Simultaneous determination of residues of six imidazolinone herbicides in adzuki beans by high performance liquid chromatography-electrospray ion trap tandem mass spectrometry

LI Cheng1 SUO Ran1 WANG Fengchi2 MA Hongying1

1. College of Food Science Agricultural University of Hebei Baoding 071000 China
2. Hebei Entry & Exit Inspection and Quarantine Bureau Shijiazhuang 050071 China

Abstract A method for the simultaneous determination of six pesticides in adzuki beans by high performance liquid chromatography-electrospray ion trap tandem mass spectrometry was developed and evaluated. The sample was extracted with 0.1 mol/L NH₄HCO₃ pH 5 methanol 70:30 v/v. The extract was partitioned with dichloromethane and cleaned up with gel permeation chromatography. The separation was performed on an Inertsil ODS-3 column with the gradient elution of methanol and 1% acetic acid as mobile phase. The identification and quantification were performed by electrospray ion trap mass spectrometry with selected ion monitoring mode. The calibration curves of imidazolinone herbicides showed good linearity in the range of 10–200 μg/L and 5–100 μg/L for imazapyr with the correlation coefficients between 0.9987 and 0.9997. The limits of detection ranged between 0.2 μg/kg and 0.5 μg/kg S/N = 3. The average recoveries of six imidazolinone herbicides spiked in adzuki beans ranged between 81.6% and 99.4% with the relative standard deviations of 3.1%–7.8%. The method has been used for the determination of 6 imidazolinone herbicides simultaneously in adzuki beans with easy operation high accuracy and good precision.

Key words gel permeation chromatography liquid chromatography-tandem mass spectrometry LC-MS/MS imidazolinone herbicides multiresidue determination adzuki beans
1  

1.1  

Agilent 1100  

ESI@ 5 × 250 mm, 5 μm  

CE-MS  

LC-MS  

GPC  

Accuprep  

22 g S-X3 Bio-Beads  

200 ~ 400 μm  

J2 Scientific  

Tedia  

0.45 μm  

Dr. Ehrenstorfer  

10 mg  

1.2  

1.2.1  

4 mL/min  

254 nm  

8 min  

8→14 min  

2 mL  

40 mL  

10 mL  

5000 r/min  

5 min  

GPC  

1 mL  

0.45 μm  

LC-MS/MS  

1.2.2  

1:1  

5 mL/min  

5 mL/min  

30 °C  

15 μL  

0.3 mL/min  

40% A→43%A→7 min  

43%A→70%A  

30 °C  

9 L/min  

350 °C  

2  

2.1  

pH 5→8  

pH 5→8  

0.1 mol/L NH₄HCO₃
70: 30 [10x185])& 85% [10x578] 1 mol/L HCl pH 5 [10x169] 6 [10x436] pH 7 [10x91] 1 mol/L NH₄HCO₃ pH 5-6 [10x43] 0.1 mol/L NH₄HCO₃ pH 5-6 [10x436] 70: 30 [10x169]

pKₐ 10 [10x578] 50% [10x436] 1 mol/L pH 5; 6 [10x436] pH 7 [10x91] 1 mol/L pH 5; 6 [10x436] pH 7.5 [10x298] 20% [10x594]

2.2 GPC


2.3

6 [10x106] 6 [10x43] 0.1% [10x43] 0.1% [10x43]

2.4

6 [10x106] 6 [10x43] 0.1% [10x43]

Table 1 The mass spectrometric operating conditions for the 6 herbicide standards

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>t_k/min</th>
<th>Collision energy/ V</th>
<th>Parent ion m/z</th>
<th>Daughter ions m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Imazapyr</td>
<td>8.5</td>
<td>0.80</td>
<td>262.2</td>
<td>220.1 * 234.1</td>
</tr>
<tr>
<td>Imazapic</td>
<td>10.1</td>
<td>0.85</td>
<td>276.2</td>
<td>234.1 * 248.2</td>
</tr>
<tr>
<td>Imazamox</td>
<td>11.7</td>
<td>0.95</td>
<td>306.2</td>
<td>264.1 * 278.1</td>
</tr>
<tr>
<td>Imazamethabenz-methyl</td>
<td>12.6</td>
<td>0.85</td>
<td>289.2</td>
<td>257.2 * 229.1</td>
</tr>
<tr>
<td>Imazethapyr</td>
<td>14.7</td>
<td>0.95</td>
<td>290.1</td>
<td>248.1 * 262.2</td>
</tr>
<tr>
<td>Imazquin</td>
<td>17.9</td>
<td>0.95</td>
<td>312.2</td>
<td>270.1 * 267.1</td>
</tr>
</tbody>
</table>

