SN

中华人民共和国出入境检验检疫行业标准

SN/T 1737.2—2007

除草剂残留量检验方法 第2部分：气相色谱/质谱法测定粮谷及油籽中二苯醚类除草剂残留量

Determination of herbicides residues—
Part 2: Determination of diphenyl ether herbicides residues in cereal and oilseed by GC/MS method

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前　言

SN/T 1737《除草剂残留量检验方法》共分为两个部分：

——第1部分：气相色谱串联质谱法测定粮谷及油籽中酰胺类除草剂残留量；

——第2部分：气相色谱/质谱法测定粮谷及油籽中二苯醚类除草剂残留量。

本部分为SN/T 1737的第2部分。

本部分的附录A为资料性附录。

本部分由国家认证认可监督管理委员会提出并归口。

本部分起草单位：中华人民共和国深圳出入境检验检疫局。

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本部分系首次发布的出入境检验检疫行业标准。

除草剂残留量检验方法 第2部分：气相色谱/质谱法测定粮谷及油籽中二苯醚类除草剂残留量

1 范围

SN/T 1737的本部分规定了粮谷与油籽中环庚草醚、甲氧除草醚、苯草醚、甲羧除草醚、氟咯草酮、乳氟禾草灵、除草醚、乙氧氟草醚、乙羧氟草醚9种二苯醚类除草剂残留量的气相色谱/质谱检测方法。

本部分适用于大米与大豆中9种二苯醚类除草剂残留量的检测与确证。

2 方法提要

试样用乙腈提取，弗罗里硅土固相萃取柱净化，气相色谱/质谱仪测定，外标法定量。

3 试剂材料

除另有说明外，所用试剂均为分析纯，水为一级水。

3.1 丙酮：色谱纯。

3.2 乙腈：优级纯。

3.3 正己烷：色谱纯。

3.4 无水硫酸钠：经650℃灼烧4 h，置于干燥器中备用。

3.5 二苯醚类除草剂标准品：甲羧除草醚（$C_{14}H_9Cl_2NO_5$，CAS No：42576-02-3）、氟咯草酮（$C_{13}H_7F_3N_2O_5$，CAS No：15457-05-3）、除草醚（$C_{12}H_7Cl_2NO_3$，CAS No：1836-75-5）、乙氧氟草醚（$C_{15}H_{11}ClF_3NO_4$，CAS No：42874-03-3）、苯草醚（$C_{12}H_9ClN_2O_3$，CAS No：74070-46-5）、乙羧氟草醚（$C_{18}H_{13}ClF_3NO_7$，CAS No：77501-90-7），纯度均大于97.0%；乳氟禾草灵（$C_{19}H_{15}ClF_3NO_7$，CAS No：77501-63-4）纯度大于91.0%。环庚草醚（$C_{18}H_{26}O_2$，CAS No：87818-31-3）和甲氧除草醚（$C_{13}H_9Cl_2NO_4$，CAS No：32861-85-1）为液体标准，浓度为10 mg/L，溶剂分别为正己烷和乙腈。

3.6 除草剂标准溶液：

a) 标准储备溶液：准确称取适量的苯草醚、甲羧除草醚、氟咯草酮、乳氟禾草灵、除草醚、乙氧氟草醚、乙羧氟草醚，分别用丙酮溶解并定容至棕色容量瓶中，浓度相当于1 000 mg/L，储备液贮存在－18℃以下；

b) 混合标准中间溶液：准确吸取适量苯草醚、甲羧除草醚、氟咯草酮、乳氟禾草灵、除草醚、乙氧氟草醚、乙羧氟草醚标准储备溶液于棕色容量瓶中，用丙酮定容至刻度，各种二苯醚类除草剂的浓度为10 mg/L，此中间溶液贮存在－18℃以下；

c) 混合标准工作溶液：用丙酮将混合标准中间溶液按需要逐级稀释，并加入与其他二苯醚类除草剂等质量浓度的环庚草醚和甲氧除草醚，配为9种二苯醚类除草剂的混合标准工作溶液，混合标准工作溶液在0℃～4℃贮存。

