SN

中华人民共和国出入境检验检疫行业标准

SN/T 3541—2013

出口食品中多种醚类除草剂残留量检测方法 气相色谱-负化学离子源-质谱法

Determination of multiple ether herbicides sesidues in foods for export—GC-MS/NCI method

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中华人民共和国
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前　言

本标准按照 GB/T 1.1—2009 给出的规则起草。

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：中华人民共和国江苏出入境检验检疫局。

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出口食品中多种醚类除草剂残留量检测方法 气相色谱-负化学离子源-质谱法

1 范围

本标准规定了食品中苯醚类除草剂的气相色谱-负化学离子源-质谱检测方法。

本标准适用于大米、大豆、菠菜、大葱、辣椒、草莓、甜豌豆、绿茶、龙虾仁、鳗鱼、猪肉、蜂蜜等12种食品中醚类除草剂残留量的测定和确证。

2 方法提要

试样经正己烷饱和过的乙腈(含1%冰醋酸)提取,分散固相萃取净化,气相色谱-负化学离子源质谱法进行测定与确证,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,水为去离子水。

3.1 乙腈:色谱纯。

3.2 正己烷:色谱纯。

3.3 丙酮:色谱纯。

3.4 冰醋酸。

3.5 无水硫酸镁。

3.6 无水乙酸钠。

3.7 提取溶剂(含1%冰醋酸的经正己烷饱和过的乙腈溶液):加10 mL冰醋酸到990 mL的(事先用正己烷饱和过)乙腈溶液中。

3.8 标准物质:三氟硝草醚(Fluorodifen,CAS号:15457-05-3)、乙氧氟草醚(Oxyfluorfen,CAS号:42874-03-3)、除草醚(Nitrofen,CAS号:1836-75-5)、苯草醚(Aclonifen,CAS号:74070-46-5)、吡草醚(Pyraflufen-ethyl,CAS号:129630-19-9)、喹氧灵(Quinoxyfen,CAS号:124495-18-7)、氯氟草醚(Ethoxyfen-ethyl,CAS号:131086-42-5)、甲氧除草醚(Chlomethoxyfen,CAS号:32861-85-1)、甲羧除草醚(Bifenox,CAS号:42576-02-3)、乳氟禾草灵(Lactofen,CAS号:77501-63-4)和乙羧氟草醚(Fluoroglycofen-ethyl,CAS号:77501-90-7):纯度大于等于98.0%。

3.9 各种农药标准储备溶液:分别准确称取适量的上述标准品,用丙酮稀释配制成1.00 mg/mL的单种标准储备液,4 ℃下保存(有效期为12个月)。

3.10 混合标准储备液:分别准确移取0.5 mL的上述单种标准储备液于10 mL容量瓶,用丙酮稀释配制成50 μg/mL的混合标准储备液,4 ℃下保存(有效期为6个月)。

3.11 混合标准工作液:根据需要用丙酮稀释成适当浓度的标准工作溶液,4 ℃下保存(有效期为1个月)。

3.12 石墨化炭黑填料:40 μm。

3.13 PSA(N-2 氨乙基)填料:40 μm。

3.14 C_{18}填料:40 μm。

3.15 微孔滤膜：0.45 μm，有机相。

4 仪器和设备

4.1 气相色谱-质谱仪：配置负化学离子源(NCI)。
4.2 分析天平：感量为 0.1 mg 和 0.01 g。
4.3 旋转蒸发器。
4.4 组织捣碎机。
4.5 粉碎机。
4.6 均质器。
4.7 振荡器。

5 试样制备与保存

5.1 试样制备

5.1.1 菠菜、大葱、辣椒、草莓和甜豌豆

取代表性样品 500 g，将其可食用部分切碎后(不可用水洗涤)，依次用捣碎机将样品加工成浆状。混匀，均分成两份作为试样，分装入容器内，密闭并标明标记。

5.1.2 绿茶、大米和大豆

取代表性样品 500 g，用粉碎机粉碎并通过 2.0 mm 圆孔筛。混匀，分装入容器内，密闭并标明标记。

5.1.3 龙虾仁、鳗鱼和猪肉

取代表性样品 500 g，将其切碎后，依次用绞碎机将样品绞碎，混匀，分装入容器内，密封并标明标记。

5.1.4 蜂蜜

取有代表性样品量 500 g，对无结晶的蜂蜜样品将其搅拌均匀；对有结晶析出的蜂蜜样品，在密闭情况下，将样品瓶置于不超过 60 ℃的水浴中温热，振荡，待样品全部融化后搅匀，迅速冷却至室温，在融化时必须注意防止水分挥发。制备好的试样均分成两份，分别装入样品瓶中，密封，并标明标记。

