SN

中华人民共和国进出口商品检验行业标准

SN 0642—1997

出口肉及肉制品中残杀威残留量检验方法

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

1997-08-15发布　　1998-01-01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》的要求进行编写的。其中测定方法是参考了国内外有关资料，经研究、改进和验证后制定的。在标准中同时制定了抽样和制样方法。

测定低限是根据国际上对肉及肉制品中残杀威残留量的最高限量和测定方法的灵敏度而制定的。

本标准的附录A为提示的附录。

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上海进出口商品检验局负责起草。

本标准主要起草人：蔡则慈、倪昕路。

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

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1 范围

本标准规定了出口肉及肉制品中残杀威残留量检验的抽样、制样和气相色谱测定方法。

本标准适用于出口猪肉中残杀威残留量的检验。

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，则可用灭菌后的锋利刀在抽出的包件中，每件割取不少于100 g，混合后置于清洁容器内，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 试样制备

从原始样品中分取出约1 kg，经捣碎机充分捣碎，混匀，均分成两份，分别装入清洁的容器内，作为试样，加封并标明标记。

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1997-08-15批准　　1998-01-01实施

3 测定方法

3.1 方法提要

试样中残留的残杀威用甲醇提取，提取液经与石油醚进行液-液分配净化。水相中被测物再用二氯甲烷提取，经脱水、浓缩后用配有氮磷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 甲醇：重蒸馏。

3.2.2 无水硫酸钠：650℃灼烧 4 h，冷却后贮于密封容器中备用。

3.2.3 硫酸钠溶液：2%水溶液。

3.2.4 石油醚：60～90℃，重蒸馏。

3.2.5 二氯甲烷：与浓硫酸充分振摇后，重蒸馏。

3.2.6 正己烷：重蒸馏。

3.2.7 残杀威标准品：纯度≥99%。

3.2.8 残杀威标准溶液：准确称取适量的残杀威标准品，用苯配制成浓度为 1.0 mg/mL 的标准储备液，再根据需要用正己烷稀释成适当浓度的标准工作溶液。

3.3 仪器和设备

3.3.1 气相色谱仪并配有氮磷检测器。

3.3.2 振荡器。

3.3.3 布氏漏斗。

3.3.4 分液漏斗。

3.3.5 水浴锅。

3.3.6 真空旋转蒸发器。

3.3.7 微量注射器：5 μL。

3.4 测定步骤

3.4.1 提取与净化

称取约 10 g 试样（精确至 0.01 g）置于 250 mL 锥形瓶中，加入 50 mL 甲醇，加塞在振荡器上振荡 1 h。用布氏漏斗抽滤，用 20 mL 甲醇分三次洗涤锥形瓶及残渣，过滤，合并滤液。将滤液移入 250 mL 分液漏斗中，用 100 mL 硫酸钠溶液（2%）分三次洗涤抽滤瓶，洗液并入上述分液漏斗。于分液漏斗中加入 50 mL 石油醚，充分振摇 1 min，静置分层。将下层水相放入另一 250 mL 分液漏斗中，弃去石油醚层。再用 25 mL 石油醚同上操作一次。于水相中加入 50 mL 二氯甲烷，剧烈振摇 2 min 后，静置分层。二氯甲烷层经无水硫酸钠柱滤入 150 mL 烧瓶中。再用 2×25 mL 二氯甲烷提取，弃去水相，合并二氯甲烷相。用少量二氯甲烷洗涤柱，洗液与提取液合并。于旋转蒸发器（水浴温度为 50℃）上浓缩至近干，然后用氮气流吹干。用 1.0 mL 正己烷溶解残渣，溶液供气相色谱测定。

3.4.2 测定

3.4.2.1 气相色谱条件

a) 色谱柱：石英毛细管柱，DB-1，10 m×0.32 mm（内径），液膜厚度 1 μm，或相当者；

b) 载气：氮气，纯度≥99.99%，2 mL/min；

c) 氢气：4.25 mL/min；

d) 空气：175 mL/min；

e) 辅助气：氮气，纯度≥99.99%，25 mL/min；

f) 色谱柱温度：程序升温，80℃保持 1 min，以 10℃/min 的速度升至 220℃，保持 5 min；

g) 进样口温度：250℃；

h) 检测器温度:300℃;

i) 进样量:1 μL;

j) 进样方式:无分流,1 min 后开阀。

3.4.2.2 气相色谱测定

根据样液中被测农药含量情况,选定与样液峰高相近的标准工作溶液。标准工作溶液和待测样液中农药的响应值均应在仪器检测的线性范围内。对标准工作液与样液应等体积参插进样测定。在上述色谱条件下,残杀威保留时间约为 8.4 min。标准品的色谱图见附录 A 中图 A1。

3.4.3 空白试验

除不加试样外,均按上述测定步骤进行。

3.5 结果计算和表述

用色谱数据处理机或按式(1)计算试样中残杀威的残留含量:

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

式中:X——试样中残杀威残留含量,mg/kg;

h——样液中残杀威的色谱峰高,mm;

h_s——标准工作液中残杀威的色谱峰高,mm;

c——标准工作液中残杀威的浓度,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

本方法测定低限为 0.05 mg/kg。

4.2 回收率

猪肉中残杀威的添加浓度及其回收率的实验数据:

在 0.05 mg/kg 时,回收率为 106%;

在 0.50 mg/kg 时,回收率为 94.8%;

在 2.00 mg/kg 时,回收率为 90.5%。

附 录 A
（提示的附录）
标准品色谱图

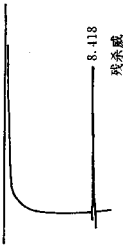


图 A1 残杀威标准品的色谱图

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 current international maximum limits for propoxur residues in meat and meat products and the sensitivity of the 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 Shanghai Import and Export Commodity Inspection Bureau of the People's Republic of China.

