Winter 1962

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Recommended Citation

Herbert L. MacDonell, Characterization of Fountain Pen Inks By Porous Glass Chromatography and Electrophoresis, 53 J. Crim. L. Criminology & Police Sci. 507 (1962)

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CHARACTERIZATION OF FOUNTAIN PEN INKS BY POROUS GLASS CHROMATOGRAPHY AND ELECTROPHORESIS

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Identification of fountain pen inks and writing fluids has long been a subject of considerable interest to the examiner of questioned documents (1-5). In order to accurately identify the various ink formulations that are commercially available, many techniques using a variety of analytical procedures have been developed (6-13). Of these, perhaps the most accepted method in current usage is that of paper chromatography (2) (12) (14-20). This separation method allows the various ink components, many of which are colored dye substances, to be separated into integral bands or zones that distribute themselves in a manner characteristic of the original combined formulation (21).

PAPER CHROMATOGRAPHY

The mechanism of paper chromatographic separations is simple from both theoretical and practical considerations. In practice, a sample spot of ink is placed near the end of a paper strip. This same end is then immersed into an appropriate solvent until the surface of the liquid is just below the sample spot. The solvent is then allowed to permeate the paper, rising by capillary action to some predetermined point above the original sample spot causing chromatographic development. During this process the components of the original sample mixture are influenced and separated by two opposing forces. One tendency is for the individual components to be washed up the strip depending upon their relative solubilities in the chosen solvent; the other is for them to deposit themselves on the cellulose support medium depending upon their individual attraction for this material and the tenaciousness with which they are bonded to it. The total effect is known as either an adsorption or distribution phenomenon and may be measured as numerical coefficients which are dependent upon the chosen combination

of solvent and support medium. If the support medium itself is active, as is the case with paper, it exhibits adsorptive properties. If, however, the support medium has been coated with some other more active substance, as is often the case with column chromatography, then the distribution of the sample between the solvent and this substance is described by a distribution coefficient.

The location, color, and intensity of the separated fractions is often of such significance that it is possible to identify an unknown ink from its paper chromatogram alone. This technique may be extended in many ways to produce variations in both the color and distribution of bands. Changing such parameters as the acidity of the solution used for development or the substitution of organic solvent systems for aqueous developers are variations often employed in paper chromatography to acquire additional data. Data obtained from such variations are often desirable, if not essential, for the correct identification of some inks. In instances when the chromatograms of two inks appear very similar, additional characteristics must be obtained to establish subtle differences.

The spectrophotometer has often been utilized to assist the technician in transforming his visual impressions into numerical values for both developed chromatograms and for single color marks on paper. Though well suited for many applications, the investigator often experiences difficulties with this instrument when attempting to obtain spectral transmission data from opaque paper chromatograms. As a result, reflectance measurements are usually taken with some compromise in accuracy (13). Transmission data has been obtained, however, by rendering the paper chromatogram either transparent or translucent using clearing oils and placing the cleared strips between glass plates for scanning (22). It must be remembered that such measurements are often subject

to error if care is not taken to equalize background due to the clearing oils themselves. An alternate technique to obtain spectral data with low background has been to physically cut the developed paper chromatogram into separate pieces and then elute samples from each cutting directly into spectrophotometer cells. Transmission measurements are then made on the resulting solutions. At best, this is a dilution method. Spectral data obtained from any of these methods will have very limited value unless performed by someone having considerable experience in the method or methods selected.

PAPER ELECTROPHORESIS

Despite the superficial resemblance of paper strip electrophoresis to paper chromatography, there are distinct differences between the two separation methods. Chromatographic separations of substances in solution depend upon their distribution between a mobile and a less-mobile or non-mobile phase. In contrast, electrophoretic separations depend upon the migration of ions or charged particles at different rates through an electrical field. In paper strip electrophoresis the paper strip serves as a carrier of the solvent or dispersion medium and is not itself significantly active in effecting separation of the sample mixture. The solvent is a buffered electrolyte of low ion strength which permits the application of a relatively high potential resulting in low current flow.

The application of paper strip electrophoresis for the characterization of inks has resulted in additional data that has proven helpful for the identification of unknown samples (9) (11). Equipment required for these separations is considerably more complex and expensive than that required for paper chromatography. It is not always necessary to purchase an expensive power supply for ink separations, however. Crown has demonstrated that a simple modification of radio receivers will provide adequate power for electrophoretic requirements (23). Nevertheless, as the results obtainable from the two methods are comparable, it is understandable that paper chromatography has found greater favor with the majority of investigators. Electrophoresis separations conducted in paper present the same problem as those obtained chromatographically; the background medium is opaque and difficulties arise when accurate spectral measurements are attempted.

POROUS GLASS

In an effort to overcome many of the inherent difficulties associated with paper as a chromatographic or electrophoretic medium, it was conceived that porous glass might offer properties which would permit such separations under a wider range of conditions. In addition, the final separations would be in a medium which was itself optically transparent. This unique glass was obtained and found to be quite acceptable for these applications (24)(25)(26). Inasmuch as porous glass is a medium unknown to many readers perhaps a brief description of its properties should be included at this time.

Porous glass is not a new product. It was discovered thirty years ago by Dr. Martin E. Nordberg and Mr. Harrison P. Hood, both of the Corning Glass Works, and is correctly known as Glass Number 7930 (27). This interesting material is not an end product but is an intermediate to the production of a 96% silica glass, Glass Number 7900. Porous glass is obtained by acid leaching a separated phase of sodium, boron, and aluminum from a low melting alkali-borosilicate glass of low chemical durability. The intermediate porous form is then consolidated at high temperatures into a non-porous or normal glass with excellent chemical durability and thermal stability. This process permits the fabrication of Vycor Brand laboratory glassware of desirable shapes at relatively low temperatures rather than at the high temperatures required to fuse and work pure silica.

Removal of sodium and boron by acid leaching results in a porous silica network with channeled openings of exceptionally small diameter. The actual size of these pores is between 20 and 100 Angstrom units or 2 to 10 millimicrons. The average pore diameter is about 40 Angstrom units, resulting in a surface area of between 150 and 200 square meters per gram of porous glass. This exceptionally high surface area is responsible for the absorption of moisture and smoke from the air into porous glass. A void space of approximately 28 percent characterizes the glass as "thirsty" as it feels very dry to the touch and may be used as a solid desiccant having about the same efficiency as silica gel.