5.2 试样的保存

大米、大豆、绿茶、蜂蜜等试样于 0 ℃～4 ℃保存；菠菜、大葱、辣椒、草莓、甜豌豆、龙虾仁、鳗鱼和猪肉等试样于－18 ℃以下冷冻保存。

在制样的操作过程中，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 称样

6.1.1 大豆、龙虾仁、鳗鱼和猪肉等试样

称取 5 g 试样(精确至 0.01 g)于 250 mL 的具塞锥形瓶中。

6.1.2 菠菜、大葱、辣椒、草莓和甜豌豆等试样

称取 10 g 试样(精确至 0.01 g)于 250 mL 的具塞锥形瓶中。

6.1.3 大米、绿茶和蜂蜜等试样

称取 5 g 试样(精确至 0.01 g)于 250 mL 的具塞锥形瓶中,并加入 4 mL 水,混匀,浸泡或溶解。茶叶需浸泡 30 min。

6.2 提取

加入 20 mL 提取溶剂(3.7),加入 15 g 无水硫酸镁(3.5)和 6 g 无水醋酸钠(3.6),振荡提取 40 min(牛肉、鳗鱼、龙虾仁等应均质提取 5 min),过滤于 150 mL 浓缩瓶中。再加入 20 mL 提取溶剂(3.7)重复提取一次,合并提取液,40 ℃下旋转浓缩至干。用 2 mL 乙腈溶解残渣,待净化。

6.3 固相分散萃取净化

6.3.1 菠菜、大葱、辣椒、草莓、甜豌豆和绿茶提取液

将 6.2 相应样品提取液转移到事先装有 50 mg PSA 填料和 200 mg 石墨化碳黑填料的 10 mL 小试管中,充分涡旋 1 min,待色素完全消除后,过滤膜,供气相色谱-质谱测定和确证。

6.3.2 大米、大豆、龙虾仁、鳗鱼、猪肉和蜂蜜提取液

将 6.2 相应样品提取液转移到事先装有 100 mg PSA 填料,50 mg 石墨化碳黑填料和 100 mg C_{18} 填料的 10 mL 小试管中,充分涡旋 1 min,过滤膜,供气相色谱-质谱测定和确证。

6.4 测定

6.4.1 气相色谱-质谱条件

6.4.1.1 色谱柱:DB-17ms 石英弹性毛细管柱,30 m×0.25 mm(i.d.),膜厚 0.25 μm,或相当者;

6.4.1.2 色谱柱温度:90 ℃ $\xrightarrow{15\ ℃/min}$ 270 ℃ $\xrightarrow{2\ ℃/min}$ 276 ℃ $\xrightarrow{48\ ℃/min}$ 300 ℃(2.5 min);

6.4.1.3 进样口温度:300 ℃;

6.4.1.4 色谱-质谱接口温度:250 ℃;

6.4.1.5 载气:氦气纯度大于等于 99.999%;流速为 1.0 mL/min;

6.4.1.6 进样量:1 μL;

6.4.1.7 进样方式:不分流进样,1.5 min 后开阀;

6.4.1.8 电离方式:NCI;

6.4.1.9 电离能量:184 eV;

6.4.1.10 离子源温度:150 ℃;

6.4.1.11 四极杆温度:150 ℃;

6.4.1.12 反应气:甲烷纯度大于等于 99.99%;反应气流速为 2 mL/min;

6.4.1.13 检测方式:分时段选择离子监测方式(SIM),参见表 1;

6.4.1.14 溶剂延迟时间:5.5 min。

表 1　分段选择离子表

农药	保留时间窗口/min	保留时间/min	定性离子(m/z)
三氟硝草醚	5.50～7.10	6.50	138*,190,298
乙氧氟草醚		6.64	296,361*,363
除草醚		6.83	283*,284,285
苯草醚		7.02	211*,228,264
吡草醚	7.11～7.85	7.26	349,376,412*
喹氧灵		7.29	271*,272,273
氯氟草醚		7.64	378*,415,450
甲氧除草醚		7.72	262,313*,315
甲羧除草醚	7.86～结束	8.04	341*,342,343
乳氟禾草灵		8.66	461*,462,463
乙羧氟草醚		8.68	294,447*,449
注：标“*”者为定量离子。			

6.4.2　气相色谱-质谱检测及确证

根据样液中待测农药残留量的情况，选定峰面积相近的标准工作溶液，对标准工作液和样液等体积参插进样。标准工作溶液和样液中待测农药的相应值均应在仪器的线性范围内。

如果样液与标准工作溶液的选择离子色谱图中，在相同保留时间处有色谱峰出现，并且在扣除背景后的样品质量色谱图中，所选离子均出现，所选择离子的丰度比与标准品对应离子的丰度比，其值在允许范围内(允许范围见表 2)。根据定量离子(见表 1 标*碎片)对其进行外标法定量。二苯醚类农药混合标准溶液的气相色谱-质谱总离子流色谱图见附录 A 中图 A.1。

