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Application News

No.C129A

Liquid Chromatography Mass Spectrometry

Analysis of Iminoctadine, Paraquat, and Diquat in Tap Water Using Triple Quadrupole LC/MS/MS [LCMS-8050]

Iminoctadine is used as an antimicrobial agent, and paraquat and diquat are used as non-selective herbicides. By the director of Water Supply Division, Health Service Bureau, Ministry of Health, Labour and Welfare (0325 No. 3 to 6) in March 2015, a notification of "simultaneous analysis using solid-phase extraction-liquid chromatograph-mass spectrometer" (appendix method 21) was issued as a method for testing the presence of these three pesticides in tap water.
This article describes an example of analysis of iminoctadine, paraquat, and diquat performed according to appendix method 21. Also described is an investigation into a simplified method that omits part of the sample pretreatment process.

Sample Pretreatment

The pretreatment process for tap water samples described in appendix method 21 involves dechlorination with sodium thiosulfate, followed by solid phase extraction in a solid phase column with divinylbenzene-N-vinylpyrrolidone copolymer with introduced carboxyl groups. The resulting eluate is then concentrated by blowing nitrogen gas, filled to volume with a mixture of acetonitrile and formic acid, then analyzed by LC/MS/MS. Fig. 1 shows a flowchart of the pretreatment process.
An important part of the pretreatment process is to prevent adsorption of sample constituents onto containers and other equipment. This is achieved by ensuring all containers and tools that come into contact with samples are made from polytetrafluoroethylene (PTFE) or polypropylene (PP) and rinsed thoroughly with purified water.

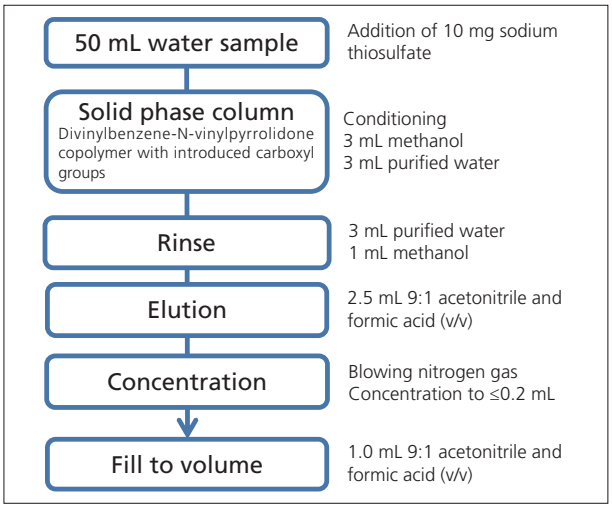

Fig. 1 Pretreatment Process

Analysis of Iminoctadine, Paraquat, and Diquat Standard Mixture

MRM chromatograms obtained from a standard mixture of iminoctadine, paraquat, and diquat (0.25 µg/L each) are shown in Fig. 2. Iminoctadine was detected at 1.5 min, paraquat at 4.9 min, and diquat at 5.7 min. The analytical conditions used are shown in Table 3.

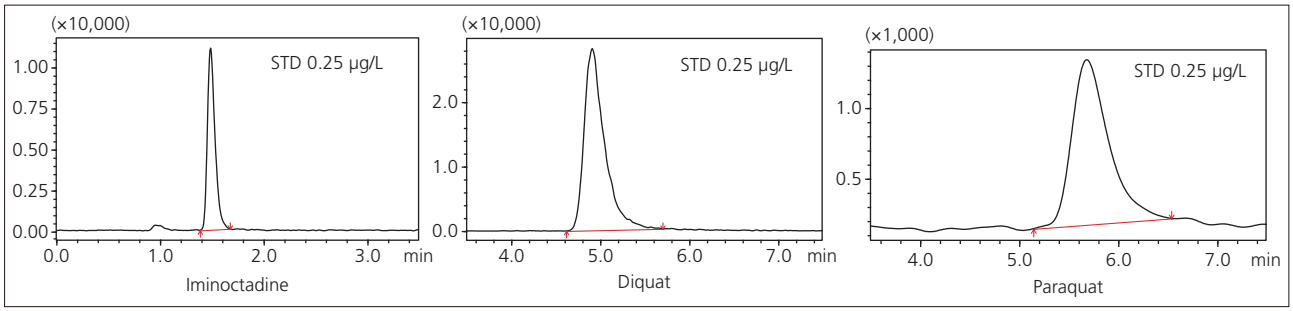

Fig. 2 MRM Chromatograms of Iminoctadine, Paraquat, and Diquat Standard Mixture

Spike and Recovery Test Using Tap Water

Spike and recovery test using tap water was performed. Chromatograms of a tap water blank, tap water spiked with each compound at 0.05 µg/L (approximately 1/100 the target threshold concentration), and tap water spiked with each compound at 0.25 µg/L (approximately 1/20 the target threshold concentration) are shown in Fig. 3, and recovery obtained during testing is shown in Table 1. There was no marked interference by contaminants present in tap water, and results were obtained that met the accuracy target (70 % to 120 %) according to validity evaluation guidelines for tap water quality test methods.

