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中华人民共和国进出口商品检验行业标准

SN 0192—93

出口水果中溴螨酯残留量检验方法

Method for determination of bromopropylate residues in fruits for export

1993-06-04发布　　1993-08-01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中溴螨酯残留量检验的抽样、制样和气相色谱测定法。

本标准适用于出口苹果中溴螨酯残留量的检验。

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、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4 kg，加封后，标明标记并及时送实验室。

2.4 试样制备

分取出部分有代表性苹果样，每个苹果取四分之一，去梗去核，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，均分成二份，装入洁净容器内，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中，必须防止样品受到污染和发生残留物含量的变化。

3 测定方法

3.1 方法提要

苹果中残留的溴螨酯(4,4′-二溴二苯乙醇酸异丙酯)用丙酮提取，提取液用正己烷萃取，弗罗里硅土柱净化，乙醚-正己烷(7+3)淋洗。净化液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 试剂和材料

除特殊规定外，试剂均为分析纯，水为蒸馏水或相适应的去离子水。

3.2.1 丙酮：重蒸馏。

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3.2.2 正己烷：重蒸后收集68～69℃馏分。

3.2.3 苯：重蒸馏。

3.2.4 乙醚。

3.2.5 无水硫酸钠：650℃灼烧4 h，冷却后，贮于密封瓶中备用。

3.2.6 硫酸钠水溶液，2%(*m*/*m*)：称取2 g无水硫酸钠，溶于100 mL蒸馏水中。

3.2.7 弗罗里硅土(牌号：Fluka)：650℃灼烧4 h，贮于密封瓶中，使用前夕在130℃烘5 h，贮于干燥器内备用。

3.2.8 溴螨酯标准品：纯度≥99%。

3.2.9 溴螨酯标准溶液：准确称取适量的溴螨酯标准品，用少量苯溶解，然后用正己烷配制成浓度为0.100 mg/mL的储备液。根据需要再稀释配制成适用浓度的标准工作液。

3.3 仪器和设备

3.3.1 气相色谱仪并配备电子俘获检测器。

3.3.2 震荡器。

3.3.3 离心管：具塞50 mL。

3.3.4 微型层析柱：15 cm×0.5 cm(内径)，带有10 mL贮液斗。

3.3.5 空气(或氮气)流浓缩装置。

3.3.6 全玻璃系统蒸馏装置。

3.3.7 无水硫酸钠柱：6 cm×18 mm(内径)，内装5 cm高无水硫酸钠。

3.3.8 微量注射器：10 μL。

3.3.9 脱脂棉：用乙醚-正己烷(7+3)回流2 h，取出挥发至干，保存在清洁容器中备用。

3.4 测定步骤

3.4.1 提取：称取约10 g试样(精确至0.1 g)于锥形瓶中。加入40 mL丙酮，震荡45 min，过滤，用丙酮洗涤滤渣，将滤液定容至100 mL。

3.4.2 净化：准确吸取10 mL提取液，于具塞离心管中，加入20 mL 2%硫酸钠水溶液，用正己烷对丙酮-水溶液相萃取二次(每次10 mL)。合并正己烷萃取液，并通过无水硫酸钠柱脱水，浓缩至约1 mL。

于微型层析柱的下端填入少量脱脂棉，依次装入0.5 cm高无水硫酸钠、1 g弗罗里硅土和1 cm高无水硫酸钠。用5 mL正己烷预淋层析柱，弃去流出液。待液面下降至上层无水硫酸钠层时，将上述浓缩液倒入柱内，并用2 mL乙醚-正己烷(7+3)洗涤器皿，倒入柱内，继用乙醚-正己烷(7+3)淋洗层析柱，收集流出液10 mL。浓缩以除尽乙醚，再以正己烷定容至10 mL，供气相色谱测定。

