Excellence in Science

Application Note

No. 16

Analytical Data for Agricultural Chemicals as Water Quality Control Target Setting Items

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Environment

1. Introduction

To protect the quality of water essential to humans, drinking water quality standards have been established. Current water quality standards in Japan were significantly revised in 2003. Water quality standards based on Ordinance 4 of Japan's Water Supply Act are specified according to "Ministerial Ordinance Concerning Water Quality Standards" (Ministry of Health, Labour and Welfare Ordinance No. 101, May 30, 2003 [Final revision, Ministry of Health, Labour and Welfare Ordinance 18, February 17, 2010]).
In addition to water quality standards, items that require considerations for water quality control are specified as water quality control target setting items. Necessary information and knowledge of these items have been continuously gathered.
This document is a collection of analytical data with respect to water quality control target setting items for 15 agricultural chemicals (102 components). Analyzing multiple types of agricultural chemicals requires experience and technical ability. It describes key considerations for preparing reagents, pretreating samples, and setting parameters for analytical instruments.

■ Reference URL for Ministry of Health, Labour and Welfare
1) Drinking water information: http://www.mhlw.go.jp/topics/bukyoku/kenkou/suido/index.html

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1-1 Water Quality Control Target Setting Items

Heterotrophic bacteria and fipronil (as one of the agricultural chemicals) were added as water quality control target setting items in April 2008. In April 2009, "Aluminum and its compounds" and "1,1-dichloroethylene" were added, the target values of "dichloroacetonitrile" and "chloral hydrate" were changed, the target values of agricultural chemicals "EPN (pesticide)" and "chlorpyrifos (pesticide)" were readjusted, and "trans-1,2-dichloroethylene" was removed. In April 2010, "1,1,2-trichloroethane" was removed, and the target values of agricultural chemicals "isoprothiolane," "dithiopyr," "mefenaset," "bromobutide," "esprocarb," "pyriproxyfen" were readjusted. Table 1 lists all of the items.

The coefficient of variations listed in the table below are based on "Exhibit 1 Setting Accuracy for Water Quality Control Target Setting Items" of the "Ministry of Health, Labour and Welfare; Health Service Bureau, Water Supply Div. Ordinance No. 1010001, October 10, 2003." This Ordinance states that "the standard value for the water quality test should be measured up to 10 %. For this, the variations of values in the vicinity of 10 % of the standard value should be retained so that the values shown are less than the coefficient of variation."

Table 1 Water Quality Control Target Setting Item List (Effective April 1, 2010)

No.	Item	Criteria	Test Method	Coefficient of Variation
1	Antimony and its compounds	0.015 mg/L or less antimony	Hydride generation-atomic absorption Hydride generation-ICP-AES ICP-MS	10 % 10 % 10 %
2	Uranium and its compounds	0.002 mg/L or less uranium (provisional)	ICP-MS Solid-phase extraction-ICP-AES	10 % 10 %
3	Nickel and its compounds	0.01 mg/L or less nickel (provisional)	Flameless atomic absorption ICP-AES ICP-MS	10 % 10 % 10 %
4	Nitrite nitrogen	0.05 mg/L max. (provisional)	Ion chromatography	10 %
5	1,2-dichloroethane	0.004 mg/L max.	PT-GC/MS HS-GC/MS	20 % 20 %
6	Deleted	Deleted	Deleted	Deleted
7	Deleted	Deleted	Deleted	Deleted
8	Toluene	0.2 mg/L max.	PT-GC/MS HS-GC/MS	20 % 20 %
9	Di-(2-ethylhexyl) phthalate	0.1 mg/L max.	Solvent extraction-GC/MS	20 %
10	Chlorite	0.6 mg/L max.	Ion chromatography Ion chromatography-post-column absorption photometry	10 % 10 %
11	Deleted	Deleted	Deleted	Deleted
12	Chlorine dioxide	0.6 mg/L max.	Ion chromatography Ion chromatography-post-column absorption photometry	10 % 10 %
13	Dichloroacetonitrile	0.01 mg/L max. (provisional)	Solvent extraction-GC/MS	20 %
14	Chloral hydrate	0.02 mg/L max. (provisional)	Solvent extraction-GC/MS	20 %
15	Agricultural chemicals	1 or less as the sum of the ratios of detected values to target values	Method specified for each individual pesticide	—
16	Residual chlorine	1 mg/L max.	Diethyl-p-phenylene diamine (DPD) method Electrical current Absorption photometry Absorption photometry by continuous automated measurement device Polarography	10 % 10 % 10 % 10 % 10 %
17	Calcium, magnesium, etc. (hardness)	10 mg/L max. 100 mg/L max.	Flame atomic absorption ICP-AES ICP-MS Ion chromatography Titration method	10 % 10 % 10 % 10 % 10 %
18	Manganese and its compounds	0.01 mg/L or less manganese (provisional)	Flameless atomic absorption ICP-AES ICP-MS	10 % 10 % 10 %
19	Free carbon dioxide	20 mg/L max.	Titration method	10 %
20	1,1,1-trichloroethane	0.3 mg/L max.	PT-GC/MS HS-GC/MS	20 % 20 %
21	Methyl t-butyl ether	0.02 mg/L max.	PT-GC/MS HS-GC/MS	20 % 20 %
22	Organic substances, etc. (potassium permanganate consumption)	3 mg/L max.	Titration method	10 %
23	Odor intensity (Threshold Odor Number (TON))	3 max.	By olfactory sense	—
24	Post-evaporation residue	30 mg/L max. 200 mg/L max.	Weight measurement	—
25	Turbidity	1 degree max.	Turbidimetric method Transmittance photometry Transmittance photometry by continuous automated spectrophotometer Integrating sphere photometry Integrating sphere photometry by continuous automated measurement device Scattered light measurement Transmission and scattered light measurement	— 10 % 10 % 10 % 10 % 10 % 10 %
26	pH value	About 7.5	Glass electrode method Glass electrode method by continuous automated measurement device	— —
27	Causticity (Langelier saturation index)	-1 or greater, as close to 0 as possible	Calculation method	—
28	Heterotrophic bacteria	2000 or fewer colonies in 1 mL of test water (provisional)	R2A agar medium method	—
29	1,1-dichloroethylene	0.1 mg/L max.	PT-GC/MS HS-GC/MS	20 % 20 %
30	Aluminum and its compounds	0.1 mg/L or less aluminum	Flameless atomic absorption ICP-AES ICP-MS	10 % 10 % 10 %

1-2 Targets for 15 Agricultural Chemicals (102 Components)

Water quality control setting items for agricultural chemicals in drinking water are specified according to the Health Sciences Council Report dated April 28, 2003, section III Water Quality Standards for Chemical Substances. (1) Water quality standards for agricultural chemicals that fit the classification conditions for water quality standards should be specified individually. (Currently, no agricultural chemicals have water quality standards specified.) (2) Agricultural chemicals that do not fall under (1) are specified as water quality control target setting items using the total pesticide method, where detection index values calculated according to the following equation must not exceed 1.

$$DI = \sum_{i} DVi / GVi$$

For the above equation, the sum of all detected value-to-target value ratios for respective agricultural chemicals must not exceed 1. In the equation, DI indicates the detection index, DVi respective detected values, and GVi respective target values for agricultural chemicals i.

Agricultural chemicals subject to measurement should be selected appropriately by companies involved in providing drinking water, based on considering the circumstances of the region where they are being inspected. Applicable agricultural chemicals should be selected based on usage quantities and past detection levels and should include agricultural chemicals with a high probability of being detected in the given drinking water.

Table 2 indicates target values for 15 target agricultural chemicals subject to the water quality control target setting items, the corresponding test methods used, quantitation lower limit values, and the coefficients of variation.

The Ministry of Health, Labour and Welfare; Health Service Bureau, Water Supply Div. Ordinance No. 1010001, October 10, 2003, Exhibit 2 Measurement Accuracy and Water Quality Testing Methods of Agricultural Chemicals (15 Water Quality Standard Items) indicates that water quality tests should measure values up to 1 % of target values. In addition, accuracy levels should ensure coefficient of variation values are less than the values indicated in the table below. In addition, guideline values for lower detection limits using standard measuring instruments and normal test methods are indicated below for respective agricultural chemicals and test methods.

Table 2 Agricultural Chemicals

No.	Agricultural Chemical	Target Value (mg/L)	Test Method	Quantitation Lower Limit	Coefficient of Variation
1	Thiuram	0.02	Solid-phase extraction-LC/MS (P)	0.0002	20 %
2	Simazine (CAT)	0.003	Solid-phase extraction-GC/MS	0.00001	20 %
3	Thiobencarb	0.02	Solid-phase extraction-GC/MS	0.00002	20 %
4	1,3-dichloropropene (D-D)	0.002	PT-GC/MS HS-GC/MS	0.0001 0.0001	20 % 20 %
5	Isoxathion	0.008	Solid-phase extraction-GC/MS	0.00001	20 %
6	Diazinon	0.005	Solid-phase extraction-GC/MS	0.00002	20 %
7	Fenitrothion (MEP)	0.003	Solid-phase extraction-GC/MS	0.00001	20 %
8	Isoprothiolane (IPT)	0.3	Solid-phase extraction-GC/MS	0.00001	20 %
9	Chlorothalonil (TPN)	0.05	Solid-phase extraction-GC/MS	0.00001	20 %
10	Propyzamide	0.05	Solid-phase extraction-GC/MS	0.00001	20 %
11	Dichlorvos (DDVP)	0.008	Solid-phase extraction-GC/MS	0.00005	20 %
12	Fenobucarb (BPMC)	0.03	Solid-phase extraction-GC/MS	0.00001	20 %
13	Chlornitrophen (CNP): outdated pesticide	0.0001	Solid-phase extraction-GC/MS	0.0001	20 %
14	CNP-amino metabolite	—	Solid-phase extraction-GC/MS	0.0001	20 %
15	Iprobenfos (IBP)	0.008	Solid-phase extraction-GC/MS	0.00005	20 %
16	EPN	0.004	Solid-phase extraction-GC/MS	0.00005	20 %
17	Bentazone: outdated herbicide	0.2	Solid-phase extraction-derivatization-GC/MS Solid-phase extraction-LC/MS (P) Solid-phase extraction-LC/MS (N)	0.00001 0.00005 0.000002	20 % 20 % 20 %
18	Carbofuran (metabolite of carbosulfan)	0.005	HPLC-post-column Solid-phase extraction-LC/MS (P)	0.00005 0.000005	20 % 20 %
19	2,4-dichlorophenoxyacetic acid (2,4-D)	0.03	Solid-phase extraction-derivatization-GC/MS Solid-phase extraction-LC/MS (N)	0.00001 0.00005	20 % 20 %

■ Reference: General policies regarding agricultural chemicals indicated in the Ministry of Health, Labour and Welfare website:
http://www.mhlw.go.jp/topics/bukyoku/kenkou/suido/suishitsu/05.html

No.	Agricultural Chemical	Target Value (mg/L)	Test Method	Quantitation Lower Limit	Coefficient of Variation
20	Tryclopyr	0.006	Solid-phase extraction-derivatization-GC/MS Solid-phase extraction-LC/MS (N)	0.00001 0.00002	20 % 20 %
21	Acephate	0.08	LC/MS (P)	0.0008	20 %
22	Isofenphos: outdated pesticide	0.001	Solid-phase extraction-GC/MS	0.00003	20 %
23	Chlorpyrifos	0.003	Solid-phase extraction-GC/MS	0.00005	20 %
24	Trichlorfon (DEP)	0.03	Solid-phase extraction-GC/MS	0.0002	20 %
25	Pyridaphenthion: outdated pesticide	0.002	Solid-phase extraction-GC/MS	0.00005	20 %
26	Iprodione	0.3	Solid-phase extraction-GC/MS Solid-phase extraction-HPLC Solid-phase extraction-LC/MS (P)	0.00002 0.001 0.0001	20 % 20 % 20 %
27	Etridiazole (Echlomezole)	0.004	Solid-phase extraction-GC/MS	0.00001	20 %
28	Oxine copper	0.04	Solid-phase extraction-LC/MS (P) LC/MS (P)	0.00005 0.0004	20 % 20 %
29	Captan	0.3	Solid-phase extraction-GC/MS	0.0001	20 %
30	Chloroneb	0.05	Solid-phase extraction-GC/MS	0.00002	20 %
31	Tolclophos-methyl	0.2	Solid-phase extraction-GC/MS	0.00001	20 %
32	Flutolanil	0.2	Solid-phase extraction-GC/MS	0.00001	20 %
33	Pencycuron	0.04	Solid-phase extraction-GC/MS	0.0001	20 %
34	Metalaxyl	0.05	Solid-phase extraction-GC/MS	0.00005	20 %
35	Mepronil	0.1	Solid-phase extraction-GC/MS	0.00001	20 %
36	Asulam	0.2	Solid-phase extraction-HPLC Solid-phase extraction-LC/MS (P) Solid-phase extraction-LC/MS (N)	0.001 0.0001 0.0005	20 % 20 % 20 %
37	Dithiopyr	0.009	Solid-phase extraction-GC/MS	0.00001	20 %
38	Terbucarb (MBPMC): outdated herbicide	0.02	Solid-phase extraction-GC/MS	0.00001	20 %
39	Napropamide	0.03	Solid-phase extraction-GC/MS	0.00001	20 %
40	Pyributicarb	0.02	Solid-phase extraction-GC/MS	0.00002	20 %
41	Butamifos	0.01	Solid-phase extraction-GC/MS	0.0001	20 %
42	Bensulide (SAP): outdated herbicide	0.1	Solid-phase extraction-LC/MS (P) Solid-phase extraction-LC/MS (N)	0.00001 0.00001	20 % 20 %
43	Benfluralin (Bethrodine)	0.08	Solid-phase extraction-GC/MS	0.00001	20 %
44	Pendimethalin	0.1	Solid-phase extraction-GC/MS	0.00001	20 %
45	Mecoprop (MCPP)	0.005	Solid-phase extraction-derivatization-GC/MS Solid-phase extraction-LC/MS (N)	0.00005 0.00002	20 % 20 %
46	Methyl daimuron: outdated pesticide	0.03	Solid-phase extraction-GC/MS	0.00005	20 %
47	Alachlor	0.01	Solid-phase extraction-GC/MS	0.00002	20 %
48	Carbaryl (NAC)	0.05	Solid-phase extraction-HPLC HPLC-post column Solid-phase extraction-LC/MS (P)	0.0005 0.0001 0.00002	20 % 20 % 20 %
49	Edifenphos (EDDP)	0.006	Solid-phase extraction-GC/MS	0.00005	20 %
50	Pyroquilon	0.04	Solid-phase extraction-GC/MS	0.00001	20 %
51	Fthalide	0.1	Solid-phase extraction-GC/MS	0.00001	20 %
52	Mefenacet	0.02	Solid-phase extraction-GC/MS	0.00001	20 %
53	Pretilachlor	0.04	Solid-phase extraction-GC/MS	0.00001	20 %
54	Isoprocarb (MIPC)	0.01	Solid-phase extraction-GC/MS	0.00005	20 %
55	Thiophanate-methyl	0.3	Solid-phase extraction-HPLC Solid-phase extraction-LC/MS (P)	0.002 0.00005	20 % 20 %
56	Thenylchlor	0.2	Solid-phase extraction-GC/MS	0.00002	20 %
57	Methidathion (DMTP)	0.004	Solid-phase extraction-GC/MS	0.00001	20 %
58	Carpropamid	0.04	Solid-phase extraction-LC/MS (P) Solid-phase extraction-LC/MS (N)	0.00002 0.00005	20 % 20 %

