SN

中华人民共和国进出口商品检验行业标准

SN 0711—1997

出口茶叶中代森锌类农药总残留量检验方法

Method for the determination of total residues of ethylene bisdithiocarbamate pesticides in tea for export

1997-12-01发布　　1998-04-01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》的要求而进行编写的。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茶叶中代森锌类农药总残留量的最高限量和测定方法的灵敏度而制定的。

本标准的附录A是标准的附录。

本标准的附录B是提示的附录。

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河南进出口商品检验局负责起草。

本标准主要起草人：杨冀州、刘亚风、杜爱荣、刘朝辉、梁稚鸿。

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

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1 范围

本标准规定了出口茶叶中代森锌类农药总残留量检验的抽样、制样和气相色谱测定方法。

本标准适用于出口茶叶中代森锌、代森锰、代森锰锌、代森联等农药的总残留量的检验。

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、规格和等级等。

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	17
1 501～2 000	18

2.3 抽样工具

2.3.1 取样勺。

2.3.2 分样布：塑料布。

2.3.3 分样板。

2.3.4 盛样器：筒或塑料袋，可密封。

2.4 抽样方法

按 2.2 规定的抽样件数从货品堆装的不同部位随机抽取样箱，逐件开启，将箱内茶叶全部倒于塑料布上，用取样铲在各部位抽取茶样，每件抽取的量约 500 g，作为一原始样。混合原始样品的总量不少于 2 kg。将所取的全部原始样品充分拌匀，用四分法缩分出约 500 g，立即装入清洁、干燥的样品筒内，密封，并标明标记，及时送实验室。

2.5 试样制备

将取回的样品全部磨碎，使通过 20 目筛。混匀，均分成两份，分别装入洁净容器内，作为试样。密封，并标明标记。

中华人民共和国国家进出口商品检验局 1997-12-01 批准　　1998-04-01 实施

2.6 试样保存

将试样于-5℃以下避光保存。

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

试样中残留的代森锌、代森锰、代森锰锌、代森联等乙撑双二硫代氨基甲酸盐类农药在密闭容器中被酸分解，定量释放出二硫化碳，用配有电子俘获检测器的气相色谱仪进行分析，外标法定量。以二硫化碳量表示这类农药的总残留量。

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 浓盐酸：密度(ρ)约 1.18 g/mL。

3.2.2 氯化亚锡：$SnCl_2 \cdot 2H_2O$。

3.2.3 正己烷：用全玻璃装置重蒸馏。

3.2.4 二硫化碳标准品：纯度≥99%。

3.2.5 氯化亚锡溶液：溶解 15 g 氯化亚锡(3.2.2)于 333 mL 浓盐酸中，用水稀释至 1 L。

3.2.6 二硫化碳标准溶液：准确称取适量的二硫化碳，用正己烷稀释成浓度为 1.0 mg/mL 的标准储备液。根据需要，再用正己烷配成适当浓度的标准工作溶液。

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 顶空瓶：250 mL。

3.3.3 气密性注射器：250 μL。

3.3.4 恒温水浴。

3.4 测定步骤

3.4.1 试样顶空瓶的制备

称取 10.0 g 试样，置于 250 mL 顶空瓶中。加入 80 mL 氯化亚锡溶液，立即封闭瓶口，置于 70℃恒温水浴中加热 2 h，期间每隔 30 min 振摇一次。取出，冷至室温，供气相色谱测定。

3.4.2 标准顶空瓶的制备

用 10 mL 水代替试样，封闭瓶口前加入适当体积(V)的二硫化碳标准工作液，按 3.4.1 所述进行操作。

3.4.3 测定

3.4.3.1 气相色谱条件

a) 色谱柱：玻璃填充柱，1.2 m×2 mm(内径)，填充物为 TENAX(60～80 目)；

b) 载气：氮气，纯度≥99.99%，40 mL/min；

c) 色谱柱温度：80℃；

d) 进样口温度：150℃；

e) 检测器温度：250℃；

f) 进样量：20 μL。

3.4.3.2 气相色谱测定

根据试样顶空瓶中二硫化碳含量情况，选定峰高相近的标准顶空瓶。标准瓶和试样瓶中二硫化碳的响应值均应在仪器检测的线性范围内，对标准瓶和试样瓶中液上气体等体积参插进样测定。在上述色谱条件下，二硫化碳保留时间约为 2.8 min。二硫化碳标准品的气相色谱图见附录 B 中图 B1。

