SN

中华人民共和国进出口商品检验行业标准

SN 0351—95

出口粮谷中丙线磷残留量检验方法

Method for the determination of ethoprophos residues in cereals for export

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1 主题内容与适用范围

本标准规定了出口粮谷中丙线磷残留量检验的抽样、制样和气相色谱测定方法。

本标准适用于出口大米中丙线磷残留量的检验。

2 抽样与制样

2.1 检验批

每批数量以不超过 4 000 袋为一检验批。

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、等级等。

2.2 抽样数量

按式(1)计算抽样袋数。

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

式中：N——全批袋数；

a——抽样袋数。

注：抽样袋数 a 值取整数，小数部分向前进位为整数。

2.3 抽样工具

2.3.1 金属单管取样器：全长 55 cm(包括手柄)，直径 1.5～2.5 cm，沟槽长度应超过袋对角线长度的二分之一。

2.3.2 取样铲。

2.3.3 分样板。

2.3.4 样品筒(袋)：可密封。

2.3.5 分样布。

2.4 抽样方法

2.4.1 袋内抽样：按 2.2 规定的应抽样数(扣除倒包抽样袋数)，在堆垛四周上、中、下各部位以曲线形走向，随机抽取。将取样器的沟槽朝下，从每袋一角依斜对角方向插入袋内，然后将沟槽旋转朝上，抽出取样器，立即倒入盛样容器内。每袋所取样品数量应基本一致。

2.4.2 倒包抽样：从堆垛各部位随机抽取 2.2 条规定的应抽样件数的 10%(每一批不少于 3 袋)，将袋口缝线全部拆开，平置于分样布或其他洁净的铺垫物上，双手紧握袋底两角，提起约成 45°倾斜角，倒拖 1 m 以上，使袋内货物全部倒出。检查货物的外观、气味、有无发霉、变质等，并查看袋内和袋间品质是否均匀。确认情况正常后，用取样铲在各部位抽取样品，每袋抽取样品数量应基本一致，立即倒入盛样容器

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内。

2.4.3 大样缩分

集中袋内和倒包所取的样品，倒于分样布上，混匀，使用分样板按四分法缩分出样品不少于 4 kg，所抽取的样品必须装入密闭容器内，以防熏蒸剂的散失。加封后，标明标记并及时送实验室。

2.5 试样制备

将样品缩分至 1 kg，全部磨碎，通过 20 目筛，混匀，均分成两份，装入洁净容器内，密封，标明标记。

2.6 试样保存

将试样在 0℃以下避光保存。

注：① 缩分样品时，操作尽量要快，以防止熏蒸剂的散失。

② 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

用甲醇提取样品中丙线磷，于提取液中加氯化钠溶液，然后用正己烷提取，经浓缩、定容后，用气相色谱氮磷检测器测定，外标法定量。

3.2 试剂和材料

3.2.1 甲醇：分析纯，经全玻璃装置重蒸馏。

3.2.2 正己烷：分析纯，经全玻璃装置重蒸馏。

3.2.3 无水硫酸钠：分析纯，经 650℃灼烧 4 h，置于干燥器内备用。

3.2.4 氯化钠：分析纯。

3.2.5 氯化钠溶液：10%，取 100 g 氯化钠溶解于 1 000 mL 蒸馏水中。

3.2.6 丙线磷标准品：纯度≥99%。

3.2.7 丙线磷标准溶液：准确称取适量的丙线磷标准品，用正己烷配成浓度为 100 μg/mL 的标准储备溶液，根据需要再配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 超声波振荡器。

3.3.3 锥形瓶：150 mL。

3.3.4 布氏漏斗。

3.3.5 旋转蒸发器。

3.3.6 分液漏斗：250 mL。

3.3.7 无水硫酸钠柱：筒形漏斗 80 mm×20 mm(内径)，内装约 50 mm 高无水硫酸钠。

3.3.8 微量注射器：10 μL。

3.4 测定步骤

3.4.1 提取

称取粉碎均匀的试样 20 g(精确到 0.1 g)于锥形瓶中，加入 50 mL 甲醇，浸渍 1 h。在超声波振荡器上提取 10 min，在布氏漏斗上过滤。残渣用 2×20 mL 甲醇按上述操作重复提取两次，过滤。合并滤液并于 50℃水浴旋转蒸发器上减压浓缩到 30 mL 左右。

3.4.2 净化

将浓缩液转入分液漏斗，加 150 mL 10%氯化钠水溶液，用 40、40、20 mL 正己烷提取 3 次。弃去水层，合并正己烷层，并使通过无水硫酸钠柱。用少量正己烷洗涤无水硫酸钠柱，合并流出液并于 45℃水浴旋转蒸发器上减压浓缩至干。用正己烷溶解并定容到 5.00 mL，供气相色谱测定。

