

# SN

## 中华人民共和国进出口商品检验行业标准

SN 0600—1996

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### 出口粮谷中氟乐灵残留量检验方法

Method for the determination of trifluralin  
residues in cereals for export

1996-11-15 发布

1997-05-01 实施

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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》的要求而进行编写的。其中测定方法采用了美国食品药品监督管理局的农药残留量分析手册中的方法。技术内容与原方法相同，经验证后，按规定格式要求作了编辑性修改。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粮谷中氟乐灵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。

本标准起草单位：中华人民共和国内蒙古进出口商品检验局。

本标准主要起草人：张曦静、包杰、潘国卿。

本标准系首次发布的行业标准。

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residues in cereals for export

### 1 范围

本标准规定了出口粮谷中氟乐灵残留量检验的抽样、制样和气相色谱测定方法。  
本标准适用于出口玉米中氟乐灵残留量的检验。

### 2 抽样和制样

#### 2.1 检验批

散积以不超过 200 t 为一检验批；袋装以约 2 200 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

##### 2.2.1 袋装货品

按式(1)计算抽样袋数：

$$a = \sqrt{N} \dots\dots\dots (1)$$

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。

##### 2.2.2 散积货品

货堆高度不超过 2 m。按货堆面积分区设点，以 50 m<sup>2</sup> 为一个取样区，每区设中心及四角（距边缘 1 m 处）5 个点，每增加一个取样区，增加 3 个点。

#### 2.3 抽样工具

2.3.1 金属双套管取样器：全长分 1 m、2 m（均包括手柄）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。内管的内径为 2.5~3.0 cm；取样器的探头长约 7 cm。

2.3.2 取样铲。

2.3.3 分样板。

2.3.4 盛样器：筒或袋，可密封。

2.3.5 分样布或适用铺垫物。

#### 2.4 抽样方法

##### 2.4.1 袋装抽样

2.4.1.1 倒包抽样：从堆垛的各部位随机抽取 2.2.1 规定的应抽样袋数的 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器内。每袋抽取样品的量应基本一致。

2.4.1.2 袋内抽样:按 2.2.1 规定的应抽样袋数(扣除倒包抽样袋数),在垛堆四周上、中、下各层以曲线形走向随机抽取。用 1 m 长的金属双套管取样器(2.3.1),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。每袋所抽取样品的量应与 2.4.1.1 基本一致。

每批所抽取的样品总量应不少 4 kg。

#### 2.4.2 散积抽样

按 2.2.2 规定的取样点,逐点抽取样品。将取样器(2.3.1)槽口关闭,以斜倾 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。抽出取样器,立即将样品倒入盛样器内。从各点所抽取的样品量应基本一致。

每批所抽取的样品总量应不少于 4 kg。

#### 2.4.3 大样缩分

袋装样品:合并从袋内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,盛于盛样器内,加封后标明标记,并及时送交实验室。

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

将样品按四分法缩分至 1 kg,全部磨碎并通过 20 目筛。混匀,均分成两份作为试样,分装入洁净的盛样器内,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

试样中残留的氟乐灵用甲醇提取,提取液经用二氯甲烷进行液液分配。二氯甲烷层经脱水、浓缩、蒸发至干。以正己烷溶解提取物,溶液过弗罗里硅土柱净化后,用电子俘获检测器-气相色谱法测定,外标法定量。

#### 3.2 试剂和材料

除另有规定外,试剂均为分析纯,水为蒸馏水。

##### 3.2.1 甲醇:重蒸馏。

##### 3.2.2 二氯甲烷:重蒸馏。

##### 3.2.3 正己烷:重蒸馏。

##### 3.2.4 苯:重蒸馏。

##### 3.2.5 氯化钠溶液:5%水溶液。

##### 3.2.6 无水硫酸钠:650℃灼烧 4 h,冷却后贮于密封容器中备用。

##### 3.2.7 弗罗里硅土:层析用,60~80 目,650℃灼烧 4 h,贮于密闭容器中。使用前一天再在 130℃下烘 5 h,冷却后,置于广口瓶中,加入 1.5%的水脱活,平衡 24 h,密封存放备用。

##### 3.2.8 氟乐灵标准品:纯度≥99%。

##### 3.2.9 氟乐灵标准贮备液:准确称取氟乐灵标准品,用苯配成浓度为 0.10 mg/mL 的标准储备液。根据需要再用苯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:配有电子俘获检测器。

