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中华人民共和国出入境检验检疫行业标准

SN/T 1990—2007

进出口食品中三唑锡和三环锡残留量的检测方法　气相色谱-质谱法

Determination of azocyclotin and cyhexatin residues in food for import and export—GC-MS method

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前　言

本标准的附录A为规范性附录、附录B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。

本标准由中华人民共和国陕西出入境检验检疫局、中华人民共和国天津出入境检验检疫局、中华人民共和国内蒙古出入境检验检疫局、中华人民共和国山东出入境检验检疫局、中华人民共和国福建出入境检验检疫局负责起草。

本标准主要起草人：李建华、何强、孔祥虹、乐爱山、葛宝坤、林安清、李刚、潘国卿、王建华、杨方。

本标准系首次发布的出入境检验检疫行业标准。

进出口食品中三唑锡和三环锡残留量的检测方法　气相色谱-质谱法

1　范围

本标准规定了食品中三唑锡和三环锡的气相色谱-质谱检测方法。

本标准适用于茶叶、韭菜、苹果、板栗、甘草、大米、食醋、蜂蜜、牛肉、鸡肉、鱼肉、猪肝中三唑锡和三环锡残留量的测定和确证。

2　方法提要

试样中残留的三唑锡在酸性条件下水解为三环锡，三环锡采用丙酮提取，经石油醚液-液分配净化后，与甲基碘化镁试剂衍生化，生成三环己基甲基锡，再用弗罗里硅土固相萃取柱净化，洗脱液浓缩并定容后，供气相色谱-质谱仪测定和确证，外标法定量。

3　试剂和材料

除非另有说明，所用试剂均为分析纯，水为蒸馏水。

3.1　丙酮。

3.2　石油醚：沸程 60℃～90℃。

3.3　无水乙醚：用金属钠脱水。

3.4　甲基碘化镁溶液：合成方法见附录 A。

3.5　氢溴酸。

3.6　无水硫酸钠：经 650℃灼烧 4 h，贮于密闭容器中备用。

3.7　10%盐酸溶液。

3.8　氯化钠水溶液：20 g/L。

3.9　三唑锡标准物质(Azocyclotin，$C_{20}H_{35}N_3Sn$，CAS No:41083-11-8)：纯度大于等于 98%。

3.10　三环锡标准物质(Cyhexatin，$C_{18}H_{34}OSn$，CAS No:13121-70-5)：纯度大于等于 98%。

3.11　标准储备溶液：准确称取适量的三环锡和三唑锡标准品，分别用丙酮配制成 100 μg/mL 的标准储备液，于 4℃保存。

3.12　标准工作溶液：根据检测要求用丙酮稀释成相应的标准工作溶液，于 4℃保存。

3.13　弗罗里硅土(Florisil)固相萃取柱：1 g，6 mL。

4　仪器和设备

4.1　气相色谱-质谱联用仪，配 EI 源。

4.2　组织捣碎机。

4.3　粉碎机。

4.4　均质器。

4.5　振荡器。

4.6　旋转蒸发器。

4.7　固相萃取装置，带真空泵。

4.8　低速离心机。

4.9 离心管:50 mL。

5 试样制备与保存

5.1 试样制备

5.1.1 水果、坚果和蔬菜

抽取苹果、韭菜、板栗等水果、坚果或蔬菜样品 500 g,去壳、去籽、去皮、去茎、去根、去冠(不可用水洗涤),将其可食用部分切碎后,用捣碎机将样品加工成浆状,混匀,装入洁净容器内,密闭并标明标记。

5.1.2 茶叶、草药及粮谷

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

5.1.3 肉类及动物内脏

取有代表性样品 500 g,取可食部分经捣碎机充分捣碎均匀,装入洁净容器内作为试样。密闭,标明标记。

5.1.4 蜂蜜及蜂产品

取有代表性样品量 500 g,对于无结晶的蜂蜜样品,将其搅拌均匀;对于有结晶析出的蜂蜜样品,在密闭情况下,将样品置于 60℃水浴中加热,待样品全部融化后搅拌均匀,迅速冷却至室温,装入洁净容器内,密闭并标明标记。

