



中华人民共和国出入境检验检疫行业标准

SN/T 1753—2016
代替 SN/T 1753—2006

出口浓缩果汁中甲基硫菌灵、噻菌灵、 多菌灵和 2-氨基苯并咪唑残留量的测定 液相色谱-质谱/质谱法

Determination of thiophanate-methyl, thiabendazole, carbendazim and
2-aminobenzimidazole residues in concentrated juices
for export—LC-MS/MS method

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前 言

本标准按照 GB/T 1.1—2009 给出的规则起草。

本标准代替 SN/T 1753—2006《进出口浓缩果汁中噻菌灵、多菌灵残留量测定方法 高效液相色谱法》。

本标准与 SN/T 1753—2006 相比主要修改如下：

——修改了标准名称；

——增加了甲基硫菌灵和 2-氨基苯并咪唑残留量的同时测定，测定方法由液相色谱法改为液相色谱-质谱/质谱法。

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、中华人民共和国上海出入境检验检疫局、中华人民共和国陕西出入境检验检疫局、广西大学。

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本标准所代替标准的历次版本发布情况为：

——SN/T 1753—2006。

出口浓缩果汁中甲基硫菌灵、噻菌灵、
多菌灵和 2-氨基苯并咪唑残留量的测定
液相色谱-质谱/质谱法

1 范围

本标准规定了出口浓缩果汁中甲基硫菌灵、噻菌灵、多菌灵和 2-氨基苯并咪唑残留量的液相色谱-质谱/质谱测定方法。

本标准适用于浓缩果汁中甲基硫菌灵、噻菌灵、多菌灵和 2-氨基苯并咪唑残留量的检测和确证。

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

试样以 0.2 mol/L 磷酸氢二钠溶液稀释、氢氧化钠溶液调节 pH 至 8.5~8.6 后,用乙腈提取,经乙二胺基-N-丙基(PSA)柱净化,用液相色谱-质谱/质谱仪检测,外标法定量。

4 试剂和材料

除非另有说明,所有试剂均为分析纯,水为 GB/T 6682 规定的一级水。

- 4.1 乙腈:色谱纯。
- 4.2 甲醇:色谱纯。
- 4.3 甲苯:色谱纯。
- 4.4 甲酸:色谱纯。
- 4.5 乙酸铵:色谱纯。
- 4.6 磷酸氢二钠: Na₂HPO₄ · 12H₂O。
- 4.7 氯化钠。
- 4.8 无水硫酸钠:用前在 650 ℃灼烧 4 h,贮于干燥器中,冷却后备用。
- 4.9 磷酸:含量≥85%。
- 4.10 甲基硫菌灵标准品: C₁₂H₁₄N₄O₄S₂,CAS 号 23564-05-8,纯度大于或等于 98%;噻菌灵标准品: C₁₀H₇N₃S,CAS 号 148-79-8,纯度大于或等于 98%;多菌灵标准品: C₁₅H₁₂N₂O,CAS 号 10605-21-7,纯度大于或等于 98%;2-氨基苯并咪唑标准品: C₇H₇N₃,CAS 号 934-32-7,纯度大于或等于 98%。
- 4.11 0.2 mol/L 磷酸氢二钠溶液:称取 17.91 g 磷酸氢二钠,用水溶解,定容至 250 mL。
- 4.12 2 mol/L 氢氧化钠溶液:称取 8.0 g 氢氧化钠,用水溶解,定容至 100 mL。
- 4.13 乙腈-甲苯(3+1):量取 300 mL 乙腈和 100 mL 甲苯,混匀。

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- 4.14 10 mmol/L 乙酸铵(含 0.1%甲酸):称取 0.77 g 乙酸铵,用水溶解,加入 1 mL 甲酸,用水定容至 1 L。
- 4.15 甲醇-10 mmol/L 乙酸铵(含 0.1%甲酸)溶液:10 mL 甲醇加入 90 mL 10 mmol/L 乙酸铵(含 0.1% 甲酸)(4.14),混匀。
- 4.16 标准储备溶液:分别准确称取 10 mg(精确到 0.1 mg)各标准品于 100 mL 棕色容量瓶中,用甲醇溶解并定容至刻度,分别配制成浓度为 100 μg/mL 的标准储备液,于-18 ℃避光保存。
- 4.17 混合标准中间液:准确吸取各标准储备液 10 mL 于 100 mL 棕色容量瓶中,用甲醇定容至刻度,配成浓度为 10 μg/mL 的混合标准中间溶液,于-18 ℃避光保存。
- 4.18 混合标准工作液:根据需要使用相应的空白样品基质配制适当浓度混合标准工作溶液。
- 4.19 PSA 固相萃取柱:500 mg/3 mL,或相当者。使用前加 1 g 无水硫酸钠,用 4 mL 乙腈-甲苯溶液(4.13)淋洗、活化柱子。
- 4.20 滤膜:0.22 μm,有机系。

