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Routine UPLC-MS/MS Quantification of Pesticide Residues in Okra with Simultaneous Acquisition of Qualitative Full-Spectrum MS and MS/MS Data

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APPLICATION BENEFITS

- Multiple pesticide residues can be detected simultaneously at legislative limits in okra samples using the ACQUITY UPLC® H-Class System coupled with Xevo® TQD MS.
- Quantitative and qualitative information can be achieved in a single injection.
- RADAR™ technology enables simultaneous full-scan data to be acquired, providing important information on matrix background ions that could potentially interfere with the analysis.
- PICS (product ion confirmation scan) provide additional confirmation for compound identification through acquisition of MS/MS spectra in the same injection.

WATERS SOLUTIONS

ACQUITY UPLC H-Class System

Xevo TQD

ACQUITY UPLC HSS T3 Column

MassLynx® Software

KEY WORDS

Pesticides, okra, QuEChERS, food safety

INTRODUCTION

Okra is an important vegetable of the tropical countries and a popular diet component in several countries including India. According to the Food and Agriculture Organization of the United Nations (FAO),[1] India is one of the largest okra producers in the world and it produced approximately 5,800 tons of okra in 2010 and 2011. Okra is susceptible to a variety of pests and diseases[2] and a wide-range of pesticides are used to treat okra plants in India. Legislative limits are in place for the presence of pesticides in domestically produced, imported, or exported okra.[3] It is, therefore, very important to monitor the presence of commonly used pesticides in okra at legislative limits.

According to the PRiF (Pesticide Residues in Food) report, import controls under regulation (EC) No 669/2009 have been increased for okra imported from India because of the frequent detection of pesticide residues, mainly monocrotophos. The consignment is supposed to be rejected if it is non-compliant with MRLs (Maximum Residue Limits). Since July 1, 2012, the frequency of testing consignments has been increased from 10% to 50%. With this frequent testing, monocrotophos, triazophos, and acetamiprid were found at 0.02 mg/kg in okra samples from India, while the MRL for these compounds is 0.01 mg/kg.[4]

In this application note, a multi-residue analysis method for the detection of 212 pesticides in okra is presented. For a complete list of all pesticides, see Appendix A.

Methods

A multi-residue MS method for the pesticides was created using Waters® Xevo TQD Quanpedia™ database. All of the pesticides were analyzed under ESI+ or ESI- mode using rapid polarity switching. Full-scan data were acquired in order to assess any matrix effects and the use of two MRMs and product ion confirmation scans were acquired to confirm and quantify the pesticide residues.

EXPERIMENTAL

UPLC conditions

LC system:	ACQUITY UPLC H-Class
Column:	ACQUITY HSS T3 2.1 X 100 mm, 1.8 µm
Column temp.:	45 °C
Injection volume:	10 µL
Flow rate:	0.45 mL/min
Mobile phase A:	10 mM ammonium acetate (pH 5) in water
Mobile phase B:	10 mM ammonium acetate (pH 5) in methanol
Weak needle wash:	50/50 Water/methanol (v/v)
Strong needle wash:	10/90 Methanol/water (v/v)
Seal wash:	90/10 water/methanol

Time (min)	Flow rate (mL/min)	%A	%B	Curve
Initial	0.450	98	2	6
0.25	0.450	98	2	6
12.25	0.450	1	99	6
13.00	0.450	1	99	6
13.01	0.450	98	2	6
17.00	0.450	98	2	6

Table 1. UPLC method for pesticide analysis.

MS conditions

MS system:	Xevo TQD
Ionization mode:	ESI+/ESI-
Capillary voltage:	3 kV
Desolvation temp.:	500 °C
Desolvation gas flow:	1000 L/Hr
Source temp.:	150 °C

Standard preparation

Pesticide standards were purchased either from Sigma-Aldrich, Fisher Scientific, or AccuStandard. A mix of all pesticides at 400 ng/mL was prepared in acetonitrile and stored at 4 °C.

Sample preparation

QuEChERS is a popular method worldwide for the multi-residue analysis of pesticides in fruits and vegetables. The AOAC official method 2007.01, was used to prepare okra samples that were purchased at a local supermarket. Briefly, okra samples were homogenized in water and 15 grams of homogenate was collected into a 50-mL centrifuge tube. Samples were extracted with acidified acetonitrile and mixed with $MgSO_4$ and NaCl (Tube 1). The tube was shaken for a minute and centrifuged at 1500 rcf for 1 minute. After centrifugation, the matrix cleanup was accomplished by dispersive solid phase extraction (d-SPE) by using 50 mg of primary secondary amine (PSA), 50 mg of C_{18} bonded silica, 150 mg of $MgSO_4$, and 7.5 mg of graphitized carbon black (GCB).[5] 1 mL of supernatant from Tube 1 was added to d-SPE cleanup tube and centrifuged at 1500 rcf for 1 minute. 1 mL of this extract was evaporated to dryness and reconstituted in 200 µL of 40/60 acetonitrile/water spiked with internal standard.