No.	Agricultural Chemical	Target Value (mg/L)	Test Method	Quantitation Lower Limit	Coefficient of Variation
59	Bromobutide	0.1	Solid-phase extraction-GC/MS	0.0001	20 %
60	Molinate	0.005	Solid-phase extraction-GC/MS	0.00001	20 %
61	Procymidone	0.09	Solid-phase extraction-GC/MS	0.0001	20 %
62	Anilofos	0.003	Solid-phase extraction-GC/MS	0.00005	20 %
63	Atrazine	0.01	Solid-phase extraction-GC/MS	0.00005	20 %
64	Dalapon	0.08	LC/MS (N)	0.001	20 %
65	Dichlobenil (DBN)	0.01	Solid-phase extraction-GC/MS	0.00001	20 %
66	Dimethoate	0.05	Solid-phase extraction-GC/MS	0.00005	20 %
67	Diquat	0.005	Solid-phase extraction-HPLC	0.001	20 %
68	Diuron (DCMU)	0.02	Solid-phase extraction-LC/MS (P) Solid-phase extraction-LC/MS (N)	0.0001 0.0001	20 % 20 %
69	Endosulfan (Benzoepin)	0.01	Solid-phase extraction-GC/MS	0.00005	20 %
70	Etofenprox	0.08	Solid-phase extraction-GC/MS	0.00005	20 %
71	Fenthion (MPP)	0.001	Solid-phase extraction-GC/MS Solid-phase extraction-LC/MS (P)	0.00001 0.00002	20 % 20 %
72	Glyphosate	2	Derivatization-HPLC HPLC-post-column	0.0005 0.002	20 % 20 %
73	Malathon (Malathion)	0.05	Solid-phase extraction-GC/MS	0.00005	20 %
74	Methomyl	0.03	HPLC-post-column Solid-phase extraction-LC/MS (P)	0.0001 0.00002	20 % 20 %
75	Benomyl	0.02	Solid-phase extraction-LC/MS (P)	0.00002	20 %
76	Benfuracarb	0.04	Solid-phase extraction-LC/MS (P)	0.000004	20 %
77	Simetryne	0.03	Solid-phase extraction-GC/MS	0.00002	20 %
78	Dimepiperate: outdated pesticide	0.003	Solid-phase extraction-GC/MS	0.00002	20 %
79	Phenthoate (PAP)	0.004	Solid-phase extraction-GC/MS	0.00004	20 %
80	Buprofezin	0.02	Solid-phase extraction-GC/MS	0.00001	20 %
81	Ethylthiomethone	0.004	Solid-phase extraction-GC/MS	0.00004	20 %
82	Probenazole	0.05	Solid-phase extraction-LC/MS (P)	0.0001	20 %
83	Esprocarb	0.03	Solid-phase extraction-GC/MS	0.0001	20 %
84	Daimuron	0.8	Solid-phase extraction-LC/MS (P) Solid-phase extraction-LC/MS (N)	0.00005 0.00005	20 % 20 %
85	Bifenox: outdated pesticide	0.2	Solid-phase extraction-GC/MS	0.0001	20 %
86	Bensulfuron methyl	0.4	Solid-phase extraction-LC/MS (P) Solid-phase extraction-LC/MS (N)	0.00001 0.00001	20 % 20 %
87	Tricyclazole	0.08	Solid-phase extraction-LC/MS (P)	0.000002	20 %
88	Piperophos: outdated pesticide	0.0009	Solid-phase extraction-GC/MS	0.00005	20 %
89	Dimethametryn	0.02	Solid-phase extraction-GC/MS	0.00001	20 %
90	Azoxystrobin	0.5	Solid-phase extraction-LC/MS (P)	0.00002	20 %
91	Iminoctadine acetate	0.006	Solid-phase extraction-HPLC-post-column Solvent extraction-HPLC-post-column	0.005 0.005	20 % 20 %
92	Fosetyl	2	LC/MS (N)	0.02	20 %
93	Polycarbamate	0.03	Derivatization-HPLC	0.002	20 %
94	Halosulfuron methyl	0.3	Solid-phase extraction-LC/MS (P) Solid-phase extraction-LC/MS (N)	0.00005 0.00005	20 % 20 %
95	Flazasulfuron	0.03	Solid-phase extraction-LC/MS (P) Solid-phase extraction-LC/MS (N)	0.000002 0.000002	20 % 20 %
96	Thiodicarb	0.08	Solid-phase extraction-LC/MS (P)	0.00005	20 %
97	Propiconazole	0.05	Solid-phase extraction-GC/MS	0.0002	20 %
98	Siduron	0.3	Solid-phase extraction-HPLC Solid-phase extraction-LC/MS (P) Solid-phase extraction-LC/MS (N)	0.002 0.00002 0.00002	20 % 20 % 20 %
99	Pyriproxyfen	0.3	Solid-phase extraction-GC/MS	0.00001	20 %
100	Trifluralin	0.06	Solid-phase extraction-GC/MS	0.00001	20 %
101	Cafenstrole	0.008	Solid-phase extraction-GC/MS	0.00001	20 %
102	Fipronil	0.0005	Solid-phase extraction-LC/MS (N)	0.000005	20 %

Note: In the test method column, P: positive mode, and N: negative mode

1-3 Test Methods for Water Quality Control Target Setting Items

Test methods for water quality control target setting items are specified in Notes on Enforcement of Ministerial Ordinance Concerning Water Quality Standards, Partial Revision of Water Supply Act Enforcement Regulations and Water Quality Control (Ministry of Health, Labour and Welfare; Health Service Bureau, Water Supply Div. Ordinance No. 1010001, October 10, 2003 [partial revision, Ministry of Health, Labour and Welfare; Health Service Bureau, Water Supply Div. Ordinance 0217, No. 1, February 17, 2010]), Exhibit 4 Test Methods of Water Quality Control Target Setting Items.
http://www.mhlw.go.jp/topics/bukyoku/kenkou/suido/suishitsu/dl/06l.pdf
Test methods for 15 target agricultural chemicals (102 components) are specified in Attached Methods 5 to 20. Analytical instruments used for the test methods include a gas chromatograph-mass spectrometer, liquid chromatograph, and liquid chromatograph-mass spectrometer. The test methods are listed in Table 3.

Table 3 List of Test Methods

Attached Method	Item	Instrument	Test Method	Page No.
Attached Method 5 Attached Method 6	Simultaneous analysis of multiple agricultural chemical components Bentazon etc.	Gas chromatograph-mass spectrometer	Simultaneous analysis using solid-phase extraction-GC/MS Simultaneous analysis using solid-phase extraction-derivatization GC/MS	8
Attached Method 9 Attached Method 11 Attached Method 12 Attached Method 14 Attached Method 17	Iprodione, etc. Diquat Glyphosate Carbofuran, etc. Iminoctadine acetate	High-performance liquid chromatograph	Simultaneous analysis using solid-phase extraction-HPLC Solid-phase extraction-HPLC Derivatization-HPLC Simultaneous analysis using HPLC-post-column Solvent extraction - HPLC-post-column	24
Attached Method 18 Attached Method 20	Simultaneous analysis of multiple agricultural chemical components Acephate, etc.	High-performance liquid chromatograph-mass spectrometer	Simultaneous analysis using solid-phase extraction-LC/MS Simultaneous analysis using LC/MS	30

2. Gas Chromatograph-Mass Spectrometer

2-1 Attached Method 5-Simultaneous Analysis Using Solid-Phase Extraction-Gas Chromatograph-Mass Spectrometer

This section introduces an example of simultaneous analysis of 83 agricultural chemicals using GC/MS. In addition to the 83 agricultural chemicals, trichlorfon (DEP) is also included in the target agricultural chemicals in Attached Method 5, but trichlorfon degrades easily and is difficult to measure using the same analytical conditions as for the other agricultural chemicals. Since trichlorfon degrades to dichlorvos (DDVP), we recommend that it be detected as dichlorvos. Table 4 shows the agricultural chemical numbers (number in the list of 102 agricultural chemicals), target values (mg/L), and the monitoring ions used during analysis for Attached Method 5.

Table 4 Monitoring Ions for 83 Agricultural Chemicals

No.	Agricultural Chemical	Target Value (mg/L)	Monitoring Ions (*m/z*)	No.	Agricultural Chemical	Target Value (mg/L)	Monitoring Ions (*m/z*)
2	Simazine	0.003	201,186	25	Pyridaphenthion	0.002	340,199
3	Thiobencarb	0.02	100,72	26	Iprodione	0.3	314,316
5	Isoxathion Isoxathion oxon	0.008	177,105 105,161	27	Etridiazole	0.004	213,211
6	Diazinon Diazinon oxon	0.005	304,179 273,137	29	Captan	0.3	79,114,149
7	Fenitrothion Fenitrothion oxon	0.003	277,260 244,261	30	Chloroneb	0.05	191,193
8	Isoprothiolane	0.3	189,118	31	Tolclophos-methyl Tolclophos-methyl oxon	0.2	265,125 249,251
9	Chlorothalonil	0.05	266,264	32	Flutolanil	0.2	173,281
10	Propyzamide	0.05	175,173	33	Pencycuron	0.04	125,180
11	Dichlorvos	0.008	185,109	34	Metalaxyl	0.05	206,160
12	Fenobucarb	0.03	121,150	35	Mepronil	0.1	119,269
13	Chlornitrophen	0.0001	319,317	37	Dithiopyr	0.009	354,306
14	CNP-amino metabolite	-	108,287	38	Terbucarb	0.02	220,205
15	Iprobenfos	0.008	204,91	39	Napropamide	0.03	128,72
16	EPN EPN oxon	0.004	157,169 141,306	40	Pyributicarb	0.02	165,108
22	Isofenphos Isofenphos oxon	0.001	213,185 229,201	41	Butamifos Butamifos oxon	0.01	286,200 244,216
23	Chlorpyrifos Chlorpyrifos oxon	0.003	314,197 270,298	43	Benfluralin	0.08	292,276

No.	Agricultural Chemical	Target Value (mg/L)	Monitoring Ions (*m/z*)
44	**Pendimethalin**	**0.1**	**252,191**
46	**Methyl daimuron**	**0.03**	**107,119**
47	**Alachlor**	**0.01**	**188,160**
49	**Edifenphos**	**0.006**	**310,109**
50	**Pyroquilon**	**0.04**	**130,144,173**
51	**Fthalide**	**0.1**	**243,241**
52	**Mefenacet**	**0.02**	**192,120**
53	**Pretilachlor**	**0.04**	**238,262**
54	Isoprocarb	0.01	136,121
56	Thenylchlor	0.2	127,288
57	Methidathion	0.004	145,85
59	Bromobutide	0.1	120,119
60	Molinate	0.005	126,98
61	Procymidone	0.09	283,96
62	Anilofos	0.003	226,125
63	Atrazine	0.01	215,200
65	Dichlobenil	0.01	171,173
66	Dimethoate	0.05	87,125
69	Endosulfan Endosulphate	0.01	α 241,195 β 195,241 272,274
70	Etofenprox	0.08	163,135

No.	Agricultural Chemical	Target Value (mg/L)	Monitoring Ions (*m/z*)
71	Fenthion (MPP) MPP sulfoxide MPP sulfone MPP oxon MPP oxon sulfoxide MPP oxon sulfone	0.001	278,153 278,125 310,231 262,247 262,247 294,215
73	Malathon Malaoxon	0.05	173,93 99,127
77	Simetryne	0.03	213,170
78	Dimepiperate	0.003	145,119
79	Phenthoate	0.004	274,125
80	Buprofezin	0.02	105,175
81	Ethylthiomethone	0.004	89,97
83	Esprocarb	0.03	222,91
85	Bifenox	0.2	310,343
88	Piperophos	0.0009	122,140
89	Dimethametryn	0.02	212,255
97	Propiconazole	0.05	259,261
99	Pyriproxyfen	0.3	136,226
100	Trifluralin	0.06	306,290
101	Cafenstrole	0.008	188,100
-	Anthracene-d10	-	188,189
-	9-bromoanthracene	-	256,258
-	Chrysene-d12	-	240,236

2-1-1 Pretreatment

Fig. 1 shows the pretreatment flow chart.

Conditioning	5 mL dichloromethane, 5 mL methyl alcohol, and 5 mL purified water are consecutively passed through a column packed with silica gel chemically bonded to styrene-divynylbenzene copolymer and octadecyl group, or a column with equivalent or better performance.
↓	
Test water 500 mL	
↓	
Solid-phase extraction	Flush with water at 10 to 20 mL/min.
↓	
Drying	Pass air or nitrogen gas for 30 min or longer.
↓	
Extraction	Pour 3 mL dichloromethane into test tube.
↓	
Concentration	Purge with nitrogen gas to concentrate to 0.8 mL or less.
↓	
Addition of the internal standard solution	Add 0.2 mL internal standard solution.
↓	
Volume adjustment	Add dichloromethane to adjust the volume to 1 mL.
↓	
GC/MS measurement	

Fig. 1 Pretreatment Procedure

2-1-2 Analytical Conditions

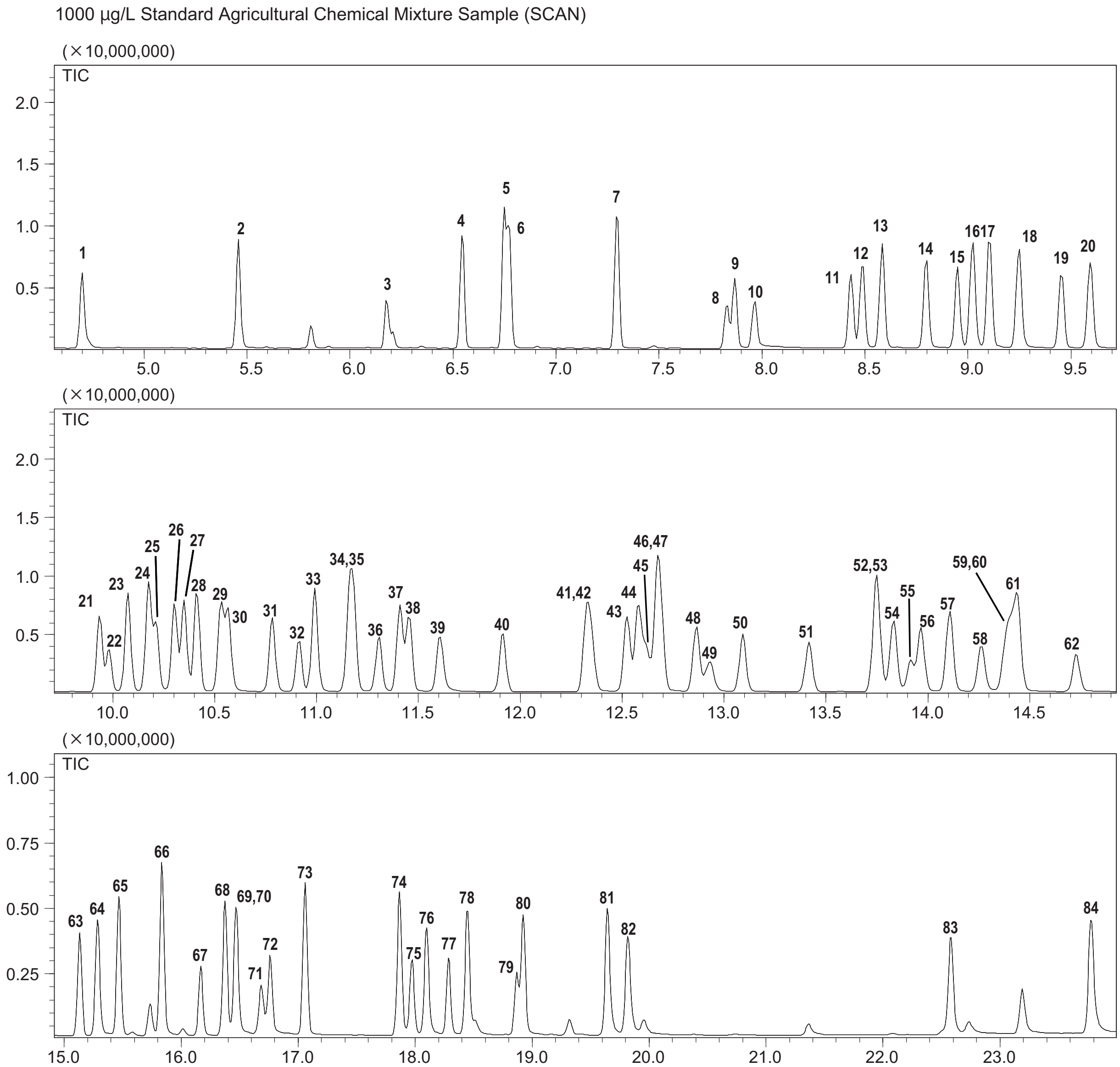
Table 5 shows the GC/MS analytical conditions.

Table 5 Analytical Conditions

Column	: Rtx-5MS (30 mL. × 0.25 mmI.D., 0.25 µm)
Injection port temp.	: 260 °C
Injection mode	: Splitless
Sampling time	: 1 min
Sample injection vol.	: 2 µL
Control mode	: Linear velocity (45 cm/sec)
Injection port advanced settings	: High pressure injection (250 kPa, 1 min)
Column oven temp.	: 80 °C (1 min) → 20 °C/min → 180 °C → 5 °C/min → 300 °C (10 min)
Ion source temp.	: 230 °C
Interface temp.	: 280 °C
Measurement mode	: SIM
Event time	: 0.3 sec
Monitoring ions	: See Table 4.

2-1-3 Results

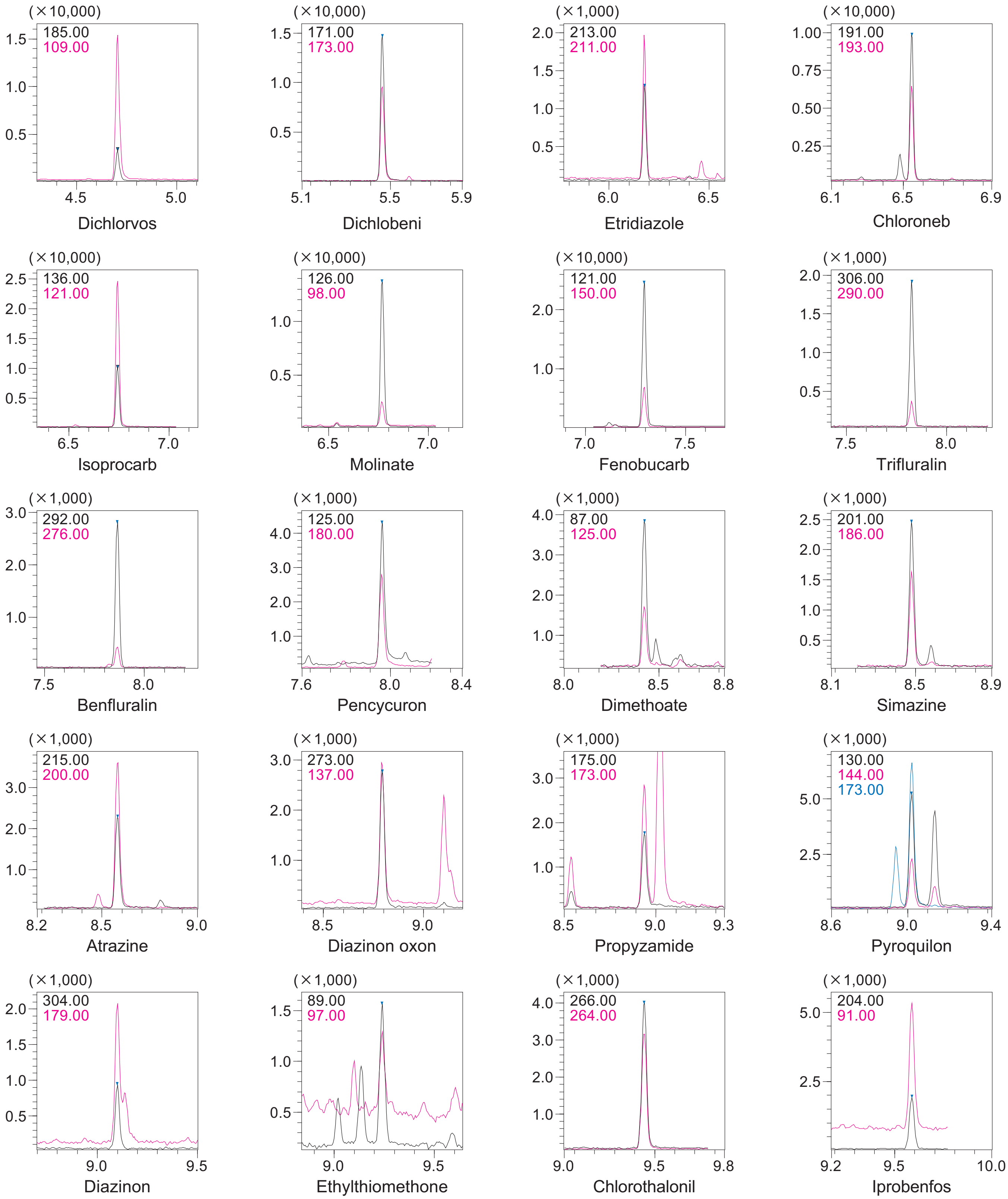
Fig. 2 shows the TIC chromatograms of the standard sample.

