RAMAN ANALYSIS IN DOCUMENT EXAMINATION

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Abstract: *Analysis of questioned documents can often be aided by chemical characterization of the ink or toner on the document. In cases where there is little visual difference between reference and questioned areas, Raman analysis can provide chemical information about the pigments and resins which may show similarities or differences in printing materials on the documents.This paper provides background information about Raman spectroscopy, as well as examples of its applicability to the analysis of inks, toners, and pencil leads on documents.*

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Keywords: Raman spectroscopy, Raman theory, Raman microscopy, Raman scattering, dipole moment, Stokes/ anti-Stokes emission, photons, polarizability

1. Introduction

Raman spectroscopy is an identification technique that uses a laser to probe a sample. Laser light is directed onto a sample through a microscope or by fiber optic cable. The sample absorbs some of the laser light, reflects some of the laser light and also re-emits or scatters the absorbed laser light. The re-emitted or scattered laser light that has interacted with the sample is collected by the microscope optics or fiber optic cable and directed to a detector. The detector measures the wavelength of collected light precisely relative to the wavelength of the laser light, producing a spectrum with bands related to the chemistry of the sample. Raman microscopy is a complementary technique to Fourier transform infrared spectroscopy analysis (FTIR); it is better suited, however, for the analysis of black materials such as carbon black, black iron oxide, and graphite because it is an emission technique rather than an absorption technique like infrared analysis. Raman spectroscopy can provide identifying information about both organic (carbon based materials such as resins, dyes and polymers) and inorganic materials (such as metal oxides or minerals). Based on rules regarding the symmetry of a molecule, we find that some compounds produce strong Raman spectra and weak infrared spectra, while some compounds produce strong infrared spectra and weak Raman spectra.

Raman analysis is also very flexible with regard to sampling. Samples can often be analyzed *in situ* without altering a document, as opposed to infrared spectroscopy analysis where the sample is typically transferred to an infrared compatible substrate such as a polished salt plate that is transparent to the infrared light. Raman analysis also provides greater spatial resolution relative to infrared microscopy. The laser beam used to probe a sample can be focused to a diameter of 1 micrometer, whereas an infrared microscope has a theoretical limit of 10 micrometers.

2. The Raman Effect

The Raman effect is named after the Indian chemist, Chandrasekhara Venkata (C.V.) Raman, who mathematically predicted a scattering effect (absorbing and re-emitting of light) in his study of optics and light during his work in the 1920s. In the early part of the 1900s, however, he had a difficult time proving that the effect was actually occurring, due to poor light sources (both in power and monochromaticity).

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Experiments that he did conduct with filtered sunlight did provide evidence of the effect (1).

In the 1960s, the advent of lasers helped further the study of the Raman scattering effect by providing bright, monochromatic light sources. The effect that Raman predicted is a type of vibrational spectroscopy based on the interaction of monochromatic light with the electron structure of a molecule. This interaction involves an inelastic collision between a photon and a molecule in which the photon is absorbed and the molecule is excited with the result that it vibrates more rapidly. As the molecule relaxes, it emits a photon. If the molecule returns to its original vibrational state, the photon emitted by the molecule is the same wavelength as the photon absorbed (same as the laser wavelength). If, however, the molecule relaxes to a vibrational state that is different from its initial state, the energy of the emitted photon is different from that of the absorbed photon. The emitted photons with different energies than the absorbed photons are Raman photons and result from the Raman effect. Approximately one photon in every 1,000,000 photons emitted is a Raman photon.

3. Raman Theory

When a photon is absorbed by a molecule it creates an induced dipole moment (μ) in the molecule. A dipole moment is a separation of positive and negative charge, in a sense similar to the North and South of a magnet. The strength of this induced dipole moment is related to the polarizability (a) of the electron structure of a molecule, and the strength of the electric field E (laser power). Mathematically, these properties are related in the following equation:

μ=áÅ

The polarizability term á is related to the polarizability of the molecule at some equilibrium state (á$_0$) and to the changes in polarizability (□á) as the molecule vibrates along its normal vibrational coordinate (Q). These terms are related mathematically as follows:

á = áo + (□á/□Q)Q + ...

Polarizability is a measure of how hard it is to deform or push apart the electrons moving around a molecule. At the (á$_0$) position for two atoms connected to each other, it is easier to deform the electrons than it is when the atoms have moved away from each other (during a normal vibration). The polarizability constant (á) is sensitive to the distance between atoms in a molecule. The distance between atoms (vibrational coordinate Q) in a molecule changes with a normal molecular oscillation (vv) and time. This vibrational coordinate term Q is defined as:

$$Q = Q_0 \mathrm{cos}2\partial v_v t$$

The strength of the electric field of the laser is equal to its maximum energy (E$_0$) times the oscillation of the laser frequency (v), multiplied by a time constant. The equation for the electric field of the laser is:

A=Å$_0$cos2∂vt

This part of the Raman theory requires us to treat the laser light as a wave that oscillates at a particular wavelength. The wavelengths that are often used are from green light (514 nanometers) to near infrared light (785 or 1065 nanometers). Also, the wavelengths of laser light fall in the spectrum of electromagnetic radiation. Electromagnetic radiation includes x-rays, UV light, visible light, infrared light, microwaves and radio waves. That is why we refer to the electric field of the laser. When we substitute the equations describing the polarizability, electric field,and coordinate function into the original equation for the polarizability, we find that we get the following equation:

μ = áo Eocos2∂□t +
0.5(□á/□Q)(Q0E0)[cos{2∂(□+□□t} + cos{2∂(
□-□$_{□□}$□)t}]

that describes both the scattering or emission of photons with the same wavelength of light as the laser (also known as Rayleigh scattering), as well as components of the equation which explain the Raman scattering which are the emitted photons that have either more or less energy than the laser photons.

