

# Development of simultaneous analysis method on organophosphorous pesticides and quaternary ammonium herbicides using LC/MS

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## Introduction

Organic pesticides are commonly used and often the related pesticide residue is analyzed by GC/MS and LC/MS. However, the measurement of ionized pesticides is more difficult than that of other pesticides. Organophosphorous pesticides and quaternary ammonium herbicides, such as glyphosate, glufosinate, paraquat and diquat, are used commonly in Japan as herbicide, because they are highly effective at blighting grass and are easy to use. However, special analytical conditions are required for LC/MS analysis of these compounds. Furthermore, it is difficult to measure them all simultaneously. We have attempted to develop a simultaneous analysis method on these organophosphorous pesticides and quaternary ammonium herbicides using LC/MS.

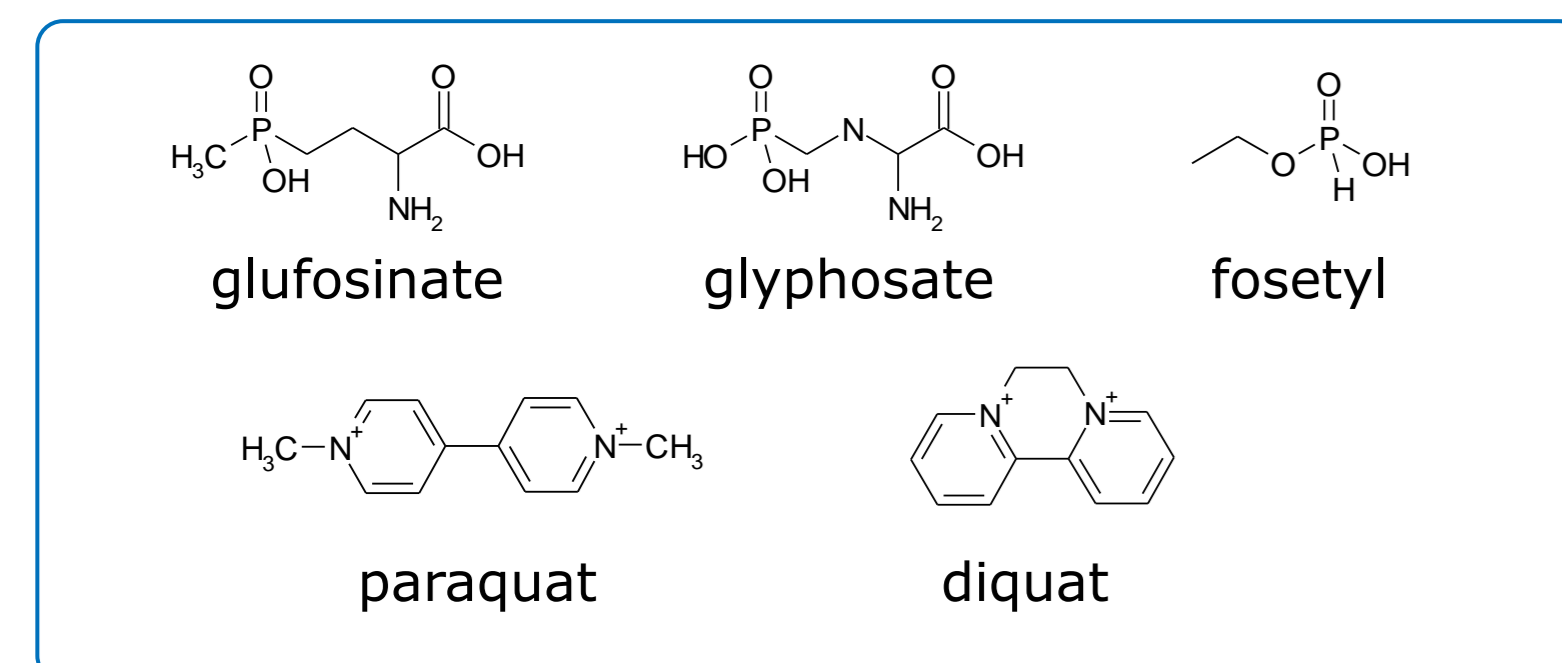


Fig. 1 Structure of pesticides

## Methods

Pesticides standards of glyphosate, glufosinate, fosetyl, paraquat and diquat were mixed and diluted then they were applied to LC/MS. Shimadzu 20A prominence HPLC system was connected to amaZon X ion trap mass spectrometer equipped with an ESI probe operated in positive / negative ion mode. When a common ODS column or HILIC column was used as a condition of HPLC, the analysis of the above pesticides was very difficult. So, we used a multimode column, Scherzo SM-C18. Pesticides were analyzed using double gradients with ammonium formate concentration and acetonitrile concentration.

