

# SN

## 中华人民共和国出入境检验检疫行业标准

SN/T 0163—2011

代替 SN 0163—1992

### 出口水果及水果罐头中二溴乙烷残留量 检验方法

Test method for ethylene dibromide residues  
in fruits and canned fruits for export

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中 华 人 民 共 和 国 发 布  
国家质量监督检验检疫总局



## 前 言

本标准按照 GB/T 1.1—2009 给出的规则起草。

本标准代替 SN 0163—1992《出口水果中二溴乙烷残留量检验方法》。

本标准与 SN 0163—1992 相比主要修改如下：

- 修改了标准名称；
- 修改了原标准的样品前处理方法；
- 将原标准中填充色谱柱改为毛细管色谱柱；
- 标准适用范围增加了菠萝、香蕉等大浆果类以及柑桔、菠萝等罐头制品；
- 增加了水果罐头的检测方法；
- 增加了水果及水果罐头中二溴乙烷气相色谱质谱联用检测方法。

请注意本文件的某些内容可能涉及专利。本文件的发布机构不承担识别这些专利的责任。

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：中华人民共和国广西出入境检验检疫局。

本标准主要起草人：吴玉杰、田继军、莫伟媛、张祖昌、刘军义、吕春秋、辛明。

本标准所代替标准的历次版本发布情况为：

- SN 0163—1992。

## 出口水果及水果罐头中二溴乙烷残留量 检验方法

### 1 范围

本标准规定了柑桔类、大浆果类水果及罐头中二溴乙烷残留检验的制样和测定方法。

本标准适用于柑桔、菠萝、香蕉及柑桔、菠萝罐头中二溴乙烷残留量的气相色谱和气质联用方法测定。

### 2 抽样和制样

#### 2.1 抽样数量

每检验批不超过1500箱,按下列规定抽样:

——1箱~25箱抽取1箱;

——26箱~100箱抽取5箱;

——101箱~250箱抽取10箱;

——251箱~1500箱抽取15箱。

抽样应按产地、分批次、论等级在不同部位随机抽样,每箱至少取500g作为原始样品,原始样品的总量不得少于2000g。

#### 2.2 试样的制备与保存

##### 2.2.1 试样制备

###### 2.2.1.1 水果样品

取代表性的可食部分样品,用粉碎机粉碎后取样。冷冻状态下的新鲜样品,应自然解冻至室温状态,再用均质器均质后取样。

###### 2.2.1.2 水果罐头样品

取代表性罐头样品,用均质器均质后取样。

##### 2.2.2 试样保存

水果及水果罐头样品应于4℃以下储存,在制样过程和保存过程中,应防止样品受到污染或发生待测物残留含量的变化。

### 3 原理

试样于硫酸钠溶液中,用丙酮和正己烷混和溶剂沸水浴蒸馏,收集液用配备电子捕获检测器(ECD)的气相色谱仪及气相-质谱联用仪检测,外标法定量。

### 4 试剂和材料

除另有规定外,所用试剂均为分析纯,水为二次蒸馏水或去离子水。

- 4.1 正己烷( $n\text{-C}_6\text{H}_{14}$ ):农残级。
- 4.2 丙酮( $\text{CH}_3\text{COCH}_3$ ):农残级。
- 4.3 无水硫酸钠( $\text{Na}_2\text{SO}_4$ ):650℃灼烧4h,冷却至室温,贮于干燥器中备用。
- 4.4 硫酸钠溶液:50 g/L。
- 4.5 硫酸钠溶液:150 g/L。
- 4.6 标准品:二溴乙烷( $\text{CH}_2\text{BrCH}_2\text{Br}$ ,密度 $\rho=2.173\text{ g/mL}$ ),纯度大于等于99%。
- 4.7 标准工作液:称取二溴乙烷标准品10.0 mg,正己烷溶解并定容至100 mL,浓度为100  $\mu\text{g/mL}$ ,根据需要用正己烷配制适当浓度的标准工作液。

## 5 仪器和设备

- 5.1 气相色谱仪:配有电子俘获检测器(ECD)。
- 5.2 气相色谱-质谱联用仪:配有电子轰击离子源(EI)。
- 5.3 粉碎机。
- 5.4 均质器。
- 5.5 涡旋混匀器。
- 5.6 低速离心机:5 000 r/min。
- 5.7 水浴锅。
- 5.8 循环水冷却器。
- 5.9 圆底蒸馏瓶:500 mL。
- 5.10 冷凝管:蛇形。
- 5.11 具塞刻度离心管:10 mL。
- 5.12 二溴乙烷蒸馏装置(见图1)。