RESULTS AND DISCUSSION

All of the pesticides were successfully detected at 10 ppb (0.01 mg/kg) in okra sample. For all of the pesticides, Appendix A lists the ionization mode, retention time, and whether or not the compound was detected in a pre-spike 1 ppb sample, as well as the 10 ppb pre-spike sample. Figure 1 shows an overlay of the total ion chromatogram (TIC) of all the pesticides at 10 ppb in okra sample.

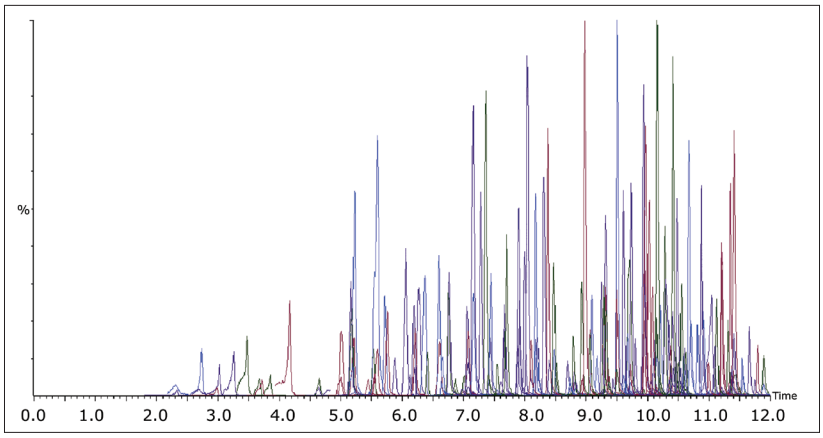

Figure 1. Overlay of MRM chromatograms of all pesticides at 10 ppb (0.01 mg/kg) in okra.

Solvent and matrix match spiked calibration (MMS) curves were prepared at concentrations that equated to the range 1 ppb to 50 ppb (*i.e.* 0.001 to 0.05 mg/kg of okra) and injected in triplicate. The majority of the compounds showed linearity with R^2 values greater than 0.99 in both the solvent and MMS curves. Ethoxyquin, milbemectin A3, and A4, oxadiazon, spiromesifen, and terbufos showed R^2 values greater than 0.970 for both solvent and MMS curves. However, fipronil, phorate, and thiabendazole showed R^2 values greater than 0.970 in MMS curves only. Figures 2 and 3 show calibration curves and residuals for an example compound (triazophos) in solvent and matrix respectively.

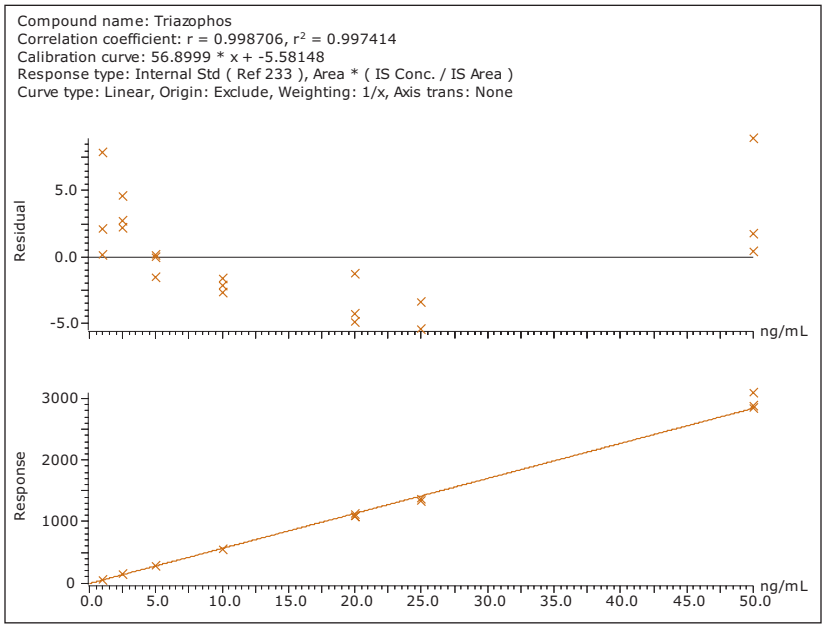

Figure 2. Calibration curve of triazophos in solvent from 1 ppb to 50 ng/mL (0.001 to 0.05 mg/kg).

