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Application News

Gas Chromatograph Mass Spectrometer

No. GCMS-1404

Analysis of Pesticides in Citrus Oil Using a Shimadzu GCMS-TQ8030

■ Introduction

Contamination of consumer products with pesticides is a growing concern because of recognized adverse health effects, increasing world-wide usage of pesticides, and imports of raw materials from foreign sources. Citrus oils have been used for centuries for a wide range of applications: flavor/fragrance, various medicinal purposes, and others. In recent years, new uses of citrus oils as cleaners and in aromatherapy and alternative medicine have become widespread.

Gas chromatography mass spectrometry (GCMS) has been used extensively to identify and quantify trace level pesticides in food and related matrices; the most significant challenges have been matrix interference and achievement of meaningful health-based detection limits for the compounds of interest. Triple quadrupole GC-MS/MS has emerged as a technique of choice for analysis of trace level contaminants in complex matrices. Operation of the triple quadrupole GC-MS/MS in the Multiple Reaction Monitoring (MRM) mode provides excellent sensitivity and specificity for detection and quantitation of target pesticides at low concentrations in the presence of background interferences. Most co-extracted matrix interferences are minimized using the MRM mode. The outstanding selectivity of the MRM mode has been illustrated previously.[1]

This application note presents instrument configuration, operating parameters, and analytical results for analysis of trace levels of 47 pesticides of various chemical classes in four orange oil samples using the Shimadzu GCMS-TQ8030 triple quadrupole GC-MS/MS (Figure 1). Results were evaluated for calibration linearity, analytical precision, sensitivity, and specificity.

Figure 1: Shimadzu GCMS-TQ8030 Triple Quadrupole GC/MS/MS

■ Experimental

The analyses were conducted using a Shimadzu GCMS-TQ8030 triple quadrupole GC/MS/MS operated in the multiple reaction monitoring (MRM) mode. Optimized MRM transitions and collision energies were obtained from three sources:

1. The Shimadzu GC/MS/MS Pesticide Database[1]
2. Previous application studies of trace level pesticides[2,3]
3. Empirical determination using the Shimadzu GCMS-TQ8030 with Smart MRM

The analytical method for detection of the target pesticides was developed using the Shimadzu GC-MS/MS Pesticide Database for the GCMS-TQ8030. Method information for 430 pesticides includes suggested MRM transitions that can be used for either quantitation or confirmation. MRM transitions were determined experimentally for pesticides not registered in the database. The Shimadzu GC/MS/MS Pesticide Database for the GCMS-TQ8030 has been described previously.

The GCMS-TQ8030 allows optimization of the collision energy for each MRM transition, providing ultimate sensitivity. In addition, the Q1 and Q3 resolution can be independently defined for each compound, to deliver individualized specificity for each analyte. The instrument configuration and operating conditions are shown in Table 1A below; MRM transitions, optimized collision energies, and Q1/Q3 resolution settings for the 47 pesticide analytes, one internal standard (IS), and one control are shown in Table 1B.

Table 1A: GCMS-TQ8030 Instrument Conditions for Analysis of Pesticides in Orange Oil

Gas Chromatograph	
Inlet	250 °C Single-taper gooseneck splitless liner with glass wool (Restek 23322.5) Splitless injection, sampling time 1 minute
Column	Rxi-5Sil MS, 30 m x 0.25 mm x 0.25 µm (Restek 13623) Helium carrier gas Constant linear velocity 47 cm/second
Oven Program	75 °C, hold 1 minute 10 °C/minute to 320 °C, hold 4.5 minutes MS interface 320 °C
Mass Spectrometer	
Ion Source	200 °C Electron ionization (EI) mode, 70 eV
Operation Mode	Simultaneous Scan/MRM Argon gas, 200 kPa Q1, Q3 resolution: Unit, Unit

Table 1B: Pesticide Analytes with MRM Transition and Q1/Q3 Resolution Details

Compound Name	MRM-1	CE-1	MRM-2	CE-2	MRM-3	CE-3	Q1/Q3 Resolution
2,4-D methyl ester	234.1>199.1	10	234.1>73.1	12	234.1>175.1	14	Unit/Unit
Phendimedipham	167.1>135.1	8	167.1>122.1	14	167.1>59.0	18	Unit/Unit
Monocrotophos	127.1>109.0	12	127.1>95.0	16	127.1>79.0	20	Unit/Unit
Cadusafos	158.9>130.9	8	158.9>97.0	18	158.9>65.0	28	Unit/Unit
Dimethoate	125.0>79.0	8	125.0>47.0	14	125.0>62.0	10	Unit/Unit
Carbofuran	164.1>149.1	8	164.1>131.1	18	164.1>103.1	24	Unit/Unit
Diazinon	304.1>179.1	10	304.1>162.1	8	304.1>137.1	26	Unit/Unit