3.4.4 空白试验

用 10 mL 水代替试样，按 3.4.1 所述测定步骤进行。

3.5 结果计算和表述

用色谱数据处理机或按式(1)计算试样中代森锌类农药的总残留含量：

$$X = \frac{h \cdot c \cdot V}{h_s \cdot m} \quad \cdots\cdots(1)$$

式中：X——试样中代森锌类农药总残留含量(以二硫化碳计)，mg/kg；

h——样品瓶中二硫化碳的色谱峰高，mm；

h_s——标准瓶中二硫化碳的色谱峰高，mm；

c——二硫化碳标准工作液的浓度，μg/mL；

V——二硫化碳标准工作液的体积，mL；

m——试样量，g。

注：计算结果需将空白值扣除。如结果超过测定低限，可按附录 A 进行确证试验。

4 测定低限、回收率

4.1 测定低限

本方法测定低限(以二硫化碳计)为 0.10 mg/kg。

4.2 回收率

茶叶中代森锌添加浓度及其回收率的实验数据：

在 0.10 mg/kg 时，回收率为 84.2%；

在 0.50 mg/kg 时，回收率为 89.3%；

在 1.00 mg/kg 时，回收率为 90.0%。

茶叶中代森锰添加浓度及其回收率的实验数据：

在 0.10 mg/kg 时，回收率为 85.0%；

在 0.50 mg/kg 时，回收率为 90.2%；

在 1.00 mg/kg 时，回收率为 92.9%。

茶叶中代森锰锌添加浓度及其回收率的实验数据：

在 0.10 mg/kg 时，回收率为 83.4%；

在 0.50 mg/kg 时，回收率为 95.5%；

在 1.00 mg/kg 时，回收率为 91.3%。

茶叶中代森联添加浓度及其回收率的实验数据：

在 0.10 mg/kg 时，回收率为 81.3%；

在 0.50 mg/kg 时，回收率为 88.6%；

在 1.00 mg/kg 时，回收率为 94.9%。

附 录 A
（标准的附录）
茶叶中代森锌类农药总残留量确证试验方法

A1 方法提要

试样中残留的代森锌、代森锰、代森锰锌、代森联等乙撑双二硫代氨基甲酸盐类农药在碱性溶液中转化为可溶性钠盐，经正己烷-三氯甲烷提取，以碘甲烷进行甲酯化，用配有紫外检测器的高效液相色谱仪测定，外标法定量。

A2 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。

A2.1 盐酸：2 mol/L。

A2.2 正己烷：经全玻璃装置重蒸馏。

A2.3 三氯甲烷：经全玻璃装置重蒸馏。

A2.4 EDTA 溶液：溶解 50 g L-半胱氨酸盐酸盐和 50 g 乙二胺四乙酸(EDTA)二钠于 800 mL 水中，用 10 mol/L 的氢氧化钠溶液调整 pH 为 9.6～10。

A2.5 四丁基硫酸氢铵溶液：溶解 13.6 g 四丁基硫酸氢铵于 100 mL 水中。

A2.6 碘甲烷溶液：溶解 14.2 g 碘甲烷于 750 mL 三氯甲烷和 250 mL 正己烷中。

A2.7 代森锌(代森锰、代森锰锌、代森联均可)标准品：≥70%，已知含量。

A2.8 代森锌标准稀释物：准确称取适量代森锌标准品和滑石粉，混合均匀，配制成相当于 1.00 mg/g 二硫化碳的代森锌标准稀释物。根据需要，取一定量的标准稀释物代替样品，按 A4.1 和 A4.2 处理，制成标准工作液。

