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中华人民共和国出入境检验检疫行业标准

SN/T 2238—2008

进出口食品中21种熏蒸剂残留量检测方法　顶空气相色谱法

Determination of twenty one fumigant residues in food for import and export—Headspace GC 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：中华人民共和国辽宁出入境检验检疫局、中华人民共和国江苏出入境检验检疫局、中华人民共和国河南出入境检验检疫局。

本标准主要起草人：姜莉、宋文斌、卫锋、荣会、金雁、于孝展、沈崇钰、杨冀洲、蒋施。

本标准系首次发布的出入境检验检疫行业标准。

进出口食品中21种熏蒸剂残留量检测方法　顶空气相色谱法

1　范围

本标准规定了食品中1,1,1-三氯乙烷、反-1,3-二氯丙烯、顺-1,3-二氯丙烯、三氯乙烯、1,2-二氯丙烷、溴二氯甲烷、1,1,2-三氯乙烷、四氯乙烯、二溴氯甲烷、溴仿、1,1,2,2-四氯乙烷、1,3-二氯苯、1,4-二氯苯、1,2-二氯苯、1,2,4-三氯苯、1,2,3-三氯苯、六氯丁二烯、1,2-二溴乙烷、1,2-二氯乙烷、四氯化碳、三氯甲烷21种熏蒸剂残留量的顶空气相色谱检测方法。

本标准适用于玉米、糙米、花生、大豆、小豆等食品中1,1,1-三氯乙烷、反-1,3-二氯丙烯、顺-1,3-二氯丙烯、三氯乙烯、1,2-二氯丙烷、溴二氯甲烷、1,1,2-三氯乙烷、四氯乙烯、三二溴氯甲烷、溴仿、1,1,2,2-四氯乙烷、1,3-二氯苯、1,4-二氯苯、1,2-二氯苯、1,2,4-三氯苯、1,2,3-三氯苯、六氯丁二烯、1,2-二溴乙烷、1,2-二氯乙烷、四氯化碳、三氯甲烷21种熏蒸剂残留量的测定。

2　方法提要

在密封容器内,易挥发的熏蒸剂分子在一定温度下在气固两相间达到动态平衡。此时熏蒸剂在气相中的浓度和它在固相中的浓度成正比,通过对气相中熏蒸剂浓度的测定,即可计算出熏蒸剂的浓度,外标法定量。

3　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。

3.1　正己烷:农残级。

3.2　无水硫酸钠:650 ℃灼烧4 h,贮于密封容器中备用。

3.3　熏蒸剂标准品:纯度大于等于99%(见表1)。

表1　熏蒸剂标准品

序号	样品名称	相对分子质量	分子式	CAS No.
1	1,1,1-三氯乙烷	133.35	CH_3CCl_3	71-55-6
2	反-1,3-二氯丙烯	110.97	$C_3H_4Cl_2$	10061-02-6
3	顺-1,3-二氯丙烯	110.97	$C_3H_4Cl_2$	10061-02-5
4	三氯乙烯	131.39	$ClCH=CCl_2$	79-01-6
5	1,2-二氯丙烷	112.9	$CH_3CHClCH_2Cl$	78-87-5
6	溴二氯甲烷	163.8	$CHBrCl_2$	75-27-4
7	1,1,2-三氯乙烷	133.4	$CHCl_2CH_2Cl$	79-00-5
8	四氯乙烯	165.82	CCl_2CCl_2	127-18-4
9	二溴氯甲烷	208.3	$CHBr_2Cl$	124-48-1
10	溴仿	252.73	$CHBr_3$	75-25-2
11	1,1,2,2-四氯乙烷	167.86	$CHCl_2CHCl_2$	79-34-5
12	1,3-二氯苯	147.00	$C_6H_4Cl_2$	541-73-1

表 1(续)

序号	样品名称	相对分子质量	分子式	CAS No.
13	1,4-二氯苯	147.00	$C_6H_4Cl_2$	106-46-7
14	1,2-二氯苯	147.00	$C_6H_4Cl_2$	95-50-1
15	1,2,4-三氯苯	181.45	$C_6H_3Cl_3$	120-82-1
16	1,2,3-三氯苯	181.45	$C_6H_3Cl_3$	87-61-6
17	六氯丁二烯	260.76	C_4Cl_6	87-68-3
18	1,2-二溴乙烷	187.88	$C_2H_4Br_2$	106-93-4
19	1,2-二氯乙烷	98.97	$C_2H_4Cl_2$	107-06-2
20	四氯化碳	153.84	CCl_4	56-23-5
21	三氯甲烷	119.38	$CHCl_3$	67-66-3

3.4 三氯甲烷、四氯化碳等 21 种熏蒸剂标准储备溶液:准确地分别移取三氯甲烷、四氯化碳、1,2-二溴乙烷等 21 种熏蒸剂的适量体积,并用其密度(见表 2)进行重量计算,用正己烷分别配置成浓度各为 1 000 μg/mL的标准储备液。该溶液在 0 ℃~4 ℃冰箱中保存。

表 2 21 种熏蒸剂的密度

编号	熏蒸剂名称	密度	编号	熏蒸剂名称	密度
1	1,1,1-三氯乙烷	1.350	12	1.3-二氯苯	1.290
2	反-1,3-二氯丙烯	1.160	13	1.4-二氯苯	1.458
3	顺-1,3-二氯丙烯	1.160	14	1.2-二氯苯	1.460
4	三氯乙烯	1.465	15	1.2.4-三氯苯	1.450
5	1,2-二氯丙烷	1.260	16	1.2.3-三氯苯	1.450
6	溴二氯甲烷	2.006	17	六氯丁二烯	1.682
7	1,1,2-三氯乙烷	4.550	18	1.2-二溴乙烷	2.177
8	四氯乙烯	1.631	19	1.2-二氯乙烷	1.260
9	二溴氯甲烷	1.440	20	四氯化碳	1.592
10	溴仿	2.889	21	三氯甲烷	1.448
11	1,1,2,2-四氯乙烷	1.600			

3.5 三氯甲烷、四氯化碳等 21 种熏蒸剂标准混合工作液:根据需要用正己烷配稀释成适用浓度的标准混合工作溶液,该溶液在 0 ℃~4 ℃冰箱中保存。

4 仪器与设备

4.1 气相色谱仪:配有电子捕获检测器。

4.2 顶空瓶:20.0 mL。

4.3 顶空进样针:1.0 mL。

4.4 顶空装置。

4.5 密封塑料离心管:50 mL。

4.6 超声波仪。

5 试样制备与保存

5.1 试样制备

取代表性样品约 500 g,装入洁净容器,密封,标明标记。

5.2 试样保存

试样于 -18 ℃以下冷冻保存。在抽样及制样的操作过程中,应防止样品受到污染或发生残留物含量的变化。

6 测定步骤

6.1 测定

6.1.1 气相色谱条件

a) 色谱柱:HP-624 石英毛细管柱,30 m×0.53 mm(内径)×2.05 μm,或相当者;

b) 色谱柱温度:40 ℃(保持 1 min)$\xrightarrow{5\ ℃/\mathrm{min}}$140 ℃(保持 30 min);

c) 进样口温度:200 ℃;

d) 检测器温度:250 ℃;

e) 载气:氮气,纯度大于等于 99.999%,流速 1.2 mL/min;

f) 进样量:200 μL。

6.1.2 分析步骤

称取样品 5 g(精确至 0.01 g)于 50 mL 具塞塑料离心管中,准确加入 15.0 mL 正己烷溶解并超声提取 5 min,离心。准确移取 10.0 mL 样液于顶空瓶中,立即用内衬聚四氟乙烯薄膜的橡皮塞密封,置于顶空装置中,于 60 ℃恒温 0.5 h,抽取 200 μL 上部气体供气相色谱分析。

6.1.3 气相色谱检测

根据样液中熏蒸剂含量情况,选定浓度相近的标准工作溶液,标准工作溶液和待测样液中熏蒸剂的响应值均应在仪器检测的线性范围内。标准工作溶液与样液等体积参插进样测定。

标准溶液及样液均按 6.1.1 规定的条件进行测定。熏蒸剂标准物质和试样的气相色谱图参见附录 A。

6.2 空白试验

除不称取试样外均按上述步骤进行。

7 结果计算和表述

用色谱数据处理机或按式(1)计算试样中熏蒸剂残留量,计算结果应扣除空白值:

