The use of a deactivated (baffled) PTV injector liner and GCMS/MS method for the quantitative determination of Captan, Folpet and their metabolites in ethyl acetate extracts of fruit samples

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Introduction

SASA (Science and Advice for Scottish Agriculture) is one of the United Kingdom's (UK) official laboratories and we participate, on behalf of the Scottish Government, in the annual UK and EU statutory surveillance programmes that monitor various UK and imported food & drink for residues of pesticides, their metabolites and other degradation products. It is mandatory for official laboratories to analyse all pesticides listed in the EU multiannual control programme and to also participate in UK and EU proficiency testing schemes.

SASA routinely screen for captan and folpet and over 100 other pesticides using an ethyl acetate multi-residue extraction followed by GCMS/MS analysis. These pesticides are notoriously challenging to analyse since they can degrade to their metabolites tetrahydrophthalimide (THPI) and phthalimide particularly during GC injection and other processes. However, use of a deactivated baffled PTV injection liner minimises degradation.

The EU pesticide residue definitions for captan and folpet changed in 2016 to include their metabolites tetrahydrophthalimide (THPI) and phthalimide, respectively. Consequently, THPI and phthalimide were included in the SASA GCMS/MS multi-residue method.

Experimental

Sample preparation

10g of cryogenically milled fruit and vegetable samples were extracted by homogenisation with ethyl acetate (matrix concentration ≡ 1g ml $^{-1}$). Gel Permeation Chromatography clean-up was employed.

Calibration standards were prepared in appropriate (organic) fruit or vegetable matrix.

Set-up for the TSQ 8000 Evo Mass Spectrometer and Trace 1310 Gas Chromatograph with PTV injector

Table 1. TSQ 8000 Evo GC/MSMS Parameters.

Injection liner	Restek Topaz Baffled PTV 2mm x 2.75mm x 120mm		
Injection mode	Splitless		
Injection volume	2µL		
Initial Inlet temperature	50°C		
Column	Thermo Scientific TG-SILMS 30m x 0.25mm x 0.25µm		
Carrier gas	He, constant flow 1.2mL/min		
MS transfer line temperature	300°C		
Ion source temperature	250°C		
Ionisation Mode	EI		
Oven programme (30min method)	Rate	Temperature/°C	Time/min
		50	2
	25 °C /min	200	0
	10 °C /min	250	0
	50 °C /min	320	16

Table 2. MRM Transitions.

Compound	Quan Peak (m/z)	Collision Energy (ev)	Qual Ion 1 (m/z)	Collision Energy (ev)	Qual Ion 2 (m/z)	Collision Energy (ev)
Captan	149>70	20	149>78.8	14	149>105	6
THPI	151.1>80.1	6	151.1>79.1	16	151.1>122.1	8
Folpet	259.9>130.1	14	104>76	10	130>102	12
Phthalimide	147.1>103.1	6	147.1>76.1	24	104.1>76.1	10

Residues of captan and folpet are quantified using multi-level matrix-matched standards containing over 100 pesticides. Transitions for THPI and phthalimide are acquired to monitor potential degradation of captan and folpet. A separate single level standard containing THPI and phthalimide is also run to screen for potential residues of these metabolites. If detected, residues are quantified using multi-level THPI and phthalimide standards.

Results

Figure 1.