表 2　使用定性气相色谱-质谱时相对离子丰度最大容许误差

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

6.5　空白试验

除不加试样外，均按上述测定步骤进行。

6.6　结果计算和表述

用色谱数据处理机或按(1)式计算试样中待测农药残留量：

$$X=\frac{A_x\times c_s\times V_x}{A_s\times m} \qquad \cdots\cdots(1)$$

式中

X ——样液中待测农药残留量的含量，单位为毫克每千克(mg/kg)；

A_x——样液中待测农药的定量离子峰面积；

c_s ——标准工作液中待测农药的浓度，单位为微克每毫升(μg/mL)；

V_x——样液最后定容体积，单位为毫升(mL)；

A_s——标准工作液中待测农药定量离子的峰面积；

m ——最终样液所代表的试样质量，单位为克(g)。

注：计算结果需将空白值扣除。

7 测定低限和回收率

7.1 测定低限

本方法各种基质的11种二苯醚类农药的测定低限均为0.01 mg/kg。

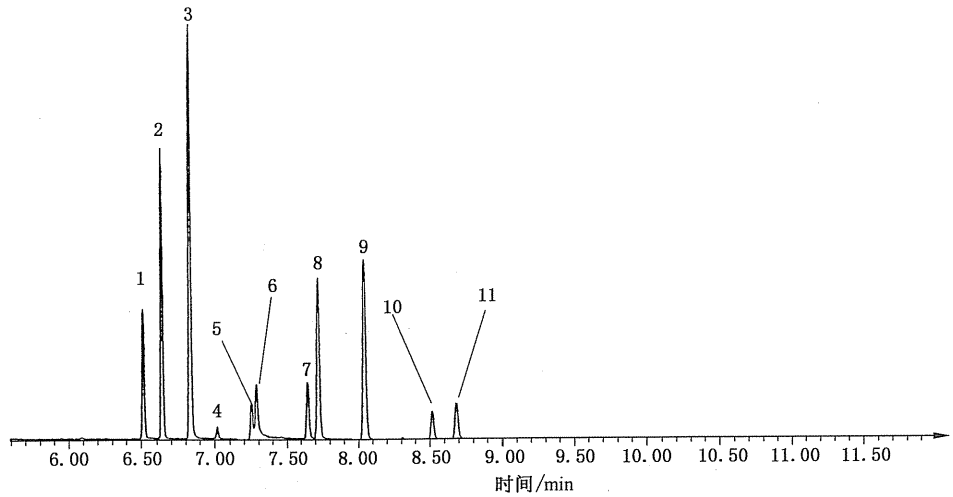
7.2 回收率

不同基质中添加浓度水平下的回收率范围参见表3。

表3 三个添加水平下食品中各种二苯醚类农药的平均回收率范围 %

样品名称	不同添加水平下的平均回收率			
	0.01 mg/kg	0.02 mg/kg	0.04 mg/kg	0.10 mg/kg
大米	80.6～87.8	96.9～106.1	87.8～100.4	97.3～109.1
大豆	91.1～114.5	87.4～97.3	85.3～99.0	88.7～107.6
菠菜	86.3～105.4	98.3～108.6	91.3～99.4	86.7～104.1
大葱	92.1～106.7	101.4～116.4	90.2～103.7	84.5～96.5
辣椒	94.4～102.3	96.2～106.9	93.3～106.0	87.5～117.8
草莓	95.0～114.3	105.2～111.1	92.0～101.7	87.7～103.9
甜豌豆	99.0～119.4	79.3～92.2	97.4～102.2	94.4～101.3
绿茶	96.5～118.9	114.3～121.5	98.8～118.9	93.9～101.8
龙虾仁	105.7～109.8	97.6～109.1	98.3～105.9	95.1～106.0
鳗鱼	92.5～113.5	92.1～108.7	87.6～99.0	94.4～102.7
猪肉	99.7～108.5	94.4～101.6	97.8～100.3	92.6～111.0
蜂蜜	93.8～103.3	100.3～108.5	98.6～106.2	104.0～117.2

附 录 A
（资料性附录）
醚类除草剂标准溶液 GC-MSD/NCI 选择离子流色谱图



说明：

1——三氟硝草醚；

2——乙氧氟草醚；

3——除草醚；

4——苯草醚；

5——吡草醚；

6——喹氧灵；

7——氯氟草醚；

8——甲氧除草醚；

9——甲羧除草醚；

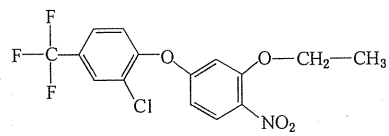
10——乳氟禾草灵；

11——乙羧氟草醚。

图 A.1 醚类除草剂混合标准溶液 GC-MS/NCI 总离子流图

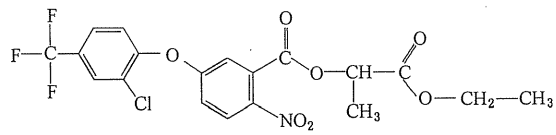
附 录 B
（资料性附录）
待测农药的分子结构式信息

B.1 Oxyfluorfen 乙氧氟草醚



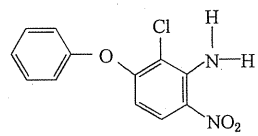
CAS 号：42874-03-3
分子式：$C_{15}H_{11}ClF_3NO_4$

