Application Note: 51880

Rapid Analysis of Pesticides in Difficult Matrices Using GC/MS/MS

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Key Words

- Fruit Preserve/Jam
- GC-MS/MS
- Multi-residue Method
- Selected Reaction Monitoring
- Pesticide Residues

Introduction

Pesticides are widely used in agriculture to protect crops and to improve efficiency of production. Consequently, governments, food producers and food retailers have a duty to ensure that any residues occurring in foods for human consumption are at or below Statutory Maximum Residue Levels (MRLs). Regulation EC 396/2005 adopted in the European Union sets MRLs for more than 500 different pesticides in over 300 different food commodities.[1] Many of these MRLs are set at a default value of 0.01 mg/kg, the typical limit of determination of routine analytical methods. Thus, there is a requirement for residue laboratories to test a wide array of foods for a large number of pesticides at concentrations at or below 0.01 mg/kg, with low costs and fast turnaround times (often < 48 hours). This is most often achieved using multi-residue methods based on the use of a combination of LC/MS/MS and GC/MS techniques to determine pesticide residues in a single generic solvent extract of the sample. One such example is the QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) procedure, which is based on acetonitrile extraction and dispersive solid phase extraction.[2] Since acetonitrile is readily compatible with LC/MS/MS and allows analysis of several hundred pesticides this approach has gained in popularity. Many of the less polar semi-volatile pesticides not amenable to LC/MS can be analysed using GC/MS. Unfortunately the analysis of acetonitrile by GC/MS is more problematic. The main issues are:

- Degradation of the GC-column phase by the polar solvent
- Poor focusing of chromatographic peaks due to the high polarity and hence the inability to create a well defined starting zone on less polar column films
- Vapor overload of the insert liner with expansion of the sample beyond insert liner dimensions due to the high thermal expansion coefficient
- Contamination of the system by co-extractives which are not removed by the simple dispersive solid phase extraction clean-up employed in QuEChERS.
- Low crop concentration in the final extracts employed by QuEChERS requiring concentration of the extracts.

Because of the above problems, the detection limits for some pesticides can be too high for analysis at the MRL. It is a common practice to overcome these difficulties by concentration of the extract by evaporation, exchanging acetonitrile to a more appropriate GC solvent, or by using large volume injection techniques. However there is the potential to lose volatile analytes (e.g. dichlorvos) during evaporation and solvent exchange. Also the use of large volume injections can lead to more rapid contamination of the injection inlet as well as degradation of the analytical column.

An alternative approach is to make use of the high sensitivity and selectivity of the Thermo Scientific TSQ Quantum XLS GC-MS/MS instrument which can achieve the 0.01 mg/kg target reporting limits even with relatively low volume injections. This also overcomes the problems associated with the thermal expansion of acetonitrile and reduces the amount of matrix injected.

This application note describes the analytical methodology for a fast multi-residue pesticide determination in a difficult matrix (fruit jam), using the QuEChERS extraction/clean-up procedure in combination with the TSQ Quantum XLS™ GC-MS/MS system as the detection system.

Experimental Conditions/Methods

Sample Preparation

The strawberry jam samples were extracted using the citrate-buffered QuEChERS procedure.[3] Homogenized sample (10 g) was mixed with water (10 mL) and acetonitrile (10 mL). After the addition of Internal Standard (triphenylphosphate, TPP) the mixture was shaken for 1 minute. Then $MgSO_4$ (4 g), NaCl (1 g), disodium hydrogen citrate (0.5 g) and trisodium citrate (1 g) were added and the mixture shaken for 1 minute and then centrifuged for 5 minutes at 3000 U/min. An aliquot of the acetonitrile portion (2 mL) was transferred to a new tube and $MgSO_4$ (300 mg) and primary-secondary amine (PSA) sorbent (50 mg) added. The mixture was shaken (1 minute) and centrifuged for 5 minutes at 3000 U/min. An aliquot of the supernatant (1 mL) was immediately transferred into a GC vial and acidified (10 µL of 5 % formic acid in acetonitrile). Then 1.0 µL of extract was injected into the GC-MS/MS system. The final concentration of sample was 1 g/mL of extract.

Instrument Setup and Conditions

Determination of pesticides was carried out using a TSQ Quantum XLS GC-MS/MS system, equipped with a split/splitless injector and TriPlus automatic liquid sampler (Thermo Fisher Scientific, Austin, USA). The analytical column used was a TR-Pesticide, 30 m x 0.25 mm i.d., 0.25 µm film thickness (Thermo Fisher Scientific, Runcorn, UK).

