



中华人民共和国出入境检验检疫行业标准

SN/T 0292—2010
代替 SN 0292—1993

进出口粮谷中灭草松残留量检测方法 气相色谱法

Determination of bentazon residues in cereals
for import and export—GC method

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气相色谱法

SN/T 0292—2010

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前 言

本标准代替 SN 0292—1993《出口粮谷中灭草松残留量检验方法》。

本标准与 SN 0292—1993 相比主要变化如下：

- 修改了标准的名称；
- 删去了抽样部分；
- 修改了气相色谱条件；
- 增加了附录 A。

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：中华人民共和国黑龙江出入境检验检疫局。

本标准主要起草人：杨长志、康庆贺、马旭、汤敏顺。

本标准于 1993 年 12 月 28 日首次发布，本次为第一次修订。

进出口粮谷中灭草松残留量检测方法

气相色谱法

1 范围

本标准规定了大米中灭草松残留量的气相色谱检测方法。

本标准适用于大米中灭草松残留量的检测。

2 方法提要

试样中残留的灭草松先在酸性溶液中用丙酮提取,然后氮气吹去丙酮,加入硫酸钠溶液,再用正己烷提取。提取液经浓缩,甲基化,硅胶固相萃取柱净化。净化液用气相色谱附电子俘获检测器检测,外标法定量。

3 试剂和材料

除另有规定外,所有试剂均为分析纯,水为蒸馏水或相当纯度的水。

3.1 丙酮:色谱纯。

3.2 正己烷:色谱纯。

3.3 甲醇:色谱纯。

3.4 乙醇。

3.5 无水乙醚:色谱纯。

3.6 无水硫酸钠:在 650 °C 灼烧 4 h,贮于干燥器中备用。

3.7 盐酸。

3.8 氢氧化钾。

3.9 丙酮-正己烷(2+98,体积比)。

3.10 硫酸钠溶液:将 20 g 灼烧过的无水硫酸钠(3.6)溶于去离子水中,稀释至 1 L。

3.11 盐酸溶液:1 mol/L。取 90 mL 盐酸(3.7)溶于 1 000 mL 去离子水中。

3.12 氢氧化钾溶液:0.6 g/mL。称取 60 g 氢氧化钾(3.8)溶于 100 mL 去离子水中。

3.13 *N*-甲基-*N*-亚硝基-*p*-甲苯磺酰胺无水乙醚溶液:21.5 g/140 mL。称 21.5 g *N*-甲基-*N*-亚硝基-*p*-甲苯磺酰胺溶于 140 mL 无水乙醚(3.5)中。

3.14 重氮甲烷溶液:将装有 10 mL 氢氧化钾溶液(3.12)、35 mL 乙醇(3.4)及 10 mL 无水乙醚的混合液的双口蒸馏瓶,置于磁力搅拌器加热板上的水浴中,水温 70 °C。将搅拌子放入瓶中。接上滴液漏斗和高效冷凝器,冷凝器后串连两个 125 mL 的烧瓶作为接收瓶。在第二个烧瓶中放入 10 mL 无水乙醚,且使入口管插到无水乙醚液面以下。在冰浴中冷却两个接收瓶。边用磁力搅拌边通过滴液漏斗滴加 *N*-甲基-*N*-亚硝基-*p*-甲苯磺酰胺无水乙醚溶液(3.13),滴完全部溶液的时间控制在 20 min 以上。当蒸馏瓶内溶液呈淡黄色时停止蒸馏。将两个接收瓶中的液体合并,在 70 °C 水浴中再蒸馏,其馏出液作为重氮甲烷溶液。此液密闭置于冰箱中保存,保存期为 1 个月。

3.15 灭草松标准品:灭草松(bentazon), $C_{10}H_{12}N_2O_3S$,CAS No. 25057-89-0,纯度 $\geq 99.5\%$ 。

