An Introduction to Gel Inks: History and Analysis

Darlene C. Florence[1] Heidi H. Harralson [2] and Joseph G.Barabe[3]

Abstract: *With the increasing use and variety of gel pens on the market, forensic document examiners may encounter problems identifying gel pens from other common pen types. This study discusses the initial findings of an investigation into the history, technology, and properties of gel pens. Microscopical (visual) and chemical methods were also evaluated as ways to characterize and identify gel inks. The results of the study demonstrate that the presence of a gel ink can often be determined, but that some gel inks resemble other types of pens, especially roller balls, upon visual examination. Further, chromatographic methods used to characterize traditional dye-based inks may be less useful with gel inks; for these, other spectrometric methods including Raman spectroscopy and energy dispersive x-ray spectrometry (EDS) were evaluated and proved useful.*

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1. Introduction

Gel pens are a relatively recent addition to the pen market. They have been widely distributed over the past decade and have become commonplace, disposable writing instruments typically sold alongside ballpoint and roller ball pens. Available in a wide range of colors and textures, the creative variety that gel pens offer undoubtedly makes them popular. Gel ink is also widely advertised as being permanent, fade-proof, and chemically resistant. A cursory visual examination of gel ink can look similar in appearance to both ballpoint and roller ball ink as all three pen types utilize a rolling ball mechanism to transfer ink to the substrate.

The popularity and manufacturing diversity of gel pens has created new challenges in ink identification for forensic document examiners. With the increasing number of gel and hybrid gel pens available, it is important for document examiners to have an awareness of the visual and chemical characteristics of gel pens in comparison to fountain, roller ball, and ballpoint pens. The scope of this paper is to examine gel pen literature, history, technology, visual characteristics, and chemical properties.

2. Definition

Gel pens can be defined as writing instruments with the following characteristics:

1. The pens utilize a rolling ball mechanism to transfer ink from the ink reservoir to the paper substrate.
2. The ink vehicle is a water-based gel.
3. The colorants may be dyes or pigments, but are typically pigments. Hybrid gel inks include both dyes and pigments.
4. A pigment can be defined as any particulate matter that modifies the color, texture or general

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look of the ink including both organic and inorganic colorants, metal powders, ground glass or other material.

3. Forensic Literature

Forensic literature about gel pens has been limited, as the brightly colored pens were not typically used in business documents, but some studies appearing in recent years have helped to fill the gap concerning forensic knowledge of gel ink. Gel pens were introduced to forensic document examiners in a preliminary study by Gemandt & Urlaub (1996) in which the authors performed limited testing on four gel pens and discussed gel ink insolubility; this study pre-dates the entrance of dye-containing (hybrid) gel pens to the market. A study conducted by Mazzella & Khanmy-Vital (2003) used filtered light examination, Raman spectroscopy, and Scanning Electron Microscopy (SEM) to examine the properties of blue gel pens in Europe. Brunelle & Crawford (2003) claimed that gel inks "are practically indestructible on paper" (p. 33) and pointed out the limitations of relative age comparison tests on gel inks since they are not solvent-based. Barabe, Smith, & Florence (2003) recognized the characterization problems in comparing gel pens with roller ball pens and performed visual characterization tests. They introduced other analytical techniques including Raman and energy dispersive x-ray spectrometry (EDS). Most recently, Wilson, LaPorte, & Cantu (2004) examined and compared black gel pens using optical and chemical techniques. This study also recognized the need to differentiate between gel pens and roller ball pens. Using gas chromatography/mass spectrometry, it was found that certain compounds in gel pens were not present in roller ball ink.

4. History

Information about the invention, manufacturing, and marketing of gel pens was obtained from manufacturers and distributors. As gel ink was invented by the Sakura Corporation of Japan and that company continues to be a leader in gel ink products manufacturing, Sakura Color Products of America was especially helpful in providing information about the history and technology of gel pens. According to Sakura, water-based, gel ink evolved from pigment ink. Sakura perfected the use of pigment in ink by producing micron sized pigment particles that could flow evenly. Water-based gel ink was invented by the Sakura Corporation in Japan and patented by that company in 1982. Because of the special requirements of water based gel ink, nearly two additional years were spent developing a pen housing to hold the ink. The first gel pen, the Ballsign 280, was introduced to the Japanese market in 1984. The Ballsign 280 was a dye-based pen that was quickly replaced by a pigment-based pen, Ballsign 150, in 1985. The first gel pen (Gelly Roll) distributed in the U.S. occurred late 1989 to early 1990 (P. Ouyang, personal communication, October, 2004). This distribution date contradicts the date reported by other literature that claims the first gel pens distributed in the U.S. occurred in 1993 (Mazzella & Khanmy-Vital, 2003; Brunelle & Crawford, 2003). However, wider distribution throughout the U.S. did not occur until the mid to late 1990s. By 1996, at least four companies were distributing gel pens in the U.S.: Pentel Hybrid, Sakura Gelly Roll, Zebra Jelly, and Uni-ball Signo by Mitsubishi (Mazzella & Khanmy-Vital, 2003; Brunelle & Crawford, 2003). Sakura reports that a surge of popularity occurred in 1997 with the release of metallic gel pens. With the limited distribution in the U.S. in the early 1990s, use of gel pens prior to 1996 is not likely; however, document examiners need to be aware of its possibility.

5. Technology

The invention of the gel pen was partially prompted by a desire to overcome some of the difficulties demonstrated by roller ball pens. The Sakura Color Products Corporation in Japan, traditionally a company that marketed art materials and pigment ink, wanted to simulate the smooth writing quality of the roller ball while creating an instrument that would provide a consistent ink flow for the life of the pen. The challenge was to overcome the roller ball ink's tendency to decrease flow rate after the initial force of the capillary system in the pen had weakened. A full ink reservoir provided the pressure necessary for the ink to flow freely. As the ink supply

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diminished from pen use, the pressure weakened, causing the appearance of a thin, faint ink line. During the early 1980s, the ink chemists at Sakura found that gel contained the properties needed to provide a consistent, flowing ink supply that resulted in smooth writing. Gel, which is a homogenous solid, becomes liquid when stirred, shaken, or disturbed; this chemical state transformation is known as *thixotropy*. This reduction in viscosity is due to a temporary breaking down of the internal gel structure under shear, which is caused by the friction of the ball on the gel ink (Roberts & Etherinton, 1965).

Gel based pens were not the first to utilize thixotropy. The Fisher Space Pen, developed in 1969, was a ballpoint pen that utilized a "thixotropic material that [was] essentially non-fluid until disturbed by rotation of the ball-point in the socket" (Brunelle & Reed, 1984, p. 17-18).Thixotropic action, a special ink formula placed within an airtight chamber, and nitrogen gas pressure were utilized to make this pen write in zero gravity conditions and maintain a 100-year shelf life. These pens were used by NASA because the zero gravity in space made other pens inoperable (Fisher Space Pen, 2003).

Gel is also an effective carrier for pigment, which opened up possibilities for creating a wide array of ink colors. In traditional ballpoint pens, pigments were not used because they do not disperse well, and the pigment particles would gravitate towards the writing end of the pen, causing it to plug up. This is due to the fundamental difference between pigments and dyes. Pigments are distinct particles; they are of a measurable size, providing color and opacity, whereas dyes are soluble colorants that exist in the medium as individual molecules, providing color but retaining the approximate refractive index of the medium and thus its transparency. Additionally, because pigments consist of individual particles, they rest on or between the paper fibers and adhere to the paper with a binding medium.

The advantages of pigments are numerous. Many are permanent (due to their light-fastness and insolubility), a greater variety of colors are possible, as are higher color saturation and opacity, and limited bleed-through. In addition to colorants, pigment-based gel ink may include powdered metals or ground glass for a glittery appearance. There are archival benefits to pigment inks as they may be acid-free, waterproof, and resistant to chemical manipulation. It is the higher viscosity of the gel that causes the pigment, and any powdered metal or glass, to suspend evenly. These characteristics make gel pens among the most technologically advanced pens available on the market today.

Gel pens are smooth writing instruments and include a wide range of ink colors, textures, and special properties including both organic and inorganic pigments, metallic (utilizing metal powders), glitter (utilizing ground glass), fluorescence under ultraviolet light, two-toned inks, and, most recently, flexographic-like textures. The proliferation of these effects shows no sign of abating. It is also reported that their resistance to solvents is an aid in preventing check washing, although the hybrid pens may not share this characteristic. However, it should be noted that at least two companies have distributed erasable gel pens (Pilot Erase-a-Gel, Sanford Eraseable Gel).

