Micro-Raman Spectroscopy of Color Inkjet Printed Documents

Williams David Mazzella, MS; Adrien Mathieu, MS; and Patrick Buzzini, MS

Ecole des Sciences Criminelles, Institut de Police Scientifique, University of Lausanne, BCH, 1015 Lausanne, Switzerland

Inkjet printed documents produced by 22 different brands and models of color inkjet printers available on the Swiss market were analyzed by micro-Raman spectroscopy using a near infrared (NIR) excitation wavelength of 785 nm. The magenta components were discriminated into 11 groups, but the cyan inks could not be further distinguished. The yellow inks did not exhibit significant Raman scattering; however, the cyan inks could not be further distinguished. The yellow inks did not exhibit significant Raman scattering, but the signals may have been concealed due to strong interference from the paper background.

Introduction

Interest in the forensic analysis of inkjet printed documents has increased with the proliferation and development of such office machines. The growing popularity and quality of color inkjet printers clearly demonstrates the need for forensic document examiners to keep abreast of this new technology to analyze suspicious color printed documents.

Inkjet printers provide an effective means of producing counterfeit and fraudulent documents, especially with respect to travel documents and currency. During the last few years, the number of cases sent to forensic laboratories that involve inkjet printing appear to have significantly increased. Since a suspect printer may not be available, the document examiner is often requested to determine the make and model of an inkjet printer used to produce a contested document or to establish a link between 2 or more questioned documents. This latter aspect is particularly useful for providing forensic intelligence to investigators. This paper describes how Raman spectroscopy may be used to make class comparisons of inkjet inks.

Many technical publications describe the inkjet printing process; however, few forensic papers refer to the analysis of inkjet printing inks by Raman spectroscopy. One of the most important technical papers relating to the inkjet printing process was written by Le Hue (1998). La Porte (2004) later wrote a comprehensive forensic overview of inkjet printing.

Raman spectroscopy involves the detection of inelastic scattering of photons due to the vibrational modes of molecular nonpolar bonds. When a molecule is irradiated by an intense monochromatic light of frequency ν_0, like a laser, it passes from a vibrational state to another vibrational state. This excitation generates a phenomenon of scattering (or diffusion) of light from the molecule. The scattered light occurs at the same frequency of the excitation source (elastic, *Rayleigh* scattering) as well as at slightly different frequencies $\nu_0 \pm \nu_m$ (inelastic, *Raman* scattering), where ν_m is the frequency of vibration (or rotation) of the molecule. Since the values of ν_m are unique to each different molecule, the Raman spectrum becomes an important tool for the characterization and identification of matter.

Advantages of micro Raman spectroscopy include high resolution and the minimal time needed to obtain data. This technique has been discussed in the literature previously for comparing and identifying pigments and dyes (Claybourn and Ansell 2000; White 2000; Andermann 2001; Mazzella 2003; Mazzella and Buzzini 2005).

Methods and Materials

Sampling and General Observations

Printed samples were randomly collected from 41 inkjet printers. Since some samples were produced using the same make and model of cartridge, samples were checked against an inkjet ink compatibility database to reduce the sample size.

Code	Brand	Serial	Model	Cartridge	Technology
1	Canon	BubbleJet	S500	Canon BCI-3e	T
3	Canon	BJC	4100	Uprint	T
4	Canon	-	i320	Canon BCI-24	T
6	Epson	Stylus Color II	ESC P2	Epson S020036	P
7	Epson	Stylus Color	440	Unknown	P
8	Epson	Stylus Color	480	Epson S020191	P
9	Epson	Stylus Color	685	Armor	P
10	Epson	Stylus Color	880	Epson T020401	P
11	Epson	Stylus Photo	Ex	Epson S020110	P
12	Epson	Stylus Photo	750	Epson S020193	P
13	Epson	Stylus Photo	950	Epson T033	P
14	HP	DesignJet	1055CM	HP 80	T
15	HP	DeskJet	610C	HP 49	T
17	HP	DeskJet	720C	HP 23	T
18	HP	DeskJet	840C	HP 17	T
21	HP	DeskJet	920C	HP 78	T
29	HP	DeskJet	5550	HP 57	T
35	HP	Business Inkjet	3000	HP 12	T
37	Lexmark	-	Z32	Lexmark 60	T
38	Lexmark	-	Z53	Lexmark 20	T
39	Lexmark	-	X73	Lexmark 20	T
41	Xerox	-	M750	Xerox	T