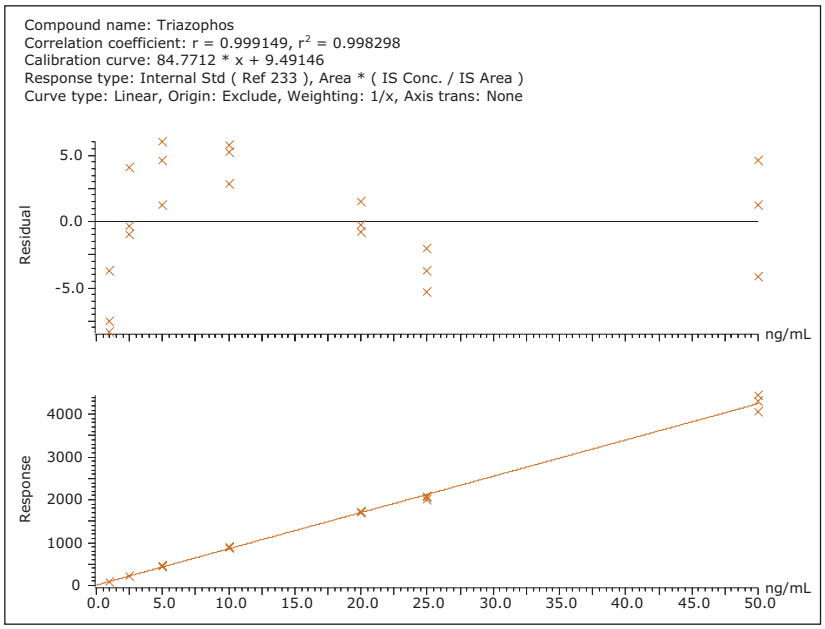

Figure 3. Matrix-match spiked calibration curve of triazophos in okra sample from 1 ppb to 50 ppb (0.01 to 0.05 mg/kg).

To evaluate the recovery, accuracy, and precision of the method, studies were carried out on spiked samples. Okra samples were pre-spiked with all the pesticides at 10 ppb (0.01 mg/kg) in triplicate, extracted, and quantified against the MMS calibration curve. Recoveries were calculated using TargetLynx™ Software. The recoveries reported are without any internal standard correction. As shown in Figure 4 (A, B, C, and D), recoveries for all of the pesticides ranged from 25% to 150%. Relative standard deviations (RSDs, shown as error bars in Figure 4) for most compounds were <20%. The RSDs for 34 compounds were found to be higher than 20%. Use of an internal standard would be likely to significantly improve repeatability for those analytes.

Figure 4. %Recovery for 212 pesticides in okra sample at 10 ppb (0.01 mg/kg).

Matrix effects

Matrix effects for all of the pesticides were calculated by taking the ratio of the slope of the MMS calibration curve to the slope of solvent calibration curve. A percent variation of + 20% was considered as no matrix effect as this variation is close to the repeatability values.[6] Values between + 20% to + 50% were considered as a medium matrix effect, and a strong matrix effect was considered to be values greater than + 50%.[7] Figure 5 shows levels of the matrix effect that were observed in the analysis of okra for all pesticides. A strong matrix effect was observed for the majority of compounds, demonstrating that the analysis of okra samples poses a challenge in regards to high matrix complexity. Even with these high matrix effects, all compounds can easily be detected at legislative limits and quantified using the matrix-matched calibration curve.

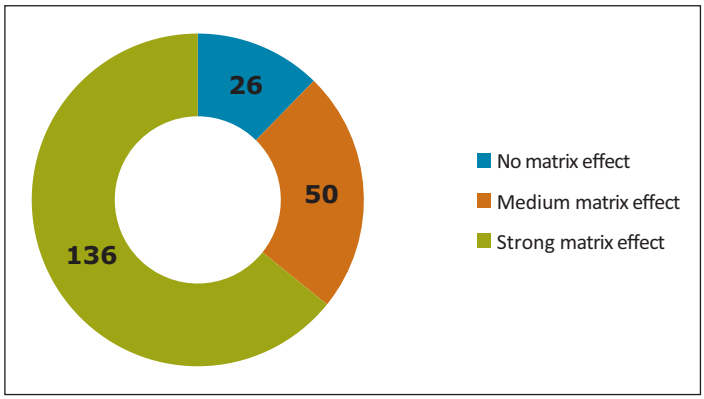

Figure 5. Matrix effects observed for okra sample.

Understanding matrix effects – RADAR

To further understand the impact of co-eluting matrix components that can compete with an analyte of interest during the ionization process, RADAR technology enables the simultaneous acquisition of full spectrum data during quantitative MS/MS analysis. Figure 6 shows an example of the use of RADAR technology. In Figure 6A, the base peak intensity (BPI) chromatogram from the full-scan background data for the okra sample is shown. At 5.08 minutes, close to the retention time of dimethoate (Figure 6B and 6C), high matrix interference was observed. The spectrum at 5.08 minute showed an intense ion at *m/z* 217.1 (Figure 6D).