5.2 试样保存

茶叶、蜂产品、调味品、草药及粮谷等试样于 4℃保存;水果蔬菜类和肉及肉制品类等试样于−18℃以下冷冻保存。

在制样的操作过程中,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

对于固态样品如茶叶、韭菜、苹果、板栗、甘草、大米、鸡肉、牛肉、鱼肉、猪肝等,称取 5 g 均匀试样(精确至 0.01 g)于 50 mL 离心管中,加入 10 mL 水,5 mL 氢溴酸,剧烈振摇 5 min,放置 2 h。加入 20 mL丙酮,均质提取 5 min,在 3 000 r/min 下离心 3 min,取上清液于 150 mL 浓缩瓶中,重复提取两次,合并提取液,于 35℃水浴中减压浓缩至约 20 mL,加入 20 mL 氯化钠水溶液(3.8),用 2×40 mL 的石油醚振摇萃取两次,每次振摇 5 min,石油醚层过无水硫酸钠柱脱水后,于 40℃水浴中减压浓缩至近干,氮气吹干至无水,加 20 mL 无水乙醚(3.3)溶解残渣。

对于液体样品如蜂蜜、食醋等,称取 5 g 均匀试样(精确至 0.01 g)于 150 mL 浓缩瓶中,加入 20 mL 水,5 mL 氢溴酸,10 mL 丙酮,振摇 10 min,用 2×30 mL 的石油醚振摇萃取两次,每次振摇 5 min,取石油醚层过无水硫酸钠柱脱水,将石油醚液于 40℃减压浓缩至近干,氮气吹干至无水,加 20 mL 无水乙醚(3.3)溶解残渣。

6.2 衍生化

向上述无水乙醚液中加入 5 mL 甲基碘化镁溶液(3.4),振摇反应 5 min,缓慢加入 10 mL 10%的盐酸溶液(3.7),振摇 2 min,静置分层,弃去水相,于 35℃水浴中减压浓缩至近干,氮气吹干,加 10 mL 石油醚溶解残渣。

6.3 净化

将弗罗里硅土固相萃取柱(柱内填约 1 cm 高的无水硫酸钠)安装在固相萃取的真空抽滤装置上,先用 5 mL 石油醚预淋洗小柱。将上述石油醚溶液倒入柱中,待液面降到硫酸钠表面时,再用 15 mL 石油醚进行洗脱,控制流速小于等于 3 mL/min,收集全部流出液,40℃减压浓缩至近干,氮气吹干,用丙酮溶解并定容至 1.0 mL,供气相色谱-质谱测定和确证。

对于基质复杂的样品如茶叶、韭菜、甘草、猪肝等，串联两根弗罗里硅土固相萃取柱进行净化。

6.4 标准溶液的制备

移取适当浓度的系列三环锡标准工作溶液各 1.0 mL 于 150 mL 浓缩瓶中，先用氮气将丙酮吹干，再加 20 mL 无水乙醚(3.3)溶解残渣，按与样品相同的方法进行衍生化(6.2)和净化(6.3)。

6.5 测定

6.5.1 气相色谱-质谱条件

a) 色谱柱：DB-5MS 石英毛细管柱，30 m×0.25 mm(内径)，0.25 μm(膜厚)，或相当者；

b) 色谱柱温度：初始温度 160℃(0 min)$\xrightarrow{25℃/min}$205℃(10 min)$\xrightarrow{25℃/min}$260℃(5 min)；

c) 进样口温度：230℃；

d) 色谱-质谱接口温度：280℃；

e) 载气：氦气，纯度大于等于 99.999%，1.0 mL/min；

f) 进样量：1 μL；

g) 进样方式：无分流进样，1 min 后开阀；

h) 电离方式：EI；

i) 电离能量：70 eV；

j) 测定方式：选择离子监测方式(SIM)；

k) 监测离子(m/z)：121，135，219，301；定量离子：219；

l) 溶剂延迟：6 min。

6.5.2 色谱测定与确证

根据样液中被测物含量情况，选定浓度相近的标准工作溶液，对标准工作溶液与样液等体积参插进样测定，标准工作溶液和待测样液中三唑锡和三环锡的衍生物三环己基甲基锡的响应值均应在仪器检测的线性范围内。

在相同实验条件下，样品中待测物质的质量色谱保留时间与标准工作液相同，并且在扣除背景后的样品质量色谱中，所选离子均出现，经过对比所选择离子的丰度比与标准品对应离子的丰度比，其值在允许范围内(允许范围见表 1)则可判定样品中存在对应的待测物。在 6.5.1 规定的色谱条件下，三唑锡和三环锡的衍生物三环己基甲基锡的保留时间是 10.8 min，其监测离子(m/z)丰度比是 121∶135∶219∶301=25∶57∶100∶44。三唑锡和三环锡的衍生物三环己基甲基锡的气相色谱-质谱的选择离子色谱图和全扫描质谱图参见附录 B 中图 B.1 和图 B.2。

