SN

中华人民共和国进出口商品检验行业标准

SN 0649—1997

出口粮谷中溴甲烷残留量检验方法

Method for the determination of methyl bromide residues in cereals for export

1997-08-15发布　　1998-01-01实施

中华人民共和国国家进出口商品检验局　发布

前　言

本标准是根据GB/T 1.1—1993《标准化工作导则　第1单元：标准的起草与表述规则　第1部分：标准编写的基本规定》及SN/T 0001—1995《出口商品中农药、兽药残留量及生物毒素检验方法标准编写的基本规定》的要求进行编写的。其中测定方法是参考国内外有关文献，经研究、改进和验证后而制定的。本标准同时制定了抽样和制样方法。

测定低限是根据国际上对粮谷中溴甲烷残留量的最高限量和测定方法的灵敏度而制定的。

本标准附录A、附录B为提示的附录。

本标准由中华人民共和国国家进出口商品检验局提出并归口。

本标准由中华人民共和国辽宁进出口商品检验局负责起草。

本标准主要起草人：宋文斌、杨鑫、张华一。

本标准系首次发布的行业标准。

中华人民共和国进出口商品检验行业标准

出口粮谷中溴甲烷残留量检验方法

SN 0649—1997

Method for the determination of methyl bromide residues in cereals for export

1 范围

本标准规定了出口粮谷中溴甲烷残留量检验的抽样、制样和气相色谱测定方法。

本标准适用于出口玉米中溴甲烷残留量的检验。

2 抽样和制样

2.1 检验批

散积玉米以不超过 200 t 为一检验批；袋装玉米(每袋约 90 kg)以约 2 200 袋为一检验批。

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

2.2.1 袋装货品

按式(1)计算抽样袋数：

$$a = \sqrt{N} \qquad \cdots\cdots(1)$$

式中：N ——全批袋数；

a ——抽样袋数。

注：a 值取整数，小数部分向前进位为整数。

2.2.2 散积货品

货堆高度不超过 2 m。按货堆面积划区设点。以 50 m^2 为一个取样区，每区设中心及四角(距边线 1 m处)5 个点。每增加一个取样区，增设 3 个点。

2.3 抽样工具

2.3.1 金属双套管取样器：全长分 1 m、2 m(均包括手柄)两种。内、外管同部位分段开几个槽口，每个槽口长 15～20 cm，口宽 2.0～2.5 cm，内管的内径为 2.5～3.0 cm；取样器的探头长约 7 cm。

2.3.2 取样铲。

2.3.3 分样板。

2.3.4 分样布或适用铺垫物。

2.3.5 样品筒(袋)：可密封。

2.4 抽样方法

2.4.1 袋装抽样

2.4.1.1 倒包抽样：从堆垛的各部位随机抽取 2.2.1 规定的应抽样袋数的 10%(每批一般不少于 3 袋)。将袋口缝线全部拆开，平置于分样布或其他洁净的铺垫物上，双手紧握袋底两角，提起约成 45°倾角，倒拖约 1 m，使袋内货物全部倒出。查看袋内和袋间品质是否均匀，确认情况正常后，用取样铲随机在各部位抽取样品，并立即将样品倒入盛样器内。每袋抽取样品的量应基本一致。

中华人民共和国国家进出口商品检验局 1997-08-15 批准　　1998-01-01 实施

2.4.1.2 袋内抽样：按 2.2.1 规定的应抽样袋数(扣除倒包抽样袋数)，在垛堆四周上、中、下各层以曲线形走向随机抽取，用 1 m 长的金属双套管取样器(2.3.1)关闭槽口，从每袋一角依斜对角方向插入袋内，然后旋转内管，开启槽口，待样品流满内管后，再旋转内管以关闭槽口。抽出取样器，立即将样品倒入盛样器内。每袋所取样品的量应与 2.4.1.1 基本一致。

每批所抽取的样品总量应不少于 4 kg。

2.4.2 散积抽样

按 2.2.2 规定的取样点，逐点抽取样品。将取样器(2.3.1)槽口关闭，以倾斜 45°角度插入货堆至相应深度，旋转取样器内管以开启槽口，待样品流满内管后，再旋转内管以关闭槽口，抽出取样器，立即将样品倒入盛样器内。从各点所抽取的样品量应基本一致。

