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TECHNICAL NOTE

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A Study to Investigate the Evidential Value of Blue Gel Pen Inks

ABSTRACT: The aim of this project was to investigate the evidential value of blue gel pen inks in Europe. For this purpose, 33 blue gel pen inks, of different brands and models, representative of those available on the European market at the time of the study, were analyzed using three techniques: filtered light examination (FLE), Raman Spectroscopy (RS), and scanning electron microscopy (SEM). First, after visual examination (naked eye and stereo microscope), it was possible to classify the 33 inks into three groups described as: milky, metallic, and normal. This paper describes in detail the results obtained for the normal gel pen group. The ability of the techniques to discriminate gel inks between and within brands varied. The results indicated that RS and SEM were more discriminating than FLE. The greatest degree of differentiation was achieved when using a combination of RS and SEM techniques (discriminating power = 0.91). This study also highlights some problems concerning the identification of the brand of a gel pen from a written text.

KEYWORDS: forensic science, document examination, inks, gel pen, evidential value

The Japanese first marketed gel pens during the mid-1980s. Gel inks were discovered by the Sakura Color Products Corp. (Osaka, Japan) in 1984.

According to Sakura (1), "Years of research resulted in the 1982 introduction of Pigma®, the first water-based pigment ink. Sakura's revolutionary Pigma inks evolved to become the first Gel Ink Rollerball launched as the Gelly Roll pen in 1984."

These pens first appeared on the U.S. market about 1993 and in the European market at approximately the same time. The Pentel Hybrid, the Sakura Gelly Roll Pen, the Zebra Jelly, and the Uniball Signo by Mitsubishi were the first four brands available.

The incorporation of colored pigments, which give the ink a full range of colors, is what differentiates the blue gel ink from traditional types of blue water-based ink. Aqueous inks primarily use organic dyestuffs to give them color. In addition to 60 to 80% water, gel inks contain a special pigment (usually copper phthalocyanine for blue ink) as well as resins, solvents (such as ethylene glycol), and additives to give the gel ink its unique characteristics.

According to U.S. Patent No. 5,993,098 (2), an example of a black gel ink contains the compounds

Composition	Parts by Weight
Carbon black	8.0
Acrylic resin molecular weight 5000	1.5
Aminomethylpropanol	0.7
Alkylphosphates	1.0
Xantam gum	0.4
Glycerin	5.0
Propylene glycol	20.0
Dezionized water	63.4

Attributes of the gel pen, such as its environmental friendliness, broad range of colors, archival qualities, low cost, and long writing, are destined to make this type of pen a popular item on the market.

The forensic community has discussed the value of various techniques for testing writing inks, and standard protocols have been proposed for conducting forensic ink examinations. However, there is little or no information available regarding the application of a sequence of analysis to the gel pen inks. A few authors (3,4) have proposed that gel pen inks be analyzed by filtered light examination (FLE) and thin layer chromatography (TLC).

Raman spectroscopy (RS) for the gel ink examination was first proposed by White (5), and Andermann (6) achieved success with this technique recently. The morphological study of gel pen inks by SEM has not yet been investigated by the forensic community.

The aim of this research was to analyze several blue gel pen inks available on the European market using FLE, RS, and SEM in order to investigate their discriminating abilities when applied to different brands. At the same time, the possibility of creating a gel pen database was also considered.

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Materials and Methods

Sampling and General Observations

The study targeted the predominant blue gel pen inks market in Europe. Sample pens were collected from supermarkets, variety stores, news agents, stationers, and pen company warehouses in Switzerland and nearby countries such Germany, France, and Italy. The goal was to create a comprehensive and representative collection of pens available throughout Europe. The samples collected are listed in Table 1. Although all 33 blue gel inks were analyzed, only the results corresponding to 17 normal blue gel pens are presented because the latter are more likely to be used to sign documents than metallic, "milky" (cloudy appearance), or normal blue-light inks.

Inks lines, for each sample, were written on unlined sheets of A4 'Xerox Business TCF' office paper. Every sample was firstly examined by the naked eye and using a stereo microscope (Wild M3Z, Leica).