表 1 使用定性气相色谱-质谱时相对离子丰度最大容许误差

相对丰度(基峰)/%	>50	>20～50	>10～20	≤10
GC/MS 时相对离子丰度最大允许误差/%	±10	±15	±20	±50

6.6 空白实验

除不加试样外，均按上述测定步骤进行。

7 结果计算和表述

测定结果以三环锡计。若以三唑锡计时将三环锡含量乘以换算系数 1.13。

用色谱数据处理机或按式(1)计算试样中三环锡的含量，计算结果须扣除空白值。

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

式中：

X——试样中三环锡的含量，单位为毫克每千克(mg/kg)；

A——样液中三环锡衍生物三环己基甲基锡的色谱峰面积；

c_S——标准工作液中三环锡的浓度，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)；

A_S——标准工作液中三环锡衍生物三环己基甲基锡的色谱峰面积；

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

本方法的测定低限为 0.020 mg/kg。

8.2 回收率

样品的添加浓度及回收率的实验数据见表 2。

表 2 样品的添加浓度及回收率的实验数据

样品	添加浓度/(mg/kg)	回收率范围/%	样品	添加浓度/(mg/kg)	回收率范围/%
茶叶	0.020	78.1～97.0	食醋	0.020	76.3～101.9
	0.040	89.0～97.6		0.040	84.1～104.5
	0.080	85.5～100.1		0.080	85.4～102.9
韭菜	0.020	92.5～99.1	蜂蜜	0.020	78.4～97.0
	0.040	91.1～99.4		0.040	89.0～97.6
	0.080	87.0～102.3		0.080	85.5～100.4
苹果	0.020	81.5～100.8	牛肉	0.020	83.5～96.1
	0.040	85.2～99.2		0.040	84.2～96.4
	0.080	84.5～102.1		0.080	85.4～98.9
板栗	0.020	72.6～99.1	鸡肉	0.020	81.1～97.9
	0.040	84.4～100.3		0.040	83.5～98.1
	0.080	76.9～100.3		0.080	83.5～100.3
甘草	0.020	80.7～99.1	鱼肉	0.020	82.3～94.9
	0.040	86.1～101.8		0.040	76.8～94.9
	0.080	90.6～100.0		0.080	77.3～97.9
大米	0.020	71.5～96.7	猪肝	0.020	71.3～99.0
	0.040	76.0～103.9		0.040	77.1～103.6
	0.080	84.2～102.1		0.080	80.7～100.4

附 录 A
（规范性附录）
甲基碘化镁溶液的合成方法

A.1 试剂和材料

A.1.1 无水乙醚：用金属钠脱水。

A.1.2 石油醚：沸程 60℃～90℃，用金属钠脱水。

A.1.3 镁带：60℃干燥 30 min。

A.1.4 碘甲烷：重蒸馏。

A.1.5 碘甲烷-无水乙醚：71 g 碘甲烷和 400 mL 无水乙醚混合均匀。

A.1.6 无水硫酸钠：经 650℃灼烧 4 h，贮于密封容器中备用。

A.2 仪器和设备

A.2.1 电热套：1 000 mL。

A.2.2 二口烧瓶：1 000 mL。

A.2.3 球形冷凝管：400 mm。

A.2.4 恒压式筒形分液漏斗：250 mL。

A.2.5 直形干燥管。

A.3 合成

将经过 60℃干燥的镁带剪成 2 mm～3 mm 宽的镁屑，称取 14 g 镁屑于二口烧瓶中，加入 100 mL 石油醚(A.1.2)，装上球形冷凝管(顶部接无水硫酸钠干燥管)和恒压式筒形分液漏斗，接通冷凝水，并开始缓慢加热。将碘甲烷-无水乙醚混合液(A.1.5)转移至恒压漏斗中，先加入 60 mL 混合液于烧瓶里，然后在 1 h 内滴加完其余混合液，使反应保持在回流状态。碘甲烷和无水乙醚混合液加完后再加热回流 1.5 h。冷却后将所得的甲基碘化镁溶液转移至干燥的棕色瓶里，于干燥器内保存备用。

