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Ultra-performance liquid chromatography for the determination of pesticide residues in foods by tandem quadrupole mass spectrometry with polarity switching

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Abstract

An ultra-performance liquid chromatographic (UPLC) electrospray ionisation tandem quadrupole mass spectrometric method has been developed for the determination of 52 pesticides in cereal-based baby foods, oranges and potatoes. The fast polarity switching capability of the mass spectrometer used enabled the determination of 44 of the compounds in the positive ionisation mode and 8 of the compounds in the negative ionisation mode in a single run. Prior to analysis, co-extractives were removed from acetonitrile extracts using dispersive solid-phase extraction with primary secondary amine (50 mg). The UPLC method separates all of the pesticides, resolves structural isomers (e.g. butocarboxim sulfoxide and aldicarb sulfoxide) and has a short (7 min) cycle time. Extracts spiked with pesticides at 0.10 and 0.01 mg kg^{-1} yielded average recoveries in the range of 66–124% with relative standard deviations less than 19% for the majority of the analytes.

Keywords: Ultra-performance liquid chromatography; Tandem mass spectrometry; Polarity switching; Pesticide residues

1. Introduction

Pesticide residue analysts are under ever increasing pressure to: expand the range of pesticides which can be monitored in a single analysis; detect analytes at lower levels and with greater precision; increase confidence in the validity of residue data; reduce analysis turnaround times and reduce usage of hazardous solvents while maintaining or reducing costs. In order to meet these demanding requirements the scope, limits of detection and quantification, efficiency and speed of multi-residue methods of analysis must be improved.

The EU residue monitoring programme 2005–2007 establishes the need to monitor 55 pesticides in various foods including potatoes, oranges and cereal-based baby foods [1]. Twenty-one of the pesticides are amenable to acetonitrile extraction and multi-residue analysis by liquid chromatography mass spectrometry. The majority of pesticides in this sub-group produce positive ions whereas fludioxonil produces a negative ion. Thus, two separate analyses are normally required, one in positive-ion mode and the other in negative-ion mode. Consequently, compounds that form negative ions are often excluded from monitoring programmes. Ideally, species of both polarities should be determined in a single analysis via polarity switching.

Polarity switching has previously been employed in the determination of ten pesticides in a single run using selected ion monitoring [2]. That study involved a single switch in the middle of the run, all of the compounds that form positive ions having eluted in the first part of the run and those that form negative ions eluting later. Subsequently, polarity switching liquid chromatography tandem quadrupole mass spectrometry (LC–MS/MS) has found use in biological applications [3,4], but has not been utilised further in pesticide residue analysis in food.

Ultra-performance liquid chromatography (UPLC), using small particles (1.7 μm) in short columns and high linear velocities (accompanied by maximum back pressures up to 15,000 psi) has been shown to give superior chromatographic resolution, reduce analysis time and increase response [5]. The

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low degree of band broadening in UPLC also benefits mass spectrometric detection, concentrating the analyte at the peak centre and thereby increasing response. Thus, UPLC coupled to mass spectrometry (MS) offers improvements in performance for quantitative analysis over existing high performance liquid chromatography–tandem MS (HPLC–MS/MS) methodologies [3,6–8]. Of these applications for the determination of pesticides using UPLC–MS/MS none have reported the use of polarity switching.

The aim of this study was to evaluate the potential of UPLC–MS/MS with fast polarity switching to improve the resolution and speed of analysis for multi-residue pesticide analysis in food. Relevant transformation products (nine sulfones and sulfoxides derivatives) of the 21 pesticides included in the EU residue monitoring programme and structural isomers (butocarboxim sulfoxide and aldicarb sulfoxide) were also included for a complete study. An extra seven pesticides that respond in the negative-ion mode were added to fully assess the capabilities of a multi-residue method with polarity switching. An additional fifteen pesticides considered relevant to potatoes and oranges for the UK monitoring programme were included in order to assess the potential for the analysis of a large and varied mixture of pesticides.

2. Experimental

2.1. Reagents, standards and samples

Pesticide reference standards (purity > 98.0%) were purchased from Qm_x (Thaxted, UK) and LGC Promochem (Teddington, UK). Working standard mixtures, containing 1 μg ml^{-1} of each compound, were prepared in acetonitrile for use as spiking solutions. Acetonitrile (HPLC fluorescence grade), methanol (HPLC fluorescence grade), acetic acid and sodium acetate were purchased from Fisher Scientific UK (Loughborough, UK). Anhydrous magnesium sulfate (analytical reagent grade) was purchased from York Glassware (York, UK). Polyethylene centrifuge tubes containing pre-weighed quantities of anhydrous magnesium sulphate (150 mg) and of bondesil-primary secondary amine (50 mg) were purchased from United Chemical Technologies (Bristol, UK).

