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Application News

LCMS-8050 High Performance Liquid Chromatograph Mass Spectrometer

Direct Analysis of Iminoctadine, Diquat and Paraquat in Tap Water Using a Triple Quadrupole Mass Spectrometer

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User Benefits

- Makes it possible to analyze concentrations down to 1/100 of the target value of the "Targets for Water Quality Management in Japan" without solid-phase extraction, thus saving time and labor in pretreatment.
- Contributes to a reduction in variation of quantitation result due to factors such as operator technical skill thanks to the elimination of the pretreatment process.

■ Introduction

Iminoctadine is a pesticide widely used as a fungicide, and diquat and paraquat are pesticides widely used as herbicides. Target values (0.006 mg/L for iminoctadine, 0.01 mg/L for diquat, 0.005 mg/L for paraquat) for water supplies in Japan are specified in “Complementary Items to Set the Targets for Water Quality Management” [1]. In Method 21 in the Appendix to “Complementary Items to Set the Targets for Water Quality Management,” a sample concentrated 50 times is analyzed by LC-MS/MS using solid-phase extraction [2]. This article introduces the analysis results obtained by directly injecting tap water without solid phase extraction.

■ Preparation for Calibration Curve Samples

Calibration curve samples were prepared in the concentrations 0.02, 0.025, 0.05, 0.25, 0.5, and 2.5 µg/L. A mixture with the ratio of ultrapure water : (acetonitrile : formic acid = 9:1) =1 : 1 was used as the sample solvent.

■ Preparation for Tap Water

The tap water was sampled in Kyoto City, and sodium thiosulfate was added at a concentration of 0.02 g/L for dechlorination. Using this dechlorinated tap water, a mixture with the ratio of tap water : (acetonitrile : formic acid = 9 : 1) = 1 : 1 was used as the sample for analysis. Spiked samples were prepared by adding 0.5 and 0.05 µg/L of each compound (equivalent to 1/10 or 1/100 of the target concentration) to the tap water.

■ Analysis Conditions

Table 1 shows the analysis conditions. A Shim-pack Velox™ HILIC analytical column was used for HPLC separation.

Table 1 LCMS Analysis Conditions

[HPLC conditions] (Nexera™ X3)	
Column	: Shim-pack Velox HILIC *1 (100 mmL. x 2.1 mmI.D., 2.7 µm)
Mobile Phases	: A) 150 mmol/L Ammonium formate buffer (pH 3.6) B) Acetonitrile Isocratic, B conc. 50%
Flowrate	: 0.40 mL/min
Column Temp.	: 30 °C
Injection Volume	: 5 µL
[MS conditions] (LCMS -8050)	
Ionization	: ESI (Positive mode)
Probe Voltage	: +0.5 kV
Mode	: MRM
Nebulizing Gas Flow	: 3.0 L/min
Heating Gas Flow	: 15.0 L/min
Drying Gas Flow	: 5 L/min
DL Temp.	: 300 °C
Heat Block Temp.	: 500 °C
Interface Temp.	: 400 °C
MRM Transitions	: Iminoctadine 178.90>69.10 Diquat 183.10>157.10 Paraquat 186.10>171.10

*1 P/N: 227-32025-03

■ Result of Standard Samples

The calibration curve samples in the range 0.02 to 2.5 µg/mL were analyzed five times, and the linearity and repeatability of the results were investigated. It was confirmed that the accuracy of each calibration point was within the range of 80 to 120%. Fig. 1 shows the calibration curves and chromatograms around the LLOQ (0.02 µg/L standard sample), and Fig. 2 shows the chromatograms of the 2.5 µg/L standard sample.

This analysis method provided good linearity, as shown by a contribution rate (R2) > 0.998 for all compounds in the range of 0.02 to 2.5 µg/L. Calibration curve ranges are shown in Table 2.

