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Application Data Sheet

No.72

GC-MS
Gas Chromatograph Mass Spectrometer

Scan/MRM Analysis of Residual Pesticides in Foods Using GC-MS/MS (3)

The GCMS-TQ8030 is a triple quadrupole GC-MS/MS system equipped with scan/MRM mode to allow simultaneous scan and MRM data measurements. This data sheet introduces the results of an investigation using the scan/MRM mode, where target pesticides were quantitatively determined using the MRM data, and concentrations of the untargeted pesticides were estimated by applying the scan data to the Compound Composer Database Software Ver.2.

Experimental

For the evaluation, analytical standards (0.001 mg/L to 0.1 mg/L) were used, as well as samples (0.01 mg/L) created by pretreating paprika with the QuEChERS method, and then adding pesticides to the obtained solution. The pesticides specified as targets and their transitions were those recommended in the results of the validity evaluations by the European Reference Laboratory[1)]. The analysis conditions are shown in Table 1.

Table 1 Analytical Conditions

GC-MS :GCMS-TQ8030
Column :Rxi-5Sil MS (30 m length, 0.25 mm I.D., df=0.25 µm)
Glass Liner :Sky Liner, Splitless Single Taper Gooseneck w/Wool (Restek Corporation, catalog # 567366)

[GC]
Injection Temp. :250 °C
Column Oven Temp. :40 °C (2 min) → (8 °C /min) → 310 °C (5 min)
Injection Mode :Splitless
Flow Control Mode :Linear velocity (40.0 cm/sec)
Injection Volume :1 µL

[MS]
Interface Temp. :300 °C
Ion source Temp. :200 °C
Data Acquisition Mode :Scan/MRM
Event Time :0.1 sec (Scan), 0.3 sec (MRM)
Scan Mass Range :*m/z* 50 – 500
Scan Speed :5,000 u/sec

MRM Monitoring *m/z*

Compound Name	Quantitative Transition Precursor>Product	CE (V)	Qualitative Transition Precursor>Product	CE (V)	Precursor>Product	CE (V)
Diphenylamine	169.10>77.00	26	169.10>115.10	30		
Ethoprophos	200.00>157.90	6	200.00>114.00	14	200.00>97.00	26
Chlorpropham	213.10>171.10	6	213.10>127.10	18		
Trifluralin	306.10>264.00	8	264.10>206.10	8	264.10>160.10	18
Dicloran	206.00>176.00	12	206.00>124.00	26	176.00>148.00	12
Propyzamide	172.90>144.90	16	172.90>109.00	26		
Chlorothalonil	265.90>230.90	14	265.90>167.90	24	263.90>167.90	24
Diazinon	304.10>179.10	12	179.20>137.20	18		
Pyrimethanil	199.10>184.10	14	199.10>158.10	14		
Tefluthrin	197.10>141.10	26	177.10>127.10	32		
Pirimicarb	238.20>166.10	10	166.10>96.00	14		
Chlorpyrifos-methyl	285.90>270.90	12	285.90>93.00	22		
Vinclozolin	212.10>172.00	14	212.10>144.90	26	212.10>109.00	30
Parathion-methyl	263.10>109.00	18	263.10>81.00	26		
Tolclofos-methyl	265.00>249.90	12	265.00>93.00	24		
Metalaxyl	206.20>162.10	8	206.20>132.10	18		
Fenitrothion	277.10>125.00	18	277.10>109.00	18		
Pirimiphos-methyl	305.10>290.10	12	290.10>125.00	24		
Dichlofluanid	332.00>167.10	6	224.00>123.00	12		
Malathion	173.10>117.00	12	173.10>99.00	18		
Chlorpyrifos	196.90>168.90	14	196.90>107.00	26		
Fenthion	278.10>125.00	22	278.10>109.00	18		
Parathion	291.10>109.00	14	291.10>81.00	26		
Tetraconazole	336.10>218.00	18	336.10>204.00	26		
Pendimethalin	252.20>162.10	12	252.20>161.10	12		
Cyprodinil	225.20>224.10	6	224.20>208.10	18		
(E)-Chlorfenvinphos	323.10>266.90	14	267.00>159.00	18		
Tolylfluanid	137.10>91.00	18	137.10>65.00	26		
Fipronil	367.00>227.90	26	367.00>212.90	26		
Captan	79.00>77.00	8	79.00>51.00	22		
(Z)-Chlorfenvinphos	323.10>266.90	14	267.00>159.00	18		
Phenthoate	274.10>125.00	18	274.10>121.10	12		
Folpet	147.10>103.10	10	147.10>76.00	26		
Procymidone	283.10>96.10	12	283.10>67.10	24		
Methidathion	145.10>85.00	8	145.10>58.00	18		
alpha-Endosulfan	240.90>205.90	14	238.90>203.90	16		
Mepanipyrim	222.20>220.10	8	222.20>193.10	26		
Profenofos	337.10>266.80	16	207.90>63.00	26		
Myclobutanil	179.10>152.00	8	179.10>125.00	16		
Flusilazole	233.10>165.10	18	233.10>152.10	18		