5 仪器和设备

- 5.1 液相色谱-质谱/质谱联用仪:配电喷雾电离源(ESI)。
- 5.2 电子天平:感量 0.1 mg,0.001
- 5.3 pH 计。
- 5.4 振荡器。
- 5.5 台式离心机:4 000 r/min
- 5.6 高速离心机:10 000 r/min。
- 5.7 旋转蒸发仪。
- 5.8 旋涡混合器。
- 5.9 固相萃取柱装置。
- 5.10 氮吹仪。
- 5.11 超纯水器。
- 5.12 螺旋盖聚丙烯离心管:50 mL、15 mL。

6 试样制备与保存

6.1 试样制备

取有代表性样品约 500 g,装入洁净容器作为试样,密封并标明标记。

6.2 试样保存

试样于-18 ℃以下保存。在制样的操作过程中,应防止样品污染或发生残留物含量的变化。

7 测定步骤

7.1 提取

称取 2 g 试样(精确到 0.001 g)于 50 mL 螺旋盖聚丙烯离心管中,加入 10 mL 0.2 mol/L 磷酸氢二钠溶液(4.11)和 3 g 氯化钠,混匀,用 2 mol/L 氢氧化钠溶液(4.12)调 pH 至 8.5~8.6,加入 10 mL 乙

腈,振荡提取 15 min,以 8 000 r/min 离心 10 min。取 10 mL 上层清液到 100 mL 鸡心瓶中,40 ℃减压浓缩至 1.5 mL~2 mL,待净化。

7.2 净化

将 7.1 中提取液转移至 PSA 固相萃取柱(4.19)中,用 2 mL 乙腈-甲苯(4.13)润洗鸡心瓶并转移至柱中,重复润洗 3 次,最后用 15mL 乙腈-甲苯(4.13)洗脱。在整个操作过程中应注意避免小柱干涸,固相萃取过程流速不超过 1 mL/min。收集全部流出液于 100 mL 鸡心瓶中,于 40℃ 减压浓缩至 1.5 mL~2 mL 后将其转移至 15 mL 的离心管中,用 3 mL 乙腈-甲苯(4.13)分两次洗涤鸡心瓶,合并洗涤液到同一离心管中,于 40 ℃水浴下氮吹至近干。残留物用 1.0 mL 的甲醇-10 mmol/L 乙酸铵(含 0.1% 甲酸)溶液(4.15)溶解,并涡旋混合 1 min,过微孔滤膜后,供测定。

7.3 测定

7.3.1 液相色谱参考条件

- 7.3.1.1 色谱柱:C18 柱,50 mm×4.6 mm(内径),1.8 μm,或相当者。
- 7.3.1.2 流动相:甲醇和 10 mmol/L 乙酸铵(含 0.1%甲酸)溶液(4.14),梯度洗脱程序见表 1。
- 7.3.1.3 进样量:10 μL。
- 7.3.1.4 柱温:40 ℃。
- 7.3.1.5 流速:0.4 mL/min。

表 1 梯度洗脱程序表

时间/min	流动相 A 甲醇/%	流动相 B 10 mmol/L 乙酸铵(含 0.1%甲酸)/%
0	10	90
7	80	20
9	80	20
10	100	0
14	100	0
15	10	90
20	10	90

7.3.2 质谱/质谱参考条件

- 7.3.2.1 电离方式:电喷雾电离,正离子。
- 7.3.2.2 质谱/质谱条件:采用多反应监测模式(MRM)检测,具体参数参见附录 A。
- 7.3.2.3 其他仪器条件:参见附录 A。

7.3.3 定性测定

按照上述条件测定试样和标准工作溶液,如果试样中的质量色谱峰保留时间与标准工作溶液一致(变化范围在±2.5%之内);样品中目标化合物的定性离子的相对丰度与浓度相当的标准溶液一致,相对丰度偏差不超过表 2 的规定,则可判断样品中存在待测物。

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%

7.3.4 定量测定

根据样液中被测物的含量,选定浓度相近的标准工作溶液,对标准工作溶液和样液等体积参插进样测定。试样中被测物的响应值应在仪器检测的线性范围内,若其响应值超过线性范围,可调整定容体积使之满足测定要求。在 7.3.2.2 液相色谱-质谱/质谱条件下,2-氨基苯并咪唑、多菌灵、噻菌灵、甲基硫菌灵的保留时间分别为 4.0 min、5.9 min、6.5 min、7.8 min,标准品的液相色谱-质谱/质谱图参见附录 B 中图 B.1。

