

# カーバメート及び含窒素系農薬の固相抽出法による精製及びGC/MS選択的イオンモニター(SIM)法を用いた測定

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**Note**

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**Study on GC/MS (SIM) for Determination of Carbamate and Organonitrogen Pesticides in Foods with Simple Clean-up by SPE Method**

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Studies to develop a GC/MS (SIM) method for the determination of 34 pesticides including carbamates and organonitrogen pesticides in foods with solid-phase extraction (SPE) were conducted.

Three kinds of SPE columns, a porous diatomaceous earth cartridge column, a diatomite column with a mini C<sub>18</sub> cartridge column and a Florisil cartridge column were used successively to clean-up the extract from foods as an alternative to a separatory funnel for liquid-liquid partition. The handling was simpler than the conventional method and gave high recoveries of the pesticides.

In GC/MS (SIM), 2 to 4 different fragment ions were selected for each pesticide so that the GC/MS (SIM) identification could be done more accurately for multi-residue analysis of carbamate and organonitrogen pesticides. This simpler method was applicable for 29 pesticides out of 34 with almost the same recoveries and detection limits as the conventional method.

**Key words:** gas chromatography/mass spectrometry (GC/MS); MS fragmentation; pesticides; solid-phase extraction (SPE); selected ion monitoring (SIM); carbamate pesticides

**Introduction**

Much attention has been paid to the levels of pesticide residues in foods in Japan because of the increasing amount of imported foods and growing concern about the safety of foods. Several GC/MS methods for newly introduced pesticides have been reported recently<sup>1)-4)</sup>. Multi-residue analyses of pesticides using the GC/MS (SIM) technique were reported in our previous papers<sup>5), 6)</sup>. *N*-Methylcarbamate pesticides are determined by an HPLC method using post column-fluorescent labeling with *o*-phthalaldehyde (OPA)<sup>7)</sup> according to the Japanese Food Sanitation Law.

This paper deals with a study of a multi-residue analytical method employing GC/MS (SIM) for 34 carbamate and organonitrogen pes-

ticides, with clean-up using three kinds of solid-phase extraction (SPE) column, to avoid the need for liquid-liquid partition with a separatory funnel. The determination limits of these pesticides were compared between the GC/MS (SIM) method and the HPLC method using post column fluorescent labeling with OPA.

**Materials and Methods***Solvent and reagent*

Acetone, *n*-hexane, methanol and acetonitrile (MeCN) were of the grade for pesticide residue analysis. Reagents were of pesticide residue grade or specified grade.

*Pesticide standard*

Standard reference materials of 34 pesticides, amitraz, aldicarb, isoprocarb, esprocarb, ethiofen-

carb, oxamyl, carbaryl (NAC), carbofuran, clofe-  
n-tezine, chlorpropham, diethofencarb, swep  
(MCC), triadimenol, pyridaben, pirimicarb, fen-  
obucarb (BPMC), flutolanil, pretilachlor, pro-  
panil (DCPA), propamocarb, propiconazole, pro-  
poxur (PHC), bendiocarb, pendimethalin, myc-  
lobutanil, methomyl, methiocarb, methiocarb sul-  
fone, methiocarb sulfoxide, metribuzin, metol-  
carb (MTMC), mefenacet, mepronil and lenacil  
were purchased from Hayashi Pure Chemical  
Industries, Ltd. (Osaka, Japan) or Wako Pure  
Chemical Industries, Ltd. (Osaka, Japan).

#### *Solid-phase extraction (SPE) columns*

Extube<sup>®</sup>20 (20 g) purchased from Varian Co.  
(U.S.A.), Extrelut<sup>®</sup> 3 (5 g) from Merck (Germany)  
with a Sep-Pak<sup>®</sup> C<sub>18</sub> (500 mg) cartridge from  
Waters Co. (U.S.A.) and Bond Elut<sup>®</sup> LRC (3 cc/  
500 mg) Florisil from Varian Co. (U.S.A.) were  
used for SPE.

#### *Samples*

Apple, cabbage, rice, potato, soybean and  
banana were obtained at markets in Japan.

#### *Gas chromatography/mass spectrometry*

A Shimadzu GC-17A gas chromatograph was  
coupled with a Parvum QP 5,000 mass spec-  
trometer and a Shimadzu AOC-17 injector. Data  
processing was done with a Sanyo AXAGE  $\nu$   
computer, Shimadzu software class 5,000 and  
MS Windows. GC conditions were as follows.  
GC column, J & W Scientific capillary column  
DB-5ms<sup>®</sup> (0.25 mm i.d.  $\times$  30 m, film thickness  
0.25  $\mu$ m); oven temp., 50°C (1.5 min) increasing  
to 300°C (10 min) at 10°C/min; injection temp.,  
250°C; transfer line temp., 280°C; carrier gas, He  
at 20 mL/min; injection volume, 1  $\mu$ L (splitless);  
sampling time, 1.00 min.

