SHIMADZU
Excellence in Science

Application News

No. C193

Liquid Chromatography Mass Spectrometry

Analyses of Agricultural Chemicals in Golf Courses Using LC/MS/MS

In order to prevent water pollution by agricultural chemicals used in golf courses, the Guideline for the Prevention of Water Pollution and Damage to Aquatic Animals and Plants by Agricultural Chemicals Used in Golf Courses (the Guideline) was established by the Ministry of the Environment (MOE) of Japan (Final amendment: Nov. 30, 2018 (No. 1811301, Issued by the Soil Environment Management Division, Environment Management Bureau, MOE)) [1].

The Guideline defines the concentration limits in drainage water for the agricultural chemicals causing water pollution as ten times greater than the registered reference values. The concentrations in drainage water at the drainage port of golf courses must not exceed the values listed in the appendix (the guideline values). The latest registered reference values are indicated on the website of the MOE [2].

The standard analysis methods for drainage water are provided in an addendum of the Guideline: 51 methods are listed under "I Standard Analysis Methods for Drainage Water (Individual Analysis)" and six methods are listed under "II Standard Analysis Methods for Drainage Water (Simultaneous Multi-Component Analysis)". [3]

This article introduces individual analyses of seven agricultural chemicals (1. I-10 Bensultap, 2. I-21 Thiophanate-methyl, 3. I-23 Validamycin, 4. I-24 Hydroxyisoxazole (Hymexazol), 5. I-27 Benomyl, 6. I-50 MCPA Isopropylamine Salt and MCPA Sodium Salt, 7. I-51 Trinexapac-ethyl), and a simultaneous multi-component analysis of 44 agricultural chemicals according to II-1, which were conducted using LC/MS/MS.

M Kobayashi

Standard Agricultural Chemicals, Reagents, and Measuring Instruments

Standard samples for pesticide residue testing by FUJIFILM Wako Pure Chemical Corporation and SIGMA-ALDRICH were used. In particular, the mixed standard sample of 44 agricultural chemicals for the simultaneous multi-component analysis II-1 was prepared by adding ethoxysulfuron (054-06821) and cumyluron (033-22051) to Pesticide Mixture Standard Solution GF-1 (LC/MS/MS) (162-25213), a mixture of 42 pesticides by FUJIFILM Wako Pure Chemical Corporation.

For the mobile phases, methanol, acetonitrile, formic acid, and acetic acid for LCMS and special grade ammonium acetate were used. The tests were conducted using the following measuring instruments: Shimadzu UHPLC Nexera™ X2, and LCMS™-8050 triple quadrupole mass spectrometer.

1. I-10 Bensultap

The guideline shows that the sensitivity must be adjusted so that 0.01 ng of nereistoxin oxalate can be measured sufficiently (see the table shown below).

Compound	Nereistoxin Oxalate
Guideline value (mg/L)	0.9
Required sensitivity (ng)	0.01
Calibration curve range (mg/L)	0.0025-0.5
Coefficient	1.8

* Nereistoxin oxalate is weighed.

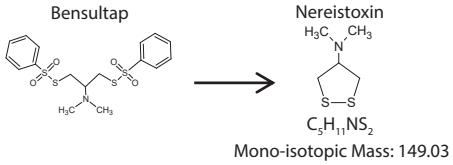


Fig. 1 Structural Formula of Bensultap and Nereistoxin

The calibration curve and a typical chromatogram of nereistoxin (0.0025 mg/L) are shown in Fig. 2. The analysis conditions are given in Table 1.

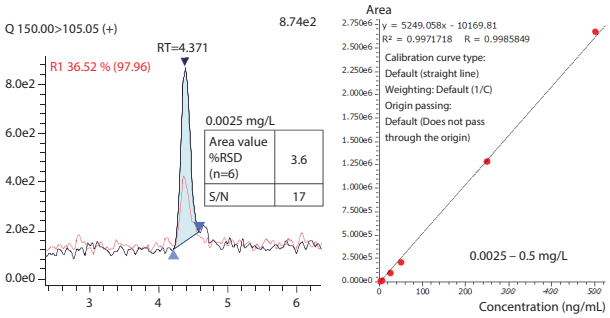


Fig. 2 Calibration Curve and a Typical Chromatogram of Nereistoxin

Table 1 Analysis Conditions of Nereistoxin Oxalate

Column	:	Shim-pack Scepter™ C18-120 (100 mm L. × 2.0 mm I.D., 1.9 µm)
Mobile phase A	:	2 mmol/L ammonium acetate-water
Mobile phase B	:	Methanol
Flow rate	:	0.2 mL/min
Time program	:	45%B. (0 min) - 95%B. (15 min) - 45%B. (15.01-20 min)
Oven temperature	:	40 °C
Injection volumn	:	4 µL
Rinse solution	:	R0: 50% methanol
Final dilution solvent	:	Methanol
Back pressure range	:	20-33 MPa
Interface polarity	:	ESI positive
IF voltage	:	+4 kV
CID gas pressure	:	270 kPa (default value)
ESI probe position	:	2 mm
Nebulizer gas	:	3 L/min
Heating/Drying gas	:	10/10 L/min
Interface/DL/HB temp.	:	300/200/400 °C
Dwell/Pause time	:	200/3 msec for each ch.
MRM transitions	:	150.00>105.05, 150.00>61.05

* S/N calculation: ASTM standards; As for noise, a time range was specified for the peak neighborhood.

