SHIMADZU APPLICATION NEWS

LAAN-A-LM-E003

● LIQUID CHROMATOGRAPHY MASS SPECTROMETRY

No. C33

# Simultaneous Analysis of Pesticides using LC-MS

The Japanese Ministry of Health, Labor and Welfare released a ministerial ordinance (No. 1010001) related to water quality standards and a partial revision to the Water Supply Law on 10th October 2003. It prescribes the inspection methods for the water-quality target values.
Water-quality target values are set for 101 pesticides. Four analysis methods use LC-MS: Additional Method 16 to 19. Additional Method 16 alone covers the simultaneous analysis of 27 components (28, including decomposition products). This Application News introduces the LC-MS methods prescribed in Additional Method 16.
As the “total pesticide method” is used for the pesticide analysis results, in principle measurements of individual pesticides are conducted on concentrations 1/100 the target value. In addition, 500× concentration using a reversed phase resin cartridge is described for analysis.

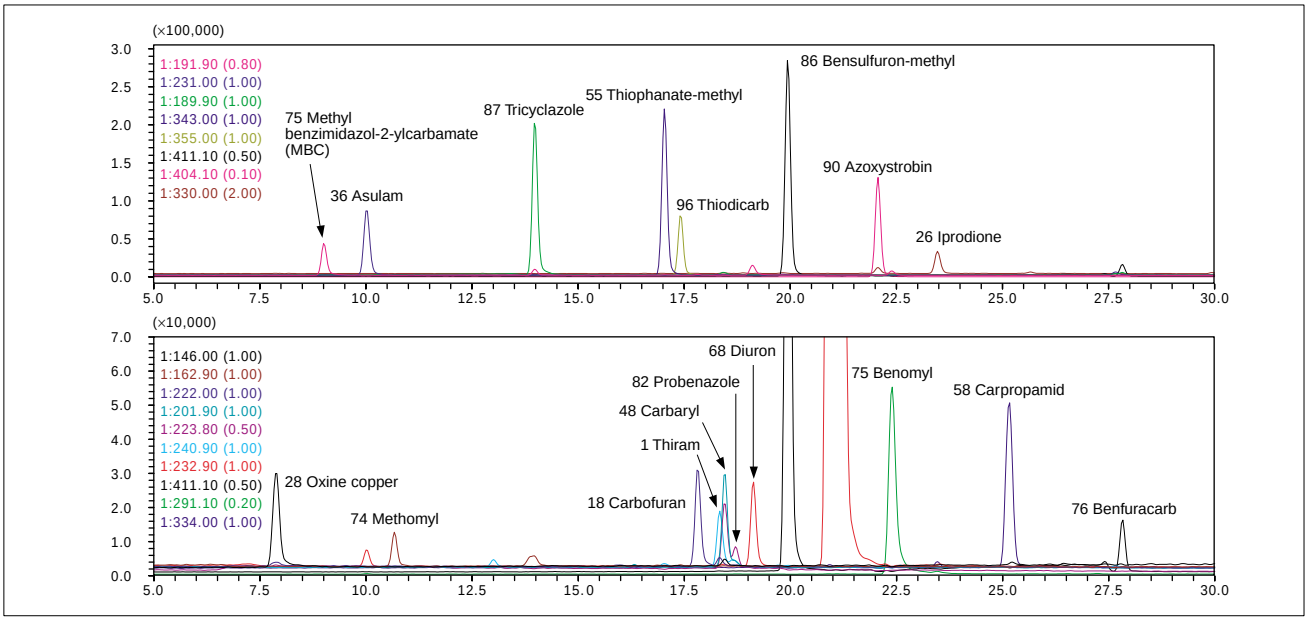


**Fig.1 SIM Chromatograms of Pesticides at 1/100 Concentration (ESI-positive) (top: target value ≥ 0.08mg/L; bottom: target value < 0.08mg/L)**