B.2 Lactofen 乳氟禾草灵



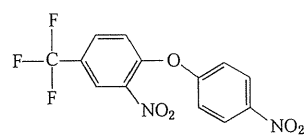
CAS 号：77501-63-4
分子式：$C_{19}H_{15}ClF_3NO_7$

B.3 aclonifen 苯草醚



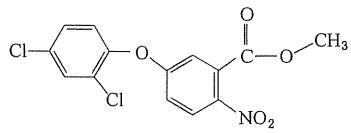
CAS 号：74070-46-5
分子式：$C_{12}H_9ClN_2O_3$

B.4 Fluorodifen 三氟硝草醚



CAS 号：15457-05-3
分子式：$C_{13}H_7F_3N_2O_5$

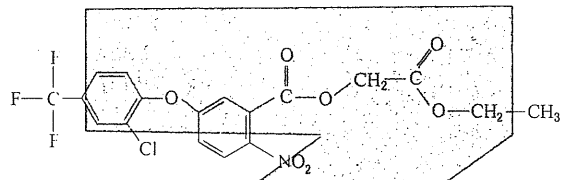
B.5 Bifenox 甲羧除草醚



CAS 号：42576-02-3

分子式：$C_{14}H_9Cl_2NO_5$

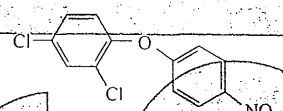
B.6 Fluoroglycofen ethyl 乙羧氟草醚



CAS 号：77501-90-7

分子式：$C_{18}H_{13}ClF_3NO_7$

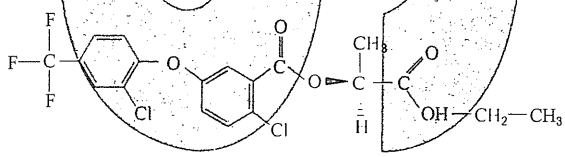
B.7 Nitrofen 除草醚



CAS 号：1836-75-5

分子式：$C_{12}H_7Cl_2NO_3$

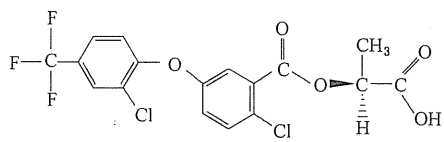
B.8 Ethoxyfen ethyl 氟乳醚



CAS 号：131086-42-5

分子式：$C_{19}H_{15}Cl_2F_3O_5$

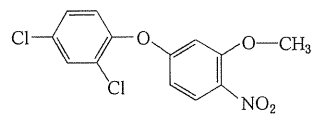
B.9 Ethoxyfen



CAS 号：188634-90-4

分子式：$C_{17}H_{11}Cl_2F_3O_5$

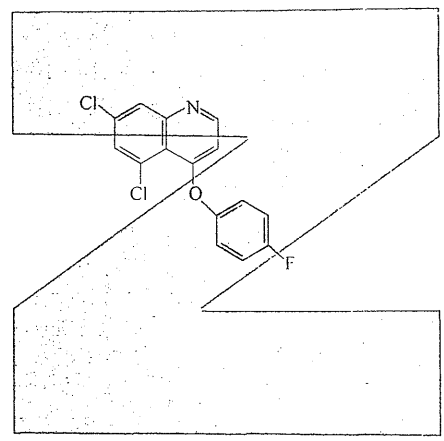
B. 10 Chlomethoxyfen 甲氧除草醚



CAS 号：32861-85-1

分子式：$C_{13}H_9Cl_2NO_4$

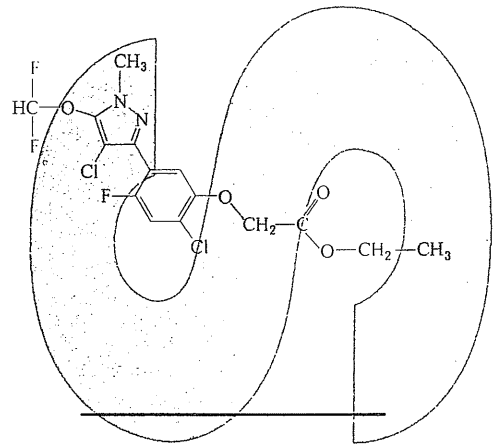
B. 11 quinoxyfen



CAS 号：124495-18-7

分子式：$C_{15}H_8Cl_2FNO$

B. 12 Paraflufen ethyl 吡草醚



CAS 号：129630-19-9

分子式：$C_{15}H_{13}Cl_2F_3N_2O_4$

Foreword

This standard was drafted according to the GB/T 1.1—2009

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

This standard was drafted by Jiangsu Entry-Exit Inspection and Quarantine Bureau.

Main drafters of this standard are Shen Weijian, Liu Han, Zhao Zengyun, Shen Chongyu, Yu Keyao, Gui Qianwen, Wu Bin, Zhang Rui.