附 录 B
（资料性附录）
三唑锡和三环锡标准物质衍生物三环己基甲基锡的选择离子色谱图、质谱图

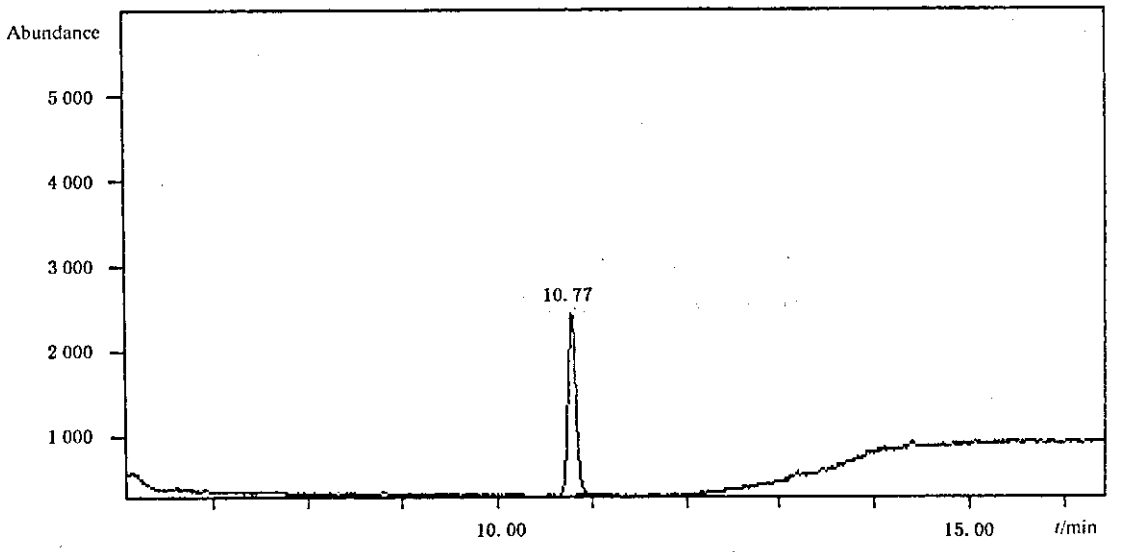

图 B.1 三环己基甲基锡的选择离子色谱图

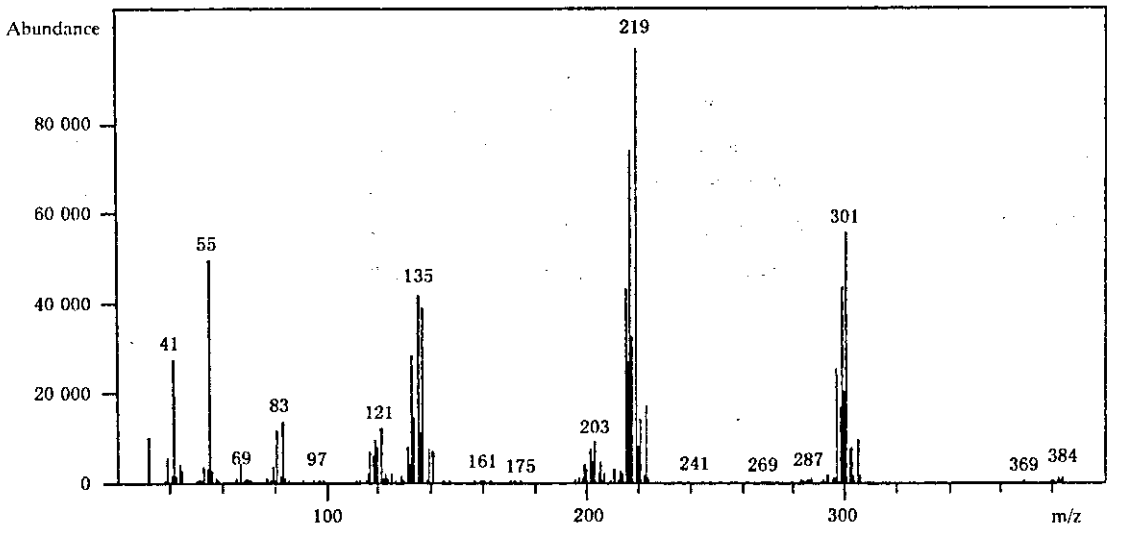

图 B.2 三环己基甲基锡的全扫描质谱图

Foreword

Annex A of this standard is normative annex and annex B is informative annex.

