SN

中华人民共和国进出口商品检验行业标准

SN 0655—1997

出口蔬菜及油籽中敌麦丙残留量检验方法

Method for the determination of dimethiphin residues in vegetables and oil seeds for export

1997-08-15发布　　1998-01-01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》的要求而进行编写的。其中测定方法是参考了国内外有关文献，经研究、改进和验证后制定的。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蔬菜及油籽中敌麦丙残留量的最高限量和本标准测定方法的灵敏度而制定的。

本标准附录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湖南进出口商品检验局负责起草。

本标准主要起草人：袁智能、黄志强、彭三和、聂洪勇。

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

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1 范围

本标准规定了出口蔬菜及油籽中敌麦丙残留量检验的抽样、制样和气相色谱测定方法。

本标准适用于出口马铃薯及油菜籽中敌麦丙残留量的检验。

2 抽样和制样

2.1 对马铃薯

2.1.1 检验批

以不超过 1 500 件商品为一检验批。

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。

2.1.2 抽样数量

批量，件	最低抽样数，件
1～25	1
26～100	5
101～250	10
251～1 500	15

2.1.3 抽样方法

按 2.1.2 规定的抽样件数，随机抽取，逐件开启。每件至少取500 g 作为原始样品，原始样品的总量不少于 4 kg。装入清洁的容器内，加封后，标明标记并及时送实验室。

2.1.4 试样制备

分取出部分有代表性马铃薯样，每个马铃薯取四分之一，切碎，用四分法缩分出 1 kg 左右。置高速组织捣碎机中，捣碎成果酱状，均分成两份，装入清洁的容器内，作为试样，密封并标明标记。

2.1.5 试样保存

将试样于－18℃冷冻保存。

2.2 对油菜籽

2.2.1 检验批

以不超过 200 t 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。

2.2.2 抽样数量

按式(1)计算抽样袋数：

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

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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。

2.2.3 抽样工具

2.2.3.1 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一半。

2.2.3.2 取样铲。

2.2.3.3 分样板。

2.2.3.4 盛样器：筒或袋，可密封。

2.2.3.5 分样布或适用的铺垫物。

2.2.4 抽样方法

2.2.4.1 倒包抽样：从堆垛的各部位随机抽取 2.2.2 规定的应抽样件数的 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，立即将样品倒入盛样器内。每袋抽取样品的量应基本一致。

2.2.4.2 袋内抽样：按 2.2.2 规定的应抽样件数(扣除倒包抽样件数)，在堆垛四周上、中、下各层以曲线形走向随机按下述方法进行取样：用金属单管取样器(2.2.3.1)槽口朝下，从每袋一角依斜对角方向插入袋内，然后将管槽旋转朝上，抽出取样器，立即将样品倒入盛样器内。

每袋所抽取的样品的量应与 2.2.4.1 基本一致。每批所抽取的样品总量应不少于 4 kg。

2.2.4.3 大样缩分：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。

2.2.5 试样制备

将样品按四分法缩分至 1 kg，用高速组织捣碎机充分捣碎混匀，均分成两份试样，装入洁净的容器内，作为试样，密封并标明标记。

2.2.6 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

以甲醇-水混合溶剂提取试样中敌麦丙，提取液经用正己烷和三氯甲烷进行液-液分配净化后，制成丙酮溶液，用配有火焰光度(硫滤光片)检测器的气相色谱仪测定，标准曲线法定量。

3.2 试剂和材料

除另有规定外，所用试剂均为分析纯，水为蒸馏水。

3.2.1 甲醇。

3.2.2 正己烷。

3.2.3 三氯甲烷。

3.2.4 丙酮。

3.2.5 甲醇-水(9＋1)。

3.2.6 氯化钠溶液：10%水溶液。

3.2.7 敌麦丙标准品：纯度≥99%。

3.2.8 敌麦丙标准溶液：准确称取适量的敌麦丙标准品(精确至 0.1 mg)，用丙酮溶解配成浓度为 100 μg/mL的标准贮备液。再根据需要用丙酮稀释成适当浓度的标准工作溶液。