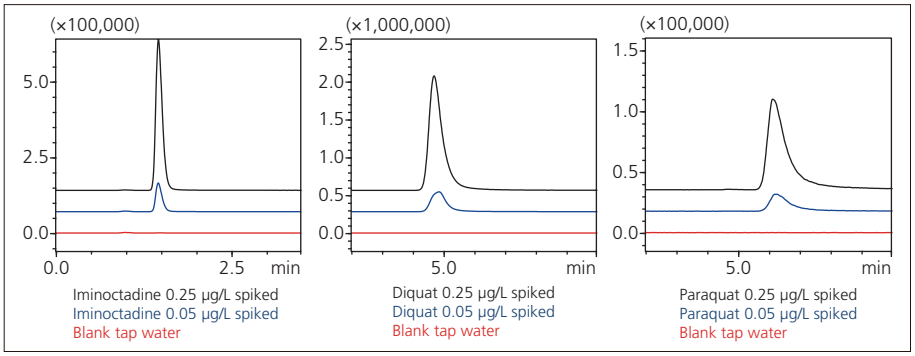

Fig. 3 MRM Chromatograms of Tap Water Blank and Tap Water Spiked with Iminoctadine, Paraquat, and Diquat

Table 1 Spike and Recovery Test Results

Compound	Recovery (%)	
	0.05 µg/L	0.25 µg/L
Iminoctadine	85.1	91.0
Paraquat	92.9	94.2
Diquat	86.8	91.7

n = 3

Simplified Sample Pretreatment by Omitting N_2 Evaporation

A simplified analytical method that omits the concentration step from sample pretreatment was investigated. After performing solid phase extraction as shown in Fig. 1, eluate was made up to 5 mL with a mixture of acetonitrile and formic acid without concentration, then analyzed by LC/MS/MS. From the results obtained from the same spike and recovery test as above, Fig. 4 shows chromatograms for each tap water sample and Table 2 shows recovery. Using a simplified analytical method that omits concentration revealed no marked interference by contaminants present in tap water, and provided results that met the accuracy target according to validity evaluation guidelines.

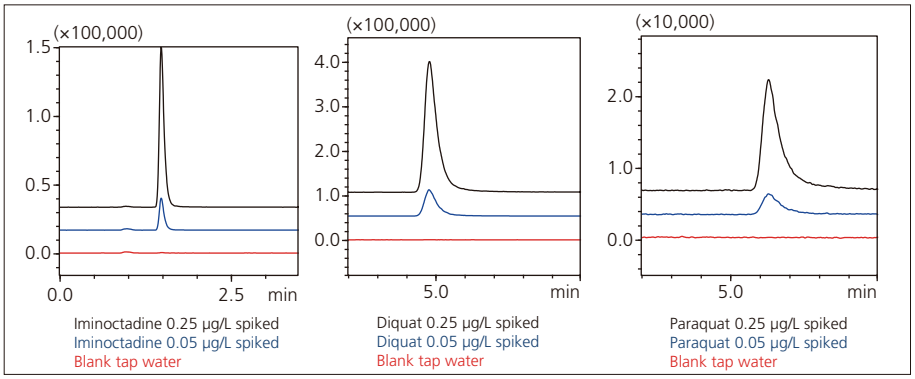

Fig. 4 MRM Chromatograms of Tap Water Samples Using a Simplified Sample Pretreatment

Table 2 Spike and Recovery Test Results Using Simplified Sample Pretreatment

Compound	Recovery (%)	
	0.05 µg/L	0.25 µg/L
Iminoctadine	85.2	85.2
Paraquat	95.5	93.7
Diquat	95.1	90.2

n = 3

Table 3 Analytical Conditions

Column	: Inertsil WP300 SIL (100 mm L. × 2.1 mm I.D., 3 µm, GL Sciences)
Mobile Phases	: 150 mmol/L Ammonium formate - water / Acetonitrile = 40 / 60 (v/v)
Flowrate	: 0.3 mL/min
Column Temperature	: 30 ˚C
Injection Volume	: 5 µL
Probe Voltage	: 1 kV (ESI-Positive)
DL Temperature	: 300 ˚C
Block Heater Temperature	: 500 ˚C
Interface Temperature	: 400 ˚C
Nebulizing Gas Flow	: 3 L/min
Drying Gas Flow	: 5 L/min
Heating Gas Flow	: 15 L/min
MRM Transition	: Iminoctadine *m/z* 179>69 Paraquat *m/z* 171>77 Diquat *m/z* 183>157

First Edition: May, 2016
(Second Edition: October 2016)

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