Porous glass which has been polished prior to leaching has every appearance of common glass. Considering the fact that the pores would have to be enlarged some 12,000 times to admit a human hair, it is not difficult to understand why they are

invisible and do not distract from the transparency of the glass. For this reason, spectral transmission measurements may be made directly on separations which have been effected in this medium. Porous glass is transparent to the ultraviolet and limited measurements may be made in the infrared as described by Little and others in recent investigations (28)(29).

POROUS GLASS CHROMATOGRAPHY— EXPERIMENTAL

Samples of five microliters each were applied directly to the surface of porous glass using a microliter syringe. The tip of the needle had been filed flat to prevent scratching the glass. Samples are placed on porous glass in the manner described earlier for paper chromatography. Individual separations were conducted on polished porous glass the size of a microscope slide, $1 \times 3 \times \frac{1}{16}$ inches. Multiple separations required a larger plate. For convenience in direct projection of the completed separations the standard lantern slide size, $3\frac{1}{4} \times 4 \times \frac{1}{16}$ inches, was adopted. In contrast to paper, porous glass is a rigid, self-supporting material. For this reason it need not be suspended but may be placed to stand upright in any convenient vessel. A 250 ml. electrolytic (tall form) beaker was found to be convenient when using the 1×3 inch slide. Larger beakers of standard shape were required for $3\frac{1}{4} \times 4$ inch plates with the exact volume of the beaker dependent upon the desired direction of development. The solvent chosen for development may be added either before or after the glass is inserted into the beaker, however, in either case the proper solvent level must be maintained slightly below the sample spot or spots. Within a few minutes a wave or solvent front may be seen rising into the porous glass and may be observed at any later time during development of the chromatogram. This migration of solvent upward into the slide is very evident due to the higher transparency of the saturated lower portion.

Chromatographic development is complete and should be terminated after the solvent has raised to the top of the glass slide. At this point, the saturated porous glass is simply withdrawn from the development vessel and carefully wiped with a clean, soft towel to remove excess solvent from its lower edge. Only that area which was actually immersed in liquid need be dried in this manner. In air, porous glass will usually dry in about four hours, however, this time may be reduced by

Figure 1
Chromatographic Separations of Five Black Inks
in Porous Glass

Developer, water; time, 12 hours. 1. Parker 5035; 2. Sheaffer 64; 3. Sanford 235; 4. Waterman (new); 5. Carter 986.

placing the slide in a warm ($40-50^{\circ}\text{C}$) drying oven. Higher temperatures will cause severe fracturing of saturated porous glass and must be avoided. A convenient drying procedure is to place the glass between a folded paper towel on top of a 110°C drying oven. One hour will usually be sufficient to effect complete drying under these conditions. Porous glass is very transparent when completely saturated but during an intermediate drying period it becomes white or opal. This condition disappears upon further drying.

POROUS GLASS CHROMATOGRAPHY—RESULTS

The time required for development of a porous glass chromatogram is considerably longer than that required for a corresponding separation in paper. Normally, from twelve to thirty hours are required for good chromatographic separation in porous glass. During this time a flow of about two to two and one-half inches is considered to be a maximum. A typical porous glass chromatogram of five black ink separations is shown in figure 1. Unfortunately, a black-and-white reproduction of this figure does not do justice to the colorful results which were actually obtained. Sample Number 5, for example, Carter's Number 986 black ink, resulted in a blue spot where the sample was placed before separation, a deep green over this, followed by orange and finally a rose or violet on top.

For purposes of recording the results of each chromatographic separation, an arbitrary system of zones was adopted as shown in figure 1. Colors present in these zones were simply recorded in tabular form to provide data characteristic of each ink sample. The first zone, called the spot, is that area covered by the original sample before

TABLE 1
DEVELOPMENT WITH WATER: BLACK INKS

Sample Identification	Spot Color	Zone 1	Zone 2	Zone 3	Zone 4
Parker Black # 5035.....		Deep Violet	Violet	Violet, Yellow	Violet
Sheaffer Black # 34.....	Black	Faint Violet	Faint Violet	Faint Violet	Faint Violet
Sheaffer Black # 64.....	Light Blue	Light Blue	Light Blue	Red, Yellow	
Carter Black # 99.....	Violet	Violet	Violet	Yellow	Violet
Carter Black # 986.....	Blue	Blue-Green	Orange	Rose	
Sanford Black # 235.....	Green-Violet	Blue-Green	Blue-Green	Violet	Orange
Sanford Black # 236.....	Black	Faint Violet	Faint Violet		
Waterman Black, New.....	Blue	Blue	Violet	Violet, Yellow	Blue
Waterman Black, Old.....	Purple	Purple	Yellow, Violet	Blue	Blue
Higgins Black # 812.....	Purple	Faint Purple	Faint Purple	Faint Purple	Faint Purple

TABLE 2
DEVELOPMENT WITH WATER: BLUE INKS

Sample Identification	Spot Color	Zone 1	Zone 2	Zone 3	Zone 4
Parker Turquoise # 5034.....	Blue	Blue	Blue	Violet	Blue
Parker Royal Blue # 5038.....	Violet	Violet	Violet	Violet	Violet
Parker Blue # 5039.....	Violet	Violet	Violet	Violet	Violet
Sheaffer Blue # 42.....	Blue	Blue	Blue	Blue	Blue
Sheaffer Blue # 44.....	Violet	Violet	Violet	Violet	Violet
Sheaffer Royal Blue # 54.....	Violet	Violet	Violet	Violet	Violet
Sheaffer Purple # 84.....	Deep Violet	Deep Violet			
Sheaffer Peacock Blue # 114.....	½ Blue-Green	Blue-Green	Blue-Green		
Carter Indigo Blue.....	Black	Blue	Faint Violet		
Carter Jewel Tone Purple # 46.....	Deep Violet				
Carter Contrast Purple # 49.....	Deep Violet				
Carter Blue # 79.....	Violet	Violet	Violet	Violet	Violet
Carter Contrast Turquoise # 119.....	Blue-Green	Blue-Green	Blue-Green		
Sanford Violet # 206.....	Deep Violet				
Sanford Royal Blue # 256.....	Blue	Blue	Blue	Blue	Blue
Sanford Peacock Blue # 266.....	½ Blue-Green	Blue-Green	Blue-Green		
Waterman Blue # 632.....	Blue	Blue	Blue	Blue	Blue