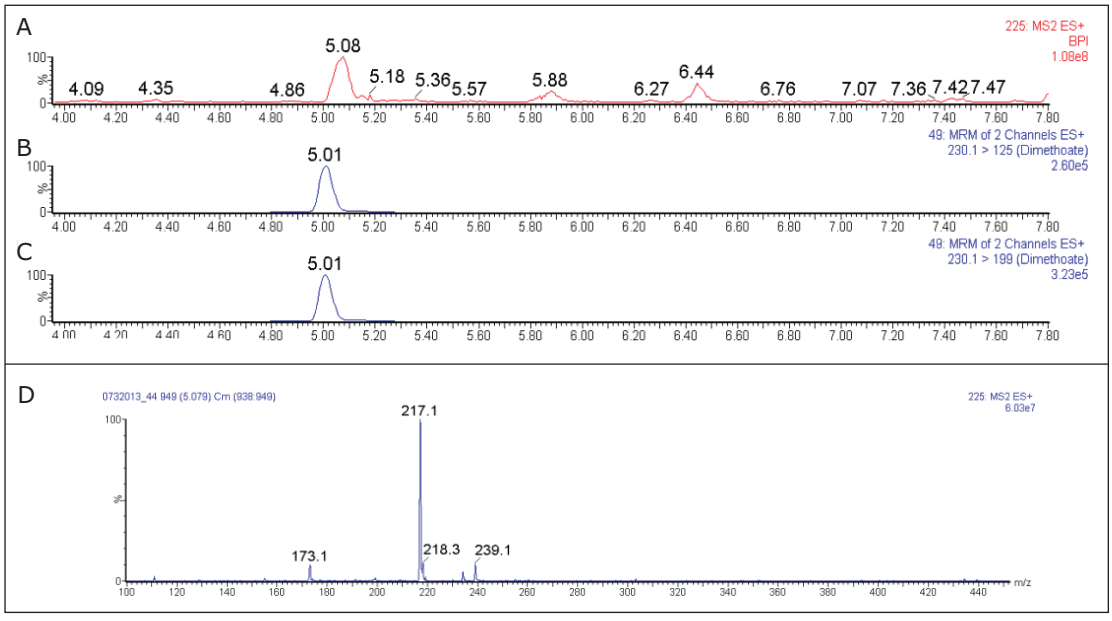

Figure 6. Use of RADAR Technology: (A) Full scan background data for okra sample, (B) and C) MRM transitions of dimethoate, (D) spectrum at retention time of dimethoate.

This interferent potentially has a large impact on the detection of dimethoate and a 48% ion suppression effect was observed for dimethoate. In the case of aldicarb, however, matrix interference was minimal (0.4%) and the RADAR data (Figure 7) showed no evidence of interferences at the retention time of aldicarb (6.13 minutes). The spectrum at the retention time of aldicarb has been expanded and zoomed in the inset (Figure 7D), clearly demonstrating that there was a much higher response from co-extracted matrix ions at the retention time of dimethoate compared to aldicarb. These data clearly demonstrate the usefulness of RADAR technology in assessing the matrix background and its potential effect on ion enhancement or suppression.

