ACQUITY UPLC™ ONE MINUTE SEPARATION OF TRIARYLMETHANE DYES AND COLORANT OF BALL POINT PEN INKS

Peter J. Lee and Alice J. Di Gioia
Waters Corporation, 34 Maple Street, Milford, MA 01757, USA

Introduction

UPLC™ combined with UV and single quadrupole MS detectors provides a powerful tool to differentiate dye components in ballpoint pen ink formulas. Important information about photo-stability of inks is obtainable by analyzing the changing profile of UPLC™ separated dye components.

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 deformulation.[1,2] The separation and analysis of the dyes from their impurities or in product formulations by conventional HPLC is 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]

This poster describes a one minute analysis of ball point pen ink dye formulas and photo-degradation of written samples using the ACQUITY UPLC™/ UV-PDA/ ZQ™ MS spectrometry system and triarylmethane dyes (**1**– **3**) as standards.

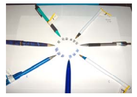
The dye components of written sample extracts and standards were separated in one minute and identified. Ink dye components and photo-stability of different ball point pens were unambiguously differentiated using the ACQUITY UPLC™ system.

Experimental

Sample Preparation:[2]

Extraction solvent: 60v% in 1.25% acetic acid, 40v% in CH_3CN
Ink extracts: Thirty lines (~1 cm long) were written with ballpoint pens on a 20lb XEROX multipurpose 4200 paper. For the photo-degradation study, the written samples were placed under a UV lamp for 3 to 24 hours. The fresh and photo-degraded written samples were cut and placed in vials with 0.5-1.5 mL of solvent. The vials were gently rotated for one hour until the paper showed no visible signs of writing. The ink extracts were used for UPLC™ analysis.

Photo-degradation setup.



Instrument and Operation System:

ACQUITY UPLC™/ 2996 ACQUITY PDA/ Waters® ZQ™ 2000/ ACQUITY UPLC™ BEH C_{18} 50 x 2.1mm/ Empower™

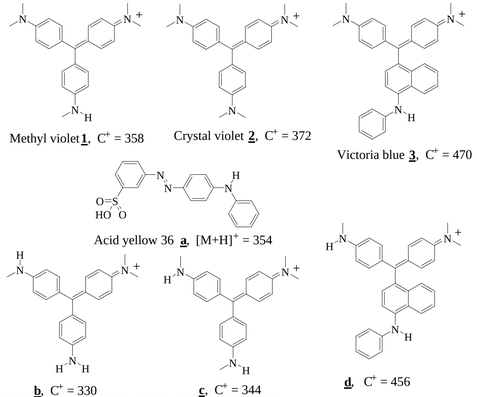
UPLC™ and ACQUITY PDA Conditions:[2]

Weak Wash : 95:5 Water: CH_3CN (500µL)
Strong Wash: 50:50 Water: CH_3CN (300µL)
Mobile Phase A: 10mM NH_4OAc in 95v% H_2O/5v% CH_3CN
Mobile Phase B: 10mM NH_4OAc in 5v% H_2O/95v% CH_3CN
Gradient Condition: 25%B to 80%B in one minute, curve 5
Flow Rate: 1 mL/min
Injection Volume: 2-5 µL; Column Temperature: 50 ^{0}C
PDA: 280-750 nm; PDA Filter Response: 0.1

Single Quad ZQ™ Mass Spectrometer (MS) Conditions:

ES capillary (kV): 3.2; Cone (V): 40
Extractor (V): 2; RF Lens (V): 0.5
Source Temp (^{0}C): 140; Desolvation Temp (^{0}C): 450
Cone Gas flow (L/Hr): 50; Desolvation Gas (L/Hr): 800
LM Resolution: 15; HM resolution: 15
Ion Energy: 0.3; Multiplier: 500
Scan Range: 150 to 500 Da; Scan time: 0.1 sec
Inter-scan delay: 0.05 sec; Probe: ES+

Chemical Structures



UPLC™ Analysis of Black and Blue Pens

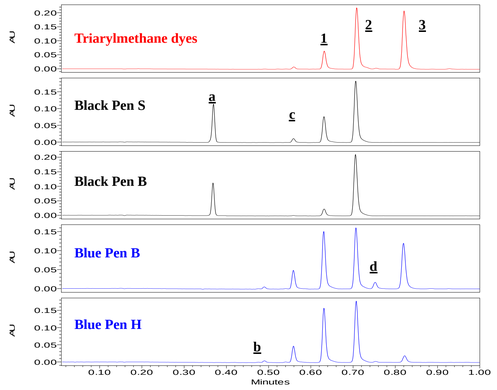


Figure 1a. *Chromatograms of freshly written sample extracts. Black pen (0 min, 415nm; 0.4 min 570nm), Blue pen (at 570nm).*

