Simple acetonitrile extraction of Quaternary Ammonium Compounds (QAC) from fruit and vegetables and quantitative analysis by UPLC-MSMS and UPLC-QTOF-MS

Pesticides & Wildlife

Authors:
Melton LM
Viezens KJ
Giela A
Taylor MJ
Reid KB

SASA, Roddinglaw Road
Edinburgh, EH12 9FJ
Scotland, U.K.

T: +44 (0) 131 244 8982
F: +44 (0) 131 244 8940

Email: laura.melton@sasa.gsi.gov.uk
www.sasa.gov.uk

Introduction

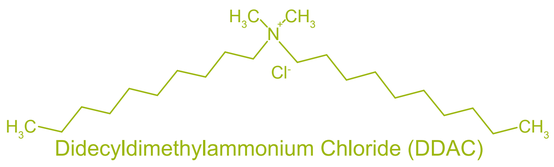
Benzalkonium chloride (BAC) and didecyl dimethyl ammonium chloride (DDAC) are quaternary ammonium compounds (QAC) used for both disinfectant and plant protection purposes. Recently in Europe unexpected residues of QAC above the current statutory maximum residue level (MRL) of 0.01 mg/kg have been found in foodstuffs. A higher non-statutory MRL of 0.5 mg/kg has been assessed for potential toxicological effects and judged to be safe. This higher MRL of 0.5 mg/kg has been adopted to enable the marketing of produce with residues of QAC above the statutory MRL. European countries are required to carry out monitoring to gather information on residues of BAC and DDAC in food and feed to allow a substantive statutory MRL to be set.

SASA (official lab) participates in the annual UK and coordinated EU pesticide residues in food surveillance programmes on behalf of the Scottish Government.

Since the introduction of a simple acetonitrile extraction single residue method for the analysis of thiophanate methyl with minimal conversion to carbendazim, we have steadily incorporated numerous other pesticides that were problematic with our principal ethyl acetate extraction e.g. chlormequat, mepiquat and propamocarb. It was relatively straightforward to incorporate BAC with chain lengths of n = 10, 12, 14 and 16 and DDAC into the acetonitrile multi-residue method.

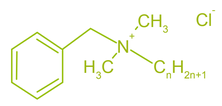
Acetonitrile extracts are injected with a methanol/water gradient elution program yielding acceptable chromatographic performance. No solvent evaporation, solvent exchange or extract clean-up is required, only the addition of internal standards.

A common acetonitrile extract is routinely analysed both by UPLC-MSMS and UPLC-QTOF-MS against separate screen and confirmation standards in order to provide simultaneous quantitative results.



Didecyldimethylammonium Chloride (DDAC)

Benzalkonium Chloride (BAC)



n = 10,12,14,16

Experimental

Extraction

QACs are extracted from 25g of cryomilled fruit or vegetable samples by homogenisation with acetonitrile. (The matrix concentration is equivalent to 0.25 g ml^{-1}). Samples are then filtered and internal standards added prior to analysis by UPLC-MSMS and UPLC-QTOF-MS.

Ultra Performance Liquid Chromatography

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, 3 µl injection, Cycle time 7 mins.

Mass Spectrometry – MSMS (screen and confirmation)

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.

Table 1. MRM transitions

QAC	Precursor ion (screen)	Product ion (screen)	Cone Voltage (V)	Collision Energy (eV)	Precursor ion (conf)	Product ion (conf)	Cone Voltage (V)	Collision Energy (eV)
BAC 10	276.3	184.0	40	20	276.3	91.0	40	25
BAC 12	304.3	212.3	40	20	304.3	91.0	40	25
BAC 14	332.3	240.3	40	25	332.3	91.0	40	30
BAC 16	360.3	268.3	40	25	360.3	91.0	40	30
DDAC	326.3	186.0	40	30	326.3	41.0	40	40

Mass Spectrometry – TOF MS (additional confirmation)

An orthogonal acceleration time-of-flight mass spectrometer with an electrospray ionisation interface was used (XEVO QTOF MS, Waters Corporation). Data acquisition 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-Da extracted mass window).

