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SN

中华人民共和国出入境检验检疫行业标准

SN/T 5144—2019

出口食品中酮脲磺草吩酯残留量的测定 液相色谱-质谱/质谱法

Determination of thiencarbazone-methyl residues in foods for export—LC-MS/MS method

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中华人民共和国海关总署　发布

前　言

本标准按照 GB/T 1.1—2009 给出的规则起草。

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。

本标准由中华人民共和国海关总署提出并归口。

本标准负责起草单位：中华人民共和国石家庄海关。

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出口食品中酮脲磺草吩酯残留量的测定 液相色谱-质谱/质谱法

1 范围

本标准规定了出口食品中酮脲磺草吩酯残留量的液相色谱-质谱/质谱测定方法。

本标准适用于玉米、小麦、大豆、糙米、马铃薯、菠菜、梨、葡萄、茶叶、鸡肉、猪肉、鱼肉、鸡肝、牛奶中酮脲磺草吩酯的确证和定量测定。

2 规范性引用文件

下列文件对于本文件的应用是必不可少的。凡是注日期的引用文件，仅所注日期的版本适用于本文件。凡是不注日期的引用文件，其最新版本(包括所有的修改单)适用于本文件。

GB/T 6682 分析实验室用水规格和试验方法

3 方法提要

试样中的酮脲磺草吩酯采用乙腈提取，提取液经石墨化炭黑固相萃取柱或 C_{18} 固相萃取柱净化，用液相色谱-质谱/质谱仪检测和确证，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，水为符合 GB/T 6682 规定的一级水。

4.1 乙腈：色谱级。

4.2 甲醇：色谱级。

4.3 二氯甲烷：色谱级。

4.4 甲酸：色谱级。

4.5 氯化钠。

4.6 无水硫酸钠：650 ℃烘烤 4 h，在干燥器内冷却至室温，贮于密封瓶中备用。

4.7 甲醇-二氯甲烷(3+7，体积比)：量取 300 mL 甲醇，加入 700 mL 二氯甲烷，混匀备用。

4.8 0.2%甲酸水溶液：量取 2 mL 甲酸(4.4)，用水定容至 1 000 mL。

4.9 酮脲磺草吩酯标准物质：thiencarbazone-methyl，CAS 号：317815-83-1，纯度大于或等于 98%。

4.10 酮脲磺草吩酯标准储备溶液：准确称取适量的标准物质，用甲醇配制成浓度为 1.0 mg/mL 的标准储备溶液，4 ℃下避光保存。

4.11 标准中间溶液：取上述标准储备液适量，用甲醇配制成 1 μg/mL 的标准工作溶液，4 ℃下避光保存。

4.12 基质空白溶液：将不同基质的阴性空白样品分别按照 7.1 和 7.2 净化处理后得到的溶液。

4.13 基质标准工作溶液：根据实验需要吸取适量的标准中间溶液(4.11)，用基质空白溶液稀释成适当浓度的标准工作溶液，现用现配。

4.14 石墨化炭黑固相萃取柱：250 mg，3 mL 或相当者。

4.15 C_{18}固相萃取柱：500 mg，3 mL或相当者。
4.16 微孔滤膜：0.22 μm，有机相型。

5 仪器和设备

5.1 高效液相色谱-质谱/质谱仪：配电喷雾正离子源(ESI+)。
5.2 组织捣碎机。
5.3 电子天平：感量分别为0.1 mg和0.01 g。
5.4 离心机：转速不低于5 000 r/min。
5.5 均质器，转速不小于10 000 r/min。
5.6 涡旋混匀器。
5.7 氮气吹干仪。
5.8 固相萃取装置。

6 样品制备和保存

6.1 制样要求

在制样的过程中，应防止样品受到污染或发生残留物含量的变化。

6.2 试样制备

6.2.1 梨、葡萄、菠菜和马铃薯

取代表性样品500 g，梨取全果去柄；葡萄取全果；菠菜取整棵去除根部；马铃薯取全薯。将其切碎后用捣碎机将样品加工成浆状。混匀，装入洁净的盛样容器内，密封并标明标记。