3.4.3 测定

3.4.3.1 色谱条件

a. 色谱柱：25 m×0.53 mm(内径)×5.0 μm(膜厚)SE-52 石英毛细管柱；

b. 色谱柱温度：220℃；

c. 进样口温度：225℃；

d. 检测器温度：250℃；

e. 氮气：纯度≥99.99%，8 mL/min；尾吹气 22 mL/min；

f. 氢气：3.5 mL/min；

g. 空气：120 mL/min。

3.4.3.2 色谱测定

根据样液中丙线磷含量情况，选定峰高相近的标准工作溶液。标准工作溶液和样液中丙线磷响应值均应在仪器检测线性范围内。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，丙线磷的保留时间约 8 min。

3.4.4 空白试验

除不加试样外，按上述测定步骤进行。

3.4.5 结果计算和表述

用色谱数据处理机或按式(2)计算：

$$X = \frac{h \cdot c \cdot V}{h_s \cdot m} \qquad \cdots\cdots(2)$$

式中：X——试样中丙线磷残留量，mg/kg；

h——样液中丙线磷的峰高，mm；

h_s——标准工作溶液中丙线磷的峰高，mm；

c——标准工作溶液中丙线磷的浓度，μg/mL；

V——样液最终定容体积，mL；

m——最终样液所代表的样品重量，g。

注：计算结果需扣除空白值。

4 方法的测定低限、回收率

4.1 测定低限

本方法测定低限为 0.005 mg/kg。

4.2 回收率

回收率的实验数据：丙线磷浓度在 0.005～0.05 mg/kg 范围，回收率为 72.0%～100.2%。

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浙江进出口商品检验局负责起草。

本标准主要起草人郑自强、徐亮、朱宏。

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

SN 0351—95

Method for the determination of ethoprophos residues in cereals for export

1 Scope and field of application

This standard specifies the methods of sampling, sample preparation and determination by gas chromatography of ethoprophos residues in cereals for export.

This standard is applicable to the determination of ethoprophos residues in rice for export.

2 Sampling and sample preparation

2.1 Inspection lot

The quantity of an inspection lot should not be more than 4 000 bags.

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

2.2 Quantity of sample taken

Calculate the number of bags to be taken by formula (1):

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

where

N—total number of bags in a lot;

a—number of bags to be taken.

Note: If value a is with decimal, round off the decimal part, which is added as unity to the integral part of a.

2.3 Sampling tools

2.3.1 Metallic sampler; Length (including handle)55 cm; diameter 1.5—2.5 cm; groove length>half of the bag's diagonal length.

2.3.2 Sampling shovel.

2.3.3 Plate for quartering.

2.3.4 Sample can (bag): Which can be sealed.

2.3.5 Cloth sheet; For sample dividing (quartering).

2.4 Sampling procedure

2.4.1 Sampling in the bag

Draw the samples from a number of the sampled bags specified in 2.2(minus the number of sam-

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pled bags by emptying out) as follows: Along the sine wave of the pile draw samples from the bags of the upper, middle and lower parts of the pile at random. Insert the sampler, with its groove facing downward, diagonally into each bag, then turn the sampler by 180℃, draw out the sampler , and promptly pour the sample into a container. The quantity of the sample drawn from each bag shall be basically the same.

2.4.2 Sampling by emptying out

Draw 10 percent of the number of bags specified in 2.2(not less than 3 bags)from different parts of the pile at random. Unseam and open the bag, and lay the bag on a clean cloth sheet(or other clean sheet). Grasp tight two corners of the bag bottom and raise up to an angle of 45°, tug backward for ca 1 m until all content of the bag is emptied out. Check the appearance, odour of the goods and whether the goods are moldy, rotten etc. Also check whether the quality of the goods is uniform within and between the bags. After confirming the goods are in normal condition, scoop up the sample from different parts of the out-poured content with a shovel, and place in sample container promptly. The quantity of the sample drawn from each bag should be basically the same.

2.4.3 Reduction of gross sample

Pour the samples (from both 2.4.1 and 2.4.2)on a clean sheet for quartering, mix and reduce to not less than 4 kg with a plate by quartering, The samples must be put into the airtight container, in order to prevent the fumigants from dissipating, sealed, labeled and sent to the laboratory in time.

2.5 Preparation of test sample

Reduce the sample to ca 1 kg, grind thoroughly and let pass through a 20-mesh sieve, mix, divide into 2 equal portions, place in clean containers, seal and label.

2.6 Storage of test sample

The test sample shall be stored below 0℃ and kept away from light.

