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Differentiation of Black Gel Inks Using Optical and Chemical Techniques*

ABSTRACT: Gel ink pens have become a common writing instrument in the United States. Questioned document examiners often attempt to optically differentiate gel inks from each other and from other non-ballpoint ink writings (e.g., those from roller-ball pens). Since early formulations were primarily pigment-based, they do not elute when analyzed by thin-layer chromatography. However, recent gel ink formulations (i.e., within the past five years) include dye-based inks that can be easily separated. This study differentiates black gel inks using optical and chemical techniques. The techniques include: microscopy, visible and near infrared reflectance, near infrared luminescence, thin-layer chromatography (TLC), spot tests, and gas chromatography/mass spectrometry (GC/MS). As a result of this study a flow chart has been developed allowing for a systematic determination of a questioned ink. In addition, an analysis of volatile compounds found in gel inks revealed that there are some unique ingredients that may be found in gel inks that are not typically found in other non-ballpoint inks.

KEYWORDS: forensic science, questioned documents, document examination, non-ballpoint inks, inks, gel inks, gel pens, thin layer chromatography, GC/MS, TLC

Gel ink pens have become a common writing instrument in the United States. Gel ink is a water-based ink that was first created in 1984 by Sakura Color Products Corporation of Japan. Prior to gel inks, non-ballpoint roller-ball inks were a popular alternative to ballpoint pens. Sakura wanted to develop an environmentally friendly ink that did not contain any volatile organic compounds like those found in roller-ball pens. The first pen produced by Sakura was the Ballsign pen, which contained a dye-based ink. The following year they changed the ink formulation to pigment-based inks, which gave them flexibility with color choices (personal communication with Sakura Color Products Corporation).

The first gel inks arrived in the United States in the late 1980s. The gel inks were pigment-based and therefore difficult to analyze using thin-layer chromatography (TLC) as outlined in American Society for Testing and Materials (ASTM) E 1422-98 (1) and E 1789-96 (2). Forensic examiners recognized the importance of characterizing this new family of inks for questioned document (QD) examinations. Gernandt and Urlaub (3) described the general characteristics of a gel pen in order to familiarize forensic scientists with the instrument and made the following observations: "All of the pens that have been tested use a clear or semitransparent outside barrel and a clear or semitransparent fill tube... At the end of the ink supply is a clear grease plug of approximately one-quarter inch in length." They also noted, "Gel inks, which normally lack any dye components, will not display any movement on the TLC plate..."

In 1995 research was conducted to examine the increasing number of gel inks found on the open market (4). The authors attempted to separate the many different colored gel inks with spectral techniques, TLC, and spot tests. The colored gel inks could be separated with spectral techniques; however, the black gel inks remained inseparable.

Recently, Mazzella and Khanmy-Vital examined 33 European blue gel inks (5). Traditional spectral techniques were used as well as Raman spectroscopy and scanning electron microscopy (SEM). Raman spectroscopy was used to help classify pigmented gel inks, but was not helpful for dye-based inks. SEM was used to examine the morphology of the ink strokes and provide guidelines for discrimination.

Modern black gel inks are both pigment and dye-based. Pen manufacturers have begun using dyes to produce colors in the inks. The use of dyes has led the authors of the present paper to consider using TLC techniques to help differentiate the dye-based black pens. Typically, when a gel ink appears on a questioned document, it is characterized as a non-ballpoint ink. It would be an advantage if the examiner could not only determine that the ink is gel based, but also determine the manufacturer of the gel pen.

In QD examinations, identifying the type of writing instrument by utilizing physical and chemical analyses can provide valuable information to the document examiner. When utilizing a library of standards to identify a writing ink(s), one of the first steps is to physically distinguish between a ballpoint and non-ballpoint ink. The non-ballpoint inks can include a number of different writing instruments such as roller-ball pens, felt tip markers, and gel pens. This step is used to determine how an ink will be extracted (e.g., ballpoints are extracted with pyridine and non-ballpoint inks with a 1:1 mixture of ethanol and water). Therefore, if the QD examiner can distinguish between other non-ballpoint inks and gel inks, this step can help narrow down the scope of analysis by eliminating inks.

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In the present study, several techniques were used to distinguish black gel inks found on the open market in the United States. It was determined that if a differentiation could be made between black gel pens, then colored gel pens would be easier to separate due to the array of colors. It was also a focus of this study to determine if there was a technique that could be used to tell the difference between gel pens and roller-ball pens.