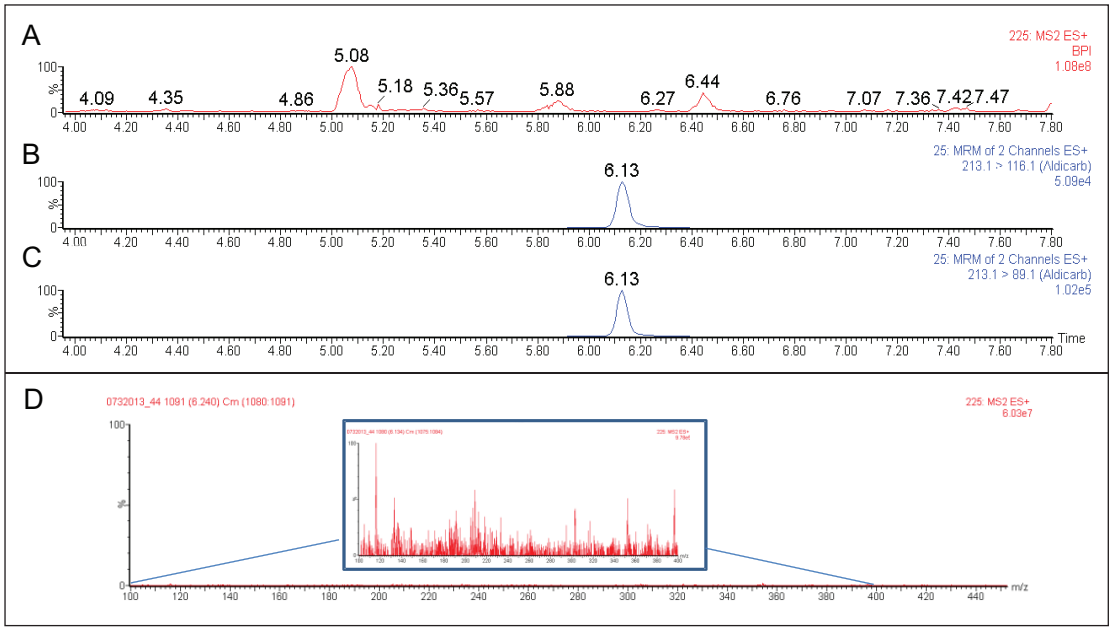

Figure 7. Use of RADAR technology. (A) Full-scan background data for okra sample, (B) and (C) MRM transitions of aldicarb, (D) Spectrum at retention time of aldicarb. The inset has been zoomed to show lower level response compared to the spectrum at the retention time of dimethoate.

Product ion confirmation (PICs)

In complex matrices, situations arise where closely-related compounds such as metabolites or matrix interferences show responses for the target compounds of interest, even in MRM mode. This can lead to ambiguity and may require an additional qualitative experiment. An alternative is to employ a product ion confirmation scan (PICs) within the quantitative MRM experiment. PICs can be used to confirm peak identity through automatic acquisition of an MS/MS spectrum after the apex of the peak has eluted. PICs, in combination with TargetLynx, provides additional confirmation of the compounds of interest through comparison of the acquired MS/MS spectrum to a reference spectrum. Figure 8 shows the TargetLynx results from the comparison of the atrazine MS/MS spectrum obtained from PICS in an okra sample versus the reference spectrum, which was obtained from MS/MS analysis of the standard in solvent.

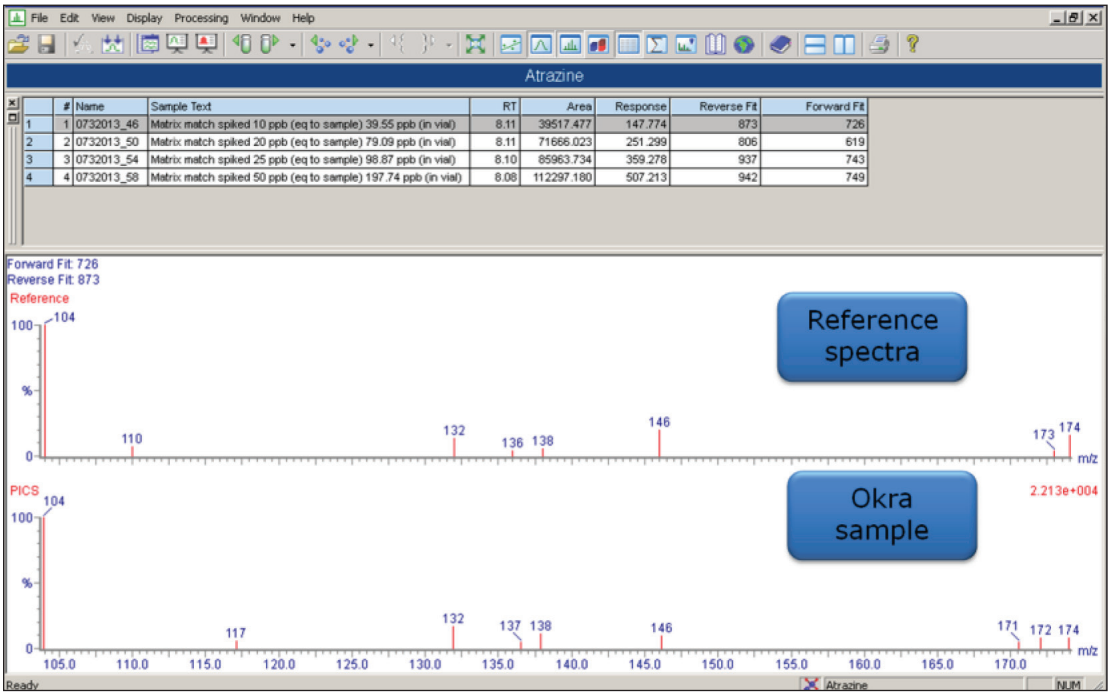

Figure 8. Product ion confirmation (PICs) data for atrazine in okra sample.

CONCLUSIONS

- The combination of ACQUITY UPLC H-Class System with the Xevo TQD tandem mass spectrometer can detect pesticides below the legislative limit in okra samples.
- Even though a strong matrix effect was observed for many compounds, detection and quantification at the legislative limit was achieved.
- Simultaneous acquisition of MRMs and RADAR full-scan data provides quantitative and qualitative information in single injection.
- Product ion confirmation (PICs) increases confidence in compound assignments, which proves highly useful when working with complex matrices.