* quantification ions. Fig. 1 Gel permeation chromatograms of a six imidazolinone herbicides standards and b sample of adzuki beans.
2.5 LC-MS/MS RSD 3.1% ~ 7.8% 0.2 ~ 0.5 μg/kg 10 6.0 μg/kg 2

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>Linear range/μg/L</th>
<th>Linear equation</th>
<th>r</th>
<th>Added/μg/kg</th>
<th>Recovery/%</th>
<th>RSD/%</th>
<th>LOD/μg/kg</th>
<th>LOQ/μg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Imazapyr</td>
<td>10 ~ 200</td>
<td>( y = 17406.4x + 192965.9 )</td>
<td>0.9997</td>
<td>10</td>
<td>87.1</td>
<td>5.8</td>
<td>0.5</td>
<td>10.0</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20</td>
<td>87.8</td>
<td>4.6</td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>50</td>
<td>85.2</td>
<td>5.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Imazamox</td>
<td>10 ~ 200</td>
<td>( y = 24869.4x + 87680.5 )</td>
<td>0.9987</td>
<td>10</td>
<td>92.5</td>
<td>6.8</td>
<td>0.5</td>
<td>10.0</td>
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<td></td>
<td></td>
<td></td>
<td>20</td>
<td>89.2</td>
<td>6.0</td>
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<td></td>
<td></td>
<td>50</td>
<td>85.4</td>
<td>3.1</td>
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</tr>
<tr>
<td>Imazapic</td>
<td>10 ~ 200</td>
<td>( y = 22263.7x + 32534.6 )</td>
<td>0.9992</td>
<td>10</td>
<td>88.1</td>
<td>5.3</td>
<td>0.5</td>
<td>10.0</td>
</tr>
<tr>
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<td></td>
<td></td>
<td>20</td>
<td>90.7</td>
<td>3.2</td>
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<td></td>
<td>50</td>
<td>88.2</td>
<td>4.3</td>
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<tr>
<td>Imazamethabenz-methyl</td>
<td>10 ~ 200</td>
<td>( y = 48304.5x + 158041.8 )</td>
<td>0.9993</td>
<td>10</td>
<td>90.2</td>
<td>7.4</td>
<td>0.3</td>
<td>10.0</td>
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<td></td>
<td></td>
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<td>89.3</td>
<td>5.6</td>
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<td>50</td>
<td>81.6</td>
<td>4.3</td>
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<tr>
<td>Imazethapyr</td>
<td>10 ~ 200</td>
<td>( y = 22196.7x + 138437.5 )</td>
<td>0.9992</td>
<td>10</td>
<td>90.3</td>
<td>5.7</td>
<td>0.5</td>
<td>10.0</td>
</tr>
<tr>
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<td>20</td>
<td>88.7</td>
<td>4.8</td>
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<td></td>
<td></td>
<td></td>
<td>50</td>
<td>89.6</td>
<td>5.7</td>
<td></td>
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<tr>
<td>Imazaquinn</td>
<td>5 ~ 100</td>
<td>( y = 10084.8x - 2965.1 )</td>
<td>0.9991</td>
<td>5</td>
<td>99.4</td>
<td>7.8</td>
<td>0.2</td>
<td>5.0</td>
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<td>10</td>
<td>94.5</td>
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<td>25</td>
<td>89.1</td>
<td>5.1</td>
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</tr>
</tbody>
</table>

**Fig. 2** Selected ion current chromatograms of adzuki beans spiked with six imidazolinone herbicide standards 5 ~ 10 μg/kg
实际样品的测定

用本文建立的方法分别测定了7份红小豆样品(采自当地农贸市场)中7种咪唑啉酮类除草剂残留,结果均未检出该类除草剂。

结论

根据咪唑啉酮类除草剂的结构特性,在提取和净化过程中选择了合适pH值的提取剂提取目标组分,使回收率达到了理想的效果;对于红小豆中的蛋白质、脂类、色素等大分子物质,采用凝胶渗透色谱净化的方法去除了大部分干扰物质,取得了理想的净化效果。本文建立的凝胶色谱净化结合高效液相色谱串联质谱对红小豆中残留的7种咪唑啉酮类除草剂的分析方法灵敏度高,选择性强,能够满足农药残留检测要求。

参考文献: