Determination of two mouldy compounds in cork by gas chromatography-mass spectrometry

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Abstract: A simple and fast method for the simultaneous determination of two mouldy compounds, 2-H[6]-trichloroanisolole (TCA) and 2-H[6]-tribromoanisolole (TBA), in cork by gas chromatography-mass spectrometry (GC-MS) was established. The analytes were extracted by ultrasonic extraction with methanol and purified then by solid phase extraction using primary secondary amine (PSA) as solid phase. After concentrating the sample was analyzed by GC-MS and quantified by the external standard method. The linear ranges were from 10 µg/L to 10 000 µg/L for TCA and TBA, the correlation coefficients \( r^2 \) of the calibration curves were above 0.99. The recoveries and the relative standard deviations (RSDs) of TCA and TBA in different kinds of corks were investigated. The recoveries ranged from 88.4% to 97.6% with the RSDs between 1.02% and 4.58%. The limits of detection (LODs) were 12 µg/L for TCA and 18 µg/L for TBA and the limits of quantification (LOQs) were 40 µg/L for TCA and 50 µg/L for TBA. The method is suitable for the determination of TCA and TBA in corks.

Key words: gas chromatography-mass spectrometry, GC-MS, 2-H[6]-trichloroanisolole (TCA), 2-H[6]-tribromoanisolole (TBA), cork
1000 mg/L \( \text{TCA} \) \( \text{BPA} \) 4 °C

1.3

5 mm \( \text{OD} \) \( \text{OD} \) \( \text{OD} \) 1 g \( \text{OD} \) \( \text{OD} \)

100 mL \( \text{OD} \) \( \text{OD} \) \( \text{OD} \) 50 mL \( \text{OD} \) \( \text{OD} \)

20 \text{min} \( \text{OD} \) \( \text{OD} \)

5 mL \( \text{OD} \) \( \text{OD} \)

1~2 \text{mL} \( \text{OD} \) \( \text{OD} \) 5 mL \( \text{OD} \)

2 \text{mL} \( \text{OD} \) \( \text{OD} \)

0.45 \text{µm} \( \text{OD} \) \( \text{OD} \)

1.4

30 m \( \times \) 0.25 mm \( \times \) 0.25 µm \( \text{OD} \) \( \text{OD} \) \( \text{OD} \) \( \text{OD} \)

280 °C \( \text{OD} \) \( \text{OD} \) \( \text{OD} \) \( \text{OD} \)

70 °C \( \text{OD} \) \( \text{OD} \) \( \text{OD} \) \( \text{OD} \)

0.5 \text{min} \( \text{OD} \) \( \text{OD} \)

10 °C/min \( \text{OD} \) \( \text{OD} \) \( \text{OD} \) \( \text{OD} \)

200 °C \( \text{OD} \) \( \text{OD} \) \( \text{OD} \) \( \text{OD} \)

2 \text{min} \( \text{OD} \) \( \text{OD} \) \( \text{OD} \) \( \text{OD} \)

15 °C/min \( \text{OD} \) \( \text{OD} \) \( \text{OD} \) \( \text{OD} \)

280 °C \( \text{OD} \) \( \text{OD} \) \( \text{OD} \) \( \text{OD} \)

5 \text{min} \( \text{OD} \) \( \text{OD} \) \( \text{OD} \) \( \text{OD} \)

0.1 \text{mL/min} \( \text{OD} \) \( \text{OD} \) \( \text{OD} \) \( \text{OD} \)

0.05 \text{µL} \( \text{OD} \)

70 eV \( \text{OD} \) \( \text{OD} \) \( \text{OD} \) \( \text{OD} \)

280 °C \( \text{OD} \) \( \text{OD} \) \( \text{OD} \) \( \text{OD} \)

230 °C \( \text{OD} \) \( \text{OD} \) \( \text{OD} \) \( \text{OD} \)

150 °C \( \text{OD} \) \( \text{OD} \) \( \text{OD} \) \( \text{OD} \)

3 \text{min} \( \text{OD} \) \( \text{OD} \) \( \text{OD} \) \( \text{OD} \)

\( \text{SIM} \) \( \text{OD} \) \( \text{OD} \) \( \text{OD} \) \( \text{OD} \)

\( \text{SIM} \) \( \text{OD} \) \( \text{OD} \) \( \text{OD} \) \( \text{OD} \)

1

Table 1 Relative molecular masses \( M_r \) and characteristic ions for TCA and TBA in selected ion monitoring \( \text{SIM} \) mode

<table>
<thead>
<tr>
<th>Analyte</th>
<th>( M_r )</th>
<th>Qualitative ion</th>
<th>Quantitative ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCA</td>
<td>211</td>
<td>210/195/167</td>
<td>195</td>
</tr>
<tr>
<td>TBA</td>
<td>345</td>
<td>344/329/301</td>
<td>344</td>
</tr>
</tbody>
</table>

TCA, 2,4,6-trichloroanisole; TBA, 2,4,6-tribromoanisole.
唐熙,等:气相色谱质谱法测定软木塞中6种霉味物质

剂,丙酮属于强极性的有机溶剂,能溶解蜡、黏结剂等聚合物,导致萃取液浑浊,不利于净化;甲醇及乙醇的萃取液均澄清,但乙醇的沸点较高,浓缩时间长;综合考虑,选择甲醇作为提取溶剂。