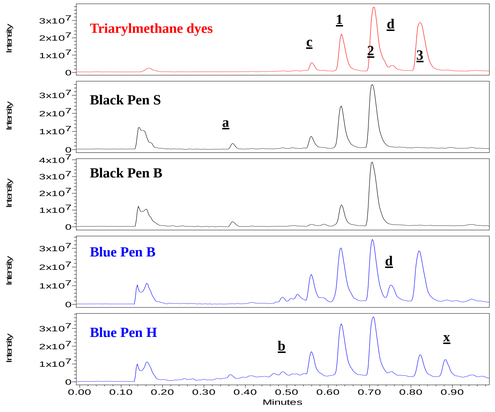


Figure 1b. *TIC chromatograms of freshly written sample extracts. (ZQ™ MS was configured in-line after PDA for peak tracking and identification: Retention time of TIC was offset -0.011 minutes to match UV chromatograms.)*

UPLC™ Analysis of Photo-Degraded Written Samples

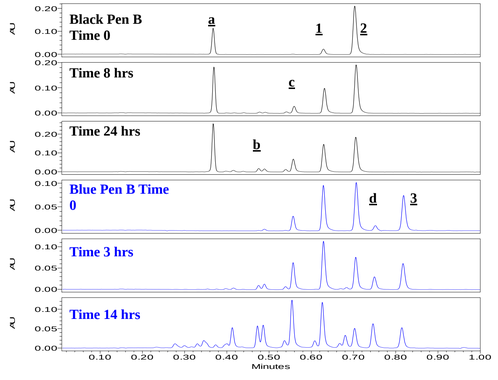


Figure 2a. *Chromatograms of photo-degraded written sample extracts. UV lamp exposure time: Black pen B samples (0, 8, 24 hours), Blue pen B samples (0, 3, 14 hours).*

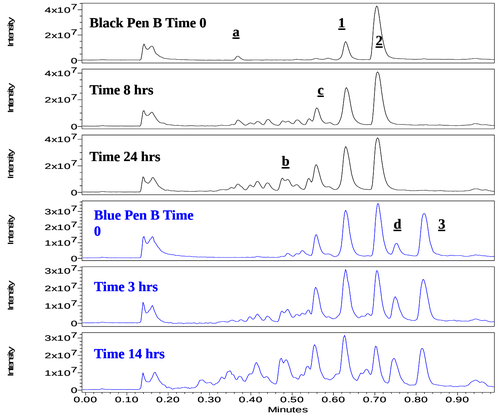


Figure 2b. *TIC chromatograms of photo-degraded written sample extracts: UV lamp exposure time: Black pen B samples (0, 8, 24 hours), Blue pen B samples (0, 3, 14 hours).*

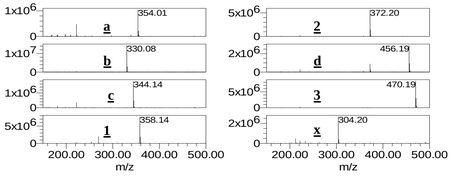


Figure 3. *Extracted mass spectra from TIC chromatograms. Retention time: 0.375 (**a**), 0.485 (**b**), 0.560 (**c**), 0.632 (**1**), 0.707 (**2**), 0.755 (**d**), 0.820 (**3**), 0.885 (**x**).*

Conclusions

- ACQUITY UPLC™ combined with UV and ZQ™ MS detectors can provide a rapid, easy-to-use and powerful tool to differentiate structurally similar dye components used in ballpoint pen inks.
- Important information about photo-stability of inks and the contribution of individual dye components to that stability can be obtained by analyzing the UPLC™ chromatograms over time.
- Potential applications of UPLC™ are competitive deformulation, forensic analysis, new product development, quality control ink dye raw materials and final ink product.
- Black pens S and B have common ink dye components: two match methyl violet (**1**) and crystal violet (**2**); the other two match **a** and **c** with m/z 354 and 344.
- Blue pens B and H have six dye components: three match methyl violet (**1**), crystal violet (**2**) and victoria blue (**3**); the other three match **b**, **c** and **d** with m/z 330, 344, and 456. Component **x** with m/z 304 is unique to the ink formulation from Pen H.
- The black written sample is more stable than the blue written sample under conditions of these experiments.
- UPLC™ analysis results confirm some photo-degradation products and pathways of triarylmethane dyes:[3] (**2**) ⇒ (**1**) ⇒ (**c**) ⇒ (**b**) ⇒; (**3**) ⇒ (**d**) ⇒

Reference

1. J. A. Zlotnick, et al., *J. Chromatogr.*, B 733, 265-272, **1999**.
2. P. J. Lee, A. J. Di Gioia, *ACQUITY UPLC™ Separation of Triarylmethane Ink Dyes (part 1)*, *Waters Corporation*, Application Note 720001262EN, **2005**.
3. R. Hofer, *J Forensic Sci*, Sept. Sept. **2004**, Vol. 49, No. 6, JFS2004056.

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