3.16 灭草松标准储备溶液:准确称取适量灭草松的标准品,用丙酮配成浓度为 100 $\mu\text{g/mL}$ 的标准储备液,标准储备液可在 -18 °C 条件下储存 6 个月。

3.17 灭草松标准工作溶液:根据需要再用丙酮稀释成适当浓度的标准工作液,标准工作液可在 0℃~4℃条件下储存 3 个月。

3.18 PT-硅胶固相萃取柱:(1 000 mg,6 mL)或相当者。

4 仪器和设备

4.1 气相色谱仪:配电子捕获检测器。

4.2 电子天平:感量 0.01 mg,0.01 g。

4.3 固相萃取装置。

4.4 粉碎机。

4.5 离心机:4 000 r/min。

4.6 旋涡混合器。

4.7 氮吹仪。

4.8 具塞玻璃离心管:20 mL、30 mL。

4.9 具磨口塞刻度试管:15 mL。

5 试样制备与保存

5.1 试样制备

取有代表性样品约 500 g,用粉碎机粉碎,过 0.21 mm 筛,混匀,装入洁净容器作为试样,密封并标明标记。

5.2 试样保存

试样于 4℃以下保存。在制样的操作过程中,应防止样品污染或发生残留物含量的变化。

6 测定步骤

6.1 提取

称取试样约 10 g(精确到 0.01 g)于 30 mL 离心管中,滴加 0.3 mL 盐酸溶液(3.11)和 10 mL 丙酮(3.1),在旋涡混合器上快速混匀 2 min,3 000 r/min 离心 3 min,用尖嘴吸管吸移丙酮层于 25 mL 容量瓶中。再用 10 mL、5 mL 丙酮重复提取两次,合并丙酮提取液于同一容量瓶中,并用丙酮定容。准确吸移 5 mL 丙酮提取液于 20 mL 离心管中,用氮气吹至 2 mL,然后加入 4 mL 硫酸钠溶液,滴加 0.3 mL 盐酸溶液(1 mol/L)和 3 mL 正己烷,在旋涡混合器上高速提取 2 min,离心 3 min(3 000 r/min),用尖嘴吸管吸移上层液于 15 mL 刻度试管中。残液再用 3 mL 正己烷提取一次。合并正己烷提取液于同一刻度试管中,在 45℃水浴中用氮气吹干。

6.2 甲基化

6.2.1 样液的甲基化

用 0.2 mL 甲醇溶解残渣,加入过量重氮甲烷溶液(约 0.3 mL),在 25℃水浴中反应 5 min,然后在 45℃水浴中用氮气吹干,用 3 mL 正己烷溶解反应产物。

6.2.2 标准溶液的甲基化

准确吸取适当浓度的标准工作液,在 45℃水浴中用氮气流下吹干,以下操作同 6.2.1。

6.2.3 净化

用 5 mL 丙酮预处理 PT-硅胶固相萃取柱,将甲基化后样液分 3 次(每次 1 mL)转移到 PT-硅胶固相萃取柱中,弃去流出液。用 10 mL 丙酮-正己烷(3.9)洗脱 PT-硅胶固相萃取柱,控制流速在 1 mL/min~2 mL/min,收集 10 mL 洗脱液。洗脱液在 45℃水浴中用氮气吹干后,用正己烷溶解并定容至 1 mL,供气相色谱分析用。

6.3 测定

6.3.1 气相色谱条件

- a) 色谱柱:Rtx-1701 石英毛细管柱,30 m×0.25 mm(内径)×0.25 μm 或相当者;
- b) 色谱柱温度:初始温度 180 ℃保持 3 min,以 15 ℃/min 升至 270 ℃,保持 3 min;
- c) 进样口温度:230 ℃;
- d) 检测器(ECD)温度:320 ℃;
- e) 载气:氮气,纯度大于 99.999%,恒流模式,1.2 mL/min;
- f) 进样量:1 μL;
- g) 进样方式:无分流进样,0.75 min 后开阀。