MS conditions were as follows. Electron  
impact ionization (EI) mode; ion source voltage,  
70 eV; detector gain, 1.75 kV; solvent elution  
time, 3.00 min; measurement time, 4.00~35.00  
min; mass range,  $m/z$  40.00~400.0.

#### *Selected ion monitoring (SIM) method*

SIM operating conditions were as follows. De-  
tector gain, 2.5 kV; maximum ion set number,  
20; solvent elution time, 3.00 min; sampling rate,  
0.30 sec; micro scan width, 0.50. GC/MS soft-

ware was class 5,000 (Shimadzu), with Windows  
3.0.

#### *Post column HPLC*

A Shimadzu carbamate pesticide-analytical  
system was used as follows. Separation unit,  
LC-10AT pump and DGU-4A degasser; FCV-10  
AL low-pressure gradient unit, and SIL-10A  
auto injector; reaction unit, LC-10AD pump,  
DGU-4A degasser and CRB-6A reaction vessel;  
detector, RF-10XL fluorescence detector; data  
processing apparatus, Fujitsu FMV-575<sub>05</sub> com-  
puter, Shimadzu software CLASS-LC10 and  
Windows-95.

HPLC conditions were as follows. Column,  
YMC-Pack<sup>®</sup> ODS-AM (150  $\times$  6.0 mm i.d.); column  
oven temp., 50°C; mobile phase, gradient elution  
(10% MeOH  $\rightarrow$  90% MeOH) increased at MeOH  
0.8 mL/min.

Fluorescence reaction was conducted by heat-  
ing with 50 mmol NaOH (A) at 100°C and then  
passing a mixture (B) of 0.25 mmol OPA and  
0.25 mmol  $\beta$ -mercaptopropionic acid in 120  
mmol boric acid buffer at 50°C at a flow rate of  
0.4 mL/min. Fluorescence intensity was meas-  
ured at wave lengths of 340 nm (excitation) and  
445 nm (emission).

#### *Preparation of the test solution*

Carbamate and organonitrogen pesticides  
were extracted twice with 100 mL of acetone  
from 20 g samples of chopped vegetables or  
fruits and ground nuts or crops. After paper  
filtration, the total volume of combined extracts  
was adjusted to 200 mL with acetone. Fifty mL  
of the acetone extract was evaporated under  
reduced pressure. The residual aqueous solu-  
tion was mixed with 5 mL of 5% NaCl solution  
and then loaded on an Extube<sup>®</sup> 20 cartridge  
column. Five minutes later, the column was  
eluted with 100 mL of a mixture of *n*-hexane  
and acetone (9 : 1). The eluate was evaporated to  
a small volume and dried with a gentle stream of  
N<sub>2</sub> gas. The residue was dissolved in 3 mL of  
hexane. All the *n*-hexane solution was loaded on  
an Extrelut<sup>®</sup> 3 cartridge column connected to a  
Sep-Pak<sup>®</sup> C<sub>18</sub> cartridge at the tip. After 10 min-  
utes, the Extrelut<sup>®</sup> 3 column was eluted with 20  
mL of MeCN saturated with *n*-hexane, and the  
eluate was concentrated and dried with a flow of

**Table 1.** Recoveries of 34 Carbamate and Organonitrogen Pesticides from Columns of Extube 20, Extrelut 3+Sep-Pak C<sub>18</sub> and Bond Elut Florisil