3.7 弗罗里硅土固相萃取柱：500 mg，3 mL。

4 仪器和设备

4.1 气相色谱-质谱联用仪，配电子轰击源。

4.2 涡旋混匀器。

4.3 离心机。

4.4 吹氮浓缩仪。

4.5 固相萃取装置。

5 样品制备与保存

分别取有代表性的大米和大豆样品约500 g，充分粉碎，混匀，装入洁净容器内，密封并标明标记，于4℃冷藏保存。

6 测定步骤

6.1 提取

称取5 g(精确至0.01 g)样品于50 mL离心管中，加入2 mL水和20 mL乙腈(3.2)，再加入2 g无水硫酸钠(3.4)，在涡旋混匀器上混匀3 min，于5 000 r/min离心5 min，将上层10 mL乙腈转移入另一15 mL离心管中，于40℃水浴中吹氮至干，用正己烷定容至1 mL。

6.2 净化

于弗罗里硅土固相萃取柱(3.7)填料上方填装1 cm高无水硫酸钠，分别用6 mL丙酮和6 mL正己烷预淋洗。将提取液转移至固相萃取柱中，以1 d/s速率过柱，弃去流出液，再用5 mL正己烷-丙酮(60+40)进行洗脱，流速为1 d/s。收集洗脱液于15 mL离心管中，于40℃水浴中吹氮浓缩至干，用正己烷溶解并定容至1 mL，供气相色谱/质谱测定。

6.3 测定

6.3.1 气相色谱条件

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

b) 色谱柱温度：70℃(2 min)$\xrightarrow{50℃/min}$180℃$\xrightarrow{10℃/min}$200℃$\xrightarrow{2℃/min}$220℃$\xrightarrow{10℃/min}$280℃(10 min)；

c) 进样口温度：270℃；

d) 载气：氦气，纯度大于99.999%，流速1.0 mL/min；

e) 进样量：1 μL；

f) 进样方式：不分流进样，1.5 min后开阀。

6.3.2 质谱条件

a) 离子源温度：230℃；

b) 传输线温度：280℃；

c) 电离方式：EI；

d) 电离能量：70 eV；

e) 监测方式：选择离子监测(SIM)，设定条件见表1；

f) 溶剂延迟：5 min。

表1 二苯醚类除草剂的保留时间和特征选择离子模式条件

保留时间/min	二苯醚类除草剂		选择离子(m/z)及丰度比
	名 称	SIM模式时间/min	
10.041	环庚草醚	5.00	105*(100)，123(44)，154(15)，169(16)
14.229	氟咯草酮	13.00	190*(100)，126(31)，162(18)，309(9)，328(9)
15.177	乙氧氟草醚	15.00	252*(100)，280(16)，300(31)，361(38)
15.680	除草醚	15.50	283*(100)，139(27)，202(49)，253(18)，285(77)
16.694	苯草醚	16.30	264*(100)，77(49)，183(38)，194(32)，212(38)

表 1(续)

保留时间/min	二苯醚类除草剂		选择离子(m/z)及丰度比
	名　称	SIM 模式时间/min	
19.584	甲氧除草醚	18.00	313[a](100),232(36),266(79),283(33)
20.404	甲羧除草醚	20.00	341[a](100),173(18),189(17),310(26),343(71)
21.616	乳氟禾草灵	21.00	344[a](100),207(24),223(26),346(40)
21.880	乙羧氟草醚	21.75	344[a](100),207(63),223(59),315(31)
[a] 为定量检测离子。			

6.3.3　气相色谱/质谱测定

根据样液中二苯醚类除草剂残留的含量情况，选定峰高相近的标准工作溶液。标准工作溶液和样液中二苯醚类除草剂残留的响应值均应在仪器的检测线性范围内。对标准工作溶液和样液等体积参差进样测定。如果样液与标准工作溶液的选择离子色谱中，在相同保留时间有色谱峰出现，同时所选择离子的丰度比与标准样品相关离子的相对丰度一致，相似度在允差之内(见表 2)，根据选择离子对其进行外标法定量。在上述气相色谱/质谱条件下，环庚草醚、氟咯草酮、乙氧氟草醚、除草醚、苯草醚、甲氧除草醚、甲羧除草醚、乳氟禾草灵、乙羧氟草醚的保留时间见表 1。0.02 mg/L 混合标准溶液总离子流色谱图参见附录 A 中图 A.1。