2.2. Apparatus

UPLC analyses were performed using a Waters Acquity Ultra-Performance LC system (Waters, Milford MA, US). Separation was performed using an Acquity UPLC BEH C_{18} column (50 mm × 2.1 mm, I.D., 1.7 μm particle size, Waters, Milford MA, US), maintained at 40 °C, with a mobile phase flow rate of 0.6 ml min^{-1}. The Acquity system operating pressure was 6500 psi at initial gradient conditions. The mobile phase contained water (A) and methanol (B) both with 17.5 mmol l^{-1} acetic acid. Gradient elution was employed, starting at 10% B and rising linearly to 100% B over 4 min. The composition was held at 100% B for 1 min before being returned to the initial conditions, followed by re-equilibration for 2 min, giving a total cycle time 7 min. The injection volume was 20 μl.

Determination was performed using a Waters Quattro Premier XE tandem quadrupole mass spectrometer (Waters). The instrument was set to collect data in multiple reaction monitoring (MRM) mode using electrospray ionisation (ESI), switching between positive and negative-ion mode during the run. The inter-scan delay for the polarity switching was 20 ms and the inter-channel delay was 5 ms. The ionisation source parameters were: capillary voltage 1.0 kV; sample cone voltage (Table 1); source temperature 120 °C; and desolvation gas temperature 400 °C at a flow rate of 1.3×10^4 ml min^{-1} (N_2). MRM conditions were optimised for each pesticide during infusion. Data acquisition and processing were performed using MassLynx 4.1 with TargetLynx.

2.3. Samples

Potato, orange and commercially available ready-to-eat cereal-based baby food samples (all labelled as organic) were used as blanks and for the preparation of fortified samples and matrix-matched calibration standards for validation experiments. Three potato samples containing incurred residues of aldicarb were used for testing the validated method.

2.4. Extraction procedure and analysis

Sub-samples (10 g) were weighed in polypropylene centrifuge tubes (40 ml) and appropriate volumes of standard solution were added to give spiking concentrations of 0.1 and 0.01 mg kg^{-1}. Acetonitrile:acetic acid (99:1, 10 ml), anhydrous magnesium sulfate (4 g) and sodium acetate (1.66 g) were added and the tubes were shaken immediately to prevent coagulation of $MgSO_4$ [9]. After centrifugation at 4300 × *g* for 5 min, an aliquot (1 ml) of the supernatant was transferred to a microcentrifuge vial containing PSA sorbent (50 mg) and anhydrous $MgSO_4$ (150 mg). The contents were vortex mixed for 30 s, centrifuged at 5000 × *g* for 1 min, and the supernatant analysed by LC–MS/MS after dilution with water (1:10).

2.5. Method performance

The precision and accuracy of the method was tested with spiked samples of potato, orange and cereal-based baby food samples. Recoveries were determined for five replicates at two spiking concentrations (0.1 and 0.01 mg kg^{-1}). For each individual food commodity matrix-matched multi-level calibration standards, bracketing the samples, were used for analyses.

3. Results and discussion

3.1. Determination of MS/MS parameters

Multiple reaction monitoring (MRM) is often used for quantification by tandem quadrupole MS. The collision energy and cone voltage employed for acquisition and the selection of MRM transitions were evaluated for best response under positive and negative mode ESI by infusing a solution of standards (Table 1) into the mobile phase using a syringe pump. Dwell times were

Table 1
Summary of retention times and MRM transitions selected for analysis of the pesticides in ESI, positive and negative mode

