SN

B31

中华人民共和国进出口商品检验行业标准

SN 0345—95

出口蔬菜中杀虫双残留量检验方法

Method for the determination of dimehypo residues in vegetables for export

1995-05-29发布　　1995-11-01实施

中华人民共和国国家进出口商品检验局　发布

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1 主题内容与适用范围

本标准规定了出口蔬菜中杀虫双残留量检验的抽样，制样和气相色谱测定方法。

本标准适用于出口青菜中杀虫双残留量的检验。

2 抽样和制样

2.1 检验批

以不超过 1 000 件为一检验批。

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

批量，件	最低抽样数，件
1～25	1
26～100	5
101～250	10
251～1 000	15

2.3 抽样方法

按 2.2 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，其总量不少于 2 kg，放入洁净容器内，加封，标明标记，及时送交实验室。

2.4 试样制备

从原始样品中取可食部分，用四分法缩分出不少于 500 g 样品放入组织捣碎机中捣碎、混匀，均分成两份试样，装入洁净容器中，加封，标明标记。

2.5 试样保存

将试样于－18℃以下冷冻保存。

注：在抽样及制样的操作过程中，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

用稀盐酸溶液提取试样中的杀虫双，在碱性条件下，以硫化钠作催化剂，使杀虫双转化为沙蚕毒素，然后用乙酸乙酯提取，液—液分配净化以后，用配有电子俘获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

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

3.2.2 乙酸乙酯：分析纯，经全玻璃系统重蒸馏。

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3.2.3 助滤剂：硅藻土(celite)545。

3.2.4 盐酸：分析纯，配成 0.1 mol/L，2 mol/L 水溶液。

3.2.5 氢氧化钠：分析纯，配成 2 mol/L，10 mol/L 水溶液。

3.2.6 硫化钠：分析纯，配成 0.2 mol/L 水溶液。

3.2.7 杀虫双标准品：纯度≥99%。

3.2.8 杀虫双标准溶液：准确称取杀虫双标准品，以蒸馏水配成 0.1 mg/mL 的标准贮备液，用时根据需要用蒸馏水稀释至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：配备电子俘获检测器。

3.3.2 微量注射器：1 μL、10 μL。

3.3.3 高速组织捣碎机：配有捣碎杯。

3.3.4 全玻璃系统蒸馏装置。

3.3.5 分液漏斗：50 mL、125 mL。

3.3.6 平底漏斗：9 cm(内径)。

3.3.7 抽滤瓶：500 mL。

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 100 g(精确至 0.1 g)，置于捣碎杯中，加入 100 mL 盐酸溶液(0.1mol/L)，用组织捣碎机匀浆 5 min，经铺有助滤剂的布氏漏斗过滤于 250 mL 圆底烧瓶内，滤渣用 2×25 mL 盐酸溶液(0.1 mol/L)洗涤并过滤，合并滤液。

3.4.2 转化及净化

用氢氧化钠(2 mol/L)将上述滤液的 pH 调至 8.5～9.0，加入 2 mL 硫化钠溶液(0.2 mol/L)，于 70℃水浴中加热 2 h。待溶液冷却，用 3×20 mL 乙酸乙酯提取，合并提取液。用 3×5 mL 盐酸溶液(2 mol/L)提取乙酸乙酯提取液，合并盐酸提取液。用氢氧化钠溶液(10 mol/L)调至碱性，立即(20 min 之内)用 5 mL 乙酸乙酯提取，提取液经无水硫酸钠脱水，供气相色谱测定。

3.4.3 标准工作溶液的处理

移取适量的杀虫双标准工作溶液，按试样提取(3.4.1)、转化和净化(3.4.2)进行处理后，供测定用。

3.4.4 测定

3.4.4.1 色谱条件

从下列 a、b、c 三种条件中任选一种：

a. 色谱柱：玻璃柱，1.1 m×3 mm(内径)，填充物 3%(*m*/*m*)OV-1 涂于 Chromosorb W HP(80～100 目)；

色谱柱温度：120℃；

进样口温度：220℃；

检测器温度：250℃；

氮气：纯度≥99.99%，70 mL/min。

在此条件下沙蚕毒素的保留时间为 2.8 min。

b. 色谱柱：玻璃柱，2.0 m×3 mm(内径)，填充物 1.5%(*m*/*m*)OV-17＋2%QF-1(*m*/*m*)涂于 Chromosorb W HP(80～100 目)；