##### 3.3.2 微量注射器:1 μL,10 μL。

3.3.3 旋转蒸发器。

3.3.4 振荡机。

3.3.5 全玻璃蒸馏装置。

3.3.6 无水硫酸钠柱:50 mL 筒形分液漏斗,内装 5 cm 高的无水硫酸钠。

3.3.7 弗罗里硅土柱:具有活塞的 20 cm×2.2 cm(内径)层析管,柱底填约 0.5 cm 脱脂棉,干法装入高 7.5 cm 弗罗里硅土(3.2.7),上填高 2.5 cm 无水硫酸钠(3.2.6)。使用前用 100 mL 正己烷预淋洗,并在柱中保持正己烷层。

3.3.8 刻度试管:具磨口塞,10 mL。

### 3.4 测定步骤

#### 3.4.1 提取

称取试样 12.5 g(精确至 0.01 g),置于 250 mL 具塞锥形烧瓶中,加入 100 mL 甲醇,振荡提取 20 min,过滤于 500 mL 分液漏斗中。用 15 mL 甲醇分三次洗涤残渣,合并提取液和洗液。加入 250 mL 5%氯化钠溶液,混匀。分别用 30,30,20 mL 二氯甲烷提取三次,合并提取液,使通过无水硫酸钠柱,收集于 250 mL 心形瓶中。再用 15 mL 二氯甲烷分三次洗涤无水硫酸钠柱,洗液并入提取液中。用旋转蒸发器在 50℃水浴中蒸去二氯甲烷。

注:二氯甲烷一蒸发完,立即取下心形瓶,以防氟乐灵损失。

#### 3.4.2 净化

加入 5 mL 正己烷,轻轻转动心形瓶,以溶解提取物。使之通过弗罗里硅土柱(3.3.7),再用 4×5 mL 正己烷冲洗心形瓶,转入柱中。用正己烷进行洗脱,前 70 mL 弃去,后 100 mL 保留。收集保留部分洗脱液于 250 mL 心形瓶中,蒸发至干。准确加入 2.0 mL 苯以溶解残渣,溶液转移至 10 mL 具塞玻璃试管中,待色谱测定。

注:避免苯溶液直接暴露在阳光下。

#### 3.4.3 测定

##### 3.4.3.1 色谱条件

a) 色谱柱:玻璃柱 1.6 m×3 mm(id),填充物为 5%(m/m)SE-30 涂于 Chromosorb W(80~100 目);

b) 色谱柱温度:180℃;

c) 进样口温度:230℃;

d) 检测器温度:230℃;

e) 载气:氮气,纯度≥99.99%,50 mL/min;

f) 进样量:0.5 μL。

##### 3.4.3.2 气相色谱测定

根据试样中被测农药含量情况,选定峰高相近的标准工作溶液。标准工作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,氟乐灵保留时间约为 2.2 min。标准品色谱图见附录 A 中图 A1。

#### 3.4.4 空白试验

除不称取试样外,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(2)计算试样中氟乐灵的残留含量:

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

式中:  $X$ ——试样中氟乐灵含量, mg/kg;  
 $h$ ——样液中氟乐灵的峰高, mm;  
 $h_s$ ——标准工作液中氟乐灵的峰高, mm;  
 $c$ ——标准工作液中氟乐灵的浓度,  $\mu\text{g/mL}$ ;  
 $V$ ——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

本方法的测定低限为 0.005 mg/kg。

##### 4.2 回收率

玉米中氟乐灵的添加浓度和回收率的实验数据:

添加浓度在 0.005 mg/kg 时, 回收率为 90.0%;

添加浓度在 0.010 mg/kg 时, 回收率为 92.0%;

添加浓度在 0.050 mg/kg 时, 回收率为 94.0%。

附录 A  
(提示的附录)  
标准品色谱图

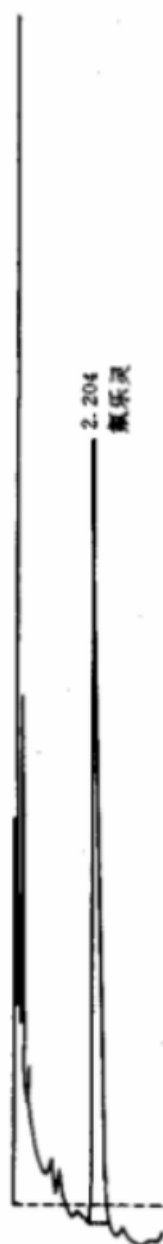


图 A1 氟乐灵标准品色谱图

## 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 testing method for trifluralin residues in "Pesticide Analytical Manual" FDA of U. S. A. is adopted as the method of determination, which is thus technically identical with that of the original; only minor editorial modification required for the stipulated format was made after going through 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 bases of the current international maximum limit for trifluralin 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 Inner Mongolia Import and Export Commodity Inspection Bureau of the People's Republic of China.

