)

样品名称	添加浓度/(μg/kg)	回收率/%	
		狄氏剂	异狄氏剂
鸡肉	5.0	77.8～91.8	87.2～102.4
	10	83.2～92.3	82.6～92.4
	100	85.5～95.2	87.3～96.5
猪肝	5.0	82.4～89.4	85.8～100.8
	10	82.0～90.5	96.5～103.2
	50	86.4～92.7	90.1～96.4
鳗鱼	狄氏剂 2.5 异狄氏剂 5.0	89.2～92.4	92.0～97.2
	10	89.6～94.6	91.2～96.1
	50	91.6～96.2	90.8～97.2
茶叶	5.0	83.2～90.8	89.6～106.4
	10	80.6～88.0	82.4～96.6
	50	88.4～97.0	90.8～95.4
板栗	5.0	81.6～92.4	89.6～96.6
	10	89.5～96.3	90.7～96.3
	50	90.4～99.8	90.2～99.2
醋	5.0	97.4～105.8	84.0～98.0
	10	92.1～98.5	95.6～102.2
	50	92.6～99.0	94.2～99.8
玫瑰花	5.0	77.2～91.4	88.2～102.6
	10	79.4～93.4	80.4～92.1
	50	84.8～97.0	85.4～98.8
蜂蜜	2.5	76.8～84.8	80.8～100.4
	10	87.5～107.3	87.9～100.6
	50	90.4～99.6	91.4～98.8

附 录 A
（资料性附录）
狄氏剂和异狄氏剂选择离子色谱图

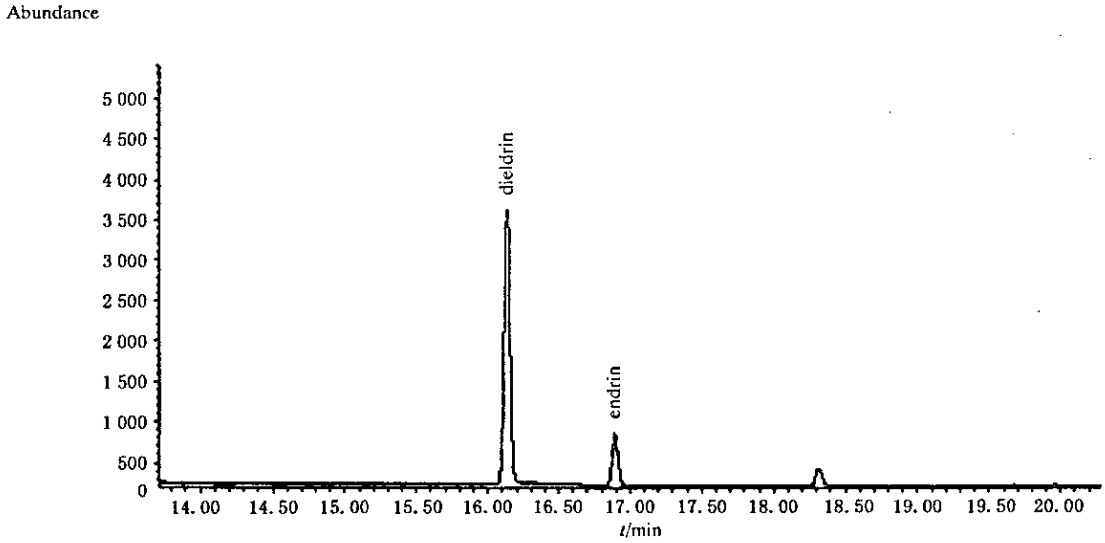

图 A.1 狄氏剂和异狄氏剂的 NCI 选择离子色谱图(TIC)

