

## 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<br>Hydride generation-ICP-AES<br>ICP-MS                                                                                                                                                                                                                                       | 10 %<br>10 %<br>10 %                              |
| 2   | Uranium and its compounds                                     | 0.002 mg/L or less uranium (provisional)                               | ICP-MS<br>Solid-phase extraction-ICP-AES                                                                                                                                                                                                                                                                           | 10 %<br>10 %                                      |
| 3   | Nickel and its compounds                                      | 0.01 mg/L or less nickel (provisional)                                 | Flameless atomic absorption<br>ICP-AES<br>ICP-MS                                                                                                                                                                                                                                                                   | 10 %<br>10 %<br>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<br>HS-GC/MS                                                                                                                                                                                                                                                                                               | 20 %<br>20 %                                      |
| 6   | Deleted                                                       | Deleted                                                                | Deleted                                                                                                                                                                                                                                                                                                            | Deleted                                           |
| 7   | Deleted                                                       | Deleted                                                                | Deleted                                                                                                                                                                                                                                                                                                            | Deleted                                           |
| 8   | Toluene                                                       | 0.2 mg/L max.                                                          | PT-GC/MS<br>HS-GC/MS                                                                                                                                                                                                                                                                                               | 20 %<br>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<br>Ion chromatography-post-column absorption photometry                                                                                                                                                                                                                                         | 10 %<br>10 %                                      |
| 11  | Deleted                                                       | Deleted                                                                | Deleted                                                                                                                                                                                                                                                                                                            | Deleted                                           |
| 12  | Chlorine dioxide                                              | 0.6 mg/L max.                                                          | Ion chromatography<br>Ion chromatography-post-column absorption photometry                                                                                                                                                                                                                                         | 10 %<br>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<br>Electrical current<br>Absorption photometry<br>Absorption photometry by continuous automated measurement device<br>Polarography                                                                                                                                        | 10 %<br>10 %<br>10 %<br>10 %<br>10 %              |
| 17  | Calcium, magnesium, etc. (hardness)                           | 10 mg/L max.<br>100 mg/L max.                                          | Flame atomic absorption<br>ICP-AES<br>ICP-MS<br>Ion chromatography<br>Titration method                                                                                                                                                                                                                             | 10 %<br>10 %<br>10 %<br>10 %<br>10 %              |
| 18  | Manganese and its compounds                                   | 0.01 mg/L or less manganese (provisional)                              | Flameless atomic absorption<br>ICP-AES<br>ICP-MS                                                                                                                                                                                                                                                                   | 10 %<br>10 %<br>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<br>HS-GC/MS                                                                                                                                                                                                                                                                                               | 20 %<br>20 %                                      |
| 21  | Methyl t-butyl ether                                          | 0.02 mg/L max.                                                         | PT-GC/MS<br>HS-GC/MS                                                                                                                                                                                                                                                                                               | 20 %<br>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.<br>200 mg/L max.                                          | Weight measurement                                                                                                                                                                                                                                                                                                 | —                                                 |
| 25  | Turbidity                                                     | 1 degree max.                                                          | Turbidimetric method<br>Transmittance photometry<br>Transmittance photometry by continuous automated spectrophotometer<br>Integrating sphere photometry<br>Integrating sphere photometry by continuous automated measurement device<br>Scattered light measurement<br>Transmission and scattered light measurement | —<br>10 %<br>10 %<br>10 %<br>10 %<br>10 %<br>10 % |
| 26  | pH value                                                      | About 7.5                                                              | Glass electrode method<br>Glass electrode method by continuous automated measurement device                                                                                                                                                                                                                        | —<br>—                                            |
| 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<br>HS-GC/MS                                                                                                                                                                                                                                                                                               | 20 %<br>20 %                                      |
| 30  | Aluminum and its compounds                                    | 0.1 mg/L or less aluminum                                              | Flameless atomic absorption<br>ICP-AES<br>ICP-MS                                                                                                                                                                                                                                                                   | 10 %<br>10 %<br>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<br>HS-GC/MS                                                                                                | 0.0001<br>0.0001               | 20 %<br>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):<br>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<br>Solid-phase extraction-LC/MS (P)<br>Solid-phase extraction-LC/MS (N) | 0.00001<br>0.00005<br>0.000002 | 20 %<br>20 %<br>20 %     |
| 18  | Carbofuran (metabolite of<br>carbosulfan)   | 0.005               | HPLC-post-column<br>Solid-phase extraction-LC/MS (P)                                                                | 0.00005<br>0.000005            | 20 %<br>20 %             |
| 19  | 2,4-dichlorophenoxyacetic acid (2,4-D)      | 0.03                | Solid-phase extraction-derivatization-GC/MS<br>Solid-phase extraction-LC/MS (N)                                     | 0.00001<br>0.00005             | 20 %<br>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<br>Solid-phase extraction-LC/MS (N)                     | 0.00001<br>0.00002          | 20 %<br>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<br>Solid-phase extraction-HPLC<br>Solid-phase extraction-LC/MS (P)     | 0.00002<br>0.001<br>0.0001  | 20 %<br>20 %<br>20 %     |
| 27  | Etridiazole (Echloomezole)            | 0.004               | Solid-phase extraction-GC/MS                                                                        | 0.00001                     | 20 %                     |
| 28  | Oxine copper                          | 0.04                | Solid-phase extraction-LC/MS (P)<br>LC/MS (P)                                                       | 0.00005<br>0.0004           | 20 %<br>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<br>Solid-phase extraction-LC/MS (P)<br>Solid-phase extraction-LC/MS (N) | 0.001<br>0.0001<br>0.0005   | 20 %<br>20 %<br>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)<br>Solid-phase extraction-LC/MS (N)                                | 0.00001<br>0.00001          | 20 %<br>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 (MCP)                        | 0.005               | Solid-phase extraction-derivatization-GC/MS<br>Solid-phase extraction-LC/MS (N)                     | 0.00005<br>0.00002          | 20 %<br>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<br>HPLC-post column<br>Solid-phase extraction-LC/MS (P)                 | 0.0005<br>0.0001<br>0.00002 | 20 %<br>20 %<br>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  | Isoprocab (MIPC)                      | 0.01                | Solid-phase extraction-GC/MS                                                                        | 0.00005                     | 20 %                     |
| 55  | Thiophanate-methyl                    | 0.3                 | Solid-phase extraction-HPLC<br>Solid-phase extraction-LC/MS (P)                                     | 0.002<br>0.00005            | 20 %<br>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)<br>Solid-phase extraction-LC/MS (N)                                | 0.00002<br>0.00005          | 20 %<br>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)<br>Solid-phase extraction-LC/MS (N)                                | 0.0001<br>0.0001            | 20 %<br>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<br>Solid-phase extraction-LC/MS (P)                                    | 0.00001<br>0.00002          | 20 %<br>20 %             |
| 72  | Glyphosate                       | 2                   | Derivatization-HPLC<br>HPLC-post-column                                                             | 0.0005<br>0.002             | 20 %<br>20 %             |
| 73  | Malathion (Malathion)            | 0.05                | Solid-phase extraction-GC/MS                                                                        | 0.00005                     | 20 %                     |
| 74  | Methomyl                         | 0.03                | HPLC-post-column<br>Solid-phase extraction-LC/MS (P)                                                | 0.0001<br>0.00002           | 20 %<br>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)<br>Solid-phase extraction-LC/MS (N)                                | 0.00005<br>0.00005          | 20 %<br>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)<br>Solid-phase extraction-LC/MS (N)                                | 0.00001<br>0.00001          | 20 %<br>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<br>Solvent extraction-HPLC-post-column                      | 0.005<br>0.005              | 20 %<br>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)<br>Solid-phase extraction-LC/MS (N)                                | 0.00005<br>0.00005          | 20 %<br>20 %             |
| 95  | Flazasulfuron                    | 0.03                | Solid-phase extraction-LC/MS (P)<br>Solid-phase extraction-LC/MS (N)                                | 0.000002<br>0.000002        | 20 %<br>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<br>Solid-phase extraction-LC/MS (P)<br>Solid-phase extraction-LC/MS (N) | 0.002<br>0.00002<br>0.00002 | 20 %<br>20 %<br>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<br>Attached Method 6                                                                    | Simultaneous analysis of multiple agricultural chemical components<br>Bentazon etc.  | Gas chromatograph-mass spectrometer                     | Simultaneous analysis using solid-phase extraction-GC/MS<br>Simultaneous analysis using solid-phase extraction-derivatization GC/MS                                                                    | 8        |
| Attached Method 9<br>Attached Method 11<br>Attached Method 12<br>Attached Method 14<br>Attached Method 17 | Iprodione, etc.<br>Diquat<br>Glyphosate<br>Carbofuran, etc.<br>Iminoctadine acetate  | High-performance liquid chromatograph                   | Simultaneous analysis using solid-phase extraction-HPLC<br>Solid-phase extraction-HPLC<br>Derivatization-HPLC<br>Simultaneous analysis using HPLC-post-column<br>Solvent extraction - HPLC-post-column | 24       |
| Attached Method 18<br>Attached Method 20                                                                  | Simultaneous analysis of multiple agricultural chemical components<br>Acephate, etc. | High-performance liquid chromatograph-mass spectrometer | Simultaneous analysis using solid-phase extraction-LC/MS<br>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 ( <i>m/z</i> ) | No. | Agricultural Chemical                       | Target Value (mg/L) | Monitoring Ions ( <i>m/z</i> ) |
|-----|-----------------------------------|---------------------|--------------------------------|-----|---------------------------------------------|---------------------|--------------------------------|
| 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<br>Isoxathion oxon     | 0.008               | 177,105<br>105,161             | 27  | Etridiazole                                 | 0.004               | 213,211                        |
| 6   | Diazinon<br>Diazinon oxon         | 0.005               | 304,179<br>273,137             | 29  | Captan                                      | 0.3                 | 79,114,149                     |
| 7   | Fenitrothion<br>Fenitrothion oxon | 0.003               | 277,260<br>244,261             | 30  | Chloroneb                                   | 0.05                | 191,193                        |
| 8   | Isoprothiolane                    | 0.3                 | 189,118                        | 31  | Tolclophos-methyl<br>Tolclophos-methyl oxon | 0.2                 | 265,125<br>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<br>EPN oxon                   | 0.004               | 157,169<br>141,306             | 40  | Pyributicarb                                | 0.02                | 165,108                        |
| 22  | Isofenphos<br>Isofenphos oxon     | 0.001               | 213,185<br>229,201             | 41  | Butamifos<br>Butamifos oxon                 | 0.01                | 286,200<br>244,216             |
| 23  | Chlorpyrifos<br>Chlorpyrifos oxon | 0.003               | 314,197<br>270,298             | 43  | Benfluralin                                 | 0.08                | 292,276                        |