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

This standard was drafted by the Shaanxi 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, Neimenggu Entry-Exit Inspection and Quarantine Bureau of the People's Republic of China, Shandong Entry-Exit Inspection and Quarantine Bureau of the People's Republic of China and Fujian Entry-Exit Inspection and Quarantine Bureau of the People's Republic of China.

The principal drafters of this standard are Li Jianhua, He Qiang, Kong Xianghong, Yue Aishan, Ge Baokun, Lin Anqing, Li Gang, Pan Guoqing, Wang Jianhua, Yang Fang.

This standard is the first special normal standard of the Entry-Exit Inspection and Quarantine of the People's Republic of China.

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

Determination of azocyclotin and cyhexatin residues in food for import and export—GC-MS method

1 Scope

This standard specifies the method for the determination and confirmation of azocyclotin and cyhexatin residues by gas chromatography-mass spectrometry in food.

This standard is applicable to the determination and confirmation of residue contents of azocyclotin and cyhexatin in tea, leek, apple, chestnut, *glycyrrhizae*, rice, vinegar, honey, beef, chicken, fish and liver.

2 Principle

Azocyclotin in the test sample are hydrolyzed to cyhexatin in acidic solution. Cyhexatin is extracted with acetone and partitioned with petroleum ether. And then the extract is methylated by methyl magnesium iodide to form tricyclohexylmethyltin. Cleaned up is performed on a florisil cartridge, and the elute solution is evaporated and made up to a definite volume. Determination and confirmation is made by GC-MS, using external standard method.

3 Reagents and materials

Unless otherwise specified, the reagents should be analytical grade, and "water" is distilled water.

3.1 Acetone.

3.2 Petroleum ether: boiling point from 60℃～90℃.

3.3 Anhydrous ether: dehydrate with sodium.

3.4 Methyl magnesium iodide solution: synthesized according to annex A.

3.5 Hydrobromic acid.

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

3.7 Hydrochloric acid solution: 10%.

3.8 Sodium chloride solution: 20 g/L.

3.9 Azocyclotin standard ($C_{20}H_{35}N_3Sn$, CAS No :41083-11-8): Purity≥98%.

3.10 Cyhexatin standard ($C_{18}H_{34}OSn$, CAS No: 13121-70-5): Purity≥98%.

3.11 Standard stock solution: Accurately weigh an adequate amount of azocyclotin standard and cyhexatin standard and dissolve in a small volume acetone respectively. Dilute with acetone to form a standard stock solution of 100 μg/mL in concentration. Store at 4℃.

3.12 Standard working solution: Then dilute the standard stock solution with acetone to the required concentration as the standard working solution. Store at 4℃.

3.13 Florisil cartridge: 1 g, 6 mL.

4 Apparatus and equipment

4.1 Gas chromatograph, equipped with mass detector.

4.2 Tissue blender.

4.3 Grinder.

4.4 Homogenizer.

4.5 Shaker.

4.6 Rotary vacuum evaporator.

4.7 Solid phase extraction with mechanical vacuum pump.

4.8 Centrifuge.

4.9 Centrifuge tube: 50 mL.

5 Preparation and storage of test samples

5.1 Preparation of test samples

5.1.1 Fruits, nut and vegetables

The combined primary samples are reduced to the ca 500 g, which has been removed shell, seed, peel, stem, root, coronal (do not wash by water). The edible portions are cut and homogenized thoroughly in a high speed blender. Keep the prepared sample into a clean container, sealed and labeled.

5.1.2 Tea and *glycyrrhizae* and grains or cereals

The combined primary samples are reduced to the ca 500 g, which is crushed with a grinder and let wholly pass through 2.0 mm sieve. Keep the prepared sample into a clean container, sealed and labeled.

5.1.3 Meats and meat products

The combined primary samples is reduced to ca 500 g, the edible potions are thoroughly ground and homogenized in a meat grinder. Keep the prepared sample into a clean container, sealed and labeled.

5.1.4 Honey

Take about 500 g of representative sample. The sample that is not crystallized shall be stirred well to produce a homogenous sample. If the sample is crystallized, it should be warmed in a waterbath at 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 melting the sample, precautious measures must be taken to avoid evaporation of water from the sample. Keep the prepared sample into a clean container, sealed and labeled.

5.2 Storage of test samples

The test samples of tea, bee products, Chinese herbs, grains or cereals should be stored below 4℃. The test samples of fresh fruits, vegetables, meat and meat products should be stored below −18℃.

In the course of sampling and sample preparation, precaution should taken to avoid contamination or any factors which may cause the change of residue content.

