

ECCO APPLICATIONS

Discriminating Printer Toners using LIBS



The discrimination of laser printer and photocopier toners present document examiners 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 ECCO to discriminate toners. The samples consisted of printed text on typical white office paper. No sample preparation was required so the toners were analysed in-situ and the results for each toner were obtained in a matter of seconds. Five spectra of each toner were obtained to ensure they were representative. The paper was also analysed, providing a background reference to assist in the interpretation.



ECCO LIBS Spectrometer

The ECCO provides elemental analysis of evidence, with little or no sample preparation, by Laser Induced Breakdown Spectroscopy (LIBS).

The LIBS technique involves the generation of optical emission spectra from the target material that are characteristic of its elemental composition.



A wide range of toners are produced by many different manufacturers

Toner Discrimination: Alternative Techniques

The ability to discriminate between printer/copier toners and to identify the machines used to produce or amend a document is highly desired by document examiners. As such many analytical techniques have been trialed during the past 30 years.

A recent in-house study using the Foster+Freeman Forum instrument, demonstrated Raman spectroscopy to be a viable, and relatively inexpensive method of toner discrimination.

Analysis of more than 20 different toners provided a discrimination rate of 84%.

To request a copy of the Forum study please contact:
sales@fosterfreeman.com

Toner Samples

The five printer toners that form the basis of this application note are listed here:

Sample	Printer
1	HP LaserJet 1022n
2	HP LaserJet Pro P1606dn A
3	HP LaserJet Pro P1606dn B
4	Brother HL-3040CN
5	Toshiba e-studio 283

Toners are highly complex materials that are manufactured to tightly controlled specifications.

At their most basic level all toners will have a certain commonality in their composition. However, there are many aspects that can be adjusted to change the overall performance of the toner which could result in observable variation between toners.

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, phthalocyanines, 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].