3.4.3 测定

3.4.3.1 色谱条件

a. 色谱柱：玻璃柱，2 m×3 mm(内径)，填充物为3%(*m*/*m*)OV-1涂于Gas Chrom Q (80～100目)；

b. 氮气：纯度≥99.99%，30 mL/min；

c. 柱温：230℃；

d. 进样口温度：250℃；

e. 检测器温度：270℃。

3.4.3.2 色谱测定

分别将等体积的标准工作液、样液注入气相色谱仪。溴螨酯出峰保留时间约4.5 min。

注：实际使用的标准工作液及待测样液中农药的响应值均应在仪器检测的线性范围之内。样液测定过程中要参插注入标准工作液，以便准确定量。

3.4.4 空白试验：除不称取试样外，均按上述测定步骤进行。

3.4.5 结果的计算和表述

用色谱数据处理机或按下式计算：

$$X = \frac{A \cdot c_s}{A_s \cdot c}$$

式中：X——试样中溴螨酯含量，mg/kg；

A——样液中溴螨酯色谱峰面积(或峰高)，mm^2(mm)；

A_s——标准工作液中溴螨酯色谱峰面积(或峰高)，mm^2(mm)；

c_s——标准工作液中溴螨酯的浓度，μg/mL；

c——最终样液所代表的试样浓度，g/mL。

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 0.04 mg/kg。

4.2 回收率

回收率的实验数据：

溴螨酯浓度在 0.0400～1.00 mg/kg 范围内，回收率为 95.3%～109.1%。

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上海进出口商品检验局负责起草。

本标准主要起草人陈余英、习娟华。

主要参考文献：

FDA-PESTICIDE ANALYTICAL MANUAL, Vol. I, Table 201-A, 1985.

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

SN 0192—93

Method for determination of bromopropylate residues in fruits for export

1 Scope and field of application

This standard specifies the methods of sampling, sample preparation and determination of bromopropylate residues by gas chromatography with electron capture detector in fruits for export.

This standard is applicable to the determination of bromopropylate residues in apples 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, specification, grade etc., should be the same.

2.2 Quantity of the 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 primary sample taken from each package shall be at least 500 g. The total weight of all primary samples should be not less than 4 kg, which shall be sealed, labeled and sent to the laboratory in time.

2.4 Preparation of test sample

Take the apples at random as representative samples. Chop one quarter of each apple, remove the stalks and kernels, cut into shreds, and then reduce the shreds to about 1 kg by quartering. The shredded sample is then ground into jam by a high-speed blender. The ground sample is divided into two test samples of equal size. Test samples shall be placed in clear stoppered and labelled containers.

2.5 Storage of the sample

The test sample should be stored under −18℃.

Note: In the course of sampling and sample preparation, precaution must be taken to avoid contamination or any

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

factors which may cause the change of the residue content.

3 Method of determination

3.1 Principle

The bromopropylate (4,4'-dibromobenzilic acid isopropyl ester) residues in apple is extracted with acetone and the extract is again extracted with n-hexane. Then the solution is cleaned up through Florisil column. Rinse with ethyl ether-n-hexane(7 : 3). The purified solution is detected by GC with electron capture detector and the residue content is determined quantitatively by external standard method.

3.2 Reagents and materials

Unless otherwise specified, the reagents should be analytically pure, "water" is distilled water or corresponding de-ionized water.

3.2.1 Acetone: Redistilled.

3.2.2 n-Hexane: Redistilled, collect the distillate of 68—69℃.

3.2.3 Benzene: Redistilled.

3.2.4 Ethyl ether.

3.2.5 Anhydrous sodium sulfate: Ignite at 650℃ for 4 h. Keep in a tightly closed container after cooling.

3.2.6 Sodium sulfate solution, 2%(*m*/*m*): Weigh 2 g of anhydrous Na_2SO_4, dissolve in 100 mL of water.

3.2.7 Florisil (trade mark Fluka): Ignite at 650℃ for 4 h. Keep in a tightly closed container. Prior to use, dry at 130℃ for 5 h and store in a desiccator.

3.2.8 Standard bromopropylate: Purity≥99%.

3.2.9 Bromopropylate standard solution: Accurately weigh an appropriate amount of standard bromopropylate, dissolve in a small volume of benzene and dilute with n-hexane to form a stock solution with a concentration of 0.100 mg/mL. Then dilute the stock solution to the required concentration as the standard working solution.

