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Rapid analytical methods for quantitative analysis and screening of 66 and 225 residual pesticide compounds, respectively, in pine needles and spices using GCMS triple quadrupole

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1. Introduction

Pesticides are indispensable in the protection of agricultural crops and products from pest infestation However, over recent years there has been an increase concern on residual pesticides found in food. Pesticides are ubiquitous through the environment and even low-level concentration can cause alarm due to these compounds acute and chronic toxicity. To that end, it is pivotal that novel instrumentation be able to measure these compounds down to trace concentration, even at the low fg/ul range.

The objective of this study is to use GCMS triple quadrupole to conduct quantitative and qualitative analysis of a cocktail of pesticides in sample matrices consisting of a mixture of pine needles and various spices. The study consisted of two sample analyses: 1) a scan analysis to determine over 200 pesticides, and 2) EI quantitation of targeted pesticides.

2. Experimental

Table 1. GCMS operating condition

Gas Chromatography	GC Nexis
Injection Mode	Split, 50:1 split ratio
Injection Temperature	250 °C
Column	SH-Rxi-5 MS (30 m x 0.25 mmID x 0.25um)
Carrier Gas	Helium
Flow Control Mode	Linear Velocity, 55 cm/sec
Oven Temperature	90 °C (1 minute), 30 °C/minute to 130 °C (0 minute), 10 °C/ minute to 330 °C (2 minute)
Mass Spectrometer	TQ8050
Acquisition Mode	MRM
Interface Temperature	290 °C
Ion Source Temperature	230 °C
Detector Voltage	Relative to Tune +0.8 kV
Loop time	Loop time 0.5 seconds
Acquisition Mode	Scan
Acquisition Range (m/z)	35 – 600
Detector Voltage	Relative to Tune +0.1 kV

Figure 1. GCMS operating condition

Spiked blind samples and standards provided by the Maryland Department of Agriculture were made in 80:20 hexane:toluene. The sample set consisted of 16 vials of extract. The extracts were spiked at the MDA laboratory with 0,10,20 and 50ppb of targeted compounds. The overall quantitative analysis of these known compounds was based on a blind test to determine what vials were spiked with the given analyte and to determine each vial spiked amount concentration.

The "Smart Pesticides Database Version 2' was used to develop an EI quantitative Smart method, which allowed for the target compound MRM analysis. In the process of SMART MRM,, the dwell time of the target compound is enhanced, and the sensitivity of the method is increased. A Shimadzu split/splitless (SPL) inlet equipped with a splitless liner was used in the analyses.

Besides being used for quantitative analysis, the Smart database was used in conjunction with full Scan analysis as an effective screening method for approximately 204 pesticides. Initially, Qudrupole3 (Q3) was used for scanning throughout the range 35.00 – 600.00 m/z. The database was then used to acquire enhanced signal for these unknowns compounds. The database consists of more than 500 compounds. Included in the smart database are retention times, retention indices, MRM transitions, SIM ions as well as reference transitions and ions. After samples in this experiment were analyzed, a datafile containing a compound table was established that consisted of known retention times, quantitative and reference ions that were established in the SMART Database. This allowed for the seamless identification of compounds based on reference ion ratios and retention times.

3. Results and Discussion

Scan analysis of unknown pesticides

The GCMS-TQ8050 Q3 was used to screen for compounds in the matrix. The results indicated that there were approximately 225 compounds, including isomers, present. Figure 2A illustrates result from a Total Ion Chromatogram (TIC) from scan analysis, while Figure 2B present MRM chromatogram results from SMART MRM analysis of more than five hundred compounds in the Shimadzu Smart Pesticides database. The smart database can be an effective tool for screening for multiple compounds in a complex matrix, since unknown compound signal is enhance compared to Full scan analysis.

Once present in the matrix, these unknowns compounds were confirmed against retention times and transition ions in the compound's processing window in post run analysis. Unknown peaks with low intensity signal in the scan data appeared as higher intensity peaks in the MRM results. Thus, having better confirmation of the unknown compounds.