| No. | Agricultural Chemical | Target Value (mg/L) | Monitoring Ions (m/z)               | No. | Agricultural Chemical | Target Value (mg/L) | Monitoring Ions (m/z) |
|-----|-----------------------|---------------------|-------------------------------------|-----|-----------------------|---------------------|-----------------------|
| 44  | Pendimethalin         | 0.1                 | 252,191                             | 71  | Fenthion (MPP)        | 0.001               | 278,153               |
| 46  | Methyl daimuron       | 0.03                | 107,119                             |     | MPP sulfoxide         |                     | 278,125               |
| 47  | Alachlor              | 0.01                | 188,160                             |     | MPP sulfone           |                     | 310,231               |
| 49  | Edifenphos            | 0.006               | 310,109                             |     | MPP oxon              |                     | 262,247               |
| 50  | Pyroquilon            | 0.04                | 130,144,173                         |     | MPP oxon sulfoxide    |                     | 262,247               |
| 51  | Fthalide              | 0.1                 | 243,241                             |     | MPP oxon sulfone      |                     | 294,215               |
| 52  | Mefenacet             | 0.02                | 192,120                             | 73  | Malathion             | 0.05                | 173,93                |
| 53  | Pretilachlor          | 0.04                | 238,262                             |     | Malaoxon              |                     | 99,127                |
| 54  | Isoprocarb            | 0.01                | 136,121                             | 77  | Simetryne             | 0.03                | 213,170               |
| 56  | Thenylchlor           | 0.2                 | 127,288                             | 78  | Dimepiperate          | 0.003               | 145,119               |
| 57  | Methidathion          | 0.004               | 145,85                              | 79  | Phenthoate            | 0.004               | 274,125               |
