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中华人民共和国出入境检验检疫行业标准

SN/T 1594—2005

进出口茶叶中噻嗪酮残留量检验方法 气相色谱法

Inspection of buprofezin residue in tea for import and export—Gas chromatographic method

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前　言

本标准的附录A为资料性附录。

本标准由国家认证认可监督管理委员会提出并归口。

本标准起草单位：中华人民共和国浙江出入境检验检疫局。

本标准主要起草人：丁慧瑛、朱晓雨、谢文、章晓氢、朱青青。

本标准系首次发布的出入境检验检疫行业标准。

进出口茶叶中噻嗪酮残留量检验方法 气相色谱法

1 范围

本标准规定了进出口茶叶中噻嗪酮残留量检验的抽样、制样和气相色谱测定方法。

本标准适用于进出口茶叶中噻嗪酮残留量的检验。

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同一特征，如包装、标记、产地、规格、等级等。

2.2 抽样数量

抽样数量见表1。

表1 抽样数量

单位为件

批量	最低抽样数
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。每件中最少取500 g作为原始样品。将所抽原始样品充分拌匀(或用分样器分取)缩分出500 g～1 000 g，装入清洁密封的样品筒内，加封后，标明标记，及时送交实验室。

2.4 试样制备

将所取全部样品磨碎，通过孔径为0.85 mm筛(20目)，均分成两份，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

在抽样和制样的操作过程中，应防止样品污染或发生残留物含量的变化。试样应于室温下保存。

3 测定方法

3.1 方法提要

样品中的噻嗪酮残留用丙酮和水提取，再经正己烷反萃取，弗罗里硅土柱净化。用配有氮磷检测器的气相色谱仪测定，外标法定量。

3.2 试剂和材料

除另有规定外，所用试剂均为分析纯，水为蒸馏水。

3.2.1 乙醚。

3.2.2 正己烷。

3.2.3 丙酮。

3.2.4 氯化钠水溶液 150 g/L。

3.2.5 洗脱液：正己烷-乙醚(7+3)。

3.2.6 无水硫酸钠：650℃灼烧 4 h，在干燥器内冷却至室温，贮于密封瓶中备用。

3.2.7 弗罗里硅土：粒度 0.075 mm～0.15 mm(100 目～200 目)。650℃灼烧 4 h，使用前一天于 130℃活化 4 h，在干燥器内冷却至室温，加 1%的水脱活，备用。

3.2.8 脱脂棉。

3.2.9 噻嗪酮标准品：纯度大于 99%。

3.2.10 噻嗪酮标准储备溶液：称取 0.010 00 g 噻嗪酮标准品(3.2.9)，用正己烷溶解定容至 100 mL，此溶液浓度为 100 μg/mL。存放在 4℃的冰箱中。根据需要用正己烷稀释至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，配有氮磷检测器。

3.3.2 旋转蒸发器。

3.3.3 均质器。

3.3.4 无水硫酸钠柱：80 mm×40 mm(内径)筒型漏斗，底部垫约 5 mm 高脱脂棉，再装约 50 mm 高无水硫酸钠。

3.3.5 净化柱：200 mm×15 mm(内径)玻璃柱，底部垫约 5 mm 高脱脂棉和约 20 mm 高无水硫酸钠，10 g 弗罗里硅土，顶端加约 20 mm 高无水硫酸钠，使用前用 30 mL 正己烷淋洗。

3.4 测定步骤

3.4.1 提取

称取 5 g 试样(精确到 0.01 g)置于 100 mL 烧杯中，加入 15 mL 蒸馏水浸泡 2 h，加入 30 mL 丙酮，在均质器中均质 2 min。过滤至 50 mL 容量瓶中，用丙酮清洗残渣，合并滤液，并定容至 50 mL。移取 20.0 mL 滤液至预先装有 50 mL 氯化钠水溶液(3.2.4)和 25 mL 正己烷的 250 mL 分液漏斗中，剧烈振摇，静置分层。水相中再加入 25 mL 正己烷，重复操作，合并正己烷相，过无水硫酸钠柱(3.3.4)至浓缩瓶中，用旋转蒸发器在 45℃水浴减压浓缩至近干。