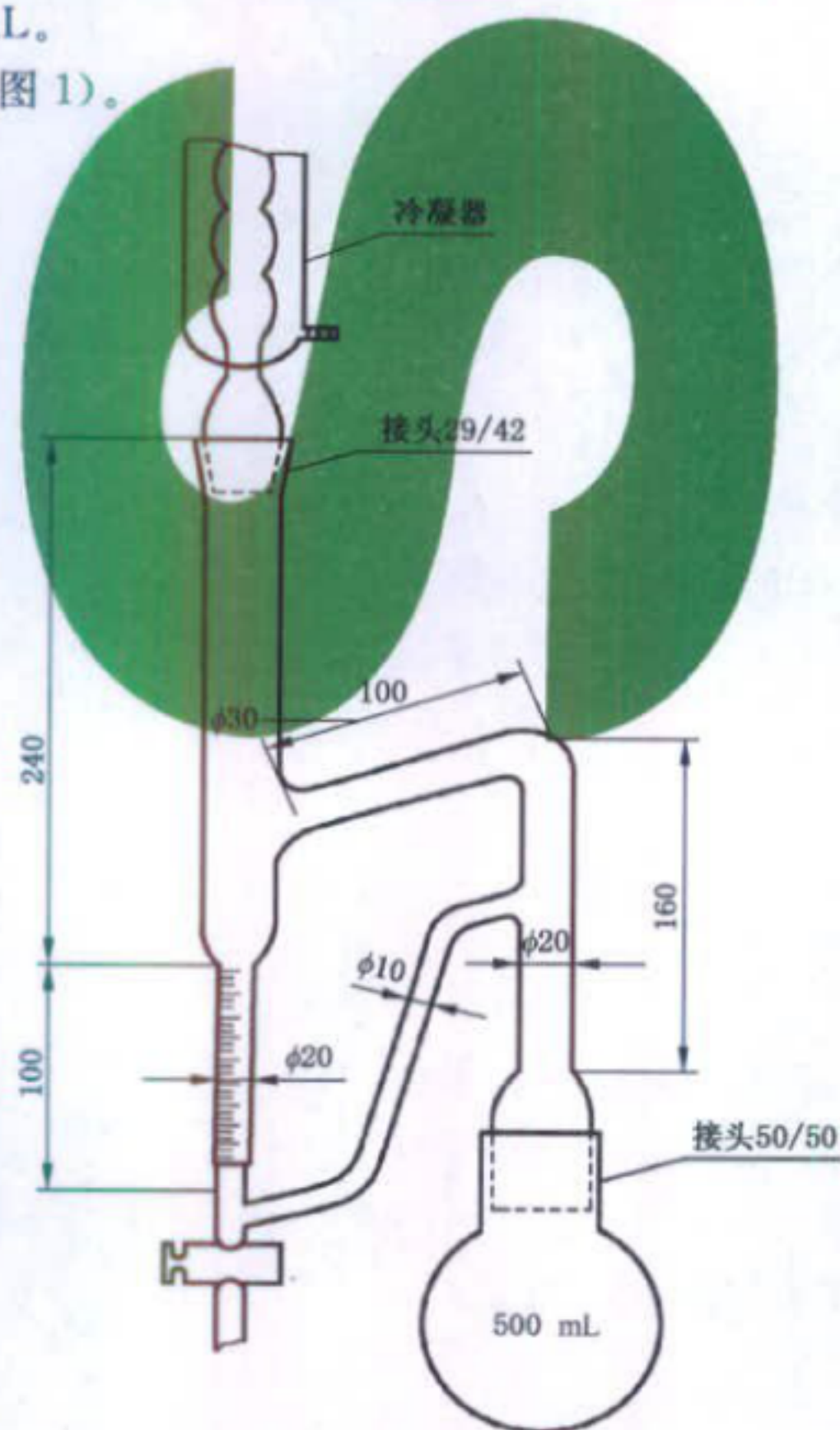


图1 二溴乙烷蒸馏装置图

## 6 测定步骤

### 6.1 提取

#### 6.1.1 水果样品

称取 20 g(精确至 0.01 g)样品于圆底烧瓶(5.9)中,加入 200 mL 硫酸钠溶液(4.5)和 10 mL 正己烷-丙酮(2+1),充分摇匀,按图 1 连接,沸水浴蒸馏,直至馏出液中有 1 mL~2 mL 水停止,流出液中加入适量无水硫酸钠(4.3)脱水,上层有机相,加正己烷至 10 mL 刻线,涡旋混匀,3 500 r/min 速度离心 3 min,上清液用气相色谱和气质联用仪测定。

#### 6.1.2 罐头样品

称取 20 g(精确至 0.01 g)样品于圆底烧瓶(5.9)中,加入 200 mL 硫酸钠溶液(4.4)和 10 mL 正己烷-丙酮(2+1),其余步骤同 6.1.1。

### 6.2 气相色谱测定

#### 6.2.1 色谱参考条件

6.2.1.1 色谱柱:HP-5 石英毛细管柱,30 m×0.25 mm(内径),膜厚 0.25 μm,或相当者。

6.2.1.2 注温程序:100 °C(6 min) $\xrightarrow{15\text{ }^{\circ}\text{C}/\text{min}}$ 250 °C(5 min) $\xrightarrow{30\text{ }^{\circ}\text{C}/\text{min}}$ 290 °C(5 min)。

6.2.1.3 进样口温度:250 °C。

6.2.1.4 检测器温度:300 °C。

6.2.1.5 载气:氮气,纯度≥99.999%;流速 1.0 mL/min。

6.2.1.6 不分流进样。

6.2.1.7 进样量:1.0 μL。

#### 6.2.2 定量测定

根据样液中被测物含量情况,绘制合适的标准工作曲线。标准工作液和样液中待测物的响应值均应在仪器检测的线性范围内。标准工作液和样液等体积穿插进样测定。外标法定量。在上述色谱条件下二溴乙烷保留时间约为 4.1 min。标准品的色谱图参见图 A.1。

### 6.3 气质联用测定

#### 6.3.1 参考条件

6.3.1.1 色谱柱:HP-5MS 石英毛细管柱,30 m×0.25 mm(内径),膜厚 0.25 μm,或相当者。

6.3.1.2 柱温:40 °C(5 min) $\xrightarrow{15\text{ }^{\circ}\text{C}/\text{min}}$ 100 °C(1 min) $\xrightarrow{20\text{ }^{\circ}\text{C}/\text{min}}$ 280 °C(10 min)。

6.3.1.3 载气:氮气,纯度≥99.999%;流速:1.0 mL/min。

6.3.1.4 进样口温度:250 °C。

6.3.1.5 离子源温度:230 °C。

6.3.1.6 GC-MS 接口温度:280 °C。

6.3.1.7 进样方式:不分流进样。

6.3.1.8 进样量:1 μL。

6.3.1.9 电离方式:EI。

- 6.3.1.10 电离能量:70 eV。
- 6.3.1.11 溶剂延迟:3 min。
- 6.3.1.12 测定方式:选择离子监测方式(SIM),选择离子及相对丰度见表 1。

表 1 选择离子及相对丰度

选择离子(m/z)	107(定量)	109	81	188
相对丰度/%	100	95	7	5

6.3.2 定量测定

根据样液中被测物含量情况,绘制合适的标准工作曲线。标准工作液和样液中待测物的响应值均应在仪器检测的线性范围内。标准工作液和样液等体积穿插进样测定。外标法定量。在上述色谱条件下,二溴乙烷保留时间约为 5.9 min。标准品的总离子流色谱图参见图 B.1。对标准工作液及样液按 6.3.1规定的条件进行测定,如样品中待测物质和外标物的保留时间相一致,并且在扣除背景后的样品谱图中均出现;同时将样品谱图中各组分定性离子的相对丰度与浓度接近的标准工作液谱图中对应的定性离子的相对丰度进行比较,若偏差在表 2 规定允许的范围,则可判定为样品中存在对应的待测物。

表 2 使用定性气相色谱-质谱时相对离子丰度最大允许偏差

相对丰度/%	>50	>20~50	>10~20	≤10
允许的相对偏差/%	±10	±15	±20	±50

6.4 空白试验

除不加试样外,均按上述步骤进行。

6.5 结果计算

水果中二溴乙烷残留量按式(1)计算:

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

式中:

- X ——标准工作曲线中得到的试样中二溴乙烷的含量,单位为毫克每千克(mg/kg);
- A ——样液中的二溴乙烷峰面积;
- c<sub>s</sub> ——标准工作液浓度,单位为微克每毫升(μg/mL);
- V ——最终样液定容体积,单位为毫升(mL);
- A<sub>s</sub> ——标准工作液中二溴乙烷峰面积;
- m ——称样量,单位为克(g)。

