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Oasis® WCX: A Novel Mixed-Mode SPE Sorbent for LC–MS Determination of Paraquat and Other Quaternary Ammonium Compounds

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Oasis® WCX, a mixed-mode weak cation-exchange SPE cartridge, provides unique retention of paraquat and related compounds. An Atlantis® HILIC column was utilized for HPLC using no ion-pairing reagents.

Paraquat and diquat, quaternary ammonium compounds (quats), are high-use agricultural chemicals. The 1997 USGS estimated use of the herbicide paraquat was over 3,000,000 lb, and the estimated use of diquat was about 200,000 lb (see Figure 1).

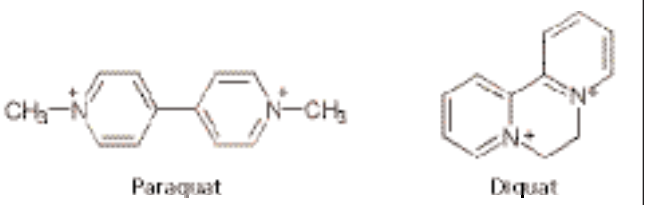

Figure 1: The structures of paraquat and diquat.

Because these substances are ionic, solid-phase extraction (SPE) and HPLC usually have been accomplished with the aid of an ion-pairing reagent such as an alkyl sulphonic acid. Liquid chromatography (LC)–mass spectrometry (MS) provides the analyst with a more sensitive and highly selective analytical method for these compounds. Strong cation exchange-based SPE methods (Oasis® MCX) that do not require ion-pairing reagents have been employed successfully for quats SPE using LC–UV, but the strong salts or strong acids used for elution are difficult to remove and are serious impediments to optimal LC–MS analysis. In order to overcome these problems, a new type of sorbent has been developed for the retention of quaternary ammonium compounds and strongly basic organic compounds. The Oasis® WCX sorbent incorporates a weak cation-exchanger bound to a polymeric reversed-phase particle.

Using the new sorbent and HILIC-based tandem LC–MS, the quantitation limit for paraquat is below 100 ng/L (ppt) using only 20 mL of sample. Prior methods required larger sample volumes and were better suited for LC–UV.

Experimental Conditions

Instruments: Waters Alliance® 2695 separations module equipped with column heater and sample chiller, Waters/Micromass Quattro Micro™ mass spectrometer, Waters 2487 dual wavelength UV detector.

Sample Preparation

A 20-mL river water sample was adjusted to pH 7 by dropwise addition of 1 M ammonium phosphate buffer.

SPE Procedure

1. Condition a 60 mg, 3 cc Oasis® WCX SPE cartridge with 1 mL methanol and 1 mL water.
2. Load 20-mL river water sample.
3. Wash the cartridge with 1 mL of 10 mM pH 7 phosphate buffer, 1 mL water, and 1 mL of methanol.
4. Elute with 1.5 mL ACN/water/TFA 84:14:2.
5. Reconstitute in 0.5-mL mobile phase.

LC Conditions

Column: Atlantis® HILIC, 2.1 × 150 mm, 3.5 µm
Mobile phase: 40% acetonitrile, 60% aqueous buffer pH 3.7 (250 mM ammonium formate)
Flow rate: 0.4 mL/min
Injection volume: 20: µL
Column temperature: 30 °C

Alternate column for LC–UV: Atlantis dC18, 2.1 × 150, 3.5 µm
Mobile phase: 25:75 acetonitrile/0.1% heptafluorobutyric acid in water
Flow rate: 0.3 mL/min
Injection volume: 20: µL
Column temperature: 30 °C

Monitored MS Transitions

Table I: MS transitions for paraquat and diquat

Compound	MW	MRM	Cone Voltage	Collision Energy
Paraquat	261	171 > 77	40	35
		171 > 155	40	35
Diquat	319	183 > 157	40	30
		183 > 168	40	35

Results and Discussion

A typical matrix-matched calibration curve was linear in the range from 0.1 to 10 µg/L using 20-mL samples of river water. Limit of quantitation is below 0.2 µg/L. Figure 2 shows a chromatogram obtained from a 0.5-µg/L spiked sample using HILIC chromatography.

A series of 1-µg/L (1 ppb) spiked samples was analyzed over a five-day period, five replicates/day. The results are summarized in Table II.