The GC-MS/MS conditions used are shown in Table 1, the list of selected reaction monitoring transitions applied is summarized in Table 2.

Results and Discussion

In this application note we present a simple and rapid method based on QuEChERS extraction and GC-tandem quadrupole mass spectrometry (GC/MS/MS) determination of 96 priority pesticides plus transformation products in jam samples. The samples of fruit jam were extracted with acetonitrile followed by dispersive SPE clean-up with PSA prior to detection by GC/MS/MS. The high sensitivity and selectivity of the TSQ Quantum XLS GC-MS/MS system has enabled direct splitless analysis using low volume (1.0 µL) aliquots of acetonitrile extracts. This has significantly simplified the sample preparation procedure, while meeting method performance criteria specified by EU method validation and quality control procedures for pesticide residues in food and feed.[4] To overcome matrix effects, calibration of the GC-MS/MS system was performed using matrix-matched standard calibration solutions.[5,6]

Validation of the methodology was carried out using samples spiked with known amounts of selected pesticides at concentrations between 0.01 and 0.05 mg/kg for 89 analytes. A further 7 analytes were spiked at higher levels (see Table 3), as reporting limits for these pesticides are correspondingly higher in UK monitoring. The recovery and precision data are summarized in Table 3. Except for chlorothalonil all of the pesticides met the EU DG SANCO method validation criteria.[4] Pesticides such as captan, dichlofluanid and iprodione, which are frequently difficult to analyse, showed good recovery and precision data. The study on the improvement of chlorothalonil recovery from the matrix is now under further investigation.

The calibration curves were linear over wide concentration ranges with correlation coefficients (r^2) > 0.98 for all analytes, except for dicofol. Also, the SRM chromatograms demonstrated high selectivity with no significant interferences observed and an excellent signal/noise ratio (> 5:1) for all analytes, even at the lowest calibrated level (5 ng/ml equivalent to 0.005 mg/kg). All analytes, except folpet and diphenylamine, could be confirmed with the second transition in the low level spiked samples. Examples of extracted ion chromatograms for dichlofluanid and deltamethrin at 0.01 mg/kg and captan at 0.02 mg/kg are illustrated in Figure 1. In all cases the detection limits comply with required MRLs.

Conclusion

The QuEChERS-GC/MS/MS multi-residue method described here is a simple, rapid and accurate approach suitable for the monitoring of GC amenable pesticides in accordance with EU requirements. Another advantage of the extraction method used is its applicability to pesticides amenable to LC analysis. During method validation it was found that recovery, % CV and linearity data were within EU DG SANCO criteria for all 96 pesticides, except chlorothalonil at 0.01 mg/kg and dicofol. However the recovery data for chlorothalonil spiked at 0.01 mg/kg (mean 63%, 11 % CV) and the consistent recovery and precision data obtained for dicofol showed that the methodology was suitable for screening purposes.

Extracted ion chromatograms of SRM traces of analytes demonstrated excellent selectivity with no interferences observed and excellent signal/noise ratios (> 5:1), for all analytes at the lowest calibrated level (typically 0.005 mg/kg).

The robustness of the system was further demonstrated during validation and analysis of pork ham samples for the UK Monitoring Programme, when similarly good quality analytical data was obtained for these analytes.

GC Trace Ultra Conditions		**TSQ Quantum MS/MS Conditions**	
Column	TR-Pesticide 30 m × 0.25 mm × 0.25 µm	Operating mode	Selected Reaction Monitoring (SRM)
Injector	Splitless	Ionization mode	EI
Injected volume	1 µL	Electron energy	70 eV
Injector temperature	225 °C	Emission current	50 µA
Carrier gas	Helium, 1mL/min	Q1/Q3 resolution	0.7 u (FWHM)
Oven program	60 °C hold 1 min 15 °C/min to 160 °C hold 1 min 2.2 °C/min to 230 °C hold 1 min 5 °C/min to 290 °C hold 5 min Run Time 57.15 min	Collision gas Collision gas pressure	Argon 1 mTorr
	Transfer line temperature 280 °C	Polarity	Positive