2. I-21 Thiophanate-methyl

The guideline shows that the sensitivity must be adjusted so that 0.02 ng of thiophanate-methyl and 0.01 ng of carbendazim can be measured sufficiently (see the table shown below).

Compound	Thiophanate-methyl
Guideline value (mg/L)	3
Required sensitivity (ng)	0.02
Calibration curve range (mg/L)	0.01-0.1
Coefficient	–

* Since thiophanate-methyl decomposes easily, the solution must be prepared at the time of use.
Prepare the standard solution of thiophanate-methyl and the standard solution of carbendazim separately.

Compound	Carbendazim
Guideline value (mg/L)	–
Required sensitivity (ng)	0.01
Calibration curve range (mg/L)	0.005-0.05
Coefficient	1.79

* For details of carbendazim, refer to "5. I-27 Benomyl."

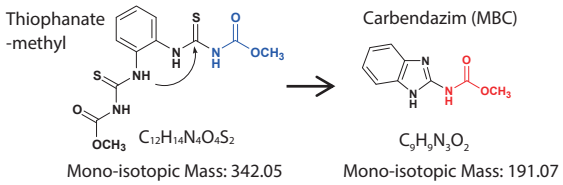


Fig. 3 Structural Formula of Thiophanate-methyl and Carbendazim

The calibration curve and a typical chromatogram of thiophanate-methyl (0.001 mg/L) are shown in Fig. 4. The analysis conditions are given in Table 2.

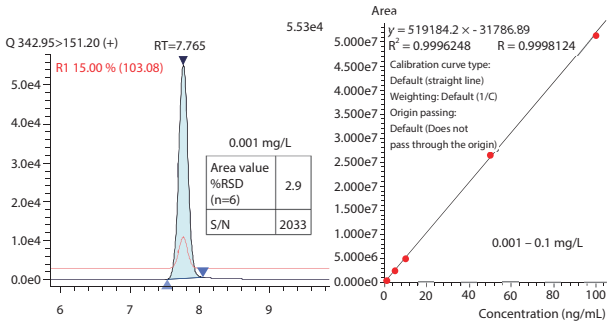


Fig. 4 Calibration Curve and a Typical Chromatogram of Thiophanate-methyl

Table 2 Analysis Conditions of Thiophanate-methyl

Column	:	Shim-pack™ XR-ODS II (100 mm L. × 2.0 mm I.D., 2.2 µm)
Mobile phase A	:	2 mmol/L ammonium acetate-water
Mobile phase B	:	Methanol
Flow rate	:	0.2 mL/min
Time program	:	40%B. (0-5 min) - 95 %B. (10-15 min) - 40%B. (15.01-20 min)
Oven temperature	:	40 °C
Injection volumn	:	2 µL
Rinse solution	:	R0: 50% methanol
Final dilution solvent	:	Methanol
Back pressure range	:	12-24 MPa
Interface polarity	:	ESI positive
IF voltage	:	+4 kV
CID gas pressure	:	270 kPa (default value)
ESI probe position	:	2 mm
Nebulizer gas	:	3 L/min
Heating/Drying gas	:	10/10 L/min
Interface/DL/HB temp.	:	300/250/400 °C
Dwell/Pause time	:	100/1 msec for each ch.
MRM transitions	:	342.95>151.2, 342.95>93.2

* S/N calculation: ASTM standards; As for noise, a time range was specified for the peak neighborhood.

3. I-23 Validamycin

The guideline shows that the sensitivity must be adjusted so that 0.025 ng of validamycin can be measured sufficiently (see the table shown below). A polypropylene vial was used to prepare the standard solution.

Compound	Validamycin
Guideline value (mg/L)	12
Required sensitivity (ng)	0.025
Calibration curve range (mg/L)	0.0025-0.05
Coefficient	–

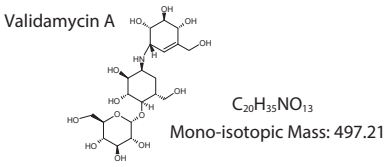


Fig. 5 Structural Formula of Validamycin A

The calibration curve and a typical chromatogram of validamycin A (0.0025 mg/L) are shown in Fig. 6. The analysis conditions are given in Table 3.

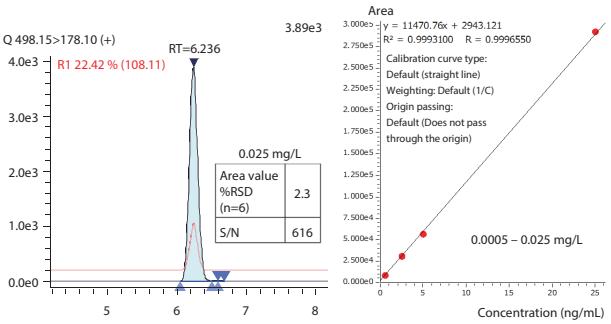


Fig. 6 Calibration Curve and a Typical Chromatogram of Validamycin A

Table 3 Analysis Conditions of Validamycin A

Column	:	Shim-pack Scepter C18-120 (100 mm L. × 2.0 mm I.D., 1.9 µm)
Mobile phase A	:	2 mmol/L ammonium acetate-water
Mobile phase B	:	Acetonitrile
Flow rate	:	0.2 mL/min
Time program	:	0%B. (0-9 min) - 50%B. (13-18 min) - 0%B. (18.01-23 min)
Oven temperature	:	40 °C
Injection volumn	:	2 µL
Rinse solution	:	R0: Water
Final dilution solvent	:	Water
Back pressure range	:	18-22 MPa
Interface polarity	:	ESI positive
IF voltage	:	+4 kV
CID gas pressure	:	270 kPa (default value)
ESI probe position	:	1 mm
Nebulizer gas	:	3 L/min
Heating/Drying gas	:	5/15 L/min
Interface/DL/HB temp.	:	200/150/500 °C
Dwell/Pause time	:	100/3 msec for each ch.
MRM transitions	:	498.15>178.10, 498.15>124.15, 498.15>336.25

