Technical Note: 10238

Multi-residue Pesticide Analysis in Onion by a Modified QuEChERS Extraction and Ion Trap GC/MS^n Analysis

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Key Words

- ITQ 700
- Food Safety
- GC/MS^n
- Pesticide
- QuEChERS

Introduction

Recently formulated pesticides are quite different in their physical properties from their predecessors such as 4,4'-DDT. Most recently formulated pesticides are smaller in molecular weight and designed to break down rapidly in the environment. Therefore, to successfully identify and quantify these compounds in foods, more careful consideration must be placed on the sample preparation for extraction and the instrument parameters for analysis. This study will cover the preparation of extracts and the optimization of the analytical parameters of the splitless injection, separation, and detection.

The determination of pesticides in fruits and vegetables has been simplified by a new sample preparation method, QuEChERS (**Qu**ick, **E**asy, **Ch**eap, **E**ffective, **R**ugged and **S**afe), published recently as AOAC Method 2007.01.[1] The sample preparation is simplified by using a single step buffered acetonitrile (MeCN) extraction and liquid-liquid partitioning from water in the sample by salting out with sodium acetate and magnesium sulfate ($MgSO_4$).[1] This technical note describes the application of the QuEChERS sample preparation procedure to analysis by gas chromatography/tandem mass spectrometry (GC/MS^n) on the Thermo Scientific ITQ 700™ GC-ion trap mass spectrometer.

The study was performed to determine the linear ranges, quantitation limits and detection limits for a long list of pesticides that are commonly used on onion crops, prepared in matrix using the QuEChERS sample preparation guidelines. A splitless injection of 46 pesticides was made in a single injection with detection in EI MS/MS. Since the extracts are prepared in MeCN, a solvent exchange was made to hexane/acetone (9:1) prior to conventional splitless injection.[2] The final solvent exchange provides a final solvent that is more amenable to splitless injection. Once the calibration curve was constructed, multiple matrix spikes were analyzed at levels of 100, 200, or 300 ng/g (ppb) and low-level spikes of 5, 10, 15, 25, or 50 ng/g (ppb) were used to verify the precision and accuracy of the analytical method.

Experimental Conditions

The sample preparation involves careful homogenization of the sample. Extraction solvents must be buffered and the powdered reagents measured at appropriate amounts for the size of sample prepared. Some reagents cause an exothermic reaction when mixed with water, which can adversely affect the recoveries of target compounds. The recommended consumables required for sample

preparation and analysis were rigorously tested (Table 1). A list of the pesticides to be studied was created that would address all of the various functional groups and different physical properties of most pesticides. MS^n parameters were optimized with the use of variable buffer gas, the testing of the isolation efficiency, and adjustment of the Collision Induced Dissociation (CID) voltage. A surge splitless injection was made into a 35 % diphenyl/ 65 % dimethyl polysiloxane column, (Thermo Scientific TRACE™ TR-35MS, 30 m x 0.25 mm ID, film thickness of 0.25 µm with a 5 m guard column).

Item Descriptions
TRACE TR-35MS 35 % diphenyl/65 % dimethyl polysiloxane column, 0.25 mm x 30 m, 0.25 µm w/5m guard column
5 mm ID splitless injection port liner, 105 mm (pk of 5)
10 µL syringe
Septa (pk of 50)
Graphite liner seal (pk of 10)
Open EI ion volume
Ion volume holder
Graphite ferrule 0.1-0.25 mm (pk of 10)
Ferrule 0.4 mm ID 1/16 G/V (pk of 10)
Blank vespel ferrule Thermo Scientific MS interface (pk of 10)
2 mL amber glass vials, silanized glass, with write-on patch (pk of 100)
Blue cap with ivory PTFE/red rubber seal (pk of 100)
Acetonitrile analytical grade (4L)
Hexane GC Resolv* Grade (4 L)
Acetone GC Resolv* Grade (4 L)
Organic bottle top dispenser
HPLC grade glacial acetic acid
50 mL FEP centrifuge tubes, Nalgene brand (pk of 2)
Initial clean up tube: 15 mL tubes ENVIRO 900 mg $MgSO_4$, 300 mg PSA 150 mg C18 (pk of 50)
50 mL PP tubes 6 g $MgSO_4$, 1.5 g $CH_3CHOONa$ (anhydrous) (pk of 250)
Final clean up tube: 2 mL tubes 150 mg $MgSO_4$, 50 mg PSA (pk of 100)

Table 1: Consumables for QuEChERS sample preparation and GC/MS analysis

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Sample Extraction and Clean Up

The QuEChERS sample prep procedure consists of the steps shown in Figure 1. There are three parts: the extraction, the clean up, and a solvent exchange. During the extraction phase of the sample preparation, an observation was made that if the MeCN extract was poured into the $MgSO_4$, poor spike recoveries were observed. This is due to the exothermic reaction of the water in the sample and $MgSO_4$. Although many vendors offer the pre-measured powder reagents in a separate capped centrifuge tube, do not add the sample to these tubes. The reagents from these tubes should instead be added directly to the sample containing the acidified MeCN. Because of this, an empty 50 mL FEP extraction tube was included in the list of consumables for sample preparation.

