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APPLICATION NOTE

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2: DISCRIMINATING TONERS WITH THE FORAM

FORAM Raman Spectral Comparator

The discrimination of laser printer and photocopier toners present the document examiner with particular challenges. Conventional analytical techniques such as visible/IR absorption which are so useful in ink examination are not applicable to toners. Other techniques such as FTIR (Fourier Transform Infrared) spectroscopy are either quite destructive to the document or are time consuming and expensive. Merrill et al [1] have described the various FTIR techniques which may be applied to toners.

In this Application Note, we demonstrate the potential of the Foster + Freeman FORAM Raman Spectral Comparator to discriminate toners. Initially, we attempt to discriminate toner in-situ on the document. Subsequently, we extract the acetone soluble components from the toner and deposit the solute onto aluminium foil. This solute is then subjected to Raman analysis in the same way.

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

Toner samples

The study reported here involved subjecting 15 types of toner to analysis using the FORAM with a laser excitation wavelength of 685 nm. Spectra were baseline-corrected using a propriety fluorescence filter.

Serial	Name	Colour on Extraction
1	HP 98X	Colourless
2	HP Color LaserJet 4600 PCL6	Colourless
3	HP Color LaserJet 9500 PCL6	Colourless
4	HP LaserJet 6P	Colourless
5	HP LaserJet 1022 Series	Grey
6	HP LaserJet 1160	Grey
7	HP LaserJet 1200	Grey
8	HP LaserJet 2300	Colourless

Serial	Name	Colour on Extraction
9	HP LaserJet 4300tn	Grey
10	HP LaserJet P3005 PCL6	Colourless
11	Kodak 235	Black
12	Konica 3340	Black
13	Lanier M6765 6755	Grey
14	Minolta CF 900	Yellow
15	Mita DC1860	Black

Toners can contain a variety of components: a fusible resin, iron oxide (Fe_3O_4), carbon black, dyes or pigments, surfactants and charge control agents [2]. Typical resins include: styrene/butadiene copolymer, polyester, styrene ethylhexylacrylate, styrene n-butylacrylate and a number of other copolymers. The colour of the toner may be modified by the addition of dyes: nigrosine, victoria blue, methyl violet, pthalocyanines, azo-pigments and quinacridones. The charge control agents are often complex organometallic compounds, which can also act as dyes, or quaternary ammonium salts (both aromatic and aliphatic) [3].

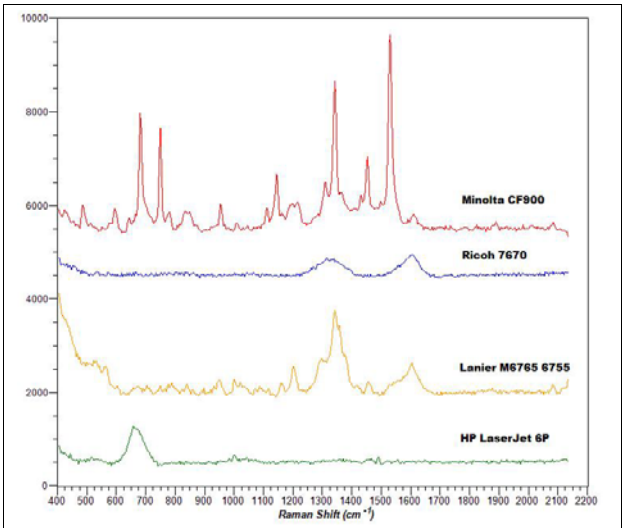
Components of the toner were extracted by immersing a small area of the document (~5 mm^2) in 2 ml of acetone (*Chromasolv Plus*, Sigma Aldrich 650501-1L) for several hours. Approximately 0.3 ml of the

resulting solution was then applied to a microscope slide covered with aluminium foil and allowed to dry. Spectra of the remaining residue were recorded using the FORAM. The aim of the extraction process was to concentrate the soluble components (resins and dyes) whilst removing possible interference from the insoluble components (carbon black and iron oxide).