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

式中:

X——试样中某一熏蒸剂残留量,单位为毫克每千克(mg/kg);

h——样液中某一熏蒸剂的色谱峰高;

h_s——标准工作液中某一熏蒸剂的色谱峰高;

c——标准工作液中某一熏蒸剂的浓度,单位为微克每毫升(μg/mL);

V——提取溶剂的体积,单位为毫升(mL);

m——称取的试样量,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：三氯甲烷、四氯化碳等21种熏蒸剂均为0.01 mg/kg。

8.2 添加浓度范围及回收率

本方法添加浓度范围及回收率见表3～表7。

表3 玉米添加浓度范围及回收率

样品名称(玉米)	添加浓度范围/(mg/kg)	回收率/%
1,1,1-三氯乙烷	0.010～0.100	78.0～95.2
反-1,3-二氯丙烯	0.010～0.100	74.0～98.5
顺-1,3-二氯丙烯	0.010～0.100	72.0～94.6
三氯乙烯	0.010～0.100	70.0～94.4
1,2-二氯丙烷	0.010～0.100	73.0～94.7
溴二氯甲烷	0.010～0.100	74.0～98.5
1,1,2-三氯乙烷	0.010～0.100	73.0～98.5
四氯乙烯	0.010～0.100	77.3～97.5
二溴氯甲烷	0.010～0.100	71.4～97.0
溴仿	0.010～0.100	78.0～96.5
1,1,2,2-四氯乙烷	0.010～0.100	70.0～97.0
1,3-二氯苯	0.010～0.100	73.0～99.0
1,4-二氯苯	0.010～0.100	75.2～98.5
1,2-二氯苯	0.010～0.100	71.0～98.0
1,2,4-三氯苯	0.010～0.100	74.0～98.5
1,2,3-三氯苯	0.010～0.100	74.0～98.0
六氯丁二烯	0.010～0.100	72.2～98.0
1,2-二溴乙烷	0.010～0.100	72.3～98.5
1,2-二氯乙烷	0.010～0.100	72.1～98.0
四氯化碳	0.010～0.100	74.0～98.5
三氯甲烷	0.010～0.100	73.0～98.5

表4 糙米添加浓度范围及回收率

样品名称(糙米)	添加浓度范围/(mg/kg)	回收率/%
1,1,1-三氯乙烷	0.010～0.100	81.0～97.5
反-1,3-二氯丙烯	0.010～0.100	74.0～98.5
顺-1,3-二氯丙烯	0.010～0.100	77.0～98.0
三氯乙烯	0.010～0.100	74.0～96.7
1,2-二氯丙烷	0.010～0.100	77.0～98.0
溴二氯甲烷	0.010～0.100	74.0～96.5
1,1,2-三氯乙烷	0.010～0.100	74.0～96.5

表 4（续）

样品名称(糙米)	添加浓度范围/(mg/kg)	回收率/%
四氯乙烯	0.010～0.100	78.0～98.0
二溴氯甲烷	0.010～0.100	74.4～97.0
溴仿	0.010～0.100	81.0～98.0
1,1,2,2-四氯乙烷	0.010～0.100	75.5～98.0
1,3-二氯苯	0.010～0.100	72.0～98.0
1,4-二氯苯	0.010～0.100	72.0～96.0
1,2-二氯苯	0.010～0.100	74.0～96.8
1,2,4-三氯苯	0.010～0.100	73.5～97.0
1,2,3-三氯苯	0.010～0.100	72.0～98.5
六氯丁二烯	0.010～0.100	71.0～98.5
1,2-二溴乙烷	0.010～0.100	72.0～98.5
1,2-二氯乙烷	0.010～0.100	72.0～98.5
四氯化碳	0.010～0.100	74.0～98.5
三氯甲烷	0.010～0.100	74.0～98.0

表 5　花生添加浓度范围及回收率

样品名称(花生)	添加浓度范围/(mg/kg)	回收率/%
1,1,1-三氯乙烷	0.010～0.100	76.5～96.1
反-1,3-二氯丙烯	0.010～0.100	75.0～98.5
顺-1,3-二氯丙烯	0.010～0.100	73.5～95.5
三氯乙烯	0.010～0.100	72.0～95.3
1,2-二氯丙烷	0.010～0.100	75.0～95.6
溴二氯甲烷	0.010～0.100	76.0～98.5
1,1,2-三氯乙烷	0.010～0.100	75.0～98.5
四氯乙烯	0.010～0.100	72.3～98.0
二溴氯甲烷	0.010～0.100	80.0～96.1
溴仿	0.010～0.100	80.0～96.1
1,1,2,2-四氯乙烷	0.010～0.100	72.0～95.1
1,3-二氯苯	0.010～0.100	71.0～95.0
1,4-二氯苯	0.010～0.100	75.7～97.0
1,2-二氯苯	0.010～0.100	78.2～98.5
1,2,4-三氯苯	0.010～0.100	79.0～98.0
1,2,3-三氯苯	0.010～0.100	72.3～98.0
六氯丁二烯	0.010～0.100	78.0～99.0
1,2-二溴乙烷	0.010～0.100	72.3～99.0
1,2-二氯乙烷	0.010～0.100	72.3～98.0
四氯化碳	0.010～0.100	72.4～98.0
三氯甲烷	0.010～0.100	75.0～91.0

表6　大豆添加浓度范围及回收率

样品名称(大豆)	添加浓度范围/(mg/kg)	回收率/%
1,1,1-三氯乙烷	0.010～0.100	79.0～98.0
反-1,3-二氯丙烯	0.010～0.100	76.8～98.0
顺-1,3-二氯丙烯	0.010～0.100	72.0～98.0
三氯乙烯	0.010～0.100	71.0～95.5
1,2-二氯丙烷	0.010～0.100	73.0～95.0
溴二氯甲烷	0.010～0.100	73.4～99.5
1,1,2-三氯乙烷	0.010～0.100	73.4～98.0
四氯乙烯	0.010～0.100	73.5～99.5
二溴氯甲烷	0.010～0.100	78.0～99.5
溴仿	0.010～0.100	79.0～97.5
1,1,2,2-四氯乙烷	0.010～0.100	72.0～97.5
1,3-二氯苯	0.010～0.100	72.8～98.0
1,4-二氯苯	0.010～0.100	73.0～98.0
1,2-二氯苯	0.010～0.100	71.0～98.5
1,2,4-三氯苯	0.010～0.100	76.8～98.0
1,2,3-三氯苯	0.010～0.100	73.4～99.5
六氯丁二烯	0.010～0.100	79.0～98.0
1,2-二溴乙烷	0.010～0.100	73.4～98.0
1,2-二氯乙烷	0.010～0.100	73.5～98.0
四氯化碳	0.010～0.100	73.4～99.5
三氯甲烷	0.010～0.100	73.3～99.5

