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Application Data Sheet

No.93

GC-MS
Gas Chromatograph Mass Spectrometer

Easy Screening for Residual Pesticides in Processed Foods Using GC-MS/MS

The analysis of residual pesticides in processed foods using GC-MS/MS, which provides excellent selectivity and sensitivity, has become a focus of attention.
Before starting GC-MS/MS measurements, it is necessary to optimize MRM transitions (precursor ions & product ions) and collision energies (CE) for each pesticide measured, which is extremely labor intensive. Furthermore, in order to calculate quantitative values, it is necessary to prepare standard samples and create calibration curves.
The Quick-DB database contains the optimal MRM conditions (MRM transitions and CE), mass spectra, retention indices, calibration curves and other information. This enables the semi-quantitative analysis of pesticides without using standard samples. Pesticide surrogates are used as the internal standard substances for calibration curves. Favorable quantitative accuracy is achieved by selecting the surrogates suited to each pesticide.
In analyzing residual pesticides in processed foods, which contain a number of contaminants, separating the pesticides from the contaminants can be impossible, even with GC-MS/MS. In this case, an effective approach to separating and detecting the pesticides is to perform the analysis with two columns respectively, which differ in their separation patterns. The information registered in Quick-DB is also compatible with analysis using two different columns for residual pesticides in processed foods. In addition, if the Twin Line MS system is used, the two columns can be attached to the MS unit simultaneously, so data can be sampled from the different columns smoothly, without compromising the MS vacuum.
This data sheet reports on the results of applying Quick-DB and the Twin Line MS system to the analysis of residual pesticides in curry.
Please also refer to Application Data Sheets No. 91 and No. 92. Application Data Sheet No. 91 introduced an example of easy screening for residual pesticides in foods using GCMS, while No. 92 introduced an example of using two columns with different separation patterns for easy screening of residual pesticides in foods.

Experiment

Using the Restek Q-sepTM, commercially-available retort-pouch curry was pretreated via the QuEChERS method. The sample solution obtained was spiked with 230 standard pesticide samples at a concentration of 10 ng/mL. The pesticide-spiked samples were then subjected to Scan/MRM analysis under the analysis conditions registered in Quick-DB. The analysis conditions are shown in Table 1. The two columns indicated in Table 1 were installed to a single GC-MS with the Twin Line MS system. The retention times for the pesticide components were estimated based on the analysis results for the n-alkane standard sample.

Table 1 Analysis Conditions

GC-MS:	GCMS-TQ8030 (Twin Line MS System)
Column 1:	Rxi-5Sil MS (30 m L., 0.25 mm I.D., df=0.25 µm) (Restek Corporation, P/N: 13623)
Column 2:	Rtx-200MS (30 m L., 0.25 mm I.D., df=0.25 µm) (Restek Corporation, P/N: 15623)
Glass Insert:	Sky Liner, Splitless Single Taper Gooseneck w/Wool (Restek Corporation, P/N: 567366)

[GC]

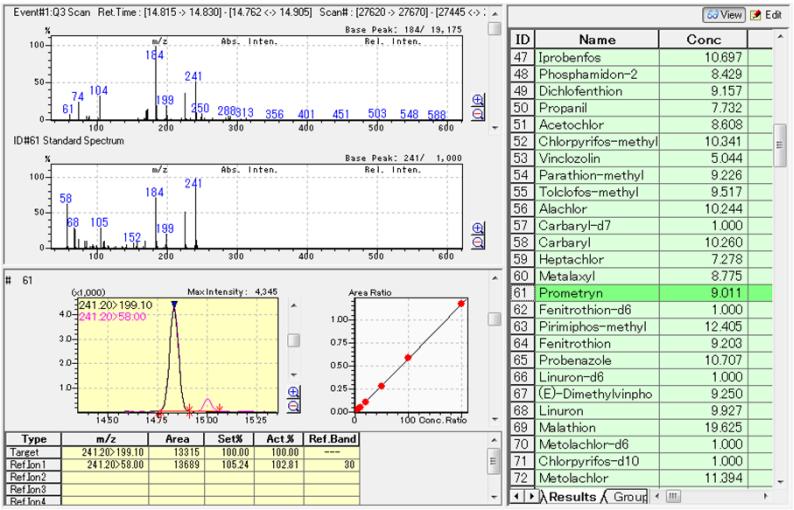
Vaporization Chamber Temperature:	250 °C
Column Oven Temperature:	60 °C (1 min) → (25 °C /min) → 160 °C → (4 °C /min) → 240 °C → (10 °C /min) → 290 °C (11 min)
Injection Mode:	Splitless
High Pressure Injection:	250 kPa (1.5 min)
Carrier Gas Control:	Linear velocity (40.0 cm/sec)
Injection Quantity:	2 µL

[MS]

Interface Temp.:	300 °C
Ion Source Temp.:	200 °C
Solvent Elution Time:	1.5 min
Measurement Mode:	FAAST (Scan/MRM simultaneous measurement)
Scan Mass Range:	m/z 50 to 330
Scan Event Time:	0.15 sec
Scan Speed	5,000 u/sec

Analysis Results

The liquid food extract spiked with pesticides was analyzed, and data processing was performed with Quick-DB. The analysis results are shown in Fig. 1. When semi-quantitative analysis was performed using the calibration curves registered in Quick-DB, favorable semi-quantitative values were obtained, close to the additive concentration of 10 ng/mL for many of the components.
To evaluate the quantitative accuracy for this analysis method, ratios were calculated for the semi-quantitative values with respect to the additive concentration. Then the pesticides were classified into those with a ratio under 50 %, 50 % to 200 %, and over 200 %, to find the distribution. The results are shown in Fig. 2. A significant 83 % of components had a semi-quantitative value 50 % to 200 % that of the concentration of the standard pesticide samples added. From this, it is evident that semi-quantitative analysis can be performed with high accuracy.