To visualize the interactions, Figure 1 shows the processes of an infrared absorption, Rayleigh scattering, and Raman scattering. In the infrared absorption, a photon of energy equal to the molecular

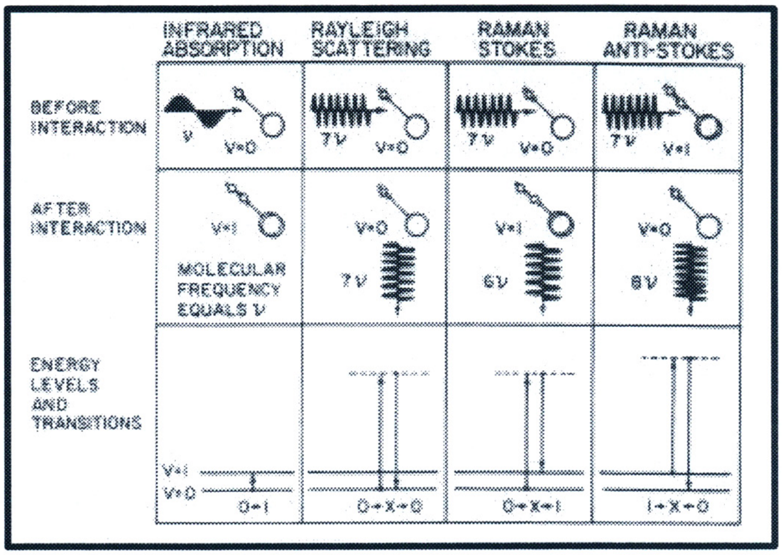

Figure 1. Energy diagrams for infrared absorption and Raman scattering. (Reprinted from Introduction to Infrared and Raman Spectroscopy, Colthup, Daly, Wiberley.)

frequency is absorbed by the molecule, exciting the molecule to the next higher energy level (v=l). The oscillation of the molecule increases after interaction with the infrared beam because it now has more energy.

In the Raman experiment, the energy of the excitation photon (laser) is much higher than the energy corresponding to a change of vibrational level from v=O to v=l. The molecule absorbs a laser photon,which excites the molecule. The molecule then relaxes, releasing a photon of energy equal to the laser, producing Rayleigh scattering. The molecule looks the same before and after interaction with the laser photon. When the molecule absorbs a photon and then subsequently releases a photon with slightly less energy than the absorbed photon, we have Raman scattering. The difference in energy is related to the return of the electron to a higher energy level than it started from. The emitted photon has less energy than the absorbed photon, and this process is referred to as a Stokes emission. At normal temperatures the majority of electrons will be in the ground state (v=O) according to the Boltzman equation:

$$n_2/n_1 = e^{-\square ERT}$$

In the Boltzman equation the ratio of electrons in a higher vibrational state (n2) to the ground state (n1) is related to temperature (T), the difference in energy between vibrational states (E) and a constant R. If an electron is in a higher vibration state (v=l or n2 from the Boltzmann equation) and is excited to the virtual excited state by a photon and then relaxed to the ground state (v=O or n1), the photon which is emitted has more energy than the photon which is absorbed. This type of an emission is called an anti-Stokes emission. The bands for anti-Stokes emissions are typically weaker than the Stokes emissions due to the statistical distribution of electrons at room temperature described by the Boltzman equation.

4. The Raman Microscope

A Raman microscope has several components. A laser is required for sample excitation and a microscope is used to direct the laser onto the sample and collect the scattered Raman emission. The spectrometer bench includes an assembly of notch filters to reduce the intensity of the laser light (and Rayleigh scattered photons) coming back to the detector. Because of the weak signal typically observed from Raman microspectroscopy, it is important to minimize the exposure of the detector to the laser. The Raman emission passes through a slit and then reflects from a mirror onto a diffraction grating. The diffraction

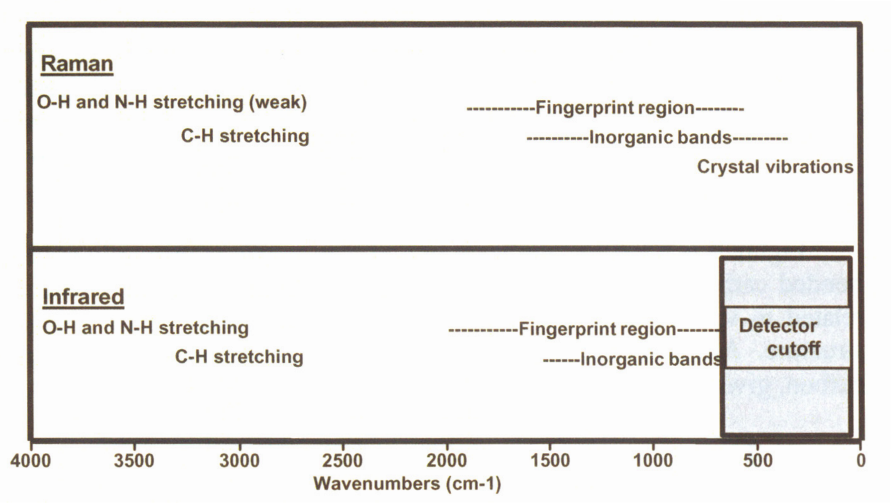

Figure 2. Spectral regions for infrared and Raman data.

grating is either held in one position to scan a region of the available Raman spectrum, or slowly rotated to scan across a larger region of the Raman spectrum. The Raman emission is finally directed to a deep depleted CCD detector.