Twenty-nine black gel pens were collected and examined. Nondestructive optical techniques such as (near) infrared reflectance (IRR) and (near) infrared luminescence (IRL) were used to separate the inks initially. The IRR mode was used to scan and measure the reflectance of the ink at several different wavelengths. The IRL mode was used to examine fluorescent characteristics of the inks. Destructive examinations such as TLC, spot testing, and gas chromatography/mass spectroscopy (GC/MS) were used to separate the pigment-based gel pens. GC/MS was also used to examine differences between gel and roller-ball inks by examining volatile organic compounds present in the ink samples. A flow chart was produced that allowed differentiation between several of the black gel pens.

Materials and Methods

Gel Pens

Twenty-nine black gel pens from 17 different companies were obtained from the United States Secret Service (USSS) International Ink Library. A complete list of pens can be found in Table 1. A sample of the gel ink was written on Whatman™ filter paper, in accordance with the ASTM standard (2), to ensure no interference from whiteners or volatiles. All inks were examined under magnification to see if there were morphological differences.

TABLE 1—*List of tested black gel pens.*

Inventory No.	Company	Model
7524	Bic	Intensity
7654	Pilot	G-2
7662	Pilot	Erase-a-gel
7841	Papermate	Gelstick
7906	Pilot	Dr. Grip Gel
7907	Rotomac Q	Gel
7908	Papermate	Gel Roller
7910	National	Gel
7911	Bic	Gel
7931	Zebra	Airlift
7932	Zebra	Sarasa
7934	RoseArt	Better Gels
7935	RoseArt	Magicolor Gels
7936	RoseArt	Curves Gel
7939	Staples	Jeller Rollers
7940	Pentech	Focus
7941	Pentel	EnerGel
7942	Pentel	Gel Ink Rollers
7943	Pentel	Hybrid Gel Roller
7944	Sanford	Get RT
7945	Sanford	Erasable Gel
7948	Cross	Gel
7949	Parker	Gel
7950	Bic	Velocity Gel
7955	Pengate	Tecco Gel
7956	Marvy	Gel Excel
7982	Sanford	Gellyz Scents
7983	Y&C	Gel Xtreme
7984	Y&C	Gel Stylist

Spectral Comparisons

The Foster and Freeman® Video Spectral Comparator 2000 High Resolution (VSC 2000 HR) was used to measure the reflectance of the inks over a range of 400–1000 nm. The ink was magnified and compared with a standard white calibration plate for the measurement. The reflectance curves were plotted for all gel inks.

The VSC 2000 HR was used to observe near infrared luminescence in the inks that had a high reflectance. The first setting utilized a 400–580 nm band-pass filter with a 610 nm cut-on filter. The second setting used the 480–620 nm band-pass filter with a 665 nm cut-on filter.

Thin Layer Chromatography

All gel inks on the filter paper were prepared for sampling by taking ten 1.3 mm punch holes from written ink lines. The samples were extracted with 20 μL of ethanol/water (1:1) for 1 min under constant agitation with a glass pipette. The extracted samples were spotted on silica gel 60 pre-coated EM Science® glass plates (EM# 5721-7) with a layer thickness of 250 μm. The plates were placed in an oven (100°C) for approximately 5 min, cooled and placed in a TLC chamber with a solvent system composed of ethyl acetate, ethanol, and water (75:35:30). The solvent front was allowed to elute for 4 cm. The VSC 2000 HR was used to examine and document the TLC plates under visible, ultraviolet, and IRR modes.

Spot Tests

Several solvents were spotted in 10 μL aliquots onto the gel ink lines on four different types of paper to include (filter, copy, coated, and bond paper). The ages of the gel ink samples were 1 day and 1 month old. The solvents used were: acetone, acetonitrile, aniline, bleach, butanol, chlorobenzene, chloroform, cyclohexane, dimethyl formamide, dimethyl sulfoxide, ethanol, 50% ethanol, ethyl acetate, ethyl ether, hexane, methyl ethyl ketone, methanol, methylene chloride, saturated NaCl solution, Na_2SO_3, 5% NaOH, petroleum ether, phenoxyethanol, propanol, propylene glycol, pyridine, tetrahydrofuran, and water. The samples were allowed to dry and observed under a microscope.

