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中华人民共和国进出口商品检验行业标准

SN 0189—93

出口水果中三硫磷残留量检验方法

Method for determination of carbophenothion residues in fruits for export

1993-06-04发布　　1993-08-01实施

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1 主题内容与适用范围

本标准规定了出口水果中三硫磷残留量检验的抽样、制样和气相色谱测定方法。

本标准适用于出口苹果、梨、杏、李子、桃和柑桔中三硫磷残留量的检验。

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，经组织捣碎机捣碎，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 ℃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

以石油醚提取，脱水、浓缩、定容后，用配有火焰光度检测器的气相色谱仪测定，外标法定量。

3.2 试剂和材料

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3.2.1 石油醚：分析纯，重蒸馏，收集 65～75 ℃馏分。

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

3.2.3 三硫磷标准品：纯度≥95%。

3.2.4 三硫磷标准溶液：准确称取适量的三硫磷标准品，用石油醚配成浓度为 1.000 mg/mL 的标准储备溶液，根据需要再配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检测器，磷滤光片(526 nm)。汽化室内的石英管和柱前端的石英棉需经常更换，以达到净化的操作要求。

3.3.2 锥形瓶：具磨口塞，250 mL。

3.3.3 刻度试管：具磨口塞，10 mL。

3.3.4 振荡器。

3.3.5 旋转蒸发器。

3.3.6 心形瓶：200 mL。

3.3.7 全玻璃系统蒸馏装置。

3.3.8 无水硫酸钠柱：筒形漏斗，内装 5 cm 高的无水硫酸钠。

3.3.9 微量注射器：10 μL、100 μL。

3.4 测定步骤

3.4.1 提取

称取试样约 20 g(精确到 0.1 g)于锥形瓶内，加 50 mL 石油醚，振荡 45 min，用已经石油醚浸洗过的滤纸过滤，再用 25 mL 石油醚分数次洗涤锥形瓶、残渣和滤纸。合并滤液，经无水硫酸钠柱脱水，收集于心形瓶内。用少量石油醚分数次洗涤无水硫酸钠柱，流出液收集于心形瓶内。在 55 ℃水浴中减压旋转浓缩后，转移至刻度试管内，用少量石油醚分数次洗涤心形瓶，并入刻度试管，定容至 10 mL，供气相色谱测定。

3.4.2 测定

3.4.2.1 色谱条件

a. 色谱柱：玻璃柱，1 m×3 mm(内径)，填充物为 3%(*m*/*m*)OV-101 涂于 Chromosorb W HP(80～100 目)；

b. 色谱柱温度：200 ℃；

c. 进样口温度：240 ℃；

d. 检测器温度：240 ℃；

e. 氮气：纯度≥99.99%，50 mL/min；

f. 氢气：50 mL/min；

g. 空气：60 mL/min。

3.4.2.2 色谱测定

根据样液中三硫磷含量情况，选定峰高相近的标准工作溶液。标准工作溶液和样液中三硫磷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，三硫磷保留时间约为 4 min。

3.4.3 空白试验

除不加试样外，按上述测定步骤进行。

3.4.4 结果计算和表述

用色谱数据处理机或按下列公式计算：

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

式中：X——试样中三硫磷残留量，mg/kg；

h——样液中三硫磷的峰高，mm；

h_s——标准工作溶液中三硫磷的峰高，mm；

c——标准工作溶液中三硫磷的浓度，μg/mL；

m——称取的试样量，g；

V——样液最终定容体积，mL。

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

本方法的测定低限为 0.1 mg/kg。

4.2 回收率

回收率的实验数据：三硫磷浓度在 0.1～5.0 mg/kg 范围，回收率为 91.4%～99.6%。

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北京、秦皇岛进出口商品检验局负责起草。

本标准主要起草人刘锦石、张军、王嘉瑞、邹连生。

主要参考文献：

FDA-PESTICIDE ANALYTICAL MANUAL，Vol. Ⅱ，180.156，1985.

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

SN 0189—93

Method for determination of carbophenothion residues in fruits for export

1 Scope and field of application

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

This standard is applicable to the determination of carbophenothion residues in fruits, such as apple, pear, apricot, peach and orange 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 and specification, shoud 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 grams. 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 portion is blended, and then divided into two equal portions. Each portion is placed in a clean container as the test sample, which is sealed and labeled.

