Examination of Gel Pen Ink by Microspectrometry

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The examination of writing inks has been an integral part of questioned document examination since its inception. The types of inks and writing instruments of concern have progressed from pencil and nib pen to ballpoint and porous-point pens. The most recent development in both ink and writing instruments has been the gel-ink pen. This instrument is a marriage of the ball pen with polymeric gel ink containing both dyes and pigments as colorant and water-based gel. This paper looks at the feasibility of using a Craic Technologies Questioned Document System II (QDS II) microspectrometer as an analysis tool for the differentiation of gel-pen inks. Using several sample preparation methodologies over the full spectral range from ultraviolet to infrared, 7 different black gel inks were examined with the QDS II. Additionally, 2 blue gel inks (with common manufacture as several of the black inks) were also examined. Results of these examinations indicate the ability to differentiate, to varying degrees, the black gel inks and consistency between those inks of common manufacture (blue and black). The preferred sample preparation methodology was also identified and elucidated.

Introduction

Gel pens became commercially available in the United States in the late 1980s (Gernandt and Urlab, 1996). They have become a popular form of writing instrument due to the great number of unique and brilliant colors that are available. Initial manufacture of gel pens used pigment-based gels, with the addition of dyes to more recent formulations. The impetus for the development of this family of pens included environmental concerns and the ability to produce a wider range of both unique and brilliant colors (Fabian, 2000). The absence of organic solvents within the gel matrix decreased safety concerns both during manufacture and for the consumer.

Since their inception, the inks from gel pens have presented a challenge for the forensic examiner. Routine examination methodologies involving the use of microscopy, infrared reflectance, infrared luminescence, chemical spot tests, and thin layer chromatography (TLC) have been of limited use in the examination of pigment-based gel inks (Jasuja, Singla, Mand, and Lyter, 2005). More specialized instrumentation and the increased use of dye-based gel ink formulations in recent years have increased the ability of the forensic examiner to discriminate inks (Mazzella and Khanmy-Vital, 2003; Andermann, 2001). In this work, another instrument, the Craic Technologies QDS II, was evaluated.

When the sample of interest is a written line upon a document, problems of sample preparation and the use of semi-destructive methodologies always exist. The methods of sample preparation available with the QDS II include microscopic direct analysis, as well as individual fiber analysis of removed portions of the written line. It is the intent of any forensic analysis to minimize the change or alteration of any evidentiary material by the process of analysis; therefore, the ability to sample in situ or with removal of small fibers is a great advantage over other chemical or instrumental methodologies. As an evaluation of this technology, a relatively difficult sample was chosen—gel ink.

Methods and Materials

The standard examination protocol for writing inks consists of both physical and chemical procedures (ASTM, 2004). The physical procedures, such as microscopy, infrared reflectance and luminescence, and the use of various filters, are still applicable to gel inks. Although chemical procedures, such as spot tests and chromatography, are not entirely applicable to the examination of gel inks due to their lack of solubility and the

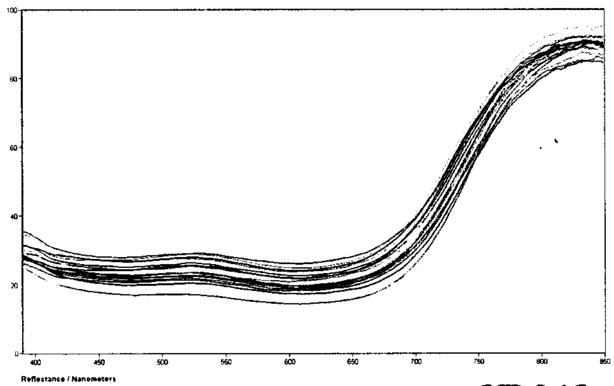

Figure 1. Overlay of diffuse reflectance spectra of 20 different locations of black Marvey GT700 ink.

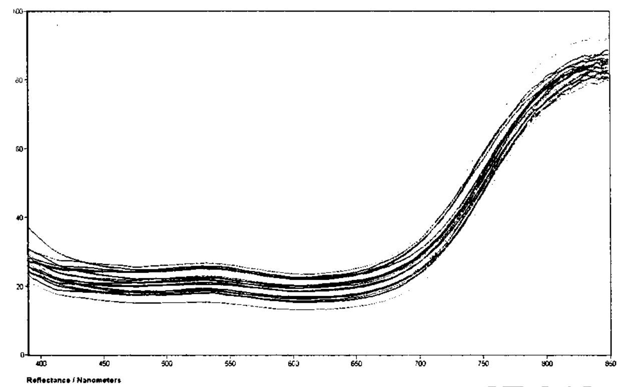

Figure 2. Overlay of diffuse reflectance spectra of 20 different locations of black Pilot G-2 0.7 ink.

