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INTRODUCTION

This application note focuses on using the Waters® ACQUITY Ultra Performance LC™ System to separate and compare the ink-jet ink dyes from generic and brand vendor printer cartridges. Chromatographic separation is the most powerful and widely used technique to assess the stability, purity and composition of dyes for product development and competitive product deformation.^{1,2} The separation and analysis of the dyes from their impurities or in product formulations by conventional HPLC can be a difficult and time-consuming task. The typical HPLC run time is approximately 20 to 30 minutes to resolve dyes with similar chemical structures.¹ The UPLC system can be used to rapidly resolve acid dyes and their impurities in less than 2 minutes and enable faster deformation of ink-jet ink dye compositions.

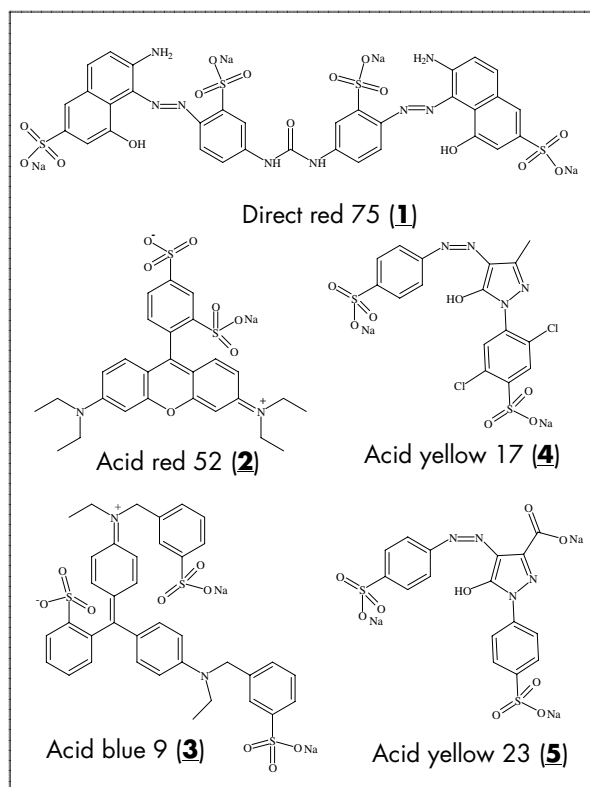


Figure 1. Structure of 5 Ink-jet Dyes.

EXPERIMENTAL

Sample Preparation

Dyes **1** to **5** were dissolved in D.I. water to make standard solutions (4-40 µg/mL). Cyan, magenta, and yellow ink-jet solutions (0.5-4 µL) were extracted from ink-jet printer cartridges by pipette and diluted with 1-2 mL of D.I. water prior to UPLC analysis. All the sample solutions were filtered with 25 mm GHP Acrodiscs filters (WAT 200514) and placed in UPLC max recovery sample vials (screw cap 12x32 mm, 186000327c) for analysis.

UPLC System and Operation Conditions

System: ACQUITY UPLC™ with an ACQUITY UV absorbance detector

Column: ACQUITY UPLC BEH SHIELD RP₁₈
2.1 x 50 mm, 2.1 x 100 mm

Column Temp: 50 °C

Weak Wash: 95:5 Water: CH₃CN (500 µL)

Strong Wash: 50:50 Water: CH₃CN (50 µL)

Seal Wash: 90:10 Water: CH₃CN (5 min)

Mobile Phase A: 10 mM NH₄HCO₃, pH 9.8

Mobile Phase B: CH₃CN

Detection: UV absorbance

Resolution: 1.2 nm

Sampling rate: 20 pts/s

Filter Response: 0.1 s

Software

Data were acquired and processed using Waters® Empower™ Chromatography Software.



Waters ACQUITY UPLC System.