7.3.5 空白试验

除不加试样外,均按 7.1、7.2、7.3.1~7.3.4 步骤进行。

8 结果计算和表述

试样中被测物的含量由色谱数据处理软件或按式(1)计算获得,计算结果需扣除空白值,并保留两位有效数字:

$$X_i = \frac{A_i \times c_i \times V \times 1\,000}{A_{si} \times m \times 1\,000} \times f \dots\dots\dots (1)$$

式中:

- X_i ——试样中被测物的残留量,单位为微克每千克(μg/kg);
- A_i ——样液中被测物的峰面积;
- c_i ——标准工作液中被测物的浓度,单位为纳克每毫升(ng/mL);
- V ——样液最终定容体积,单位为毫升(mL);
- A_{si} ——标准工作液中被测物的峰面积;
- m ——试样的质量,单位为克(g);
- f ——稀释倍数。

9 测定低限、回收率

9.1 测定低限

本方法的测定低限:2-氨基苯并咪唑为 2 μg/kg,多菌灵、噻菌灵、甲基硫菌灵均为 1 μg/kg。

9.2 回收率

样品的添加浓度及回收率的数据参见附录 C。

附 录 A
(资料性附录)
质谱参考条件¹⁾

质谱参考条件：
a) 毛细管电压:4 000 V；
b) 雾化气温度:350 ℃；
c) 雾化气流速:12 L/min；
d) 雾化气压力:0.276 MPa(40 psi)。
多反应监测模式(MRM)条件见表 A.1。

表 A.1 多反应监测模式(MRM)条件

化合物	离子对 <i>m/z</i>	裂解电压 V	碰撞能量 V
2-氨基苯并咪唑	134/65 ^a	120	25
	134/92		35
多菌灵	192/160 ^a	110	15
	192/132		30
噻菌灵	202/175 ^a	120	25
	202/131		35
甲基硫菌灵	343/151 ^a	80	4
	343/311		15
* 定量离子对。			

1) 非商业性声明:附录所列参考质谱条件是在 Agilent 6410B 型液质联用仪上完成的,此处列出试验型号仅为提供参考,并不涉及商业目的,鼓励标准使用者尝试使用不同厂家或型号的仪器。