6 Method of determination

6.1 Extraction

For solid sample, such as tea, leek, apple, chestnut, *glycyrrhizae*, rice, beef, chicken, fish and liver, weigh 5 g(accurate to 0.01g) of the test sample into a 50 mL centrifuge tube. Add 10 mL water and 5 mL hydrobromic acid, stand for 2 h after shake 30 s drastically. Add 20 mL acetone, extract for 5 min on a high speed homogenizer, and centrifuge for 3 min under 3 000 r/min. Transfer the upper extract solution into a 150 mL concentrating bottle by passing through anhydrous sodium sulfate column. Repeat above extract procedure with 20 mL of acetone twice. Combine acetone extracts, evaporate to 20 mL in a rotary evaporator with a bath temperature below 35℃. Add 20 mL NaCl solution(3.8) and 2×40 mL petroleum ether, shake 5 min, transfer the upper organic phase into another 150 mL concentrating bottle through anhydrous sodium sulfate column. Add another 2×40 mL pe-

troleum ether and shake 5 min, discard the lower aqueous layer, combine the organic phase and evaporate to approach dryness in a rotary evaporator with a bath temperature below 40℃ and blow to dryness. Dissolve the residue with 20 mL anhydrous ether (3.3).

For liquid sample such as vinegar and honey, weigh 5 g(accurate to 0.01 g) of the test sample into a 150 mL concentrating bottle. Add 20 mL water, 5 mL hydrobromic acid, 10 mL acetone and shake 10 min. Extract for 5 min with 2×30 mL petroleum ether twice by shaking. Transfer the upper organic phase into another 150 mL concentrating bottle by passing through anhydrous sodium sulfate column. Evaporate to approach dryness in a rotary evaporator with a bath temperature below 40℃ and blow to dryness. Dissolve the residue with 20 mL anhydrous ether(3.3).

6.2 Derivation

Add 5 mL methyl magnesium iodide solution(3.4) into above anhydrous ether solution(6.1), shake 5 min, then add 10 mL 10% hydrochloric acid solution(3.7) and shake 2 min. Stand for separate into two layers and discard the lower aqueous layer. Evaporate to dryness in a rotary evaporator with a bath temperature below 35℃. Dissolve the residue with 10 mL petroleum ether.

6.3 Clean up

Set up the solid phase extraction vacuum manifold and mechanical pump(about 1 cm thickness anhydrous sodium sulfate was put into the florisil cartridge). Rinse the cartridge with 5 mL petroleum ether and then transfer the above solution(6.2) into cartridge. Elute with 15 mL petroleum ether with the flow rate below 3 mL/min. Collect all the eluted solution in a 150 mL concentrating bottle and evaporate to approach dryness in a rotary evaporator with a bath temperature below 40℃ and blow dryness with nitrogen. Dissolve the residue and dilute exactly to 1.0 mL with acetone for GC/MSD.

For complex test sample matrix, such as tea, leek, *glycyrrhizae*, and liver, cleaning up operate with two florisil cartridges connecting in series.

6.4 Prepare standard solution

Transfer 1.0 mL cyhexatin standard working solution in appropriate concentration into a 150 mL concentrating bottle. Blow out acetone with nitrogen and dissolve the residue with 20 mL anhydrous ether(3.3). The following operation procedures are same as that of test sample with derivate (6.2) and clean up(6.3).

6.5 Determination

6.5.1 GC/MSD operating conditions

a) Column: DB-5 ms fused quartz capillary column, 30 m × 0.25 mm (id), film thickness 0.25 μm or the equivalent;

b) Column temperature: 160℃ (0 min) $\xrightarrow{25℃/min}$ 205℃ (10 min) $\xrightarrow{25℃/min}$ 260℃ (5 min);

c) Injection port temperature: 230℃;

d) GC/MS interface temperature: 280℃;

e) Carrier gas: Helium, purity≥99.999%, 1.0 mL/min;

f) Injection volume: 1 μL;

g) Injection mode: Splitless, purge after 1 min;

h) Ionization mode: EI;

i) Ionization energy: 70 eV;

j) Acquistion mode: SIM;

k) Monitor ion (m/z): 121, 135, 219, 301; quantitative ion: 219;

l) Sovlent delay: 6 min.

