SN

中华人民共和国进出口商品检验行业标准

SN 0204—93

出口粮谷中除草醚残留量检验方法

Method for determination of nitrofen residues in grains for export

1993-06-04发布　　1993-08-01实施

中华人民共和国国家进出口商品检验局　发布

中华人民共和国进出口商品检验行业标准

出口粮谷中除草醚残留量检验方法

SN 0204—93

Method for determination of nitrofen residues in grains for export

1 主题内容与适用范围

本标准规定了出口粮谷中除草醚残留量检验的抽样、制样和气相色谱测定方法。

本标准适用于出口大米中除草醚残留量的检验。

2 抽样和制样

2.1 检验批

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、规格和等级等。

2.2 抽样数量

按一批总袋数的平方根抽取：

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

式中：N——全批袋数；

a——抽样袋数。

注：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二分之一。

2.3.2 取样铲：见图 1。

2.3.3 分样板：见图 2。

2.3.4 样品筒(袋)：可密封。

2.3.5 分样布或适用铺垫物。

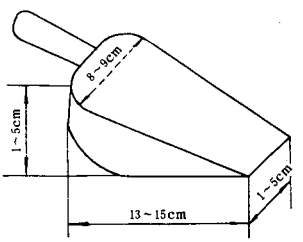


图 1 取样铲

中华人民共和国国家进出口商品检验局 1993-06-04 批准　　1993-08-01 实施

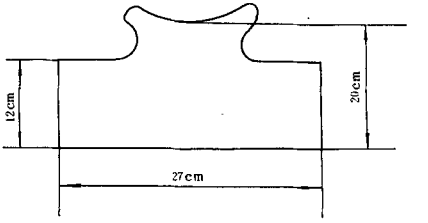


图 2 分样板

2.4 抽样方法

2.4.1 袋内抽样：按 2.2 规定计算抽样袋数，在堆垛四周上、中、下各部位以曲线形走向，随机抽取。将扦槽朝下，从每袋一角依斜对角方向插入袋内，然后将扦槽旋转朝上，抽出扦样器，立即倒入盛样容器内。每袋扦取样品数量应基本一致。

2.4.2 倒包抽样：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后，用取样铲在各部位扦取样品约 100 g，立即倒入盛样容器内。

2.4.3 大样缩分：集中袋内或倒包所取样品，倒于分样布上，使用分样板，按四分法缩分样品不少于 4 kg，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

将试样于 5℃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

大米中除草醚的残留量用丙酮和石油醚提取。洗去丙酮后，提取液用硫酸净化。将净化液浓缩后，残渣用环氧七氯内标溶液溶解，用配有电子俘获检测器的气相色谱仪定量测定。

3.2 试剂和材料

3.2.1 丙酮：分析纯，重蒸馏。

3.2.2 石油醚：分析纯，重蒸馏，收集 65～75℃馏分。

3.2.3 浓硫酸：密度 1.84 g/mL。

3.2.4 硫酸：于 200 mL 烧杯中加 5.0 mL 蒸馏水，缓缓加入 95.0 mL 浓硫酸，冷却后贮于玻璃瓶内。

3.2.5 无水硫酸钠：分析纯，650℃灼烧 4 h。冷却后贮于密闭容器中。

3.2.6 硫酸钠水溶液(20 g/L)：将灼烧过的无水硫酸钠 20 g 溶于热水中，最后以水定容至 1 L。

3.2.7 除草醚和环氧七氯(内标物)：纯度≥99.5%。

3.2.8 除草醚和环氧七氯标准溶液：准确称取适量除草醚和环氧七氯标准品，用石油醚配制成 0.5 mg/mL的标准贮备溶液，根据需要分别配制成适用浓度标准工作溶液和混合农药标准工作溶液。

3.3 仪器和设备

3.3.1 气相色谱仪配备有电子俘获检测器。

3.3.2 振荡器或匀浆器。

3.3.3 旋转蒸发器。

3.3.4 布氏漏斗和减压过滤装置。

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

3.4 测定步骤

3.4.1 提取

称取试样约 10 g(精确至 0.1 g)于具塞锥形瓶内，加 5 mL 丙酮，充分振摇后加 20 mL 石油醚，匀浆 2～3 min 或置于振荡器上，振荡提取 30 min。在有快速滤纸的布氏漏斗上过滤。残渣分别用 2 份 20 mL 石油醚，按上述操作重复提取两次，过滤。合并滤液和提取液于分液漏斗内，加 50 mL 热硫酸钠水溶液洗涤，分层后，弃去水溶液。

