SHIMADZU

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Simultaneous Analysis of Pesticides in Food With GC-MS/MS Using Hydrogen Carrier Gas

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1. Introduction

In GC-MS/MS analysis, helium gas is generally used as the carrier gas; however, in recent years the shortage of supply and the soaring price of helium gas have resulted in a need to pivot to other options. To address this problem, hydrogen gas is being used as an alternative carrier gas. The characteristics of hydrogen gas are different from those of helium gas, however, and methods using helium gas must be adjusted to appropriate conditions for hydrogen gas. We have developed a quantitative analysis method for 216 pesticides with GC-MS/MS using hydrogen gas. Using this method, good recovery results were obtained in food samples.

2. Methods

2-1. Samples and reagents

Oranges and spinach were bought at a grocery store and the whole fruit, including the peel, was freeze-ground. Freeze crushing was performed using Frestent FST-4000 (AiSTI SCIENCE).

Freeze-ground samples were extracted and cleaned up using the QuEChERS method. The Q-sep QuEChERS extraction salt kit (Restek, AOAC 2007.01, P/N: 25852) was used for extraction and the Q-sep QuEChERS extraction solution purification dSEP (Restek, AOAC 2007.01, P/N: 26222 for orange, P/N: 26219 for spinach) was used for cleanup.

2-2. Extraction and purification

15 g of frozen ground sample were weighed into a 50 mL tube and 15 mL of acetic acid/acetonitrile solution (1:100, v/v) were added. Next, Q-sep QuEChERS extract salt was added and immediately shaken vigorously by hand for 1 minute. Centrifugation was performed at 3,000 rpm for 5 minutes at room temperature. Acetonitrile layer was transferred to a dSEP tube containing a purification filler and shaken vigorously by hand for 1 minute. Supernatant was collected by centrifugation at 3,000 rpm for 5 minutes at room temperature.

5 mL of cleaned-up sample solution was concentrated to 0.5 mL or less using a nitrogen gas blowdown concentrator TurboVap LV (Biotage), and then adjusted to 5 mL with an acetone/hexane solution (1:1, v/v)*1 before GC-MS/MS analysis. Pesticide standard solutions were spiked at a final concentration of 10 ng/mL to verify recovery.

*1 Since precipitation occurred in the sample solution treated with orange, the sample was centrifuged at 3,000 rpm for 5 minutes at room temperature, and the supernatant was used as the sample for analysis.