计算结果应将空白值扣除。

7 测定低限、回收率及精密度

7.1 测定低限

本方法新鲜水果和水果罐头样品中二溴乙烷残留量的气相色谱法测定低限均为 0.000 5 mg/kg,气

质联用方法测定低限均为 0.001 mg/kg。

## 7.2 回收率及精密度

样品中添加二溴乙烷测定的回收率及精密度结果参见附录 C。

附录 A  
(资料性附录)  
二溴乙烷标准品气相色谱图

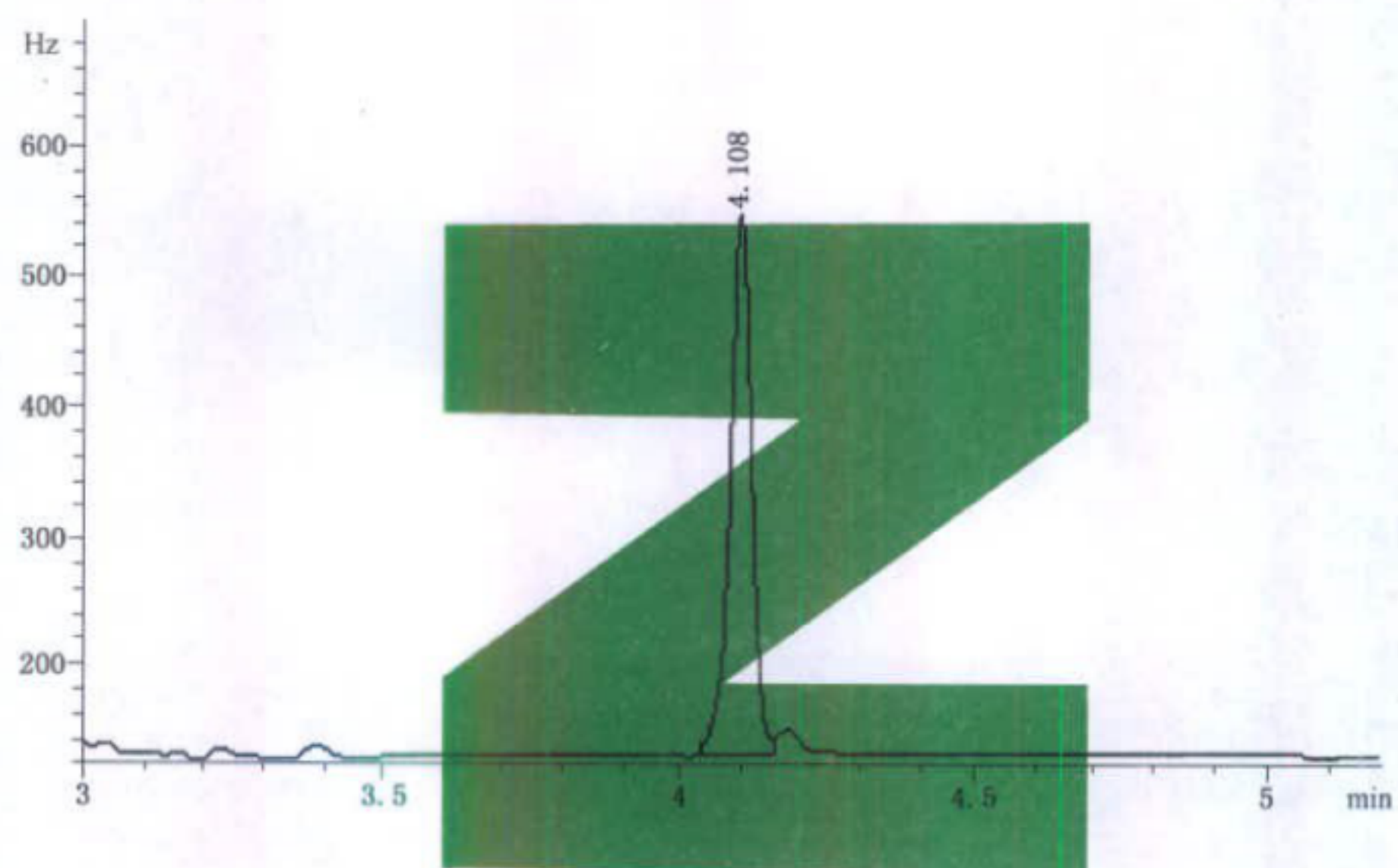


图 A.1 二溴乙烷标准品气相色谱图

## 附录 B

(资料性附录)