Due to the water-based gel ink formula in comparison to the solvent-based ballpoint ink, gel ink is considered ecologically and environmentally safe. While gel ink may limit harmful pollutants, gel pens do not last as long as ballpoint pens. It is reported that it takes eight gel pens to write as much as one ballpoint pen (Schwartz, 2001). It seems that while gel ink may be environmentally safer than ballpoint ink, the increase in the number of disposable pens may offset the positive environmental effects of gel ink. There has, however, been an influx of refillable gel pens on the market, which may help to offset their disposal rate.

6. Gel Pen Characteristics

Writing performance problems can result from poorly manufactured ink and/or pen housing. To help create the gel pen's smooth writing capability, the metal ball tip needs to be more highly polished in a gel pen than it does in a ballpoint pen. This highly polished surface is necessary to facilitate the flow of the gel ink through thixotropy it also makes the gel pens more expensive to manufacture. Because gel ink is water-based (usually over 60- 80% of the ink formula is water), air bubble contamination within the gel causes the ink to dry out quickly. Centrifuging techniques

Figure 1. Irregular line quality in the writing performance of Sanford Uni Ball Signo Gel Stick, which is a common problem in gel pens as they age.

are frequently employed to eliminate this. The gel pen housing is designed as an airtight container to prevent the water-based gel ink from drying out. Many gel pens also have removable, protective seals on the tips of the pen nibs to help retain moisture and prolong the shelf life of the pen. After this protective seal is removed for everyday use, manufacturers usually recommend that the cap be placed on the pen to prevent drying out. Despite precautions taken by manufacturers to prevent moisture loss, many gel pens dry out quickly and do not have a long shelf life. As a result, problems associated with starting, hesitation, and skipping in the ink line may occur. Gel inks vary in viscosity and those with higher viscosity may exhibit gooping on the ink line. A combination of skipping and gooping produces a highly irregular line quality in the writing performance of some gel inks (Figure 1).

The light colors and metallic appearances introduced by some gel pen manufacturers have created legibility problems for schools, businesses, and banks. Many of the lighter gel pen colors are barely legible on shades of paper that do not provide adequate contrast and the metallic pens can have a glittery appearance that decreases legibility. Digital imaging of checks for the Check 21 Act has created additional problems in legibility because some of the lighter colors such as yellow may not scan legibly even if they are legible on the original check (A. Garner, personal communication, October, 2004). Some schools and businesses prohibit the use of gel pens for reasons of poor legibility and the unprofessional appearance of certain colors and textures. However, because of the tendency for distributors to market colorful gel pens so that they appeal to school children, document examiners should expect cases involving children's writing to possibly include unusual gel pen colors and textures.

7. Forensic Ink Identification: Visual Methods

In addressing the forensic challenges associated with the identification of gel inks, visual analysis and examination must be undertaken with caution, as gel inks exhibit characteristics similar to other types of inks.

7.1 Methods and Materials

The goal of this study was to investigate the visual and chemical characteristics of gel pens so that they could be differentiated from one another and from other types of pens. The pens chosen for this study came from eight manufacturers: Bic, PaperMate, Pentel, Pilot, Sailor, Sakura, Sanford, and Zebra. Although the study began with black and blue inks, the colors traditionally used to sign business documents, it soon became apparent, through digital imaging

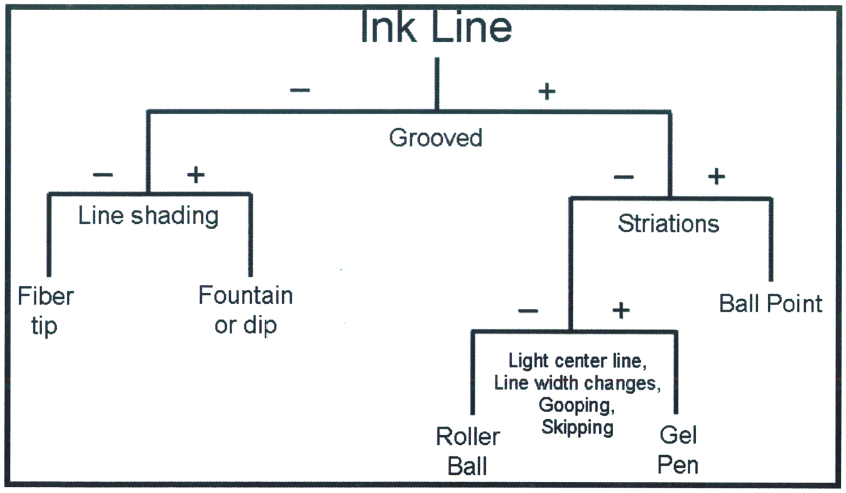

Figure 2. A decision tree to aid in determining the type of pen used to create a body of writing.

problems with the Check 21 Act, that other colors such as red, green, and even yellow were also being used. In response, research was expanded to include these colored pens. The tests performed included microscopic analysis, polarized light microscopy (PLM), Raman spectroscopy, and energy dispersive x-ray spectrometry (EDS). Also discussed is the use of other tests such as thin layer chromatography (TLC) and information that can be gathered from Material Safety Data Sheets (MSDS). In accordance with ASTM standards, the ink was written on filter paper to ensure that the substrate is free of additives that may interfere with analysis (ASTM E 1789-04 7.1.2.1). For each ink, the brand, model, point size, color, date acquired, date written, and type (gel, roller ball, ballpoint) was written on the filter paper, and the above information, along with data obtained from the instrumentation, was entered into a Microsoft Excel™ database file.

7.2 Microscopic Analysis

The exemplars were examined with an Olympus SZH stereomicroscope with magnifications ranging from 7.5X to 64X. Both oblique and ring illumination was provided by an Olympus Highlight 3000 fiber optic source. An Olympus BH-2 polarizing light microscope was also used for higher magnification examinations; this microscope was equipped with metallurgical objectives providing magnifications ranging from 50X to 500X. The samples were examined without a coverglass and with both oblique and co-axial illumination. Although more information can be gathered using higher magnifications, it was found that the stereomicroscope was usually adequate. A decision tree to aid the analyst in determining the nature of the pen and ink type is included as Figure 2. This decision tree should be considered as suggestive rather than definitive, and should be used with caution, with full consideration of the range of variation between both pens and writers. Discriminating between gel pens and roller balls may, in many cases, be impossible, especially with the growing number of gel/roller ball hybrids.

A collimated light source such as a fiber optic illuminator, spot lamp, or flashlight at a low, grazing angle (raking light), is first used to distinguish between pens that use a rolling ball mechanism, such as ballpoint, roller ball, and gel, which leave a deep furrow (Figure 3) in the paper, from those that do not, such as fiber tip, dip, and fountain pens. With raking light, a shadowed furrow can be seen on tracks made with a rolling ball mechanism. The maximum width of the furrow is determined by the diameter of the ball, and the depth of the furrow is largely determined by the pressure provided by the writer and the deformability of the paper substrate.

Between the three pen types that use a rolling ball mechanism, the easiest pen to identify is ballpoint, recognizable by the striated ink deposits on the paper

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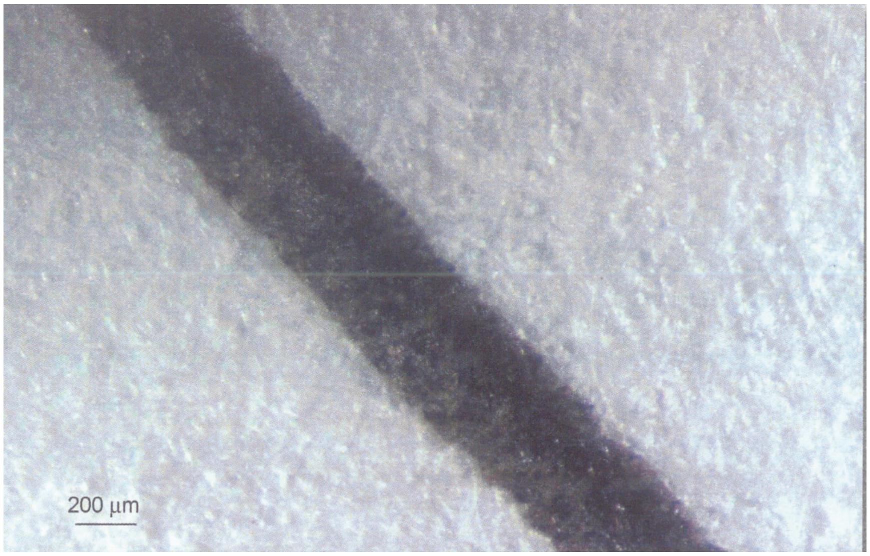

Figure 3. The deep furrow, characteristic of roller ball mechanism, illuminated with oblique light.