表 2　定性确证时相对离子丰度的最大允许偏差

相对离子丰度/%	>50	>20～50	>10～20	≤10
允许的相对偏差/%	±20	±25	±30	±50

6.3.4　空白试验

除不加标样外，按上述测定步骤进行。

7　结果计算和表述

按式(1)计算试样中二苯醚类除草剂的含量，计算结果需扣除空白值。

$$X=\frac{A\times c\times V}{A_S\times m} \qquad \cdots\cdots(1)$$

式中：

X——样品中二苯醚类除草剂含量，单位为毫克每千克(mg/kg)；

A——样液中二苯醚类除草剂峰面积；

A_S——标准工作溶液中二苯醚类除草剂峰面积；

c——标准工作溶液中二苯醚类除草剂浓度，单位为毫克每升(mg/L)；

m——最终样液代表的试样质量，单位为克(g)；

V——样液最终定容体积，单位为毫升(mL)。

8　方法的测定低限和回收率

8.1　测定低限

本方法的测定低限为 0.025 mg/kg。

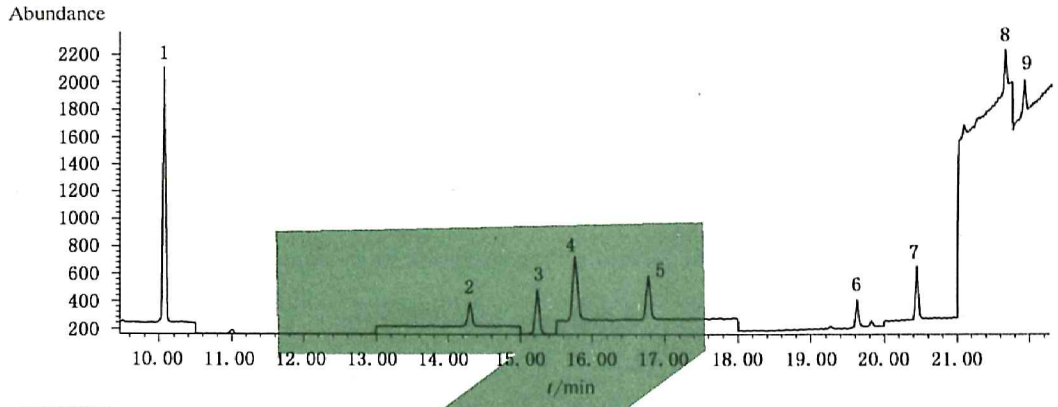
8.2　回收率

0.025 mg/kg～0.100 mg/kg 添加浓度范围内，大米与大豆中二苯醚类除草剂回收率数据见表 3。

表 3　大米与大豆中二苯醚类除草剂不同添加水平回收率数据

化合物名称	添加水平/(mg/kg)	大米中回收率范围/%	大豆中回收率范围/%
环庚草醚	0.025	72.0～100.0	76.0～100.0
	0.050	76.0～96.0	74.0～100.0
	0.100	73.0～97.0	72.0～104.0
氟咯草酮	0.025	76.0～104.0	72.0～104.0
	0.050	76.0～110.0	70.0～108.0
	0.100	74.0～97.0	72.0～92.0
乙氧氟草醚	0.025	72.0～96.0	72.0～100.0
	0.050	70.0～98.0	72.0～94.0
	0.100	72.0～93.0	70.0～106.0
除草醚	0.025	72.0～96.0	72.0～104.0
	0.050	74.0～98.0	70.0～102.0
	0.100	75.0～107.0	71.0～89.0
苯草醚	0.025	72.0～96.0	72.0～100.0
	0.050	74.0～98.0	72.0～102.0
	0.100	72.0～105.0	71.0～96.0
甲氧除草醚	0.025	72.0～100.0	72.0～96.0
	0.050	70.0～104.0	74.0～92.0
	0.100	74.0～107.0	75.0～91.0
甲羧除草醚	0.025	72.0～100.0	72.0～92.0
	0.050	72.0～102.0	76.0～108.0
	0.100	72.0～107.0	72.0～92.0
乳氟禾草灵	0.025	72.0～92.0	72.0～96.0
	0.050	70.0～106.0	72.0～104.0
	0.100	71.0～97.0	71.0～94.0
乙羧氟草醚	0.025	72.0～96.0	72.0～92.0
	0.050	72.0～104.0	70.0～98.0
	0.100	74.0～90.0	71.0～104.0

附 录 A
（资料性附录）
9种二苯醚类除草剂总离子流色谱图



1——环庚草醚；
2——氟咯草酮；
3——乙氧氟草醚；
4——除草醚；
5——苯草醚；
6——甲氧除草醚；
7——甲羧除草醚；
8——乳氟禾草灵；
9——乙羧氟草醚。

图 A.1 0.02 mg/L 二苯醚类除草剂标准溶液总离子流色谱图

Foreword

Annex A of this part is an informative annex.