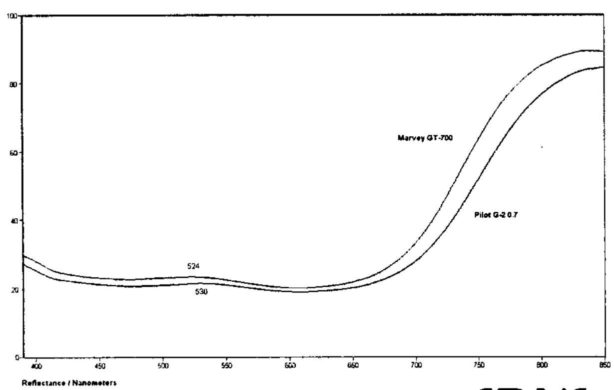

Figure 3. Overlay of averaged diffuse reflectance spectra of the Marvey and Pilot inks.

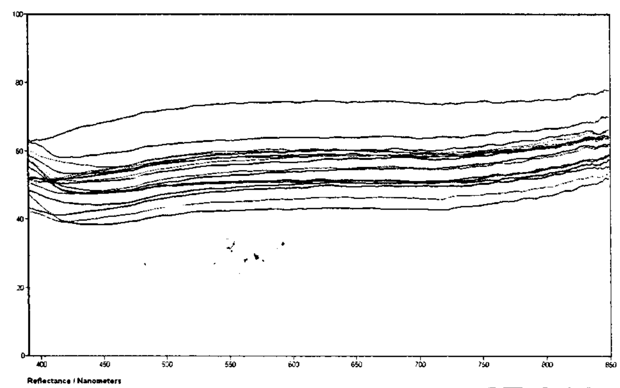

Figure 4. Overlay of diffuse reflectance spectra of 20 different locations of black Uniball Gel Grip ink.

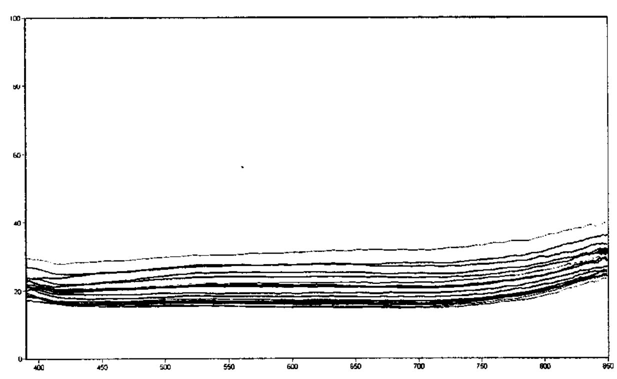

Figure 5. Overlay of diffuse reflectance spectra of 20 different locations of black Pentel Hybrid Gel ink.

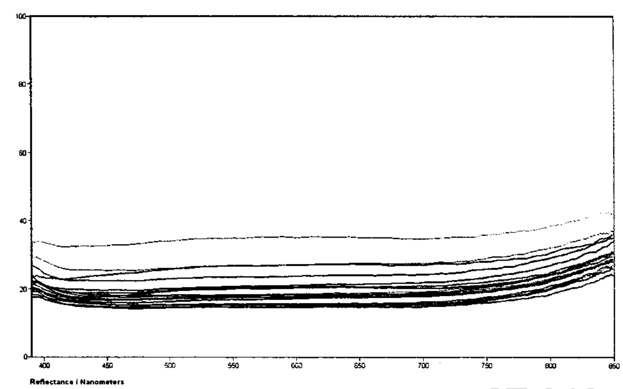

Figure 6. Overlay of diffuse reflectance spectra of 20 different locations of black Papermate ink.

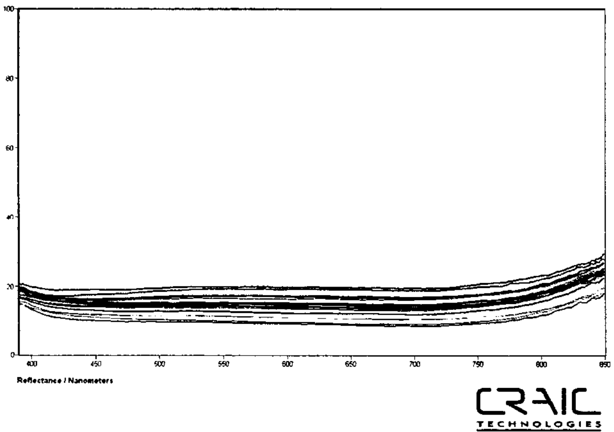

Figure 7. Overlay of diffuse reflectance spectra of 20 different locations of black Uniball Gel Impact ink.