3.3 仪器和设备

3.3.1 气相色谱仪并配有火焰光度(硫滤光片,394 nm)检测器。

3.3.2 快速混匀器或匀浆机。

3.3.3 多功能微量化样品处理仪或相当者。

3.3.4 离心机:4 000 r/min。

3.3.5 微量可调移液管:40～200 μL,200～1 000 μL。

3.3.6 离心管:15 mL。

3.3.7 微量进样器:10 μL。

3.4 测定步骤

3.4.1 提取

称取约 2 g 试样(精确至 0.01 g)于 15 mL 离心管中,加入 6 mL 甲醇-水,于快速混匀器匀浆2 min,然后以 3 000 r/min 离心2 min。将上清液倾入第二支 15 mL 离心管中。再用 5 mL 甲醇-水提取残渣,离心后,提取液并入第二支离心管中。将提取液于 60℃浴温浓缩至约 2 mL。

3.4.2 净化

于第二支离心管中加入 1 mL 氯化钠溶液和 3 mL 正己烷,在快速混匀器上剧烈混合 2 min。离心 2 min后,用尖嘴吸管移去正己烷层,并弃去。再用 3 mL 正己烷重复处理一次。加入 4 mL 水,用 2×4 mL三氯甲烷剧烈混合以从水相中提取敌麦丙。离心 3 min 后,用尖嘴吸管将下层有机相转入第三支离心管中。将提取液于 60℃浴温吹干。以 0.50 mL 丙酮溶解残渣,经离心后,澄清液供气相色谱测定。

3.4.3 测定

3.4.3.1 气相色谱条件

a) 色谱柱:石英毛细管柱,农残Ⅱ号柱,30 m×0.53 mm(内径)×1.0 μm(膜厚)或相当者;

b) 载气:氮气,纯度≥99.99%,5.0 mL/min;

c) 尾吹:氮气,纯度≥99.99%,30 mL/min;

d) 氢气:50 mL/min;

e) 空气:90 mL/min;

f) 色谱柱温度:180℃;

g) 进样口温度:250℃;

h) 检测器温度:250℃;

i) 进样量:2.0 μL;

j) 进样方式:无分流进样。

3.4.3.2 标准曲线的绘制

根据试样中被测农药含量情况,分别等体积地注入 5 个不同适用浓度系列的敌麦丙标准工作液于气相色谱仪中,按上述色谱条件进行色谱分析,测定峰面积。标准工作液中农药的响应值均应在仪器检测的线性范围内。以峰面积的对数对敌麦丙的浓度绘制标准曲线。在上述色谱条件下,敌麦丙保留时间约为 3.4 min。标准品色谱图见附录 A 中图 A 1。

3.4.3.3 样液测定

准确注入上述等体积的样液于气相色谱仪中,求得峰面积,再从标准曲线上求得样液中敌麦丙的浓度。其响应值应在标准曲线的线性范围之内。

3.4.4 空白试验

除不加试样外,均按上述测定步骤进行。

3.5 结果的计算和表述

用色谱数据处理机,或按式(2)计算试样中敌麦丙残留含量:

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

式中：X——试样中敌麦丙残留含量，mg/kg；

c——从标准曲线上求得样液中敌麦丙的浓度，μg/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 0.05 mg/kg。

4.2 回收率

敌麦丙的添加浓度及其回收率的实验数据：

在马铃薯中：0.05 mg/kg 时，回收率为 94.9%；

0.10 mg/kg 时，回收率为 95.4%；

1.00 mg/kg 时，回收率为 91.0%。

在油菜籽中：0.05 mg/kg 时，回收率为 95.7%；

0.10 mg/kg 时，回收率为 94.0%；

1.00 mg/kg 时，回收率为 92.2%。

附 录 A
（提示的附录）
标准品色谱图

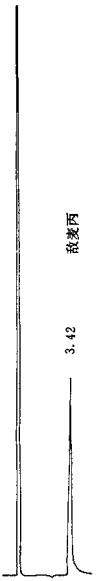


图 A1　敌麦丙标准品气相色谱图

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 limits for dimethiphin residues in vegetables and oil seeds 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 the Hunan Import and Export Commodity Inspection Bureau of the People's Republic of China.

This main drafters of this standard are Yuan Zhineng, Huang Zhiqiang, Peng Sanhuo and Nie Hongyong.

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

Method for the determination of dimethiphin residues in vegetables and oil seeds for export

SN 0655—1997

1 Scope

This standard specifies the methods of sampling, sample preparation and determination of dimethiphin residues by gas chromatography in vegetables and oil seeds for export.

