Determination of paraquat residue in plant-derived foodstuffs by high performance liquid chromatography-tandem mass spectrometry

BO Haibo *

Hebei Entry-Exit Inspection and Quarantine Bureau· Shijiazhuang 050051· China

Abstract A sensitive and selective method is presented for the determination of paraquat residue in fruits, vegetables, beans and grain by high performance liquid chromatography-tandem mass spectrometry. Paraquat in samples was extracted with water and cleaned-up with a weak cation exchange column to obtain an extract suitable for analysis using HPLC-MS/MS. The paraquat was separated by a CAPCELL PAK ST column 150 mm × 2.0 mm and with acetonitrile-10 mmol/L ammonium acetate solution adjusted to pH 4.0 by formic acid as the mobile phase and multiple reaction monitoring. MRM was used with electrospray ionization in the positive ion mode. The calibration curve was linear between the peak area and the mass concentration of paraquat from 0.01 to 0.1 mg/L with the correlation coefficient of 0.993. Recoveries of paraquat spiked in samples at three levels ranged from 84.0% to 106.0% with the relative standard deviations of 7.8%–18.8%. The limits of detection of paraquat were 0.01 mg/kg in fruits and vegetables and 0.05 mg/kg in beans and grain. The LODs can meet the requirements of international maximum residue limit.

Key words weak cation exchange high performance liquid chromatography-tandem mass spectrometry HPLC-MS/MS paraquat residue plant-derived foodstuffs

* Corresponding author. Tel: +86-311-85980504 E-mail: bohb1212@163.com
草枯的高效液相色谱分析方法采用紫外检测器检测。由于百草枯结构特殊，国内外多残留分析方法难以被憎水性的反相色谱柱保留，以反相高效液相色谱法等。现行检验检疫行业标准或相关研究中均不包括百草枯的测定。百草枯为碱性的强极性有机化合物，在水溶液中，提取方法十分复杂，需要在强酸或强碱条件下进行还原反应，操作费时、繁琐，回收率和灵敏度低。现有的标准方法如美国环保局EPA 549.2，美国分析化学家学会AOAC 992.17，植物源性食品中百草枯残留测定方法十分必要。百草枯标准储备液:准确称取百草枯于聚丙烯离心管中，加水至257 mm，室温溶解，转移至50 mL容量瓶，定容摇匀。储存在4 ℃条件下。储备液可稳定1 个月。根据不同的样品基质，取储备液0.1 ～ 1.0 g/L,0 ～ 4 ℃条件下预处理。

## 1.2

### 1.2.1

**仪器与试剂**

- HPLC-MS/MS系统: Waters WCX (150 mm×4.6 mm，5 μm)配CEM固相萃取柱
- Teflon毛细管(Skyline)：10 μm
- 串联质谱仪
- 电离模式: 具有多反应监测(DM)的ESI
- 碰撞气(氩气)流量: 0.1 L/min
- 锥孔气(氮气)流量: 0.1 L/min
- 电离电压: 0.4 kV
- 毛细管电压: -40 V
- 流速: 0.2 μL/min
- 进样量: 2 μL
- 质谱扫描范围: m/z 186
- *m/z 186 >77

### 1.3

#### 1.3.1

**样品溶液的制备**

植物源性食品中有很多种，很难用一种固定相或一种流动相用于百草枯残留分析，解决了上述方法中流动相与质谱仪的兼容性问题。百草枯为碱性的强极性有机化合物，在水溶液中，提取方法十分复杂，需要在强酸或强碱条件下进行还原反应，操作费时、繁琐，回收率和灵敏度低。现有的标准方法如美国环保局EPA 549.2，美国分析化学家学会AOAC 992.17，植物源性食品中百草枯残留测定方法十分必要。百草枯标准储备液:准确称取百草枯于聚丙烯离心管中，加水至257 mm，室温溶解，转移至50 mL容量瓶，定容摇匀。储存在4 ℃条件下。储备液可稳定1 个月。根据不同的样品基质，取储备液0.1 ～ 1.0 g/L,0 ～ 4 ℃条件下预处理。
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do not reach a concentration of 100 μmol/L, paraquat cannot be eluted under these conditions. During this period, a large amount of crystalline buffer salt is deposited at the ion source orifice. Thus, it is unsuitable for routine analysis of paraquat. Using a HILIC column, the addition of acetic ammonium to the mobile phase can make paraquat effectively separated with a retention time of about 1 min. Therefore, the HILIC column is selected as the analysis column for paraquat.

In the ESI positive ionization mode, by adjusting the capillary voltage, cone voltage, ion source temperature, desolvation gas temperature and flow, and cone gas flow, etc., the parent ion (m/z 186.1 > 77.1, 155.2 > 77.1, 171.1 > 77.1) with the maximum abundance can be obtained. Through the daughter ion scan, the main daughter ions were found at m/z 186.1 > 77.1, 155.2 > 77.1, 171.1 > 77.1. The relative abundance of the largest daughter ion m/z 186.1 > 77.1 was selected as the quantitative ion, and the collision energy, collision gas flow, and fragmentation voltage were optimized to obtain a higher sensitivity.

The total ion chromatogram and spectrum of paraquat in the blank sample and the sample spiked with different levels of paraquat are shown in Fig. 1. Therefore, it is selected as the purification column for this method.

Table 1  Recoveries and precisions of paraquat spiked in four samples (n = 6)

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Added/ Found/</th>
<th>Recovery/ RSD/</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/kg</td>
<td>%</td>
</tr>
<tr>
<td></td>
<td>mg/kg</td>
<td>%</td>
</tr>
<tr>
<td>Apple</td>
<td>0.01</td>
<td>0.092</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>0.042</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>0.089</td>
</tr>
<tr>
<td>Cabbage</td>
<td>0.01</td>
<td>0.010</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>0.046</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>0.088</td>
</tr>
<tr>
<td>Pea[dried]</td>
<td>0.01</td>
<td>0.0086</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>0.053</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>0.092</td>
</tr>
<tr>
<td>Rice</td>
<td>0.01</td>
<td>0.0086</td>
</tr>
<tr>
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<td>0.047</td>
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<tr>
<td></td>
<td>0.1</td>
<td>0.091</td>
</tr>
</tbody>
</table>

2.4 Regression analysis and detection limits

Accurately吸取paraquat standard reserve solution an appropriate amount, using blank basal solution diluted to 0.01, 0.02, 0.05, and 0.1 mg/L concentration levels respectively, and each concentration level was measured in triplicate under the above conditions. The linear regression equation was obtained by linear regression analysis of the quantitative ion peak area and paraquat concentration, with a linear range of 0.01 to 0.1 mg/L, and the equation was $y = 20300x + 3180$, the correlation coefficient was 0.993.

The detection limit was obtained by the 3σ method, which was 0.01 mg/kg. Therefore, the detection limit in this method is 0.05 mg/kg.

RSD 7.8% ~ 18.8%
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薄海波: 液相色谱串联质谱法快速测定植物源性食品中的百草枯

图 a: 空白样品及 b: 空白添加样品的 HPLC-MS/MS 图

Fig. 2 HPLC-MS/MS chromatograms of (a) a blank sample and (b) a spiked sample

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1. SN 0340-95
3. US EPA National Environmental Methods 549, 2 Revision 1. 0, June 1997
4. AOAC Official Method 992. 17