SN

中华人民共和国进出口商品检验行业标准

SN 0198--93

出口蔬菜中复硝盐残留量检验方法

Method for determination of nitrophenol salt residues in vegetables 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

中华人民共和国进出口商品检验行业标准

出口蔬菜中复硝盐残留量检验方法

SN 0198—93

Method for determination of nitrophenol salt residues in vegetables for export

1 主题内容与适用范围

本标准规定了出口蔬菜中复硝盐残留量检验的抽样、制样和气相色谱测定方法。

本标准适用于出口蕃茄中复硝盐残留量的检验。

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 500 g，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，密封，作为试样，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

硝基苯酚的钠盐，在碱性水溶液中与乙酸酐衍生化反应，生成相对应的酯类化合物，用石油醚提取，定容后，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

中华人民共和国国家进出口商品检验局 1993-06-04 批准　　1993-08-01 实施

3.2.1 丙酮:分析纯。

3.2.2 磷酸:分析纯。

3.2.3 石油醚(60～90 ℃):分析纯,重蒸馏。

3.2.4 乙醚:分析纯。

3.2.5 碳酸钠:分析纯。

3.2.6 乙酸酐:分析纯。

3.2.7 Celite 545 助滤剂。

3.2.8 邻硝基苯酚钠、对硝基苯酚钠和 5-硝基邻甲氧基苯酚钠标准品:纯度≥99%。

3.2.9 蒸馏水或相当纯度的去离子水。

3.2.10 标准储备溶液:准确称取适量的邻硝基苯酚钠、对硝基苯酚钠和 5-硝基邻甲氧基苯酚钠标准品,用蒸馏水溶解定容,配成各组分浓度为 3.5×10^{-5} g/mL 的混合标准储备液。

3.3 仪器和设备

3.3.1 气相色谱仪并配有电子俘获检测器。

3.3.2 高速组织捣碎机。

3.3.3 匀质器。

3.3.4 摆动式振荡器。

3.3.5 真空旋转蒸发器。

3.3.6 层析柱。

3.4 测定步骤

3.4.1 提取和净化

称取经捣碎的蕃茄浆试样约 40 g(精确到 0.1 g)于烧杯中,加 70 mL 丙酮,匀质抽提 5 min,抽滤。滤渣移入烧杯中,重复提取二次,每次使用丙酮 40 mL。合并三次滤液,在真空旋转蒸发器上浓缩至仅存水相(水浴温度为 40 ℃)。水相通过 Celite545 助滤剂层析柱(用约 1 mL 蒸馏水淋洗),流出液收集于 250 mL 分液漏斗中,加 4 mL 磷酸,分别用 50 mL、50 mL 石油醚和 40 mL 乙醚提取,合并三次有机相。再分别用 0.2 mol/L 碳酸钠水溶液 30 mL、20 mL、20 mL 提取,每次应充分静置分层,合并这三次碳酸钠提取液。

3.4.2 衍生化

在盛有约 70 mL 上述碳酸钠提取液的分液漏斗中,加入 2 mL 乙酸酐,充分振荡(必须放气),直至无气泡产生,衍生化反应即完毕。后用石油醚提取三次,每次 20 mL。合并提取液,浓缩,定容,供气相色谱测定。

3.4.3 标准工作溶液制备

取标准储备溶液 1 mL,加到盛有 70 mL0.2 mol/L 碳酸钠水溶液的分液漏斗中,按 3.4.2 操作,制备成组分浓度为 1.5×10^{-7} g/mL 的标准工作溶液,供气相色谱外标法测定使用。使用前临时制备。

3.4.4 测定

3.4.4.1 色谱条件

a. 色谱柱:玻璃柱,1 m×4 mm(内径),填充 15%(*m*/*m*)FFAP Chromosorb 880A DMCS(80～100 目);

b. 色谱柱温度:175 ℃;

c. 进样口温度:230 ℃;

d. 检测器温度:220 ℃;