## 二溴乙烷全扫描总离子流图及质谱图

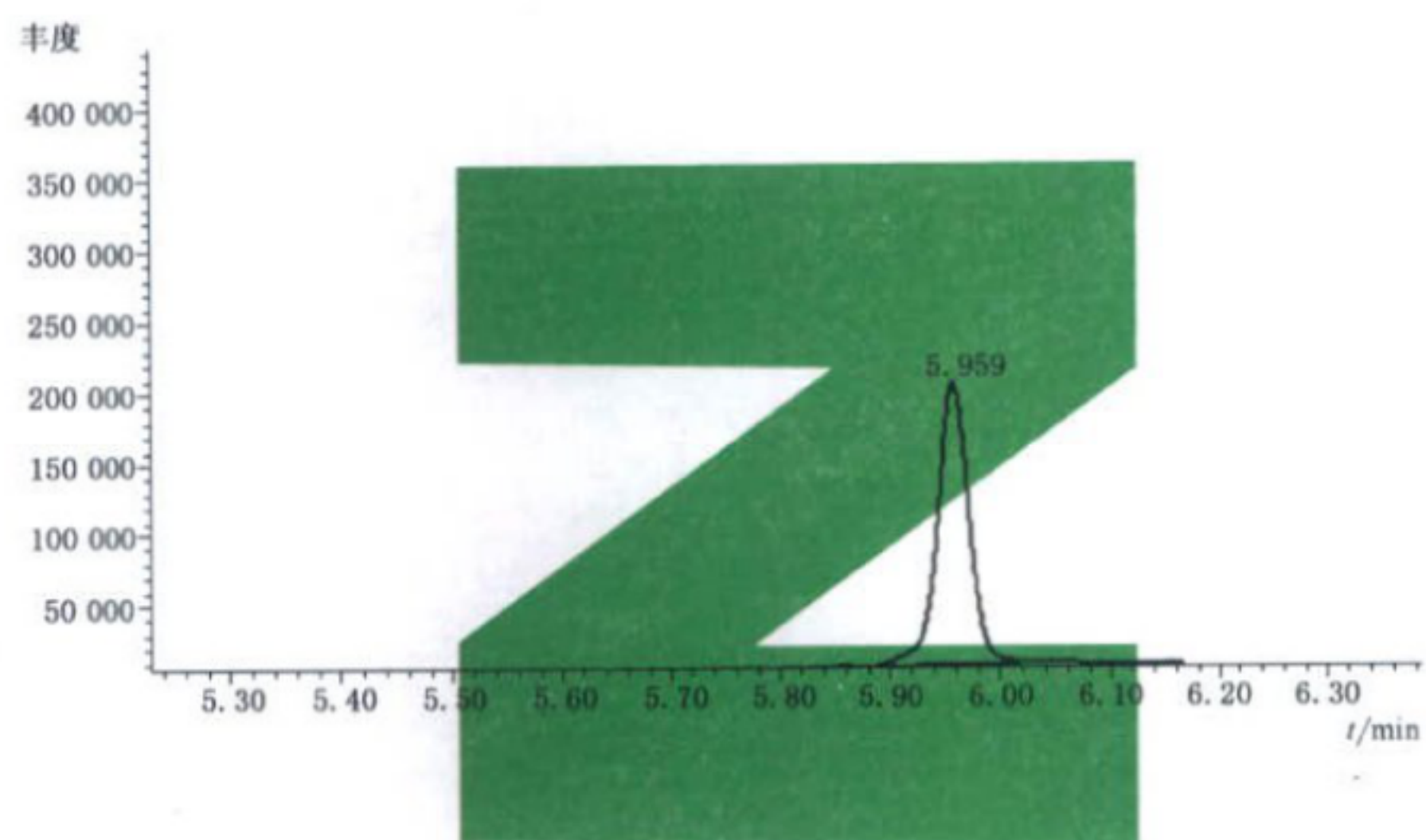


图 B.1 二溴乙烷全扫描总离子流图

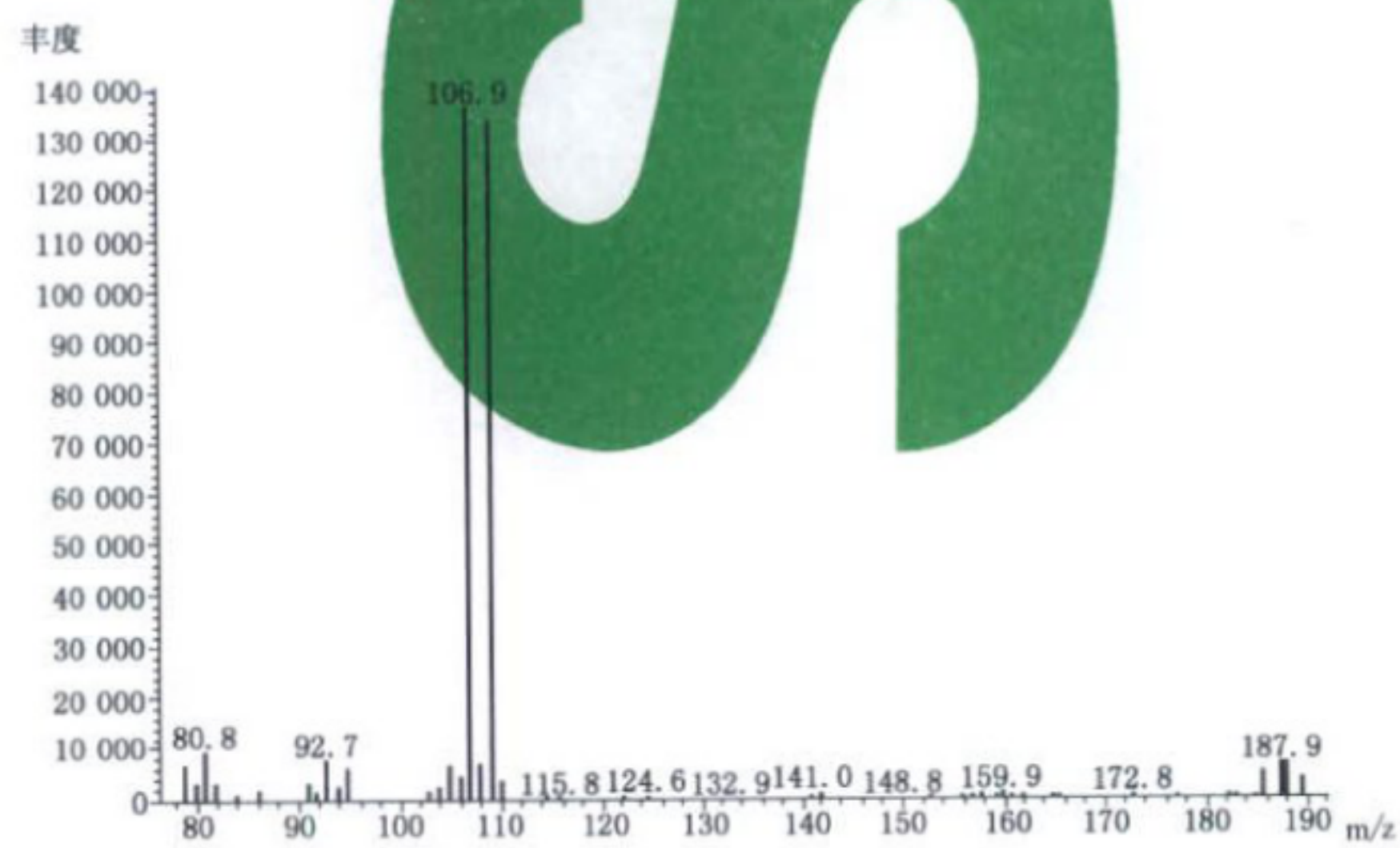


图 B.2 二溴乙烷质谱图

附 录 C  
(资料性附录)

二溴乙烷在不同样品中 3 个浓度添加测得的回收率及精密度

表 C.1 二溴乙烷在水果及水果罐头中 3 个添加浓度水平  
气相色谱法和气质联用法测得的回收率及精密度

测定方法	样品名称	添加水平 $\mu\text{g/kg}$	回收率范围 %	相对标准偏差 %
GC-ECD	柑桔	0.5	102.00~109.40	3.19
		10	85.48~100.11	6.66
		20	88.29~98.77	4.64
	菠萝	0.5	95.40~103.40	3.45
		10	90.10~109.10	8.04
		20	101.02~110.62	3.52
	香蕉	0.5	90.80~107.60	6.40
		10	88.54~109.45	8.34
		20	102.36~106.69	1.58
	柑桔罐头	0.5	92.20~108.40	6.54
		10	92.11~108.41	6.70
		20	105.05~120.85	5.90
	菠萝罐头	0.5	88.00~106.40	7.00
		10	89.31~109.07	7.72
		20	118.44~125.31	2.27
GC-MS	柑桔	1.0	87.60~105.50	6.62
		10	88.81~105.96	6.71
		20	96.87~114.62	7.47
	菠萝	1.0	97.30~116.70	8.41
		10	95.08~121.03	10.51
		20	98.06~120.64	9.67
	香蕉	1.0	94.00~106.20	4.68
		10	95.24~105.08	4.30
		20	97.06~115.16	6.79
	柑桔罐头	1.0	84.10~101.20	7.38
		10	86.85~110.66	9.66
		20	106.14~115.01	3.05
	菠萝罐头	1.0	86.30~113.00	10.25
		10	96.06~108.51	4.37
		20	104.14~117.88	4.75

## Foreword

This standard was drafted in accordance with the GB/T 1.1—2009.