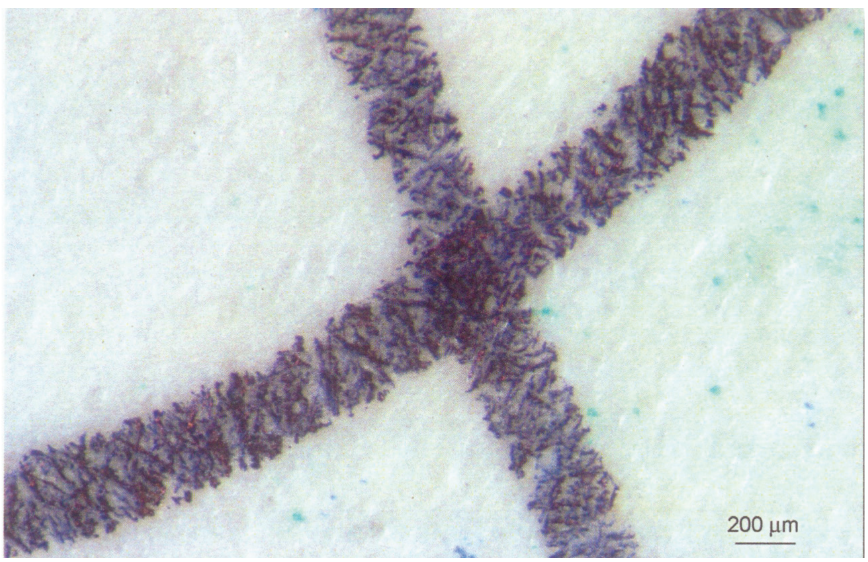

Figure 4. Striations in ballpoint ink, which are perpendicular to the travel direction of the pen. This identifying characteristic results from the catching of the thick, oily ink on the leading edge of the paper fibers.

fibers perpendicular to the travel direction of the pen (figure 4). The thick, oily ink of a ballpoint is caught on the leading edges of the paper fibers and lacks the fluidity to saturate the paper fibers other than by direct contact; very little capillary action, or wicking, is evident. Other identifying characteristics include occasional gooping of the ink and a somewhat limited range of colors.

Roller ball pens also utilize a rolling ball mechanism, but the ink is water-based, which is much more fluid than ballpoint ink. The colorants are often the same dyes as found in ballpoint. Under magnification, the ink line is seen as a solid line of color. The line is so ink-filled, that it is often difficult to determine the direction of the writing movement. Extensive wicking can often be seen, but not always, as quick-drying resins may be present to retard excessive fluid travel along the paper fibers (Figure 5).

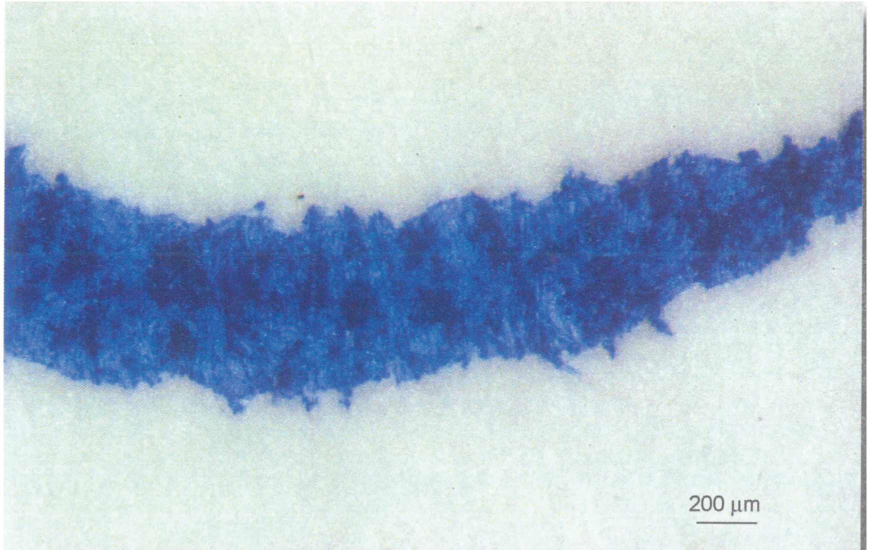

Figure 5. Wicking along the paper fibers of a roller ball ink. The water based ink also fills in the ink line, often making it difficult or impossible to determine the pen's direction of travel.

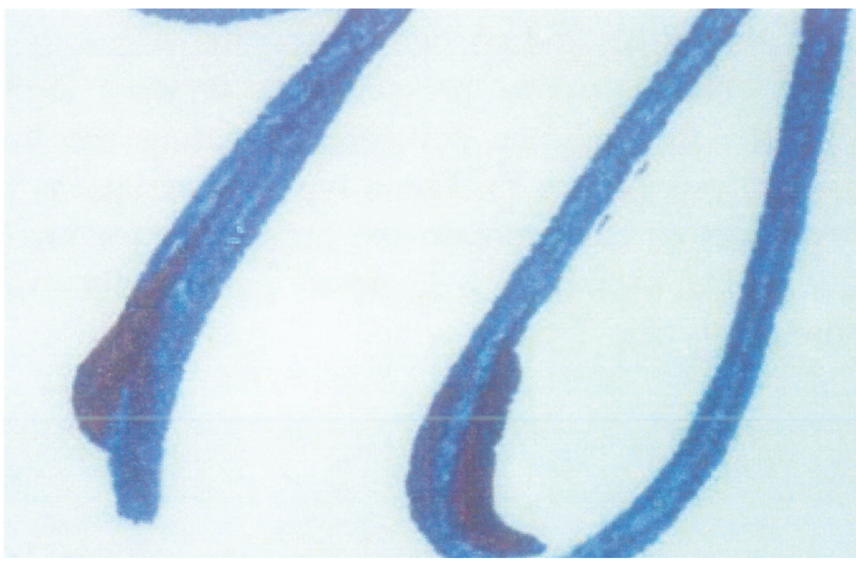

Figure 6. Gooping of Sanford Gel pen when the stroke direction changes quickly, such as in the lower loops of 'g,' 'y,' 'j,' and 'q.' This phenomenon was observed with other gel pens, and may been seen throughout the line depending on the ink formulation, writer, and age of the pen.

7.3 Visual Characteristics

Gel pens can exhibit a variety of characteristics, many of which may be visible with the naked eye or low magnification. Glitter and metallic inks are achieved through the introduction of cosmetic grade glass and powdered metal. Black light effects are visible with fluorescent pigments, and flexographic-like raised lettering is present in some gel pen varieties used in arts and crafts. All these characteristics are unique to gel pens.

Other characteristics are best evaluated with a stereo or conventional compound microscope. Among the frequently observed characteristics are those related to the increased viscosity of the ink and the need for greater pressure to overcome the ball's

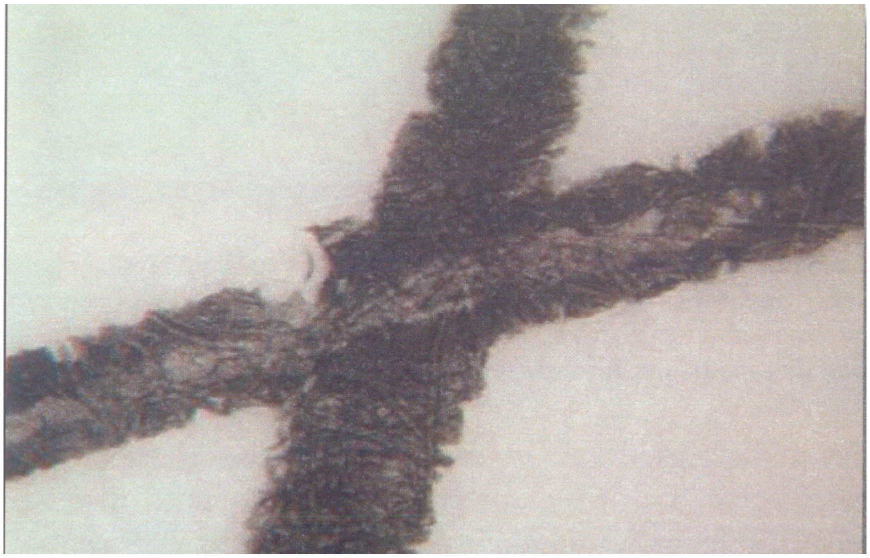

Figure 7. Light center line in Pentel Sunburst Gel K-906. The downward pressure of the writing causes the ink to flow away from the center of the nib and concentrate on the edges. Changes in pressure can produce significantly different results with the same pen.