	Pesticide	t_R (min)	MRM transitions (m/z)[a]	Dwell time (s)	Cone voltage (V)	Collision energy (eV)	Polarity
1	**Methamidophos**	0.41	142–94 142–125	0.015	22	14 13	+
2	**Acephate**	0.50	184–143 184–125	0.015	16	8 18	+
3	*Omethoate*	0.58	214–183 214–155	0.015	20	12 15	+
4	Butocarboxim sulfoxide	0.59	207–75 207–132	0.015	17	12 6	+
5	Pymetrozine	0.61	218–105 218–79	0.015	25	17 36	+
6	*Aldicarb sulfoxide*	0.64	207–89 207–132	0.015	16	14 10	+
7	Butoxycarboxim (butocarboxim sulfone)	0.68	223–106 223–166	0.015	17	10 7	+
8	*Aldoxycarb (aldicarb sulfone)*	0.72	223–86 223–76	0.015	23	12 7	+
9	**Methomyl**	0.85	163–88 163–106	0.025	15	8 10	+
10	**Oxydemeton-methyl**	0.86	247–169 247–109	0.025	20	14 28	+
11	*Demeton-S-methyl sulfone*	0.90	263–169 263–121	0.025	26	17 17	+
12	**Carbendazim**	1.01	192–160 192–132	0.025	25	18 30	+
13	**Imidacloprid**	1.15	256–209 256–175	0.020	22	16 20	+
14	**Thiabendazole**	1.18	202–175 202–131	0.020	40	25 32	+
15	*Methiocarb sulfoxide*	1.26	242–185 242–168	0.020	22	13 24	+
16	**Dimethoate**	1.27	230–125 230–199	0.020	17	20 10	+
17	Acetamiprid	1.32	223–126 223–56	0.020	27	20 15	+
18	*Methiocarb sulfone*	1.40	258–122 258–107	0.020	22	20 37	+
19	Cymoxanil	1.41	199–128 199–111	0.020	17	8 18	+
20	*Thiacloprid*	1.49	253–126 253–90	0.020	28	20 37	+
21	Butocarboxim	1.61	213–75 213–156	0.020	24	15 10	+
22	**Aldicarb**	1.64	208–116 208–89	0.020	7	7 7	+
23	**Carbaryl**	2.08	202–145 202–127	0.020	18	10 28	+
24	*Thiodicarb*	2.19	355–88 355–108	0.020	15	16 16	+
25	Phorate sulfoxide	2.25	277–97 277–143	0.020	18	32 20	+

Table 1 (*Continued*)

	Pesticide	t_R (min)	MRM transitions (m/z)[a]	Dwell time (s)	Cone voltage (V)	Collision energy (eV)	Polarity
26	Phorate sulfone	2.29	293–97 293–115	0.020	18	30 24	+
27	Lenacil	2.30	233–151 233–107	0.030	44	24 32	–
28	**Azinphos-methyl**	2.46	318–160 318–261	0.020	14	8 8	+
29	**Imazalil**	2.52	297–159 297–69	0.020	30	20 20	+
30	Linuron	2.56	249–160 249–182	0.020	28	16 15	+
31	**Azoxystrobin**	2.60	404–372 404–329	0.020	22	15 30	+
32	**Methiocarb**	2.63	226–169 226–121	0.020	16	10 19	+
33	**Fludioxonil**	2.65	247–180 247–126	0.030	45	28 35	–
34	**Triadimefon**	2.77	294–69 294–197	0.015	22	21 15	+
35	Iprovalicarb	2.84	321–119 321–203	0.015	15	18 8	+
36	*Triadimenol*	2.85	296–70 296–99	0.015	14	10 16	+
37	**Dichlofluanid**	2.86	333–123 333–224	0.015	22	24 10	+
38	**Fenhexamid**	2.86	302–97 302–55	0.015	35	25 35	+
39	Flufenacet	2.88	364–152 364–194	0.015	17	20 10	+
40	**Cyprodinil**	2.95	226–93 226–108	0.015	45	33 25	+
41	Diflubenzuron	2.96	309–156 309–289	0.100	20	11 9	–
42	Fenoxycarb	3.00	302–88 302–116	0.015	21	20 12	+
43	**Spiroxamine**	3.04	298–144 298–100	0.015	32	20 32	+
44	**Tolylfluanid**	3.06	347–137 347–238	0.015	19	28 10	+
45	Zoxamide	3.11	336–187 336–159	0.015	25	24 41	+
46	Phorate	3.15	261–75 261–97	0.015	11	12 32	+
47	Hexaflumuron	3.31	459–276 459–175	0.020	22	22 39	–
48	Teflubenzuron	3.47	379–196 379–339	0.020	18	25 15	–
49	Lufenuron	3.49	509–175 509–326	0.020	22	40 22	–
50	Fluazinam	3.50	463–416 463–398	0.020	26	21 17	+

Table 1 (*Continued*)

	Pesticide	t_R (min)	MRM transitions (m/z)[a]	Dwell time (s)	Cone voltage (V)	Collision energy (eV)	Polarity
51	Flucycloxuron	3.58	482–156 482–462	0.020	34	14 13	–
52	Flufenoxuron	3.62	487–156 487–329	0.020	27	16 22	–

Note: Pesticides in bold are the 21 pesticides from the EU guidelines and in italic their relevant transformation products.
[a] The MRM transitions are shown in the following order: quantification transition and confirmation transition.

set so that approximately 10–15 data points were acquired for each chromatographic peak. The number of data points collected is directly related to the MRM cycle time which is defined by the summation of the dwell times of all the MRM channels, inter-channel delay times between successive MRM channels, and inter-scan delay times during polarity switching. The mass spectrometer used has a unique collision cell (T-wave design) that enables data collection with very short dwell times (5 ms) and inter-scan delay (20 ms) without loss of signal intensity. The electronics and detection system of the mass spectrometer have been designed to ensure that voltages are stabilised rapidly following switches of polarity, allowing very short inter-channel delays (5 ms) to be used, minimising losses in signal intensity.

