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Application News

LCMS™-8050 High Performance Liquid Chromatograph Mass Spectrometer

Analysis of Glufosinate, Glyphosate, and AMPA in Tap Water Using Triple Quadrupole LC/MS/MS

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User Benefits

- Direct analysis of glufosinate, glyphosate, and AMPA is possible after derivatization.
- Analysis is possible at a concentration (0.2 µg/L) of no more than 1/100 of the target values specified in "Complementary Items to Set the Targets for Water Quality Management" (MHLW).
- Compounds in tap water can be analyzed with a satisfactory recovery rate.

■ Introduction

Glufosinate is widely used as an amino acid-based herbicide, and glyphosate is a widely-used foliage-applied herbicide. Glyphosate forms the aminomethylphosphonic acid (AMPA) when metabolized in soil or water.

As of March 2021, glufosinate, glyphosate, and AMPA are included in "Pesticides" (Item 15) of the target setting items in "Complementary Items to Set the Targets for Water Quality Management" established by Japan's Ministry of Health, Labour and Welfare (MHLW), with targets values of 0.02 mg/L for glufosinate and 2 mg/L for glyphosate and AMPA. As the analysis method, "Simultaneous analysis by derivatization-solid phase extraction-liquid chromatograph-mass spectrometer" is specified in Appendix Method 22 [(1)] of Inspection Methods for Complementary Items.

This article introduces an example of an analysis of glufosinate, glyphosate, and AMPA without concentration by solid-phase extraction (SPE) specified in Appendix Method 22 using a Shimadzu LCMS-8050. A satisfactory recovery rate was obtained for all three compounds at a concentration of 0.2 µg/L, which is 1/100 of the target value or less, confirming that highly precise analysis is possible.

■ Derivatization of Samples

The samples were derivatized using 9-fluorenylmethyl chloroformate (FMOC-Cl) under a basic condition in accordance with Appendix Method 22. Fig. 1 shows the structural formulas of the derivatized glufosinate, glyphosate, and AMPA. Fig. 2 shows the workflow of derivatization.

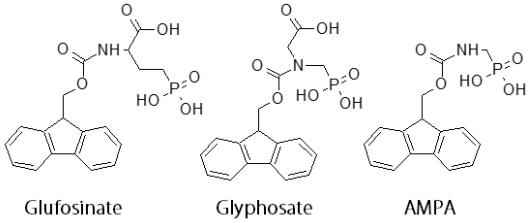

Fig. 1 Structures of FMOC Derivatives

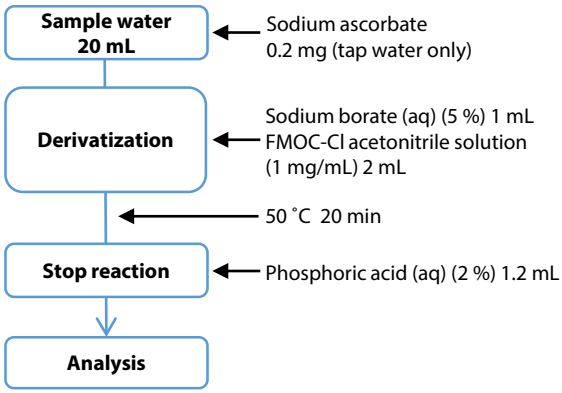

Fig. 2 Workflow of Derivatization

■ MRM Chromatogram of Glufosinate, Glyphosate, and AMPA

A mixed standard solution of glufosinate, glyphosate, and AMPA (0.1 µg/L each) was derivatized in accordance with the derivatization workflow in Fig. 2. Fig. 3 shows the MRM chromatogram of the sample measured under the conditions shown in Table 1. The results confirmed that detection of all three compounds is amply possible, even at a concentration of no more than 1/100 of the target values.