6.2.2 玉米、小麦、大豆、糙米和茶叶

取有代表性样品500 g，玉米、小麦、大豆取整粒，用粉碎机粉碎，混匀，装入洁净的盛样容器内，密封并标明标记。

6.2.3 猪肉、鸡肉、鱼肉和鸡肝

取代表性样品500 g，猪肉去除骨，包括脂肪含量小于10%的脂肪组；鸡肉去除骨；鱼肉去除骨和鳞；鸡肝取整付。用捣碎机充分捣碎均匀，装入洁净的盛样容器内，密封并标明标记。

6.3 试样保存

玉米、小麦、大豆、糙米和茶叶于0 ℃～4 ℃下保存，梨、葡萄、菠菜、马铃薯、猪肉、鸡肉、鱼肉、鸡肝和牛奶于－18 ℃下保存。

7 测定步骤

7.1 提取

7.1.1 茶叶

称取1.0 g试样(精确至0.01 g)于50 mL离心管中，加入4 mL水，于混匀器上混匀2 min，放置

30 min。加入 2 g 氯化钠和 10 mL 乙腈，10 000 r/min 均质 1 min，以 5 000 r/min 离心 5 min，取上层清液转移至 25 mL 容量瓶中，再用 10 mL 乙腈重复以上提取过程，最后用 5 mL 乙腈再次重复提取，合并三次提取液于同一容量瓶中，并用乙腈定容至刻度。分取 5 mL 提取液于 40 ℃下氮气流吹至近干，待净化。

7.1.2 玉米、小麦、大豆、糙米、菠菜、马铃薯、猪肉、鸡肉、鱼肉和鸡肝

称取 2.0 g 试样(精确至 0.01 g)于 50 mL 离心管中，对于玉米、小麦、大豆、糙米加入 4 mL 水，于混匀器上混匀 2 min，放置 30 min。加入 2 g 氯化钠和 10 mL 乙腈，10 000 r/min 均质 1 min，以 5 000 r/min离心 5 min，取上层清液转移至 25 mL 容量瓶中，再用 10 mL 乙腈重复以上提取过程，最后用 5 mL 乙腈再次重复提取，合并三次提取液于同一容量瓶中，并用乙腈定容至刻度。分取 5 mL 提取液于 40 ℃下氮气流吹至近干，待净化。

7.1.3 梨、葡萄和牛奶

称取 5.0 g 试样(精确至 0.01 g)于 50 mL 离心管中，加入 2 g 氯化钠和 10 mL 乙腈，10 000 r/min 均质 1 min，以 5 000 r/min 离心 5 min，取上层清液转移至 25 mL 容量瓶中，再用 10 mL 乙腈重复以上提取过程，最后用 5 mL 乙腈再次重复提取，合并三次提取液于同一容量瓶中，并用乙腈定容至刻度。分取 5 mL 提取液于 40 ℃下氮气流吹至近干，待净化。

7.2 净化

7.2.1 玉米、小麦、大豆、糙米、马铃薯、猪肉、鸡肉、鱼肉和牛奶

用 2 mL 乙腈(4.1)溶解 7.1 步骤中所获得的浓缩液。在 C_{18} 固相萃取柱上端装入 1 cm 高的无水硫酸钠，先用 5 mL 乙腈预淋洗小柱，弃去淋洗液。然后将复溶后的样品提取液过柱，并用 6 mL 乙腈洗脱，控制流速为 0.5 mL/min，收集所有流出液，在 40 ℃下氮吹浓缩至近干。用 1.0 mL 乙腈溶解残渣，过 0.22 μm 滤膜供液相色谱-质谱/质谱仪测定。

7.2.2 梨、葡萄、菠菜、鸡肝和茶叶

用 2 mL 甲醇-二氯甲烷混合液(4.7)溶解 7.1 步骤中所获得的浓缩液。在石墨化炭黑固相萃取柱上端装入 1 cm 高的无水硫酸钠，先用 5 mL 甲醇-二氯甲烷混合液(4.7)预淋洗小柱，弃去淋洗液。然后将复溶后的样品提取液过柱，并用 6 mL 甲醇-二氯甲烷混合液(4.7)洗脱，控制流速为 0.5 mL/min，收集所有流出液，在 40 ℃下氮吹浓缩至近干。用 1.0 mL 乙腈溶解残渣，过 0.22 μm 滤膜供液相色谱-质谱/质谱仪测定。