附 录 B
(资料性附录)
色 谱 图

标准品的液相色谱-质谱 质谱图见图 B.1。

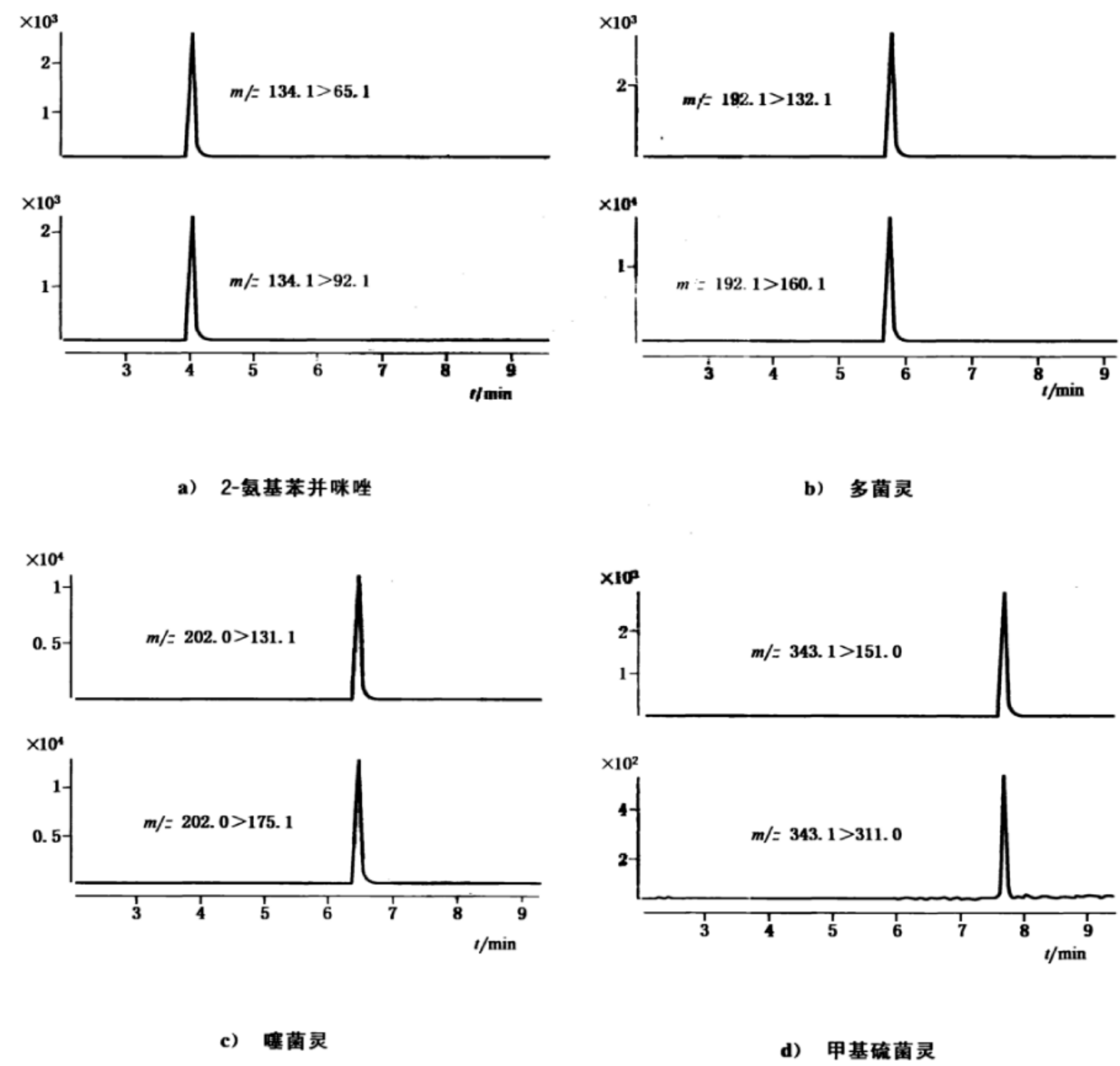


图 B.1 标准品的液相色谱-质谱/质谱色谱图(MRM 检测)

附 录 C
(资料性附录)
回 收 率

果汁样品的添加浓度及回收率的数据见表 C.1。

表 C.1 添加样品回收率及精密度(n=6)

杀 菌 剂	添加水平 μg/kg	浓缩苹果汁		浓缩梨汁		浓缩芒果汁		浓缩西番莲汁		浓缩橙汁		浓缩荔枝汁		浓缩菠萝汁	
		平均回收率 %	RSD %	平均回收率 %	RSD %	平均回收率 %	RSD %	平均回收率 %	RSD %	平均回收率 %	RSD %	平均回收率 %	RSD %	平均回收率 %	RSD %
2-氨基苯并咪唑	2	83.9	3.1	82.8	3.4	90.8	4.8	86.2	5.2	87.5	4.9	88.1	6.0	92.5	2.6
	4	85.4	4.7	90.2	2.9	86.7	6.9	88.0	6.6	86.5	5.3	90.5	3.8	86.5	8.2
	20	92.1	3.3	94.8	1.2	92.8	3.0	93.0	2.6	95.0	3.4	92.5	3.2	91.4	3.7
多菌灵	1	84.3	2.4	82.6	5.2	94.7	7.5	86.1	6.2	86.6	6.5	84.8	7.1	86.2	5.9
	2	88.2	4.2	86.1	4.0	87.1	6.1	87.8	4.0	95.5	5.9	95.7	5.6	94.6	5.2
	10	90.7	6.6	89.2	3.5	92.6	4.9	89.0	6.9	90.4	4.9	92.7	5.4	90.5	7.3
噻菌灵	1	91.6	6.1	92.7	9.4	91.2	6.6	95.4	8.4	94.0	8.6	92.1	7.5	86.1	5.5
	2	94.3	3.8	94.4	5.8	84.5	5.3	88.4	6.4	93.4	4.4	90.9	3.8	96.5	5.9
	10	91.0	4.2	93.7	2.4	90.0	4.0	91.4	5.0	91.0	5.1	88.1	4.7	9.07	4.9
甲基硫菌灵	1	81.8	5.2	96.0	6.8	94.3	6.5	88.5	8.7	89.5	5.8	93.2	7.8	94.8	6.2
	2	89.9	2.6	94.1	3.8	94.1	3.8	92.7	3.7	94.6	5.3	91.4	2.9	94.5	5.1
	10	98.3	5.7	91.2	4.6	91.2	4.6	91.4	4.0	96.9	4.6	91.3	4.5	95.0	6.2

Foreword

This standard is drafted allording to GB/T 1.1—2009.

This standard replaced SN/T 1753—2006 *Determination of thiabendazole and carbendazim residues in concentrated fruit juices for import and export—High performance liquid chromatographic method*.

Compared with SN/T 1753—2006, this standard has the main changes which are as follows:

—Modify the name of the standard;

—Measuring method changed by high performance liquid chromatography (HPLC) to the liquid chromatography-mass spectrometry/mass spectrometry (LC-MS/MS). This standard increased thio-phanate-methyl and 2-aminobenzimidazole residues determination at the same time.

