SHIMADZU

LC-MS Application Data Sheet No. 047

Analysis of Phenoxyproprionic Type Herbicides using LC-MS

Fluazifop, quizalofop-butyl, and other phenoxyproprionic agricultural chemicals are used widely throughout the world because they have strong herbicidal effects at low doses. The compound inhibits the biosynthesis of fatty acid by acetyl CoA carboxylase inhibition with the active substance as carboxylic acid type. In Japan, the residues of quizalofop-ethyl, cyhalofop-butyl and fluazifop are known to be problems and test methods are prescribed by regulations. To determine the total amount of agrochemical residues, the amount of quizalofop content is measured by HPLC/LC-MS analysis after hydrolysis of quizalofop-ethyl. Fluazifop is detected by the GC/GC-MS analysis of the esters formed from butyl esterification after hydrolysis.

This data sheet introduces a simultaneous analysis of fluazifop, fluazifop-butyl, quizalofop and quizalofop-ethyl using electrospray ionization (ESI). The ESI method effectively ionizes carboxylic acid types (fluazifop and quizalofop) with negative ions, and the ester types (fluazifop-butyl and quizalofop-ethyl) by positive ions. The mass spectra of these compounds are shown in Fig. 1. These spectra confirm the deprotonated molecules (M-H) of the carboxylic type agricultural chemicals in negative ion mode, and the protonated molecules (M+H) of the ester type agricultural chemicals in positive ion mode.

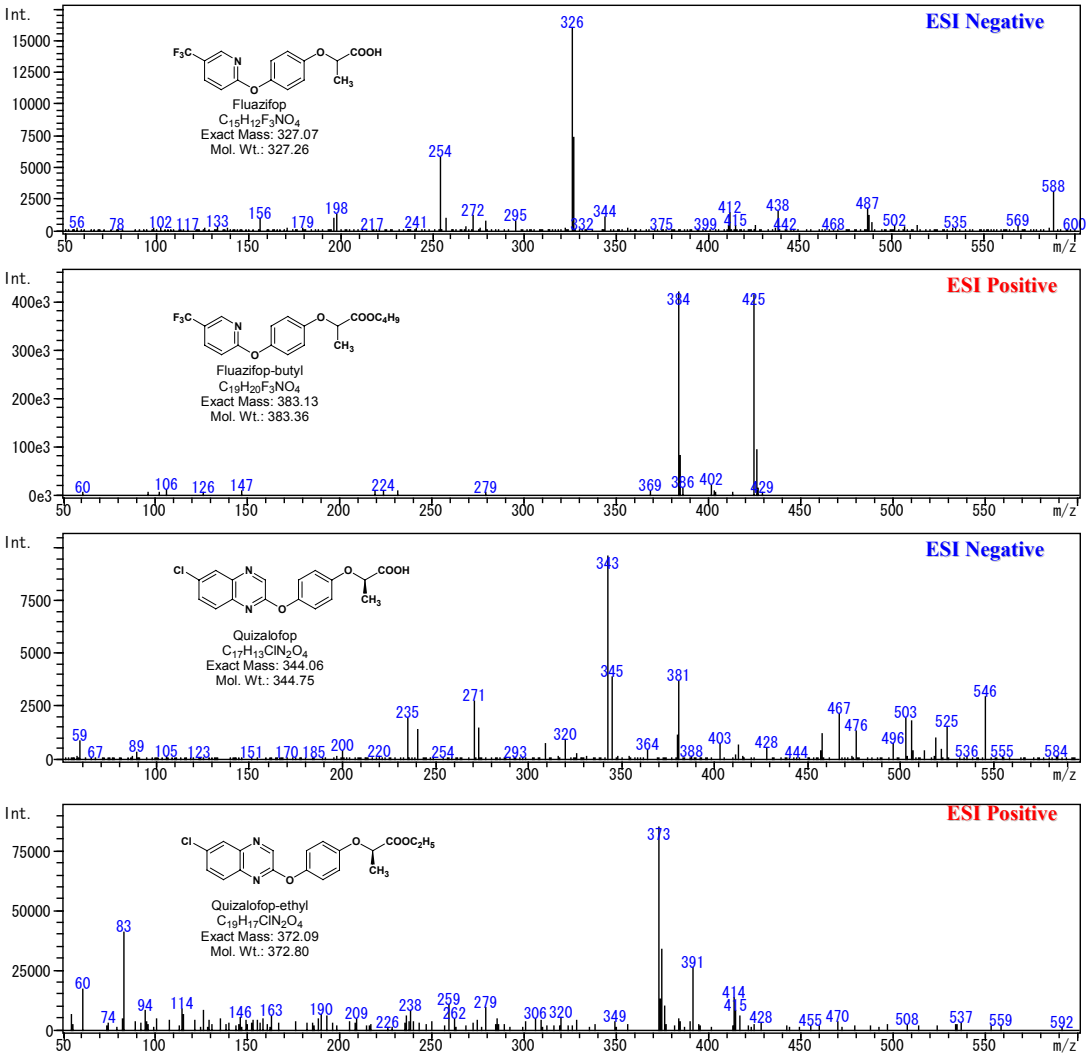

Fig. 1 ESI Mass Spectra of Phenoxypropionic Type Herbicides

When using a reversed-phase column, the retention time of ester types is longer than that of carboxylic acids. Therefore, it is possible to simultaneously analyze both carboxylic acid type and ester type agricultural chemicals, by first selecting negative ion detection, and then, after the carboxylic acid elution is complete, switching to positive ion detection (Fig. 2). This analysis produced a good calibration curve for each substance in concentration between 0.8 ppb to 500 ppb. Fig. 3 shows the calibration curve for fluazifop and the SIM chromatogram at 0.8 ppb.

