SN

中华人民共和国进出口商品检验行业标准

SN 0701—1997

出口粮谷中磷胺残留量检验方法

Method for the determination of phosphamidon residues in cereals 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》的要求进行编写的。其中，测定方法是参考国内外有关文献，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。

测定低限是根据国际上对粮谷中磷胺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深圳进出口商品检验局负责起草。

本标准主要起草人：谢丽琪、蓝芳、潘坤永。

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

出口粮谷中磷胺残留量检验方法

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Method for the determination of phosphamidon residues in cereals for export

1 范围

本标准规定了出口粮谷中磷胺残留量检验的抽样、制样和气相色谱测定方法。

本标准适用于出口大米、玉米中磷胺残留量的检验。

2 抽样和制样

2.1 检验批

以不超过 200 t 为一检验批。200 t 袋装大米约 4 000 袋；袋装玉米约 2 200 袋。玉米有时为散装品。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

2.2.1 袋装货品

按式(1)计算抽样袋数：

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

式中：a ——抽样袋数；

N ——全批袋数。

注：a 值取整数，小数部分向前进位为整数。

2.2.2 散装货品

货堆高度不超过 2 m。按货堆面积划区设点，以 50 m^2 为一个取样区，每区设中心和四角(距边沿 1 m处)5 个点。每增加一个抽样区，增设 3 个点。

2.3 抽样工具

2.3.1 单管取样器：不锈钢管，全长 55 cm(包括手柄)，直径 1.5～2.0 cm，沟槽长度应超过袋对角线长度的一半。

2.3.2 双套管取样器：不锈钢管，全长 1 m、2 m(包括手柄)两种。内外管同部位分段开几个槽口，每个槽口长 15～20 cm，口宽 2.0～2.5 cm。内管的内径 2.5～3.0 cm；取样器的探头长约 7 cm。

2.3.3 取样铲或取样勺。

2.3.4 分样板。

2.3.5 盛样器，筒或袋，可密封。

2.3.6 分样布或适用铺垫物。

2.3.7 磨碎机。

2.4 抽样方法

2.4.1 袋装抽样

2.4.1.1 袋内抽样：按 2.2.1 条规定的应抽样袋数的 90%，在堆垛四周的上、中、下各层以曲线形走

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向，随机抽取。对大米用金属单管取样器(2.3.1)槽口朝下，从每袋一角依斜对角线方向插入袋内，然后将管槽旋转朝上，抽出取样管，立即将样品倒入盛样容器内。每袋抽取的样品数量应基本一致。对玉米，用 1 m 长的金属双套管(2.3.2)，关闭槽口，从每袋一角依斜对角方向插入袋内，然后旋转内管以开启槽口，待样品流满内管后，再旋转内管以关闭槽口。抽出取样器，立即将样品倒入盛样器内。每袋抽取的样品数量应基本一致。

2.4.1.2 倒包抽样：从堆垛的各部位随机抽取 2.2.1 规定的应抽件数的 10%(每批一般不少于 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°倾角，倒拖约 1 m，使袋内货物全部倒出。查看袋内和袋间品质是否均匀。确认情况正常后，用取样铲随机在各部位抽取样品，并立即将样品倒入盛样容器内。每袋所取样品量应与 2.4.1.1 基本一致。

每批样品总量应不少于 4 kg。

2.4.2 散积抽样

按 2.2.2 所设定的取样点，逐点抽取样品。将取样器(2.3.2 中 1 m 或 2 m)关闭槽口，以倾斜 45°角度插入粮堆至相应深度，旋转取样器内管以开启槽口，待样品流满内管后，再旋转内管以关闭槽口。抽出取样管，立即将样品倒入盛样器内。从各个点所抽取的样品量应基本一致。每批所抽取样品总量应不少于 4 kg。