每批所抽取的样品总量应不少于 4 kg。

2.4.3 大样缩分

袋装样品：合并从袋内和倒包抽取全部样品，倒于分样布上，用分样板按四分法缩分样品至不少于 2 kg，盛于盛样器内，加封后标明标记，并及时送交实验室。

散积样品：将抽取的全部样品，倒于分样布上，以下按上述袋装样品方法进行。

2.5 试样制备

将样品按四分法缩分至 1 kg，混匀，均分成两份，立即装入清洁容器内，作为试样。密封并标明标记。

2.6 试样保存

试样于−18℃以下避光保存。

注

1 缩分样品时，操作尽量要快，以防止溴甲烷的散失。

2 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

试样中的溴甲烷残留于回流提取器中，在氮气流下与硫酸溶液一起加热而被蒸发出，吸收于冰盐浴中的异辛烷中。异辛烷溶液经定容后，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

除另有规定外，所用试剂均为分析纯，水为蒸馏水。

3.2.1 异辛烷：在 1 000 mL 烧瓶内加入 500 mL 异辛烷，再加入金属钠片 5～10 g，接上磨口冷凝器，回流 6～8 h。然后用全玻璃蒸馏装置蒸馏，收集 97.5～99.5℃之间的馏分。

3.2.2 硫酸溶液：0.05 mol/L。

3.2.3 蒸馏水：用前煮沸 20 min，冷却备用。

3.2.4 无水硫酸钠：650℃灼烧 4 h，冷却后过筛，取 10～20 目颗粒，储于密闭容器中，备用。

3.2.5 溴甲烷标准品：纯度≥99%，密度 ρ 约 1.730 g/mL(0℃时)。

3.2.6 溴甲烷标准溶液：准确称取适量的溴甲烷标准品，用异辛烷配成浓度为 1.00 mg/mL 的标准储备溶液。根据需要再以异辛烷稀释成适用浓度的标准工作溶液。

3.3 仪器和设备

3.3.1 气相色谱仪：配有电子俘获检测器。

3.3.2 酸回流提取器：见附录 B 中图 B1。

3.3.3 容量瓶：25 mL。

3.3.4 电热套：调温型，500 mL，200 W。

3.3.5 全玻璃蒸馏装置。

3.3.6 气体流量计。

3.3.7 冰盐浴。

3.3.8 恒温水浴循环器。

3.4 测定步骤

3.4.1 提取

如附录B中图B1安装好酸回流提取装置。干燥管下部垫少许玻璃棉，装入10 g左右无水硫酸钠。上口用2 mm(内径)聚乙烯管联通到通气管，通气管内加入6～7 cm高的无水硫酸钠。通气管插入25 mL预先装好20 mL异辛烷的容量瓶中，埋入冰盐浴中冷却。冷凝器接到恒温水浴循环器，水浴温度为56～59℃。接通后使冷凝水保持恒温。移开冷凝器，称取试样50.0 g(精确至0.1 g)于提取器的烧瓶中，并同时加入200 mL硫酸溶液，混匀后迅速联接好冷凝器。通入氮气，调整流量为20～30 mL/min，缓缓加热到微沸(约20～30 min)，保持微沸通气2 h。加热完毕，关闭氮气流，将通气管抽离吸收液液面，用少量异辛烷多次冲洗通气管内外。取出容量瓶，待容量瓶温度平衡到室温后，定容，溶液供气相色谱分析。

注

1 通气管下口不宜多塞玻璃棉，以硫酸钠不落出为度，否则易发生通气堵塞。

2 冷凝器中水温不能超过60℃，否则水汽带出过多，造成通气管内结冰。

3 因溴甲烷极易挥发，测定前试样应冷冻后再称量。

3.4.2 测定

3.4.2.1 色谱条件

a) 色谱柱：玻璃柱，1.5 m×3.2 mm(内径)，填充物为10%(m/m)DC-200涂于Chromosorb W AW-DMCS(60～80目)；

b) 色谱柱温度：70℃；

c) 进样口温度：150℃；

d) 检测器温度：150℃；

e) 载气：氮气，纯度≥99.99%，20 mL/min。

3.4.2.2 色谱测定

根据样液中溴甲烷含量情况，选定峰高相近的标准工作溶液。标准工作溶液和样液中溴甲烷响应值均应在仪器检测线性范围内，对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，溴甲烷保留时间约为1.0 min。溴甲烷标准品的色谱图见附录A中图A1。