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

The part was drafted by shenzhen Entry-Exit Inspection and Quarantine Bureau of the People's Republic of China.

The main drafters of this part are Jin Baohui, Xie Liqi, Lin Yankui, Lan Fang, Chen Peijin, Wu Weidong, Lin Li and Zhao Qionghui.

This part is a professional standard for entry-exit inspection and quarantine promulgated for the first time.

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

Determination of herbicides residues— Part 2: Determination of diphenyl ether herbicides residues in cereal and oilseed by GC/MS method

1 Scope

This part of SN/T 1737 specifies the methods of determination by gas chromatography-mass spectrometry of 9 kinds of diphenyl ester herbicides residues including cinmethylin, fluorodifen, oxyfluorfen, nitrofen, aclonifen, chlomethoxyfen, bifenox, lactofen, fluoroglycofen-ethyl in cereals and oilseeds.

This part is applicable to the qualitative and quantitative determination of 9 diphenyl ester herbicides residues of in rice and soybean.

2 Abstract

The residues of diphenyl ester herbicides in the test sample are extracted with acetonitrile. After concentrating the acetonitrile extract to dry under nitrogen, And the residues dissolved with hexane is cleaned up by passing through a florisil cartridge or equivalent and determined by a GC-MS, using external standard method.

3 Reagents and materials

Unless otherwise specified, all reagents should be of analytical grade; water is the first grade water.

3.1 Acetone: Grade for GC residue analysis.

3.2 Acetonitrile: GR.

3.3 Hexane: Grade for GC residue analysis.

3.4 Anhydrous sodium sulfate: Ignite at 650℃ for 4 h, and keep in a tightly closed container.

3.5 Diphenyl ester herbicides standard: Bifenox ($C_{14}H_9Cl_2NO_5$, CAS No: 42576-02-3), fluorodifen ($C_{13}H_7F_3N_2O_6$, CAS No: 15457-05-3), nitrofen ($C_{12}H_7Cl_2NO_3$, CAS No: 1836-75-5), oxyfluorfen ($C_{15}H_{11}ClF_3NO_4$, CAS No: 42874-03-3), aclonifen ($C_{12}H_9ClN_2O_3$, CAS No: 74070-46-5), fluoroglycofen-ethyl ($C_{18}H_{13}ClF_3NO_7$, CAS No: 77501-90-7), purity more than 97.0%. lactofen ($C_{19}H_{15}ClF_3NO_7$,

CAS No:77501-63-4), purity more than 91.0%. Cinmethylin($C_{18}H_{26}O_2$, CAS No:87818-31-3) and chlomethoxyfen($C_{13}H_9Cl_2NO_4$, CAS No:32861-85-1) is liquid standard with concentration of 10 mg/L and the solvent of cinmethylin is hexane, the solvent of chlomethoxyfen is acetonitrile.

3.6 Herbicides standard solution:

a) Standard stock solution: Accurately weigh herbicides standard of bifenox, fluorodifen, nitrofen, oxyfluorfen, fluoroglycofen-ethyl, aclonifen, lactofen respectively, dissolve in acetone to make a standard stock solution of 1 000 mg/L in concentration. The solution can be preserved in the temperature below −18℃;

b) Intermediate standard mixture solution: Accurately measure and adequate volume herbicides standard stock solution, dilute with acetone to make an intermediate standard mixture solution of 10 mg/L in concentration. The solution can be preserved in the temperature below −18℃;

c) Standard working solution: According to the requirement, accurately measure an adequate volume of herbicides intermediate standard mixture solution and the standard of cinmethylin and chlomethoxyfen, dilute with acetone and prepare a standard working solution of appropriate concentration. The solution can be preserved in the temperature at 0℃～4℃.

3.7 Florisil cartridge: 500 mg, 3 mL or equivalent.

4 Apparatus and equipment

4.1 GC-MS, equipped with EI.

4.2 Mechanical Shaker.

4.3 Centrifuge.

4.4 Evaporator.

4.5 Solid phase extraction.

5 Sample preparation and storage

Reduce the rice and soybean sample to ca. 500 g, churn up and mix thoroughly, place in clean containers, seal and label, stored below 4℃.