This standard replaced SN 0163—1992《Method for determination of ethylene dibromide residue in fruit for export》.

The mainly differences between this standard and SN 0163—1992 are as follows:

- Modified the standard name;
- Modified method for the original standard sample pretreatments;
- Chromatographic column in the original standard replaced by capillary column;
- The standard applicability has increased big bacca kinds of pineapple, bananas and canned products such as orange, pineapple;
- Added the testing method of canned fruit;
- Added the inspection method for ethylene dibromide residues in fruits and canned fruits by GC-MS.

Please note: some patents may be included in this standard, while the agency who releases the standard will not be charged with it.

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

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

This standard was mainly drafted by Wu Yujie, Tian Jijun, Mo Weiyuan, Zhang Zuchang, Liu Junyi, Lv Chunqiu, Xin Ming.

This standard replaced the previous version of the release of the standard as follows:

- SN 0163—1992.

## Test method for ethylene dibromide residues in fruits and canned fruits for export

### 1 Scope

This standard specifies the method of sampling and determination of ethylene dibromide residues in citrus, big bacca fruits and canned fruits.

This standard is applicable to the determination of ethylene dibromide residues in orange, pineapple, bananas and canned citrus, canned pineapple by GC and GC-MS.

### 2 Sampling

#### 2.1 Sum of the sampling

No more than 1 500 boxes, sampling as follows:

- 1~25, take 1 box;
- 26~100, take 5 boxes;
- 101~250, take 10 boxes;
- 251~1 500, take 15 boxes.

Sample should be taken according to place of origin, in batches, on the level in the different parts of the sample immediately, the original samples must be no less than 500 g, and the total original samples no less than 2 000 g.

#### 2.2 Sample preparation and storage

##### 2.2.1 Sample preparation

##### 2.2.1.1 Fruit samples

Take appropriate typical edible part sample after crashed. The frozen fresh sample should be defrosted first, then weighed after homogen.

### 2.2.1.2 Canned fruit samples

Take appropriate canned samples after being homogen.

### 2.2.2 Storage

The samples shall be stocked sealed below 4 °C. Avoid contaminating the sample or change the residue concentration of the analyses during sampling and stocking.

## 3 Principle

The analytes in the sodium sulfate solution, with acetone and *n*-hexane mixed solvent are distilled by boiling water bath, then detected by GC with ECD detector, and quantitation by external standard.

## 4 Reagents and materials

Unless specified, all reagents used should be of analytical grade. "water" is the secondary water or deionized water.

4.1 Hexane(*n*-C<sub>6</sub>H<sub>14</sub>): Pesticide grade.

4.2 Acetone(CH<sub>3</sub>COCH<sub>3</sub>): Pesticide grade.

4.3 Sodium sulfate anhydrous(Na<sub>2</sub>SO<sub>4</sub>): Burned at 650 °C for 4 h, then cool to room temperature, storing in desiccator for use.

4.4 Sodium sulfate solution: 50 g/L.

4.5 Sodium sulfate solution: 150 g/L.

4.6 Standards: Ethylene dibromide(CH<sub>2</sub>BrCH<sub>2</sub>Br, density,  $\rho = 2.173$  g/mL). Purity  $\geq 99\%$ .

4.7 Standard stock solution: Dissolve 10.0 mg ethylene dibromide in 100 mL hexane(4.1), respectively. Which concentrations of the solutions are 100  $\mu$ g/mL, preparation the standard working solutions with the standard stock solutions.

## 5 Apparatus and equipment

5.1 Gas chromatography: Equipped with ECD detector.

5.2 GC-MS: Equipped with EI source.

- 5.3 Bucker.
- 5.4 Homogenizer.
- 5.5 Vortex mixer.
- 5.6 Rotary evaporator; 5 000 r/min.
- 5.7 Water bath boiler.
- 5.8 Recycled water cooler.
- 5.9 Round-bottomed distillation bottle; 500 mL.
- 5.10 Condense pipe; S-shaped.
- 5.11 Plug-scale centrifuge tube; 10 mL.
- 5.12 Ethylene dibromide distillation unit(see figure 1).

