Comparison of RAMAN Microscopy and ASAP Mass Spectrometry for Identification of Selected Fountain Pen Inks

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Abstract

There has been a rise of counterfeit and forgery crimes. For forensic purposes, research on fountain pen inks include identifying and distinguishing between samples. Raman spectroscopy analyzes the vibrations of molecules, and the spectra can act as a "fingerprint" for different fountain pen ink. A sample size of fourteen blue-black inks were analyzed. Ink spectra were added to an OMNIC database to compare and recognize similar inks to a certain confidence. It is anticipated that inks of the same brand or similar color will have a lower differentiation by the OMNIC software. If successful, the next phase will include a larger sample size with more brands. If inks are indistinguishable via Raman spectroscopy, inks will be diluted and compared to results from a RADIAN Atmospheric Pressure Solids Analysis Probe (ASAP) Direct Mass Spectrometer.

Background

Once the Raman microscope is focused on a sample of ink, the focused laser beam bounces off the vibrating covalent bonds of the molecules present in the sample. These vibrational modes are characteristic of each kind of molecule present, allowing us to identify the molecules if we have a pure sample of each chemical for comparison. For the inks, we don't even know which compounds are used in each ink, so we treat each spectrum as a "fingerprint" for qualitative identification.

The Direct Mass Spec involves dipping a capillary into sample before loading into the instrument. A stream of hot nitrogen gas is used to desorb the sample from the capillary, and a corona discharge ionizes the molecules in the gas stream. This ion source is most similar to an atmospheric pressure chemical ionization (APCI) source. A quadrupole mass analyzer allows the instrument to recognize individual ions by m/z.

Experimental

Raman Microscope procedure:

- Swatch each ink on a control paper
- Focus lens, locate saturated portion of paper, and pinpoint data point for sampling
- Collect and save one round of spectra
- Subsequently, add three more collections of each ink to the library

Direct Mass Spectrometry Procedure:

- Mix one drop of ink with 1/3 vial of distilled water
- Insert capillary
- Run sample to completion
- Repeat three cycles

References

- Jones, R; Cody, R.; McClelland, J. Differentiating Writing Inks Using Direct Analysis in Real Time Mass Spectrometry. *Journal of Forensic Sciences* **2006**, 51(4),915-918
- Jones, R.; McClelland, J. Analysis of Writing Inks on Paper Using Direct Analysis in Real Time Mass Spectrometry. *Forensic Science International* **2013**, 231(1-3) 73-81
- Saviello, D.; et al. A combined Surface Enhanced Raman Spectroscopy (SERS)/UV-vis approach for the investigation of dye content in commercial felt tip pen inks. *Talanta* **2018**, 181, 448-453