7.3 测定

7.3.1 液相色谱参考条件

液相色谱参考条件如下：

a) 色谱柱：C_{18} 柱，150 mm×2.1 mm(内径)，粒度 5 μm，或相当者；
b) 流动相：梯度洗脱程序见表 1：
c) 流速：200 μL/min；
d) 柱温：30 ℃；
e) 进样量：10 μL。

表 1　流动相梯度洗脱程序

时间/min	0.2%甲酸/%	乙腈/%
0.00	90	10
1.00	90	10
3.00	40	60
5.00	10	90
8.00	10	90
8.01	90	10
10.00	90	10

7.3.2　质谱参数

参见附录 A。

7.3.3　液相色谱-质谱/质谱检测

本方法采用外标校准曲线法定量测定。为减少基质对定量测定的影响，定量用标准曲线应采用基质标准工作溶液绘制的标准工作曲线，并且保证所测样品中酮脲磺草吩酯的响应值均在线性范围内。在上述液相色谱-质谱条件下，酮脲磺草吩酯的保留时间约为 6.15 min，多反应离子监测色谱图参见附录 B 中图 B.1。

7.3.4　液相色谱-质谱/质谱确证

按照上述色谱和质谱条件下进行测定，试液中待测物色谱峰保留时间与基质标准工作溶液保留时间偏差在±2.5%之内，各离子对的相对丰度应与标准品的相对丰度一致，且样品中各离子对的相对丰度与浓度接近的基质标准工作液中对应的离子对的相对丰度进行比较，偏差不超过表 2 规定的范围，则可判定为样品中存在对应的待测物。

表 2　定性确证时相对离子丰度的最大允许误差

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

7.4　空白试验

除不加样品外，按上述相同条件和步骤进行。

7.5　结果计算和表述

酮脲磺草吩酯残留量的测定结果按照式(1)计算，计算结果需扣除空白值：

$$X_i = \frac{C_i \times V}{m} \times \frac{1\,000}{1\,000} \qquad \cdots\cdots(1)$$

式中：

X_i ——试样中酮脲磺草吩酯残留量，单位为微克每千克(μg/kg)；

C_i ——从基质标准工作曲线上得到的酮脲磺草吩酯溶液浓度，单位为纳克每毫升(ng/mL)；

V ——样品溶液定容体积，单位为毫升(mL)；

m ——最终样品溶液所代表试样的质量，单位为克(g)。

8 测定低限和回收率

8.1 测定低限

本方法酮脲磺草吩酯农药测定低限为 5 μg/kg。

8.2 回收率

玉米、小麦、大豆、糙米、马铃薯、菠菜、梨、葡萄、茶叶、鸡肉、猪肉、鱼肉、鸡肝、牛奶中酮脲磺草吩酯农药的添加浓度及回收率数据见附录 C。

附 录 A
（资料性附录）
参考质谱条件

A.1 参考条件

参考质谱条件如下：

a） 离子源：电喷雾离子源；
b） 扫描模式：正离子扫描；
c） 检测方法：多反应监测（MRM）；
d） 鞘气压力：30 unit；
e） 辅助气压力：8 unit；
f） 正离子模式电喷雾电压（IS）：4 000 V；
g） 毛细管温度：320 ℃；
h） 源内诱导解离电压：10 V；
j） Q1，Q3 分辨率：0.7；
j） 碰撞气：高纯氩气；
k） 碰撞气压力：1.5mTorrj
l） 其他质谱参数见表 A.1。

表 A.1 被测物的参考保留时间、监测离子对和裂解能量

分析物	保留时间（min）	检测离子对（m/z）	裂解能量（eV）
酮脲磺草吩酯	6.15	391.0/229.8*	18
		391.0/129.9	23
注：* 为定量离子对，对于不同质谱仪器，仪器参数可能存在差异，测定前应将质谱参数优化到最佳。			