3.4.2 净化

浓缩瓶中残留物用 2 mL、2 mL 正己烷溶解洗涤 2 次，将溶液移入净化柱中(3.3.5)，用 100 mL 洗脱液(3.2.5)洗脱。收集全部洗脱液，用旋转蒸发器在 45℃水浴减压浓缩至近干，加入 2.0 mL 正己烷溶解，供气相色谱测定。

3.4.3 测定

3.4.3.1 色谱条件

进行测定色谱条件如下：

a) 色谱柱：石英毛细管柱，HP-Ultra2 25 m×0.32 mm(直径)×0.52 μm(膜厚)，固定相为：(5%)二苯基-(95%)二甲基硅氧烷共聚物，或相当者；

b) 载气和尾吹气：氮气(纯度大于 99.999%)，载气流量：5.0 mL/min，尾吹气流量：20 mL/min，空气流量：110 mL/min；氢气流量：3.5 mL/min；

c) 柱温：初始温度 70℃保持 1 min，以 25℃/min 升至 280℃，保持 8 min；

d) 进样口温度：250℃；

e) 检测器温度：300℃；

f) 开阀时间：1 min；

g) 进样方式：不分流进样；

h) 进样量：2 μL；

i) 铷盐珠的电压应调整至最佳状态。

3.4.3.2 色谱测定

根据样液中噻嗪酮含量的情况，选定峰面积相近的标准工作溶液。标准工作溶液和样液中噻嗪酮的响应值应在仪器检测的线性范围内。标准工作溶液和样液等体积穿插进样测定。在上述色谱条件下，噻嗪酮的保留时间约为 12.3 min。噻嗪酮标准品的气相色谱图参见附录 A 中图 A.1。

3.4.3.3 空白试验

除不加试样外，均按上述操作步骤进行。

3.4.3.4 结果计算和表述

计算结果需扣除空白值，用色谱数据处理机或按式(1)计算试样中噻嗪酮的残留含量：

$$X = \frac{A \times c \times V}{A_s \times m} \qquad \cdots\cdots(1)$$

式中：

X——试样中噻嗪酮的残留量，单位为毫克每千克(mg/kg)；

A——样液中噻嗪酮的峰面积，单位为平方毫米(m^2)；

A_s——标准工作液中噻嗪酮的峰面积，单位为平方毫米(m^2)；

c——标准工作液噻嗪酮的浓度，单位为微克每千克(μg/mL)；

V——样液最终定容体积，单位为毫升(mL)；

m——最终样液所代表的试样质量，单位为克(g)。

4 测定低限和回收率

4.1 测定低限

本方法的测定低限为 0.01 mg/kg。

4.2 回收率

噻嗪酮添加浓度在 0.01 mg/kg 时，回收率为 82%～100%；

噻嗪酮添加浓度在 0.02 mg/kg 时，回收率为 80%～100%；

噻嗪酮添加浓度在 0.2 mg/kg 时，回收率为 85%～100%。

附 录 A
（资料性附录）
标准品色谱图

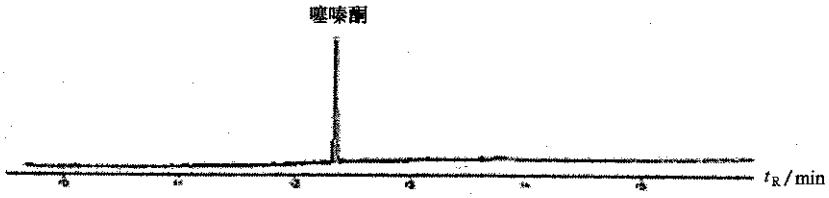

图 A.1 噻嗪酮标准品气相色谱图

Foreword

Annex A of this standard is an informative annex.