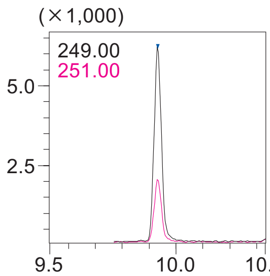


1: Dichlorvos
2: Dichlobenil
3: Etridiazole
4: Chloroneb
5: Isoprocarb
6: Molinate
7: Fenobucarb
8: Trifluralin
9: Benfluralin
10: Pencycuron
11: Dimethoate
12: Simazine
13: Atrazine
14: Diazinon oxon
15: Propyzamide
16: Pyroquilon
17: Diazinon
18: Ethylthiomethone
19: Chlorothalonil
20: Iprobenfos
21: Tolclophos-methyl oxon
22: Fenitrothion oxon
23: Bromobutide
24: Terbucarb
25: Malaoxon
26: Simetryne
27: Tolclophos-methyl
28: Alachlor
29: Metalaxyl
30: MPP oxon
31: Dithiopyr
32: Fenitrothion
33: Esprocarb
34: Malathon
35: Thiobencarb
36: Chlorpyrifos oxon
37: Fenthion (MPP)
38: Chlorpyrifos
39: Isofenphos oxon
40: Fthalide
41: Dimethametryn
42: Pendimethalin
43: Methyl daimuron
44: Isofenphos
45: Captan
46: Dimepiperate
47: Phenthoate
48: Procymidone
49: Butamifos oxon
50: Methidathion
51: α-endosulfan
52: Butamifos
53: Napropamide
54: Flutolanil
55: Isoxathion oxon
56: Isoprothiolane
57: Pretilachlor
58: MPP oxon sulfoxide
59: CNP-amino metabolite
60: MPP oxon sulfone
61: Buprofezin
62: Isoxathion
63: β-endosulfan
64: MPP sulfoxide
65: MPP sulfone
66: Mepronil
67: Chlornitrophen
68: Edifenphos
69: Propiconazole-1
70: Endosulphate
71: Propiconazole-2
72: EPN oxon
73: Thenylchlor
74: Pyributicarb
75: Iprodione
76: Pyridaphenthion
77: EPN
78: Piperophos
79: Bifenox
80: Anilofos
81: Pyriproxyfen
82: Mefenacet
83: Cafenstrole
84: Etofenprox

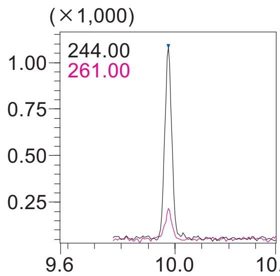
Fig. 2 TIC Chromatograms

Fig. 3 shows the SIM chromatograms obtained from analysis of a 5 µg/L standard solution.

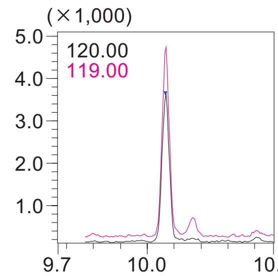




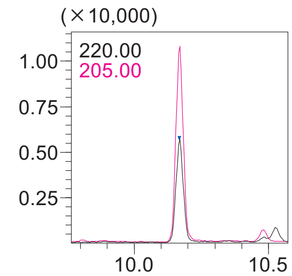
Tolclophos-methyl oxon



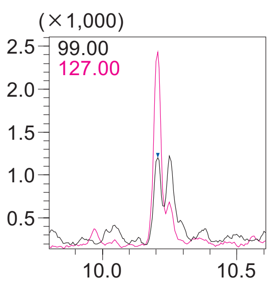
Fenitrothion oxon



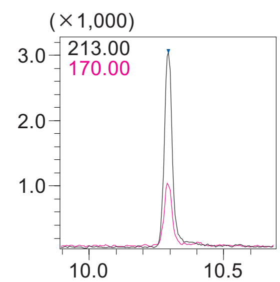
Bromobutide



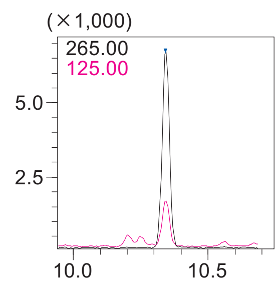
Terbucarb



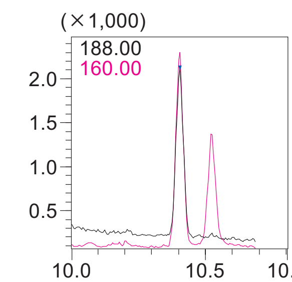
Malaoxon



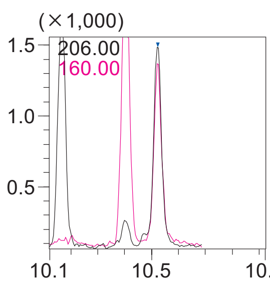
Simetryne



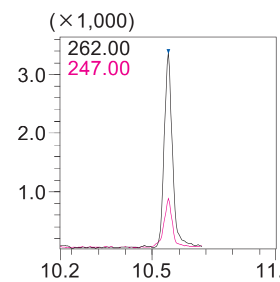
Tolclophos-methyl



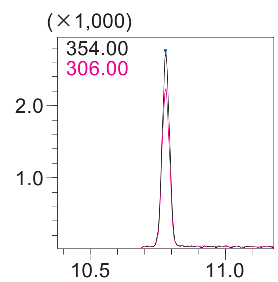
Alachlor



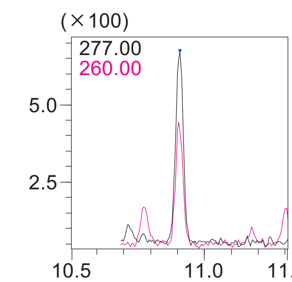
Metalaxyl



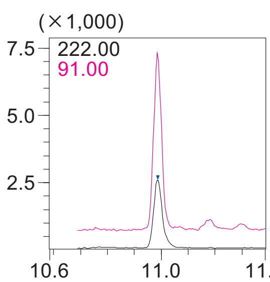
MPP oxon



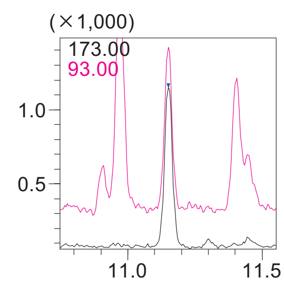
Dithiopyr



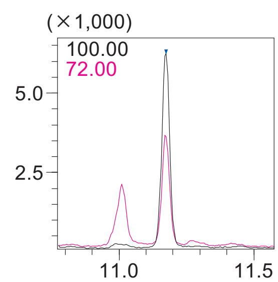
Fenitrothion



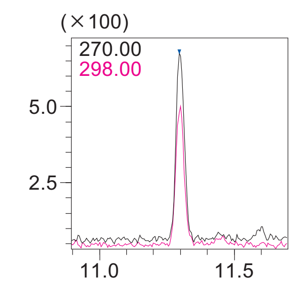
Esprocarb



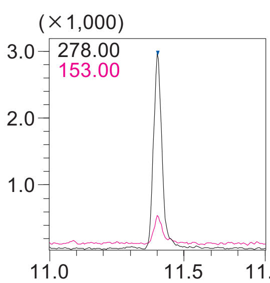
Malathon



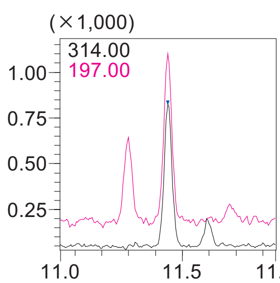
Thiobencarb



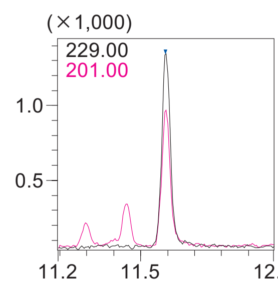
Chlorpyrifos oxon



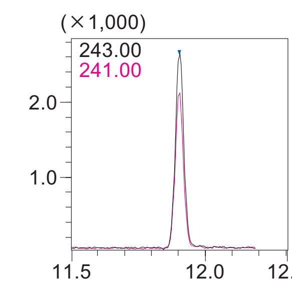
Fenthion (MPP)



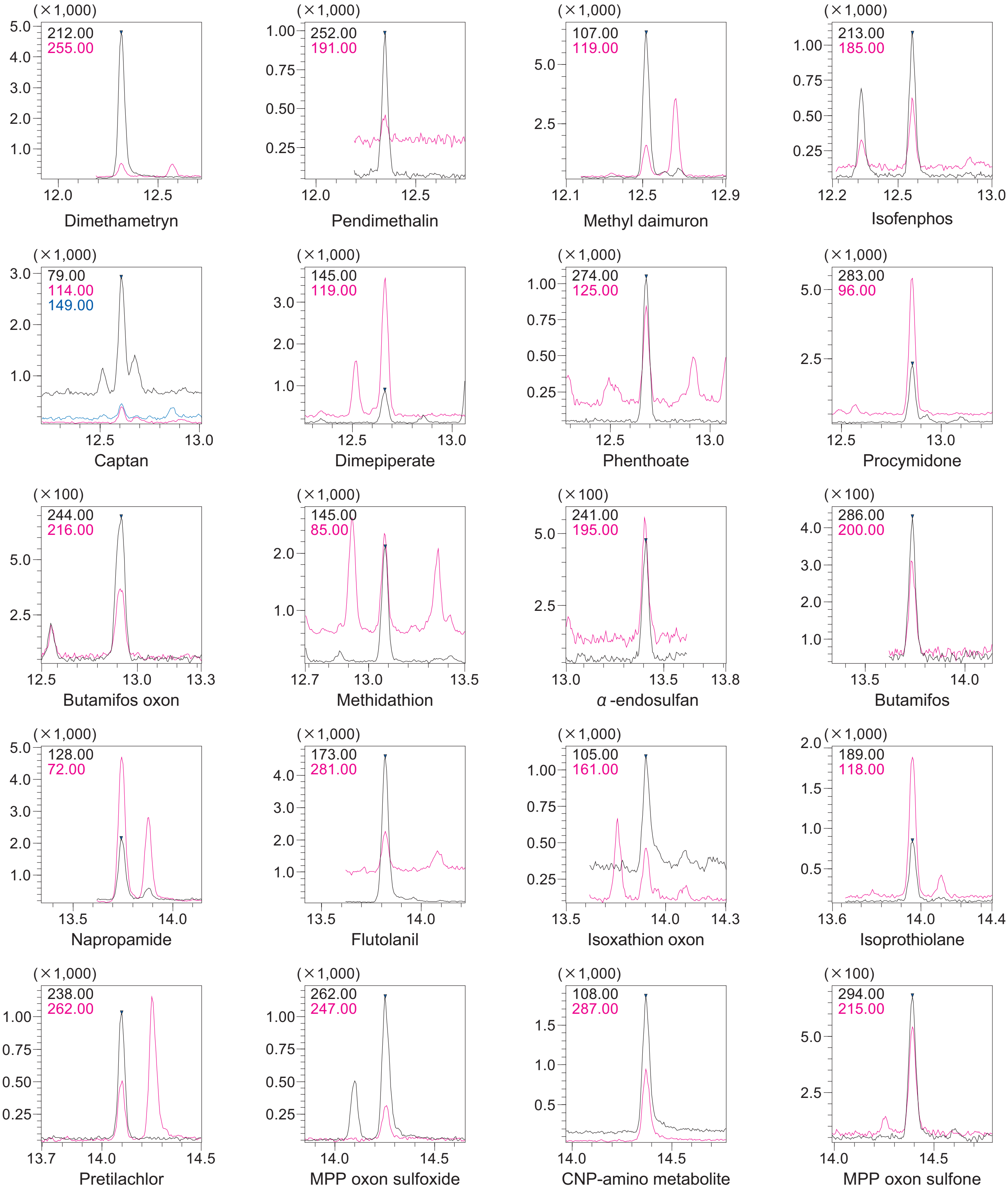
Chlorpyrifos



Isofenphos oxon



Fthalide



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255.00
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(×1,000)
252.00
191.00
Pendimethalin
(×1,000)
107.00
119.00
Methyl daimuron
(×1,000)
213.00
185.00
Isofenphos
(×1,000)
79.00
114.00
149.00
Captan
(×1,000)
145.00
119.00
Dimepiperate
(×1,000)
274.00
125.00
Phenthoate
(×1,000)
283.00
96.00
Procymidone
(×100)
244.00
216.00
Butamifos oxon
(×1,000)
145.00
85.00
Methidathion
(×100)
241.00
195.00
α -endosulfan
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286.00
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Butamifos
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72.00
Napropamide
(×1,000)
173.00
281.00
Flutolanil
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105.00
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118.00
Isoprothiolane
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Pretilachlor
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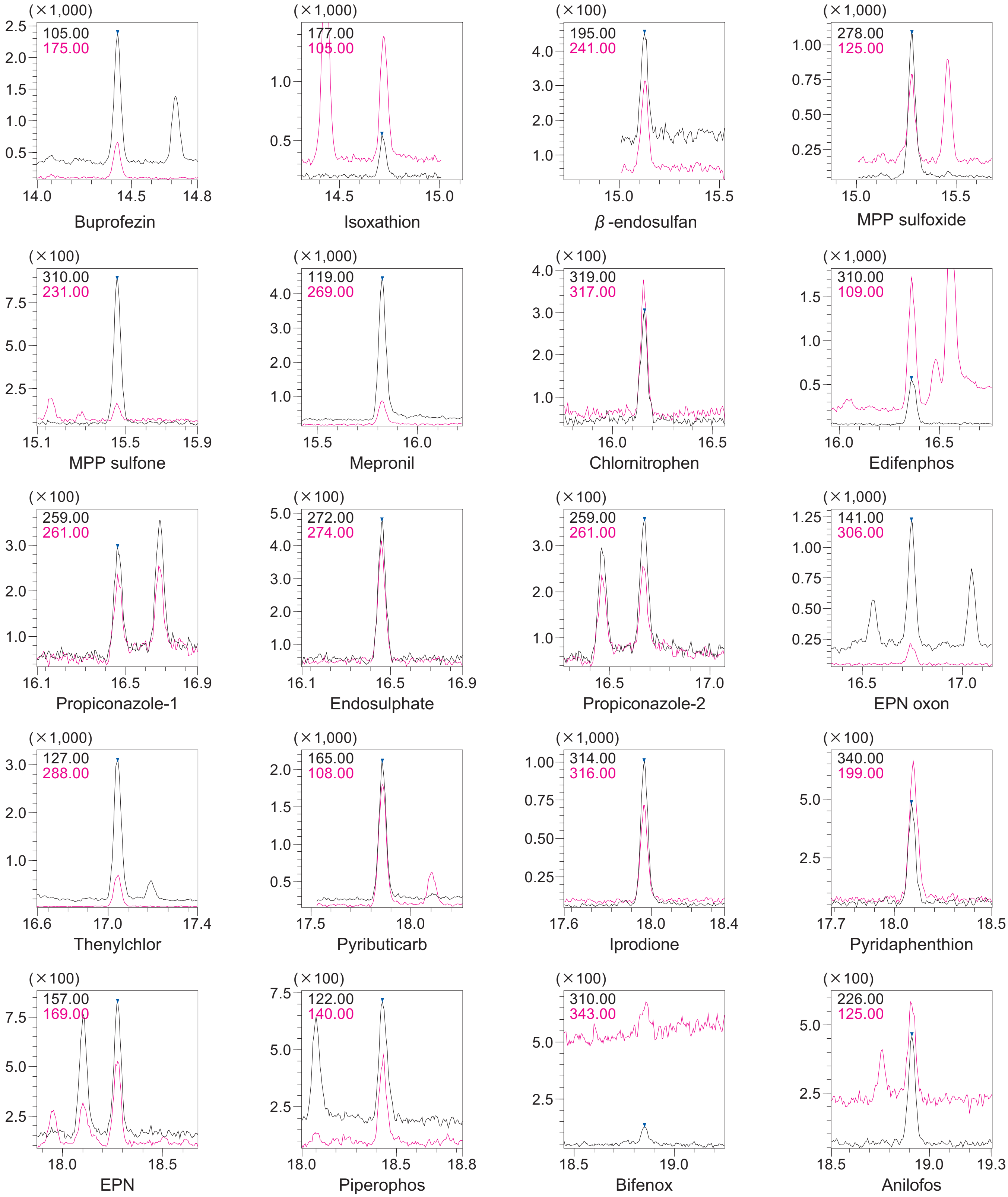
MPP oxon sulfone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105.00
Isoxathion
(×100)
195.00
241.00
β-endosulfan
(×1,000)
278.00
125.00
MPP sulfoxide
(×100)
310.00
231.00
MPP sulfone
(×1,000)
119.00
269.00
Mepronil
(×100)
319.00
317.00
Chlornitrophen
(×1,000)
310.00
109.00
Edifenphos
(×100)
259.00
261.00
Propiconazole-1
(×100)
272.00
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Endosulphate
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Propiconazole-2
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306.00
EPN oxon
(×1,000)
127.00
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Thenylchlor
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165.00
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Pyributicarb
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Pyridaphenthion
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EPN
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Anilofos

