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中华人民共和国进出口商品检验行业标准

SN 0193.1—93

出口皮革及皮革制品中五氯酚残留量检验方法 乙酰化-气相色谱法

Method for determination of pentachlorophenol residues in leather and leather products for export —Acetylation-gas chromatography

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中华人民共和国国家进出口商品检验局　发布

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1 主题内容与适用范围

本标准规定了出口皮革及皮革制品中五氯酚残留量检验的抽样、制样和气相色谱测定方法。

本标准适用于出口皮革及皮革制品中五氯酚残留量的检验。

2 抽样和制样

出口皮革及皮革制品中五氯酚残留量的检验样品可取自于原料皮革。

2.1 检验批

以不超过1万件为一检验批。同一检验批的商品应具有相同特征，如包装、标记、产地、规格和等级等。

2.2 抽样数量

抽样件数可按式(1)计算：

$$n = 0.5\sqrt{N} \qquad \cdots\cdots(1)$$

式中：n——抽样件数；

N——每个检验批内的总件数。

取样件数不得少于3件，每一检验批内取样总量不得少于500 g。

2.3 抽样工具

割刀，剪刀。

2.4 抽样方法

在检验批中抽取样品时，先数清整批革的数量，而后顺次每隔N/n件取一件，割下或剪下部分作为原始样品。同一取样单位的原始样品放在同一塑料袋或容器内，加封后，标明标记，并及时送实验室。

2.5 试样制备

将皮革样品剪成约1 cm见方的小块，混和并以四分法缩分出50 g以上样品，于食品粉碎机中粉碎，使全部通过2 mm直径孔筛，制成均匀样品。制备好的试样盛于500 mL广口具磨口塞样品瓶中。

2.6 试样保存

试样于室温下保存。

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。

3 测定方法

3.1 方法提要

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样品中残留的五氯酚及其钠盐在硫酸溶液中均成五氯酚，用正己烷提取。经浓硫酸净化后，再以四硼酸钠水溶液反提取。加入乙酸酐生成五氯酚乙酯，最后以正己烷提取。用配有电子俘获检测器的气相色谱仪检测，以艾氏剂作内标进行定量。

3.2 试剂和材料

除特殊规定外试剂均为分析纯，水为蒸馏水或相适应的去离子水。

3.2.1 浓硫酸。

3.2.2 硫酸溶液：6 mol/L。

3.2.3 四硼酸钠溶液：0.1 mol/L。

3.2.4 正己烷：全玻璃仪器加碱重新蒸馏。

3.2.5 无水硫酸钠：经 650 ℃4 h 灼烧。

3.2.6 无水硫酸钠柱：类似筒形漏斗的柱，内装 5 cm 高的无水硫酸钠。

3.2.7 乙酸酐。

3.2.8 内标及五氯酚标准品：纯度＞99%。

3.2.9 内标及五氯酚标准溶液的配制

3.2.9.1 内标溶液配制：称取 0.05 g 艾氏剂，精确至 0.000 1 g，于 100 mL 容量瓶中，用正己烷溶解并定容，再用正己烷定量稀释至浓度为 0.500 μg/mL。

3.2.9.2 五氯酚标准溶液的配制：称取 0.10000 g 五氯酚标准品，精确至 0.1 mg，于 100 mL 容量瓶中，用正己烷溶解并定容作为贮备液，五氯酚浓度为 1.000 mg/mL。定量稀释，并移取一定量稀释液按测定步骤 3.4.3 乙酰化后制成标准工作液（使五氯酚浓度与样液中被测组分浓度相近，内标物艾氏剂浓度约为 0.050 0μg/mL）。

3.3 仪器和设备

3.3.1 气相色谱仪并配备电子俘获检测器。

3.3.2 积分仪或记录仪。

3.3.3 食品粉碎机。

3.3.4 离心机。

3.3.5 混合器。

3.3.6 微量注射器：10 μL。

3.4 测定步骤

3.4.1 提取

称取试样约 1.0 g（精确至 0.01 g）于 50 mL 离心管中，加 20 mL 6 mol/L 硫酸，在混合器上混匀 2 min。加入 20 mL 正己烷，振摇 3 min 后在混合器上混匀 2 min，并在 3 000 r/min 下离心 2 min。用吸管吸取正己烷层移入另一 50 mL 离心管中，残液再用 10 mL 正己烷重复提取一次，合并正己烷提取液在同一离心管内。