* S/N calculation: ASTM standards; As for noise, a time range was specified for the total analysis time.

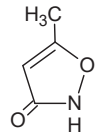
4. I-24 Hydroxyisoxazole

The guideline shows that the sensitivity must be adjusted so that 0.025 ng of hydroxyisoxazole can be measured sufficiently (see the table shown below). In addition to the SIM mode mentioned in the guideline, the MRM mode can be used for the analysis as well.

A polypropylene vial was used to prepare the standard solution.

Compound	Hydroxyisoxazole
Guideline value (mg/L)	1
Required sensitivity (ng)	0.025
Calibration curve range (mg/L)	0.0025-0.1
Coefficient	–

Hydroxyisoxazole



$C_4H_5NO_2$

Mono-isotopic Mass: 99.03

Fig. 7 Structural Formula of Hydroxyisoxazole

Calibration curves and typical chromatograms (0.0025 mg/L) of hydroxyisoxazole are shown in Fig. 8. The analysis conditions are given in Table 4.

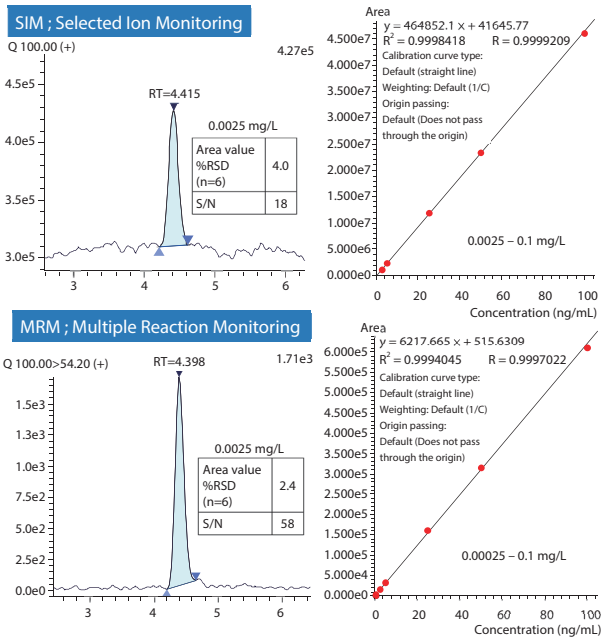


Fig. 8 Calibration Curves and Typical Chromatograms of Hydroxyisoxazole (SIM & MRM)

Table 4 Analysis Conditions of Hydroxyisoxazole

Column	:	Shim-pack XR-ODS II (100 mm L. × 2.0 mm I.D., 2.2 µm)
Mobile phase A	:	0.01% formic acid-water
Mobile phase B	:	Acetonitrile
Flow rate	:	0.2 mL/min
Time program	:	4%B. (0-6 min)
Oven temperature	:	40 °C
Injection volumn	:	2 µL
Rinse solution	:	R0: Water
Final dilution solvent	:	Water
Back pressure range	:	15 MPa
Interface polarity	:	ESI positive
IF voltage	:	+1 kV
CID gas pressure	:	270 kPa (default value)
ESI probe position	:	2 mm
Nebulizer gas	:	3 L/min
Heating/Drying gas	:	10/10 L/min
Interface/DL/HB temp.	:	300/250/400 °C
Dwell/Pause time	:	100/3 msec for each ch.
SIM transition	:	100
MRM transitions	:	100.00>54.20, 100.00>44.05

* S/N calculation: ASTM standards; As for noise, a time range was specified for the peak neighborhood.

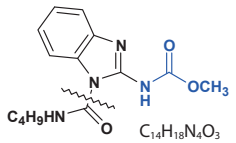
5. I-27 Benomyl

The guideline shows that the sensitivity must be adjusted so that 0.001 ng of carbendazim can be measured sufficiently (see the table shown below).

Compound	Carbendazim
Guideline value (mg/L)	0.2
Required sensitivity (ng)	0.001
Calibration curve range (mg/L)	0.0005-0.05
Coefficient	1.52

* Carbendazim is weighed.

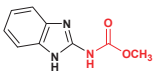
Benomyl



$C_{14}H_{18}N_4O_3$

Mono-isotopic Mass: 290.14

Carbendazim (MBC)



$C_9H_9N_3O_2$

Mono-isotopic Mass: 191.07

Fig. 9 Structural Formula of Benomyl and Carbendazim

The calibration curve and a typical chromatogram of carbendazim (0.0005 mg/L) are shown in Fig. 10. The analysis conditions are given in Table 5.