| 59  | Bromobutide           | 0.1                 | 120,119                             | 80  | Buprofezin            | 0.02                | 105,175               |
| 60  | Molinate              | 0.005               | 126,98                              | 81  | Ethylthiomethone      | 0.004               | 89,97                 |
| 61  | Procymidone           | 0.09                | 283,96                              | 83  | Esprocarb             | 0.03                | 222,91                |
| 62  | Anilofos              | 0.003               | 226,125                             | 85  | Bifenox               | 0.2                 | 310,343               |
| 63  | Atrazine              | 0.01                | 215,200                             | 88  | Piperophos            | 0.0009              | 122,140               |
| 65  | Dichlobenil           | 0.01                | 171,173                             | 89  | Dimethametryn         | 0.02                | 212,255               |
| 66  | Dimethoate            | 0.05                | 87,125                              | 97  | Propiconazole         | 0.05                | 259,261               |
| 69  | Endosulfan            | 0.01                | $\alpha$ 241,195<br>$\beta$ 195,241 | 99  | Pyriproxyfen          | 0.3                 | 136,226               |
|     | Endosulphate          |                     |                                     | 100 | Trifluralin           | 0.06                | 306,290               |
| 70  | Etofenprox            | 0.08                | 163,135                             | 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.

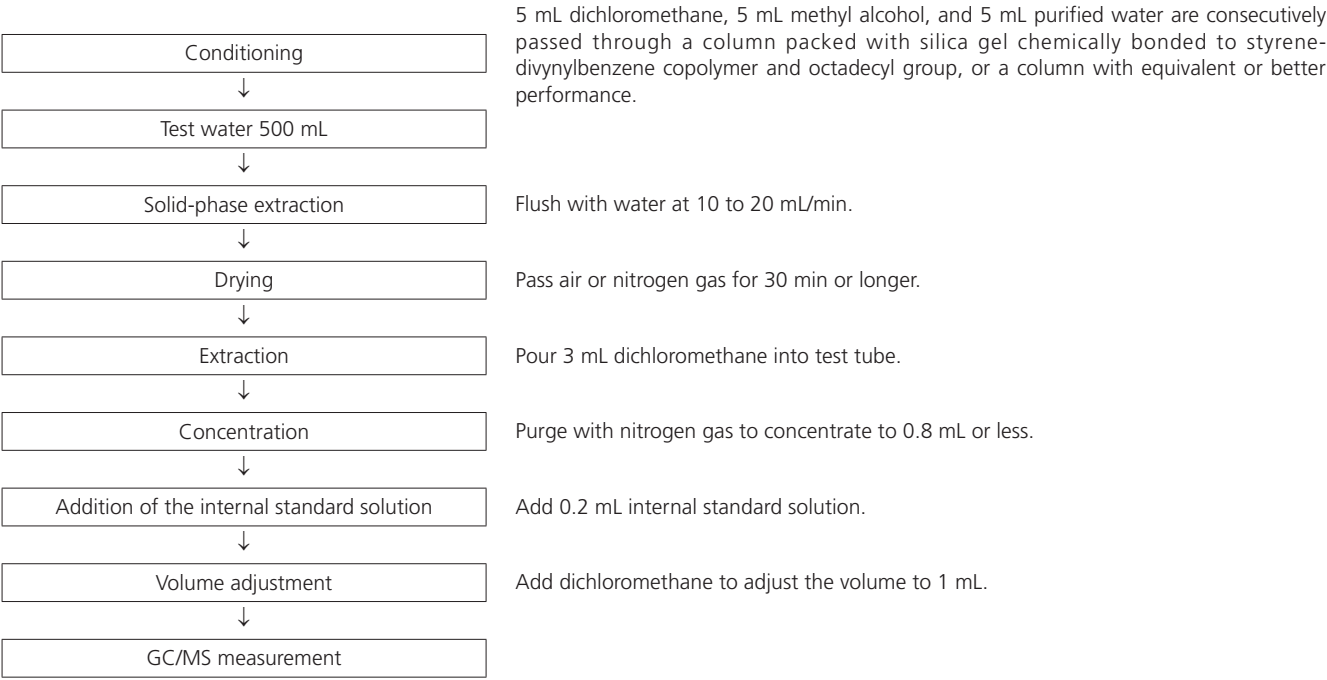


Fig. 1 Pretreatment Procedure

2-1-2 Analytical Conditions

Table 5 shows the GC/MS analytical conditions.

Table 5 Analytical Conditions

|                                  |                                                                   |
|----------------------------------|-------------------------------------------------------------------|
| Column                           | : Rtx-5MS (30 mL. × 0.25 mml.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.

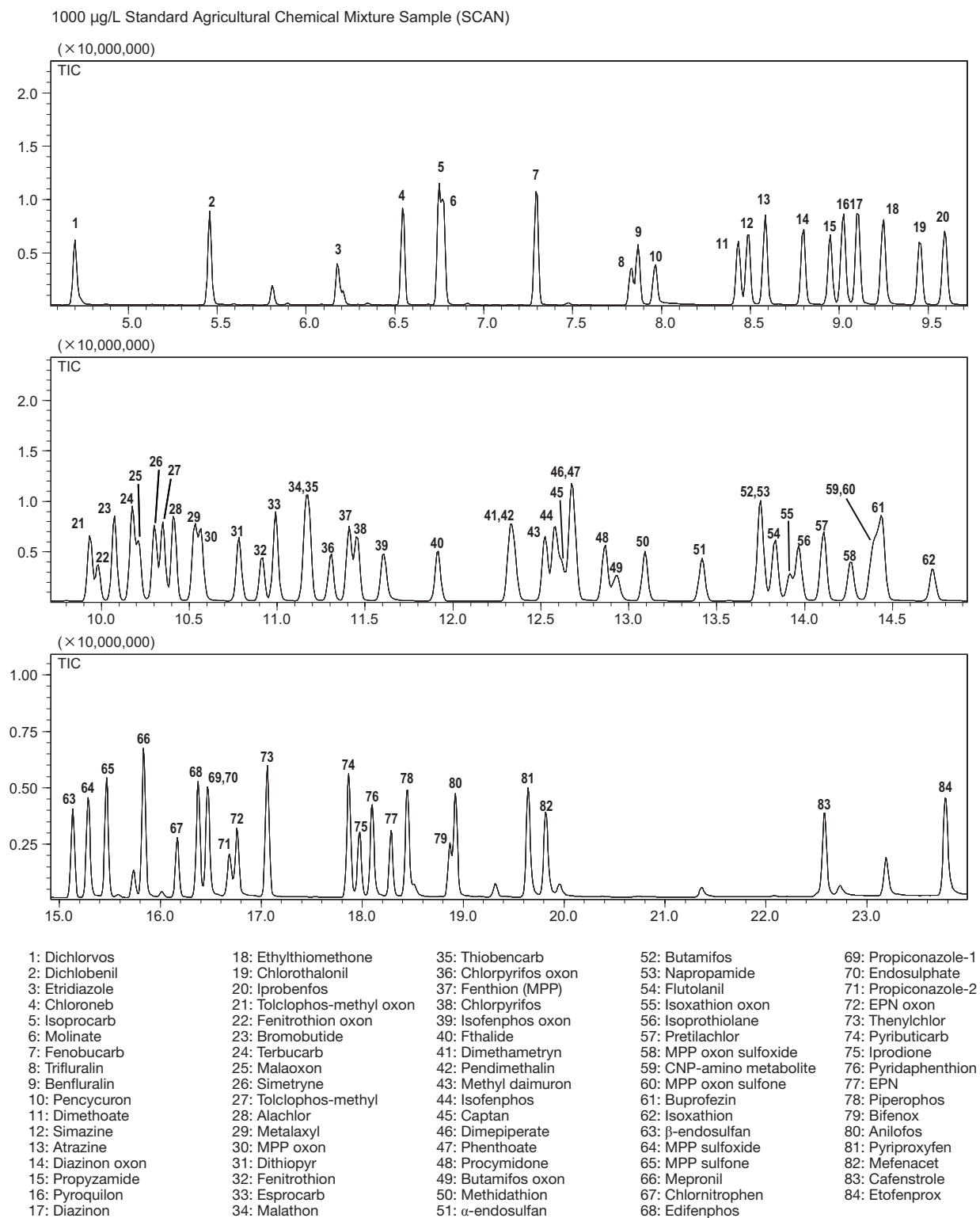
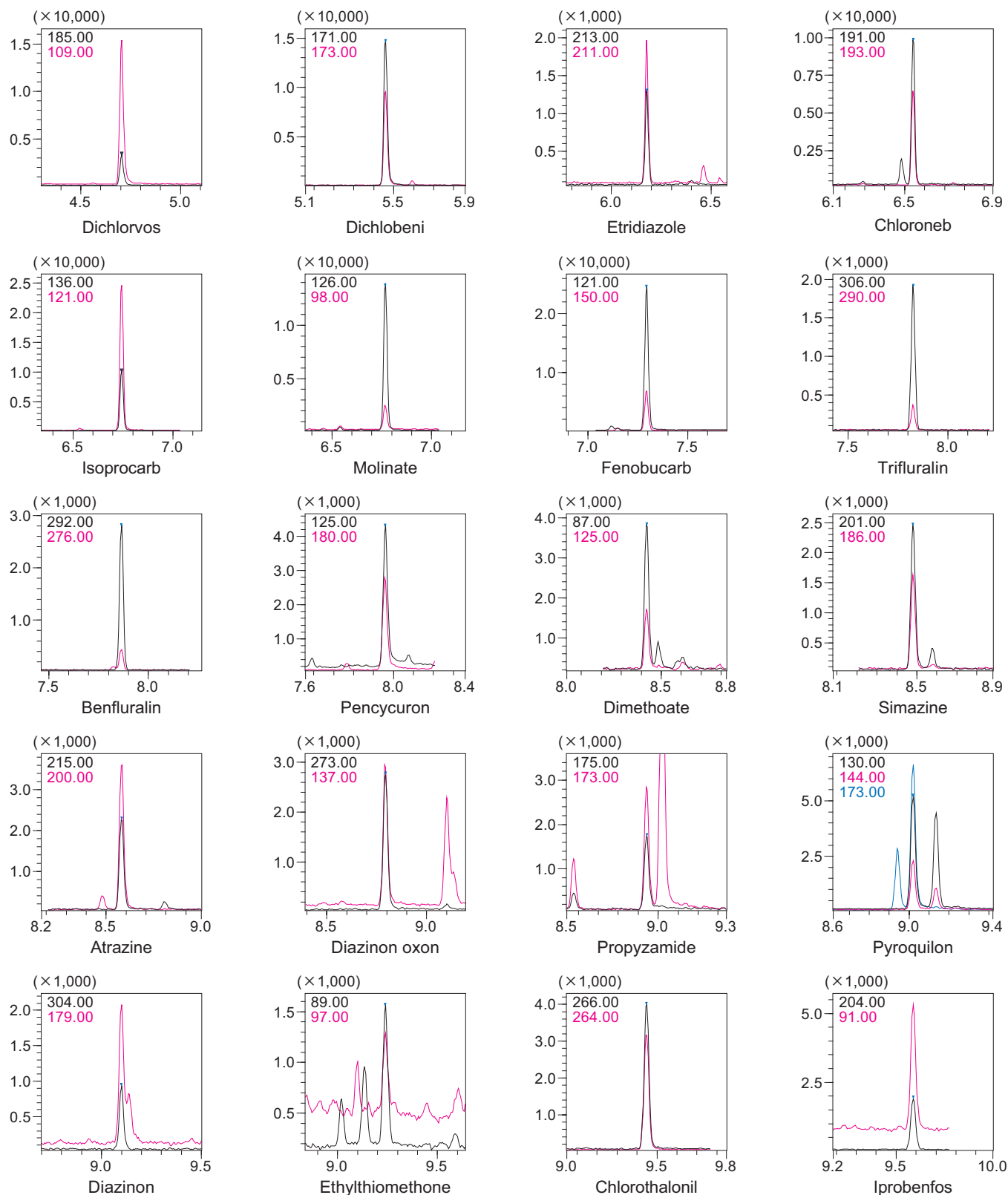
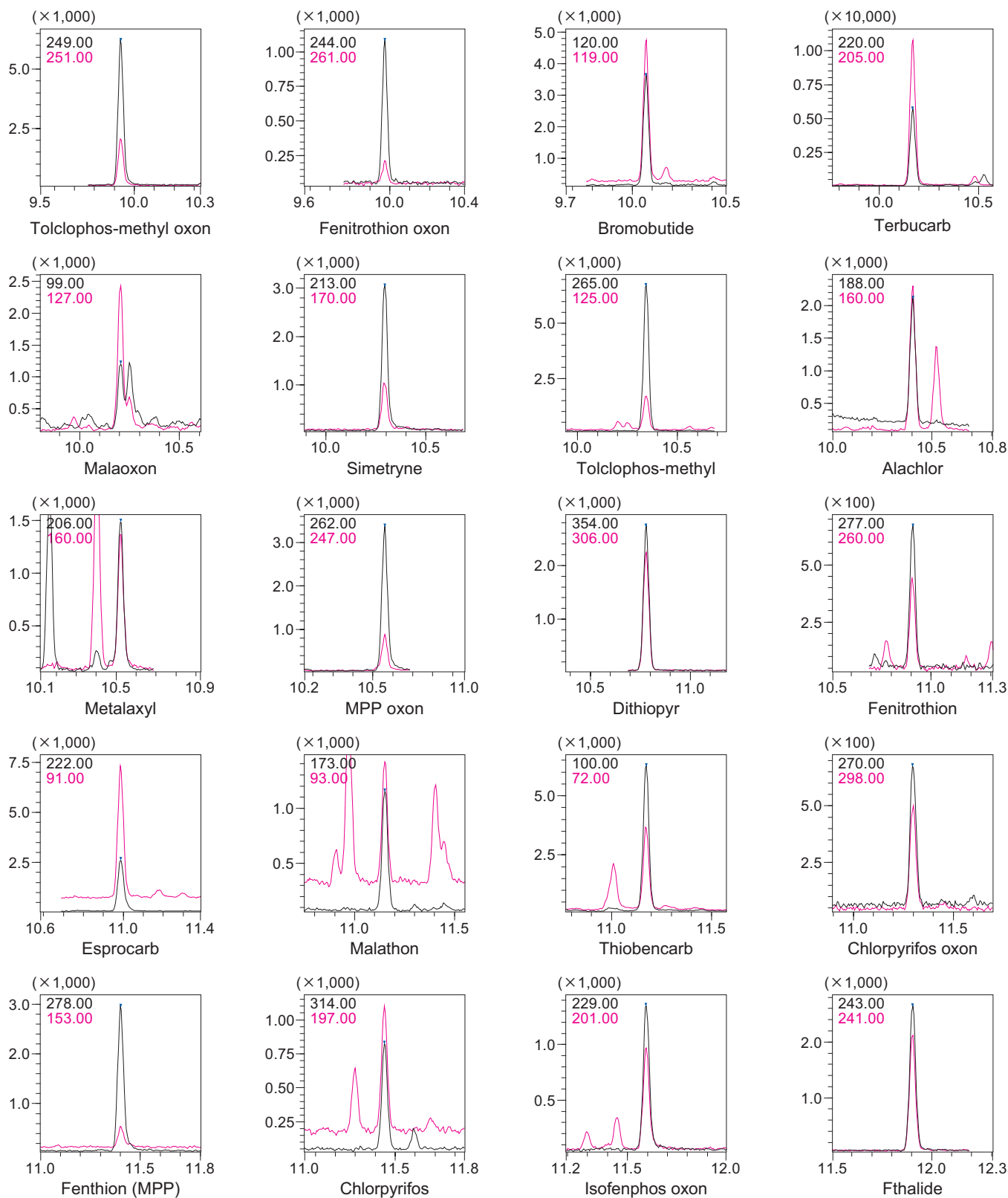
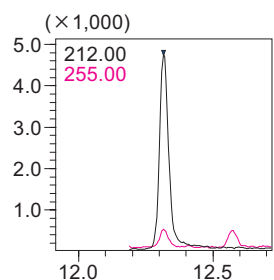