Filtered Light Examination (FLE)

Filtered light examination (FLE) was undertaken using the video spectral comparator Docucenter 3000 (Projectina, Herbrugg, Switzerland). The following optical properties of the inks were assessed:

- Infrared reflectance (IRR) was done by illuminating the inks with a tungsten light source and observing the region of interest using a 780 nm barrier filter. In order to obtain a maximum of objectivity, only two definitions of the IRR were selected: "absorbs" and "reflects."
- For the infrared luminescence (IRL), the following conditions were chosen:

Excitation Filter (bandwidth), nm	Emission Barrier Filters, nm
380–570 (Projectina "DOCU-Filter")	780
590–620	780

The camera integration was set up in an automated mode for optimized brightness and contrast control. The inks were initially viewed collectively and their infrared luminescence graded as either strong, weak, similar to the paper, or none at all. Following this and in order to obtain maximum of objectivity, only three definitions of the observed luminescence were selected: "yes" = luminescence, "no" = absorption (no luminescence), and "yes/no" = luminescence/absorption.

Raman Spectroscopy (RS)

Raman spectroscopy was carried out using a Renishaw Raman microscope "RM 1000" for confocal spectroscopy (Renishaw plc, Gloucestershire, UK), equipped with a 50 X Leica objective. All the measurements were achieved using an excitation wavelength of 514.5 nm from an argon ion laser (output 20 mW) and 830 nm from a diode laser (output 300 mW).

TABLE 1—*Gel pen inks collected and analyzed.*

Brand	Model	Ink Type	Color	Code
Edding	Crystaljelly 2185	Metallic	blue-violet	1
Beifa		Metallic	blue-violet	27
Edding	Crystaljelly 2185	Metallic	blue-violet	2
Beifa		Metallic	blue-violet	25
Edding	Crystaljelly tec 2185	Metallic	blue	4
Online	Gel Refill	Metallic	blue	8
Pentel	K108 Hybrid	Metallic	blue	12
Rotring	Star Gels	Metallic	blue	16
Beifa		Metallic	blue	26
Tratto	Genius Metal	Metallic	blue	20
Sanford	Star Gels Grip	Milky	blue-light	18
Pentel	K118 Hybrid	Milky	blue-light	23
Uniball Mitsubishi	Signo scent	Milky	blue-light	21
Uniball Mitsubishi	Signo scent	Milky	violet	28
Edding	Crystaljelly tec 2185	Normal	blue	3
Edding	Gel Stick 2170	Normal	blue	33
Flair	Gel Tech 250	Normal	blue	5
Schneider	Gel-Tops	Normal	blue	19
Uniball Mitsubishi	Signo broad	Normal	blue	22
Mondial LUS	Gelus	Normal	blue	31
Herlitz	Geltec	Normal	blue	6
Papermate	Gel roller	Normal	blue	9
Pentel	K106 Hybrid	Normal	blue	10
Pentel	K227C	Normal	blue	11
Sakura	Gelly Roll	Normal	blue	30
Pilot	G-2	Normal	blue	13
Pilot	G-1	Normal	blue	24
Reynolds	InkGEL	Normal	blue	15
Rotring	Star Gels	Normal	blue	17
Fila	Tratto Genius	Normal	blue	32
Stypen	Gel Grip	Normal	blue	29
Herlitz	Geltec	Normal	blue-light	7
Reynolds	InkGEL	Normal	blue-light	14

Scanning Electron Microscopy (SEM)

The morphological and structural study of the blue ink strokes was performed with a JEOL JSM 6300 Field Emission Scanning Electron Microscope. A magnification range between 1000X and 10 000X was used to explore the structural morphology of the inks. All the samples were coated with a thin gold film (5 nm), an acceleration voltage of 5 kV, and a working distance of 15 mm.

Discriminating Power (DP)

The discriminating powers (DP) of the different ink brands and different samples of the same brand were calculated according to the method of Smalldon and Moffat (7), where:

$$DP = \frac{\text{Number of discriminated pairs}}{\text{Number of possible pairs}}$$

Results and Discussion

The 33 samples could be separated into three groups by inspecting them with both the unaided eye and the stereomicroscope. These groups are described as: milky, metallic, and normal (see Table 1). It is interesting to note that a continuous line could be seen on both edges of all the milky and the metallic ink strokes. This phenomenon is also very useful for determining the writing sequence of intersecting pen strokes (Fig. 1).