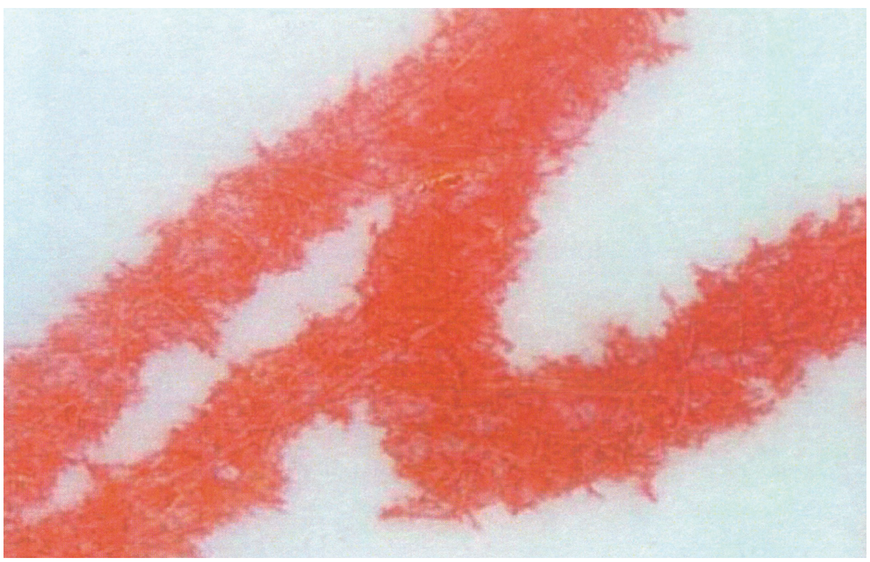

Figure 8. Wicking of the Pentel Energel Liquid Gel, which is similar to that of roller ball ink, which is also water-based.

inertia. Gel pens often exhibit variable line width, sudden discontinuities, or ink deposits with slight changes in writing pressure, around sharp curves, or with flaws on the ball's surface. These ink deposits are reminiscent of the gooping so characteristic of ballpoint pens, but exhibit different patterns. This gooping was observed particularly when the stroke direction changed quickly, such as in the lower loops of *g*, *y*, *j*, *q*, and the cursive *z* (Figure 6). Loops in upper letter extensions may also show this effect, but none were observed in this study. In contrast, no instances of gooping by roller ball pens were observed.

Deposits of dried ink in the spaces between paper fibers is characteristic of both roller ball and gel pens, but roller ball ink will generally leave a relatively uniform deposit, well soaked into the fibers, often with abundant wicking. Gel inks will frequently leave pools of pigment deposits between the fibers, or even

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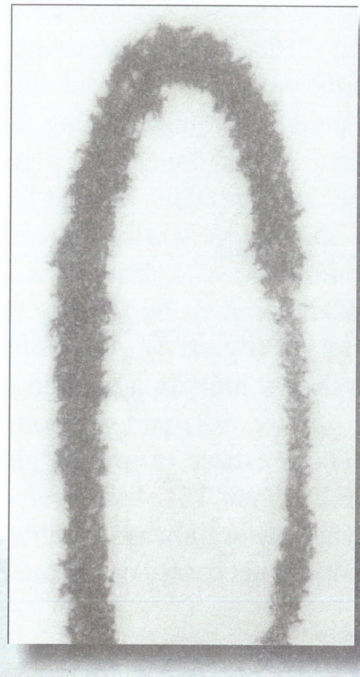

Figure 9. sudden change in line width in the Pented Energel liquid gel.

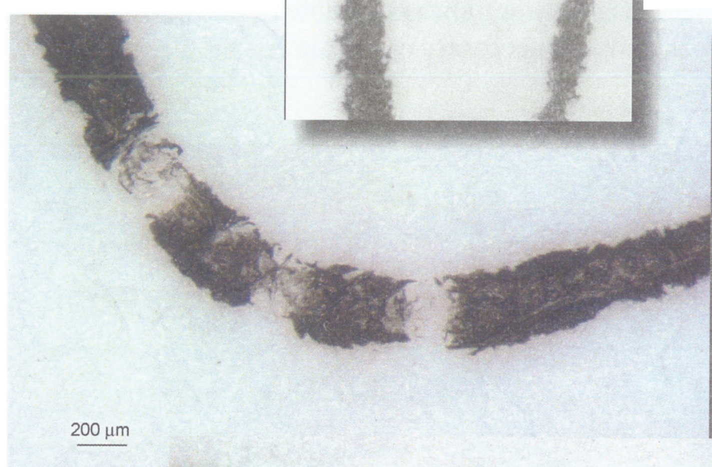

Figure 10. Skipping of the ink line.

Figure 11. Pigment pooling between the paper fibers.

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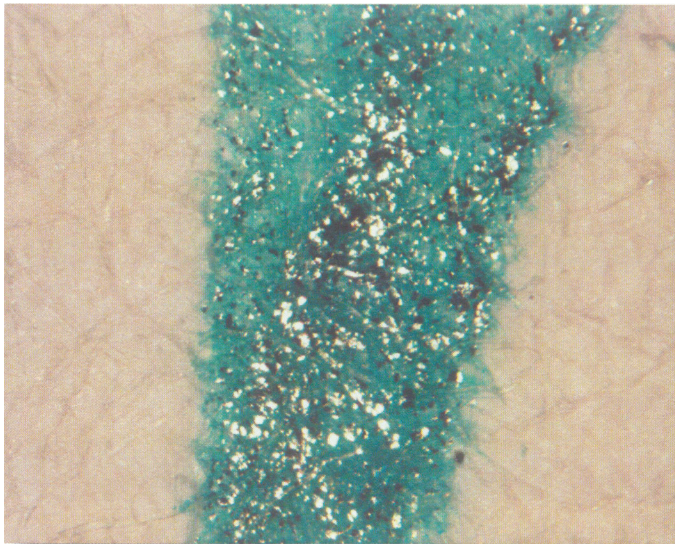

Figure 12. Metallic particles in the Pentel Sunburst Gel Metallic K908. The high viscosity of the gel ink allows for this addition and creates a look not seen in other types of ink.

heaped on top of the paper fibers in some cases. A very light touch with an extremely fine-tipped tungsten or eyelash needle will demonstrate the presence of pigment deposits as material separate from the fibers. High quality microscope optics are helpful when evaluating a feature of this subtlety; magnifications of 100X or more may be necessary to evaluate this feature.

The center line characteristic has frequently been mentioned in gel pen literature as an identifying characteristic. Brunelle & Crawford (2003) point out that "heavy writing pressure often leaves a lightly inked center portion in the ink line" (p. 53). The unique nib construction combined with the viscous gel ink may be responsible for the light center line. The downward pressure of writing causes the ink to flow away from the center of the nib, when it is in closest contact with the paper, and concentrate on the edges. It was also noted that a change in pen pressure can produce significantly different results in the same gel pen, indicating the limitations of a visual analysis (Figure 7). These types of variations based on pen pressure factors can increase the possibility for error in pen identification when examining a document purportedly written with two or more pen types.

It is often difficult to discriminate between gel and roller ball pens. A summary of microscopical characteristics comparing roller ball and gel pens including wicking, line width, line discontinuity, central line artifact, and deposits of pigments and metal can be found in Table 1. Gel pens typically exhibit less wicking than do roller ball pens, as gel inks are generally more viscous than roller ball inks, but with the increase of hybrid pens available on the market, the degree of wicking cannot be reliably used to discriminate between roller ball and gel (Figure 8). Additional features commonly found in gel pen writings include a sudden change in line width (Figure 9), skipping (Figure 10), and a pooling of the pigment particles (Figure 11). The presence of ground glass or metallic particles also point to gel ink (Figure 12). And, even after careful study of known exemplars, one may not always be able to discriminate between the two types with the necessary confidence.