附 录 B
（资料性附录）
狄氏剂和异狄氏剂全扫描质谱图

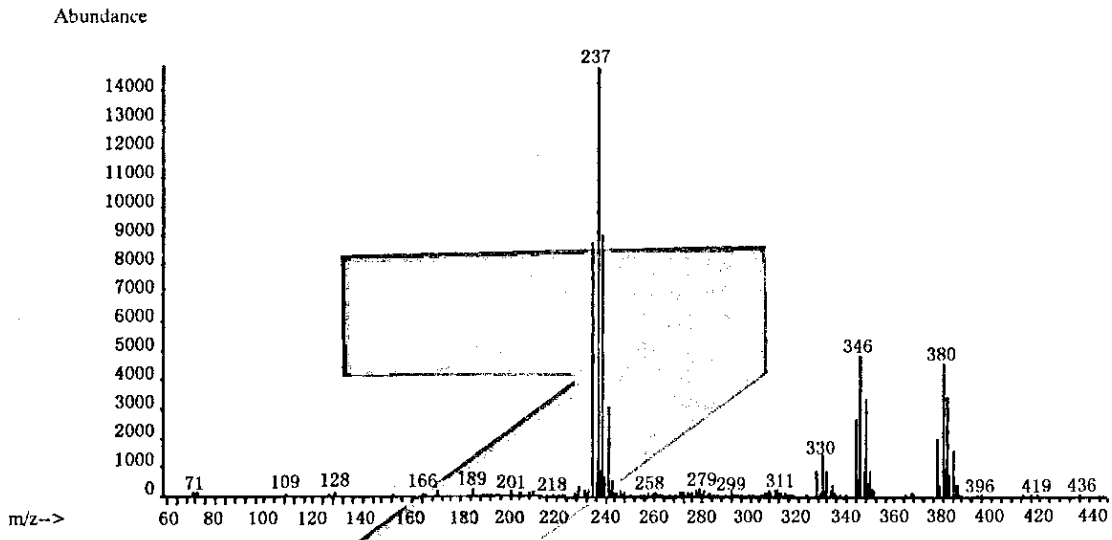

图 B.1 狄氏剂 NCI 全扫描质谱图

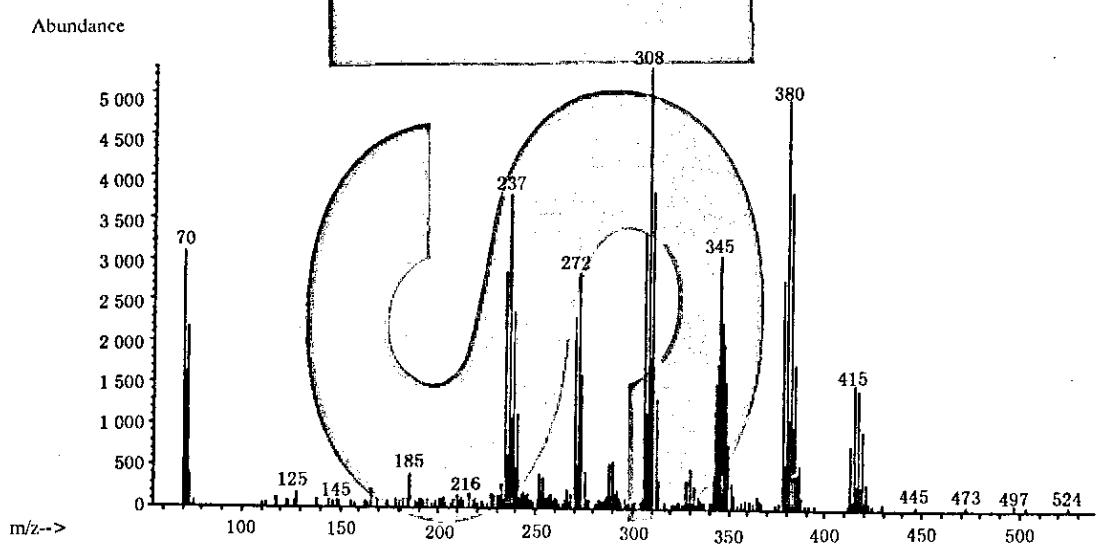

图 B.2 异狄氏剂 NCI 全扫描质谱图

Foreword

Annex A of this standard is an informative annexe.

This standard was proposed by and is under the charged of the Certification and Accreditation Administration of the people's Republic of China.

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

The main drafters of this standard are Chen Jie, Xie Jianjun, Wang Zhiyuan, Wang Yunfeng, Wang Mingtai, Ge Baokun, Zhu liuming and Wang Fengchi.