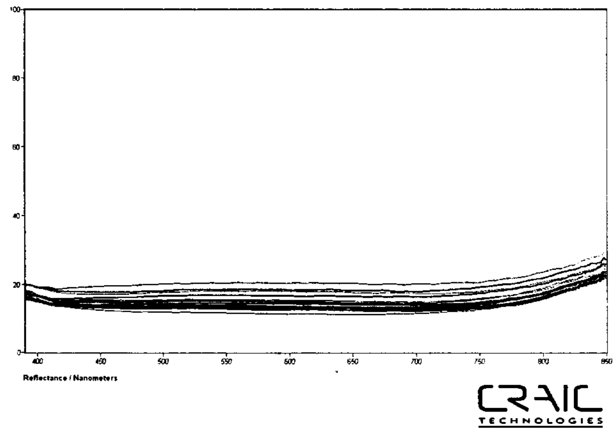

Figure 8. Overlay of diffuse reflectance spectra of 20 different locations of black Sakura Gelly Roll ink.

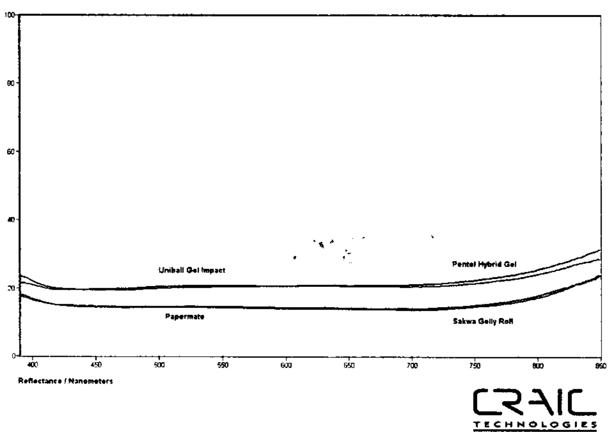

Figure 9. Overlay of average of diffuse reflectance spectra of the black Papermate, Pentel, Sakura, and Uniball inks.

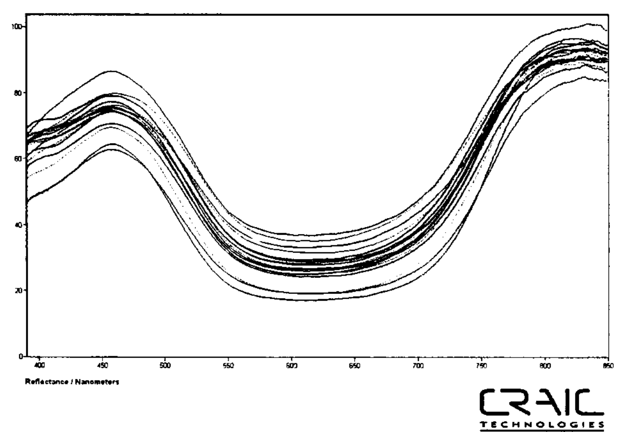

Figure 10. Overlay of diffuse reflectance spectra of 20 different locations of blue Pilot G2 0.7 ink.

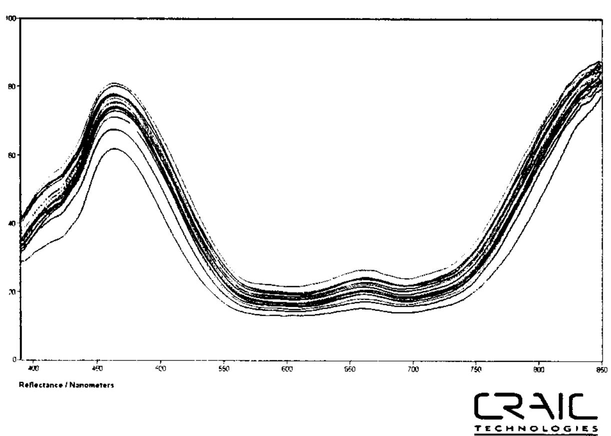

Figure 11. Overlay of diffuse reflectance spectra of 20 different locations of blue Uniball Gel Impact RT ink.