Fig. 2 TIC Chromatograms

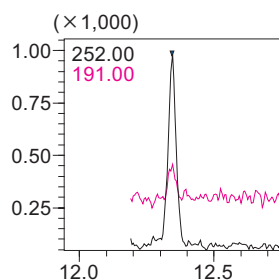
Fig. 3 shows the SIM chromatograms obtained from analysis of a 5 µg/L standard solution.



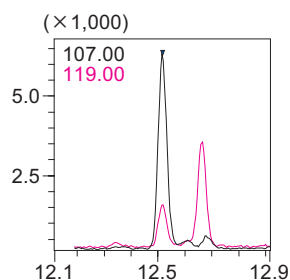




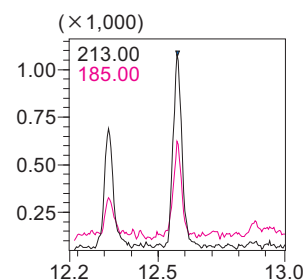
Dimethametryn



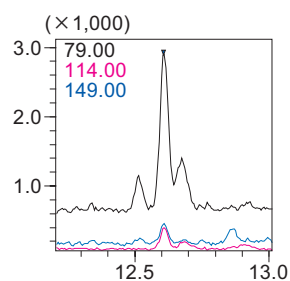
Pendimethalin



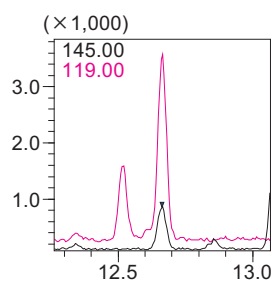
Methyl daimuron



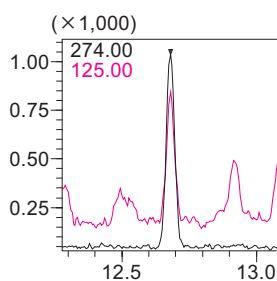
Isofenphos



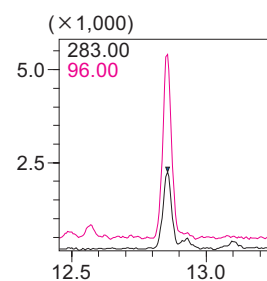
Captan



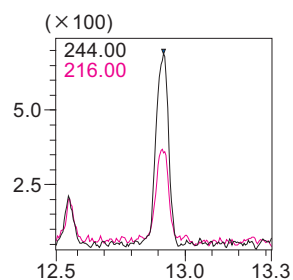
Dimepiperate



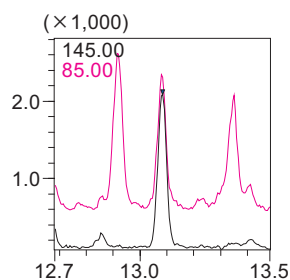
Phenthoate



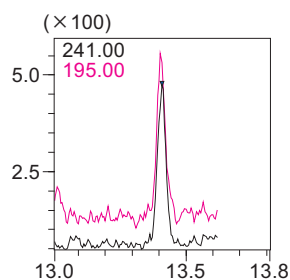
Procymidone



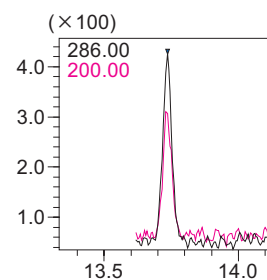
Butamifos oxon



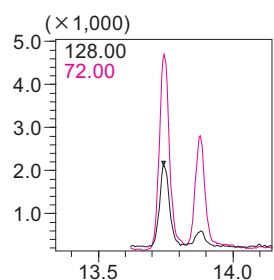
Methidathion



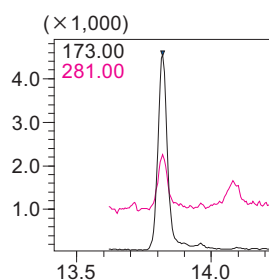
$\alpha$ -endosulfan



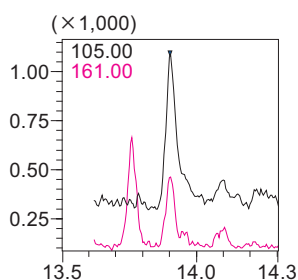
Butamifos



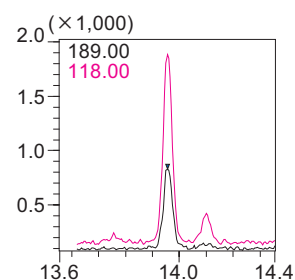
Napropamide



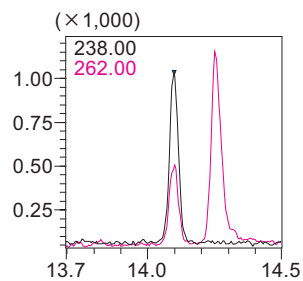
Flutolanil



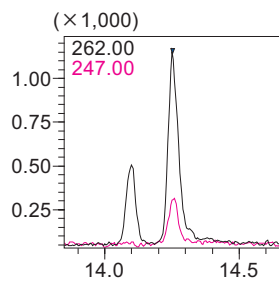
Isoxathion oxon



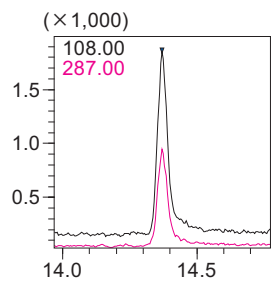
Isoprothiolane



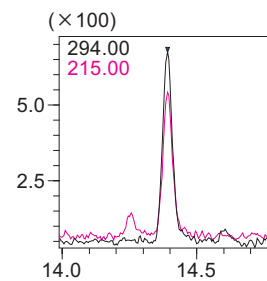
Pretilachlor



MPP oxon sulfoxide

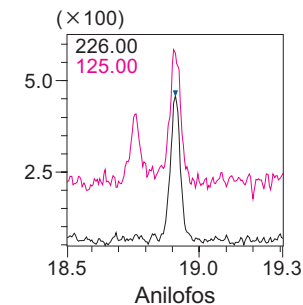
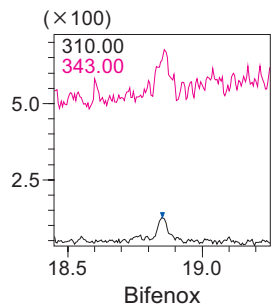
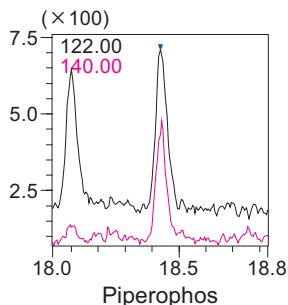
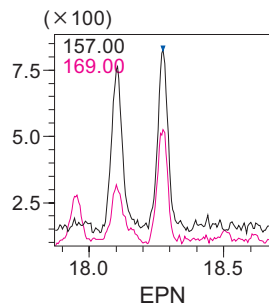
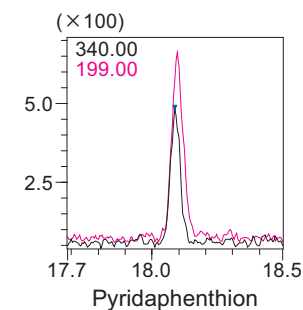
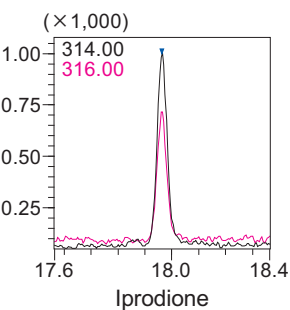
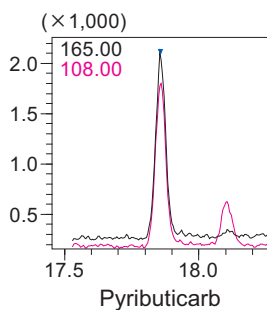
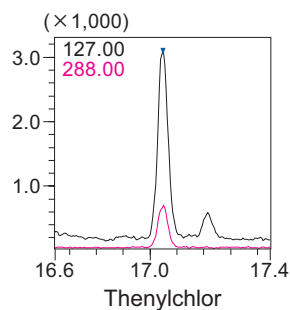
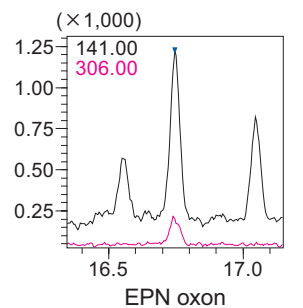
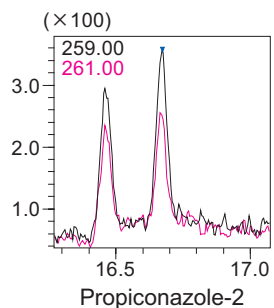
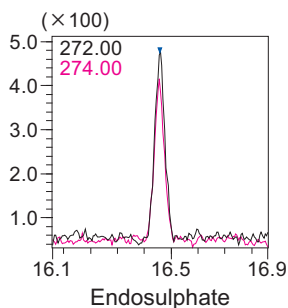
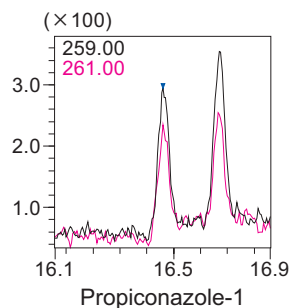
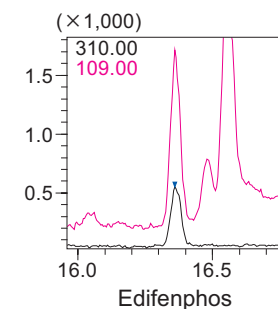
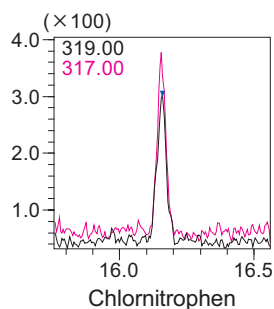
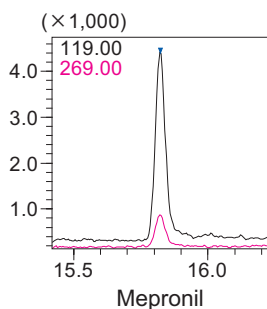
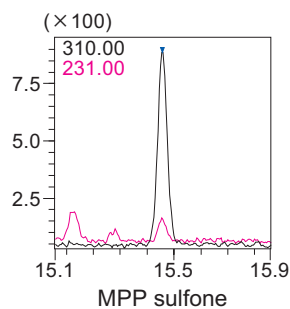
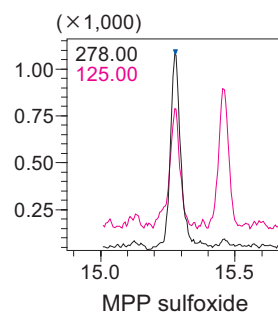
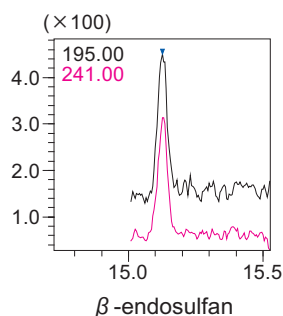
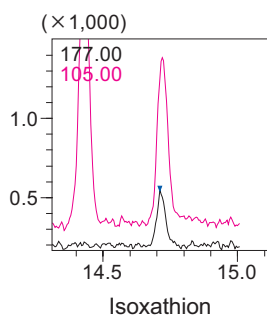
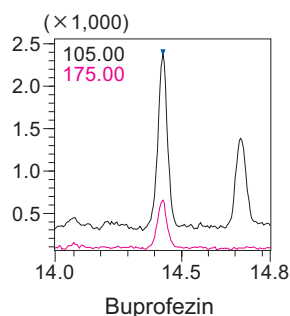


CNP-amino metabolite



MPP oxon sulfone





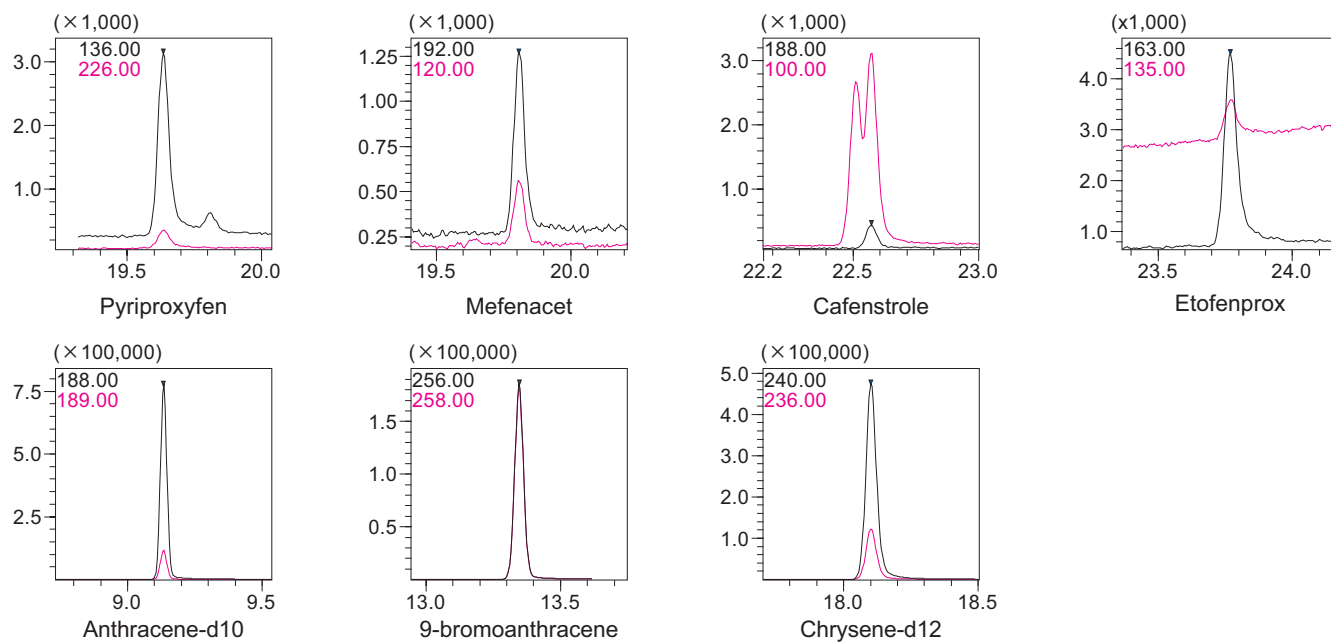


Fig. 3 SIM Chromatograms (5 µg/L)

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  | Isoproc carb                  | 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 | $\alpha$ -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 (MCP)        | 0.005               | 228,169               |
| 19  | 2,4-dichlorophenoxyacetic acid (2,4-D) | 0.03                | 234,199               | -   | Anthracene-d10        | -                   | 188,189               |
| 20  | Tryclopvr                              | 0.006               | 210,212               | -   | -                     | -                   | -                     |