Table 1: Instrumental conditions

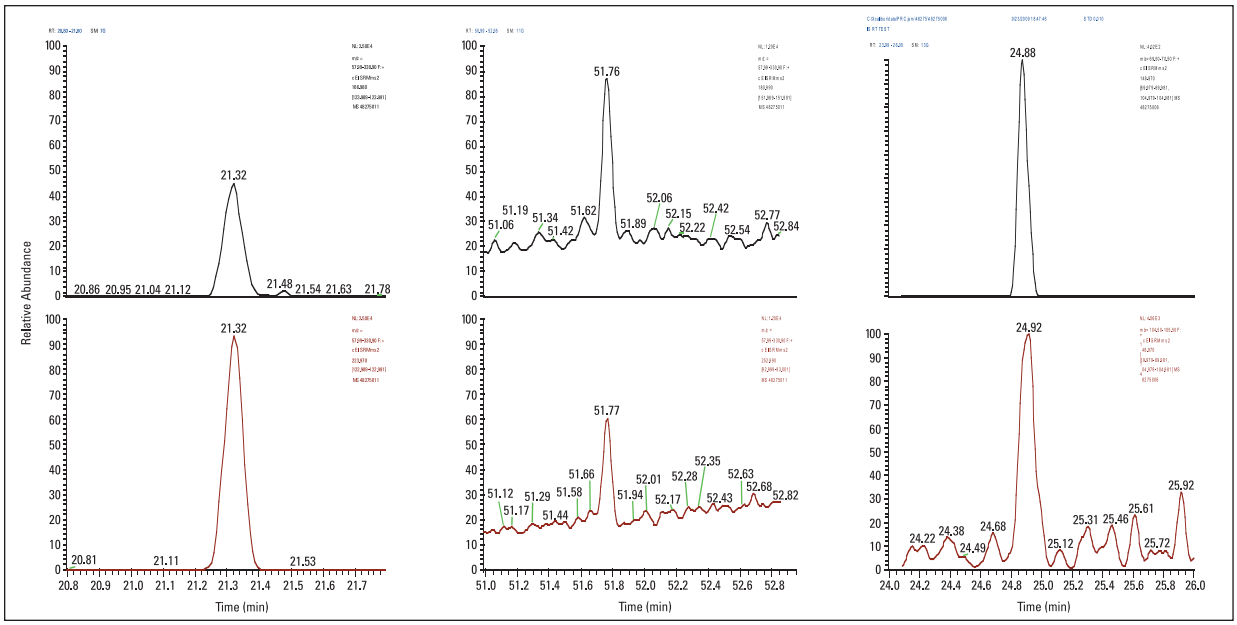

Figure 1: Extracted ion chromatogram of quantifier (upper trace) and qualifier ions (lower trace) for (A) dichlofluanid, (B) deltamethrin in a fruit preserve sample spiked at 0.01 mg kg^{-1} and (C) captan at 0.02 mg kg^{-1}. Transitions used are summarized in Table 2.

Name	Rt (min)	Transition	Precursor Ion (*m/z*)	Product Ion (*m/z*)	Collision Energy (eV)	Timed SRMs Start (min)	Timed SRMs End (min)	Polarity
dichlorvos	6.44	Quant	184.95	92.98	17	5.44	7.44	Pos
dichlorvos	6.44	Qual	219.95	184.95	10	5.44	7.44	Pos
propham	8.90	Quant	179.09	137.07	10	7.90	9.90	Pos
propham	8.90	Qual	137.07	93.05	8	7.90	9.90	Pos
phthalimide (folpet bd*)	9.05	Quant	147.03	103.02	10	8.05	10.05	Pos
phthalimide (folpet bd*)	9.05	Qual	147.03	76.02	10	8.05	10.05	Pos
tetrahydrophthalimide (captan bd*)	9.35	Quant	151.06	122.05	10	8.35	10.35	Pos
tetrahydrophthalimide (captan bd*)	9.35	Qual	151.06	79.03	10	8.35	10.35	Pos
methacrifos	9.62	Quant	208.02	180.02	10	8.62	10.62	Pos
methacrifos	9.62	Qual	240.02	208.02	10	8.62	10.62	Pos
tecnazene	11.69	Quant	260.88	202.90	15	10.69	12.69	Pos
tecnazene	11.69	Qual	258.88	200.90	15	10.69	12.69	Pos
propachlor	11.80	Qual	176.06	120.04	10	10.80	12.80	Pos
propachlor	11.80	Qual	196.07	120.04	10	10.80	12.80	Pos
diphenylamine	12.02	Quant	167.09	139.07	25	11.02	13.02	Pos
ethoprophos	12.19	Quant	200.05	158.04	10	11.19	13.19	Pos
ethoprophos	12.19	Qual	158.04	114.03	10	11.19	13.19	Pos
chlorpropham	12.59	Quant	213.06	171.04	10	11.59	13.59	Pos
chlorpropham	12.59	Qual	213.06	127.03	15	11.59	13.59	Pos
dicrotophos	13.02	Quant	127.04	109.04	10	12.02	14.02	Pos
dicrotophos	13.02	Qual	193.06	127.04	10	12.02	14.02	Pos
trifluralin	13.14	Quant	306.10	264.09	15	12.14	14.14	Pos
trifluralin	13.14	Qual	264.09	160.05	15	12.14	14.14	Pos
cadusafos	13.41	Quant	159.05	131.04	10	12.41	14.41	Pos
cadusafos	13.41	Qual	159.05	97.03	20	12.41	14.41	Pos
hexachlorobenzene	14.27	Quant	283.81	248.84	20	13.27	15.27	Pos
hexachlorobenzene	14.27	Qual	285.81	250.83	20	13.27	15.27	Pos
dicloran	14.48	Quant	205.97	175.97	10	13.48	15.48	Pos
dicloran	14.48	Qual	207.96	177.97	10	13.48	15.48	Pos
simazine	14.80	Quant	201.08	173.07	10	13.80	15.80	Pos
simazine	14.80	Qual	201.08	138.05	10	13.80	15.80	Pos