Ion Set	No.	Pesticide	Target ion (m/z)	Recovery (%) <sup>1)</sup>		
				Extube 20	Extrelut 3+ Sep-Pak C <sub>18</sub>	Bond Elut Florisil
#1 <sup>d)</sup>	1	Aldicarb	100	104.2±3.7	97.1±12.1	95.1±9.2
	2	Methomyl	105	N.D.	86.3±6.8	N.D.
	3a	Metolcarb	108	97.1±4.8	101.6±8.7	87.1±6.5
	4	Clofentezine	137	103.0±7.3	81.3±0.9	92.4±7.1
	5	Propoxur (PHC)	110	95.7±12.0	81.4±1.4	100.1±14.0
#2 <sup>d)</sup>	6a	Bendiocarb	151	100.1±7.9	97.5±1.9	98.0±11.0
	7a	Carbofuran	164	94.2±7.9	81.6±1.2	102.1±18.8
	8a	Swep (MCC)	187	94.8±8.7	101.0±5.6	89.6±10.3
	9	Propamocarb	58	16.4±11.4	14.9±1.1	3.4±1.6
	10	Ethiofencarb	107	99.6±8.1	91.0±5.4	93.2±11.5
#3 <sup>d)</sup>	3b	Metolcarb	108	110.1±14.4	105.8±8.8	94.6±11.1
	11	Carbaryl (NAC)	115	89.6±8.3	98.7±7.9	98.0±11.5
	12	Oxamyl	98	35.2±8.3	102.4±6.4	28.7±6.4
	13	Isoprocarb (MIPC)	121	105.7±11.0	106.7±5.3	95.5±16.5
	14a	Methiocarb	168	107.1±7.1	92.7±3.5	98.2±11.5
#4 <sup>d)</sup>	15	Fenobucarb (BPMC)	121	110.8±4.9	106.9±6.7	94.1±12.6
	5b	Propoxur (PHC)	110	107.3±9.4	106.5±1.4	100.3±19.0
	16	Chlorpropham	127	101.3±7.4	98.1±8.7	94.8±13.4
	6b	Bendiocarb	151	104.4±9.9	102.5±6.8	88.0±8.6
	7b	Carbofuran	164	105.6±0.6	103.9±10.5	94.1±15.3
#5 <sup>d)</sup>	8b	Swep (MCC)	187	102.0±6.0	103.0±7.3	90.2±13.9
	17	Pirimicarb	166	104.0±5.7	104.6±6.4	96.6±16.3
	10b	Ethiofencarb	107	94.8±14.3	104.8±2.2	88.6±10.7
	18	Propanil (DCPA)	161	101.3±5.0	97.8±7.4	88.3±7.2
	19	Metribuzin	198	107.8±1.7	102.2±5.4	93.8±19.0
#6 <sup>d)</sup>	20	Methiocarb-sulfoxide	168	7.3±8.0	103.9±4.2	N.D.
	21	Methiocarb-sulfone	121	N.D.	103.6±3.5	33.4±22.6
	14b	Methiocarb	153	101.3±5.6	101.5±6.6	89.1±9.5
	22	Esprocarb	91	105.0±9.2	108.9±6.5	99.7±13.4
	23	Diethofencarb	151	108.3±4.7	105.6±6.5	83.7±8.8
#7 <sup>d)</sup>	24	Pendimethalin	252	100.4±7.1	101.6±4.9	90.5±15.6
	25a	Triadimenol	112	93.3±8.4	99.2±6.3	86.6±5.0
	25b	Triadimenol	112	104.7±3.8	96.8±4.4	89.6±18.6
	26	Flutolanil	173	103.4±6.5	96.1±7.8	92.2±21.1
	27	Pretilachlor	162	106.4±6.2	99.1±2.2	98.2±6.9
#7 <sup>d)</sup>	28	Myclobutanil	179	105.2±5.4	98.3±3.8	78.5±18.9
	29	Mepronil	119	104.1±5.0	103.0±6.7	99.4±7.6
	30a	Propiconazole	173	97.0±1.9	101.1±3.4	90.1±2.4
	30b	Propiconazole	173	97.0±13.0	100.8±8.9	94.0±0.9
	31	Lenacil	153	105.1±4.3	99.0±13.1	98.5±12.2
	32	Amitraz	162	102.6±11.6	98.0±13.3	89.2±12.2
	33	Mefenacet	192	96.2±9.1	94.6±15.9	89.7±10.5
	34	Pyridaben	147	101.8±7.6	98.8±3.6	89.3±6.7

<sup>1)</sup> Each value represents the mean±SD of 3 trials  
Each pesticide (1 µg) was loaded on the column.

N<sub>2</sub> gas. The residue was dissolved in 5 mL of *n*-hexane. The *n*-hexane solution was applied to a Bond Elut<sup>®</sup> Florisil column conditioned with 2 mL of *n*-hexane, and the column was eluted with 5 mL of *n*-hexane (fraction 1), and then with 5 mL of *n*-hexane/acetone (17:3) (fraction 2). Each eluate was evaporated under N<sub>2</sub> gas, and the residue was dissolved in 5 mL of *n*-hexane (for GC/MS) or MeOH (for post column HPLC).

#### Recovery test

Thirty-four carbamate and organonitrogen pesticides were spiked into 6 kinds of agricultural products (including apple, cabbage, rice, potato, soybean and banana) at the concentration of 0.2 ppm. Each recovery was obtained as the average of three trials ( $n=3$ ).

### Results and Discussion

#### 1. Elution pattern on SPE

The usual multi-residue analyses of pesticides have employed three steps of purification, of which the first step is solvent extraction for liquid-liquid partition, followed by partition between MeCN and *n*-hexane and finally column chromatography. Our method adopted SPE purification only. First, elution on an Extube 20 cartridge was used instead of liquid-liquid partition. Secondly, elution on an Extrelut 3 column with Sep-Pak C<sub>18</sub> replaced MeCN partition. Finally, elution with Bond Elut Florisil was employed as column chromatography.