Pyrimethanil	198.1>183.1	14	198.1>158.1	18	198.1>118.1	28	Unit/Unit
Parathion-methyl	263.0>109.0	14	263.0>136.0	8	263.0>246.0	6	Unit/Unit
Carbaryl	144.1>116.1	12	144.1>89.0	38	144.1>65.0	28	Unit/Unit
Metalaxyl (Mefenoxam)	249.2>190.1	8	249.2>146.1	22	249.2>217.1	6	Unit/Unit
Primiphos-methyl	305.1>180.1	6	305.1>290.1	12	305.1>125.0	26	Unit/Unit
Methiocarb	168.1>153.0	8	168.1>109.0	14	168.1>45.0	22	Unit/Unit
Malathion	173.1>99.0	14	173.1>127.0	6	173.1>145.0	6	Unit/Unit
Chlorpyrifos	313.9>257.9	14	313.9>285.9	8	313.9>193.9	28	Unit/Unit
Fenthion	278.0>109.0	20	278.0>125.0	20	278.0>169.0	14	Unit/Unit
Parathion	291.1>109.0	14	291.1>137.0	6	291.1>81.0	24	Unit/Unit
Kelthane (Dicofol)	250.1>139.1	12	250.1>215.1	4	250.1>111.1	30	Unit/Unit
Triphenylmethane (IS)	244.1>167.1	10	244.1>243.1	10			Unit/Unit
Pendimethalin (Penoxaline)	252.1>162.1	10	252.1>191.1	8	252.1>208.1	6	Unit/Unit
Phenthoate	273.9>125.0	20	273.9>246.0	6	273.9>93.0	14	Unit/Unit
Thiabendazole	201.1>174.1	16	201.1>130.1	26	201.1>92.0	28	Unit/Unit
Methidathion	145.0>85.0	8	145.0>58.0	14	145.0>71.0	6	Unit/Unit
Napropamide	128.1>72.0	6	128.1>57.0	12	128.1>100.0	8	Unit/Unit
Imazalil	215.00>173.0	6	215.0>159.0	6	215.0>145.0	26	Unit/Unit
Pymetrozine	113.2>98.2	11	113.2>70.0	23		0	Unit/Unit
2,4-D ethylhexyl ester	332.1>220.1	9	332.1>162.1	24	332.1>57.2	22	Unit/Unit
Fenthion sulfone	310.1>109.1	20	310.1>136.1	16	310.1>105.2	12	Unit/Unit
Ethion	231.0>174.9	23	231.0>203.0	16	231.0>185.0	15	Unit/Unit
Triazophos	257.0>162.0	8	257.0>134.0	22	257.0>119.0	26	Unit/Unit
Trifloxystrobin	222.1>190.1	4	222.1>162.1	10	222.1>130.1	12	Unit/Unit
Triphenyl Phosphate (Control)	326.1>170.1	15	326.1>215.1	20			Unit/Unit
Propargite-1	135.1>107.1	16	135.1>77.0	24	135.1>95.0	14	Unit/Unit
Pyridaphenthion	340.0>199.1	8	340.0>109.1	22	340.0>125.1	20	Unit/Unit
Acetamiprid	152.0>116.0	18	152.0>89.0	26	152.0>125.0	14	Unit/Unit
Imidan (Phosmet)	160.0>133.0	14	160.0>77.0	24	160.0>105.0	18	Unit/Unit
Fenoxycarb	186.1>109.1	14	186.1>129.1	14	186.1>81.0	26	Unit/Unit
Bromopropylate	340.9>157.0	30	340.9>184.9	20	340.9>182.9	18	Unit/Unit
Fenpropathrin	265.1>210.1	12	265.1>172.1	14	265.1>89.0	28	Unit/Unit
Tetradifon	355.9>228.9	12	355.9>159.0	18	355.9>127.0	16	Unit/Unit

Azinphos-methyl	160.1>132.1	6	160.1>77.0	20	160.1>51.0	28	Unit/Unit
Pyriproxyfen	136.1>78.0	20	136.1>96.0	14	136.1>108.0	6	Unit/Unit
Spirodiclofen	312.0>109.0	20	312.0>277.0	6	312.0>259.0	12	Unit/Unit
Pyridaben	147.1>117.1	22	147.1>132.1	14	147.1>119.1	10	Unit/Unit
Prochloraz	180.1>138.1	12	180.1>69.0	20	180.1>95.0	20	Unit/Unit
Fenbuconazole	198.1>129.1	10	198.1>102.1	24	198.1>78.0	28	Unit/Unit
Pyraclostrobin	164.1>132.1	14	164.1>77.0	28	164.1>104.1	26	Unit/Unit
Azoxystrobin	344.1>183.1	24	344.1>329.1	16	344.1>156.1	32	Unit/Unit
Famoxadone	330.1>224.1	10	330.1>196.1	22	330.1>237.1	10	Unit/Unit

Calibration employed the matrix-matched internal standard procedure. A sample of organic orange oil was used as the sample matrix; an organic variety was selected so it would be free from background pesticide contamination. The samples were diluted 10-fold into methylene chloride for analysis; no other pretreatment or cleanup of the samples was attempted in this study. Concentrations are expressed in ng/mL (parts-per-billion, ppb) in the original sample.

■ Results and Discussion

Chromatography

The total ion chromatogram (TIC) of the pesticide standard (20 µg/mL in methylene chloride) acquired in the Q3 full-scan mode is shown in Figure 2A, and illustrates the chromatographic separation of the target pesticides in this study. A full-scan chromatogram of the organic orange oil acquired under the same conditions is shown in Figure 2B, and shows a broad, intense signal for limonene before 7.5 minutes, intense chromatographic peaks from 7.5 - 12 minutes, and illustrates the significant matrix interference in the raw orange oil.