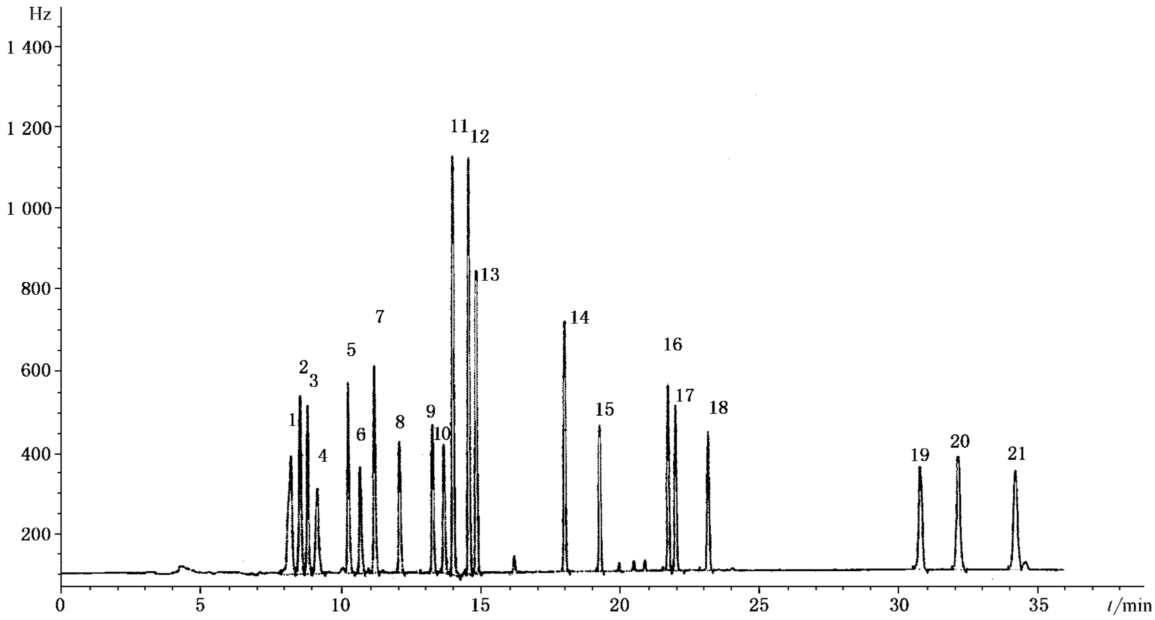
表7　小豆添加浓度范围及回收率

样品名称(小豆)	添加浓度范围/(mg/kg)	回收率/%
1,1,1-三氯乙烷	0.010～0.100	73.0～98.0
反-1,3-二氯丙烯	0.010～0.100	72.3～98.5
顺-1,3-二氯丙烯	0.010～0.100	72.0～98.0
三氯乙烯	0.010～0.100	72.0～94.4
1,2-二氯丙烷	0.010～0.100	73.0～94.7
溴二氯甲烷	0.010～0.100	70.2～98.5
1,1,2-三氯乙烷	0.010～0.100	70.2～98.0
四氯乙烯	0.010～0.100	72.8～98.5
二溴氯甲烷	0.010～0.100	70.1～98.0
溴仿	0.010～0.100	77.8～98.0
1,1,2,2-四氯乙烷	0.010～0.100	72.8～98.0
1,3-二氯苯	0.010～0.100	73.0～98.0

表 7（续）

样品名称(小豆)	添加浓度范围/(mg/kg)	回收率/%
1,4-二氯苯	0.010～0.100	71.7～97.5
1,2-二氯苯	0.010～0.100	70.1～97.5
1,2,4-三氯苯	0.010～0.100	71.7～97.5
1,2,3-三氯苯	0.010～0.100	72.8～98.5
六氯丁二烯	0.010～0.100	75.0～98.0
1,2-二溴乙烷	0.010～0.100	73.0～97.5
1,2-二氯乙烷	0.010～0.100	70.2～98.0
四氯化碳	0.010～0.100	70.2～97.5
三氯甲烷	0.010～0.100	70.3～98.5

附 录 A
（资料性附录）
熏蒸剂标准气相色谱图



1——三氯甲烷；
2——1,1,1-三氯乙烷；
3——四氯化碳；
4——1,2-二氯乙烷；
5——三氯乙烯；
6——1,2-二氯丙烷；
7——溴二氯甲烷；
8——顺-1,3-二氯丙烯；
9——反-1,3-二氯丙烯；
10——1,1,2-三氯乙烷；
11——四氯乙烯；
12——二溴氯甲烷；
13——1,2-二溴乙烷；
14——溴仿；
15——1,1,2,2-四氯乙烷；
16——1,3-二氯苯；
17——1,4-二氯苯；
18——1,2-二氯苯；
19——1,2,4-三氯苯；
20——六氯丁二烯；
21——1,2,3-三氯苯。