### 2-2-1 Derivatization Reaction

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

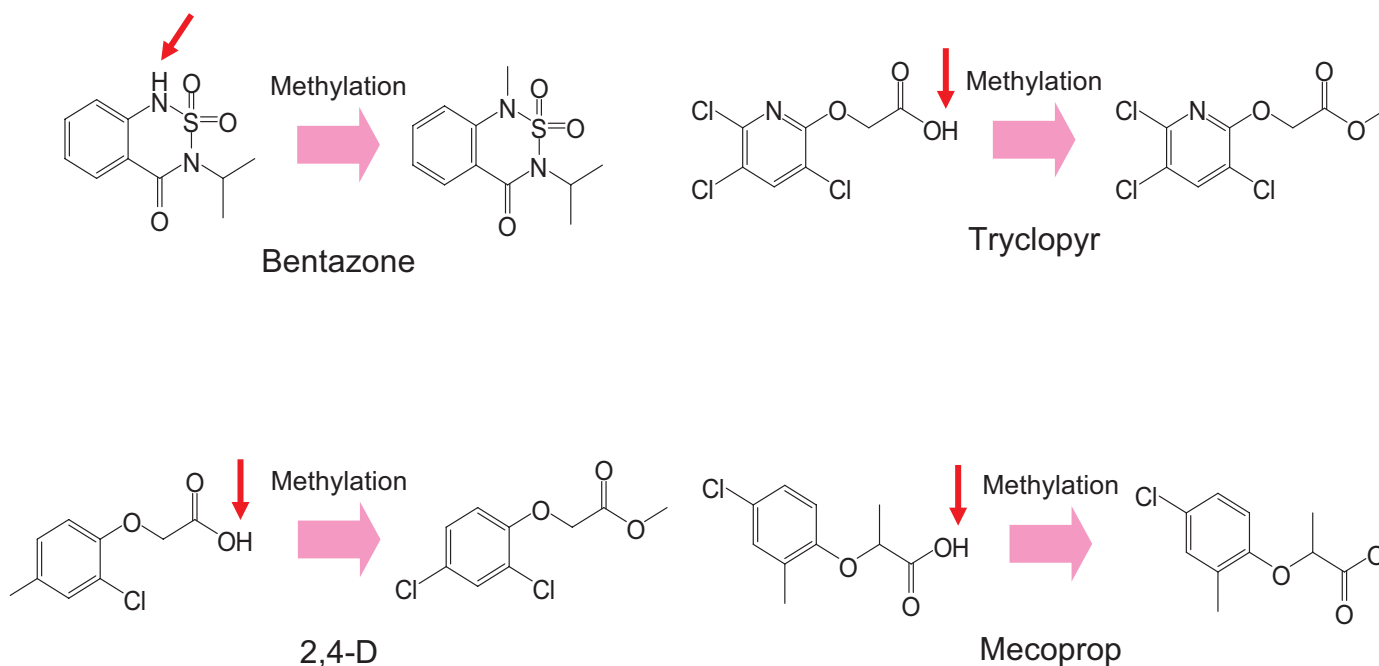
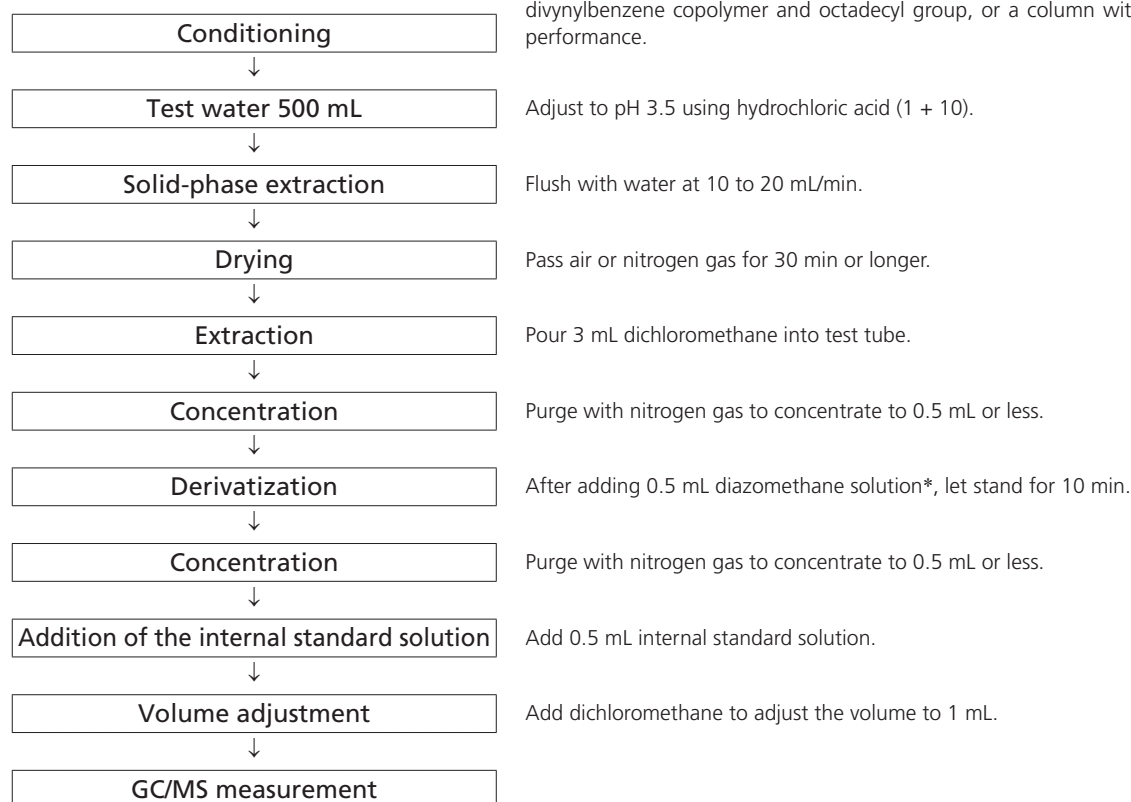


Fig. 4 Derivatization Reactions for Each Agricultural Chemical

## 2-2-2 Pretreatment

Fig. 5 shows the pretreatment flow chart.



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

Fig. 5 Pretreatment Procedure

## 2-2-3 Analytical Conditions

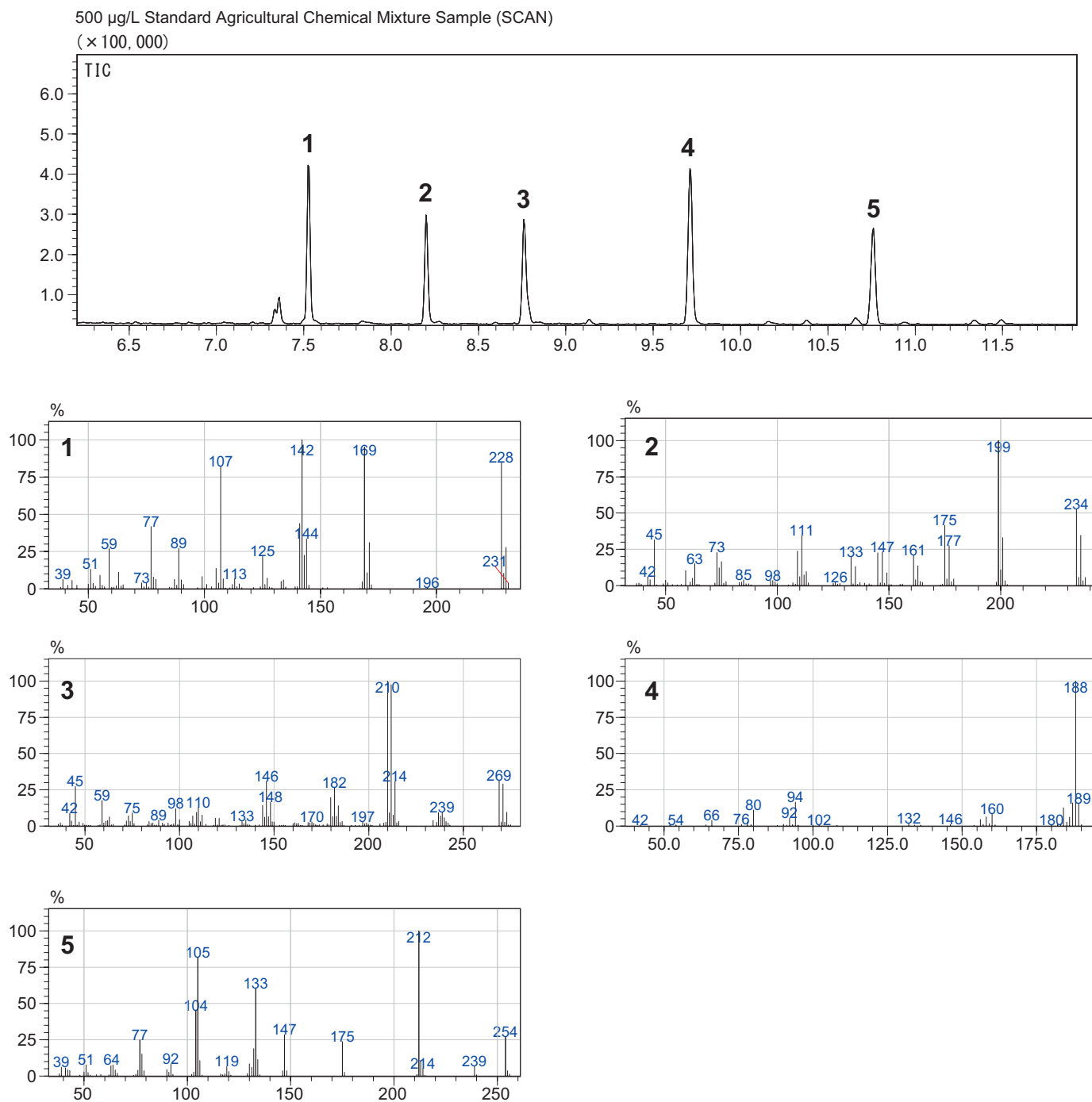
Table 8 shows the GC/MS analytical conditions.

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: Tryclopypyr 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.

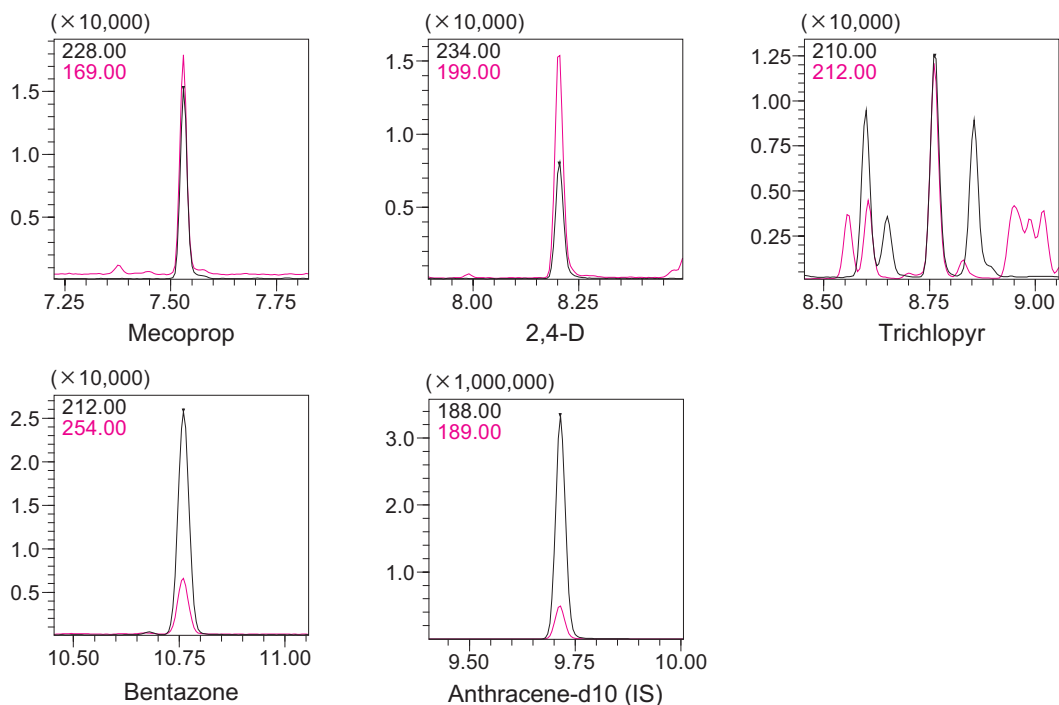


Fig. 7 SIM Chromatograms (10 µg/L)

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.