6.5.2 GC/MSD determination and confirmation

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

According to the GC/MSD operating conditions (6.5.1), if the retention time of sample chromatogram peaks are consistent with the standards, and subtracted from background compensation, selected ions are all present and the relative ion abundance of the selected ions according with that of the calibration standard, at comparable concentrations, within the tolerances (seen table 1). Under

the above GC/MSD operating conditions, the retention time oftricyclohexylmethyltin is 10.8 min, and the ratio of the monitoring ions (m/z) is 121 : 135 : 219 : 301 = 25 : 57 : 100 : 44. For GC-MS chromatogram (TIC) and mass spectrum of the standard, see figure B.1 and B.2 in annex B.

Table 1—Maximum permitted tolerances for relative ion abundance while confirmation

Relative abundance (base peak)/%	>50	>20~50	>10~20	≤10
Permitted tolerances/%	±10	±15	±20	±50

6.6 Blank test

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

7 Calculation and expression of result

The determination result is calculated as cyhexatin. If the determination result calculated as azocyclotin, then the final result should time a cosfficient 1.13.

The calculation of cyhexatin in the sample is carried out by GC-MS data processor or according to the following formula (1). The blank value should be subtracted from the above result of calculation.

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

where

X—the residue content of azocyclotin or cyhexatin in the test sample, mg/kg;

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

c_s—the concentration of azocyclotin or cyhexatin in the standard working solution, μg/mL;

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

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

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

8 Limit of determination and recovery

8.1 Limit of determination

The limit of determination of this method is 0.020 mg/kg.

8.2 Recovery

Fortifying concentrations in test samples and recovery experimental data are list in table 2.

Table 2—Fortifying concentrations in test samples and recovery experimental data

Sample	Fortifying concentration/(mg/kg)	Range of recovery/%	Sample	Fortifying concentration/(mg/kg)	Range of recovery/%
tea	0.020	78.4～97.0	vinegar	0.020	76.3～101.9
	0.040	89.0～97.6		0.040	84.1～104.5
	0.080	85.5～100.4		0.080	85.4～102.9
leek	0.020	92.5～99.1	honey	0.020	78.4～97.0
	0.040	91.4～99.4		0.040	89.0～97.6
	0.080	87.0～102.3		0.080	85.5～100.4
apple	0.020	81.5～100.8	beef	0.020	83.5～96.1
	0.040	85.2～99.2		0.040	84.2～96.4
	0.080	84.5～102.1		0.080	85.4～98.9
chestnut	0.020	72.6～99.1	chicken	0.020	81.1～97.9
	0.040	84.4～100.3		0.040	83.5～98.1
	0.080	76.9～100.3		0.080	83.5～100.3
glycyrrhizae	0.020	80.7～99.4	fish	0.020	82.3～94.9
	0.040	86.1～101.8		0.040	76.8～94.9
	0.080	90.6～100.0		0.080	77.3～97.9
rice	0.020	71.5～96.7	liver	0.020	71.3～99.0
	0.040	76.0～103.9		0.040	77.1～103.6
	0.080	84.2～102.1		0.080	80.7～100.4

Annex A
(normative)
Synthesis of methyl magnesium iodide solution

A.1 Reagents and materials

A.1.1 Anhydrous ether: dehydrate with sodium.

A.1.2 Petroleum ether: boiling point from 60℃ to 90℃, dehydrate with sodium.

A.1.3 Magnesium ribbon: dried 30 min at 60℃.

A.1.4 Iodomethane: redistill.

A.1.5 Iodomethane-anhydrous: 71 g iodomethane and 400 mL anhydrous ether ether mixture solution.

A.1.6 Anhydrous sodium sulfate: Ignite at 650℃ for 4 h, and keep in a desiccator.

A.2 Apparatus and equipment

A.2.1 Heater sheath: 1 000 mL.

A.2.2 Double neck flask: 1 000 mL.

A.2.3 Spherical condenser: 400 mm.

A.2.4 Isobarically funnel: 250 mL.

A.2.5 Dryness tube.

A.3 Synthesis

Cut the dried magnesium ribbon into 2 mm~3 mm chips, weigh ca 14 g of magnesium chips into a 1 000 mLdouble necks flask, add 100 mL petroleum ether (A.1.2). Set up spherical condenser (with dryness tube packed anhydrous calcium chloride) and isobarically funnel, inlet cooling water into condenser, and heat slowly. Transfer iodomethane-anhydrous ether mixture solution (A.1.5) into the funnel, add 60 mL mixture solution (A.1.5) into the flask first and add the other mixture solution during 1 h. Keep the reaction in fluxing 1.5 h. Transfer the methyl magnesium iodide solution into a brown bottle after cooling to room temperature and place in a desiccator.

Annex B
(informative)
SIM chromatogram and mass spectrum of tricyclohexyimethyitin of the standard derivative

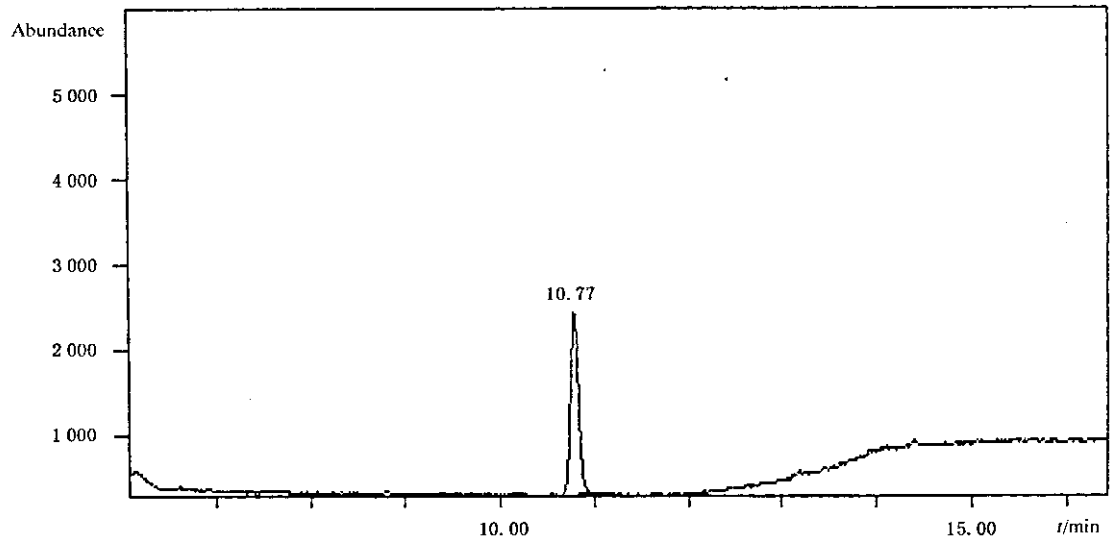

Figure B. 1—SIM chromatograph of tricyclohexylmethyltin

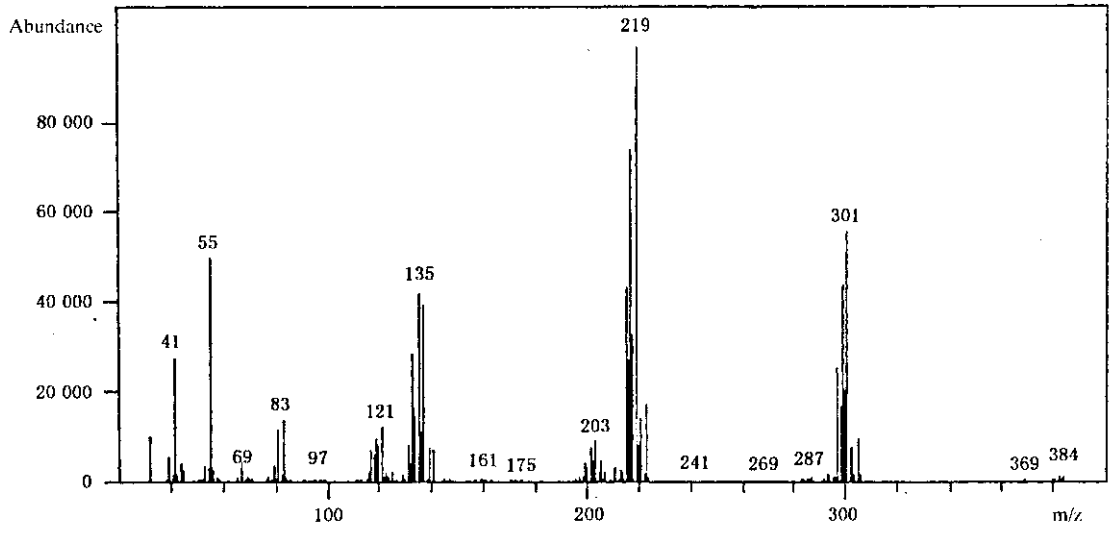

Figure B. 2—Mass spectrum of tricyclohexylmethyltin

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