The protonated molecule $[M+H]^+$ was base peak in the spectra of most compounds in positive mode and the deprotonated molecule $[M-H]^-$ in negative mode. Two compounds exhibited a propensity to form adducts. Thus, $[M+Na]^+$ (m/z 213) was base peak for butocarboxim and $[M+NH_4]^+$ (m/z 208) for aldicarb.

The MRM cycle time is critical for analysis of compounds when polarity switching is used, particularly where they elute closely (e.g. phorate sulfone and lenacil and cyprodinil, diflubenzuron and fenoxycarb). The very fast (20 ms) switching between negative and positive ESI mode allowed phorate sulfone (ESI+) and lenacil (ESI−), two close eluting pesticides (Fig. 1) with peak widths of approximately 5 s, to be determined with 10 data points for each of two MRM transitions across each peak. The requirement to monitor all four MRM transitions simultaneously gives an acquisition time of only 0.125 s for each transition, inclusive of the dwell and switching times. Similarly, cyprodinil (ESI+), diflubenzuron (ESI−) and fenoxycarb (ESI+) have similar retention times and average peak widths of 9 s. Thus, the total acquisition time to monitor each MRM transition for each analyte is only 0.15 s. Such measurement would not have been possible using older instruments, where switching times are in the order 0.2–0.3 s.

Although diflubenzuron and flufenoxuron respond under both positive and negative ESI mode (Fig. 2), both gave the finest response in negative-ion mode. Clearly, the ability to monitor these analytes in negative mode and other analytes in positive mode has benefits in terms of improved limits of detection and quantification.

3.2. Method performance, recoveries and selectivity

The critical parameter controlling the UPLC separation of the pesticides of interest was determined to be the pH of the mobile phase. For multi-analyte quantification the pH needs to be suitable for use across the range of chemistry represented. For example, thiabendazole is a very basic compound and ionises best at low pH. Methanol:water with ammonium acetate at a final concentration of 5 mmol l^{-1} gave a very poor peak shape for thiabendazole and a split peak for tolylfluanid. Acetonitrile with 17.5 mmol l^{-1} acetic acid gave the best response for thiabendazole and a very good peak shape. Under those conditions, however, a few compounds, including tolylfluanid, gave no response. The final choice of mobile phase, methanol:water with 17.5 mmol l^{-1} acetic acid, gave a good peak shape for thiabendazole without compromising response or peak shape for the other pesticides, allowing quantification for all analytes. A 10-fold dilution of acetonitrile extracts with water also improved the peak shape and was employed routinely.

The UPLC–MS/MS calibration curves for all analytes were linear over the range 0.005–0.250 μg ml^{-1} (equivalent to 0.005–0.250 mg kg^{-1}) and correlation coefficients were >0.99. Method recoveries (Table 2) obtained for the majority of the pesticides spiked at concentrations of 0.10 and 0.01 mg kg^{-1} in potatoes (73–124%, RSD < 18%), oranges (66–118%, RSD < 17%) and cereal-based baby food (73–114%, RSD < 19%) were satisfactory according to the EU guidelines [10]. In the orange validation study, but not in the baby food and potato validations, poor precision affected the late eluting pesticides at both spiked concentrations. This suggests that the high RSDs obtained for these six pesticides are caused by matrix interferences only present in oranges. Nevertheless, the results are still satisfactory for the purposes of screening.

The UPLC method developed gave an analysis time for the 52 pesticides of interest of less than 4 min, an improvement in speed by a factor of approximately 12.5 compared to a typical HPLC separation [11].

Butocarboxim sulfoxide and aldicarb sulfoxide are structural isomers that share one MRM transition (m/z 207–132). A single transition is not sufficient for confirmation of an analyte, hence, chromatographic resolution is necessary for determination and confirmation. The UPLC method gives adequate resolution of butocarboxim sulfoxide and aldicarb sulfoxide (Fig. 3), enabling confirmation of identity of these two pesticides.