The main drafters of this standard are Zhang Xijing, Bao Jie, Pan Guoqing.

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 0600—1996

**Method for the determination of trifluralin  
residues in cereals for export**

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**1 Scope**

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

This standard is applicable to the determination of trifluralin residue content in maize for export.

**2 Sampling and sample preparation**

**2.1 Inspection lot**

For the cargo in bulk, each inspection lot should not exceed 200 t. For the cargo in bags, each inspection lot is about 2 200 bags.

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**

**2.2.1 Cargo in bags**

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

$$a = \sqrt{N} \dots\dots\dots (1)$$

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  $a$ .

**2.2.2 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<sup>2</sup> is considered as an area, in which 5 spots shall be fixed, one in the centre and four at four corners (1 m from the margins) of the area. For an additional area, 3 more sampling spots should be fixed.

**2.3 Sampling tools**

**2.3.1 Metallic double casing sampler:** Length 1 m and 2 m (both including handle), with some slots on different sections at the same heights for both inner and outer casings; length of slots: 15—20 cm; width of the slots 2.0—2.5 cm; inside diameter of the inner casing: 2.5—3.0 cm; the probe length of the sampler: ca 7 cm.

**2.3.2 Sampling shovel.**

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Approved by the State Administration of  
Import and Export Commodity Inspection of  
the People's Republic of China on Nov. 15, 1996

Implemented from May. 1, 1997

2.3.3 Plate for quartering.

2.3.4 Sample container; Can or bag, which can be sealed.

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

2.4 Sampling procedure

2.4.1 For cargo in bags

2.4.1.1 Sampling by emptying out; Draw 10 percent of the number of bags specified in 2.2.1 (not less than 3 bags) at any part of the pile at random. Unseam and open the bag, and lay 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  $45^\circ$ , tug backward for ca 1 m until all content of the bag is emptied out. Check whether the quality of 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 at random, and promptly place in a sample container. The quantity of sample drawn from each bag should be basically the same.

2.4.1.2 Sampling from inside the bags; Draw the samples from the number of bags specified in 2.2.1 (by deducting the number of bags drawn in 2.4.1.1) as follows; Along the sine wave of the pile, draw samples from the bags of upper, middle and lower parts around the pile at random. Insert the metallic double casing sampler (2.3.1, length 1 m) (the slots should be 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 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 of each lot should be not less than 4 kg.

2.4.2 Sampling from the cargo in bulk; Insert the double casing sampler (2.3.1) successively into the pile at the spots specified in 2.2.2 to an appropriate depth at  $45^\circ$  (the slots should be closed while inserting in). 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 quantity of the sample drawn from all the spots shall be basically the same.

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

2.4.3 Reduction of gross sample

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

For cargo in bulk; Pour all the drawn samples onto a clean sheet and proceed as for cargo in bags described above.

2.5 Preparation of test sample

Reduce the sample to ca 1 kg by quartering, grind thoroughly and let pass through a 20-mesh sieve, Mix thoroughly and divide into two equal portions, place in clean sample containers as the test samples, seal and label.

2.6 Storage of test sample

The test samples should be stored below  $-5^\circ\text{C}$  and kept away from light.

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

### 3 Method of determination

#### 3.1 Principle

The trifluralin residues in sample is extracted with methanol, the extract is treated by methanol-dichloromethane partitioning, then the dichloromethane solution is dehydrated, concentrated and evaporated to dryness. The residue is dissolved with n-hexane and cleaned up by passing through a florisil column. The trifluralin is determined by GC-ECD, using external standard method.

### 3.2 Reagents and materials

Unless otherwise specified, all reagents should be of analytical grade, "water" is distilled water.

3.2.1 Methanol, Redistilled.

3.2.2 Dichloromethane, Redistilled.

3.2.3 n-Hexane, Redistilled.

3.2.4 Benzene, Redistilled.

3.2.5 Sodium chloride solution, 5% aqueous solution.

3.2.6 Anhydrous sodium sulfate: Ignite at 650°C for 4 h and keep in a tightly closed container after cooling.

3.2.7 Florisil: For chromatographic use, 60—80 mesh. Ignite at 650°C for 4 h, keep in a closed container. Before use, it is activated again at 130°C for 5 h, then deactivated after cooling by adding 1.5% of distilled water. Keep in a tightly closed container and let stand overnight.

