

J33 Minimally Destructive Ink Analysis Using Miniaturized Ultraviolet/Visible (UV/Vis) Spectroscopy

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Learning Overview: After attending this presentation, attendees will understand a UV/Vis spectrometric methodology for the minimally destructive chemical analysis of different ink types.

Impact on the Forensic Science Community: This presentation will impact the forensic science community by providing a method of ink classification by miniaturized UV/Vis spectroscopy that utilizes a new sampling technique in order to allow for smaller sample sizes that thereby maintain most of the physical characteristics of handwriting after chemical analysis.

Questioned document analysis often deals with the validation of legal documents and other such forms that may contain a particularly small sample of handwriting. It is possible that a Forensic Document Examiner (FDE) is faced with a sample as small as a set of initials. Conventional destructive chemical analysis is unfavorable as it often utilizes an organic solvent extraction of the entire sample. When working with a particularly small sample or a sample where it is also important to be able to do non-destructive visual and microscopic analysis of physical characteristics, an FDE may elect not to perform conventional chemical testing.

Conventional UV/Vis spectroscopy is another established method for chemical ink analysis, but faces the same issues of large sample size and original document destruction. Additionally, the conventional solvent used in UV/Vis ink analysis, pyridine, produces a nauseating odor and is a systemic toxicant.^{1,2} UV/Vis spectroscopy is ideal in that it is possible to determine important information from a visual examination of the spectra that does not necessarily require in-depth molecular analysis.

This new analytical method utilizes a 0.7mm steel mechanical pencil tip as a micro-punch to transfer tiny ink-on-paper samples from written characters and test them on a significantly smaller scale with a micro-volume UV/Vis spectrometer. Using a safe and mild detergent as a solvent, six micro-punches generate recognizable and repeatable spectra that allow for differentiation between types of pens. Testing began with a variety of brands of black and blue ballpoint, gel, and porous point pens. The analysis later expanded to thermochroic, or “erasable,” gel pens and alcohol-based porous point permanent markers due to their forensic relevance. These samples are not commonly tested early in the development of a method for chemical analysis, but it makes sense to include them because questioned documents frequently looks at evidence material where handwriting is meant to have intense staying power, as in “permanent” inks, or is meant to be easily destroyed, as lay-people feel they achieve with pigment that deactivates. Additionally, these formulations are popular among consumers.³⁻⁴

After the micro-punch samples are taken, it is still possible to see general physical and microscopic characteristics of the characters, and samples can be taken with strategic placement in order to preserve the most relevant or distinctive aspect of any given character being examined. The larger a sample is the more spread out the six punches can be and the less it disturbs the original writing pattern; however, this method works on a sample as small as a set of initials and leaves them readable with some lines of ink still present for further analysis

The results of these tests were found to be replicable when analysis was in keeping with the set procedure. It was found that ballpoint, gel, and porous point pen inks were differentiable from one another, and the spectra for ink formulations were clearly different from the spectra obtained by running paper blanks, showing the ink spectra were notable due to the ink itself and not any paper interference. The method was additionally found to work on deactivated thermochroic pigment and on alcohol-based porous point pen inks, indicating this form of analysis is suitable for a wide variety of samples, in contrast to conventional methods. The intention of this research is to develop an accessible and replicable methodology for minimally destructive chemical ink analysis, and to use the existing testing that has been performed and further testing to establish a searchable database of reference UV/Vis spectra.

Reference(s):

1. Standard Guide for Forensic Examination of Non-Reactive Dyes in Textile Fibers by Thin-Layer Chromatography. *ASTM International*, E 2227 – 02: 2-5.
2. U.S. EPA. *Health And Environmental Effects Profile for Pyridine*. U.S. Environmental Protection Agency, Washington, D.C., EPA/600/X-86/168 (NTIS PB89123384), 1986.
3. *The Science Behind FriXion Erasable Pens*. Na., accessed October 4, 2020, <https://www.nippon.com/en/features/c00520/>.
4. *Sharpie—About Us*. Na., accessed October 4, 2020, <https://www.sharpen.com/about>.

Ink Analysis, Miniaturized UV/Vis, Minimally Destructive