This standard is an Entry-Exit Inspection and Quarantine professional standard promulgated for the first time.

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

Determination of dieldrin and endrin residues in food for import and export—GC-MS method

1 Scope

The standard specifies the determination and confirmation of dieldrin and endrin residues in foods by Gas chromatography-mass spectrometry.

This standard is applicable to the determination and confirmation of dieldrin and endrin residues in rice,mung bean,spinage,string bean,orange,grape, chestnut,vinegar, rose,tea, pork,chicken,pork liver, eel and honey.

2 Principle

The residues in test samples are extracted with acetonitrile-ethyl acetate or *n*-Hexane-ethyl acetate or ethyl acetate. The extracts are cleaned up by neutral alumina SPE cartridge or florisil SPE cartridge or active carbon SPE cartridge. Determination and confirmation made by GC-MS in NCI mode and using external standard method.

3 Reagents and materials

Unless otherwise specified,all regents used should be analytical grade, "water" is distilled water.

3.1 Acetone.

3.2 Ethyl acetate.

3.3 *n*-Hexane.

3.4 Acetonitrile: chromatogram grade.

3.5 Methanol

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

3.7 Sodium chloride.

3.8 Acetonitrile-ethyl acetate (4+1, *V*/*V*): Mix 80 mL of acetonitrile with 20 mL of ethyl acetate.

3.9 Acetonitrile-ethyl acetate (2+3, *V*/*V*): Mix 40 mL of acetonitrile with 60 mL of ethyl acetate.

3.10 *n*-Hexane-ethyl acetate (1+4, *V*/*V*): Mix 20 mL of *n*-Hexane with 80 mL of ethyl acetate.

3.11 *n*-Hexane-acetone (4+1, *V*/*V*): Mix 80 mL of *n*-Hexane with 20 mL of acetone.

3.12 Standards and standard solutions:

a) Dieldrin: Purity≥99.0%(CAS: 60571) Endrin: Purity≥99.0%, (CAS:72208);

b) Standard stock solution: Accurately weigh adequate amount of dieldrin and endrin standards separately, dissolve with ethyl acetate and prepare a solution of 1.00 mg/mL as standard stock solution. Standard stock solution stored at −18℃ in a refrigerator;

c) Standard middle solution: pipette adequate amount of standard stock solution, dilute with ethyl acetate to prepare a solution of 10 μg/mL as standard working solution. Stored at −18℃ in a refrigerator;

d) Standard working solutions: pipette adequate amount of standard stock solution, dilute with ethyl acetate to prepare appropriate concentration standard working solutions. Stored at −18℃ in a refrigerator.

3.13 Neutral alumina SPE cartridge: 2 500 mg, 6 mL

3.14 Florisil SPE cartridge: 1 000 mg, 3 mL

3.15 Active carbon SPE tubes: 200 mg, 3 mL, ENVI-Carb, or equivalent.

3.16 Strata SDB-L SPE cartridge: Styrene-Divinylbenzene Polymer, 200 mg, 3 mL, or equivalent.

4 Apparatus and equipment

4.1 Gas chromatograph-mass spectrometry with negative chemical ionization. interface.

4.2 High Speed Homogenizer.

4.3 Ultrasonic water bath.

4.4 Centrifuge: 4 000 r/min, 6 000 r/min.

4.5 Rotary vacuum evaporator.

4.6 Nitrogen evaporator.

4.7 Solid phase extraction vacuum manifold.

4.8 Vortex mixer.

4.9 Glass tube with scale, 5 mL with stopper.

4.10 Centrifuge tube, polytetrafluoroethylene, 50 mL.

4.11 Sand funnel.

5 Sample preparation and storage

5.1 Preparation of test sample

5.1.1 spinage,string bean,orange,grape

Representative sample,about 500 g. Edible part is minced and prepare to be starchy with a blender. The sample is mixed and placed in a clean container,which is sealed and. labeled.

5.1.2 rice,mung bean, chestnut, rose,tea

Representative sample,about 500 g, which is crushed and passed through a 2.0mm mesh sieve. The sample is mixed and placed in a clean container,which is sealed and. labeled.

