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Application Data Sheet

No.106

GC-MS
Gas Chromatograph Mass Spectrometer

Simultaneous Analysis of 477 Residual Pesticides in Agricultural Crops Using GC-MS/MS - Part 1

GC-MS/MS systems can measure more than 400 residual pesticides in foods. However, analyzing more than 400 pesticides simultaneously requires a short dwell time (data loading time) during MRM measurements, which results in problems with inadequate sensitivity and the tedious process of creating MRM measurement programs. Consequently, several different methods are used for target pesticides and the same sample is measured multiple times to analyze all components. That can decrease productivity, due to the time required for analyzing all the components involved in the large number of pesticides being inspected. This Application Data Sheet describes a solution to these problems with the creation of a method for simultaneously analyzing 477 components and evaluating the resulting sensitivity and accuracy.

Experiment

Matrix solutions were prepared by processing soy bean, orange, brown rice, and spinach samples according to a pretreatment procedure for residual pesticide analysis, and then purifying them using the GPC Cleanup System (from Shimadzu Corporation).[1)] Measurement sample solutions (1 g/mL sample concentration) were then prepared by spiking the prepared matrix solutions with 477 components (including internal standard substances) to a concentration of 5 ppb (or 200 ppb for the internal standard substances). 19 kinds*1 of surrogate pesticides were used as the internal standard substances.
The GCMS-TQ8040 combined with the Twin Line MS System was used to measure samples based on the analytical conditions listed in Table 1. Two transitions were specified for each component, one for quantitation and the other for confirmation, and Smart MRM was used to automatically create a measurement program.

Table 1: Analysis Conditions

GC-MS:	GCMS-TQ8040 (Twin Line MS System)
Column 1:	SH-Rxi-5Sil MS (30m L., 0.25 mm I.D., df=0.25 μm) (Shimadzu, P/N: 221-75954-30)
Column 2:	SH-Rtx-200 MS (30m L., 0.25 mm I.D., df=0.25 μm) (Shimadzu, P/N: 221-75811-30)
Glass Insert :	Sky Liner, Splitless Single Taper Gooseneck w/Wool (Restek, P/N: 567366)

[GC]		[MS]	
Injection Temp.:	250 °C	Interface Temp.:	300 °C
Column Oven Temp.:	60 °C (1 min) → (25 °C /min) → 160 °C → (4 °C /min) → 240 °C → (10 °C /min) → 290 °C (11 min)	Ion Source Temp.:	200 °C
		Measurement Mode:	MRM
Injection Mode:	Splitless	Loop Time:	0.4 sec
High Pressure Injection:	250 kPa (1.5 min)	Processing Time Required:	0.3 min
Carrier Gas Control:	Linear Velocity (40.0 cm/sec)		
Injection Volume:	2 μL		

Analysis Results

The relationship between the dwell time and retention time in the measurement program created using Smart MRM is shown in Fig. 1. The average dwell time for all components was 12.3 msec, with over 6.5 msec provided even for retention time bands where a high number of pesticides were eluted. Consequently, compared to conventional measurement methods that divide analysis into segments, Smart MRM provides, on average, 2.5 time longer dwell times and makes it easy to create optimal MRM measurement programs.

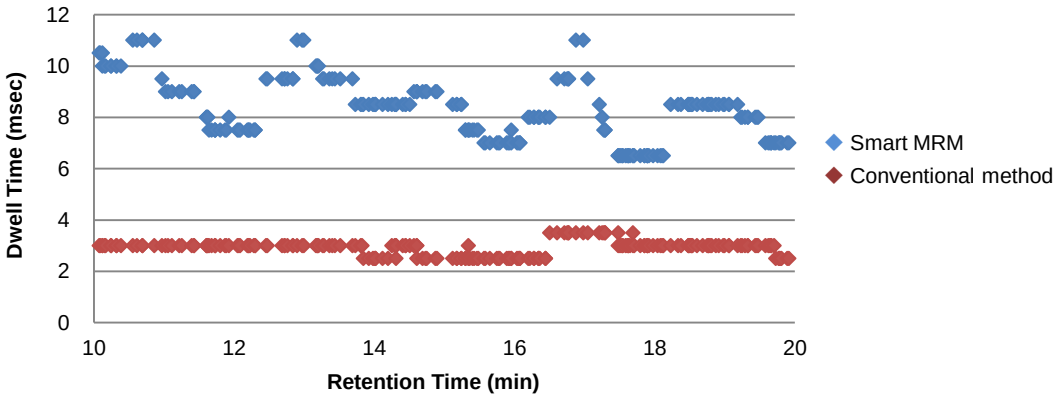

Fig. 1 Relationship Between Retention Time and Dwell Time (for retention times from 10 to 20 minutes)