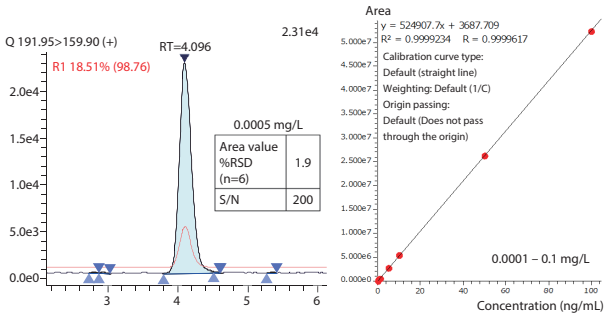


Fig. 10 Calibration Curve and a Typical Chromatogram of Carbendazim

Table 5 Analysis Conditions of Carbendazim

Column	:	Shim-pack XR-ODS II (100 mm L. × 2.0 mm I.D., 2.2 µm)
Mobile phase A	:	2 mmol/L ammonium acetate-water
Mobile phase B	:	Methanol
Flow rate	:	0.2 mL/min
Time program	:	40%B. (0-5 min) - 95%B. (10-15 min) - 40%B. (15.01-20 min)
Oven temperature	:	40 °C
Injection volumn	:	2 µL
Rinse solution	:	R0: 50% methanol
Final dilution solvent	:	Methanol
Back pressure range	:	12-24 MPa
Interface polarity	:	ESI positive
IF voltage	:	+4 kV
CID gas pressure	:	270 kPa (default value)
ESI probe position	:	2 mm
Nebulizer gas	:	3 L/min
Heating/Drying gas	:	10/10 L/min
Interface/DL/HB temp.	:	300/250/400 °C
Dwell/Pause time	:	100/1 msec for each ch.
MRM transitions	:	191.95>159.90, 191.95>132.05

* S/N calculation: ASTM standards; As for noise, a time range was specified for the peak neighborhood.

6. I-50 MCPA Isopropylamine Salt and MCPA Sodium Salt

The guideline shows that the sensitivity must be adjusted so that 0.025 ng of MCPA can be measured sufficiently (see the table shown below).

Compound	MCPA
Guideline value (mg/L)	0.051
Required sensitivity (ng)	0.025
Calibration curve range (mg/L)	0.005-0.5
Coefficient	–

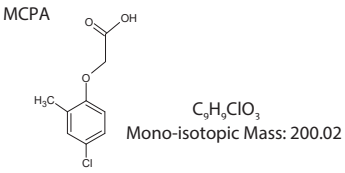


Fig. 11 Structural Formula of MCPA

The calibration curve and a typical chromatogram of MCPA (0.001 mg/L) are shown in Fig. 12. The analysis conditions are given in Table 6.

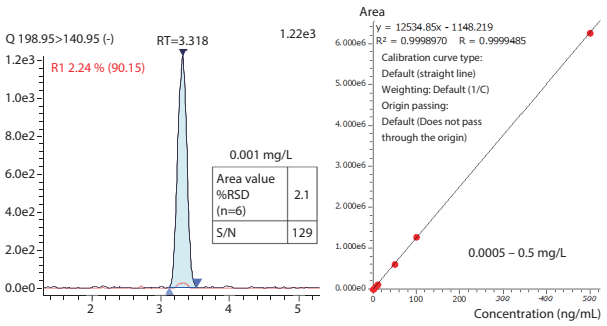


Fig. 12 Calibration Curve and a Typical Chromatogram of MCPA

Table 6 Analysis Conditions of MCPA

Column	:	Shim-pack XR-ODS II (100 mm L. × 2.0 mm I.D., 2.2 µm)
Mobile phase A	:	5 mmol/L ammonium acetate-water
Mobile phase B	:	Methanol
Flow rate	:	0.2 mL/min
Time program	:	40%B. (0 min) - 95%B. (10-12 min) - 40%B. (12.01-17 min)
Oven temperature	:	40 °C
Injection volumn	:	2 µL
Rinse solution	:	R0: 50% methanol
Final dilution solvent	:	Methanol
Back pressure range	:	12-24 MPa
Interface polarity	:	ESI negative
IF voltage	:	–3 kV
CID gas pressure	:	270 kPa (default value)
ESI probe position	:	2 mm
Nebulizer gas	:	3 L/min
Heating/Drying gas	:	5/15 L/min
Interface/DL/HB temp.	:	200/150/500 °C
Dwell/Pause time	:	200/3 msec for each ch.
MRM transitions	:	198.95>140.95, 198.95>104.90

* S/N calculation: ASTM standards; As for noise, a time range was specified for the peak neighborhood.

Fig. 13 LCMS™-8050 High Performance Liquid Chromatograph Mass Spectrometer

7. I-51 Trinexapac-ethyl

The guideline shows that the sensitivity must be adjusted so that 0.025 ng of trinexapac and trinexapac-ethyl can be measured sufficiently (see the table shown below).

Compound	Trinexapac Trinexapac-ethyl
Guideline value (mg/L)	0.15
Required sensitivity (ng)	0.025
Calibration curve range (mg/L)	–
Coefficient	1.13

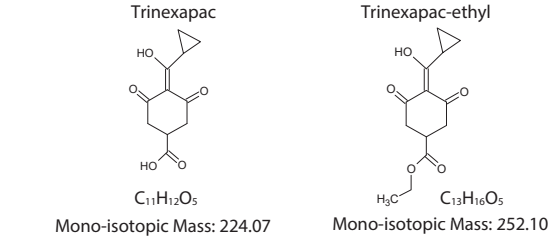


Fig. 14 Structural Formula of Trinexapac and Trinexapac-ethyl

The calibration curve and a typical chromatogram of trinexapac and trinexapac-ethyl (0.005 mg/L) are shown in Fig. 15. The analysis conditions are given in Table 7.