Table 2: Selected Reaction Monitoring transitions used

Name	Rt (min)	Transition	Precursor Ion (*m/z*)	Product Ion (*m/z*)	Collision Energy (eV)	Timed SRMs Start (min)	Timed SRMs End (min)	Polarity
carbofuran	14.88	Quant	164.08	149.07	10	13.88	15.88	Pos
carbofuran	14.88	Qual	221.11	164.08	5	13.88	15.88	Pos
HCH-gamma	15.53	Quant	218.89	182.91	15	14.53	16.53	Pos
HCH-gamma	15.53	Qual	180.91	108.95	25	14.53	16.53	Pos
quintozene	15.80	Quant	248.86	213.88	10	14.80	16.80	Pos
quintozene	15.80	Qual	294.84	236.87	20	14.80	16.80	Pos
fonofos	15.97	Quant	246.03	137.02	10	14.97	16.97	Pos
fonofos	15.97	Qual	137.02	109.01	10	14.97	16.97	Pos
diazinon	16.48	Quant	152.00	137.00	10	15.48	17.48	Pos
diazinon	16.48	Qual	304.10	179.06	15	15.48	17.48	Pos
tefluthrin	17.12	Quant	177.02	127.02	20	16.12	18.12	Pos
tefluthrin	17.12	Qual	197.03	141.02	15	16.12	18.12	Pos
chlorothalonil	17.14	Quant	265.88	169.92	20	16.14	18.14	Pos
chlorothalonil	17.14	Qual	265.88	132.94	20	16.14	18.14	Pos
etrimfos	17.35	Quant	292.06	181.04	10	16.35	18.35	Pos
etrimfos	17.35	Qual	292.06	153.03	10	16.35	18.35	Pos
formothion	17.94	Quant	126.00	93.00	8	16.94	18.94	Pos
formothion	17.94	Qual	224.00	125.00	15	16.94	18.94	Pos
chlorpyrifos-methyl	19.23	Quant	285.91	92.97	15	18.23	20.23	Pos
chlorpyrifos-methyl	19.23	Qual	124.96	78.97	10	18.23	20.23	Pos
parathion-methyl	19.23	Quant	263.00	109.00	15	18.23	20.23	Pos
parathion-methyl	19.23	Qual	263.00	127.00	20	18.23	20.23	Pos
vinclozolin	19.25	Quant	285.00	212.00	15	18.25	20.25	Pos
vinclozolin	19.25	Qual	212.00	172.00	15	18.25	20.25	Pos
tolclofos-methyl	19.48	Quant	264.96	249.96	18	18.48	20.48	Pos
tolclofos-methyl	19.48	Qual	264.96	219.97	20	18.48	20.48	Pos
fenitrothion	21.01	Quant	277.02	260.02	10	20.01	22.01	Pos
fenitrothion	21.01	Qual	277.02	109.01	20	20.01	22.01	Pos
pirimiphos-methyl	21.21	Quant	290.09	233.07	10	20.21	22.21	Pos
pirimiphos-methyl	21.21	Qual	305.10	290.09	15	20.21	22.21	Pos
ethofumesate	21.25	Quant	286.11	207.08	12	20.25	22.25	Pos
ethofumesate	21.25	Qual	207.08	161.06	10	20.25	22.25	Pos
dichlofluanid	21.45	Quant	223.97	122.99	15	20.45	22.45	Pos
dichlofluanid	21.45	Qual	166.98	123.99	12	20.45	22.45	Pos
aldrin	21.71	Quant	262.91	192.93	32	20.71	22.71	Pos
aldrin	21.71	Qual	292.90	257.91	20	20.71	22.71	Pos
chlorpyrifos	22.40	Quant	196.96	168.96	15	21.40	23.40	Pos
chlorpyrifos	22.40	Qual	313.93	257.95	15	21.40	23.40	Pos
dichlorobenzophenone, 4,4'- (dicofol bd*)	22.47	Quant	139.00	111.00	15	21.47	23.47	Pos
dichlorobenzophenone, 4,4'- (dicofol bd*)	22.47	Qual	250.00	139.00	10	21.47	23.47	Pos
parathion-ethyl	22.47	Quant	291.03	109.01	15	21.47	23.47	Pos
parathion-ethyl	22.47	Qual	125.01	97.01	8	21.47	23.47	Pos
chlorthal-dimethyl	22.71	Quant	331.90	300.91	15	21.71	23.71	Pos
chlorthal-dimethyl	22.71	Qual	300.91	222.93	25	21.71	23.71	Pos
isocarbofos	22.89	Quant	119.98	92.30	10	21.89	23.89	Pos
isocarbofos	22.89	Qual	135.96	108.34	10	21.89	23.89	Pos
nitrothal-isopropyl	23.10	Quant	236.08	194.07	10	22.10	24.10	Pos
nitrothal-isopropyl	23.10	Qual	236.08	148.05	20	22.10	24.10	Pos
pirimiphos-ethyl	24.08	Quant	304.12	168.06	15	23.08	25.08	Pos
pirimiphos-ethyl	24.08	Qual	318.12	166.06	13	23.08	25.08	Pos
isofenphos-methyl	24.22	Quant	199.06	121.04	15	23.22	25.22	Pos
isofenphos-methyl	24.22	Qual	241.07	199.06	10	23.22	25.22	Pos
oxychlordane	24.47	Quant	386.79	262.86	15	23.47	25.47	Pos
oxychlordane	24.47	Qual	386.79	322.83	15	23.47	25.47	Pos