3.3. Application

The method was tested by application in the analysis of potato samples known to contain residues of aldicarb. The concentrations of residues of aldicarb sulfoxide and aldoxycarb detected in three different potato samples, between 0.011

Table 2
Recoveries (%) and relative standard deviations, RSD (%), obtained by UPLC–MS/MS (MRM mode) analysis of three different samples fortified with a standard solution containing 52 pesticides, at a spiking level of 0.01 and 0.1 mg kg^{-1} ($n = 5$)

	Pesticide	Potato				Orange				Cereal-based baby food			
		0.01 mg kg^{-1}		0.1 mg kg^{-1}		0.01 mg kg^{-1}		0.1 mg kg^{-1}		0.01 mg kg^{-1}		0.1 mg kg^{-1}	
		Rec (%)	RSD (%)	Rec (%)	RSD (%)	Rec (%)	RSD (%)	Rec (%)	RSD (%)	Rec (%)	RSD (%)	Rec (%)	RSD (%)
1	Methamidophos	77	11	81	6	81	12	82	2	79	4	91	5
2	Acephate	91	3	91	4	78	7	87	3	89	6	101	7
3	Omethoate	85	8	96	4	82	9	95	3	88	8	103	4
4	Butocarboxim sulfoxide	91	12	97	4	80	11	94	3	90	5	102	5
5	Pymetrozine	73	6	82	3	67	9	76	3	76	7	87	3
6	Aldicarb sulfoxide	97	6	96	3	85	14	94	3	93	6	107	2
7	Butoxycarboxim	102	11	103	2	92	6	102	3	101	6	112	3
8	Aldoxycarb (aldicarb sulfone)	102	8	104	3	90	7	102	3	103	8	108	5
9	Methomyl	92	8	99	4	97	8	104	1	100	3	106	3
10	Oxydemeton-methyl	90	4	93	3	83	6	91	2	91	5	102	3
11	Demeton-S-methyl sulfone	101	4	102	2	92	4	100	3	96	2	107	2
12	Carbendazim	102	3	99	1	87	6	98	2	97	4	103	2
13	Imidacloprid	110	18	100	2	106	6	101	6	100	9	104	3
14	Thiabendazole	89	2	93	2	73	11	95	5	87	4	99	4
15	Dimethoate	103	6	105	2	92	6	102	4	103	3	106	3
16	Methiocarb sulfoxide	95	2	96	3	92	3	96	4	95	4	101	5
17	Acetamiprid	102	5	101	2	85	7	101	3	97	4	105	4
18	Cymoxanil	106	6	104	3	105	11	105	5	93	11	110	2
19	Methiocarb sulfone	103	8	103	2	99	6	103	5	100	6	104	2
20	Thiacloprid	101	4	102	2	99	9	98	4	101	3	106	3
21	Butocarboxim	107	5	105	5	95	7	107	3	106	6	106	7
22	Aldicarb	102	10	104	5	105	8	102	5	104	7	107	10
23	Carbaryl	105	2	103	1	94	6	105	3	101	5	107	3
24	Thiodicarb	100	6	98	2	99	4	103	4	99	3	104	5
25	Phorate sulfoxide	99	8	93	4	102	6	107	5	102	6	107	6
26	Lenacil	96	5	96	3	96	7	102	8	94	3	101	4
27	Phorate sulfone	110	1	103	3	102	6	109	3	106	5	107	4
28	Azinphos-methyl	92	7	90	8	99	17	111	7	113	19	93	9
29	Linuron	103	9	106	2	97	13	115	3	104	3	107	3
30	Imazalil	105	10	95	7	110	4	111	4	105	6	106	7
31	Methiocarb	102	3	101	2	103	4	108	3	103	5	107	4
32	Azoxystrobin	105	4	103	3	99	10	110	3	104	5	110	4
33	Fludioxonil	102	11	107	6	115	12	109	5	107	5	107	6
34	Triadimefon	101	4	102	2	101	10	106	2	104	9	106	4
35	Iprovalicarb	101	4	104	3	99	8	105	1	100	7	104	4
36	Triadimenol	101	5	101	3	96	9	106	3	93	6	103	4
37	Dichlofluanid	104	5	105	5	*65*	*24*	89	16	73	14	87	10
38	Fenhexamid	100	5	97	3	101	10	108	1	93	8	104	2
39	Flufenacet	101	7	104	2	105	9	108	3	99	8	108	4
40	Cyprodinil	110	6	104	5	104	7	107	1	95	6	102	6

Table 2 (*Continued*)

