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SN

中华人民共和国进出口商品检验行业标准

SN 0499—95

出口水果蔬菜中百菌清残留量检验方法

Method for the determination of chlorothalonil residues in fruits and vegetables for export

1995-11-28发布　　　　1996-01-01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

本标准规定了出口水果蔬菜中百菌清残留量检验的抽样、制样和气相色谱测定方法。

本标准适用于出口柑桔和青刀豆中百菌清残留量的检验。

2 抽样和制样

2.1 检验批

以不超过1 500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
251～1 500	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，原始样品总量不得少于2 kg。加封后，标明标记，及时送实验室。

2.4 试样制备

将所取原始样品缩分出1 kg，取可食部分，经组织捣碎，均分成两份，装入洁净容器内，作为试样，密封，并标明标记。

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

试样经磷酸酸化，以石油醚提取，在石油醚-中性氧化铝-乙醚体系中净化，用配有电子俘获检测器的气相色谱仪测定，外标法定量。

3.2 试剂

除特殊规定外，所用试剂均为分析纯，水为重蒸馏水。

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3.2.1 磷酸。

3.2.2 石油醚（30～60℃）。

3.2.3 乙醚。

3.2.4 磷酸溶液：1+1（V/V）。

3.2.5 氧化铝：中性、层析用，70～325 目，常态。

3.2.6 百菌清标准品：纯度≥99%。

3.2.7 百菌清标准溶液：准确称取适量的百菌清标准品，用石油醚配成 0.100 mg/mL 的标准溶液，根据需要再配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，配有电子俘获检测器。

3.3.2 高速组织捣碎机。

3.3.3 旋涡混匀器。

3.3.4 离心机：0～5 000 r/min。

3.3.5 多功能微量化样品处理仪或相当者。

3.3.6 离心管：50 mL、25 mL。

3.3.7 微量注射器：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 50 mL 离心管中，加入 1 mL 磷酸溶液（1+1），混匀，加入 4 mL 石油醚，在旋涡混匀器上混匀 1 min。以 3 000 r/min 离心 2 min，将石油醚层移至 25 mL 离心管中。残渣再用 4 mL 石油醚以同样步骤提取一次，合并有机相。

3.4.2 净化

于石油醚提取液中加入 1 g 中性氧化铝，在旋涡混匀器上混匀 1 min，以 3 000 r/min 离心 2 min，将石油醚层全部倾弃。氧化铝层用 3×4 mL 乙醚提取，将乙醚层合并于另一支 25 mL 离心管中，置多功能微量化样品处理仪上，于 40℃通氮气挥发浓缩至干，用石油醚定容至 1.00 mL，供气相色谱测定。

3.4.3 测定

3.4.3.1 色谱条件

a. 毛细管色谱柱：HP-1（dimethylpolysiloxane，Gum）10 m×0.53 mm（id）×2.65 μm 石英柱或相当的色谱柱；

b. 色谱柱温：190℃；

c. 进样口温度：230℃；

d. 检测器温度：300℃；

e. 载气、尾吹气：氮气（纯度≥99.99%）；载气流速 4 mL/min；尾吹气流速 40 mL/min；

f. 进样方式：填充柱进样口进样；

g. 进样量：2 μL。

3.4.3.2 色谱测定

根据样液中百菌清含量情况，选择峰高相近的标准工作溶液。标准工作溶液和样液中百菌清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。在上述色谱条件下百菌清保留时间约为 2.2 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下式计算试样中百菌清含量：

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

式中：X——试样中百菌清含量，mg/kg；
h——样液中百菌清的峰高，mm；
h_s——标准工作溶液中百菌清的峰高，mm；
c——标准工作液中百菌清的浓度，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 0.01 mg/kg。

4.2 回收率

回收率的实验数据：百菌清添加浓度在 0.01～2.0 mg/kg 范围内，回收率为 90.4%～100.2%。

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厦门进出口商品检验局负责起草。
本标准主要起草人周昱、刘胜利。

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

SN 0499—95

Method for the determination of chlorothalonil residues in fruits and vegetables for export

1 Scope and field of application

This standard specifies the methods of sampling, sample preparation and determination by gas chromatography (GC) of chlorothalonil residues in fruits and vegetables for export.

This standard is applicable to the determination of chlorothalonil residues in oranges and green beans for export.