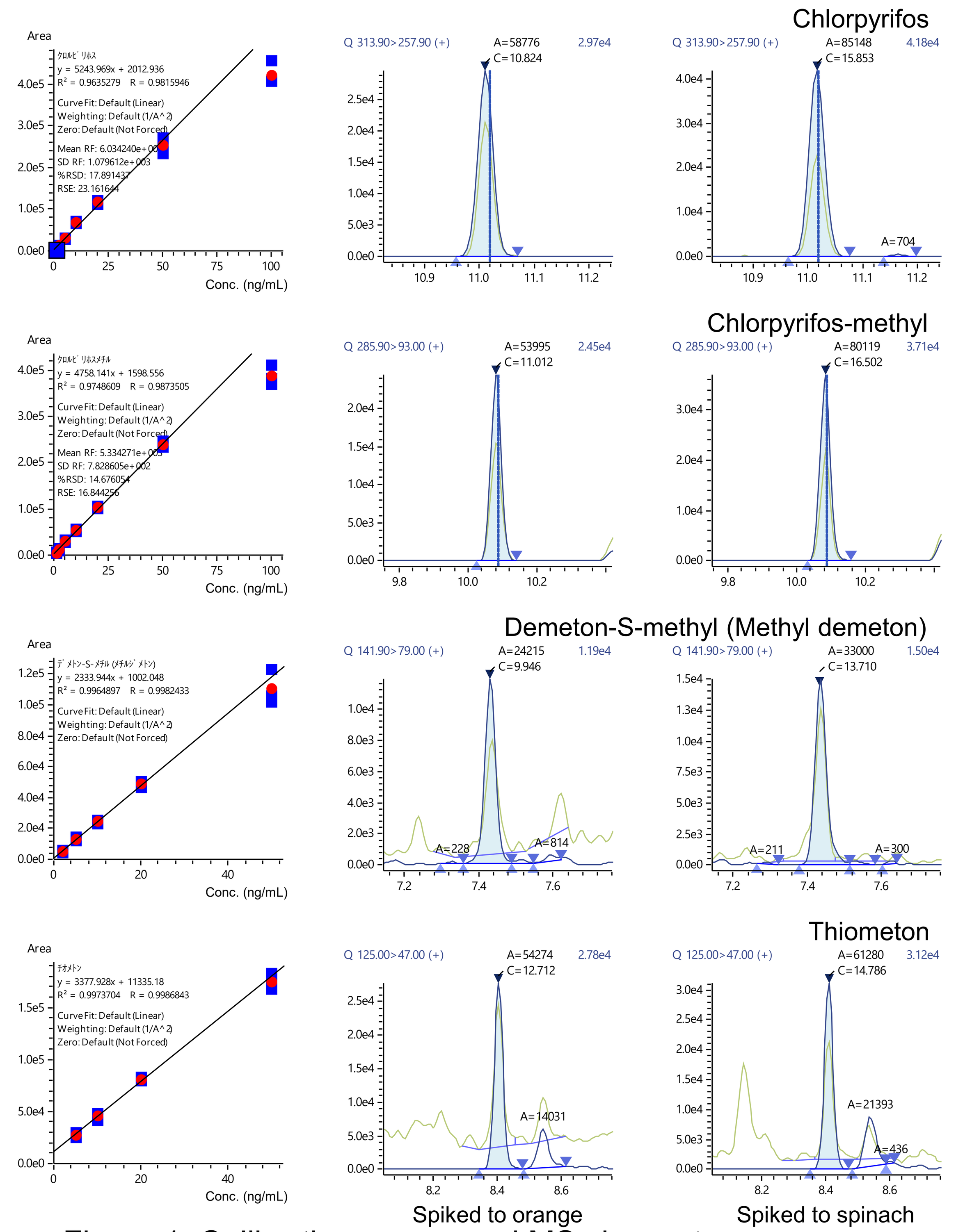

Figure 1. Calibration curves and MS chromatograms

Table 1. System and analysis conditions

System	
GC-MS Model	: GCMS-TQ8050 NX
Autoinjector	: AOC-30i + AOC-20s U
GC Conditions	
Carrier Gas	: H_2 (Hydrogen gas generator, Peak Scientific)
Carrier Gas Control	: Linear Velocity (60.5 cm/sec)
Column	: SH-I-5Sil MS (30 m x 0.25 mm I.D., 0.25 μm)
Guard Column	: Rxi Guard Column (5 m x 0.25 mm I.D.)
Column Temp.	: 70℃ (1 min) → (40℃/min) → 125℃ → (10℃/min) → 300℃ (20 min)
Injection Mode	: Spitless
Sampling Time	: 1.0 min
High Pressure Injection	: 200 kPa (1.5 min)
Injection Volume	: 1 μL
Injector Temp.	: 250℃
MS Conditions	
Ionization	: EI
Data Acquisition Mode	: MRM
Ion Source Temp.	: 230℃
Interface Temp.	: 250℃
Emission Current	: 150 μA