RESULTS AND DISCUSSIONS

Five dyes (**1** to **5**, Figure 1) that are typical components in ink-jet inks were used to demonstrate the utility of UPLC for rapid identification and impurity profiling.³ Figure 2 shows that the dyes and their impurities can be rapidly resolved with a 2-minute linear gradient (5% to 55%B, 1 mL/min, 5 μ L injection, and a 2.1 x 50 mm UPLC BEH SHIELD RP₁₈ column). The optimum separation was with pH 9.8 ammonium bicarbonate, mobile phase A.

The same chromatographic conditions were used to profile dye components in yellow and magenta ink-jet ink printer cartridge solutions from five vendors. Figure 3 shows the chromatograms of yellow ink-jet inks. There are two major yellow dye components in Vendor E with retention time 0.66 and 1.14 minutes, respectively. The UPLC data show that the peak at 1.14 minutes is found in the yellow ink-jet ink formulations of Vendors C, E and CE; whereas Vendor H and Vendor E have the 0.66 minute peak dye component in their yellow ink-jet ink formulations. The first two peaks at 0.15 and 0.20 minutes in the Vendors L and CE yellow ink-jet inks are consistent with acid yellow 23 and its impurity peak.

Figure 4 shows that one or two major red dye components were used to formulate magenta ink-jet inks. Acid red 52, retention time 1.22 minutes, was used by Vendors E, H and CE.

The chromatograms of the cyan ink-jet inks are very different from the other inks. To provide more details about the cyan ink dye compositions, a 2.1 x 100 mm UPLC BEH SHIELD RP₁₈ column with a 10-minute linear gradient from 5% to 40%B at 0.5 mL/min (10 μ L injection), was used.

Figure 5 shows that, although the cyan ink-jet ink dye formulations are more complicated than the yellow and magenta ink dyes, the cyan color components are well resolved by UPLC. Qualitatively, the cyan ink-jet chromatograms of Vendors E, H and L are strikingly similar. All of the cyan ink-jet ink dye chromatographic profiles suggest a polymeric distribution.

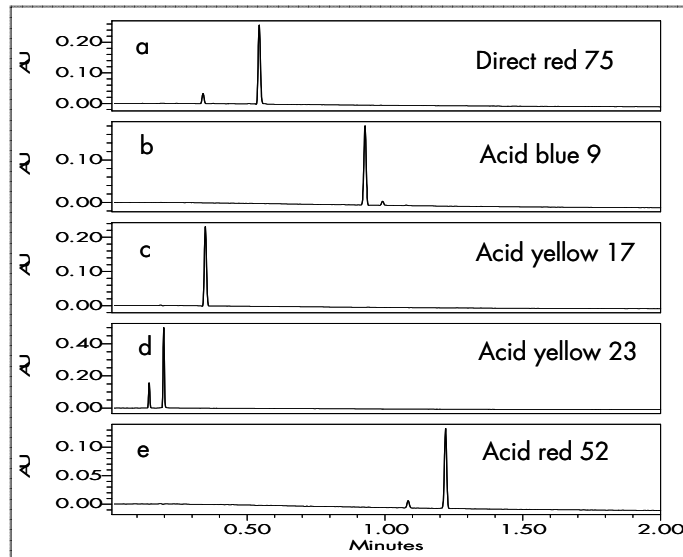


Figure 2. Impurity Profiles of Commercial Dyes. Chromatograms: **a** 535 nm, **b** 625 nm, **c** 400 nm, **d** 420 nm, **e** 550 nm.

