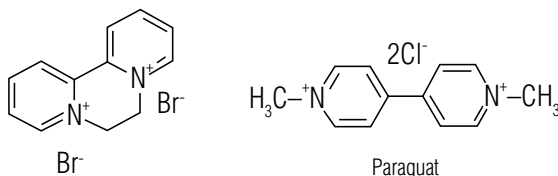


Improved Separation of Diquat and Paraquat Using the Acclaim Mixed-Mode HILIC-1 Column

Introduction

Mixtures of diquat and paraquat—quaternary ammonium herbicides—are widely used to control crop and aquatic weeds. The structures of these herbicides are shown below. High-performance liquid chromatography (HPLC) is one commonly used method for the determination of diquat and paraquat. The U.S. Environmental Protection Agency (EPA) has published EPA Method 549.2, a method for the analysis of these herbicides in aqueous samples.¹



The separation of diquat and paraquat is difficult due to their very weak retention on a conventional reversed-phase (RP) C18 column; therefore, ion-pairing reagents are added to the mobile phase.¹⁻⁴ These reagents are also added to improve peak shape.⁵ A stationary phase that may be used in the hydrophilic interaction liquid chromatography (HILIC) mode can be used for this separation in the absence of an ion-pairing reagent.⁶ However, the only separation that shows a baseline separation of diquat and paraquat is the one reported in reference 5 that uses a special column and a commercial buffer.

The Thermo Scientific Acclaim Mixed-Mode HILIC-1 column, based on high-purity spherical silica functionalized with a silyl ligand containing both hydrophilic and hydrophobic functionalities, may be used either in HILIC mode (high organic conditions) or RP mode (high aqueous conditions). In HILIC mode, this column has been used for the determination of urea and allantoin in cosmetics.⁷

The work shown here describes an efficient method for the baseline separation of diquat and paraquat with improved peak shape. Experiments performed on an Acclaim™ Mixed-Mode HILIC-1 column (3.0 × 150 mm, 3 μm) show that when increasing the pH value of mobile phase buffer from 3.5 to 5.5 or decreasing the proportion of organic mobile phase (methanol), both retention time (t_R) and peak resolution (R_s) increase, whereas peak symmetry (A_s) decreases. This method uses the column in RP mode with an ammonium formate (160 mM, pH 4.7)–methanol (87:13, v/v) mobile phase to separate diquat and paraquat. Figure 1 shows the chromatogram with baseline separation ($R_s = 3.2$).

Equipment

Thermo Scientific Dionex UltiMate 3000 RSLC system, including:

HPG 3400RS Pump

WPS 3000RS Autosampler

TCC-3000RS Thermostatted Column Compartment

DAD-3000RS UV-vis Detector

Thermo Scientific Dionex Chromeleon Chromatography Data System (CDS) software Version 6.80 SR9

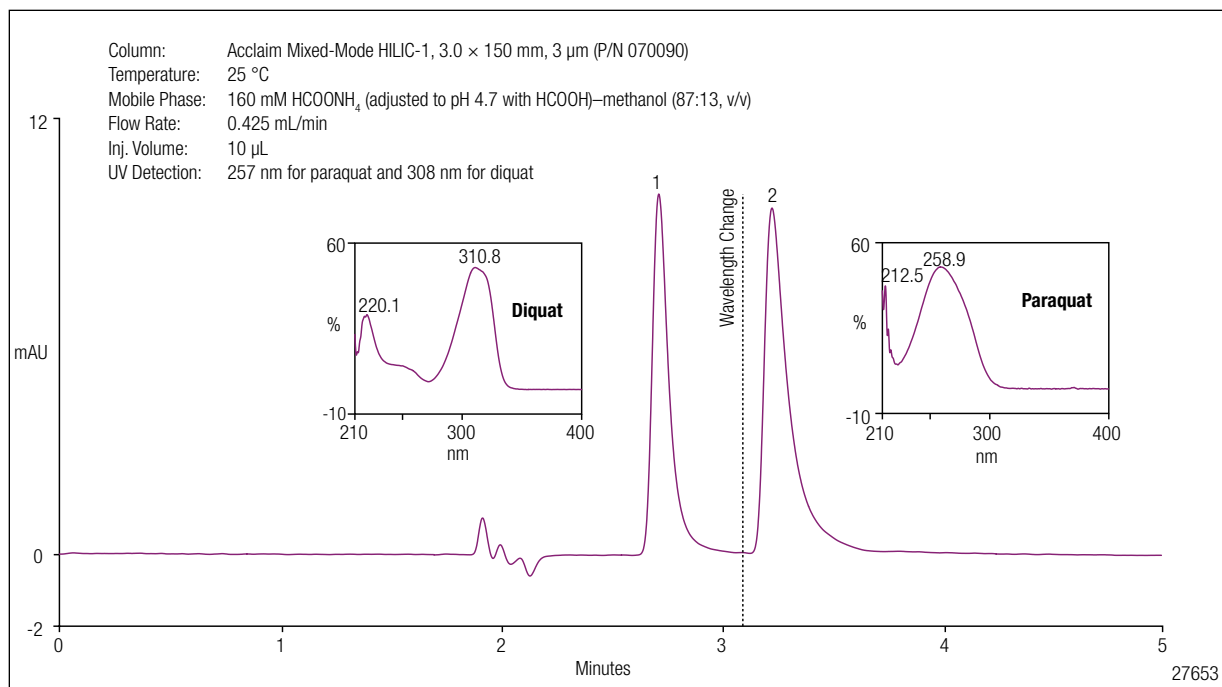


Figure 1. Chromatogram of diquat (peak 1) and paraquat (peak 2) (1.0 μg/mL each) with the UV spectrum for each.

References

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