3.4.2 净化

有机相加入 6 mL 硫酸(3.2.4)，振荡 20 s。分层后，弃去硫酸层。石油醚层分别再用 2 份 6 mL 硫酸(3.2.4)，剧烈振摇 0.5 min，净化两次。弃去硫酸层。然后分别用 25 mL 硫酸钠水溶液，洗涤有机相两次。分层后弃去水溶液。石油醚层通过无水硫酸钠柱，滤入心形瓶内。用 10 mL 石油醚洗涤分液漏斗和无水硫酸钠柱。合并滤液和洗液，接心形瓶于旋转蒸发器上，在 50℃水浴内减压浓缩至近干。加 2.00 mL 环氧七氯标准工作溶液，溶解残渣后移入具塞刻度试管内。加约 0.2 g 无水硫酸钠，供气相色谱测定。

3.4.3 测定

3.4.3.1 色谱条件

a. 色谱柱：玻璃柱，2 m×3 mm(内径)，填充物为 0.27%(*m*/*m*)OV-17 和 2.8%(*m*/*m*)QF-1 混合液，涂于 Chromosorb W HP(80～100 目)；

b. 色谱柱温度：200℃；

c. 进样口温度：230℃；

d. 检测器温度：250℃；

e. 氮气：纯度≥99.99%，50 mL/min。

3.4.3.2 色谱测定

根据样液中除草醚含量，选定峰高相近的混合标准工作溶液。混合标准工作溶液和样液中除草醚响应值应在仪器检测线性范围内。混合标准工作溶液和样液等体积进样。在上述色谱条件下，除草醚的保留时间约 8.3 min，环氧七氯的保留时间约 3 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：

$$X = \frac{A \cdot A_i' \cdot c' \cdot c_i}{A' \cdot A_i \cdot c \cdot c_i'} \qquad \cdots\cdots(2)$$

式中：X——除草醚残留量，mg/kg；

A——样液中除草醚的峰面积，mm^2；

A'——混合农药标准工作溶液中除草醚的峰面积，mm^2；

A_i——样液中内标物的峰面积，mm^2；

A_i'——混合农药标准工作溶液中内标物的峰面积，mm^2；

c——样液浓度，g/μL；

c'——混合农药标准工作溶液中除草醚的浓度，μg/μL；

c_i——样液中内标物的浓度，μg/μL；

c_i'——混合农药标准工作溶液中内标物的浓度，μg/μL。

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：10 μg/kg。

4.2 回收率

回收率的实验数据：除草醚 0.01～0.15 mg/kg 范围，回收率为 82.3%～91.7%。

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湖北进出口商品检验局负责起草。

本标准主要起草人卢康全。

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

SN 0204—93

Method for determination of nitrofen residues in grains for export

1 Scope and field of application

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

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

2 Sampling and sample preparation

2.1 Inspection lot

Each inspection lot should not exceed 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

The square root of the total number of bags in a lot shall be taken as the number of bags to be sampled:

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

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: See fig. 1.

2.3.3 Plate for quartering: See fig. 2.

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

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

Approved by the State Administration of Import and Export Commodity Inspection of the People's Republic of China on Jun. 4, 1993

Implemented from Aug. 1, 1993

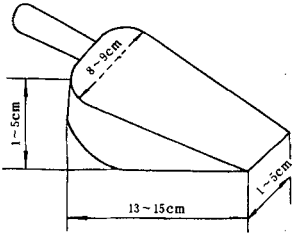


Fig. 1 Sampling shovel

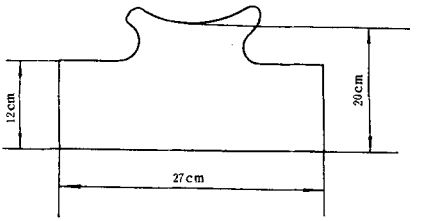


Fig. 2 Plate for quartering

2.4 Sampling procedure

2.4.1 Sampling from the bag

Draw the samples from a number of bags specified in 2.2 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. Mix all the samples from different bags to form a gross sample.

2.4.2 Sampling by emptying out

Unseam and open the bag, and erect it 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. Scoop up the sample from different parts of the out-poured content with a shovel, totalling ca 100 g, and place in sample container promptly. Mix all the samples from different bags to form a gross sample.

2.4.3 Reduction of gross sample

Pour the sample (either from 2.4.1 or 2.4.2) on a clean sheet for quartering, reduce to not less than 4 kg with a plate by quartering. Place in a sample container, seal, label and send 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, divide into 2 equal portions, place in clean containers, seal and label.

2.6 Storage of test sample

The test sample shall be stored at 5℃ and kept away from light.

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

3 Method of determination

3.1 Principle

The nitrofen residues in sample is extracted with acetone and petroleum ether. The extract is washed with sodium sulfate solution, and clean-up with 95% sulfuric acid. Evaporate the cleaned up solution to near dryness. Add 2.00 mL internal standard working solution to dissolve the residues. The solution is measured by gas chromatography with a electron capture detector.