A3 仪器和设备

A3.1 液相色谱仪配有紫外检测器。

A3.2 旋转蒸发器。

A3.3 磁力搅拌器。

A4 测定步骤

A4.1 提取

称取试样约 5 g(精确至 0.01 g)于 250 mL 具塞锥形瓶中，加入 100 mL EDTA 溶液，振荡 15 min。过滤，残渣用 20 mL EDTA 溶液洗涤，合并滤液于另一具塞锥形瓶中。

A4.2 甲酯化

上述滤液在磁力搅拌器上，加入 5 mL 四丁基硫酸氢铵溶液，用 2 mol/L 盐酸溶液，调整 pH 为 7.5～8.0。加 40 mL 碘甲烷溶液，搅拌 10 min，过滤于分液漏斗中，分层。水相再用 20 mL 碘甲烷溶液提取一次。合并有机相，放置 30 min 后，于旋转蒸发器 30℃下减压蒸至近干。用 1.0 mL 乙腈溶解残渣，供液相色谱测定。

A4.3 测定

A4.3.1 液相色谱条件

a) 色谱柱：C_{18}柱，5 μm，250 mm×4.6 mm(内径)或相当的色谱柱；

b) 流动相：乙腈-水(2+3)；

c) 流速:1.0 mL/min;

d) 紫外检测器,波长:272 nm;

e) 进样量:20 μL。

A4.3.2 色谱测定

根据试样中被测农药含量情况,选定浓度相近的标准工作液。标准工作液和待测样液中农药的响应值均应在仪器检测的线性范围内。对标准工作液与样液等体积参插进样测定。在上述色谱条件下,乙撑双二硫代氨基甲酸二甲酯的保留时间约为 9.5 min。乙撑双二硫代氨基甲酸二甲酯的液相色谱图见图 A1。

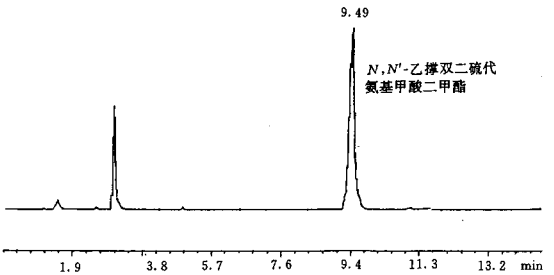


图 A1 N,N'-乙撑双二硫代氨基甲酸二甲酯标准品液相色谱图

A4.3.3 空白试验

除不称取试样外,均按上述测定步骤进行。

A5 结果计算和表述

用色谱数据处理机或按式(A1)计算试样中代森锌、代森锰、代森锰锌、代森联等的总残留含量:

$$X = \frac{h \cdot c \cdot V}{h_s \cdot m} \qquad \cdots\cdots(A1)$$

式中:X——试样中代森锌、代森锰、代森锰锌、代森联等的总含量(以二硫化碳计),mg/kg;

h——样液中乙撑双二硫代氨基甲酸二甲酯的色谱峰高,mm;

h_s——标准工作液中乙撑双二硫代氨基甲酸二甲酯的色谱峰高,mm;

c——代森锌标准工作液的浓度(以二硫化碳计),μg/mL;

V——最终样液体积,mL;

m——试样量,g。

注:计算结果需将空白值扣除。

A6 测定低限、回收率

A6.1 测定低限

本确证试验的测定低限(以二硫化碳计)为 0.10 mg/kg。

A6.2 回收率

茶叶中代森锌添加浓度及其回收率的实验数据:

在 0.10 mg/kg 时,回收率为 85.1%;

在 0.50 mg/kg 时,回收率为 84.3%;