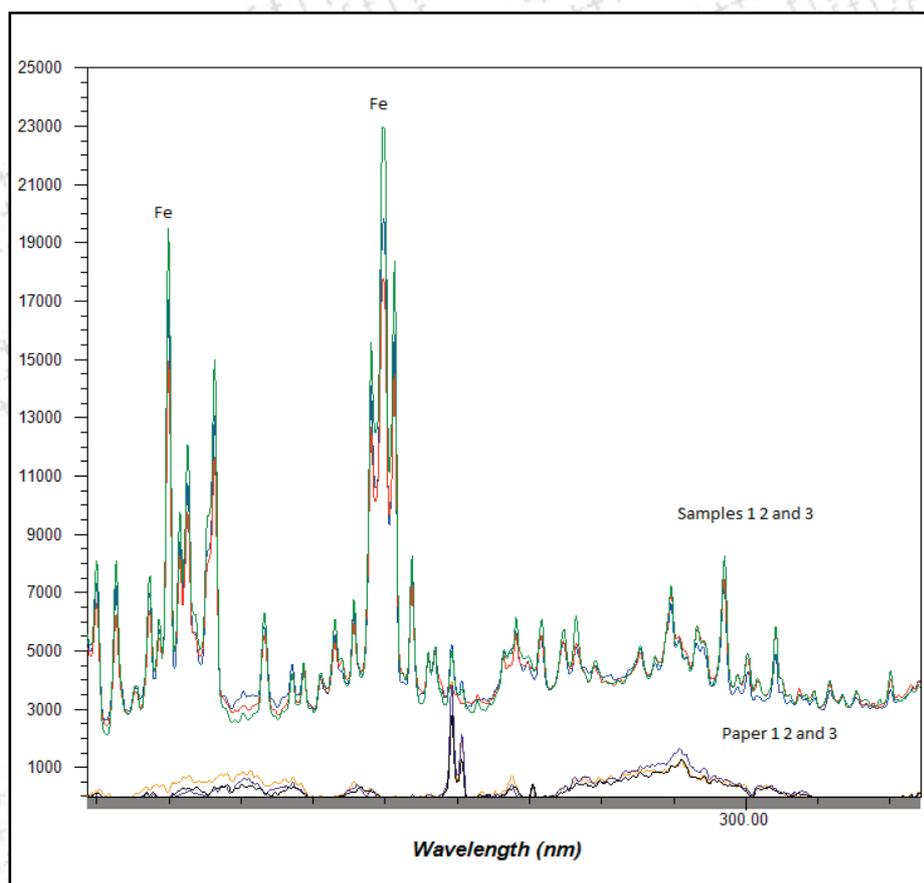
Results and discussion

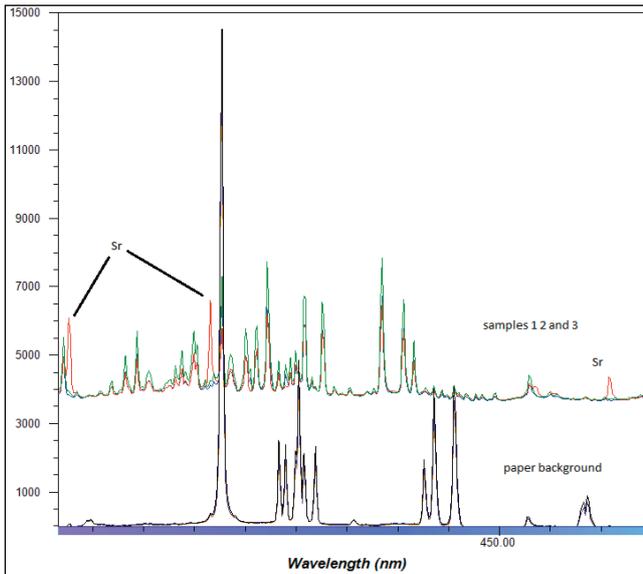
There were 10 possible pairs in this mini study ($5 \times 4/2$).

Nine pairs were discriminated, giving a discrimination power of 90%.

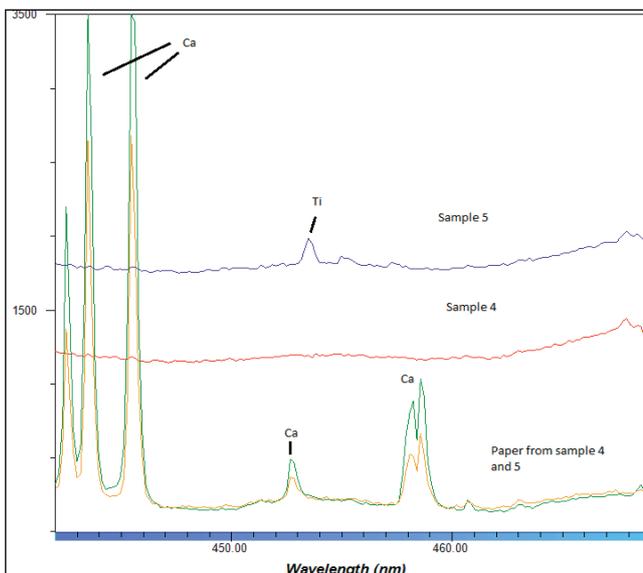
Toners 1, 2 and 3 all showed iron peaks, which is typical of toner containing iron oxide.

On this basis they could be discriminated from the remaining samples as they did not contain iron.