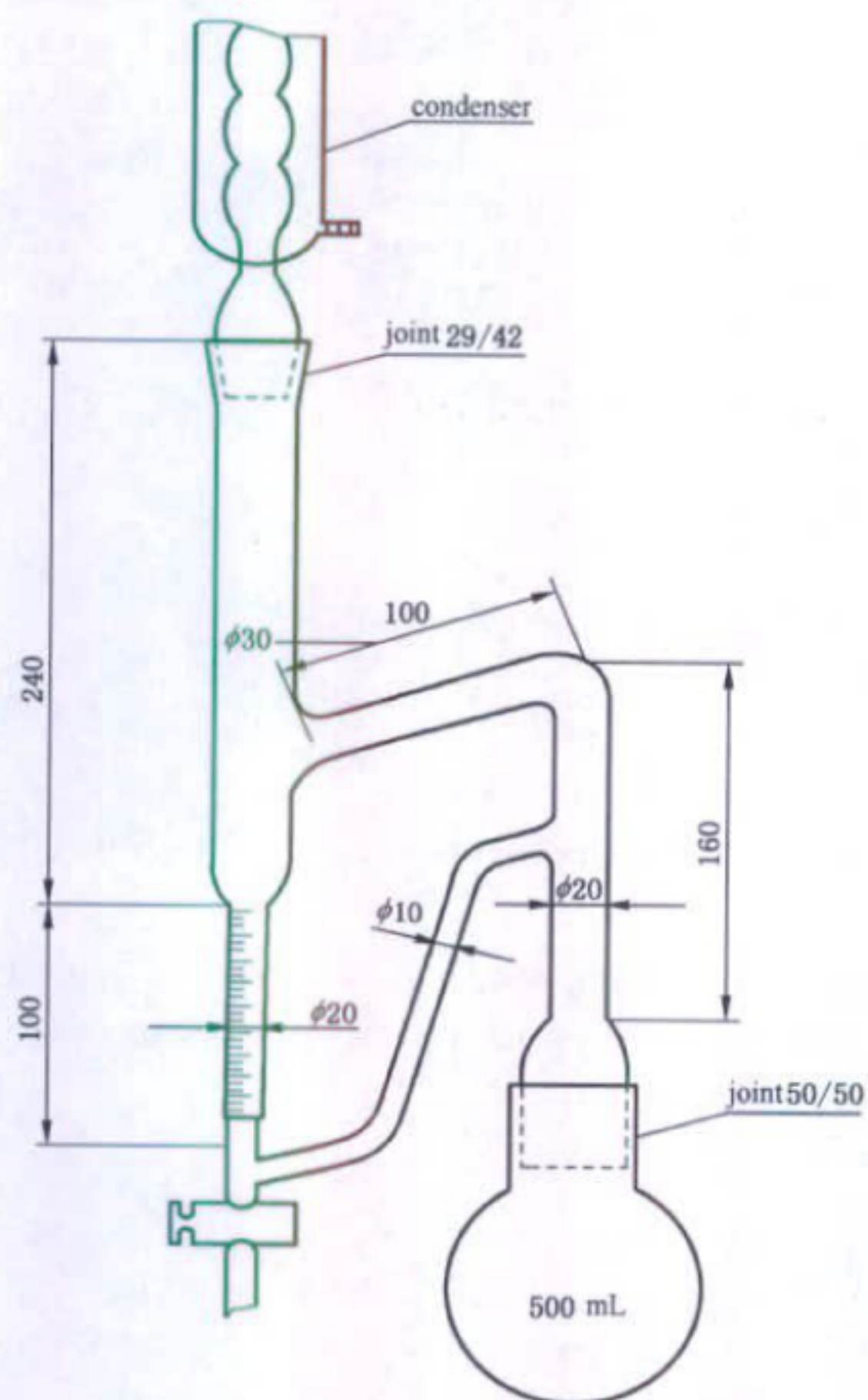


Figure 1—Ethylene dibromide distillation unit

## 6 Procedure of determination

### 6.1 Extraction

#### 6.1.1 Fruit sample

20.0 g sample (accurate to 0.01 g) were weighed into 500 mL round-bottomed distillation bottle (5.9), then adding 200 mL sodium sulfate solution (4.5) and 10 mL hexane-acetone mixture (2 + 1), fully shaken, according to figure 1 to connect, the distillation bottle put in the boiling water bath until the liquid has slipped out of the 1 mL ~ 2 mL of water. The solution slipped out were added appropriate anhydrous sodium sulfate (4.3) to remove water, dissolve the upper organic phase with hexane to 10 mL, vortex mixing, centrifuged at 3 500 r/min for 3 min, then the upper layers detected by GC and GC-MS.

#### 6.1.2 Canned samples

20.0 g sample (accurate to 0.01 g) were weighed into 500 mL round-bottomed distillation bottle (5.9), then adding 200 mL sodium sulfate solution (4.4) and 10 mL hexane-acetone mixture (2 + 1), the others step is the same as 6.1.1.

### 6.2 GC determination

#### 6.2.1 GC operating condition

6.2.1.1 Chromatographic column: Fused silica capillary column, HP-5 30 m × 0.25 mm (i. d.) × 0.25 μm (film thickness) or equivalent.

6.2.1.2 Temperature programme: 100 °C (6 min)  $\xrightarrow{15\text{ }^{\circ}\text{C/min}}$  250 °C (5 min)  $\xrightarrow{30\text{ }^{\circ}\text{C/min}}$  290 °C (5 min).

6.2.1.3 Injection port temperature: 250 °C.

6.2.1.4 Detector temperature: 300 °C.

6.2.1.5 Carrier gas: Nitrogen (purity ≥ 99.999%), flow rate: 1.0 mL/min.

6.2.1.6 Injection mode: Splitless.

6.2.1.7 Injection volume: 1 μL.

#### 6.2.2 Quantitation determination

Use the standard working solutions based on estimating the concentration of analyses in the sample.

The responses of analyses in the standard working solution and sample solutions should be within the linear range of the instrumental detection. The standard working solution should be randomly injected in-between the injections of the sample solution of equal volume, and quantitation by external standard. Under the above operating condition, the ethylene dibromide retention time is about 4.1 min. The chromatograms of ethylene dibromide are in annex A. 1.

### 6.3 GC-MS determination

#### 6.3.1 GC-MS operation condition

6.3.1.1 Chromatographic column: Fused silica capillary column, HP-5MS, 30 m × 0.25 mm (i. d.) × 0.25 μm (film thickness) or equivalent.

6.3.1.2 Temperature programme: 40 °C (5 min)  $\xrightarrow{15\text{ }^{\circ}\text{C/min}}$  100 °C (1 min)  $\xrightarrow{20\text{ }^{\circ}\text{C/min}}$  280 °C (10 min).

6.3.1.3 Carrier gas: Nitrogen (purity ≥ 99.999%), flow rate: 1.0 mL/min.

6.3.1.4 Injection port temperature: 250 °C.

6.3.1.5 Ion source temperature: 230 °C.

6.3.1.6 GC-MS transfer temperature: 280 °C.

6.3.1.7 Injection mode: Splitless.

6.3.1.8 Injection volume: 1 μL.

6.3.1.9 Ionization mode: EI.

6.3.1.10 Ionization energy: 70 eV.

6.3.1.11 Solvent delay: 3 min.

6.3.1.12 Detection mode: SIM (see table 1).

Table 1—Selected ion and relative abundance

Selected ion (m/z)	107 (quantitation)	109	81	188
Relative abundance/%	100	95	7	5

#### 6.3.2 Quantitation determination

Use the standard working solutions based on estimating the concentration of analyses in the sample.

The responses of analyses in the standard working solution and sample solutions should be within the linear range of the instrumental detection. The standard working solution should be randomly injected in-between the injections of the sample solution of equal volume, and quantitation by external standard. Under the above operating condition, the ethylene dibromide retention time is about 5.9 min. The total ion current chromatograms of ethylene dibromide are in annex B. 1. Determinating the standard working solutions and sample solutions based on condition on section 6.3.1. If the retention time of the analyses are the same to that of the external standards when subtraction the background, in the same time the ion relative abundance of the compounds from samples are similar to that of the standards' at the deviation as table 2, it can be inferred that is positive sample.

Table 2—Maximum deviation of the ion relative abundance qualitative by GC-MS

Relative abundance/%	>50	>20~50	>10~20	≤10
Permit relative deviation/%	±10	±15	±20	±50

#### 6.4 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.

#### 6.5 Calculation and expression of result

Calculation of the content of ethylene dibromide residues in the test sample according to the formula(1):

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

Where

$X$  —the residue content of ethylene dibromide in the standard working curve, mg/kg;

$A$  —the peak area of ethylene dibromide in sample solution;

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

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

$A_s$  —the peak area of ethylene dibromide in standard solution;

$m$  —mass of the test sample, g.

The calculation results shall deduct the blank value.

## 7 Limit of determination, recovery and precision

### 7.1 Limit of determination

Limits of determination of ethylene dibromide is 0.000 5 mg/kg in fresh fruit and canned fruit samples by GC method. Limits of determination is 0.001 mg/kg by GC-MS method.

### 7.2 Recovery and precision

The recovery and precision result that ethylene dibromide added in the sample consult annex C.