Extube 20, a cartridge column filled with porous diatomaceous earth, was able to separate 29 carbamate and organonitrogen pesticides out of 34 from the aqueous layer retained in the diatomaceous earth with 100 mL of a mixture of *n*-hexane and acetone (9:1). It appears that liquid-liquid partition between aqueous solvent and non-polar solvent occurred on the diatomaceous earth surface in the column in a short time without generating an emulsion. Recoveries of the 29 pesticides through the Extube 20 column were over 80%, but those of the 5 remaining pesticides, methomyl, propamocarb, oxamyl, methiocarb-sulfoxide and methiocarb-sulfone, were low (Table 1).

At the second step, an Extrelut<sup>®</sup> 3 column with Sep-Pak<sup>®</sup> C<sub>18</sub> was successful in separation of the residues from oil and lipophilic constitu-

ents, using a slight modification of a clean-up method reported by Di Muccio *et al.*<sup>8)</sup>. In the preliminary test, when 100  $\mu$ g of olive oil was loaded on the column and eluted with 20 mL of MeCN saturated *n*-hexane, over 98% of the oil was found on the column. Thirty-two pesticides out of 34 were eluted with over 80% recoveries, though propamocarb and oxamyl showed low recovery (Table 1). This step effectively replaced on-column *n*-hexane-MeCN partition to eliminate lipophilic materials.

At the third step, as shown in Table 1, most of the pesticides were eluted in fraction 2 with a mixture of *n*-hexane and acetone (17:3). Most of these pesticides were eluted through the Bond Elut-Florisil column with over 80% recovery, except for methomyl, propamocarb, oxamyl, methiocarb-sulfoxide and methiocarb sulfone. These five water-soluble pesticides showed low recoveries, as in the first step with Extube 20.

#### 2. GC/MS (SIM)

In order to obtain suitable target ions of the pesticides on GC/MS (SIM), 2 to 4 different fragment ions for each pesticide were selected, as listed in Table 2. The proposed ion assignments and determination limits corresponding to the target ions are listed in Table 2. Most of the pesticides gave three characteristic ions which afforded almost the same quantitative values, and were observed at similar relative intensity in both standard solution and test solution.

The 34 pesticides were divided into 7 groups (#1-#7) of ion sets for effective SIM measurement on the basis of their retention times in GC. Consequently, 31 pesticides were detectable by GC/MS (SIM) at levels of 1/5 to 1/10 of the maximum residue limits in the Japanese Law of Food Sanitation, though methomyl, oxamyl and mfenacet gave low sensitivity. Propoxur and pirimicarb, which could not be separated from each other in HPLC analysis according to the official method, could be separated well in this GC/MS (SIM) analysis.

When linear least-squares regression analysis was used, most of the pesticides showed good linearity in the range of 0.01 to 1  $\mu$ g/mL. The shown determination limits of 34 pesticides were 0.01 to 0.1  $\mu$ g/mL as shown in Table 1.