e. 氮气:纯度≥99.99%,55 mL/min。

3.4.4.2 色谱测定

分别将样液及标准工作液以等体积注入气相色谱仪,进行气相色谱测定。标准工作溶液和样液应穿

插进样，并要求标准工作溶液和样液中待测组分的响应值在仪器检测线性范围内。在上述色谱条件下，各待测组分的衍生物的保留时间为：

邻硝基苯酚钠 1.85 min；

对硝基苯酚钠 2.80 min；

5-硝基邻甲氧基苯酚钠 10.75 min。

3.4.5 空白试验

除不加入试样外，按上述测定步骤进行。

3.4.6 结果计算和表述

用色谱数据处理机或按下列公式计算各待测组分的残留量：

$$X = \frac{h \cdot V_s \cdot V_0 \cdot c}{h_s \cdot V \cdot m}$$

式中：X——复硝盐中单一组分的残留量，mg/kg；

h——样液中待测组分的峰高，mm；

h_s——标准工作溶液中有关标准组分的峰高，mm；

V——样液的进样体积，μL；

V_s——标准工作溶液的进样体积，μL；

V_0——样液的最终定容体积，mL；

c——标准工作溶液中待测组分的浓度，μg/mL；

m——称取的试样量，g。

注：计算结果需扣除空白值。

4 方法的测定低限和回收率

4.1 测定低限

邻硝基苯酚钠：0.01 mg/kg；

对硝基苯酚钠：0.02 mg/kg；

5-硝基邻甲氧基苯酚钠：0.01 mg/kg。

4.2 回收率

回收率的实验数据：

邻硝基苯酚钠添加浓度在 0.001～0.100 mg/kg 范围，回收率为 91.2%～99.0%；

对硝基苯酚钠添加浓度在 0.005～0.100 mg/kg 范围，回收率为 99.3%～107.4%；

5-硝基邻甲氧基苯酚钠添加浓度在 0.005～0.100 mg/kg 范围，回收率为 74.0%～100.0%。

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、深圳进出口商品检验局和浙江农业大学负责起草。

本标准主要起草人庄无忌、潘坤永、陈忠明、谢丽琪、罗荣杰、李淑娟、储可铭。

主要参考文献：

Asahi Chemical MFG. CO. LTD. Japan. Residue Analysis of Atonik in Farm Products. 1986.

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

Method for determination of nitrophenol salt residues in vegetables for export

SN 0198—93

1 Scope and field of application

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

This standard is applicable to the determination of nitrophenol salt residues in tomatoes 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, specification, grade 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—1 000	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 be at least 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 of which is blended and then divided into two equal portions, each portion is placed in a clean container as test sample, which is sealed and labeled.

2.5 Storage of sample

The test samples should be stored at −18 ℃.

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

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

3 Method of determination

3.1 Principle

The sodium salts of nitrophenol are converted to the corresponding ester compouns of nitrophenol with acetic anhydride in alkaline solution. Resultants are extracted with petroleum ether, and diluted to a definite volume. The esterified derivatives are determined by GC with electron capture detector and quantified by using the external standard.

3.2 Reagents and materials

3.2.1 Acetone: A. R..

3.2.2 Phosphoric acid: A. R..

3.2.3 Petroleum ether (boiling range 60—90 ℃): A. R., redistilled.

3.2.4 Ethyl ether: A. R., redistilled.

3.2.5 Sodium carbonate: A. R..

3.2.6 Acetic anhydride: A. R..

3.2.7 Filter aid, e. g. Celite 545.

3.2.8 Standard sodium salts of ortho-nitrophenol, para-nitrophenol, and 5-nitroguaiacol: Purity $\geqslant 99\%$.

3.2.9 Distilled water of corresponding de-ionized water.

3.2.10 Nitrophenol salt standard stock solutions:

Accurately weigh an adequate amount of standard salts of ortho-nitrophenol, para-nitrophenol and 5-nitroguaiacol, dissolve them in distilled water and make up to a given volume with the concentration of each component as 3.5×10^{-5} g/mL in the mixed standard stock solution.