色谱柱温度：170℃；

进样口温度：220℃；

检测器温度：250℃；

氮气：纯度≥99.99%，70 mL/min。

在此条件下沙蚕毒素的保留时间为 2.4 min。

c. 色谱柱：石英毛细管色谱柱，5 m×0.53 mm(内径)，HP-1 键合固定相，2.6 μm(膜厚)；

色谱柱温度：130℃；

进样口温度：220℃；

检测器温度：250℃；

氮气：纯度≥99.99%，14 mL/min。

在此条件下沙蚕毒素的保留时间为 2.1 min。

3.4.4.2 色谱测定

分别注入 5 μL 标准工作溶液和样品溶液的待测液于气相色谱仪中，按 3.4.4.1 的色谱条件进行分析。样品溶液和标准工作液的响应值应在仪器的检测线性范围之内。否则应对样液和标准工作溶液进行适当稀释。

3.5 空白试验

除不加试样外，按上述测定步骤进行。

3.6 结果计算和表述

用色谱数据处理机或按下式计算试样中杀虫双含量：

$$X = \frac{h \cdot c \cdot V}{h_s \cdot m}$$

式中：X——试样中杀虫双的含量，mg/kg；

h——样液中杀虫双转化物(沙蚕毒素)的峰高，mm；

h_s——标准工作溶液中杀虫双转化物(沙蚕毒素)的峰高，mm；

c——标准工作溶液浓度，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

本方法测定低限为 0.01 mg/kg。

4.2 回收率

回收率的实验数据：杀虫双添加浓度在 0.01～0.5 mg/kg 范围内，回收率为 72%～103%。

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。

本标准由中国进出口商品检验技术研究所负责起草。

本标准主要起草人庄无忌、邱月明。

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

SN 0345—95

Method for the determination of dimehypo residues in vegetables for export

1 Scope and field of application

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

This standard is applicable to the determination of dimehypo residues in green cabbage for export.

2 Sampling and sample preparation

2.1 Inspection lot

The quantity of an inspection lot should not be more than 1,000 packages.

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

2.2 Quantity 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—1 000	15

2.3 Sampling procedure

A number of packages specified in 2.2 are taken at random and opened one by one. At least 500 grams of the sample should be taken from each package as the primary sample. The total weight of all primary samples should not be less than 2 kg, which should be sealed, labeled and sent to laboratory in time.

2.4 Preparation of test sample

From the combined primary sample, the edible portions are taken and reduced to not less than 500 g by quartering, which is homogenized by blending and then divided into two equal portions. Each portion is placed in a clean container as test sample, which is then sealed and labeled.

2.5 Storage of test sample

The test samples should be stored below −18℃.

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

Approved by the State Administration of Import and Export Commodity Inspection of the People's Republic of China on May 29, 1995

Implemented from Nov. 1, 1995

3 Method of determination

3.1 Principle

Dimehypo, extracted by dilute hydrochloric acid solution, is converted into nereistoxin in alkaline medium with sodium sulfide added as catalyst. The nereistoxin is extracted by ethyl acetate, purified by liquid-liquid partition and finally detected by gas chromatograph equipped with electron capture detector. External standard method is used for quantitation.

3.2 Reagents and materials

3.2.1 Sodium sulfate: Anhydrous, analytical grade, heated at 650℃ for more than 4 h, kept in a desiccator.

3.2.2 Ethyl acetate: Analytical grade, redistilled in all glass system.

3.2.3 Filter aid: Celite 545.

3.2.4 Hydrochloric acid: Analytical grade, from which 2 mol/L and 0.1 mol/L aqueous solutions are prepared.

3.2.5 Sodium hydroxide: Analytical grade, from which 10 mol/L and 2 mol/L aqueous solutions are prepared.

3.2.6 Sodium sulfide: Analytical grade, from which 0.2 mol/L aqueous solution is prepared.

3.2.7 Dimehypo standard: Purity≥99%.

3.2.8 Dimehypo standard solution: Accurately weigh an adequate amount of standard dimehypo, dissolve in distilled water to prepare a standard stock solution of 0.1 mg/mL. According to the concentration requirement, prepare a standard working solution by diluting the stock solution with distilled water.