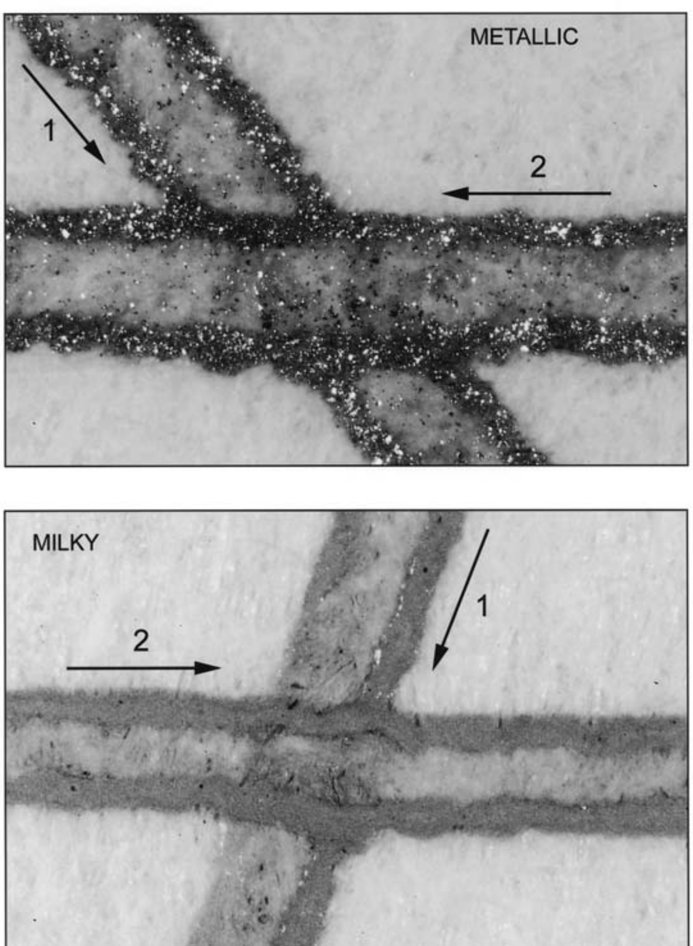

FIG. 1—*The continuous line on both edges of the gel pen ink indicates the sequence of the crossing (arrow 1: first line, arrow 2: second line).*

FLE is frequently used in forensic ink analysis because of its nondestructive nature. The results of the infrared luminescence (IRL) and infrared reflectance (IRR) examinations were considered in combination. However, these results should be considered cautiously because the optical properties of inks can change with time or under certain environmental conditions. The quantity of ink or the nature of the support medium can also influence the optical characteristics of inks. In order to reduce the influence of some of these factors, the observed reflections were classified as "absorbs" and "reflects" (independently of their intensity) and the observed luminescence was classified as "yes" = luminescence, "no" = absorption (no luminescence), and "yes/no" = luminescence/absorption.

In order to classify an ink correctly, the results should be compared with a suitable standard, including, respectively, the two IRR definitions and the three IRL definitions. A major limitation of this technique is that the FLE is "substrate dependent." In other words, the same ink may provide a different result when written on different surfaces. To determine the extent of this influence, the inks were examined on ten different white plain papers, randomly selected from the mail we receive daily. The results were consistent; i.e., an ink classified as "yes" displays the same definition of luminescence regardless of which paper it is written on. The discriminating power (DP) of the FLE was calculated to be 0.72.

It must be emphasized that ink numbers 13 and 24 (Pilot), 15 (Reynolds), 17 (Rotring), 29 (Stypen), and 32 (Fila) are soluble in methanol and contain dyes rather then pigments. This was confirmed by thin layer chromatography (TLC). Some companies introduced gel pens because their competitors offered gel pen products. Most gel pen inks are patented in Japan and the technical knowledge to develop new formulations is scarce. The license fees for using Japanese patents are high and in most cases too prohibitive for secondary manufacturers. We understand that these are some of the reasons why it is possible to find soluble dyes in gel pens. Some companies don't know how or are not allowed to put pigments in gel pens. Another reason for using soluble dyes is that they facilitate tuning the hue of inks. Special hues and bright colors can be produced by varying the quantity of dye in a formulation. For dye-based gel inks, the RS method was found to be inefficient.