Please pay attention that some of the content of this document may involve patents, the publisher of this document does not assume the responsibility to identify these patents.

This standard was proposed by and was 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, Shanghai Entry-Exit Inspection and Quarantine Bureau, Shanxi Entry-Exit Inspection and Quarantine Bureau of the People’s Republic of China, Guangxi University.

This standard was mainly drafted by Liu Xiaosong, Zhen Ling, Li Yon, Ling Jingchang, Lv Chunqiu, Ning Enchuang, Huang Wenwen, Kong Xianghong, Fang Xiaoming.

This standard replaces the previous version:

—SN/T 1753—2006.

Determination of thiophanate-methyl, thiabendazole, carbendazim and 2-aminobenzimidazole residues in concentrated juices for export—LC-MS/MS method

1 Scope

This standard specifies the determination of thiophanate-methyl, thiabendazole, carbendazim and 2-aminobenzimidazole residues in concentrated juices for import and export—LC-MS/MS method

This standard is applicable to the determination and confirmation of thiophanate-methyl, thiabendazole, carbendazim and 2-aminobenzimidazole residues in concentrated juices.

2 Normative reference documents

The following documents for the application of this document is indispensable. For documents which note date, only note date version applicable to this standard. For those which doesn't note date, the latest version (including all the modified single) applicable to this document.

GB/T 6682 Water for Analysis laboratory use—Specifications and test methods

3 Principle

Dilute the test sample with 0.2 mol/L disodium hydrogen phosphate solution, and adjust pH to 8.5~8.6 with sodium hydroxide solution. Extract with acetonitrile, and clean up with an ethylene diamine base-N-propyl (PSA) column. HPLC-MS/MS is used to determine using external standard method for quantity.

4 Reagents and materials

Unless specified, all the reagents used should be analytical grade, and “water” is the top level in GB/T 6682.

4.1 Acetonitrile: HPLC grade.

4.2 Methanol; HPLC grade.

4.3 Toluene; HPLC grade.

4.4 Formic acid; HPLC grade.

4.5 Ammonium acetate; HPLC grade.

4.6 Disodium hydrogen phosphate; $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$.

4.7 Sodium chloride.

4.8 Anhydrous sodium sulfate; Burn at 650 °C for 4 hours before using, store in the dryer, and reserve after cooling.

4.9 Phosphoric acid; Content $\geq 85\%$

4.10 Thiophanate-methyl standard: $\text{C}_{12}\text{H}_{14}\text{N}_4\text{O}_4\text{S}_2$, CAS No.23564-05-8, purity $\geq 98\%$; thiabendazole standard: $\text{C}_{10}\text{H}_7\text{N}_3\text{S}$, CAS No.148-79-8, purity $\geq 98\%$; carbendazim standard: $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}$, CAS No.10605-21-7, purity $\geq 98\%$; 2-aminobenzimidazole standard: $\text{C}_7\text{H}_7\text{N}_3$, CAS No.934-32-7, purity $\geq 98\%$.

4.11 0.2 mol/L disodium hydrogen phosphate solution; take 17.91 g disodium hydrogen phosphate and dilute with water to 250 mL.

4.12 2 mol/L sodium hydroxide solution; take 8.0 g sodium hydroxide and dilute with water to 100 mL.

4.13 Acetonitrile-toluene (3 + 1); blend 300 mL acetonitrile with 100 mL toluene.

4.14 10 mmol/L ammonium acetate solution (including 0.1% formic acid); take 0.77 g ammonium acetate, and dilute with water, then add 1 mL formic acid, and dilute with water to 1L.

4.15 Methanol-10 mmol/L ammonium acetate solution containing 0.1% formic acid; Add 10 mL methanol into 90 mL 10 mmol/L ammonium acetate solution containing 0.1% formic acid (4.14), and mix well.

4.16 Standard stock solutions; Accurately weigh 10 mg (accurate to 0.1 mg) of the standard to a 100 mL brown volumetric flask and dissolve with methanol to the volume, obtaining 100 $\mu\text{g/mL}$ of the standard stock solution, respectively. The solutions are stored at $-18\text{ }^\circ\text{C}$, and avoid light.

4.17 Mixed standard intermediate solution; Accurately pipette 10 mL of each standard stock solution to a 100 mL brown volumetric flask, and dissolve with methanol to the volume, obtaining 10 $\mu\text{g/mL}$ of the mixed standard intermediate solution. The solution is stored at $-18\text{ }^\circ\text{C}$, and avoid light.

4.18 Mixed standard working solution: make the corresponding blank sample substrate prepare appropriate concentration mixed standard working solutions. These solutions should be prepared before use.

