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中华人民共和国进出口商品检验行业标准

SN/T 0348.1-95

出口茶叶中三氯杀螨醇残留量检验方法 气 相 色 谱 法

Method for the determination of dicofol residues
in tea for export—Gas chromatography

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1 主题内容与适用范围

本标准规定了出口茶叶中三氯杀螨醇残留量的抽样、制样和气相色谱测定方法。
本标准适用于出口茶叶中三氯杀螨醇残留量的检验。

2 抽样和制样

2.1 检验批

以不超过 2 000 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。

2.2 抽样数量

批量,件	最低抽样数,件
1~5	1
6~50	2
51~500	11
501~1 000	16
1 001~1 500	19
1 501~2 000	20

2.3 抽样方法

按 2.2 规定的抽样件数随机抽取,逐件开启。每件最少取 500 g 为原始样品。将所抽原始样品充分拌均(或用分样器分取)缩分出 500~1 000 g,装入清洁密封的样品筒内,加封后,标明标记,及时送实验室。

2.4 试样制备

将取回样品全部磨碎、通过 20 目筛,匀分成两份,装入洁净的容器内,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

用丙酮-正己烷提取茶叶中的三氯杀螨醇,经弗罗里硅土、酸性硅藻土混合柱净化,与氢氧化钾溶液进行碱解,转化为双-(对氯苯基)-甲酮(DBP)。用配有电子俘获检测器的气相色谱仪测定,内标法定量。

3.2 试剂和材料

- 3.2.1 正己烷:分析纯,重蒸馏,收集 67~69℃馏分。
- 3.2.2 丙酮:分析纯,重蒸馏,收集 55~57℃馏分。
- 3.2.3 二氯甲烷:分析纯,重蒸馏,收集 38~40℃馏分。
- 3.2.4 无水乙醇:优级纯。
- 3.2.5 弗罗里硅土:层析用,粒度 60~100 筛目。在 650℃灼烧 4 h,置于干燥器内备用。用前在 140℃烘箱中烘 2 h。
- 3.2.6 无水硫酸钠:分析纯,在 650℃灼烧 4 h,置于干燥器内备用。
- 3.2.7 酸性硅藻土:10 g 硅藻土(或 celite)545,加入 3 mL 发烟硫酸搅拌均匀。
- 3.2.8 氢氧化钾:分析纯。
- 3.2.9 氢氧化钾溶液:10 mol/L。称取 56.1 g 氢氧化钾(3.2.8),溶于 100 mL 蒸馏水中。
- 3.2.10 硫酸钠溶液:2%。称取 2 g 无水硫酸钠(3.2.6),溶于 100 mL 重蒸馏水中。
- 3.2.11 三氯杀螨醇标准品:纯度 $\geq 96.2\%$ 。
- 3.2.12 内标物标准品:艾氏剂,纯度 $\geq 99\%$ 。
- 3.2.13 三氯杀螨醇标准溶液:准确称取适量的三氯杀螨醇标准品,用正己烷配成浓度为 1.00 mg/mL 的标准储备液,根据需要再配成适当浓度的标准工作液。
- 3.2.14 内标物标准溶液:准确称取适量的艾氏剂标准品,用正己烷配成浓度为 1.00 mg/mL 的内标物标准储备液,根据需要再配成适当浓度的内标物标准工作液。

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和热式毛细管柱头进样器。
- 3.3.2 微量注射器:1 μ L,10 μ L。
- 3.3.3 多功能微量样品处理仪或相当的设备。
- 3.3.4 振荡器。
- 3.3.5 离心机:转速 5 000 r/min。
- 3.3.6 刻度试管:具磨口塞,10 mL。
- 3.3.7 净化柱:100 mm \times 6 mm(内径)玻璃柱。柱底部填约 0.5 cm 高脱脂棉[脱脂棉经正己烷-二氯甲烷(4+1)抽取 2 h],依次装入 1 cm 无水硫酸钠(3.2.6),4 cm 酸性硅藻土(3.2.7),2 cm 弗罗里硅土(3.2.5),1 cm 无水硫酸钠。用前经正己烷-二氯甲烷(4+1)5 mL 淋洗。

3.4 测定步骤

3.4.1 提取

称取试样 10 g(精确到 0.01 g)于 100 mL 具塞锥形瓶内,加丙酮-正己烷(1+4)混合液 40 mL,振荡 45 min,滤纸过滤,再用 50 mL 上述混合液分数次清洗锥形瓶、残渣和滤纸,滤液定量收集于 100 mL 容量瓶中,定容。准确吸取 10 mL 滤液于试管(3.3.6)中,在多功能微量样品处理仪中浓缩至约 1 mL,待净化。

3.4.2 净化

将上述浓缩液定量移入净化柱(3.3.7)中,用正己烷-二氯甲烷(4+1)10 mL 以 1 mL/min 的流速淋洗,收集淋洗液于试管中,在多功能微量样品处理仪中,浓缩至近干。