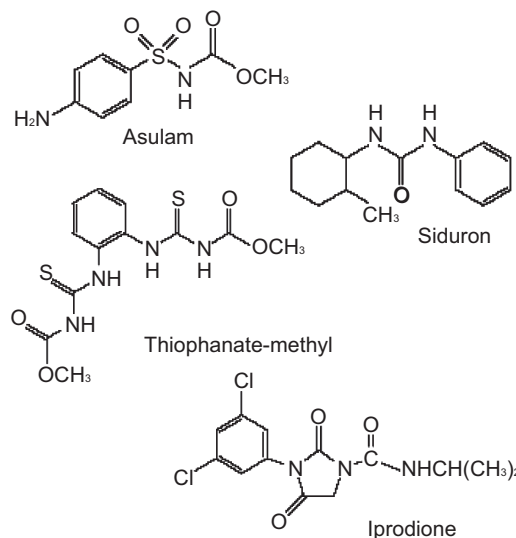


Fig. 8 Structural Formulas

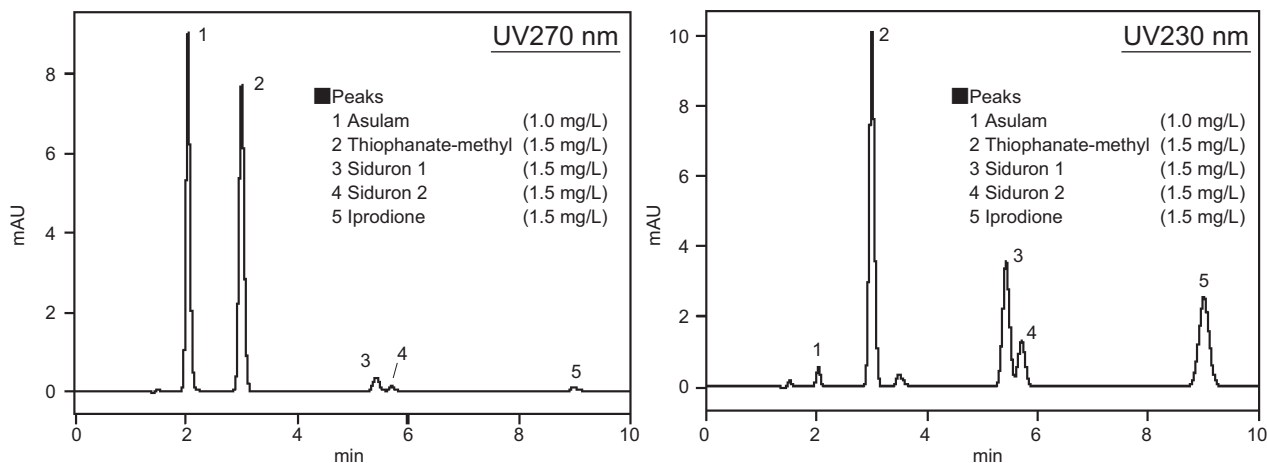


Fig. 9 Chromatograms of the Standard Sample

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.

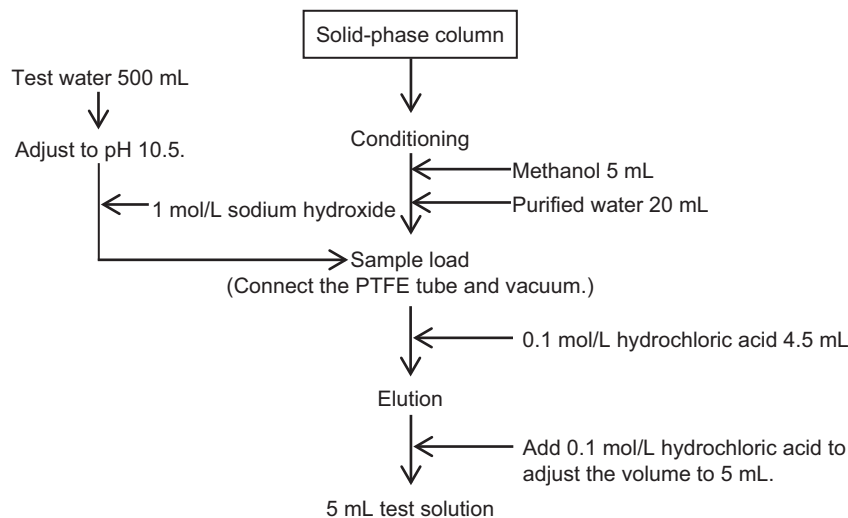


Fig. 10 Pretreatment

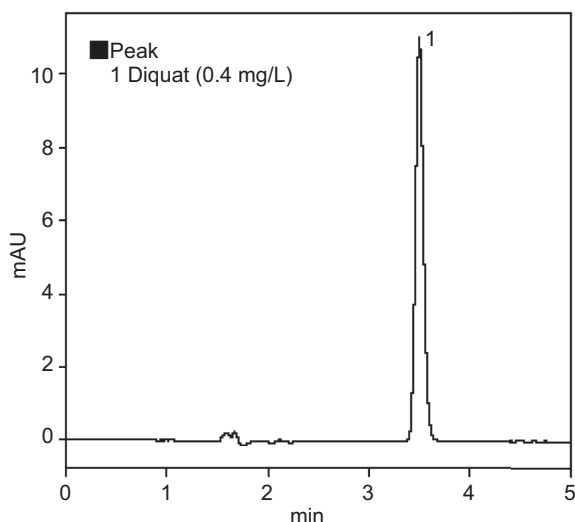


Fig. 11 Chromatogram of Diquat

Table 11 Analytical Conditions

|                |                                                                                                                                         |
|----------------|-----------------------------------------------------------------------------------------------------------------------------------------|
| Column         | : Shim-pack VP-ODS<br>(150 mmL. × 4.6 mmL.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.

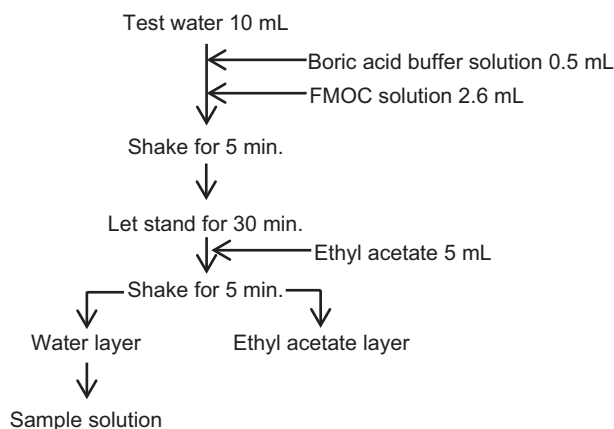


Fig. 12 Pretreatment

#### 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.

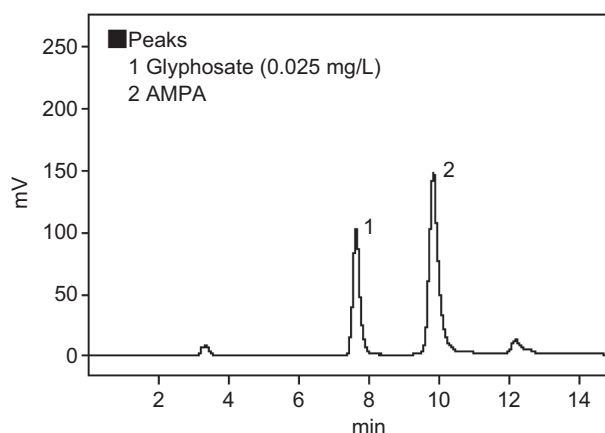


Fig. 13 Chromatogram of Glyphosate and AMPA Standard Samples

Table 12 Analytical Conditions

|                |                                                                                                                       |
|----------------|-----------------------------------------------------------------------------------------------------------------------|
| Column         | : Shim-pack VP-ODS<br>(150 mmL. × 4.6 mmL.D., 5 μm)                                                                   |
| Mobile phase   | : 50 mmol/L potassium phosphate monobasic<br>(pH = 2.5, adjusted with phosphoric acid)<br>/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.

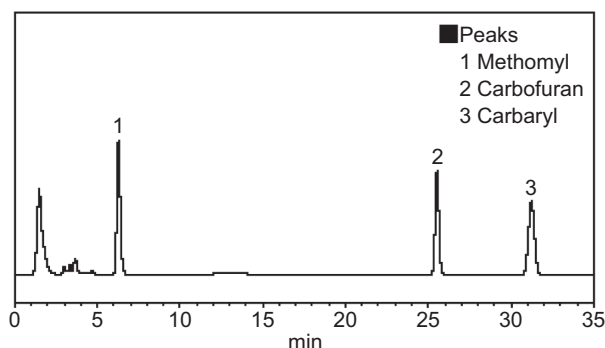


Fig. 14 Chromatogram of the Standard Samples (5 µg/L each)

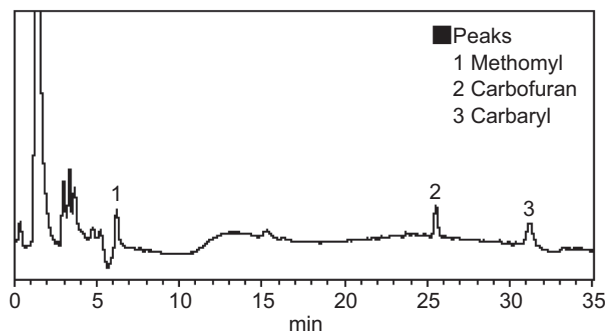


Fig. 15 Chromatogram of the Standard Samples (0.1 µg/L each)

#### 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. x 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.

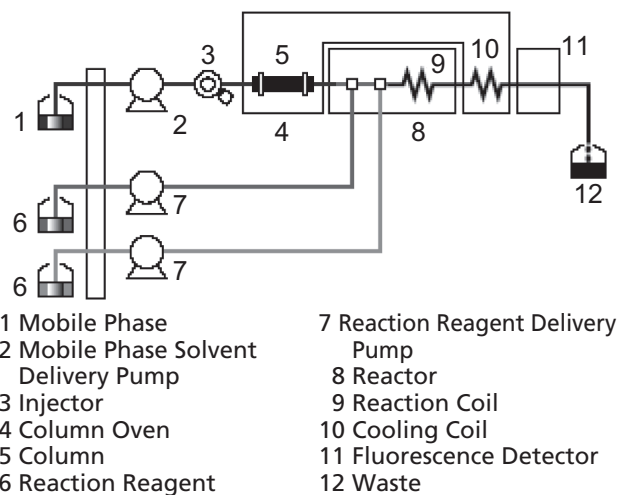


Fig. 16 Flow Diagram

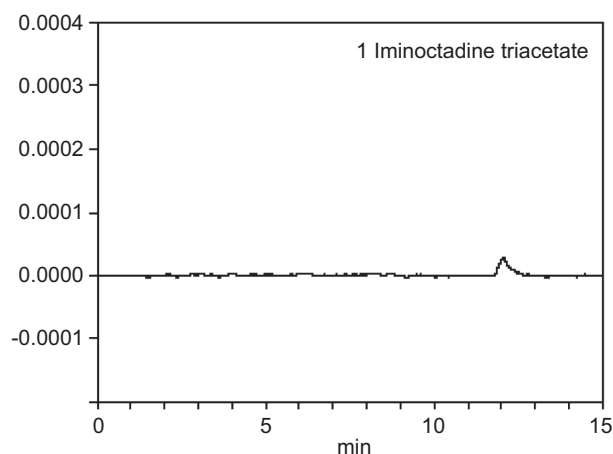


Fig. 17 Chromatogram of Iminoctadine Triacetate (0.01 mg/L)

