SN

中华人民共和国进出口商品检验行业标准

SN 0692—1997

出口肉及肉制品中氯化松节油残留量检验方法

Method for the determination of strobane residues in meats and meat products for export

1997-12-01发布　　1998-04-01实施

中华人民共和国国家进出口商品检验局　发布

前　言

本标准是根据GB/T 1.1—1993《标准化工作导则　第1单元：标准的起草与表述规则　第1部分：标准编写的基本规定》及SN/T 0001—1995《出口商品中农药、兽药残留量及生物毒素检验方法标准编写的基本规定》的要求而进行编写的。其中测定方法是参考国内外有关资料，经研究、改进和验证后制定的。本标准同时制定了抽样和制样方法。

测定低限是根据测定方法的灵敏度而制定的。

本标准的附录A是提示的附录。

本标准由中华人民共和国国家进出口商品检验局提出并归口。

本标准由中华人民共和国湖南进出口商品检验局负责起草。

本标准起草人：戴华、黄志强、袁智能。

本标准系首次发布的行业标准。

中华人民共和国进出口商品检验行业标准

出口肉及肉制品中氯化松节油残留量检验方法

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Method for the determination of strobane residues in meats and meat products for export

1 范围

本标准规定了出口肉及肉制品中氯化松节油残留量检验的抽样、制样和气相色谱测定方法。

本标准适用于出口猪肉和牛肉中氯化松节油残留量的检验。

2 抽样和制样

2.1 检验批

以不超过 2 500 件为一检验批。

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

批量，件	最低抽样数，件
1～25	1
26～100	5
101～250	10
251～500	15
501～1 000	17
1 001～2 500	20

2.3 抽样方法

按 2.2 规定的抽样件数，随机抽取，逐件开启。从每件中取一袋作为原始样品，其总量不少于 2 kg，放入清洁的容器内，加封后，标明标记，及时送交实验室。

如每件中无小包装或有小包装但每袋重量超过 2 kg 者，可用灭菌锋利刀，在抽出的包件中，每件割取不少于 100 g，混合后置于洁净容器中，作为混合原始样。混合原始样的重量不少于 2 kg。加封后，标明标记，及时送交实验室。

2.4 样品制备

从所取全部样品中取出代表性样品约 1 kg，取可食部分充分绞碎，混匀，均分成两份，装入清洁的容器内。密封，作为试样，并标明标记。

2.5 试样保存

将试样于－18℃以下冷冻保存。

注：在抽样和制样的操作过程中，必须防止样品受到污染或发生残留物含量的变化。

中华人民共和国国家进出口商品检验局 1997-12-01 批准　　1998-04-01 实施

3 测定方法

3.1 方法提要

试样中残留的氯化松节油用正己烷经索氏提取器提取，提取液经浓硫酸处理以除去部分杂质，加氢氧化钾-甲醇溶液，回流，以脱去部分氯化氢，再用正己烷提取碱解液，经浓缩、浓硫酸处理定容后，溶液供配有电子俘获检测器的气相色谱仪测定氯化松节油经脱氯化氢后的主峰，用外标法进行定量。

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 正己烷：优级纯。

3.2.2 无水硫酸钠：650℃灼烧 4 h，置于密闭容器内备用。

3.2.3 氢氧化钾-甲醇溶液：50 g 氢氧化钾中加入 100 mL 甲醇。

3.2.4 浓硫酸：优级纯，密度(ρ)约 1.84 g/mL。

3.2.5 氯化松节油标准品，100%。

3.2.6 氯化松节油标准溶液：准确称取适量的氯化松节油标准品，用正己烷溶解，并配成 100 μg/mL 的标准储备液。根据需要，用正己烷将氯化松节油标准储备溶液稀释成适当浓度的标准工作溶液。以下按 3.4.3 脱氯化氢和 3.4.4 再净化，步骤与试样分析同时进行。