6.3.2 色谱检测

根据样液中被测物的含量情况,选定浓度与样液相近的标准工作溶液。标准工作溶液和样液中灭草松响应值均应在仪器检测线性范围内。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,灭草松甲酯的保留时间约为 7.24 min。标准品的色谱图参见附录 A 中图 A.1。

6.4 空白试验

除不加试样外,均按上述步骤进行。

7 结果计算和表达

用 GC 色谱数据处理机或按式(1)计算试样中灭草松残留含量,计算结果需扣除空白值。

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

式中:

X ——试样中灭草松残留量,单位为毫克每千克(mg/kg);

A ——样液中灭草松甲酯的峰面积;

c ——标准工作液中灭草松甲酯的浓度,单位为微克每毫升(μg/mL);

V ——样液最终定容体积,单位为毫升(mL);

A_s ——标准工作液中灭草松甲酯的峰面积;

m ——最终样液所代表的试样质量,单位为克(g)。

8 测定低限和回收率

8.1 测定低限

本方法的测定低限为 0.04 mg/kg。

8.2 回收率

样品的添加浓度及回收率的数据见表 1。

表 1 样品的添加浓度及回收率的数据

样 品	添加浓度/(mg/kg)	回收率/%
大米	0.04	82.7~91.9
	0.05	85.5~91.0
	0.5	80.4~94.8

附 录 A
(资料性附录)
灭草松甲酯标准品气相色谱图

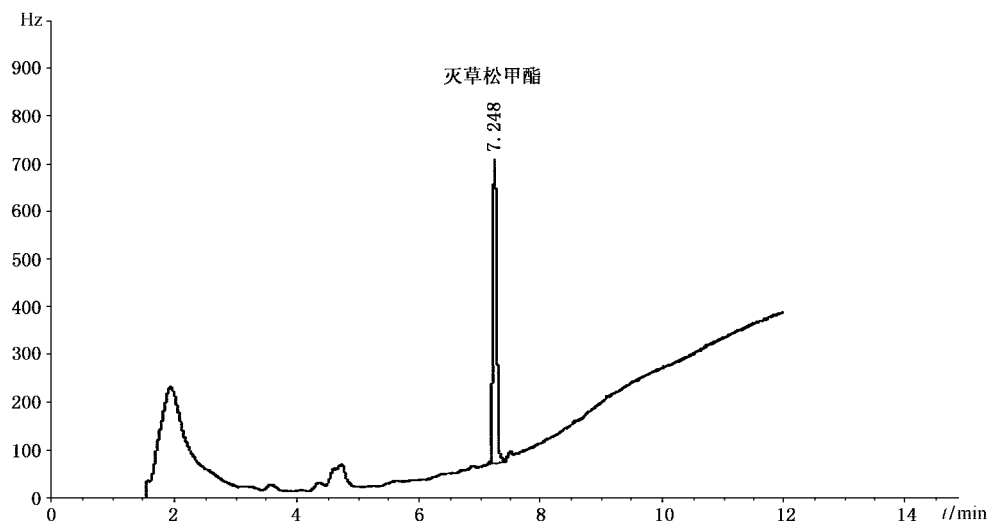


图 A.1 灭草松甲酯标准品气相色谱图

Foreword

This standard replace SN 0292—1993 “method for determination of bentazon residues in cereals for export”.

The main technique course and method for determination are not changed in this standard. Compare this standard with original standard SN 0292—1993,main change of this standard to be as follows:

- Revised the standard name;
- Sampling parts is cancelled;
- The GC operation conditions are modified;
- Annex A of this standard is added.

Annex A of this standard is an informative annex.

This standard was proposed by and is under the charge of National Regulatory Commission for Certification and Accreditation.

This standard was drafted by Heilongjiang Entry-Exit Inspection and Quarantine Bureau of the People's Republic of China.

This main drafters of this standard are Yang Changzhi,Kang Qinghe.

Original standard was approved on Dec. 28,1993 for the first time,amend the standard for the first time.