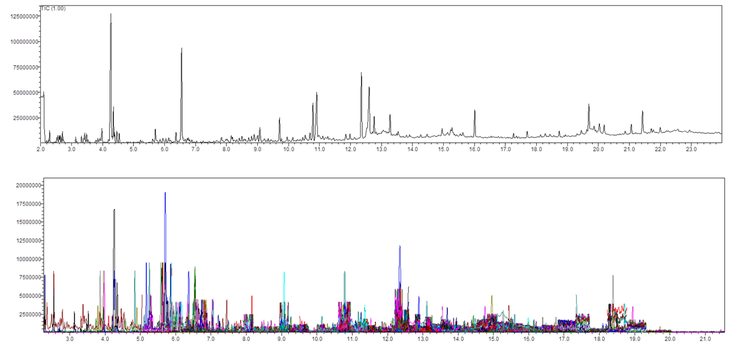

Figure 2. Total Ion Chromatogram (TIC) for scan analysis(Figure 2A, top) and MRM chromatogram of over 225 pesticides in pine needle and spice matrix (Figure 2B, bottom).

Positive EI quantitation of targeted pesticides

EI quantitative analysis of targeted compounds in pine needle and spices was conducted as per the method and summarized in Table 1. For each compound, calibration curve ranged from 2.5 to 80 ppb. Linear responses were obtained from 0.9859 to 0.9999. RF %RSD ranged from 2.892 to 57.495 (Table 2). The calibration curve was used to calculate concentration of each analyte. Calibration curves for selected compounds are displayed in Figure 2.

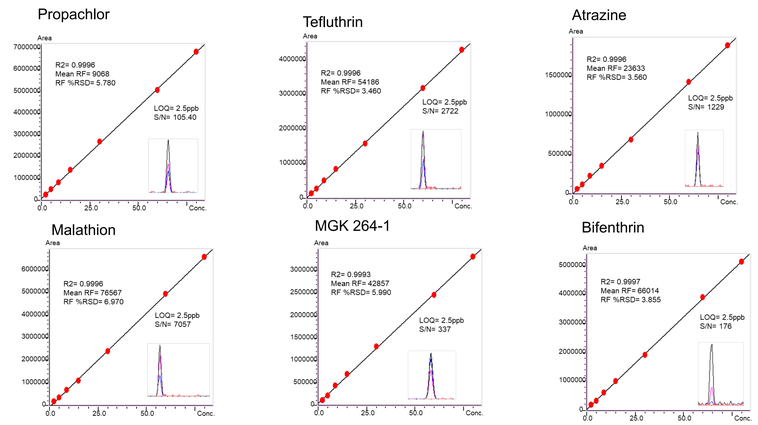

Figure 3. Calibration curves for selected compounds

Samples vial 3, 5, 13 and 15 were determined to be spiked with 10 ppb pesticide standards. Samples vials 1, 2, 7 an 12 were spiked at 20 ppb , sample vials 8, 9, 16 and 18 were spiked at 50 ppb and sample vials 4, 6, 14 and 20 were blanks. The average concentration for each of the spiked sample sets were calculated and the average percent recoveries were determined. (Table 2).

Table 2. Blind sample analysis results showing average percent recoveries from spiked samples and precision within with in the analysis.