3.3 仪器和设备

3.3.1 气相色谱仪：配有电子俘获检测器(^{63}Ni)。

3.3.2 微量注射器：10 μL。

3.3.3 离心机。

3.3.4 混匀器。

3.3.5 离心管：50 mL，具塞。

3.3.6 索氏提取器。

3.4 测定步骤

3.4.1 提取

称取 10 g 试样(准确至 0.01 g)置于盛有 30 g 无水硫酸钠的研钵内，研磨成干粉状。然后移入滤纸筒内，装入 150 mL 索氏提取器中，用 100 mL 正己烷分两次洗涤研钵，洗液倒入提取瓶内，置水浴中浸提 16 h(每小时回流 10～12 次)。取出滤纸筒，将提取瓶内溶液蒸发至约 5 mL，并将其转入到 50 mL 具塞离心管中，用 2×5 mL 正己烷洗涤提取瓶，洗液并入同一离心管中。

3.4.2 净化

于上述离心管中加 1 mL 浓硫酸，在混匀器上混匀 1 min 后，于 2 000 r/min 下离心 5 min，用吸管吸出下层酸相并弃去。再用 3×1 mL 浓硫酸处理正己烷溶液。经处理过正己烷溶液于 50℃以下用空气流浓缩至约 5 mL。

3.4.3 脱氯化氢

加 10 mL 氢氧化钾-甲醇溶液于上述离心管中，接上冷凝管，在 92(±2)℃水浴中回流 1 h。取下离心管并冷却至室温。加入 10 mL 水和 5 mL 正己烷，在混匀器上混匀 1 min，于 2 000 r/min 离心 3 min。用吸管移上层正己烷于另一刻度离心管中。水层再用 2×5 mL 正己烷提取，合并正己烷提取液于同一刻度离心管中，在 50℃以下用空气流浓缩至近干。

3.4.4 再净化

在刻度离心管中加入正己烷至近 2 mL，溶解残渣，然后加入 0.25 mL 浓硫酸，在混匀器上混匀 1 min后，于 2 000 r/min 下离心 3 min，用吸管吸取下层酸相并弃去。再用 2×0.25 mL 浓硫酸处理正己烷溶液两次，处理后的正己烷溶液定容至 2.0 mL，供气相色谱测定。

3.4.5 测定

3.4.5.1 色谱条件

a) 色谱柱：OV-1701，35 m×0.53 mm(内径)，膜厚 1 μm；或等效色谱柱；

b) 柱温：210℃；

c) 进样口温度：300℃；

d) 检测器温度：300℃；

e) 载气：氮气，纯度≥99.99%；载气流速：20 mL/min；尾吹气流速：30 mL/min；

f) 进样量：1～2 μL；

g) 进样方式：无分流进样。

3.4.5.2 色谱测定

根据样液中氯化松节油含量情况，选定峰高相近的标准工作溶液(经脱氯化氢及净化)。标准工作溶液和待测样液中脱氯化氢后的氯化松节油响应值均应在仪器检测的线性范围内。对标准工作溶液和样液等体积参插进样测定。在上述色谱条件下，脱氯化氢后的氯化松节油主峰的保留时间约为 6 min。标准品色谱图见附录 A 中图 A1。