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September 2013 720004789en AG-PDF

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Appendix A

In order to determine that the method was fit-for-purpose for the analytes listed, the analysis of pre-spiked samples at 1 ppb (0.01 mg/kg) and 10 ppb (0.01 mg/kg) was undertaken. All compounds were detected at 10 ppb. Those compounds that were also detected at 1 ppb are indicated in the fourth column. Some early eluting compounds showed compromised peak shapes, owing to the sample diluent (40% acetonitrile). Signal-to-noise improvements (and therefore lower LODs) can be gained from reducing the organic content of the sample diluent, however, some risk lies with ensuring that non-polar analytes remain in solution. For this work 40% organic was utilized. Atrazine desethyldesisopropyl, dinotefuran, methamidophos, and oxydemeton methyl showed compromised chromatographic peaks. In addition, for seven compounds, the second transition peak was not apparent at the lowest level. These compounds are shown by an asterisk in the table below.

Name	Ionization mode	Retention time (minute)	Pre-spike level detected
2,4-D	ESI -	6.10	10 ppb
6-Benzyl Adenine*	ESI +	6.63	1 ppb
Acephate	ESI +	2.33	10 ppb
Acetachlor	ESI +	9.80	10 ppb
Acetamiprid	ESI +	5.19	1 ppb
Acifluorfen*	ESI -	8.49	10 ppb
Aldicarb	ESI +	6.16	1 ppb
Aldicarb sulfone	ESI +	3.27	1 ppb
Aldicarb Sulfoxide	ESI +	3.00	1 ppb
Allethrin	ESI +	11.73	1 ppb
Atrazine	ESI +	8.10	1 ppb
Atrazine desethyldesisopropyl	ESI +	1.81	10 ppb
Atrazine desisopropyl	ESI +	4.33	1 ppb
Atrazine-desethyl	ESI +	5.61	1 ppb
Azoxystrobin	ESI +	8.98	1 ppb
Barban/Barbamate*	ESI +	9.25	1 ppb
Bendiocarb	ESI +	7.19	1 ppb
Benalaxyl	ESI +	10.41	1 ppb
Benfuracarb	ESI +	11.20	1 ppb
Bensulfuron methyl	ESI +	8.51	1 ppb
Bifenazate	ESI +	9.53	1 ppb
Bitertanol	ESI +	10.50	1 ppb
Boscalid	ESI +	9.19	1 ppb
Bromacil	ESI +	7.03	1 ppb
Bromodialone	ESI +	10.11	10 ppb
Buprofezin	ESI +	11.37	1 ppb
Butachlor	ESI +	11.43	1 ppb
Carbaryl	ESI +	7.42	1 ppb
Carbendazim	ESI +	5.61	1 ppb

Name	Ionization mode	Retention time (minute)	Pre-spike level detected
Carbofuran	ESI +	7.18	1 ppb
Carbofuran 3 keto	ESI +	6.22	1 ppb
Carbofuran-3-hydroxy	ESI +	5.23	1 ppb
Carbosulfan	ESI +	12.46	1 ppb
Carboxin	ESI +	7.46	1 ppb
Chlorantraniliprole	ESI +	8.73	1 ppb
Chlorfenvinphos	ESI +	10.51	1 ppb
Chlorimuron ethyl	ESI +	7.94	1 ppb
Chlorpyriphos /Dursban	ESI +	11.52	1 ppb
Chlorsulfuron	ESI +	5.46	1 ppb
Clothianidin	ESI +	4.68	1 ppb
Coumachlor	ESI +	8.57	1 ppb
Coumatetralyl	ESI +	7.49	1 ppb
Cruformate	ESI +	9.98	1 ppb
Cyazofamide/ cyazofamid	ESI +	9.81	1 ppb
Cycloxidim	ESI +	10.17	1 ppb
Cymoxanil	ESI +	5.55	1 ppb
Cyprazine	ESI +	8.19	1 ppb
Cyproconazole I	ESI +	9.36	1 ppb
Cyproconazole II	ESI +	9.52	1 ppb
Diafenthiuron	ESI +	11.89	10 ppb
Diazinon	ESI +	10.43	1 ppb
Dichlofluanid	ESI +	9.64	10 ppb
Dichlorvos	ESI +	6.89	10 ppb
Diclofop methyl	ESI +	11.19	10 ppb
Difenconazole I	ESI +	10.35	10 ppb
Difenconazole II	ESI +	10.74	1 ppb
Difenoxuron	ESI +	8.32	1 ppb
Diflubenzuron	ESI +	10.15	1 ppb
Diflufenican	ESI +	10.82	1 ppb
Dimethoate	ESI +	5.04	1 ppb
Dimethomorph I	ESI +	9.09	1 ppb
Dimethomorph II	ESI +	9.29	1 ppb
Diniconazole	ESI +	10.62	1 ppb
Dinotefuran	ESI +	2.99	10 ppb
Dioxathion	ESI +	11.25	1 ppb
Diuron	ESI +	8.20	1 ppb
DMSA	ESI +	6.23	1 ppb
Edifenfos	ESI +	10.28	1 ppb