Compound Name	Quantitative Transition Precursor>Product	CE (V)	Qualitative Transition Precursor>Product	CE (V)	Precursor>Product	CE (V)
Buprofezin	172.10>57.10	18	105.10>104.10	4		
Bupirimate	273.10>193.20	8	273.10>108.00	18		
beta-Endosulfan	240.90>205.90	14	238.90>203.90	14		
Oxadixyl	163.10>132.10	10	163.10>117.10	24		
Ethion	231.00>174.90	14	231.00>128.90	26		
Triazophos	161.10>134.10	8	161.10>106.10	14		
Endosulfan sulfate	386.90>252.90	10	386.90>216.90	26		
Propiconazole-1	259.10>190.90	8	259.10>172.90	18	259.10>69.10	12
Propiconazole-2	259.10>190.90	8	259.10>172.90	18	259.10>69.10	12
Tebuconazole	252.10>127.00	24	250.10>125.10	24		
Iprodione	314.10>244.90	12	314.10>56.10	24		
Bromopropylate	340.90>184.90	18	182.90>154.90	16		
Bifenthrin	181.10>166.10	16	181.10>165.10	22	181.10>153.10	10
Fenpropathrin	265.10>210.10	12	181.10>152.10	24	181.10>127.10	26
Fenazaquin	160.20>145.10	8	145.20>115.10	24	145.20>91.10	24
Tebufenpyrad	333.20>276.10	8	333.20>171.00	22		
Tetradifon	355.90>158.90	12	353.90>159.00	12	228.90>200.90	14
Phosalone	182.00>138.00	8	182.00>111.00	18	182.00>102.10	18
Pyriproxyfen	136.10>96.00	12	136.10>78.00	24		
Cyhalothrin	181.10>152.10	24	163.10>127.00	14	163.10>91.00	22
Fenarimol	251.00>139.00	18	139.10>111.00	16		
Acrinathrin	289.10>93.10	12	181.10>152.10	24	208.10>181.10	8
Permethrin-1	183.10>168.10	12	183.10>153.10	18	183.10>115.10	24
Pyridaben	147.20>132.10	14	147.20>117.10	22		
Permethrin-2	183.10>168.10	12	183.10>153.10	18	183.10>115.10	24
Cyfluthrin-1	206.10>151.20	24	163.10>127.10	6	163.10>91.00	14
Cyfluthrin-2	206.10>151.20	24	163.10>127.10	6	163.10>91.00	14
Cyfluthrin-3	206.10>151.20	24	163.10>127.10	6	163.10>91.00	14
Cyfluthrin-4	206.10>151.20	24	163.10>127.10	6	163.10>91.00	14
Cypermethrin-1	181.10>152.10	24	163.10>127.10	6	163.10>91.00	14
Cypermethrin-2	181.10>152.10	24	163.10>127.10	6	163.10>91.00	14
Cypermethrin-3	181.10>152.10	24	163.10>127.10	6	163.10>91.00	14
Cypermethrin-4	181.10>152.10	24	163.10>127.10	6	163.10>91.00	14
Ethofenprox	163.20>135.00	10	163.20>107.10	18		
Fenvalerate-1	125.10>99.00	22	125.10>89.00	22		
tau-Fluvarlinate-1	250.10>200.10	16	250.10>55.00	18		
Fenvalerate-2	125.10>99.00	22	125.10>89.00	22		
tau-Fluvarlinate-2	250.10>200.10	16	250.10>55.00	18		
Deltamethrin-1	252.90>93.10	18	181.10>152.10	24		
Deltamethrin-2	252.90>93.10	18	181.10>152.10	24		

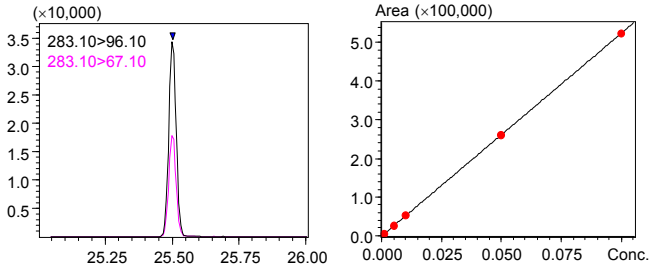
Results

An example of the results of the analysis of the analytical standards (0.001 mg/L to 0.1 mg/L) and the pesticide-spiked samples (0.01 mg/L) in scan/MRM mode are shown in Fig. 1. As with Procymidone, shown in Fig. 1, strict quantification of the targeted pesticides could be performed by creating calibration curves from the MRM data. Furthermore, since the scan data was sampled simultaneously, the pesticides could be confirmed from the mass spectrum.

