

Simultaneous Analysis of Carbamate Pesticides with LC-MS

In expectation of revising the Public Water Law, the Japanese Ministry of Health, Labour and Welfare announced a draft guideline entitled "On the Review of Water Quality Standards" on March 14th, 2003, to solicit opinions from the public. This draft specifies 101 agricultural chemicals for which water quality target values are set. In accordance with this list, agricultural chemicals that may be used in a water catchment area are specified to perform intensive inspections in the season when they are sprayed. The evaluation will be made using the "total agricultural chemicals" method, where the detection index (DI) should not exceed 1.

$$DI = \sum (DVi \text{ detected value} / GVi \text{ target value})$$

Measurement will be made using GC-MS, HPLC or LC-MS, among which the optimal method should be selected for different agricultural chemicals.

Agricultural chemicals are categorized according to their chemical structures. Carbamate agrichemicals, which are generally unstable against heat, are effectively analyzed by HPLC or LC-MS. Using the Selective Ion Monitoring (SIM) method allows simultaneous analysis of multiple components. This Data Sheet introduces an analysis example of the following carbamate agrichemicals: 1)

carbendazim (as benomyl and thiophanate methyl decomposition products; not added as carbendazim), 2) asulam, 3) oxamyl, 4) mesomyl, 5) thiofanate methyl, 6) thiodicarb, 7) carbaryl, 8) XMC, 9) thiuram, 10) isoprocarb, 11) benomyl, 12) dimepiperate, 13) benfuracarb, 14) carbofuran (benfuracarb decomposition products; not added as carbofuran).

Fig. 1 shows the SIM chromatogram of these agricultural chemicals. To ensure the separation of adjacent peaks, the Shim-pack FC-ODS separation column with excellent separation performance was used. Ionization was conducted by the electrospray ionization (ESI) method using positive ions. The mass number of the protonated molecule of each substance was used as the selective ion mass number. Even immediately after sample preparation, carbendazim generated by the decomposition of benomyl and thiophanate methyl, and carbofuran generated by the decomposition of benfuracarb were detected. Therefore, it is recommended to monitor also decomposition products when preparing samples by concentration and pretreatment.

Under these conditions, good linearity was obtained for each substance in the range of 0.0008 to 0.8 mg/L (3 μ L