A difference between Raman microspectroscopy and infrared microspectroscopy is the spectral ranges normally examined. Figure 2 shows typical regions for types of vibration in both infrared and Raman spectroscopy. The units of the x-axis of the figures are in wave numbers or reciprocal centimeters (cm^{-1}). The wavenumber is the number of waves of the infrared light in a one-centimeter wavetrain. Wavenumber is inversely related to wavelength, and the typical infrared spectrum covering a range of 400 to 650 cm^{-1} corresponds to 2500 to 15,400 nanometers. A cut-off of the low end of the infrared spectrum is typical for most mid-infrared instruments due to the normal characteristics of the detectors used. Raman spectroscopy, however, measures the photons emitted from the sample that have shifted away from an excitation wavelength (the laser wavelength). Using holographic notch filters to eliminate nearly all of the light from the laser, *x* spectroscopic data that has shifted as little as 100 cm^{-1} from the laser wavelength can be collected. Spectral bands between 100 and 600 cm^{-1} can provide significant information for inorganic and crystalline materials.

Sample preparation for Raman microscopy is typically very minimal. The samples can either be analyzed directly if they are small enough to fit on the microscope stage, or a small amount of material may be transferred from a document using a tungsten needle. Material transferred from a document can be placed on a glass microscope slide, polished beryllium, or carbon planchets, or even on salt plates normally used for infrared analysis.

A Renishaw Raman Microscope System 1000 was used to collect the data presented in this paper. The system is outfitted with a 30- milliwatt, 514 nanometer argon ion laser, and a 50 milliwatt, 782 nano meter near infrared diode laser. The data presented in this paper was collected using the 514 nanometer laser for excitation. The use of the microscope with a 50X objective allows focusing of the laser to a spot size as small as 1 micrometer. This allows in situ, nondestructive analysis of some documents, or multiple collections from small samples taken from others.

5. Toner Analysis

Photocopiers and faxes use toners to produce printing on paper. Toners are often applied in a relatively thick layer compared to inks. These toner layers are composed of particles that can be analyzed individually if required. Figure 3 is a photomicrograph of toner particles from a copier on paper. The particles are approximately 5-10 micrometers in diameter and are present in a fairly thick coating on the paper. Pigments found in toners usually include carbon black

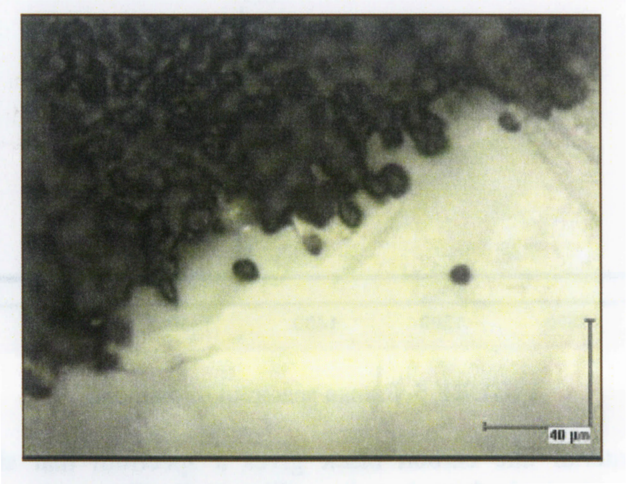

Figure 3. Toner particles on paper.

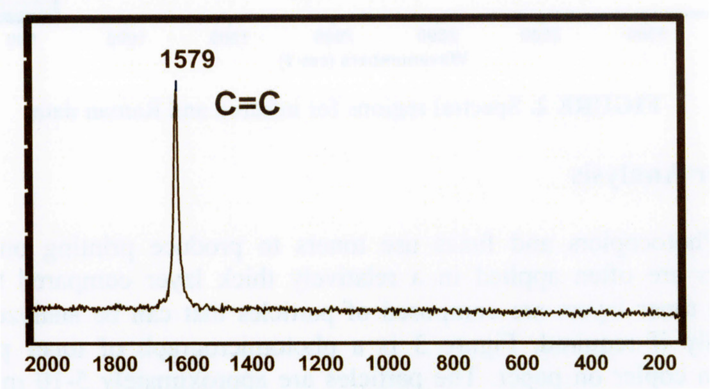

Figure 4. Raman spectrum of graphite.

and in some cases iron oxide. These materials can be discerned using Raman spectroscopy.

Raman spectroscopy is particularly useful in analyzing black materials because it is an emission technique. Black carbonaceous materials generally show two major bands related to graphitic carbon (carbon atoms connected with double bonds) and amorphous carbon (carbon atoms connected with single bonds, but which are not crystalline like diamond).