2.4.3 大样缩分

袋装样品：集中袋内抽样和倒包抽样所取全部样品，倒于分样布上，用分样板按四分法缩分样品至不少于 2 kg。放入盛样容器内，加封，并标明标记，及时送交实验室。

散积样品：将抽取的全部样品，倒于分样布上，以下按上述袋装样品方法进行。

2.5 试样制备

将取回样品用四分法缩分至约 1 kg，用磨碎机全部磨碎并通过 20 目筛，混匀后均分成两份，分装入清洁的容器内，作为试样。密封，标明标记。

2.6 试样保存

将试样于－5℃以下避光保存。

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

试样中的磷胺用丙酮提取，提取液经浓缩、定容后，用配有火焰光度检测器的气相色谱仪进行测定，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。

3.2.1 丙酮：重蒸馏。

3.2.2 磷胺标准品：纯度≥99.0%(顺式异构体 70%，反式异构体 30%)。

3.2.3 磷胺标准溶液：准确称取适量的磷胺标准品，用丙酮配成浓度为 100 μg/mL 的贮备液。根据需要再用丙酮稀释贮备液成适当浓度的标准工作液。

3.3 仪器和设备

3.3.1 气相色谱仪，配有火焰光度检测器(带磷滤光片)。

3.3.2 旋转蒸发器。

3.3.3 旋涡混匀器。

3.3.4 微量注射器：10 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 0.1 g)于 50 mL 具塞锥形瓶中,加 20 mL 丙酮,混匀,放置 30 min,然后在旋涡混匀器上混匀 10 min,将丙酮提取液过滤入梨形瓶中。残渣再用丙酮提取二次,每次用 10 mL 丙酮。合并丙酮提取液于梨形瓶中,用旋转蒸发器于 50℃浓缩,并用丙酮定容至 5.0 mL。溶液供气相色谱测定。

3.4.2 测定

3.4.2.1 色谱条件

a) 色谱柱:HP-5,10 m×0.53 mm(id),膜厚度 2.65 μm,石英毛细管柱,或相当者;

b) 色谱柱温度:程序升温:100℃保持 1 min,以 20℃/min 升至 260℃,保持 10 min;

c) 进样口温度:270℃;

d) 检测器温度:270℃;

e) 载气:氮气:纯度≥99.99%,20 mL/min;

f) 氢气:40 mL/min;

g) 空气:120 mL/min;

h) 进样方式:不分流进样;

i) 进样量:2 μL。

3.4.2.2 色谱测定

根据样液中磷胺含量情况,选定峰面积相近的标准工作溶液。标准工作溶液和样液中磷胺的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,磷胺的保留时间反式-磷胺为 5.8 min,顺式-磷胺为 6.2 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,按上述测定步骤进行。

3.4.4 结果计算和表述

用色谱数据处理机或按式(2)计算试样中磷胺残留含量:

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

式中:X ——试样中磷胺残留含量,mg/kg;

A ——样液中磷胺的峰面积(顺式、反式异构体峰面积之和),mm^2;

A_s ——标准工作液中磷胺的峰面积(顺式、反式异构体峰面积之和),mm^2;

c ——标准工作溶液中磷胺的浓度,μg/mL;

V——样液最终定容体积,mL;

m——称取的试样量,g。

注:计算结果需扣除空白值。

4 测定低限、回收率

4.1 测定低限

本方法的测定低限为 0.02 mg/kg。

4.2 回收率

大米中磷胺添加浓度及其回收率的实验数据:

在 0.02 mg/kg 时,回收率为 90.5%;

在 0.05 mg/kg 时,回收率为 92.0%;

在 0.10 mg/kg 时,回收率为 99.5%;

在 1.00 mg/kg 时,回收率为 96.0%。

玉米中磷胺添加浓度及其回收率的实验数据:

在 0.02 mg/kg 时，回收率为 86.3%；
在 0.05 mg/kg 时，回收率为 97.4%；
在 0.10 mg/kg 时，回收率为 97.1%；
在 1.00 mg/kg 时，回收率为 101.3%。