Table 1 Analytical Conditions

[HPLC conditions] (Nexera™ X3)		
Column	: Mastro 2 C18 (Shimadzu GLC) (100 mm × 2.0 mm I.D., 3 µm) P/N: 370-01005-64	
Mobile phases	: A) 5 mmol/L Ammonium acetate in H_2O B) Acetonitrile	
Gradient Program	: B 5 % (0 min) – 50 % (7.00 min) – 95 % (7.01 – 11 min) – 5 % (11.01 – 13 min)	
Flow rate	: 0.25 mL/min	
Column Temp.	: 40 ˚C	
Injection volume	: 20 µL	
[MS conditions] (LCMS-8050)		
Ionization	: ESI (Negative mode)	
Probe Voltage	: -3 kV	
Nebulizing gas flow	: 2 L/min	
Drying gas flow	: 10 L/min	
Heating gas flow	: 10 L/min	
DL temp.	: 150 ˚C	
Heat Block Temp.	: 400 ˚C	
Interface Temp.	: 300 ˚C	
MRM transition	: Glufosinate	*m/z* 402.10>180.10
	Glyphosate	*m/z* 390.05>168.05
	AMPA	*m/z* 332.05>110.05

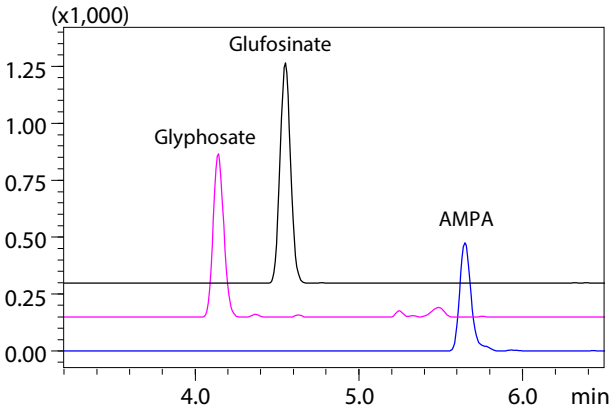

Fig. 3 MRM Chromatogram of Compounds (0.1 µg/L each)

■ Calibration Curves of Glufosinate, Glyphosate, and AMPA

Fig. 4 shows the calibration curves for glufosinate, glyphosate, and AMPA in the concentration range of 0.1 to 3 µg/L (4 points).

The correlation coefficient (r^2) of the calibration curves was $r^2 > 0.998$ for the three compounds, confirming satisfactory linearity of all calibration curves.

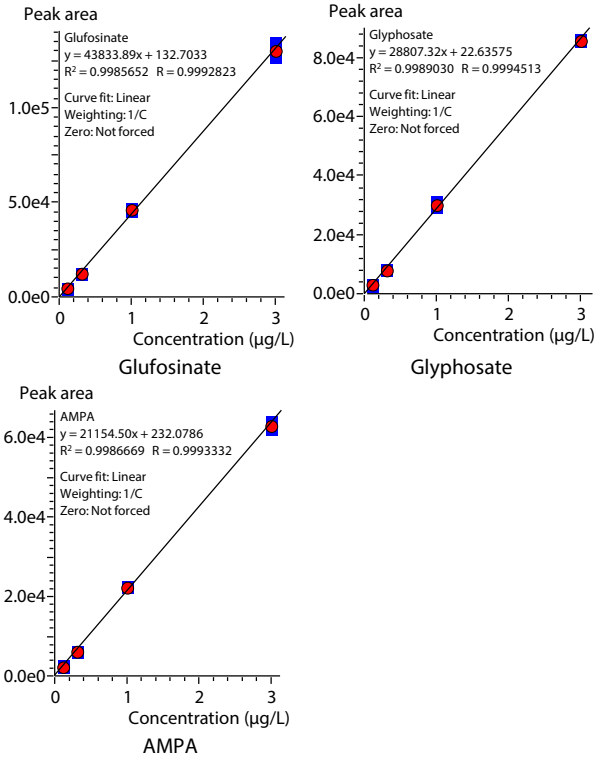

Fig. 4 Calibration Curves of Compounds

■ Analysis of Tap Water

A spike-and-recovery test was conducted using tap water sampled in Kanagawa Prefecture. The sampled tap water was dechlorinated by adding sodium ascorbate. The concentrations of glufosinate, glyphosate, and AMPA in the dechlorinated samples were then adjusted to 0.2 µg/L, and the derivatization was carried out by the derivatization procedure in Fig. 2.