Table 1. A list of inkjet printers used to print documents that were subsequently analyzed by micro Raman spectroscopy

Consequently, if the same ink was used in several inkjet printers, only 1 sample was chosen for use in the study, with the exception of samples #38 and #39. As a result, 22 printers using different cartridges were analyzed (Table 1).

Despite efforts to obtain original equipment manufacturer (OEM) inks, samples #3, #7, and #9 were printed with non-OEM inks. To facilitate the preliminary investigation, all of the 22 analyzed samples were printed on "test pages"; i.e., the 4 main colors (cyan, magenta, yellow, and black) were printed separately. Each separate color was then cut and glued to a microscopic glass plate (Figure 1).

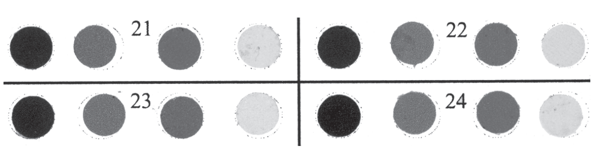

Figure 1. The 4 main colors (cyan, magenta, yellow, and black) were cut and glued to a microscopic glass plate.

Micro Raman Spectroscopy

Analysis using Raman spectroscopy was carried out using a Renishaw RM 1000 Raman spectrometer (Renishaw plc, Gloucestershire, UK), equipped with a Leica DM research microscope (with 5x, 20x, 50x, and 100x lens objectives). Four laser wavelengths were available using: a 514.5 nm Argon ion laser (20 mW maximum output power), 632.8 nm Helium-Neon laser (14-17 mW maximum output power), and 2 near-infrared (NIR) diode array lasers at 785 nm and 830 nm respectively (both 300 mW maximum output power). The instrument was also equipped with a 1200 1/mm grating and a thermo-cooled charge-coupled device (CCD). Data was collected over the spectral range 2000 and 200 cm^{-1}. Laser power varied from sample to sample and was modulated at 100%, 50%, 10%, and 1% to obtain the best

