J13 Raman Spectroscopy of Blue Ballpoint Pen Inks and Dyes Found in Inks: Investigation of the Effects of Varying Laser Wavelength

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After attending this presentation, attendees will understand the main dyes used in blue ballpoint pens and their spectra using different excitation lasers. The Raman spectra of blue ballpoint inks mainly result from one dye or a mixture of several of dyes. The reason why the Raman spectra at 514nm was not influenced by fluorescence but the discriminative power was poor will be explained clearly. A 633nm laser was chosen as a balance between the fluorescence and discriminative power. A 785nm laser can also be used as a complement to differentiate inks. Dyes in inks can be revealed by an analysis of their Raman spectra obtained using different wavelengths.

This presentation will impact the forensic science community by demonstrating how blue ballpoint pen inks and dyes found in inks should be analyzed by Raman spectra obtained using lasers of three different wavelengths in a systematic manner.

Raman spectroscopy can be helpful for characterizing and discriminating inks based on their composition. However, fluorescence interference is a problem that is sometimes encountered and may result in poor analytical performance. The applicability of Raman spectroscopy to the analysis of 50 blue ballpoints and 8 synthetic dyes commonly found in blue ballpoint inks was investigated in this study. Excitation wavelengths varying from 514nm, 633nm, and 785nm were used to identify the dyes and caution of fluorescence observed in spectra of inks. Methyl violet derivatives are commonly used in blue ballpoint inks, which include crystal violet, methyl violet, pararosaniline, and so on. Copper phthalocyanine is another kind of dye found in many blue ballpoint inks. Basic blue 7, Victoria blue, acid blue, aniline blue, and pigment blue 7 are also added by some manufacturers.

All dyes were measured by focusing through test drops deposited on the surface of the microscope slides and inks were detected by focusing on ink lines on paper. The spectra of Methyl violet derivatives obtained at 514nm are almost identical, which are similar to basic blue 7 and stronger than Victoria blue. Other dyes produced intense Raman scattering. For seven dyes, fluorescence and weak bands were observed in the 633 nm spectra and high levels of fluorescence were in the 785 nm spectra. Only copper phthalocyanine responded well to both laser wavelengths showing consistent peaks of high intensity.

For 50 blue ballpoint inks, the Raman spectra at 514nm did not provide adequate discriminative power and the tested inks could be divided into only eight groups. Spectra of 35 blue ballpoint inks dominated by methyl violet derivatives whose main peaks were at 1619cm-1D1584 cm-1D1540 cm-1D1372 cm-1D1173 cm-1D911 cm-1
and 801cm-1 were included in the MV group. Spectra of four inks were similar with the MV group (two of them whose Raman signal near 1175cm-1 split to 1362 cm-1 and 1389 cm-1, and the other two had different peaks at 692cm-1 and 1647cm-1 respectively). According to peaks at 1070 cm-1, 1157 cm-1, 1175 cm-1, 1197 cm-1, the spectra of nine blue ballpoints were dominated by Basic blue 7, which could be divided into one group with two inks and one group with seven inks because of the different bands at 1175 cm-1 and 1197 cm-1. There was one ballpoint whose spectrogram was matched with that of pigment blue 15. And the last spectrogram was dominated by a fluorescent background and weak Raman shifts at 1645 cm-1 and 1615 cm-1. The discriminative power by 514nm laser was 0.50 because 70% of spectra were methyl violet derivatives.

Upon excitation at 633 nm, the inks were separated into 11 groups. One group contained ten inks which belonged to the MV group whose Raman signal at 514nm was submerged by inflorescence. One ink had a weak peak at 1616cm-1 and another one had weak peaks at 1616cm-1 and 796cm-1 on the strong inflorescence background. The remaining 37 inks produce abundant Raman shifts, the different ratio of height 1616cm-1 versus 1539cm-1 suggested the different ratio of methyl violet and copper phthalocyanine in ink. Twenty-eight inks with higher 1616cm-1 peaks were divided into five groups by slight peak difference. Ten inks with lower 1616cm-1 peaks were divided into two groups by the weak and stable peak at 681cm-1. The ink matched pigment 15 upon 514nm laser showed both Raman signals of pigment blue 15 and copper phthalocyanine. The discriminative power by the 633nm laser was 0.84, which was higher than that of the 514nm laser.

The Raman spectra obtained using the 785 nm laser allowed division of the inks into seven groups and resulted in a lower discriminative power (0.77) than that of the 633nm laser. Fluorescence played stronger influence on spectra and 16 inks were dominated by it. The other 22 inks generated main Raman scattering bands at 1544cm-1, 1341cm-1 and 749cm-1 from the influence background and certain shifts classified inks into three3 groups. Only eight inks produced a strong Raman signal and could be separated into three types, one of them was

almost the same with copper phthalocyanine.

Conclusions: Raman spectra at 514nm were not influenced by fluorescence, whereas the discriminative power was not good since the widely used dye methyl violet derivatives generated strong Raman scattering at 514nm. Raman spectra at 633nm showed the fluorescence of basic blue 7 or acid blue as well as the mixture of methyl violet and copper phthalocyanine and gave the best discriminative power of the three lasers. The weak bands at 785nm could distinguish more inks than 514nm excitation although the spectra were susceptible by fluorescence. The main dyes used in blue ballpoint pen inks could be inferred by Raman spectra. Liquid Chromatography-Mass Spectrometry/Mass

Spectrometry (LC-MS/MS) could be considered for further research to identify the exact dyes.

Blue Ballpoint Pen Inks, Dyes, Raman Spectroscopy