This standard is applicable to the determination of dimethiphin residues in potato and rape-seed for export.

2 Sampling and sample preparation

2.1 For potato

2.1.1 Inspection lot

The quantity of an inspection lot should not be more than 1 500 packages.

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

2.1.2 Quanity of sample taken

Number of packages in each inspection lot	Minimum number of packages to be taken
1—25	1
26—100	5
101—250	10
251—1 500	15

2.1.3 Sampling procedure

A number of packages specified in 2.1.2 are taken at random and opened one by one. The sample weight taken as the primary sample from each package should be at least 500 g. The total weight of all primary samples should be at least 4 kg, which shall be sealed, labeled and sent to laboratory in time.

2.1.4 Preparation of test sample

Take a portion of the potato as the representative sample. Chop out one quarter of each potato, cut into shreds, and then reduce to about 1 kg by quartering, which shall be ground to jam by a high-speed blender. The ground sample shall be then divided into two equal portions. Each portion is placed in a clean sample container as a test sample, which shall be sealed and labeled.

2.1.5 Storage of test sample

The test samples should be stored below −18 C.

Approved by the State Administration of Import and Export Commodity Inspection of the People's Republic of China on Aug. 15, 1997

Implemented from Jan. 1, 1998

2.2 For rape-seed

2.2.1 Inspection lot

Each inspection lot should not exceed 200 t.

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

2.2.2 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.

2.2.3 Sampling tools

2.2.3.1 Metallic sampler: Length (including handle): 55 cm; diameter: 1.5—2.0 cm; groove length: longer than half the diagonal length of the bag.

2.2.3.2 Sampling shovel.

2.2.3.3 Plate for quartering.

2.2.3.4 Sample container: Can or bag, which can be sealed.

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

2.2.4 Sampling procedure

2.2.4.1 Sampling by emptying out: Draw 10 percent of the number of bags specified in 2.2.2 (not less than 3 bags) 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°C, 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 at random, and promptly place in a sample container. The quantity of the sample drawn from each bag should be basically the same.

2.2.4.2 Sampling from inside the bags: Draw the samples from the number of bags specified in 2.2.2 (by deducting the number of bags drawn in 2.2.4.1) 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. Using the metallic sampler (2.2.3.1), insert it with its groove facing downward, diagonally into each bag, then turn the sampler 180°, draw out the sampler, and promptly pour the sample into a sample container.

The amount of sample drawn from each bag shall be basically the same as in 2.2.4.1. The total weight of the sample of each lot should be not less than 4 kg.

2.2.4.3 Reduction of gross sample

Pour all the samples (from both 2.2.4.1 and 2.2.4.2) on a clean sheet, reduce to not less than 2 kg with a plate by quartering. Place the sample in a sample container, seal, label and send to the laboratory in time.

2.2.5 Preparation of test sample

Reduce the sample to ca 1 kg by quartering, blend and homogenize thoroughly with a high-speed blender, and divide into two equal portions. Each portion is placed in a clean sample container as the test sample, which shall be sealed and labeled.

2.2.6 Storage of test sample

The test sample should be stored below −5℃ and kept away from light.

Note: In the course of sampling and sample preparation, precautions 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 dimethiphin residues in the test sample are extracted with methanol-water, the extract is cleaned up by liquid-liquid partitioning with *n*-hexane and chloroform. Finally the analyte is dissolved in acetone and determined by gas chromatograph with flame photographic detector(sulphur filter), using standard curve method.

3.2 Reagents and materials

Unless otherwise specified, all the reagents used should be analytically pure, "water"is distilled water.

3.2.1 Methanol.

3.2.2 *n*-Hexane.

3.2.3 Chloroform.

3.2.4 Acetone.

3.2.5 Methanol-water(9+1).

3.2.6 Sodium chloride solution: 10% aqueous solution.

3.2.7 Dimethiphin standard: Purity≥99%.

3.2.8 Dimethiphin standard solution: Accurately weigh an adequate amount of dimethiphin standard (accurrate to 0.1 mg), dissolve in acetone to prepare a solution of 100 μg/mL in concentration as the standard stock solution. According to the requirement, prepare standard working solutions of appropriate concentrations by diluting the stock solution with acetone.