Determination of bentazon residues in cereals for import and export—GC method

1 Scope

This standard specifies the method of determination of bentazon residues in rice by GC.

This standard is applicable to the determination of bentazon residues in rice.

2 Principle

The bentazon residues in the test sample is extracted in acidic aqueous solution with acetone. After acetone is expelled in nitrogen evaporator, sodium sulfate solution is added to the extract, and then extract with *n*-hexane, the hexane extract is concentrated to dryness and the residue is methylated. The methylated residue is cleaned up by silica-gel cartridge and analysis by GC with electron capture detector, using external standard method.

3 Reagents and materials

Unless otherwise specified, all reagents are analytical pure, “water” is distilled water or equivalent purity water.

3.1 Acetone; LC grade.

3.2 *n*-hexane; LC grade.

3.3 Methanol; LC grade.

3.4 Ethanol.

3.5 Anhydrous ether; LC grade.

3.6 Anhydrous sodium sulfate; Ignite at 650 °C for 4 h and store in a desiccators.

3.7 Hydrochloric acid.

3.8 Potassium hydroxide.

- 3.9 Acetone-hexane solution (2+98, V/V).
- 3.10 Sodium sulfate solution; Dissolve 20 g of anhydrous sodium sulfate (3.6) in water and dilute to 1 L with deionized water.
- 3.11 Hydrochloric acid solution; 1 mol/L. Transfer 90 mL of hydrochloric acid (3.7) into a 1 000 mL Volumetric flask, dilute to volume with deionized water and mix well.
- 3.12 Potassium hydroxide solution; 0.6 g/mL. weigh 60 g of potassium hydroxide (3.8) into a 100 mL Volumetric flask, dilute to volume with deionized water and mix well.
- 3.13 *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide in anhydrous ether solution; 21.5 g/140 mL. weigh 21.5 g of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide into a 200 mL Volumetric flask, dilute to volume with anhydrous ether (3.5) and mix well.
- 3.14 Diazomethane solution; Add 35 mL of ethanol (3.4), 10 mL of anhydrous ether and 10 mL of potassium hydroxide solution (3.12) into a double-mouth distilling flask. Immerse the flask in a water bath (70 °C) on hot plate with a magnetic stirring device. Place a magnetic stirring bar in the flask. Attach the flask with a dropping funnel and an efficient condenser. Connect the end of the condenser with two 125 mL receiving conical flasks in series. Place 10 mL of anhydrous ether in the secondary receiving conical flask and let the tip of the inlet tube dip below the surface of anhydrous ether. Cool both receiving flasks in an ice bath. Add dropwise a *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide in anhydrous ether solution (3.13) through the dropping funnel while stirring the contents of the flask with the magnetic stirring bar. It should take more than 20 min to add all of the solution into the flask. When the solution in the distilling flask turns pale yellow, stop the distillation. Combine the contents of the two receiving flasks and redistill the combined distillate in a 70 °C water bath, the distillate is the diazomethane solution. The solution is kept in an air-tight container and preserved in a refrigerator not exceeding one month.
- 3.15 Bentazon standard; bentazon, $C_{10}H_{12}N_2O_3S$, CAS No. 25057-89-0, Purity $\geq 99.5\%$.
- 3.16 Bentazon standard stock solution; Accurately weigh an adequate amount of bentazon standard, dissolve in acetone and prepare a solution of 100 $\mu\text{g/mL}$ as the standard stock solution. The standard stock solution can be preserved in the refrigerator between $-18\text{ }^{\circ}\text{C}$ for 6 month.
- 3.17 Bentazon standard working solution; According to the requirement, dilute a standard working solution of appropriate concentration with acetone. The standard working solution can be preserved in the refrigerator between $0\text{ }^{\circ}\text{C} \sim 4\text{ }^{\circ}\text{C}$ for 3 month.
- 3.18 PT-silica-gel cartridge; 1 000 mg, 6 mL, or equivalent.