Extraction begins by adding 15 g of a thoroughly homogenized sample of onion into this 50 mL FEP extraction tube. Care must be taken to adequately and thoroughly homogenize the sample. Then 15 mL of 1 % glacial acetic acid MeCN extraction solvent was poured into the tube on top of the sample. For the method validation (MVD) and method detection limit (MDL) samples, the surrogate and the pesticide solutions were spiked into this MeCN layer.

The tube was capped and vortexed for 30 seconds. The cap was removed and the powder reagents were poured slowly into the MeCN layer. The cap was tightened securely on the 50 mL extraction tube, and was vortexed for 30 seconds until all of the powder reagents were mixed with the liquid layers. The tube was placed on a mechanical shaker for 5 minutes and then centrifuged for 5 minutes at 3000 rpm. Next, 11 mL of the top MeCN layer was removed and transferred to a 15 mL clean-up tube. This tube was capped and vortexed for 30 seconds and centrifuged for 5 minutes at 3000 rpm. A 5 mL aliquot of the top layer was transferred into a clean test tube for solvent exchange.

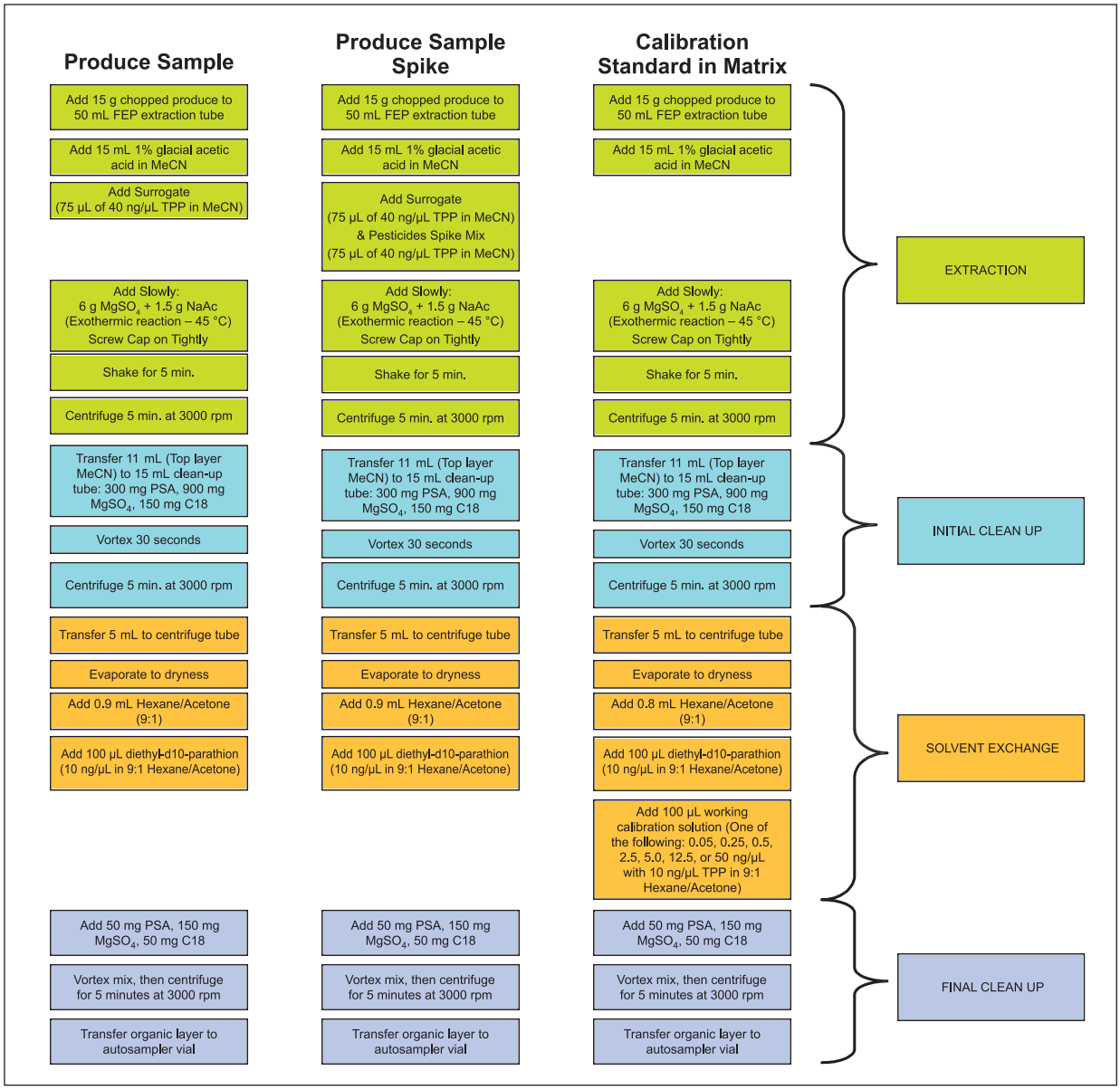

Figure 1: Flow diagram of a modified QuEChERS sample preparation process

Solvent Exchange

The 5 mL aliquot of cleaned up extract was evaporated to dryness under a gentle stream of nitrogen at 40 °C (about one hour). Care was taken to remove the tube immediately when dried. A 900 µL aliquot of hexane/acetone (9:1) was added and 100 µL of the internal standard, d10-parathion, was spiked into the organic solution. The tube was capped and vortexed for 15 seconds. The 1 mL of extract was transferred to a 2 mL clean-up tube, capped tightly, and vortexed for 30 seconds. After centrifuging for 5 minutes at 3000 rpm, 200 µL of the clear extract was transferred to an autosampler vial with a small glass insert for injection on the ITQ 700. The individual calibration levels were spiked into each extract for the calibration curve in matrix before the final cleanup step (Figure 1).