Pilot's Erase-a-Gel has characteristics significantly unlike those described. The ink is deposited as small spheres about 10 micrometers in diameter (Figure 13). In the written line, the spheres are randomly distributed throughout, creating a look similar to laser jet. However, Erase-a-Gel can be easily distinguished from laser jet by several characteristics: the Erase-a-Gel spheres are only loosely attached to the paper fibers (thus their erasability), and, if touched with any small instrument, such as a tungsten needle, will remove easily. Additionally, this pen incorporates a rolling ball mechanism, so the characteristic groove

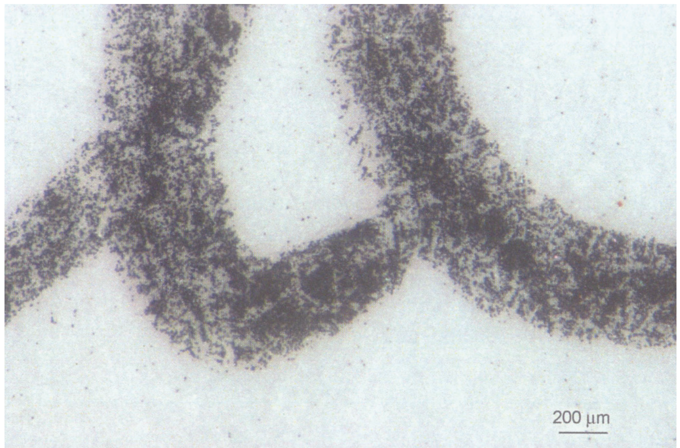

Figure 13. Pilot Erase-a-Gel with small, 10 micrometers diameter spheres that look more like a laser jet line than one from a pen. The two distinguishing features are that the spheres are loosely attached and there is a furrow from the rolling ball mechanism.

Characteristic	Roller Ball	Gel Pen	Figure
Wicking along paper fibers	Moderate to Strong	Weak to Moderate	9
Light central line	Absent	Sometimes present	7
Line width changes abruptly	Absent	Often present	10
Skipping	Rare	Sometimes present	11
Ink gooping	Absent	Often present	6
Pigment deposits between paper fibers	Rare	Often present	12
Powdered metal, ground glass, fluorescent ink	Absent	Sometimes present	13

Table 1: Microscopical Characteristics of Roller Ball and Gel Pen Lines.

in the paper is present. Even after an area has been erased, oblique illumination can be used to highlight the groove from the erased section.

7.4 Polarized Light Microscopy (PLM)

Polarized light microscopy is widely employed in the analysis of paint, fibers, and many kinds of trace evidence. It is less often used in forensic automotive paint analysis, where spectrometric methods are preferred. PLM provides mostly morphological information such as color, size, shape, and crystallographic information, such as refractive indices and birefringence. The method is of some use in characterizing larger particles, such as those in the metallic and glitter inks, but less useful in characterizing pigment particles (other than helping determine that they indeed are pigments). Most of the pigments were too small (in the sub-micrometer range) to be adequately characterized with PLM.

8. Forensic Ink Identification: Instrumental Methods

8.1 Thin Layer Chromatography (TLC)

Traditionally, chromatographic methods, such as thin layer chromatography (TLC), have been used to characterize inks; it remains one of the standard tests used in forensic document examination. Chromatographic methods are ideal for dye separation and characterization, such as with ballpoint inks, but the insolubility of many pigments limits their effectiveness in the identification of gel inks, especially when dyes are completely absent. There have been a number of hybrid pens that have recently entered the marketplace; these may contain dyes as well as (or even instead of) pigments. The possibility of encountering dyes in inks suggests that chromatographic methods such as TLC remain useful, even when it is clear that a gel pen was used. The more important implication is that chromatography may not be sufficient to distinguish between two questioned inks as it may give little or no discriminating information.

8.2 Raman Spectroscopy

Raman is becoming an increasingly popular choice for ink analysis due to its non-destructive nature and ease of sample preparation. Ink analysis can be performed directly on the paper surface without the need to remove the ink through extraction or physical methods. This *in-situ* analysis can give a usable spectrum from samples as small as 1 micrometer; a spectrum is obtained within minutes and can then be compared against references in a library or other known samples. Interference from paper substrate materials is generally trivial.

Additional advantages of the Raman instrument are its ability to analyze inorganic pigments, colored substances, and different forms of carbon, which may be useful in differentiating black inks. The scattering effect that produces a Raman spectrum, however, is weak and the use of a laser causes the process to be prone to fluorescence, which may overwhelm the signal from the sample. Chemicals to reduce or eliminate fluorescence are beginning to appear on the market, greatly enhancing the usefulness of this technique. For a more detailed discussion of Raman methods in forensic document examination see Smith (2003).

8.3 Energy Dispersive X-Ray Spectrometry (EDS)

Energy dispersive x-ray spectrometry (EDS) provides elemental information about materials; this analytical method generates a spectrum listing nearly all of the elements present in the sample (only the first four elements - hydrogen, helium, lithium and beryllium - are too light to be detected). EDS analysis works best with inorganic compounds, as it is unable to differentiate between the forms of carbon or the overall structure of an organic compound. While not a traditional method for ink characterization, the increased use of inorganic pigments and additives such as colorants, opacifiers (titanium dioxide), and modifiers (magnesium carbonate) in gel ink formulas are easy to identify and have greatly enhanced the usefulness of this technique.

As with Raman, elemental analysis requires only a very small sample and tests can be completed in a short amount of time. This technique requires transferring the ink to a suitable substrate, such as beryllium, but the amount necessary for analysis is much less than that needed for chromatographic analysis making the test minimally destructive.

8.4 Raman and EDS

These two techniques are best used in combination with one another, as each provides information that the other does not. The EDS, for example, can provide additional information about trace elements in samples that primarily contain carbon black pigment. The Raman spectrum for Sakura Gelly Roll (brown) (Figure 14) similar to the spectrum for Pentel Sunburst Gel K908 (black) (Figure 15), but the EDS of the Sakura ink (Figure 16) shows a bromine peak that is absent in the EDS spectrum of the Pentel ink (Figure 17).

Conversely, the EDS spectrum for the Bic Velocity Gel (black) (Figure 18) is similar to the spectrum of the black-colored Pentel Sunburst Gel K908. It is in the Raman spectrum that a "shoulder" appears at 1094 cm-1 (Figure 19) differentiating it from the Pentel Hybrid Gel. A similar shoulder also appears in the Raman spectrum of the Sandford Uni-ball Signo 207 and Sanford Uni-ball Gel Grip, both black. The EDS spectra of the three inks are also similar to one another, displaying few trace elements. As expected, there are also inks for which both the Raman and EDS spectra are different from other black inks. Pentel Energel Liquid Gel best illustrates this. The Raman spectrum (Figure 20) is in the same region as carbon black, but there are numerous peaks as opposed to the usual two peaks for amorphous carbon. Looking at the EDS spectrum, there are also sulfur and sodium peaks as major components (>5%). These two additional peaks also appear in the inks of Pentel Energel (black), Pilot G2 (black) and Pilot Neo Gel (black), all of which did not give a Raman spectrum.

In examining blue inks, it was found that copper phthalocyanine blue is the predominant pigment.

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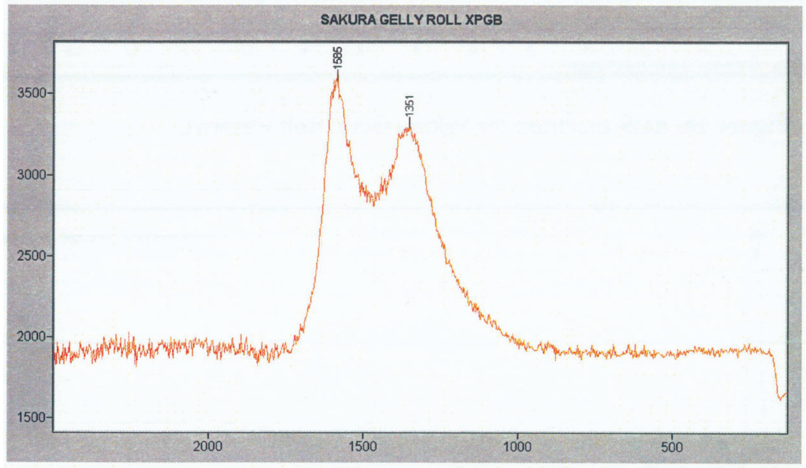

Figure 14. Raman spectrum for Sakura Gelly Roll (brown).

