

Carbon Tetrachloride in Folpet Formulations by Headspace GC-MS

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Introduction

Folpet is a widely used protective fungicide in Switzerland.

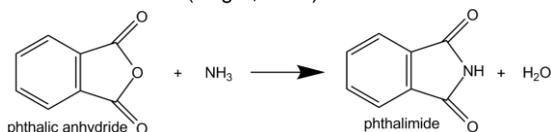
Approx. 84 products with folpet as single a.i. formulation or in combination with systemic fungicides are registered and on the market.

In a pesticide quality control campaign in 2011 focused on folpet products, among other parameters, the two relevant impurities carbon tetrachloride (CCl₄) and perchloro methyl mercaptan (PCMM) were determined.

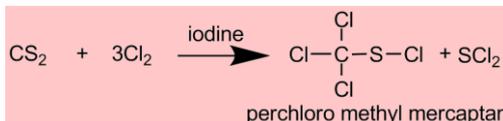
CCl₄ as sideproduct in the synthesis of folpet

Step 1

(Unger, 1996)



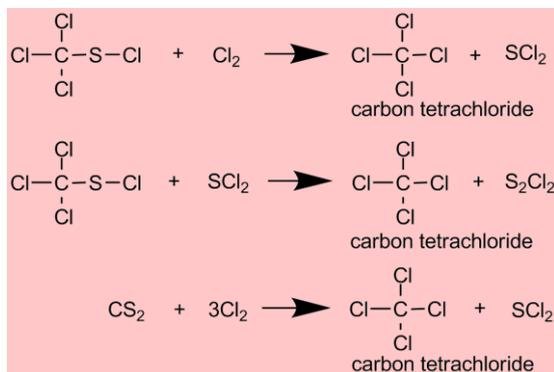
Step 2



Step 3



Side reactions of step 2 (www.freepatentsonline.com)



Relevance of carbon tetrachloride

IARC (International Agency for Research on Cancer):

- carbon tetrachloride induces hepatic cell proliferation and DNA synthesis
- carbon tetrachloride has a mutagenic effect and induces aneuploidy in several in-vitro systems
- carbon tetrachloride is possibly carcinogenic to humans (Group 2B)

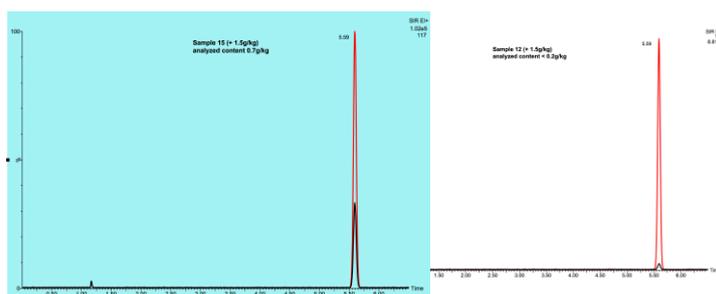
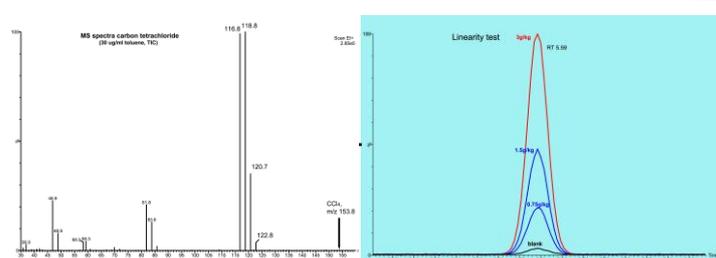
In conclusion the EU considers CCl₄ as relevant impurity in folpet and captan technical (SANCO/10032/2006).

References

- IARC, International Agency for Research on Cancer, monograph 71, p. 422, www.iarc.fr
- Thomas A. Unger, Pesticide Synthesis Handbook, Noyes Publications 1996
- www.freepatentsonline.com/3968155.html
- folpet, SANCO/10032/2006 – rev. 5, 03. July 2006

Method description

- headspace GC-MS, SIM m/z 117 with standard addition
- column: Restek Rtx-624 (6% cyanopropylphenyl, 94% dimethyl polysiloxane), 30m x 0.32mm x 1.8 µm film th.
- carrier gas: He 20 kPa (constant pressure)
- incubator 50°C, 2 min, 500 rpm
- injection vol.: 500 µl, injector 200°C, syringe temp. 50°C
- split ratio 20:1
- oven: 40°C 2 min, 5°C/min to 70°C, 30°C/min to 130°C
- filament off 6.5 min (toluene peak)
- sample preparation: 100mg ai, add 1ml water, 2 min sonication, add 10ml toluene, shake well, pipet 100 µl off organic layer in a head-space vial and close immediately, analyse



Results:

- 20 formulations (WP, WG, SC) were analyzed
- residues detected ranged from <0.2 – 0.7g/kg folpet
- EU specification max. 4 g/kg folpet

Validation:

- linearity evaluated with matrix free and WG, SC samples (concentration range: 0.0, 0.75, 1.5, 3.0 g/kg): correlation coefficient r: 0.997 – 0.999
- repeatability: 6 repetitions, mean 0.53g/kg ± 0.16 (95% confidence interval)

Conclusions folpet

- approx. 84 formulations are registered and sold in Switzerland
- EU specification: 2 relevant impurities are identified – perchloro methyl mercaptan and carbon tetrachloride
- a headspace GC-MS method for determination carbon tetrachloride was developed and validated
- in all 20 formulations analyzed, the CCl₄ content found was < 4.0g/kg a.i. and met the EU specification
- S₂Cl₂ and SCl₂ are readily hydrolyzed and not expected to occur in folpet TC and formulations