图 A.1 熏蒸剂标准气相色谱图

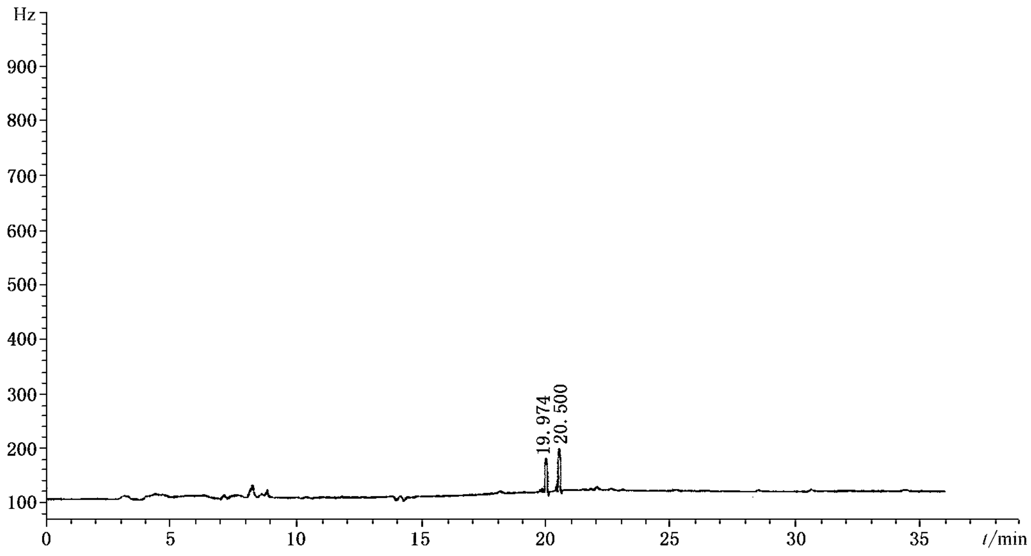


图 A.2　大豆空白样品气相色谱图

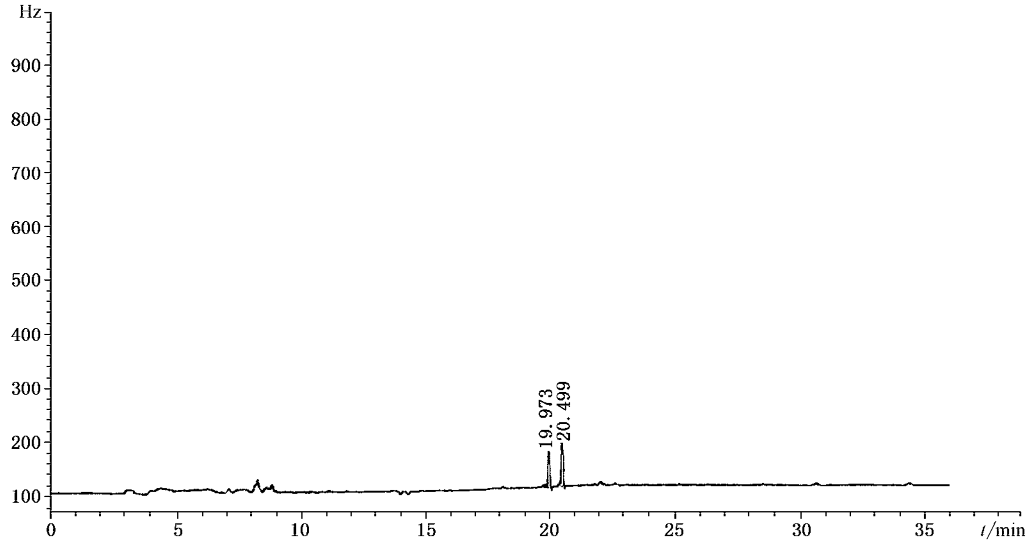


图 A.3　小豆空白样品气相色谱图

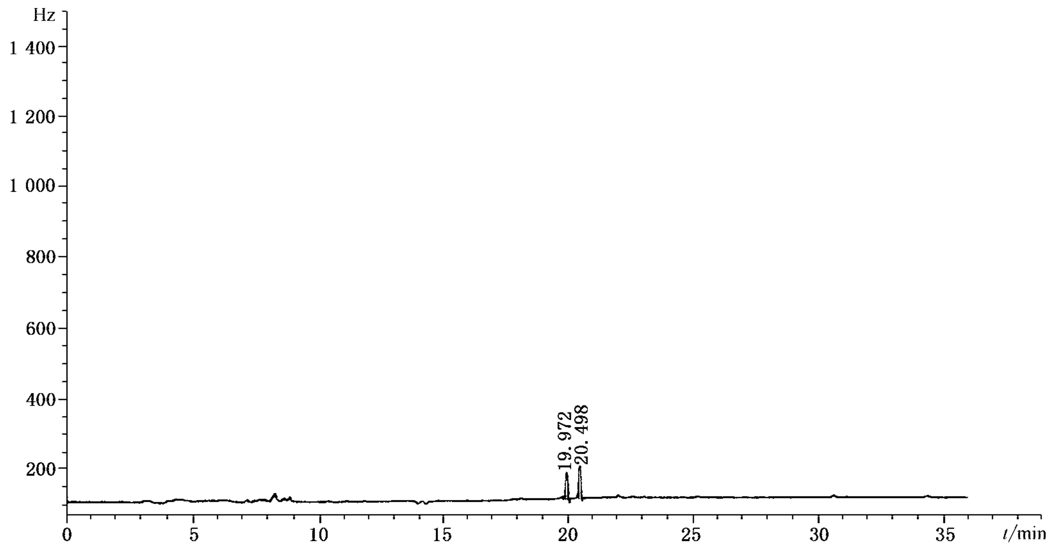


图 A.4 花生空白样品气相色谱图

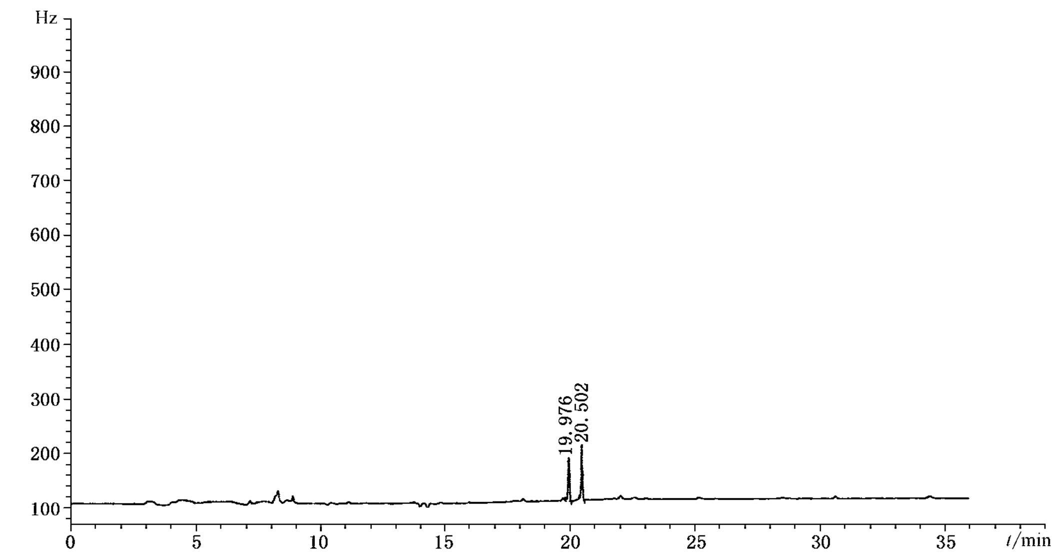


图 A.5 糙米空白样品气相色谱图

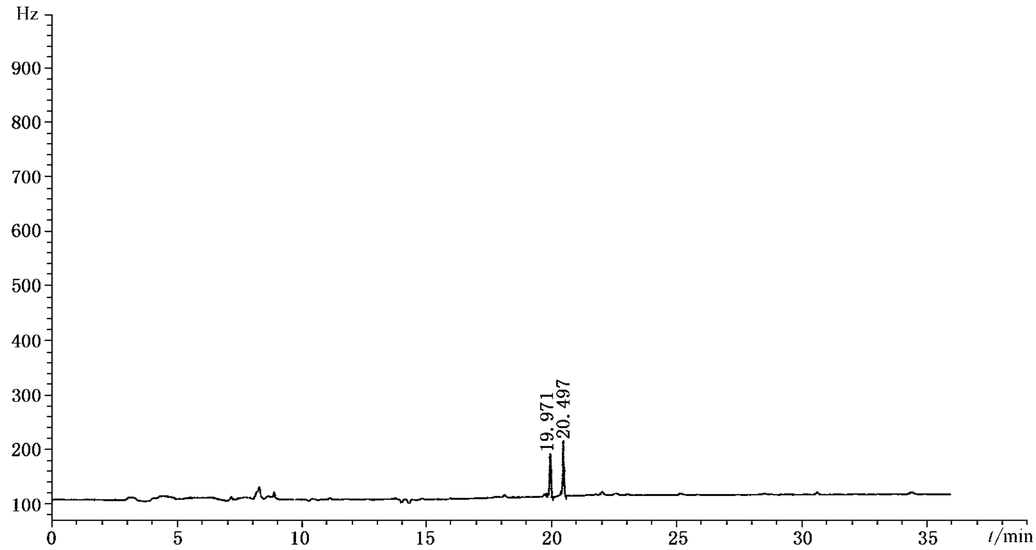


图 A.6　玉米空白样品气相色谱图

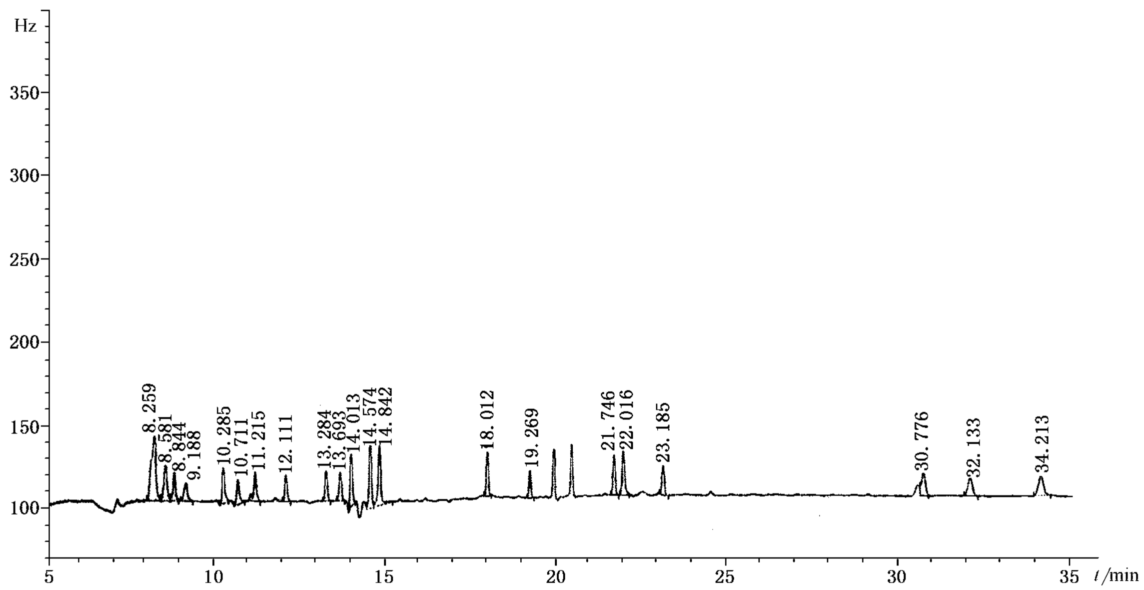


图 A.7　添加测定低限样品的气相色谱图

Foreword

Annex A of this standard is an informative annex.

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

This standard was drafted by the Liaoning Entry－Exit Inspection and Quarantine Bureau，Jiangsu Entry-Exit Inspection and Quarantine Bureau and Henan Entry－Exit Inspection and Quarantine Bureau.

This main drafters of this standard are：Jiang Li，Song Wenbin，Rong Hui，Jin Yan，Yu Xiaozhan，Shen Chongyu，Yang Jizhou，Jiang Shi.

This standard is an inspection and quarantine professional standard promulgated for the first time.