**Table 2.** Target Ions and Determination Limits of Carbamate and Organonitrogen Pesticides by GC/MS (SIM)

GC/MS (SIM)								
Ion set	No.	Pesticide	Retention time (min)	Molecular weight	Target ion <sup>a)</sup> ( <i>m/z</i> )	Proposed ion assignments	Determination limit ( $\mu\text{g/mL}$ )	Other target ion <sup>b)</sup> ( <i>m/z</i> )
#1 <sup>c)</sup>	1	Aldicarb	4.48	190	100	$[\text{C}_3\text{H}_5\text{O}_2\text{N}_2^{-1}]^+$	0.01	115
	2	Methomyl	7.39	162	105	$[\text{C}_3\text{H}_5\text{OSN}^{+1}]^+$	0.5	88
	3a <sup>j)</sup>	Metolcarb	7.63	165	108 <sup>*k)</sup>	$[\text{C}_7\text{H}_7\text{O}^{+1}]^+$	0.05	90
	4	Clofentezine	9.25	303	137	$[\text{C}_7\text{H}_4\text{NCl}]^+$	0.01	102
	5a <sup>j)</sup>	Propoxur (PHC)	9.25	152	110	$[\text{C}_6\text{H}_6\text{O}_2]^+$	0.01	152
	Measurement time (min): 4.00–10.00 Monitoring ion ( <i>m/z</i> ): 88, 90, 100, 102, 105, 108, 110, 115, 137, 152							
#2 <sup>d)</sup>	6a <sup>j)</sup>	Bendiocarb	10.79	223	151*	$[\text{C}_8\text{H}_6\text{O}_3^{+1}]^+$	0.01	126, 166
	7a <sup>j)</sup>	Carbofuran	11.21	221	164*	$[\text{C}_8\text{H}_7\text{O}_3\text{N}^{-1}]^+$	0.01	131, 149
	8a <sup>j)</sup>	Swep (MCC)	11.37	220	187*	$[\text{C}_7\text{H}_4\text{ONCl}_2]^+$	0.05	124, 159
	9	Propamocarb	12.61	188	58*	$[\text{C}_3\text{H}_7\text{O}^{-1}]^+$	0.05	
	10a <sup>j)</sup>	Ethiofencarb	13.00	225	107*	$[\text{C}_7\text{H}_6\text{O}^{+1}]^+$	0.05	168
	3b <sup>j)</sup>	Metolcarb	13.58	165	108*	$[\text{C}_7\text{H}_7\text{O}^{+1}]^+$	0.05	90
Measurement time (min): 10.00–13.80 Monitoring ion ( <i>m/z</i> ): 58, 90, 107, 108, 124, 126, 131, 149, 151, 159, 164, 166, 168, 187								
#3 <sup>e)</sup>	11	Carbaryl (NAC)	14.27	201	115*	$[\text{C}_9\text{H}_7]^+$	0.05	144
	12	Oxamyl	14.43	219	98*	$[\text{C}_4\text{H}_6\text{N}_2\text{O}]^+$	0.1	72, 115, 145
	13	Isoprocarb (MIPC)	14.57	193	121*	$[\text{C}_8\text{H}_8\text{O}^{+1}]^+$	0.01	136
	14a <sup>j)</sup>	Methiocarb	14.73	225	168*	$[\text{C}_9\text{H}_{11}\text{OS}^{+1}]^+$	0.01	109, 153
	15	Fenobucarb (BPMC)	15.47	207	121*	$[\text{C}_7\text{H}_4\text{O}_2^{+1}]^+$	0.01	150, 207
	5b <sup>j)</sup>	Propoxur (PHC)	15.48	209	110*	$[\text{C}_6\text{H}_6\text{O}_2]^+$	0.01	152, 209
Measurement time (min): 13.80–15.80 Monitoring ion ( <i>m/z</i> ): 72, 98, 109, 110, 115, 121, 136, 144, 145, 150, 152, 153, 168, 207, 209								
#4 <sup>f)</sup>	16	Chlorpropham	16.12	213	127*	$[\text{C}_6\text{H}_5\text{NCl}^{+1}]^+$	0.01	171, 213
	6b <sup>j)</sup>	Bendiocarb	16.27	223	151*	$[\text{C}_8\text{H}_6\text{O}_3^{+1}]^+$	0.01	126, 166
	7b <sup>j)</sup>	Carbofuran	17.07	221	164*	$[\text{C}_8\text{H}_7\text{O}_3\text{N}^{-1}]^+$	0.01	149
	8b <sup>j)</sup>	Swep (MCC)	17.19	220	187*	$[\text{C}_7\text{H}_4\text{ONCl}_2^{-1}]^+$	0.05	124, 219
	17	Pirimicarb	18.18	238	166*	$[\text{C}_8\text{H}_{12}\text{N}_3\text{O}]^+$	0.01	238
	10b	Ethiofencarb	18.36	225	107*	$[\text{C}_7\text{H}_6\text{O}^{+1}]^+$	0.05	168, 225
Measurement time (min): 15.80–18.45 Monitoring ion ( <i>m/z</i> ): 107, 124, 126, 127, 149, 151, 164, 166, 168, 171, 187, 213, 219, 225, 238								
#5 <sup>g)</sup>	18	Propanil (DCPA)	18.60	218	161*	$[\text{C}_6\text{H}_4\text{NCl}_2^{+1}]^+$	0.05	217
	19	Metribuzin	18.72	214	198	$[\text{C}_8\text{H}_{12}\text{ON}_3\text{S}]^+$	0.01	
	20	Methiocarb-sulfoxide	18.84	241	168	$[\text{C}_9\text{H}_{11}\text{OS}^{+1}]^+$	0.5	153
	21	Methiocarb-sulfone	19.20	257	121*	$[\text{C}_8\text{H}_9\text{O}]^+$	0.05	137, 200
	14b <sup>j)</sup>	Methiocarb	19.41	225	153	$[\text{C}_8\text{H}_9\text{OS}]^+$	0.01	168, 225
	22	Esprocarb	19.55	265	91*	$[\text{C}_7\text{H}_7]^+$	0.01	222, 265
23	Diethofencarb	19.69	267	151	$[\text{C}_8\text{H}_9\text{O}_2\text{N}]^+$	0.01	207, 267	
Measurement time (min): 18.45–20.00 Monitoring ion ( <i>m/z</i> ): 91, 121, 137, 151, 153, 161, 168, 198, 200, 207, 217, 225, 265, 267								
#6 <sup>h)</sup>	24	Pendimethalin	20.38	281	252*	$[\text{C}_{11}\text{H}_{14}\text{N}_3\text{O}_4]^+$	0.01	162, 281
	25a <sup>j)</sup>	Triadimenol	20.78	296	112	$[\text{C}_6\text{H}_4\text{Cl}^{+1}]^+$	0.05	128, 168
	25b <sup>j)</sup>	Triadimenol	20.95	296	112	$[\text{C}_6\text{H}_4\text{Cl}^{+1}]^+$	0.05	128, 168
	26	Flutolanil	21.52	323	173*	$[\text{C}_8\text{H}_4\text{OF}_3]^+$	0.05	145, 323
	27	Pretilachlor	21.62	312	162*	$[\text{C}_{11}\text{H}_{15}\text{N}^{+1}]^+$	0.01	176, 311
Measurement time (min): 20.00–22.00 Monitoring ion ( <i>m/z</i> ): 112, 128, 145, 150, 162, 168, 173, 176, 179, 252, 281, 288, 311, 323								