## Results

At first we tried to analyze pesticides with standard reversed phase ODS columns in HPLC conditions. The result was that organophosphorous pesticides were eluted almost with void volume and quaternary ammonium herbicides were eluted with broad peak shapes, so this approach was not suitable. Then, the analysis was examined with Scherzo SM-C18, a multimode column with anion exchange, cation exchange, normal phase, and reversed phase. In this condition, all compounds were retained and had excellent peak shape. After investigating the concentration of salt and organic solvent in mobile phase, time program of gradient, etc, the five compounds that were targeted for this analysis were able to be separated under HPLC conditions.

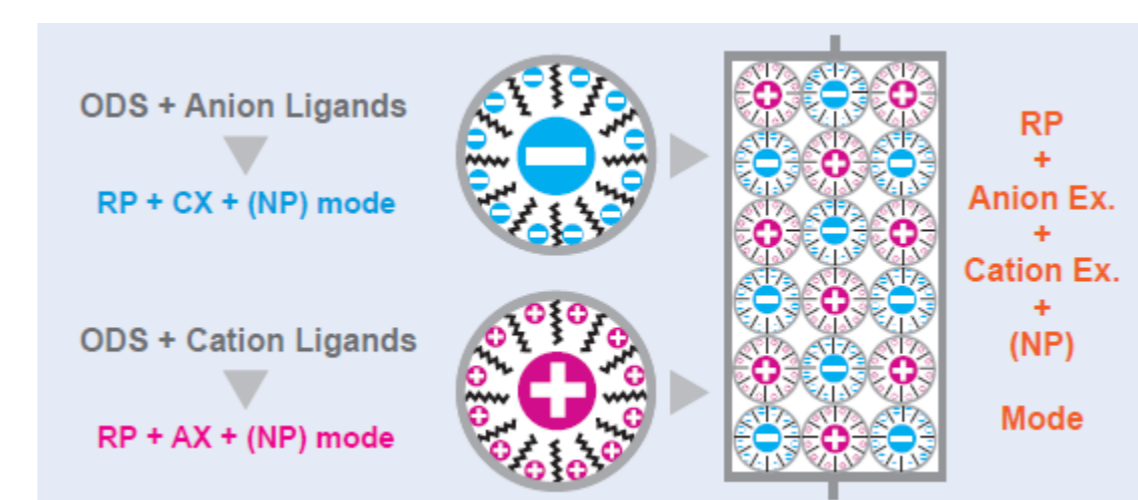


Fig. 2 Scherzo SM-C18 column; ODS column consists of C18+anion+cation ligand SM-C18 contains ODS+cation+anion ligands and can be used to separate highly polar compounds. Unlike other mixed-mode RP columns, Scherzo SM-C18 contains ODS ligands, and shows similar behavior to conventional ODS columns for non-ionic compounds. In addition, the IEX ligands on SM-C18 are highly polar and provide normal phase mode. This allows for both RP + NP separation mode.