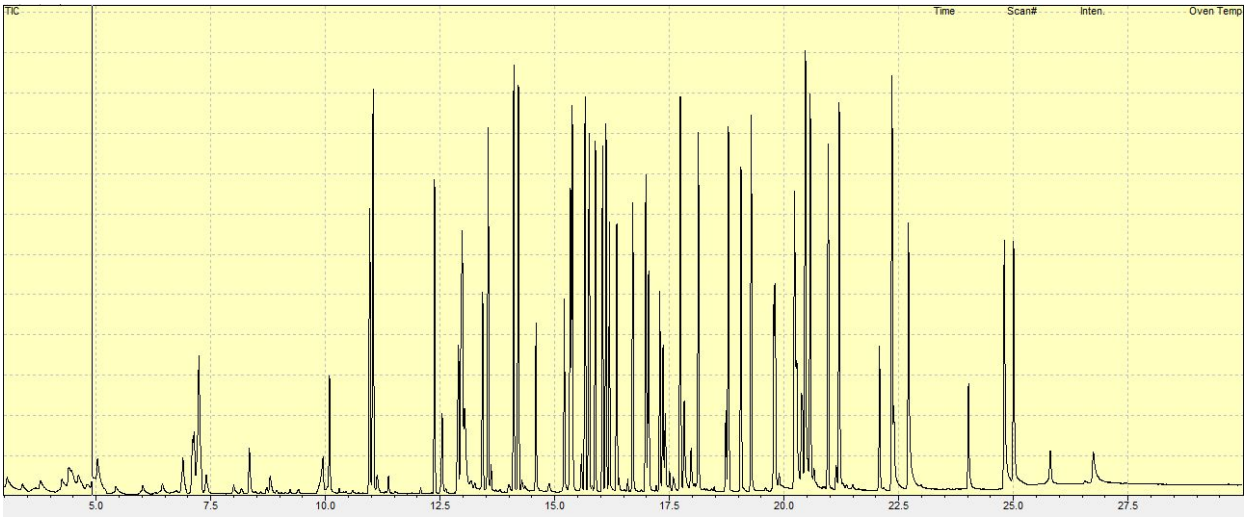

Figure 2A: Total Ion Chromatogram of Pesticide Standard – Q3 Scan Mode

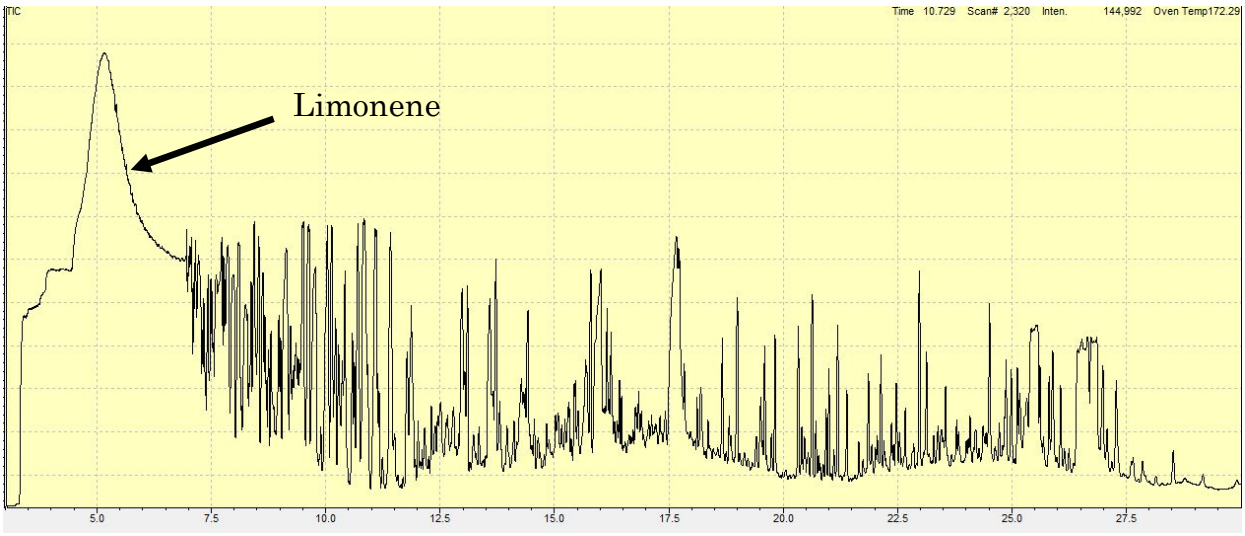

Figure 2B: Total Ion Chromatogram of Organic Orange Oil – Q3 Scan Mode

Calibration and Assessment of Precision

Calibration employed the matrix-matched internal standard procedure. Nine calibration standards were prepared in diluted organic orange oil over the range of 5-5000 ng/mL (ppb) expressed as concentration in the original orange oil (corresponding to mass of 0.5-500 pg on column for each analyte). Triphenylmethane was used as the internal standard and was held at a constant concentration of 500 ng/mL; triphenyl phosphate was used as a control standard, and was also held at a constant concentration of 500 ng/mL in all standards. The calibration standards were analyzed using the instrument conditions outlined in Table 1 above. The detector (electron multiplier) was adjusted to give acceptable response at the lowest calibration level and avoid saturation at the highest calibration level.

Response factors were calculated and relative standard deviation (RSD) was determined by the GCMSsolution software. Mean response factors for the initial calibration are presented in Table 2 below. The precision of the calibration was evaluated using the RSD of the response factors and the correlation coefficient (r) for each of the analytes. The RSD and correlation coefficient values for the multi-point calibration(s) are also included in Table 2. Linearity as evaluated by the correlation coefficient was acceptable for the multi-point calibration. In cases where the RSD for the response factors was greater than 20%, chromatographic interferences contributed to the signal for the lowest concentration standards. Matrix interference for some compounds was significant at the lowest calibration ranges, so lower calibration levels were omitted and the calibration range was adjusted accordingly. The lowest calibration point for each compound is listed in Table 2. For the purpose of this study, the level of quantitation (LOQ) is defined as the lowest point in the multi-point calibration.