However, Raman spectroscopy, which is virtually a nondestructive technique, could be performed well for the eleven pigmented normal blue gel inks and gave information that supplemented the results of the FLE observations. Examination of the eleven pigmented normal blue gel pens with the 514.5-nm laser separated them into three classes (Fig. 2). By using the 830-nm laser, the inks could be divided into four classes and by using both lasers, the eleven tested inks could be separated into five classes. The DP for the RS technique was calculated as 0.76.

The testing of the gel inks with the SEM showed that they could be discriminated further according to the morphology of the ink strokes. The main structures of the normal blue-pigmented gel pen ink lines are shown in Fig 3. Based on these structures and differences within each main group, it was possible to discriminate almost all of the pigmented blue gel pen inks (cf. Fig. 6).

It is interesting to note that even inks of the same brand could be discriminated. For example, Pentel inks 10 and 11 have a different structure, and the size of their micro spheres is also different (Fig. 4).

Concerning the dye-based gel pen ink, only ink 15 could be distinguished from the other five inks (13, 17, 24, 29, 32). The morphological structure of this ink was found to be distinct and quite uncommon (Fig. 5).

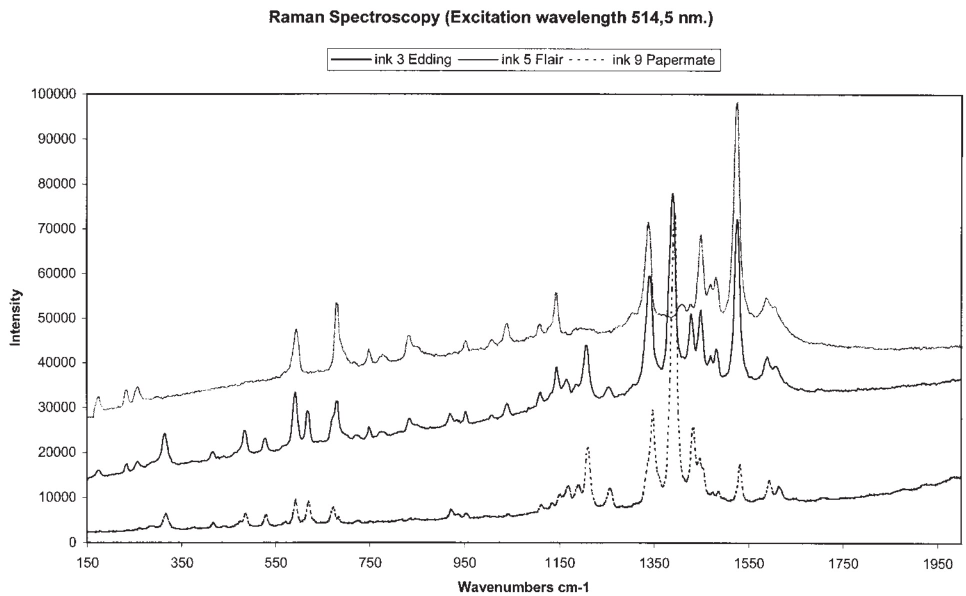

FIG. 2—*Raman spectra groups obtained with an excitation laser at 514.5 nm.*

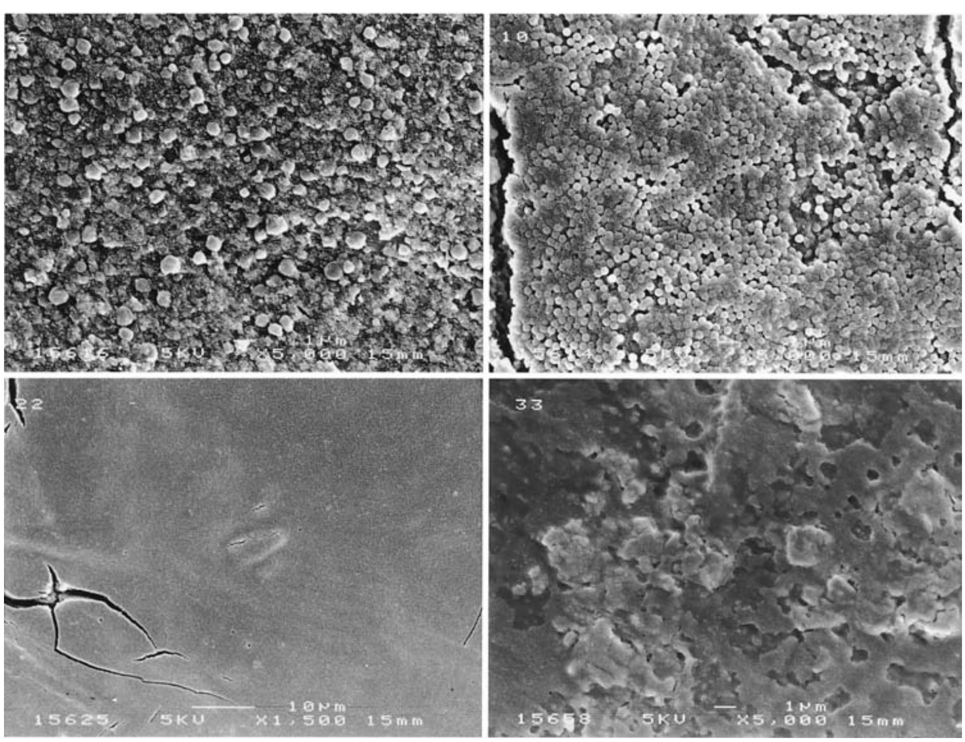

FIG. 3—*SEM microphotograph, the four main morphological structures of the normal blue pigmented gel pen inks. (ink 6: Herlitz, ink 10: Pentel, ink 22: Uniball Mitsubishi and ink 33: Edding).*

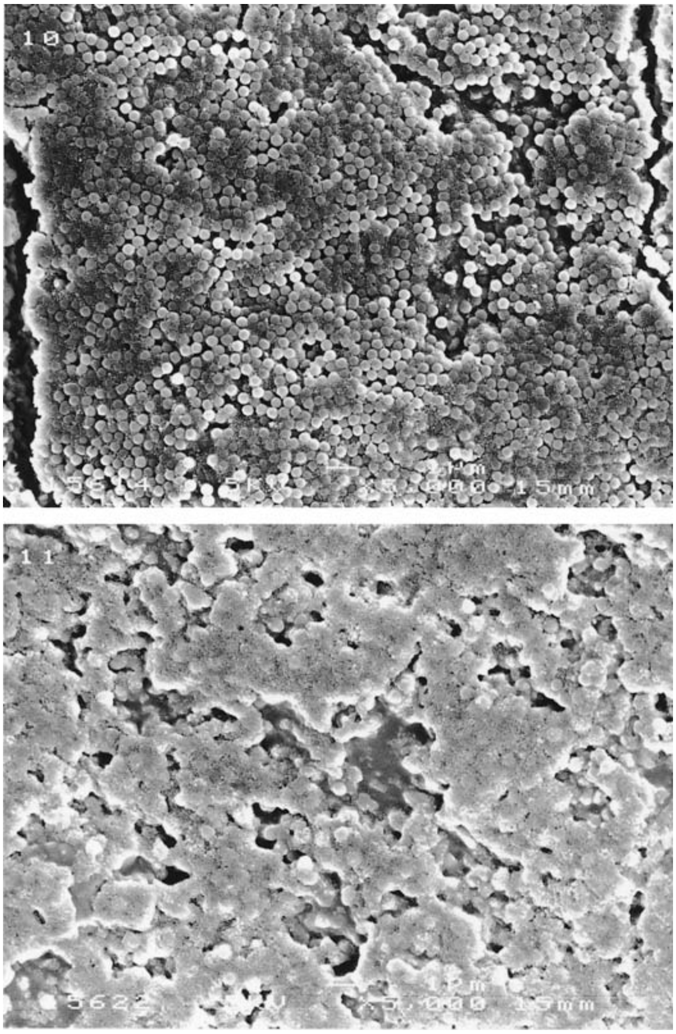

FIG. 4—*SEM microphotograph, two inks of the same Pentel brand (inks 10 and 11) showing a different structure.*