TABLE 3
DEVELOPMENT WITH WATER: BLUE-BLACK INKS

Sample Identification	Spot Color	Zone 1	Zone 2	Zone 3	Zone 4
Parker Blue-Black # 5033.....	Violet	Violet	Violet	Violet	Violet
Carter Blue-Black.....	Blue	Blue	Blue	Blue	Blue
Carter Blue-Black # 816.....	Blue	Blue	Blue	Blue	Blue
Carter Blue-Black # 919.....	Blue	Blue	Blue	Blue	Blue
Sanford Blue-Black # 276.....	Blue	Blue	Blue	Blue	Blue
Sheaffer Blue-Black # 22.....	Blue	Blue-Green	Blue-Violet	Violet	½ Violet
Waterman Blue-Black.....	Blue	Blue	Blue	Blue	Blue
Higgins Blue-Black # 822.....	Blue	Blue	Blue	Blue	Blue

TABLE 4
DEVELOPMENT WITH WATER: RED INKS

Sample Identification	Spot Color	Zone 1	Zone 2	Zone 3	Zone 4
Parker Red #5037.....	Faint Red	Red	Red Band	Red	Red
Sheaffer Red #04.....	Deep Red		Red		
Carter Red #39.....	Red		Red	Red Band	Red
Carter Carmine Red #382.....	Orange				
Sanford Cardinal Red #246.....	Orange				
Sanford Dubonnet #286.....	Purple		Red	Red	

TABLE 5
DEVELOPMENT WITH WATER: BROWN INKS

Sample Identification	Spot Color	Zone 1	Zone 2	Zone 3	Zone 4
Sheaffer Brown #14.....		Blue	Violet-Brown	Yellow	
Carter Sunset Brown #526..	Dark Brown	Dark Brown	Red-Brown	Red-Brown	
Sanford Brown #296.....	Purple	Purple	Rose-Brown	Yellow	

TABLE 6
DEVELOPMENT WITH WATER: GREEN INKS

Sample Identification	Spot Color	Zone 1	Zone 2	Zone 3	Zone 4
Parker Emerald Green #5043..	Blue-Green	Blue-Green	Blue-Green	Yellow	Blue-Green
Sheaffer Emerald Green #74...	½ Blue-Green	Blue-Green	Blue-Green	Yellow	
Carter Green #56.....	Green	Green			
Carter Contrast Green #59....	Green	Green			
Carter Jewel Tone Green #56..	Green	Green			
Carter Green #959.....	Green	Green			
Sanford Green #216.....		Blue-Green	Blue-Green		

separation. The remaining distance from this spot to the extent of the solvent front during development was divided into four equal sections designated as zone 1, zone 2, zone 3, and zone 4, respectively. In many cases no component will migrate into zone 4 (such as ink #2 in figure 1). Nevertheless, during development the wave front of complete solvent saturation is clearly visible and the extent of its migration well defined. For this reason it is possible to determine the proper "zone classification" of a particular component even though only one ink is being separated. When no component has migrated into the fourth zone (immediately following the wave front), the extent of solvent migration must be marked before drying the slide. Without such a mark there would be no way of knowing proportional distances and the correct assignment of "zone classification" would be impossible. Data obtained on fifty-one

commercially available fountain pen inks following their chromatographic separation in porous glass is contained in tables 1 to 6.

It is important to realize that these tables are at best a guide rather than a firm rule for the identification and location of various bands. No two individuals would agree completely on the exact color or position of these bands, therefore, a liberal interpretation of position of these characteristics is essential.

Additional data was obtained through the use of solvent systems other than water. The color of certain ink dyes is known to be pH sensitive and for this reason both dilute acids and dilute bases were evaluated as porous glass chromatographic developers (30). Generally speaking, however, there was very little difference between development with dilute acid and water. For this reason dilute acid chromatographic results will be omitted

Figure 2

Spectral Transmittance Curves of Porous Glass Chromatograms of Sheaffer No. 14 Brown Ink
Developing solution (1) distilled water, and (2) 1:20 HCl. (Percentage transmittance vs. wavelength in millimicrons). (Reprinted from *Analytical Chemistry*, Vol. 33, p. 1553, 1961 with permission of the American Chemical Society.)

from this report. Organic solvents may be used for chromatographic development in porous glass, however, considerably more time is required to achieve worthwhile separations. Although these non-aqueous systems yield a wide variety of colors establishing further characteristics, they also permit excessive lateral diffusion during the 200 to 300 hours development time (25).

Characteristic color results using dilute ammonium hydroxide (1 part 28% ammonia to 19 parts water) as a developer are given in tables 7 to 12. The same arbitrary manner of description is used in these tables as used before in tables 1 to 6.

The optical transparency of porous glass permits direct spectral measurements to be made on separated chromatograms. Marked differences which are produced by changing the pH of the development solution may be seen graphically in figure 2. This figure shows the direct spectral transmission obtained on both a neutral and an acidic separation of the same ink. A rather generous sample of ink (10 ml) was applied to these porous glass slides to more completely cover the spectrophotometer slit. Usually, a spot was used for visual observations rather than the wide strip shown in this figure.