This standard was proposed by and is under the charged of The Certification and Accreditation Administration of the People's Republic of China.

This standard was drafted by Zhejiang Entry-Exit Inspection and Quarantine Bureau.

The standard was mainly drafted by Ding Huiying, Zhu Xiao yu, Xie Wen, Zhang Xiao Dong and Zhu Qing Qing.

This standard is a professional standard for entry-exit inspection and quarantine promulgated for the first time.

Inspection of buprofezin residue in tea for export and import ——Gas chromatographic method

1 Scope

This standard specifies the methods of sampling, sample reparation and determination by gas chromatography(GC) of buprofezin residue in tea for export and import

This standard is applicable to the determination of buprofezin residues in tea for export and import Sampling and sample preparation.

2 Sampling and sample preparation

2.1 Inspection lot

Each inspection lot should not be exceed 2 000 packages.

The characteristics of the cargo within the same inspection lot, such as packing, mark, origin, specification and grade etc. should be the same.

2.2 Quantity of sample taken

Quantity of sample taken(see Table 1.

Table 1

Number of packages in an 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

Draw a number of packages specified in 2.2 are taken at random and open the packages. The least sample weight as the primary sample from each package should be at 500 g. The combine primary sample is fully mixed, reduced to 500－1000 g, placed in a clean sample canister, 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 throughly crushed and wholly

passed through a 0.85 mm(id) sieve (20 mesh), 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

In the course of sampling and sample preparation, precautions must be taken to avoid contamination or any factors which may cause the change of residue content. The test samples should be stored at room temperature.

3 Method of determination

3.1 Principle

Buprofezin residue are extracted from the tea sample by acetone, and re-extracted by hexane, and cleaned up by passing through a florisil column. The solution is used for GC-NPD determination. External standard method is used for quantitative measurement.

3.2 Reagents and materials

Unless otherwise specified, all the reagent used should be analytical. grade, "water" is distilled water.

3.2.1 ethyl ether.

3.2.2 n-hexane.

3.2.3 acetone.

3.2.4 Sodium chloride solution 150 g/L.

3.2.5 Eluting solution: n-hexane-ethyl ether(7+3).

3.2.6 Anhydrous sodium sulfate: ignite for 4 h at 650℃, and keep in a tightly closed container.

3.2.7 Florisil: granule size 0.075 mm~0.15 mm (100 mesh~200 mesh), ignite for 4 h at 650℃, and keep in a tightly closed container, then heat for 4 h at 130℃ in an oven, cooling to room temperature in desiccator and add 1% of water before use.

3.2.8 Absorbent cotton.

3.2.9 Satandard of buprofezin: purity >99%.

3.2.10 Stock satandard solution of buprofezin: accurately weight 0.010 00 g Satandard(3.2.9), dissolve with n-hexane and quantitatively on 100 mL, the concentration of solution is 100 μg/mL. The solution shall be stored in 4℃ refrigeratory. According to the requirement, is prepared from the

stock standard solution by n-hexane and diluted to the required concentration.

3.3 Apparatus and equipment

3.3.1 Gas chromatography, equipped with Nitrogen phosphorus detector.

3.3.2 Rotary vacuum evaporator

3.3.3 High speed blender.

3.3.4 Column of anhydrous sodium sulfate: 80 mm × 40 mm(id) cylinder funnel, pack with ca 5 mm absorbent cotton at the bottom of the column and fill in 50 mm anhydrous sodium sulfate.

3.3.5 Column for clean-up: 200 mm × 15 mm(id) glass cloumn , pack with 5 mm absorbent cotton at the bottom of the column and fill in 20 mm anhydrous sodium sulfate, 10 g florisil, fill in 20 mm anhydrous sodium sulfate at top. Add 30 mL of n-hexane wash before use.