	Pesticide	Potato				Orange				Cereal-based baby food			
		0.01 mg kg^{-1}		0.1 mg kg^{-1}		0.01 mg kg^{-1}		0.1 mg kg^{-1}		0.01 mg kg^{-1}		0.1 mg kg^{-1}	
		Rec (%)	RSD (%)	Rec (%)	RSD (%)	Rec (%)	RSD (%)	Rec (%)	RSD (%)	Rec (%)	RSD (%)	Rec (%)	RSD (%)
41	Diflubenzuron	94	16	96	3	104	8	109	5	100	11	103	9
42	Fenoxycarb	99	15	91	6	112	3	116	8	102	7	106	5
43	Spiroxamine	97	8	95	6	118	6	114	6	98	7	108	8
44	Tolylfluanid	100	11	104	4	66	12	100	13	85	13	92	9
45	Zoxamide	105	5	101	3	108	7	118	4	100	8	104	5
46	Phorate	*113*	*24*	*170*	22	104	8	*114*	*5*	96	6	95	7
47	Hexaflumuron	*128*	*25*	113	13	*102*	*39*	*110*	*25*	*124*	*9*	109	8
48	Teflubenzuron	*124*	*4*	*111*	*5*	*106*	*34*	117	17	107	6	89	11
49	Fluazinam	*120*	*11*	105	16	*116*	*37*	*107*	*25*	99	4	99	6
50	Lufenuron	*122*	*14*	*120*	*5*	*113*	*43*	*127*	*27*	109	5	95	3
51	Flucycloxuron	*115*	*14*	*113*	*11*	*108*	*41*	*123*	*28*	105	9	92	6
52	Flufenoxuron	*120*	*14*	*118*	*9*	*114*	*45*	*131*	*27*	*114*	*3*	93	6

Note: Values in italic fall outside the EU AQC guidelines [10] but are satisfactory for the purposes of screening. The EU AQC guidelines set criteria for recoveries as follows: (i) at 0.1 mg kg^{-1}, 70–110% ± 20%; (ii) at 0.01 mg kg^{-1}, 70–110% ± 30%.