3.4.2 净化

在正己烷提取液内徐徐加入 10 mL 浓硫酸，振摇 0.5 min，在 3 000 r/min 下离心 2 min。用吸管将正己烷提取液移入 125 mL 分液漏斗中，再用 2 mL 正己烷冲洗离心管管壁，静置分层后，用吸管将正己烷冲洗液合并于同一分液漏斗中。弃去硫酸层。

在上述正己烷中加 30 mL 0.1 mol/L 四硼酸钠溶液，振摇 1 min，静置分层。将下层水相放入另一 125 mL 分液漏斗中。正己烷层再以 20 mL 0.1 mol/L 四硼酸钠溶液提取一次，合并下层水相于同一分液漏斗。弃去正己烷层。

3.4.3 乙酰化

在上述四硼酸钠水溶液中加入 0.5 mL 乙酸酐，振摇 1 min，再加入 10 mL 正己烷，振摇 1 min，静置分层。弃去下层水相。于正己烷溶液中，再每次用 20 mL 0.1 mol/L 四硼酸钠水溶液洗涤正己烷层，共

二次，振摇，静止分层，弃去水层。从分液漏斗上口将正己烷层经无水硫酸钠柱脱水后收集于具塞10 mL试管内，定量地加入适量内标溶液（一般为0.5 μg艾氏剂），此溶液供气相色谱测定。

3.4.4 测定

3.4.4.1 色谱条件

a. 色谱柱：玻璃柱，2 m×3 mm（内径），填充物为1.6%（*m*/*m*）OV-17+6.4%（*m*/*m*）OV-210涂于Chromosorb W HP（80～100目）；

b. 氮气：纯度≥99.99%，80 mL/min；

c. 柱温：210 ℃；

d. 进样口温度：250 ℃；

e. 检测器温度：250 ℃。

3.4.4.2 色谱测定

分别将标准工作溶液、样液注入气相色谱仪，进样量各5 μL。标准工作溶液中被测组分的浓度应与样液相近。出峰保留时间：五氯酚乙酯约为3.3 min；艾氏剂约为5.6 min。

3.4.5 空白试验：除不加试样外，按上述测定步骤进行。

3.4.6 结果的计算和表述

用色谱数据处理机按内标法计算或按式（2）计算：

$$X=\frac{c_s\cdot A\cdot A_{si}\cdot m_i}{c_{si}\cdot A_i\cdot A_s\cdot m} \quad \cdots\cdots(2)$$

式中：X——试样中五氯酚含量，mg/kg；

c_s——标准工作液中五氯酚乙酯（以五氯酚计）浓度，μg/mL；

c_{si}——标准工作液中艾氏剂浓度，μg/mL；

A——样液中五氯酚乙酯色谱峰面积，mm^2；

A_i——样液中艾氏剂色谱峰面积，mm^2；

A_s——标准工作液中五氯酚乙酯色谱峰面积，mm^2；

A_{si}——标准工作液中艾氏剂色谱峰面积，mm^2；

m_i——样液中艾氏剂总量，μg；

m——试样总量，g。

注：计算结果须扣除空白值。

4 测定低限、回收率

4.1 测定低限

本方法的测定低限为0.1 mg/kg。

4.2 回收率

回收率实验数据：五氯酚浓度在0.102～18.1 mg/kg范围内，回收率为92.9%～101.7%。

附加说明：

本标准由中华人民共和国国家进出口商品检验局提出。

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。

本标准主要起草人葛修丽。

参考文献：

Determination of Pentachlorophenol in Animal Tissues, JAOAC 73, 838—841 1990.

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

Method for determination of pentachlorophenol residues in leather and leather products for export —Acetylation-gas chromatography

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1 Scope and field of application

This standard specifies the method of sampling, sample preparation and determination of pentachlorophenol residues by gas chromatography in leather and leather products for export.

This standard is applicable to the determination of pentachlorophenol residues in leather and leather products for export.