Figure 4 is a Raman spectrum of graphite, which is primarily doubly bonded carbon. Graphite gives a sharp band around 1580 cm^{-1} which is related to vibrations of the carbon-carbon double bonds in the graphite structure. Alternatively, diamond, which is a hexagonal, singly bound carbon, gives a Raman band at 1330 cm^{-1} as seen in Figure 5.

A material like carbon black gives a spectrum that shows both graphitic and singly bound carbon (Figure 6). The peaks tend to be broader than either pure graphite or diamond, due to the more complex molecular environments of a material like carbon black, because it is produced from a combustion process. However, we can still examine materials like carbon black that show bands at 1598 and 1340 cm^{-1} and discern them from other materials such as charcoal or soot. The Raman spectrum of a toner sample (Figure 7) that has a carbon black pigment shows both the graphitic and amorphous carbon bands. The Raman spectra of several sites on the toner sample are very reproducible, as shown in Figure 8, where the bands related to carbon black filler show consistent intensity and position. These spectra were collected from different letters on the page at positions that ranged from top to middle to edge.

We do not see evidence in Figure 8 of the resin of the toner because the bands from the carbon black overwhelm the response of the organic resin. Extended analysis time may reveal bands related to the toner resin.

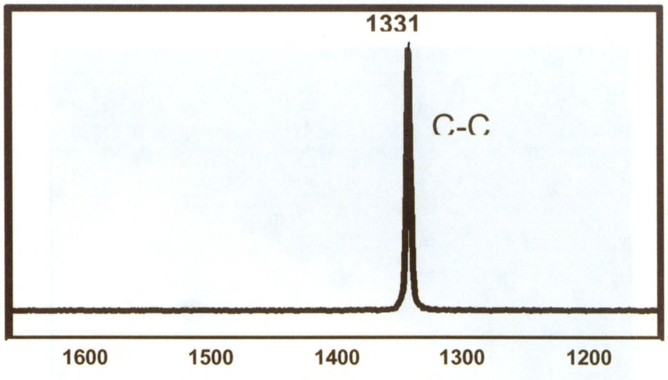

Figure 5. Raman spectrum of diamond.

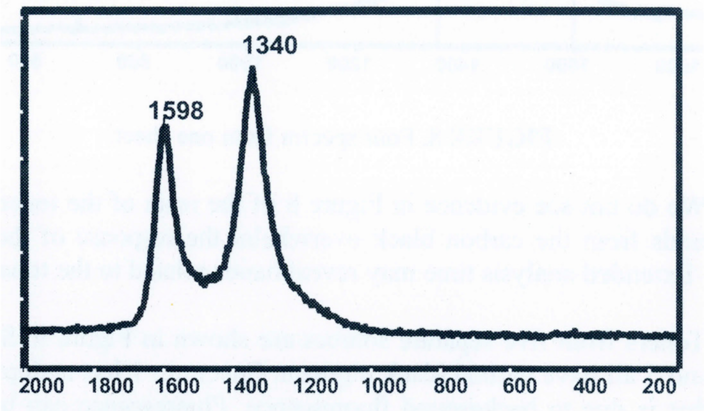

Figure 6. Raman spectrum of carbon black.

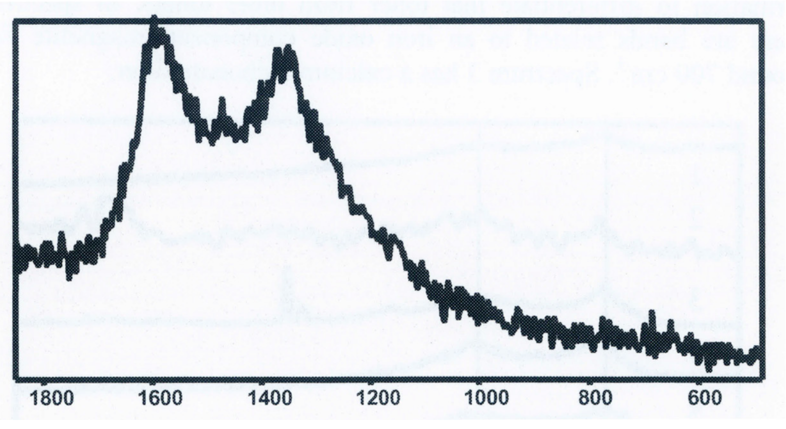

Figure 7. Raman spectrum of toner particle.

Toners from five separate sources are shown in Figure 9. Spectra 1, 3, 4 and 5 all have carbon black pigment. Spectrum 1 has a sloping base line that is due to background fluorescence. Fluorescence can be a difficult characteristic to deal with when performing a Raman analysis. In this case, it is indicative of the sample and can be used as a piece of information to differentiate that toner from other toners. In spectrum 2, there are bands related to an iron oxide component (magnetite $Fe3O4$) around 700 cm^{-1}. Spectrum 3 has a calcium carbonate filler.

Spectra 4 and 5 are similar carbon black pigmented toners. We do see some variation in the peak intensities of the graphitic and amorphous carbon bands. This difference can also be used to differentiate between toners that are very similar.

