## A182 Use of Surface Enhanced Raman Spectroscopy (SERS) Applied to the Study of Fluorescing Pigments and Dyes

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After attending this presentation, attendees will know a limitation of Raman spectroscopy (fluorescence) and learn a technique to overcome the limitation–Surface Enhanced Raman Spectroscopy (SERS).

This presentation will impact the forensic science community by demonstrating a technique that may be useful in overcoming a limitation of Raman spectroscopy and may be applied to samples in both civil and criminal cases.

Raman micro-spectroscopy provides a means to classify and identify colorants *in situ.* The laser-based analysis method affords a small analytical volume (as small as a few cubic micrometers), requires minimal sample preparation, and is generally non-destructive. Past presentations have illustrated the ways in which Raman spectroscopy can be advantageously applied to the study of pigments in automotive and architectural paint samples. The most significant limitation to Raman spectroscopy is sample fluorescence. Fluorescence can easily overwhelm a Raman spectrum. While there are various analytical approaches to minimizing or avoiding fluorescence (*e.g.* different laser wavelengths, fluorescence bleaching, etc.), the issue remains a major limitation, in many instances. Surface Enhanced Raman Spectroscopy (SERS) offers another alternative to overcome this problem.

SERS is based upon enhancing the Raman scattering from a particle through resonance effects created by the addition of a metal colloid. In practice, preparation of a SERS sample is relatively straightforward. A capillary drop of a metal colloid solution (typically gold or silver), which can be prepared in a laboratory or purchased, is applied to an area of interest on the sample. Once the colloid solution has dried, the sample is analyzed by Raman spectroscopy. The technique can be extremely sensitive (spectra have been obtained by researchers from a single molecule) and due to the strong resonance enhanced scattering, fluorescence can be overcome. The downsides to this technique are that:

(1) not all molecules resonate with all metals and so a metal colloid must be matched to a molecule; and, (2) the SERS spectrum can show peak shifts and different peak intensities than a corresponding Raman spectrum. The latter point makes identification of unknown samples by SERS a difficult prospect (since a regular Raman spectral database is not applicable).

The research into forensic applications of SERS that was conducted and will be presented here consisted of several components. First, colloidal solutions of gold and silver were precipitated. Reference dyes known to produce SERS spectra were analyzed to ensure that the effect was being observed. Various colloid application techniques were evaluated. Once a suitable technique had been developed, numerous reference spectra were collected from common dyes. Many of the dyes examined (e.g., erythrosine B, methyl violet, and pararosaniline), which have virtually no Raman spectrum due to fluorescence, produced excellent SERS spectra. Pigments studied, in general, were less amenable to producing a useful SERS spectrum. Still, certain pigments produced SERS spectra when a corresponding traditional Raman analysis showed only fluorescence. A small database of SERS spectra was developed.

Over the course of twelve months, SERS was applied to various casework samples in an attempt to find practical applications of this method as a forensic technique. In one case, requiring the identification of an unknown solid floating in a liquid product, FTIR analysis suggested the presence of a dyestuff. Analysis of the solid by Raman spectroscopy produced only fluorescence. Application of a gold colloid solution to a small, isolated fraction of the unknown material produced an intense SERS spectrum. The SERS spectrum was identified, by comparison to reference spectra, as erythrosine, a food dye that has been largely phased out of U.S. usage. This identification was supported by elemental data obtained by EDS analysis.

The successful application of SERS to a civil forensic matter illustrates the potential value of this technique in specific circumstances. Although SERS will never be used as commonly in the forensic field, it deserves consideration and use as a valuable micro-analytical accessory to Raman spectroscopy in specific instances.

**Pigment, Raman Spectroscopy, Surface Enhanced**

 ** Presenting Author*