1) E. Ueno, et al., *J. AOAC INT.* **87**, (2004) 1003-1015

*1 Dichlorvos-d_6, acephate-d_6, diazinon-d_{10}, iprobenfos-d_7, carbaryl-d_7, fenitrothion-d_6, linuron-d_6, metolachlor-d_6, chlorpyrifos-d_{10}, diethofencarb-d_7, fosthiazate-d_5, pendimethalin-d_5, thiabendazole-$^{13}C_6$, imazalil-d_5, isoprothiolane-d_4, isoxathion-d_{10}, EPN-d_5, etofenprox-d_5, and esfenvalerate-d_7

The repeatability for each matrix was used to evaluate whether the measurement program created using Smart MRM provided adequate sensitivity. The %RSD distribution obtained for each matrix is shown in Fig. 2 and the %RSD values for 100 of the 477 components are tabulated in Table 2. These results show that %RSD (n = 5) was 10 % or less for 88 % of targets (1618 of the 1832 components in four types of matrix), which indicates that high analytical accuracy was achieved when analyzing as many as 477 components simultaneously. By eliminating the need to split the analysis using multiple methods, the number of injections is reduced and productivity increased. This also allows maintenance frequency and costs to be minimized.
Though matrix interference was identified for a few components, high-accuracy detection was possible by using the Twin Line MS system, which uses two columns with different separation characteristics. For information regarding the Twin Line MS System, refer to Application Data Sheet 107.

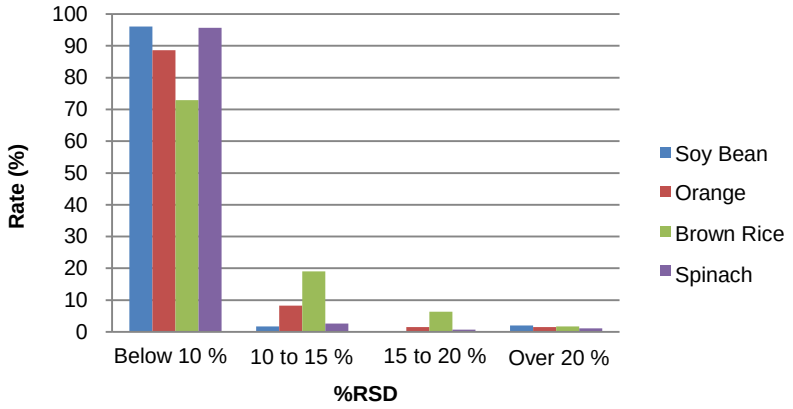

Fig. 2 %RSD Distribution for Each Matrix

Table 2: %RSD (n = 5) of Samples Spiked with Pesticides (5 ppb)