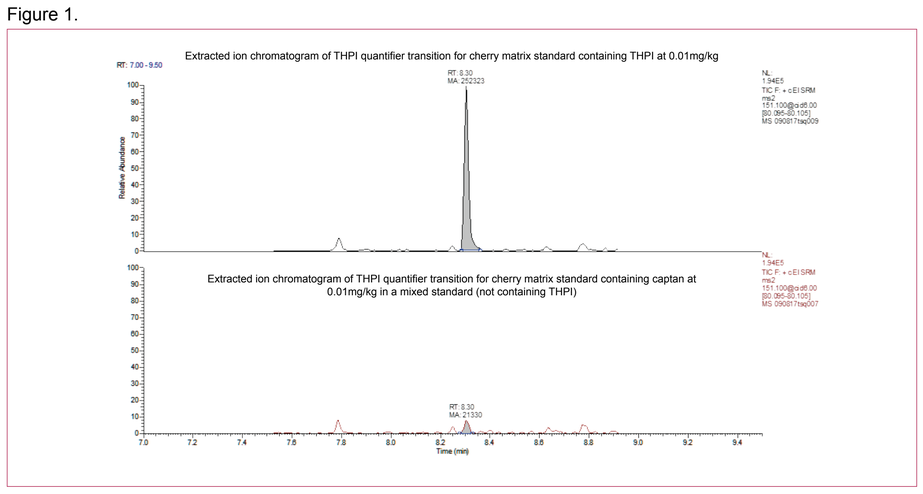

Figure 2.

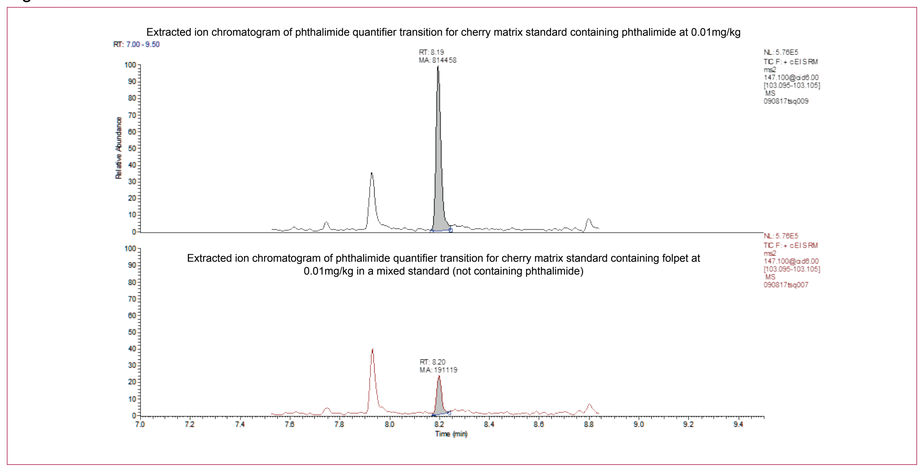

Table 3. Summary of 2017 Cherry Validation data.

	Reporting level (RL)/mg/kg^{-1}	Fortification level =RL (n=6)		Fortification level =2RL (n=6)	
		mean recovery	% RSD	mean recovery	% RSD
Phthalimide	0.01	94	5	86	6
THPI	0.01	89	3	85	5
	Reporting level (RL)/mg/kg^{-1}	Fortification level =RL (n=5)		Fortification level =2RL (n=5)	
		mean recovery	% RSD	mean recovery	% RSD
Folpet	0.01	89	6	83	4
Captan	0.01	84	6	79	11

Table 4. Results from a 2017 Cherry Sample.

Compound	Residues mg/kg^{-1}
Captan	0.056
THPI	0.029

Table 5. Preliminary results from 2017 European Union Proficiency test on strawberry homogenate (EUPTSRM12).

Compound	Reported Value (mg/kg^{-1})	Assigned value (mg/kg^{-1})	Z-Score
Captan	0.0723	0.085	-0.6
Folpet	0.295	0.334	-0.5
Phthalimide	0.4545	0.446	0.1
THPI	0.0874	0.11	-0.8

Conclusion

This method has demonstrated minimal degradation of Captan and Folpet; the approach taken quantifies the metabolites using separate calibration standards. The quantitative determination of Captan, Folpet, THPI and Phthalimide has been successfully validated in cauliflower, cherries, cucumber, kale, kiwi, onion and parsnip. The method has been routinely used to quantify residues of Captan and THPI in cherry and to achieve good z-scores for Captan, Folpet, THPI and Phthalimide in a recent European Union proficiency test on strawberry homogenate.

Designed by Sylvia Breslin & printed in-house by SASA Digital Imaging & Presentation.

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