2.5 Storage of test sample

The test samples should be stored at −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 Jun. 4, 1993

Implemented from Aug. 1, 1993

3 Method of determination

3.1 Principle

After the sample is extracted by petroleum ether, the water in the extract is removed, then the solution is concentrated and diluted to a definite volume. Finally, the solution is analyzed by GC with flame photometric detector and phosphorous filter (526 nm), using external standard method.

3.2 Reagents and materials

3.2.1 Petroleum ether: A. R., redistill and collect the distillate of 65—75 ℃.

3.2.2 Anhydrous sodium sulfate: A. R., ignite at 650 ℃ for 4h, and keep in a tightly closed container after cooling.

3.2.3 Carbophenothion standard: Purity≥95%.

3.2.4 Carbophenothion standard solution:

Accurately weigh an adequate amount of carbophenothion standard, dissolve in petroleum ether and prepare a solution of 1.000 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 Chromatograph: Equiped with flame photometric detector and phosphorous filter (526 nm), the quartz tube in the vaporizer and the quartz wool for the column shall be frequently replaced with the new ones in order to meet the requirements for the clean up.

3.3.2 Conical flask: 250 mL, with ground stopper.

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

3.3.4 Shaker.

3.3.5 Rotary evaporator.

3.3.6 Heart-shape bottle: 200 mL.

3.3.7 All-glass distilling system.

3.3.8 Column of anhydrous sodium sulfate: A cylindrical shape funnel, filled with 5 cm height of anhydrous sodium sulfate.

3.3.9 Micro syringe: 10 μL, 100 μL.

3.4 Procedure

3.4.1 Extraction

Weigh ca 20 g of the test sample (accurate to 0.1 g) into a conical flask, add 50 mL of petroleum ether, stopper and shake for 45 min by a shaker. Filter the extract with a filter paper which had been immersed with petroleum ether, rinse the conical flask with 25 mL of petroleum ether in several portions and filter, combine the filtrates, pass the combined filtrates through the column of anhydrous sodium sulfate to remove water, and rinse the column several times with petroleum ether, combine the solution and rinsings and collect in a heart-shape bottle. The combined solution is concentrated in the rotary evaporator under reduced pressure in a 55 ℃ water-bath. The concentrated solution is transfered quantitatively into a graduated test tube, and exactly diluted to 10 mL. The solution is used for chromatographic determination.

3.4.2 Determination

3.4.2.1 GC operating condition

a. Column: glass, 1m × 3 mm (id), packed with 3%(*m*/*m*) OV-101 on Chromosorb W HP (80—100 mesh);

b. Column temperature: 200 ℃;

c. Injection port temperature: 240 ℃;

d. Detector temperature: 240 ℃;

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

f. Hydrogen: 50 mL/min;

g. Air: 60 mL/min.

3.4.2.2 GC determination

According to the approximate concentration of carbophenothion in the sample solution, select the standard working solution with similar peak height to that of sample solution. The responses of carbophenothion in the standard solution and sample solution should be in the linear range of the instrumental detection. The standard working solution should be injected in-between occasionally with the sample solution of equal volume. Under the above chromatographic condition, the retention time of carbophenothion is about 4 min.

3.4.3 Blank test

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

3.4.4 Calculation and expression of result

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

$$X = (h \cdot c \cdot V)/(h_s \cdot m)$$

where

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

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

h_s—the peak height of carbophenothion in the standard working solution, mm;

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

m—the mass of test sample, g;

V—the final volume of test sample solution, mL.

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 0.1 mg/kg.

4.2 Recovery

According to the experimental data, when the concentration of carbophenothion is in the range of 0.1—5.0 mg/kg, the recovery is 91.4%—99.6%.

Additional explanations:

This standard was proposed by the State Administration of Import and Export Commodity Inspection Bureau of the People's Republic of China.

This standard was drafted by the Beijing and Qinhuangdao Import and Export Commodity Inspection Bureau of the People's Republic of China.

This standard was mainly drafted by Liu Jinshi, Zhang Jun, Wang Jiarui, Zhou Liansheng.

Reference:

FDA-PESTICIDE ANALYTICAL MANUAL, Vol. Ⅰ, 180.156, 1985.

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