### 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.

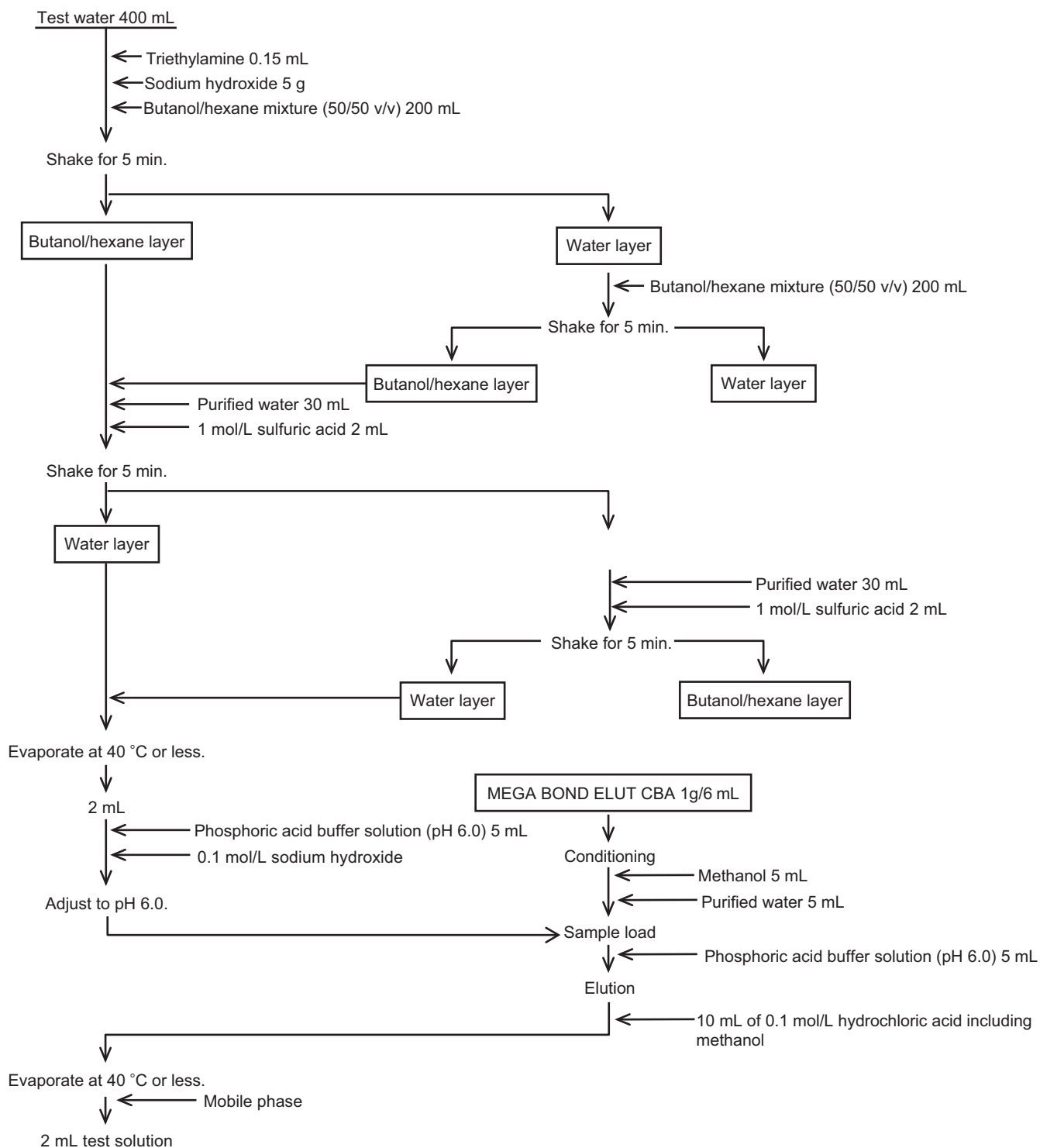


Fig. 18 Pretreatment

## 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 ( <i>m/z</i> ) |
|----------|-----|----------------------------------------|---------------------|--------------------------------|
| 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)                         | 0.001               | 279                            |
|          |     | MPP sulfoxide                          |                     | 295                            |
|          |     | MPP sulfone                            |                     | 311                            |
|          |     | MPP oxon                               |                     | 263                            |
|          |     | MPP oxon sulfoxide                     |                     | 279                            |
|          |     | MPP oxon sulfone                       |                     | 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  | Tryclopypyr                            | 0.006               | 254                            |
|          | 42  | Bensulide (SAP)                        | 0.1                 | 396                            |
|          | 45  | Mecoprop (MCP)                         | 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 (MCP), 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)

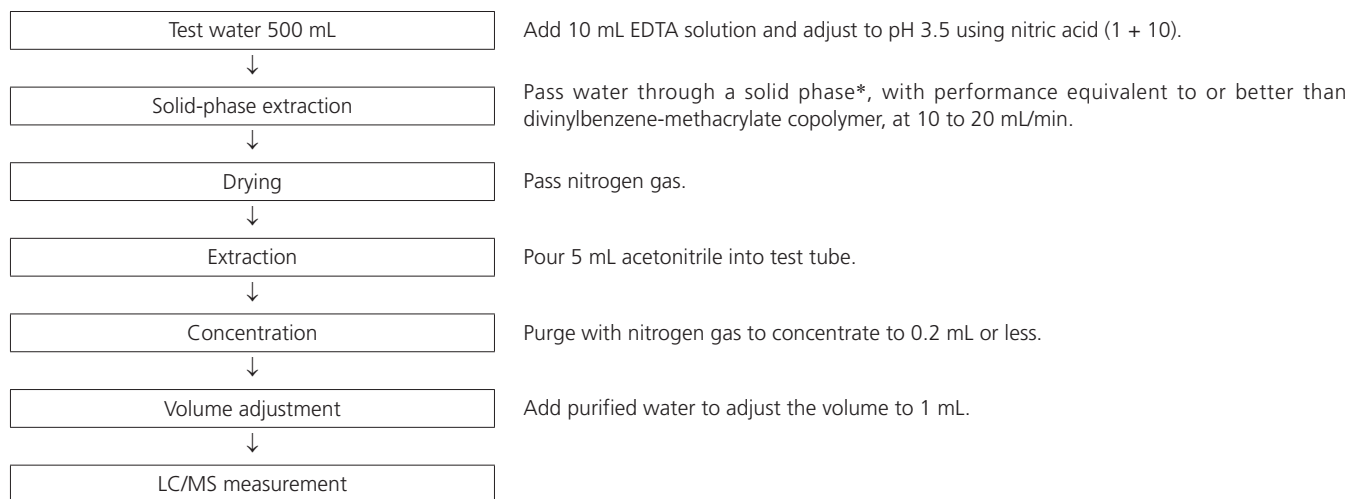
Place 100  $\mu$ L each of agricultural chemical standard stock solutions for thiuram, bentazon, carbofuran (carbosulfan metabolite), 2,4-dichlorophenoxyacetic acid (2,4-D), trichlopyr, asulam, bensulide (SAP), mecoprop (MCP), carbaryl (NAC), carpropamid, diuron (DCMU), fenthion (MPP), methomyl, daimuron, 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  $\mu$ g of each agricultural chemical except iprodione and probenazole. It contains 100  $\mu$ g 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.



\* 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                                                                     |
| DI 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)

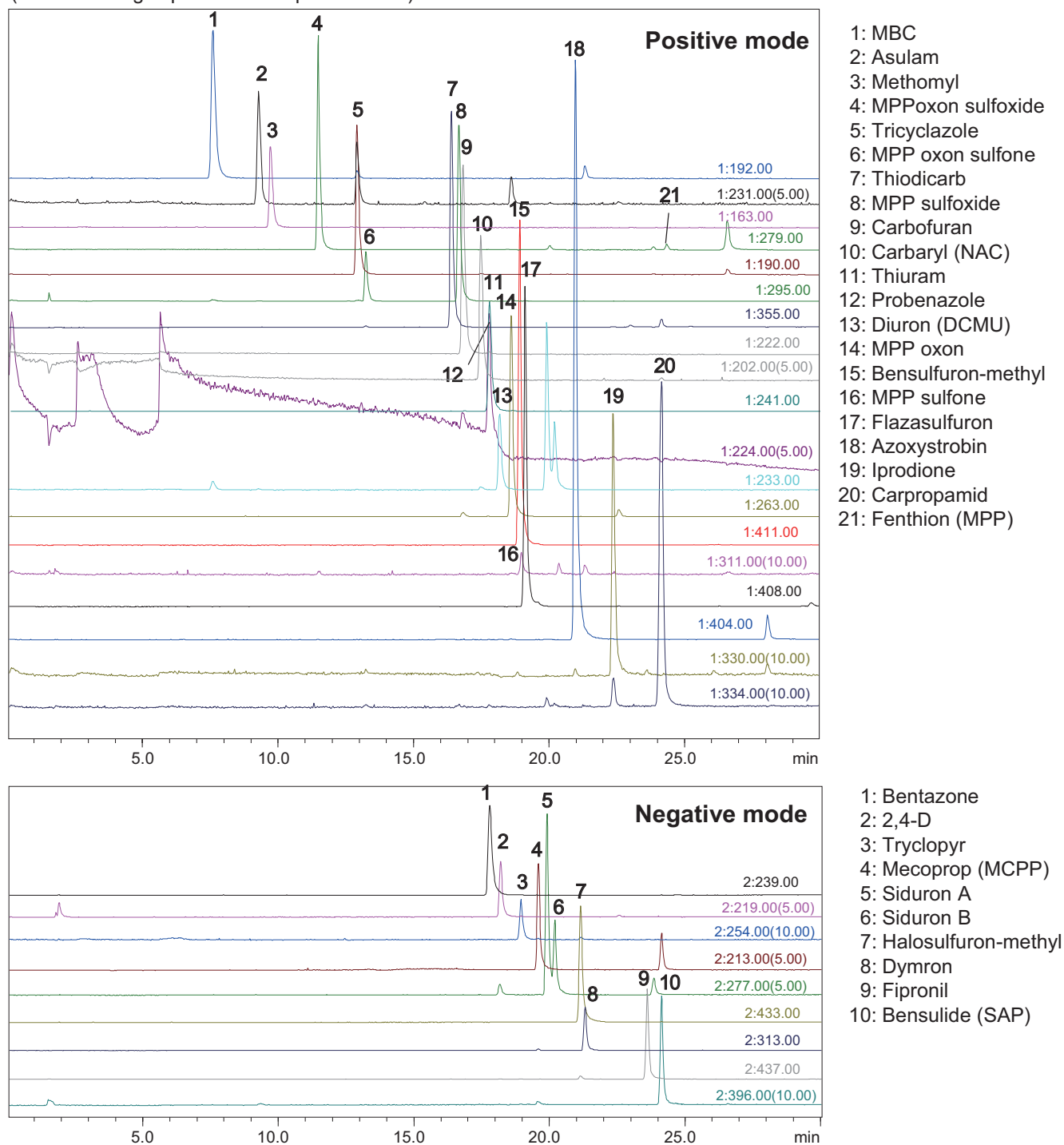
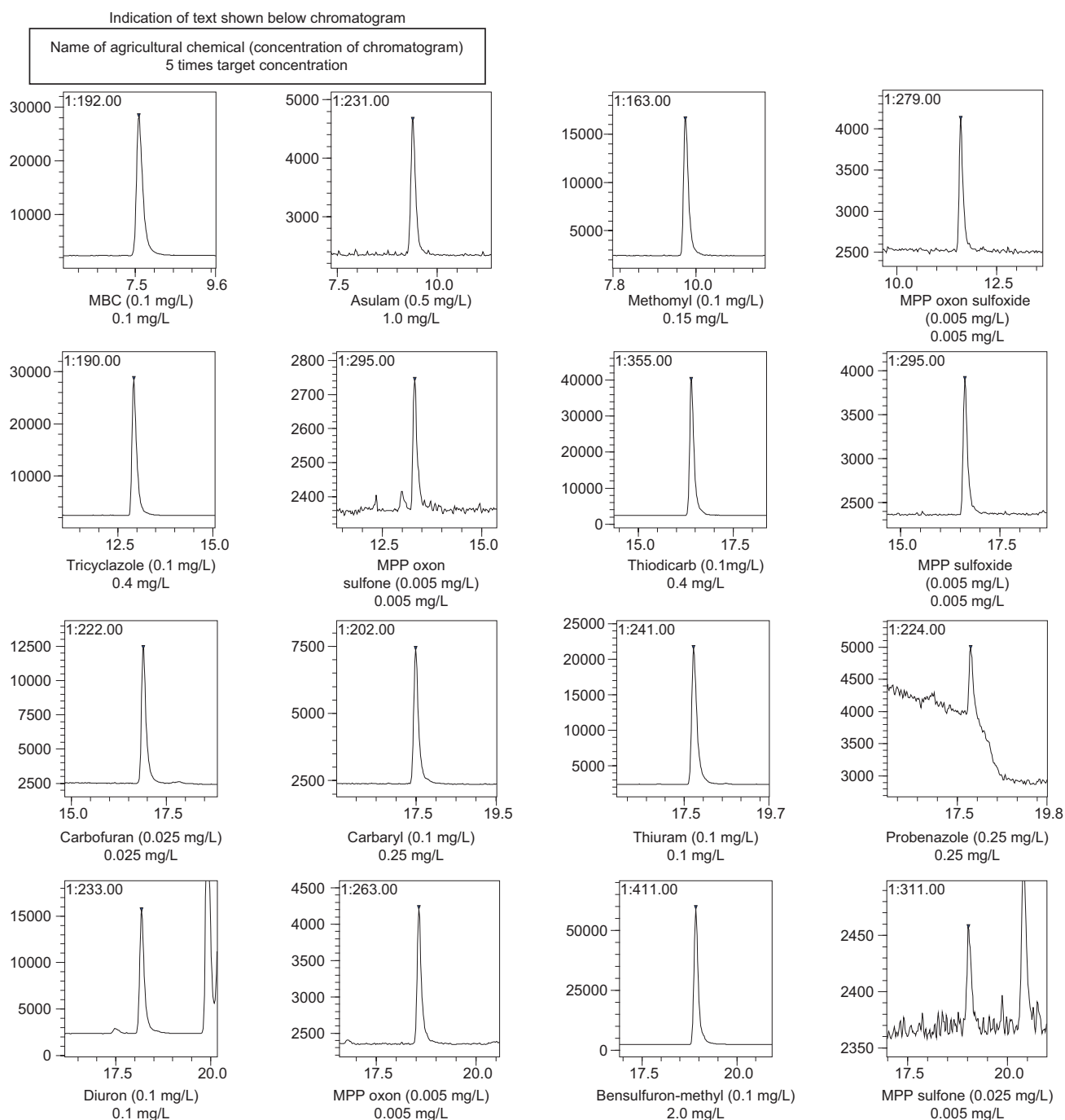