附 录 A
（提示的附录）
标准品色谱图

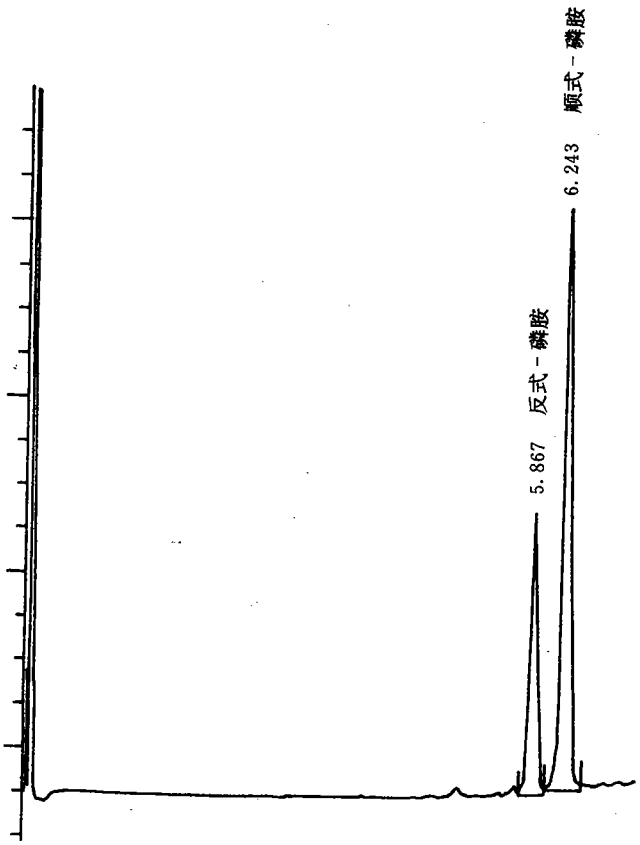

图 A1 磷胺标准品气相色谱图

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". The method of determination of this standard 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 limit for phosphamidon residues in cereals 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 Shenzhen Import and Export Commodity Inspection Bureau of the People's Republic of China.

The main drafters of this standard are Xie Liqi, Lan Fang and Pan Kunyong.

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 0701—1997

Method for the determination of phosphamidon residues in cereals for export

1 Scope

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

This standard is applicable to the determination of phosphamidon residues in rice and maize for export.

2 Sampling and sample preparation

2.1 Inspection lot

Each inspection lot should not exceed 200 t. An inspection lot of 200 t for rice in bags shall be ca 4 000 bags, that for maize in bags shall be ca 2 200 bags. The cargo of maize is sometimes in bulk.

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

2.2.1 Cargo in bags

The number of bags to be sampled shall be calculated according to the formula(1):

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

where

N —total number of bags in a lot;

a—number of bags to be sampled.

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

2.2.2 Cargo in bulk

The height of the cereal pile should not exceed 2 m. Set up areas and spots for sampling on the pile surface. 50 m^2 is considered as an area, in which 5 spots should be fixed, one in the center and four at four corners, but 1 m from the margins of the area. For an additional area, three more sampling spots should be fixed.

2.3 Sampling tools

2.3.1 Metallic sampler: Stainless steel tube, length (including handle): 55 cm; diameter: 1.5 cm—2.0 cm; groove length: longer than half of the bag's diagonal length.

2.3.2 Double-casing sampler: Consists of two stainless steel tubes; length 1 m, 2 m (both including handle), with some slots on different sections and respectively at the same height for both inner and outer casing; length of slots: 15—20 cm, width of the slots: 2.0—2.5 cm; inside diameter of the inner

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

casing:2.5—3.0 cm,the probe length of the sampler:ca 7 cm.

2.3.3 Sampling shovel or ladle.

2.3.4 Plate for quartering.

2.3.5 Sample container:Can or bag which can be sealed.

2.3.6 Cloth(or other material)sheet:For sample dividing(quartering).

2.3.7 Grinder.

2.4 Sampling procedure

2.4.1 For cargo in bags

2.4.1.1 Sampling from inside the bags:Draw the samples from 90 percent of the number of bags specified in 2.2.1 as follows:Along the sine wave of the pile,draw samples from the bags of the upper,middle and lower parts around the pile at random. For rice,insert the metallic sampler (2.3.1) 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 sample container. The amount of the sample drawn from each bag should be basically the same. For maize,insert the metallic double casing sampler(2.3.2, length 1 m),with the slots closed while inserting in,diagonally into each bag. Turn the inner casing to open the slots so that the sample may fill up the inner tube. Again turn the inner casing to close the slots and draw out the sampler. Promptly pour the sample into a sample container. The amount of sample drawn from each bag should be basically the same.