After the multi-point calibration, ten replicate injections of the 5, 10, and 50 ng/mL standards were analyzed to assess the precision and accuracy of measurement near the low end of the calibration range. The mean concentration and RSD for the replicate analyses are presented in Table 2. In cases where the spike level fell below the LOQ for a compound, precision data are not presented (e.g. the LOQ for Cadusafos is 50 ppb, so spike results are not presented for the 5 and 10 ppb spikes).

Table 2: Calibration, Precision, and Accuracy Results for Pesticides in Orange Oil

Compound Name	Calibration Results				5 ppb Spike		10 ppb Spike		50 ppb Spike	
	Mean RRF	RRF %RSD	Linearity (r)	Low Cal (ppb)	Mean Conc.	%RSD	Mean Conc.	%RSD	Mean Conc.	%RSD
2,4-D methyl ester	0.511	12	>0.999	5	9	11.1	7	53	2	9
Phendimedipham	0.509	14	>0.999	100	xxx	xxx	xxx	57	5	xxx
Monocrotophos	1.463	2	>0.999	10	xxx	12.8	4	46	2	xxx
Cadusafos	1.366	15	>0.999	50	xxx	xxx	xxx	53	6	xxx
Dimethoate	0.169	3	>0.999	50	xxx	xxx	xxx	47	7	xxx
Carbofuran	0.940	28	>0.999	50	xxx	xxx	xxx	61	6	xxx
Diazinon	0.441	5	>0.999	5	9	10.9	8	53	4	9
Pyrimethanil	0.434	11	>0.999	5	5	10.1	7	52	3	5
Parathion-methyl	0.089	11	>0.999	50	xxx	xxx	xxx	58	2	xxx
Carbaryl	1.950	18	>0.999	5	7	13.9	4	56	3	7
Metalaxyl (Mefenoxam)	0.388	9	>0.999	50	xxx	xxx	xxx	60	12	xxx
Primiphos-methyl	0.271	5	>0.999	5	12	10.6	6	52	3	12
Methiocarb	1.404	3	>0.999	50	xxx	xxx	xxx	60	4	xxx
Malathion	1.232	17	>0.999	50	xxx	xxx	xxx	80	2	xxx
Chlorpyrifos	0.272	22	>0.999	5	10	13.6	9	54	6	10
Fenthion	1.200	12	>0.999	5	7	11.7	5	53	1	7
Parathion	0.430	5	>0.999	5	12	10.6	4	47	3	12
Kelthane (Dicofol)	0.627	15	>0.999	5	5	12.1	5	53	3	5
Triphenylmethane (IS)	NA	NA	NA	NA	N/A	NA	NA	NA	NA	N/A
Pendimethalin (Penoxaline)	0.364	10	>0.999	5	14	8.4	7	43	3	14
Phenthoate	0.788	13	>0.999	5	2	12.2	2	54	2	2
Thiabendazole	3.004	5	>0.999	5	8	12.3	17	49	5	8
Methidathion	3.066	3	>0.999	10	xxx	15.9	3	56	1	xxx
Napropamide	0.515	4	>0.999	50	xxx	xxx	xxx	54	5	xxx
Imazalil	0.758	4	>0.999	5	15	10.3	10	48	3	15
Pymetrozine	0.808	8	>0.999	5	19	9.6	10	47	5	19
2,4-D ethylhexyl ester	0.086	8	>0.999	10	xxx	7.7	13	47	10	xxx
Fenthion sulfone	0.422	13	>0.999	5	14	10.7	6	52	3	14
Ethion	0.440	14	>0.999	5	6	12.9	8	55	2	6
Triazophos	0.772	7	>0.999	5	11	11.5	3	51	2	11
Trifloxystrobin	0.405	7	>0.999	5	9	10.1	7	49	4	9
Triphenyl Phosphate (Control)	0.666	1	>0.999	NA	N/A	N/A	N/A	N/A	N/A	N/A
Propargite-1	1.155	12	>0.999	100	xxx	xxx	xxx	xxx	xxx	xxx
Pyridaphenthion	0.802	6	>0.999	5	7	11.3	8	52	2	7
Acetamiprid	0.438	7	>0.999	10	xxx	8.3	11	45	4	xxx
Imidan (Phosmet)	2.174	17	>0.999	5	7	14.4	6	52	2	7
Fenoxycarb	0.265	16	>0.999	10	xxx	16.0	9	58	3	xxx
Bromopropylate	0.265	11	>0.999	50	xxx	xxx	xxx	65	3	xxx
Fenpropathrin	0.274	11	>0.999	5	17	12.6	12	54	3	17
Tetradifon	0.173	11	>0.999	5	12	11.9	8	55	2	12

Azinphos-methyl	2.071	10	>0.999	5	11	12.5	4	51	3	11
Pyriproxyfen	1.158	16	>0.999	10	xxx	14.1	5	55	2	xxx
Spirodiclofen	0.147	21	>0.999	5	13	10.6	10	58	5	13
Pyridaben	4.292	5	>0.999	10	xxx	11.8	11	55	4	xxx
Prochloraz	0.562	18	>0.999	10	xxx	12.3	14	51	3	xxx
Fenbuconazole	3.670	8	>0.999	5	6	8.9	9	51	3	6
Pyraclostrobin	1.573	9	>0.999	10	xxx	17.5	7	61	3	xxx
Azoxystrobin	0.703	8	>0.999	10	xxx	5.7	15	47	8	xxx
Famoxadone	0.111	21	>0.999	10	xxx	3.8	12	43	6	xxx

Qualitative Specificity and Chromatographic Interferences

The MRM chromatograms for all analytes at the LOQ calibration standard were examined for matrix interference. For many of the analytes, minimal chromatographic interference was observed at the lowest calibration level (LOQ), and did not interfere with quantitation (Figure 4A and 4B). For other analytes however, significant matrix interference was observed even at higher concentrations (Figures 5A and 5B).