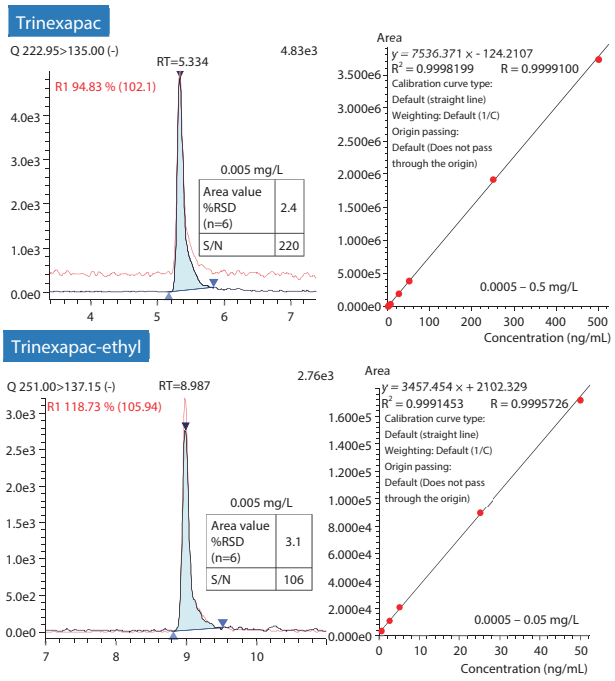


Fig. 15 Calibration Curve and a Typical Chromatogram of Trinexapac and Trinexapac-ethyl

Table 7 Analysis Conditions of Trinexapac and Trinexapac-ethyl

Column	:	L-column 2 ODS METAL FREE (100 mm L. × 2.0 mm, 3 µm)
Mobile phase A	:	0.1% acetic acid-water
Mobile phase B	:	Acetonitrile
Flow rate	:	0.2 mL/min
Time program	:	20%B. (0 min) - 80%B. (15 min) - 20%B. (15.01-20 min)
Oven temperature	:	40 °C
Injection volumn	:	2 µL
Rinse solution	:	R0: Acetonitrile
Final dilution solvent	:	Water and acetonitrile (4:1)
Back pressure range	:	5-9 MPa
Interface polarity	:	ESI negative
IF voltage	:	–3 kV
CID gas pressure	:	270 kPa (default value)
ESI probe position	:	2 mm
Nebulizer gas	:	3 L/min
Heating/Drying gas	:	10/10 L/min
Interface/DL/HB temp.	:	300/250/400 °C
Dwell/Pause time	:	100/3 msec for each ch.
MRM transitions	:	222.95>135.00, 222.95>179.15 251.00>137.15, 251.00>177.05

* S/N calculation: ASTM standards; As for noise, a time range was specified for the peak neighborhood.

Summary of the Analyses by the Individual Methods

Table 8 summarizes the guideline values, area values (%RSD) obtained from tests repeated 6 times, calibration curve ranges, and the coefficient of determination and the correlation coefficient of calibration curves regarding the seven individual analyses.

Agricultural chemicals in golf courses can be analyzed at or below the required sensitivity of each individual method by using the LCMS-8050 liquid chromatograph mass spectrometer.

Table 8 Calibration Curve Range, Area Value Reproducibility, and Guideline Value of Each Individual Method

(n=6, unit: mg/L)

	Compound	Guideline Value	Water Quality Reference Value	Area Value %RSD Calculated Concentration	Area Value %RSD	Calibration Curve Range	Coefficient of Determination	Correlation Coefficient
10	Bensultap (Nereistoxin)	0.9	–	0.0025	3.6	0.0025-0.5	0.9972	0.9986
21	Thiophanate-methyl	3	–	0.0010	2.9	0.001-0.1	0.9996	0.9998
23	Validamycin	12	–	0.0025	2.3	0.0005-0.025	0.9993	0.9997
24	Hydroxyisoxazole SIM	1	–	0.0025	4.0	0.0025-0.1	0.9998	0.9999
24	Hydroxyisoxazole MRM	1	–	0.0025	2.4	0.0025-0.1	0.9994	0.9997
27	Benomyl (Carbendazim)	0.2	–	0.0005	1.9	0.0001-0.1	0.9999	1.0000
50	MCPA	0.051	–	0.0010	2.1	0.0005-0.5	0.9999	0.9999
51	Trinexapac-ethyl	0.15	–	0.0050	2.4	0.0005-0.5	0.9998	0.9999
51	Trinexapac	–	–	0.0050	3.1	0.0005-0.05	0.9991	0.9996

Simultaneous Multi-Compound Analysis II-1

The simultaneous multi-compound analysis II-1 is a simultaneous positive/negative ionization analysis method for analyzing 44 agricultural chemicals. The mixed standard sample was prepared by adding ethoxysulfuron (054-06821) and cumyluron (033-22051) to Pesticide Mixture Standard Solution GF-1 (LC/MS/MS) (162-25213), a mixture of 42 pesticides by FUJIFILM Wako Pure Chemical Corporation.