3.4.3 空白试验

除不加试样外，按上述测定步骤进行。

3.4.4 结果计算和表述

用色谱数据处理机或按式(2)计算：

$$X = \frac{h \cdot c \cdot V}{h_s \cdot m} \qquad \cdots\cdots(2)$$

式中：X——试样中溴甲烷残留含量，mg/kg；

h——样液中溴甲烷的峰高，mm；

h_s——标准工作液中溴甲烷的峰高，mm；

c——标准工作液中溴甲烷的浓度，μg/mL；

V——样液最终定容体积，mL；

m——称取试样量，g。

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 0.02 mg/kg。

4.2 回收率

玉米中溴甲烷添加浓度及其回收率的实验数据：

在 0.02 mg/kg 时，回收率为 82.50%；

在 0.10 mg/kg 时，回收率为 90.90%；

在 0.50 mg/kg 时，回收率为 92.36%。

附 录 A
（提示的附录）
标准品色谱图

图 A1 溴甲烷标准品色谱图

附 录 B
（提示的附录）
回流提取器

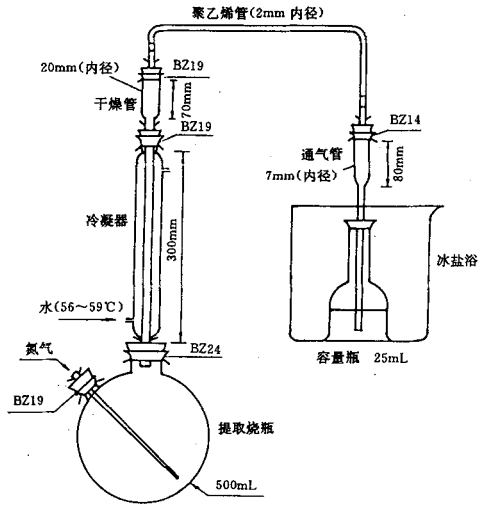

图 B1 酸回流提取器装置图

Foreword

This standard was drafted in accordance with the requirements of GB/T 1.1—1993 "Directives for the work of standardization—Unit 1:Drafting and presentation of standards—Part 1:General rules for drafting standards" and SN/T 0001—1995 "General rules for drafting the standard methods for the determination of pesticide, veterinary drug residues and biotoxins in commodities for export". The method of determination of this standard was drafted by referring to the relevant domestic and foreign literatures through research, modification and verification. In addition, the methods of sampling and sample preparation are also specified in this standard.

The limit of determination in this standard is defined on the basis of the current international maximum limits for methyl bromide residues in cereals and the sensitivity of the method.

Annex A and B of this standard are informative annexes.

This standard was proposed by and is under the charge of the State Administration of Import and Export Commodity Inspection of the People's Republic of China.

This standard was drafted by Liaoning Import and Export Commodity Inspection Bureau of the People's Republic of China.

The main drafters of this standard are Song Wenbin, Yang Xin, Chang Huayi.

This standard is a professional standard promulgated for the first time.

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

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

SN 0649—1997

Method for the determination of methyl bromide residues in cereals for export

1 Scope

This standard specifies the methods of sampling, sample preparation and determination of methyl bromide residues by gas chromatography in cereals for export.

This standard is applicable to the determination of methyl bromide residues in maize for export.

2 Sampling and sample preparation

2.1 Inspection lot

For the cargo in bulk, each inspection lot should not exceed 200 t, for the cargo in bags (ca 90 kg/bag), each inspection lot shall be about 2 200 bags.

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

2.2.1 Cargo in bags

Calculate the number of bags to be taken by formula(1):

$$a = \sqrt{N} \qquad \cdots\cdots(1)$$

where

a—number of bags to be taken;

N —tatal number of bags in a lot.

Note: if value a is with decimal, round off the decimal part, which is added as unity to the integral part of a.

2.2.2 Cargo in bulk

The height of the cargo pile should not exceed 2 m. Set up areas and spots for sampling on the pile surface, 50 m^2 is considered as an area in which 5 spots shall be fixed, one in the center and four at the four corners (1 m from the margins) of the area. For an additional area, three more sampling spots should be fixed.

2.3 Sampling tools

2.3.1 Metallic double-casing sampler: Length 1 m and 2 m (both including handle) with some slots on different sections and respectively at the same heights for both inner and outer casings; length of slots: 15—20 cm; width of the slot: 2.0—2.5 cm; inside diameter of the inner casing: 2.5—3.0 cm; probe length of the sampler: ca 7 cm.

2.3.2 Sampling shovel.

2.3.3 Plate for quartering.

Approved by the State Administration of Import and Export Commodity Inspection of the People's Republic of China on Aug. 15, 1997

Implemented from Jan. 1, 1998

2.3.4 Cloth(or other suitable materials)sheet:For sample dividing(quartering).

2.3.5 Sample container:Can or bag,which can be sealed.

2.4 Sampling procedure

2.4.1 For cargo in bags

2.4.1.1 Sampling by emptying out:Draw 10 percent of the number of bags specified in 2.2.1(not less than 3 bags)at any part of the pile at random. Unseam and open the bag,and lay it on a clean cloth sheet(or other clean sheet). Grasp tight two corners of the bag bottom and raise up to an angle of 45°, tug backword for ca 1 m until all content of the bag is emptied out. Check whether the quality of the goods is uniform within and between the bags. After confirming the goods are in normal condition, scoop up the sample from different parts of the out-poured content with a shovel at random,and place in a sample container promptly. The quantity of sample drawn from each bag should be basically the same.