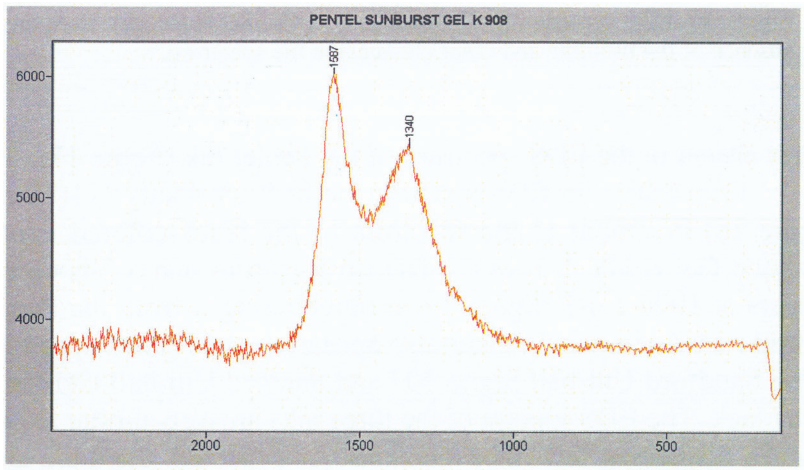

Figure 15. Raman spectrum for Pentel Sunburst Gel K908 (black). Note the similarities to the brown Sakura ink (Figure 14).

Raman provides the clearer identification as there are distinct peaks at approximately 1528 cm-1, 1450 cm-1, and 1339 cm-1 (Raman Group at LENS, 2000). Additional peaks may also be present in varying intensities at 1142 cm-1, 680 cm-1, and 593 cm-1. The majority of the Sanford pens used copper phthalocyanine blue including Uni-ball Signo Gel Stick (Figure 21), Uni-ball Gel Grip, and Uni-ball Gel Impact. The EDS of the Sanford Uni-ball Signo Gel Stick (Figure 22) illustrates the copper peak that is suggestive of copper phthalocyanine blue, but not always an indicator, as the Pentel Sunburst Gel K908 contains copper (Figure 23). However, the Raman spectrum (Figure 24) is not a match for copper phthalocyanine blue. The identification of the pigment in Pentel Sunburst Gel K908 ink is currently unknown, but, as more pigments are added to the library, it will likely be identified.

Several red, violet, green, and tangerine inks were also examined. With the use of the 514 (green) laser, all of the red inks analyzed resulted in fluorescence. The tangerine-colored ink, Sanford Uni-ball Gel Stick, also resulted in Raman fluorescence and the EDS spectrum contained mainly carbon and oxygen, with only trace amounts of additional elements (Figure 25). A number of the violet/ lavender inks also produced Raman fluorescence, with the exception of Sanford Uni-ball Signo Gel Stick (violet), which did not match any spectrum currently in the library. Pentel Sunburst Gel Metallic K908 (lavender) also resulted in fluorescence in the Raman, but the EDS analysis showed aluminum metal as the source of the metallic nature of the pen (Figure 26). The green pen of the same model also showed aluminum in the EDS (Figure 27) as well as minor amounts of copper, chlorine and bromine, which indicates that the

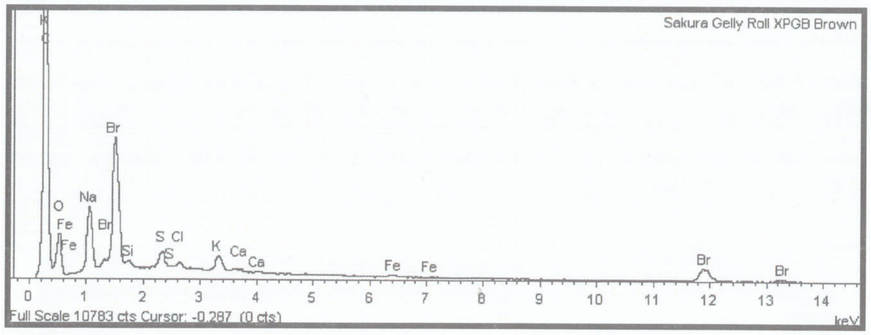

Figure 16. EDS spectrum for Sakura Gelly Roll (brown).

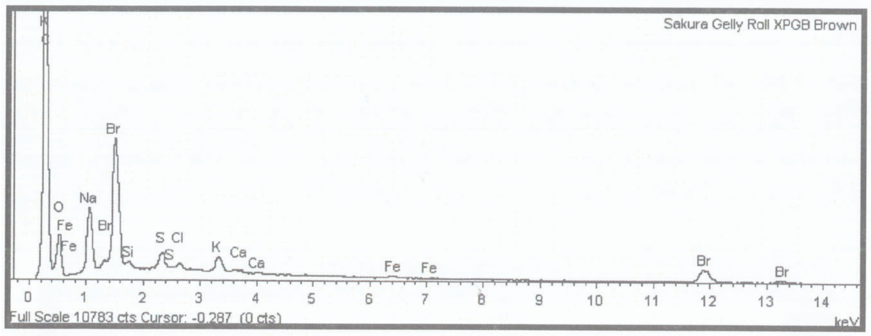

Figure 17. EDS spectrum for Pentel Sunburst Gel K908 (black). Note the absence of the bromine and other elements in the spectrum.

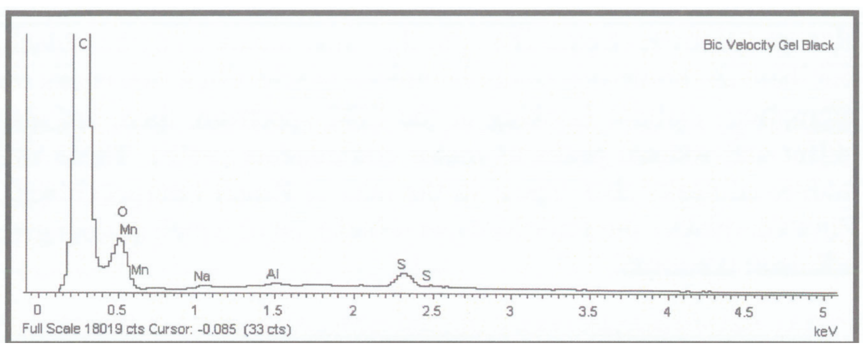

Figure 18. EDS spectrum for the Bic Velocity Gel (black). Note the similarity to black Pentel Sunburst Gel K908 (Figure 17).

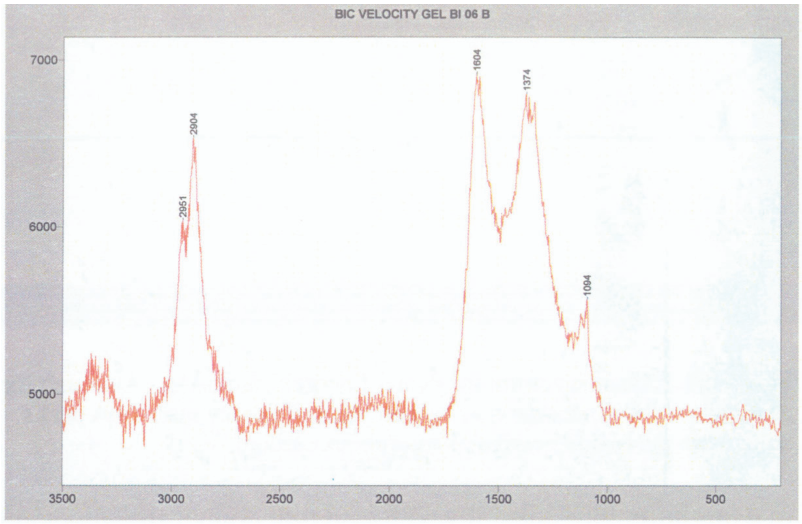

Figure 19. Raman spectrum for Bic Velocity Gel, note the shoulder at 1094 cm·', which is not present in the spectrum for black Pentel Sunburst Gel K908 (Figure 15).