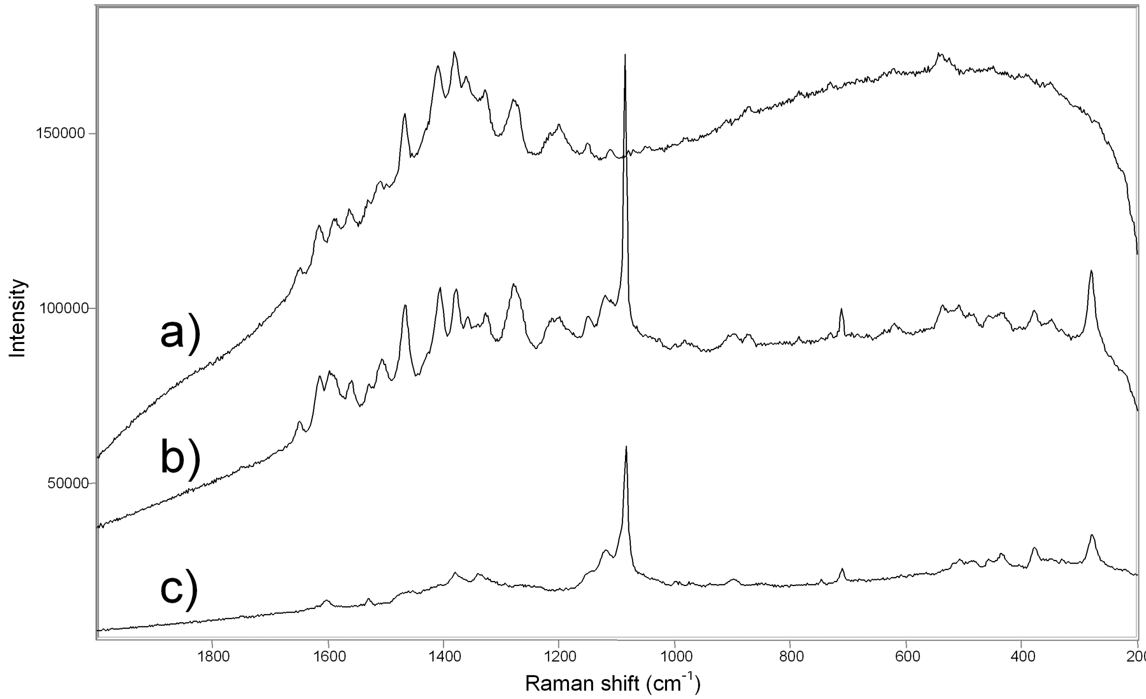

Figure 2. Raman spectra of: a) the extracted magenta dye from the OEM HP 23 cartridge; b) the magenta dot of a printed document using the HP DeskJet 720 printer; and c) the paper used as support (laser source: ëexc = 785 nm). The spectrum of the printed document shows Raman bands coming from both the ink and the paper.

signal-to-noise ratio and to avoid burning the sample. The Raman spectra were collected and managed using the GRAMS/32 software by Galactic Industries Corporation.

Results

Preliminary Tests

Only colored inks were analyzed during this study by focusing on the pure dots of cyan, magenta, and yellow. Preliminary measurements were conducted on samples #4 (Canon i320), #13 (Epson Stylus Photo 950), #21 (HP DeskJet 920 C), and #38 (Lexmark Z53) to find the best analytical conditions. The NIR diode array laser source operating at 785 nm was found to be the best choice, and the microscope was focused on the samples using a 100x objective lens. Under these conditions, and using maximum laser power, a value of 70 mW was recorded for each sample. The 830 nm NIR laser gave the same results as the 785 nm NIR diode array laser, while lasers operating in the visible range (i.e., at 514.5 nm and 632.8 nm) generated fluorescence that concealed Raman spectral information.

Paper Interference

One factor investigated in this study was whether paper components influenced the quality of the Raman spectra of the inks. To investigate this problem, 31 different kinds of plain papers were analyzed. All 31 Raman paper spectra had very similar results.

Magenta, cyan, and yellow inks originating from the printer HP DeskJet 720 (sample #17) were extracted from the cartridge and spotted on a glass microscope slide. Raman spectra produced by the pure ink samples were then compared to spectra from the papers. The interference caused by the paper was most noticeable in the spectral regions 1080 to 1100 cm-1 and 660 to 200 cm-1 (Figure 2). The majority of the Raman bands obtained from printed samples were attributed to the ink and not to the paper itself.

Reproducibility

The reproducibility of the technique was tested by doing 10 consecutive analyses of 10 different areas printed by each colored ink of an Epson Stylus Photo 950 (sample #13) printer. In general, the best spectra were obtained by focusing on a

Group	Code	Inkjet Printers
1	1	Canon Bubblejet S500
	4	Canon i320
2	3	Canon BJC 4100
3	6	Epson Stylus Color II ESC 2
4	7	Epson Stylus Color 440
5	8	Epson Stylus Color 480
	10	Epson Stylus Color 880
	11	Epson Stylus Photo Ex
	12	Epson Stylus Photo 750
	13	Epson Stylus Photo 950
6	9	Epson Stylus Color 685
7	14	HP Designjet 1055CM
	21	HP DeskJet 920C
	35	HP Business Inkjet 3000
8	15	HP DeskJet 610C
	17	HP DeskJet 720C
	18	HP DeskJet 840C
9	29	HP DeskJet 5550C
10	37	Lexmark Z32
	38	Lexmark Z53
	39	Lexmark X73
11	41	Xerox M750

Table 2. Inkjet printers grouping of the magenta inks Raman analysis.

straight and flat fiber in the printed sample. The ink must be present in sufficient quantity (e.g., full coverage over the paper fibers), and tested regions must exclude other color inks. The importance of using a 100x lens objective while focusing on an area for analysis cannot be emphasized enough since it facilitates the isolation of a small, homogenous area.