2.4.1.2 Sampling from inside the bags:Draw the samples from the number of the bags specified in 2.2.1(by deducting the number of the bags drawn in 2.4.1.1) as follows:Along the sine wave of the pile,draw the samples from the bags of the upper,middle and lower parts around the pile at random. Insert the sampler(2.3.1,length 1 m),the slots should be closed while inserting diagonally into each bag. Turn the inner casing to open the slots so that the sample may fill up the inner tube. Again turn the inner casing to close the slots and draw out the sampler. Promptly pour the sample into a sample container. The quantity of the sample drawn from each bag should be basically the same as in 2.4.1.1.

The total weight of the gross sample of each lot should be not less than 4 kg.

2.4.2 Sampling from the cargo in bulk

Insert the sampler(2.3.1)successively into the pile at the spots specified in 2.2.2 to appropriate depth at 45℃(the slots should be closed while inserting in). Turn the inner casing to open the slots so that the sample may fill up the inner tube. Again turn the inner casing to close the slots and draw out the sampler. Promptly pour the sample into a sample container. The quantity of the sample drawn from all the spots shall be basically the same.

The total weight of the sample of each lot should be not less than 4 kg.

2.4.3 Reduction of gross sample

For cargo in bags:Pour all the samples(from both 2.4.1.1 and 2.4.1.2)on a clean sheet,reduce to not less than 2 kg with a plate by quartering. Place in a sample container,seal,label and send to the laboratory in time.

For cargo in bulk:Pour all the samples on a clean sheet and proceed as for cargo in bags described above.

2.5 Preparation of test sample

Reduce the sample to ca 1 kg by quartering,mix thoroughly and divide into two equal portions. Place in clean containers as the test samples,seal and label.

2.6 Storage of test sample

The test samples should be stored below −18℃ and kept away from light.

Note

1 Sample reduction operation must be conducted as quickly as possible to avoid the loss of methyl bromide.

2 In the course of sampling and sample preparation,precautions must be taken to avoid contamination or any factors that may cause the change of residue content.

3 Method of dedermination

3.1 Principle

The methyl bromide residues in the test sample are evaporated under a stream of nitrogen by heating with sulfuric acid solution in a reflux extractor and absorbed in *iso*-octane, which is cooled in an ice-salt bath. After diluting to a definite volume with *iso*-octane, the solution is analyzed by GC with electron capture detector, using external standard method.

3.2 Reagents and materials

Unless otherwise specified, all reagents should be analytically pure, "water" is distilled water.

3.2.1 *iso*-Octane: Add 500 mL of *iso*-octane and 5—10 g of metallic sodium flakes into a 1 000 mL flask. Connect the flask with the condenser and reflux for 6—8 h. The reagent is then distilled with an all-glass distilling apparatus and the fractions of 97.5—99.5℃ are collected.

3.2.2 Sulfuric acid solution: 0.05 mol/L.

3.2.3 Distilled water: Before use, the distilled water is boiled for 20 min and cooled down.

3.2.4 Anhydrous sodium sulfate: 10—20 mesh. Ignite at 650℃ for 4 h, after cooling, let pass through a 10—20 mesh sieve, and keep in a tightly closed container .

3.2.5 Methyl bromide standard: Purity≥99.9%, density ρ ca 1.730 g/mL (at 0℃).

3.2.6 Methyl bromide standard solution: Accurately weigh a suitable amount of methyl bromide standard and dissove in *iso*-octane to prepare a solution of 1.00 mg/mL in concentration as the standard stock solution. According to the requirement, prepare a standard working solution of appropriate concentration by diluting the stock solution with *iso*-octane.