5.1.3 pork,chicken,pork liver, eel

Representative sample,about 500 g, the bone and tegument should be discarded. Sample is blended with a blender,mixed and placed in a clean container,which is sealed and. labeled.

5.1.4 vinegar

Representative sample,about 500 g, mixed and placed in a clean container,which is sealed and. labeled.

5.1.5 honey

Representative sample,about 500 g. The sample which is not crystallized shall be stirred well to make homogeneous. If the sample is crystallized,it must be warmed in a water-bath below 60℃ with the sample bottle covered tightly,mix thoroughly when all sample has melted, then cool immediately to room temperature. In the course of samle melting, precautions must be taken to avoid evaporation of water from the smple. Place in a clean container,which is labeled and sealed.

5.2 Storage of sample

Tea, honey,viegar,grain and nut should be stord 0℃～4℃;vegetable and fruit The test should be

stord below −18℃. In the course of sampleing and sample preparation, precaution should be taken to avolid contamination or any factors that may cause change of the residue content.

6 Procedure

6.1 Extraction

6.1.1 Rice, mung bean

Weigh 5.0 g (accurate to 0.01 g) of test sample into a 50 mL centrifuge tube, add 3 g of sodium chloride, 20 mL of acetonitrile-ethyl acetate (4 ∶ 1, *V*/*V*) (3.8) and 3 g of anhydrous sodium sulfate. Homogenize the sample for 1 min, and sonicate for 10 min. After centrifugation for 5 min at 4 000 r/min, the supernatant layer was transfered into a heart-shaped flask. Residue was rinsed twice with 10 mL of acetonitrile-ethyl acetate (4 ∶ 1, *V*/*V*) and combined the organic solvent. Evaporate the organic solvent to dryness with rotary evaporator at 45℃. Dissolve the residue with 1.0 mL of *n*-hexane for clean up.

6.1.2 spinage, string bean, orange, grape

Weigh accurately 20.0 g (accurate to 0.01 g) of test sample into a 100 mL conical flask with stopper, add 6 g of sodium chloride and mix. Extraction with 20 mL of ethyl acetate, vortex for 1 min, add 10 g of anhydrous sodium sulfate, vortex for 1 min and sonicate for 10 min.

Sample and extracted solution were passed through a sand funnel which was added 40 g of anhydrous sodium. Rinse the residue with 15 mL × 3 of ethyl acetate, collect the filtrate into a 50 mL of colorimetric tube and make up to the mark with ethyl acetate. Mix well and transfer 10 mL of ethyl acetate into a 20 mL glass tube for clean up.

6.1.3 Pork, chicken, pork liver

Weigh 5.0 g (accurate to 0.01 g) of test sample into 50 mL centrifuge tube, add 10 g of anhydrous sodium sulfate, 25 mL of acetonitrile-ethyl acetate (2 ∶ 3, *V*/*V*) (3.9). Homogenize the sample for 1 min, and sonicate for 10 min. After centrifugation for 5 min at 6 000 r/min. ,transfer 10 mL of the supernatant layer into a 20 mL tube for clean up.

6.1.4 Eel, chestnut

Weigh 5.0 g (accurate to 0.01 g) of test sample into a 50 mL centrifuge tube, add 10 g of anhydrous sodium sulfate and 25 mL of acetonitrile-ethyl acetate (4 ∶ 1, *V*/*V*). Homogenize the sample for 1 min, and sonicate for 10 min. After centrifugation for 5 min at 6 000 r/min, transfer 10 mL of the supernatant layer into a 20 mL tube for a clean up.

6.1.5 Tea, rose

Weigh 0.5 g (accurate to 0.001 g) of test sample into a 10 mL centrifuge tube, dipped in 1.5 mL water for 20 min. Add 0.2 g of sodium chloride and 0.2 g of anhydrous sodium sulfate, vortex to mix and add 2 mL×3 of *n*-hexane-ethyl acetate (4 : 1, *V*/*V*) (3.10), vortex for 2 min, centrifuge at 4 000 r/min for 3 min, and combined the supernatants for a clean up.