Magenta colors

The magenta samples were organized into 11 groups according to the presence or absence of Raman bands at specific Raman shift values. While this banding was reproducible and exploitable for the comparison of inkjet samples, the intensity of the Raman bands often varied. At least 10 measurements of each sample were taken to evaluate the intra-variability of band intensities. Raman spectra for the 11 groups shown in Table 2 appear in Figures 3 and 4.

Considering that 22 printed samples were analyzed, the number of possible pairs was 231 using the formula N x (N-1)/2. Although it was possible to discriminate 211 pairs (92%) using Raman spectroscopy, 20 pairs (8%) could not be discriminated using this method.

Cyan colors

Repeated frequency measurements conducted on each cyan ink sample were reproducible; however, the analysis of the different cyan ink samples was not discriminatory (Figure 5). Differences in intensity, mainly due to weak fluorescence, were encountered amongst the samples analyzed, but these differences were not of sufficient magnitude to form separate groupings.

Yellow colors

Interference caused by the paper was much stronger for yellow samples than the cyan and magenta. When visualized with the microscope, it was difficult to distinguish the paper from the yellow colored area due to their similar appearance. Consequently, measurements of yellow ink samples were the most difficult to achieve and interpret. In most cases, only the Raman bands due to the paper were present in the spectrum (Figure 6).

Discussion

Generally, results obtained by analyzing color inkjet inks using micro-Raman spectroscopy were reproducible. However, it was observed that magenta inks were more easily discriminated than cyan or yellow inks. As previously mentioned, several measurements of an ink sample were necessary to evaluate possible sample differences in intensity. Despite this limitation, the location of Raman bands was found to be reproducible.

Concerning the analysis of several paper backgrounds, the fact that they regularly generated the same Raman bands, easily distinguished the magenta ink bands, constituting an advantage for the spectra interpretation (even if the reference analysis of the paper was always recommended). Raman analysis is an ideal method for analyzing inkjet inks *in situ*. A research microscope equipped with a 100x objective lens was of