Gas Chromatography / Mass Spectrometry

The gel inks were prepared for the GC/MS by taking ten 1.3 mm punch holes from the filter paper samples. The inks were sampled fresh (approximately 1 h), 1 week, and 1 month old. The samples were allowed to age in an open air and ambient (fluorescent) light environment and were then extracted with 20 μL of ethanol for 1 min under constant agitation with a glass pipette. The ethanol extract was removed and transferred into a vial. Injection volumes of 1 μL were analyzed on a Perkin Elmer® Autosystem XL Gas Chromatograph in series with a Perkin Elmer® Turbomass Mass Spectrometer. The column used was a fused silica capillary column Hewlett Packard HP-5 (30 m × 0.25 mm × 0.25 μm). The injector and detector temperatures were set at 250°C and 300°C, respectively. The analytical conditions were: initial temperature 50°C for 1 min, ramp 10°C/min to 200°C with a 2 min hold, then 25°C/min to 300°C with a final hold time of 2 min.

Results and Discussion

Microscopic Examination

When the samples were examined under magnification, besides different line thickness, some samples had a flat black appearance

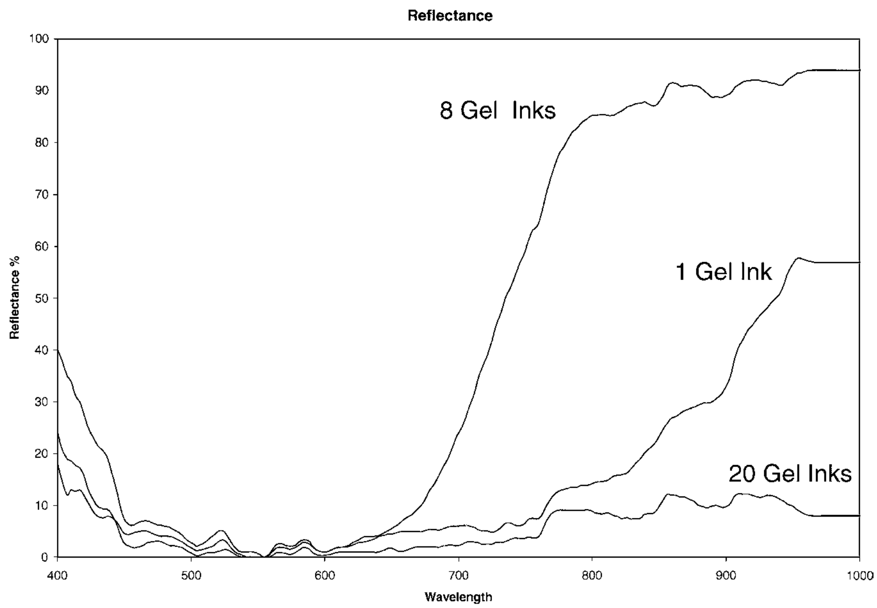

FIG. 1—*Three representative reflectance curves measured from the group of 29 gel inks. The inks were differentiated into the first groups by the percent reflectance at 1000 nm.*

compared with the others and two samples had a glitter-like appearance. The line thickness was not a distinguishing characteristic since the thickness can change based on such factors as the pressure of the pen or the type of paper used. It was decided that the microscopic differentiation would be made in the latter part of the flow chart since reference gel ink samples were needed for comparisons.

Visible and Near Infrared Reflectance

Each sample on the filter paper was placed into a VSC 2000 HR and a reflectance curve between 400 to 1000 nm was generated. Three representative reflective curves are shown in Fig. 1. Twenty samples reflected little or minimal light and remained at the 10% reflectance area over the entire light spectrum. One sample had about 50% reflectance at 1000 nm. The remaining eight samples had increased reflectance beginning at 700 nm and ending at 1000 nm with about 90% reflectance. It was decided that the first separation for the flow chart of the black gel inks would be made using the reflectance at 1000 nm. Additionally, it was determined that the nine inks that had an increased reflectance at 1000 nm were at least partially dye-based. The inks that remained in the 10% reflectance region were the pigment-based gel inks.

