J1 A Study on Discrimination Methods of Black Ballpoint Pen Ink Lines on Paper

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The goal of this presentation is to compare ink discrimination methods UV light by VIS spectrum, thin layer chromatography (TLC), and high pressure liquid chromatography – electrospray tandem mass spectrometry (HPLC-ESI-MS).

This presentation will impact the forensic science community by making a comparison of different ink discrimination methods using UV light by VIS spectrum, TLC, and HPLC-ES as well as detailing how these methods can provide methodology, classification, and identification of ballpoint ink lines.

In forensic examinations of question documents, analyses of ink components and the dating of ink entries are often of considerable importance. Forensic ink examinations are principally concerned with the classification and comparison of complex chemical mixtures. The inks on a questioned document may be examined through analyses that include spectral examination, thin layer chromatography (TLC), high pressure liquid chromatography/mass spectrometry (HPLC/MS), and gas chromatograph/mass spectrometry (GC/MS). Fifty-six different types of black ballpoint pens manufactured from five country groups were collected. Experimental sampling was conducted by extracting samples from ink lines produced on white copy paper. The goal of this work is to investigate the degradation pathways of ballpoint ink dyes using UV light irradiation, TLC, and HPLC-ESI/MS. To study the effects of aging, the fifty-six ink samples on paper were created and stored with varying elapsed-time periods of one, two, and three years. As ink age determination is highly dependent on the composition of the ink and storage conditions of the document, two variables usually unknown in forensic document examination, the study samples were kept in darkness to simulate natural aging and to minimize variance in exposure to UV irradiation.

Individual characteristic data was identified among all of the fifty-six different types of black ballpoint pen ink samples on paper using the Infrared luminescence, ultraviolet light features, TLC, HPLC-ESI/MS, and GC/MS. Ink samples were first totally dissolved in methanol. Ink component reactions were observed and recorded using light radiation and filter pair sets in five groupings of (① 580nm, 420nm; ② 580nm, 550nm, 420nm; ③ 550nm, 580nm, 660nm, 380nm; ④ 580nm; and ⑤ 580nm, 550nm.) A mobile phase system for TLC analysis was conducted using n-butanol: ethanol: water: acetic acid at ratios of 6: 1: 2: 0.05, which were effective in separating nearly all dye mixture samples. In this system, the spot capacity more than 21 was achieved. Dyes of black ballpoint ink lines were analyzed using HPLC-ESI/MS and completely detected 15 samples of which the ten violet dyes indentified were: ① crystal violet (CV, Hexamethyl pararosaniline); ② CV-CH2 (Pentamethyl pararosaniline; ③ CV-2CH2 (Tetramethyl pararosaniline); ④ CV-3CH2 (Trimethyl pararosaniline); ⑤ CV-4CH2 (Dimethyl pararosaniline; ⑥ CV+OH-2CH2 (Tetrahydroxy methyl pararosaniline); ⑦ DLPM-3CH2(bis(4-(dimethylamino)phenyl)methanone; ⑧ DLPM-CH2; ⑨ DLPM+OH-2CH2; and ⑩ basic violet 14 and basic yellow 33, basic yellow 2 of yellow dye, basic blue 26, basic blue 9 of blue dye, and Megawhite PL of fluorescence. The results of this study indicated that analysis of UV-VIS spectrum, TLC and HPLC-ESI/MS could make a discriminating tool of ballpoint inks dye for forensic purposes and can supply methodology for the classification and identification of ballpoints pen ink lines.

The absorption maximum of the spectral bands shifts hypsochromically from 580 to 560nm with UV irradiation. This hypsochromic shift (blue shift) of crystal violet absorption band is presumed to result from the formation of series of N-demethylated intermediates in a stepwise manner. Aging curves for the N-demethylated intermediates of crystal violet and equations from elapsed time and UV irradiation samples were identified. Crystal violet (hexamethyl pararosalinine) was transformed to its decomposition product pentamethyl pararosalinine by demethylation. Pentamethyl pararosalinine is transformed to tetramethyl pararosalinine and latter to trimethyl pararosalinine. UV accelerated aging mimics natural aging from a dye perspective and can be characterized by UV-Vis spectrum and HPLC-ESI/MS. Irradiation for 1.6h produces the same extent of degradation as what occurs naturally over a period of one year. The relative abundance of the intact dye molecule (m/z 372) decreases as the relative abundances of the degradation products (m/z 358, 344) increase with irradiation time.

Question Document, Black Ballpoint Pen Ink, Discrimination

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