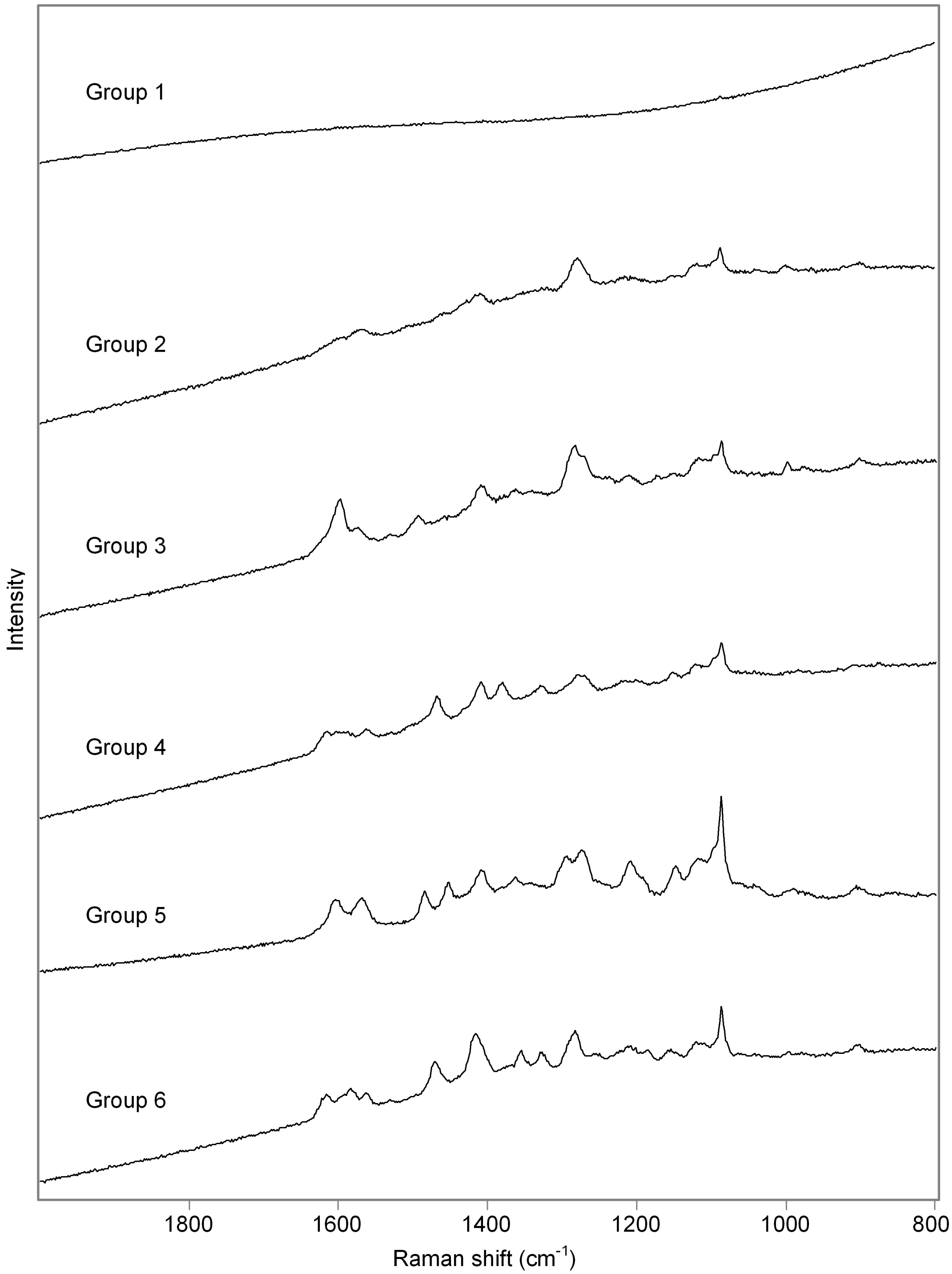

Figure 3. Groups 1 through 6 obtained for the magenta colors.