Results and Discussion

There are 15x14/2 = 105 sample pairs in the study.

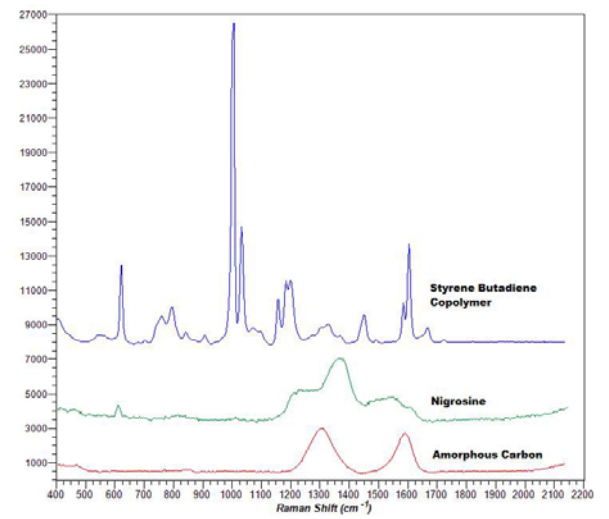
Toner (in situ): discrimination 72%



Raman spectra of toners

Most of the spectral pairs showed clear differences, yielding an overall visual discrimination rate of 72% (76 pairs).

Toner components



Raman spectra of toner components

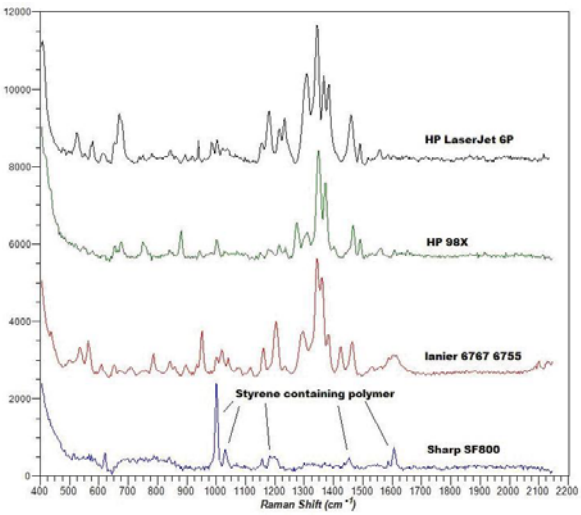
Many of the components either yielded no Raman spectrum or fluoresced too intensely to enable one to be obtained.

Note that the spectrum of Ricoh 7670 correlates well with that of amorphous carbon. It is surprising, however, that despite the toner containing as much as 60% resin [3], no spectral peaks corresponding to the resin component are observed. It is likely that the peak at 668 cm^{-1} in the spectrum of HP 6P LaserJet arises from magnetite [4].

Toner residue: discrimination 84%

Most of the spectral pairs showed clear differences, yielding an overall visual discrimination rate of 84% (88 pairs).

Note that peaks attributable to styrene are observed in the spectrum of the Sharp SF800 toner extract, which is presumably attributable to a styrene containing copolymer.



Raman spectra of toner extract

Conclusions

The FORAM spectrometer has the ability to discriminate between different types of toner, both in situ on the document, and extracted into acetone. Discrimination rates of 72% and 84% were achieved. As the FORAM spectrometer requires only very tiny amounts of material, the method for extracting and concentrating the toner extracts could be optimised further, reducing the amount of material removed from the document. The instrumentation is cost effective, compact and almost free of maintenance.

References

[1] R.A.Merrill, E.G.Bartick and W.D.Mazella, Journal of Forensic Sciences, Vol.41, No.2 March 1996.

[2] “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.

[3] “Electro-photography and Development Physics”, L.B.Schein, Laplacian Press 1996, pp. 85 – 87.

[4] A.Zoppi, C.Lofrumento, E.M.Castellucci and M.G.Migliorini, Spectroscopy Europe 14/5 (2002), pp. 16 - 20.

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