Name of Compound	Soy Bean	Orange	Brown Rice	Spinach	Name of Compound	Soy Beas	Orange	Brown Rice	Spinach	Name of Compound	Soy Bean	Orange	Brown Rice	Spinach
Methamidophos	4.82	7.66	8.84	1.86	Fthalide	6.92	5.01	12.09	4.79	Trifloxystrobin	6.80	8.83	8.84	5.89
Acephate	4.72	4.29	4.85	6.89	Fosthiazate-1	9.53	4.33	14.06	3.16	Tebuconazole	6.63	4.46	9.34	5.18
Propham	4.55	3.84	15.43	3.13	Fosthiazate-2	7.90	3.44	15.15	8.60	Piperonyl butoxide	4.41	3.91	9.63	2.78
Clothianidin	3.66	4.84	7.53	2.92	Pendimethalin	9.80	5.24	9.81	6.47	Acetamiprid	7.56	7.09	8.10	3.44
Chloroneb	4.35	2.74	12.91	5.54	Fipronil	9.68	11.76	9.33	9.72	Iprodione	8.26	3.90	9.09	3.65
Fenobcarb	2.95	3.02	7.72	2.14	Heptachlor-exo-epoxide	5.92	13.72	8.89	7.93	EPN	7.68	9.03	5.85	7.96
Phorate	6.20	4.87	10.62	4.72	Thiabendazole	4.22	3.90	9.34	5.03	Bromopropylate	4.58	3.65	9.49	3.71
Dimethoate	7.03	5.21	8.75	6.91	Captan	14.99	3.41	5.66	10.28	Bifenthrin	4.52	2.87	8.77	2.67
gamma-BHC	9.73	3.38	9.13	7.18	Phenthoate	8.96	1.92	9.77	5.60	Bifenazate	9.05	7.67	9.58	6.96
Cyanophos	5.89	3.82	8.64	4.01	Quinalphos	6.63	5.12	8.38	7.46	Fenpropathrin	8.53	4.96	9.79	9.01
Terbufos	2.89	4.37	7.94	5.04	Procymidone	4.31	5.49	12.58	5.87	Tebufenpyrad	3.66	4.18	9.73	2.88
Diazinon	8.13	4.68	9.35	7.42	Triflumizole	7.71	7.73	7.93	8.74	Tetradifon	8.47	4.02	8.83	7.17
Pyrimethanil	2.80	3.38	8.13	5.52	Chinomethionat	7.98	4.48	11.60	1.82	Azinphos-methyl	7.95	8.06	8.35	5.72
Iprobenfos	3.77	3.83	12.89	3.25	Trichlamide	7.78	3.23	9.93	5.82	Pyriproxyfen	4.25	6.00	5.30	3.39
Benoxacor	7.31	1.86	8.91	4.25	Butachlor	9.05	5.75	8.79	5.25	Fenarimol	1.45	4.13	9.64	2.72
Acetochlor	6.74	6.94	8.74	3.01	Alpha-endosulfan	8.92	3.48	9.39	3.12	Acrinathrin	5.27	9.02	8.37	8.17
Parathion methyl	7.86	4.91	7.77	3.41	Mepanipyrim	4.63	3.89	9.55	3.77	Coumaphos	5.15	6.18	7.79	4.18
Tolclofos-methyl	8.51	7.87	8.79	1.95	Hexaconazole	5.49	8.17	8.81	5.20	Pyridaben	6.42	3.16	7.25	1.59
Carbaryl	4.44	8.21	8.83	6.73	Imazalil	8.84	5.09	8.01	4.24	Cypermethrin-1	8.23	8.70	7.71	1.42
Heptachlor	7.92	3.29	8.59	4.05	Flutolanil	4.88	3.61	9.69	1.93	Boscalid	5.29	14.34	9.02	3.51
Metalaxyl	2.88	6.82	14.92	5.22	Prothiofos	9.31	4.77	10.21	4.80	Cypermethrin-2	8.68	5.80	8.49	7.71
Prometryn	4.48	5.90	8.83	7.87	Isoprothiolane	3.65	4.46	8.04	5.86	Cypermethrin-3	9.28	5.31	8.79	5.44
Pirimiphos-methyl	7.24	9.41	9.11	6.64	Dieldrin	9.55	8.16	9.39	6.59	Cypermethrin-4	4.59	12.36	2.67	7.80
Fenitrothion	9.87	6.55	5.77	7.20	Myclobutanil	4.80	5.72	9.55	2.11	Ethofenprox	4.72	7.17	7.04	3.51
Linuron	7.87	6.27	13.16	4.65	o,p'-DDD	5.51	3.71	11.30	3.02	Silafluofen	3.09	10.17	8.81	2.84
Malathion	9.97	7.47	7.37	2.98	Flusilazole	7.51	7.35	8.85	5.56	Fenvalerate-1	8.28	14.86	9.21	6.41
Metolachlor	3.77	3.78	12.20	4.78	Kresoxim-methyl	6.77	6.34	13.15	3.58	Fenvalerate-2	8.60	16.74	8.23	4.30
Chlorpyrifos	7.22	3.28	9.78	6.08	Chlorfenapyr	10.54	7.30	5.37	7.93	Difenoconazole-1	1.52	9.27	7.86	2.83
Thiobencarb	7.77	2.08	9.59	4.36	Isoxathion	9.10	7.85	12.21	9.12	Difenoconazole-2	5.84	9.25	7.16	7.27
Diethofencarb	5.44	4.17	12.25	6.75	Beta-endosulfan	8.66	8.25	12.65	4.06	Azoxystrobin	5.01	4.22	4.54	5.80
Fenthion	4.11	5.06	9.33	5.36	Ethion	5.81	4.81	9.01	4.22					
Parathion	7.43	8.93	9.05	5.05	Triazophos	6.42	4.64	8.64	2.63	Among Total of 458 Components*2				
Triadimefon	5.66	7.30	9.52	9.15	Edifenphos	7.40	6.61	9.89	7.70	Number of Components with 10 % or Lower	440	406	334	438
Tetraconazole	9.01	8.56	9.70	6.59	Endosulfan sulfate	8.23	4.19	7.14	5.54	Average %RSD (excluding N.D.)	6.62	6.46	9.90	5.55
Dicofol degradation products	4.91	3.99	11.87	7.33	Quinoxyfen	4.23	8.59	12.91	2.30					

Items determined to have 20 % or more overlap (area values) between pesticide-spiked and blank samples are underlined (reference data).
*2 Excludes the 19 internal standard substances.

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