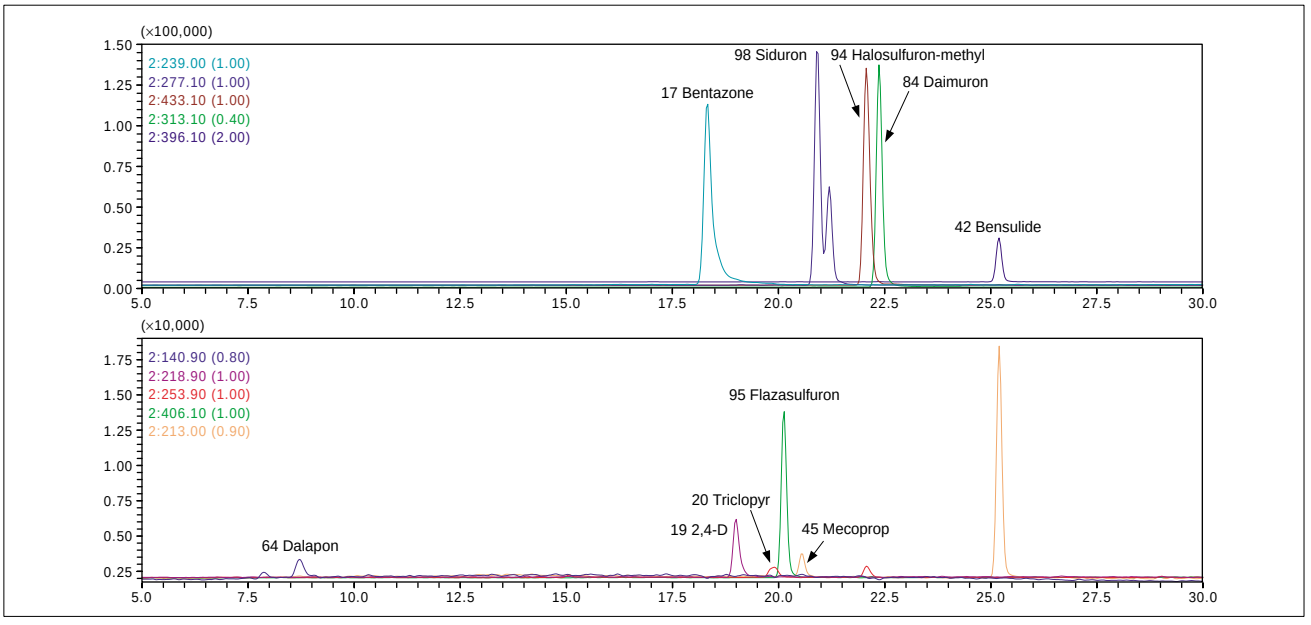


**Fig.2 SIM Chromatograms of Pesticides at 1/100 Concentration (ESI-negative) (top: target value ≥ 0.1mg/L; bottom: target value < 0.1mg/L)**

Acetonitrile-0.1%(w/v) formic acid water or acetonitrile-0.15%(w/v) acetic acid water can be selected as the mobile phase. However, the type of mobile phase affects the mass number of the monitored ions and sensitivity for electrospray ionization (ESI) and causes differences in elution behavior during chromatography. Investigations by Shimadzu have revealed an acetonitrile-formic acid mobile phase to be superior overall for this analysis.
Using this mobile phase, all pesticides detectable as positive ions can be monitored with protonated molecules $[M+H]^+$ and most pesticides detectable as negative ions can be monitored with deprotonated molecules $[M-H]^-$. Highly selective chromatography is possible for Benomyl, Benfuracarb, and Azoxystrobin (detectable as positive ions) and 2,4-D, Triclopyr, and Bensulide (detectable as negative ions), which can be directly observed as molecular ion species, not only as fragment ions. Care is required with Daimuron and Siduron (both phenylurea-based pesticides), which are observable as molecules with attached negative formic acid ions $[M+HCOO]^-$. Table 1 summarizes the mass numbers of the monitor ions for each pesticide, when an acetonitrile–formic acid-based mobile phase is used.
Figs.1 and 2 show the batch analysis (SIM chromatograms) of pesticide samples prepared to the equivalent of 1/100 each target concentration value for each of the 28 components. They show that all components were detected with a satisfactory S/N ratio.