The main drafters of this standard are Cai Zeci and Ni Xinlu.

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 0642—1997

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

1 Scope

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

This standard is applicable to the determination of propoxur residues in pork for export.

2 Sampling and sample preparation

2.1 Inspection lot

Each inspection lot of cargo 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 each 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 package, at least one bag shall be taken as a 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 the laboratory in time.

In case the meat pieces are not contained in small bags inside each package, or if there are small bags inside 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. Place in a clean container, seal, label, and send to the laboratory in time.

2.4 Preparation of test sample

Approved by the State Administration of Import and Export Commodity Inspection of the People's Republic of China on Aug. 15, 1997

Implemented from Jan. 1, 1998

Reduce the combined primary sample to ca 1 kg. Blend with a blender and homogenize thoroughly. Mix and divide 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 sample should be stored below −18℃.

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

3 Method of determination

3.1 Principle

The propoxur residues in test sample are extracted with methanol, the extract is cleaned up by partitioning with petroleum ether. The analyte in aqueous solution is then extracted with dichloromethane. After dehydration and concentration, the solution is used for determination by gas chromatograph with nitrogen-phosphorus detector, using external standard method.

3.2 Reagents and materials

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

3.2.1 Methanol: Redistilled.

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

3.2.3 Sodium sulfate solution: 2% aqueous solution.

3.2.4 Petroleum ether: 60—90℃, redistilled.

3.2.5 Dichloromethane: Shake violently with concentrated sulfuric acid and redistill.

3.2.6 *n*-Hexane: Redistilled.

3.2.7 Propoxur standard: Purity≥99%.

3.2.8 Propoxur standard solution: Accurately weigh an adequate amount of propoxur standard, dissolve in benzene to prepare a solution of 1.0 mg/mL in concentration as the standard stock solution. According to the requirment, prepare a standard working solution of appropriate concentration by diluting the stock solution with *n*-hexane.

3.3 Apparatus and equipment

3.3.1 Gas chromatograph: Equipped with nitrogen-phosphorus detector.

3.3.2 Shaker.

3.3.3 Buchner funnel.

3.3.4 Separatory funnel.

3.3.5 Water-bath.

3.3.6 Rotary vacuum evaporator.

3.3.7 Micro-syringe: 5 μL.

3.4 Procedure

3.4.1 Extraction and cleanup

Weigh ca 10 g of the test sample (accurate to 0.01 g)into a 250 mL conical flask, add 50 mL of methanol, stopper and shake for 1 h with a shaker. Filter the extract by suction through a Buchner funnel. Rinse the conical flask and pad three times with 20 mL of methanol in total and filter. Transfer the combined flitrate into a 250 mL separatory funnel. Wash the flask three times with 100 mL in total of sodium sulfate solution (2%) and combine the washings into the separatory funnel. Add 50

mL of petroleum ether into the separatory funnel, shake violently for 1 min and let stand to separate clearly. Transfer the lower layer into another 250 mL separatory funnel, discard the petroleum ether layer. Repeat the above procedure with 25 mL of petroleum ether. Add 50 mL of dichloromethane into the aqueous phase, shake violently for 2 min and let stand to separate clearly. Pass the dichlorlmethane layer through an anhydrous sodium sulfate column to remove the water, let drain into a 150 mL flask. Extract with 2×25 mL of dichloromethane as described above, discard the aqueous phase and combine dichloromethane phases. Rinse the column with a small amount of dichloromethane and combine the rinsing with the extracts. Concentrate the combined extract to near dryness in a rotary vacuum evaporator (in 50℃ water-bath), then blow to dryness under a nitrogen current. Add exactly 1.0 mL of *n*-hexane to dissolve the residue, the solution is ready for GC determination.

3.4.2 Determination

3.4.2.1 GC operating condition

a) GC column: Fused-silica capillary column, DB-1 10 m×0.32 mm (id), film thickness 1 μm, or equivalent.

b) Carrier gas: Nitrogen, purity≥99.99%, 2 mL/min;

c) Hydrogen: 4.25 mL/min;

d) Air: 175 mL/min;

e) Make-up gas: Nitrogen, purity≥99.99%, 25 mL/min;

f)Column temperature: Keep at 80℃ for 1 min, then raise (10℃/min) to 220℃, keep at 220℃ for 5 min;

g) Injection port temperature: 250℃;

h) Detector temperature: 300℃;

i) Injection volume: 1 μL;

j) Injection mode: Splitless, purge on after 1 min.

3.4.2.2 GC determination

According to the approximate concentration of pesticide in the sample solution, select the standard working solution with similar peak height to that of the sample solution. The responses of propoxur 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 propoxur is about 8.4 min. For chromatogram of the standard, see fig. A1 in annex A.

3.4.3 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.

3.5 Calculation and expression of the result

Calculate the content of propoxur residues in the test sample by GC 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 residue content of propoxur in the test sample, mg/kg;

h—the peak height of propoxur in the sample solution, mm;

h_s—the peak height of propoxur in the standard working solution, mm;

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

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

m—the corresponding mass of 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 0.05 mg/kg.

4.2 Recovery

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

0.05 mg/kg, the recovery 106%;

0.50 mg/kg, the recovery 94.8%;

2.00 mg/kg, the recovery 90.5%.

Annex A

(informative)

Chromatogram of the standard

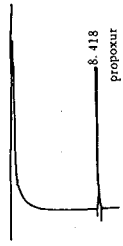


Fig. A1 Chromatogram of the propoxur standard