Near Infrared Luminescence

The next step in the differentiation of the gel inks was to examine the dye-based inks, which had 90% reflectance at 1000 nm when examined with the IRR mode. The pigment-based inks did not have these properties and reflected approximately 10% of all wavelengths of light. The dye-based ink samples were illuminated with 400–580 nm light using a band-pass filter. A 610 nm cut-on filter was placed in front of the camera, allowing only fluorescent emission to reach the detector. Three of the eight dye-based gel inks were fluorescent under these conditions. An example of a fluorescent ink sample is shown in Fig. 2. The other five were illuminated with 480–620 nm light and imaged with a 665 nm cut-on filter. Two of these gel inks appeared transparent and the other three remained opaque. Of the two transparent samples, one was observed to sparkle under magnification (e.g., $\times 10$) while the other did not. Examples of a transparent and an opaque ink sample are shown in Fig. 2.

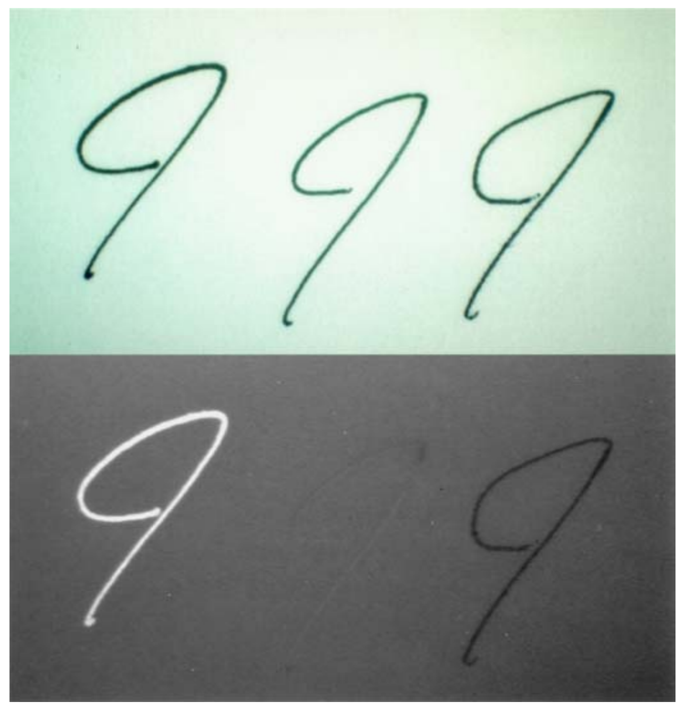

FIG. 2—*Three different dye-based gel pens were photographed first under normal light conditions* (top)*, and under a near infrared luminescent mode* (bottom). *The ink will fluoresce, appear transparent, or remain opaque depending on the inks components.*

Thin Layer Chromatography

Following the optical examinations, TLC was performed on all of the gel ink samples. The nine dye-based gel inks were previously separated into five groups using IRR, microscopy, and IRL. Using slight differences in banding patterns on the TLC plates, the