非商业性声明：附录 A 所列参考质谱条件是在 Thermo TSQ Quantum Ultra 型液质联用仪上完成的，此处列出试验用仪器型号仅为提供参考，并不涉及商业目的，鼓励标准使用者尝试不同厂家或型号的仪器。

附　录　B
（资料性附录）
标准物质多反应监测质量色谱图

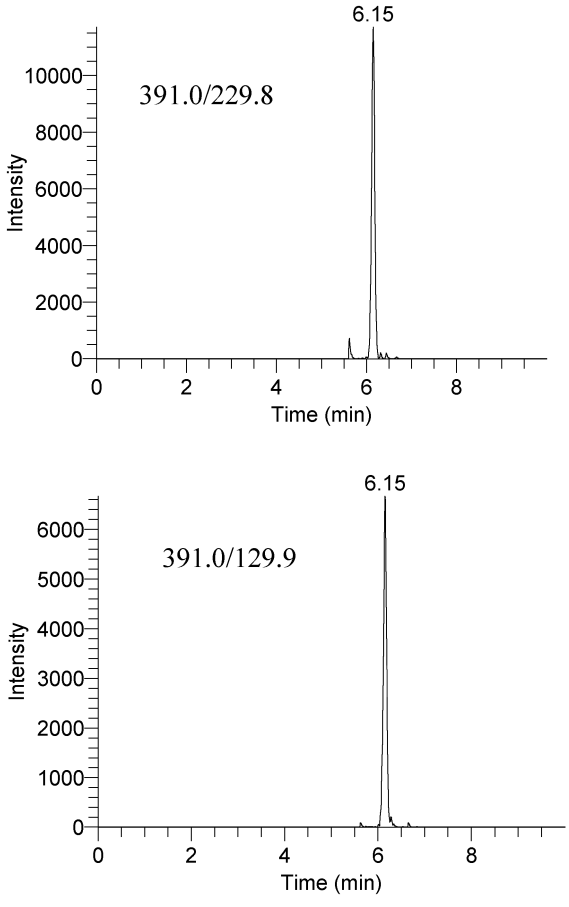

图 B.1　酮脲磺草吩酯标准溶液多反应监测色谱图（1 ng/mL）

附 录 C
（资料性附录）
回收率

表 C.1 酮脲磺草吩酯在 14 种样品基质中添加浓度及回收率数据

样品	添加浓度（μg/kg）	回收率（%）	样品	添加浓度（μg/kg）	回收率（%）
玉米	5	76.0～92.2	葡萄	5	82.2～103.2
	10	80.5～95.4		10	86.7～106.0
	50	84.0～97.7		50	81.1～98.6
小麦	5	73.4～97.2	茶叶	5	78.4～97.8
	10	80.4～98.8		10	81.6～102.5
	50	83.2～96.6		50	87.6～103.6
大豆	5	76.6～94.8	鸡肉	5	76.8～103.0
	10	76.0～94.6		10	83.2～106.0
	50	81.0～94.4		50	89.0～104.6
糙米	5	78.8～96.2	猪肉	5	87.0～105.2
	10	84.1～98.2		10	75.9～93.1
	50	82.8～99.6		50	84.6～101.8
马铃薯	5	73.8～97.0	鱼肉	5	81.8～104.4
	10	78.0～96.2		10	85.6～105.3
	50	85.9～98.3		50	85.9～99.0
菠菜	5	72.0～97.0	梨	5	82.6～102.8
	10	86.3～108.5		10	90.3～105.1
	50	91.8～104.3		50	85.3～99.2
鸡肝	5	74.0～97.6	牛奶	5	74.2～97.4
	10	75.7～98.0		10	87.4～114.6
	50	84.6～99.7		50	89.6～106.0

Foreword

This standard was drafted according to the principle of the GB/T 1.1—2009《Directives for standardization—Part 1: Structure and drafting of standards》, GB/T 20001.4—2001《Rules for drafting standards—Part 4: Methods of chemical analysis》and SN/T 0001—1995《General rules for drafting the standards of biological method for the determination of pesticide, veterinary drug residues and biotoxins in commodities for export》Some parts of the standard may have relationship with some patents. The release department have no responsibility to recognize these patents.