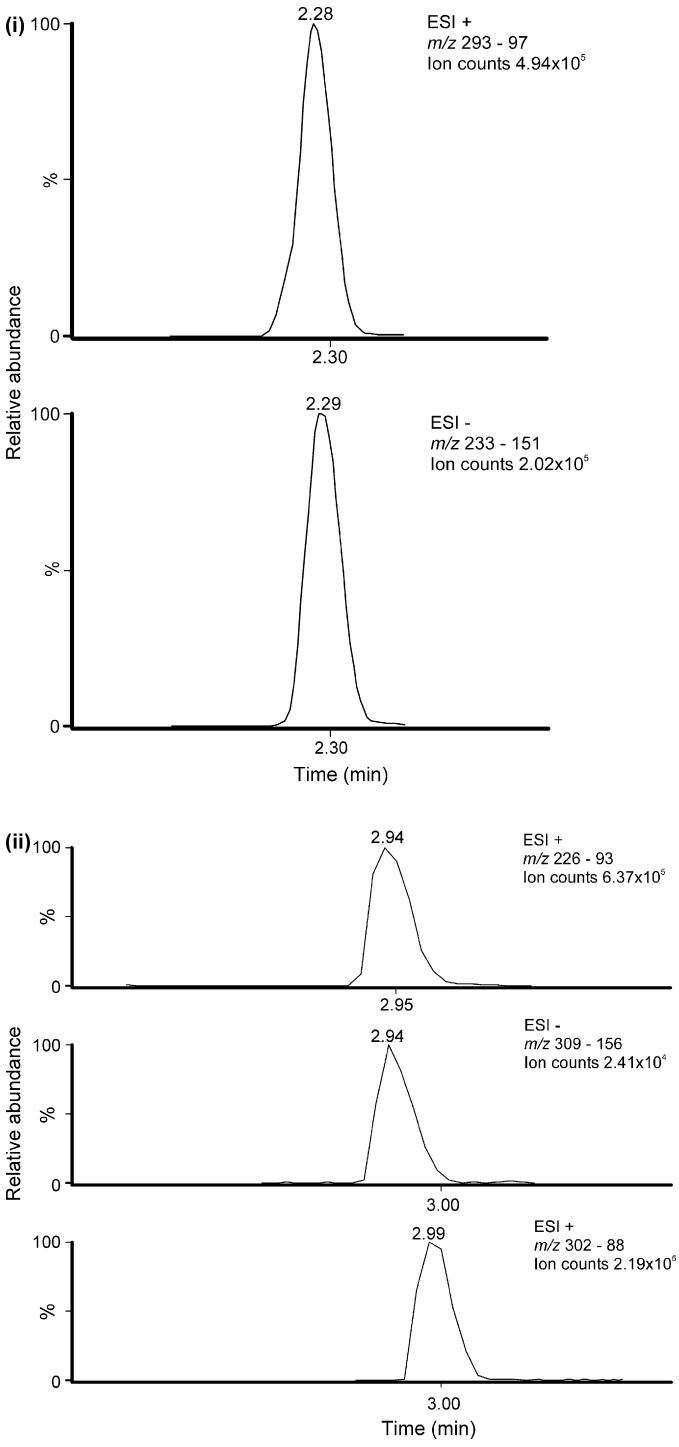

Fig. 1. Reconstructed partial UPLC–MS/MS chromatograms (using quantification transition) for a cereal-based baby food matrix fortified at 0.1 mg kg^{-1}. Region shown contains closely eluting compounds giving positive and negative ions (i) phorate sulfone (*m/z* 293–97) and lenacil (*m/z* 233–151) and (ii) cyprodinil (*m/z* 226–93), diflubenzuron (*m/z* 309–156) and fenoxycarb (*m/z* 302–88).

and 0.034 mg kg^{-1}, do not exceed the UK maximum residue limits in potatoes (Table 3). The resolution capability of the UPLC–MS/MS method was crucial in discriminating aldicarb sulfoxide from butocarboxim sulfoxide in all of the unknown samples tested. Furthermore, a signal-to-noise (S/N) ratio > 3:1 for the confirmation transition was achieved in all cases. The

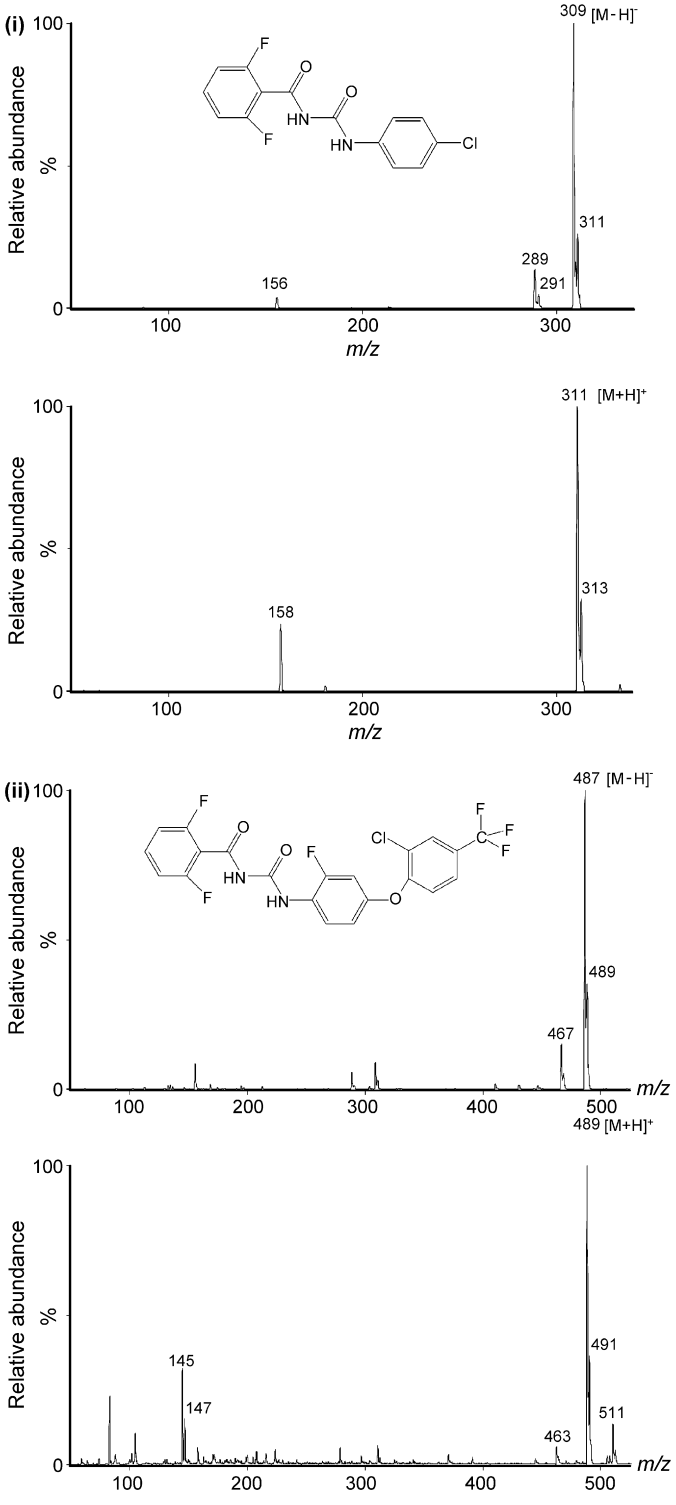

Fig. 2. Mass spectra for (i) diflubenzuron and (ii) flufenoxuron in ESI negative and positive mode.