4.19 PSA solid-phase extraction column: 500 mg, 3 mL, or rather a person. Before use, add 1 g anhydrous sodium sulfate on the top of the column, and 4 mL acetonitrile-toluene (4.13) to rinse.

4.20 Microporous membrane filter: 0.22 μm , organic system.

5 Apparatus and equipment

5.1 LC-MS/MS: equipped with electrospray ionization (ESI).

5.2 Electronic balance: accurate to 0.01 mg and 0.01g.

5.3 pH meter.

5.4 Oscillator.

5.5 Bench centrifuge: 4 000 r/min.

5.6 High speed centrifuge: 10 000 r/min.

5.7 Rotary evaporation apparatus.

5.8 Vortex mixer.

5.9 Solid phase extraction column device.

5.10 Nitrogen blow apparatus.

5.11 Ultrapure water device.

5.12 Screw cap polypropylene centrifuge tube: 50 mL, 15 mL.

6 Sample preparation and storage

6.1 Preparation of test samples

Take a representative sample of about 500 g, into clean containers as a test sample, seal and mark it.

6.2 Storage of test samples

The test samples are stored under $-18\text{ }^{\circ}\text{C}$. In the operation of the sample preparation process, the sample pollution or the change in the content of residues should be avoided.

7 Method of determination

7.1 Extraction

Weigh 2 g (accurate to 0.001 g) test sample in a 50 mL screw cap polypropylene centrifuge tube, add 10 mL 0.2 mol/L disodium hydrogen phosphate solution (4.11) and 3 g sodium chloride, and mix. Adjust pH to 8.5 – 8.6 with NaOH solution (4.12). Add 10 mL acetonitrile, and vortex for 15 min. Centrifuge for 10 min at 8 000 r/min. Transfer 10 mL supernatant to a 100 mL bottle of heart, and condense to 1.5 mL—2 mL using the rotary evaporation apparatus at $40\text{ }^{\circ}\text{C}$, followed by clean-up.

7.2 Clean-up

Transfer the 7.1 solutions to a PSA solid-phase extraction column (4.19). Rinse the bottle three times with 2 mL of acetonitrile-toluene (4.13), and transfer to the column. Elute with 15 mL acetonitrile-toluene (4.13). In the whole operation process, avoid the column dry, and the flow rate of the liquid should be less than 1 mL/min. Collect the eluent in a 100 mL bottle of heart, and condense to 1.5 mL—2 mL using the rotary evaporation apparatus at $40\text{ }^{\circ}\text{C}$. Transfer the solutions to a 15 mL centrifuge tube. Rinse the bottle two times with 3 mL of acetonitrile-toluene (4.13), and transfer to the tube. Condense the solutions in the tube to nearly dry under nitrogen blow at $40\text{ }^{\circ}\text{C}$. Dissolve the residues with 1.0 mL methanol – 10 mmol/L ammonium acetate solution containing 0.1% formic acid (4.15), and vortex for 1 min. Filter the solutions through a microporous membrane filter for determination.

7.3 Determination

7.3.1 HPLC reference conditions

7.3.1.1 Chromatographic column: C18 column, 50 mm × 4.6 mm (i. d), 1.8 μm , or rather a person.

7.3.1.2 Mobile phase: methanol and 10 mmol/L ammonium acetate solution containing 0.1% formic acid (4.14). Gradient elution procedure is shown in Table 1.

7.3.1.3 Injection volume: 10 μL .

7.3.1.4 Column temperature: $40\text{ }^{\circ}\text{C}$.

7.3.1.5 Flow rate: 0.4 mL/min.

Table 1 Gradient elution procedure list

Time/min	Mobile phase A (Meyhanol)/%	Mobile phase B (Ammonium acetate solution)/%
0	10	90
7	80	20
9	80	20
10	100	0
14	100	0
15	10	90
20	10	90

7.3.2 MS-MS reference condition

7.3.2.1 Ionization method: electrospray ionization, positive ion.

7.3.2.2 MS/MS mode: multiple reaction monitoring (MRM), the condition is shown in appendix A.

7.3.2.3 Other instruments conditions are shown in appendix A.

7.3.3 Qualification

Test sample and standard working solution according to the above conditions, if the retention time of the sample chromatographic peak is equal to that of the standard working solution (range within $\pm 2.5\%$); the tolerances between the relative abundance of the qualification ions of the test sample and that of the standard working solution is not over the range described in table 2, the targeted compound existed in the sample is confirmed.

