J22 The Application of Raman Spectroscopy to the Analysis of Blue, Red, and Black Gel Pen Writing Inks

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After attending this presentation, attendees will understand the basic principles of Raman Spectroscopy and how it can be applied to ink analysis for questioned document casework, as well as the benefits and drawbacks of the technique.

This presentation will impact on the forensic science community by providing practitioners with an overview of the most suitable excitation wavelengths and ideal operating conditions for the analysis of common colours of gel ink on white office paper. It will extend the existing body of research which has already demonstrated the potential of Raman Spectroscopy for the analysis of gel pen writing inks where traditional techniques have been found to not be as effective. It will also demonstrate for the first time, to the best of the authors' knowledge and belief, the use of a multivariate statistical approach to discriminate between different brand and model combinations of gel pens.

During the past 15 years, the gel pen has become an increasingly popular choice of writing instrument around the globe, primarily due to its relatively low cost, long writing life, and environmentally friendly ink composition. The gel pen utilizes water based ink composed of either pigments or dyestuffs, giving a wide selection of colors. With this increased popularity, comes a need within the forensic community to find a suitable analytical approach by which to identify and classify different brands and/or models of gel pen ink. Among other analytical techniques investigated for this purpose, Raman Spectroscopy has been shown to provide a good ability to discriminate between different pigment-based gel pen inks. The technique can be performed *in situ* and involves directing a laser of specific excitation wavelength onto an ink sample in order to detect scattered light at longer wavelength to generate a Raman spectrum characteristic of its molecular structure, thus providing a molecular fingerprint for comparison. Different spectra of the same ink sample can be produced by using different excitation wavelengths providing additional discriminating ability.

A selection of over 450 gel ink pens in blue, red, and black colors, representing a variety of different brand/model combinations available on the worldwide market were analyzed using different Raman Spectrometer systems and several different excitation wavelengths (514nm; 633nm; 685nm; 785nm and 830nm). Resulting spectra were first grouped according to visual pattern recognition. Then, the application of a multivariate statistical approach in the form of hierarchical cluster analysis (HCA) was used in an attempt to discriminate between different brand/model combinations. The data presented here discusses some of the findings from this investigation and makes some recommendations as to the use of Raman Spectroscopy in gel ink analysis.

This work forms part of a wider investigation into the ability of other analytical techniques to discriminate within and between batches of different gel pen inks, focusing in particular on the potential of stable isotope analysis at a natural abundance level of the elements C, N, H, and O by Isotope Ratio Mass Spectrometry (IRMS) for this purpose. It is envisaged that this will lead to the development and validation of a reliable analytical methodology for the analysis of gel pens inks within forensic casework.

Questioned Documents, Raman Spectroscopy, Gel Pen Inks