This standard was proposed by and is under the charge of General Administration of Customs, P.R. China.

This standard was drafted by Shijiazhnang Customs District, P.R.China.

Main drafters of this standard are: Ma Yusong, Zhang Haichao, Ai Lianfeng, Dou Caiyun, Li Wei, Wang Jing, Chen Ruichun, Guo Chunhai.

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

Determination of thiencarbazone-methyl residues in foodstuffs for export—LC-MS/MS method

1 Scope

This standard specifies the determination method for residues of thiencarbazone-methyl residues in foodstuffs for export by liquid chromatography-tandem mass spectrometry.

This standard is applicable to the determination and confirmation of thiencarbazone-methyl residues in corn, wheat, soybean, brown rice, potato, spinach, pear, grape, tea, chicken, pork, fish, chicken liver and milk for export.

2 Normative references

The following documents are necessary for this standard. For dated references, only dated editions shall apply to this standard. For undated references, the latest of the normative document (including subsequent amendments) referred to applies.

GB/T 6682 Water for laboratory use-Specification and test methods.

3 Principle

The residues in the test sample are extracted with acetonitrile. The solution is cleaned up with Envi-Carb cartridge or C_{18} cartridge, thiencarbazone-methyl is then detected and confirmed by liquid chromatography-tandem mass spectrometry, quantified by external standard method.

4 Reagents and materials

All reagents were of analytical grade unless otherwise specified and "water" is the first grade water prescribed by GB/T 6682.

4.1 Acetonitrile: HPLC grade.

4.2 Methanol: HPLC grade.

4.3 Dichloromethane: HPLC grade.

4.4 Formic acid: HPLC grade.

4.5 Sodium chloride.

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

4.7 Methanol-dichloromethane (3 + 7, v/v): transfer 300 mL methanol (4.2) into 700 mL dichloromethane (4.3), mix adequately.

4.8 0.2% formic acid solution: Accurately measure 2.0 mL formic acid (4.4) into a 1 000 mL volumetric flask, dilute with water to 1 000 mL.

4.9 Thiencarbazone-methyl standard: CAS NO. 317815-83-1 are no less than 98%.

4.10 Thiencarbazone-methyl standard solution: Accurately weigh an adequate amount of standard (4.9), dissolve in methanol and prepare a solution of 1.0 mg/mL. The solutions should be stored below 4 ℃.

4.11 Middle working solution: Prepare a standard working solution of 1 μg/mL by diluting the above stock solution (4.10) with methanol. The solutions should be stored below 4 ℃.

4.12 Blank matrix extract solution: Prepare different samples without thiencarbazone-methyl, following as 7.1 and 7.2.

4.13 Matrix standard working solution: According to the requirement, dilute middle standard solution (4.11) to appropriate concentration with blank matrix solution just before use.

4.14 Envi-carb cartridge: 3 mL, 250 mg or equivalent.

4.15 C_{18} cartridge: 3 mL, 500 mg or equivalent.

4.16 Membrane filter: 0.22 μm, organic type.

5 Apparatus and equipment

5.1 Liquid chromatography-tandem mass spectrograph: equipped with electrospray ion source.

5.2 Organ blender.

5.3 Balance: accuracy to 0.1 mg and 0.01 g.

5.4 Centrifuge, speed of no less than 5 000 r/min.

5.5 Homogenizer, speed of no less than 10 000 r/min.

5.6 Vortex mixer.

5.7 Nitrogen evaporator.

5.8 Solid-phase extraction.

6 Preparation and storage of test sample

6.1 Requirement

In the course of sample preparation, precaution must be taken avoid the contamination or any factors which may cause the charge of residue content.