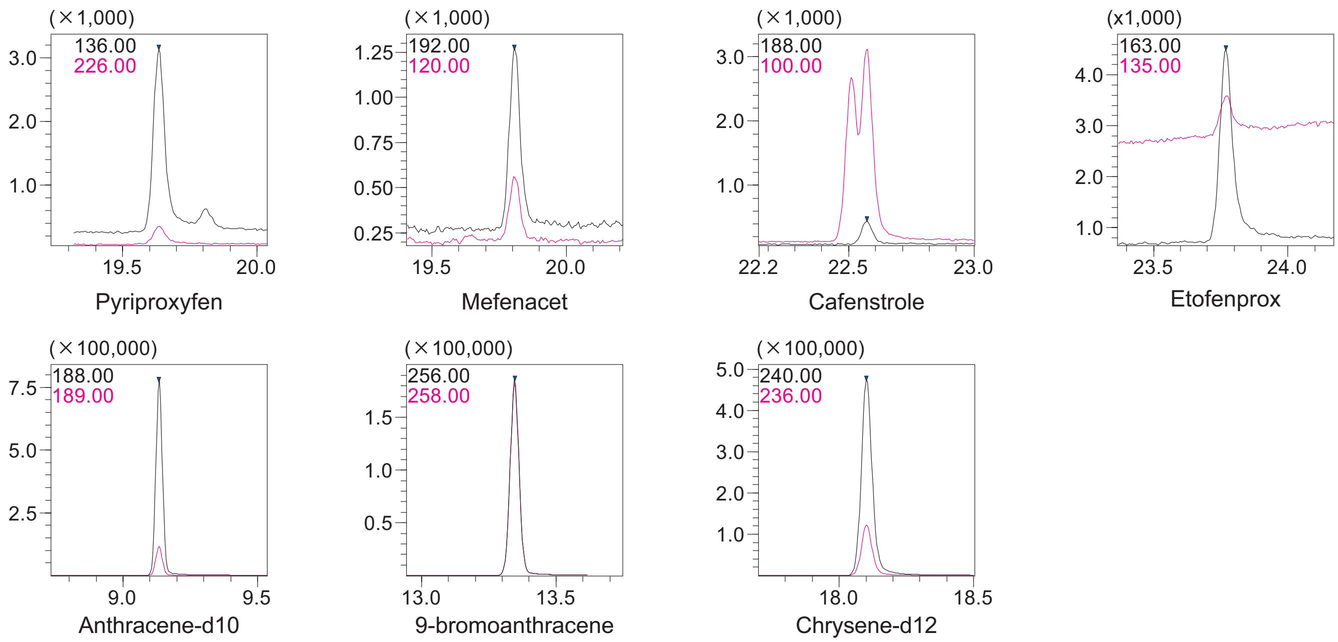


Fig. 3 SIM Chromatograms (5 μg/L)

Table 6 shows the repeatability obtained from five consecutive measurements of 5 μg/L concentrations of each agricultural chemical.

Table 6 Repeatability (area ratio with respect to internal standard, n = 5)

ID	Compound Name	ISTD Group	1st Measurement	2nd Measurement	3rd Measurement	4th Measurement	5th Measurement	Average	Standard Deviation	CV Value (%)
1	Dichlorvos	1	0.0032432	0.0033023	0.0031307	0.0032386	0.0033550	0.0032539	0.00008382	2.58
2	Dichlobenil	1	0.0143558	0.0142362	0.0140189	0.0143891	0.0149033	0.0143806	0.00032618	2.27
3	Etridiazole	1	0.0010937	0.0010960	0.0010845	0.0011223	0.0011760	0.0011145	0.00003715	3.33
4	Chloroneb	1	0.0084734	0.0084616	0.0083606	0.0085872	0.0089420	0.0085650	0.00022552	2.63
5	Isoprocarb	1	0.0088332	0.0086397	0.0086349	0.0089090	0.0089403	0.0087914	0.00014601	1.66
6	Molinate	1	0.0129342	0.0126181	0.0126553	0.0129837	0.0130498	0.0128482	0.00019784	1.54
7	Fenobucarb	1	0.0242070	0.0241116	0.0237093	0.0243825	0.0247256	0.0242272	0.00037234	1.54
8	Trifluralin	1	0.0019440	0.0018998	0.0018562	0.0019082	0.0019346	0.0019086	0.00003449	1.81
9	Benfluralin	1	0.0028433	0.0027697	0.0027618	0.0027977	0.0028109	0.0027967	0.00003285	1.17
10	Pencycuron	1	0.0049468	0.0049257	0.0049951	0.0045798	0.0048167	0.0048528	0.00016600	3.42
11	Dimethoate	1	0.0042975	0.0042023	0.0043582	0.0043679	0.0043016	0.0043055	0.00006596	1.53
12	Simazine	1	0.0029419	0.0029169	0.0028695	0.0029663	0.0030055	0.0029400	0.00005119	1.74
13	Atrazine	1	0.0026437	0.0026097	0.0026582	0.0026345	0.0027115	0.0026515	0.00003788	1.43
14	Diazinon oxon	1	0.0033604	0.0033121	0.0033020	0.0032919	0.0032250	0.0032983	0.00004868	1.48
15	Propyzamide	1	0.0020501	0.0019847	0.0019805	0.0019708	0.0020456	0.0020063	0.00003826	1.91
16	Pyroquilon	1	0.0065220	0.0065506	0.0065086	0.0067533	0.0066214	0.0065912	0.00010056	1.53
17	Diazinon	1	0.0010009	0.0010111	0.0010617	0.0010017	0.0009673	0.0010086	0.00003406	3.38
18	Ethylthiomethone	1	0.0017815	0.0017909	0.0017843	0.0018463	0.0019123	0.0018231	0.00005650	3.10
19	Chlorothalonil	1	0.0051004	0.0051556	0.0050787	0.0051885	0.0053998	0.0051846	0.00012795	2.47
20	Iprobenfos	1	0.0023988	0.0025173	0.0025476	0.0025332	0.0025632	0.0025120	0.00006554	2.61
21	Tolclophos-methyl oxon	1	0.0086581	0.0084992	0.0085996	0.0086476	0.0087167	0.0086242	0.00008137	0.94
22	Fenitrothion oxon	1	0.0013882	0.0013311	0.0013470	0.0013281	0.0013483	0.0013486	0.00002398	1.78
23	Bromobutide	1	0.0048325	0.0049655	0.0048915	0.0047995	0.0048847	0.0048747	0.00006337	1.30
24	Terbucarb: outdated pesticide	1	0.0079926	0.0077683	0.0077900	0.0079166	0.0078628	0.0078661	0.00009209	1.17
25	Malaoxon	1	0.0013749	0.0013559	0.0013381	0.0012561	0.0013384	0.0013327	0.00004539	3.41
26	Simetryne	1	0.0044534	0.0043157	0.0044680	0.0044228	0.0043786	0.0044077	0.00006176	1.40
27	Tolclophos-methyl	1	0.0093378	0.0091783	0.0092441	0.0092416	0.0093569	0.0092717	0.00007419	0.80

ID	Compound Name	ISTD Group	1st Measurement	2nd Measurement	3rd Measurement	4th Measurement	5th Measurement	Average	Standard Deviation	CV Value (%)
28	Alachlor	1	0.0027616	0.0027216	0.0026816	0.0026213	0.0026966	0.0026966	0.00005183	1.92
29	Metalaxyl	1	0.0019143	0.0018848	0.0019874	0.0019654	0.0019380	0.0019380	0.00004058	2.09
30	Fenthion oxon	1	0.0050328	0.0049610	0.0050455	0.0051197	0.0049633	0.0050245	0.00006585	1.31
31	Dithiopyr	1	0.0038857	0.0041001	0.0041530	0.0040871	0.0041269	0.0040706	0.00010639	2.61
32	Fenitrothion	1	0.0009475	0.0009105	0.0009208	0.0009181	0.0009582	0.0009310	0.00002064	2.22
33	Esprocarb	1	0.0042248	0.0043375	0.0046483	0.0042070	0.0044656	0.0043766	0.00018377	4.20
34	Malathon	1	0.0016643	0.0016617	0.0017304	0.0016243	0.0016290	0.0016619	0.00004241	2.55
35	Thiobencarb	1	0.0094884	0.0096681	0.0095612	0.0096500	0.0097436	0.0096223	0.00009905	1.03
36	Chlorpyrifos oxon	1	0.0010143	0.0010036	0.0009947	0.0009676	0.0009913	0.0009943	0.00001737	1.75
37	Fenthion	1	0.0046930	0.0047086	0.0048238	0.0047345	0.0047969	0.0047513	0.00005664	1.19
38	Chlorpyrifos	2	0.0036966	0.0036532	0.0035880	0.0037941	0.0036456	0.0036755	0.00007675	2.09
39	Isofenphos oxon	2	0.0066893	0.0066169	0.0064727	0.0066629	0.0063409	0.0065565	0.00014671	2.24
40	Fthalide	2	0.0131347	0.0125165	0.0124506	0.0125592	0.0131161	0.0127554	0.00034001	2.67
41	Dimethametryn	2	0.0252894	0.0248232	0.0250086	0.0260876	0.0250800	0.0252578	0.00049301	1.95
42	Pendimethalin	2	0.0041267	0.0041376	0.0038280	0.0041408	0.0041566	0.0040779	0.00014011	3.44
43	Methyl daimuron: outdated pesticide	2	0.0326642	0.0324041	0.0320688	0.0331143	0.0335235	0.0327550	0.00057489	1.76
44	Isofenphos: outdated pesticide	2	0.0050629	0.0047119	0.0049946	0.0049465	0.0049153	0.0049262	0.00013214	2.68
45	Captan	2	0.0118534	0.0115640	0.0115262	0.0120733	0.0121990	0.0118432	0.00029918	2.53
46	Dimepiperate: outdated pesticide	2	0.0040899	0.0041145	0.0039712	0.0042189	0.0042205	0.0041230	0.00010357	2.51
47	Phenthoate	2	0.0051320	0.0052469	0.0049756	0.0052468	0.0051018	0.0051406	0.00011335	2.20
48	Procymidone	2	0.0097740	0.0097235	0.0098143	0.0104717	0.0100555	0.0099678	0.00030918	3.10
49	Butamifos oxon	2	0.0044810	0.0044259	0.0045924	0.0044924	0.0044172	0.0044818	0.00007008	1.56
50	Methidathion	2	0.0103950	0.0106461	0.0102355	0.0101494	0.0107811	0.0104414	0.00026790	2.57
51	α-endosulfan	2	0.0020174	0.0021703	0.0019456	0.0020265	0.0020106	0.0020341	0.00008256	4.06
52	Butamifos	2	0.0019737	0.0020665	0.0019582	0.0020143	0.0019237	0.0019873	0.00005493	2.76
53	Napropamide	2	0.0108528	0.0106968	0.0114315	0.0105962	0.0108015	0.0108758	0.00032597	3.00
54	Flutolanil	2	0.0240749	0.0238776	0.0239137	0.0230333	0.0234578	0.0236714	0.00042332	1.79
55	Isoxathion oxon	2	0.0047018	0.0044143	0.0045250	0.0045412	0.0045296	0.0045424	0.00010281	2.26
56	Isoprothiolane	2	0.0039910	0.0042944	0.0041523	0.0038137	0.0042205	0.0040944	0.00019284	4.71
57	Pretilachlor	2	0.0049663	0.0050117	0.0049946	0.0050637	0.0051248	0.0050322	0.00006275	1.25

ID	Compound Name	ISTD Group	1st Measurement	2nd Measurement	3rd Measurement	4th Measurement	5th Measurement	Average	Standard Deviation	CV Value (%)
58	Fenthion oxon sulfoxide	2	0.0059601	0.0060242	0.0061400	0.0060110	0.0058632	0.0059997	0.00010078	1.68
59	CNP-amino metabolite	2	0.0093714	0.0103716	0.0098228	0.0100102	0.0096570	0.0098466	0.00037575	3.82
60	Fenthion oxon sulfone	2	0.0036414	0.0035794	0.0035627	0.0036550	0.0036329	0.0036143	0.00004063	1.12
61	Buprofezin	2	0.0115084	0.0116770	0.0117726	0.0114288	0.0121274	0.0117028	0.00027329	2.34
62	Isoxathion	2	0.0018172	0.0019719	0.0018403	0.0019044	0.0017781	0.0018624	0.00007647	4.11
63	β-endosulfan	2	0.0019553	0.0019050	0.0017814	0.0019386	0.0018139	0.0018788	0.00007716	4.11
64	Fenthion sulfoxide	3	0.0018069	0.0017409	0.0018338	0.0017868	0.0017776	0.0017892	0.00003457	1.93
65	Fenthion sulfone	3	0.0015135	0.0015405	0.0016319	0.0016572	0.0015193	0.0015725	0.00006714	4.27
66	Mepronil	3	0.0076559	0.0074934	0.0076384	0.0076497	0.0071844	0.0075244	0.00020159	2.68
67	Chlornitrophen: outdated pesticide	3	0.0004648	0.0004864	0.0004767	0.0004874	0.0004651	0.0004761	0.00001100	2.31
68	Edifenphos	3	0.0009540	0.0009663	0.0009817	0.0009884	0.0009418	0.0009665	0.00001921	1.99
69	Propiconazole-1	3	0.0004899	0.0004879	0.0004841	0.0004946	0.0005088	0.0004931	0.00000957	1.94
70	Endosulphate	3	0.0008206	0.0007703	0.0008541	0.0008031	0.0007889	0.0008074	0.00003200	3.96
71	Propiconazole-2	3	0.0005229	0.0005430	0.0005327	0.0005145	0.0004932	0.0005213	0.00001900	3.64
72	EPN oxon	3	0.0018356	0.0019616	0.0019067	0.0019061	0.0018181	0.0018856	0.00005850	3.10
73	Thenylchlor	3	0.0057306	0.0055776	0.0057634	0.0053452	0.0051415	0.0055117	0.00026476	4.80
74	Pyributicarb	3	0.0034051	0.0034193	0.0034468	0.0034121	0.0032625	0.0033892	0.00007256	2.14
75	Iprodione	3	0.0017424	0.0017097	0.0017508	0.0016436	0.0015505	0.0016794	0.00008347	4.97
76	Pyridaphenthion: outdated pesticide	3	0.0008020	0.0007775	0.0008177	0.0007546	0.0008092	0.0007922	0.00002578	3.25
77	EPN	3	0.0012395	0.0012900	0.0012511	0.0012771	0.0011993	0.0012514	0.00003537	2.83
78	Piperophos: outdated pesticide	3	0.0011133	0.0011231	0.0010729	0.0010043	0.0009988	0.0010625	0.00005873	5.53
79	Bifenox: outdated pesticide	3	0.0001341	0.0001488	0.0001242	0.0001400	0.0001514	0.0001397	0.00001107	7.92
80	Anilofos	3	0.0007525	0.0007441	0.0007596	0.0007236	0.0007210	0.0007402	0.00001721	2.33
81	Pyriproxyfen	3	0.0061804	0.0062702	0.0064906	0.0060179	0.0058727	0.0061663	0.00023685	3.84
82	Mefenacet	3	0.0020099	0.0019224	0.0019385	0.0019259	0.0018665	0.0019326	0.00005130	2.65
83	Cafenstrole	3	0.0007496	0.0007376	0.0007468	0.0006179	0.0006282	0.0006960	0.00006687	9.61
84	Etofenprox	3	0.0087340	0.0098688	0.0105586	0.0086691	0.0088301	0.0093321	0.00084287	9.03
85	Anthracene-d10	1	-	-	-	-	-	-	-	-
86	9-bromoanthracene	2	-	-	-	-	-	-	-	-
87	Chrysene-d12	3	-	-	-	-	-	-	-	-

2-2 Attached Method 6-Simultaneous Analysis Using Solid-Phase Extraction-Derivatization-Gas Chromatograph-Mass Spectrometer

This section introduces an example of simultaneous analysis of 4 agricultural chemicals, targeted in Attached Method 6, using GC/MS. Since these agricultural chemicals have high polarity, this method derivatizes the samples (methyl esterification) before measurement. The same analytical conditions can be used for measurements as for agricultural chemicals targeted in Attached Method 5. Table 7 shows the agricultural chemical numbers (number in the list of 102 agricultural chemicals), target values (mg/L), and the monitoring ions used during analysis for Attached Method 6.