Determination of twenty one Fumigants residues in food for import and export—Headspace GC method

1 Scope

This standard specifies the method of testing twenty one kinds of fumigants residue, such as 1,1,1-trichloroethane, Trans-1,3-dichloropropene, Cis-1,3-dichloropropene, Trichloroethylene, 1,2-dichloropropane Monobromo-dichloro-methane, 1,1,2-trichloroethane, Tetrachloroethylene, Dibromochloromethane, Tribromomethane, 1,1,2,2-Tetrachloroethane, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,2-dichloroenzene, 1,2,4-trichlorobenzene, 1,2,3-trichlorobenzene ,Hexachloro-1,3-butadiene, 1,2-dibromoethane, Carbon disulfide, Carbon tetrachloride, Trichloromethane in corn, brown rice, peanut, soybean and red bean by headspace gas chromatography in foods for import and export.

This standard is applicable to the determination and confirmation of residue content of twenty onekinds of fumigants, such as trichloromethane, carbon tetrachloride, 1,2-dibromoethane and so on, in corn, brown rice, peanut, soybean, apple, spinach, scallion, carrot, pine – nut kernel, walnut, tea, honey, fish, cattle liver, chicken kidney, corn, rice, licorice and hot chili paste for import and export.

2 Principle

In the sealed vessel, the volatile fumigant poison molecules realize homeostasis between gas phase and solid phase at a certain temperature. At this moment the concentration of fumigants in the gas phase is direct ratio to that in the solid phase. Through the concentration determination of fumigants in the gas phase, the concentration of fumigants can be calculated by using external standard method.

3 Reagents and materials

All the reagents used should be analytically pure unless otherwise specified. "Water" is redistilled water.

3.1 Hexane: Residue grade.

3.2 Anhydrous sodium sulfate: Ignited at 650 ℃ for 4 hours, and kept in a sealed container.

3.3 Fumigants standard: Purity≥99%(see Table 1).

Table 1—Fumigants standard

Number	Standard name	Molar weight	Molecular formula	CAS No.
1	1,1,1-trichloroethane	133.35	CH_3CCl_3	71-55-6
2	Trans-1,3-dichloropropene	110.97	$C_3H_4Cl_2$	10061-02-6
3	Cis-1,3-dichloropropene	110.97	$C_3H_4Cl_2$	10061-02-5
4	Trichloroethylene	131.39	$ClCH=CCl_2$	79-01-6
5	1,2-dichloropropane	112.9	$CH_3CHClCH_2Cl$	78-87-5
6	Monobromo-dichloro-methane	163.8	$CHBrCl_2$	75-27-4
7	1,1,2-trichloroethane	133.4	$CHCl_2CH_2Cl$	79-00-5
8	Tetrachloroethylene	165.82	CCl_2CCl_2	127-18-4
9	Dibromochloromethane	208.3	$CHBr_2Cl$	124-48-1
10	Tribromomethane	252.73	$CHBr_3$	75-25-2
11	1,1,2,2-Tetrachloroethane	167.86	$CHCl_2CHCl_2$	79-34-5
12	1,3-dichlorobenzene	147.00	$C_6H_4Cl_2$	541-73-1
13	1,4-dichlorobenzene	147.00	$C_6H_4Cl_2$	106-46-7
14	1,2-dichlorobenzene	147.00	$C_6H_4Cl_2$	95-50-1
15	1,2,4-trichlorobenzene	181.45	$C_6H_3Cl_3$	120-82-1
16	1,2,3-trichlorobenzene	181.45	$C_6H_3Cl_3$	87-61-6
17	Hexachloro-1,3-butadiene	260.76	C_4Cl_6	87-68-3
18	1,2-dibromoethane	187.88	$C_2H_4Br_2$	106-93-4
19	Carbon disulfide	98.97	$C_2H_4Cl_2$	107-06-2
20	Carbon tetrachloride	153.84	CCl_4	56-23-5
21	Trichloromethane	119.38	$CHCl_3$	67-66-3

3.4 Fumigand poisons stock solution: Accurately weigh a certain amount of fumigand poisons standard, calulate their weights with density (Their density values are shown on Table 2) and dilute with hexane to make the standard stock solution of 1 000 μg/mL. The storage period is 12 months in a refrigerator at 0 ℃～4 ℃.

Table 2—The density values of fumigands

Number	Fumigand name	Density	Number	Fumigand name	Density
1	1,1,1-trichloroethane	1.350	12	1,3-dichlorobenzene	1.290
2	Trans-1,3-dichloropropene	1.160	13	1,4-dichlorobenzene	1.458
3	Cis-1,3-dichloropropene	1.160	14	1,2-dichlorobenzene	1.460
4	Trichloroethylene	1.465	15	1,2,4-trichlorobenzene	1.450
5	1,2-dichloropropane	1.260	16	1,2,3-trichlorobenzene	1.450
6	Monobromo-dichloro-methane	2.006	17	Hexachloro-1,3-butadiene	1.682
7	1,1,2-trichloroethane	4.550	18	1,2-dibromoethane	2.177
8	Tetrachloroethylene	1.631	19	Carbon disulfide	1.260
9	Dibromochloromethane	1.440	20	Carbon tetrachloride	1.592
10	Tribromomethane	2.889	21	Trichloromethane	1.448
11	1,1,2,2-Tetrachloroethane	1.600			

3.5 Standard working solution: Then dilute the standard stock solution with hexane to the required concentration as the standard working solution. The storage period is 12 months in a refrigerator at 0 ℃～4 ℃.

4 Apparatus and equipment

4.1 Gas chromatography equipped with the Electron Capture Detector.

4.2 Headspace: 20.0 mL.

4.3 Headspace injector: 1.0 mL.

4.4 Headspace equipment.

4.5 Conical plastic centrifuge tube: 50 mL.

4.6 Ultrasonic extraction.

5 Preparation and storage of test sample

5.1 Preparation of test sample

Take representative approximately 500 g of sample and place them in a clean container, which is sealed and labeled, as the test sample.

5.2 Storage of test sample

The test samples should be stored below −18 ℃. While sampling and sample preparation, precaution must be taken to avoid contamination or any factors that may cause the change of residue content.

6 Procedure

6.1 Determination

6.1.1 GC operating condition

a) Chromatographic column: HP−624 quartz capillary column, 30 m × 0.53 mm (i.d.) × 2.05 μm or equivalent;

b) Column temperature: 40 ℃ (1 min) $\xrightarrow{5\ ℃/\text{min}}$ 140 ℃ (30 min);

c) Injection port temperature：200 ℃；

d) Detector temperature：250 ℃；

e) Carrier gas：Helium，purity≥99.999%，flow rate 1.2 mL/min；

f) Injection volume：1 μL.

6.1.2 Analysis procedure

Weigh the test sample ca. 5.0 g(The precision is 0.01 g)into a 50 mL conical plastic centrifuge tube，add 15.0 mL hexane to dissolve，and then ultrasonic extraction is carried out for 3 min，and at last the centrifugal effect. Accurately transfer 10.0 mL the test sample solution into the headspace bottle，seal it rightly with rubberstopper containing polytetrafluoroethylene film inside，and place it in the headspace equipment at 60 ℃ for 0.5 h. Filter the extract into a 250 mL concentrate bottle under vacuum. Extract the residue with 50 mL of acetone once more，filter and combine the washings into the same concentrate bottle. Condense to 20 mL by a rotary evaporator with a 40 ℃ water bath temperature. The extractive top 200 μL gas is for GC analysis.

6.1.3 GC determination and confirmation

According to the approximate concentration of the fumigants pesticide in the sample solution，select the standard working solution with a similar concentration of the sample solution. The standard working solution should be injected in-between the injections of the sample solutions with one common volume. The responses of fumigants in the standard working solution and in the sample solution should be within the linear range of the instrumental detection.

The standard solution and the sample solution are determined under the above 6.1.1 condition，the GC chromatogram of the fumigants standard and the sample solution are shown respectively in annex A.

6.2 Blank experiment

The procedure is same with the above procedure without the sample being used.

7 Calculation and expression of the result

Calculate the content of fumigants residue in the test sample by GC data processor or according to the followed formula(1). The blank value should be subtracted from the calculated results.