Table 2 Continued: Selected Reaction Monitoring transitions used

Name	Rt (min)	Transition	Precursor Ion (*m/z*)	Product Ion (*m/z*)	Collision Energy (eV)	Timed SRMs Start (min)	Timed SRMs End (min)	Polarity
pendimethalin	24.57	Quant	252.12	162.08	12	23.57	25.57	Pos
pendimethalin	24.57	Qual	252.12	191.09	12	23.57	25.57	Pos
pyrifenox-e (peak 1)	24.93	Quant	262.03	200.02	20	23.93	27.72	Pos
pyrifenox-e (peak 1)	24.93	Qual	262.03	192.02	20	23.93	27.72	Pos
tolylfluanid	24.98	Quant	238.09	137.05	15	23.98	25.98	Pos
tolylfluanid	24.98	Qual	137.05	91.03	20	23.98	25.98	Pos
chlozolinate	25.08	Quant	331.00	259.00	8	24.08	26.08	Pos
chlozolinate	25.08	Qual	259.00	188.00	8	24.08	26.08	Pos
captan	25.10	Quant	148.97	104.98	10	24.10	26.10	Pos
captan	25.10	Qual	148.97	69.98	15	24.10	26.10	Pos
isofenphos	25.31	Quant	213.07	121.04	17	24.31	26.31	Pos
isofenphos	25.31	Qual	213.07	185.06	10	24.31	26.31	Pos
quinalphos	25.44	Quant	146.03	118.02	15	24.44	26.44	Pos
quinalphos	25.44	Qual	157.03	129.02	13	24.44	26.44	Pos
folpet	25.54	Quant	259.91	129.96	16	24.54	26.54	Pos
folpet	25.54	Qual	146.95	102.97	10	24.54	26.54	Pos
furalaxyl	25.78	Quant	242.11	95.04	15	24.78	26.78	Pos
furalaxyl	25.78	Qual	301.13	225.10	10	24.78	26.78	Pos
procymidone	25.90	Quant	283.02	96.01	15	24.90	26.90	Pos
procymidone	25.90	Qual	283.02	255.02	10	24.90	26.90	Pos
chlordane (*cis/trans*)**	26.05	Quant	373.00	264.00	15	25.05	28.14	Pos
chlordane (*cis/trans*)**	26.05	Qual	372.81	265.87	15	25.05	28.14	Pos
methidathion	26.34	Quant	144.98	84.99	10	25.34	27.34	Pos
methidathion	26.34	Qual	144.98	57.99	15	25.34	27.34	Pos
bromophos-ethyl	26.56	Quant	358.89	302.91	20	25.56	27.56	Pos
bromophos-ethyl	26.56	Qual	358.89	330.90	10	25.56	27.56	Pos
endosulfan (I)	26.88	Quant	240.89	205.91	20	25.88	27.88	Pos
endosulfan (I)	26.88	Qual	271.88	236.89	10	25.88	27.88	Pos
tetrachlorvinphos	27.17	Quant	328.91	108.97	22	26.17	28.17	Pos
tetrachlorvinphos	27.17	Qual	330.91	315.91	22	26.17	28.17	Pos
hexaconazole	28.07	Quant	214.05	187.04	15	27.07	29.07	Pos
hexaconazole	28.07	Qual	214.05	159.04	15	27.07	29.07	Pos
prothiofos	28.41	Quant	308.97	238.97	5	27.41	29.41	Pos
prothiofos	28.41	Qual	266.97	238.97	10	27.41	29.41	Pos
dieldrin	28.74	Quant	276.91	240.92	10	27.74	29.74	Pos
dieldrin	28.74	Qual	262.91	192.93	26	27.74	29.74	Pos
DDE-pp	28.89	Quant	245.95	175.97	25	27.89	29.89	Pos
DDE-pp	28.89	Qual	317.94	247.95	20	27.89	29.89	Pos
fludioxonil	29.04	Quant	248.04	154.02	20	28.04	30.04	Pos
fludioxonil	29.04	Qual	248.04	182.03	15	28.04	30.04	Pos
buprofezin	29.74	Quant	249.13	193.10	10	28.74	30.74	Pos
buprofezin	29.74	Qual	305.16	172.09	10	28.74	30.74	Pos
flusilazole	29.84	Quant	233.07	152.05	20	28.84	30.84	Pos
flusilazole	29.84	Qual	233.07	165.05	20	28.84	30.84	Pos
bupirimate	30.16	Quant	273.14	193.10	10	29.16	31.16	Pos
bupirimate	30.16	Qual	316.16	208.10	10	29.16	31.16	Pos
endosulfan (II)	30.98	Quant	240.89	205.91	20	29.98	31.98	Pos
endosulfan (II)	30.98	Qual	271.88	236.89	18	29.98	31.98	Pos
chlorobenzilate	31.33	Quant	251.02	139.01	20	30.33	32.33	Pos
chlorobenzilate	31.33	Qual	251.02	111.01	20	30.33	32.33	Pos
DDD-pp/DDT-op	31.95	Quant	234.97	164.98	20	30.95	32.95	Pos
DDD-pp/DDT-op	31.95	Qual	234.97	198.97	18	30.95	32.95	Pos
ethion	32.45	Quant	230.99	174.99	15	31.45	33.45	Pos
ethion	32.45	Qual	230.99	129.00	20	31.45	33.45	Pos