TABLE 7
DEVELOPMENT WITH 1:20 NH_4OH : BLACK INKS

Sample Identification	Spot Color	Zone 1	Zone 2	Zone 3	Zone 4
Parker Black #5035.....	Violet	Violet	Red-Brown	Violet	Violet
Sheaffer Black #34.....	Black	Purple	Purple	Purple	Purple
Sheaffer Black #64.....		Blue-Green	Black	Black	Blue-Green
Carter Black #99.....	Deep Violet	Violet	Brown	Brown	Violet
Carter Black #986.....	Purple	Blue	Blue	Blue	Rose-Brown
Sanford Black #235.....	Brown	Blue-Green	Dark Yellow	Dark Yellow	Blue-Green
Sanford Black #236.....	Purple	Purple	Purple	Purple	Purple
Waterman Black, New.....	Light Brown	Light Brown	Yellow to Orange	Orange	Light Blue
Waterman Black, Old.....	Brown	Light Brown	Light Brown	Light Brown	Light Brown
Higgins Black #812.....	Purple-Black	Purple			

TABLE 8
DEVELOPMENT WITH 1:20 NH_4OH : BLUE INKS

Sample Identification	Spot Color	Zone 1	Zone 2	Zone 3	Zone 4
Parker Turquoise #5034....	Blue	Blue	Blue	Blue	Blue
Parker Royal Blue #5038...					
Parker Blue #5039.....	Blue	Blue	Blue	Blue	Blue
Sheaffer Blue #42.....					
Sheaffer Blue #44.....					
Sheaffer Royal Blue #54....	Brown				
Sheaffer Purple #84.....	Purple	Purple	Purple	Purple	Purple
Sheaffer Peacock Blue #114..	Blue-Green	Blue-Green	Blue-Green	Blue-Green	Blue-Green
Carter Indigo Blue.....	Blue	Blue	Blue	Blue	Blue
Carter Jewel Tone Purple #46.....	Faint Purple Ring	Blue			
Carter Contrast Purple #49..	Faint Purple Ring	Blue			
Carter Blue #79.....	Brown	Brown	Brown	Brown	Brown
Carter Contrast Turquoise #119.....	Blue		Blue-Green	Blue-Green	Blue-Green
Sanford Violet #206.....	Purple Ring				
Sanford Royal Blue #256....	Brown Ring				
Sanford Peacock Blue #266..	Blue-Green	Blue-Green	Blue-Green	Blue-Green	Blue-Green
Waterman Blue #632.....					

TABLE 9
DEVELOPMENT WITH 1:20 NH_4OH : BLUE-BLACK INKS

Sample Identification	Spot Color	Zone 1	Zone 2	Zone 3	Zone 4
Parker Blue-Black #5033....	Blue	Blue	Blue	Blue	Blue
Carter Blue-Black.....	Brown-Black	Faint Violet	Faint Violet	Faint Violet	Faint Violet
Carter Blue-Black #816....	Brown	Faint Brown	Faint Brown	Faint Brown	Faint Brown
Carter Blue-Black #919.....	Brown-Black	Blue	Blue	Blue	Blue
Sanford Blue-Black #276....	Brown-Black Rings	Blue	Blue	Blue	Blue
Sheaffer Blue-Black #22....	Brown	Blue	Blue to Rose	Rose to Blue	Blue
Waterman Blue-Black.....	Light Brown	Light Brown	Yellow	Yellow	Light Blue
Higgins Blue-Black #822....	Brown Ring & Brown Spot				

TABLE 10
DEVELOPMENT WITH 1:20 NH_4OH : RED INKS

Sample Identification	Spot Color	Zone 1	Zone 2	Zone 3	Zone 4
Parker Red #5037.....	Orange	Light Red	Red	Red	
Sheaffer Red #04.....	Deep Red	Red	Red-Orange		Deep Red
Carter Red #39.....	Red-Orange	Red	Red	Red	Red Band
Carter Carmine Red #382.....	Rose	Light Rose	Red	Red	Red
Sanford Cardinal Red #246.....	Red	Light Red	Red	Red	Red
Sanford Dubonnet #286.....	Purple			Red	Red

TABLE 11
DEVELOPMENT WITH 1:20 NH_4OH : BROWN INKS

Sample Identification	Spot Color	Zone 1	Zone 2	Zone 3	Zone 4
Sheaffer Brown #14.....		Blue	Yellow to Brown	Brown to Yellow	
Carter Sunset Brown #526..	Dark Brown	Brown	Brown	Brown	Light Brown
Sanford Brown #296.....	Dark Purple	Purple	Yellow	Yellow-Brown	Yellow

TABLE 12
DEVELOPMENT WITH 1:20 NH_4OH : GREEN INKS

Sample Identification	Spot Color	Zone 1	Zone 2	Zone 3	Zone 4
Parker Emerald Green #5043.....	Blue	Blue	Green	Blue-Green	
Sheaffer Emerald Green #74.....	Blue-Green	Blue-Green	Green	Green	Blue-Green
Carter Green #56.....	Blue	Blue	Blue	Blue	Blue
Carter Contrast Green #59.....	Blue	Blue	Blue	Blue	Blue
Carter Jewel Tone Green #56.....	Blue	Blue	Blue	Blue	Blue
Carter Green #959.....	Blue Ring	Blue	Blue	Blue	Blue
Sanford Green #216.....	Faint Blue				

POROUS GLASS ELECTROPHORESIS— EXPERIMENTAL

Electrophoresis separations were conducted in porous glass in a manner similar to that of conventional paper strip electrophoresis. Porous glass, however, as a rigid medium, does not require additional support by being clamped between glass plates. The apparatus used during this investigation is illustrated in figure 3. This assembly consists of a 4 x 6 x $\frac{3}{8}$ " Plexiglas sheet that supports two spring clips. The clips are modified by the addition of stainless steel strips to increase the jaw width to four inches. Light platinum foil may be added to the stainless steel and folded back inside the jaws to insure a corrosion-free liner. This is not a requirement and is not shown in

figure 3; however, it is recommended. Likewise, the stainless steel additions are not diagramed in the figure for the sake of simplicity.

Both spring clips are bolted to the Plexiglas as shown, one through a hole and the other through a slot. The clip on the right in figure 3 is secured in the slot by a large terminal nut which may be loosened to allow adjustment of this clip. Four one and one-half inch 10-24 brass bolt legs are used in the corners of the Plexiglas, as indicated.

Electrophoresis separations were conducted in polished porous glass slides and plates of the same size discussed under chromatography. Ink samples were applied directly to the glass surface as before. The slide or plate was then saturated from the side opposite the sample by placing the slide, sample

Figure 3
Porous Glass Electrophoresis Cell

Figure 4

Electrophoresis Separation of Five Black Inks in Porous Glass

Buffer, pH 8.6 Veronal; potential, 160 volts; current flow, 8 ma.; time, 2 hours. Migration was toward the anode (top). 1. Parker 5035; 2. Sheaffer 64; 3. Sanford 235; 4. Waterman (new); 5. Carter 986.

side up, into either a large watch glass or a petri dish. If the petri dish is used some provision must be made to support the under side of the porous glass above the bottom of the dish. Cementing several glass beads with epoxy cement was found convenient for this purpose.