2.4.1.2 Sampling by emptying out:Draw 10 percent of the number of bags specified in 2.2.1(not less than 3 bags)of any part of the pile at random. Unseam and open the bag,and lay it on a 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 whether the quality of the goods is uniform within and between the bags. After confirming that the goods are in normal condition,scoop up the sample from different parts of the out-poured content with a shovel,and place in a sample container promptly. The quantity of the sample drawn from each bag should be basically the same as in 2.4.1.1.

The total weight of the sample drawn from each lot should not be less than 4 kg.

2.4.2 Sampling for cargo in bulk

Fix the sampling spots as specified in 2.2.2,draw the samples from the spots successively by inserting the double casing sampler (1 m or 2 m in 2.3.2) into the pile to an appropriate depth at 45°, with the slots closed while inserting in. Turn the inner casing to open the slots so that the sample may fill up inner tube. Again turn the inner casing to close the slots and draw out the sampler. Promptly pour the sample into a sample container. The amount of sample drawn from each spot should be basically the same.

The total weight of the sample drawn from each lot should be not less than 4 kg.

2.4.3 Reduction of gross sample

For cargo in bags:Pour all of the samples(from both 2.4.1.1 and 2.4.1.2)onto a clean sheet. Reduce to not less than 2 kg with a plate by quartering. Place in a sample container,seal,label and send to the laboratory in time.

For cargo in bulk:Pour all the drawn sample onto a clean sheel and proceed as for cargo in bags described above.

2.5 Preparation of test sample

Reduce the sample taken back by quartering to ca 1 kg,Grind with a grinder to let all pass through a 20 mesh sieve. Mix thoroughly and divide into two equal portions,place in clean containers

as the test samples, seal and label.

2.6 Storage of test sample

The test samples should be stored blow −5℃ and kept away from light.

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

3 Method of determination

3.1 Principle

The phosphamidon residues in the test sample are extracted with acetone. The acetone extract is concentrated and made up to a definite volume. Determination is made by gas chromatography with flame photometric detector (FPD), using external standard method.

3.2 Reagents and materials

Unless otherwise specified, all the reagents used should be analytically pure.

3.2.1 Acetone: Redistilled.

3.2.2 Phosphamidon standard: Purity ≥99.0% (Z-phosphamidon: 70%, E-phosphamidon: 30%).

3.2.3 Phosphamidon standard solution: Accurately weigh an adequate amount of phosphamidon standard, dissolve and dilute with acetone to prepare a standard stock solution of 100 μg/mL in concentration. Then according to the requirement prepare a standard working solution of appropriate concentration by diluting the standard stock solution with acetone.

3.3 Apparatus and equipment

3.3.1 Gas chromatography, equipped with FPD (with P filter).

3.3.2 Rotary evaporator.

3.3.3 Vortex mixer.

3.3.4 Micro-syringe: 10 μL.

3.4 Procedure

3.4.1 Extraction

Weigh ca 10 g of the test sample (accurate to 0.1 g) into a 50 mL conical flask with stopper, add 20 mL of acetone, mix and let stand for 30 min. Blend intensely in a vortex mixer for 10 min. Filter the extract into a pear-shaped flask. Reextract the residue twice with 10 mL portions of acetone. Combine the acetone extracts into the same pear-shaped flask. Rotary-evaporate at 50℃ to concentrate and make-up to 5.0 mL with acetone. The solution is used for GC determination.

3.4.2 Determination

3.4.2.1 GC operating condition

a) Column: HP-5, fused quartz capillary column, 10 m × 0.53 mm (id) × 2.65 μm film thickness or equivalent;

b) Column temperature: Programmed, 100℃ (1 min) $\xrightarrow{20℃/min}$ 260℃ (10 min);

c) Injection port temperature: 270℃;

d) Detector temperature: 270℃;

e) Carrier gas: Nitrogen: Purity ≥99.99%, 20 mL/min;

f) Hydrogen: 40 mL/min;

g) Air: 120 mL/min;

h) Injection mode: Splitless;

i) Injection volume: 2 μL.