3.3 Apparatus and equipment

3.3.1 Gas chromatograph, equipped with flame photometric detector (sulphur filter, 394 nm).

3.3.2 Vortex mixer.

3.3.3 Multifunction sample treatment unit for microchemical method, or equivalent.

3.3.4 Centrifuge: 4000 r/min.

3.3.5 Micro-adjustable pipets: 40—200 μL, 200—1 000 μL.

3.3.6 Centrifuge tube: 15 mL.

3.3.7 Micro-syringe: 10 μL.

3.4 Procedure

3.4.1 Extraction

Weigh ca 2 g of the test sample (accurate to 0.01 g)into a 15 mL centrifuge tube. Add 6 mL of methanol-water, blend with a vortex mixer for 2 min, centrifuge at 3 000 r/min for 2 min. Pour the supernatant extract into a second 15 mL centrifuge tube. Repeat the extraction once more with 5 mL of methanol-water, centrifuge and combine the extracts into the second centrifuge tube. Concentrate to ca 2 mL with 60℃ bath temperature.

3.4.2 Cleanup

Add 1 mL of sodium chloride solution and 3 mL of *n*-hexane into the second centrifuge tube and mix on the vortex mixer for 2 min. Centrifuge for 2 min and discard the *n*-hexane layer with a pointed

pipet. Add 3 mL of *n*-hexane and repeat the above process. Add 4 mL of water and extract the dimethiphin from the aqueous layer with 2×4 mL of chloroform by intense mixing. Centrifuge for 3 min. Transfer the lower organic phase into a third centrifuge tube with a pointed pipet. Evaporate to dryness with 60 C bath temperature. Dissolve the residue in 0.50 mL of acetone and centrifuge. The supernatant solution is ready for gas chromatographic determination.

3.4.3 Determination

3.4.3.1 GC operating condition

a) GC column: Pesiticide residue No. Ⅰ, fused quartz capillary column, 30 m×0.53 mm(id)×1.0 μm(film thickness)or equivalent.;

b) Carrier gas: Nitrogen, purity≥99.99%, 5.0 mL/min;

c) Make-up gas: Nitrogen, purity≥99.99%, 30 mL/min;

d) Hydrogen: 50 mL/min;

e) Air: 90 mL/min;

f) Column temperature: 180 C;

g) Injection port temperature: 250 C;

h) Detector temperature: 250 C;

i) Injection volume: 2.0 μL;

j) Injection mode: Splitless.

3.4.3.2 Plotting of standard curve

According to the approximate concentration of pesticide in the sample solution, inject accurately 5 suitable dimethiphin standard working solutions with different concentrations of equal volume separately into gas chromatogragh, and carry out the analysis under the above condition. The responses of the pesticide in the different standard working solutions should be within the linear range of instrumental detection. Determine the peak areas and plot the logarithm of peak area against concentrations of dimethiphin to prepare a standard curve. Under the above operating condition, the retention time of dimethiphin is about 3.4 min. For chromatogram of the standard, see fig. A1 in annex A.

3.4.3.3 Determination of sample solution

Inject accurately the sample solution of equal volume as that of the above into the gas chromatograph. From the peak area, obtain the concentration of dimethiphin in sample solution from the standard curve. The responses of pesticide should be within the linear range of the standard curve.

3.4.4 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.

3.5 Calculation and expression of the result

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

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

where

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

c—the concentration of dimethiphin in the sample solution obtained from the standard curve, μg/mL;

V—the final volume of the 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 0.05 mg/kg.

4.2 Recovery

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

In potato: 0.05 mg/kg, the recovery 94.9%;

0.10 mg/kg, the recovery 95.4%;

1.00 mg/kg, the recovery 91.0%.

In rape seed: 0.05 mg/kg, the recovery 95.7%;

0.10 mg/kg, the recovery 94.0%;

1.00 mg/kg, the recovery 92.2%.

Annex A

(informative)

Chromatogram of the standard

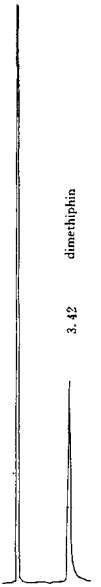


Fig. A 1 Gas chromatogram of dimethiphin standard