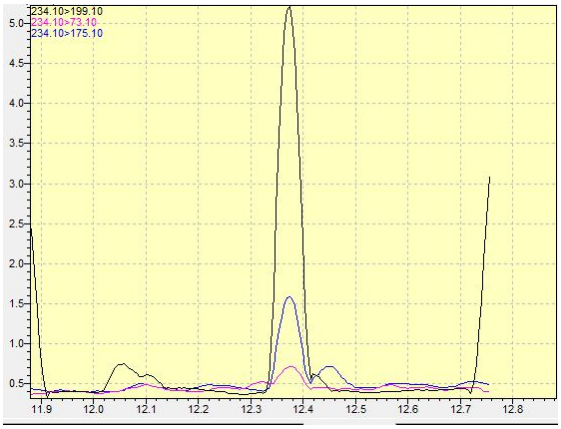

Figure 4A: MRM Chromatograms of 2,4-DMethyl Ester at 5 ppb in Orange Oil

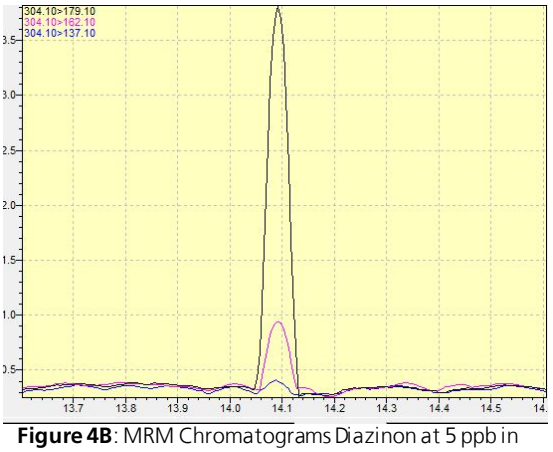

Figure 4B: MRM Chromatograms Diazinon at 5 ppb in Orange Oil

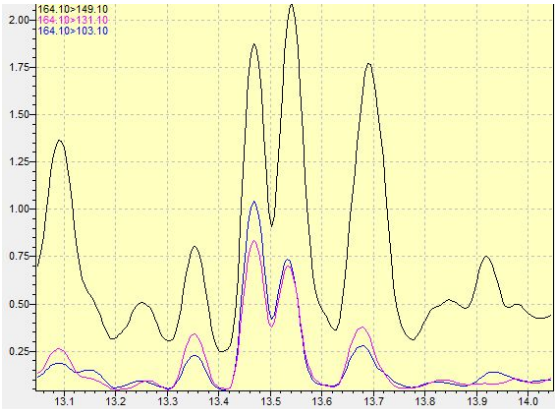

Figure 5A: MRM Chromatograms Carbofuran at 50 ppb in Orange Oil

Figure 5B: MRM Chromatograms Metalaxyl at 50 ppb in Orange Oil

Two compounds, bromopropylate and pyraclostrobin, exhibited unusual chromatographic interferences. The primary (most intense) MRM transitions suggested that background concentrations in the organic orange oil sample exceeded 1000 ng/mL. However, close examination of the results revealed that chromatographic interferences were present only with the primary MRM transition; the secondary and tertiary transitions were not affected. Acceptable quantitative results were obtained when a minor alternate MRM transition was chosen for quantitation.

The calibration for bromopropylate using the usual primary transition of 340.9>184.9 is shown in Figure 6A below. The high positive y-intercept in the calibration curve is consistent with background concentration of the analyte at approximately 1000 ppb in the unspiked sample.

However, close examination of the data shows that ratio of the less intense 340.9>157.0 transition increases with increasing concentration. This trend is shown graphically in Figure 6B; MRM chromatograms are displayed for each of the calibration standards with the highest concentration at the top. When the 340.9>157.0 transition is used for quantitation, a normal calibration is obtained, as shown in figure 6C. The results indicate interference with the 340.9>184.9 transition from a coeluting compound in the sample matrix. The results point out the need for comparing the ratio of transitions when confirming the qualitative identity of analytes in the MRM mode.