Table 2. Continued

GC/MS (SIM)									
Ion Set	No.	Pesticide	Retention time (min)	Molecular weight	Target ion <sup>a)</sup> ( <i>m/z</i> )	Proposed ion assignments	Determination limit ( $\mu\text{g/mL}$ )	Other target ion <sup>b)</sup> ( <i>m/z</i> )	
#7 <sup>i)</sup>	28	Myclobutanil	21.89	289	179*	[C <sub>11</sub> H <sub>13</sub> Cl <sup>-</sup> ] <sup>+</sup>	0.05	150, 288	
	29	Mepronil	22.92	91	119*	[C <sub>8</sub> H <sub>7</sub> ] <sup>+</sup>	0.01	91, 269	
	30a <sup>j)</sup>	Propiconazole	23.22	342	173*	[C <sub>7</sub> H <sub>3</sub> OCl <sub>2</sub> ] <sup>+</sup>	0.05	259	
	30b <sup>j)</sup>	Propiconazole	23.22	342	173*	[C <sub>7</sub> H <sub>3</sub> OCl <sub>2</sub> ] <sup>+</sup>	0.05	259	
	31	Lenacil	23.37	234	153*	[C <sub>8</sub> H <sub>11</sub> O <sub>2</sub> N] <sup>+</sup>	0.01		
	32	Amitraz	23.37	293	162	[C <sub>10</sub> H <sub>13</sub> N <sub>2</sub> <sup>+1</sup> ] <sup>+</sup>	0.05	147, 132, 293	
	33	Mefenacet	25.32	298	192*	[C <sub>9</sub> H <sub>6</sub> O <sub>2</sub> NS] <sup>+</sup>	0.1	120, 298	
	34	Pyridaben	26.43	366	147*	[C <sub>11</sub> H <sub>15</sub> ] <sup>+</sup>	0.05	364	
	Measurement time (min): 22.00–35.00								
	Monitoring ion ( <i>m/z</i> ): 91, 119, 120, 132, 147, 153, 162, 173, 192, 259, 269, 293, 298, 364								

<sup>a)</sup>: Target ions for quantitative analysis were the base peak or a peak of high intensity.

<sup>b)</sup>: Other target ions were used for identification.

<sup>c)</sup>: #1 is grouped according to measurement time: 4.00–10.00.

Monitoring ion *m/z* 88, 90, 100, 102, 105, 108, 110, 115, 137, 152

<sup>d)</sup>: #2 is grouped according to measurement time: 10.00–13.80.

Monitoring ion *m/z* 58, 90, 107, 108, 124, 126, 131, 149, 151, 159, 164, 166, 168, 187

<sup>e)</sup>: #3 is grouped according to measurement time: 13.80–15.80.

Monitoring ion *m/z* 72, 98, 109, 110, 115, 121, 136, 144, 145, 150, 152, 153, 168, 207, 209

<sup>f)</sup>: #4 is grouped according to measurement time: 15.80–18.45.

Monitoring ion *m/z* 107, 124, 126, 127, 149, 151, 164, 166, 168, 171, 187, 213, 219, 225, 238

<sup>g)</sup>: #5 is grouped according to measurement time: 18.45–20.00.

Monitoring ion *m/z* 91, 121, 137, 151, 153, 161, 168, 198, 200, 207, 217, 225, 265, 267

<sup>h)</sup>: #6 is grouped according to measurement time: 20.00–22.00.

Monitoring ion *m/z* 112, 128, 145, 150, 162, 168, 173, 176, 179, 252, 281, 288, 311, 323

<sup>i)</sup>: #7 is grouped according to measurement time: 22.00–35.00.

Monitoring ion *m/z* 91, 119, 120, 132, 147, 153, 162, 173, 192, 259, 269, 293, 298, 364

<sup>j)</sup>: Isomer or decomposition was observed.