Note: ① Sample reduction operation must be conducted as quickly as possible to avoid the dissipation of fumigants.

② During sampling and preparation of sample, precautions must be taken to avoid contamination of any factors that may cause the change of residue content.

3 Method of determination

3.1 Principle

The ethoprophos residues in sample is extracted with methanol. The extract is combined with sodium chloride solution, and then extracted with n-hexane. Evaporate the extract to near dryness, then dilute to a definte valume. The solution is measured by gas chromatography with nitrogen phosphorus detector, using external standard method.

3.2 Reagents and materials

3.2.1 Methanol: A. R. , redistilled.

3.2.2 n-Hexane: A. R. , redistilled.

3.2.3 Anhydrous sodium sulfate: A. R. , ignited at 650℃ for 4 h, and stored in a desiccator.

3.2.4 Sodium chloride: A. R. .

3.2.5 Sodium chloride solution(10%): Dissolve 100 g of sodium chloride in 1 000 mL of distilled water.

3.2.6 Ethoprophos: Purity≥99%.

3.2.7 Ethoprophos standard solution: Accurately weigh a suitable amount of ethoprophos standard, and dissolve in n-hexane to prepare a stock solution with a concentration of 100 μg/mL. According to

the concentration requirement, prepare a standard working solution of appropriate concentration.

3.3 Apparatus and equipment

3.3.1 Gas chromatograph with nitrogen phosphorus detector.

3.3.2 Supersonic shaker.

3.3.3 Conical flask: 150 mL.

3.3.4 Buchner funnel.

3.3.5 Rotary evaporator.

3.3.6 Separatory funnel: 250 mL.

3.3.7 Column of anhydrous sodium sulfate: 80 mm×20 mm(id)cylindrical funnel, filled with 50 mm height of anhydrous sodium sulfate.

3.3.8 Micro syringe: 10 μL.

3.4 Procedure

3.4.1 Extraction

Weigh ca 20 g of the mixed test sample(accurate to 0.1 g)into a conical flask with stopper. Add 50 mL of methanol, and let stand for one hour, then shake for 10 min by a supersonic shaker. Filter the extract through a Buchner funnel under reduced pressure. Reextract the residues twice with 20 mL of methanol each time and filter. The combined filrate is concentrated to ca 30 mL in the rotary evaporator under reduced pressure in a 50℃ water-bath.

3.4.2 Cleanup

Transfer the concentrate into a separatory funnel. Add 150 mL of 10% sodium chloride solution and then successively extract with 40、40 and 20 mL of n-hexane. Draw off and discard the aqueous layer. Combine the n-hexane layers and pass through the column of anhydrous sodium sulfate. Rinse the column with a small amount of n-hexane, combine the rinsing with the extract. Concentrate the extract to dryness in the rotary evaporator under reduced pressure in a 45℃ water-bath. Dissolve the residue and dilute exactly to 5.00 mL with n-hexane. The solution is used for chromatographic determination.

3.4.3 Determination

3.4.3.1 Gas chromatographic operation condition

a. Column: 25 m×0.53 mm(id)×5.0 μm(film thickness) SE 52 fused-silica capillary column;

b. Column temperature: 220℃;

c. Injection port temperature: 225℃;

d. Detector temperature: 250℃;

e. Nitrogen: Purity≥99.99%, 8 mL/min; make up gas 22 mL/min;

f. Hydrogen: 3.5 mL/min;

g. Air: 120 mL/min.

3.4.3.2 Gas chromatographic determination

According to the approximate concentration of ethoprophos in the sample solution, select a standard working solution with similar peak height to that of sample solution. The response values of ethoprophos in the standard working solution and sample solution should be in linear range of the instrument detection. The standard working solution should be injected randomly in-between the injections of the sample solution of equal volume.

Under the above chromatographic condition, the retention time of ethoprophos is about 8 min.

3.4.4 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.

3.4.5 Calculation of result and expression:

The calculation of result is carried out by GC data processor or according to formula (2):

$$X = \frac{h \cdot c \cdot V}{h_s \cdot m} \qquad \cdots\cdots(2)$$

where

X—the residue content of ethoprophos in the test sample, mg/kg;

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

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

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

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

m—the corresponding mass of the sample in the final test 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 0.005 mg/kg.

4.2 Recovery

According to the experimental data, when the concentration of ethoprophos residues is in the range of 0.005—0.05 mg/kg, the recovery is 72.0%—100.2%.

Additional explanations:

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 the Zhejiang Import and Export Commodity Inspection of Bureau of the People's Republic of China.

This standard was mainly drafted by Zheng Ziqiang, Xu Liang, Zhu Hong.

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