Table 2 Continued: Selected Reaction Monitoring transitions used

Name	Rt (min)	Transition	Precursor Ion (*m/z*)	Product Ion (*m/z*)	Collision Energy (eV)	Timed SRMs Start (min)	Timed SRMs End (min)	Polarity
benalaxyl	34.07	Quant	266.14	148.08	10	33.07	35.07	Pos
benalaxyl	34.07	Qual	234.12	174.09	10	33.07	35.07	Pos
endosulfan-sulphate	34.17	Quant	227.01	212.01	15	33.17	35.17	Pos
endosulfan-sulphate	34.17	Qual	271.88	236.89	15	33.17	35.17	Pos
methoxychlor bd	34.17	Quant	228.01	213.01	15	33.17	35.17	Pos
methoxychlor bd	34.17	Qual	273.88	238.89	15	33.17	35.17	Pos
DDT-pp	34.68	Quant	234.94	164.96	20	33.68	35.68	Pos
DDT-pp	34.68	Qual	234.94	198.95	15	33.68	35.68	Pos
TPP (IS)	36.19	Quant	326.07	325.00	10	35.19	37.19	Pos
TPP (IS)	36.19	Qual	326.07	215.00	25	35.19	37.19	Pos
propargite	36.26	Quant	135.06	107.05	15	35.26	37.26	Pos
propargite	36.26	Qual	173.08	105.05	12	35.26	37.26	Pos
diflufenican	36.55	Quant	394.07	266.05	10	35.55	37.55	Pos
diflufenican	36.55	Qual	266.05	246.05	10	35.55	37.55	Pos
iprodione	38.21	Quant	314.03	245.03	15	37.21	39.21	Pos
iprodione	38.21	Qual	314.03	271.03	10	37.21	39.21	Pos
phosmet	38.26	Quant	160.00	133.00	15	37.26	39.26	Pos
phosmet	38.26	Qual	160.00	77.00	20	37.26	39.26	Pos
pyridaphenthion	38.40	Quant	340.06	199.04	10	37.40	39.40	Pos
pyridaphenthion	38.40	Qual	340.06	203.04	25	37.40	39.40	Pos
bromopropylate	38.60	Quant	184.98	156.98	20	37.60	39.60	Pos
bromopropylate	38.60	Qual	342.96	184.98	20	37.60	39.60	Pos
EPN	38.70	Quant	169.02	141.02	10	37.70	39.70	Pos
EPN	38.70	Qual	157.02	110.01	15	37.70	39.70	Pos
dicofol	39.08	Quant	138.97	110.97	15	38.08	40.08	Pos
dicofol	39.08	Qual	164.09	107.06	17	38.08	40.08	Pos
tetramethrin	39.08	Quant	164.09	135.07	10	38.08	40.08	Pos
tetramethrin	39.08	Qual	250.94	138.97	15	38.08	40.08	Pos
methoxychlor	39.25	Quant	227.01	169.01	20	38.25	40.25	Pos
methoxychlor	39.25	Qual	227.01	212.01	15	38.25	40.25	Pos
TPE (alternative IS)	39.44	Quant	332.21	253.13	15	38.44	40.44	Pos
TPE (alternative IS)	39.44	Qual	332.21	254.14	15	38.44	40.44	Pos