<sup>k)</sup>: Base peak

### 3. Recoveries

Pesticides equivalent to 0.2 ppm were spiked into 20 g samples to investigate recoveries from apple, cabbage, rice, potato, soybean and banana. Twenty-nine pesticides gave good recoveries of over 80%, except for 5 water-soluble pesticides as previously described under SPE extraction from (see Results and Discussion, section 1). The recoveries of metribuzin and amitraz from apple were low (57.37%, 32.95%) (Table 3). These two pesticides may be decomposed by components in apples.

Since no interference peak derived from agricultural foods was detected in GC/MS (SIM), this method is effective for multi-residue analyses of carbamate and organonitrogen pesticides.

### 4. Comparison between GC/MS (SIM) and post column HPLC

Although the sensitivities of the GC/MS (SIM) method for *N*-methyl carbamate pesticides were almost equivalent to those of the post column HPLC method, the GC/MS (SIM) method is applicable to more pesticides than the post column HPLC method. Furthermore, identification by the GC/MS (SIM) method adopting multiple target ions was more selective than in the post column HPLC method.

### Conclusions

- Multi-residue analysis of 29 pesticides by a GC/MS (SIM) method was developed to replace the conventional post column HPLC method and GC equipped with a selective

Table 3. Recoveries of Carbamate and Organonitrogen Pesticides from 6 Agricultural Foods

Ion set	No.	Pesticide	Target ion (m/z)	Recovery (%) <sup>1)</sup>					
				Apple	Cabbage	Rice	Potato	Soybean	Banana
#1 <sup>d)</sup>	1	Aldicarb	100	95.5±4.7	87.1±1.1	86.4±3.9	85.0±4.0	93.3±10.2	86.4±3.9
	2	Methomyl	105	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3a	Metolcarb	108	91.2±2.8	88.0±0.6	88.7±8.3	91.1±6.3	88.2±5.4	89.9±10.2
#2 <sup>d)</sup>	4	Clofentezine	137	87.0±5.2	89.2±2.5	93.1±9.4	73.7±3.3	64.5±5.1	102.1±2.9
	5a	Propoxur (PHC)	110	79.6±2.7	81.1±3.4	72.4±8.4	80.9±0.3	54.7±8.9	82.1±1.7
	6a	Bendiocarb	151	85.7±4.2	101.9±5.2	80.8±1.0	87.1±5.9	73.2±5.5	91.6±9.7
	7a	Carbofuran	164	79.3±3.8	84.8±6.3	71.1±10.1	82.7±2.1	57.1±7.0	79.9±3.5
	8a	Swep (MCC)	187	83.3±2.6	86.8±3.7	81.8±3.4	89.2±2.3	84.8±1.5	84.7±2.4
	9	Propamocarb	58	6.4±1.7	2.2±0.6	1.9±0.4	2.2±0.6	36.8±42.6	N.D.
#3 <sup>d)</sup>	10a	Ethiofencarb	107	38.1±3.4	62.0±7.0	61.2±9.8	91.3±5.9	71.6±7.9	62.9±2.4
	3b	Metolcarb	108	67.8±3.3	86.8±6.4	96.8±5.3	82.6±1.4	95.4±4.4	101.6±4.8
	11	Carbaryl (NAC)	115	94.5±11.9	89.3±4.0	91.9±5.5	94.8±4.2	94.3±2.2	99.8±5.5
	12	OxamyI	98	18.9±5.6	N.D.	N.D.	N.D.	N.D.	N.D.
	13	Isoprocarb (MIPC)	121	79.8±2.9	93.6±5.9	99.2±4.2	84.6±1.0	100.5±4.7	95.2±12.3
#4 <sup>d)</sup>	14a	Methiocarb	168	83.0±2.8	85.9±6.3	80.9±4.8	101.5±7.9	79.1±4.3	73.5±6.0
	15	Fenobucarb (BPMC)	121	81.2±3.0	87.8±5.9	102.4±2.3	91.8±1.2	90.4±4.8	95.0±7.0
	5b	Propoxur (PHC)	110	81.3±2.7	85.7±5.9	103.4±2.1	83.2±2.3	103.2±10.3	98.1±7.6
	16	Chlorpropham	127	83.6±1.7	90.9±9.9	103.4±3.6	85.9±1.3	96.3±10.4	98.1±5.4
	6b	Bendiocarb	151	76.7±3.2	72.5±7.3	101.3±4.2	81.1±0.7	107.1±0.9	97.8±4.1
	7b	Carbofuran	164	82.8±3.3	82.5±5.3	101.3±6.9	85.4±2.0	103.6±9.4	96.6±7.5
#5 <sup>d)</sup>	8b	Swep (MCC)	187	88.0±7.5	87.2±2.7	100.0±9.1	95.2±3.8	95.4±10.3	98.4±8.3
	17	Pirimicarb	166	80.7±3.7	82.7±4.9	85.9±9.3	82.8±2.2	99.2±8.9	90.4±7.4
	10b	Ethiofencarb	107	41.0±3.4	53.6±5.9	97.0±12.1	70.2±3.3	88.4±6.7	84.8±5.2
	18	Propanil (DCPA)	161	81.2±1.1	84.5±5.8	98.6±5.8	90.6±6.4	92.3±8.9	85.1±4.5
	19	Metribuzin	198	57.4±22.1	83.9±7.2	86.8±4.8	82.4±1.8	92.6±11.0	88.0±10.7
	20	Methiocarb-sulfoxide	168	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	21	Methiocarb-sulfone	121	8.2±2.2	8.3±2.8	12.5±2.8	8.0±1.6	20.2±2.8	13.0±3.8
14b	Methiocarb	153	84.0±5.3	83.1±5.4	99.4±7.2	83.6±2.1	101.0±12.9	98.7±12.6	
	Esprocarb	91	89.6±4.4	82.1±5.8	100.3±1.7	90.7±1.2	106.6±3.9	91.9±1.8	
	Diethofencarb	151	88.7±4.8	81.9±2.4	100.2±2.4	352.7±64.6	100.7±8.4	102.7±5.2	



