A complementary acetonitrile extraction procedure for multi-residue pesticide screening without solvent evaporation, solvent exchange or extract clean-up.

SASA
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Introduction

Science and Advice for Scottish Agriculture (SASA) participates in the annual UK and coordinated EU surveillance programmes that monitor various UK and imported food & drink for the presence of pesticide residues and their metabolites on behalf of the Scottish Government. Monitoring is essential in order to support enforcement of legislation, ensure good agricultural practice and to assess the pesticide load in our diet.

Analytical methodologies employed in the determination of multiple pesticide residues in foodstuffs must be capable of quantifying very low levels of incurred residues and confirming the identity and magnitude of these residues in compliance with rigorous Analytical Quality Control (AQC) guidelines. We are also obliged to participate in relevant EU and FAPAS proficiency tests.

SASA established a simple acetonitrile extraction single residue method (SRM) for the analysis of thiophanate-methyl with minimal conversion to carbendazim. We have successfully incorporated other pesticides that were problematic when subject to our principal ethyl acetate extraction e.g. carbosulfan, diafenthiuron, chlormequat, mepiquat and propamocarb.

Experimental

Extraction
Pesticides are extracted from 25g of cryomilled fruit or vegetable samples by homogenisation with acetonitrile. (The matrix concentration is equivalent to 0.25g ml^{-1}). Crude extracts are then filtered and analysed using liquid chromatography - mass spectrometric detection with electrospray ionisation and multiple reaction monitoring (MRM) or accurate mass measurement (TOF).

Acetonitrile extracts are injected with a methanol / water gradient elution program yielding acceptable chromatographic performance. No solvent evaporation, solvent exchange or extract clean-up is required, only the addition of internal standards (carbendazim-d4, methomyl-d3, pendimethalin-d5).

Ultra Performance Liquid Chromatography – UPLC
UPLC was performed using a Waters ACQUITY Ultra-Performance LC system with H2O/MeOH/5mM ammonium acetate gradient elution, 0.48ml/min, BEH C18 Column, Cycle time 6.5mins.

Mass Spectrometry – MSMS
Electrospray ionisation was achieved using a Quattro Premier-XE tandem mass spectrometer (Waters Corporation) operated in +ve ion polarity during multiple reaction monitoring (MRM) acquisition in accordance with time-scheduled sequencing.

Mass Spectrometry – TOF MS
An orthogonal acceleration time-of-flight mass spectrometer with an electrospray ionisation interface was used (XEVO QTOF MS, Waters Corporation). Data acquisition was performed using +ve ionisation mode over a mass range of m/z 50 to 1000 at a nominal instrument resolution of 9500 (FWHM). Peak responses were derived from extracted ion chromatograms of selected compounds (20milli-m/z extraction mass window).

Results

Validation was performed in accordance with SANCO /10684/2009 and latterly SANCO/12495/2011 guidelines. TOF validation only carried out when required for confirmation.

Acetonitrile 2010 Validation Data Summary for Leeks Using Premier (MRM)

	Ave Rec (%)	%RSD	Ave Rec (%)	%RSD
Pesticide	0.02mg/kg	0.02mg/kg	0.01mg/kg	0.01mg/kg
carbendazim	74	6	76	6
fenamidone	76	5	73	6
propamocarb	67	9	80	6
thiophanate-methyl	99	11	103	15
triazamate ester	74	2	81	9

*n = 6

Acetonitrile 2010 Validation Data Summary for Carbendazim in Leeks Using Xevo (TOF)

	Ave Rec (%)	%RSD	Ave Rec (%)	%RSD
Pesticide	0.02mg/kg	0.02mg/kg	0.01mg/kg	0.01mg/kg
carbendazim	73	6	82	10

*n = 6

Proficiency Test Results for Leeks

			MRM	TOF	Assigned
	Commodity	Pesticide	mg/kg	mg/kg	Value
EUPT FV12	Leek	Carbendazim	0.307	0.323	0.320
EUPT FV12	Leek	Thiophanate-methyl	<0.01	N/A	not added
FAPAS 19-108	Leek	Carbendazim	0.157	0.157	0.177
FAPAS 19-108	Leek	Thiophanate-methyl	<0.01	N/A	not added

Acetonitrile 2012 Validation Data Summary for Green Beans Using Premier (MRM)

	Ave Rec (%)	%RSD	Ave Rec (%)	%RSD
Pesticide	0.02mg/kg	0.02mg/kg	0.01mg/kg	0.01mg/kg
carbendazim	77	5	81	7
carbosulfan	85	2	90	5
propamocarb	81	3	100	2
thiophanate-methyl	106	6	97	1
triazamate ester	81	6	83	9
chlormequat	71	10	94	9
mepiquat	70	5	84	6
formetanate hydrochloride	75	6	71	8
DMPF	71	5	61	17
DMF	85	9	83	7
clethodim	98	15	104	20
metolachlor	90	6	89	13
diafenthiuron	80	5	70	10

*n = 6

Acetonitrile 2012 Validation Data Summary for Propamocarb Green Beans Using Xevo (TOF)

	Ave Rec (%)	%RSD	Ave Rec (%)	%RSD
Pesticide	0.02mg/kg	0.02mg/kg	0.01mg/kg	0.01mg/kg
propamocarb	96	6	78	3

*n = 6

Propamocarb Residue Summary for Green Beans Survey (2012)

		MRM	TOF
Sample	Pesticide	mg/kg	mg/kg
0205	Propamocarb	0.011	0.014
4517	Propamocarb	0.024	0.020
4747	Propamocarb	0.019	0.020
2954	Propamocarb	0.023	0.018

Conclusion

The method has been validated for a range of commodities including Broccoli, Green Beans, Cherry, Strawberry, Leek, Cucumber, and Spinach. We are now able to perform ethyl acetate and acetonitrile validation exercises simultaneously for new and obligatory analytes and also continually extend our pesticide inventories.

The Scottish Government