Table 7 Monitoring Ions for 4 Agricultural Chemicals

No.	Agricultural Chemical	Target Value (mg/L)	Monitoring Ions (*m/z*)	No.	Agricultural Chemical	Target Value (mg/L)	Monitoring Ions (*m/z*)
17	Bentazone	0.2	212,254	45	Mecoprop (MCPP)	0.005	228,169
19	2,4-dichlorophenoxyacetic acid (2,4-D)	0.03	234,199	-	Anthracene-d10	-	188,189
20	Tryclopyr	0.006	210,212	-	-	-	-

2-2-1 Derivatization Reaction

Fig. 4 shows the methyl derivatization reaction used by this test method.

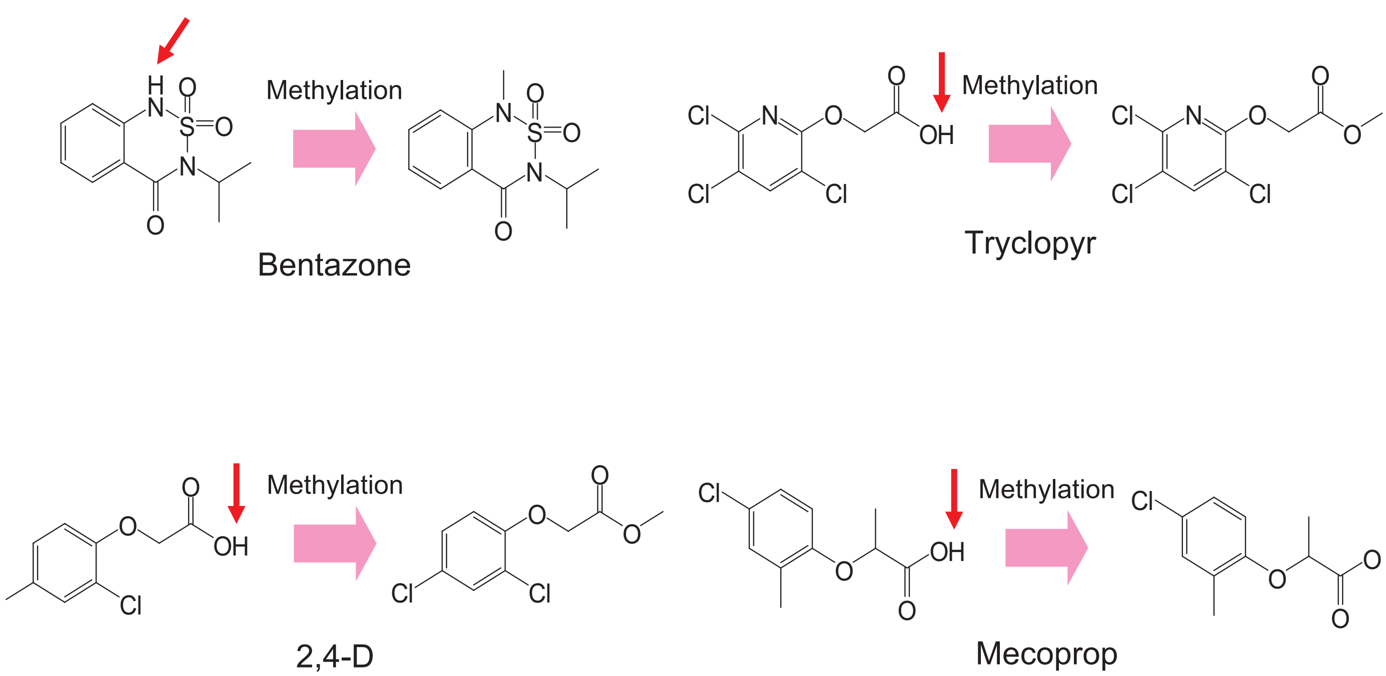


Fig. 4 Derivatization Reactions for Each Agricultural Chemical

2-2-2 Pretreatment

Fig. 5 shows the pretreatment flow chart.

Conditioning	5 mL dichloromethane, 5 mL methyl alcohol, and 5 mL purified water are consecutively passed through a column packed with silica gel chemically bonded to styrene-divynylbenzene copolymer and octadecyl group, or a column with equivalent or better performance.
↓	
Test water 500 mL	Adjust to pH 3.5 using hydrochloric acid (1 + 10).
↓	
Solid-phase extraction	Flush with water at 10 to 20 mL/min.
↓	
Drying	Pass air or nitrogen gas for 30 min or longer.
↓	
Extraction	Pour 3 mL dichloromethane into test tube.
↓	
Concentration	Purge with nitrogen gas to concentrate to 0.5 mL or less.
↓	
Derivatization	After adding 0.5 mL diazomethane solution*, let stand for 10 min.
↓	
Concentration	Purge with nitrogen gas to concentrate to 0.5 mL or less.
↓	
Addition of the internal standard solution	Add 0.5 mL internal standard solution.
↓	
Volume adjustment	Add dichloromethane to adjust the volume to 1 mL.
↓	
GC/MS measurement	

* In accordance with Example 1-(5) in Attached Table 17 of the test method notification.

Fig. 5 Pretreatment Procedure

2-2-3 Analytical Conditions

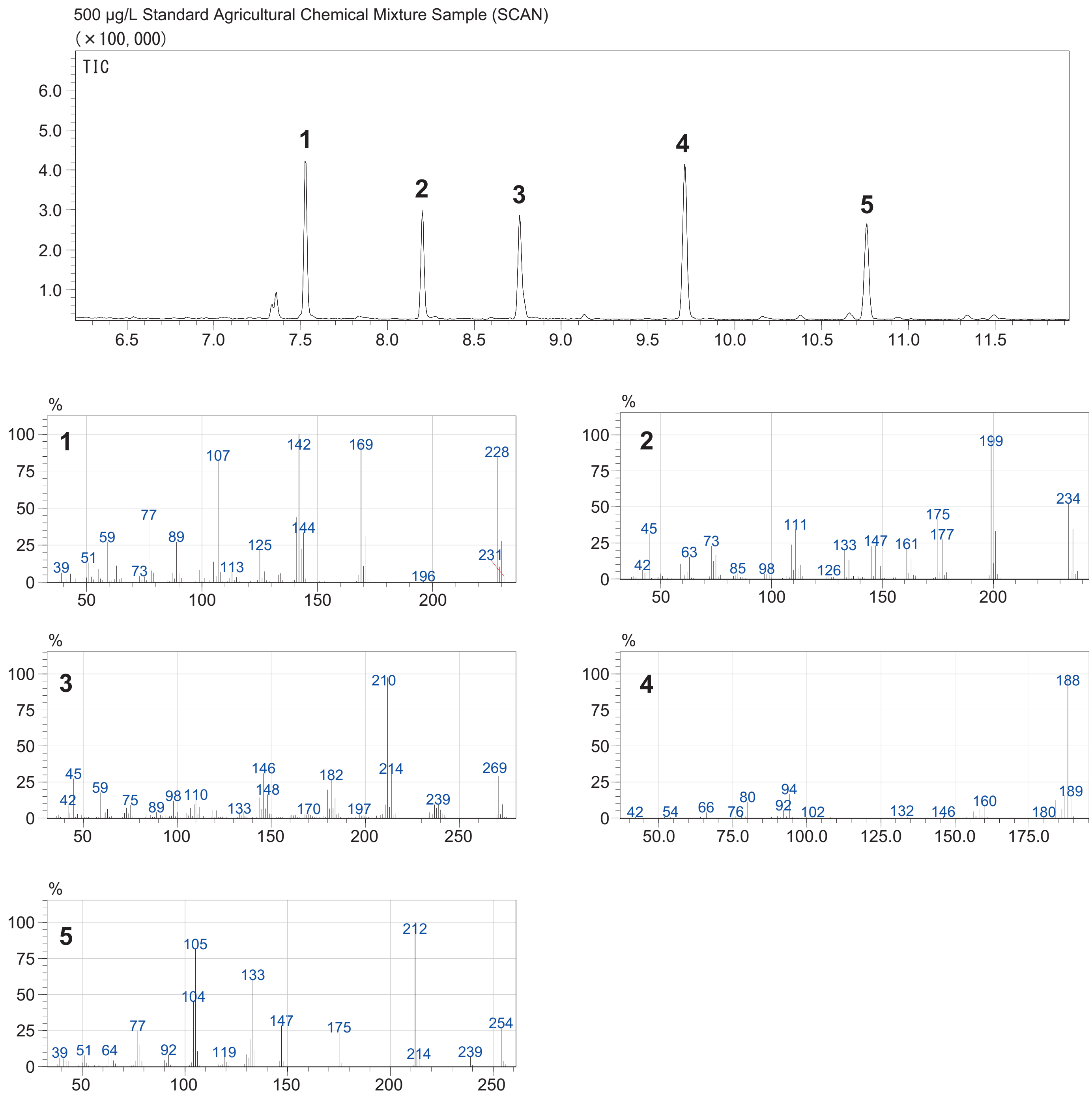
Table 8 shows the GC/MS analytical conditions.

Table 8 Analytical Conditions

Column	: Rtx-5MS (30 mL. × 0.25 mmI.D., 0.25 μm)
Injection port temp.	: 250 °C
Injection mode	: Splitless
Sampling time	: 2 min
Sample injection vol.	: 2 μL
Control mode	: Linear velocity (44.5 cm/sec)
Injection port advanced settings	: High pressure injection (250 kPa, 2 or 3 min)
Column oven temp.	: 80 °C (2 min) → 20 °C/min → 180 °C → 5° C/min → 280 °C (3 min)
Ion source temp.	: 230 °C
Interface temp.	: 250 °C
Measurement mode	: SIM
Event time	: 0.3 sec
Monitoring ions	: See Table 7.

2-2-4 Results

Fig. 6 shows the TIC chromatogram and mass spectra of the standard sample.



1: Mecoprop 2: 2,4-D 3: Tryclopyr 4: Anthracene-d10 (IS) 5: Bentazone

Fig. 6 TIC Chromatogram

Fig. 7 shows the SIM chromatograms obtained from analysis of a 10 µg/L standard solution.

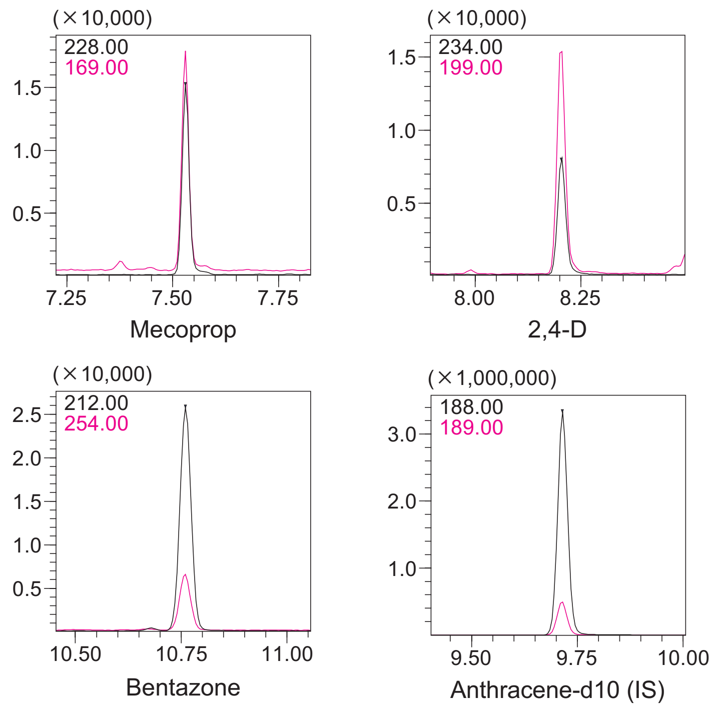


Fig. 7 SIM Chromatograms (10 µg/L)

Table 9 shows the repeatability obtained from five consecutive measurements of 10 µg/L concentrations of each agricultural chemical.

Table 9 Repeatability (area ratio with respect to internal standard, n = 5)

ID	Compound Name	ISTD Group	1st Measurement	2nd Measurement	3rd Measurement	4th Measurement	5th Measurement	Average	Standard Deviation	CV Value (%)
1	Mecoprop	1	0.0034207	0.0034716	0.0033198	0.0034180	0.0036803	0.0034621	0.0001338	3.86
2	2,4-D	1	0.0020649	0.0020719	0.0019648	0.0021026	0.0022441	0.0020897	0.0001007	4.82
3	Trichlopyr	1	0.0032496	0.0033034	0.0032312	0.0033283	0.0034951	0.0033215	0.0001047	3.15
4	Bentazone	1	0.0088797	0.0091469	0.0087811	0.0089618	0.0096077	0.0090754	0.0003264	3.60
5	Anthracene-d10	1	-	-	-	-	-	-	-	-

3. High-Performance Liquid Chromatograph

3-1 Attached Method 9-Simultaneous Analysis of Iprodione, Asulam, Thiophanate-methyl, and Siduron

Of the agricultural chemicals specified as water quality control target setting items, four components-iprodione, asulam, thiophanate-methyl, and siduron, can be analyzed using the solid-phase extraction-HPLC method indicated in Attached Method 9. This section introduces an example of simultaneous analysis of these four agricultural chemicals using Attached Method 9.

3-1-1 Simultaneous Analysis of Standard Sample

Fig. 8 shows structural formulas for iprodione, asulam, thiophanate-methyl, and siduron. A target value of 0.3 mg/L is specified for iprodione, thiophanate-methyl, and siduron and 0.2 mg/L is specified for asulam. Fig. 9 shows chromatograms for the standard sample and Table 10 shows the analytical conditions. The concentration of each component in Fig. 9 is equivalent to 1/100 of the target value specified in Attached Method 9 for solid-phase extraction (test water concentration: 500 times). The method specifies detecting asulam at 270 nm and the other three components at 230 nm. In this example, the SPD-10AVP detector's simultaneous dual wavelength measurement function was utilized to detect them.

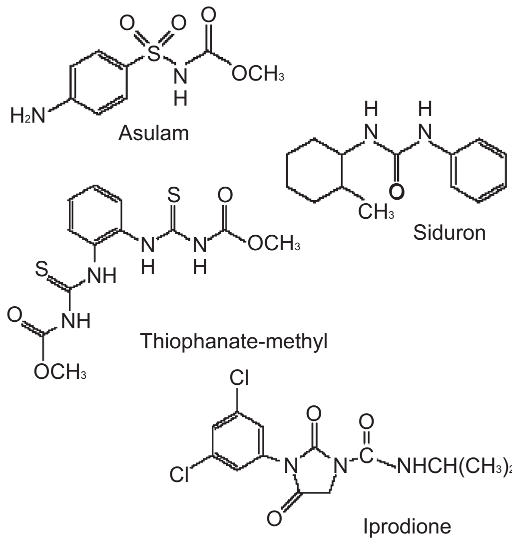


Fig. 8 Structural Formulas

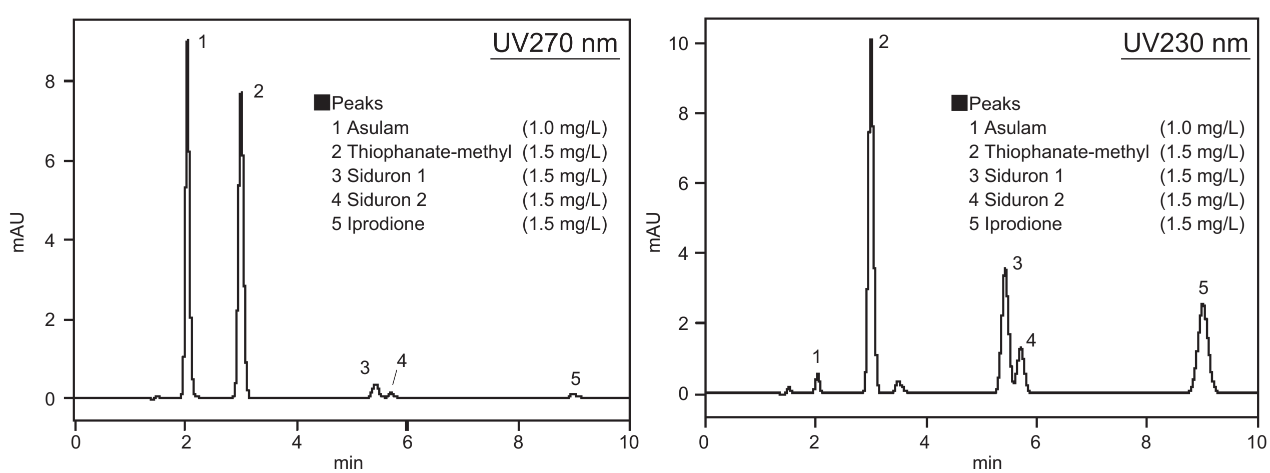


Fig. 9 Chromatograms of the Standard Sample

Table 10 Analytical Conditions

Column	: Shim-pack VP-ODS (150 mmL. × 4.6 mmI.D., 5 µm)
Mobile phase	: Acetonitrile/50 mmol/L potassium phosphate monobasic (pH 3.0) = 55/45 (v/v%)
Flow rate	: 1.0 mL/min
Column temp.	: 40 °C
Detector	: UV-VIS detector at 230 nm, 270 nm
Injection vol.	: 10 µL

3-2 Attached Method 11-Diquat Using Solid-Phase Extraction-HPLC

Of the agricultural chemicals specified as water quality control target setting items, diquat is analyzed using solid-phase extraction-HPLC method indicated in Attached Method 11. This section introduces an analysis example of diquat using Attached Method 11.

3-2-1 Analysis of Standard Sample

The target value specified in Attached Method 11 for diquat is 0.005 mg/L. In addition, it also specifies preparing test water by using solid-phase extraction to concentrate it by 100 times. Fig. 10 shows a flow diagram of the pretreatment process. Fig. 11 shows the results from analyzing a 0.4 mg/L standard diquat sample that was not pretreated by concentrating it by 100 times. Table 11 shows analytical conditions.