Table 2. Recovery rate of 216 pesticides

Compound	Recovery rate (%, n=3)	
	Orange	Spinach
1,1-Dichloro-2,2-bis(4-ethylphenyl)ethane	118.6	120.6
2,6-Dichlorobenzamide	95.2	98.9
2-Phenylphenol	74.6	96.3
Acetochlor	83.4	102.6
Alachlor	97.0	122.4
Allidochlor	93.0	103.0
Ametryn	87.0	102.0
Anilofos	90.9	129.6
Atrazine	112.5	113.7
Azaconazole	72.4	114.4
Benfuresate	58.7	83.3
Bifenazate	78.8	165.9
Bifenthrin	89.6	111.6
Biphenyl	80.6	76.7
Bitertanol-1	58.0	102.8
Bitertanol-2	67.9	116.0
Bromobutide	81.6	98.9
Bromophos	109.4	121.7
Bromophos-ethyl	102.4	98.8
Bromopropylate	109.8	157.3
Bromuconazole-1	84.2	132.7
Bromuconazole-2	116.6	186.4
Bupirimate	57.6	88.0
Buprofezin	74.9	90.8
Butachlor	38.6	92.0
Butylate	104.9	87.2
Cadusafos	113.8	108.5
Carbophenothion	102.3	120.9
Carboxin	68.1	88.5
Chlorbenside	88.3	99.6
Chlorfenson	93.3	124.5
(E)-Chlorfenvinphos	101.3	135.8
(Z)-Chlorfenvinphos	84.9	141.0
Chlormephos	113.6	119.0
Chlorobenzilate	116.4	161.2
Chloroneb	63.7	80.7
Chlorpropham	106.4	108.7
Chlorpyrifos	96.1	122.3
Chlorpyrifos-methyl	109.1	130.4
Chlorthal-dimethyl	79.9	99.2
Chlorthiophos-1	56.8	77.2
Chlorthiophos-2	92.7	116.4
Chlorthiophos-3	96.6	106.2
Cinmethylin	93.3	85.0
Clomazone	117.6	120.9
Clomeprop	69.9	107.8
Crimidine	69.5	92.6
Cyanofenphos	104.2	139.9
Cyanophos	73.8	92.5
Cyhalofop-butyl	110.5	195.2
Cyproconazole-1	77.0	102.8
Cyproconazole-2	77.3	103.2
Cyprodinil	73.5	94.6
DCIP	81.2	85.7
Demeton-S-methyl (Methyl demeton)	100.4	135.3
Di-allate-1	112.0	113.5
Di-allate-2	114.2	96.3
Diazinon	85.3	98.8
Dichlobenil	75.0	92.2
Dichlofenthion	90.4	101.8
Diclobutrazol	72.5	110.0
Diclocymet-1	50.0	88.5
Diclocymet-2	58.8	87.9
Dicrotophos	100.7	117.5
Diethofencarb	100.3	133.1
Difenoconazole-1	44.2	106.1
Difenoconazole-2	46.6	94.6
Diflufenican	90.2	132.1
Dimepiperate	92.6	105.4
Dimethametryn	77.5	82.2
Dimethenamid (Dimethenamid-P)	86.7	104.8
Dimethomorph-1	35.9	84.1
Dimethomorph-2	36.6	78.3
(E)-Dimethylvinphos	112.2	188.2
(Z)-Dimethylvinphos	120.0	183.5
Diniconazole	73.2	103.3
Dioxabenzofos (Salithion)	105.9	120.8
Dioxathion	41.3	93.7
Diphenamid	56.8	83.1
Diphenylamine	61.9	80.8
Disulfoton	100.2	108.3
Dithiopyr	73.2	90.9
Epoxiconazole	59.7	105.3
EPTC	106.0	95.5
Esprocarb	95.9	101.7
Ethion	100.2	112.2
Ethofumesate	56.0	86.9
Ethoprophos	137.6	97.4
Etobenzanid	76.6	134.2
Etofenprox	58.0	78.8
Etoxazole	76.1	132.7
Etrimfos	91.5	110.3
Fenamidone	57.3	119.1
Fenamiphos	79.0	141.9
Fenarimol	69.4	96.0
Fenbuconazole	51.6	115.4
Fenchlorphos	104.7	112.9
Fenitrothion	115.4	177.7
Fenothiocarb	62.8	89.3
Fenoxycarb	75.8	109.4
Fenpropimorph	95.1	85.3
Fensulfothion	68.7	93.3
Fenthion	93.5	132.7
Ferimzone	56.1	111.1
Flamprop-methyl	90.1	105.7
Fludioxonil	-288.6	110.5
Fluridone	41.9	94.1
Flusilazole	75.5	134.4
Flusilazole metabolite	89.9	66.1
Flutolanil	64.8	94.4
Flutriafol	83.6	120.8
Fonofos	96.7	108.9
Furametpyr	59.6	101.7
Furametpyr metabolite	48.4	85.3
Furilazole	115.7	136.3
Hexaconazole	79.7	92.6
Hexazinone	50.4	93.6
Indanofan	65.9	119.7
Iprobenfos	71.1	96.5
Isazofos	91.9	106.3
Isofenphos	88.1	110.6
Isofenphos oxon	119.8	198.3
Isoprothiolane	87.8	96.9
MCPB-ethyl	76.7	89.9
Mefenacet	69.7	118.7
Mepronil	70.9	96.2
Metalaxyl (Mefenoxam)	51.1	98.6
Methacrifos	82.0	112.9
Methidathion	93.4	140.1
Methoprene	111.3	122.6
Metolachlor (S-Metolachlor)	82.4	109.8
(E)-Metominostrobin	79.9	110.6
(Z)-Metominostrobin	64.6	118.0
Metribuzin	95.3	146.8
Mevinphos-1	91.2	144.2
Mevinphos-2	91.2	144.2
Molinate	85.2	85.2
Monocrotophos	85.1	161.6
Myclobutanil	67.6	94.0
Napropamide	73.1	96.8
Nereistoxin	130.0	117.7
Norflurazon	70.7	94.6
Oxadiazon	79.2	93.3
Oxadixyl	53.7	98.1
Oxpoconazole	45.5	111.0
Paclobutrazol	69.5	113.8
Penconazole	73.2	83.8
Permethrin-1	116.1	147.7
Permethrin-2	80.8	99.8
Phenothrin-1	116.8	185.5
Phenothrin-2	134.1	136.7
Phenthoate	95.1	142.6
Phorate	109.3	114.3
Picolinafen	63.1	90.1
Piperonyl butoxide	62.1	88.7
Piperophos	54.0	99.5
Pirimiphos-methyl	92.8	123.0
Pretilachlor	116.5	132.6
Procymidone	61.3	86.7
Prohydrojasmon-1	90.6	84.6
Prohydrojasmon-2	75.7	79.9
Prometryn	85.3	97.9
Propachlor	58.5	86.4
Propanil	85.6	105.7
Propaphos	72.1	110.3
Propazine	109.2	108.7
Propiconazole-1	82.3	93.4
Propiconazole-2	64.5	101.0
Propyzamide	85.9	116.3
Pyributicarb	92.4	115.3
Pyridaben	74.0	95.8
(E)-Pyrifenox	68.7	109.5
(Z)-Pyrifenox	64.3	87.2
Pyrimethanil	74.3	87.9
Pyrimidifen	76.0	104.6
(E)-Pyriminobac-methyl	60.8	102.6
(Z)-Pyriminobac-methyl	65.0	110.7
Pyriproxyfen	76.5	98.7
Pyroquilon	53.4	81.6
Quinalphos	62.0	84.7
Quinoclamine	102.5	237.0
Quinoxyfen	74.9	88.1
Resmethrin-1	88.5	9.6
Resmethrin-2 (Bioresmethrin)	73.5	92.1
Silafluofen	66.6	86.0
Simazine	86.4	89.9
Simeconazole	89.0	133.1
Simetryn	77.3	109.5
Spiroxamine-1	85.1	89.4
Spiroxamine-2	75.9	77.8
Sulfotep	102.1	118.9
Sulprofos	99.6	129.0
Tebuconazole	61.2	97.9
Tebufenpyrad	65.0	93.7
Tebupirimfos	100.7	100.4
Tefluthrin	84.4	87.8
Terbacil	113.1	172.2
Terbufos	95.8	97.6
Terbutryn	81.3	103.5
Tetraconazole	73.8	115.1
Tetradifon	114.7	152.1
Thenylchlor	62.3	92.5
Thiabendazole	-842.7	117.3
Thifluzamide	81.5	134.6
Thiobencarb	98.9	124.1
Thiocyclam	124.8	114.8
Thiometon	119.7	127.3
Tolclofos-methyl	79.2	103.8
Tolfenpyrad	45.4	86.3
Triadimefon	88.6	106.5
Triadimenol-1	71.4	93.3
Triadimenol-2	78.7	106.9
Tri-allate	116.4	110.0
Triazophos	76.8	138.0
Uniconazole (Uniconazole-P)	75.0	122.5
Vinclozolin	84.0	108.1