在 1.00 mg/kg 时，回收率为 83.7%。

茶叶中代森锰添加浓度及其回收率的实验数据：

在 0.10 mg/kg 时，回收率为 81.6%；

在 0.50 mg/kg 时，回收率为 80.1%；

在 1.00 mg/kg 时，回收率为 84.6%。

茶叶中代森锰锌添加浓度及其回收率的实验数据：

在 0.10 mg/kg 时，回收率为 88.6%；

在 0.50 mg/kg 时，回收率为 84.3%；

在 1.00 mg/kg 时，回收率为 86.6%。

茶叶中代森联添加浓度及其回收率的实验数据：

在 0.10 mg/kg 时，回收率为 82.4%；

在 0.50 mg/kg 时，回收率为 88.0%；

在 1.00 mg/kg 时，回收率为 82.3%。

附 录 B
（提示的附录）
标准品色谱图

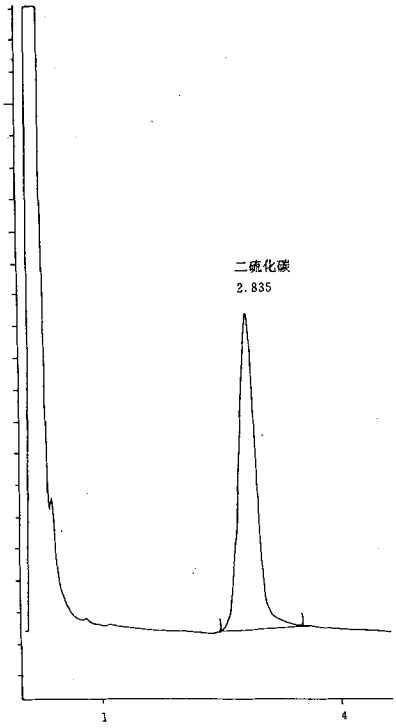


图 B1 二硫化碳标准品气相色谱图

Foreword

This standard was drafted in accordance with the requirements of the 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 relevant domestic and foreign literatures through research, modification and verification. In addition, methods of sampling and sample preparation are also defined in this standard.

The limit of determination is defined in the standard on the basis of the current international maximum limits for total pesticide residues of ethylene bisdithiocarbamate pesticides in tea and the sensitivity of the method.

Annex A of this standard is a normative annex.

Annex B is an informative annex.

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

The main drafters of the standard are Yang Jizhou, Liu Yafeng, Du Airong Liu Zhaohui and Liang Zhihong.

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

Method for the determination of total residues of ethylene bisdithiocarbamate pesticides in tea for export

SN 0711—1997

1 Scope

This standard specifies the methods of sampling, sample preparation and determination of total residues of ethylene bisdithiocarbamate pesticides by gas chromatography in tea for export.

This standard is applicable to the determination of total residue content of zineb, maneb, mancozeb metiram etc. 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, specification 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—5	1
6—50	2
51—500	11
501—1 000	16
1 001—1 500	17
1 501—2 000	18

2.3 Sampling tools

2.3.1 Sampling ladle.

2.3.2 Sheet: Plastic sheet.

2.3.3 Plate for quartering.

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

2.4 Sampling procedure

Draw a number of sample packages specified in 2.2 from different parts of the pile at random and open the packages one by one. Pour the tea from each packages on a clean plastic sheet and take up the sample from different parts of the out-poured tea as the primary sample. The amount taken from

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Implemented from Apr. 1, 1998

each package is ca 500 g, the total quantity of the primary samples should be at least 2 kg. Mix thoroughly the primary samples and reduce to ca 500 g by quartering, promotly place in a clean, dry sample container, seal, label and send to laboratory in time.

2.5 Preparation of test sample

The mixed primary sample is crushed with a grinder and let wholly pass through a 20-mesh sieve. Mix well and divide into two equal portions. Each portion is placed in a clean container as the test sample, which is then sealed and labeled.

2.6 Storage of test sample

The test samples shall be stored below −5℃ and kept away from light.

Note: 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 determination

3.1 Principle

The residues of ethylene bisdithiocarbamate pesticides csuch as zineb, maneb, mancozeb and metiram etc. in test sample are decomposed with acid in a closed container, releasing carbon disulfide quantitatively. Determination is carried out by gas chromatography with electron capture detector, using external standard method.

3.2 Reagents and materials

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

3.2.1 Concentrated hydrochloric acid: Density (ρ) ca 1.18 g/mL.

3.2.2 Stannous chloride: $SnCl_2 \cdot 2H_2O$.

3.2.3 *n*-Hexane: Redistilled with all glass apparatus.