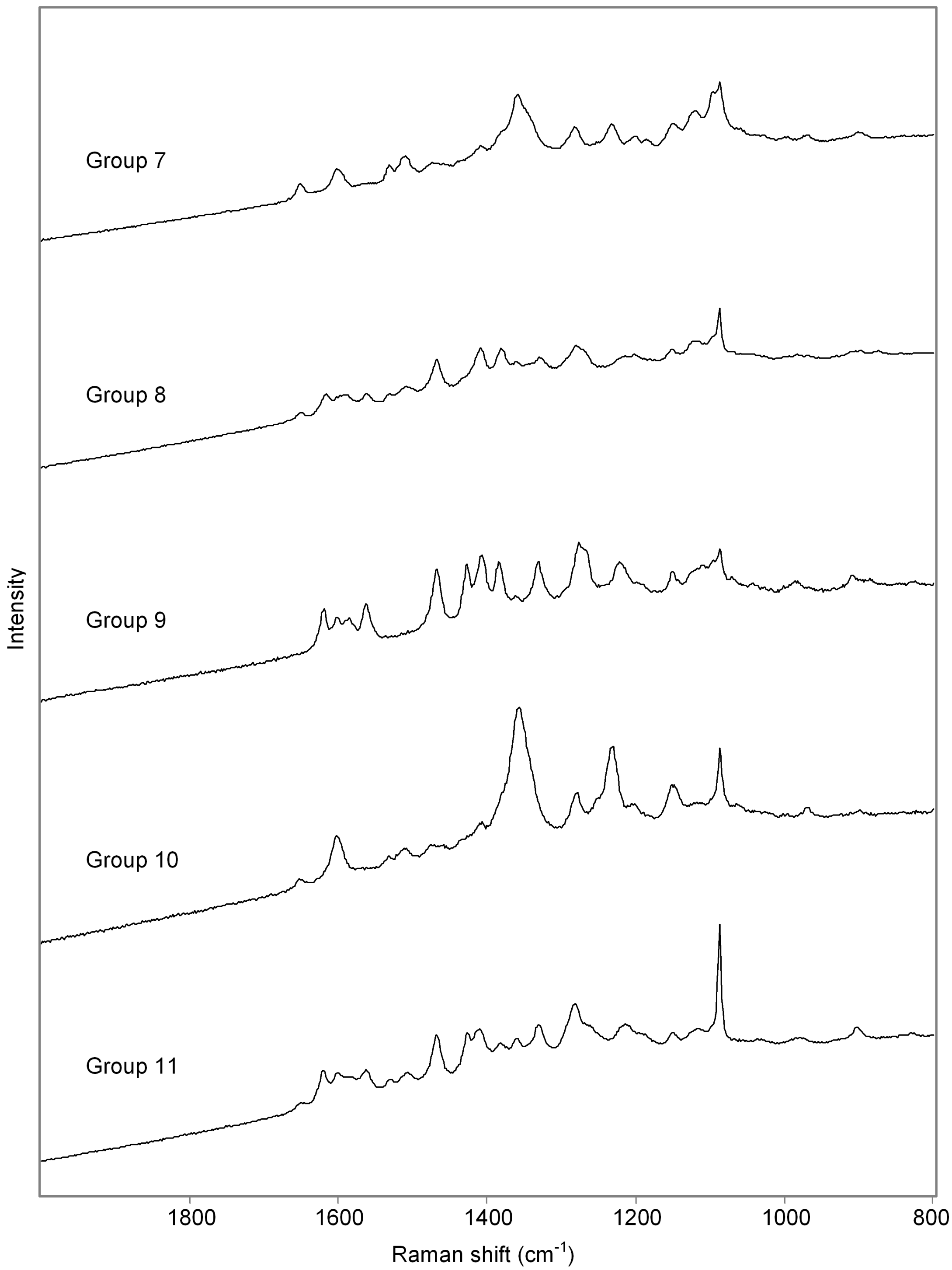

Figure 4. Groups 7 through 11 obtained for the magenta colors.