3.4.3 碱解

在上述试管中依次加入 1 mL 内标物溶液,0.5 mL 无水乙醇和 1 mL 10 mol/L 的氢氧化钾溶液,振荡 5 min,在 3 000 r/min 下离心 5 min,移取正己烷相于另一试管中。正己烷相用 1 mL 2%硫酸钠溶液洗涤两次,弃去水相。加入少量无水硫酸钠脱水,供气相色谱测定。

3.4.4 标准物碱解

取适用浓度的标准工作液,吹干,按 3.4.3 步骤进行碱解。

3.4.5 测定

3.4.5.1 色谱条件

- 色谱柱: LZ 农残-Ⅰ 石英毛细管柱, 25 m×0.53 mm(内径), 或相当的色谱柱;
- 色谱柱温度: 180℃;
- 进样口温度: 220℃;
- 检测器温度: 250℃;
- 载气、尾吹气: 氮气(纯度≥99.99%); 柱载气流量 2 mL/min, 尾吹气流量 30 mL/min;
- 进样方式: 柱头进样。

3.4.5.2 气相色谱测定

根据样液中三氯杀螨醇含量情况, 选定峰高相近的标准工作液。标准工作溶液和样液中三氯杀螨醇的碱解产物(DBP)的响应值均在仪器检测线性范围内, 对标准溶液和样液等体积参插进样测定。在上述色谱条件下, DBP 的保留时间约为 13 min。

3.4.6 空白试验。

除不加试样外, 按上述测定步骤进行。

3.4.7 结果计算和表述

用色谱数据处理机或按下列公式计算:

$$X = \frac{h \cdot c_s \cdot h_{n1} \cdot c_1}{h_s \cdot c_{n1} \cdot h_i \cdot c}$$

式中: X——试样中三氯杀螨醇含量, mg/kg;

h ——样液中 DBP 峰高, mm;

h_s ——标准工作液中 DBP 峰高, mm;

h_i ——样液中内标物峰高, mm;

h_{n1} ——标准工作液中内标物峰高, mm;

c ——样液中样品浓度, g/mL;

c_s ——标准工作液中三氯杀螨醇浓度, $\mu\text{g/mL}$;

c_1 ——样液中内标物浓度, $\mu\text{g/mL}$;

c_{n1} ——标准工作液中内标物浓度, $\mu\text{g/mL}$ 。

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 0.05 mg/kg。

4.2 回收率

回收率的实验数据: 三氯杀螨醇浓度在 0.05~3 mg/kg 范围内, 回收率为 78.1%~104.2%。

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安徽进出口商品检验局负责起草。

本标准主要起草人朱梦桐、王勇。

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

Method for the determination of dicofol residues SN/T 0348.1-95 in tea for export—Gas chromatography

1 Scope and field of application

This standard specifies the method of sampling, sample preparation and determination by gas chromatography of dicofol residues in tea for export.

This standard is applicable to the determination of dicofol residues in tea for export.

2 Sampling and sample preparation

2.1 Inspection lot

The quantity of an inspection lot should not be more than 2 000 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—5	1
6—50	2
51—500	11
501—1 000	16
1 001—1 500	19
1 501—2 000	20

2.3 Sampling procedure

A number of package 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 combined primary sample is fully mixed, reduced to 500—1 000 g, placed in a clean sample can, sealed, labeled and sent to laboratory in time.

2.4 Preparation of test sample

The mixed primary sample is crushed with a grinder or mortar until thoroughly crushed and wholly passed through a 20-mesh sieve, and then 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 sample should be stored below -18°C .

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 dicofol is extracted from the tea sample with acetone-hexane, and cleaned up on a column of florisil and acid siliceous earth mixture. Dicofol is converted with potassium hydroxide solution into p, p'-dichlorobenzophenone (DBP), which is determined by gas chromatography with electron capture detector, using internal standard.

3.2 Reagents and materials

3.2.1 n-Hexane; A. R., redistill and collect the distillate of 67—69°C.

3.2.2 Acetone; A. R., redistill and collect the distillate of 55—57°C.

3.2.3 Dichloromethane; A. R., redistill and collect the distillate of 38—40°C.

3.2.4 Alcohol, absolute; G. R.

3.2.5 Florisil; Used for chromatography, 60—100 mesh granule size, ignite at 650°C for 4 h, and store in a desiccator, then heat at 140°C for 2 h in an oven before use.

3.2.6 Anhydrous sodium sulfate; A. R., ignite at 650°C for 4 h, and keep in a desiccator.

3.2.7 Acid siliceous earth; Add 3 mL of fuming sulfuric acid to 10 g of siliceous earth or celite 545, and mix thoroughly.

3.2.8 Potassium hydroxide; A. R.

3.2.9 Potassium hydroxide solution; 10 mol/L. Weigh 56.1 g of potassium hydroxide (3.2.8) and dissolve it in 100 mL of redistilled water.

3.2.10 Sodium sulphate solution; 2%. Weigh 2 g of anhydrous sodium sulfate (3.2.6) and dissolve it in 100 mL redistilled water.