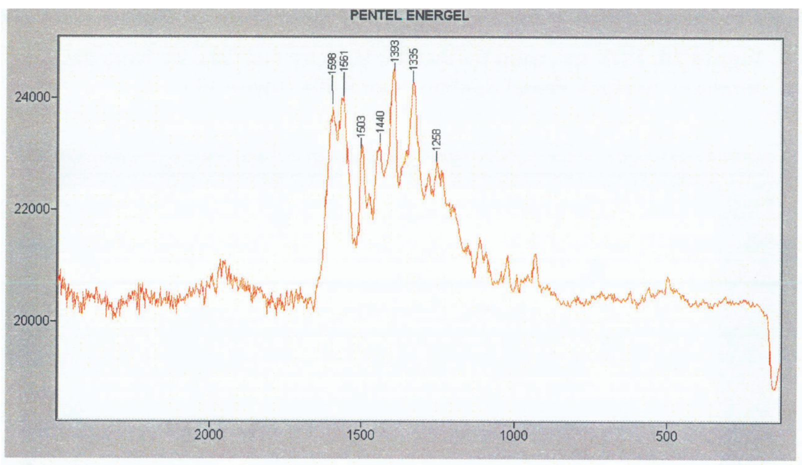

Figure 20. Raman spectrum for Pentel Energel Liquid Gel. Although the peaks are in the same region as carbon black, there are numerous peaks rather than the two indicative of amorphous carbon.

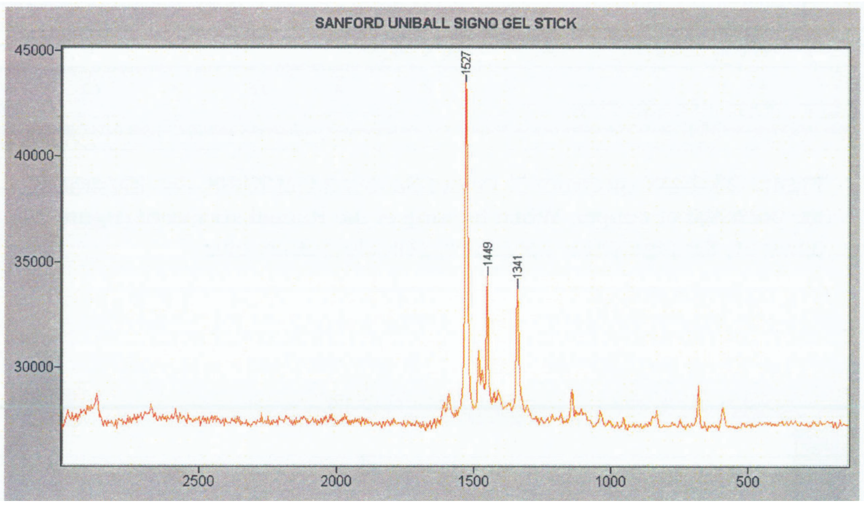

Figure 21. Raman spectrum of Uni-ball Signo Gel Sick, which uses copper phthalocyanine blue as a colorant.

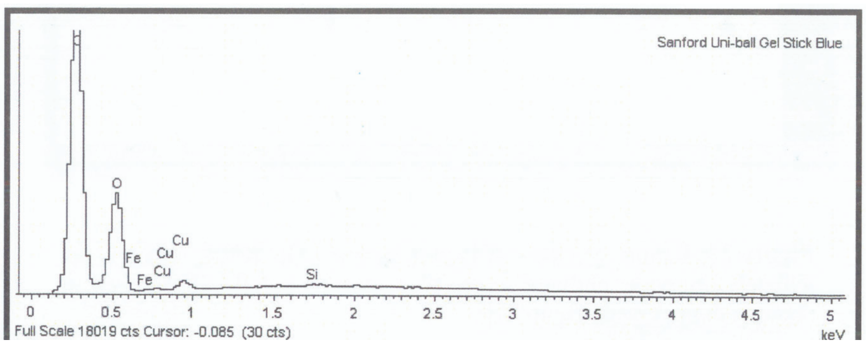

Figure 22. EDS spectrum of Sanford Uni-ball Signo Gel Stick illustrating the presence of copper that is suggestive of copper phthalocyanine blue.

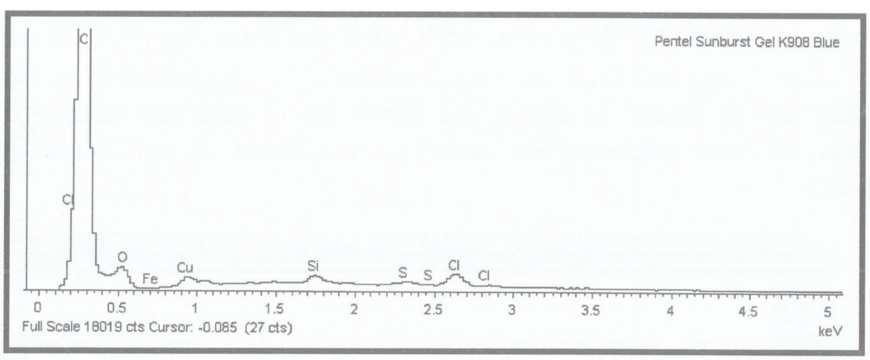

Figure 23. EDS spectrum of Pentel Sunburst Gel K908 also illustrating the presence of copper. When looking at the Raman spectrum (Figure 24), however, the pigment is not copper phthalocyanine blue.

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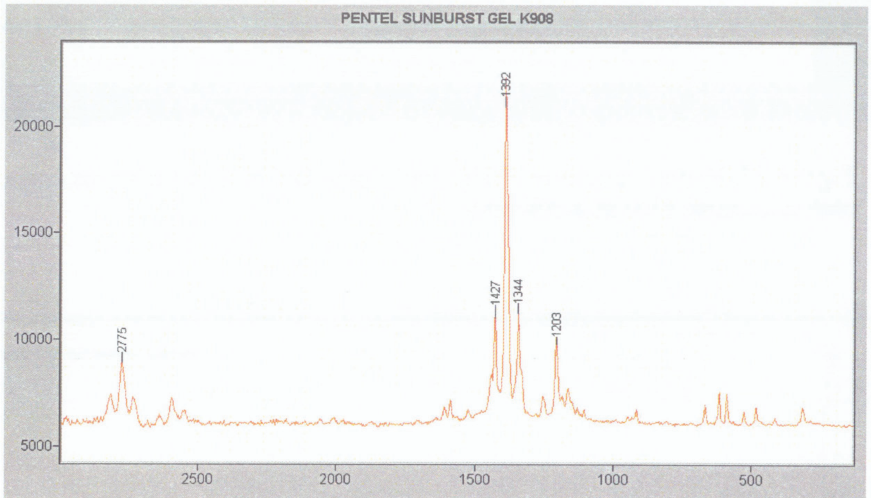

Figure 24: Raman spectrum of Pentel Sunburst Gel K908, which is not a match for copper phthalocyanine blue, even though the EDS spectrum shows a copper peak (figure 23).

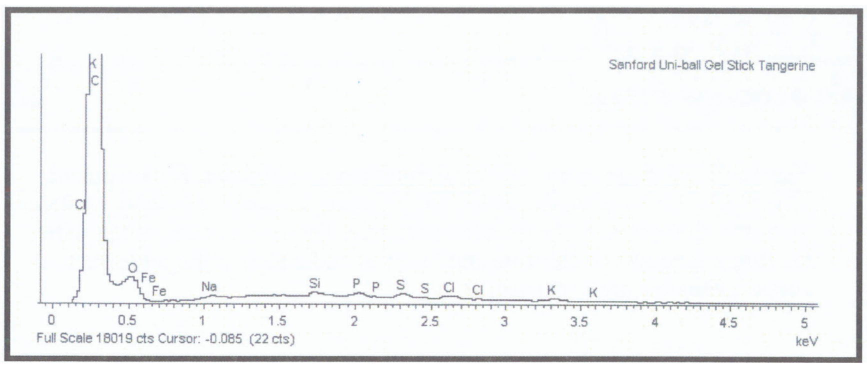

Figure 25. EDS spectrum of Sanford Uni-ball Gel Stick (tangerine) with trace amounts of a number of elements.