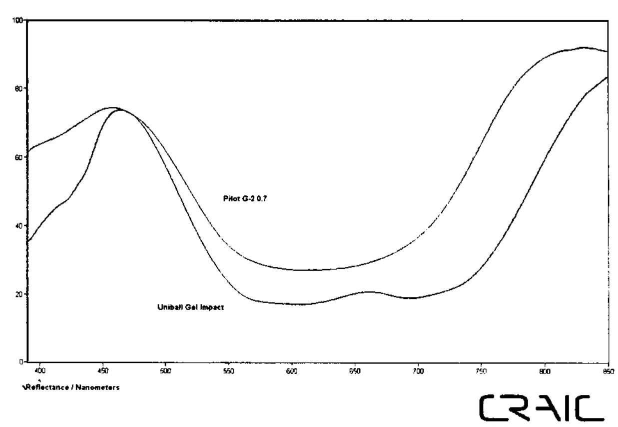

Figure 12. Overlay of average of diffuse reflectance spectra of the blue Pilot and Uniball inks.

nature of the colorant used, they have been reported in recent works. Instrumental methods have also been reported, ranging from scanning electron microscopy to Raman spectroscopy to gas chromatography/mass spectrometry (Jasuja, Singla, Mand, and Lyter, 2005; Mazzella and Khanmy-Vital, 2003; Wilson and LaPorte, 2004).

The examination of 7 black gel-pen ink writings and 2 blue gel-pen ink writings was conducted with a Craic Technologies QDS II. The gel-pen writings were prepared on white copy paper by scribing 4 horizontal lines for each type of ink. The gel ink samples were found in instruments manufactured by the companies listed in Table 1. Instrumental analysis was conducted upon neat written lines on paper with no additional sample preparation. Diffuse reflectance illumination was employed, and spectra from 390 nm to 850 nm were collected from 5 different locations on 4 different pen strokes for each sample. Each collection was an averaging of 50 spectra, with each scan taking approximately 20 milliseconds. The white copy paper on which the lines were scribed was used as the reference. Fluorescence microspectroscopy was also obtained. Each ink sample was excited with 365, 405, and 436 nm light. Each collection was an average of 50 spectra, with each scan taking an average of 50 milliseconds.

Results

The spectra generated from the gel ink samples by the Craic Technologies QDS II yielded excellent reproducibility with very little deviation, either within a single line or among various written lines from the same writings. The signal-to-noise ratio was also acceptable in spite of the opaque nature of the ink line. Figures 1 through 9 illustrate the spectra from the black gel-pen ink samples. It is clear from an evaluation of the spectral shape that the Marvy GT–700 and Pilot G-2 gel pens are very different from the other black ink samples due to their increased absorbance in the near infrared region (700 to 850 nm) and their weak reflectance around 530 nm. The remaining inks appeared spectrally similar. Figures 11 and 12 represent the spectral results of the blue gel ink samples, demonstrating that these samples are easily differentiated from each other.

The near infrared region of the spectra of both Pilot G-2 samples (black and blue) are consistent (Figures 10 and 12). For the most part, the inks examined did not fluoresce. When comparing the fluorescent emission spectra of paper with that of the inks, the spectra were identical in shape and relative peak intensity to that of paper. The only real difference was that the overall intensity of the emissions was weaker, an effect caused by the ink itself acting as a filter. The only exception was the Marvey GT-700 gel ink, which exhibited a very weak emission at 767 nm. The blue inks did differ. The Pilot G-2 0.7 gel ink also exhibited a weak emission at 783 nm, in addition to variations in the major peak.

Conclusion

The methodology employing the Craic Technologies QDS II provides excellent reproducibility and

Company	Designation	Color
Marvy	GT-700	Black
Pilot	G-2 0.7	Black
Uniball	Gel Grip	Black
Pentel	Hybrid Gel	Black
Papermate	None	Black
Uniball	Gel Impact RT	Black
Sakura	Gelly Roll	Black
Pilot	G-2 0.7	Blue
Uniball	Gel Impact RT	Blue

Table 1.

signal-to-noise ratios that are capable of differentiating certain previously indistinguishable ink writings. Due to the capabilities of the QDS II to measure along the entire visible spectra, its impact appears to be even greater when samples with colors different from black are involved. A correlation of different color inks by manufacturer is possible, but additional examinations are required. Sample preparation is minimal. However, given the relatively small sample population of gel inks examined, this advantage over other sample preparation schemes is difficult to gauge. It is expected that this technology is appropriate for the analysis of other written lines, and future investigation will include both additional gel ink samples including samples of ball-pen and nonball-pen ink as well.

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