2-3. Equipment

Quantification was performed with a triple quadrupole mass spectrometer GCMS-TQ8050 NX equipped with AOC-30i and AOC-20s U as injectors (Shimadzu Corporation). The column was the same size as that commonly used when helium gas is used. The system configuration is shown table 1. This system enables accurate simultaneous analysis of multiple components. LabSolutions Insight^{TM}, a quantitative analysis support software optimized for multi-analyte and multi-component analysis, was used for the analysis.

3. Results

Recovery tests were conducted in triplicate at 10 ng/mL to verify the recovery rates and repeatability. For calculation of recovery rate, the peak area values of compounds were compared with the standard solution. Table 2 shows the recovery rate of pesticides spiked into orange and spinach. The recovery rate was within 70 to 120% for 151 compounds (70%) in orange and 159 in spinach (74%). Also, there were 173 compounds in the reference standard, 144 in orange, and 182 in spinach that had a repeatability (%RSD) of 10% or less in 3 replicates (data not shown in the table).

In addition, using standard solutions, calibration curves could be generated at 1 to 100 ng/mL for 152 compounds (70%) and at 2 to 100 ng/mL for 28 compounds (13%). The calibration curves and MS chromatograms of some compounds are shown in figure 1. The middle column shows MS chromatograms of samples spiked into orange and the right column shows MS chromatograms of samples spiked into spinach.

Figure 2. GCMS-TQ8050 NX

4. Conclusions

- Using hydrogen gas as an alternative carrier gas, we simultaneously analyzed 216 food-borne agrochemicals using an ultra-sensitive triple-quadrupole mass spectrometer GCMS-TQ8050 NX combined with AOC-30i and AOC-20s U as injectors.
- Good recovery rate within 70 ~ 120% were obtained for 70% to 74% of the compounds. This system enables simultaneous analysis of multiple pesticides with high sensitivity and accuracy.