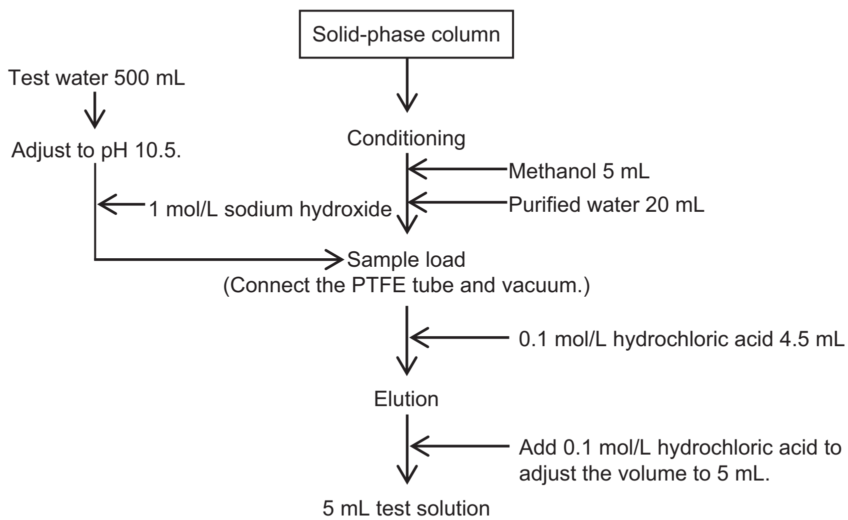


Fig. 10 Pretreatment

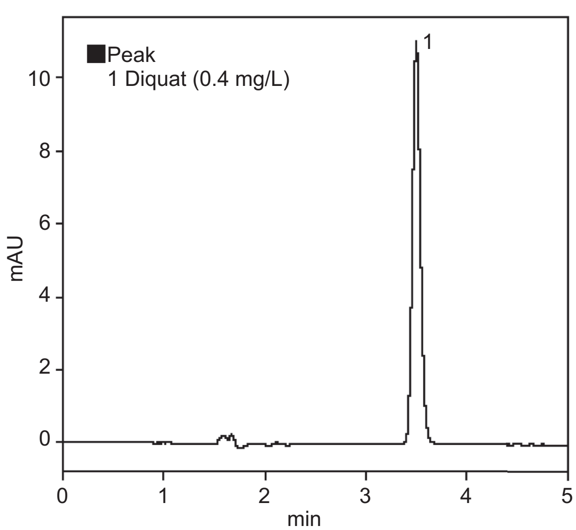


Fig. 11 Chromatogram of Diquat

Table 11 Analytical Conditions

Column	: Shim-pack VP-ODS (150 mmL. × 4.6 mmI.D., 5 µm)
Mobile phase	: Aqueous solution of 13.5 mL phosphoric acid, 10 mL diethylamine and 3.0 g sodium 1-pentanesulfonate, with the total volume of 1000 mL
Flow rate	: 1.0 mL/min
Column temp.	: 40 °C
Detector	: UV-VIS detector at 313 nm
Injection vol.	: 50 µL

3-3 Attached Method 12-Glyphosate Using Derivatization-HPLC

Of the agricultural chemicals specified as water quality control target setting items, glyphosate can be analyzed using the derivatization-HPLC method indicated in Attached Method 12. In the case of glyphosate, it is specified that its metabolite amino-methylphosphonic acid (AMPA) is also measured. This section introduces an analysis example of glyphosate using Attached Method 12.

3-3-1 Analysis of Standard Sample

The 2 mg/L target value specified for glyphosate is for the total of glyphosate and its metabolite AMPA. These components are pretreated by reaction with FMOC reagent, then detected with a fluorescence detector. Fig. 12 shows a flow diagram of the pretreatment process. In addition, Fig. 13 shows results from analyzing a standard sample with 0.025 mg/L each of glyphosate and AMPA and Table 12 shows the corresponding analytical conditions.

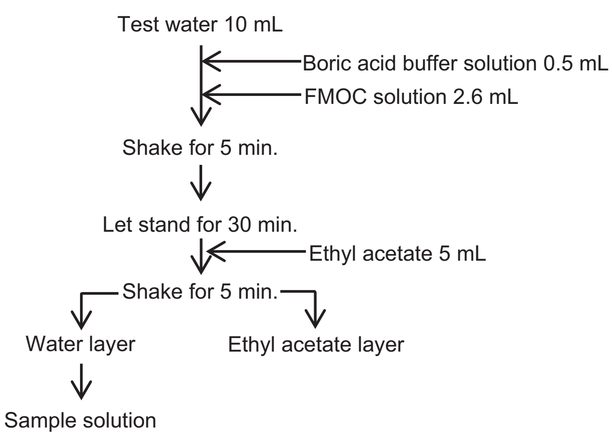


Fig. 12 Pretreatment

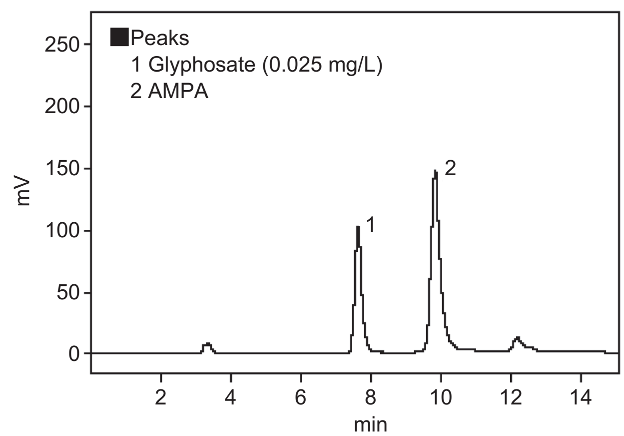


Fig. 13 Chromatogram of Glyphosate and AMPA Standard Samples

Table 12 Analytical Conditions

Column	: Shim-pack VP-ODS (150 mmL. × 4.6 mmI.D., 5 µm)
Mobile phase	: 50 mmol/L potassium phosphate monobasic (pH = 2.5, adjusted with phosphoric acid) /acetonitrile = 70/30 (v/v)
Flow rate	: 0.7 mL/min
Column temp.	: 40 °C
Detector	: Fluorescence detector, Ex. at 270 nm, Em. at 315 nm
Injection vol.	: 20 µL

3-4 Attached Method 14-Simultaneous Analysis of Carbofuran, Carbaryl, and Methomyl Using HPLC-Post-Column

Of the agricultural chemicals specified as water quality control target setting items, three components-carbofuran (carbosulfan metabolite), carbaryl (NAC), and methomyl, can be analyzed using the HPLC-post-column method indicated in Attached Method 14. This section introduces an analysis example using post-column derivatization and fluorescence detection based on Attached Method 14.

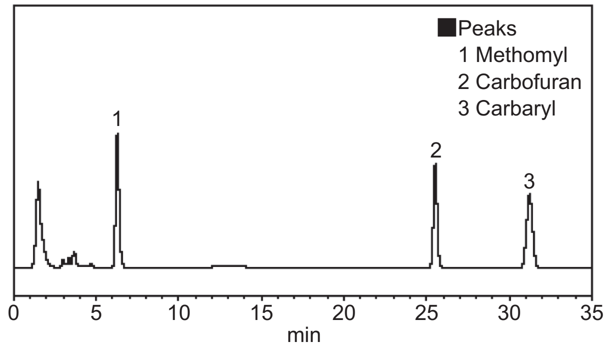


Fig. 14 Chromatogram of the Standard Samples (5 μg/L each)

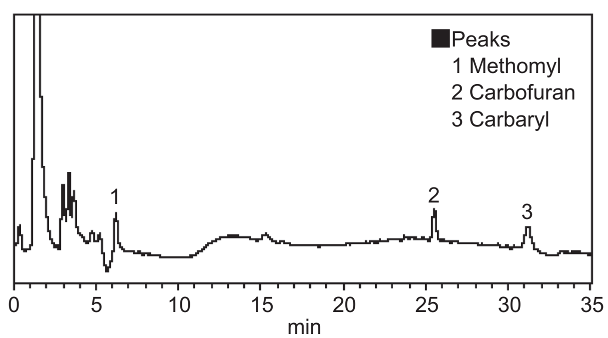


Fig. 15 Chromatogram of the Standard Samples (0.1 μg/L each)

3-4-1 Analysis of Standard Sample

Carbofuran (carbosulfan metabolite), carbaryl (NAC), and methomyl are detected using post-column derivatization with a reaction solution of o-phthalaldehyde. This method detects the agricultural chemical components by hydrolyzing each component eluted from an analytical column with sodium hydroxide, then reacting them with o-phthalaldehyde. Fig. 14 and 15 show the results from analyzing standard samples of the three components-carbofuran (carbosulfan metabolite), carbaryl (NAC), and methomyl, using a system specified in the given method. Fig. 14 shows the results from analyzing 5 μg/L standard samples of each component, whereas Fig. 15 is from 0.1 μg/L standard samples. Table 13 and 14 show analytical conditions.

Table 13 Analytical Conditions

Separation	
Column	: Shim-pack FC-ODS (75 mmL. × 4.6 mmI.D., 3 μm)
Mobile phase	: A→B gradient elution
	A : water
	B : 2-propanol
Flow rate	: 1.0 mL/min
Column temp.	: 50 °C
Detection	
Primary reaction	
Reagent	: 0.05 mol/L sodium hydroxide
Flow rate	: 0.5 mL/min
Reaction temp.	: 100 °C
Secondary reaction	
Reagent	: OPA solution
Flow rate	: 0.5 mL/min
Reaction temp.	: 50 °C
Detector	: Fluorescence detector, Ex. at 339 nm, Em. at 455 nm
Injection vol.	: 500 μL

Table 14 Gradient Program

B solution initial concentration 2 %

Time (min)	Item	Concentration (%)
6.00	B solution concentration	2
20.00	B solution concentration	15
32.00	B solution concentration	15
32.01	B solution concentration	2
44.00	End of analysis	

3-5 Attached Method 17-Iminoctadine Acetate Using Solvent Extraction-HPLC-Post-Column

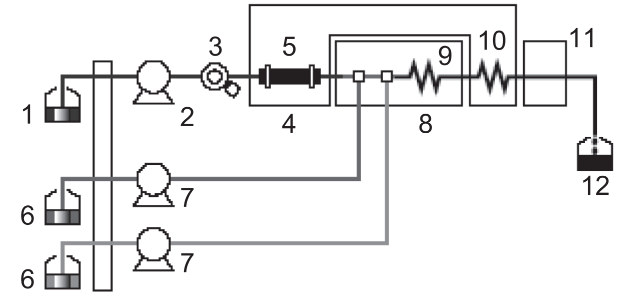
Of the agricultural chemicals specified as water quality control target setting items, Attached Methods 16 and 17 are specified for analyzing Iminoctadine acetate, using a solid-phase extraction-HPLC-post-column method and solvent extraction-HPLC-post-column method, respectively. This section introduces an analysis example of iminoctadine acetate using a Prominence iminoctadine acetate analysis system based on Attached Method 17.

Table 15 Analytical Conditions

Separation	
Column	: Shim-pack VP-ODS (150 mmL. × 4.6 mmI.D., 5 μm)
Mobile phase	: A/B = 17/5 (v/v)
	A : 1000 mL aqueous solution prepared to contain 14.1 g sodium perchlorate, 1.8 mL lactate, and 400 mg sodium hydroxide
	B : Acetonitrile
Flow rate	: 0.6 mL/min
Column temp.	: 50 °C
Detection	
Primary reaction	
Reagent	: 0.5 mmol/L sodium hydroxide
Flow rate	: 0.2 mL/min
Secondary reaction	
Reagent	: 3 g/L ninhydrin solution
Flow rate	: 0.1 mL/min
Reaction temp.	: 90 °C
Detector	: Fluorescence detector, Ex. at 395 nm, Em. at 500 nm
Cell temp.	: 20 °C

3-5-1 Analysis of Standard Sample

Table 15 shows analytical conditions and Fig. 16 shows a flow diagram of the Prominence iminoctadine acetate analysis system. The target value specified for iminoctadine triacetate is 0.006 mg/L, but Attached Method 17 requires pretreating test water by concentrating it by 200 times. Fig. 17 shows the results for injecting 20 μL of a 0.01 mg/L standard iminoctadine triacetate solution.



1 Mobile Phase
2 Mobile Phase Solvent Delivery Pump
3 Injector
4 Column Oven
5 Column
6 Reaction Reagent
7 Reaction Reagent Delivery Pump
8 Reactor
9 Reaction Coil
10 Cooling Coil
11 Fluorescence Detector
12 Waste

Fig. 16 Flow Diagram

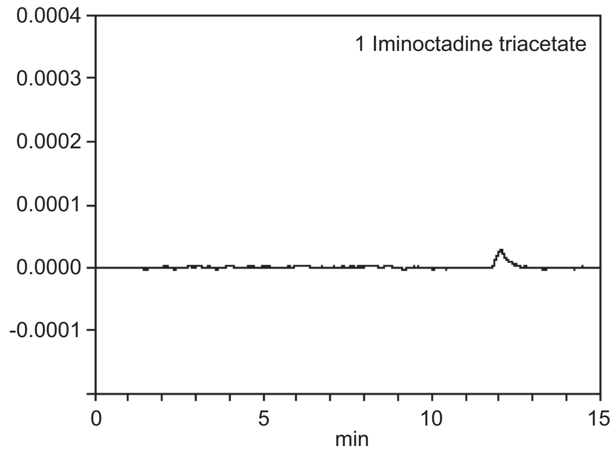


Fig. 17 Chromatogram of Iminoctadine Triacetate (0.01 mg/L)

3-5-2 Pretreatment

Fig. 18 shows a flow diagram of the test water pretreatment process. Iminoctadine triacetate tends to adhere to glass containers, so equipment and containers made of PTFE are used.

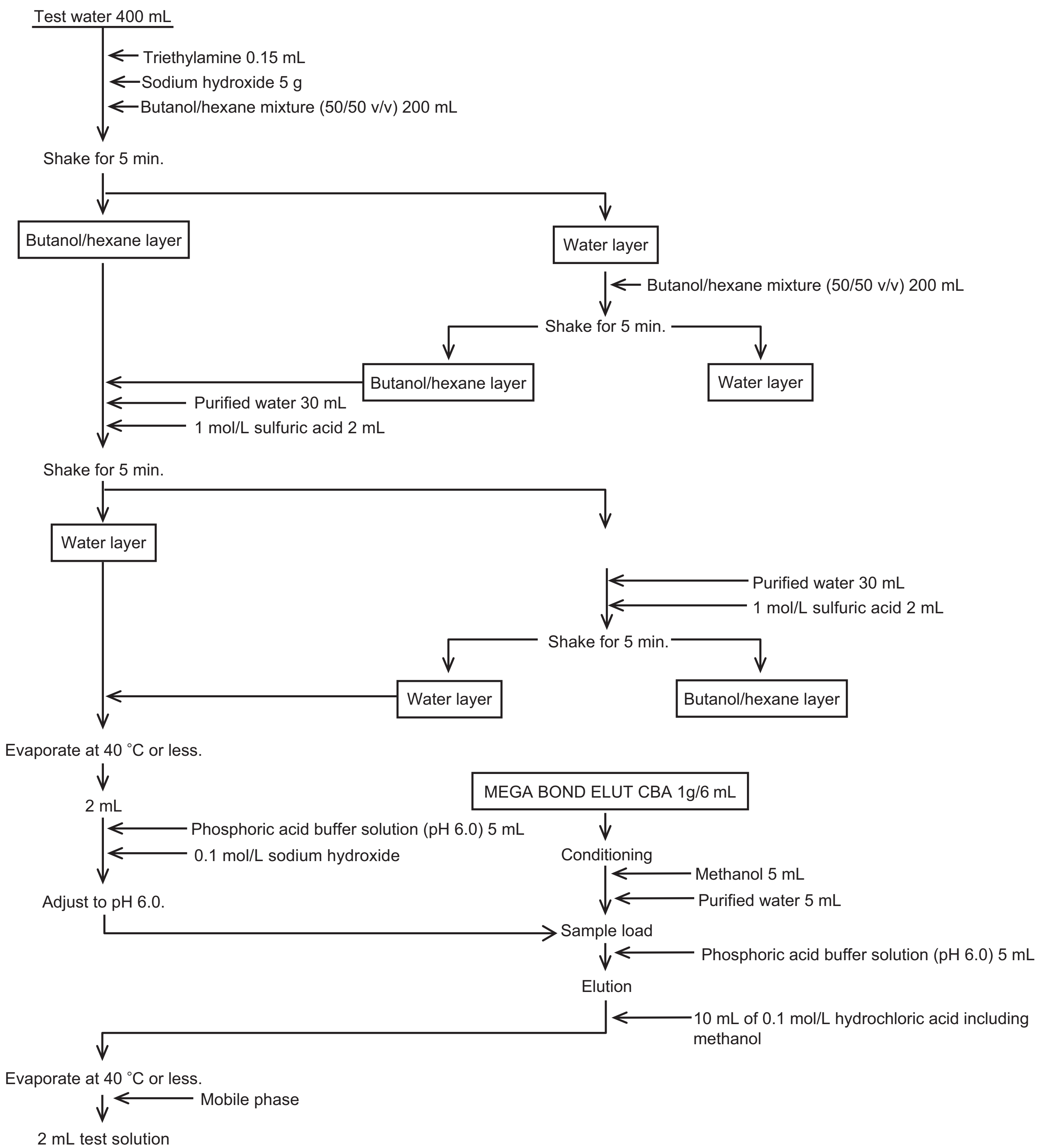


Fig. 18 Pretreatment

4. Liquid Chromatograph - Mass Spectrometer

4-1 Attached Method 18-Simultaneous Analysis Using Solid-Phase Extraction-Liquid Chromatograph-Mass Spectrometer

This section introduces an example of simultaneous analysis of 30 agricultural chemicals using LC/MS. 21 agricultural chemicals were detected using the positive mode and 9 using the negative mode.