Typical chromatograms of the 44 agricultural chemicals (each chemical: 0.04 mg/L) are shown in Fig. 16 and the analysis conditions are given in Table 9.

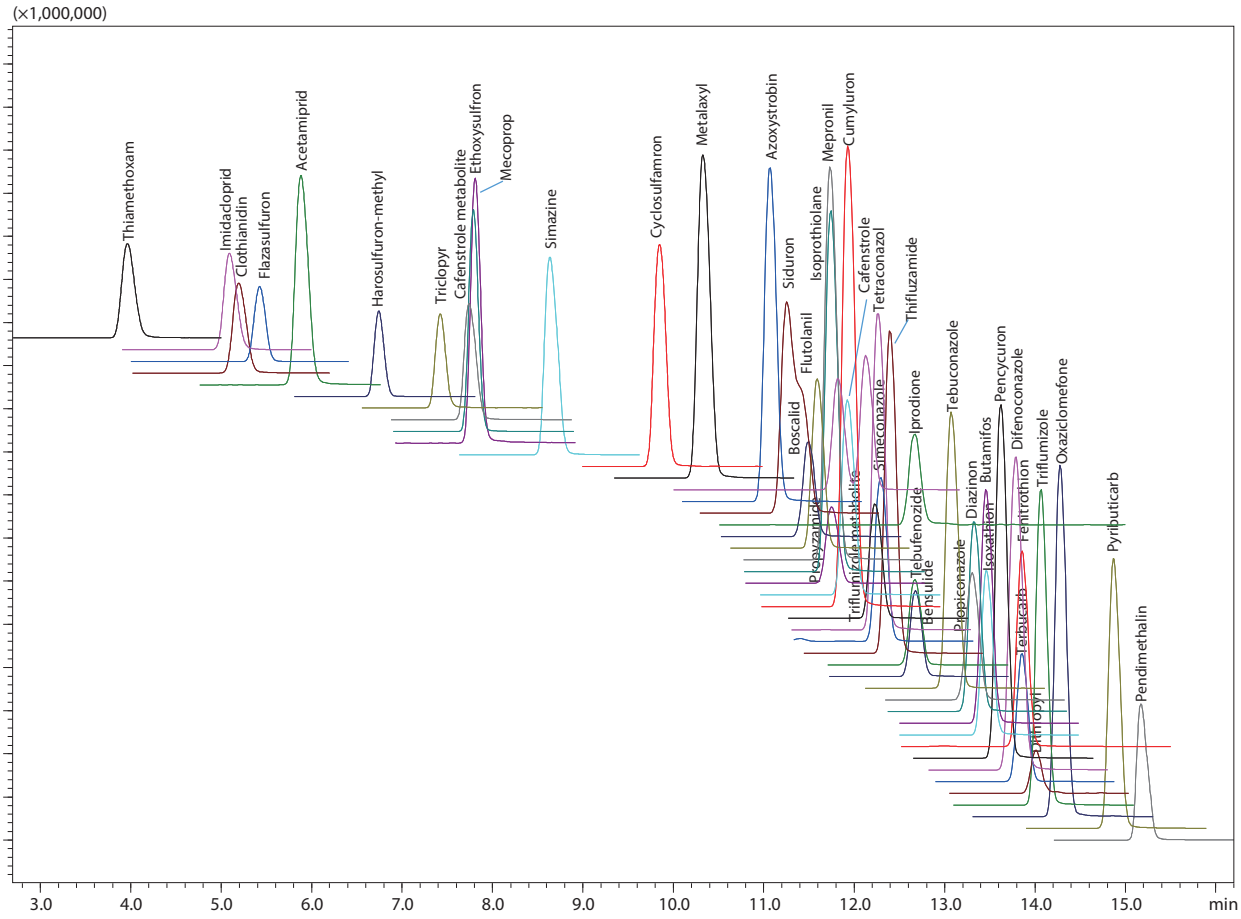


Fig. 16 Typical Chromatograms of 44 Agricultural Chemicals (Each Compound: 0.04 mg/L)

Table 9 Analysis Conditions of Simultaneous Multi-Compound Analysis II-1

Column	: Shim-pack XR-ODS II (100 mm L. × 2.0 mm I.D., 2.2 µm)	Interface polarity	: ESI positive/negative
Mobile phase A	: 5 mmol/L ammonium acetate-water	IF voltage	: +4 kV/–3 kV (Iprodione –1 kV)
Mobile phase B	: Methanol	CID gas pressure	: 270 kPa (default value)
Flow rate	: 0.2 mL/min	ESI probe position	: 1 mm
Time program	: 20%B. (0 min) - 90%B. (13-17 min) - 20%B. (17.01-22 min)	Nebulizer gas	: 3 L/min
Oven temperature	: 40 °C	Heating / Drying gas	: 10/10 L/min
Injection volumn	: 5 µL	Interface /DL/HB temp.	: 100/150/300 °C
Rinse solution	: R0: 50% methanol	Dwell / Pause time	: 25/1 msec for each ch.
Final dilution solvent	: 50% methanol	MRM transitions	: 44 event (max loop time 1.076 sec)
Back pressure range	: 20-24 MPa		

Typical chromatograms of the 44 agricultural chemicals (0.002 mg/L) are shown individually in Fig. 17. The chromatograms are presented in the order of elution.