6.1.6 Honey, vinegar

Weigh 1.0 g(accurate to 0.01 g) of test sample into a 10 mL glass tube, add 5 mL water to mix. The diluted solution was passed through a SDB-L SPE column (wash the culumn with 2 mL of methanol and 2 mL of water before use)(3.16), and then rinse the column with 15 mL of water at a flow rate of 3 mL/min, dry the column for 2 min. And then,elute the column with 2 mL of acetone and 3 mL of ethyl acetate at a flow rate of 1 mL/min. Collect the eluents into a heart-shaped flask. Evaporate nearly to 0.5 mL with rotary evaporator at 45℃ for a clean up.

6.2 Clean-up

6.2.1 Rice, mung bean, honey, vinegar

Setting SPE vacuum manifold, fill 0.5 g anhydrous sodium sulfate on the top of the florisil SPE column (3.14). Condition the florisil SPE column with 3 mL of *n*-hexane-acetone(4 : 1, *V*/*V*) (3.11) before use. Pass the sample extraction solution through the column and rinse the column with 1.0 mL×4 of *n*-hexane -acetone(4 : 1, *V*/*V*) at a flow rate of 1 mL/min. Collect the eluents in a 10 mL glass tube and evaporate under nitrogen to dryness at 45℃. Dissolve the residue and dilute to 1.0 mL with ethyl acetate for GC-MS analysis.

6.2.2 spinage,string bean,orange,grape

Setting SPE vacuun manifold. Condition the ENVI-Carb SPE column(3.15) with 2 mL×2 of ethyl acetate before use. Pass the sample extraction solution through the column and rinse the column with 2.0 mL×2 of ethyl acetate at a flow rate of 1 mL/min. Collect the eluents in a 10 mL glass tube and evaporate under nitrogen to dryness at 45℃. Dissolve the residue and dilute to 1.0 mL with ethyl acetate for GC-MS analysis.

6.2.3 Pork, chicken, pork liver, Eel, chestnut

Setting SPE vacuum manifold, add 1.0 g of anhydrous sodium sulfate into a neutral alumina SPE column (3.13). Condition the florisil column with 4 mL of acetonitrile-ethyl acetate (4 : 1, *V*/*V*) before use. Pass the sample extraction solution through the column and rinse the column with 2.0 mL of acetonitrile-ethyl acetate (4 : 1, *V*/*V*) at a folw rate of 1 mL/min. Collect the eluents in a 10 mL glass tube and evaporate under nitrogen to dryness at 45℃, and reconstitute with 1.0 mL of *n*-hexane-acetone (4 : 1, *V*/*V*),then pass through the florisil column (fill 0.5 g anhydrous sodium sulfate

on the top of column bed). Follow the same operation as that described in 6.2.1.

6.2.4 Tea, rose

Setting SPE manifold. Condition the ENVI-Carb column with 2 mL × 2 of ethyl acetate before use. Pass the sample extraction solution through the column and rinse the column with 1.0mL of ethyl acetate at a flow rate of 1 mL/min. Collect the eluents and evaporate under nitrogen to near 0.5 mL at 45℃, then pass through the florisil column (fill 0.5 g anhydrous sodium sulfate on the top of column bed). Rinse the column with 1.0 mL × 4 of *n*-hexane-acetone (4 : 1, *V*/*V*) at a flow rate of 1 mL/min. Collect the eluents in a 10 mL glass tube and evaporate under nitrogen to dryness at 45℃. Dissolve the residue and dilute to 1.0 mL with ethyl acetate for GC-MS analysis.

6.3 Determination

6.3.1 GC and MS operating conditions

a) Gc column: Capillary column, DB-XLB, 0.25 mm(i.d.) × 30 m with 0.25 μm particle size, or equivalent;

b) Carrier gas: Nitrogen, purity≥99.999%; Fow rate: 1.5 mL/min; Pressure: 14.6 Psi;

c) Injection mode: Splitless, purge on after 1 min;

d) Injection volumn: 1 μL;

e) Injection port temperature: 270℃;

f) Interface temperature: 280℃;

g) Temperature increasing programme: Column temperature: 80℃ (1.5 min) $\xrightarrow{20℃/min}$ 220℃ (3 min) $\xrightarrow{5℃/min}$ 255℃ $\xrightarrow{20℃/min}$ 280℃ (4 min);

h) Electron ionization mode: NCI;

i) Ion source temperature: 150℃;

j) Quadrupole temperature: 150℃;

k) Solvent protection delay: 5 min;

l) Reaction Gas: methane; Flow rate: 40%;

m) Determination mode: SIM;

n) Monitor ions(m/z): See table 1.