6 Procedure

6.1 Extraction

Accurately weigh 5 g of the test sample(accurate to 0.01 g) in 50 mL centrifuge tube, add 2 mL dis-

tilled water, 20 mL acetonitrile(3.2)and 2 g anhydrous sodium sulfate(3.4), blend for 3 min in vortex mixer, centrifuge for 5 min. (5 000 r/min.). Transfer 10 mL of the upper anhydrous extract into another 15 mL centrifuge tube. Concentrate the extract to dry under nitrogen at 40℃. Dissolve the residues and dilute exactly to 1 mL with hexane.

6.2 Cleanup

Transfer the sample residue(6.1)into the florisil cartridge(3.7)to the height of 1 cm. Prior to use, rinse the cartridge with 6 mL acetone and 6 mL hexane. Load the sample on the cartridge, and keep the flow rate at 1 d/s.

Discard the column eluate. Rinse the cartridge with 5 mL hexane-Acetone(60+40)and keep the flow speed at 1 d/s. Collect the washings with the total eluent into a 15 mL centrifuge tube and blow nearly dry under nitrogen at 40℃. Dissolve the residues and dilute exactly to 1 mL with hexane for GC/MS.

6.3 Determination

6.3.1 GC operating conditions

a) Column: HP-5MSI capillary column, 30 m × 0.25 mm × 0.25 μm or equivalent;

b) Column temperature: 70℃ (2 min) $\xrightarrow{50℃/min}$ 180℃ $\xrightarrow{10℃/min}$ 200℃ $\xrightarrow{2℃/min}$ 220℃ $\xrightarrow{10℃/min}$ 280℃ (10 min);

c) Injection port temperature: 270℃;

d) Carrier gas: Helium, Purity≥99.999%, 1.0 mL/min;

e) Injection volume: 1 μL;

f) Injection mode: Splitless, purge on after 1.5 min.

6.3.2 MS operating conditions

a) Ion source temperature: 230℃;

b) Transferline temperature: 280℃;

c) Ionization mode: EI;

d) Ionization energy: 70 eV;

e) Test mode:SIM,condition setup can be found in table 1;

f) Solvent delay:5 min.

Table 1—Retention time and SIM condition of diphenyl ester compounds

Retention time/min	Diphenyl ether compounds		Selected ions and abundance ratio
	Name	Time in SIM/min	
10.041	cinmethylin	5.00	105[a](100),123(44),154(15),169(16)
14.229	fluorodifen	13.00	190[a](100),126(31),162(18),309(9),328(9)
15.177	oxyfluorfen	15.00	252[a](100),280(16),300(31),361(38)
15.680	nitrofen	15.50	283[a](100),139(27),202(49),253(18),285(77)
16.694	aclonifen	16.30	264[a](100),77(49),183(38),194(32),212(38)
19.584	chlomethoxyfen	18.00	313[a](100),232(36),266(79),283(33)
20.404	bifenox	20.00	341[a](100),173(18),189(17),310(26),343(71)
21.616	lactofen	21.00	344[a](100),207(24),223(26),346(40)
21.880	fluoroglycofen-ethyl	21.75	344[a](100),207(63),223(59),315(31)
[a] are ions for quantitative determination.			

6.3.3 GC-MS determination

According to the approximate concentration of diphenyl ether herbicides in the test sample solution, the standard working solution is selected with similar peak area to that of sample solution. The response of herbicides in the standard working solution and 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 sample solution of equal volume. If there is a peak appeared at the same retention time for both of the sample solution and standard working solution in the mass spectrogram figure, the relative intensity ratios of each qualitative ions are also consistent with standard at a similar concentration. The similarity degree of their relative abundance ratio in permitted tolerance (see table 2). Under the above GC-MS conditions, the retention time of cinmethylin, fluorodifen, oxyfluorfen, nitrofen, aclonifen, chlomethoxyfen, bifenox, lactofen, fluoroglycofen-ethyl can be found in table 1. The chromatogram of 0.02 mg/L standard working solution can be found in annex A.

Table 2—Miximum permitted tolerance for relative ion intensities using a range of mass spectrometric techniques

Relative intensiy(% of base peak)	>50	>20~50	>10~20	≤10
GC-MS(relative)/%	±20	±25	±30	±50

6.3.4 Blank test

The operation of the blank test is the same as that described in the method of determination, but

with omission of sample addition.