3.2.4 Carbon disulfide standard: Purity≥99%.

3.2.5 Stannous chloride solution: Dissolve 15 g of stannous chloride (3.2.2) in 333 mL of concentrated hydrochloric acid and make up to 1 L with water.

3.2.6 Carbon disulfide standard solution: Accurately weigh an adequate amount of carbon disulfide standard, dissolve in *n*-hexane to prepare a solution of 1.0 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 *n*-hexane.

3.3 Apparatus and equipment

3.3.1 Gas chromatography, equipped with electron capture detector.

3.3.2 Head-space bottle: 250 mL.

3.3.3 Gas-tight syringe: 250 μL.

3.3.4 Thermostatic water-bath.

3.4 Procedure

3.4.1 Preparation of head-space bottle of the test sample

Weigh 10.0 g of the test sample into a 250 mL head-space bottle. Add 80 mL of stannous chloride solution and close the bottle immediately. Place the bottle in a thermostatic water-bath at 70℃ for 2 h. Shake at an interval of ca 30 min. Take it out and allow to cool to room temperature.

3.4.2 Preparation of head-space bottle of the standard

Instead of the test sample use 10 mL of water as the matrix. Add a suitable volume (V) of carbon

disulfide standard working solution, then proceed as described in 3.4.1.

3.4.3 Determination

3.4.3.1 GC operating condition

a) Column: Glass, 1.2 m×2 mm(id), packed with TENAX(60—80 mesh);

b) Carrier gas: Nitrogen, purity≥99.99%, 40 mL/min;

c) Column temperature: 80℃;

d) Injection port temperature: 150℃;

e) Detector temperature: 250℃;

f) Injection volume: 20 μL.

3.4.3.2 GC determination

According to the approximate concentration of carbon disulfide in the head space bottle of the test sample, select the head space bottle of standard with similar peak height to that of the sample bottle. The responses of carbon disulfide in the standard bottle and the test sample bottle should be within the linear range of the instrumental detection. Head space gas in the standard bottle should be injected occasionally in-between the injections of head space gas in the test sample bottle of equal volume. Under the above operating condition, the retention time of carbon disulfide is about 2.8 min. For chromatogram of carbon disulfide standard see fig. B1 in annex B.

3.4.4 Blank test

The operation of the blank test is the same as that described in 3.4.1 but the test sample is replaced by 10 mL of water.

3.5 Calculation and expression of the result

Calculate the total residue content of ethylene bisdithiocarbamate pesticides in the test sample by data processor or according to formula (1):

$$X = \frac{h \cdot c \cdot V}{h_s \cdot m} \qquad \cdots\cdots(1)$$

where

X—the total content (calculated as carbon disulfide) of zineb, maneb, mancozeb and metiram residues in the test sample, mg/kg;

h—the peak height of carbon disulfide in the sample bottle, mm;

h_s—the peak height of carbon disulfide in the standard bottle, mm;

c—the concentration of carbon disulfide in the standard working solution, μg/mL;

V—the volume of the standard working solution, mL;

m—the mass of the test sample, g.

Note: The blank value should be subtracted from the above result of calculation. If the result is over the limit of determination, the confirmatory test should be detected according to the annex A.

4 Limit of determination and recovery

4.1 Limit of determination

The limit of determination of this method is 0.10 mg/kg (as carbon disulfide).

4.2 Recovery

According to the experimental data, the fortifying concentrations of zineb in tea and its corresponding recoveries are:

0.10 mg/kg, the recovery 84.2%;

0.50 mg/kg, the recovery 89.3%;

1.00 mg/kg, the recovery 90.0%.

According to the experimental data, the fortifying concentrations of maneb in tea and its corresponding recoveries are:

0.10 mg/kg, the recovery 85.0%;

0.50 mg/kg, the recovery 90.2%;

1.00 mg/kg, the recovery 92.9%.