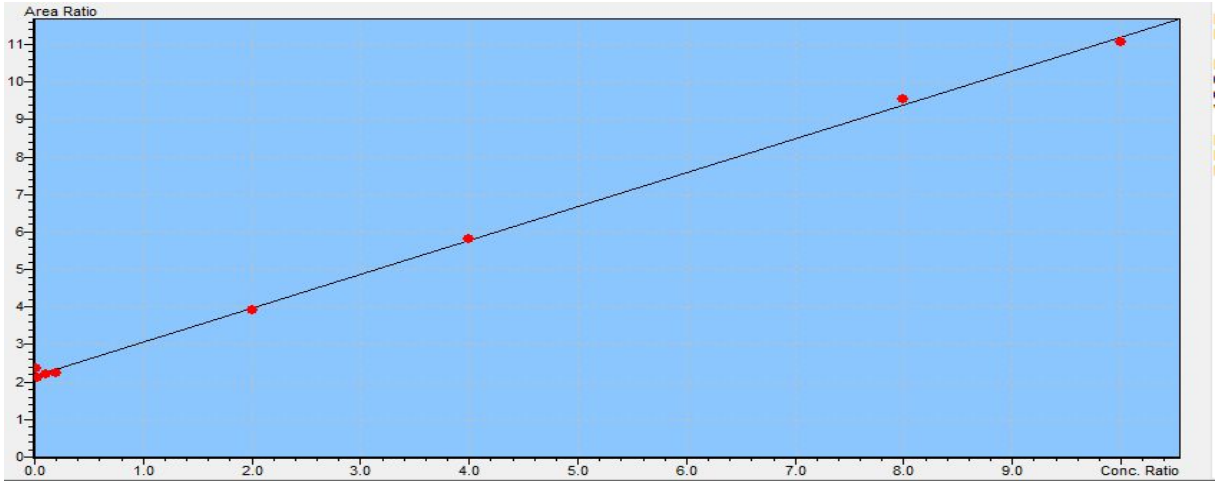

Figure 6A: Calibration for Bromopropylate Using the 340.9>184.9 MRM Transition

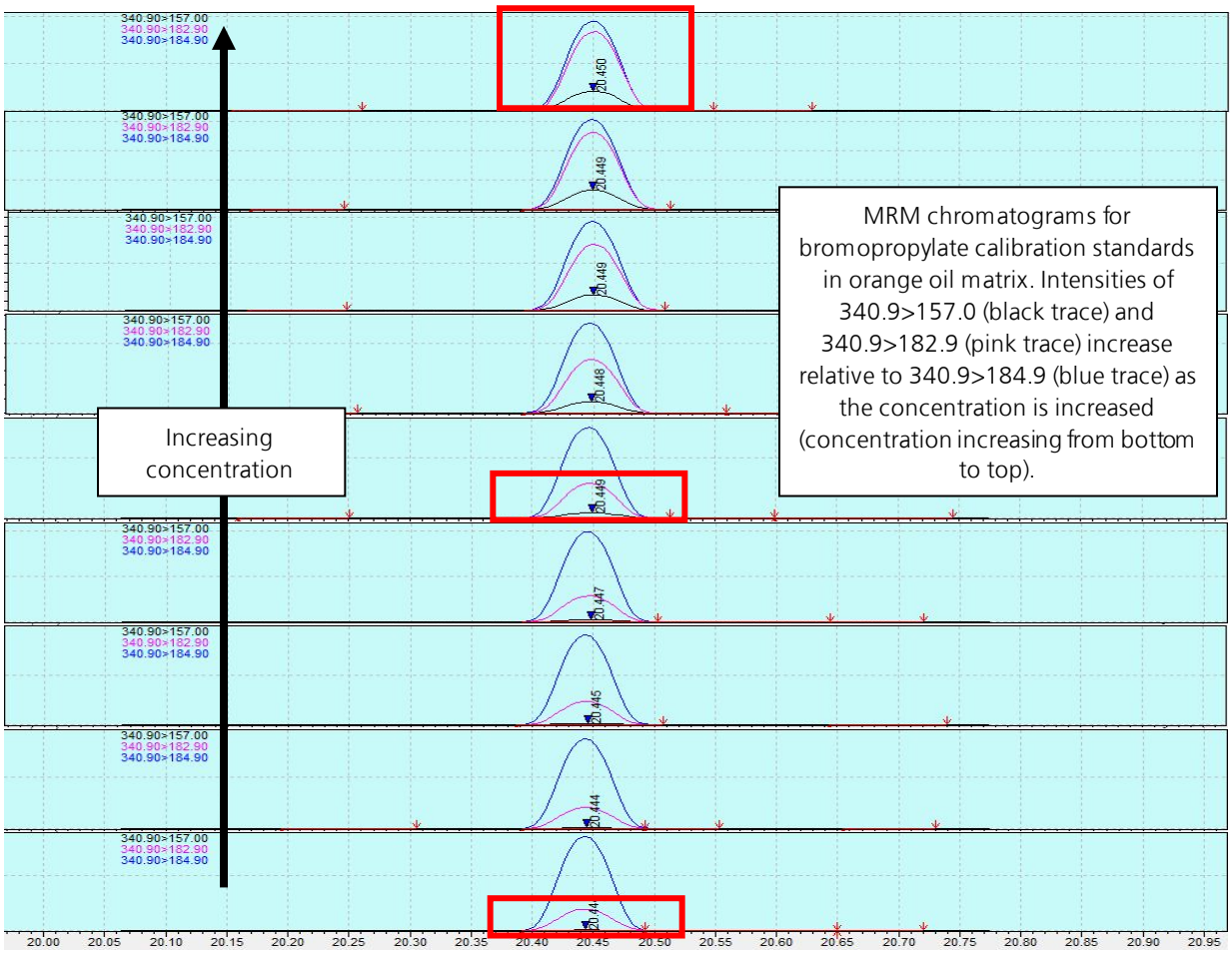

Figure 6B: Variable Transition Ratios vs. Concentration of Bromopropylate

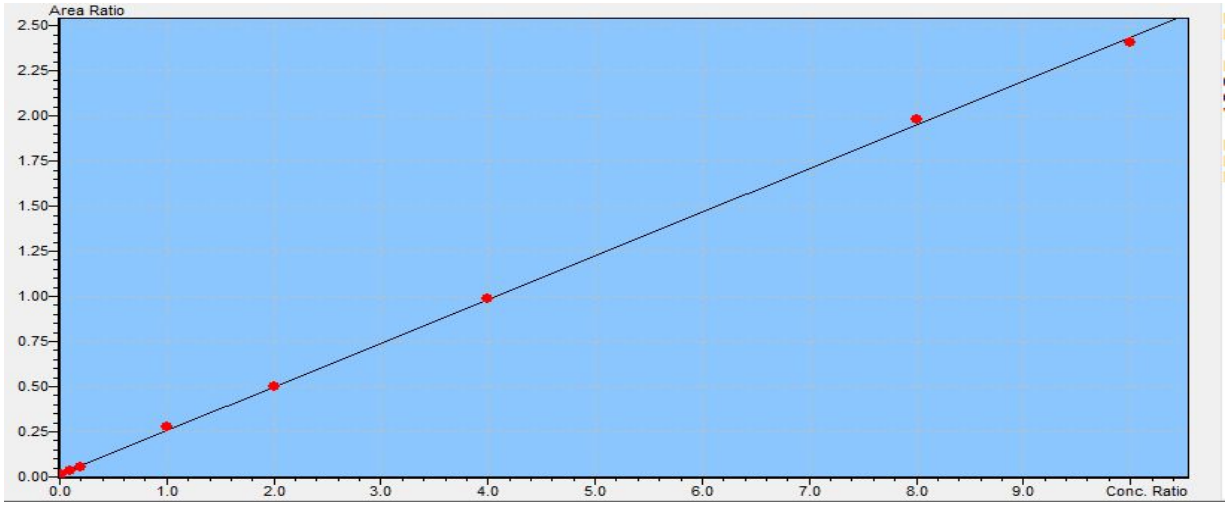

Figure 6C: Calibration for Bromopropylate Using the 340.9>157.0 Transition

Sample Results

Four real-world orange oil samples were analyzed using the conditions described above. Two of the oils were considered "organic", or free of pesticides, and two were not. Four replicates of each sample were analyzed to assess precision of the results. Results are presented in Table 3 below. In Table 3, the reported concentration is the mean result of the four analyses, expressed as concentration in the original sample; the RSD of the four measurements is also included.

None of the target pesticides were detected above the quantitation limit in the two organic orange oil samples (Samples 3 and 4), but several target pesticides were detected at various levels in the other two samples.

Table 3: Analytical Results for Four Orange Oils

Compound Name	LOQ (ppb)	Sample 1 Non-Organic		Sample 2 Non-Organic		Sample 3 Organic		Sample 4 Organic	
		Mean Conc. (ppb)	%RSD	Mean Conc. (ppb)	%RSD	Mean Conc. (ppb)	%RSD	Mean Conc. (ppb)	%RSD
2,4-D methyl ester	5	ND		ND		ND		ND	
Phendimedipham	100	ND		ND		ND		ND	
Monocrotophos	10	ND		ND		ND		ND	
Cadusafos	50	ND		ND		ND		ND	
Dimethoate	50	ND		ND		ND		ND	
Carbofuran	**50**	**240**	**1%**	**210**	**1%**	**ND**		**ND**	
Diazinon	5	ND		ND		ND		ND	
Pyrimethanil	5	ND		ND		ND		ND	
Parathion-methyl	50	ND		ND		ND		ND	
Carbaryl	**5**	**ND**		**2600**	**1%**	**ND**		**ND**	
Metalaxyl (Mefenoxam)	50	ND		ND		ND		ND	
Primiphos-methyl	5	ND		ND		ND		ND	
Methiocarb	50	ND		ND		ND		ND	
Malathion	**50**	**120**	**2%**	**770**	**1%**	**ND**		**ND**	
Chlorpyrifos	**5**	**360**	**1%**	**1900**	**2%**	**ND**		**ND**	
Fenthion	5	ND		ND		ND		ND	
Parathion	5	ND		ND		ND		ND	
Kelthane (Dicofol)	**5**	**970**	**1%**	**55**	**4%**	**ND**		**ND**	
Triphenylmethane (IS)	NA	ND		ND		ND		ND	