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

Where：

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

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

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

c—the concentration of fumigants in the standard working solution, μg/mL;
V—the final volume of the sample solution, mL;
m—the corresponding mass of the test sample representing the final sample solution, g.

8 Limit of determination and recovery

8.1 Limit of determination

The determination limit of this method is 0.005 mg/kg for all the 21 kinds of fumigants.

8.2 The limit of determination and confirmation and recovery

The limit of determination and confirmation and recovery of this method is showed in table 3～table 7.

Table 3—The limit of determination and confirmation and recovery range

Sample name(Corn)	The limit of determination and confirmation/(mg/kg)	Recovery/%
1,1,1-trichloroethane	0.010～0.100	78.0～95.2
Trans-1,3-dichloropropene	0.010～0.100	74.0～98.5
Cis-1,3-dichloropropene	0.010～0.100	72.0～94.6
Trichloroethylene	0.010～0.100	70.0～94.4
1,2-dichloropropane	0.010～0.100	73.0～94.7
Monobromo-dichloro-methane	0.010～0.100	74.0～98.5
1,1,2-trichloroethane	0.010～0.100	73.0～98.5
Tetrachloroethylene	0.010～0.100	77.3～97.5
Dibromochloromethane	0.010～0.100	71.4～97.0
Tribromomethane	0.010～0.100	78.0～96.5
1,1,2,2-Tetrachloroethane	0.010～0.100	70.0～97.0
1,3-dichlorobenzene	0.010～0.100	73.0～99.0
1,4-dichlorobenzene	0.010～0.100	75.2～98.5
1,2-dichlorobenzene	0.010～0.100	71.0～98.0
1,2,4-trichlorobenzene	0.010～0.100	74.0～98.5
1,2,3-trichlorobenzene	0.010～0.100	74.0～98.0
Hexachloro-1,3-butadiene	0.010～0.100	72.2～98.0
1,2-dibromoethane	0.010～0.100	72.3～98.5
Carbon disulfide	0.010～0.100	72.1～ 98.0
Carbon tetrachloride	0.010～0.100	74.0～98.5
Trichloromethane	0.010～0.100	73.0～98.5

Table 4—The limit of determination and confirmation and recovery range

Sample name(Brown rice)	The limit of determination and confirmation/(mg/kg)	Recovery/%
1,1,1-trichloroethane	0. 010～0. 100	81. 0～97. 5
Trans-1,3-dichloropropene	0. 010～0. 100	74. 0～98. 5
Cis-1,3-dichloropropene	0. 010～0. 100	77. 0～98. 0
Trichloroethylene	0. 010～0. 100	74. 0～96. 7
1,2-dichloropropane	0. 010～0. 100	77. 0～98. 0
Monobromo-dichloro-methane	0. 010～0. 100	74. 0～96. 5
1,1,2-trichloroethane	0. 010～0. 100	74. 0～96. 5
Tetrachloroethylene	0. 010～0. 100	78. 0～98. 0
Dibromochloromethane	0. 010～0. 100	74. 4～97. 0
Tribromomethane	0. 010～0. 100	81. 0～98. 0
1,1,2,2-Tetrachloroethane	0. 010～0. 100	75. 5～98. 0
1,3-dichlorobenzene	0. 010～0. 100	72. 0～98. 0
1,4-dichlorobenzene	0. 010～0. 100	72. 0～96. 0
1,2-dichlorobenzene	0. 010～0. 100	74. 0～96. 8
1,2,4-trichlorobenzene	0. 010～0. 100	73. 5～97. 0
1,2,3-trichlorobenzene	0. 010～0. 100	72. 0～98. 5
Hexachloro-1,3-butadiene	0. 010～0. 100	71. 0～98. 5
1,2-dibromoethane	0. 010～0. 100	72. 0～98. 5
Carbon disulfide	0. 010～0. 100	72. 0～98. 5
Carbon tetrachloride	0. 010～0. 100	74. 0～98. 5
Trichloromethane	0. 010～0. 100	74. 0～98. 0

Table 5—The limit of determination and confirmation and recovery range

Sample name(Peanut)	The limit of determination and confirmation/(mg/kg)	Recovery/%
1,1,1-trichloroethane	0. 010～0. 100	76. 5～96. 1
Trans-1,3-dichloropropene	0. 010～0. 100	75. 0～98. 5
Cis-1,3-dichloropropene	0. 010～0. 100	73. 5～95. 5
Trichloroethylene	0. 010～0. 100	72. 0～95. 3
1,2-dichloropropane	0. 010～0. 100	75. 0～95. 6
Monobromo-dichloro-methane	0. 010～0. 100	76. 0～98. 5
1,1,2-trichloroethane	0. 010～0. 100	75. 0～98. 5
Tetrachloroethylene	0. 010～0. 100	72. 3～98. 0
Dibromochloromethane	0. 010～0. 100	80. 0～96. 1
Tribromomethane	0. 010～0. 100	80. 0～96. 1

Table 5 (continue)

Sample name(Peanut)	The limit of determination and confirmation/(mg/kg)	Recovery/%
1,1,2,2-Tetrachloroethane	0.010～0.100	72.0～ 95.1
1,3-dichlorobenzene	0.010～0.100	71.0～95.0
1,4-dichlorobenzene	0.010～0.100	75.7～97.0
1,2-dichlorobenzene	0.010～0.100	78.2～98.5
1,2,4-trichlorobenzene	0.010～0.100	79.0～98.0
1,2,3-trichlorobenzene	0.010～0.100	72.3～98.0
Hexachloro-1,3-butadiene	0.010～0.100	78.0～99.0
1,2-dibromoethane	0.010～0.100	72.3～99.0
Carbon disulfide	0.010～0.100	72.3～98.0
Carbon tetrachloride	0.010～0.100	72.4～98.0
Trichloromethane	0.010～0.100	75.0～91.0

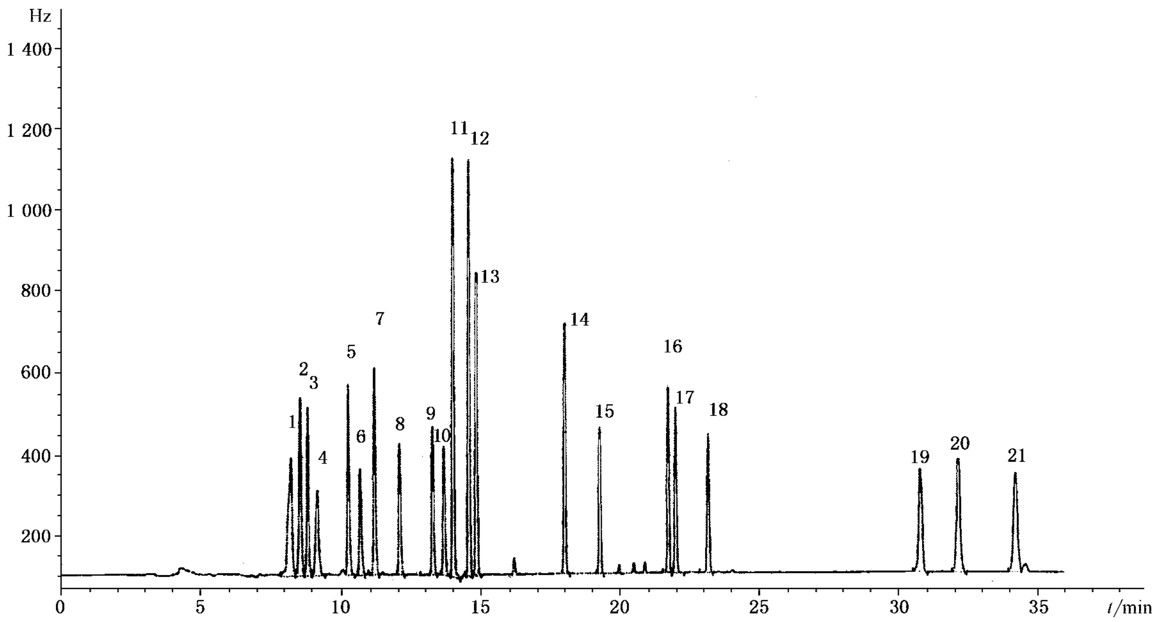
Table 6—The limit of determination and confirmation and recovery range