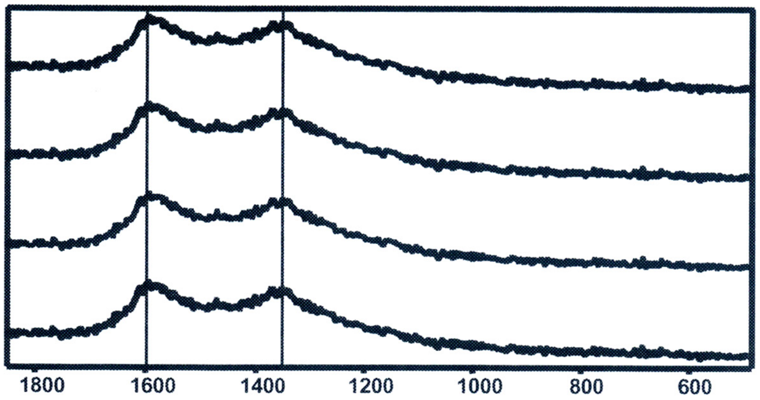

Figure 8. Four spectra from one sheet.

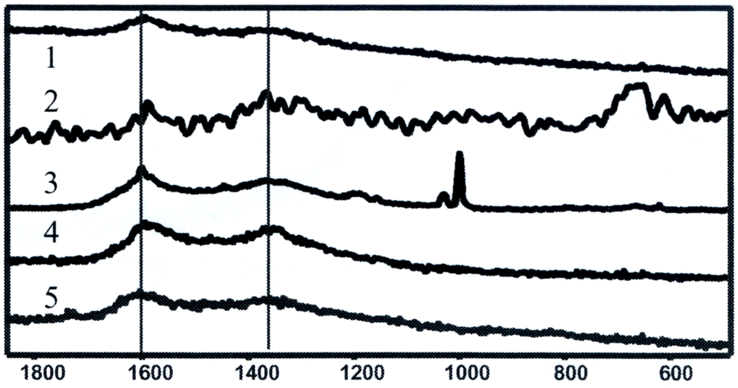

Figure 9. Assorted toner spectra.

Overall, toners generally have low fluorescence, which makes them good candidates for Raman analysis. Consistency of spectra is generally good over an entire page. It is possible to differentiate between types of toners or toner manufacturers based on variations in carbon black, fillers, and other pigmentations such as iron oxides. In some cases, we can get resin information for the toner material from the Raman analysis.

6. Ink Analysis

Ink analysis presents some different problems in that the samples are much thinner relative to toner samples, and there are greater potentials for interference from the paper under the ink. Interference may be related to oxidation of aged fibers or optical brighteners added to the page, which can cause background fluorescence that in some cases may overwhelm the ink spectrum. Paper coating materials may contribute additional peaks to the ink spectrum. In Figure 10, a black ink applied to paper is shown.

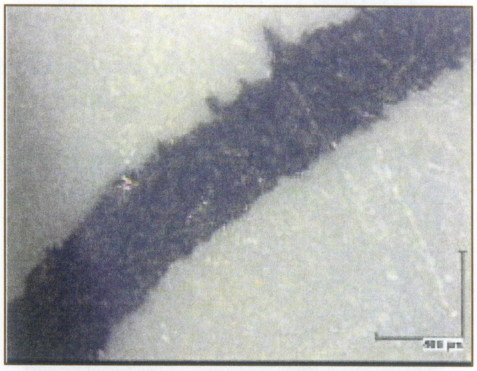

Figure 10. Black ink 1.

Samples were collected from various sites on this line to determine the reproducibility of the black ink spectrum and to see what type of interference may be present from the paper. Figure 11 shows Raman spectra from three sites on this line. There is very good reproducibility of the Raman spectra. We see both

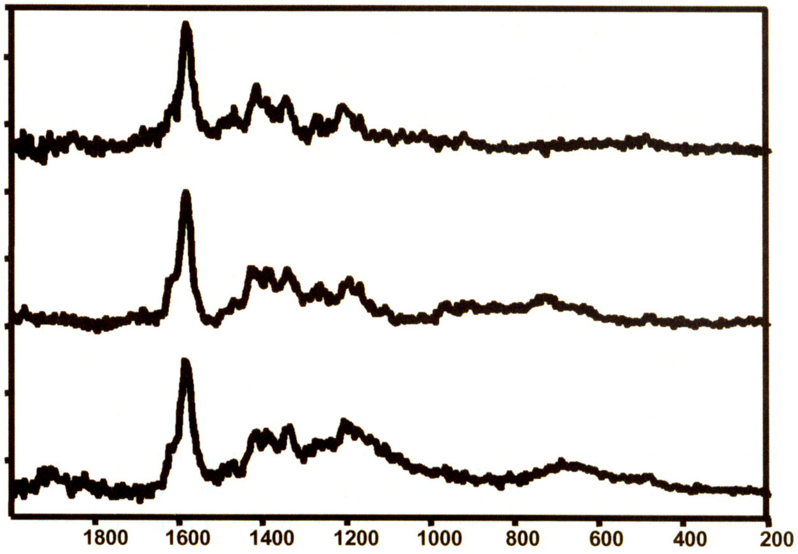

Figure 11. Black ink 1 spectra.

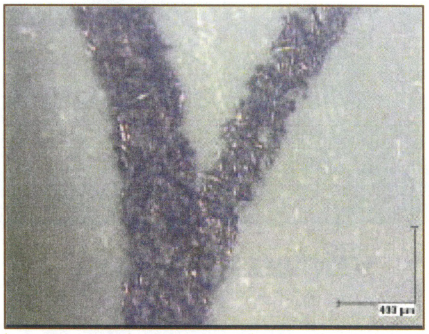

Figure 12. Black ink 2.