4 Apparatus and equipment

- 4.1 Gas chromatography equipped with ECD-detector.
- 4.2 Electronic balance; accurate to 0.1 mg and 0.01 g.
- 4.3 SPE-12G Column Processor.
- 4.4 Grinder.
- 4.5 Centrifuge; 4 000 r/min.
- 4.6 Vortex mixer.
- 4.7 Nitrogen evaporator.
- 4.8 Centrifuge tubes with ground stopper; 20 mL, 30 mL.
- 4.9 Graduated tubes with ground stopper; 15 mL.

5 Preparation and storage of sample

5.1 Preparation of test sample

Take approximately 500 g of representative sample, grind thoroughly with a grinder, let pass through a 0.21 mm mesh sieve and mix thoroughly. The sample is placed in clean containers as the test sample, which is sealed and labeled.

5.2 Storage of test sample

The test sample should be stored at 4 °C refrigerator. In the course of sampling and sample preparation, precautions should be taken to avoid contamination or any factors which may cause the change of residue content.

6 Procedure

6.1 Extraction

Weigh ca. 10 g (accurate to 0.01 g) of the test sample into a 30 mL centrifuge tube. Add 0.3 mL of hydrochloric acid solution (3.11) and 10 mL of acetone (3.1) and mix at high speed on a vortex

mixer for 2 min, and centrifuge at 3 000 r/min for 3 min. Transfer the acetone layer with capillary-tipped pipet into a 25 mL volumetric flask. The remaining solution is extracted twice more with 10 mL, 5 mL acetone. Combine the acetone extracts into the same volumetric, and dilute to volume with acetone. Accurately pipet 5 mL of the extract into a 20 mL centrifuge tube, blow to 2 mL in nitrogen evaporator below 45 °C, followed by addition of 4 mL of sodium sulfate solution (3.10). Add 0.3 mL of hydrochloric acid solution and 3 mL of *n*-hexane (3.2), extract on a mixer for 2 min and centrifuge (3 000 r/min) for 3 min. Pipet the supernate into a 15 mL graduated tube. Extract the remaining solution with 3 mL of *n*-hexane once more. Combine the *n*-hexane extracts. In the same graduated tube and evaporate to dryness in nitrogen evaporator below 45 °C.

6.2 Methylation

6.2.1 Methylation of the sample solution

Dissolve the residue in 0.2 mL of methanol (3.3), and add an excess of diazomethane solution (about 0.3 mL). Let the mixture react in a water bath at 25 °C for 5 min. The reaction mixture is evaporated to dryness in nitrogen evaporator below 45 °C. Dissolve the residue in 3 mL of *n*-hexane.

6.2.2 Methylation of the standard solution

Accurately pipet 1 mL of bentazon standard working solution is evaporated to dryness in nitrogen evaporator below 45 °C and proceed according to 6.2.1 finally, dilute exactly to volume (1 mL) with *n*-hexane.

6.2.3 Clean up

Pre-wash PT-silica-gel cartridge with 5 mL acetone. The methylated sample solution in *n*-hexane is transferred to PT-silica-gel cartridge in three portions (1 mL for each portion), and the *n*-hexane is discarded. PT-silica-gel cartridge is eluted at 1 mL/min~2 mL/min with 10 mL of acetone-hexane solution (3.9). Collect 10 mL of the eluate and concentrated to dryness in nitrogen evaporator below 45 °C, and then dilute exactly to volume (1 mL) with *n*-hexane for gas chromatographic analysis.

6.3 Determination

6.3.1 GC operation conditions

- a) Column: Rtx-1701 fused quartz capillary column, 30 m × 0.25 mm (i. d.), film thickness 0.25 μm, or the equivalent;
- b) Column temperature: Initial temperature 180 °C hold for 3 min, ramp at 15 °C/min to 270 °C, hold for 3 min;
- c) Inlets temperature: 230 °C;

- d) Detector temperature(ECD):320 ℃ ;
- e) Carrier gas:Nitrogen,purity $\geq$ 99.999% ,flow rate=1.2 mL/min;
- f) Injection volumn:1 μ L;
- g) Injection mode:splitless,purge after 0.75 min.