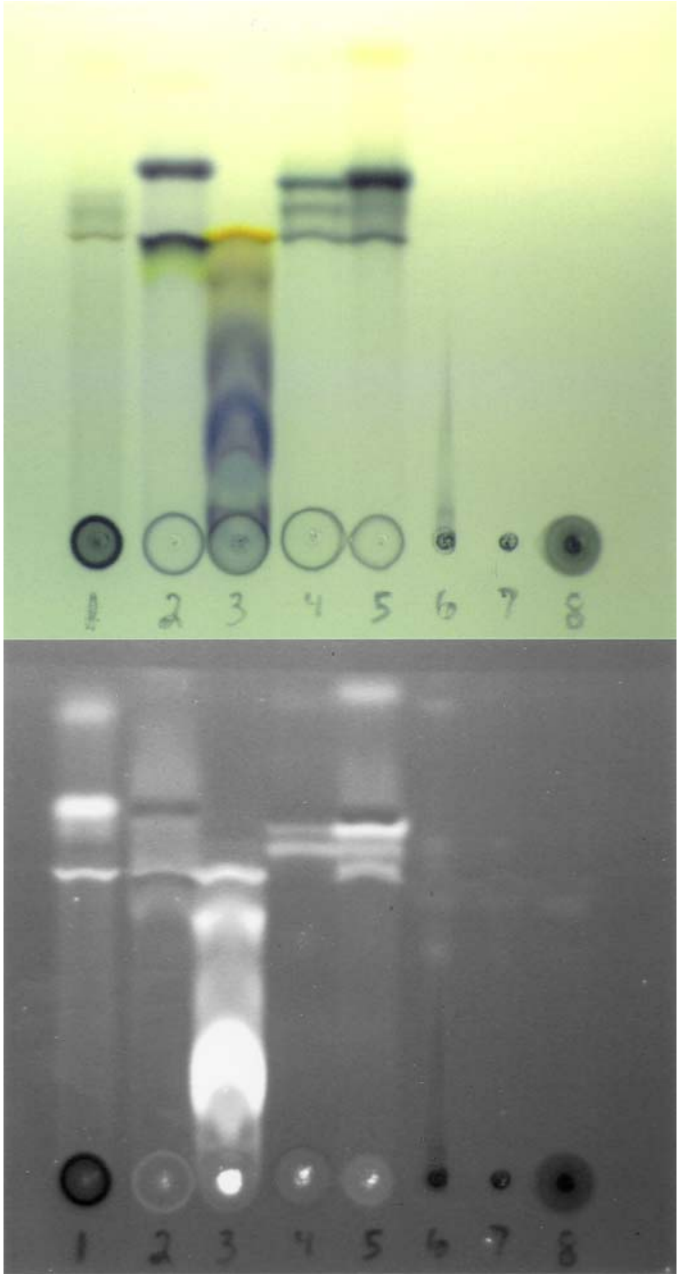

FIG. 3—*The five main banding patterns of the dye-based inks are shown as the first five spots on the TLC plate viewed left to right under visible* (top) *and IRL* (bottom). *The erasable gel pens are shown as dark black spots at the origin, one with a streaking pattern (samples 6 and 7). Sample 8 is the typical pigment-based gel ink that will not migrate on the TLC plate.*

dye-based gel inks were further separated into eight groups. The five main TLC banding patterns for the dye-based gel inks are shown as samples 1–5 in Fig. 3.

It was theorized that the pigment-based gel inks would not run on the aforementioned TLC, which is commonly utilized for separating dyes. Nonetheless, all the pigment-based inks were run on TLC because occasionally differences are seen at the origin when pigment-based inks are spotted. Eighteen of the 20 inks did not migrate up the plate, but two of the inks did make a unique spot at the origin approximately the diameter of the pipette. One of the two spots made an upward streaking pattern. The pattern was observed on samples that were fresh as well as samples 7 months old. The TLC of these two pigment-based inks is shown as samples 6 and 7 in Fig. 3. Interestingly, these two unique pigment-based gel inks were both from pens that were advertised as being erasable gel inks (Pilot Erase-a-Gel and Uni-ball Signo Erasable Gel). The other 18 pigment-based inks made a darkened circle with a larger diameter than the pipette when spotted on the plate (see Fig. 3).

Spot Tests

There were 17 pigment-based gel inks that were not distinguishable following previous examinations. The inks were placed on filter, copy, bond, and coated paper. All solvents mentioned in the Materials and Methods section were spotted onto the fresh ink lines. The solvents $NaSO_3$ and 5% NaOH were the only two solvents that caused eight of the inks to smear. Samples were allowed to age for 1 month and spotted again. After allowing the inks to age, only two of the inks smeared with 5% NaOH. It was decided that the spot test would be used only to differentiate these two inks because the aged sample represented a more typical questioned document since it is rare to examine a document that is only 1 day old.

Gas Chromatography/Mass Spectrometry

The remaining 15 pigment-based gel inks were analyzed using both fresh and aged samples (e.g., 1 week and 1 month in open air and ambient fluorescent light). The chromatograms revealed many different components for each sample. The most noticeable peak was from glycerin, which had a retention time (RT) of ~6.0 min. This peak was very large and broad. Of the 15 pigment-based samples, 10 contained glycerin. The glycerin peak was very abundant in the fresh sample, as well as in the week-old sample, and was detectable in samples aged 6 months. A typical total ion chromatogram (TIC) from a 1-h sample showing the glycerin peak is illustrated in Fig. 4.

After differentiation by detection of a glycerin peak, other major peaks were used to separate the samples. Other major peaks include triethylene glycol (RT-12.3), pentaethylene glycol (RT-15.4, 18.8, 21.0), and triethanolamine (RT-11.7). The five samples that did not contain any glycerin were separated into four groups based on the presence or absence of triethylene glycol and triethanolamine. The ten samples that contained glycerin were separated into three groups using pentaethylene glycol and triethanolamine peaks. The time that these peaks remained in the sample was examined and determined to be less than that of glycerin. Triethanolamine and triethylene glycol were detected in some quantity in samples that were 3 months old. However, pentaethylene glycol dissipated after approximately two weeks.