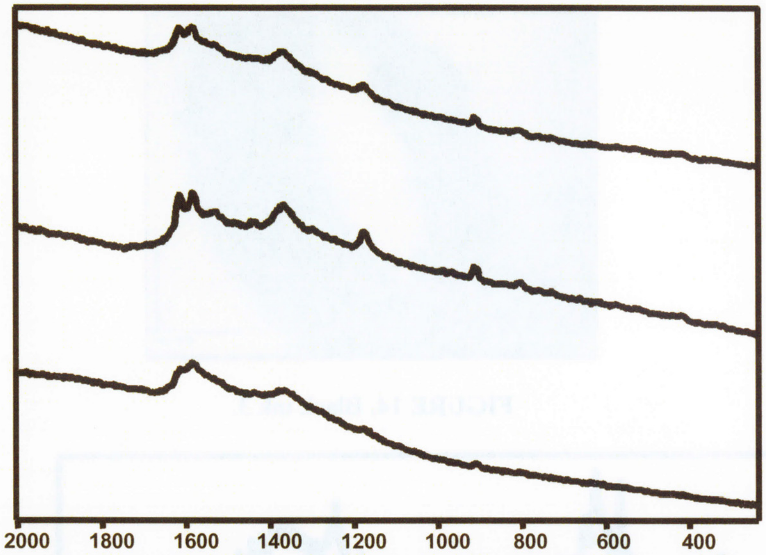

Figure 13. Black ink 2 spectra.

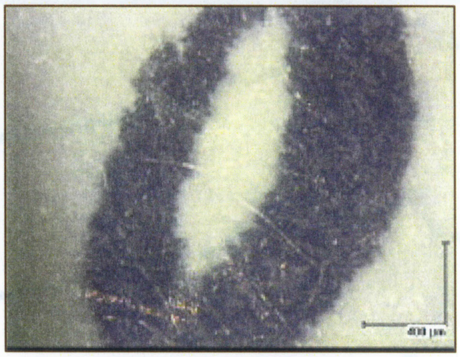

Figure 14. Black ink 3.

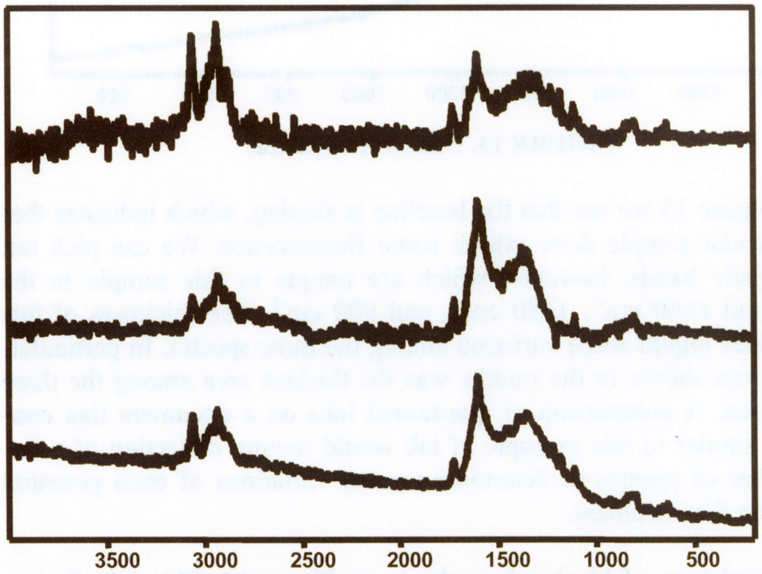

Figure 15. Black ink 3 spectra.

indications of carbon black as well as spectral features related to the resin system in the ink around 1300-1420 cm·1. Common coating materials such as calcium carbonate are strong Raman scatterers that produce a sharp spectral feature around 1085 cm^{-1}. There does not appear to be any significant interference from anything coming from the paper in this particular sample.

A second black ink sample, shown in Figure 12, is slightly thinner and produced the Raman spectra shown in Figure 13.

In Figure 13 we see that the baseline is sloping, which indicates that this particular sample does exhibit some fluorescence. We can pick out characteristic bands, however, which are unique to this sample in the area around 1600 cm^{-1} 1380 cm^{-1}, and 900 cm^{-1}. The thickness of this sample does impart some variation among the three spectra. In particular, the spectrum shown in the middle was the thickest area among the three sites chosen. A comparison of questioned inks on a document that contains ink similar to this example of ink would require collection of a larger number of spectra to determine normal variations of each potential ink type on the document.

A third type of black ink is shown in Figure 14. This ink, from a permanent marker, has saturated the paper fibers fairly well. The Raman spectra of this third black ink (Figure 15) show carbon black and some indication of the resin system. These spectra are fairly noisy, but we can still discern some aromatic structure (carbon rings such as those observed in benzene) to the resin system based on the band at 3100 cm^{-1} and 1620 cm^{-1}.

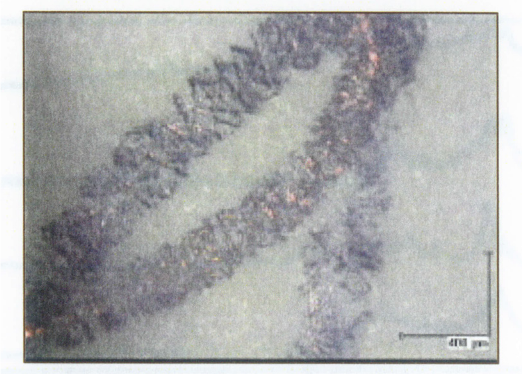

Figure 16. Black ink 4.