Targeted compounds	Samples 3, 5, 13, 15 (10ppb spk.)		Samples 1, 2, 7, 12 (20 ppb spk.)		Samples 8, 9, 16, 18 (50ppb spk.)	
	AVG % recovery	%RSD	AVG %Recovery	%RSD	AVG % Recovery	%RSD
Propachlor	95	8.62	89.1	8.24	92.52	3.60
Benfluralin	134.2	2.83	74.3	2.50	108.42	3.67
Atrazine	108.6	5.41	101.35	3.66	96.14	1.78
Profluralin	126.8	10.33	74.65	2.30	107.46	1.68
Tefluthrin	92	16.00	84.7	11.67	81.52	5.34
Acetochlor	86.4	20.26	87.9	7.44	79.48	2.09
Vinclozolin	95.9	9.14	91.9	4.56	91.02	3.26
Chlorpyrifos-methyl	134.7	6.38	124.35	1.65	113.58	2.85
Parathion-methyl	150.6	5.30	137.15	4.00	126.22	1.48
Transfluthrin	71.8	3.80	78.85	2.74	73.22	2.77
Metalaxyl (Mefenoxam)	108.1	11.61	96.35	6.75	100.22	2.65
Malathion	104.5	3.48	108.1	1.50	97.64	1.42
Anthraquinone	99.1	11.08	90.9	7.02	80.36	2.80
Metolachlor (S-Metolachlor)	79.7	3.49	79.4	2.55	78.9	2.91
Chlorpyrifos	164.7	4.05	125.85	14.14	106.18	3.76
Parathion	175.3	8.30	130.35	18.32	130.6	13.75
MGK 264-1	128.3	10.45	100.8	1.26	95.76	5.47
MGK 264-2	97.9	6.26	94.5	4.75	88.18	3.20
(E)-Chlorfenvinphos	88.6	12.19	98.15	2.39	92.54	4.11
(Z)-Chlorfenvinphos	100.1	6.39	102.1	5.28	95.92	1.64
Captan	89.5	56.27	84.9	18.59	73.92	5.34
Fipronil	134.9	8.87	124.25	4.38	111.3	4.68
o,p'-DDE	90.3	6.06	98.25	4.81	95.78	2.69
Fenamiphos	126.8	7.96	127.5	5.54	112.54	4.04
p,p'-DDE	101.9	4.50	98.6	3.94	94.76	2.93
o,p'-DDD	98	3.89	97.65	2.48	95.2	3.59
p,p'-DDD	108.3	4.02	105.1	0.89	100.2	2.17
o,p'-DDT	107.8	8.65	107.25	3.83	98.2	1.34
Carfentrazone-ethyl	117.1	5.67	109.25	3.82	101.76	2.54
p,p'-DDT	108.8	9.97	98.2	6.58	94.08	3.43
Propargite-1	77.2	36.47	75.7	16.85	63.66	9.10
Propargite-2	91	6.42	75.75	16.85	63.66	9.10
Piperonyl butoxide	136.1	28.60	102	3.47	94.78	2.97
Iprodione	101.3	14.53	100.45	16.14	95.04	1.74
Tetramethrin-1	158.1	17.22	92.8	10.16	80.72	2.97
Tetramethrin-2	96.1	9.45	92.05	6.06	80.6	4.63
Bifenthrin	128.4	26.92	112.35	8.92	86.76	6.34
Phenothrin-2	98.9	2.72	98.85	10.45	83.94	5.29
Cyhalothrin-1	137.1	2.84	110.3	4.21	94.46	1.30
Acrinathrin-1	131.6	15.81	104.1	13.30	79.24	2.81
Cyhalothrin-2	141.3	2.62	112.25	4.11	94.92	1.29
Acrinathrin-2	131.8	3.54	109.95	7.08	95.12	2.88
cis-Permethrine	103.2	6.09	87.5	2.29	80.84	3.08
trans-Permethrine	106.3	10.75	95.25	3.93	80.58	3.64
Cyfluthrin-1	109.1	8.84	102.25	2.38	87.64	3.06
Cyfluthrin-2	137.6	5.71	106.5	7.57	95.58	3.56
Cyfluthrin-3	98	8.13	108.75	5.66	94.68	5.68
Cyfluthrin-4	114.9	6.50	108.1	16.23	91.24	9.32
Flucythrinate-1	123	2.48	109.45	8.71	94.98	3.86
Flucythrinate-2	118.3	7.09	105.3	6.31	98.16	1.56
Fenvalerate-1	118.1	5.06	102.2	7.56	93.84	4.51
tau-Fluvalinate-1	136.7	6.01	115.85	4.22	106.96	2.36
Fenvalerate-2	119.4	3.56	101.65	3.92	92.7	5.92
tau-Fluvalinate-2	132.4	3.26	112.15	6.31	101.46	3.97
Deltamethrin-2	144.6	11.01	115.65	10.22	99.66	6.59

Conclusion

The results from this performance study indicates that the GCMS TQ-8050 is capable of quantitation and screening of target and unknown compounds in pine needle and spices. A Shimadzu Smart pesticides database was also used for developing the screening method for approximately 225 pesticides. Qudrupole3 (Q3) was used for scanning throughout the range 35.00 – 600.00 m/z. For EI quantitative analysis, calibration curve ranged from 2.5 to 80 ppb. Linear responses were obtained from 0.9859 to 0.9999. RF %RSD ranged from 2.892 to 57.495.