A simple, fast and accurate method by GC-µECD to determine the relevant impurity carbon tetrachloride in captan technical materials and formulations

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Introduction

- Captan is a dicarboximide fungicide used on fruits and other crops. This active substance is registered under Regulation (EC) No 1107/2009 with a minimum purity of 910 g/kg and 3 relevant impurities are specified (Regulation EU No 540/2011):
  - Perchloromethylmercaptan: maximum 5 g/kg
  - Folpet: maximum 10 g/kg
  - Carbon tetrachloride: maximum 0.1 g/kg

- Carbon tetrachloride (CCl₄) has a high acute oral, dermal and inhalation toxicity and causes damages to organs through prolonged or repeated exposure

Analytical method

- For TC and WG: sample weighing containing 30 mg captan dissolved with 25 mL toluene by ultrasonication
- For SC: sample weighing containing 250 mg captan dissolved with 25 mL methanol by ultrasonication, 10 times dilution in toluene
- Determination by GC-µECD with external standard calibration

Chromatographic conditions

- Column: DB-WAX (100% polyethylene glycol), 30 m x 0.25 mm i.d., 1 µm film
- Carrier gas: Helium 1.5 mL/min
- Inlet temperature: 250°C, Split ratio: 15:1, Injection volume: 1 µL
- Oven temperature: 50°C for 5.5 min, 40°C/min to 250°C, 250°C for 5 min
- Detector temperature: 260°C, Make-up gas: Argon / Methane (95/5) 60 mL/min

Validation results

- Specificity and non-analyte interference
  RT difference between sample and calibration solutions < 1%
  No interference affecting the peak of CCl₄
  Peak of CCl₄ free from co-eluant

- Accuracy (standard addition on WG n = 3)
<table>
<thead>
<tr>
<th>Fortification level</th>
<th>Marginal recovery</th>
<th>RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.06 g/kg</td>
<td>78.4%</td>
<td>2.72%</td>
</tr>
<tr>
<td>0.08 g/kg</td>
<td>74.9%</td>
<td>2.21%</td>
</tr>
</tbody>
</table>

Analysis of samples

- 500 samples of captan TC, WG and SC from the EU market were analysed during December 2019 - July 2022
- The accuracy and reproducibility of the method was confirmed by analysing QC samples of captan WG concurrently with the analysis of unknown samples

<table>
<thead>
<tr>
<th>Captan</th>
<th>No. of samples analysed</th>
<th>No. of compliant samples</th>
<th>No. of samples out of specification</th>
<th>% of non-compliance</th>
</tr>
</thead>
<tbody>
<tr>
<td>TC</td>
<td>117</td>
<td>97</td>
<td>20</td>
<td>17.1%</td>
</tr>
<tr>
<td>WG</td>
<td>349</td>
<td>327</td>
<td>22</td>
<td>6.3%</td>
</tr>
<tr>
<td>SC</td>
<td>34</td>
<td>22</td>
<td>12</td>
<td>35.3%</td>
</tr>
<tr>
<td>Total</td>
<td>500</td>
<td>446</td>
<td>54</td>
<td>10.8%</td>
</tr>
</tbody>
</table>

Conclusions

- This method by GC-µECD after toluene or methanol extraction for determination of CCl₄ in captan formulations is simple, fast and accurate
- Method validation results complies with the requirements of the EU document SANCO/3030/99 rev.5 for all validation parameters

Captan

Gas chromatography with ⁶³Ni micro electron capture detection (GC-µECD)