Determination of multiple ether herbicides residues in foodstuffs for export—GC-MS/NCI method

1 Scope

This standard specifies preparation of test sample, determination and confirmation of multiple ether herbicides residue by gas chromatography-negative chemical ionization mass spectrometry (GC-MS/NCI) in foods for export.

This standard is applicable to the determination and confirmation of multiple ether herbicides residue in rice, soybean, spinach, welsh, capsicum, strawberry, sweet pea, green tea, red swamp crayfish, eel, pork, bee honey.

2 Principle

Diphenyl ether pesticides residues are extracted with acetonitrile containing 1% acetic acid and simultaneous liquid-liquid partitioning formed by adding anhydrous magnesium sulfate plus sodium acetate following by a simple cleanuo step knownby dispersive solid-phase extraction. The aliquot is determined and confirmed by gas chromatography-negative chemical ionization mass spectrometry (GC-MS/NCI) using external standard method.

3 Reagents and materials

Unless otherwise specified, all the reagents used should be analytical grade. "Water" is redistilled water.

3.1 Acetonitrile: HPLC Grade.

3.2 Hexane: HPLC Grade.

3.3 Acetone: HPLC Grade.

3.4 Acetic acid.

3.5 Magnesium sulfate anhydrous.

3.6 Sodium acetate anhydrous.

3.7 Acetonitrile (satured by *n*-hexane) containing 1% acetic acid: Add 10 mL acetic acid to 990 mL acetonitrile (satured by *n*-hexane)

3.8 Standards: Fluorodifen (CAS. 15457-05-3), Oxyfluorfen (CAS: 42874-03-3), Nitrofen (CAS: 1836-75-5), Aclonifen (CAS: 74070-46-5), Pyraflufen-ethyl (CAS: 129630-19-9), Quinoxyfen (CAS: 124495-18-7), Ethoxyfen-ethyl (CAS: 131086-42-5), Chlomethoxyfen (CAS: 32861-85-1), Bifenox (CAS: 42576-02-3), Lactofen (CAS: 77501-63-4) and Fluoroglycofen-ethyl (CAS: 77501-90-7), all purities≥98.0%.

3.9 Standard stock solution: Accurately weight an adequate amount of each standard and dissolve in a small volume of acetone respectively. Dilute with acetone to form a standard stock solution of 1.00 mg/mL in concentration (Be stored below 4 ℃ for 12 months).

3.10 Mixture standard stock andworking solution: accurately transfer 0.5 mL each stock standard solution into 10 mL volumetric flask, then make up to graduation with acetone, prepare a solution of 50 μg/m as the mixture standard stock solution, stored below 4 ℃ for 6 month.

3.11 Mixture standard working solution: Then dilute the mixture standard stock solution with acetone to the required concentration as the standard working solution (Be stored below 4 ℃ for 1 months).

3.12 Graphitized Carbon Black: 40 μm.

3.13 Bondesil-PSA(Primary secondary amine): 40 μm.

3.14 C_{18}: 40 μm.

3.15 0.45 μm organic phase fiber.

4 Apparatus and equipment

4.1 Gas chromotograph/msss spectrometry(MSD) equipped with negative chemical ionization.

4.2 Balances (0.1 mg, 0.01 g).

4.3 Rotatory evaporator.

4.4 Tissue triturator.

4.5 Grinding machine.

4.6 Homogenizer.

4.7 Vortex mixer.

5 Sample preparation and storage

5.1 Preparation of test sample

5.1.1 Vegetables or fruits, such as Spinach, welsh, capsicum, strawberry and sweet pea, etc.

About 500 g representative samples should be taken from all samples, the edible parts are selected, cut into mince and homogenized thoroughly into pulp by a high speed tissue triturator. Then divide the pulp into two equal portions. Each portion is put in a clean container which is sealed and labled.

5.1.2 Green Tea, rice, soybean and feedstuff.

About 500 g representative samples should be taken from all samples, and grounded into powder and then passed through a mesh with 2.0 mm round holes. The passed powder is mixed and divided into two portions. Each portion is put into one clean sample bottle which is sealed and labled.

5.1.3 Meats and meat products, such as red swamp crayfish, eel and pork etc.

About 500 g representative samples should be taken from all samples, the edible parts are cut into mince and homogenized by a high speed tissue triturator. The mixed primary sample is divided into two equal portion. Each portion is put into one clean sample bottle which is sealed and labled.

5.1.4 Bee honey

About 500 g representative samples should be taken from all samples, and the sample that is not crystallized shall be stirred well to make homogeneous. If the sample is crystallized, it must be warmed in a water-bath below 60 ℃ with the sample bottle covered tightly, mix thoroughly when all sample has melted, then cool immediately to room temperature. In the course of melting the sample, precautions must be taken to avoid evaporation of water from the sample. Then divide the pulp into two equal portions. Each portion is put in a clean container which is sealed and labled.