Table 3. Continued

Ion set	No.	Pesticide	Target ion ( $m/z$ )	Recovery (%) <sup>1)</sup>						
				Apple	Cabbage	Rice	Potato	Soybean	Banana	
#6 <sup>b)</sup>	24	Pendimethalin	252	90.3±8.7	83.4±5.6	84.7±4.0	97.9±2.9	90.9±7.4	91.0±8.9	
	25a	Triadimenol	112	97.8±1.0	83.3±2.6	97.7±12.0	96.5±1.9	95.5±5.8	97.8±11.0	
	25b	Triadimenol	112	88.2±2.6	80.7±8.7	86.1±9.0	83.4±1.2	97.6±6.2	94.7±11.6	
	26	Flutolanil	173	84.6±4.1	68.1±9.1	100.0±3.5	82.3±1.0	99.1±8.4	90.8±6.1	
	27	Pretilachlor	162	84.6±3.8	79.9±4.2	105.3±1.9	85.0±3.2	94.1±1.4	97.1±10.2	
#7 <sup>b)</sup>	28	Myclobutanil	179	87.3±11.3	308.3±40.7	88.4±24.6	83.1±1.7	93.9±3.8	89.3±7.4	
	29	Mepronil	119	98.7±6.7	81.9±5.6	101.6±11.9	97.4±4.8	99.7±7.2	99.8±10.8	
	30a	Propiconazole	173	89.8±7.0	91.5±10.9	94.8±6.8	98.7±4.1	95.5±9.1	97.1±12.6	
	30b	Propiconazole	173	104.2±1.7	91.2±7.6	101.0±4.4	94.0±7.0	100.9±8.7	94.4±12.1	
	31	Lenacil	153	94.4±7.4	84.2±6.2	92.7±5.2	83.6±1.1	97.9±5.9	102.6±5.9	
	32	Amitraz	162	32.9±3.8	83.7±3.6	100.2±13.5	87.4±5.6	99.7±4.3	95.9±1.8	
	33	Mefenacet	192	91.8±8.2	80.3±10.6	98.7±12.1	86.8±4.8	107.7±3.5	96.2±9.8	
	34	Pyridaben	147	103.7±3.7	92.1±2.5	101.4±6.1	99.7±2.9	107.7±3.8	92.9±9.1	

<sup>1)</sup> Each value represents the mean±SD of 3 trials

Pesticides equivalent to 0.2 ppm were spiked into 20 g of samples.

detector.

2. Three kinds of SPE columns, a porous diatomaceous earth cartridge column, a diatomite column with a C<sub>18</sub> cartridge column and a Florisil cartridge column were used successively to clean-up the extract containing pesticides from foods as an alternative to the use of a separatory funnel for liquid-liquid partition.
3. In this GC/MS (SIM) experiment, 2 to 4 different fragment ions for each pesticide were selected to allow precise identification. The determination limits of 31 pesticides were 0.01 to 0.1 µg/mL and the determination limits of *N*-methylcarbamate pesticides were almost the same as in the HPLC method.
4. Twenty-nine out of the 34 carbamate and organonitrogen pesticides gave high recoveries (over 80%) from 6 kinds of agricultural foods. The exceptions were five aqueous carbamate pesticides (methomyl, propamocarb, oxamyl, methiocarb-sulfoxide and methiocarb-sulfone).

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