Table 1—Monitor ions and Quantitative ions

Analyte	Time/min	Detected ion(m/z)	Quantitative ions(m/z)
dieldrin	16.1	237,380,239,346	346
endrin	16.9	380,70,308,345	380

6.3.2 GC-MS determination and confirmation

According to approximate concentration of analyte, select the staandard working solution with similar response to that of sample solution. The responses of dieldrin and endrin in the standard working solution and samole 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.

According to the operating condition assinged in 6.3.1, analyze the standard solution and sample solution. If there is a peak appeared at the same retention time for the both of sample solution and standard working solution, the confirmation test should be conducted. All the detected ions shall be presence after background correction and the relative intensities of the detected ions of each analyst, shall correspond to those of the calibration standard at comparable concentrations, within the tolerances shown in table2, then the corresponding analyte must be present in the sample. For GC-MS chromatogram (TIC) and mass spectrum of dieldrin and endrin standards, see annex A and annex B.

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

Relative intensity/%	>50	>20~50	>10~20	≤10
Permitted tolerances/%	±20	±25	±30	±50

6.4 Blank test

The operation of the blank test is the same as the described in the method of determination, but with the omission of sample addition.

7 Calculation and expression of result

Calculation the content of dieldrin and endrin residues in the test sample by GC-MS data processor or according to the formula (1). The blank value should be substracted from the above result of calculation:

$$X = \frac{A \times c \times V}{A_S \times m} \quad \cdots\cdots(1)$$

where

X—the residue content of dieldrin and endrin in the test sample, μg/kg;

A—the peak area of dieldrin and endrin in the sample solution;

A_S—the peak area of dieldrin and endrin in the standard working solution;

c—the concentration of dieldrin and endrin in the standard working solution, μg/L;

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 determination and recovery

8.1 Limit of determination

The limit determination of this method for dieldrin and endrin in eel and honeybee is 2.5 μg/kg, and the limit determination of this method for dieldrin and endrin in the other foods mentioned obove is 5.0 μg/kg.

8.2 Recovery

According to the experimental data, the fortifying concentrations of dieldrin and endrin and their corresponding recoveries of are shown in tabe 3.

Table 3—The recovery of dieldrin and endrin

Sample	Fortified concentration/(μg/kg)	Recovery/%	
		Dieldrin	Endrin
rice	5.0	80.6～93.2	85.0～99.2
	10	84.5～98.6	86.5～97.4
	50	88.8～99.8	87.9～99.5
mung bean	5.0	82.8～93.6	88.6～98.4
	10	88.5～97.6	88.3～98.2
	50	90.4～98.2	87.6～98.4

Table 3 (continued)

Sample	Fortified concentration/(μg/kg)	Recovery/%	
		Dieldrin	Endrin
spinage	5.0	77.2～86.8	80.4～93.4
	10	87.6～95.4	83.2～94.7
	50	89.6～97.1	89.0～98.2
string bean	5.0	79.6～91.4	80.8～92.2
	10	88.7～94.4	89.0～94.1
	50	91.4～100.2	91.2～97.0
orange	5.0	76.2～87.2	76.8～84.0
	10	83.2～92.3	83.3～92.0
	50	85.2～95.6	89.4～96.4
grape	5.0	77.4～87.4	77.0～84.4
	10	86.5～94.0	83.2～95.7
	50	89.8～97.6	88.4～96.2
pork	5.0	80.4～88.4	87.0～100.6
	50	80.2～86.9	88.4～102.0
	100	85.9～93.2	90.5～94.7
chicken	5.0	77.8～91.8	87.2～102.4
	10	83.2～92.3	82.6～92.4
	100	85.5～95.2	87.3～96.5
pork liver	5.0	82.4～89.4	85.8～100.8
	10	82.0～90.5	96.5～103.2
	50	86.4～92.7	90.1～96.4
eel	Dieldrin2.5 Endrin5.0	89.2～92.4	92.0～97.2
	10	89.6～94.6	91.2～96.1
	50	91.6～96.2	90.8～97.2
tea	5.0	83.2～90.8	89.6～106.4
	10	80.6～88.0	82.4～96.6
	50	88.4～97.0	90.8～95.4
chestnut	5.0	81.6～92.4	89.6～96.6
	10	89.5～96.3	90.7～96.3
	50	90.4～99.8	90.2～99.2