Sample name (soybean)	The limit of determination and confirmation/(mg/kg)	Recovery/%
1,1,1-trichloroethane	0.010～0.100	79.0～98.0
Trans-1,3-dichloropropene	0.010～0.100	76.8～98.0
Cis-1,3-dichloropropene	0.010～0.100	72.0～98.0
Trichloroethylene	0.010～0.100	71.00～95.5
1,2-dichloropropane	0.010～0.100	73.0～95.0
Monobromo-dichloro-methane	0.010～0.100	73.4～99.5
1,1,2-trichloroethane	0.010～0.100	73.4～98.0
Tetrachloroethylene	0.010～0.100	73.5～99.5
Dibromochloromethane	0.010～0.100	78.0～99.5
Tribromomethane	0.010～0.100	79.0～97.5
1,1,2,2-Tetrachloroethane	0.010～0.100	72.0～97.5
1,3-dichlorobenzene	0.010～0.100	72.8～98.0
1,4-dichlorobenzene	0.010～0.100	73.0～98.0
1,2-dichlorobenzene	0.010～0.100	71.0～98.5
1,2,4-trichlorobenzene	0.010～0.100	76.8～98.0
1,2,3-trichlorobenzene	0.010～0.100	73.4～99.5
Hexachloro-1,3-butadiene	0.010～0.100	79.0～98.0
1,2-dibromoethane	0.010～0.100	73.4～98.0
Carbon disulfide	0.010～0.100	73.5～98.0
Carbon tetrachloride	0.010～0.100	73.4～99.5
Trichloromethane	0.010～0.100	73.3～99.5

Table 7—The limit of determination and confirmation and recovery range

Sample name(Red bean)	The limit of determination and confirmation/(mg/kg)	Recovery/%
1,1,1-trichloroethane	0.010～0.100	73.0～98.0
Trans-1,3-dichloropropene	0.010～0.100	72.3～98.5
Cis-1,3-dichloropropene	0.010～0.100	72.0～98.0
Trichloroethylene	0.010～0.100	72.0～94.4
1,2-dichloropropane	0.010～0.100	73.0～94.7
Monobromo-dichloro-methane	0.010～0.100	70.2～98.5
1,1,2-trichloroethane	0.010～0.100	70.2～98.0
Tetrachloroethylene	0.010～0.100	72.8～98.5
Dibromochloromethane	0.010～0.100	70.1～98.0
Tribromomethane	0.010～0.100	77.8～98.0
1,1,2,2-Tetrachloroethane	0.010～0.100	72.8～98.0
1,3-dichlorobenzene	0.010～0.100	73.0～98.0
1,4-dichlorobenzene	0.010～0.100	71.7～97.5
1,2-dichlorobenzene	0.010～0.100	70.1～97.5
1,2,4-trichlorobenzene	0.010～0.100	71.7～97.5
1,2,3-trichlorobenzene	0.010～0.100	72.8～98.5
Hexachloro-1,3-butadiene	0.010～0.100	75.0～98.0
1,2-dibromoethane	0.010～0.100	73.0～97.5
Carbon disulfide	0.010～0.100	70.2～98.0
Carbon tetrachloride	0.010～0.100	70.2～97.5
Trichloromethane	0.010～0.100	70.3～98.5

Annex A
(informative)
GC chromatogram of the fumigants standard



1—Trichloromethane;
2—1,1,1-trichloroethane;
3—Carbon tetrachloride;
4—1,2-dichloroethane;
5—Trichloroethylene;
6—1,2-dichloropropane;
7—Monobromo-dichloro-methane;
8—Cis-1,3-dichloropropene;
9—Trans-1,3-dichloropropene;
10—1,1,2-trichloroethane;
11—Tetrachloroethylene;
12—Dibromochloromethane;
13—1,2-dibromoethane;
14—Tribromomethane;
15—1,2,2-tetrachloroethane;
16—1,3-dichlorobenzene;
17—1,4-dichlorobenzene;
18—1,2-dichlorobenzene;
19—1,2,4-trichlorobenzene;
20—Hexachloro-1,3-butadiene;
21—1,2,3-trichlorobenzene.