图1不同溶剂对软木塞中-bottom-#和-$#的提取效率

图2不同提取方式下软木塞中-bottom-#和-$#的提取效率

提取方法的选择

文献$%对软木塞中的-bottom-#采用微波提取方式。本文选择了-bottom-#、索氏萃取、快速加压溶剂萃取、超声波萃取种方式对提取效果进行了比较,结果见图#。结果表明,虽然索氏萃取是最经典的固液萃取方法,但效果却不令人满意,尤其在低浓度时回收率很低。分析原因,主要是-bottom-#和-bottom-#属于半挥发性化合物,索氏萃取需经历长时间的加热回流,此过程造成了-bottom-#和-bottom-#的损失。快速加压溶剂萃取在高压条件下进行萃取,由于全程密闭,回收率满意;但是软木有很好的吸湿性,在高压条件下经溶剂浸泡后膨胀严重,造成系统压力过高,操作困难。微波萃取和超声波萃取效率相似,二者相比超声波萃取设备简单、操作简便,且提取过程中的小幅升温不会造成目标化合物的损失,经两次提取后回收率可达8%以上。考虑到简单、便利的原则,我们确定采用超声波对软木塞中的-bottom-#和-bottom-#进行萃取,分两次萃取,每次#%。

净化条件的选择

采用固相萃取方式对提取液进行净化。软木等木制品中可馏出物主要有酚类、醇类和一些有机酸。根据杂质类型,研究比较了-bottom-#、硅胶、弗罗里硅藻土、-bottom-#种填料的-bottom-#柱对木制品馏出物的净化效果。实验表明硅胶、-bottom-#、-bottom-#的净化效果都较满意,弗罗里硅藻土的净化效果较差。在空白样品溶液中添加-bottom-#和-bottom-#混合标准工作液分经-bottom-#、硅胶、-bottom-#固相萃取柱处理,考察回收率,结果见表#。

表1空白样品溶液中-bottom-#和-bottom-#经-bottom-#、硅胶、-bottom-#固相萃取柱处理后的回收率

<table>
<thead>
<tr>
<th>针对物</th>
<th>平均回收率（%）</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCA</td>
<td>89.3</td>
</tr>
<tr>
<td>TBA</td>
<td>90.6</td>
</tr>
</tbody>
</table>

考虑到目标物残留在-bottom-#柱上造成损失,在上样后用适量甲醇淋洗-bottom-#柱。考察了不同淋洗体积对回收率的影响,结果见表*。

表2不同甲醇淋洗体积下-bottom-#和-bottom-#的回收率

<table>
<thead>
<tr>
<th>针对物</th>
<th>淋洗体积（mL）</th>
<th>平均回收率（%）</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCA</td>
<td>2</td>
<td>81.3</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>87.6</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>90.6</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>93.1</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>95.3</td>
</tr>
<tr>
<td>TBA</td>
<td>2</td>
<td>81.9</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>93.1</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>95.7</td>
</tr>
</tbody>
</table>

考虑到目标物残留在-bottom-#柱上造成损失,在上样后用适量甲醇淋洗-bottom-#柱。考察了不同淋洗体积对回收率的影响,结果见表*。
2.3 TCA and TBA

TCA and TBA were used for GC-MS/MS and GC-ECD detection. The sensitivity of TCA is high, but TBA has a lower sensitivity.

2.4 Methods

2.4.1 Sample Treatment

Sample treatment methods were optimized using blank matrices. Sample recovery was determined using the method described in Section 2.4.2.

2.4.2 Analysis of target compounds

The purity level of the target compound was determined by comparing the peak area of the target compound to the peak area of the internal standard.

Table 4 Linear relationships, limits of detection (LODs) and limits of quantification (LOQs) for TCA and TBA

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Linear range μg/L</th>
<th>Calibration equation</th>
<th>Correlation coefficient $r^2$</th>
<th>LOD μg/L</th>
<th>LOQ μg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCA</td>
<td>10 – 100</td>
<td>$Y = 66651X - 42287$</td>
<td>0.9978</td>
<td>12</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>100 – 1000</td>
<td>$Y = 64416X - 891.51$</td>
<td>0.9999</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1000 – 10000</td>
<td>$Y = 62.98X - 78.668$</td>
<td>0.9980</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TBA</td>
<td>10 – 100</td>
<td>$Y = 30175X - 26165$</td>
<td>0.9928</td>
<td>18</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>100 – 1000</td>
<td>$Y = 30630X - 2518.1$</td>
<td>0.9996</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1000 – 10000</td>
<td>$Y = 31.02X - 245.3$</td>
<td>0.9943</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$Y$ peak area, $X$ mass concentration in μg/L.

2.5 Results

2.5.1 TCA and TBA

The recovery of TCA and TBA was determined using the method described in Section 2.5.2.

Table 5 Recoveries and relative standard deviations (RSD) of TCA and TBA

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Added μg/kg</th>
<th>Recovery/%</th>
<th>RSD/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCA</td>
<td>50</td>
<td>88.4</td>
<td>3.18</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>96.6</td>
<td>1.28</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>97.6</td>
<td>1.17</td>
</tr>
<tr>
<td>TBA</td>
<td>50</td>
<td>89.4</td>
<td>4.58</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>96.3</td>
<td>1.76</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>97.1</td>
<td>1.02</td>
</tr>
</tbody>
</table>

3 Conclusions

The proposed method is quick, easy, and suitable for the detection of TCA and TBA in softwood samples.