3.3 Apparatus and equipment

3.3.1 Gas chromatograph, equipped with electron capture detector.

3.3.2 Shaker.

3.3.3 Centrifuge tube(with stopper): 50 mL.

3.3.4 Chromatographic micro-column: 15 cm×0.5 cm(id), with a 10 mL reservoir funnel.

3.3.5 Air (or N_2)-flow concentrator.

3.3.6 All-glass distillation apparatus.

3.3.7 Column of anhydrous sodium sulfate: 6 cm×18 mm(id), prepacked with 5 cm height of anhydrous sodium sulfate.

3.3.8 Micro-syringe: 10 μL.

3.3.9 Absorbent cotton: Reflux with ethyl ether-n-hexane (7 : 3) for 2 h. Take out and air-dry. Store in a clean container.

3.4 Procedure

3.4.1 Extraction: Weigh ca 10.0 g of the sample (accurate to 0.1 g) into a conical flask. Add 40 mL of acetone, stopper and shake for 45 min, filter, then wash the residue with acetone. Quantitatively transfer the filtrate to a 100 mL volumetric flask and dilute to the mark.

3.4.2 Clean up: Accurately pipet 10 mL of the extract into a centrifuge tube (with stopper). Add 20 mL of 2% aqueous solution of sodium sulfate. Extract the aceton-aqueous solution twice with n-hexane (10 mL for each time). Combine the n-hexane extracts, let it pass through the anhydrous Na_2SO_4 to remove the water and concentrate to about 1 mL.

Place a small amount of absorbent cotton at the lower end of the chromatographic micro-column. Then pack successively with 0.5 cm of anhydrous sodium sulfate, 1 g of Florisil and 1 cm of anhydrous sodium sulfate. At first rinse the chromatographic column with 5 mL of n-hexane, and discard the effluent. When the liquid level lowers to the upper surface of anhydrous sodium sulfate, pour the above concentrated solution into the column. Wash the container with 2 mL of ethyl ether-n-hexane (7 : 3) and pour the washings into the column. Rinse the chromatographic column with ethyl ether-n-hexane (7 : 3). Collect 10 mL of the effluent. Concentrate the solution to expel the ethyl ether. Quantitatively dilute with n-hexane to 10 mL for GC determination.

3.4.3 Determination

3.4.3.1 GC operating conditions:

a. GC column: Glass, 2 m×3 mm (id), packed with 3% (*m*/*m*) OV-1 on Gas Chrom Q (80—100 mesh);

b. Nitrogen: Purity≥99.99%, 30 mL/min;

c. Column temperature: 230℃;

d. Injection port temperature: 250℃;

e. Detector temperature: 270℃.

3.4.3.2 GC determination

Inject the standard working solution and sample solution of equal volume separately into the gas chromatograph. Retention time for bromopropylate: ca 4.5 min.

Note: The response values of the pesticide in both the standard working solution and sample solution for determination should be within the linear range of the instrumental detection. The standard working solutions should be injected in-between occasionally with the sample solutions of equal volume to check the sensitivity of the detector.

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.

3.4.5 Calculation and expression of the result

Calculate the content of bromopropylate in the sample by GC data processor or according to the following formula:

$$X = \frac{A}{A_s} \times \frac{c_s}{c}$$

where

X—Bromopropylate content in the sample, mg/kg;

A—Peak area (or peak height) of bromopropylate in the sample solution, mm^2(mm);

A_s—Peak area (or peak height) of bromopropylate in the standard working solution, mm^2(mm);

c_s—Concentration of bromoopropylate in the standard working solution, μg/mL;

c—Concentration in terms of sample mass in the final test solution, g/mL.

Note: The response value of the blank test should be subtracted from the result.

4 Limit of determination and recovery

4.1 Limit of determination: 0.04 mg/kg.

4.2 Recovery

According to the experimental data, when the concentration of bromopropylate is in the range of 0.040 0—1.00 mg/kg, the recovery is 95.3%—109.1%.

Additional explanation:

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

This standard was mainly drafted by Chen Yuying, Xi Juanhua.

Reference:

FDA-PESTICIDE ANALYTICAL MANUAL, Vol. I, Table 201-A, 1985.

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