Table 2 Maximum permitted tolerances for relative ion intensities using a range of mass spectrometric techniques

Relative ion intensity	>50%	>20% to 50%	>10% to 20%	$\leq 10\%$
Maximum permitted tolerances	$\pm 20\%$	$\pm 25\%$	$\pm 30\%$	$\pm 50\%$

7.3.4 Quantification

According to the content of sample solution, select the standard working solution with similar peak height to that of the sample solution. The responses of per analytes in the standard working solution and sample solution should be within 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. Under the 7.3.2.2 LC-MS conditions, the reference retention time of analytes are 2-amino-benzimidazole 4.0 min, carbendazim 5.9 min, thiabendazole 6.5 min, thiophanate-methyl 7.8 min,

respectively. LC-MS/MS multiple reaction monitoring chromatogram of the standard substance is shown in appendix B figure. B.1.

7.3.5 Blank test

Blank test will be conducted according to the 7.1、7.2、7.3.1—7.3.4 procedures,without sample addition.

8 Calculation and expression of the result

Calculate the content of thiophanate-methyl, thiabendazole, carbendazim and 2-aminobenzimidazole in the test sample by LC-MS data processor or according to the formula(1). The result of calculation should be deducted with blank value. and keep the two significant figures:

$$X_i = \frac{A_i \times c_i \times V \times 1\,000}{A_{si} \times m \times 1\,000} \times f \quad \dots\dots\dots(1)$$

where

X_i —the residue content of analytes in the test sample, $\mu\text{g/kg}$;

A_i —the peak area (height) of analytes in the sample solution;

c_i —the concentration of analytes in the standard working solution, ng/mL ;

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

A_{si} —the peak area (height) of analytes in the standard working solution;

m —the mass of the test sample, g ;

f —dilution ratio.

9 Limit of quantification and recovery

9.1 Limit of quantification (LOQ)

The method limits of quantification (LOQ) are $2\,\mu\text{g/kg}$ for 2-aminobenzimidazole, and $1\,\mu\text{g/kg}$ for thiophanate-methyl, thiabendazole and carbendazim.

9.2 Recovery

The ranges of fortification and recovery of this method are shown in appendix C.

Annex A
(informative annex)
Reference mass spectrum conditions¹⁾

LC-MS conditions:

- a) Capillary voltage: 4 000 V;
- b) Atomization temperature: 350 ℃ ;
- c) Atomizing gas velocity:12 L/min;
- d) Ion source gas;0.276 MPa(40 psi) ;

Multiple reaction monitoring conditions are shown in Table A.1.

Table A.1 Multiple reaction monitoring conditions

Compound	Qualitative ion pair <i>m/z</i>	Cracking voltage V	Collision energy V
2-aminobenzimidazole	134/65*	120	25
	134/92		35
carbendazim	192/160*	110	15
	192/132		30
thiabendazole	202/175*	120	25
	202/131		35
thiophanate-methyl	343/151*	80	4
	343/311		15
* Quantitative ion pair.			

1) Non-commercial statement: the reference mass parameters in Section A are accomplished by Agilent 6410B 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 equipments of different corporation or different type.

Annex B
(informative annex)
Chromatogram

LC-MS/MS chromatograms(MRM)of the standard are shown in Figure B.1.