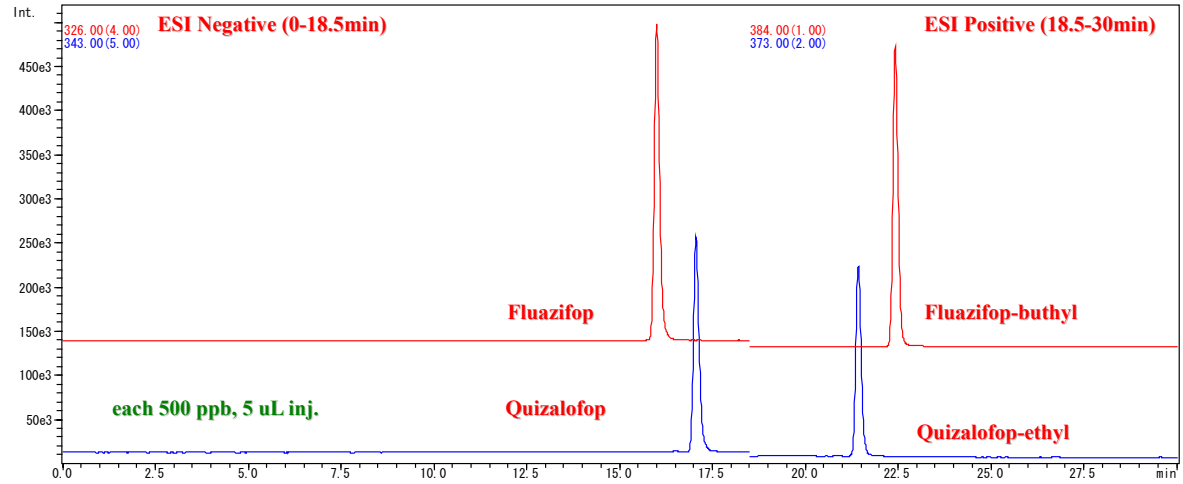

Fig. 2 ESI Mass Chromatograms of Phenoxypropionic Type Herbicides

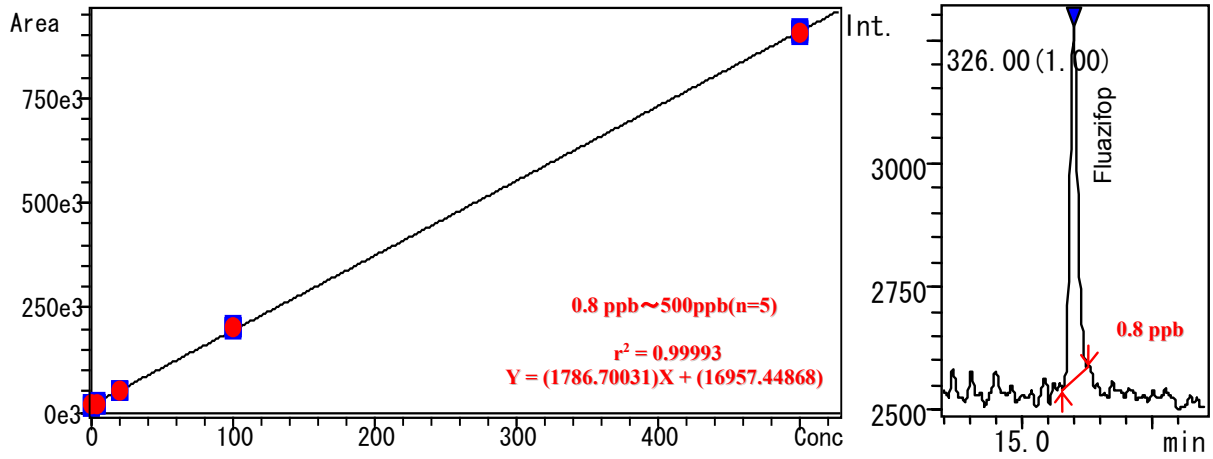

Fig. 3 Calibration curve and SIM Chromatogram of Fluazifop

Table 1 Analytical conditions for LC-MS

Column	: Shimadzu Shim-pack VP-ODS (2.0mmI.D.x 150mmL.)		
Mobile phase A	: water containing 0.1% formic acid		
Mobile phase B	: acetonitrile containing 0.1% formic acid		
Time program	: 20%B (0min)→ 90%B (20-30min)		
Flow late	:0.2mL/min		
Injection volume	: 5μL	**Column temperature**	: 40 ℃
Probe voltage	: -3.5kV (ESI-Negative mode), +4.5 kV (ESI-Positive mode)		
CDL temperature	: 200 ℃	**Block heater temperature**	: 200 ℃
Nebulizing gas flow	: 4.5 L/min		
Q-array DC voltage	: -30V, 10V	**Q-array RF voltage**	: 150
Scan range	: m/z 50-600(1.0sec/scan)		
SIM	: m/z 326, 343, 384, 373(0.5sec/ch)		

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