Table 3 (continued)

Sample	Fortified concentration/(μg/kg)	Recovery/%	
		Dieldrin	Endrin
vinegar	5.0	97.4～105.8	84.0～98.0
	10	92.1～98.5	95.6～102.2
	50	92.6～99.0	94.2～99.8
rose	5.0	77.2～91.4	88.2～102.6
	10	79.4～93.4	80.4～92.1
	50	84.8～97.0	85.4～98.8
honey	2.5	76.8～84.8	80.8～100.4
	10	87.5～107.3	87.9～100.6
	50	90.4～99.6	91.4～98.8

Annex A
(informative)
GC-MS chromatogram of the dieldrin and endrin standard(TIC)

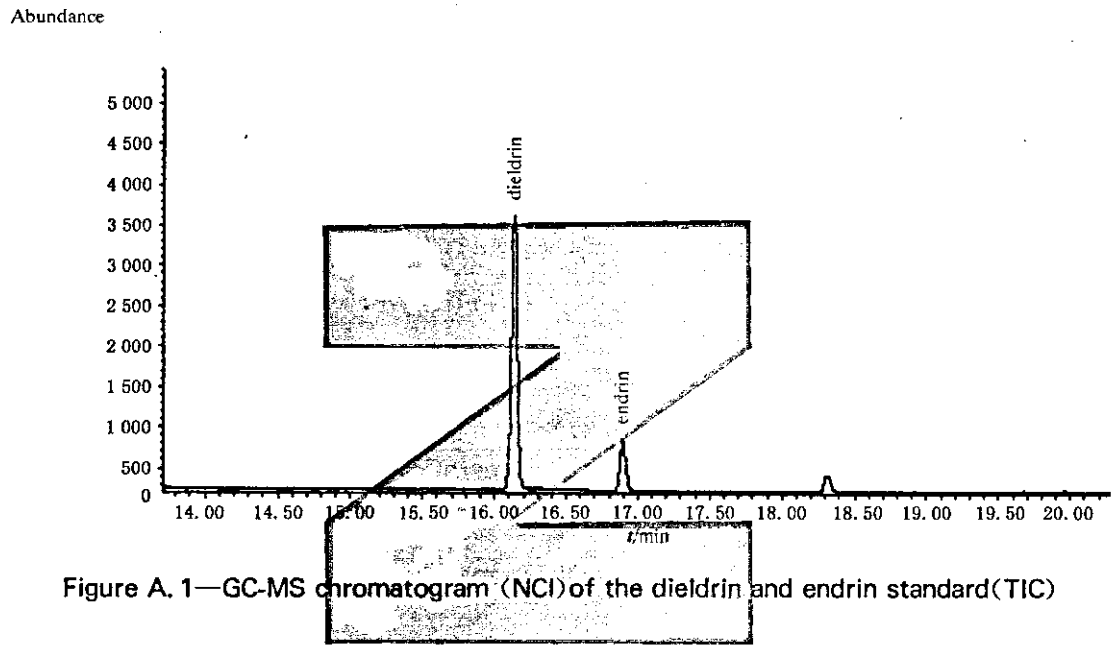

Figure A.1—GC-MS chromatogram (NCI)of the dieldrin and endrin standard(TIC)