Results

Table 2. Summary of 2013 Leek Validation data

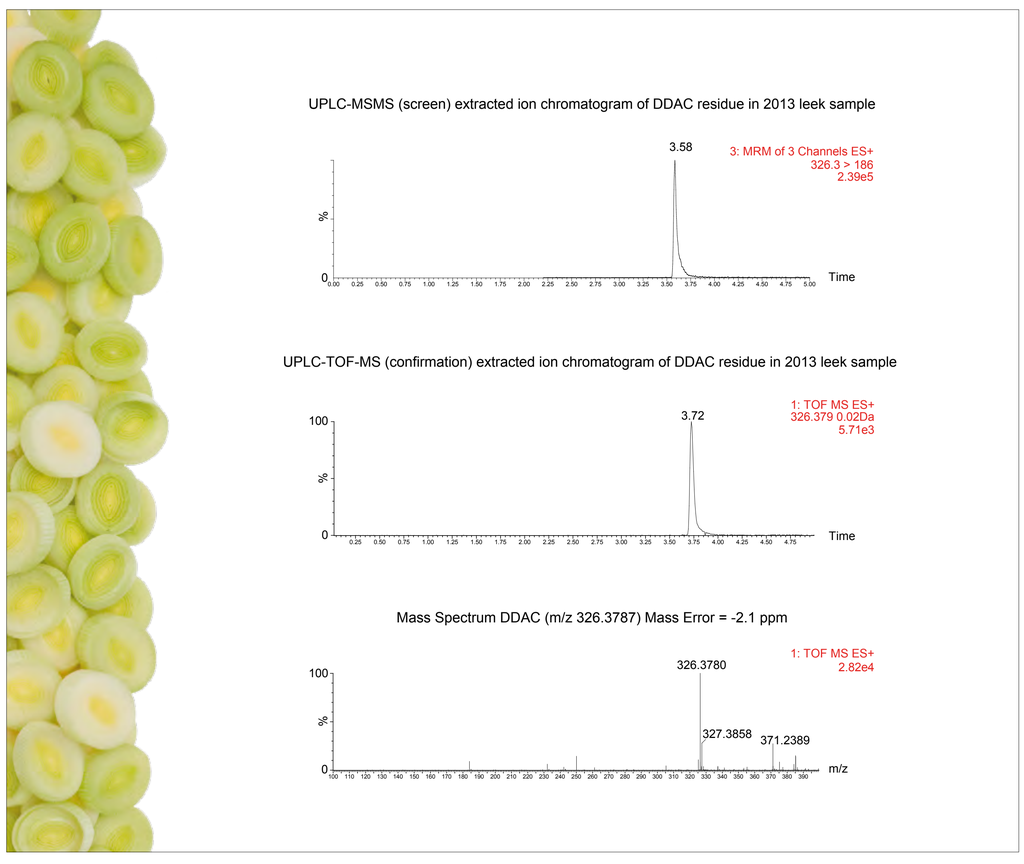
QAC	Reporting Level (RL) / $mgkg^{-1}$	Fortification level = RL (n=6)		Fortification level = 2RL (n=6)	
		Mean recovery	%RSD	Mean recovery	%RSD
BAC (sum)	0.1	81	12	87	16
DDAC	0.01	73	8	77	6

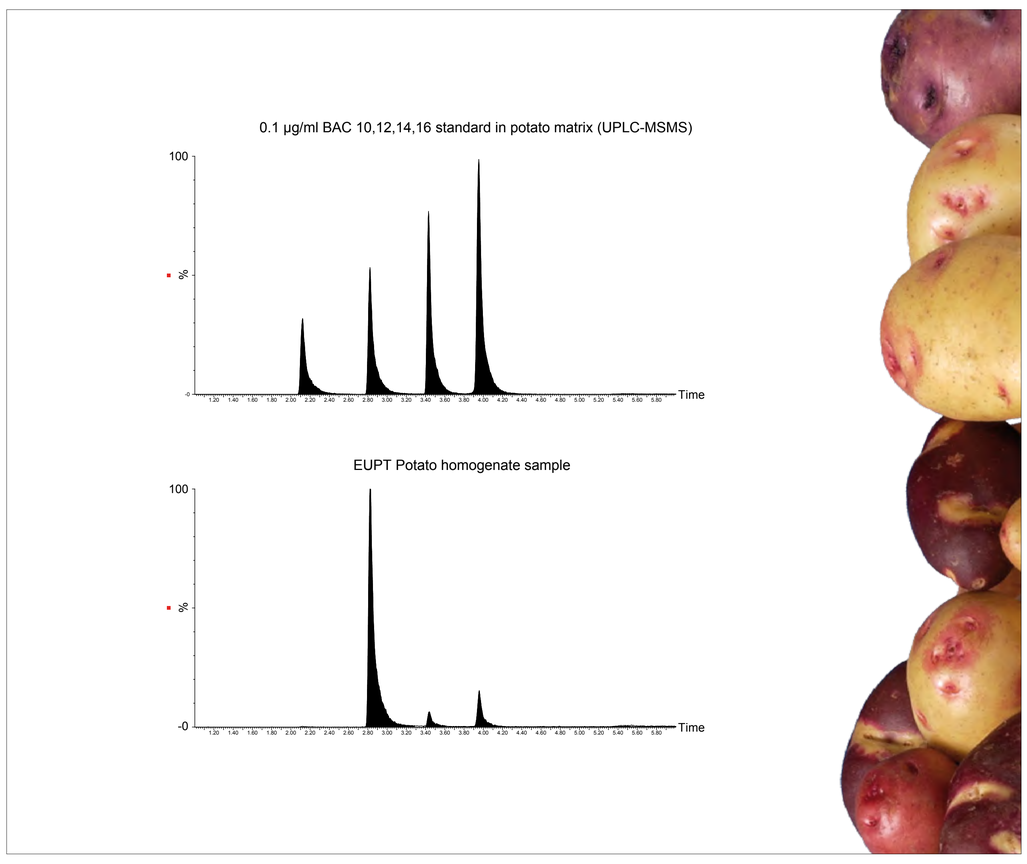
Table 3. Results from 2013 Leek Sample

	MSMS Screen Result (326.3>186.0)	QTOF Confirmation Result (326.3787)	Mean Result
DDAC in 2013 Leek Sample	0.0210 $mgkg^{-1}$	0.0197 $mgkg^{-1}$	0.020 $mgkg^{-1}$

Table 4. Preliminary Results from 2013 European Union Proficiency Test on Potato Homogenate (EUPT SRM8)

QAC	Reported Value ($mgkg^{-1}$)	Assigned Value ($mgkg^{-1}$)	z-score
BAC 10	Detected below RL	0	-
BAC 12	0.413	0.568	-1.09
BAC 14	Detected below RL	0	-
BAC 16	Detected below RL	0	-
DDAC	0.364	0.380	-0.17





Conclusion

The quantitative determination of BAC and DDAC has been successfully validated in aubergine, cherries, green beans, leeks, peas and strawberries. The method has since been used to quantify residues of DDAC in leek and to achieve good z-scores for BAC and DDAC in a recent European Union proficiency test on potato homogenate.