Application Note: ANCCSDIQPAQSYN

HILIC Method for the Separation of Diquat and Paraquat

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Key Words

- Paraquat
- Diquat
- Quaternary amines
- Syncronis HILIC
- EPA

Abstract

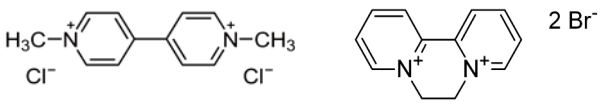
This application note demonstrates the use of the Thermo Scientific Syncronis HILIC column for the fast analysis of the quaternary ammonium herbicides paraquat and diquat.

Introduction

Paraquat and diquat are non-selective contact herbicides, widely used to control crop and aquatic weeds [1]. Paraquat and diquat have high water solubility, making them easily absorbed into the soil and potentially into drinking water supplies. Because of their significant toxicity to humans, these compounds have been banned, or their use restricted, in several European countries and in Japan.

The World Health Organization considers paraquat and diquat moderately hazardous pesticides and they must be routinely monitored [2].

The structures of these compounds are shown in Figure 1.



A. B.

Figure 1: Structure of paraquat (A) and diquat (B)

These highly charged quaternary amines cannot be retained in conventional reversed-phase.

An alternative separation and retention method is offered by hydrophilic interaction liquid chromatography (HILIC), a technique suitable for the retention of very polar and hydrophilic compounds. In HILIC the stationary phase is hydrophilic and often charged; the mobile phase typically consists of 60-95% acetonitrile in water, or a volatile buffer. In HILIC, water (or the aqueous buffer) acts as the strong eluent, necessary to establish a water-rich liquid layer near the stationary phase surface. Separation is achieved by partitioning of analytes from the mobile phase to the water-rich layer. When using charged HILIC stationary phases, secondary electrostatic interactions can also contribute to retention and selectivity. Zwitterionic stationary phases are successfully employed in HILIC because the overall effect they provide is of weak electrostatic interactions and lower buffer concentrations are required to disrupt these interactions.

Experimental Details

The separation of paraquat and diquat was achieved on a Syncronis HILIC column specifically designed for the retention of polar and hydrophilic compounds.

Chemicals and Reagents	Part Number
Fisher Scientific HPLC grade water	W/0106/17
Fisher Scientific HPLC grade acetonitrile	A/0626/17
Thermo Scientific 2 mL clear vial and Si/PTFE seal	60180-600

Sample Preparation

A 1400 µg/mL standard solution of paraquat and 1800 µg/mL standard solution of diquat were prepared in mobile phase; these solutions were then mixed in a 50:50 ratio and used for the analysis.

Separation Conditions		Part Number
Instrumentation:	Thermo Scientific Accela HPLC/UHPLC	
Column:	Syncronis HILIC 5 µm, 100 x 2.1mm	97505-102130
Column Temperature:	45 °C	
Injection volume:	1 µL	
Flow rate:	0.3 mL/min	
UV detection:	254 nm (for paraquat) and 308 nm (for diquat)	
Mobile phase:	20:80 (v/v) water/acetonitrile + 0.1% TFA	

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Syncronis™ HILIC columns are based on highly pure 100 Å silica, with a surface area of 320 m^2/g. The zwitterionic modified stationary phase results in total charge equalisation and therefore a neutral but highly polar surface, which offers enhanced retention of polar and hydrophilic analytes.

This application note shows an efficient and reproducible HILIC method for the analysis of paraquat and diquat, with excellent peak shape and baseline resolution.

Results

The herbicides paraquat and diquat were retained and separated on the Syncronis HILIC column, using an isocratic method with 0.1% TFA added to the mobile phase. Figure 2 shows the chromatogram obtained employing Syncronis HILIC 5 µm, 100 x 2.1 mm column, with paraquat eluting at 1.30 min and diquat eluting at 1.47 min.

The following chromatographic parameters were monitored: retention time t_R, peak area, and resolution Rs. Mean and % RSD values for the above parameters were based on data derived from six replicate injections, and they are reported in Table 1.

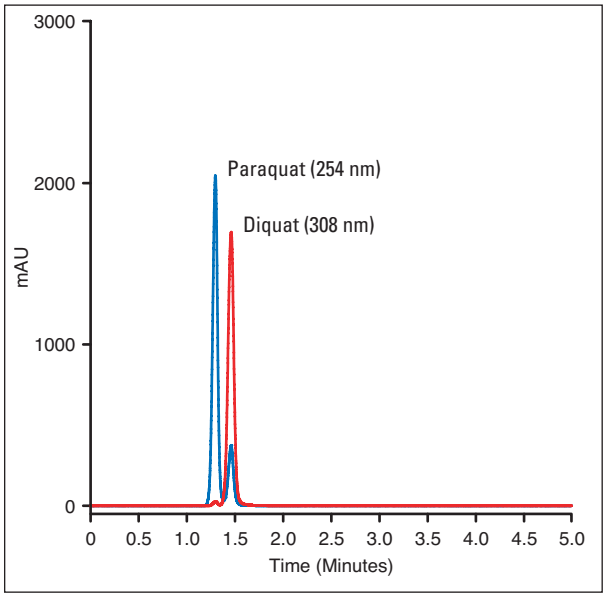

Figure 2: Chromatogram of paraquat and diquat, separated on a Syncronis HILIC 5 µm, 100 x 2.1 mm column

Conclusions

The use of a Syncronis HILIC column allowed the successful retention and separation of the quaternary ammonium compounds paraquat and diquat. Syncronis HILIC columns are an excellent choice for the HILIC separation of paraquat and diquat, affording highly reproducible analysis

References

[1] Determination of diquat and paraquat in drinking water by Liquid-Solid Extraction and High Performance Liquid Chromatography with Ultraviolet Detection; U.S. EPA Method 549.2, Revision 1.0, Environmental Protection Agency: Cincinnati, OH, 1997.
[2] http://www.who.int/whosis/en/ World Health Organization.

Paraquat	t_R (min)	Peak Area
Mean	1.30	7361563
SD	0.01	98638.00
% RSD	0.43	1.34

Diquat	t_R (min)	Peak Area	R_S
Mean	1.47	7414798	1.61
SD	0.01	104719.97	0.01
% RSD	0.50	1.41	0.66

Table 1: Average and Method Precision (%RSD) of chromatographic parameters, derived from the analysis of paraquat and diquat on a Syncronis HILIC 5 µm, 100 x 2.1 mm column (data calculated from six replicate injections)

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