5.2 Storage of test sample

The test samples of rice, soybean, green tea, bee honey and feedstuff should be stored between 0 and 4 ℃. The test samples of spinach, welsh, capsicum, strawberry, sweet pea, red swamp crayfish, eel and pork should be stored below −18 ℃.

In the course of sampling and sample preparation, precaution must be taken to avoid contamination or

any factors which may cause the change of residue content.

6 Procedure

6.1 Weight

6.1.1 Soybean, red swamp crayfish, eel, and pork

Weigh 5 g (accurate to 0.01 g) of the test sample into 250 mL stoppered conical flask.

6.1.2 Spinach, welsh, capsicum, strawberry and sweet pea

Weigh 10 g (accurate to 0.01 g) of the test sample into 250 mL stoppered conical flask.

6.1.3 Rice, green tea and bee honey

Weigh 5 g (accurate to 0.01 g) of the test sample into 250 mL stoppered conical flask, and add 4 mL water, and blend homogeneous, soak or dissolve into 250 mL stoppered conical flask.

Green tea need be soaked for 30 min.

6.2 Extraction

Add 20 mL acetonitrile with 1% acetic acid and 15 g anhydrous magnesium sulfate (3.5) and 6 g anhydrous sodium acetate (3.6), vibrating for 40 min in the oscillator (pork eel, and red swamp crayfish be homogemized for 5 min). Filter the extract into a 150 mL condensor. The residue is extracted with 20 mL extracted solution (3.7) again, filter and combine the extracts into the same condensor. Evaporate the extract to dry by a rotary evaporator with a water bathing temperature of 40 ℃. Add 2 mL acetonitrile to dissolve the residue and waiting for cleanup operation.

6.3 Dispersive SPE cleanup

6.3.1 Extraction solution from high pigments content sample, such as spinach, welsh, capsicum, strawberry, sweet pea and green tea

An aliquat of the extract (6.2) is transferred into the 10 mL tube which contains 50 mg PSA and 200 mg graphitized carbon, and shake vigorously by hand for 1 minute, and filter 0.45 μm organic phase fiber, and wait for GC-MS determination and confirmation.

6.3.2 Extraction solution from rice, soybean, red swamp crayfish, eel and pork

Transfer the sample extract of high oil content sample into the 10 mL tube which contains 100 mg

PSA,50 mg graphitized carbon and 100 mg C_{18} and shake vigorously by hand for 1 minute,and filter 0.45 μm organic phase fiber,and wait for GC-MS determination and confirmation.

6.4 Determination

6.4.1 GC-MSD operation conditions

6.4.1.1 Column: DB-17ms fused quartz capillary column,30 m × 0.25 mm(i.d.),film thickness 0.25 μm,or the equivalent;

6.4.1.2 Column temperature:90 ℃ $\xrightarrow{15\ ℃/min}$ 270 ℃ $\xrightarrow{2℃/min}$ 276 ℃ $\xrightarrow{48\ ℃/min}$ 300 ℃(2.5 min);

6.4.1.3 Inlet temperature: 300 ℃;

6.4.1.4 Interface temperature: 250 ℃;

6.4.1.5 Carrier gas: Helium,purity≥99.999%,flow rate=1.0 mL/min;

6.4.1.6 Injection volumn: 1 μL;

6.4.1.7 Injection mode: splitless,purge after 1.5 min;

6.4.1.8 Ionization mode: NCI;

6.4.1.9 Ionization energe: 184 eV;

6.4.1.10 Ionization source temperature: 150 ℃;

6.4.1.11 Quadropole temperature: 150 ℃;

6.4.1.12 Reagent gas: methane,purity≥99.99%, flow rate: 1.0 mL/min;

6.4.1.13 Acquisition mode: Selected Ion Monitoring (SIM) mode see Table 1;

6.4.1.14 Solvent delay time: 5.5 min.

Table 1—RT (window)and mornitoring ion of pesticide

Pesticide	Retention time window/min	Retention time/min	Identification ions(m/z)
Fluorodifen	5.50～7.10	6.50	138,190,298*
Oxyfluorfen		6.64	361*,362,363
Nitrofen		6.83	283*,284,285
Aclonifen		7.02	211,228,264*
Pyraflufen-ethyl	7.11～7.85	7.26	349,376,412*
Quinoxyfen		7.29	271*,272,273
Ethoxyfen ethyl		7.64	378*,414,449
Chlomethoxyfen		7.72	262,313*,315
Bifenox	7.86～End	8.04	341*,342,343
Lactofen		8.66	461*,462,463
Fluoroglycofen-ethyl		8.68	294*,330,447
Attention: Ion with symbol of "*"is the qualitative ion of the pesticide			

6.4.2 GC-MS determination and confirmation

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

If there is a peak appeared at the same retention time for both of sample solution and standard working solution, and the qualification ions for every compound must be found, and for the same analysis batch and the same compound, the variation range of the ion ratio for the unknown sample and the standard working solution at the similar concentration cannot be out of range of Table 2. According to qualitative ion (Ion with symbol of "*"in table 1), quantitate the anlytes with external standard method is the qualitative ion of the pesticide. The GC-MS total ion chromatogram of diphenyl ether standard solution are shown respectively by figure A.1 in annex A.