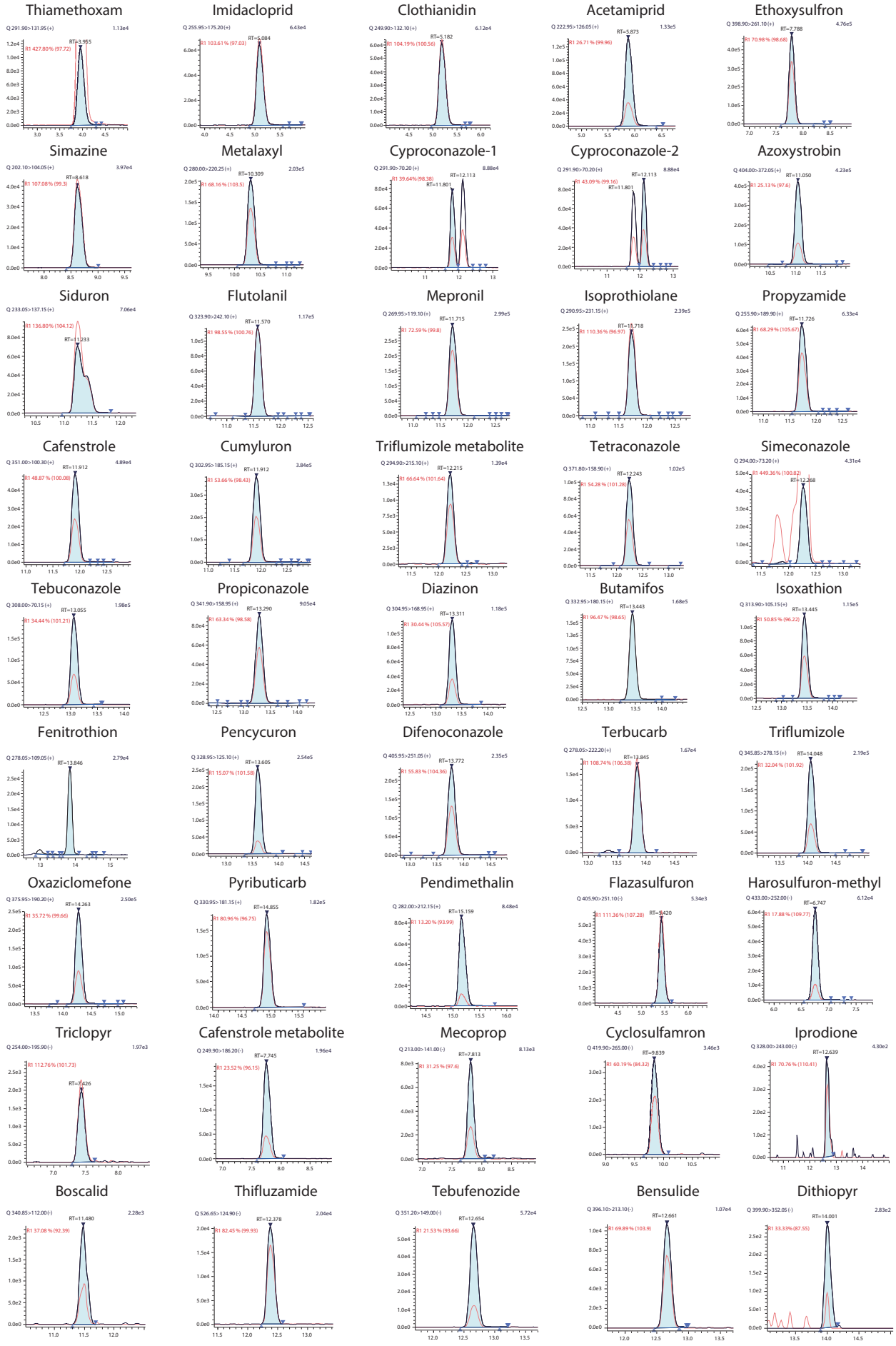


Fig. 17 Typical Chromatograms of All Agricultural Chemicals (0.002 mg/L)

Summary of the Analyses by Simultaneous Multi-Compound Analysis II-1

Table 10 summarizes the guideline values, area values (%RSD) obtained from tests repeated 6 times, calibration curve ranges, and the coefficient of determination and the correlation coefficient of calibration curves of the 44 agricultural chemicals. The calibration curve range of all agricultural chemicals was between 0.0002 to 0.04 mg/L (0.002 to 0.04 mg/L for iprodione, boscalid, and dithiopyl).

All agricultural chemicals can be inspected at one-hundredth of the guideline value when using the LCMS-8050 liquid chromatograph mass spectrometer. (When performing the simultaneous multi-compound analysis II-1, the concentration of samples is doubled by sample preparation.)