Injection

The ITQ 700 is paired with the Thermo Scientific FOCUS GC gas chromatograph, which is a single-channel GC with a standard split/splitless (SSL) injection port. The SSL inlet temperature was set to 250 °C. A 5 mm ID splitless liner with a volume of 1.6 mL was selected for the surged pressure injection. For the surge splitless injection, the inlet pressure was held at an elevated pressure of 250 kPa for the 0.5 minute injection (splitless) time. This technique reduces the vapor cloud of a 2 µL injection from 0.37 mL to 0.19 mL. At an elevated injection flow rate of 4.6 mL/min, the liner was swept several times during injection. The target compounds moved through the inlet so rapidly that they had less time to interact with the inside walls of the liner. This minimized the amount of breakdown of the more fragile pesticides.

A Performance Solution consisting of DFTPP, endrin and 4,4'-DDT was analyzed as a daily check to determine system activity. The analysis of endrin and its breakdown products as part of daily quality control can alert the analyst that the system has developed active sites and maintenance is needed. Without performing a breakdown analysis of endrin, the laboratory may need to continually maintain the equipment and replace consumables, even when it may not be needed. This can decrease the cost of running the analysis and save significant amounts of time. Endrin breakdown is determined by adding up the response for the two breakdown products: endrin aldehyde and endrin ketone and dividing by the total response for the breakdown products and endrin in percent. The breakdown check results showed < 5 % endrin breakdown on a daily basis. For routine use the liner would be changed when the breakdown reaches > 20%. The injection port liner tested showed very good results over a long period of time without the need for maintenance (Figure 2).

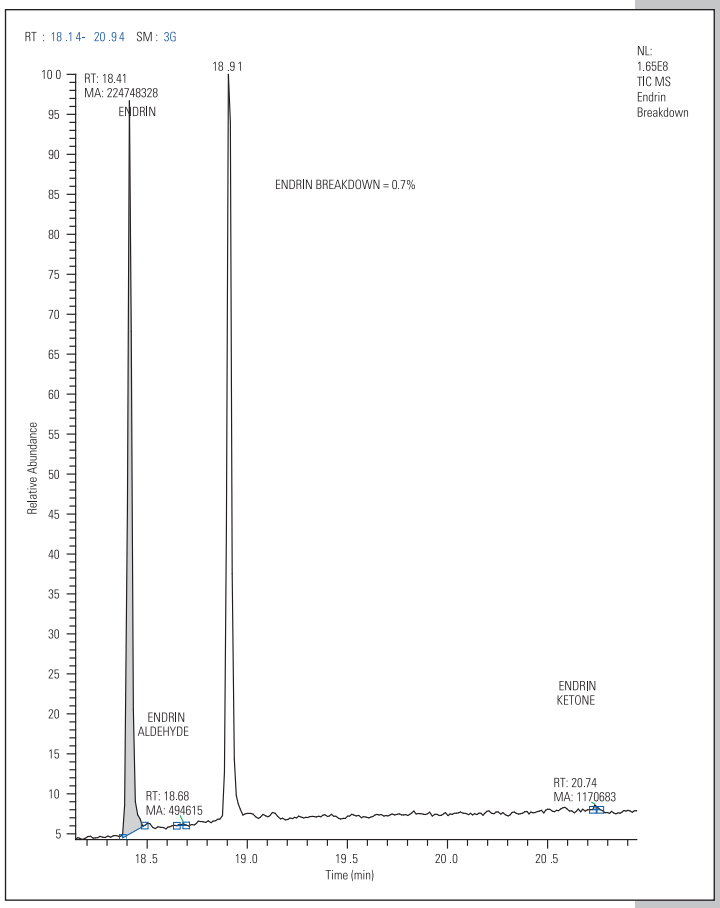

Figure 2: Chromatogram of endrin breakdown, demonstrating low breakdown and good system inertness