ID	Name	Conc
47	Iprobenfos	10.697
48	Phosphamidon-2	8.429
49	Dichlofenthion	9.157
50	Propanil	7.732
51	Acetochlor	8.608
52	Chlorpyrifos-methyl	10.341
53	Vinclozolin	5.044
54	Parathion-methyl	9.226
55	Tolclofos-methyl	9.517
56	Alachlor	10.244
57	Carbaryl-d7	1.000
58	Carbaryl	10.260
59	Heptachlor	7.278
60	Metalaxyl	8.775
61	Prometryn	9.011
62	Fenitrothion-d6	1.000
63	Pirimiphos-methyl	12.405
64	Fenitrothion	9.203
65	Probenazole	10.707
66	Linuron-d6	1.000
67	(E)-Dimethylvinpho	9.250
68	Linuron	9.927
69	Malathion	19.625
70	Metolachlor-d6	1.000
71	Chlorpyrifos-d10	1.000
72	Metolachlor	11.394

Type	m/z	Area	Set%	Act%	Ref.Band
Target	241.20>199.10	13315	100.00	100.00	---
Ref.Ion1	241.20>58.00	13689	105.24	102.81	30
Ref.Ion2					
Ref.Ion3					
Ref.Ion4					

As a result of calculation of the semi-quantitative values using the calibration curves preregistered in Quick-DB, favorable quantitative values were obtained.
(*The concentration of the internal standard is indicated as 1 ng/mL.)

Fig. 1 Analysis Results for the Pesticide-Spiked Samples (10 ng/mL concentration)

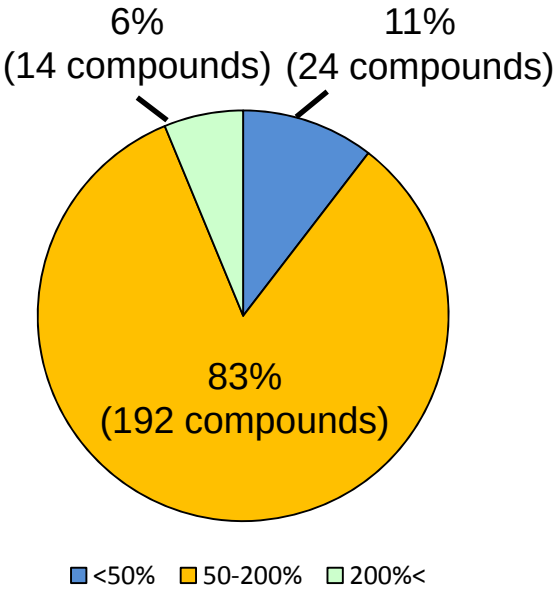


Fig. 2 Percentage Distribution of Semi-Quantitative Values with Respect to the Additive Concentration

In the analysis of residual pesticides in foods, when pesticide peaks are detected, it is necessary to check whether contaminants have been misidentified as pesticides, and whether contaminant overlap has inflated the size of the quantitative values. One confirmation method is to analyze the samples with columns with different separation patterns, and then check that essentially the same quantitative values are obtained for the pesticides detected in the respective columns. As an example, Fig. 3 shows the analysis results for dimethoate. With the Rxi-5Sil MS, there was an impact from contaminants, but with the Rts-200MS, there was not. Semi-quantitative value obtained from the calibration curves registered in Quick-DB was favorable, 9.6 ng/mL, for the use of the Rtx-200MS column. In this way, even for pesticides of which separation from contaminants is difficult, separation is possible if using columns with different separation patterns, enabling highly reliable semi-quantitative analysis.

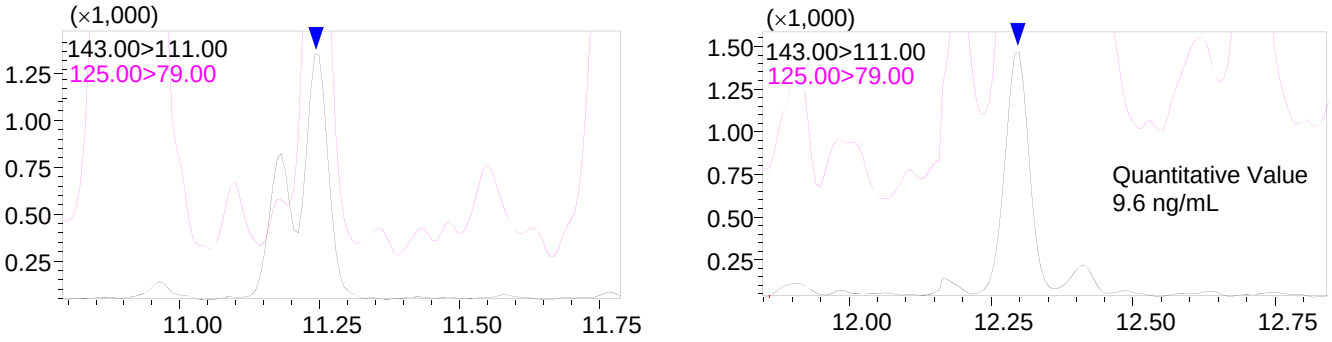


Fig. 3 Chromatograms for Liquid Curry Extract, Spiked with Dimethoate (10 ng/mL Concentration)
(Left: Rxi-5Sil MS; Right: Rtx-200MS)

High-accuracy semi-quantitative analysis was achieved quickly and easily, by attaching two columns to the GCMS-TQ8030 utilizing the Twin Line MS system, and then screening for residual pesticides in processed foods using Quick-DB.

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