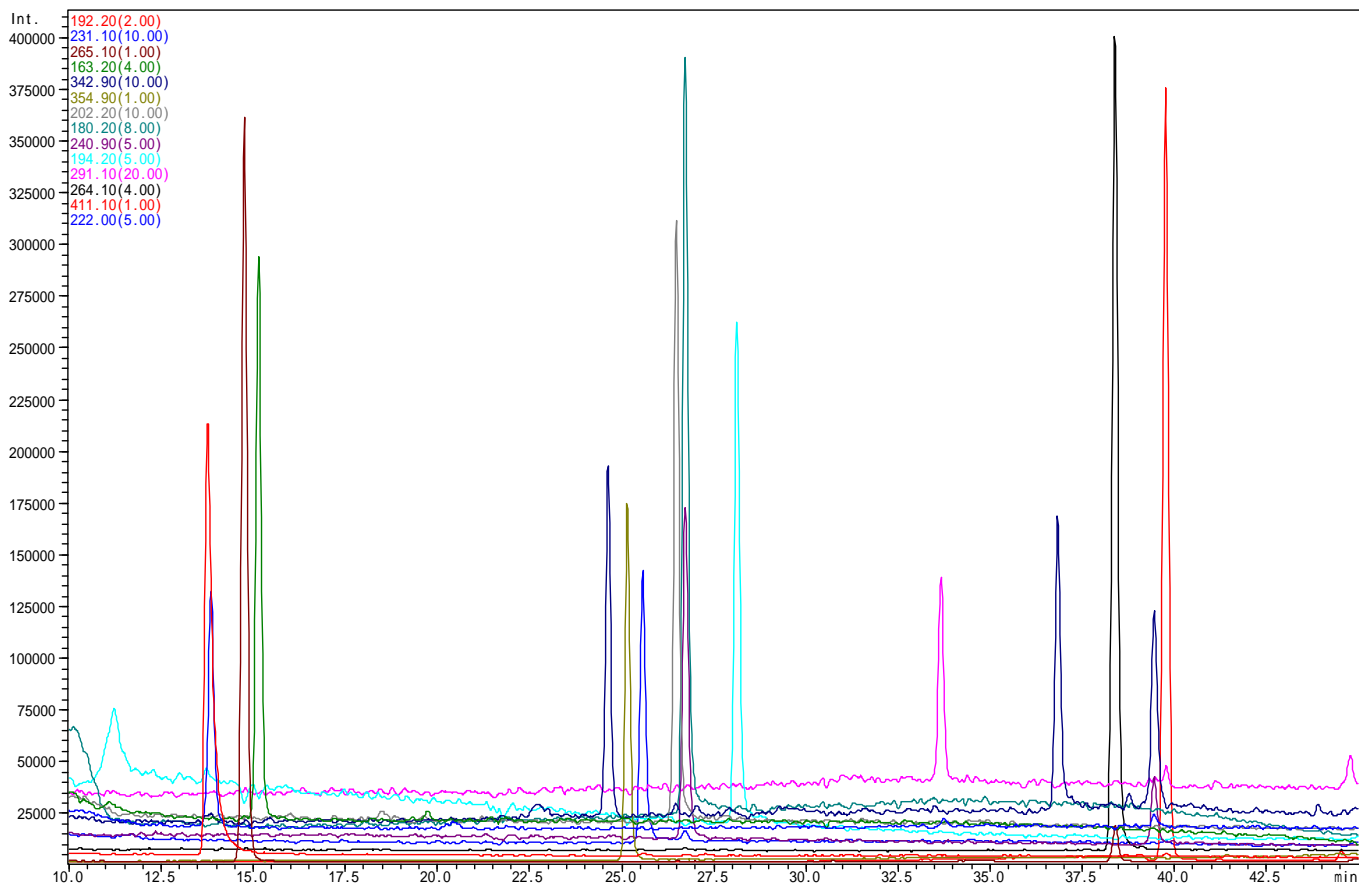


Fig. 1 SIM Chromatogram of Carbamate Agrichemicals

injection). Target values for thiuram, carbofuran, asulam, carbaryl, isoprocarb, thiofanate methyl, mesomyl, benomyl, benfuracarb, dimepiperate and thiodicarb are listed as 0.02 , 0.005 , 0.2 , 0.05 , 0.01 , 0.3 , 0.03 , 0.02 , 0.04 , and 0.003 mg/L respectively. If the influence of the matrices is small, 1/10 of target values can be detected. (Concentration is necessary when considering repeatability.)

Fig. 2 shows the peaks for 0.02 mg/L of each pesticide

(3 μ L injection). (This data is for reference because the analysis includes substances subject to natural decomposition and those generated by decomposition. It is necessary to understand the degradability of each agricultural chemical to acquire accurate data.) Because these analytical conditions are quite typical, they can be applied to other agricultural chemicals.

