J2 Study on the Dye Components of Black Gel Pen Inks by HPLC-Tandem/MS

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After attending this presentation, attendees will learn about black gel pen discrimination methods.

This presentation will impact the forensic science community by identifying the dye components in black gel pen ink using high pressure liquid chromatography- tandem/mass spectrometry (HPLC-Tandem/MS).

In order to determine and identify the dye components in black gel pen ink, sixteen black gel pen inks produced from three different countries (Korea, Japan, and Germany) using an HPLC-Tandem/MS were analyzed. Nine different dyes at varying compositions within the sample inks were detected. The dye types included: methyl violet B base (MVB), crystal violet (CV), methyl violet (MV), acid orange 10 (AO10), sudan black B (SBB), victoria pure blue BO (VPBBO), patent blue VF (PBVF), acid red 52 (AR52), and aniline blue diammonium salt (ABDS). Among the dyes, CV, AO10, SBB, and VPBBO were found in all inks, while the other dyes were differentially observed. MV was detected in samples 6-8 (Korea), 11 and 14 (Japan); ABDS was detected in samples 1-3 (Korea) and 11 (Japan); and AR52 was detected in samples 1 (Korea) and 12 (Japan). PBVF was only detected in the Japanese ink sample 13.

Sample inks were divided into five groups by statistical analysis. Group 1: GP1, GP2, GP3 (Dong-A, Korea), and GP11 (Pental, Japan); Group 2: GP4 (Dong-A, Korea), GP5, GP9 (Monami, Korea), and GP10 (Japan); Group 3: GP6, GP7, GP8 (Monami, Korea), GP14 (Sakura, Japan), GP15, and GP16 (Germany); Group 4: GP13 (Zebra, Japan); and Group 5: GP12 (Pental, Japan).

An accelerated weathering test was performed with the black gel pens and the dye components of black gel pen ink were analyzed using HPLC-Tandem/MS (Table 23). The MVB and CV dyes in sample 1, 2, 3, 4, 5, 6, and 7 were significantly decreased by UV light in a time-dependent manner. After one hour UV of light treatment, MLB dye detected 6.476 µg/kg at sample 1, 3.85 µg/kg at sample 2, 4.461 µg/kg at sample 3, 7.113 µg/kg at sample 4 and 10.547 µg/kg at sample 5. After seven hours UV light treatment, MLB dye detected 2.924 µg/kg at sample 1, 2.149 µg/kg at sample 2, 2.601 µg/kg at sample 3, 4.855 µg/kg at sample 4 and 3.652 µg/kg at sample 5. After one hour UV of treatment, CV dye detected 3.572 µg/kg at sample 1, 3.51 µg/kg at sample 2, 2.488 µg/kg at sample 3, 1.794 µg/kg at sample 4 and 2.479 µg/kg at sample 5. After seven hours of UV treatment, CV dye detected 2.803 µg/kg at sample 1, 1.15 µg/kg at sample 2, 1.224 µg/kg at sample 3, 1.09 µg/kg at sample 4, and 0.915 µg/kg at sample 5. The increased detection of several dyes following the weathering test might be caused by the degradation of some dyes into shared components or could be due to the sample pretreatment process for the HPLC-Tandem/MS trace-level analysis.

In this report, it was established an HPLC-Tandem/MS method for simultaneous determination of the dye components in black gel pen ink, and showed that black gel pen inks produced from three different countries contained common as well as unique dyes. It was also demonstrated that MVB and CV dye contents were significantly reduced by UV light. Based on the data described here, it may be possible to classify the manufacturing origin of black gel pens based on the ink dye components and provide a scientific foundation for dating of documents written with ink from black gel pens.

Question Document, Black Gel Pen Ink, HPLC-Tandem/MS

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