Fig. 20 SIM Chromatograms of 30 Agricultural Chemicals

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.



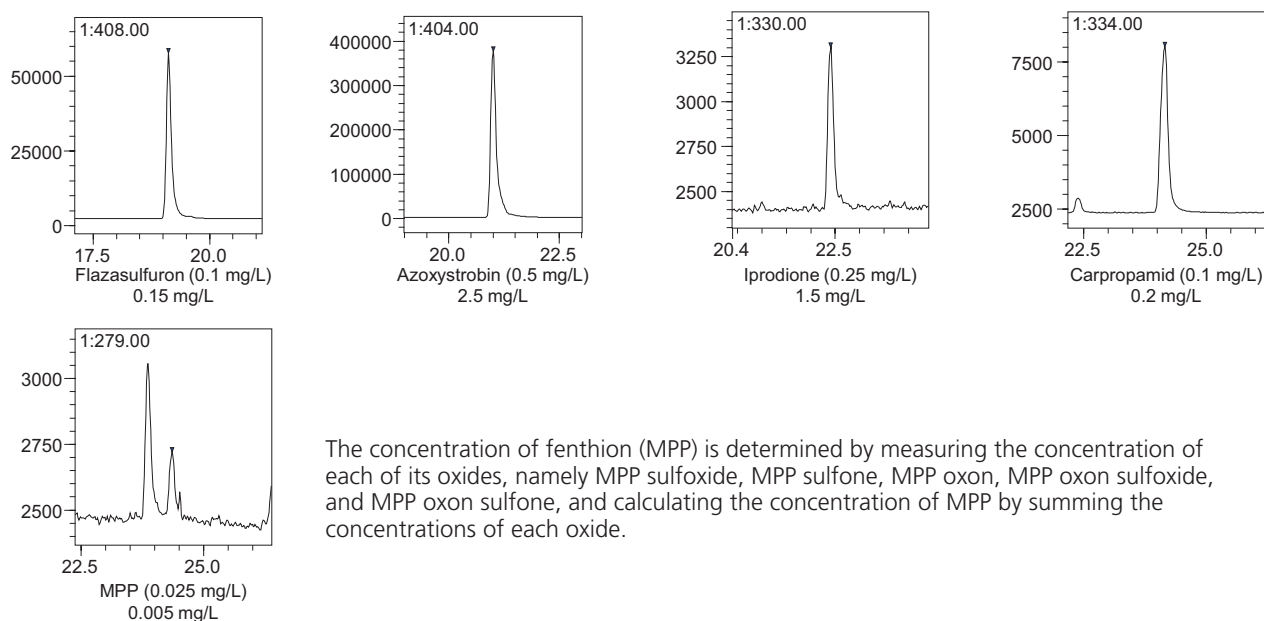


Fig. 21 SIM Chromatograms (Positive Mode)

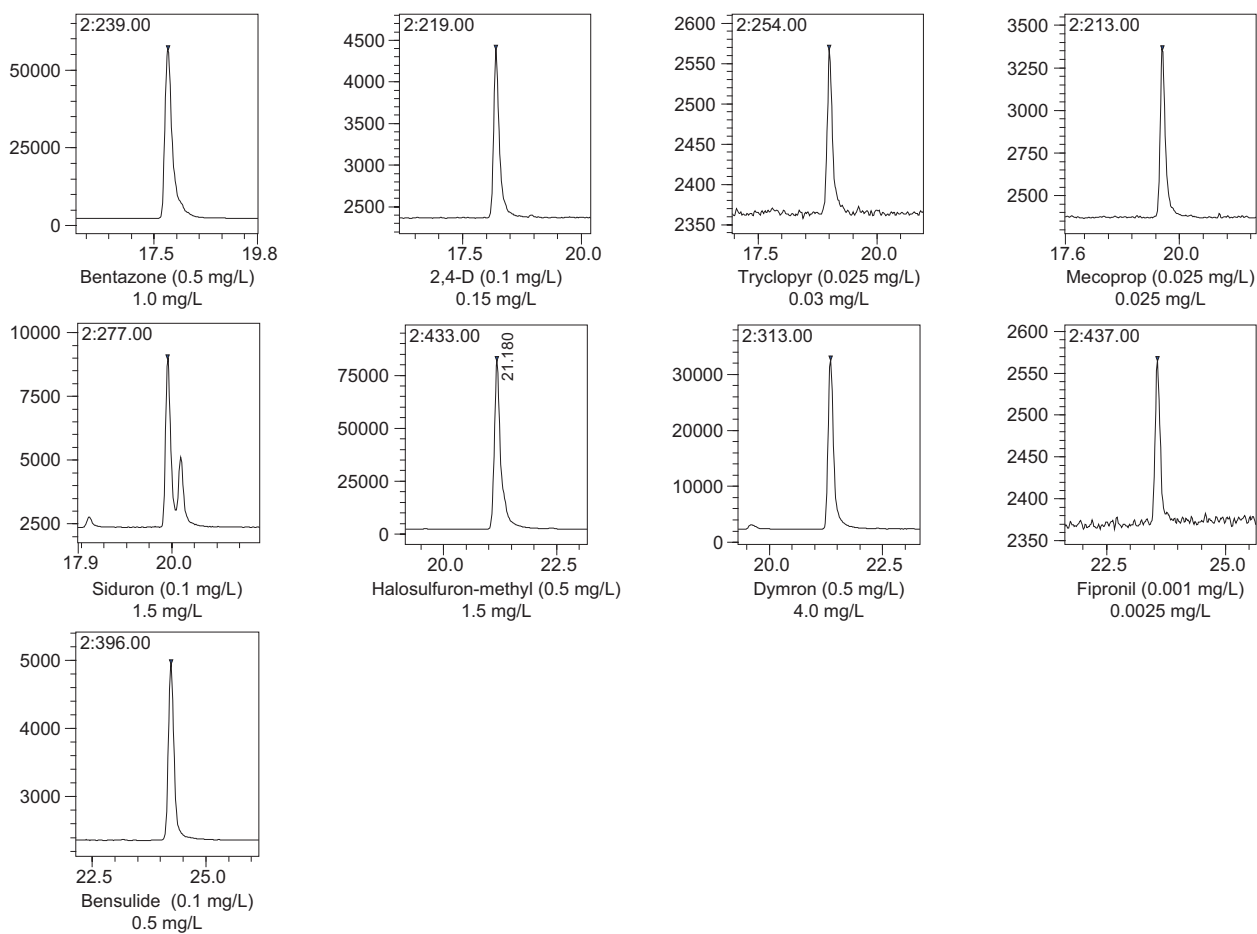


Fig. 22 SIM Chromatograms (Negative Mode)

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  | Tryclopypyr           | –    | 254                  | 0.025                | 1673               | 103.84             | 6.21         |
| 25  | Mecoprop (MCP)        | –    | 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 ( <i>m/z</i> ) |
|----------|-----|-----------------------|---------------------|-------------------------------|
| 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

Place 100 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

Place 100 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

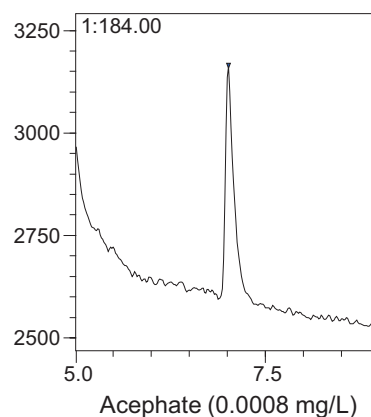
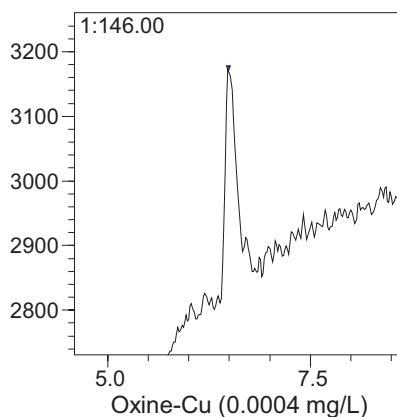
|                         |                                                                          |
|-------------------------|--------------------------------------------------------------------------|
| Column                  | : L-Column ODS (150 mmL. × 2.1 mmI.D., 5 µm)                             |
| 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.

##### Positive mode



##### Negative mode

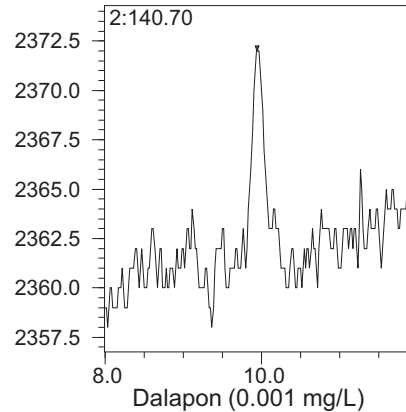
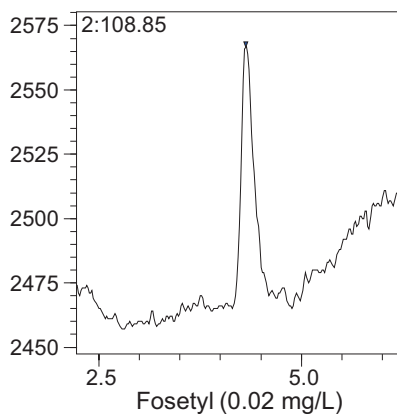


Fig. 23 SIM Chromatograms of Agricultural Chemicals

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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