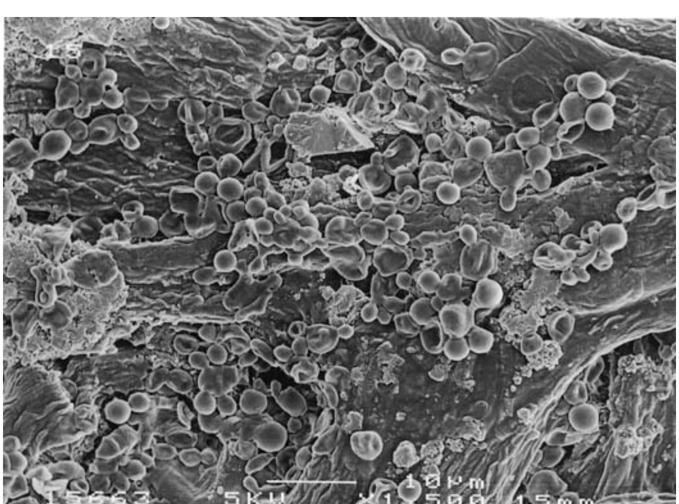

FIG. 5—*SEM microphotograph, the particular and uncommon structure of a dyed gel pen ink (ink 15: Reynolds).*

The results indicate that, contrary to the aspect of ink deposits of other writing instruments such as ballpoint pens, rollerball pens, and fiber tip pens (8), gel pen inks show a more complex and individual morphology.

The results show that the SEM method provides the highest discriminating score ($DP = 0.88$) compared with the other methods (FLE and RS). The discriminating power for each technique appears below.

Technique	DP for Normal Blue
FLE	0.72
RS	0.76
SEM	0.88
Combined sequence	0.91

A database was created containing all the pertinent information associated with gel pens, i.e., the FLE results, RS spectra, and the SEM microphotographs. Two blind tests were conducted in order to verify the utility of the database. A first test consisted of testing four gel pen inks taken from our collection. The brand and model of each ink were identified correctly. In the second test, four new gel pens were purchased and tested using the method described. In this instance, a 100% success rate was also achieved. The ability to correctly identify a particular brand of gel pen can be useful for dating purposes.

As with many forensic examinations, the ability to reach meaningful conclusions very much depends on the size, content, and completeness of a database. In order to state that an unknown or questioned writing was produced by a pen from a certain company or group of companies during a certain period of time, excluding all others, an analyst must have knowledge of all possible manufacturers and distributors, their ink formulations, and their years of production. Realistically, databases will seldom represent all possible products, and gaps will inevitably exist in the available information. This leads to an inherent uncertainty that must be considered when drawing conclusions.

In practical work, a normal blue gel pen can be confused with a liquid ink pen such a roller pen or a porous tip pen. In order to assess the extent of this problem, we purchased all the different blue roller pens available on the Swiss market (eleven inks) as well as two pigmented blue porous tip pens.

All the blue roller inks were soluble in methanol and can be distinguished from normal blue-pigmented gel pens. However, it was difficult to distinguish them from the dyed-based blue gel pens. Therefore, the two pigmented porous tip pens can be assimilated to the gel pens and were also integrated into the database. Further studies are presently underway in our laboratory to determine if it will be possible to distinguish pen strokes produced by pigmented porous tip pens from those written by normal blue gel pens.

The global results of this research and the grouping for the blue normal gel pens are presented in Table 2.

Figure 6 illustrates the schematic and sequential procedure to discriminate the normal blue gel pen.