6.3.2 GC determination

According to the estimated approximate concentration of bentazon in the sample solution,select the standard working solution of similar concentration to that of sample solution. The responses of bentazon in the standard working solution and the sample solution should be in the linear range of the instrumental detection. The standard working solution should be injected randomly in-between the injections of the sample solution of equal volume. Under the above chromatographic condition, the retention time of *N*-methyl bentazon is ca. 7.24 min. For the chromatogram of bentazon standard, see figure A.1 in annex A.

6.4 Blank test

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

7 Calculation and expression of result

Calculate the content of bentazon residue in the test sample by GC data processor or using the followed formula (1). The blank value should be sutracted from the calculated result.

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

Where:

X—the residue content of bentazon in the test samples,mg/kg;

A—the peak area of *N*-methyl bentazon in the test sample solution;

c— the concentration of bentazon in the standard working solution, μ g/mL;

V—the final volume of sample solution,mL;

A_s —the peak area of *N*-methyl bentazonin in the standard working solution;

m —the corresponding mass of test sample in the final sample solution, g.

8 Limit of determination and recovery

8.1 Limit of determination

The limit of determination of this method is 0.04 mg/kg.

8.2 Recovery

Recovery and the fortifying concentration of bentazon in the test sample is shown in the table 1.

Table 1—Recovery and the fortifying concentration of bentazon in the test sample

Sample	Spike/(mg/kg)	Recovery/%
rice	0.04	82.7~91.9
	0.05	85.5~91.0
	0.5	80.4~94.8

Annex A
(informative)
Chromatogram of *N*-methyl bentazon standard

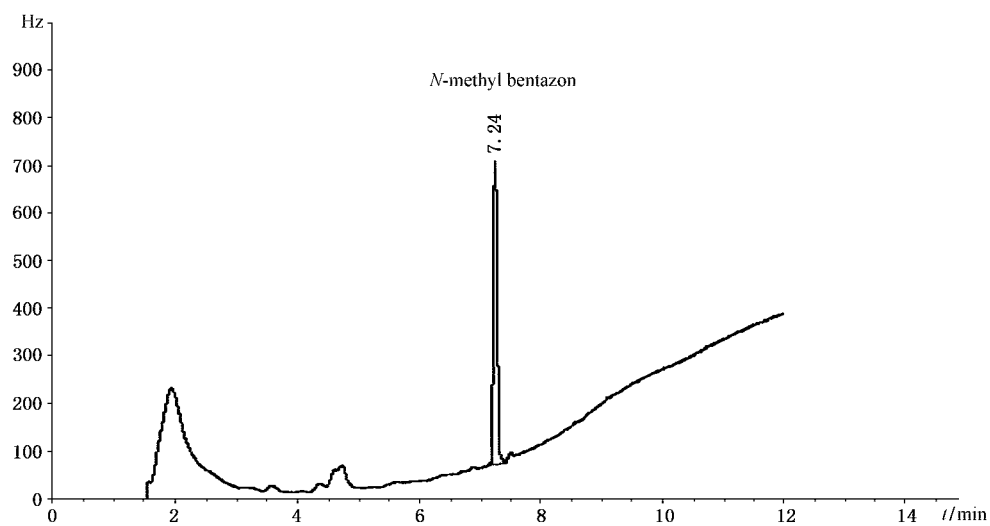
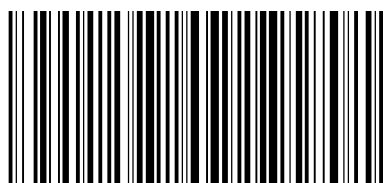


Figure A. 1—Gas Chromatogram of *N*-methyl bentazon standard



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