Name	Ionization mode	Retention time (minute)	Pre-spike level detected
Emamectin Benzoate	ESI +	11.81	1 ppb
Ethiofencarb	ESI +	7.68	1 ppb
Ethion	ESI +	11.42	1 ppb
Ethoxyquin	ESI +	9.79	10 ppb
Ethoxysulfuron	ESI +	7.73	1 ppb
Etrimphos	ESI +	10.25	1 ppb
Famoxadone	ESI +	10.37	1 ppb
Fenamidone	ESI +	9.11	1 ppb
Fenamiphos	ESI +	9.97	1 ppb
Fenarimole	ESI +	9.64	1 ppb
Fenazaquin	ESI +	12.11	1 ppb
Fenchlorphos-oxon	ESI +	9.61	10 ppb
Fenobucarb	ESI +	8.79	1 ppb
Fenoxaprop-p-ethyl	ESI +	11.16	1 ppb
Fenoxycarb	ESI +	9.95	1 ppb
Fenpropathrin	ESI +	11.79	1 ppb
Fenpyroximate	ESI +	11.91	1 ppb
Fenthion	ESI +	10.21	10 ppb
Fenthion sulfoxide	ESI +	7.45	1 ppb
Fenthion-sulfone	ESI +	7.67	1 ppb
Fipronil*	ESI +	10.01	1 ppb
Fipronil carboximide	ESI -	8.54	1 ppb
Fipronil desulfinyl	ESI -	9.81	1 ppb
Fipronil sulfone	ESI +	8.77	10 ppb
Fipronil sulphide	ESI -	10.12	1 ppb
Flonicamid	ESI +	3.69	1 ppb
Fluazifop	ESI +	7.65	1 ppb
Fluazifop-p-butyl	ESI +	11.24	1 ppb
Flubendazole	ESI +	8.42	1 ppb
Flufenacet	ESI +	9.76	1 ppb
Flufennoxuron (flufenoxuron)	ESI +	11.66	1 ppb
Flufenzine *	ESI +	10.06	1 ppb
Fluopicolide	ESI +	9.32	1 ppb
Fluopyram	ESI +	9.61	1 ppb
Flusilazole	ESI +	9.94	1 ppb
Halosulfuron-methyl	ESI +	6.82	1 ppb
Haloxyfop	ESI +	8.85	10 ppb
Hexaconazole	ESI +	10.37	1 ppb
Hexazinone	ESI +	7.17	1 ppb

Name	Ionization mode	Retention time (minute)	Pre-spike level detected
Hexythiazox	ESI +	11.54	1 ppb
Imazalil	ESI +	10.06	1 ppb
Imazaquin	ESI +	5.28	10 ppb
Imazosulfuron	ESI +	6.69	1 ppb
Imidachloprid	ESI +	4.65	1 ppb
Indoxacarb	ESI +	10.81	1 ppb
Iodosulfuran-methyl	ESI +	6.64	1 ppb
Iprobenfos	ESI +	10.15	1 ppb
Iprodione	ESI +	9.91	10 ppb
Iprovalicarb	ESI +	9.72	1 ppb
Isoprothiolane	ESI +	9.32	1 ppb
Isoproturon	ESI +	8.18	1 ppb
Linuron	ESI +	8.83	1 ppb
Lufenuron	ESI -	11.28	1 ppb
Malaoxon	ESI +	7.37	1 ppb
Malathion	ESI +	9.33	1 ppb
Mandipropamid	ESI +	9.25	1 ppb
Mesosulfuron methyl	ESI +	7.31	1 ppb
Metaflumizone	ESI -	11.08	10 ppb
Metalaxyl	ESI +	8.38	1 ppb
Methabenzthiazuron	ESI +	8.09	1 ppb
Methamidophos	ESI +	1.76	10 ppb
Methidathion	ESI +	8.47	1 ppb
Methiocarb	ESI +	8.92	1 ppb
Methomyl	ESI +	3.71	1 ppb
Metolachlor + S-metolachlor	ESI +	9.94	1 ppb
Metoxuron	ESI +	6.30	1 ppb
Metribuzin	ESI +	7.08	10 ppb
Metsulfuron methyl	ESI +	5.19	1 ppb
Mevinphos I	ESI +	5.22	1 ppb
Mevinphos II	ESI +	5.88	1 ppb
Milbemectin A3*	ESI +	12.26	10 ppb
Milbemectin A4 *	ESI +	12.53	10 ppb
Molinate	ESI +	9.37	1 ppb
Monocrotophos	ESI +	4.18	1 ppb
Monolinuron	ESI +	7.55	1 ppb
Mycobutanil	ESI +	9.38	1 ppb
Novaluron	ESI +	10.99	1 ppb
Omethoate	ESI +	2.73	1 ppb