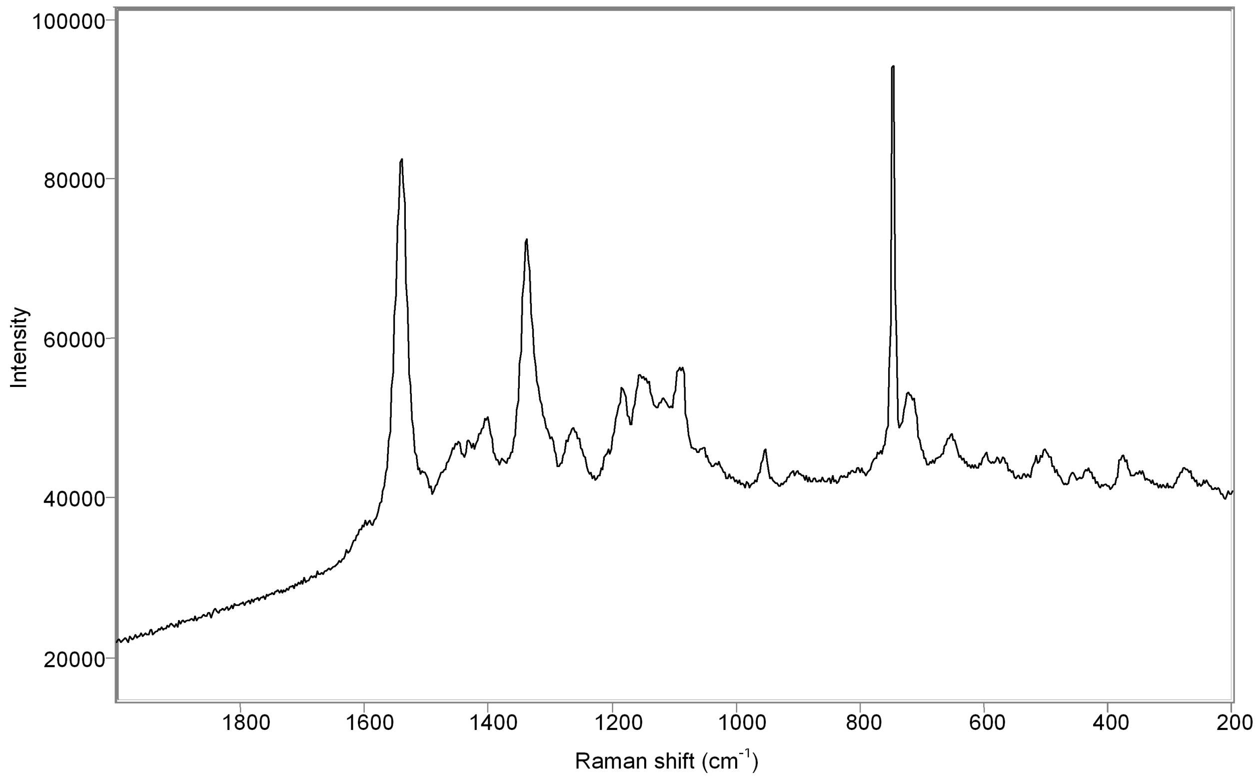

Figure 5. An example of a Raman spectrum for a cyan color.