Numerous smaller peaks were detected on the TIC and may be used to differentiate the pigmented inks further; however, the small peaks were usually detected only in fresh samples and could not be detected a few days later. These peaks would not be of interest in most casework since it is unlikely that documents are received for analysis in this time frame. Future work should include examining these small peaks and their ratios over time.

The dye-based inks that were not characterized after all previous tests were extracted in the same manner and run on the GC/MS. There were no notable differences in these samples that would lead to further characterization.

Gel Inks versus Roller-Ball Inks

Twenty roller-ball inks were randomly selected from the United States Secret Service (USSS) International Ink Library, extracted,

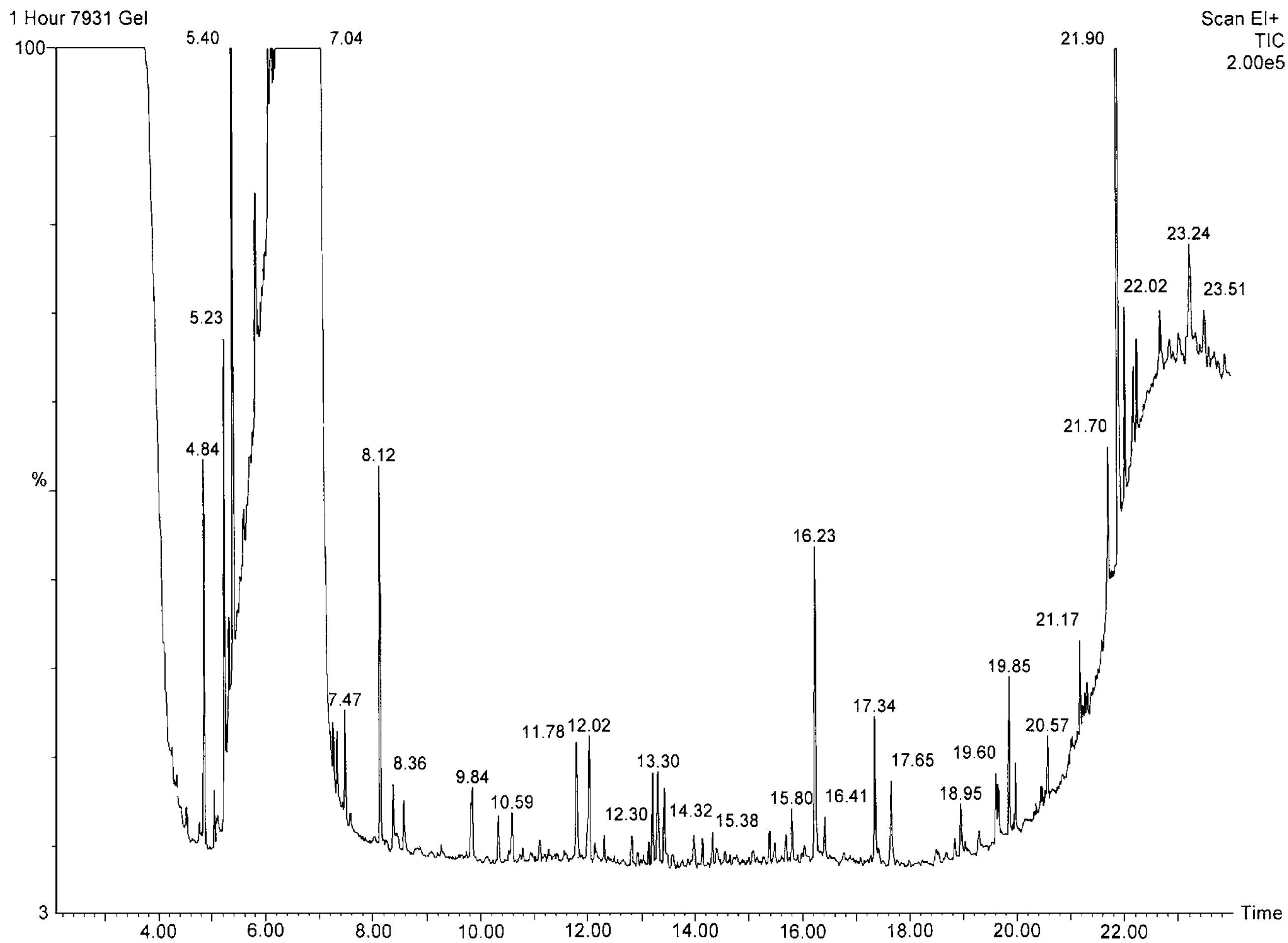

FIG. 4—*Typical gas chromatogram of 1-h old gel ink that contains glycerin. The very large, broad peak is glycerin, while the other smaller peaks are other volatile organic compounds.*