According to the experimental data, the fortifying concentrations of mancozeb in tea and its corresponding recoveries are:

0.10 mg/kg, the recovery 83.4%;

0.50 mg/kg, the recovery 95.5%;

1.00 mg/kg, the recovery 91.3%.

According to the experimental data, the fortifying concentrations of metiram in tea and its corresponding recoveries are:

0.10 mg/kg, the recovery 81.3%;

0.50 mg/kg, the recovery 88.6%;

1.00 mg/kg, the recovery 94.9%.

Annex A
(normative)
Method for the confirmatory test of total residues of ethylene bisdithiocarbamate pesticide in tea

A1 Principle

The residues of ethylene bisdithiocarbamate (such as zineb, maneb, mancozeb, metiram etc.) in the test sample were transformed into water-soluble sodium salts in an alkaline solution. The water-soluble sodium salts are extracted with *n*-hexane-chloroform, methylated by methyl iodide and determination is carried out by HPLC with UV detector, using external standard method.

A2 Reagents and materials

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

A2.1 Hydrochloric acid: 2 mol/L.

A2.2 *n*-Hexane: Redistill with all glass apparatus.

A2.3 Chloroform: Redistill with all glass apparatus.

A2.4 EDTA solution: Dissolve 50 g *L*-cysteine hydrochloric acid salt and 50 g ethylenediamine tetraacetic acid (EDTA) disodium salt in 800 mL of water. The pH of the solution is adjusted to 9.6—10 by add 10 mol/L NaOH.

A2.5 Tetrabutylammonium hydrogen sulfate solution: Dissolve 13.6 g tetrabutylammonium hydrogen sulfate in 100 mL of water.

A2.6 Methyl iodide solution: Dissolve 14.2 g methyl iodide in 750 mL of chloroform and 250 mL *n*-hexane.

A2.7 Zineb (maneb, mancozeb and metiram can also be use) standard: ≥70% of known content.

A2.8 Zineb standard dilution: Accurately weigh an adequate amount of zineb standard and talc, mix well and prepare a 1.00 mg/mL in concentration as carbon disulfide of the zineb standard dilution. Then according to the requirement prepare a standard working solution of appropriate concentration, proceed as described in A 4.1 and A 4.2, and use the standard dilution instead of the test sample for the preparation.

A3 Apparatus and equipment

A3.1 High performance liquid chromatograph, equipped with a UV detector.

A3.2 Rotary evaporator.

A3.3 Magnetic stirrer.

A4 Procedure

A4.1 Extraction

Weigh ca 5 g(accurate to 0.01 g) of the test sample into a 250 mL conical flask with stopper, add 100 mL of EDTA solution and shake for 15 min. Filter the extract. The residue is washed with 20 mL of EDTA solution. Combine the filtrates into another conical flask.

A4.2 Methylation

5 mL of the tetrabutylammonium hydrogen sulfate solution 5 mL is added to the filtrate on a magnetic stirrer. The pH is cautiously adjusted to 7.5—8.0 with 2 mol/L hydrochloric acid. Add 40 mL of methyl iodide solution into the filtrate. Stir for 10 min, filter into a separatory funnel. The two phases are separated. The aqueous layer is again extracted with 20 mL of the methyl iodide solution. Combine the organic layers and after setting aside for 30 min, evaporate the solvent to dryness in a rotary vacuum evaporator at 30℃. Dissolve the residue with 1.0 mL of acetonitrile for HPLC determination.

A4.3 Determination

A4.3.1 HPLC operating condition

a) Chromatographic column: C_{18} column, 5 μm, 250 mm×4.6 mm(id), or any other equivalent column;

b) Mobile phase: Acetonitrile-water(2+3);

c) Flow rate: 1.0 mL/min;

d) UV detector, wave length: 272 nm;

e) Injection volume: 20 μL.

A4.3.2 HPLC determination

According to the approximate concentration of pesticide in the sample solution, select the standard working solution with similar peak height to that of the sample solution. The responses of pesticide 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 injected randomly inbetween the injections of the sample solution of equal volume. Under the above HPLC operating condition, the retention time of dimethyl *N*,*N*′-ethylenebis (dithiocarbamate) is about 9.5 min. For chromatogram of dimethyl *N*,*N*′-ethylenebis (dithiocarbamate), see fig. A1.