Attached Method 18 specifies that benomyl is detected as methyl-2-benzimidazolecarbamate (MBC). Since oxine copper requires dissolving the standard reagent with hydrochloric acid and the hydrochloric acid can cause other agricultural chemicals to degrade, it cannot be mixed with other agricultural chemicals. It must be analyzed by itself. Another method for analyzing oxine copper, Attached Method 20, is described below. Table 16 shows the agricultural chemical numbers (number in the list of 102 agricultural chemicals), target values (mg/L), and the monitoring ions used during analysis for Attached Method 18.

Table 16 Monitoring Ions for 30 Agricultural Chemicals (using formic acid water as the mobile phase)

Mode	No.	Agricultural Chemical	Target Value (mg/L)	Monitoring Ions (*m/z*)
Positive	1	Thiuram	0.02	241
	18	Carbofuran (metabolite of carbosulfan)	0.005	222
	26	Iprodione	0.3	330
	36	Asulam	0.2	231
	48	Carbaryl (NAC)	0.05	202
	58	Carpropamid	0.04	334
	68	Diuron (DCMU)	0.02	233
	71	Fenthion (MPP) MPP sulfoxide MPP sulfone MPP oxon MPP oxon sulfoxide MPP oxon sulfone	0.001	279 295 311 263 279 295
	74	Methomyl	0.03	163
	75	Methyl-2-benzimidazolecarbamate (MBC)	0.02	192
	82	Probenazole	0.05	224
	86	Bensulfuron methyl	0.4	411
	87	Tricyclazole	0.08	190
	90	Azoxystrobin	0.5	404
	95	Flazasulfuron	0.03	408
	96	Thiodicarb	0.08	355
Negative	17	Bentazone	0.2	239
	19	2,4-dichlorophenoxyacetic acid (2,4-D)	0.03	219
	20	Tryclopyr	0.006	254
	42	Bensulide (SAP)	0.1	396
	45	Mecoprop (MCPP)	0.005	213
	84	Daimuron	0.8	313
	94	Halosulfuron methyl	0.3	433
	98	Siduron	0.3	277
	102	Fipronil	0.0005	437

Note: Verify monitoring ions by Scan analysis and specify the optimal *m/z* position for the instrument being used.

4-1-1 Preparing Reagents

The following describes the reagent preparation method. Prepare agricultural chemical stock solutions of thiuram, probenazole, and iprodione, just before use, to avoid degradation. Prepare diluted standard agricultural chemical mixture solutions before use as well. Standard agricultural chemical mixture solutions were diluted with 8/2 mixtures of water and acetonitrile. When diluted with water, adequate calibration curve linearity could not be obtained in some cases for thiuram and probenazole. HPLC grade acetonitrile and methanol reagents were used to prepare reagents.

□ Standard Agricultural Chemical Stock Solution

Place 100 mg each of bentazon, carbofuran (carbosulfan metabolite), 2,4-dichlorophenoxyacetic acid (2,4-D), trichlopyr, asulam, bensulide (SAP), mecoprop (MCPP), carbaryl (NAC), carpropamid, diuron (DCMU), fenthion (MPP), methomyl, daimuron, bensulfuronmethyl, tricyclazole, azoxystrobin, halosulfuron methyl, flazasulfuron, thiodicarb, siduron, fipronil, MPP sulfoxide, MPP sulfone, MPP oxon, MPP oxon sulfoxide, and MPP oxon sulfone in separate volumetric flasks and dissolve in acetonitrile to make 100 mL. Store these solutions in a freezer.
Prepare stock solutions of thiuram, probenazole, and iprodione in the same manner just before use.

□ MBC Standard Solutions

Place 10 mg of methyl-2-benzimidazolecarbamate (MBC) in a volumetric flask, and dissolve with methanol to make 100 mL. Store this solution in a freezer.

□ Standard Agricultural Chemical Mixture Solution (prepare by diluting just before use)

Place 100 µL each of agricultural chemical standard stock solutions for thiuram, bentazon, carbofuran (carbosulfan metabolite), 2,4-dichlorophenoxyacetic acid (2,4-D), trichlopyr, asulam, bensulide (SAP), mecoprop (MCPP), carbaryl (NAC), carpropamid, diuron (DCMU), fenthion (MPP), methomyl, daimuron, bensulfuron methyl, tricyclazole, azoxystrobin, halosulfuron methyl, flazasulfuron, thiodicarb, siduron, fipronil, MPP sulfoxide, MPP sulfone, MPP oxon, MPP oxon sulfoxide, and MPP oxon sulfone and 1 mL each of iprodione, probenazole, and MBC standard stock solutions in a volumetric flask, then add acetonitrile to make 10 mL. Prepare this solution just before use. 1 mL of this standard agricultural chemical mixture contains 10 µg of each agricultural chemical except iprodione and probenazole. It contains 100 µg of each iprodione and probenazole.

□ Preparing Calibration Curves (prepare by diluting just before use)

Add the standard agricultural chemical mixture to a volumetric flask in stages, adding 8/2 mixture of water and acetonitrile at each stage to make 10 mL. Prepare this solution just before use.

4-1-2 Pretreatment

Fig. 19 shows the pretreatment flow chart.

Test water 500 mL	Add 10 mL EDTA solution and adjust to pH 3.5 using nitric acid (1 + 10).
↓	
Solid-phase extraction	Pass water through a solid phase*, with performance equivalent to or better than divinylbenzene-methacrylate copolymer, at 10 to 20 mL/min.
↓	
Drying	Pass nitrogen gas.
↓	
Extraction	Pour 5 mL acetonitrile into test tube.
↓	
Concentration	Purge with nitrogen gas to concentrate to 0.2 mL or less.
↓	
Volume adjustment	Add purified water to adjust the volume to 1 mL.
↓	
LC/MS measurement	

* Condition in advance with 10 mL acetonitrile, 10 mL methanol, and 10 mL purified water. Backflushing methods may be more appropriate for some types of solid phases.

Fig. 19 Pretreatment Procedure

4-1-3 Analytical Conditions

Table 17 shows the LC/MS analytical conditions.

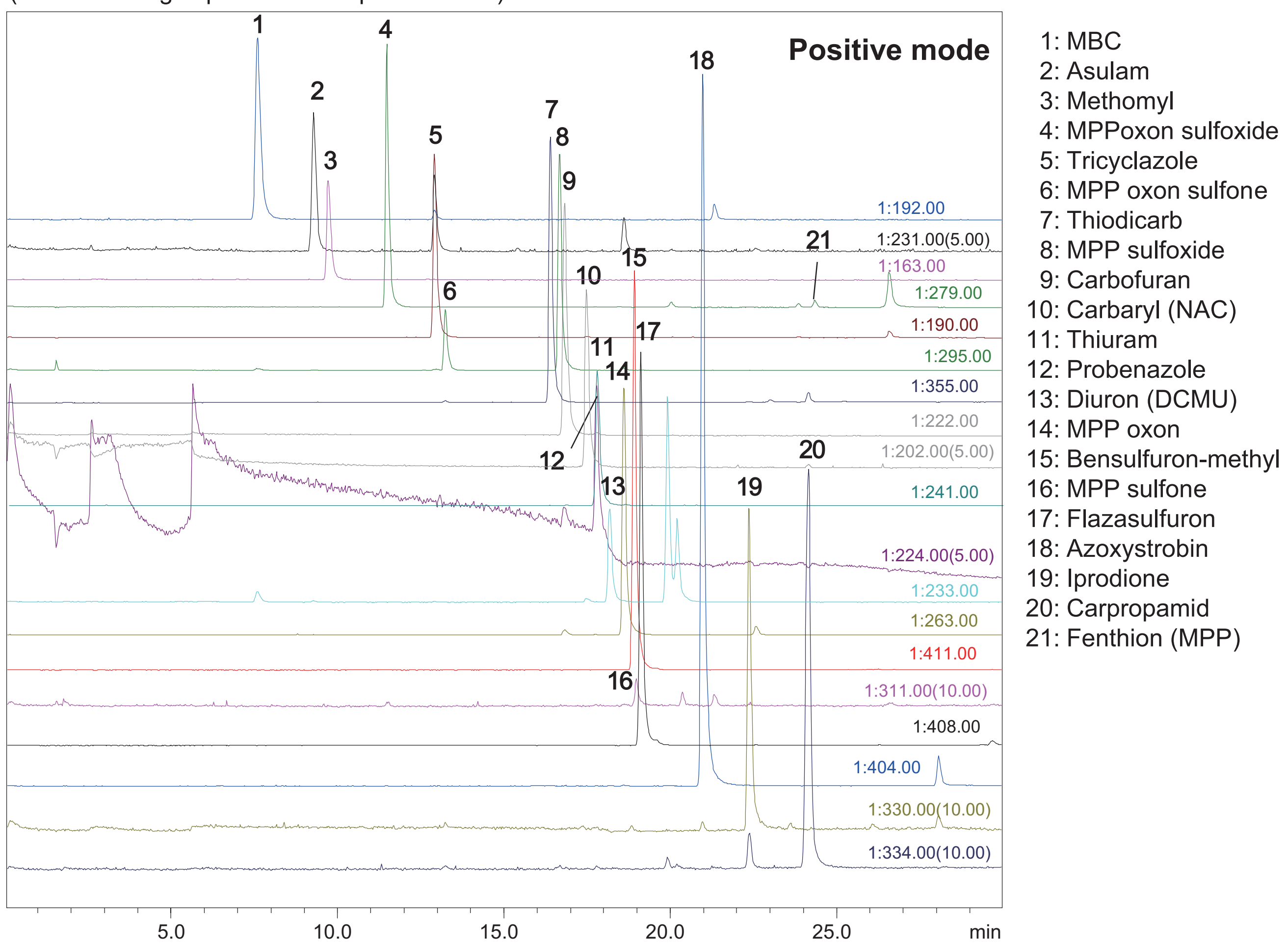
Table 17 Analytical Conditions

Column	: L-Column ODS (150 mmL. × 2.1 mmI.D., 5 µm)
Mobile phase A	: 0.1 % aqueous formic acid
Mobile phase B	: Acetonitrile
Time program	: B. Conc. 0 % (0 min) → 100 % (30 – 35 min) → 0 % (35.01 min) → STOP (45 min)
Flow rate	: 0.2 mL/min
Injection vol.	: 10 µL
Column temp.	: 40 °C
Probe voltage	: 4.5 kV/-3.5 kV (ESI-Positive mode/ESI-Negative mode)
Nebulizer gas Flow rate	: 1.5 L/min
Drying gas Flow rate	: 15 L/min
Dl temp.	: 250 °C
Heat block temp.	: 400 °C
Monitoring ions	: See Table 16.
Event time	: 0.5 sec (posi)/0.5 sec (nega)

4-1-4 Results

Fig. 20 shows the SIM chromatograms of the standard sample.

0.1 mg/L Standard Agricultural Chemical Mixture Sample
(contains 1 mg/L iprodione and probenazole)



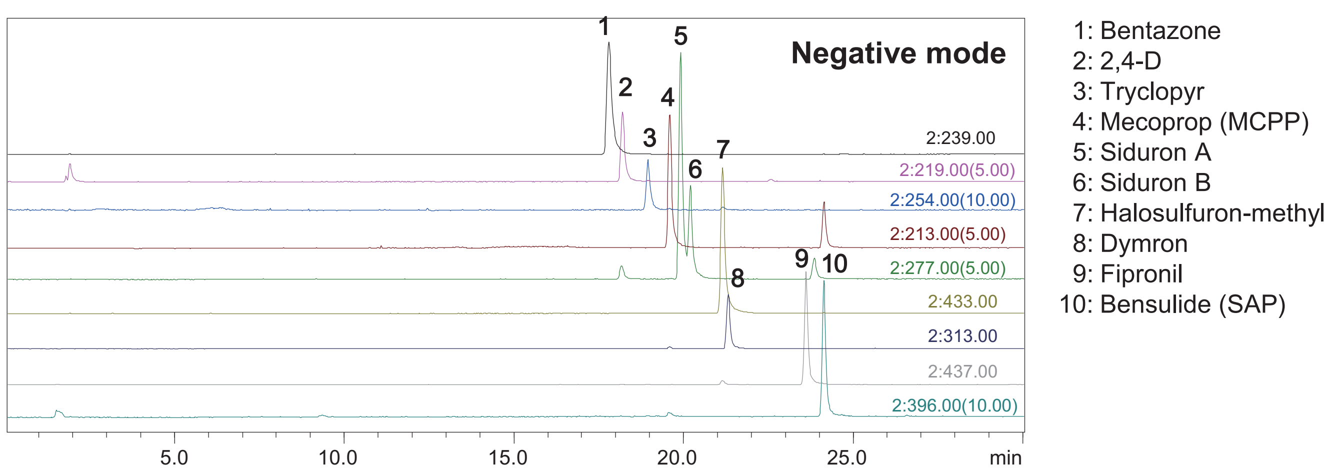
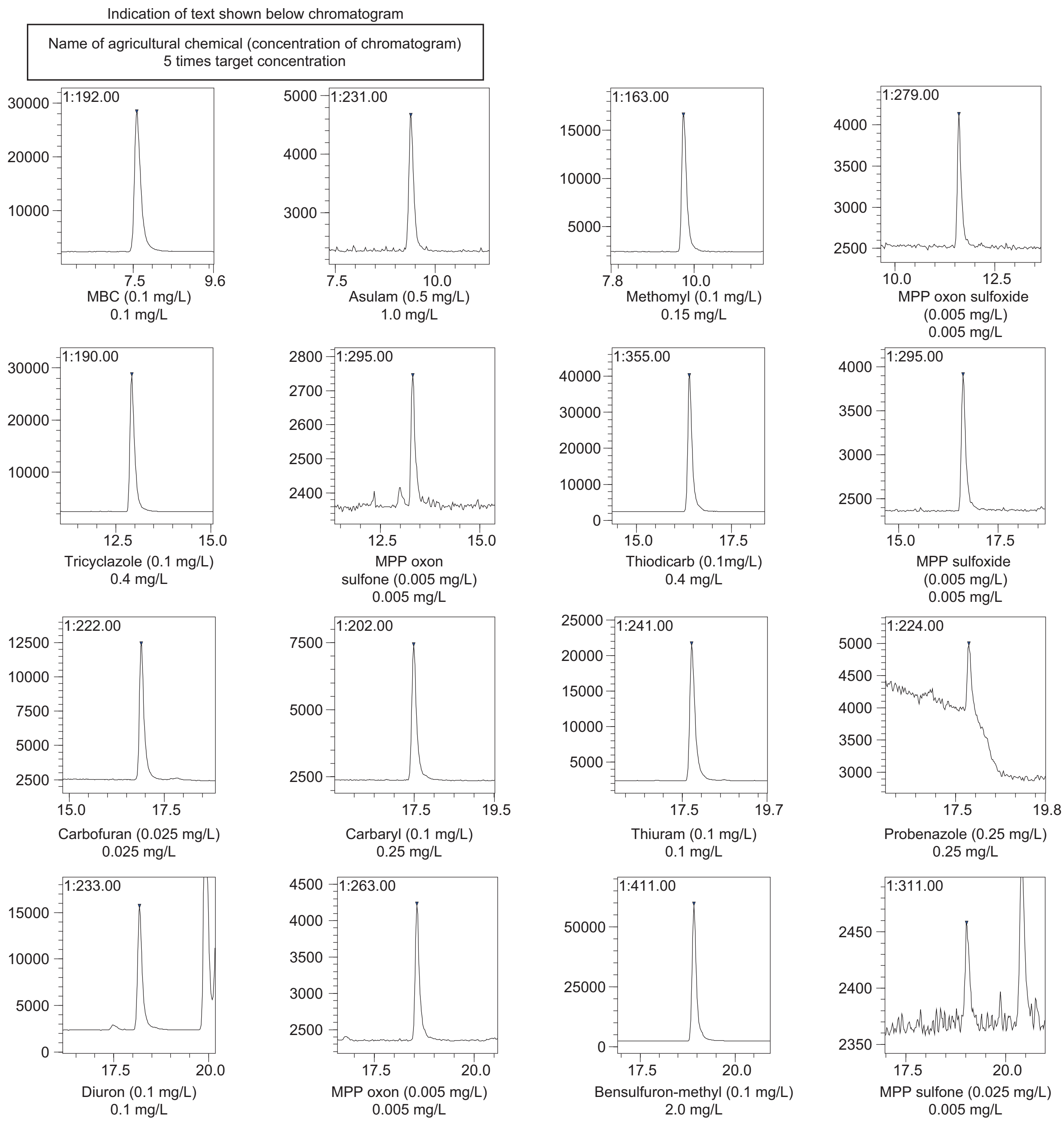
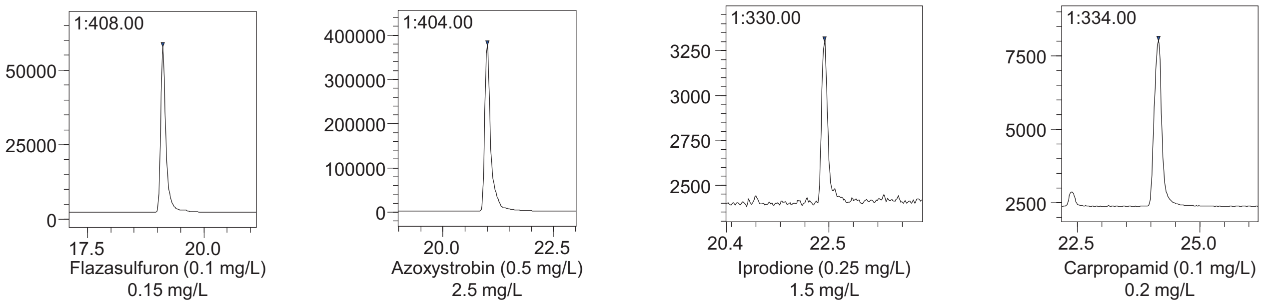


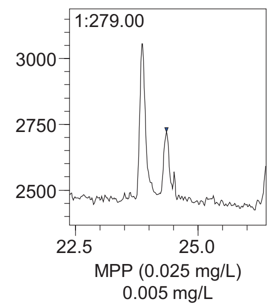
Fig. 20 SIM Chromatograms of 30 Agricultural Chemicals

Fig. 21 and 22 show SIM chromatograms of respective agricultural chemicals at about 5 times the target concentration. When analyzing actual samples, detection requires 1/100 the concentration of target values. Actual samples are concentrated by 500 times by pretreatment using a solid-phase column.