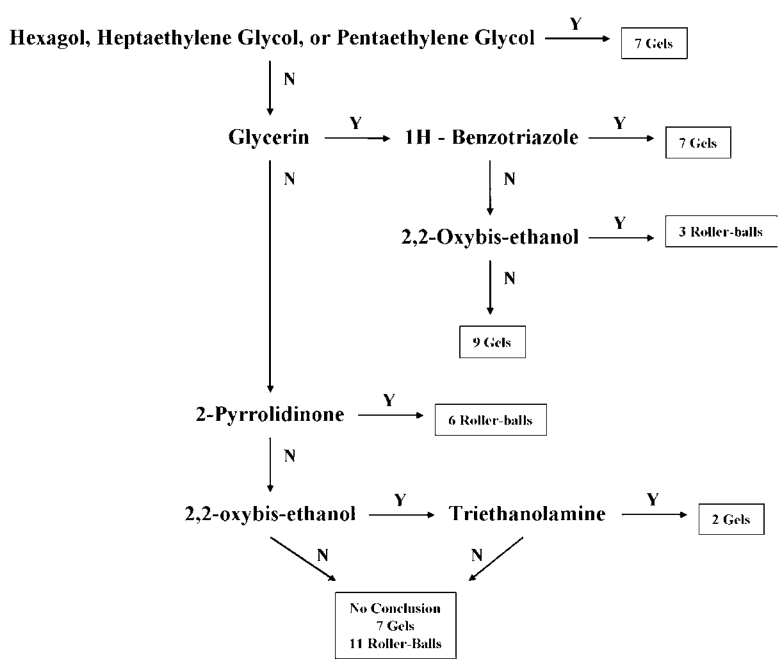

FIG. 5—*Flow chart for the characterization of an ink as a gel or a roller-ball using major compounds detected with the GC/MS. Thirty-two gel and 20 roller-ball inks were examined. The quantity of each type of ink is noted in the flow chart.*