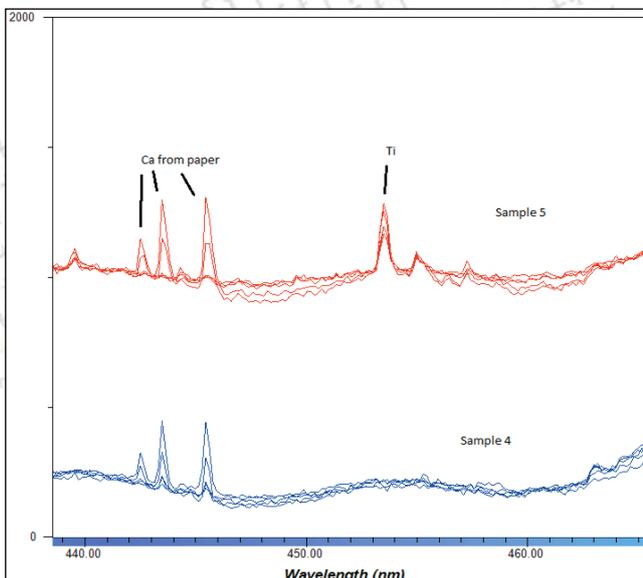




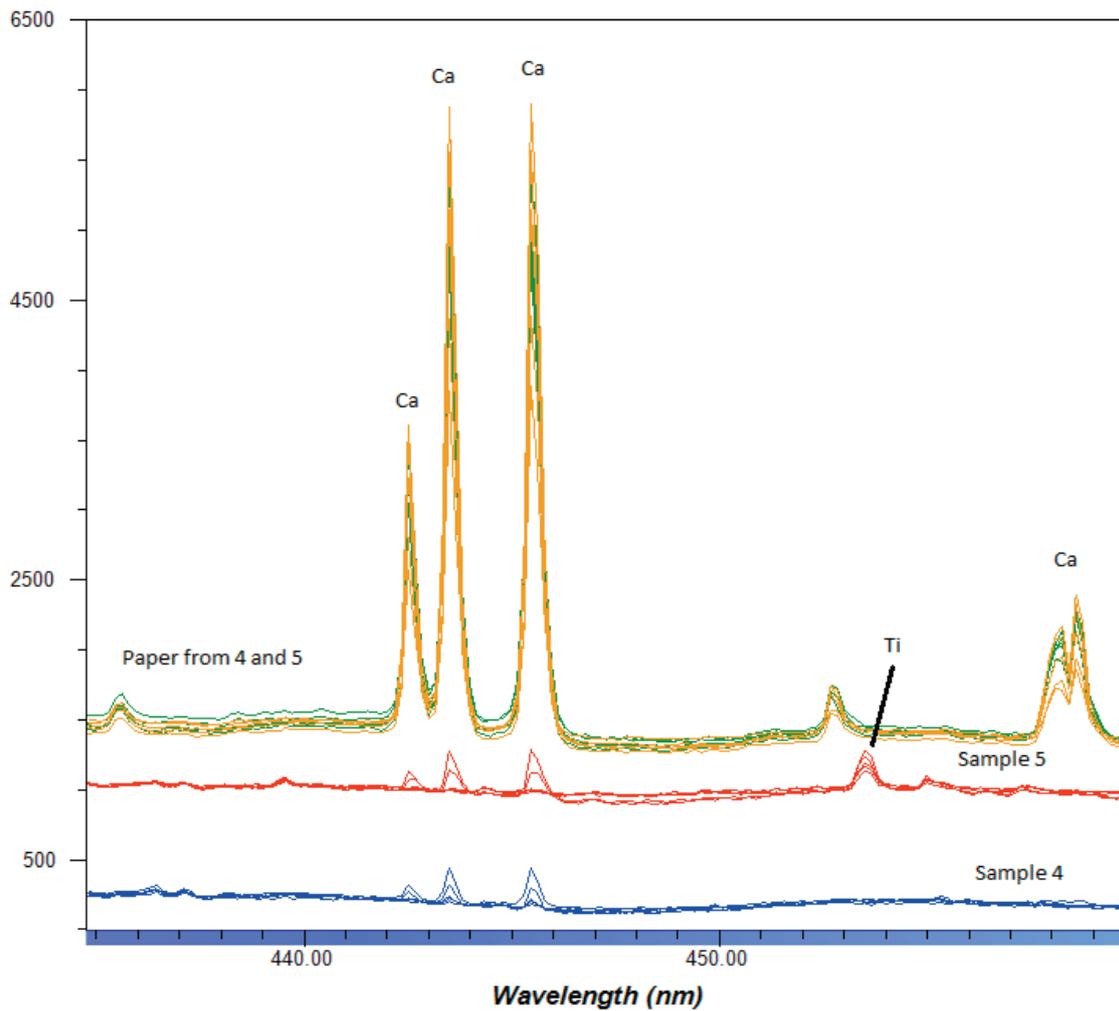
Toner 2 (shown in red) could be further discriminated from 1 and 3, based on the presence of strontium.



Toner 5 showed weak titanium peaks and could therefore be discriminated from the other samples (spectra off-set for clarity).



The spectra also show some weak peaks from calcium which is probably from the paper. Typical office paper uses calcium carbonate as an optical brightener.



Conclusion

Five toners from different printers were investigated in this mini study and a discrimination power of 90% was achieved.

Laser printers and photocopiers can present the document examiner with particular challenges, however the ECCO has demonstrated the ability to discriminate toners from different printers.

Although classed as a minimally destructive technique, the ECCO only requires very small amounts of toner to be consumed and no sample preparation was required. The results were therefore obtained quickly and easily.

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.