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APPLICATION NOTE

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3: DISCRIMINATING PRINTER INKS WITH THE FORAM

FORAM Raman Spectral Comparator

The low cost and ready availability of inkjet printers has greatly increased the frequency with which documents produced by these machines are encountered by document examiners. Conventional analytical techniques such as visible/IR absorption which are normally so useful in ink examination are not as effective with printed documents produced by inkjet printers. Other techniques such as chromatography involve the destruction of a small portion of the document.

Whilst the application of Raman and SERRS (Surface Enhanced Resonance Raman Scattering) spectroscopy to the analysis of questioned documents is widely discussed in the scientific literature [1, 2, 3, 4], the application of these techniques to the analysis of black inkjet inks is somewhat limited. Littleford et al [4] have used SERRS spectroscopy to probe the structural changes of the chromophore present in black inkjet inks when deposited onto paper. They also give examples of the types of dye that are likely to be found in inkjet inks.

In this Application Note, we demonstrate the potential of the Foster + Freeman FORAM Raman Spectral Comparator to discriminate black inkjet inks when used in conjunction with the SERRS technique.

Raman spectroscopy involves the scattering of laser light from a target material, the analysis of which provides the user with a spectral “fingerprint” of the molecular composition of the material

Ink samples

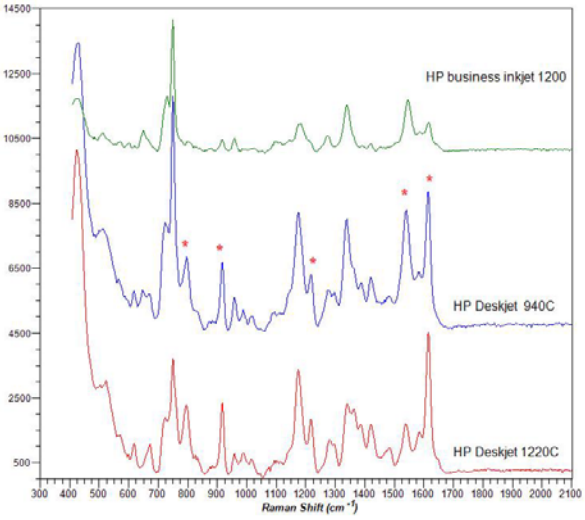
The study reported here involved subjecting 15 types of ink to analysis using the FORAM with a laser excitation wavelength of 685 nm. The SERRS technique was effected by applying poly-L-lysine (Sigma-Aldrich) and gold colloid (British Biocell) to the ink mark on the document [5] prior to recording each Raman spectrum. Spectra were baseline-corrected using a propriety fluorescence filter.

Serial	Inkjet Printer
1	Canon M610
2	Canon Pixma MP520
3	Epson Stylus C64
4	Epson Stylus C66
5	Epson Stylus DX7450
6	HP Business Inkjet 1200
7	HP C4180
8	HP Deskjet 820 Cxi

Serial	Inkjet Printer
9	HP Deskjet 940c
10	HP Deskjet 1220c
11	HP Deskjet 6122
12	HP Deskjet F2180
13	HP Photosmart 7150
14	Lexmark 4300
15	Lexmark Black Inkjet Cartridge #70

Results and Discussion

There are 15x14/2 = 105 sample pairs in the study. Most of the spectral pairs showed clear differences, yielding an overall visual discrimination rate of 84% (88 pairs).



Raman spectra of inks using SERRS

Brunelle and Crawford [6] describe the various types of dyes, solvents, dye complexing agents and surfactants typically found in inkjet inks. The dye component, which is the component expected to give rise to the spectra shown above, is frequently an azo dye with a very broad visible absorption profile. The differences between the dyes are often due to modification or addition of side chain groups [4] to improve properties such as light fastness or solubility. Although it has not been possible to identify the dyes giving rise to the different spectra shown, the small spectral differences observed are consistent with the assertion that the dye molecules have a similar basic molecular structure, but have different side chain groups. Further work is needed to prove this assertion.

Conclusions

The FORAM spectrometer has the ability to discriminate between different types of printer ink when the SERRS technique is applied. A discrimination rate of 84% was achieved. The instrumentation is cost effective, compact and almost free of maintenance.

References

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[4] R.E.Littleford, M.P.Hughes, G.Dent, D.Tackley and W.E.Smith, Applied Spectroscopy, Volume 57, Number 8 (2003), pp. 977 – 983.

[5] E.Wagner and S.Clement, Problems of Forensic Sciences, Volume 46 (2001), Pages 437 – 441.

[6] "Advances in the forensic analysis and dating of inks", R.L.Brunelle and K.R.Crawford, published by Charles C Thomas, Springfield, Illinois 2003, pp. 41 – 44.

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