6.2 Preparation of test sample

6.2.1 Pear, grape, spinach, potato

Take approximately 500 g of representative sample, take the whole pear without the handle, take the whole grape, take the whole spinach without the root, take the whole potato. Cut into minces and crush with a crusher into pulp and mix thoroughly. The sample is placed in clean containers as the test sample, which sealed and labeled.

6.2.2 Corn, wheat, soybean, brown rice, tea

Take approximately 500 g of representative sample, take the whole grain of corn, wheat and soybean, smash thoroughly by a pulverizer, mix thoroughly. The sample is placed in clean containers as the test sample, which is sealed and labeled.

6.2.3 Pork, chicken, fish, chicken liver

Take approximately 500 g of representative sample. Remove the bone of pork, including fat content less than ten percent fat group, remove the bone of chicken, remove the bone and scale of fish, take the whole chicken liver. Then blender thoroughly with a tissue homogenizer. The sample is placed in clean containers as the test sample, which is sealed and labeled.

6.3 Preservation of test sample

Corn, wheat, soybean, brown rice and tea shall be preserved at 0 ℃～4 ℃. Pear, grape, spinach, potato, pork, chicken, fish, chicken liver and milk shall be preserved below －18 ℃.

7 Procedure

7.1 Extraction

7.1.1 Tea

Weigh 1.0 g (accurate to 0.01 g) in a 50 mL centrifuge tube. Add 4 mL deionized water to soak the sample. Mix for 2 rain on vortex mixer and allow standing for 30 min. then add 2 g sodium chloride and 10 mL acetonitrile to the sample, homogenize it for 1 min (10 000 r/min), and then centrifuge the sample solution for 5 min at 5 000 r/min. Transfer the supernatant into a 25 mL volumetric flask, repeat the above extract procedure twice with 10 mL acetonitrile and 5 mL acetonitrile, combined the supernatant, dilute the extract to 25 mL. Accurately draw 5.0 mL extract into a centrifuge tube, concentrate the extract to dryness under nitrogen at 40 ℃ for further cleanup.

7.1.2 Com, wheat, soybean, brown rice, spinach, potato, pork, chicken, fish, chicken liver

Weigh 2.0 g (accurate to 0.0lg) in a 50 mL centrifuge tube. For corn, wheat, soybean and brown rice add 4 mL deionized water to soak the sample. Mix for 2 min on vortex mixer and allow standing for 30 min. then add 2 g sodium chloride and 10 mL acetonitrile to the sample,homogenize it for 1 min (10 000 r/min), and then centrifuge the sample solution for 5 min at 5 000 r/min. Transfer the supernatant into a 25 mL volumetric flask, repeat the above extract procedure twice with 10 mL acetonitrile and 5 mL acetonitrile, combined the supematant, dilute the extract to 25 mL. Accurately draw 5.0 mL extract into a centrifuge tube, concentrate the extract to dryness under nitrogen at 40 ℃ for further cleanup.

7.1.3 Pear, grape, milk

Weigh 5.0 g (accurate to 0.01g) in a 50 mL centrifuge tube. Add 2 g sodium chloride and 10 mL acetonitrile to the sample, homogenize it for 1 min (10 000 r/min), and then centrifuge the sample solution for 5 min at 5 000 r/min. Transfer the supernatant into a 25 mL volumetric flask, repeat the above extract procedure twice with 10 mL acetonitrile and 5 mL acetonitrile, combined the supematant, dilute the extract to 25 mL. Accurately draw 5.0 mL extract into a centrifuge tube, concentrate the extract to dryness under nitrogen at 40 ℃ for further cleanup.

7.2 Cleaning-up

7.2.1 Corn, wheat, soybean, brown rice, potato, pork, chicken, fish, milk

The residue (7.1) is reconstituted with 2 mL acetonitrile (4.1). Set up the solid phase extraction vacuum manifold and mechanical pump (about 1 cm thickness anhydrous sodium sulfate was put into C_{18} cartridge). First wash C_{18} cartridge with 5 mL acetonitrile, discard the effluent. Transfer the extracts into the cartridge. Wash the test tube with 6 mL acetonitrile and into the cartridge, keep flow

speed at 0.5 mL/min. Collect the total eluent and blow nearly dry with nitrogen at 40 ℃. Dissolve the residue with 1.0 mL acetonitrile and filtrate through the 0.22 μm filter membrane. The filtrate is ready for LC-MS/MS determination.