Table 2 shows the results of the spike-and-recovery test of the tap water. Fig. 5 shows the MRM chromatograms of the unspiked tap water (blank) and samples spiked with 0.2 µg/L of each of the target compounds.

Satisfactory results were obtained, as the recovery rates were 97 % for glufosinate, 91 % for glyphosate, and 89 % for AMPA, and the repeatability accuracy (concentration %RSD) of all three compounds satisfied <10 %. Thus, this experiment confirmed that tap water can also by analyzed with good precision.

Table 2 Results of Spike-and-Recovery Test of Tap Water (n = 5)

Compound	Recovery rate (%) (0.2 µg/L)	Repeatability accuracy (concentration %RSD)
Glufosinate	97	2.0
Glyphosate	91	6.3
AMPA	89	4.0

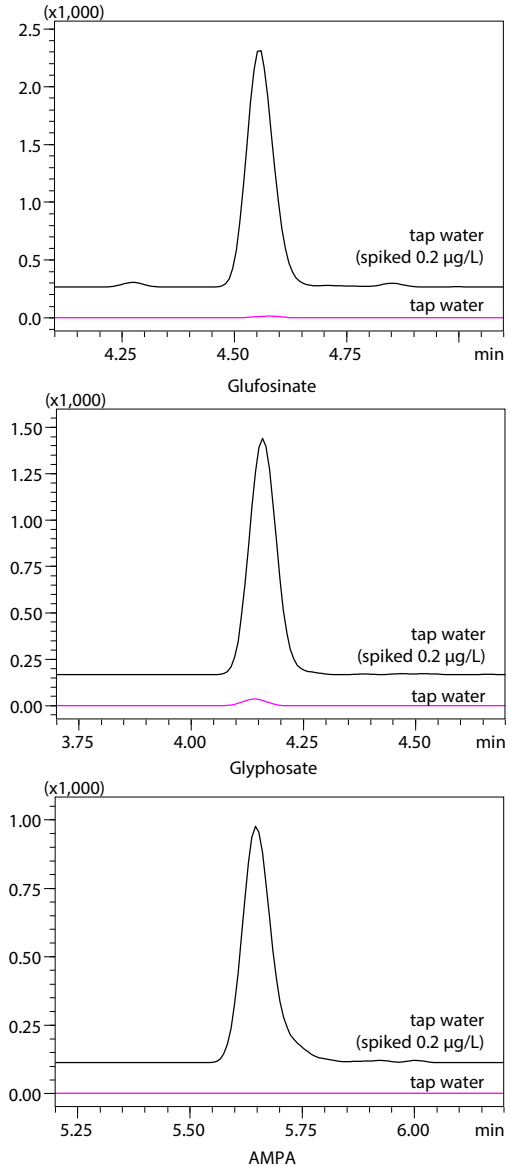

Fig. 5 MRM Chromatograms of Tap Water (Blank) and Spiked Tap Water Samples

■ Conclusion

- In an analysis using a Shimadzu LCMS-8050, high sensitivity was obtained at a concentration (0.1 µg/L) of no more than 1/100 of the target values specified in "Complementary Items to Set the Targets for Water Quality Management."
- Satisfactory recovery rates and repeatability were obtained in a spike-and-recovery test of tap water samples, demonstrating that glufosinate, glyphosate, and AMPA in tap water can be analyzed with high precision by this method after derivatization, without the solid-phase extraction process specified in Appendix Method 22.

<Reference>

(1) Enactment of Ministerial Ordinances on Water Quality Standards and Partial Revisions to Waterworks Law Enforcement Regulations, and Points to Note in Waterworks Water Quality Control (October 10, 2003, Kensui No. 1010001 [Final revision March 30, 2020, Yakuseisui 0330, No. 1]), Appendix 4 Inspection Methods for Complementary Items to Set the Targets for Water Quality Management.

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