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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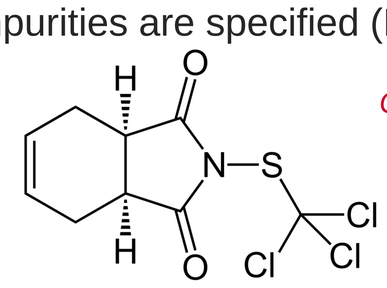
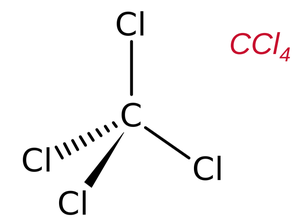
Introduction

- **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



Captan



CCl_4

- **Carbon tetrachloride** (CCl_4) has a high acute oral, dermal and inhalation toxicity and causes damages to organs through prolonged or repeated exposure

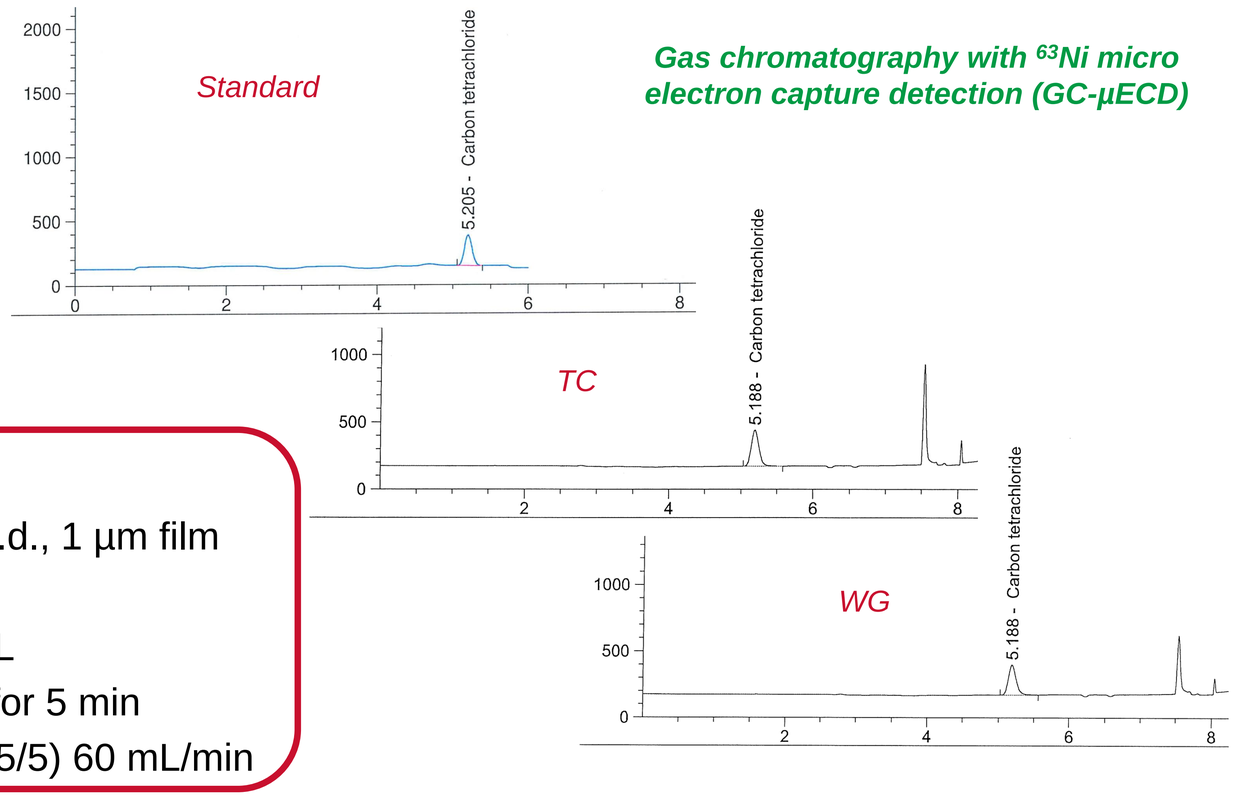
Analytical method

- 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

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

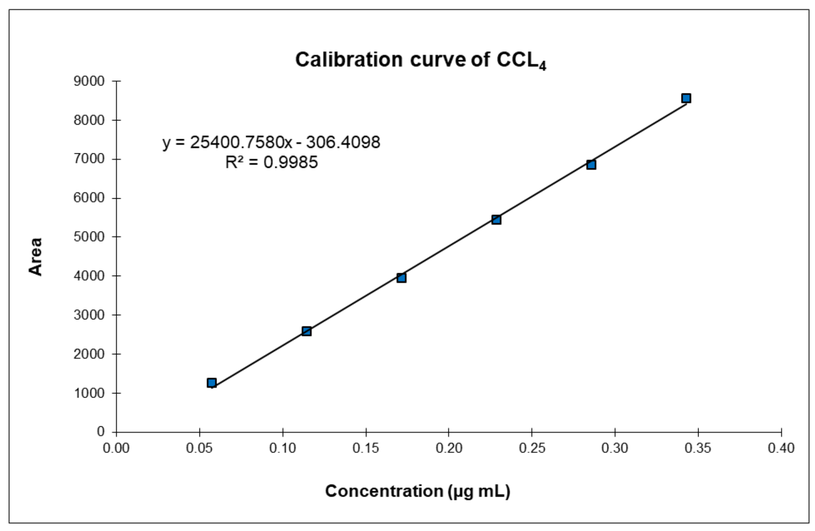


Validation results

- **Specificity and non-analyte interference**
  RT difference between sample and calibration solutions < 1%
  No interference affecting the peak of CCl_4
  Peak of CCl_4 free from co-eluant
- **Accuracy** (standard addition on WG n = 3)

Fortification level	Marginal recovery	RSD
0.06 g/kg	78.4%	2.72%
0.08 g/kg	74.9%	2.21%

- **Linearity**
- **Range**
  0.06 - 0.36 g CCl_4 / kg captan
- **LOQ**
  0.06 g/kg



- **Interlaboratory comparison**
  4 samples of captan WG were analysed by the WFSR (Wageningen Food Safety Research, The Netherlands) using a toluene / GC-MS method and by the CRA-W using this toluene / GC-µECD method and **results of analysis are very similar**

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

Captan	No. of samples analysed	No. of compliant samples	No. of samples out of specification	% of non-compliance
TC	117	97	20	17.1%
WG	349	327	22	6.3%
SC	34	22	12	35.3%
Total	**500**	**446**	**54**	**10.8%**

Conclusions

- This method by **GC-µECD** after toluene or methanol extraction for determination of **CCl_4** 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

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