Buffer should be carefully poured into the watch glass (or petri dish) until it just wets the bottom side of the sample slide. As the slide becomes saturated with buffer a noticeable meniscus develops from all sides. This phenomenon disappears entirely when complete saturation is achieved; usually within five minutes. The glass is then removed from the container and excess buffer is wiped from the bottom side, using a clean, soft cloth. Filter paper strips are placed over the ends of the glass and the slide is inserted into the clamps as shown in figure 3. All filter paper should be immediately saturated with buffer to retard sur-

face evaporation from and provide intimate electrical contact with the porous glass. A medicine dropper facilitates this operation.

After these conditions have been satisfied, the cover of the cell should be secured and a potential applied to effect separation of the samples. All separations were conducted at 160 volts with a resulting current flow of 2 to 3 ma for a 1" strip and 6 to 10 ma for a 3¼ x 4" plate. After separation is complete, the sample slide is removed from the cell, wiped dry with a soft cloth, and placed in a warm drying oven at 40-50°C until completely dry.

POROUS GLASS ELECTROPHORESIS—RESULTS

Separations achieved from porous glass electrophoresis are rapid, distinct, and do not develop distortion during drying. Figure 4 illustrates the porous glass electrophoresis separations of five black inks shown earlier as chromatograms in figure 1. By comparing these two figures it is evident that better resolution and more complete separations are possible when the electrophoresis technique is employed. An additional comparison between the two methods is shown in figure 5.

The electrophoresis characterization of fifty-one commercially available fountain pen inks are listed in tables 13 to 18. Results are expressed in the same system as used in the preceding tables.

ADDITIONAL CHARACTERISTICS

Initial experiments using porous glass as a chromatographic medium disclosed an unexpected and interesting aspect of this material. After a sample has been placed on porous glass an almost instantaneous drying occurs due to the extremely large surface area. When dry the sample spot of

Figure 5

Comparison of Electrophoresis and Chromatography Patterns in Porous Glass

Chromatography (left); developer, water; time, 12 hours. Electrophoresis (right); buffer, pH 8.6 Veronal; potential, 160 volts; current flow, 8 ma.; time, 2 hours. Migration (electrophoresis) was toward the anode (top). 1. Parker 5037 Red; 2. Sheaffer 04 Red; 3. Carter 39 Red; 4. Parker 5043 Green; 5. Sanford 296 Brown.

TABLE 13
ELECTROPHORESIS PATTERNS: BLACK INKS

Sample Identification	Spot Color	Zone 1	Zone 2	Zone 3	Zone 4
Parker Black #5035.....	Faint Grey	Violet	Black	Yellow	Rose
Sheaffer Black #34.....	Black	Purple	Blue		Red
Sheaffer Black #64.....	Blue-Green	Blue-Green to Purple		Red to Orange	Yellow
Carter Black #99.....	Purple	Purple	Purple	Red	Yellow
Carter Black #986.....	Dark Green	Orange	Purple		
Sanford Black #235.....	Blue-Green	Blue-Green	Blue	Blue & Yellow	Orange & Yellow
Sanford Black #236.....	Black	Purple	Blue		
Waterman Black, New.....	Blue	Blue	Blue	Purple	Yellow
Waterman Black, Old.....	Black	Purple	Yellow & Purple	Blue	Yellow
Higgins Black #812.....	Black	Purple	Purple		

TABLE 14
ELECTROPHORESIS PATTERNS: BLUE INKS

Sample Identification	Spot Color	Zone 1	Zone 2	Zone 3	Zone 4
Parker Turquoise #5034.....	Blue-Green	Blue-Green	Blue	Blue	
Parker Royal Blue #5038...	Blue	Blue	Blue	Blue	
Parker Blue #5039.....	Blue	Blue	Blue	Blue	Blue
Sheaffer Blue #42.....	Blue	Blue	Blue	Blue & Purple	
Sheaffer Blue #44.....	Blue	Blue	Blue	Blue & Purple	
Sheaffer Royal Blue #54....	Blue	Blue	Blue	Blue & Purple	
Sheaffer Purple #84.....	Blue				
Sheaffer Peacock Blue #114..	Faint Blue- Green	Green	Green		
Carter Indigo Blue.....	Black	Blue	Faint Purple	Faint Purple	Faint Purple
Carter Jewel Tone Purple #46.....	Strong Violet				
Carter Contrast Purple #49..	Purple	Blue & Purple ¹			
Carter Blue #79.....	Blue	Blue	Blue	Faint Blue	Blue
Carter Contrast Turquoise #119.....	Blue	Blue	Faint Blue	Blue-Green	
Sanford Violet #206.....	Purple	Purple ²			
Sanford Royal Blue #256...	Blue	Blue	Blue	Blue & Purple	Violet to Rose
Sanford Peacock Blue #266..	Blue	Blue	Faint Blue	Blue-Green	
Waterman Blue #632.....	Blue	Blue	Blue	Blue & Purple	

¹ Purple migrated toward the cathode; blue toward the anode.

² Purple migrated toward the cathode.

some inks exhibited a characteristic appearance which can best be described as a "metallic luster". The color of this luster and the frequent occurrence of colored concentric rings within the spot pattern are often sufficient to correctly identify the ink without further analysis. This effect is due

in part to the fact that some of the constituents in certain samples are of molecular sizes greater than that of the pore openings. Therefore, diffusion into the glass is simply not possible and the sample is, in effect, subjected to a micro-filtration.