fenpropathrin	39.60	Quant	181.09	152.07	23	38.60	40.60	Pos
fenpropathrin	39.60	Qual	265.13	210.10	15	38.60	40.60	Pos
fenazaquin	39.77	Quant	145.08	117.07	15	38.77	40.77	Pos
fenazaquin	39.77	Qual	160.09	117.07	20	38.77	40.77	Pos
tetradifon	40.61	Quant	355.88	228.93	10	39.61	41.61	Pos
tetradifon	40.61	Qual	226.93	198.94	18	39.61	41.61	Pos
phosalone	41.32	Quant	181.99	111.00	15	40.32	42.32	Pos
phosalone	41.32	Qual	366.99	181.99	10	40.32	42.32	Pos
fenarimol	43.10	Quant	139.01	111.01	15	42.10	44.10	Pos
fenarimol	43.10	Qual	251.02	139.01	15	42.10	44.10	Pos
pyrazophos	43.85	Quant	221.05	193.04	10	42.85	44.85	Pos
pyrazophos	43.85	Qual	232.05	204.05	10	42.85	44.85	Pos
bitertanol	45.06	Quant	170.09	141.07	20	44.06	46.06	Pos
bitertanol	45.06	Qual	170.09	115.06	25	44.06	46.06	Pos
permethrin *cis/trans***	45.36	Quant	183.04	168.03	15	44.36	46.36	Pos
permethrin *cis/trans***	45.36	Qual	183.04	165.03	15	44.36	46.36	Pos
pyridaben	45.58	Quant	147.06	117.04	20	44.58	46.58	Pos
pyridaben	45.58	Qual	309.12	147.06	15	44.58	46.58	Pos
cyfluthrin**	47.13	Quant	163.02	91.01	12	46.13	48.13	Pos
cyfluthrin**	47.13	Qual	226.03	206.03	5	46.13	48.13	Pos
cypermethrin**	47.94	Quant	181.03	152.03	25	46.94	48.94	Pos
cypermethrin**	47.94	Qual	163.03	127.02	10	46.94	48.94	Pos
fenvalerate-e/z**	50.14	Quant	167.05	125.04	10	49.14	51.14	Pos
fenvalerate-e/z**	50.14	Qual	419.13	225.07	10	49.14	51.14	Pos

Table 2 Continued: Selected Reaction Monitoring transitions used

Name	Rt (min)	Transition	Precursor Ion (*m/z*)	Product Ion (*m/z*)	Collision Energy (eV)	Timed SRMs Start (min)	Timed SRMs End (min)	Polarity
deltamethrin	51.85	Quant	180.99	151.99	20	50.85	52.85	Pos
deltamethrin	51.85	Qual	252.99	93.00	18	50.85	52.85	Pos
famoxadone	52.52	Quant	330.11	224.08	10	51.52	53.52	Pos
famoxadone	52.52	Qual	330.11	237.08	15	51.52	53.52	Pos

** bd* *breakdown product not in standard mix*
*** rt cis-chlordane* *27.11*
*** Rt permethrin-trans* *45.77*
*** Rt cyfluthrin-II – IV* *47.51 – 47.72*
*** Rt cypermethrin-II – IV* *48.22 – 48.61*
*** Rt fenvalerate-z* *50.64*