3.2 Reagents and materials

3.2.1 Acetone: A. R., redistilled.

3.2.2 Petroleum ether: A. R., redistilled and collect the distillate of 65～75℃.

3.2.3 Concentrated sulfuric acid: Density 1.84 g/mL.

3.2.4 Sulfuric acid: Add 95.0 mL concentrated sulfuric acid into 5.0 mL water in a 200 mL beaker.

3.2.5 Anhydrous sodium sulfate: A. R., ignit at 650℃ for 4 h, and stored an air-tight container after cooling.

3.2.6 Sodium sulfate solution (20 g/L): Dissolve 20 g anhydrous sodium sulfate in hot water, then dilute to 1 L.

3.2.7 Nitrofen and heptachlorepoxide (internal standard): Purity≥99.5%.

3.2.8 Nitrofen and heptachlorepoxide standard solution:

Accurately weigh a suitable amount of heptachlorepoxide and nitrofen respectively, and dissolve in petroleum ether to prepare a stock solution with a concentration of 0.50 mg/mL. According to the concentration requirement, prepare a standard working solution, heptachlorepoxide standard working solution and mixed pesticides standard working solution of appropriate concentration, respectively.

3.3 Apparatus and equipment

3.3.1 Gas chromatograph with Ni^{63} electron capture detector.

3.3.2 Homogenizer or shaker.

3.3.3 Rotary evaporator.

3.3.4 Buchner funnel.

3.3.5 Column of anhydrous sodium: Sulfate: 80×20 mm (id) cylindrical funnel, filled with 5 cm height of anhydrous sodium sulfate.

3.4 Procedure

3.4.1 Extraction

Weigh ca 10 g of the test sample (accurate to 0.1 g)into stoppered conical flask. Add 5 mL acetone shake for 0.5 min, then add 20 mL petroleum ether and homogenize for 3 min (or shake for 30 min). Filter the extract through a rapid filter paper on a Buchner funnel under reduce pressure. The residues re-extract twice with 20 mL petroleum ether each time. Transfer the filtrate into a 250 mL separatory funnel. Add 50 mL warm sodium sulfate solution, and shake 10 s. Let stand to separtate, discard the aqueous phase.

3.4.2 Clean up

Add 6 mL sulfuric acid (3.2.4) into the petroleum ether layer, shake 20s and let stand to separate. Discard the acid layer. Repeat the above procedure 1 or 2 time by shaking for 0.5 min each time. Then wash the petroleum ether layer with 25 mL sodium sulfate solution. Shake for 10 s, and stand to

separate. Discard the aqueous layer. Repeat the above washing procedure once again. Pass the petroleum ether layer through an anhydrous sodium sulfate column into a heart-shaped bottle. Wash the column with petroleum ether for several times. Combine the solution and rinsings and collect in the heart-shaped bottle. The combined solution is concentrated in a rotary evaportor under reduced pressure in a 50 C water bath to near dryness. Add 2.00 mL internal standard working solution to dissolve the rasidues, and transferred into a stoppered test tube. Add 0.2 g anhydrous sodium sulfate. The solution is used for chromatographic determination.

3.4.3 Determination

3.4.3.1 Gas chromatographic operation conditions

a. Column: 2 m×3 mm(id)glass column, packed with 0.27%(*m*/*m*)OV-17+2.8%(*m*/*m*)QF-1 on chromosorb W HP (80—100 mesh);

b. Column temperature: 200℃;

c. Injection port temperature: 230℃;

d. Detector temperature: 250℃;

e. Nitrogen: Purity≥99.99%, 50 mL/min.

3.4.3.2 Gas chromatographic determination

According to the approximat concentration of nitrofen in the sample solution, selecte a mixed standard working solution with similar peak hight to that of sample solution. The response values of nitrofen in mixed standard working solution and sample solution should be in linear range of the instrument detection. The mixed standard working solution should be injected with the sample solution of equal volume.

Under the above chromatographic condition, the retention time of nitrofen is about 8.3 min and heptachlorepoxide is about 3 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

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

$$X = \frac{A \cdot A_i' \cdot c' \cdot c_i}{A' \cdot A_i \cdot c \cdot c_i'} \qquad \cdots\cdots(2)$$

where

X—the residue content of nitrofen, mg/kg;

A—the peak area of nitrofen in sample solution, mm^2;

A'—the peak area of nitrofen in the mixed pesticides standard working solution, mm^2;

A_i'—the peak area of heptachlorepoxide in the mixed pesticides standard working solution, mm^2;

A_i—the peak area of heptachlorepoxide in the sample solution, mm^2;

c'—the concentration of nitrofen in the mixed pesticides standard working solution, μg/μL;

c—the concentration of sample solution, g/μL;

c_i—the concentration of heptachlorepoxide in the sample solution, μg/μL;

c_i'—the concentration of heptachlorepoxide in the mixed pesticides standard working solution, μg/μL.

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

4 Limit of determination and recovery

4.1 Limit of determination: 10 μg/kg.

4.2 Recovery

According to the experimental data, when the concentration of nitrofen residues is in the range of 0.01—0.15 mg/kg, the recovery is 82.3%—91.7%.

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

This standard was mainly drafted by Lu Kangguan.

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