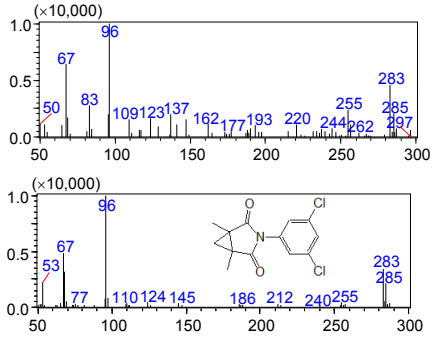
For the untargeted pesticides, data analysis was performed utilizing the Compound Composer Database Software (P/N: 225-13106-92). The simultaneous analysis database software contains information (mass spectra, retention times, and calibration curves) on more than 450 pesticides. As a result, it is possible to identify pesticides from their estimated retention times and mass spectra without using analytical standards, and then calculate semi-quantitative values from the calibration curves. Also in this investigation, it was possible to confirm the detection and semi-quantification of untargeted pesticides such as Quinoxyfen.

Analysis Results for Target Compounds

Procymidone: Quantitative value 0.0098 mg/L

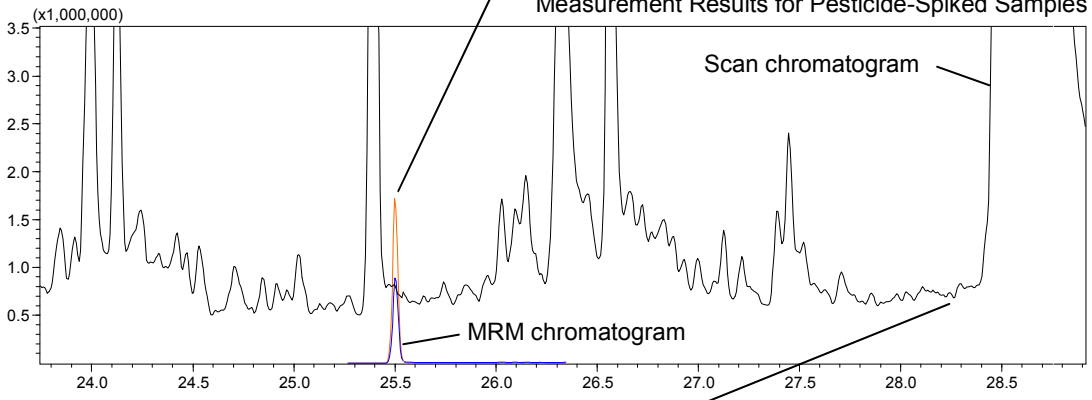


Quantitative determination by creating calibration curves from the MRM data



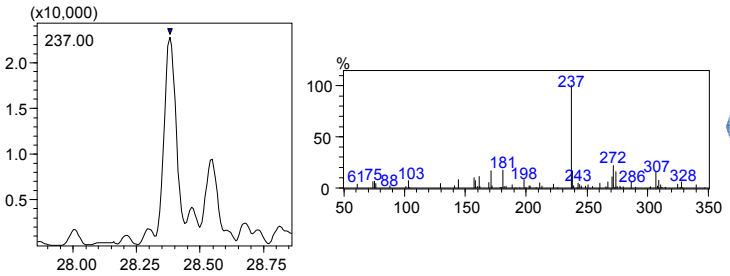
Mass spectral confirmation is possible with the scan data.
(Upper: Sampled mass spectrum; Lower: Mass spectrum in the library)

Measurement Results for Pesticide-Spiked Samples

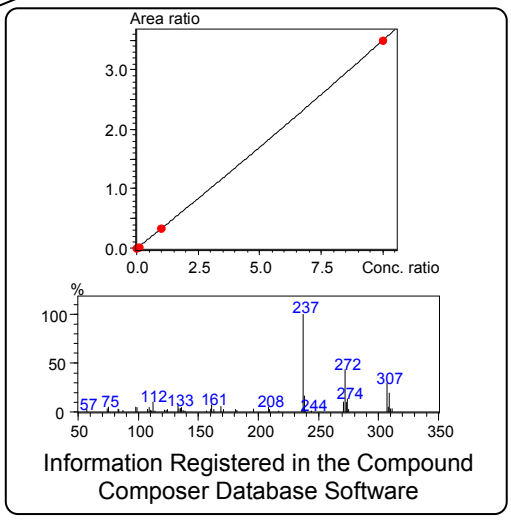


Screening Results for Other Pesticides

Quinoxyfen: Quantitative value 0.0134 mg/L



Compound identification and semi-quantitative calculations can be performed utilizing the information contained in the simultaneous analysis database software.



Information Registered in the Compound Composer Database Software

Fig. 1 Scan/MRM Analysis Results

Reference
1) EURL-FV Multiresidue Method using QuEChERS followed by GC-QqQ/MS/MS and LC-QqQ/MS/MS for Fruits and Vegetables (European Reference Laboratory, 2010-M1)

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