Separation

Chromatographic separation was achieved by using a 35 % diphenyl/65 % dimethyl polysiloxane column (30 m x 0.25 mm ID, film thickness of 0.25 µm with a 5m guard column). This column was chosen to improve the resolution of the more polar compounds. Interactions within the stationary phase showed a loss of certain pesticides at concentrations below 100 pg. The oven was programmed as follows:

Initial Temp: 40 °C, initial hold of 1.5 min
First Ramp: 25 °C/min to 150 °C; hold 0.0 min
Second Ramp: 5 °C/min to 225 °C; hold 7.5 min
Final Ramp: 25 °C/min to 290 °C; final hold time of 12 min

A constant column flow rate of 1 mL/min was used for the duration of the run. The entire set of instrument parameters is listed in Table 2.

Detection

The detection of the pesticides was performed using the ITQ 700 ion trap mass spectrometer with optional MS^n mode. This scanning mode offers enhanced selectivity over scanning modes such as full scan and selected ion monitoring (SIM). In SIM at the elution time of each pesticide, the ratio of the intensity of matrix ions increases exponentially versus that of the pesticide ions as the concentration of the pesticide approaches the detection limit, decreasing the accuracy at lower levels. The ITQ 700 operated in the MS^n mode

performs tandem MS functions by injecting ions into the ion trap and destabilizing matrix ions, isolating only the pesticide ion. These pesticide ions are give sufficient energy to further fragment and are then scanned. This process provides the product ion spectrum. This is done by setting up a stable field for the pesticide precursor ion. Once the precursor ion is isolated from the matrix ions, Collision Induced Dissociation (CID) energy is applied to fragment it into its respective product ions. Finally these unique product ions are scanned out to generate the product ion spectrum. Because of the elimination of matrix interferences, this process produces more accurate results at the lower levels. The MS″ parameters for the ITQ 700 are listed in Table 3. Figures 3 and 4 show a comparison between a Full Scan and MS″ TIC.

AS 3000 Autosampler	
Sample Volume	2 µL
Plunger Strokes	5
Viscous Sample	No
Sampling Depth in Vial	Bottom
Injection Depth	Standard
Pre-inj Dwell Time	0
Post-inject Dwell Time	0
Pre-inject Solvent Wash Vial Position	A + B
Pre-inject Solvent Wash Cycles	3
Sample Rinses	3
Post-inject Solvent	A
Post-inject Solvent Cycles	3
FOCUS GC	
Column	TRACE TR-35 35 % diphenyl/65 % dimethyl polysiloxane (30 m x 0.25 mm x 0.25 µm w/ 5m guard column)
Column Constant Flow	1 mL/min
Oven Program	40 °C, 1.5 min, 25 °C/min; 150 °C, 0.0 min, 5 °C/min; 225 °C, 7.5 min, 25 °C/min; 290 °C, 12 min
S/SL Temperature	250 °C
S/SL Mode	Splitless with Surge Pressure
Surge Pressure	250 kPa
Inject Time	0.5 min
Split Flow	50 mL/min
Transferline Temperature	290 °C
ITQ Mass Spectrometer	
Damping Gas Flow	2
Source Temperature	250 °C
Ion Volume	Open EI
Emission Current	250 µA
Detector Gain	3 (1367 V)
Lens 1	-25V
Lens 3	-25V
Gate Lens On	-100
Gate Lens Off	100
Electron Lens On	15V
Electron Lens Off	85
Electron Energy	-70 eV
Trap Offset	-10
Waveforms	Off

Table 2: Instrument parameters for the AS 3000 autosampler, FOCUS GC, and ITQ-700 MS system

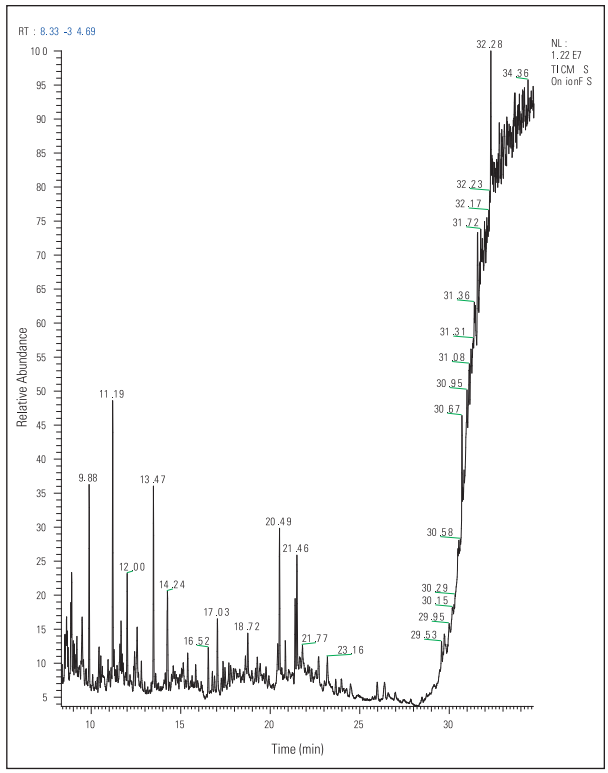

Figure 3: Total ion chromatogram of full scan data for 50 ng/g of pesticides in onion matrix