Annex A  
(Informative annex)  
GC chromatogram of EDB standard

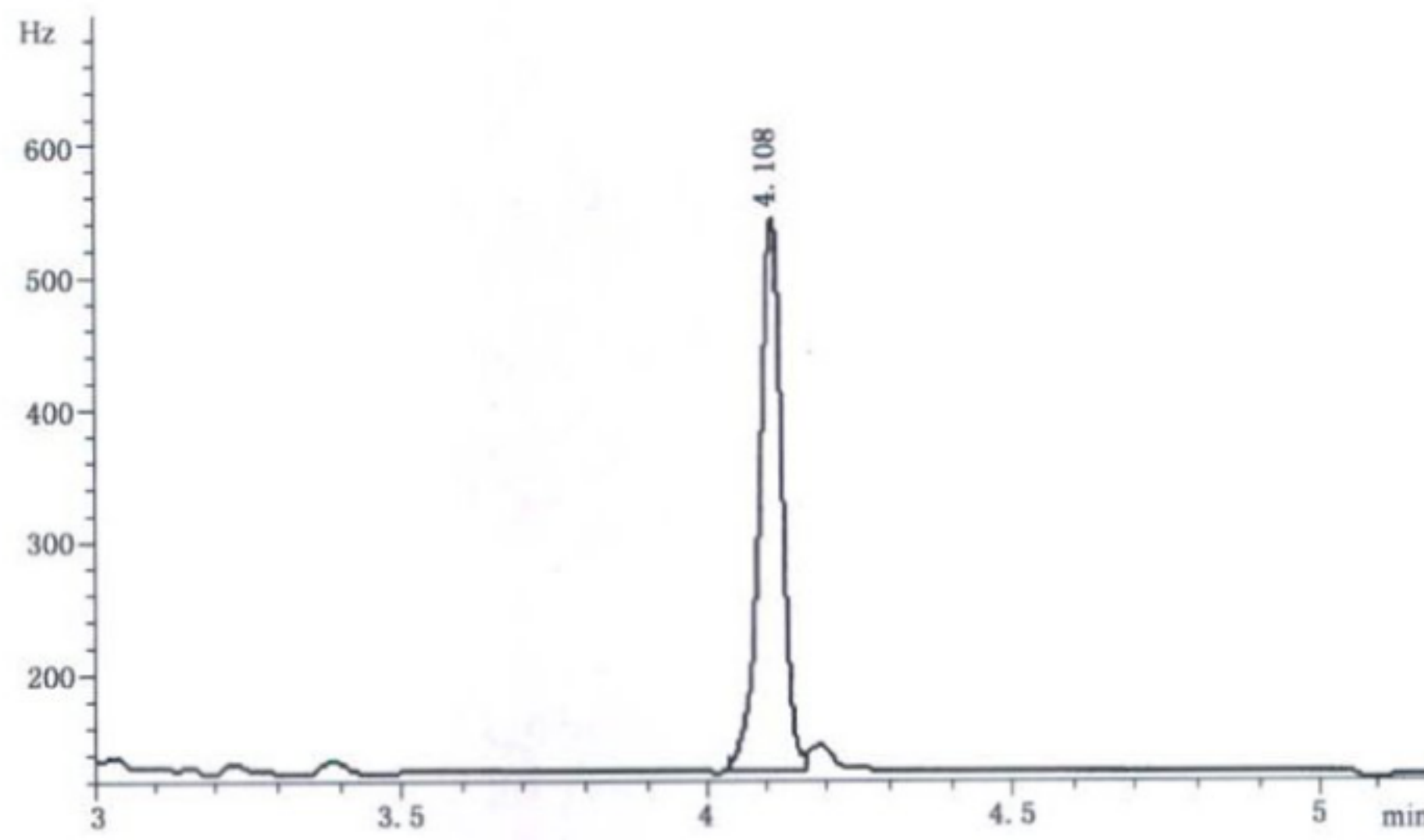


Figure A. 1—GC chromatogram of EDB standard

Annex B  
(Informative annex)  
TIC of SCAN and MS spectra of EDB

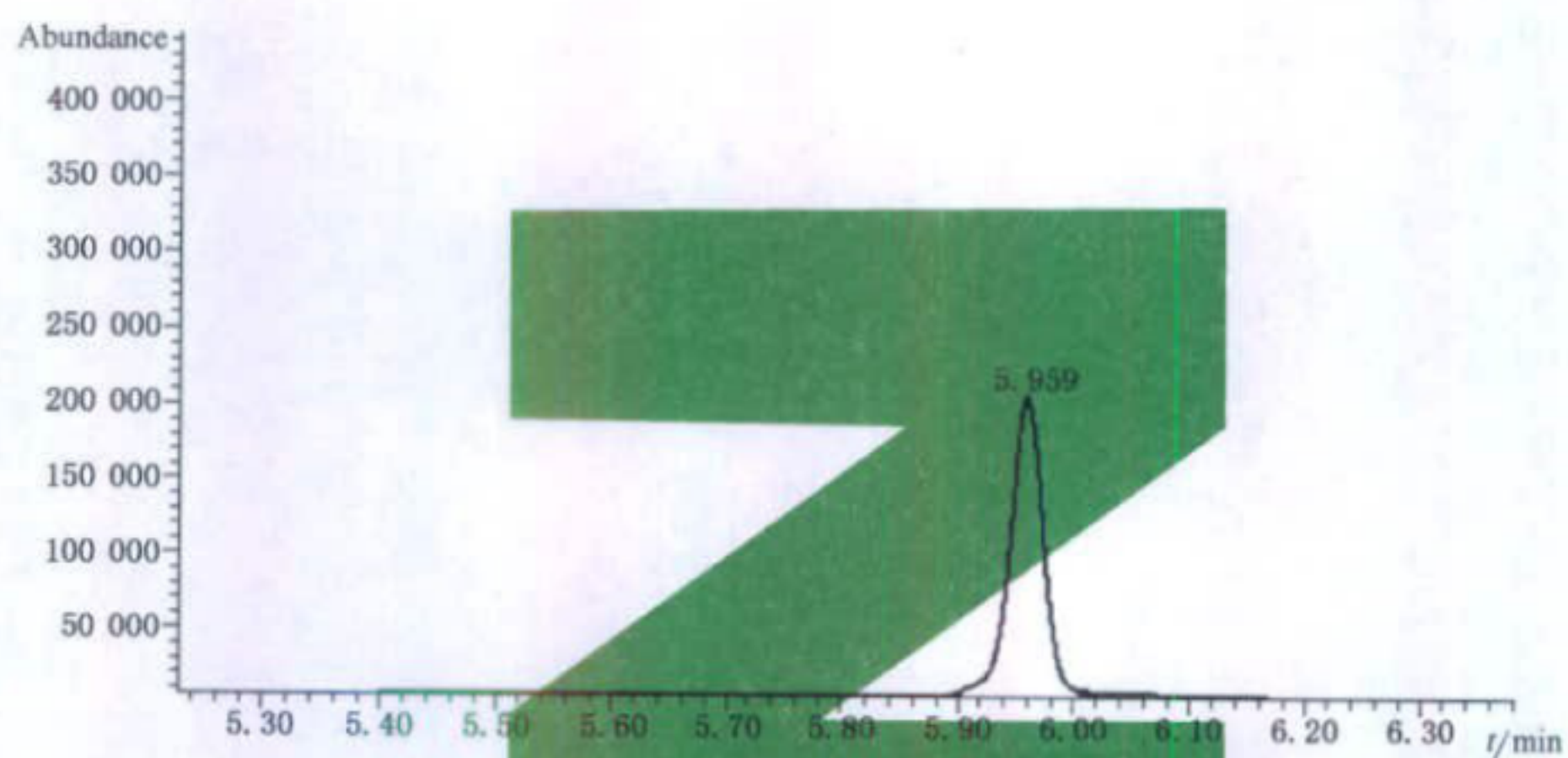


Figure B. 1—Total ion chromatogram of EDB at Full SCAN mode

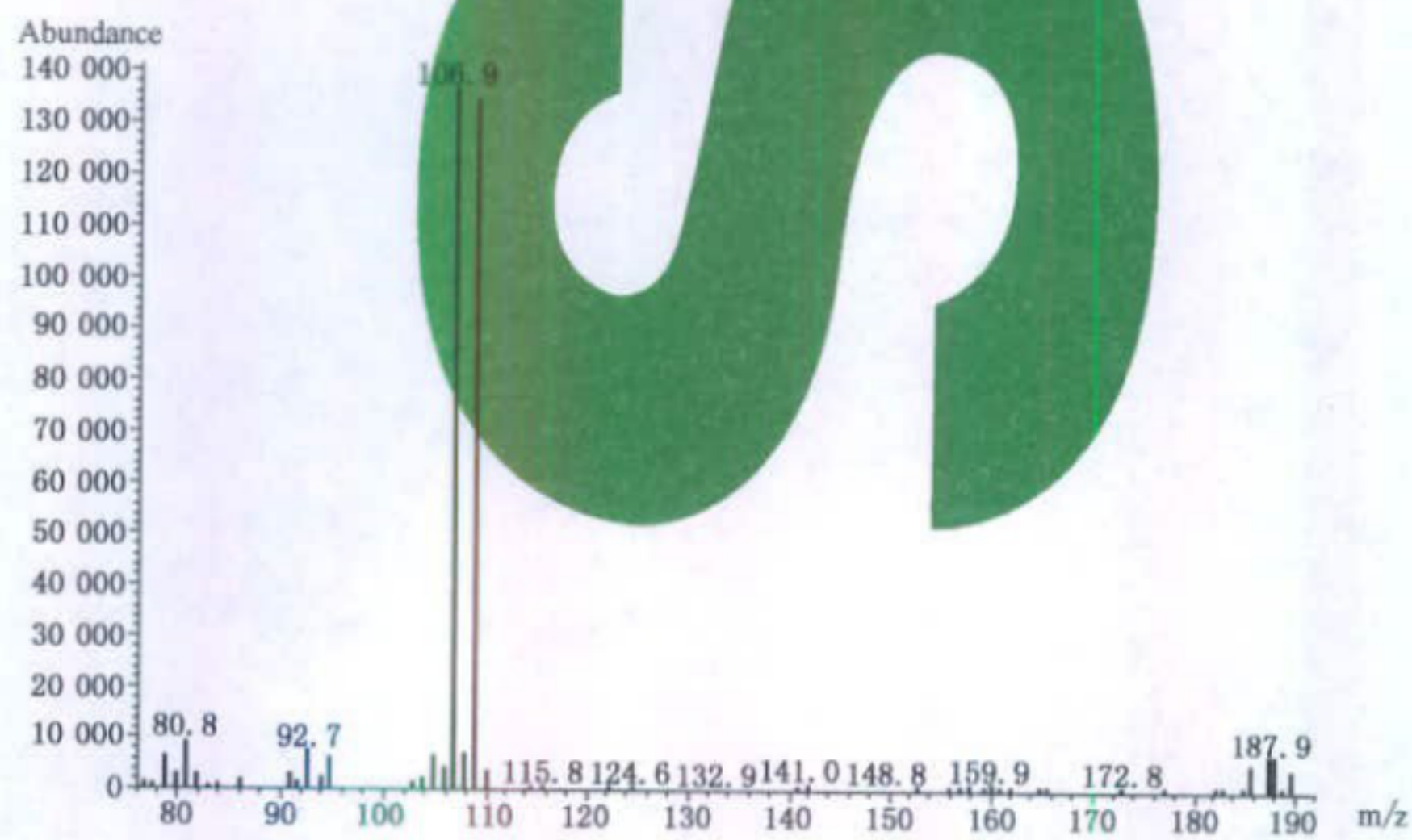


Figure B. 2—Mass sepectrogram of EDB standard

## Annex C

(Informative annex)

Recovery and precision of EDB from different added samples  
at three levels by GC and GC-MS methods

Table C. 1—Recovery and precision of EDB from different added samples  
at three levels by GC and GC-MS methods

Method	Sample	Added level μg/kg	Recovery %	Relative standard deviate %
GC-ECD	Orange	0.5	102.00~109.40	3.19
		10	85.48~100.11	6.66
		20	88.29~98.77	4.64
	Pineapple	0.5	95.40~103.40	3.45
		10	90.10~109.10	8.04
		20	101.02~110.62	3.52
	Banana	0.5	90.80~107.60	6.40
		10	88.54~109.45	8.34
		20	102.36~106.69	1.58
	Canned orange	0.5	92.20~108.40	6.54
		10	92.11~108.41	6.70
		20	105.05~120.85	5.90
	Canned pineapple	0.5	88.00~106.40	7.00
		10	89.31~109.07	7.72
		20	118.44~125.31	2.27
GC-MS	Orange	1.0	87.60~105.50	6.62
		10	88.81~105.96	6.71
		20	96.87~114.62	7.47
	Pineapple	1.0	97.30~116.70	8.41
		10	95.08~121.03	10.51
		20	98.06~120.64	9.67
	Banana	1.0	94.00~106.20	4.68
		10	95.24~105.08	4.30
		20	97.06~115.16	6.79
	Canned orange	1.0	84.10~101.20	7.38
		10	86.85~110.66	9.66
		20	106.14~115.01	3.05
	Canned pineapple	1.0	86.30~113.00	10.25
		10	96.06~108.51	4.37
		20	104.14~117.88	4.75

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