In addition to the visible spectrum, fluorescent

TABLE 15
ELECTROPHORESIS PATTERNS: BLUE-BLACK INKS

Sample Identification .	Spot Color	Zone 1	Zone 2	Zone 3	Zone 4
Parker Blue-Black # 5033.....	Blue	Blue	Blue & Purple	Blue	Yellow
Carter Blue-Black.....	Dark Blue	Blue	Blue	Blue	Very Faint Yellow
Carter Blue-Black # 816.....	Blue	Blue	Blue	Blue	
Carter Blue-Black # 919.....	Blue	Blue	Blue	Blue	Yellow
Sanford Blue-Black # 276.....	Blue	Blue	Blue	Blue	
Sheaffer Blue-Black # 22.....	Blue-Green	Blue	Blue	Rose-Purple	
Waterman Blue-Black.....	Blue	Blue	Blue	Blue	
Higgins Blue-Black # 822.....	Strong Blue	Blue	Blue	Blue	

TABLE 16
ELECTROPHORESIS PATTERNS: RED INKS

Sample Identification	Spot Color	Zone 1	Zone 2	Zone 3	Zone 4
Parker Red # 5037.....	½ Faint Red		Orange	Orange	Orange
Sheaffer Red # 04.....	½ Orange ⅓ Rose				
Carter Red # 39.....	Orange		Orange		Orange
Carter Carmine Red # 382.....	Orange				
Sanford Cardinal Red # 246....	Orange	Rose	½ Rose		
Sanford Dubonnet # 286.....	Purple	Faint Purple	Faint Purple	Red	Red

TABLE 17
ELECTROPHORESIS PATTERNS: BROWN INKS

Sample Identification	Spot Color	Zone 1	Zone 2	Zone 3	Zone 4
Sheaffer Brown # 14.....	Blue-Green	Brown Faint Purple	Brown	Yellow-Brown	Red Yellow
Carter Sunset Brown # 526..	Dark Brown		Purple		
Sanford Brown # 296.....	Purple		Purple	Rose	

TABLE 18
ELECTROPHORESIS PATTERNS: GREEN INKS

Sample Identification	Spot Color	Zone 1	Zone 2	Zone 3	Zone 4
Parker Emerald Green # 5043....	Blue	Green	Violet	Yellow	
Sheaffer Emerald Green # 74....	Blue-Green		Yellow		
Carter Green # 56.....	Green	½ Blue-Green			
Carter Contrast Green # 59.....	Green	½ Green			
Carter Jewel Tone Green # 56....	Green	½ Blue-Green			
Carter Green # 959.....	Green	½ Blue-Green			
Sanford Green # 216.....	Blue-Green	Blue-Green			

activity of the developed porous glass separations was observed. Also, the infrared opacity was obtained by observing the developed chromatograms through an infrared "sniperscope" image con-

verter while holding the glass slides in front of a 100 watt incandescent bulb. Data obtained from these observations are recorded in tables 19 to 24, as follows.

DISCUSSION

The data outlined above are sufficient to differentiate between any two of the fifty-one commercially available fountain pen inks acquired for this investigation. Combination of the two separation methods provides adequate characterization for any one of these samples to distinguish it from all of the others. Undoubtedly, the methods are not restricted to just these particular inks but could also provide similar data for all other fountain pen inks as well.

The data in the above tables are reported to provide the examiner of questioned documents with a guide for effecting the probable identification or

differentiation of an unknown ink. However, this data is not to be considered or used as an absolute means for establishing identification of a particular sample. Rather, it should be used as a guide for selecting the most probable standard which is known to produce patterns similar to those of the unknown sample. Ideally, the investigator would have a supply of porous glass and run standards on all available inks by both chromatography and electrophoresis. More practically, he might have but a few slides and run the unknown under several conditions. A comparison of his results with the data in this report could indicate the probable identity of the unknown ink. These

TABLE 19
ADDITIONAL CHARACTERISTICS: BLACK INKS

Ink	Fluorescence*		IR Opacity†	Luster
	Chromatography	Electrophoresis		
Parker #5035.....	No Fluorescence	No Fluorescence	Transparent	No Luster
Sheaffer #34.....	No Fluorescence	No Fluorescence	Opaque	Strong Grey
Sheaffer #64.....	Overall with a bright spot at top	Strong First $\frac{1}{4}$	Transparent	No Luster
Carter #99.....	No Fluorescence	No Fluorescence	Opaque	Strong Neutral Ring
Carter #986.....	No Fluorescence	No Fluorescence	Transparent	Strong Neutral Rings
Sanford #235.....	No Fluorescence	No Fluorescence	Transparent	No Luster
Sanford #236.....	No Fluorescence	Faint second $\frac{1}{4}$	Opaque	Strong Violet
Waterman (New).....	No Fluorescence	No Fluorescence	Transparent	Red Ring
Waterman (Old).....	No Fluorescence	No Fluorescence	Transparent	Faint Neutral Lines
Higgins #812.....	No Fluorescence	No Fluorescence	Opaque	Strong Yellow

* @ 357 m μ .

† Sniperscope image converter.

TABLE 20
ADDITIONAL CHARACTERISTICS: BLUE-BLACK INKS

Ink	Fluorescence*		IR Opacity†	Luster
	Chromatography	Electrophoresis		
Parker #5033.....	No Fluorescence	No Fluorescence	Transparent	No Luster
Carters.....	No Fluorescence	No Fluorescence	Semi-Transparent	Red-Yellow Ring
Carter #816.....	No Fluorescence	No Fluorescence	Semi-Transparent	Silver White Spot
Carter #919.....	No Fluorescence	No Fluorescence	Transparent	Faint Red Rings
Sanford #276.....	No Fluorescence	No Fluorescence	Semi-Transparent	Violet Spot
Sheaffer #22.....	Bottom $\frac{1}{4}$	Fluorescent in middle	Transparent	No Luster
Waterman #24...	No Fluorescence	No Fluorescence	Transparent	Faint Violet Rings
Higgins #822.....	No Fluorescence	No Fluorescence	Transparent	Red-Violet Spot

* @ 357 m μ .

† Sniperscope image converter.

