Determination of trace carbaryl and carbofuran in water by online column enrichment-ultra high performance liquid chromatography

WANG Enzhi1, YANG Xinlei2, YE Mingli2, WANG Qiong2, CAI Xiaojun3,*

1. Taizhou Hospital of Integrated Traditional and Western Medicine, Zhejiang District, Wenzhou, 317523, China
2. Shanghai Laboratory of Application and Research Center, Shionix China Limited, Shanghai, 201203, China
3. School of Pharmacy, Wenzhou Medical College, Wenzhou, 325035, China

Abstract An online column enrichment-ultra high performance liquid chromatography (UHPLC) method was developed to determine trace carbaryl and carbofuran in water. The sample was injected into a UHPLC system directly after filtration with 0.22 μm membrane and then enriched by online solid phase extraction (SPE) column. The analyte was back-flushed into the analytical column Acclaim RSLC C18 (100 mm × 2.1 mm, 2.2 μm) by valve switching method. The mobile phases were 10 mmol/L ammonium acetate buffer/μL pH 5.0 adjusted by acetic acid and acetonitrile in a gradient elution mode with a flow rate of 0.8 mL/min and detected by a diode array detector with the detection wavelength of 280 nm. The good linear ranges of carbaryl and carbofuran were 1.0 – 100 μg/L with the correlation coefficients r2 larger than 0.999 and the limits of detection S/N = 3 were 0.5 μg/L and 0.25 μg/L respectively. The average spiked recoveries were in the range of 76.0% – 120.0%. The method has been applied to determine trace carbaryl and carbofuran in water samples with satisfactory results.

Key words dual gradient online column enrichment ultra high performance liquid chromatography UHPLC carbaryl carbofuran
用环己烷和乙酸乙酯等有机试剂。生活饮用水检验光检测方法测定了水样中的呋喃丹。甲萘威,采用液液萃取方法农药指标。前处理方法对蔬菜中氨基甲酸酯类农药,该方法虽无需样品前处理,但仪器操作较为繁琐。陈剑刚等

### 实验部分

#### 1.1 基甲酸酯类农药,该方法虽无需样品前处理,但仪器操作较为繁琐。陈剑刚等

#### 1.2 基甲酸酯类农药,该方法虽无需样品前处理,但仪器操作较为繁琐。陈剑刚等

#### 1.3 基甲酸酯类农药,该方法虽无需样品前处理,但仪器操作较为繁琐。陈剑刚等

#### 1.4 基甲酸酯类农药,该方法虽无需样品前处理,但仪器操作较为繁琐。陈剑刚等

#### 1.5 基甲酸酯类农药,该方法虽无需样品前处理,但仪器操作较为繁琐。陈剑刚等

#### 1.6 基甲酸酯类农药,该方法虽无需样品前处理,但仪器操作较为繁琐。陈剑刚等

### 表 1 梯度洗脱程序和阀切换时间

<table>
<thead>
<tr>
<th>Loading pump</th>
<th>Analytical pump</th>
<th>Valve</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time(min)</td>
<td>% B</td>
<td>Time(min)</td>
</tr>
<tr>
<td>0</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>2.0</td>
<td>30</td>
<td>2.2</td>
</tr>
<tr>
<td>3.2</td>
<td>100</td>
<td>4.0</td>
</tr>
<tr>
<td>4.4</td>
<td>100</td>
<td>4.1</td>
</tr>
<tr>
<td>4.5</td>
<td>30</td>
<td>4.7</td>
</tr>
<tr>
<td>5.0</td>
<td>30</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>5.0</td>
</tr>
</tbody>
</table>

For loading pump[I] mobile phase B was methanol[,] and mobile phase A was water. For analytical pump[A] mobile phase B was acetonitrile[,] and mobile phase A was 10 mmol/L ammonium acetate buffer[pH 5.0] adjusted by acetic acid[I].
1.0 mg/L [100.0, 50.0, 10.0 μg/L] 

100.0 μg/L [5.0, 1.0, 0.5 μg/L] 

0.22 μm [10 mL] 

-20 °C 

2

2.1

SoilEx RSLC HRH [20 mm] × 2.1 mm [12 ~ 14 μm] 

pH [100%] 80 MPa [0 ~ 14 μm] 

2.3

1.0 ~ 100 μg/L 

Y = 0.99999 0.056 2X - 0.001 0.001 Y = 0.023 1X + 0.002 4Y μg/L mAU 

S/N = 3 RSDs = 0.07% 

2.4

\[ Y = 0.056X + 0.001 \]

\[ Y = 0.023X + 0.002 \]
样经过淋洗、洗脱、氮气吹干后,用

分析系统进行测定,被测物的灵敏度与离线方法处

理

道,虽然进样量只有

解残留物待测,此时富集倍数为

定

率,结果见表

表 2 Recoveries of carbaryl and carbofuran in 3 samples at different spiked levels

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Spiked/ µg/L</th>
<th>Tap water</th>
<th>Pond water</th>
<th>Penstock water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbofuran</td>
<td>1.0</td>
<td>82.0</td>
<td>98.5</td>
<td>99.4</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>99.4</td>
<td>99.4</td>
<td>98.5</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>100.0</td>
<td>99.7</td>
<td>96.1</td>
</tr>
<tr>
<td>Carbaryl</td>
<td>5.0</td>
<td>105.0</td>
<td>95.4</td>
<td>95.2</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>92.6</td>
<td>96.1</td>
<td>98.1</td>
</tr>
</tbody>
</table>

2.5

100 mL 0.22 µm

1.2

3

20 mL 10.0 µg/L

5

2.3%

RSDs 0.9%

n = 3

Table 2 Recoveries of carbaryl and carbofuran in 3 samples at different spiked levels

Fig. 2 Chromatograms of a blank tap water sample and samples spiked with carbaryl and carbofuran

a. tap water
b. tap water spiked with standards at 1 µg/L

c. tap water spiked with standards at 5 µg/L.