3.5 空白试验

除不加试样外，均按上述测定步骤进行。

3.6 结果的计算和表述

用色谱数据处理机或按式(1)计算试样中氯化松节油残留含量：

$$X = \frac{h \cdot c \cdot V}{h_s \cdot m} \qquad \cdots\cdots(1)$$

式中：X——试样中氯化松节油残留含量，mg/kg；

h——样液中经脱氯化氢后的氯化松节油色谱主峰高，mm；

h_s——标准工作液中经脱氯化氢后的氯化松节油色谱主峰高，mm；

c——标准工作液中氯化松节油的浓度，μg/mL；

V——样液最终定容体积，mL；

m——最终样液所代表的试样量，g。

注：计算结果需将空白值扣除。

4 测定低限、回收率

4.1 测定低限

本方法的测定低限为 0.2 mg/kg。

4.2 回收率

猪肉中氯化松节油添加浓度及其回收率的实验数据：

在 0.20 mg/kg 时，回收率为 99.3%；

在 0.50 mg/kg 时，回收率为 84.6%；

在 2.00 mg/kg 时，回收率为 81.0%。

牛肉中氯化松节油添加浓度及其回收率的实验数据：

在 0.20 mg/kg 时，回收率为 99.5%；

在 0.50 mg/kg 时，回收率为 93.7%；

在 2.00 mg/kg 时，回收率为 99.2%。

附 录 A
（提示的附录）
标准品色谱图

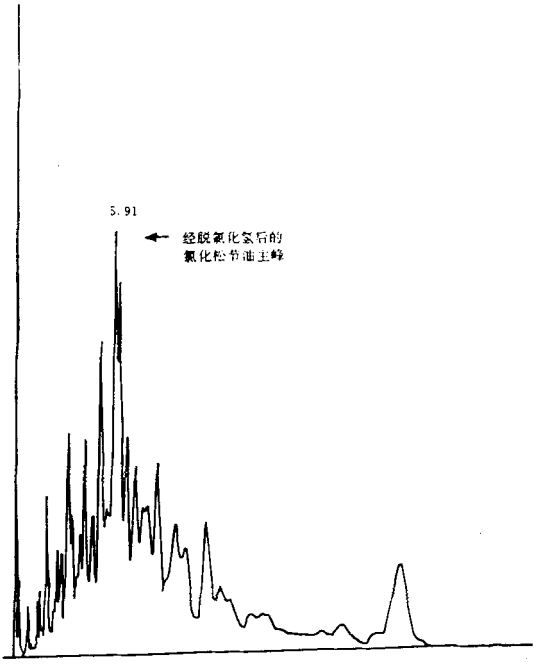


图 A1 氯化松节油标准品经脱氯化氢后的气相色谱图

Foreword

This standard was drafted in accordance with the requirements of GB/T 1.1—1993"Directives for the work of standardization —Unit 1:Drafting and presentation of standards—Part 1:General rules for drafting standards"and SN/T 0001—1995"General rules for drafting the standard methods for the determination of pesticide,veterinary drug residues and biotoxins in commodities for export". In this standard,the method of determination was drafted by referring to relevant domestic and foreign literatures through research, modification and verification. In addition, methods of sampling and sample preparation are also specified in this standard.

The limit of determination in this standard is defined on the basis of the sensitivity of this method.

Annex A of this standard is an informative annex.

This standard was proposed by and is under the charge of the State Administration of Import and Export Commodity Inspection of the People's Republic of China.

This standard was drafted by Hunan Import and Export Commodity Inspection Bureau of the People's Republic of China.

The main drafters of this standard are Dai hua, Huang Zhiqiang and Yuan Zhineng.

This standard is a professional standard promulgated for the first time.

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

Professional Standard of the People's Republic of China
for Import and Export Commodity Inspection

SN 0692—1997

Method for the determination of strobane residues in meats and meat products for export

1 Scope

This standard specifies the methods of sampling, sample preparation and determination of strobane residues in meats and meat products by gas chromatography for export.

This standard is applicable to the determination of strobane residues in pork and beef for export.

2 Sampling and sample preparation

2.1 Inspection lot

Each inspection lot should not exceed 2 500 packages.

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

2.2 Quantity of sample taken

Number of packages in an inspection lot	Minimum number of packages to be taken
1—25	1
26—100	5
101—250	10
251—500	15
501—1 000	17
1 001—2 500	20

2.3 Sampling procedure

A number of packages specified in 2.2 are taken at random and opened one by one. From each, at least one bag shall be taken as the primary sample. The total weight of all the primary samples should not be less than 2 kg, which shall be placed in a clean container, sealed, labeled and sent to laboratory in time.

In case the meat-pieces are not contained in small bags inside each package, or if there are small bags inside the package but the content of the bag exceeds 2 kg, cut out a part from the meat in each package of not less than 100 g with a disinfected sharp knife. Mix the parts of the meat as the mixed primary sample, which shall not be less than 2 kg. Seal, label and sendl to the laboratory in time.