Table 2—Maximum permitted tolerances for relative ion intensities while confirmation

Relative intensity	>50%	20%～50%	10%～20%	≤10%
Permitted tolerances	±20%	±25%	±30%	±50%

6.5 Blank test

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

6.6 Calculation and expression of the result

Calculate the content of diphenyl ether residue in the test sample by GC-MSD data processor or using the formula (1):

$$X = \frac{A_x \cdot c_s \cdot V_x}{A_s \cdot m} \quad \cdots\cdots (1)$$

Where:

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

A_x —the total area of quantitative ion for two diphenyl ether peaks in the sample solution;

c_s —the concentration of diphenyl ether in the standard working solution, μg/mL;

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

A_s —the total area of quantitative ion for two diphenyl ether peaks in the standard working solution;

m —the corresponding weight of the test sample in the final sample solution, g.

7 Limit of determination and recovery

7.1 Limit of determination

The limit of determination of this method is 0.01 mg/kg.

7.2 Recovery

Recoveries of different matrices at three spiked levels are shown respectively in table 3.

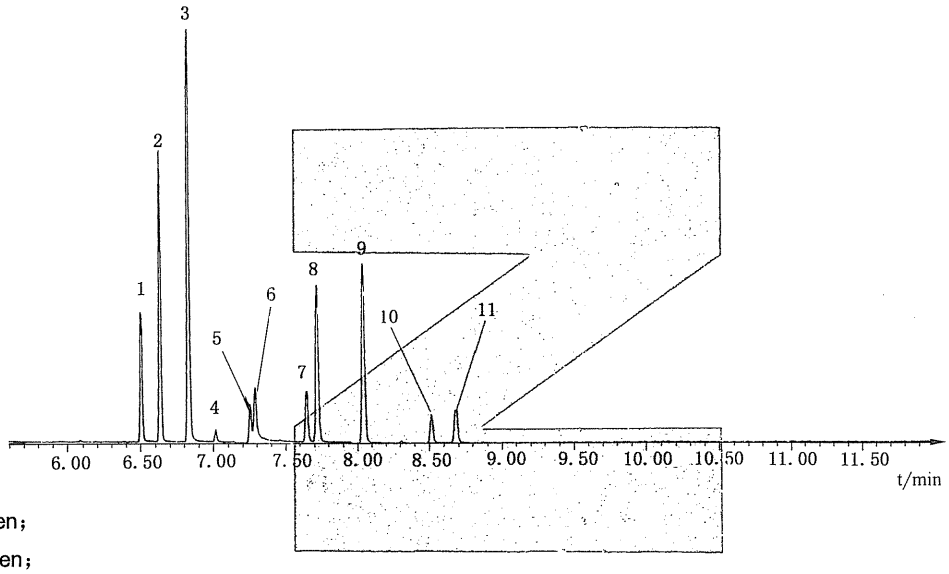
Table 3 Recoveries data of ether herbicides at three spiked levels in foods %

Sample	Range of Recovery			
	0.01 mg/kg	0.02 mg/kg	0.04 mg/kg	0.10 mg/kg
Rice	80.6～87.8	96.9～106.1	87.8～100.4	97.3～109.1
Soybean	91.1～114.5	87.4～97.3	85.3～99.0	88.7～107.6
Spinach	86.3～105.4	98.3～108.6	91.3～99.4	86.7～104.1

Table 3 (continued) %

Sample	Range of Recovery			
	0.01 mg/kg	0.02 mg/kg	0.04 mg/kg	0.10 mg/kg
Welsh	92.1～106.7	101.4～116.4	90.2～103.7	84.5～96.5
Capsicum	94.4～102.3	96.2～106.9	93.3～106.0	87.5～117.8
Strawberry	95.0～114.3	105.2～111.1	92.0～101.7	87.7～103.9
Sweet pea	99.0～119.4	79.3～92.2	97.4～102.2	94.4～101.3
Green tea	96.5～118.9	114.3～121.5	98.8～118.9	93.9～101.8
Red swamp crayfish	105.7～109.8	97.6～109.1	98.3～105.9	95.1～106.0
Eel	92.5～113.5	92.1～108.7	87.6～99.0	94.4～102.7
Pork	99.7～108.5	94.4～101.6	97.8～100.3	92.6～111.0
Bee honey	93.8～103.3	100.3～108.5	98.6～106.2	104.0～117.2

Annex A
(informative annex)
Total ion chromatogram of GC-MS/NCI for the mixture pesticides standard solution

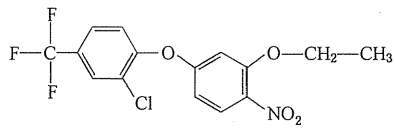


1—Fluorodifen;
2—Oxyfluorfen;
3—Nitrofen;
4—Aclonifen;
5—Pyraflufen-ethyl;
6—Quinoxyfen;
7—Ethoxyfen ethyl;
8—Chlomethoxyfen;
9—Bifenox;
10—Lactofen;
11—Fluoroglycofen-ethyl.