TABLE 21
ADDITIONAL CHARACTERISTICS: BLUE INKS

Ink	Fluorescence*		IR Opacity†	Luster
	Chromatography	Electrophoresis		
Parker # 5034.....	No Fluorescence	No Fluorescence	Transparent	No Luster
Parker # 5038.....	No Fluorescence	No Fluorescence	Transparent	Red ring & Lines
Parker # 5039.....	No Fluorescence	Faint first $\frac{1}{4}$	Transparent	No Luster
Sheaffer # 42.....	Over-all with a bright spot at top	Spot & middle	Transparent	No Luster
Sheaffer # 44.....	Over-all with a bright spot at top	Spot & middle	Transparent	No Luster
Sheaffer # 54.....	Faint over-all with a faint spot at top	In middle	Transparent	No Luster
Sheaffer # 84.....	No Fluorescence	First $\frac{1}{4}$	Transparent	Strong Yellow-gold
Sheaffer # 114.....	Over-all with a bright spot at top	Overspot & middle	Transparent	No Luster
Carter Indigo.....	No Fluorescence	No Fluorescence	Opaque	Faint red ring
Carter # 46.....	No Fluorescence	No Fluorescence	Transparent	Strong yellow-green ring
Carter # 49.....	No Fluorescence	No Fluorescence	Transparent	Strong yellow-green ring
Carter # 79.....	No Fluorescence	No Fluorescence	Transparent	No Luster
Carter # 119.....	No Fluorescence	No Fluorescence	Transparent	Strong blue
Sanford # 206.....	No Fluorescence	No Fluorescence	Transparent	Strong yellow-green ring
Sanford # 256.....	No Fluorescence	No Fluorescence	Transparent	Red-violet rings
Sanford # 266.....	No Fluorescence	No Fluorescence	Transparent	No Luster
Waterman # 632.....	No Fluorescence	No Fluorescence	Transparent	No Luster

* @ 357 m μ

† Sniperscope image converter

TABLE 22
ADDITIONAL CHARACTERISTICS: RED INKS

Ink	Fluorescence*		IR Opacity†	Luster
	Chromatography	Electrophoresis		
Parker # 5037.....	No Fluorescence	No Fluorescence	Transparent	Faint lines
Sheaffer # 04.....	Yellow over-all (only when acidic, not when basic.)	Faint first $\frac{1}{4}$	Transparent	Strong yellow ring
Carter # 39.....	No Fluorescence	No Fluorescence	Transparent	Strong yellow
Carter # 382.....	No Fluorescence	No Fluorescence	Transparent	Strong yellow-red rings
Sanford # 246.....	No Fluorescence	No Fluorescence	Transparent	No Luster
Sanford # 286.....	No Fluorescence	No Fluorescence	Transparent	Faint lines

* @ 357 m μ

† Sniperscope image converter

two inks, standard and unknown, should then be subjected to porous glass under neutral, acidic, and basic conditions and also electrophoretic separation. The fluorescent activity, infrared

opacity, and original character of the dried sample spot should also be determined.

If the unknown ink sample and the known ink standard are actually the same, all characteristics

TABLE 23
ADDITIONAL CHARACTERISTICS: GREEN INKS

Ink	Fluorescence*		IR Opacity†	Luster
	Chromatography	Electrophoresis		
Parker #5043.....	No Fluorescence	No Fluorescence	Transparent	No Luster
Sheaffer #74.....	Over-all with a bright spot at top	First half	Transparent	No Luster
Carter #959.....	No Fluorescence	No Fluorescence	Transparent	Strong yellow
Carter #56.....	No Fluorescence	No Fluorescence	Transparent	Strong red-violet
Carter Jewel Tone #56.....	No Fluorescence	No Fluorescence	Transparent	Strong red-violet
Carter #59.....	No Fluorescence	No Fluorescence	Transparent	Strong red-violet
Sanford #216.....	No Fluorescence	No Fluorescence	Transparent	No Luster

* @ 357 mμ

† Sniperscope image converter

TABLE 24
ADDITIONAL CHARACTERISTICS: BROWN INKS

Ink	Fluorescence*		IR Opacity†	Luster
	Chromatography	Electrophoresis		
Sheaffer #14.....	Over-all with a bright spot at top	First ¼	Transparent	No Luster
Carter #526.....	No Fluorescence	No Fluorescence	Opaque	Strong yellow-green
Sanford #296.....	No Fluorescence	No Fluorescence	Opaque	Strong grey spot

* @ 357 mμ

† Sniperscope image converter

should be found identical. Application of additional reagents to the porous glass slides will result in similar reactions by corresponding bands of the two separated samples. Exposure to hydrogen sulfide, ammonia, or hydrogen thiocyanide vapors should produce similar alterations provided the two samples themselves are identical (15). Likewise, other high dielectric developing solvents may be used for obtaining additional data to further establish probable identification (25).

Unlike paper chromatography, comparison between known and unknown may even be extended to include fractional pyrolysis. When two samples of the same ink are separated in porous glass, and these chromatograms are subjected to gradual heating, the individual bands will char and darken in an identical manner. The chemical inertness and thermal stability of porous glass suggest still further characterization procedures should they ever be required (31)(32).

Limited investigation has indicated that no significant problems are encountered in characterization of ink samples which have been eluted

from the surface of documents. In some instances the pattern obtained from an eluted sample will differ from that obtained with the liquid ink standard. This results when some constituents of a given ink are so tenaciously bonded to the document that they simply can not be easily eluted into solution. Often this difficulty may be overcome by the proper choice of solvent and/or comparison of the unknown pattern with standards which have also been eluted from paper.

CONCLUSION

Porous glass offers an unique medium in which to conduct chromatographic and electrophoretic separations. The inert nature of this optically transparent material offers several advantages over conventional separation media. Separation patterns achieved in porous glass have provided sufficient data to correctly identify unknown ink samples provided a standard sample of the same ink is also available. It must be emphasized, however, that such identification was based upon the knowledge that every unknown ink was, in fact,

one of the several samples which had been characterized during the course of this investigation. When one considers that there are hundreds of other ink formulations which have not been so characterized, it is apparent that in other instances a final conclusion must be limited to a "presumptive identification." Nevertheless, differences between two samples definitely may be established using porous glass separation techniques. Very often it is this information which is of more significant evidential value to the examiner of questioned documents.

ACKNOWLEDGEMENTS

The author expresses his appreciation to Corning Glass Works for providing both the porous glass and laboratory facilities used throughout this research. Thanks are extended to the following companies for their consideration in supplying many of the ink samples: Higgins Ink Company, The Parker Pen Company, Sanford Ink Company, and W. A. Shaeffer Pen Company. Encouragement and advice from Dr. J. P. Williams during many phases of the investigation are also acknowledged. The typing efforts of Miss Patricia A. Hyland are greatly appreciated.