Approved by the State Administration of Import and Export Commodity Inspection of the People's Republic of China on Dec. 1, 1997

Implemented from Apr. 1, 1998

2.4 Preparation of test sample

The combined primary sample is reduced to 1 kg, the edible portions are blended, and then divided into two equal portions. Each portion is placed in a clean container as the test sample, which is then sealed and labeled.

2.5 Storage of test sample

The test samples should be stored below −18℃.

Note: In the course of sampling and sample preparation, precautions must be taken to avoid the contamination or any factors which may cause the change of residue content.

3 Method of determination

3.1 Principle

The strobane residues in the test sample are extracted with *n*-hexane in a Soxhlet extractor and the extract is treated with concentrated sulfuric acid to remove some impurities. Reflux with potassium hydroxide-methanol solution for partial dehydrochlorination. Extract with *n*-hexane, the *n*-hexane extract is concentrated, cleaned up again with concentrated sulfuric acid and dilute to a definite volume. Determination is made by gas chromatograph with electron capture detector, using external standard method by measuring the major peak of dehydrochlorinated strobane.

3.2 Reagents and materials

Unless otherwise specified, all the reagents used should be analytically pure, "water" is distilled water.

3.2.1 *n*-Hexane, G.R.

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

3.2.3 Potassium hydroxide-methanol solution: Dissolve 50 g of potassium hydroxide in 100 mL of methanol.

3.2.4 Concentrated sulfuric acid, GR. densidy (ρ) ca 1.84 g/mL.

3.2.5 Strobane, 100%.

3.2.6 Strobane standard solution: Accurately weight an adequate amount of storbane standard, dissolve in *n*-hexane to prepare a solution of 100 μg/mL in concentration as the standard stock solution. According to the requirement, prepare a standard working solution of appropriate concentration by diluting the stock solution with *n*-hexane. Then proceed according to the procedure 3.4.3 for dehydrochlorination and 3.4.4 for cleanup at the same time with the sample treatment.

3.3 Apparatus and equipment

3.3.1 Gas chromatograph, equipped with electron capture detector (^{63}Ni).

3.3.2 Micro-syringe: 10 μL.

3.3.3 Centrifuge.

3.3.4 Mixer.

3.3.5 Centrifuge tube: 50 mL, with ground stopper.

3.3.6 Soxhlet extractor.

3.4 Procedure

3.4.1 Extraction

Grind carefully ca 10 g (accurate to 0.01 g) of the test sample with 30 g of anhydrous sodium sulfate in a mortar into dry powder, then transfer to a filfer-paper thimble, and place the thimble into a 150 mL Soxhlet extractor. Wash twice the pestle and mortar with 100 mL in total of *n*-hexane, and

pour the washings into the extractor. Extract for 16 h in a water-bath (reflux 10—12 times per hour). Take out the thimble and the extract is evaporated to ca 5 mL. Transfer the extract into a 50 mL centrifuge tube. Rinse the extracting flask with 2×5 mL of *n*-hexane, combine the rinsings into the same centrifuge tube.

3.4.2 Cleanup

Add 1 mL of concentrated sulfuric acid into the above centrifuge tube, mix on a mixer for 1 min, centrifugalize at 2 000 r/min for 5 min, draw out the acid layer with a capillarytipped pipet and discard. Treat again the *n*-hexane layer with 3×1 mL of concentrated sulfuric acid as described above. Evaporate the *n*-hexane extract to ca 5 mL with an air flow below 50℃.

3.4.3 Dehydrochlorination

Add 10 mL of potassium hydroxide-methanol solution into the above centrifuge tube, connect with a condenser and reflux for 1 h on a water-bath at (92±2)℃. Remove the centrifuge tube and let cool to the room temperature. Add 10 mL of water and 5 mL of *n*-hexane, shake violently for 1 min and centrifugalize at 2 000 r/min for 3min. Transfer the *n*-hexane layer into another graduated centrifuge tube with a capillary-tipped pipet. Extract the water layer again with 2×5 mL of *n*-hexane, combine the *n*-hexane extracts in the same graduated tube, then evaporate to near dryness with an air flow below 50℃.