Figure A. 1—Total ion chromatogram of GC-MS/NCI for the mixture pesticides standard solution

Annex B
(informative annex)
Molecular structure of interested pesticides

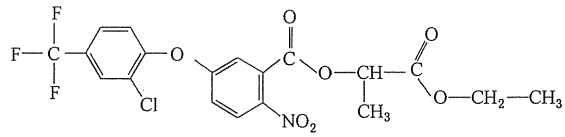
B.1 Oxyfluorfen



CAS:42874-03-3

$C_{15}H_{11}ClF_3NO_4$

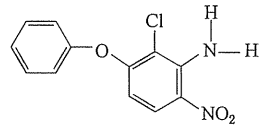
B.2 Lactofen



CAS:77501-63-4

$C_{19}H_{15}ClF_3NO_7$

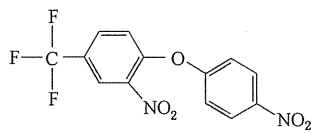
B.3 aclonifen



CAS:74070-46-5

$C_{12}H_9ClN_2O_3$

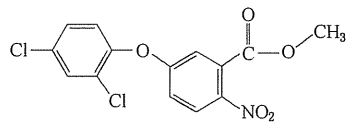
B.4 Fluorodifen



CAS:15457-05-3

$C_{13}H_7F_3N_2O_5$

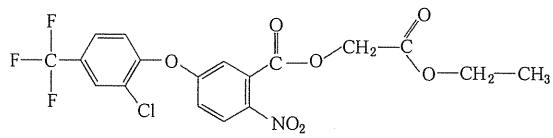
B.5 Bifenox



CAS：42576-02-3

$C_{14}H_9Cl_2NO_5$

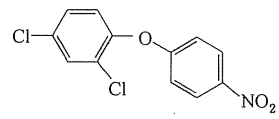
B.6 Fluoroglycofen ethyl



CAS：77501-90-7

$C_{18}H_{13}ClF_3NO_7$

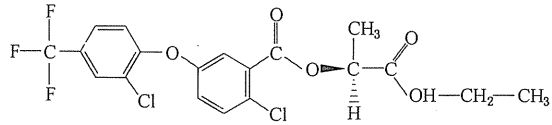
B.7 Nitrofen



CAS：1836-75-5

$C_{12}H_7Cl_2NO_3$

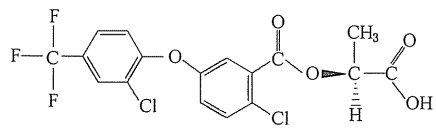
B.8 Ethoxyfen ethyl



CAS：131086-42-5

$C_{19}H_{15}Cl_2F_3O_5$

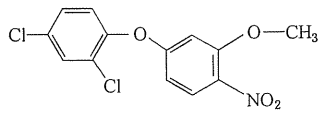
B.9 Ethoxyfen



CAS：188634-90-4

$C_{17}H_{11}Cl_2F_3O_5$

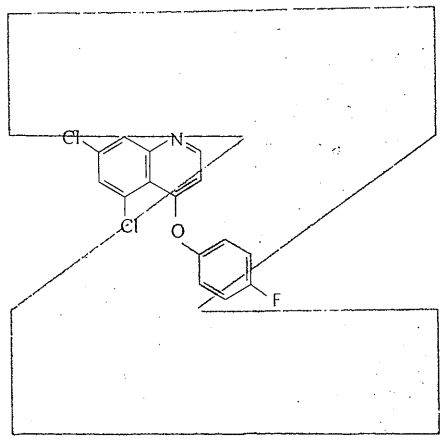
B. 10 Chlomethoxyfen



CAS：32861-85-1

$C_{13}H_9Cl_2NO_4$

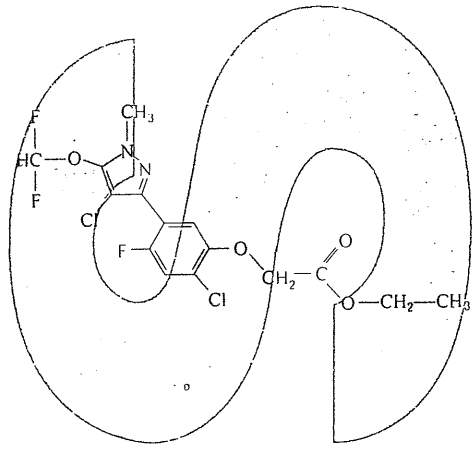
B. 11 quinoxyfen



CAS：124495-18-7

$C_{15}H_8Cl_2FNO$

B. 12 Paraflufen ethyl



CAS：129630-19-9

$C_{15}H_{13}Cl_2F_3N_2O_4$