Therefore, to detect 1/100 concentration of the target values requires being able to detect 5 times the target value. Fig. 21 and 22 show that, except for MPP and MPP sulfone, there is more than adequate capacity to detect agricultural chemicals at those concentrations. Chromatograms for MPP and MPP sulfone are shown for a concentration of 0.025 mg/L.







The concentration of fenthion (MPP) is determined by measuring the concentration of each of its oxides, namely MPP sulfoxide, MPP sulfone, MPP oxon, MPP oxon sulfoxide, and MPP oxon sulfone, and calculating the concentration of MPP by summing the concentrations of each oxide.

Fig. 21 SIM Chromatograms (Positive Mode)

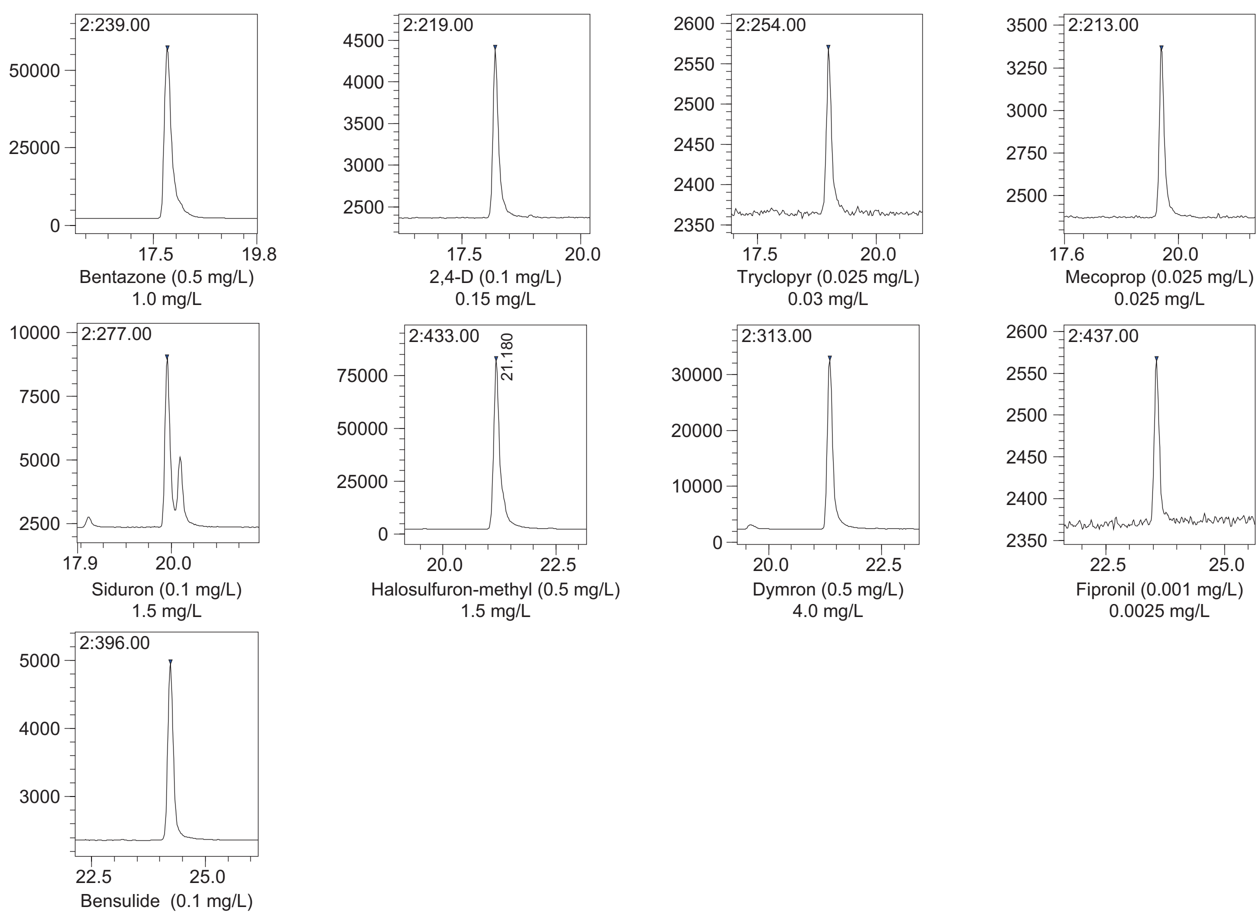


Fig. 22 SIM Chromatograms (Negative Mode)

Table 18 shows the repeatability obtained from six consecutive measurements of each agricultural chemical standard sample. CV values for all agricultural chemicals were within 20 %. Since probenazole and iprodione both degrade easily, a key point for the analysis is to finish their analysis within the same day they are prepared.

Table 18 Repeatability (n = 6)

No.	Agricultural Chemical	Mode	Monitoring Ion (*m/z*)	Concentration (mg/L)	Average Area Value	Standard Deviation	CV Value (%)
1	MBC	+	192	0.1	292262	4292.68	1.47
2	Asulam	+	231	0.5	148464	5640.39	3.80
3	Methomyl	+	163	0.1	131497	3382.78	2.57
4	MPP oxon sulfoxide	+	279	0.005	14488	453.88	3.13
5	Tricyclazole	+	190	0.1	270231	5287.00	1.96
6	MPP oxon sulfone	+	295	0.005	3406	169.07	4.96
7	Thiodicarb	+	355	0.1	348024	4135.78	1.19
8	MPP sulfoxide	+	295	0.005	13614	341.05	2.51
9	Carbofuran	+	222	0.025	84339	1001.40	1.19
10	Carbaryl (NAC)	+	202	0.1	41792	1276.55	3.05
11	Thiuram	+	241	0.1	198659	2659.50	1.34
12	Probenazole	+	224	0.25	15202	2012.53	13.24
13	Diuron (DCMU)	+	233	0.1	127135	1769.55	1.39
14	MPP oxon	+	263	0.005	15259	452.73	2.97
15	Bensulfuron-methyl	+	411	0.1	455223	6055.44	1.33
16	MPP sulfone	+	311	0.05	1868	72.57	3.89
17	Flazasulfuron	+	408	0.1	489809	10098.54	2.06
18	Azoxystrobin	+	404	0.5	3436307	171432.26	4.99
19	Iprodione	+	330	0.25	15590	883.59	5.67
20	Carpropamid	+	334	0.1	62868	714.98	1.14
21	MPP	+	279	0.025	2971	323.36	10.88
22	Bentazone	–	239	0.5	701871	6979.48	0.99
23	2,4-D	–	219	0.1	21003	312.60	1.49
24	Tryclopyr	–	254	0.025	1673	103.84	6.21
25	Mecoprop (MCPP)	–	213	0.025	9381	203.60	2.17
26	Siduron A	–	277	0.1	54414	2214.23	4.07
27	Siduron B	–	277	0.1	26175	951.31	3.63
28	Halosulfuron-methyl	–	433	0.5	921502	87936.10	9.54
29	Dymron	–	313	0.5	441545	2773.54	0.63
30	Fipronil	–	437	0.001	1541	125.49	8.15
31	Bensulide (SAP)	–	396	0.1	24408	624.44	2.56

4-2 Attached Method 20-Simultaneous Analysis Using Liquid Chromatograph-Mass Spectrometer

This section introduces an example of simultaneous analysis of acephate, oxine copper, dalapon, and fosetyl. Acephate and oxine copper were detected using the positive mode and dalapon and fosetyl using the negative mode. Actual samples are filtered through a membrane filter and analyzed directly using the LC/MS system without concentrating. Table 19 shows their corresponding agricultural chemical number, target values (mg/L), and monitoring ions (*m/z*).

Table 19 Monitoring Ions for 4 Agricultural Chemicals (when using formic acid as the mobile phase)

Mode	No.	Agricultural Chemical	Target Value (mg/L)	Monitoring Ion (*m/z*)
Positive	21	Acephate	0.08	184
	28	Oxine copper	0.04	146
Negative	64	Dalapon	0.08	141
	92	Fosetyl	2	109

Note: Verify monitoring ions by Scan analysis and specify the optimal *m/z* position for the instrument being used.

4-2-1 Preparing Reagents

The following describes the reagent preparation method.

☐ Standard Acephate Stock Solution

Dissolve 100 mg acephate in acetonitrile to make 100 mL. 1 mL of this solution contains 1 mg of acephate. Store this solution in a freezer.

☐ Standard Oxine Copper Stock Solution

Place 100 mg oxine copper in a volumetric flask and dissolve it with a small amount of hydrochloric acid, then add acetonitrile to make 100 mL. 1 mL of this solution contains 1 mg of oxine copper. Store this solution in a freezer.

☐ Standard Dalapon Stock Solution

Place100 mg dalapon in a volumetric flask and dissolve it with purified water to make 100 mL. 1 mL of this solution contains 1 mg of dalapon. Store this solution in a refrigerator.

☐ Standard Fosetyl Stock Solution

Place100 mg of fosetyl in a volumetric flask and dissolve it with purified water to make 100 mL. 1 mL of this solution contains 1 mg of fosetyl. Store this solution in a refrigerator.

☐ Standard Agricultural Chemical Mixture Solution (prepare just before use)

Place 0.08 mL acephate, 0.04 mL oxine copper, 0.1 mL dalapon, and 2 mL fosetyl in a volumetric flask and add purified water to make 10 mL. Prepare this solution just before use.

☐ Preparing Calibration Curves (prepare just before use)

Add the standard agricultural chemical mixture solution to a volumetric flask in stages, adding some purified water at each stage to make 10 mL. Prepare this solution just before use.

4-2-2 Pretreatment

Filter 100 mL of test water through a membrane filtering system. Discard the first 10 mL of the filtered water.

4-2-3 Analytical Conditions

Table 20 shows the LC/MS analytical conditions.

Table 20 Analytical Conditions

Column	: L-Column ODS (150 mmL. × 2.1 mmI.D., 5 µm)
Mobile phase A	: 0.1 % aqueous formic acid
Mobile phase B	: Acetonitrile
Time program	: B. Conc. 0 % (0 min) → 35 % (15 min) → 0 % (15.01 min) → STOP (25 min)
Flowrate	: 0.2 mL/min
Injection vol.	: 50 µL
Column temp.	: 40 °C
Probe voltage	: 4.5 kV/-3.5 kV (ESI-Positive mode/ ESI-Negative mode)
Nebulizer gas Flow rate	: 1.5 L/min
Drying gas Flow rate	: 20 L/min
DI temp.	: 250 °C
Heat block temp.	: 400 °C
Monitoring ions	: See Table 19.
Event time	: 0.5 sec (posi)/0.5 sec (nega)

4-2-4 Results

Fig. 23 shows SIM chromatograms of respective agricultural chemicals at about 1/100 the target concentration. Since Attached Method 20 does not include a concentrating step, the components must be detected at 1/100 the concentration of the target value. Table 21 shows the repeatability obtained from six consecutive measurements of each agricultural chemical standard sample.

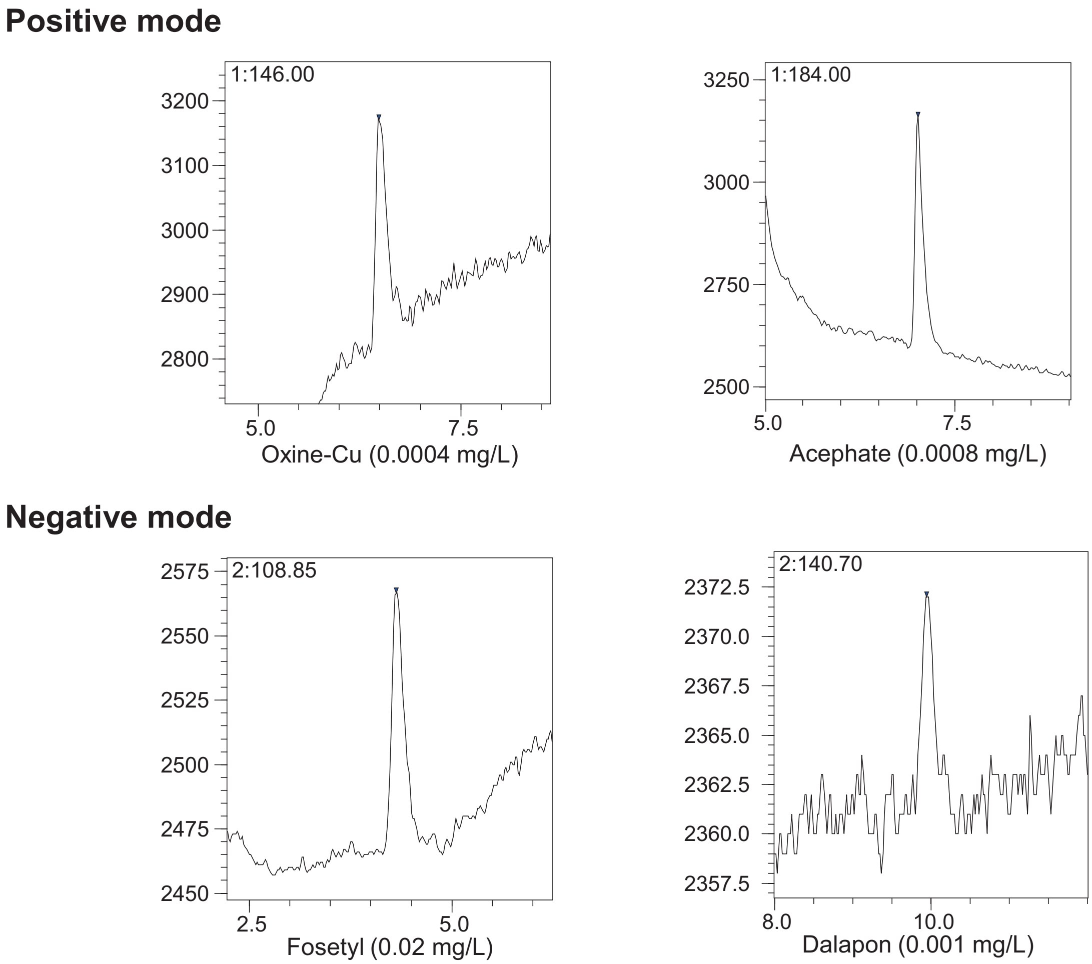


Fig. 23 SIM Chromatograms of Agricultural Chemicals

Table 21 Repeatability (n = 6)

No.	Agricultural Chemical	Mode	Monitoring Ion (*m/z*)	Average Retention Time (min)	Concentration (mg/L)	Average Area Value	Standard Deviation	CV Value (%)
1	Fosetyl	–	108.85	4.317	0.02	1185	106.05	8.95
2	Oxine-Cu	+	146.00	6.490	0.0004	3391	302.78	8.93
3	Acephate	+	184.00	6.987	0.0008	4271	206.27	4.83
4	Dalapon	–	140.70	9.940	0.001	132	24.71	18.79

5. Summary

The ability for safe use of drinking water depends on the water quality tests that are required to be conducted by companies that supply water. The water quality standards established by the Water Supply Act dates back to 1958. Since then, it has gone through several revisions, the most comprehensive of which was in 2003. This revision served to greatly strengthen water quality control for drinking water. Since 2003, revisions have been conducted when necessary.
Inspection items include items that relate to health and the water-related characteristics of drinking water. Also, inspection target items are wide-ranging, and include bacteria, organic and inorganic materials, and metals.
In addition, they require that the proportional agricultural chemical levels detected for all agricultural chemicals mentioned in this Application Note, expressed in terms of a ratio of their respective target values, must not add up to more than 1. Rather than regulating individual agricultural chemical levels, this aggregate agricultural chemical method is arguably a more realistic approach. However, it requires the analytical instruments used be capable of detecting trace agricultural chemical levels at high sensitivity.
As a manufacturer of integrated analytical instruments, we offer a range of measuring instruments for water quality control for laboratories to conduct water quality tests.
Furthermore, our instruments offer plenty of performance to enable measuring agricultural chemicals with high sensitivity.
This Application Note was issued as a follow-up to our previously published Application Note entitled "Data on Drinking Water Quality Standards" to provide a summary update of the latest measurement results, and their corresponding analytical conditions, from testing drinking water for agricultural chemicals using Shimadzu analytical instruments.
Our efforts would be rewarded if the information offered in this Application Note proves useful and interesting to those involved in water quality testing, and to people with an interest in testing the quality of drinking water.

November, 2010
From everyone in the Environmental Project

*This document is based on information valid at the time of publication. It may be changed without notice.

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