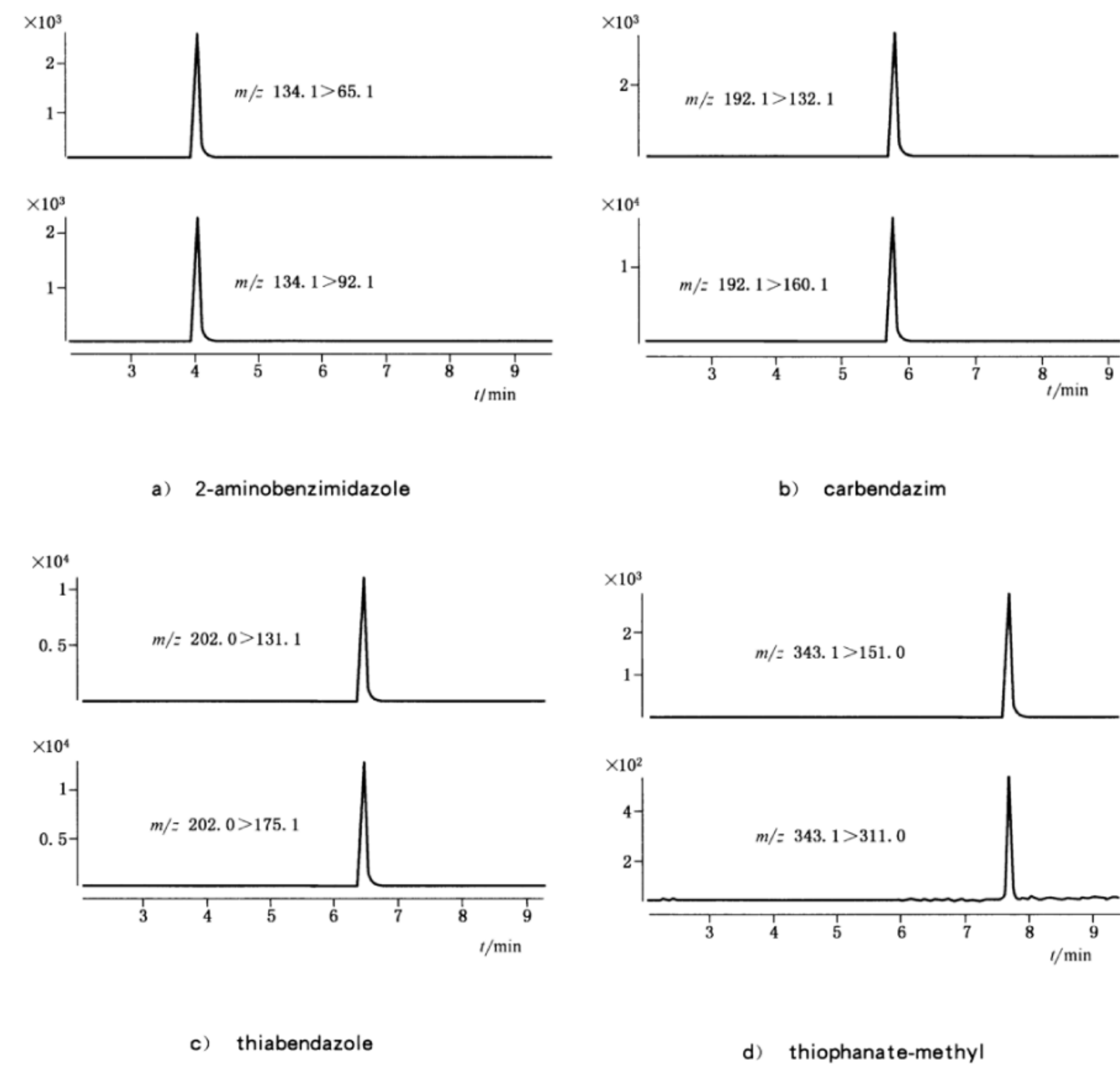


Figure B.1 LC-MS/MS chromatograms(MRM)of the standard

Annex C
(informative annex)
Recovery

Recovery of samples in various fortified concentrations is shown in Table C.1.

Table C.1 Recovery of samples in various fortified concentrations(*n* =6)

Fungicide	Spiked concentration μg/kg	Concentrated apple juice		Concentrated pear juice		Concentrated mango juice		Concentrated passion fruit juice		Concentrated orange juice		Concentrated litchi juice		Concentrated pineapple juice	
		Recovery %	RSD %	Recovery %	RSD %	Recovery %	RSD %	Recovery %	RSD %	Recovery %	RSD %	Recovery %	RSD %	Recovery %	RSD %
2-aminoben-zimidazole	2	83.9	3.1	82.8	3.4	90.8	4.8	86.2	5.2	87.5	4.9	88.1	6.0	92.5	2.6
	4	85.4	4.7	90.2	2.9	86.7	6.9	88.0	6.6	86.5	5.3	90.5	3.8	86.5	8.2
	20	92.1	3.3	94.8	1.2	92.8	3.0	93.0	2.6	95.0	3.4	92.5	3.2	91.4	3.7
Carbendazim	1	84.3	2.4	82.6	5.2	94.7	7.5	86.1	6.2	86.6	6.5	84.8	7.1	86.2	5.9
	2	88.2	4.2	86.1	4.0	87.1	6.1	87.8	4.0	95.5	5.9	95.7	5.6	94.6	5.2
	10	90.7	6.6	89.2	3.5	92.6	4.9	89.0	6.9	90.4	4.9	92.7	5.4	90.5	7.3
Thiabendazole	1	91.6	6.1	92.7	9.4	91.2	6.6	95.4	8.4	94.0	8.6	92.1	7.5	86.1	5.5
	2	94.3	3.8	94.4	5.8	84.5	5.3	88.4	6.4	93.4	4.4	90.9	3.8	96.5	5.9
	10	91.0	4.2	93.7	2.4	90.0	4.0	91.4	5.0	91.0	5.1	88.1	4.7	9.07	4.9
Thiophan-ate-methyl	1	81.8	5.2	96.0	6.8	94.3	6.5	88.5	8.7	89.5	5.8	93.2	7.8	94.8	6.2
	2	89.9	2.6	94.1	3.8	94.1	3.8	92.7	3.7	94.6	5.3	91.4	2.9	94.5	5.1
	10	98.3	5.7	91.2	4.6	91.2	4.6	91.4	4.0	96.9	4.6	91.3	4.5	95.0	6.2

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