Raman

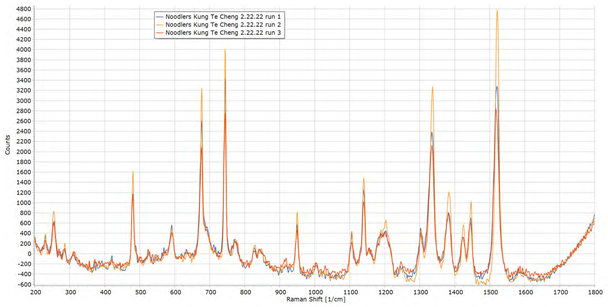

Figure 4: Multiple runs of Noodler's Kung Te Cheng ink analyzed by Raman

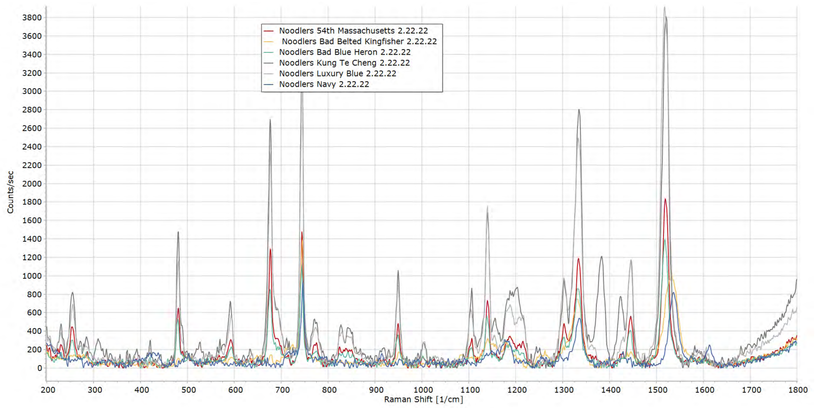

Figure 5: All Noodler's Ink Samples Analyzed by Raman

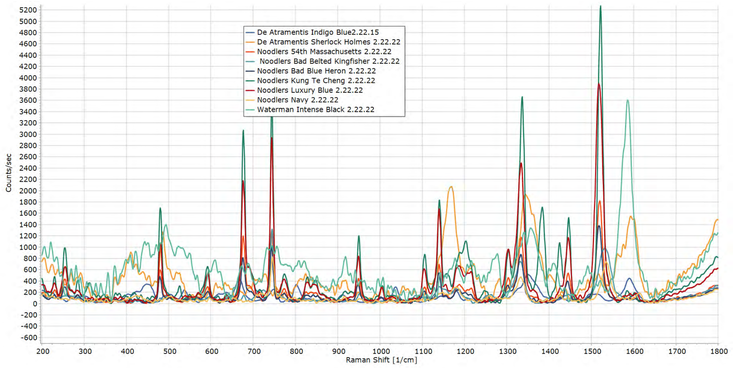

Figure 6: Inks analyzed by Raman

RADIAN ASAP Direct Mass Spectrometer

Figure 7: RADIAN ASAP Direct Mass Detector

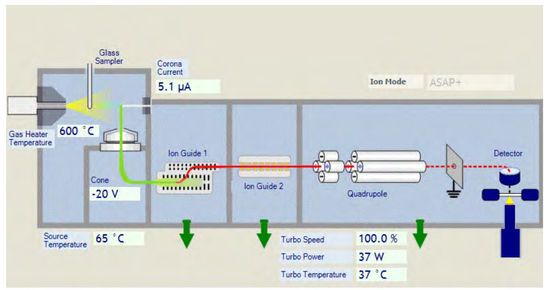

Figure 8: Mass Spectrometer Schematic Diagram

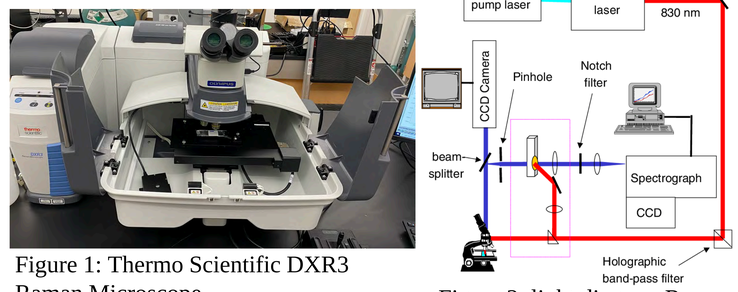

Figure 1: Thermo Scientific DXR3 Raman Microscope

Figure 2: light diagram Raman

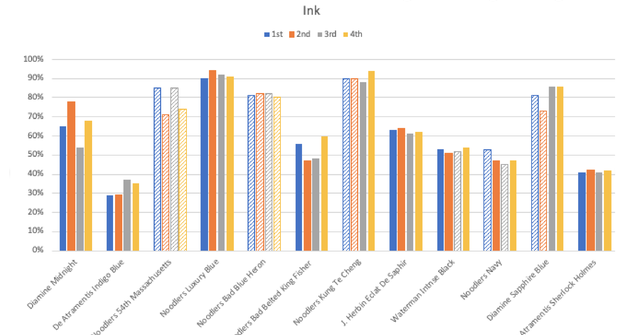

Figure 3: Bar graph of ink accuracy as data is inputted. Solid shading indicates accurate match. Bars with stripes indicate inaccurate identification

Conclusion

Ink differentiation with the Raman microscope resulted in inconclusive results. Inks of the same brand had identical peak locations which made it difficult for OMNIC software to differentiate using the Library search feature. Multiple of Noodler's inks were misidentified as Noodler's Luxury Blue. The other brands' black ink were also misidentified as each other.

The Direct ASAP Mass spectrometry instrument produced more comprehensible differentiation. Multiple 3-D charts show a clear delineation between the Noodler's inks and the De Atramentis inks.

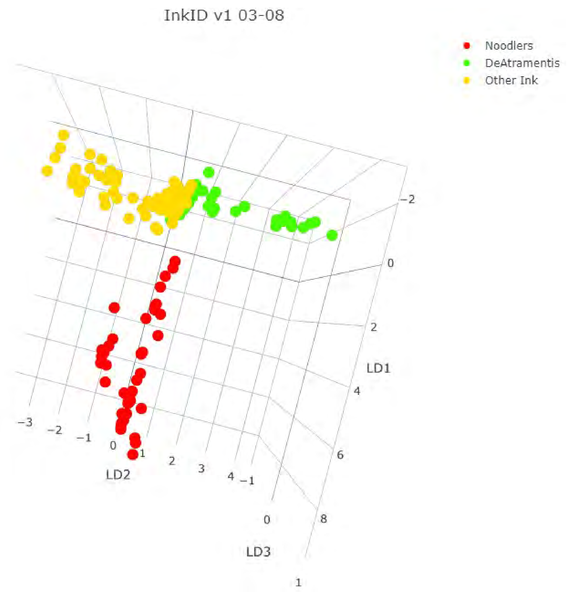

Figure 9: 3-D model analysis of Noodler's brand and De Atramentis