results were in good agreement with those obtained using an established HPLC–MS/MS method [11]. Residues of aldicarb sulfoxide and aldoxycarb were confirmed at similar concentrations (Table 3). Therefore, this application confirms the benefits of the developed UPLC–MS/MS method to resolve aldicarb sulfoxide and aldoxycarb in less than 1 min and to confirm the presence of pesticide residues in the tested samples.

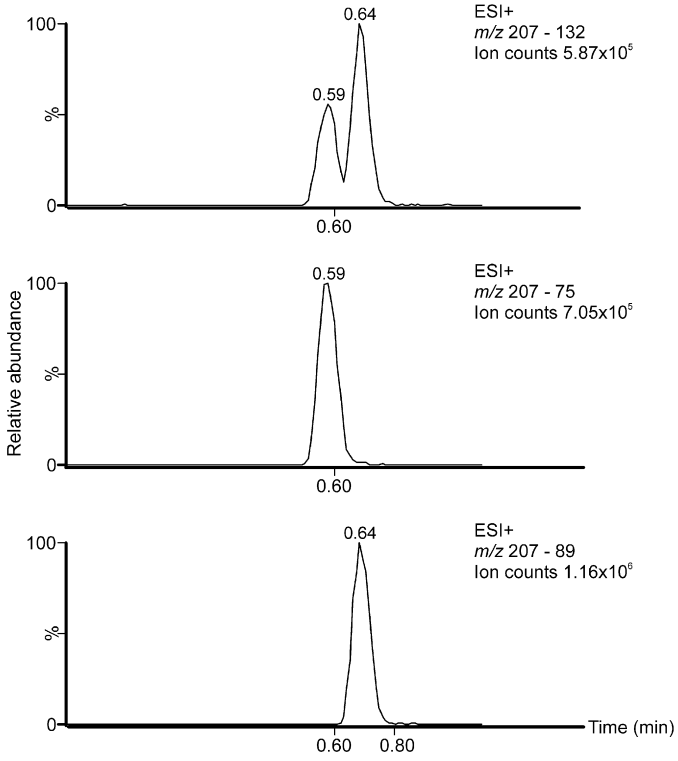

Fig. 3. Reconstructed UPLC–MS/MS chromatogram for cereal-based baby food matrix-matched calibrant (0.250 mg kg^{-1}) using the MRM transitions for butocarboxim sulfoxide and aldicarb sulfoxide (Table 1).

Table 3
UPLC–MS/MS and HPLC–MS/MS results for the analysis of three different potato samples containing incurred residues ($n = 2$)

Sample	Analyte	Amount detected (mg kg^{-1}) by UPLC–MS/MS	Amount detected (mg kg^{-1}) by HPLC–MS/MS
A	Aldicarb sulfoxide	0.020	0.020
	Aldoxycarb	0.017	<0.020
B	Aldicarb sulfoxide	0.034	0.030
	Aldoxycarb	0.002	<0.020
C	Aldicarb sulfoxide	0.021	0.025
	Aldoxycarb	0.011	<0.020

4. Conclusions

A fast and simple UPLC–MS/MS method involving switching of the polarity of ionisation has been developed for the determination of 52 pesticides including 20 of the pesticides listed in the EU residue monitoring programme 2005–2007. The method has been applied to three representative matrices, potatoes, oranges and cereal-based baby foods, giving satisfactory recoveries for the majority of the pesticides. Poor precision obtained for the late eluting compounds in the orange extracts is attributed to matrix interferences.

The facility for very fast switching of the polarity of ionisation allows simultaneous determination of compounds that are amenable to analysis as positive and negative ions. Furthermore, the rapid voltage stabilisation in the electronics and detection

system of the mass spectrometer used, following switches of polarity, ensured that very short inter-channel delays could be used minimising losses in response.

The high resolution capacity of the UPLC method combined with the extremely short analysis times for the determination of pesticide residues in food offers significant benefit for this type of analysis, as exemplified in the case of the structural isomers butocarboxim sulfoxide and aldicarb sulfoxide.

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