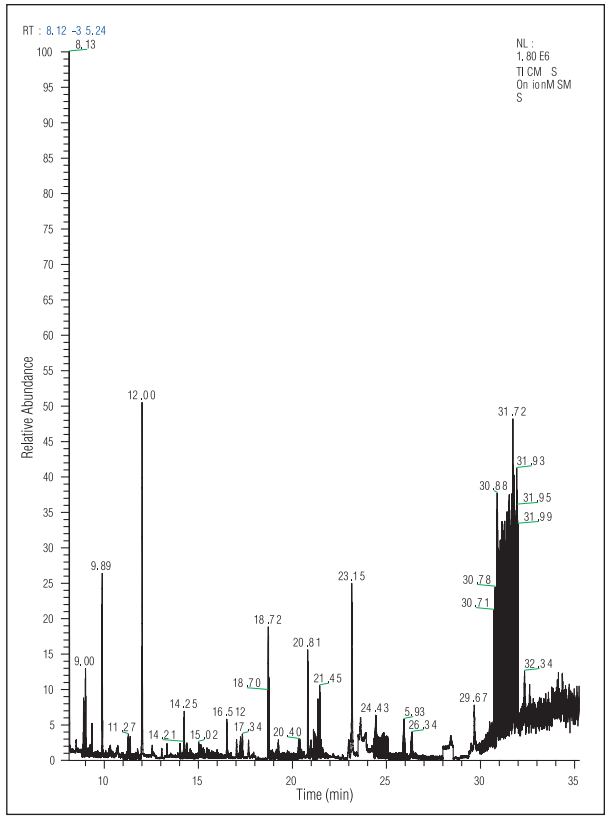

Figure 4: Total ion chromatogram of the MS/MS analysis of 50 ng/g pesticides in onion matrix

Compound	Precursor *(m/z)*	Isolation Width *(m/z)*	CID Voltage	Excitation Energy (q)	Product Ion Range *(m/z)*	Product Ion *(m/z)*	Qualifiers *(m/z)*
Dichlorovos	185	1	3	0.225	53-195	93	131, 109, 170, 63
EPTC	128	3	2	0.3	73-138	86	83, 84, 85
Mevinphos	127	1	7	0.3	69-137	109	95, 79
Etridazole	211	5	3	0.225	173-221	183	185, 184
Molinate	126	2	3	0.3	45-136	98	83, 55, 82, 81
Trifluralin	264	2	3	0.225	150-274	206	188, 160, 171, 177
Cyanophos (Thionazin)	140	2	3	0.3	95-150	107	105, 106, 112, 125
Ethoprophos	158	2	2	0.225	84-168	114	130, 94, 140
Di-allate	234	3	3	0.225	140-244	192	150,193
Propazine	214	5	4	0.225	162-224	172	174, 173
Atrazine	200	6	4	0.225	84-210	122	132, 94, 134, 158
Diazanon	179	1	4	0.225	86-189	137	164, 138, 161, 96
Gamma-BHC (Lindane)	219	4	3	0.225	171-229	181	183, 182, 184
Disulfoton	153	3	3	0.225	87-163	125	124, 123, 97
Heptachlor	272	2	3	0.225	225-282	237	235, 268, 266, 264
Vinclozolin	212	1	4	0.225	131-224	172	177, 141, 149
Prometryn	241	6	4	0.225	156-251	199	226, 198, 184, 166
Metalaxyl	160	1	3	0.225	120-170	145	130, 132
Metribuzin	198	2	4	0.225	93-208	151	103, 110, 153, 128
Triadimefon	208	3	3	0.225	129-218	180	181, 172, 139, 144
Thiobencarb	100	3	5	0.45	52-110	72	71, 73, 99, 62
Dursban (Chlorpyrifos)	314	5	3	0.225	248-324	286	258, 287, 288, 285
Sevin (Carbaryl)	144	1	3	0.3	105-154	116	115, 142, 109
Malathion	173	3	4	0.225	125-183	136	145, 137, 138, 127
Methiocarb	168	1	3	0.225	99-178	153	109
Parathion	291	4	3	0.225	99-301	142	263, 137, 109, 114
Heptachlor-2,3-exo-epoxide	353	4	4	0.225	251-363	263	261, 317, 315, 325
Cyprodinil	224	1	5	0.225	173-234	208	209, 207, 197, 183
Cyanazine	225	5	4	0.225	162-235	189	172, 198, 174
trans-Chlordane	375	4	4	0.225	256-385	301	266, 337, 303, 339
Terbufos (Sulfone)	199	7	3	0.225	133-209	171	172, 153, 143, 173
cis-Chlordane	373	5	4	0.225	254-383	301	337, 299, 264, 335
Endosulfan A	241	1	4	0.225	160-251	206	170, 204, 205
Tetrachlorvinphos (Stirofos)	331	1	4	0.225	99-341	316	109, 318, 301, 268
p,p-DDE	246	1	5	0.225	167-256	177	211, 213, 212, 176
Thiabendazole	201	1	4	0.3	164-211	174	175, 169, 168
Dieldrin	277	3	4	0.225	197-287	241	242, 239, 207, 217
Chlorobenzilate	251	4	3	0.225	129-261	139	141, 140
Endrin	263	1	5	0.225	183-273	228	230, 226, 229, 193
Endosulfan B	195	2	4	0.225	148-205	159	160, 158, 157
p,p-DDT	235	4	4	0.225	156-245	166	200,199,201, 202
Endosulfan Sulfate	387	2	3	0.225	241-397	289	253, 254, 251, 277
Bifenthrin	181	7	4	0.225	143-191	166	165, 167, 178, 153
Methoxychlor	227	7	5	0.225	175-237	212	195, 196, 185, 197
cis-Permethrin	183	3	4	0.225	143-193	168	165, 155, 153, 154
trans-permethrin	183	3	4	0.225	143-193	168	165, 155, 153, 154