7.2.2 Pear, grape, spinach, chicken liver, tea

The residue (7.1) is reconstituted with 2 mL methanol-dichloromethane(4.7). Set up the solid phase extraction vacuum manifold and mechanical pump(about 1 cm thickness anhydrous sodium sulfate was put into Carbon cartridge). First wash the graphitized carbon black cartridge with 5 mL methanol-dichloromethane(4.7), discard the effluent. Transfer the extracts into the cartridge.Wash the test tube with 6 mL methanol-dichloromethane(4.7) and into the cartridge, keep flow speed at 0.5 mL/min. Collect the total eluent and blow nearly dry with nitrogen at 40 ℃. Dissolve the residue with 1.0 mL acetonitrile and filtrate through the 0.22 μm filter membrane. The filtrate is ready for LC-MS/MS determination.

7.3 Determination

7.3.1 LC operating conditions

Reference LC operating conditions are as follows:

a) Column: C_{18} 150 mm×2.1 mm (i.d.), 5 μm, or equivalent.

b) Mobile phases and gradient elution conditions are listed in table 1.

c) Flow rate: 200 μL/min

d) Column temperature:30 ℃.

e) Injection volume: 10 μL.

Table 1—Mobile phase and gradient elution condition

Time/min	0.2% Formic acid/%	Acetonitrile/%
0.00	90	10
1.00	90	10
3.00	40	60
5.00	10	90
8.00	10	90
8.01	90	10
10.00	90	10

7.3.2 MS conditions

See annex A.

7.3.3 LC-MS/MS determination

This method uses external standard to quantitative. To reduce the influence of matrix, the standard calibration curve uses sample blank solution to make the matrix standard working solution. The response of thiencarbazone-methyl should be in the linear range of the instrumental detection. Under this conditions, the reference retention time of thiencarbazone-methyl is about 6.15 min, the multiple reaction monitor(MRM)chromatogram of thiencarbazone-methyl is shown as Figure B.1 in annex B.

7.3.4 LC-MS/MS confirmation

Under above determinations conditions, the deviation of retention time for analyte between test sample and standard solution is within ±2.5%. For the same analysis batch and the same compound, the variation range of the ion ratio between the two daughter ions for the unknown sample and the standard working solution at the similar concentration can not be out of range of table 2, and then the corresponding analyte must be present in the sample.

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

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

7.4 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.

7.5 Calculation an expression of result

Calculation the content of thiencarbazone-methyl residues in test sample by standard curve method according to formula (1), the blank value should be subtracted from the result of calculation:

$$X_i = \frac{C_i \times V}{m} \times \frac{1\,000}{1\,000} \qquad \cdots\cdots(1)$$

where:

X_i ——the residue content of thiencarbazone-methyl in the test sample, μg/kg;

C_i ——the concentration of thiencarbazone-methyl in the matrix standard working solution, ng/ml;

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

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

8 Limit of determination and recovery

8.1 Limit of determination

Under this method to determine thiencarbazone-methyl is 5 μg/kg in all matrix.

8.2 Recovery

According to the experimental data for corn, wheat, soybean, brown rice, potato, spinach, pear, grape, tea, chicken, pork, fish, chicken liver and milk, the fortifying concentration of thiencarbazone-methyl for each sample and the range of recovery is shown in annex C.

Annex A
（Informative）

A.1 Reference mass conditions

Reference mass conditions are as follows：

a） ionsource：ESI；

b） Scan mode：Positive ion；

c） Detection mode:Multiple reaction monitoring（MRM）；

d） Sheath Gas：30unit；

e） Auxilliar Gas：8unit；

f） Ion spay voltage in ESI＋mode：4 000 V；

g） Capillary temperature：320 ℃；

h） Source CID：10 V；

i） Width of Q1 and Q3:0.7；

j） Collision gas:Argon with high purity；

k） Collision gas pressure:l.5 mTorr；

l） Other mass operating conditions are list in table A. 1.