2 Sampling and sample preparation

2.1 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, grade, specification etc., 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—1 500	15

2.3 Sampling procedure

A number of packages specified in 2.2 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 not be less than 2 kg, which shall be sealed, labeled and sent to laboratory in time.

2.4 Preparation of test sample

The combined primary sample is reduced to 1 kg, the edible portions are blended, and divided into two equal portions. Each portion is placed in a clean container as the test sample, which is then sealed and labeled.

2.5 Storage of test sample

The test samples should be stored below —18℃.

Approved by the State Administration of Import and Export Commodity Inspection of the People's Republic of China on Nov. 28, 1995

Implemented from Jan. 1, 1996

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.

3 Method of determination

3.1 Principle

After being acidified with phosphoric acid, the sample is extracted by petroleum ether, the extract is cleaned up in a petroleum ether-aluminum oxide-diethyl ether system. Finally, the solution is analyzed by GC with electron capture detector (ECD). Using external standard method.

3.2 Reagents

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

3.2.1 Phosphoric acid.

3.2.2 Petroleum ether (b. p. 30—60℃).

3.2.3 Diethyl ether.

3.2.4 Phosphoric acid solution: 1+1(*V*/*V*).

3.2.5 Aluminum oxide: Neutral, for chromatography, 70—325 mesh, in normal state.

3.2.6 Chlorothalonil standard: Purity≥99%.

3.2.7 Chlorothalonil standard solution: Accurately weigh an adequate amount of chlorothalonil standard, dissolve in petroleum ether and prepare a solution of 0.100 mg/mL as the standard stock solution. According to the requirement, prepare a standard working solution of appropriate concentration.

3.3 Apparatus and equipment

3.3.1 Gas chromatograph, equipped with electron capture detector (ECD).

3.3.2 High speed blender.

3.3.3 Vortex mixer.

3.3.4 Centrifuge: 0—5 000 r/min.

3.3.5 Multifunction sample treatment unit for microchemical method, or the equivalent.

3.3.6 Centrifuge tube: 50 mL, 25 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 50 mL centrifuge tube, add 1 mL of phosphoric acid solution (1+1), mix well, add 4 mL of petroleum ether, mix vigorously by a vortex mixer for 1 min. Centrifuge for 2 min at 3 000 r/min, transfer the petroleum ether layer to a 25 mL centrifuge tube. Repeat once the extraction in the same way with 4 mL of petroleum ether, and then combine the organic layers.

3.4.2 Cleanup

Add 1 g of neutral aluminum oxide to the combined organic layer, and mix vigorously by a vortex mixer for 1 min, centrifuge for 2 min at 3 000 r/min and discard all the petroleum ether layer. Then the aluminum oxide layer is extracted with 3×4 mL of diethyl ether, and the combined ether layer is evaporated to dryness under nitrogen stream at 40℃. Dissolve the residue in 1.00 mL of petroleum ether, and the solution is used for gas chromatographic determination.

3.4.3 Determination

3.4.3.1 GC operating condition

a. Capillary column: HP-1 (dimethylpolysiloxane, Gum), 10 m×0.53 mm(id)×2.65 μm fused silica column, or the equivalent;

b. Column temperature: 190℃;

c. Injection port temperature: 230℃;

d. Detector temperature: 300℃;

e. Carrier gas and make-up gas: Nitrogen, purity≥99.99%, Flow rate: carrier gas 4 mL/min; make-up gas: 40 mL/min;

f. Injection mode: On packed column injection;

g. Injection volume: 2 μL.

3.4.3.2 GC determination

According to the approximate concentration of chlorothalonil in the sample solution, select the standard working solution with similar peak height to that of sample solution. The responses of chlorothalonil in the standard working solution and sample solution should be in the linear range of the instrumental detection. The standard working solution should be injected randomly in-between the injections of the sample solution of equal volume. Under the above operating condition the retention time of chlorathalonil is about 2.2 min.

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 sample.

3.4.5 Calculation and expression of result

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

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

Where

X—Content of chlorothalonil in test sample, mg/kg;

h—Peak height of chlorothalonil in the sample solution, mm;

h_s—Peak height of chlorothalonil in the standard working solution, mm;

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

V—Final volume of the 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 fortifying concentration of chlorothalonil is in the range of 0.01—2.0 mg/kg, the recovery is 90.4%—100.2%.

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

This standard was mainly drafted by Zhou Yu, Liu Shengli.

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