Annex B
(informative)
NCI mass spectrogram of dieldrin and endrin standard

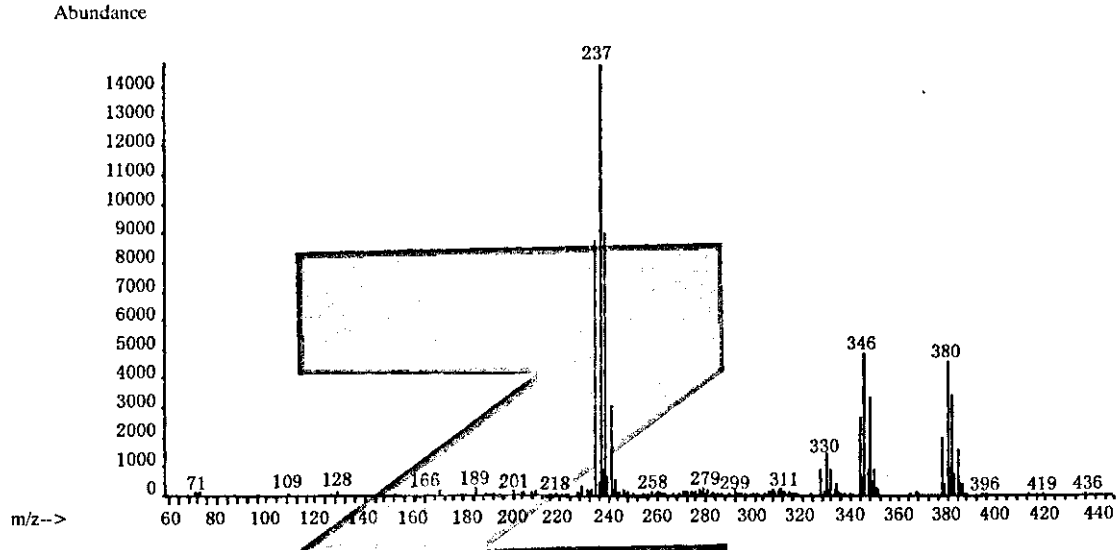

Figure B. 1—NCI mass spectrogram of dieldrin standard

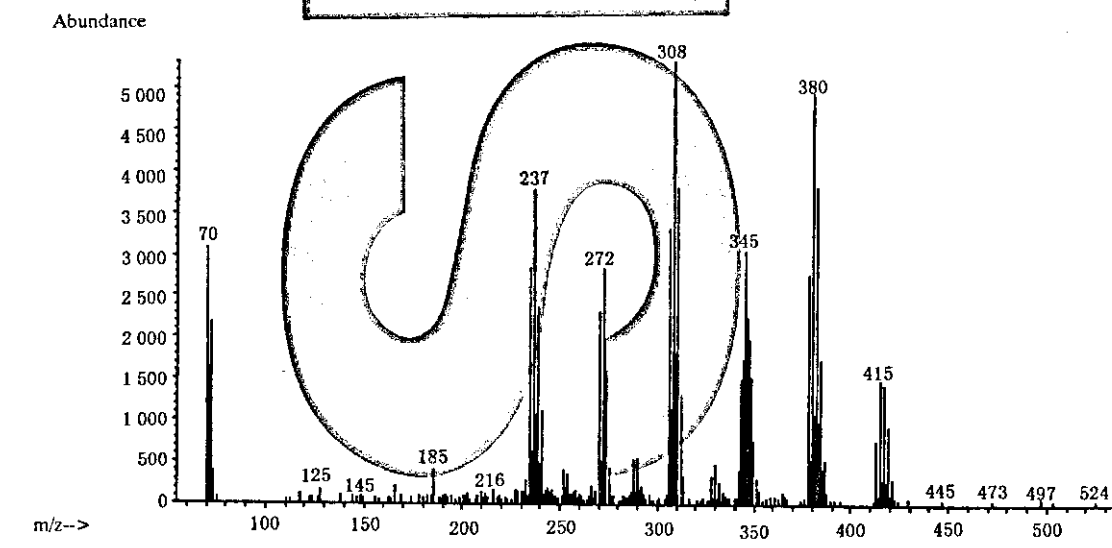

Figure B. 2—NCI mass spectrogram of endrin standard

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行 业 标 准
进出口食品中狄氏剂和异狄氏剂残留量
检测方法 气相色谱-质谱法
SN/T 1978—2007
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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 1.75 字数 40 千字
2007年11月第一版 2007年11月第一次印刷
印数 1—2 000
*
书号:155066·2-18259 定价 14.00 元