**Table 1 Monitor ions of 28 pesticides using 0.1%(w/v) formic acid-water as mobile phase**

| Mode | No. | Pesticide name | Target value (mg/L) | Monitor ion (m/z) | |
|---|---|---|---|---|---|
| Positive | 1 | Thiram | 0.02 | 241 | $[M+H]^+$ |
| | 18 | Carbofuran | 0.005 | 222 | $[M+H]^+$ |
| | 26 | Iprodione | 0.3 | 330 | $[M+H]^+$ |
| | 28 | Oxine copper | 0.04 | 146 | $[M+H]^+$ |
| | 36 | Asulam | 0.2 | 231 | $[M+H]^+$ |
| | 48 | Carbaryl (NAC) | 0.05 | 202 | $[M+H]^+$ |
| | 55 | Thiophanate-methyl | 0.3 | 343 | $[M+H]^+$ |
| | 58 | Carpropamid | 0.04 | 334 | $[M+H]^+$ |
| | 68 | Diuron (DCMU) | 0.02 | 233 | $[M+H]^+$ |
| | 74 | Methomyl | 0.03 | 163 | $[M+H]^+$ |
| | 75 | Benomyl | 0.02 | 291 | $[M+H]^+$ |
| | 76 | Benfuracarb | 0.04 | 411 | $[M+H]^+$ |
| | 82 | Probenazole | 0.05 | 224 | $[M+H]^+$ |
| | 86 | Bensulfuron-methyl | 0.4 | 411 | $[M+H]^+$ |
| | 87 | Tricyclazole | 0.08 | 190 | $[M+H]^+$ |
| | 90 | Azoxystrobin | 0.5 | 404 | $[M+H]^+$ |
| | 96 | Thiodicarb | 0.08 | 355 | $[M+H]^+$ |
| | | Methyl benzimidazol-2-ylcarbamate (MBC) (decomposition product of Benomyl) | – | 192 | $[M+H]^+$ |
| Negative | 17 | Bentazone | 0.2 | 239 | $[M-H]^-$ |
| | 19 | 2,4-dichlorophenoxyacetic acid (2,4-D) | 0.03 | 219 | $[M-H]^-$ |
| | 20 | Triclopyr | 0.006 | 254 | $[M-H]^-$ |
| | 42 | Bensulide (SAP) | 0.1 | 396 | $[M-H]^-$ |
| | 45 | Mecoprop (MCPP) | 0.005 | 213 | $[M-H]^-$ |
| | 64 | Dalapon | 0.08 | 141 | $[M-H]^-$ |
| | 84 | Daimuron | 0.8 | 313 | $[M+HCOO]^-$ |
| | 94 | Halosulfuron-methyl | 0.3 | 433 | $[M-H]^-$ |
| | 95 | Flazasulfuron | 0.03 | 406 | $[M-H]^-$ |
| | 98 | Siduron | 0.3 | 277 | $[M+HCOO]^-$ |

**Table 2 Analytical conditions**

| | | | |
|---|---|---|---|
| Column | : L-column ODS (150 mmL. × 2.1 mm I.D.) | Probe voltage | : +4.5/ −3.5 kV (ESI-Positive mode/ ESI-Negative mode) |
| Mobile phase A | : 0.1%(w/v) formic acid-water | CDL temperature | : 200˚C |
| Mobile phase B | : acetonitrile | Block heater temperature | : 200˚C |
| Gradient program | : 0%B (0 min)→ 100%B (30-35 min) | Nebulizing gas flow | : 1.5 L/min |
| Flow rate | : 0.2 mL/min | Drying gas pressure | : 0.2MPa |
| Injection volume | : 10µL | CDL, Q-array voltages | : using default values |
| Column temperature | : 40˚C | SIM | : see Table 1 |

SHIMADZU

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