Table A. 1——the scan segment，ion pairs and collision enerev of the analvtes

compound	Retention time（min）	Ion pairs（*m*/*z*）	Collision energy（eV）
thiencarbazone-methy1	6.15	391.0/229.8*	18
		391.0/129.9	23
Note：* mark is the quantification ion pair.for the different MS equipment,the parameters may be different,and the MS parameters should be optimized to the best before analysis.			

Non-commercial statement：the reference mass parameters in Annex A are accomplished by Thermo TSQ Quantum Ultra LC-MS/MS，the equipment and its type involved in the standard method is only for reference and not related to any commercial aim，and the analysts are encouraged to use equipment of different corporation or different type.

Annex B
（Informative）
MRM chromatogram of standard

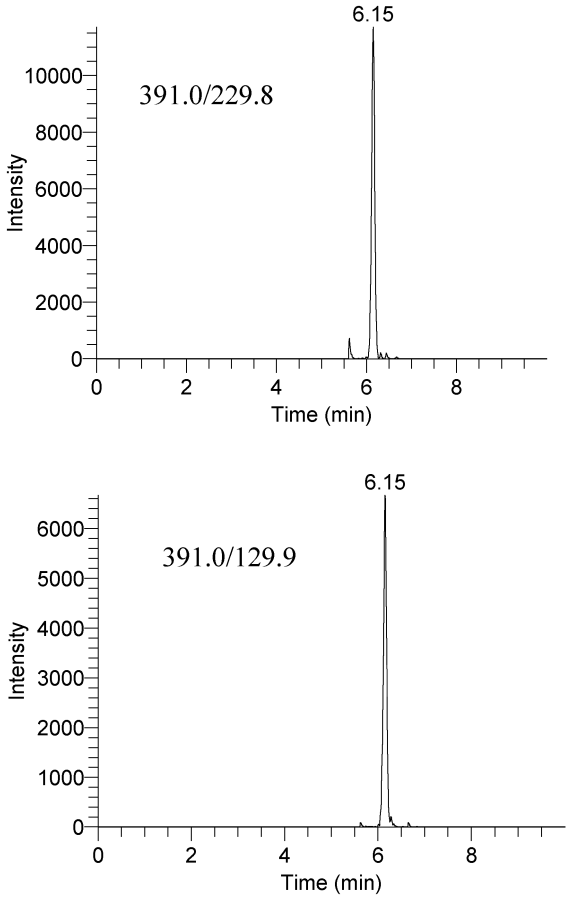

Fig.B.1—the MRM chromatogram of standard working solution（1 ng/mL）

Annex C
（informative）
Recovery ranges

Table C.1—Recovery ranges

Sample	Spiked level/（μg/kg）	Recoveries（%）	Sample	Spiked level/（μg/kg）	Recoveries（%）
corn	5	76.0～92.2	grape	5	82.2～103.2
	10	80.5～95.4		10	86.7～106.0
	50	84.0～97.7		50	81.1～98.6
wheat	5	73.4～97.2	tea	5	78.4～97.8
	10	80.4～98.8		10	81.6～102.5
	50	83.2～96.6		50	87.6～103.6
soybean	5	76.6～94.8	chicken	5	76.8～103.0
	10	76.0～94.6		10	83.2～106.0
	50	81.0～94.4		50	89.0～104.6
brown rice	5	78.8～96.2	port	5	87.0～105.2
	10	84.1～98.2		10	75.9～93.1
	50	82.8～99.6		50	84.6～101.8
potato	5	73.8～97.0	fish	5	81.8～104.4
	10	78.0～96.2		10	85.6～105.3
	50	85.9～98.3		50	85.9～99.0
spinach	5	72.0～97.0	pear	5	82.6～102.8
	10	86.3～108.5		10	90.3～105.1
	50	91.8～104.3		50	85.3～99.2
chicken liver	5	74.0～97.6	milk	5	74.2～97.4
	10	75.7～98.0		10	87.4～114.6
	50	84.6～99.7		50	89.6～106.0