7 Calculation and expression of result

The calculation of diphenyl ether content in the sample is according to the following formula(1), the blank value should be subtracted from the result of calculation:

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

where

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

A—Peak area of diphenyl ether in the sample solution;

A_s—Peak area of diphenyl ether in the standard working solution;

c—the concentration of diphenyl ether in the standard working solution, mg/L;

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

V—the final volume of sample solution, mL.

8 Limit of determination and recovery

8.1 Limit of determination

The limit of determination of testing diphenyl ether herbicides is 0.025 mg/kg.

8.2 Recovery

According to the experimental data for rice and soybean, when the concentration of diphenyl ether is in the range of 0.025 mg/kg~0.100 mg/kg, recovery is shown in table 3.

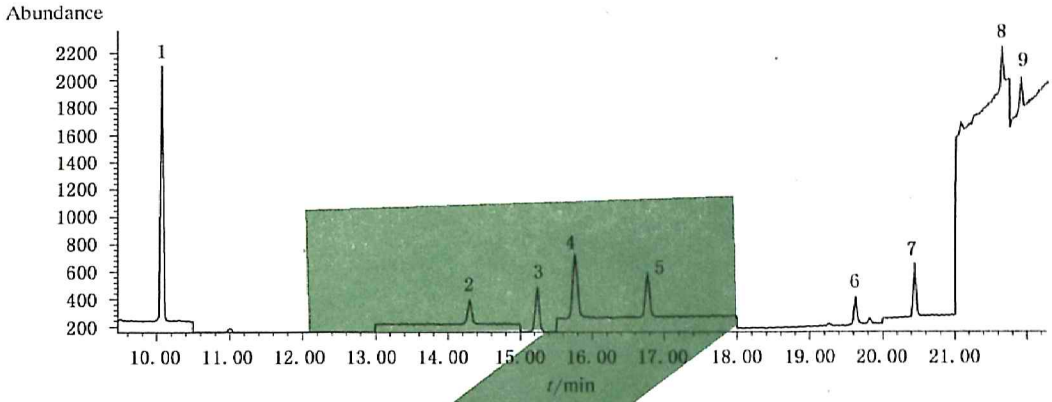
Table 3—The range of recovery of diphenyl ether in rice and soybean

Name	Spike level/(mg/kg)	Range of recovery(rice)/%	Range of recovery(soybean)/%
cinmethylin	0.025	72.0~100.0	76.0~100.0
	0.050	76.0~96.0	74.0~100.0
	0.100	73.0~97.0	72.0~104.0
fluorodifen	0.025	76.0~104.0	72.0~104.0
	0.050	76.0~110.0	70.0~108.0
	0.100	74.0~97.0	72.0~92.0
oxyfluorfen	0.025	72.0~96.0	72.0~100.0
	0.050	70.0~98.0	72.0~94.0
	0.100	72.0~93.0	70.0~106.0

Table 3 (continued)

Name	Spike level/(mg/kg)	Range of recovery(rice)/%	Range of recovery(soybean)/%
nitrofen	0.025	72.0～96.0	72.0～104.0
	0.050	74.0～98.0	70.0～102.0
	0.100	75.0～107.0	71.0～89.0
aclonifen	0.025	72.0～96.0	72.0～100.0
	0.050	74.0～98.0	72.0～102.0
	0.100	72.0～105.0	71.0～96.0
chlomethoxyfen	0.025	72.0～100.0	72.0～96.0
	0.050	70.0～104.0	74.0～92.0
	0.100	74.0～107.0	75.0～91.0
bifenox	0.025	72.0～100.0	72.0～92.0
	0.050	72.0～102.0	76.0～108.0
	0.100	72.0～107.0	72.0～92.0
lactofen	0.025	72.0～92.0	72.0～96.0
	0.050	70.0～106.0	72.0～104.0
	0.100	71.0～97.0	71.0～94.0
fluoroglycofen-ethyl	0.025	72.0～96.0	72.0～92.0
	0.050	72.0～104.0	70.0～98.0
	0.100	74.0～90.0	71.0～104.0

Annex A
(informative)
SIM Chromatogram of the 9 kinds of diphenyl ester compound



1—cinmethylin;
2—fluorodifen;
3—oxyfluorfen;
4—nitrofen;
5—aclonifen;
6—chlomethoxyfen;
7—bifenox;
8—lactofen;
9—fluoroglycofen-ethyl.

Figure A. 1—SIM Chromatograph of 0. 02 mg/L diphenyl ester standard solution