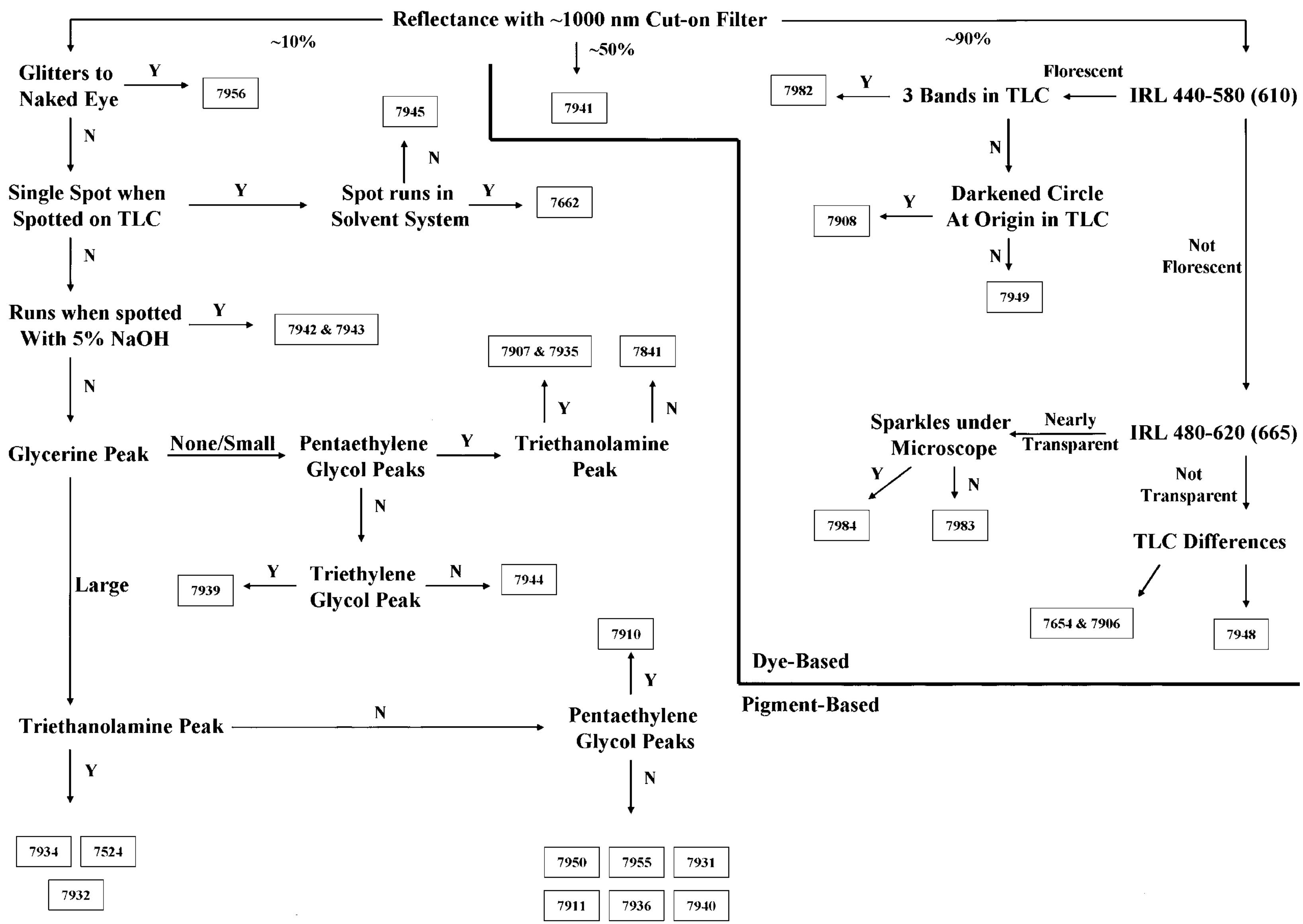

FIG. 6—*Flow chart for identification of gel inks. The flow chart is separated between dye and pigment-based inks. The nondestructive examinations are performed before the destructive.*

and run on the GC/MS to determine the volatile compounds in the inks. Several major peaks were detected in the roller-ball samples that were similar to those of the gel inks. It was found that the presence of the compounds of hexagol, heptaethylene glycol, and pentaethylene glycol most likely indicated a gel pen as these compounds were not found in the roller-ball samples. The combination of other major peaks helped to determine the likelihood of an ink being either a gel or a roller-ball. A flow chart with the conclusions is shown in Fig. 5. Future work will include the examination of the major and minor peaks and the time that the peaks remain in a sample.

Gel Ink Flow Chart

A flow chart was made to summarize the examinations incorporated in this study (Fig. 6). The chart is organized with the nondestructive techniques (e.g., microscopy, IRR, IRL) followed by the destructive examinations (e.g., TLC, spot tests, GC/MS). A division occurs in the chart that distinguishes the pigment from the dye-based gel inks. The samples are labeled with an inventory number corresponding to the International Ink Library maintained by the USSS. The 29 inks have been separated into 19 groups. The number of groups can increase on a sample that is fresh since they contain many additional components which can be identified with GC/MS, thus giving an increased discrimination.

Conclusions

Gel ink pens have become more prevalent in the market over the past several years. As these writing instruments are dispersed throughout the population, a questioned document examiner can expect an increase of cases that include gel ink. It is important for the examiner to be able to not only conclude that the ink is a gel ink, but also to identify the gel ink individually and determine the brand of writing instrument.

In this study, several black gel inks were collected and differentiated with optical, spectral, and chemical techniques. Since black inks are common and difficult to differentiate, black gels were the focus of this study. Similar work on colored inks should begin with a separation based on colors, followed by optical and TLC examinations. GC/MS could be incorporated if needed.

The 29 inks collected for this study were differentiated into 19 groups. Some of the inks that were narrowed down into groups of two were produced by the same manufacturer and may have been the same formulation. The inks were compared against common black roller-ball pens found on the open market. A flow chart was developed that can be used to determine if a questioned ink is a gel or a roller-ball. A second flow chart was prepared that separates open market gel inks using optical and chemical techniques.

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