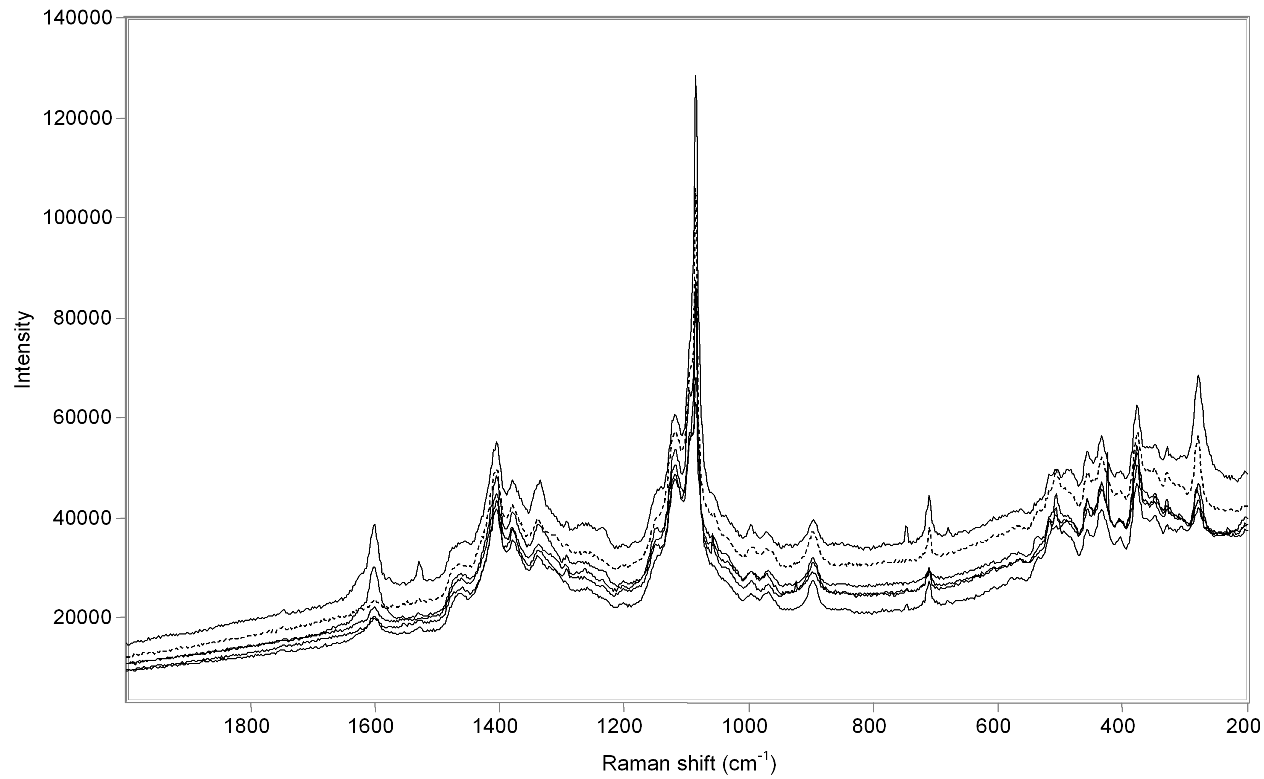

Figure 6. Examples of Raman spectra for yellow colors. The dashed line corresponds to the paper background.

tremendous assistance because of its ability to isolate and focus on a single inkjet dot. This is especially important considering the improvements by inkjet printer manufacturers to improve printing quality by reducing the size of the cartridge nozzles.

Printed documents, in general, can be separated into different groups based on the make and/or model of printer (Table 2). Moreover, OEM inks can be differentiated from those produced by other manufacturers. The major contribution of Raman spectroscopy is the discrimination of ink samples. The analyst has to take into account that these results are based on class characteristics and that many cartridges produced by a specific manufacturer will contain the same ink. Another advantage of Raman spectroscopy is that it is possible to produce a list of ink cartridges that could have created a given printed text. This information can be very useful for investigators tasked with the responsibility of locating the source of an unknown document.

As with many forensic examinations, the ability to reach meaningful conclusions very much depends on the size, content, and value of a database. To state that an unknown or questioned document was printed using a specific inkjet ink during a certain period of time, excluding all others, an analyst must have knowledge of all possible manufacturers and distributors, their ink formulations, and their years of production. Realistically, databases seldom contain all this information, and gaps will inevitably exist. This leads to an inherent uncertainty that must be considered when drawing conclusions. Raman spectroscopy of colored inkjet inks can be very useful for detecting inks produced by different manufacturers.

Conclusion

Twenty-two inkjet inks of different brands and models were analyzed with Raman spectroscopy using a NIR excitation source at 785 nm. Spectra obtained by analyzing the magenta inks were most valuable in that they permitted the 22 inks to be classified into 11 groups. Cyan inks could not be effectively discriminated by this method, and the paper substrate interfered with spectral peaks produced by yellow inks. This research has shown that micro-Raman spectroscopy provides a nondestructive, noninvasive, and rapid technique for analyzing color inkjet inks.

References

Andermann, T. (2001). Raman spectroscopy of ink on paper. *Problems of Forensic Sciences, Special Issue*. Proceedings of the Second European Academy of Forensic Science Meeting, 2000 Sept 12-16, Krakow, pp. 335-344.

Claybourn, M. and Ansell, M. (2000). Using Raman Spectroscopy to Solve Crime: Inks, Questioned Documents and Fraud. *Science & Justice*, Vol. 40, No. 4, pp. 261-271.

Le Hue, P. (1998). Progress and Trends in Inkjet Printing Technology. *Journal of Imaging Science and Technology*, Vol. 42, No. 1, pp. 49-62.

LaPorte, G. (2004). Modern Approaches to the Forensic Analysis of Inkjet Printing—Physical and Chemical Examinations. *Journal of the American Society of Questioned Document Examiners,* Vol. 7, No. 1, pp. 22-36.

Mazzella, W. D. and Khanmy, A. (2003). A Study to Investigate the Evidential Value of Blue Gel Pen Inks, *Journal of Forensic Sciences*, Vol. 48, No. 2, pp. 419-424.

Mazzella, W. D. and Buzzini, P. (2005). Raman Spectroscopy of Blue Gel Pen Inks. *Forensic Science International,* Vol. 152, No. 2-3, pp. 241-247.

White, P. C. (2000). SERRS Spectroscopy—A New Technique for Forensic Science? *Science & Justice*, Vol. 40, No. 2, pp. 113-119.