Pendimethalin (Penoxaline)	5	ND		ND		ND		ND	
Phenthoate	5	ND		ND		ND		ND	
Thiabendazole	5	ND		ND		ND		ND	
Methidathion	**10**	**4900**	**1%**	**280**	**1%**	**ND**		**ND**	
Napropamide	50	ND		ND		ND		ND	
Imazalil	5	ND		ND		ND		ND	
Pymetrozine	5	ND		ND		ND		ND	
2,4-D ethylhexyl ester	10	ND		ND		ND		ND	
Fenthion sulfone	5	ND		ND		ND		ND	
Ethion	5	ND		ND		ND		ND	
Triazophos	5	ND		ND		ND		ND	
Trifloxystrobin	**5**	**170**	**1%**	**230**	**3%**	**ND**		**ND**	
Triphenyl Phosphate	**NA**	**500**	**1%**	**500**	**1%**	**496**	**1%**	**497**	**1%**

(Control)									
Propargite-1	100	ND		ND		ND		ND	
Pyridaphenthion	5	ND		ND		ND		ND	
Acetamiprid	10	ND		ND		ND		ND	
Imidan (Phosmet)	**5**	**370**	**1%**	**6100**	**<1%**	**ND**		**ND**	
Fenoxycarb	10	ND		ND		ND		ND	
Bromopropylate	50	ND		ND		ND		ND	
Fenpropathrin	**5**	**77**	**3%**	**740**	**1%**	**ND**		**ND**	
Tetradifon	5	ND		ND		ND		ND	
Azinphos-methyl	5	ND		ND		ND		ND	
Pyriproxyfen	**10**	**32**	**1%**	**ND**		**ND**		**ND**	
Spirodiclofen	**5**	**15**	**5%**	**22**	**6%**	**ND**		**ND**	
Pyridaben	10	ND		ND		ND		ND	
Prochloraz	10	ND		ND		ND		ND	
Fenbuconazole	**5**	**ND**		**190**	**1%**	**ND**		**ND**	
Pyraclostrobin	**10**	**790**	**1%**	**320**	**2%**	**ND**		**ND**	
Azoxystrobin	**10**	**32**	**2%**	**140**	**2%**	**ND**		**ND**	
Famoxadone	**10**	**20**	**4%**	**ND**		**ND**		**ND**	

■ Alternate Approaches for Minimizing Interferences from Complex Matrices

As illustrated above, chromatographic interferences from complex matrices can significantly impact data quality, even when the specificity of GC-MS/MS in the MRM mode is employed. Several additional approaches for minimizing matrix interferences can be considered for similar applications:

- Sample pretreatment ("cleanup")
- Selection of alternate MRM transitions
- Use of an alternate chromatographic mobile phase with the Shimadzu Twin Line MS Kit

Sample pretreatment can be effective in removing chromatographic interferences, but it is sometimes not possible or desirable. In the case of citrus oils, the QuEChERS procedure may be possible, but it was not employed for this study.