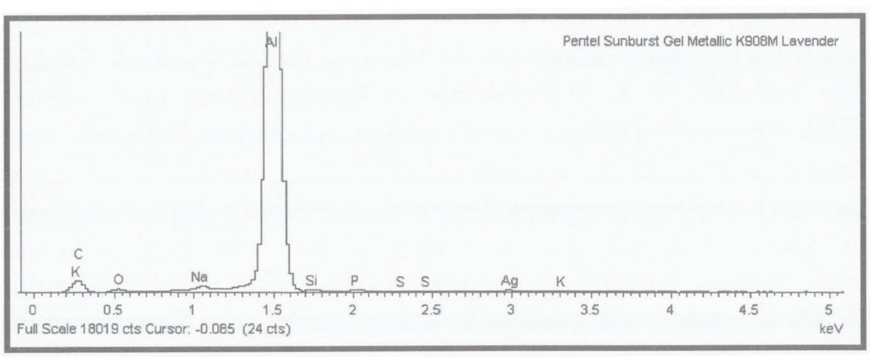

Figure 26. EDS spectrum of Pentel Sunburst Gel Metallic K908 (lavender). The strong aluminum peak shows the source of the metallic nature of the metal flakes in the ink.

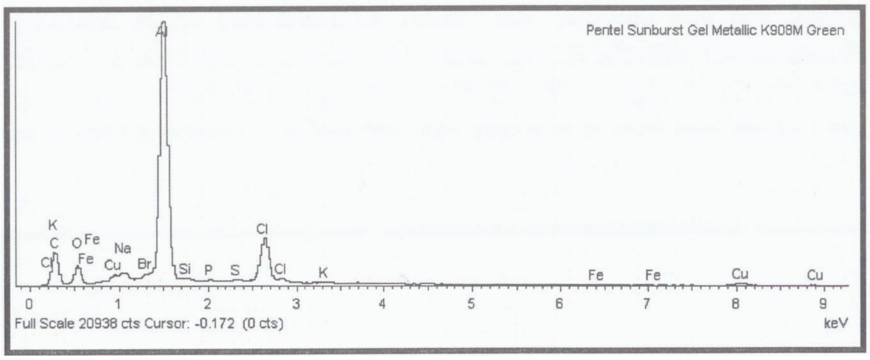

Figure 27. EDS spectrum of Pentel Sunburst Gel Metallic K908 (green). This pen is the same model as the one in Figure 26 and predictably contains the same aluminum as the metallic particles. The copper peak along with the minor amounts of chlorine and bromine indicate that the pigment is a copper phthalocyanine derivative.

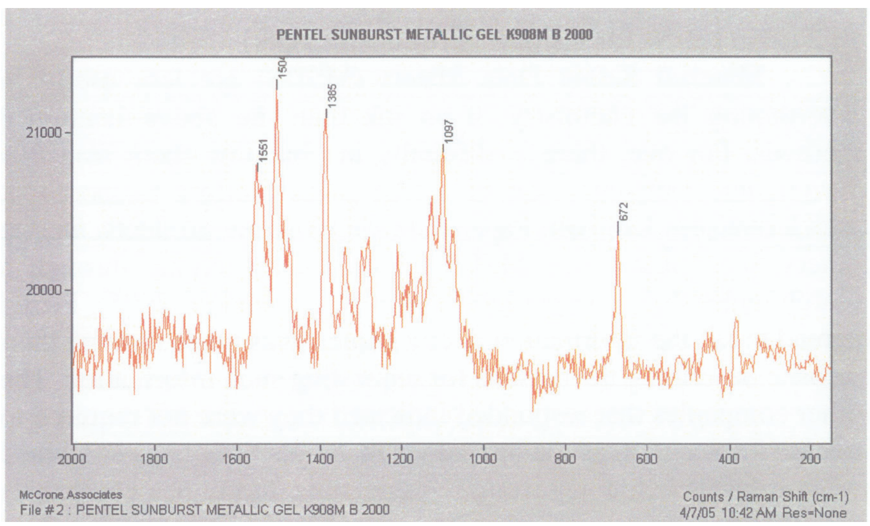

Figure 28. Raman spectrum of Pentel Sunburst Gel Metallic K908 (green). The likely colorant is copper phthalocyanine green, which is a chlorinated copper phthalocyanine.

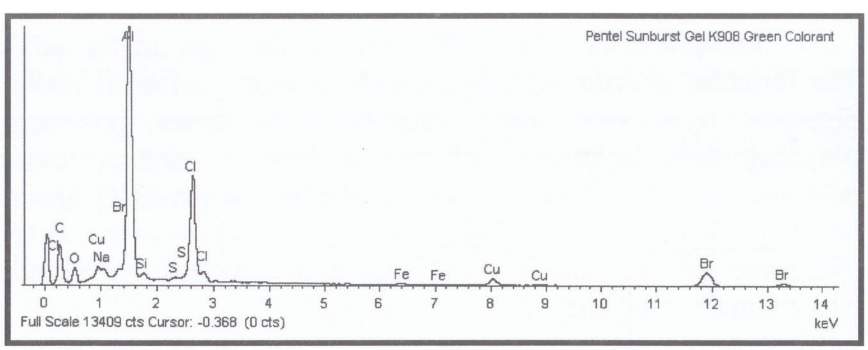

Figure 29. EDS spectrum of Pentel Sunburst Gel K908 (green). Since the pen is the same model as the metallic pen in Figure 27 and the EDS spectrums are similar, it is likely that the colorants are the same, a copper phthalocyanine derivative, although a confirming Raman spectrum was unable to be obtained for comparison due to fluorescence.

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pigment is likely a copper phthalocyanine derivative. From the Raman spectrum (Figure 28) it is likely that the colorant is phthalocyanine green, which is a chlorinated copper phthalocyanine. From the same series, but non-metallic, the Pentel Sunburst Gel K908 results in fluorescence with the Raman and minor levels of chlorine and sulfur with the EDS (Figure 29). Sulfonated copper phthalocyanines are also green and thus it is likely that the ink is a combination of the chlorinated and sulfonated copper phthalocyanines.

9. Material Safety Data Sheets (MSDS)

Material Safety Data Sheets (MSDS) are less useful in determining the chemistry of an ink than the above-mentioned methods. For one, there is difficulty in obtaining them from the various ink companies. An exception is the Sanford Corporation, which oversees Uni-ball, PaperMate, and Sharpie products, among others, who make their MSDS files available online through a search under their product tab (Sanford Corporation, 2005). Pentel agreed to fax the information after a request was made through their website describing the reasons for requesting such information. The other companies that responded indicated they were not required to release information as the hazardous materials their pens contained were at levels below reporting requirements. Many pen companies thought that sharing such information would be akin to releasing their ink formulas. The chemicals that were listed (in total) are ethylene glycol, diethylene glycol, glycerol (glycerin), propylene glycol, and triethanolamine. All have hydroscopic properties (absorb/retain water) and also have uses listed as solvents for dyes, inhibitor of mold growth, and increasing the penetration of organic liquids into paper. The Merck Index (Budavari, 1996) also specifically stated that ethylene glycol was used in the ink of ballpoint pens.

Brunelle & Crawford (2003) provide three gel ink formulas. The formulas contain ingredients such as water, solvents, resins, pigments, dyes, surfactants, pseudoplasticity agents, polymers, pH controllers, lubricants, antispectics, biocides, and corrosion inhibitors (p. 34-36). The addition of the pseudoplasticity agents help to produce a “shear-thinning viscosity” in the flow of the ink (p. 34). Some gel inks contain a combination of colorants that include both pigments and dyes.

10. Conclusion

Currently, the authors have collected and catalogued approximately 100 inks. This, however, is only the beginning as the focus thus far has been on gel pens. The inks are indexed by company, with each having a company and number identifier; although it has been suggested that the preferred arrangement for a collection is organized by ink and color (Brunelle & Crawford, 2003). As more samples are added, this will become a consideration. Data generation is currently in the preliminary stages. While a number of Raman and EDS spectra have been obtained, there are also photomicrographs at low and high magnification to be collected as well as spectral response data from IR reflectance, IR luminescence, and UV fluorescence. Upon the addition of more types of pens, it is likely that TLC tests will be conducted, as it is an industry standard. Infrared spectroscopy is often preformed as a complement to Raman and works well in characterizing many of the pigments encountered in this study. Limited testing of IR was unsuccessful because, once the ink has been attached to a paper substrate, the cellulose in paper overpowers the more subtle ink signal. In examining the inks reported in this study, it was found that a multi-technique approach was most helpful, using the visual data as a starting point and combining it with both Raman and EDS data to create a set of unique identifiers.

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