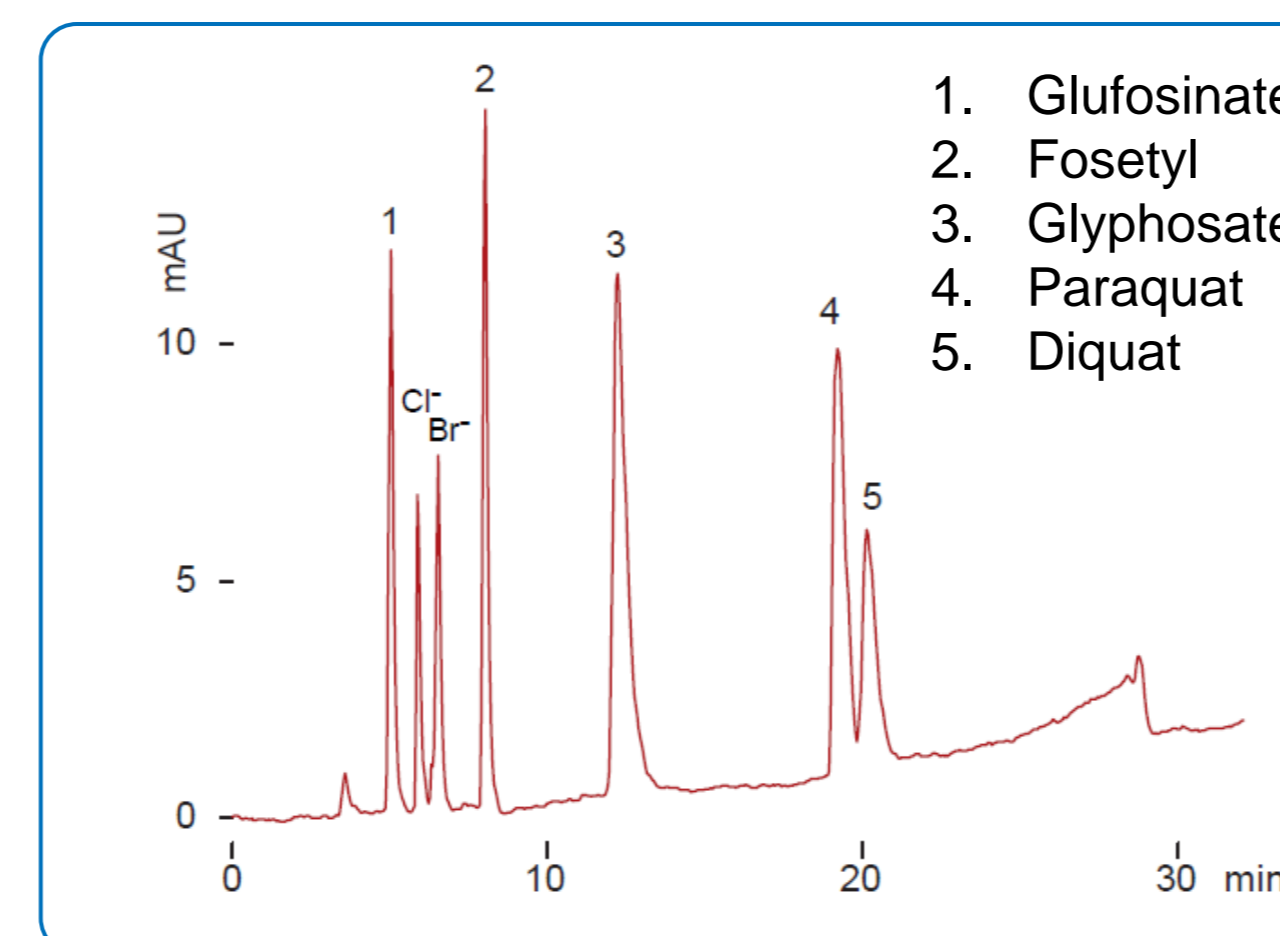


Fig. 3 HPLC simultaneous analysis of pesticides using Scherzo SM-C18 column  
HPLC condition; column size 250 x 3mm  
A: 5 mM ammonium formate  
B: 100 mM ammonium formate / acetonitrile = 25 / 75  
0-100 %B (0-25min), 0.4 mL/min (12MPa)  
37 deg.C, ELSD (spray chamber 10 deg.C, drift tube 50 deg.C)  
Sample amount: 5 uL (0.5-2ug)

Glufosinate, fosetyl, paraquat and diquat were able to be detected in one run of LC/MS by using ion trap mass spectrometer. The organophosphorous pesticides were detected in negative ion mode with MS, while quaternary ammonium herbicides were detected in positive ion mode.