3.3 Apparatus and equipment

3.3.1 Gas chromatography equipped with electron capture detector.

3.3.2 High-speed blender.

3.3.3 Homogenizer.

3.3.4 Mechanical shaker.

3.3.5 Rotary vacuum evaporator.

3.3.6 Chromatographic column.

3.4 Procedures

3.4.1 Extraction and clean up

Weigh ca 40 g of the sample (accurate to 0. 1 g) into a 500 mL jar, homogenize with 70 mL acetone to extract for 5 min. Filter the homogenate with suction. Transfer the filter cake into the jar, re-extract twice with acetone (40 mL each time). Combine the filtrates of three times, and concentrate in the rotary vacuum evaporator (in a 40 ℃ water bath) to remove acetone. Let the aqueous phase pass through the celite 545 column and rinse the column with ca 1 mL distilled water. The effluent is collected in a 250 mL separatory funnel. Add 4 mL phosphoric acid and extract twice with petroleum ether (each 50 mL) and then once with 40 mL ethyl ether. Combine the organic extracts and extract successively with 30 mL, 20 mL, 20 mL of 0. 2 mol/L Na_2CO_3. After shaking let stand to allow the phases to separate for each extraction. Collect the aqueous phase of three extractions.

3.4.2 Derivatization

Transfer the above combined extracts of Na_2CO_3 solution into a 250 mL separatory funnel, add 2 mL acetic anhydride; Shake vigorously with frequent release of gas until bubbling has ceased. The derivatives are extracted with three portions petroleum ether, each 20 mL. Combine the extracts and make up to a definite volume for GC determination.

3.4.3 Preparation of standard working solution

Pipe 1 mL of the mixed standard stock solution into a separatory funnel containing 70 mL 0.2 mol/L Na_2CO_3 solution. Carry out derivatization and extraction according to 3.4.2 and dilute the concentration of this standard working solution to 1.5×10^{-7} g/mL for GC external standard. Prepare this solution just before use.

3.4.4 Determination

3.4.4.1 GC operating conditions

a. Column: Glass, 1 m×4 mm(id), packed with 15%(*m*/*m*)FFAP on Chromosorb 880 A DMCS (80—100 mesh);

b. Column temperature: 175 ℃;

c. Injection port temperature: 230 ℃;

d. Detector temperature: 250 ℃;

e. Carrier gas: Nitrogen, purity ≥99.99%, 55 mL/min.

3.4.4.2 GC determination

GC determination is performed by injecting in-between occasionally the sample solutions and the standard working solutions of equal volume. The responses of the components to be determined should be in the linear range of the detector. Under the above GC conditions, the retention times of the derivatives:

Of O-nitrophenol sodium salt is 1.85 min;

Of P-nitrophenol sodium salt is 2.80 min;

Of 5-nitroguaiacol sodium salt is 10.75 min。

3.4.5 Blank test

Perform the blank test with the same procedures as that described in the method of determination but without of addition of test sample.

3.4.6 Calculation and expression of results

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

$$X = \frac{h \cdot V_s \cdot V_0 \cdot c}{h_s \cdot V \cdot m}$$

Where

X—Residue content of a component of nitrophenol salts in the test sample, mg/kg;

h—Peak height of a component measured from the sample solution, mm;

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

V_0—Final volume of sample solution for GC determination, μL;

V—Volume of sample injected into GC, μL;

V_s—Volume of standard working solution injected into GC, μL;

m—Test sample weight, g;

c—Concentration of nitrophenol sodium in the standard working solution, μg/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

Ortho-nitrophenol(ONPNa)0.01 mg/kg;

Para-nitrophenol(PNPNa)0.02 mg/kg;

5-nitroguaiacol(5NGNa)0.01 mg/kg。

4.2 Recovery

According to the experimental data,for different fortifying levels,the recoveries are as follows:

Component of nitrophenol salts	Fortified(mg/kg)	Recovery(%)
Ortho-nitrophenol(ONPNa)	0.001—0.100	91.2—99.0
Para-nitrophenol(PNPNa)	0.005—0.100	99.3—107.4
5-nitroguaianol(5NGNa)	0.005—0.100	74.0—100.0

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 China Import and Export commodity Inspection Technology Institute, the Shenzhen Import and Export Commodity Inspection Bureau of the People's Republic of China and Zhejiang Agricultural University.

This standard was mainly drafted by Zhuang Wuji, Pan Kun yong, Chen Zhongming, Xie Liqi, Luo Rongjie, Li Shujuan, Chu Keming.

Reference:

Asahi Chemical MFG. CO. LTD. Japan. Residue Analysis of Atonik in Farm Products. 1986.

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

(京)新登字 023 号

SN 0198—93

中国标准出版社出版　中国标准出版社北京印刷厂印刷

1993 年 12 月第一版　1993 年 12 月第一次印刷　书号：155066・2-9159