BIBLIOGRAPHY

- OSBORN, ALBERT S., *QUESTIONED DOCUMENTS*, Second Edition, Boyd, New York, 1929.
- GODOWN, LINTON, *Differentiation and Identification of Writing Inks by Chromatographic Analysis*. Unpublished Paper, American Society of Questioned Documents Examiners, Rochester, New York, 1951.
- SOMERFORD, ALBERT W., *Comparison of Writing Inks by Chromatography*, *IDENTIFICATION NEWS*, 2, p. 4 (April), 1952.
- GROSS, HANS, *CRIMINAL INVESTIGATION*, Fourth Edition, Sweet & Maxwell, Ltd., London, 1950, p. 297-301.
- SODERMAN, HARRY, AND O'CONNELL, JOHN J., *MODERN CRIMINAL INVESTIGATION*, Fourth Edition, Funk & Wagnalls Company, New York, 1952, p. 445-449.
- O'HARA, CHARLES E., AND OSTERBURG, JAMES W., *AN INTRODUCTION TO CRIMINALISTICS*, MacMillan Company, New York, 1949, p. 457-479.
- FEIGL, FRITZ, *SPOT TESTS IN INORGANIC ANALYSIS*, Fifth Edition, Elsevier, Amsterdam, 1958, p. 479-481.
- FINN, JOHN, AND CORNISH, ROBERT E., *Determination of Age of Inks by the Chloride Method*, *INDUSTRIAL AND ENGINEERING CHEMISTRY*, 10, p. 524-525, 1938.
- GODOWN, LINTON, *Report on Experiments on Examination of Ink by Electrophoresis*. Unpublished Paper, American Society of Questioned Documents Examiners, Chicago, Illinois, 1956.
- CROWN, DAVID A., et al., *Differentiation of Ball-Point Pen Inks*, *JOURNAL OF CRIMINAL LAW, CRIMINOLOGY, AND POLICE SCIENCE*, 52, p. 338-343, 1961.
- BROWN, CHARLOTTE, AND KIRK, PAUL L., *Paper Electrophoresis in the Identification of Writing Inks*, *JOURNAL OF CRIMINAL LAW, CRIMINOLOGY, AND POLICE SCIENCE*, 45, p. 473-480, 1954.
- SOMERFORD, ALBERT W., *Comparison of Writing Inks by Paper Chromatography*, *JOURNAL OF CRIMINAL LAW, CRIMINOLOGY, AND POLICE SCIENCE*, 43, p. 124-127, 1952.
- BAILEY, C. F., AND CASEY, ROBERT S., *Spectrophotometric Evaluation of the Color of Ink Marks on Paper*, *INDUSTRIAL & ENGINEERING CHEMISTRY, ANALYTICAL EDITION*, 19, p. 1020-1022, 1947.
- MCBAY, ARTHUR J., *Chromatographic Methods of Analysis Applied to Forensic Problems*, *JOURNAL OF FORENSIC SCIENCES*, 3, p. 364-369, 1958.
- BRACKETT, JAMES W., AND BRADFORD, LOWELL W., *Comparison of Ink Writing on Documents by Means of Paper Chromatography*, *JOURNAL OF CRIMINAL LAW, CRIMINOLOGY, AND POLICE SCIENCE*, 43, p. 530-539, 1952.
- BROWN, CHARLOTTE, AND KIRK, PAUL L., *Horizontal Paper Chromatography in the Identification of Ball-Point Pen Inks*, *JOURNAL OF CRIMINAL LAW, CRIMINOLOGY, AND POLICE SCIENCE*, 45, p. 334-339, 1954.
- COLDWELL, B. B., *The Comparison of Inks and Writings by Paper Chromatography*, *ANALYST*, 80, p. 68-72, 1955.
- SOUDER, WILMER, AND SMITH, W. HAROLD, *Comparisons of Writing Inks by Paper Chromatography*, *IDENTIFICATION NEWS*, 1, p. 4, 1951.
- BOSCH, K., AND MUELLER, B., *To What Extent Can Ball Pen Inks be Differentiated by Paper Chromatography*, *ARCHIV FÜR KRIMINOLOGIE*, 126, p. 77-86, 1960.
- DOUD, DONALD, *Chromatographic Analysis of Inks*, *JOURNAL OF FORENSIC SCIENCES*, 3, p. 486-492, 1958.
- LEDERER, EDGAR, AND LEDERER, MICHAEL, *CHROMATOGRAPHY*, Second Edition, Elsevier, Amsterdam, 1957, p. 115-146.
- SMITH, IVOR, *CHROMATOGRAPHIC AND ELECTROPHORETIC TECHNIQUES*, Volume II, Zone Electrophoresis, William Heinemann Medical Books, Ltd., London, p. 69, 1960.
- CROWN, DAVID A., *Simple Power Sources for Electrophoresis*. Paper, American Academy of Forensic Sciences Annual Meeting, Chicago, Illinois, 1962.
- MACDONELL, HERBERT L., *Porous Glass Chromatography*, *NATURE*, 189, 302, 1961.
- MACDONELL, H. L., AND WILLIAMS, J. P., *Porous Glass Chromatography Used for the Characterization of Water-Soluble Inks*, *ANALYTICAL CHEMISTRY*, 33, p. 1552-1554, 1961.
- MACDONELL, H. L., *Porous Glass Electrophoresis*, *ANALYTICAL CHEMISTRY*, 33, p. 1554-1555, 1961.
- NORDBERG, MARTIN E., *Properties of Some Vycor-Brand Glasses*, *JOURNAL OF THE AMERICAN CERAMIC SOCIETY*, 27, p. 229-305, 1944.
- LITTLE, L. H., et al., *Infrared Spectra of Chemisorbed Molecules*, *PROCEEDINGS OF THE ROYAL SOCIETY, A*, 259, p. 242-256, 1960.
- LITTLE, L. H., et al., *An Infrared Study of the Adsorption of Butenes on Surfaces of Porous Vycor Glass*, *CANADIAN JOURNAL OF CHEMISTRY*, 39, p. 42-60, 1961.
- CASEY, ROBERT S., *Ink, Writing*, *ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY*, p. 870-877, Interscience, New York, 1951.
- BENARIE, MICHAEL M., *Chromatography of Molten Salts on a Glass Powder Column*, *SCIENCE*, 128, p. 1008, 1958.
- Anon, *Glass Paper Aids Chromatography*, *CHEMICAL AND ENGINEERING NEWS*, 33, February 22, 1960, p. 51.