3.2.11 Dicofol standard; Purity $\geq 96.2\%$.

3.2.12 Internal standard; Aldrin, purity $\geq 99\%$.

3.2.13 Dicofol standard solution; Accurately weigh an adequate amount of dicofol standard, dissolve in n-hexane and prepare a solution of 1.00 mg/mL as the standard stock solution. According to the requirement, prepare a standard working solution of appropriate concentration.

3.2.14 Internal standard solution; Accurately weigh an adequate amount of aldrin standard, dissolve in n-hexane and prepare a solution of 1.00 mg/mL as the internal 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 and thermal type capillary on-column injector.

3.3.2 Micro syringe; 1 μ L, 10 μ L.

3.3.3 Multifunction sample treatment unit for microchemical method or equivalent.

3.3.4 Shaker.

3.3.5 Centrifuge; 5 000 r/min.

3.3.6 Graduated test tube; 10 mL, with ground stopper.

3.3.7 Column for cleanup; 100 mm \times 6 mm (id) glass column, pack with ca 0.5 cm absorbent cotton (extracted with hexane-dichloromethane (4+1) for 2 h) at the bottom of the column and fill in 1 cm of anhydrous sodium sulfate (3.2.6), 4 cm of acid siliceous earth (3.2.7), 2 cm of florisil (3.2.5) and 1 cm of anhydrous sodium sulfate in turn. Rinse the column with 5 mL of hexane-dichloromethane (4+1) before use.

3.4 Procedure

3.4.1 Extraction

Weigh 10 g of the test sample (accurate to 0.01 g) into a 100 mL conical flask with stopper. Add 40 mL of acetone-n-hexane (1+4) and shake for 45 min by a shaker. Filter the extract with a filter paper, rinse the conical flask and filter paper with 50 mL of acetone-n-hexane (4+1) in several portions and filter, collect the filtrates quantitatively in a 100 mL volumetric flask. Dilute to the mark. Pipet accurately 10 mL of the filtrate into a test tube (3.3.6), concentrate it to ca 1 mL in the multifunction sample treatment unit, and the solution is ready for cleanup.

3.4.2 Cleanup

Transfer quantitatively the above concentrated solution into the cleanup column (3.3.7). Add into the column 10 mL of n-hexane-dichloromethane (4+1), the flow rate is 1 mL/min. Collect the solution into a test tube, and concentrate to dryness in a multifunction sample treatment unit for microchemical method.

3.4.3 Alkaline hydrolysis

Accurately add 1 mL of internal standard solution, 0.5 mL of absolute alcohol and 1 mL of 10 mol/L potassium hydroxide solution into the above test tube. Shake the tube for 5 min and centrifugalize at 3 000 r/min for 5 min. Transfer the hexane layer into another tube. Wash the hexane layer two times, each with 1 mL of 2% sodium sulphate solution. Discard the water layer and dehydrate with a little anhydrous sodium sulfate. The solution is used for gas chromatographic determination.

3.4.4 Alkaline hydrolysis of the standard

Accurately pipet the standard working solution of suitable concentration into a tube and blow to dry. Then proceed with the alkaline hydrolysis as in 3.4.3.

3.4.5 Determination

3.4.5.1 GC operating condition

- Column: LZ pesticide- I, the fused silica capillary column, 25 m × 0.53 mm (id) or equivalent;
- Column temperature: 180°C;
- Injection port temperature: 220°C;
- Detector temperature: 250°C;
- Carrier gas and make-up gas: Nitrogen, purity ≥ 99.99%, flow rate of carrier gas 2 mL/min, flow rate of make-up gas 30 mL/min;
- Mode of injection: On-column injection.

3.4.5.2 GC determination

According to the approximate concentration of dicofol in the sample solution, select the standard working solution with similar peak height to that of sample solution. The responses of alkaline hydrolyzed product (DBP) of dicofol in the standard working solution and sample solution should be in the linear range of the instrumental detection. The standard working solution shall be randomly injected in-between the injections of the sample solution of equal volume. Under the above chromatographic condition, the retention time of dicofol is about 13 min.

3.4.6 Blank test

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

3.4.7 Calculation and expression of result

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

$$X = \frac{h \cdot c_s \cdot h_{si} \cdot c_i}{h_s \cdot c_{si} \cdot h_i \cdot c}$$

where

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

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

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

h_i —The peak height of internal standard in the sample solution, mm;

h_{si} —The peak height of internal standard in the standard working solution, mm;

c —The concentration of sample in the sample solution, g/mL;

c_s —The concentration of dicofol in the standard working solution, $\mu\text{g/mL}$;

c_i —The concentration of internal standard in the sample solution, $\mu\text{g/mL}$;

c_{si} —The concentration of internal standard in the standard working solution, $\mu\text{g/mL}$.

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 0.05 mg/kg.

4.2 Recovery

According to the experimental data, when the concentration of dicofol is in the range of 0.05—3.0 mg/kg, the recovery is 78.1%—104.2%.

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

This standard was mainly drafted by Zhu Mengxu, Wang Yong.

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