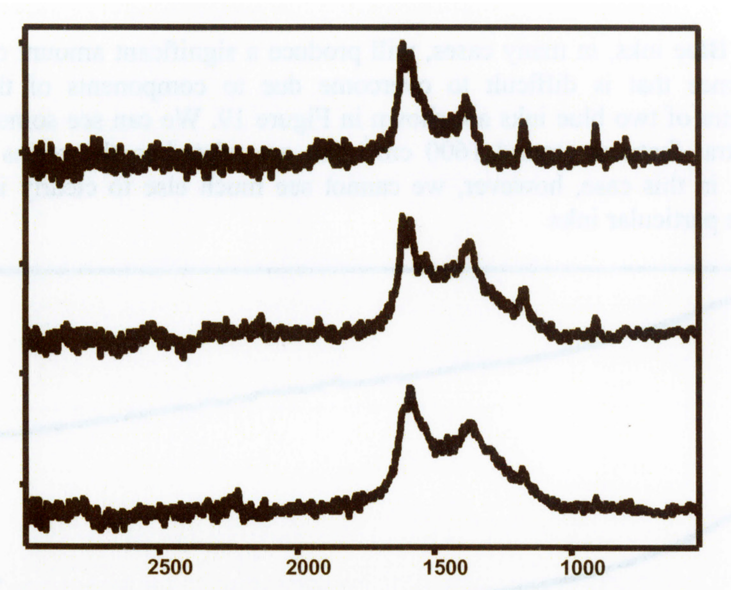

Figure 17. Black ink 4.

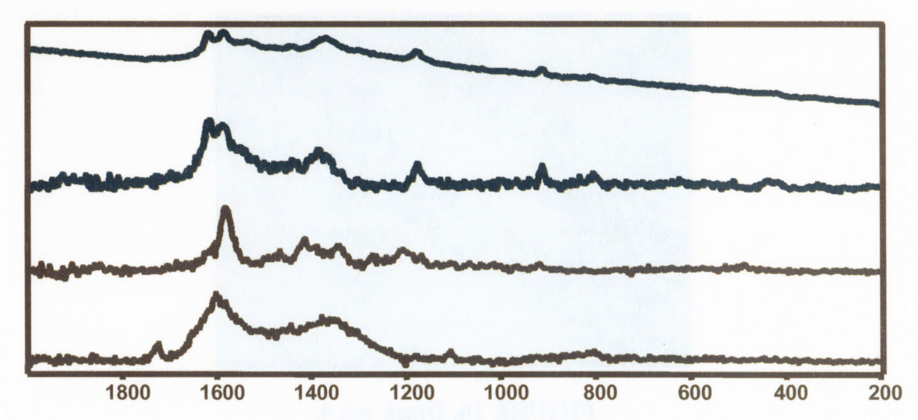

Figure 18. Black inks 1 through 4.

Finally, a fourth black ink sample that is very thin, shown in Figure 16, produced the Raman spectra shown in the Figure 17. These spectra have primarily carbon black bands with some smaller shoulder bands behind. There is also an indication from the bands around 1086 cm^{-1} that the paper is coated with calcium carbonate.

When we compare the ink from the four samples in Figure 18, we can see that each ink is unique. The uniqueness is related to the materials used to produce

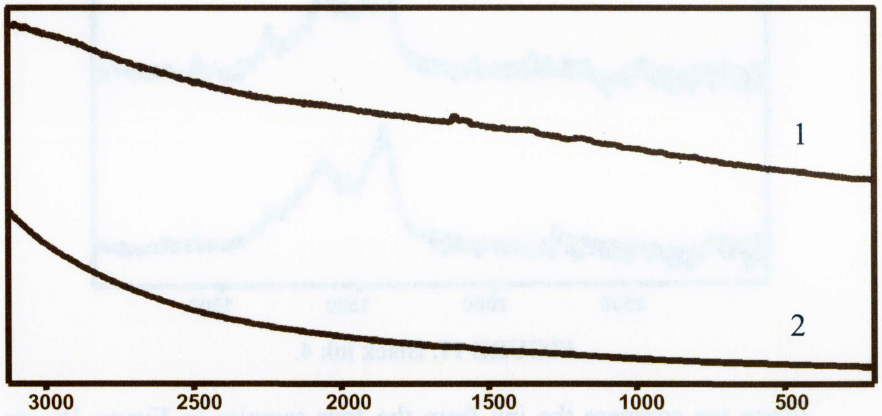

Figure 19. Blue ink on paper.