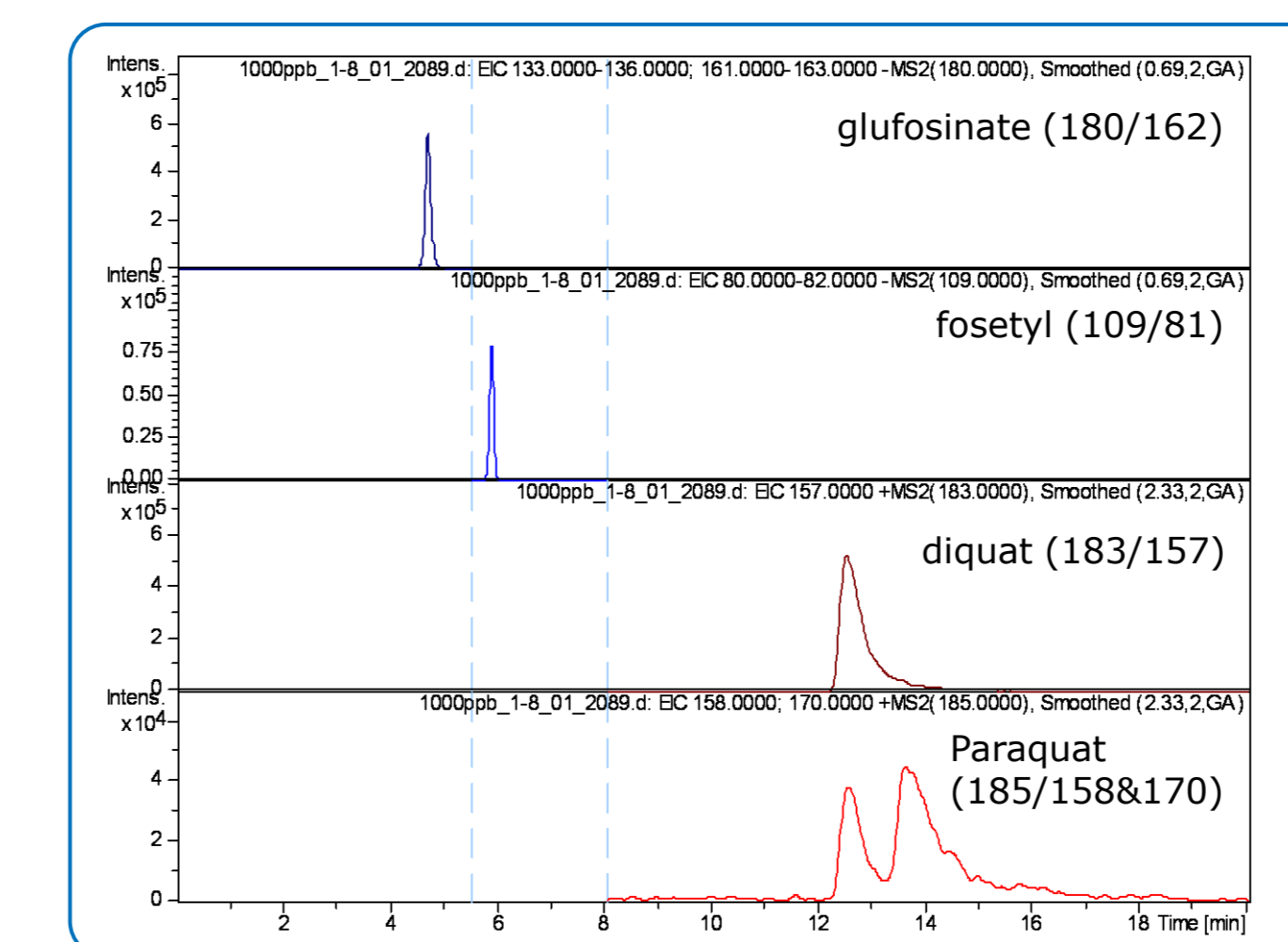


Fig. 4 LC/MS simultaneous analysis of pesticides  
HPLC condition; column size 250 x 3mm  
A: H<sub>2</sub>O  
B: 100 mM ammonium formate / acetonitrile = 10 / 90  
1-95 %B (0-10min), 0.4 mL/min  
40 deg.C  
Sample concentration: 1ppm each  
MS condition; amaZon X  
ESI, negative (0-8min) / positive (8-20min)