Figure A.1—GC chromatogram of the fumigants standard

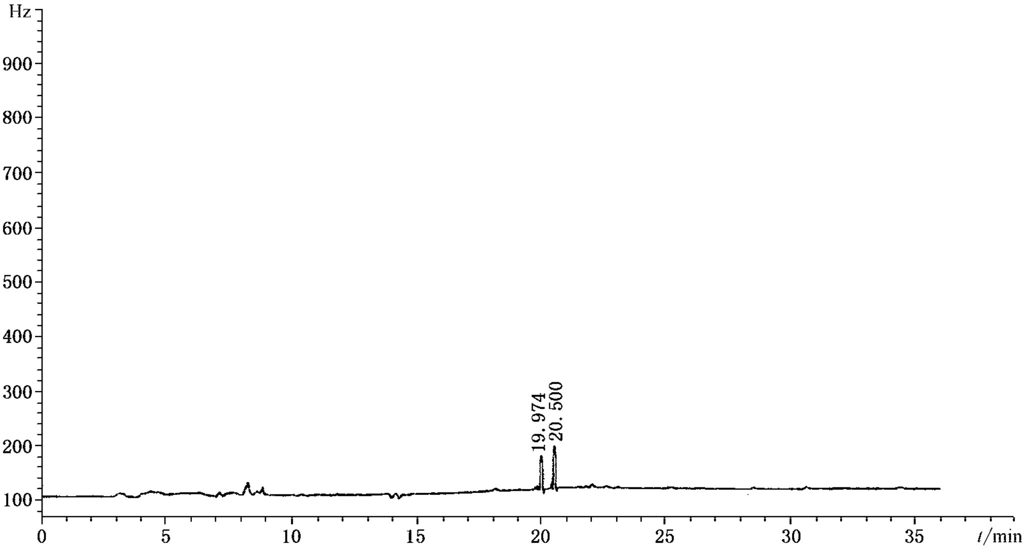


Figure A.2—GC chromatogram of the soybean sample

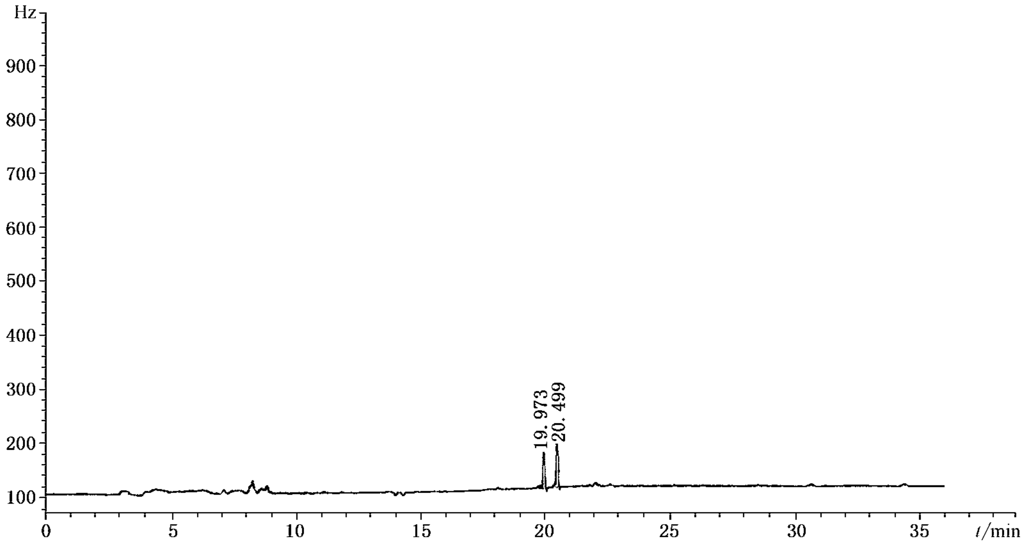


Figure A.3—GC chromatogram of the red bean sample

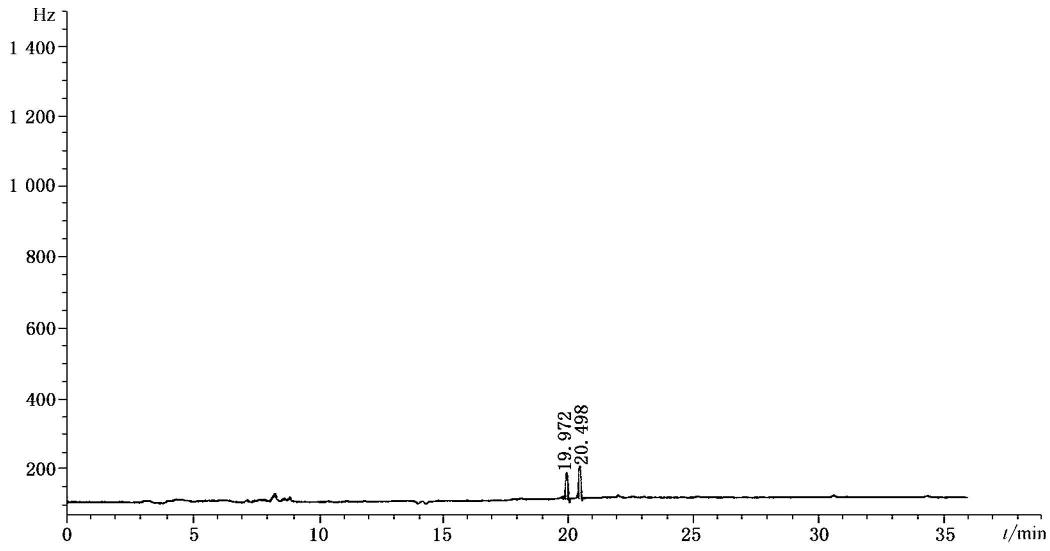


Figure A. 4—GC chromatogram of the peanut sample

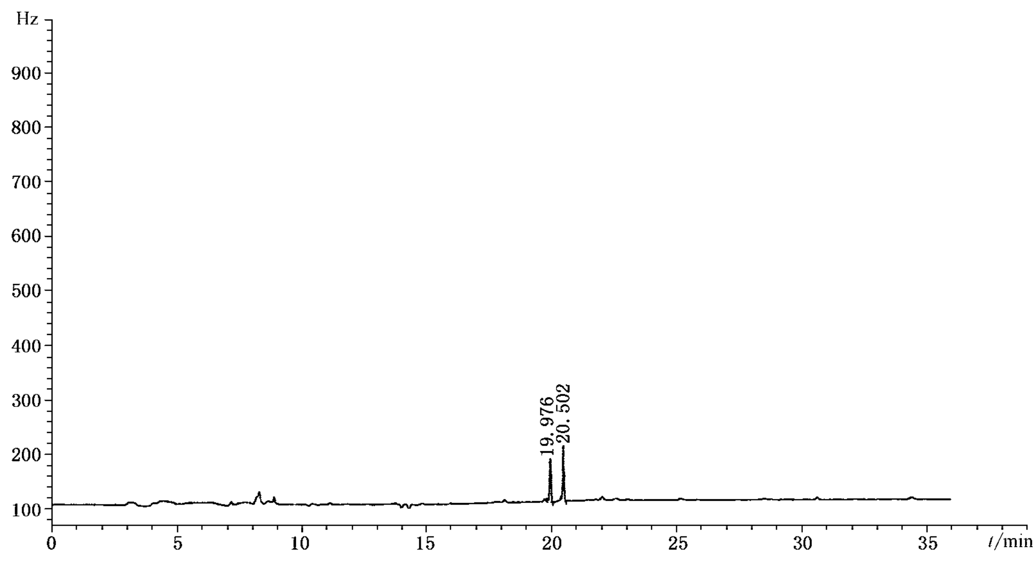


Figure A. 5—GC chromatogram of the brown rice sample

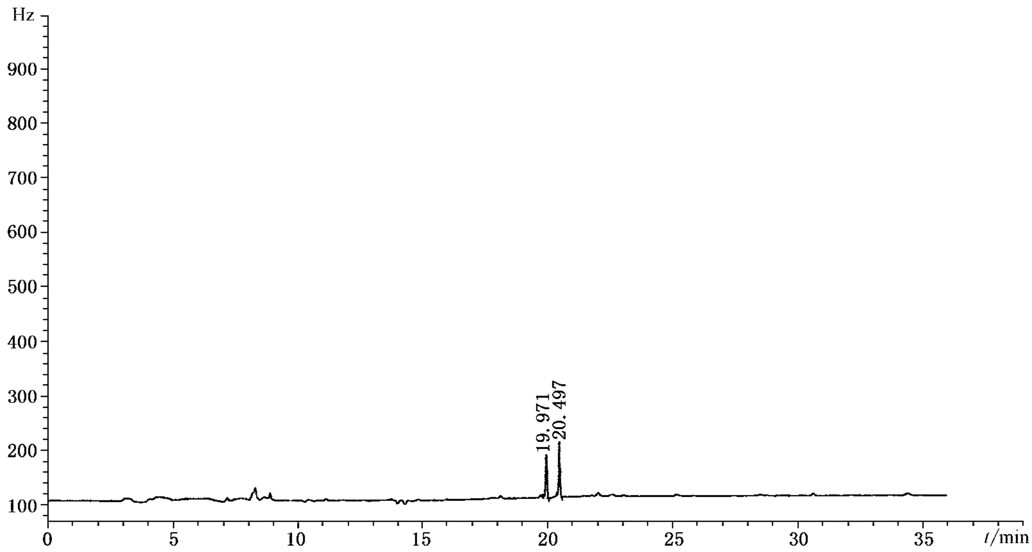


Figure A. 6— GC chromatogram of the corn sample

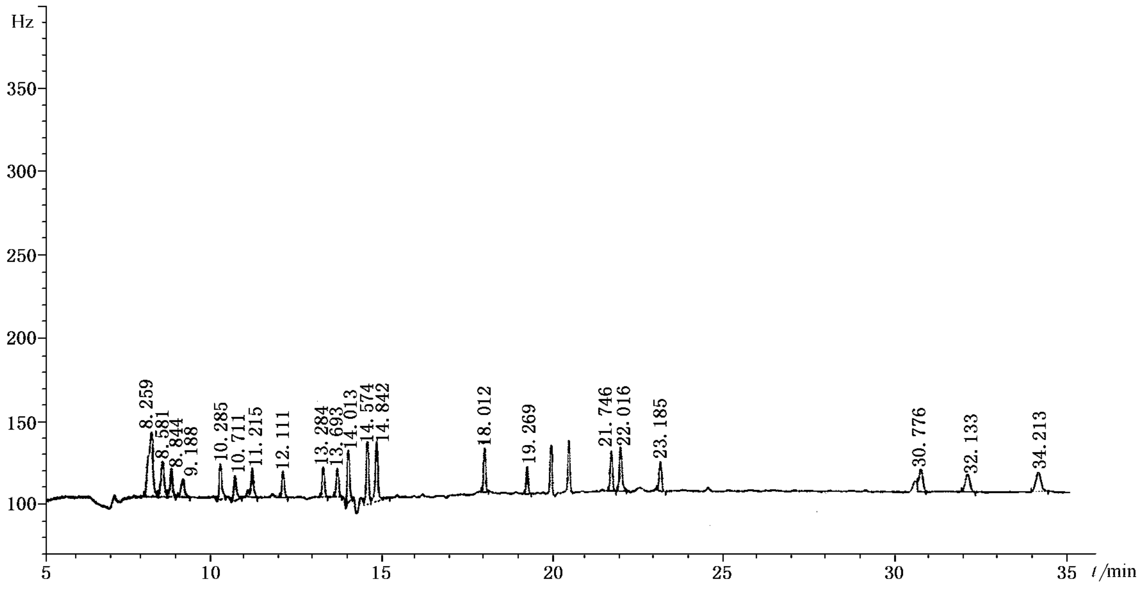


Figure A. 7—GC chromatogram of the determination limit of the sample

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