Table 3: Detailed MS/MS settings for the ITQ 700 with optional MS^n

Results and Discussion

Linearity

The calibration curve was spiked into the onion matrix. Levels ranged from 1 ng/g to 1200 ng/g, depending on the compound and its MRL in onion. The linearity for most compounds was R^2>0.995. The results of the linearity for the full set of pesticides analyzed are shown in Table 4. Figures 5 and 6 show calibration curves for atrazine and molinate.

Limits of Detection and Quantitation

The actual limit of detection (LOD) and limit of quantitation (LOQ) were determined by preparing matrix spikes at a level near or below the MRL. Concentrations of 5, 10, 15, 25, and 50 ng/g were analyzed in ten matrix samples and the LOD and LOQ calculated from these results by multiplying the standard deviation by 2.821 and 10 respectively. The recovery of the 10 standards ranged from 79-159% with an average of 116%. The results are shown in Table 5.

Method Validation Results

The method validation (MVD) calculations were performed using Thermo Scientific EnviroLab™ Forms data analysis and reporting software on twelve matrix samples spiked at concentrations of 100, 200, and 300 ng/g. These samples had an average recovery of 104%, with an average % RSD of 22%. MVD results are shown in Table 6.

Conclusions

The Thermo Scientific ITQ 700 GC-ion trap MS was thoroughly evaluated and showed excellent accuracy at low concentrations for a large number of pesticide residues analyzed in onion. Using the instrument's MS^n functionality allows the user to identify, confirm, and quantify in one analytical run. The injector demonstrated low endrin breakdown (< 5%) on a daily basis, proving that the system can analyze active compounds without the need for continual, expensive, and time-consuming maintenance. Calibration curves for the pesticides studied met a linear least squares calibration with a correlation coefficient of R^2 > 0.995 for most compounds. The Method Validation Study generated an average % RSD of 22% for twelve replicate analyses at 100, 200, and 300 ng/g and a calculated average LOD of 8 ng/g in onion, based on 10 replicate analyses of 5, 10, 15, 25, and 50 ng/g.

References

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2. Rapid Method for the Determination of 180 Pesticide Residues in Foods by Gas Chromatography/Mass Spectrometry and Flame Photometric Detection, M. Okihashi, Journal Pesticide Science, 304 (4), (2005) 368-377
3. Commission Decision of August 12, 2002 Implementing Council Directive 96/23/EC Concerning the Performance of Analytical Methods and the Interpretation of Results, Official Journal of European Communities, 17.8.2002
4. MRLs for lettuce as listed at http://www.codexalimentarius.net/mrls/pestdes/jsp/pest_q-e.jsp

Compound	(R^2)	Compound	(R^2)	Compound	(R^2)	Compound	(R^2)
Dichlorvos	0.9995	Gamma-BHC	0.9999	Methiocarb	0.9998	Dieldrin	0.9995
EPTC	1.0000	Disulfoton	0.9993	Parathion	0.9983	Chlorobenzilate	0.9996
Mevinphos	0.9999	Heptachlor	0.9977	Heptachlor-2,3-exo-epoxide	0.9918	Endrin	0.9998
Etridazole	0.9988	Vinclozolin	0.9998	Cyprodinil	0.9997	Endosulfan B	0.9997
Molinate	0.9994	Prometryn	0.9991	Cyanazine	0.9972	p,p-DDT	0.9985
Trifluralin	0.9978	Metalaxyl	0.9998	*trans*-Chlordane	0.9928	Endosulfan Sulfate	0.9971
Cyanophos (Thionazin)	1.0000	Metribuzin	0.9995	Terbufos_Sulfone	0.9996	Bifenthrin	0.9975
Ethoprophos	0.9995	Triadimefon	0.9992	*cis*-Chlordane	0.9998	Methoxychlor	0.9999
Di-allate	0.9996	Thiobencarb	0.9985	Endosulfan_A	0.9998	*cis*-Permethrin	0.9977
Propazine	0.9993	Dursban (Chlorpyrifos)	0.9994	Tetrachlorvinphos (Stirofos)	0.9989	*trans*-Permethrin	0.9977
Atrazine	0.9996	Sevin (Carbaryl)	0.9997	p,p-DDE	0.9994		
Diazanon	0.9999	Malathion	0.9999	Thiabendazole	0.9997	**Average**	**0.9989**