3.4.2.2 GC determination

According to the approximate concentration of phosphamidon in the sample solution, select the standard working solution with similar peak area to that of the sample solution. The responses of phosphamidon in the standard working solution and sample solution should be within the linear range of the instrumental detection. The standard working solution should be injected in-between the injections of the sample solution of equal volume. Under the above operating condition, the retention time of Ephosphamidon is ca 5.8 min and Z-phosphamidon is ca 6.2 min. For chromatogram of the standard, see figure 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.

3.4.4 Calculation and expression of the result

The calculation of the content of phosphamidon residues in the test sample is carried out by GC data processor or according to the formula(2):

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

where

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

A —peak area of phosphamidon in the sample solution (the total area of E-phosphamidon and Z-phosphamidon), mm^2;

A_s —peak area of phosphamidon in the standard working solution (the total area of E-phosphamidon and Z-phosphamidon), mm^2;

c —concentration of phosphamidon in the standard working solution, $\mu g/mL$;

V —final volume of the sample solution, mL;

m —mass of test sample, 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 0.02 mg/kg.

4.2 Recovery

According to the experimental data, the fortifying concentrations of phosphamidon and its corresponding recoveries are:

In rice:

0.02 mg/kg, the recovery 90.5%;

0.05 mg/kg, the recovery 92.0%;

0.10 mg/kg, the recovery 99.5%;

1.00 mg/kg, the recovery 96.0%.

In maize:

0.02 mg/kg, the recovery 86.3%;

0.05 mg/kg, the recovery 97.4%;

0.10 mg/kg, the recovery 97.1%;

1.00 mg/kg, the recovery 101.3%.

Annex A

(informative)

Chromatogram of the standard

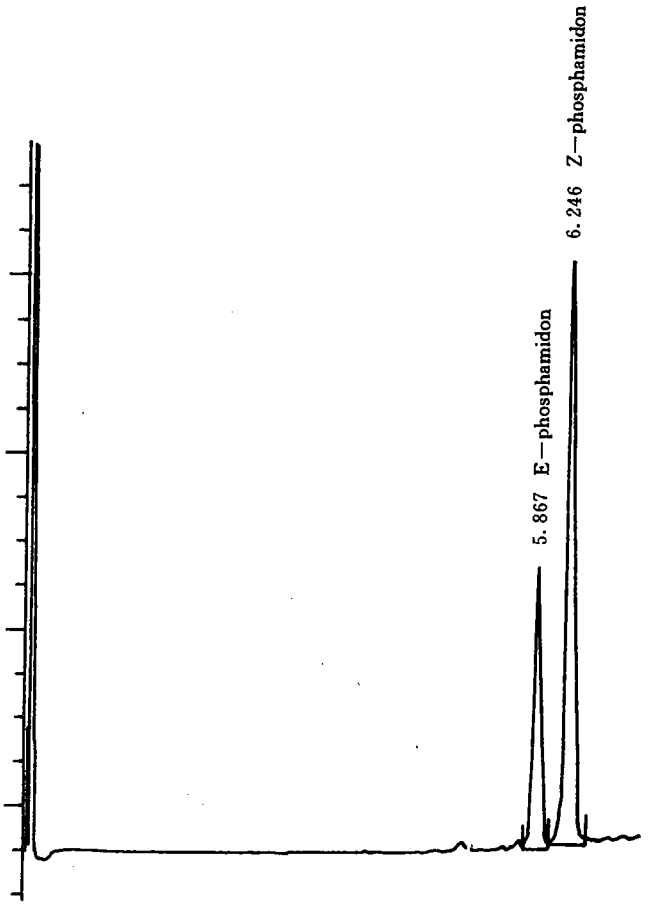

Fig. A1 Gas chromatogram of phosphamidon standard

中国标准出版社出版　中国标准出版社秦皇岛印刷厂印刷

1998 年 2 月第一版　1998 年 2 月第一次印刷　书号:155066・2-11962