Name	Ionization mode	Retention time (minute)	Pre-spike level detected
Oryzalin	ESI +	9.69	10 ppb
Oxadiargyl	ESI +	10.52	10 ppb
Oxadiazon	ESI +	11.38	1 ppb
Oxamyl	ESI +	3.49	1 ppb
Oxycarboxin	ESI +	5.56	1 ppb
Oxydemeton methyl	ESI +	3.78	10 ppb
Oxyfluorfen	ESI +	8.83	1 ppb
Paclobutrazole	ESI +	9.26	1 ppb
Parathion ethyl	ESI +	9.98	10 ppb
Paraxon methyl	ESI +	6.42	1 ppb
Penconazole	ESI +	10.16	1 ppb
Pencycuron	ESI +	10.67	1 ppb
Pendimethalin	ESI +	11.57	10 ppb
Phenthoate	ESI +	10.09	1 ppb
Phorate	ESI +	5.36	10 ppb
Phorate sulfone	ESI +	8.04	1 ppb
Phorate sulfoxide	ESI +	7.93	1 ppb
Phosalone	ESI +	10.56	1 ppb
phosmet	ESI +	8.70	1 ppb
Phosphamidon	ESI +	6.77	1 ppb
Picoxystrobin	ESI +	10.02	1 ppb
Pirimiphos methyl	ESI +	10.65	1 ppb
Pretilachlor	ESI +	11.04	1 ppb
Primicarb	ESI +	8.06	1 ppb
Prochloraz	ESI +	10.55	10 ppb
Profenofos	ESI +	11.11	1 ppb
Propanil	ESI +	8.81	1 ppb
Propetamphos	ESI +	9.44	1 ppb
Propiconazole (Tilt)	ESI +	10.36	1 ppb
Propoxur	ESI +	7.09	1 ppb
Pyraclostrobin	ESI +	10.48	1 ppb
Pyridalyl	ESI +	12.91	1 ppb
Pyrimethanil	ESI +	8.97	10 ppb
Pyriproxyfen	ESI +	11.40	1 ppb
Pyrithiobac sodium	ESI +	7.01	10 ppb
Quinalphos	ESI +	10.11	1 ppb
Quizalfop free acid	ESI +	8.53	10 ppb
Quizalfop-p-ethyl	ESI +	11.14	1 ppb
Rimsulfuron	ESI +	5.79	1 ppb

Name	Ionization mode	Retention time (minute)	Pre-spike level detected
Simazine	ESI +	7.09	1 ppb
Spinosad A	ESI +	12.40	1 ppb
Spinosad D	ESI +	12.62	1 ppb
Spiromesifen	ESI +	11.76	10 ppb
Spirotetramat	ESI +	9.75	10 ppb
Spiroxamine	ESI +	10.20	1 ppb
Sulfosulfuron	ESI +	6.26	1 ppb
Tebuconazole	ESI +	10.21	1 ppb
Temephos	ESI +	11.33	1 ppb
Terbufos	ESI +	11.26	10 ppb
Tetraconazole	ESI +	9.68	1 ppb
Tetradifon	ESI +	9.40	1 ppb
Thiabendazole	ESI +	6.38	1 ppb
Thiacloprid	ESI +	5.73	1 ppb
Thiobencarb	ESI +	10.59	1 ppb
Thiodicarb	ESI +	7.87	1 ppb
Thiomethoxam (Thiamethoxam)	ESI +	3.87	1 ppb
Thiophanate methyl	ESI +	7.09	10 ppb
Tralkoxydim	ESI +	10.52	1 ppb
Triademefon	ESI +	9.41	1 ppb
Triademenol	ESI +	9.52	1 ppb
Triallate	ESI +	11.61	10 ppb
Triazophos	ESI +	9.50	1 ppb
Trichlorfon	ESI +	5.04	1 ppb
Tricyclazole	ESI +	6.07	1 ppb
Tridemorph	ESI +	12.84	1 ppb
Trifloxystrobin	ESI +	10.88	1 ppb
Triflumizole	ESI +	10.94	1 ppb
Triticonazole	ESI +	9.72	10 ppb
Vamidathion (Vamidothion)	ESI +	5.24	1 ppb