Table 4: Calibration curve result summary for pesticides in onions

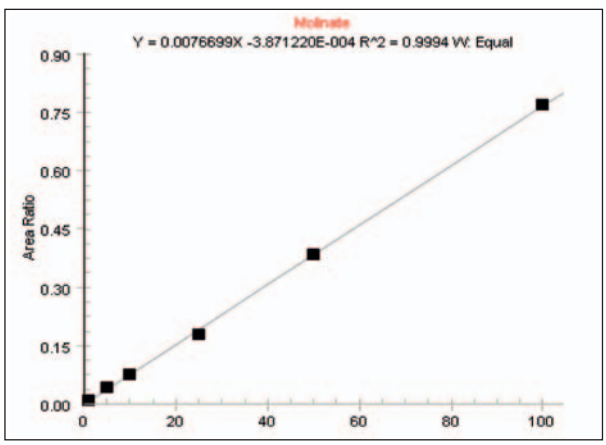

Figure 5: Calibration curve for molinate, from 1 ng/g to 100 ng/g, R^2 = 0.9994

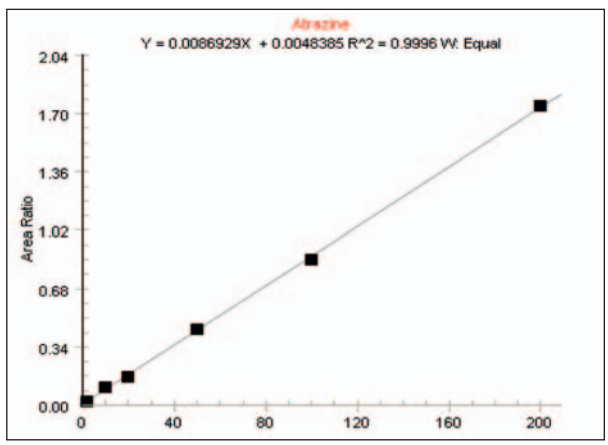

Figure 6: Calibration curve for atrazine, from 1 ng/g to 200 ng/g, R^2 = 0.9996

Component	Ave. Conc. (ng/g)	Std. Dev.	% Recovery	% RSD	LOD (ng/g)	LOQ (ng/g)	Japan[1] MRL (ng/g)	US-EPA[2] MRL (ng/g)	EU[3] MRL (ng/g)	EU[3] LOD[3]	WHO[4] MRL (ng/g)
Dichlorvos	63	3.00	126	5	8	30	100		100		
EPTC	22	1.95	86	9	6	20	40				
Mevinphos	48	3.84	96	8	11	38	100		100		
Etridazole	34	2.46	135	7	7	25	100				
Molinate	6	0.62	123	10	2	6	20				
Trifluralin	31	1.55	126	5	4	16	50				
Cyanophos (Thionazin)	27	3.16	108	12	9	32	50				
Ethoprophos	28	1.90	111	7	5	19	20				
Di-allate	31	2.47	125	8	7	25	50		50	50	
Propazine	66	6.47	132	10	18	65	100				
Atrazine	12	1.56	116	13	5	16	20		100	100	
Diazanon	15	0.88	149	6	3	9	50	750			50
Gamma-BHC (Lindane)	12	1.40	121	12	4	14	2000	1000	10	10	
Disulfoton	15	1.81	152	12	6	18	50		20	20	
Heptachlor	5	1.21	92	26	4	12	30		10	10	
Vinclozolin	13	1.03	130	8	3	10	1000	1000	1000	50	1000
Prometryn	60	7.45	120	12	21	74	50				
Metalaxyl	22	3.04	88	14	9	30	2000	3000	500	50	2000
Metribuzin	30	2.54	120	8	7	25	500				
Triadimefon	28	2.24	111	8	6	22	500		500	100	
Thiobencarb	30	3.00	120	10	8	30	200				
Dursban (Chlorpyrifos)	15	2.07	102	13	7	21	50	300	200	50	200
Sevin (Carbaryl)	23	2.45	92	11	7	25	3000		100		
Malathion	29	4.41	114	15	12	44	8000	8000	3000		1000
Methiocarb	26	2.63	103	10	7	26	50				500
Parathion	31	2.45	124	8	7	24	300		50	50	
Heptachlor-2,3-exo-epoxide	4	1.08	79	27	3	11		30			
Cyprodinil	32	4.17	128	13	12	42	50	600			300
Cyanazine	27	3.40	108	13	10	34	50				
trans-Chlordane	3	0.84	54	31	3	8	20				
Terbufos Sulfone	14	2.20	138	16	7	22	50				
cis-Chlordane	5	0.55	99	11	2	5	20				
Endosulfan A	26	3.24	103	13	9	32	200				
Tetrachlorvinphos (Stirofos)	34	2.26	136	7	6	23	300				
p,p-DDE	29	2.74	116	9	8	27		500			
Thiabendazole	28	3.54	111	13	10	35	2000				
Dieldrin	28	2.58	114	9	7	26		50			
Chlorobenzilate	14	1.20	138	9	4	12	20		20	20	
Endrin	5	0.96	104	18	3	10	10		10	10	
Endosulfan B	31	2.37	125	8	7	24	200		50	50	
p,p-DDT	40	2.09	159	5	6	21	500				
Endosulfan Sulfate	40	7.77	79	20	22	78	200				
Bifenthrin	33	3.15	134	9	9	32	50		50	50	
Methoxychlor	7	2.12	135	31	7	21	10		10	10	
cis-Permethrin	60	5.32	120	9	15	53	3000*	100*	50*	50*	
trans-Permethrin	13	3.091	133	23	10	31					
Average			**116**	**12**	**8**	**27**					