Alternate MRM transitions can be used to mitigate interferences. In the example of bromopropylate described above, three MRM transitions are listed in the Shimadzu GC-MS/MS Pesticide Database. While the 340.9>184.9 transition shows significant matrix interference, the 340.9>157.0 and 340.9>182.9 transitions show minimal interferences. The NIST library mass spectrum of bromopropylate, shown in Figure 7 below, suggests that additional transitions may be available, either by selecting alternate precursor ions (m/z 338.9 or 342.9) or alternate product ions (m/z 155, 104, or 76).

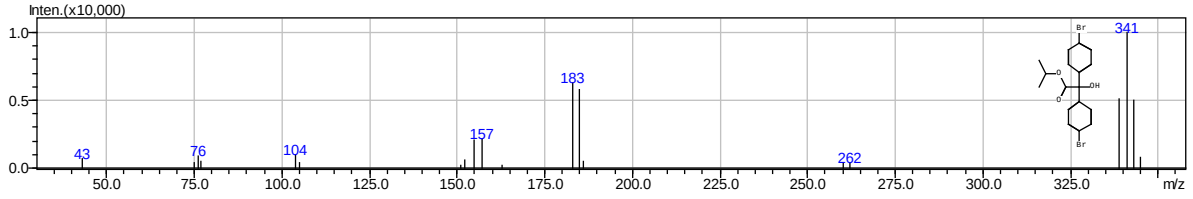

Figure 7: NIST Library Mass Spectrum of Bromopropylate

Alternate chromatographic columns can also be employed to separate chromatographic interferences from the analytes of interest. While changing chromatographic columns can be cumbersome and time-consuming, the Shimadzu Twin Line MS System provides a convenient means for simultaneously maintaining two chromatographic columns connected to the MS. This configuration employs two injection ports with two dissimilar chromatographic columns connected to the mass spectrometer by means of a two-hole ferrule. The two-hole ferrule connection is shown in Figure 8 below.

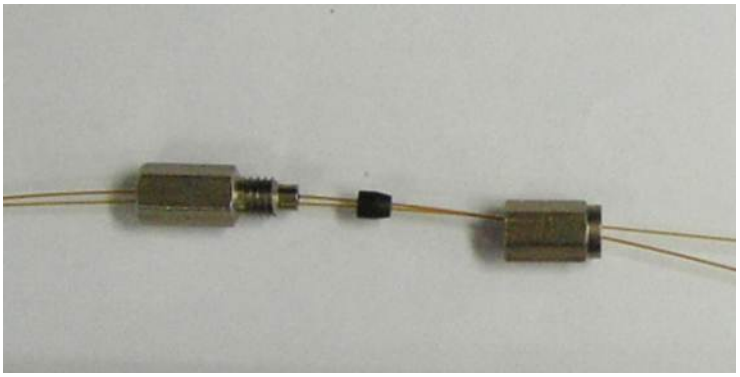

Figure 8: Tw in Line MS Kit Connection w ith 2-Hole Ferrule

■ Conclusion

Detection of pesticides was demonstrated at low ng/mL (ppb) levels in orange oil using a Shimadzu GCMS-TQ8030 GC-MS/MS. Calibration was conducted using the matrix-matched internal standard procedure. Nine calibration standards were prepared and analyzed in diluted organic orange oil over the range of 5-5000 ng/mL (ppb), although some compounds could not be accurately quantitated at the low concentrations due to matrix interference. Precision and accuracy were demonstrated by replicate analyses of matrix spiked aliquots at 5, 10 and 50 ng/mL.

Results were evaluated for calibration linearity, analytical precision, sensitivity, and specificity. Chromatographic interferences in the MRM mode were variable, depending on the individual analyte. Quantitation levels (LOQ's) were variable, depending upon the analyte, from 5 to 100 ng/mL.

A Shimadzu GCMS-TQ8030 system was shown to be a rapid, sensitive, and selective technique for analysis of various classes of pesticides in orange oil. Operation of the GC/MS/MS in the MRM mode provided accurate, precise results for the sample matrix. Reliable, precise measurements were obtained for 47 pesticides. The Shimadzu GC/MS/MS Pesticide Database simplified development of the MRM method.

■ References

1. Shimadzu GC-MS/MS Pesticide Database (October, 2012).
2. Analysis of Organophosphorus Pesticides in Baby Foods Using a Triple-Quadrupole GC/MS/MS System, Shimadzu Application News No. GCMS-1304 (February, 2013).
3. Analysis of Pesticides in Baby Food Using a GCMS-TQ8030 GC/MS/MS, Part II, Shimadzu Application News No. GCMS-1402 (March 2014).
4. AOAC Official Method 2007.01, Pesticide Residues in Foods by Acetonitrile Extraction and Partitioning with Magnesium Sulfate (2007)

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