3.3 Apparatus and equipment

3.3.1 Gas chromatograph: Equipped with electron capture detector.

3.3.2 Micro-syringe: 1 μL, 10 μL.

3.3.3 High speed blender: Equipped with glass blending cup.

3.3.4 All glass distilling system.

3.3.5 Separatory funnel: 50 mL, 125 mL.

3.3.6 Buchner funnel: 9 cm(id).

3.3.7 Vacuum filtration flask: 500 mL.

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

3.4 Procedure

3.4.1 Extraction

Weigh 100 g(accurate to 0.1 g) of the test sample into a blending cup, add 100 mL of 0.1 mol/L hydrochloric acid solution, homogenize and extract the sample for 5 min. Filter the homogenized sample by suction through a Buchner funnel with filter aid into a 250 mL round-bottom flask. Wash the residue with 2×25 mL of 0.1 mol/L hydrochloric acid solution, combine the filtrates.

3.4.2 Conversion and cleanup

Adjust the combined solution with 2 mol/L sodium hydroxide solution to pH 8.5—9.0, add 2 mL of 0.2 mol/L sodium sulfide solution, heat at 70℃ for 2 h in a water-bath. After cooled, extract the reaction product 3 times, each with 20 mL of ethyl acetate, Combine the extracts and extract it 3 times, each with 5 mL of 2 mol/L hydrochloric acid solution. Combine the extracts and adjust with 10 mol/L sodium hydroxide solution to alkaline, instantly (within 20 min) extract it with 5 mL of ethyl acetate,

Dehydrate the organic extract with anhydrous sodium sulfate and the solution is used for gas chromatographic determination.

3.4.3 Treatment of standard working solution:

Transfer a suitable amount of dimehypo standard working solution into a container, proceed with the same procedures used for the sample extraction (3.4.1), conversion and cleanup (3.4.2) and the solution is used as an external standard for GC determination.

3.4.4 Determination

3.4.4.1 GC operating condition

Chose one of the following three conditions of a, b, c:

a. Column: Glass, 1.1 m×3 mm(id), packed with 3%(*m*/*m*) OV-1 on Chromosorb W HP (80—100 mesh);

Column temperature: 120℃;

Injection port temperature: 220℃;

Detector temperature: 250℃;

Nitrogen: Purity≥99.99%, 70 mL/min.

Under the above mentioned conditions, the retention time of nereistoxin is 2.8 min.

b. Column: Glass, 2.0 m×3 mm(id), packed with 1.5%(*m*/*m*)OV-17+2%(*m*/*m*)QF-1 on Chromosorb W HP(80—100 mesh);

Column temperature: 170℃;

Injection port temperature: 220℃;

Detector temperature: 250℃;

Nitrogen: Purity≥99.99%, 70 mL/min.

Under the above mentioned conditions, the retention time of nereistoxin is 2.4 min.

c. Column: Fused silica capillary, 5 m×0.53 mm(id), HP-1 bonded stationary phase, film thickness 2.6 μm;

Column temperature: 130℃;

Injection port temperature: 220℃;

Detector temperature: 250℃;

Nitrogen: Purity≥99.99%, 14 mL/min.

Under the above mentioned conditions, the retention time of nereistoxin is 2.1 min.

3.4.4.2 GC determination

Accurately inject 5 μL of the test sample solution and standard working solution respectively into the gas chromatograph and carry out the analysis under the condition indicated in 3.4.4.1. The responses of nereistoxin in the test sample solution and standard working solution should be in the linear range of the instrumental detection. Otherwise, suitable dilution should be made to the sample solution and standard working solution.

3.5 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.

3.6 Calculation and expression of result

The calculation of result is carried out by GC data processor or according to the following formula:

$$X = \frac{h \cdot c \cdot V}{h_s \cdot m}$$

where

X—Residue content of dimehypo in test sample, mg/kg;

h—Peak height of converted dimehypo (nereistoxin) in the test sample solution, mm;

h_s—Peak height of converted dimehypo (nereistoxin) in the standard working solution, mm;

c—Concentration of dimehypo in the standard working solution, μg/mL;

V—Final volume of test 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 0.01 mg/kg.

4.2 Recovery

According to the experimental data, when the concentration of dimehypo is in the range of 0.01—0.5 mg/kg, the recovery is 72%—103%.

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 China Import & Export Commodity Inspection Technology Insititute.

This standard was mainly drafted by Zhuang Wuji, Qiu Yueming.

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