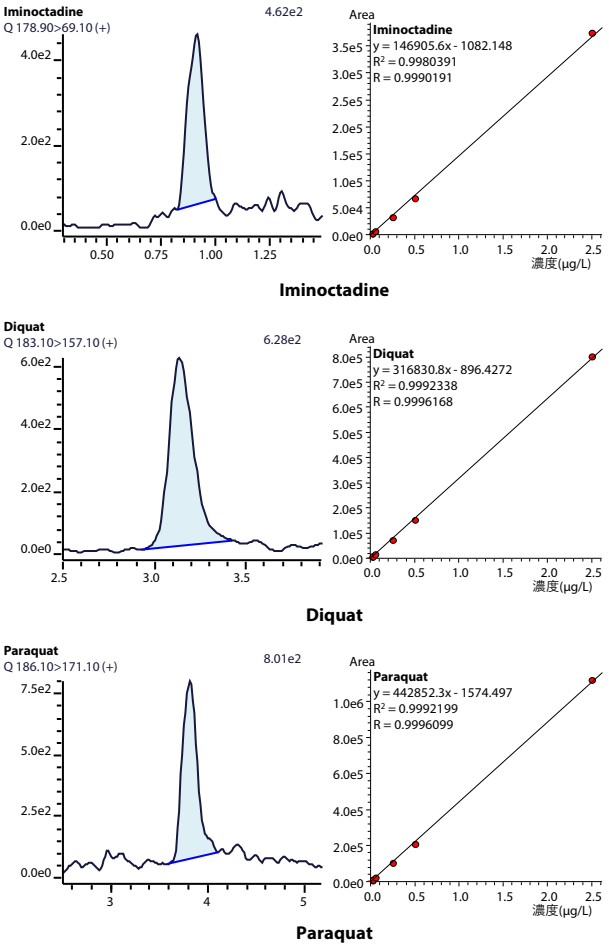

Fig.1 Chromatograms and calibration curves of 0.02 µg/L standard sample

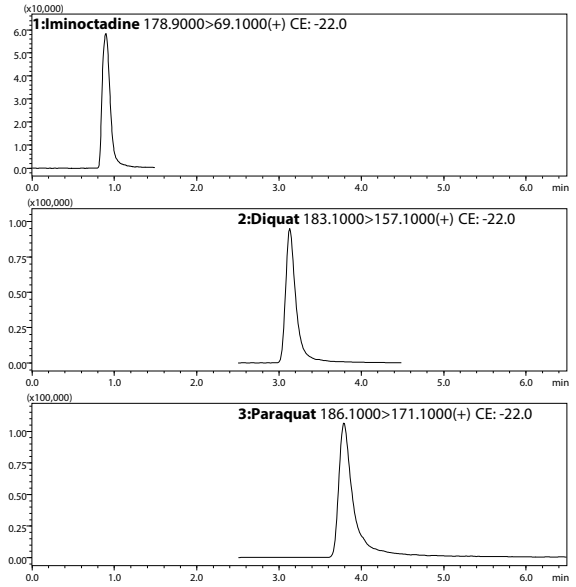

Fig.2 Chromatograms of 2.5 µg/L standard sample

Table 2 Calibration Curve Range and Contribution Ratio (R^2)

Compound	Calibration curve (µg/L)			Contribution ratio (R^2)
Iminoctadine	0.02	-	2.5	0.998
Diquat	0.02	-	2.5	0.999
Paraquat	0.02	-	2.5	0.999

■ Spike and Recovery Test on Tap Water

Table 3 shows accuracy and repeatability after analyzing spike and recovery test samples five times. Figure 3 shows the chromatograms of blank tap water and spiked tap water. For all the compounds, no interference peaks due to impurities in the tap water were identified, and good results were obtained at concentrations that included 1/100 of the target value, which meets the accuracy targets set out in the guidelines for the appropriateness of a tap water quality test in Japan.

Table 3 Accuracy and Repeatability

Compound	Spiked at 0.05 µg/L		Spiked at 0.5 µg/L	
	Accuracy (Average)	Repeatability (Conc. CV%)	Accuracy (Average)	Repeatability (Conc. CV%)
Iminoctadine	106.5%	5.9%	103.0%	4.4%
Diquat	104.6%	6.1%	94.7%	2.8%
Paraquat	106.3%	5.5%	98.7%	3.4%

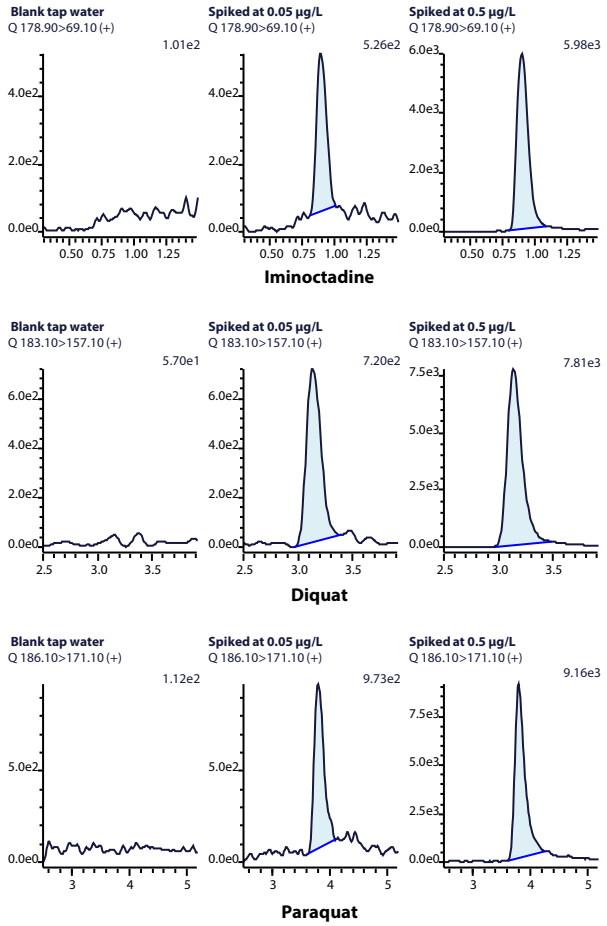

Fig.3 Chromatograms of Blank Tap Water and Spiked Tap Water

■ Conclusion

- Good recovery rates and repeatability were obtained in the spike and recovery test for tap water samples.
- We confirmed that this analysis method can accurately analyze iminoctadine, diquat, and paraquat in tap water even if the solid-phase extraction process specified in Appendix Method 21 is omitted.

<References>
1) Notice from Ministry of Health, Labour and Welfare ""Enactment of the Ministerial Ordinance on Water Quality Standards and Partial Amendment to the Enforcement Regulations of the Water Supply Act, etc. "" (October 10, 2003, No. 1010004, Health Service Bureau [last revision: March 26, 2021, No. 0326-8, Policy Planning Division for Environmental Health and Food Safety) Appendix 2: Targeted pesticides list of Pesticides (Complementary Items to Set the Targets for Water Quality Management No. 15)
2) Notice from Ministry of Health, Labour and Welfare ""Appendix 4 Inspection Methods for Complementary Items to Set the Targets for Water Quality Management"" (October 10, 2003, No. 1010001, Health Service Bureau [last revision: March 26, 2021])

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