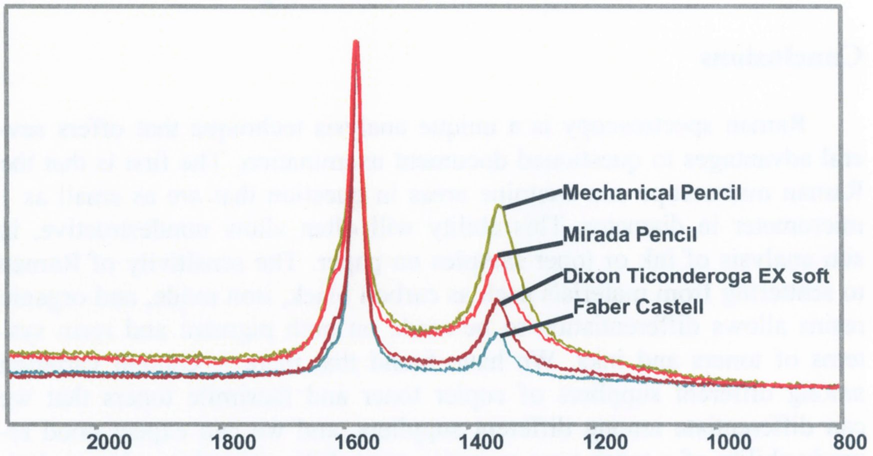

Figure 20. Multiple pencil leads.

the color of the ink, the intensity of the color as related to the amount of pigmentation, the resin systems used, and the presence or absence of fluorescence from the ink.

Blue inks, in many cases, will produce a significant amount of fluorescence that is difficult to overcome due to components of the ink. Spectra of two blue inks are shown in Figure 19. We can see some minor spectral features around 1600 cm^{-1} that are related to the resins in the inks; in this case, however, we cannot see much else to clearly identify these particular inks.

For ink samples overall, we are looking at a thinner material which is more susceptible to variations in the paper and in the ink, as well as paper defects and paper coatings. Fluorescence is a more significant problem in inks than in toners, in particular colored inks such as blues, which may contain organic dyes that are more susceptible to fluorescence.

7. Pencil Leads

Because of the strength of Raman microscopy in analyzing carbonaceous materials, we undertook a short experiment to determine if it is possible to differentiate pencil leads based on their Raman spectra. With pencil writing, the samples are very thin. The mixtures are fairly simple, however, generally composed of a wax and graphite.

Figure 20 shows an overlay of Raman spectra from four different pencil types. Each spectrum is normalized to the 1580 cm^{-1} graphite carbon band. Among these four we see significant variations in the singly bonded carbon band around 1380 cm^{-1}. There is also some variation on the front shoulder of the graphite band that result from the type of pencil lead.

A single pencil lead analysis did show good reproducibility over the course of a page (Figure

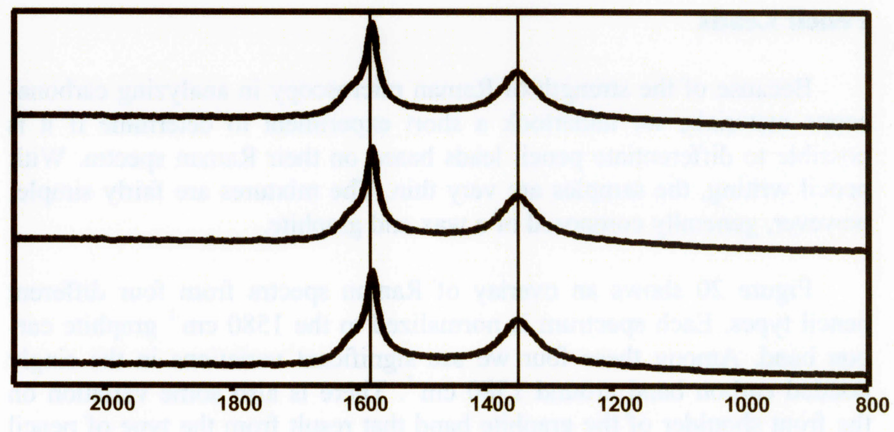

Figure 21. Pencil over one page.

21). These results indicate that it may be possible to examine questioned documents written in pencil and look for variations in the graphitic carbon (1580 cm^{-1}) to amorphous carbon (1360 cm^{-1}) ratios as a means to differentiate among pencil lead types. Fluorescence is typically not a problem because of the simple mixtures used in pencil lead although fluorescence may occur on older papers as the paper becomes oxidized, and the thin coating of pencil lead on the paper may not cover the paper well enough to hide the fluorescence coming from the paper fibers.

8. Conclusions

Raman spectroscopy is a unique analysis technique that offers several advantages to questioned document examination. The first is that the Raman microscope can examine areas in question that are as small as 1 micrometer in diameter. This ability will often allow nondestructive, *in situ* analysis of ink or toner samples on paper. The sensitivity of Raman to scattering from materials such as carbon black, iron oxide, and organic resins allows differentiation to be made on both pigment and resin systems of toners and inks. We have found that there is enough variation among different suppliers of copier toner and facsimile toners that we can differentiate among different suppliers, and we can expect good reproducibility of a toner over an entire page. Like any other microanalytical technique, Raman would not be expected to discriminate between inks from one pen versus another pen if both pens are from the same manufacturer using inks from the same batch. On the other hand, if subtle differences are suspected as a result of a microscopical or alternate light source photographic comparison, the sensitivity and chemical specificity of Raman spectroscopy will likely assist in confirming the suspected differences.

At this point, libraries of Raman spectra of inks and toners from different manufacturers are essentially nonexistent. In a questioned document case, however, one would be comparing the spectra of various printing or writing on a document and would not necessarily need to identify a specific source or type of ink or toner. A combined approach to questioned document examination using a light microscopy examination and Raman spectroscopic analysis would provide a more complete characterization of a sample with regard to its inconsistencies and variations in chemistry.

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