Table 2 Continued: Selected Reaction Monitoring transitions used

Pesticide	0.01 mg/kg mean	0.01 mg/kg CV	0.05 mg/kg mean	0.05 mg/kg CV
aldrin	89	11	94	3
benalaxyl	101	6	108	3
bromophos-ethyl	93	10	101	4
bromopropylate	93	6	104	5
bupirimate	97	9	110	3
buprofezin	97	9	110	3
cadusafos	97	6	105	4
carbofuran	95	7	107	5
chlordane-cis	90	13	104	1
chlordane-trans	94	5	101	2
chlorobenzilate	103	7	108	2
chlorothalonil	63	11	84	5
chlorpyrifos	91	8	102	1
chlorpyrifos-methyl	95	4	103	3
chlorthal-dimethyl	87	9	102	3
chlozolinate	98	15	107	5
DDD-pp	94	6	103	3
DDE-pp	85	6	97	3
DDT-op	92	7	101	3
DDT-pp	94	5	102	2
deltamethrin	93	18	104	5
diazinon	97	7	107	5
dichlofluanid	80	9	94	6
dichlorvos	95	9	105	3
dicloran	92	5	105	5
dicrotophos	89	9	103	3
dieldrin	89	7	100	3
diflufenican	101	7	109	1
endosulfan-I	94	14	101	3
endosulfan-II	94	14	105	6
endosulfan-sulfate	102	8	109	3
EPN	95	9	105	3
ethion	103	9	105	3
ethofumesate	95	5	107	4
ethoprophos	102	9	108	4
etrimfos	94	4	106	4
famoxadone	92	8	100	6
fenarimol	95	7	105	3
fenazaquin	95	13	98	5
fenitrothion	93	8	106	7
fenpropathrin	95	13	107	4
fenvalerate	97	6	103	3
fludioxonil	103	7	104	5
flusilazole	93	11	111	6
folpet	93	9	97	8
fonofos	94	8	103	3
formothion	93	7	105	3
furalaxyl	96	6	108	5
HCB	72	10	86	4
HCH-gamma	94	5	103	3
hexaconazole	99	13	105	8
iprodione	101	6	110	3
isocarbofos	97	9	111	7
isofenphos	99	5	107	2
isofenphos-methyl	100	8	105	3
methacrifos	93	7	107	3
methidathion	100	8	104	3
methoxychlor	94	10	103	2
nitrothal-isopropyl	101	9	103	5
oxychlordane	99	21	99	6
parathion-ethyl	98	6	102	3
pendimethalin	97	9	103	4
parathion-methyl	100	8	105	5
permethrin	90	7	99	3
phosalone	103	7	105	3
phosmet	102	6	105	6
pirimiphos-ethyl	97	2	106	2
pirimiphos-methyl	95	7	104	3
procymidone	93	9	105	7
propachlor	92	11	107	2
propargite	98	11	107	4
propham	95	5	104	4
prothiofos	80	7	102	4
pyrazophos	97	7	106	3
pyridaben	100	6	104	3
pyridaphenthion	97	8	107	2
pyrifenox	97	6	107	1
quinalphos	102	9	102	3
quintozene	86	9	94	5
simazine	91	7	105	7
tecnazene	81	5	95	5
tefluthrin	90	8	103	3
tetrachlorvinphos	99	3	110	3
tetradifon	97	6	107	2
tetramethrin	97	8	106	2
tolclofos-methyl	95	8	101	3
tolylfluanid	98	8	100	3
trifluralin	97	8	104	2
vinclozolin	92	5	104	6

	0.02 mg/kg		0.10 mg/kg	
captan	108	8	96	9
cyfluthrin	110	5	105	4
	0.05 mg/kg		**0.25 mg/kg**	
chlorpropham	98	7	108	5
bitertanol	98	7	103	4
cypermethrin	103	6	102	3
dicofol	108	10	94	10
diphenylamine	94	6	99	4

Table 3: Validation data for fruit preserve (jam), n = 5

References and Acknowledgements

1. REGULATION (EC) No 396/2005 and amendments, Feb. 23 2005
2. M. Anastassiades, S. Lehotay D. Steinbacher, F. Schenck, J. AOAC Int. 86 (2) (2003) 412.
3. http://www.quechers.com
4. European Commission, Doc No. SANCO/10684/2009
5. Godula M. et al, J. High Resol. Chromatogr. 1999, 22, (7) 395–402
6. Hajšlová J. et al, J. Chromatogr. A, 800 (1998) 283–295

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