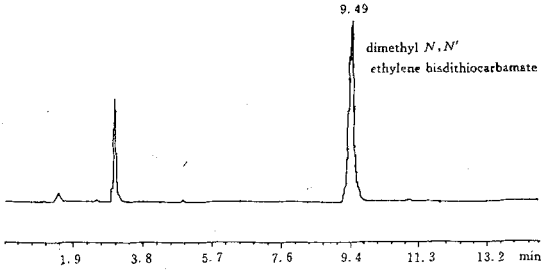


Fig. A1 Liquid chromatogram of dimethyl *N*,*N*′-ethylene bisdithiocarbamate standard

A4.4 Blank test

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

A5 Calculation and expression of the result

Calculate the total content of zineb, maneb, mancozeb and metiram residues in the test sample by chromatographic data processor or according to formula (A1):

$$X = \frac{h \cdot c \cdot V}{h_s \cdot m} \qquad \text{(A1)}$$

where

X—the total content (calculated as carbon disulfide)of zineb, maneb, mancozeb and metiram residues in the test sample, mg/kg;

h—the peak height of dimethyl N,N'-ethylene bisdithiocarbamate in the sample solution, mm;

h_s—the peak height of dimethyl N,N'-ethylene bisdithiocarbamate in the standard working solution, mm;

c—the concentration of zineb (calculated as carbon disulfide) in the standard working solution, μg/mL;

V—the final volume of the sample solution, mL;

m—the mass of the test sample, g.

Note: The blank value should be subtracted from the above result of calculation.

A6 Limit of determination and recovery

A6.1 Limit of determination

The limit of determination of this confirmatory test is 0.10 mg/kg (as carbon disulfide).

A6.2 Recovery

According to the experimental data, the fortifying concentrations of zineb in tea and its corresponding recoveries are:

0.10 mg/kg, the recovery 85.1%;

0.50 mg/kg, the recovery 84.3%;

1.00 mg/kg, the recovery 83.7%.

According to the experimental data, the fortifying concentrations of maneb in tea and its corresponding recoveries are:

0.10 mg/kg, the recovery 81.6%;

0.50 mg/kg, the recovery 80.1%;

1.00 mg/kg, the recovery 84.6%.

According to the experimental data, the fortifying concentrations of mancozeb in tea and its corresponding recoveries are:

0.10 mg/kg, the recovery 88.6%;

0.50 mg/kg, the recovery 84.3%;

1.00 mg/kg, the recovery 86.6%.

According to the experimental data, the fortifying concentrations of metiram in tea and its corresponding recoveries are:

0.10 mg/kg, the recovery 82.4%;

0.50 mg/kg, the recovery 88.0%;

1.00 mg/kg, the recovery 82.3%.

Annex B

(informative)

Chromatogram of the standard

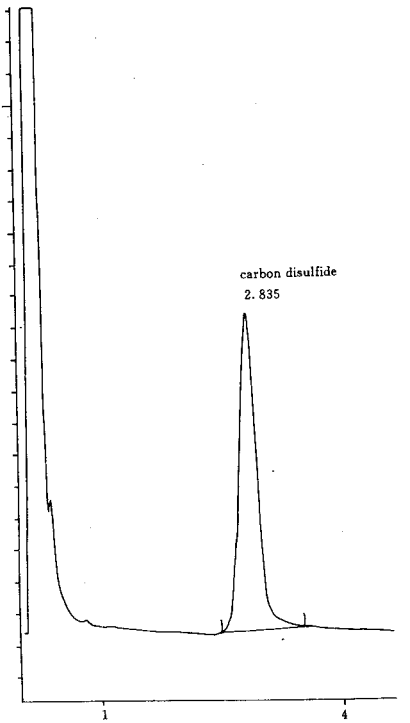


Fig. B1 Gas chromatogram of carbon disulfide standard