Table 10 Calibration Curve Ranges, Area Value Reproducibility, and Guideline Values of the 44 Agricultural Chemicals

(n=6, unit: mg/L)

	Compound	Guideline Value	Water Quality Reference Value	Area Value %RSD Calculated Concentration	Area Value %RSD	Calibration Curve Range	Coefficient of Determination	Correlation Coefficient
1	Acetamiprid	1.8	0.18	0.0002	0.8	0.0002-0.04	0.99982	0.99991
2	Azoxystrobin	4.7	0.47	0.0002	1.2	0.0002-0.04	0.99979	0.99989
3	Boscalid	1.1	0.11	0.002	2.8	0.002-0.04	0.99997	0.99998
4	Butamifos	0.2	0.02	0.0002	3.4	0.0002-0.04	0.99909	0.99954
5	Cafenstrole	0.07	0.007	0.0002	3.4	0.0002-0.04	0.99502	0.99751
6	Clothianidin	2.5	0.25	0.0002	2.0	0.0002-0.04	0.99901	0.99951
7	Cumyluron	0.2	0.02	0.0002	2.6	0.0002-0.04	0.99248	0.99623
8	Cyproconazole	0.3	–	0.0002	4.6	0.0002-0.04	0.99850	0.99930
9	Diazinon	0.05	–	0.0002	3.5	0.0002-0.04	0.99995	0.99997
10	Difenoconazole	0.3	0.025	0.0002	2.2	0.0002-0.04	0.99715	0.99858
11	Ethoxysulfron	1	0.14	0.0002	1.3	0.0002-0.04	0.99983	0.99991
12	Flazasulfuron	0.3	–	0.0002	7.8	0.0002-0.04	0.99838	0.99919
13	Flutolanil	2.3	0.23	0.0002	3.0	0.0002-0.04	0.99819	0.99909
14	Harosulfuron-methyl	2.6	0.26	0.0002	2.0	0.0002-0.04	0.99722	0.99861
15	Imidacloprid	1.5	0.15	0.0002	1.2	0.0002-0.04	0.99922	0.99961
16	Iprodione	3	–	0.002	13.7	0.002-0.04	0.99676	0.99838
17	Isoprothiolane	2.6	0.26	0.0002	2.5	0.0002-0.04	0.99963	0.99982
18	Isoxathion	0.08	–	0.0002	3.1	0.0002-0.04	0.99942	0.99971
19	Mecoprop	0.47	0.047	0.0002	8.2	0.0002-0.04	0.99986	0.99993
20	Mepronil	1	0.1	0.0002	5.0	0.0002-0.04	0.99550	0.99775
21	Metalaxyl	0.58	0.058	0.0002	1.9	0.0002-0.04	0.99984	0.99992
22	Oxaziclomefone	0.24	0.024	0.0002	1.8	0.0002-0.04	0.99902	0.99951
23	Pencycuron	1.4	0.14	0.0002	3.7	0.0002-0.04	0.99860	0.99930
24	Pendimethalin	3.1	0.31	0.0002	3.0	0.0002-0.04	0.99979	0.99989
25	Propiconazole	0.5	0.05	0.0002	2.1	0.0002-0.04	0.99862	0.99931
26	Propyzamide	0.5	0.05	0.0002	4.1	0.0002-0.04	0.99165	0.99582
27	Pyributicarb	0.23	0.023	0.0002	1.9	0.0002-0.04	0.99978	0.99989
28	Siduron	3	–	0.0002	3.3	0.0002-0.04	0.99919	0.99960
29	Simazine	0.03	–	0.0002	2.5	0.0002-0.04	0.99984	0.99992
30	Simeconazole	0.22	0.022	0.0002	5.3	0.0002-0.04	0.99589	0.99794
31	Tebuconazole	0.77	0.077	0.0002	1.8	0.0002-0.04	0.99833	0.99916
32	Tebufenozide	0.42	0.042	0.0002	3.4	0.0002-0.04	0.99873	0.99936
33	Tetraconazole	0.1	–	0.0002	3.1	0.0002-0.04	0.98094	0.99042
34	Thiamethoxam	0.47	0.047	0.0002	4.2	0.0002-0.04	0.99979	0.99990
35	Thifluzamide	0.5	0.037	0.0002	11.0	0.0002-0.04	0.99993	0.99996
36	Triflumizole	0.5	0.039	0.0002	3.4	0.0002-0.04	0.99932	0.99966
37	Cyclosulfamron	0.8	–	0.0002	6.8	0.0002-0.04	0.99745	0.99873
38	Dithiopyr	0.095	0.0095	0.002	17.5	0.002-0.04	0.99999	1.00000
39	Fenitrothion	0.03	–	0.0002	6.0	0.0002-0.04	0.99938	0.99969
40	Triclopyr	0.06	–	0.0002	17.0	0.0002-0.04	0.99995	0.99997
41	Bensulide	–	–	0.0002	7.6	0.0002-0.04	0.99977	0.99988
42	Terbucarb	–	–	0.0002	7.7	0.0002-0.04	0.99934	0.99967
43	Cafenstrole metabolite	–	–	0.0002	2.2	0.0002-0.04	0.99384	0.99692
44	Triflumizole metabolite	–	–	0.0002	6.9	0.0002-0.04	0.99993	0.99997

<References>

1) Guideline for the Prevention of Water Pollution and Damage to Aquatic Animals and Plants by Agricultural Chemicals Used in Golf Courses (Final amendment: Nov. 30, 2018 (No. 1811301, Issued by the Soil Environment Management Division, Environment Management Bureau, MOE))
2) Website of the MOE http://www.env.go.jp/water/dojo/noyaku/odaku_kijun/kijun.html (Accessed on April 18, 2019)
3) Addendum of No. 1811301, Issued by the Soil Environment Management Division, Environment Management Bureau, MOE (Standard Analysis Methods for Drainage water) http://www.env.go.jp/water/dojo/noyaku/golf_course/attach/guidelines_an.pdf (in Japanese) (Accessed on April 18, 2019)

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