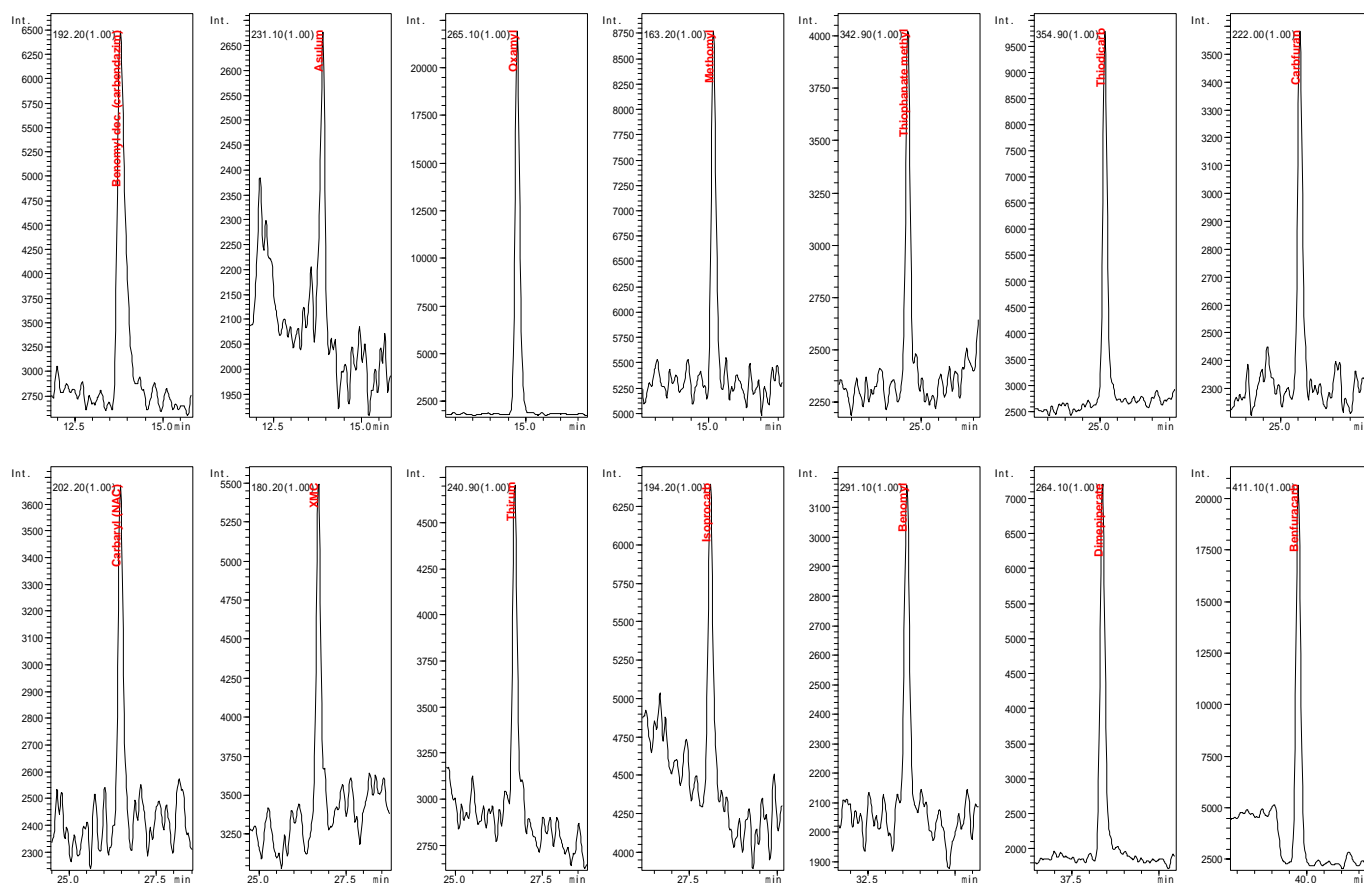


Fig. 2 SIM Chromatograms of Carbamate Agricultural Chemicals (0.02 mg/L)

Table 1 Analytical Conditions for LC-MS

Column	: Shimadzu Shim-pack FC-ODS (2.0ml.D.x 150 mmL.)		
Mobile phase A	: 0.1% formic acid-water		
Mobile phase B	: acetonitrile		
Time program	: 0%B (0 min) -> 95%B (45 – 50 min)		
Flow rate	: 0.2mL/min		
Injection volume	: 3 μ L	Column temperature	: 40 $^{\circ}$ C
Probe voltage	: +4.5 kV (ESI-Positive mode)		
Nebulizing gas flow	: 1.5 L/min	Drying gas pressure	: 0.1 MPa
CDL temperature	: 200 $^{\circ}$ C	Block heater temperature	: 200 $^{\circ}$ C
CDL, Q-array voltages	: using default values		
SIM	: m/z 192.2, 231.1, 265.1, 163.2, 342.9, 354.9, 202.2, 180.2, 240.9, 291.1, 264.1, 411.1, 222.0		

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