1. Japanese Food Chemical Research Foundation (www.m5.ws001.squarestart.ne.jp/foundation/search.html)

2. Informal coordination of MRLs established in Directives 76/895/EEC, 86/362/EEC, 86/363/EEC, and 90/642/EEC (5058/VI/98

3. 40CFR180 (www.access.gpo.gov/nara/cfr/waisidx_02/40cfr180_02.html)

4. CODEX alimentarius (www.codexalimentarius.net/mrls/pesticides/jsp/pest-q-e.jsp)

**Total Permethrins*

Table 5: Comparison of LODs and LOQs to published MRLs from various agencies

Component	Avg Conc	Theo Conc	% Recovery	% Difference	% RSD
Dichlorvos	214	200	107	7.12	16.64
EPTC	112	100	112	12.33	24.48
Mevinphos	193	200	96	-3.54	19.36
Etridazole	112	100	112	11.94	17.12
Molinate	120	100	120	20.00	19.34
Trifluralin	80	100	80	-19.51	19.09
Cyanophos (Thionazin)	101	100	101	1.36	21.82
Ethoprophos	114	100	114	13.87	20.90
Di-allate	111	100	111	10.67	21.27
Propazine	229	200	114	14.50	20.42
Atrazine	257	200	128	28.36	24.38
Diazanon	228	200	114	14.10	22.53
Gamma-BHC (Lindane)	223	200	111	11.39	20.86
Disulfoton	247	200	123	23.47	22.14
Heptachlor	124	100	124	24.06	22.85
Vinclozolin	233	200	116	16.31	22.60
Prometryn	193	200	96	-3.74	20.98
Metalaxyl	77	100	77	-23.22	25.68
Metribuzin	99	100	99	-1.21	22.83
Triadimefon	86	100	86	-13.68	23.48
Dursban (Chlorpyrifos)	364	300	121	21.17	22.38
Thiobencarb	110	100	110	9.75	21.79
Sevin (Carbaryl)	98	100	98	-2.21	24.95
Malathion	117	100	117	17.00	25.17
Methiocarb	90	100	90	-10.14	23.42
Parathion	87	100	87	-12.96	22.42
Heptachlor-2,3-exo-epoxide	125	100	125	25.23	24.25
Cyprodinil	108	100	108	7.56	26.09
Cyanazine	94	100	94	-5.90	22.36
trans-Chlordane	104	100	104	3.98	17.04
Terbufos Sulfone	209	200	105	4.67	25.76
cis-Chlordane	109	100	109	8.94	23.67
Endosulfan A	106	100	106	5.61	23.16
Tetrachlorvinphos (Stirofos)	107	100	107	7.03	23.07
p,p-DDE	102	100	102	2.00	21.46
Thiabendazole	99	100	99	-0.62	24.37
Dieldrin	102	100	102	2.27	22.48
Chlorobenzilate	160	200	80	-19.79	27.40
Endrin	93	100	93	-7.26	25.35
Endosulfan B	94	100	94	-5.52	23.00
p,p-DDT	97	100	97	-2.74	20.85
Endosulfan Sulfate	203	200	102	1.57	28.03
Bifenthrin	105	100	105	4.57	22.49
Methoxychlor	100	100	100	0.34	24.71
cis-Permethrin	189	200	95	-5.34	20.97
trans-Permethrin	197	200	99	-1.32	19.13
Average			**104**		**22**

Table 6: Results of the method validation study, performed in onion matrix

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TN10238_E 09/08M