3.4.4 Recleanup

Dissolve the residue with ca. 2 mL of *n*-hexane in the same tube, add 0.25 mL of concentrated sulfuric acid, mix on a mixer for 1 min, then centrifugalize at 2 000 r/min for 3 min. Draw off the acid layer with a capillary-tipped pipet and discard. Treat the *n*-hexane layer again with 2×0.25 mL of concentrated sulfuric acid as described above and dilute exactly to 2.0 mL with *n*-hexane. The *n*-hexane layer is used for gas chromatographic analysis.

3.4.5 Determination

3.4.5.1 GC operating condition

a) GC column: OV-1701 capillary column, 35 m×0.53 mm(id); film thickness 1 μm, or equivalent;

b) Column temperature: 210℃;

c) Injection port temperature: 300℃;

d) Detector temperature: 300℃;

e) Carrier gas: Nitrogen, purity≥99.99%; flow rate: 20 mL/min; make-up gas flow rate: 30 mL/min;

f) Injection volume: 1—2 μL;

g) Injection mode: Splitless.

3.4.5.2 GC determination

According to the approximate concentration of strobane in the sample solution, select the standard working solution with similar peak height to that of sample solution. The responses of dehydrochlorinated strobane in the standard working solution and sample solution should be within the linear range of the instrumental detection. The standard working solution should be randomly injected in-between the injections of the sample solution of equal volume. Under the above operating condition, the retention time of the major peak of dehydrochlorinated strobane is about 6 min. For the chromatogram of the standard, see fig. A1 in annex A.

3.5 Blank test

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

3.6 Calculation and expression of result

Calculate the content of strobane residues in the test sample by data processor or according to formula(1):

$$X = \frac{h \cdot c \cdot V}{h_s \cdot m} \qquad \cdots\cdots(1)$$

where

X—the content of strobane residues in the test sample, mg/kg;

h—the major peak height of dehydrochlorinated strobane in the sample solution, mm;

h_s—the major peak height of dehydrochlorinated strobane in the standard working solution, mm;

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

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

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

Note: The blank value should be subtracted from the above result of calculation.

4 Limit of determination and recovery

4.1 Limit of determination

The limit of determination of this method is 0.2 mg/kg.

4.2 Recovery

According to the experimental data, the fortifying concentrations of strobane in pork and its corresponding recoveries are:

0.20 mg/kg, the recovery 99.3%;

0.50 mg/kg, the recovery 84.6%;

2.00 mg/kg, the recovery 81.0%.

According to the experimental data, the fortifying concentration of strobane in beef and its corresponding recoveries are:

0.20 mg/kg, the recovery 99.5%;

0.50 mg/kg, the recovery 93.7%;

2.00 mg/kg, the recovery 99.2%.

Annex A

(informafive)

Chromatogram of the standard

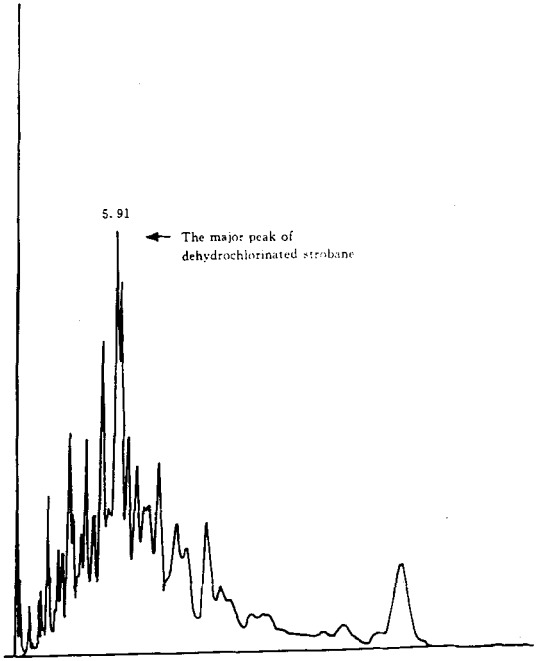


Fig. A1 Gas chromatogram of dehydrochlorinated strobane standard