3.3 Apparatus and equipment

3.3.1 Gas chromatagraph: Equipped with an electron capture detector (ECD).

3.3.2 Acid reflux extractor: See fig. B1 in annex B.

3.3.3 Volumetric flask: 25 mL.

3.3.4 Electrothermal oven: With adjustable temperature, 500 mL, 200 W.

3.3.5 All-glass distilling apparatus.

3.3.6 Gas flowmeter.

3.3.7 Ice-salt bath.

3.3.8 Constant temperature cycle water-bath

3.4 Procedure

3.4.1 Exraction

The acid reflux extractor is installed as fig. B1 in annex B. A little glass-wool is placed at the bottom of dry-tube, then add ca 10 g of anhydrous sodium sulfate into the tube. Connect the dry-tube and the gas-tube with polyethylene tube of 2 mm (id) and add 6—7 cm height of anhydrous sodium sulfate in the gas-tube. Pour 20 mL of *iso*-octane into the volumetric flask, and insert the gas-tube into the volumetric flask, which is placed in an ice-salt bath, Connect the condenser and the constant temperature cycle water-bath in place. The temperature of the water-bath is controlled at 56—59℃. Transfer quickly the well-mixed 50.0 g (accurate to 0.1 g) of test sample and 200 mL of sulfuric acid solution into the extracting flask. Connect the condenser promptly, then pass in a stream of nitrogen (flow rate: 20—30 mL/min). Heat slowly the flask on an electrothermal oven to gentle boilling (ca 20—30 min), with the nitrogen streams still passing through for 2 h. Close the nitrogen current and stop heating. Take off the gas-tube from the volumetric flask. Rinse the gas tube several times with a few millilitres

of *iso*-octane. Take off the volumetric flask from the ice-bath. Let stand for temperature equilibrium, then exactly diluted to the mark with *iso*-octane. The solution is used for chromatographic determination.

Note

1 A little glass wool should be placed at the lower end of the gas-tube, to keep Na_2SO_4 in the tube, but not to block the gas passage.

2 The temperature of water-bath should be controlled≤60℃ for preventing excess steam to be distilled out.

3 Before weighing, the test sample should be frozen to avoid the loss of methyl bromide due to its volalility.

3.4.2 Determination

3.4.2.1 GC operating condition

a) Column: Glass, 1.5 m×3.2 mm(id), packed with 10%(*m*/*m*)DC-200 on•Chromosorb W AW-DMCS(60—80 mesh);

b) Column temperature: 70℃;

c) Injection port temperature: 150℃;

d) Detector temperature: 150℃;

e) Nitrogen: Purith≥99.99%, 20 mL/min.

3.4.2.2 GC determination

According to the approximate concentration of methyl bromide in the sample solution, select the standard working solution with similar peak height to that of sample solution. The responses of methyl bromide in the standard working solution and sample solution should be in the linear range of the instrumental detection. The standard working sodution should be injected randomly in-between the injections of the sample solution of equal volume. Under the above mentioned chomatographic condition, the retention time of methyl bromide is about 1.0 min. For chromatogram of methyl bromide standard, see fig. A1 in annex A.

3.4.3 Blank test

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

3.4.4 Calculation and expression of result

The calculation of result is carried out by GC data processor or according to formula(2):

$$X = \frac{h \cdot c \cdot V}{h_s \cdot m} \qquad \cdots\cdots(2)$$

where

X—the residue content of methyl bromide in test sample, mg/kg;

h—the peak height of methyl bromide in the sample solution, mm;

h_s—the peak height of methyl bromide in the standard working solution, mm;

c—the concentration of methyl bromide in the standard working solution, μg/mL;

V—the final volume of sample solution, mL;

m—the mass of the test sample, g.

Note: The blank vulue 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 0.02 mg/kg.

4.2 Recovery

According to the experimental data, the fortifying concentrations of methyl bromide in maize and its corresponding recoveries are:

0.02 mg/kg, the recovery 82.50%;

0.10 mg/kg, the recovery 90.90%;

0.50 mg/kg, the recovery 92.36%.

Annex A

(informative)

Chromatogram of the standard

Fig. A1 Chromatogram of methyl bromide standard

Annex B
(informative)
Reflux extractor

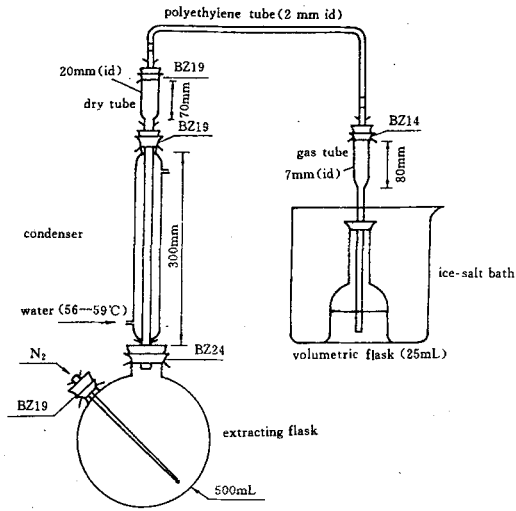

Fig. B1 Acid reflux extractor