Conclusions

Thirty-three blue gel pen inks of different brands and models available on the European market were analyzed using a new forensic protocol, including filtered light examinations, Raman spectroscopy, and scanning electron microscopy. The combined discriminating power calculated for this protocol when applied to a population of normal blue gel pen inks was 0.91. Scanning electron microscopy showed the highest discriminating power (0.88) of all

TABLE 2—*The global results of the normal blue gel pen inks analysis.*

Brand	Code	Extraction In MeOH	Docucenter 3000 (IR/barrier 780) IRR	Docucenter 3000 (Ex.docu /Em. 780) IRL 1	Docucenter 3000 (Ex.590–620/Em. 780) IRL 2	Groups Docucenter 3000 IRR + IRL 1 & 2	Groups Raman (514 nm)	Groups Raman (830 nm)	Groups Raman (514 + 830 nm)	Groups SEM	Groups All Techniques
Edding	3	Pigment	absorbs	Yes/No	No	1	1	1	1	1	3
Edding	33	Pigment	absorbs	Yes/No	No	1	1	1	1	2	33
Flair	5	Pigment	absorbs	No	No	2	2	1	2	3	5,22,31
Schneider	19	Pigment	absorbs	No	No	2	2	1	2	1	19
Uniball Mitsubishi	22	Pigment	absorbs	No	No	2	2	1	2	3	
Mondial LUS	31	Pigment	absorbs	No	No	2	2	1	2	3	6
Herlitz	6	Pigment	reflects	Yes	Yes	3	3	2	3	4	9
Papermate	9	Pigment	reflects	Yes	Yes	3	3	2	3	5	10
Pentel	10	Pigment	reflects	Yes	Yes/No	4	3	3	4	6	11
Pentel	11	Pigment	reflects	Yes	Yes/No	4	3	3	4	7	30
Sakura	30	Pigment	reflects	Yes	Yes/No	4	3	4	5	8	
							TLC				
Pilot	13	Dyes	reflects	Yes	Yes	1	1			1	13,17,24,32
Pilot	24	Dyes	reflects	Yes	Yes	1	1			2	15
Reynolds	15	Dyes	reflects	Yes	Yes	1	1			1	
Rotring	17	Dyes	reflects	Yes	Yes	1	1			1	29
Fila	32	Dyes	reflects	Yes	Yes	1	1			1	
Stypen	29	Dyes	reflects	Yes*	Yes*	2	2			1	

* Very strong.

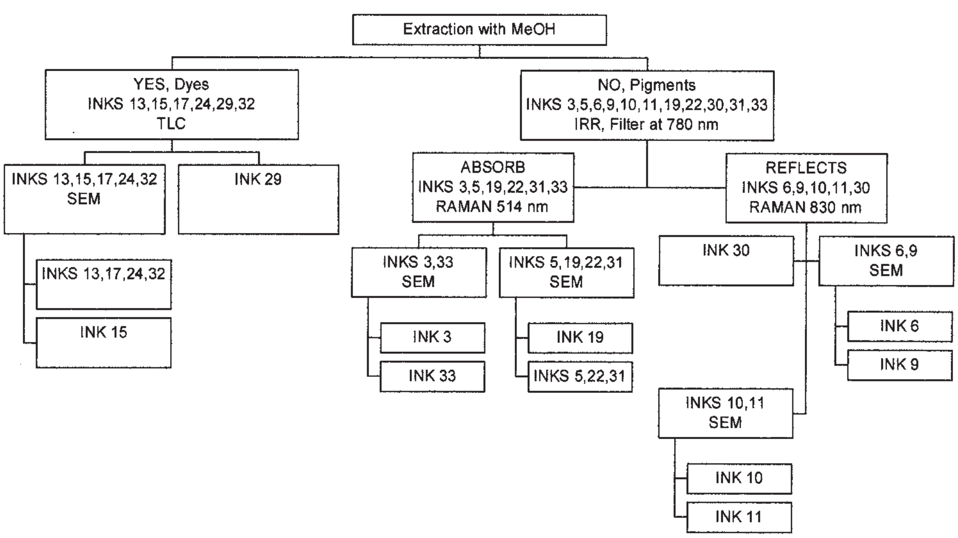

FIG. 6—*Schematic and sequential procedure to discriminate the normal blue gel pens.*

three techniques. Raman spectroscopy combined with scanning electron microscopy is a very useful approach for pigmented blue gel inks and leads to highly reliable gel pen ink classification.

Acknowledgments

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