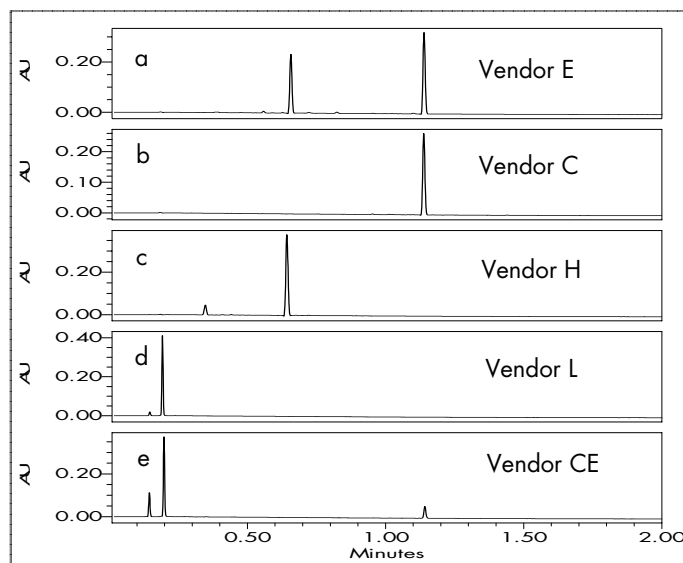


Figure 3. UPLC Separation of Yellow Ink-jet Inks. Chromatograms: **a**, **b**, **c** 400 nm and **d**, **e** 420 nm.

It is plausible that all the products examined use chromophore-incorporated functional polymers for the cyan ink-jet inks.

For the analysis of dye components that are not in a standard mix or confirmation of chromophore-incorporated functional polymer, UPLC with an MS detector offers the potential to more easily provide additional details for competitive product analysis. Conventional analyses are time consuming.⁴⁻⁵

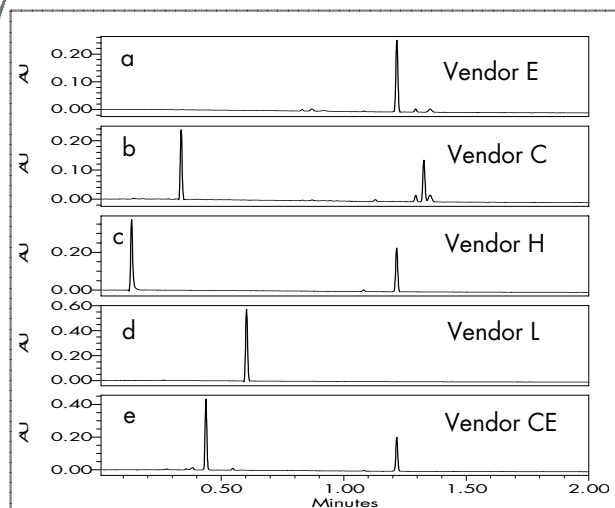


Figure 4. UPLC Separation of Magenta Ink-jet Inks.
Chromatograms: **a** 550 nm, **b** 540 nm, **c, d, e** 550 nm.

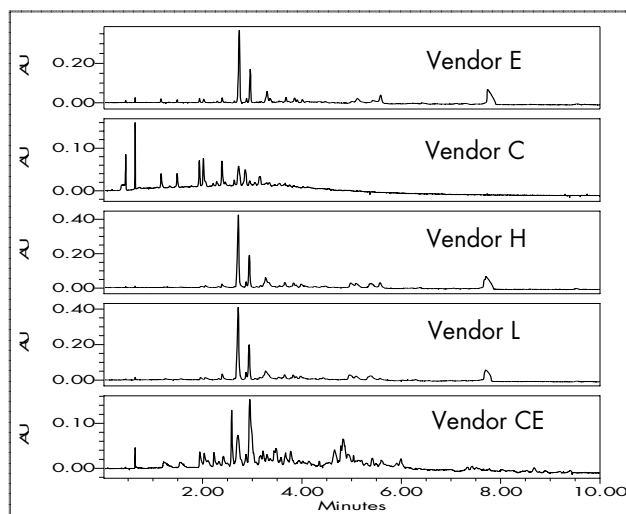


Figure 5. UPLC Separation of Cyan Ink-jet Inks.
Chromatograms: 670 nm.

CONCLUSION

The Waters ACQUITY Ultra Performance LC system provides an easy and fast method for sensitive separation and comparison of ink-jet ink dyes. The UPLC BEH column technology enables the use of pH 9.8 for excellent selectivity and resolution power. UPLC is a powerful tool to resolve ink-jet ink dyes from printer cartridges of generic and brand vendors. Potential applications for analyzing the stability, purity and composition of dyes are product development, competitive analysis, patent infringement, quality control, and also forensic analysis.

REFERENCE

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