2 Sampling and sample preparation

The sample for determination of pentachlorophenol residue in leather and leather products for export may be taken from leather raw materials.

2.1 Inspection lot

The quantity of an inspection lot should not be more than 10 000 pieces.

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

The number of pieces taken may be calculated according to formula (1):

$$n = 0.5\sqrt{N} \quad \cdots\cdots (1)$$

where

n—number of pieces taken;

N—total number of pieces within one inspection lot.

The number of pieces taken should be not less than 3, and the sample taken from each inspection lot should be not less than 500 g.

2.3 Sampling tools

Bark hack and scissors.

2.4 Sampling procedure

When sample is taken from the inspection lot, count the number of pieces of the whole lot at first, then successively take one piece from every N/n pieces and cut or clip part of it as primary sample. Put the primary samples of the same lot into the same plastic bag or container, seal and label and send to the laboratory in time.

2.5 Preparation of test sample

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Implemented from Aug. 1, 1993

Clip the sample into small pieces of ca 1 cm^2, mix and reduce the pieces to not less than 50 g by quartering. Then grind the sample with a food mill and pass through the sieve of 2 mm diameter apertures to form a uniform sample. The prepared sample is put into a 500 mL widemouth sample bottle with a ground glass stopper.

2.6 Storage of sample

The test sample is stored at room temperature.

Note: In the course of sampling and sample preparation, precaution 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 pentachlorophenol and its sodium salt residues in the sample will all turn to pentachlorophenol in sulphuric acid solution, which is then extracted with n-hexane. After cleaned up by concentrated sulphuric acid, extract with sodium tetraborate solution. Acetylate with acetic anhydride and finally extract with n-hexane. Determination is made by gas chromatorgraph with electron capture detector. Aldrin is used as internal standard for quantitative measurement.

3.2 Reagents and materials

Unless otherwise specified, all reagents should be of analytical grade, "water" is distilled water or corresponding de-ionized water.

3.2.1 Concentrated sulphuric acid.

3.2.2 Sulphuric acid solution: 6 mol/L.

3.2.3 Sodium tetraborate solution: 0.1 mol/L.

3.2.4 n-Hexane: Redistilled with alkali by glass apparatus.

3.2.5 Anhydrous sodium sulfate: Ignite at 650 ℃ for 4 h.

3.2.6 Column of anhydrous sodium sulfate: A 6 cm × 18 mm(id) glass column, filled with 2.5 cm height of anhydrous sodium sulfate.

3.2.7 Acetic anhydride.

3.2.8 Internal standard and pentachlorophenol standard: Purity > 99%.

3.2.9 Preparation of internal standard and pentachlorophenol standard solution.

3.2.9.1 Internal standard solution: Weigh 0.05 g of pure aldrin, accurate to 0.000 1 g, into a 100 mL volumetric flask, add n-hexane to dissolve it and dilute to volume. Further dilute this solution to a concentration of 0.500 μg/mL.

3.2.9.2 Pentachlorophenol standard solution: Weigh 0.100 00 g of standard pentachlorophenol (accurate to 0.1 mg) into a 100 mL volumetric flask. Add n-hexane to dissolve it and dilute to volume as the standard stock solution with a concentration of 1.000 mg/mL. Dilute quantitatively and transfer certain amount of the solution and prepare the standard working solution after acetylation according to the procedure in 3.4.3 (with a pentachlorophenol concentration closing to that of the sample solution and aldrin concentration as internal standard being ca 0.050 0 μg/mL).

3.3 Apparatus and equipment

3.3.1 Gas chromatograph with electron capture detector.

3.3.2 Integrator or recorder.

3.3.3 Food mill.

3.3.4 Centrifuge.

3.3.5 Mixer.

3.3.6 Micro-syringe: 10 μL.

3.4 Procedure

3.4.1 Extraction

Weigh ca 1.0 g of the sample (accurate to 0.001 g) into a 50 mL centrifuge tube. Add 20 mL of 6 mol/L suphuric acid and mix thoroughly on the mixer for 2 min. Add 20 mL of n-hexane, shake for 3 min and mix thoroughly on the mixer for another 2 min. Centrifugalize at 3 000 r/min for 2 min. Transfer the n-hexane layer with a pipette into a second 50 mL centrifuge tube. Re-extract the remaining solution with 10 mL of n-hexane and combine the n-hexane extract with that in the second centrifuge tube.