3.4 Procedure

3.4.1 Extraction

Weigh ca 5 g of the test sample(accurate to 0.01 g) into a 100 mL beaker. Add 15 rnL water and stand to 2 hours. Add 30 mL acetone , mixed 2 min in high speed blender, filter the extracted solution with a filter paper, collect the filtrates quantitatively in 50 mL volunetric flask with acetone. Transfer 20.0 mL filter solution into a 250 mL separatory funnel which is added 50 mL sodium chloride solution(3.2.4) and 25 mL n-hexane, shake vigorously for 2 min,let stand to separating, Add 25 mL n-hexane to water layer, repeat the operation again. Combine the n-hexane layers through column of anhydrous sodium sulfate(3.3.4) into a 100 mL round bottom flask to nearly dryness at rotary vacuum evaporator bleow 45℃.

3.4.2 Cleanup

Add 2 mL n-hexane and 2 mL n-hexane to dissolve the residue, transfer the above solution into column(3.3.5), eluted with 100 mL eluting solution(3.2.5). Collect all the eluted solution and rotary vacuum evaporate to dryness below 45℃.

Add exactly 2.0 mL n-hexane to dissolve the residue, the solution is ready for GC determination.

3.4.3 Determination

3.4.3.1 GC operating condition

a) Chromatographic column: Fused silica capillary column, Ultra 2 25 m × 0.32 mm (id) × 0.52 μm (film thickness),composition: 5% diphenyl and 95%dimethyl polysiloxane;

b) Carrier gas and make-up gas: Nitrogen(purity>99.999%), Flow rate of carrier gas: 5.0 mL/min, flow rate of make-up gas: 20 mL/min, flow rate of hydrogen: 3.5 mL/min, flow rate of air: 110 mL/min;

c) Temperature programme: 70℃ (keep 1 min), 25℃/min to 280℃ (keep 8 min);
d) Injection port temperature: 250℃;
e) Detector temperature: 300℃;
f) Purge valve: 1 min on;
g) Inection mode: Splitless;
h) Injection volume: 2 μL;
i) The voltage of the bead should be adjusted good condition.

3.4.3.2 GC determination

According to the concentrations of buprofezin, select the standard working solution with similar peak area to that of sample solution. The responses of buprofezin in the standard working solution and the sample solution should be within the linear range of the instrumental detection. The standard working solution should be randomly injected in between the injections of sample solution of equal volume. Under the above GC operating condition, the retention time of buprofezin is about 12.3 min. For chromatogram of the standard see Figure A.1 in annex A.

3.4.3.3 Blank test

The operation of the blank test is the same as the described in the method of determination, but with the omission of sample addition.

3.4.3.4 Calculation and expression of result

The blank value should be subtracted from the above result of calculation. calculation the content of buprofezin residue in the test sample by GC data processor or according to the formula (1):

$$X = \frac{A \times c \times V}{A_s \times m} \qquad \cdots\cdots(1)$$

Where:

X——the residue content of buprofezin in the test sample, mg/kg;
A——the peak area of buprofezin in sample solution, m^2;
A_s——the peak area of multi organophosphorus in standard working solution, m^2;
C——the concentration of multi organophosphorus in working solution, μg/mL;
V——the final volume of the sample solution, mL;
m——Mass of test sample, g.

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

buprofezin 0.01 mg/kg, the recovery is 82%～100%;
buprofezin 0.02 mg/kg, the recovery is 80%～100%;
buprofezin 0.2 mg/kg, the recovery is 85%～100%.

Annex A
(informative)
Chromatogram of the standard

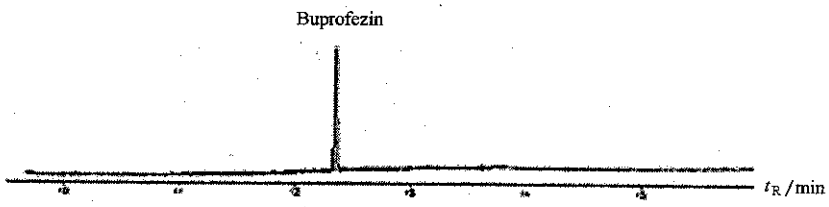

Fig. A. 1 Gas chromatogram of buprofezin

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