Table II: Intraday results obtained from spiked river water samples (spike level 1.0 µg/L)

Paraquat	Diquat
Day 1 1.08 µg/L (8.1% RSD)	Day 1 1.05 µg/L (2.9% RSD)
Day 4 1.10 µg/L (8.0% RSD)	Day 4 1.09 µg/L (5.9% RSD)
Day 5 0.95 µg/L (7.1% RSD)	Day 5 1.08 µg/L (4.4% RSD)
Overall (n = 15) 1.04 mg/L (9.8% RSD)	Overall (n = 15) 1.08 mg/L (4.8% RSD)

Although LC–MS might be preferable for this analysis, the Oasis® WCX SPE protocol is certainly compatible with ion-pair LC–UV analysis. Figure 3 shows a typical separation for a 0.5-µg/L spiked sample using ion-pairing chromatography on an Atlantis® dC18 column. However, the ion-pairing method should not be used for high sensitivity LC–MS analysis. The inset (Figure 2) shows the relative LC–MS response obtained for the same standard using the HILIC method compared with the ion-pairing method.

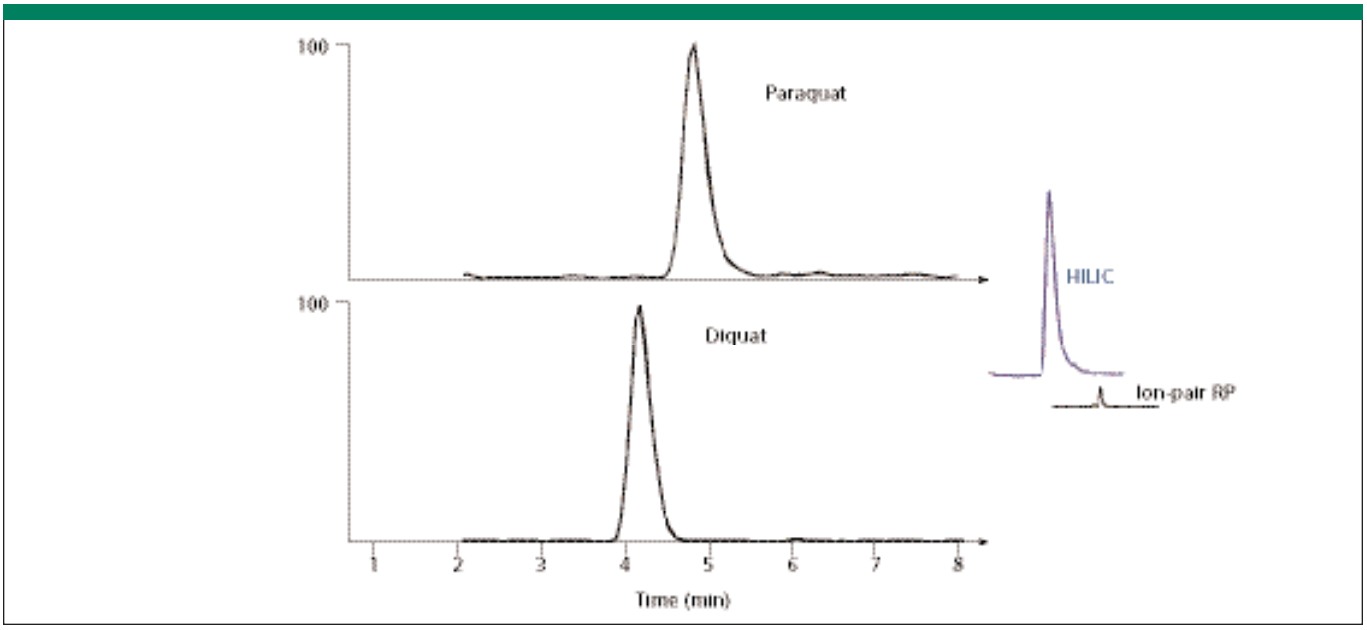

Figure 2: LC–MS chromatogram showing the separation of paraquat and diquat at 0.5 µg/L using the Atlantis HILIC analytical column. Inset shows the relative LC–MS response for HILIC compared with ion-pair reversed-phase chromatography.

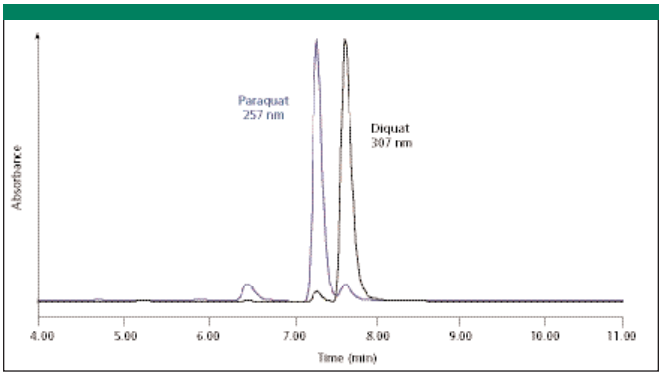

Figure 3: LC–UV chromatogram showing the separation of paraquat and diquat at 0.5 µg/L using the Atlantis dC18 analytical column. The aqueous mobile phase contained 0.1% heptafluorobutyric acid as ion-pairing reagent.

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