3.4.2 Clean up

Add 10 mL of concentrated sulphuric acid to n-hexane extract and shake for 0.5 min, then centrifugalize at 3 000 r/min for 2 min. Transfer the n-hexane extract into a 125 mL separatory funnel with a pipette. Add 2 mL of n-hexane to rinse the centrifuge tube wall, and let stand to separate. Combine the n-hexane rinse solution in the separatory funnel with a pipette. Discard the sulphuric acid layer.

Add slowly 30 mL of 0.1 mol/L sodium tetraborate solution to the above n-hexane solution, shake for 1 min and let stand to separate. Transfer the lower aqueous layer into another 125 mL separatory funnel, the n-hexane layer is then extracted once more with 20 mL of 0.1 mol/L sodium tetraborate solution. Combine the lower aqueous layers in the same separatory funnel. Discard the n-hexane layer.

3.4.3 Acetylation

Add 0.5 mL of acetic anhydride to the above sodium tetraborate solution and shake for 1 min, then add 10 mL of n-hexane and shake for 1 min. Let stand to separate. Discard the lower aqueous layer. Wash it twice, each with 20 mL of 0.1 mol/L sodium tetraborate solution. Shake and let stand to separate. Discard the aqueous washings. From the upper mouth of the separatory funnel pass the n-hexane layer through an anhydrous sodium sulfate column to remove the water and collect the effluent in a 10 mL test tube with a stopper. Add adequate internal standard solution quantitatively (generally 0.5 μg for aldrin) to the n-hexane layer.

The sample solution is thus ready for GC determination.

3.4.4 Determination

3.4.4.1 Gas chromatographic operating conditions

a. GC Column: Glass, 2m × 3 mm (id), packed with 1.6%(*m*/*m*) OV-17 + 6.4%(*m*/*m*) OV-210 on chromosorb W HP (80—100 mesh);

b. Nitrogen: Purity ≥ 99.99%, 80 mL/min;

c. Column temperature: 210 ℃;

d. Injection port temperature: 250 ℃;

e. Detector temperature: 250 ℃.

3.4.4.2 GC determination

Inject separately the standard working solution and sample solution into the gas chromatograph. Injection volume: 5 μL each. The concentration of the constituent to be determined in the standard working solution should be close to that of the sample solution. Retention time: ethyl pentachlorophenolate: ca 3.3 min; aldrin: ca 5.6 min under above GC condition.

3.4.5 Blank test

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

3.4.6 Calculation and expression of the result

Calculate the content of pentachlorophenol in the sample by GC data processor or according to formula (2):

$$X = \frac{c_s \cdot A \cdot A_{si} \cdot m_i}{c_{si} \cdot A_i \cdot A_s \cdot m} \quad \cdots\cdots(2)$$

where

X—Content of pentachlorophenol in the test sample, mg/kg;

c_s—Concentration of ethyl pentachlorophenolate (calculated as pentachlorophenol) in the standard working solution, μg/mL;

c_{si}—Concentration of aldrin in the standard working solution, μg/mL;

A—Peak area of ethyl pentachlorophenolate in the sample solution, mm^2;

A_i—Peak area of aldrin in the sample solution, mm^2;

A_s—Peak area of ethyl pentachlorophenolate in the standard working solution, mm^2;

A_{si}—Peak area of aldrin in the standard working solution, mm^2;

m_i—Total mass of aldrin in the sample solution, μg;

m—Total mass of sample, g.

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

4 Limit of determination and recovery

4.1 Limit of determination

The limit of determination of this method is 0.1 mg/kg.

4.2 Recovery

According to the experimental data, when the concentration of pentachlorophenol is in the range of 0.102—18.1 mg/kg, the recovery is 92.9%—101.7%.

Additional explanation:

This standard was proposed by 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.

This standard was mainly drafted by Ge Xiuli.

Reference:

Determination of Pentachlorophenol in Animal Tissues, JAOAC 73, 838—841, 1990.

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