3D Ion Trap MS system  
amaZon X

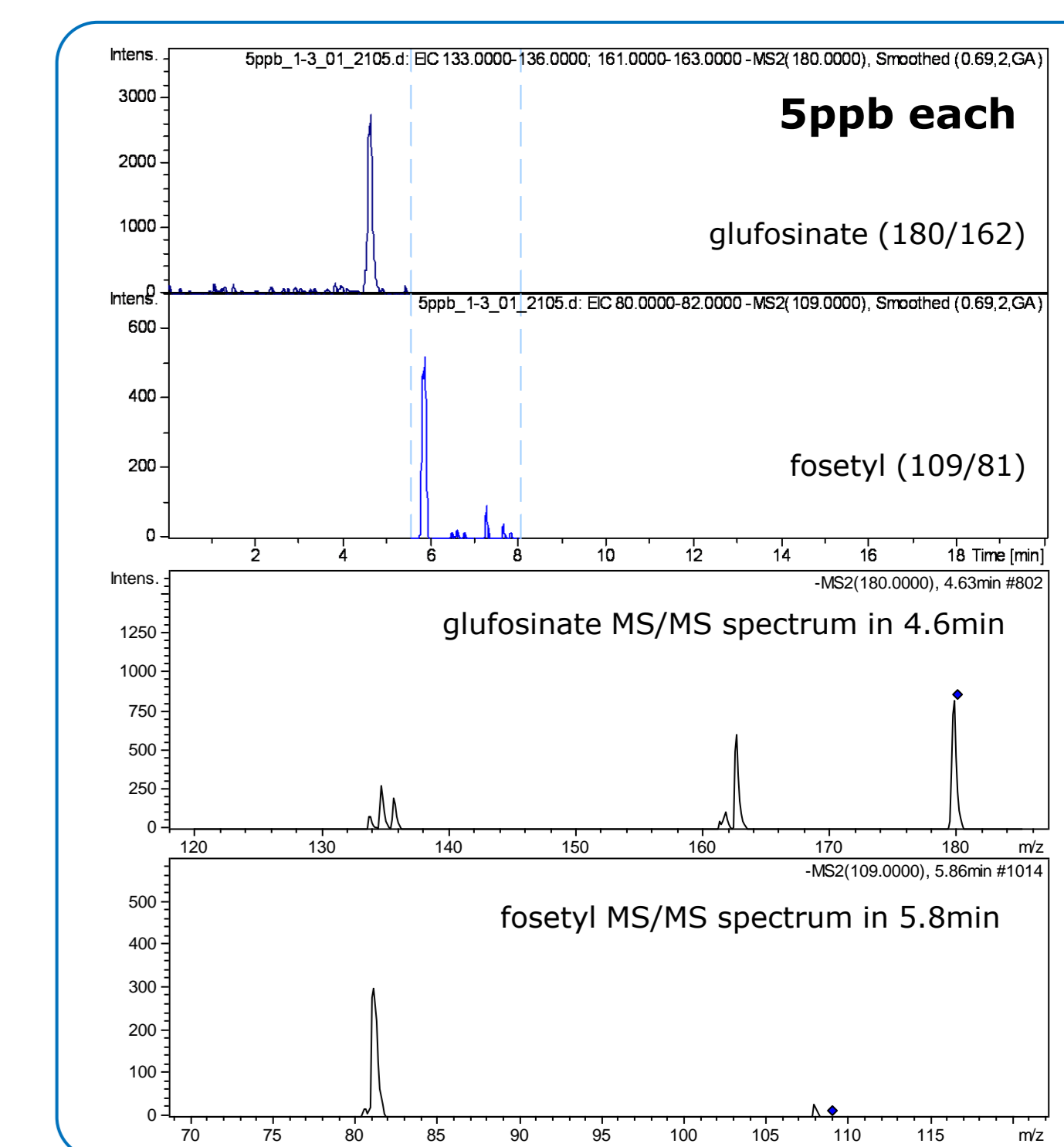


Fig. 5 LC/MS simultaneous analysis (2)  
LC/MS conditions were the same as that in Fig.4. 5ppb of each compounds were applied to LC/MS. This resulted in very high sensitivity analysis on glufosinate and fosetyl, which were acquired in ESI negative ion mode.

## Conclusions

- Organophosphorous pesticides and quaternary ammonium herbicides were analyzed simultaneously by multi-mode column Scherzo.
- These compound were detected in high sensitivity by 3D ion trap mass system, amaZon X.