3.2.8 Trifluralin standard, Purity  $\geq 99\%$ .

3.2.9 Trifluralin standard solution: Accurately weigh an adequate amount of trifluralin standard, dissolve in benzene and prepare a solution of 0.10 mg/mL in concentration as the standard stock solution. According to the requirement, prepare a standard working solution of appropriate concentration by diluting the stock solution with benzene.

### 3.3 Apparatus and equipment

3.3.1 Gas chromatograph, equipped with electron capture detector.

3.3.2 Micro-syringe: 1  $\mu$ L, 10  $\mu$ L.

3.3.3 Rotary vacuum evaporator.

3.3.4 Shaker.

3.3.5 All-glass distilling system.

3.3.6 Anhydrous sodium sulfate column: A cylinder-shaped funnel of 50 mL in capacity, filled with 5 cm height of anhydrous sodium sulfate.

3.3.7 Florisil column: 20  $\times$  2.2 cm (id) glass column, with round stopper, packed with 0.5 cm height of absorbent cotton at the bottom of the column and packed with 7.5 cm height of florisil (3.2.7) then covered with 2.5 cm height of anhydrous sodium sulfate (3.2.6). Wash the column with 100 mL of n-hexane before use and retain a layer of hexane on the column.

3.3.8 Graduated test-tube: 10 mL, with ground stopper.

### 3.4 Procedure

#### 3.4.1 Extraction

Weigh ca 12.5 g of the test sample (accurate to 0.01 g) into a 250 mL conical flask with ground stopper, add 100 mL of methanol, stopper and shake for 20 min by a shaker. Filter the extract into a 500 mL separatory funnel. Rinse the residue on the filter for three times with methanol (15 mL in total), combine the filtrates into the same separatory funnel, then add 250 mL of 5% sodium chloride solution, mixed. The solution is extracted successively with 30, 30 and 20 mL of dichloromethane. Let the combined extract pass through the column of anhydrous sodium sulfate, then rinse the column for three times with 15 mL of dichloromethane in total. Collect the solution in a heart-shaped flask and evaporate off the dichloromethane

with rotary evaporator in a 50°C water-bath.

Note: The heart-shaped flask must be removed as soon as the dichloromethane is evaporated to prevent loss of trifluralin.

### 3.4.2 Cleanup:

Add 5 mL of n-hexane to a heart-shaped flask (3.4.1), swirl to dissolve the content and transfer the solution to the florisil column. Wash the heart-shaped flask with 4×5 mL of n-hexane and pour the washings into the column. Elute the column with n-hexane, collect the eluate in a 250 mL heart-shape flask (Normally the first 70 mL is discarded and the next 100 mL is retained). Evaporate the solution just to dryness in a water-bath. Dissolve the residue with 2.0 mL benzene and transfer the solution into the 10 mL graduated test tube. The solution shall be used for chromatographic determination.

Note: Avoid exposure of benzene solution to direct sunlight.

### 3.4.3 Determination

#### 3.4.3.1 GC operating condition

a) GC column: Glass, 1.6 m×3 mm(id), packed with 5% (m/m) SE-30 on Chromosorb W(80—100 mesh);

b) Column temperature: 180°C;

c) Injection port temperature: 230°C;

d) Detector temperature: 230°C;

e) Carrier gas: Nitrogen, purity ≥ 99.99%, 50 mL/min;

f) Injection volume: 0.5 μL.

#### 3.4.3.2 GC determination

According to the approximate concentration of trifluralin in the sample solution, select the standard working solution with similar peak height to that of the sample solution. The responses of trifluralin 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 chromatographic operating condition, the retention time of trifluralin is about 2.2 min. For chromatogram of the standard, see fig. A1 in annex A.

#### 3.4.4 Blank test

The operation of the blank test is the same as that described in the method of determination but without addition of the sample.

### 3.5 Calculation and expression of the result

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

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

where

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

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

h<sub>s</sub>—the peak height of trifluralin in standard working solution, mm;

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

V—the final volume of sample solution, mL;

m—the corresponding mass of the 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 0.005 mg/kg.

##### 4.2 Recovery

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

0.005 mg/kg, the recovery 90.0%;

0.010 mg/kg, the recovery 92.0%;

0.050 mg/kg, the recovery 94.0%.

**Annex A**  
(informative)  
**Chromatogram of the standard**



Fig. A1 Chromatogram of trifluralin standard

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