Ink Analysis by Capillary Electrophoresis

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Table of Contents

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I wish to acknowledge Dr. Jay Siegel, Michigan State University for his willingness to take me into his lab, Michael Jahnke, for his brainstorming and problem solving skills that helped get this project off the ground, and Matthew Miller for his assistance in familiarizing Mike and I with the CE. Thank you to Dr. Joan Esson for reviewing this Senior Individualized Project.

Abstract

Ink analysis plays an important role in the examination of questioned/fraudulent documents in a forensic lab. Recent studies of a fairly new analytical technique, capillary electrophoresis (CE), have been conducted and have proven CE to be an efficient analytical technique for the separation of inks. CE is known for its high resolution power and efficiency, requiring a small sample volume, and its capability of separating charged compounds.

In this study, capillary electrophoresis was proven successful in the separation of ballpoint and felt tip pen inks using two buffer systems; a 50mM borate buffer, pH 9.3, with 30mM SDS and 25% acetonitrile, as well as a 50mM borate buffer, pH 9.3, with 20% methanol. Electropherograms of 10 inks of various colors and origin were analyzed and sufficiently distinguished from each other.

List of Tables

List of Figures

Introduction.

I. *Ink Analysis*

Ink analysis plays an important role in the examination of questioned/fraudulent documents in a forensic lab (1, 2, 3). Analysis of the inks used on a document can give insight into many aspects of the preparation of that document. Alterations and addition of text, determination of date and origin, identification of writing tool, and the possibility of forgery and counterfeiting can all be accessed in regards to documents such as insurance claims, tax returns, checks, bank notes, contracts, wills, ransom notes, and threats (1, 2, 3).

Numerous physical and chemical methods to distinguish, compare, and separate inks have been developed. Optical microscopy, microspectrophotometry, and IR, UV, and visible spectroscopy are among the physical, non-destructive techniques of ink analysis (3). Chemical analysis techniques include paper chromatography, thin layer chromatography, high performance liquid chromatography, gas chromatography, chemical spot tests, scanning electron microscopy, and x-ray fluorescence spectroscopy (3). These chemical tests are semi-destructive to the documents that often serve as evidence in criminal and civil cases. The destructive nature of these methods can destroy distinguishing characteristics such as handwriting and fingerprints. It is for this reason that it is essential to minimize the size and amount of sample that must be extracted from a questioned document for analysis.

Several studies have been completed using Thin Layer Chromatography (TLC), the primary method of ink analysis in forensic labs due to its simple and fast technique and sufficient resolution, while High Performance Liquid Chromatography (HPLC) has

also been proven to be a sensitive method (3). However, recent studies of a fairly new analytical technique, capillary electrophoresis (CE), have been conducted and have proven CE to a have a higher resolution power and efficiency, require a smaller sample volume, and have the capability of separating charged compounds (1, 2, 3, 4).

Inks are composed of a complex mixture of several chemical compounds including inorganic and organic color pigments, surfactants, antioxidants, resins, viscosity adjusters, lubricants, glycol and glycerol, azoic compounds, and synthetic acidic and basic dyes (2, 3). It is the possibility of separating these charged dyes that makes CE an appealing analytical technique.

A few studies have begun to address the use of CE in ink analysis, and promising results have been obtained in the characterization of inks. Ink samples were successfully separated using CE, and this technique was proficient in distinguishing between various samples (1, 3, 4). This investigation will attempt to obtain distinguishable and reproducible results for the characterization of several ballpoint pen and felt tip pen inks by capillary electrophoresis, as groundwork for further analysis to minimize sample size requirements and in preparation of a library of electropherograms of ink samples.

II. *Capillary Electrophoresis*

Capillary electrophoresis is a chemical separation technique that is capable of separating charged molecules based on their movement through a fluid under the influence of an applied electric field. Separation occurs when the components of the mixture have differing electrophoretic mobilities, meaning they move at different speeds through the fluid based on their charge and size. The fluid that is required to carry out

the separation is called the carrier or background electrolyte (BGE) but is more commonly referred to as the run buffer. The buffer maintains the pH of the system and allows the passage of ions, or current, that is required for separation to occur. A voltage is applied to the system and protons are produced at the anode, while hydroxide ions are produced at the cathode. A current flows with anions migrating toward the anode and cations toward the cathode, allowing for the separation of charged molecules present in solution. A schematic diagram of a CE system follows in Figure 1.

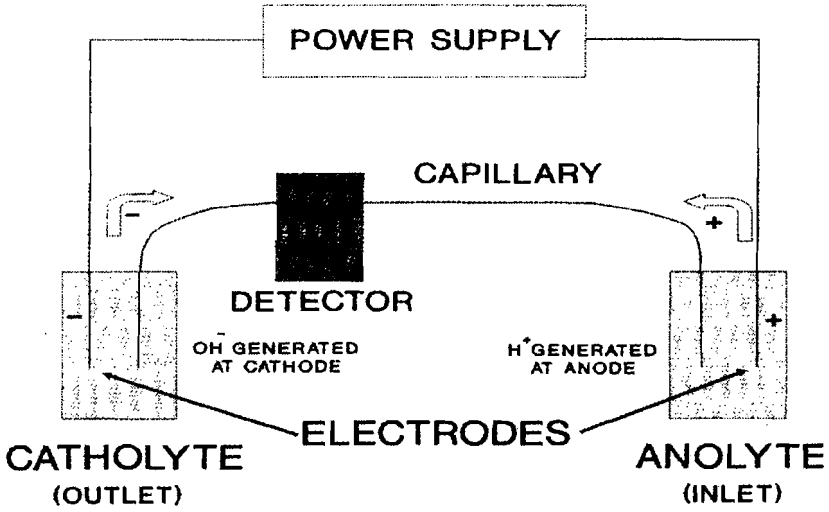


Figure 1. Schematic diagram of a capillary electrophoresis system.

Separation occurs inside a capillary composed of fused silica with a diameter in the range of 25-100μm. A protective polyimide coating surrounds the capillary with the exception of a small window where detection takes place. Capillary lengths vary depending on the separation taking place, but typically are approximately 50cm in length. The effective length is the length from the beginning of the capillary to the detector window, while the total length includes the extension of the capillary beyond the detector window. This extension is necessary to submerge the ends of the capillary in the buffer and make electrical contact to produce a current.

Unlike a retention time in chromatography, CE produces a migration time as each of the components passes the detector window. Direction of net flow inside the capillary is largely dictated by the composition of the capillary itself. The fused silica creates a layer of negative charge around the edge of the capillary. Cations flowing through the capillary are attracted to the capillary wall creating an adsorbed layer of cations closest to the wall. Further from the wall is a compact and mobile layer rich in cations. Even further from the wall, the solution is electrically neutral, as the charge of the column wall loses its effect with distance. The mobile cations migrate in the direction of the negative electrode, which pull along the remaining fluid due to the solvation of the ions by water. This net flow of fluid in the capillary is termed the electroosmotic flow, or EOF. The EOF always flows toward the cathode, and, depending on the direction chosen for the voltage, can aid or deter the flow of ions toward the end of the capillary. A diagram demonstrating the effects causing the EOF follows in Figure 2.

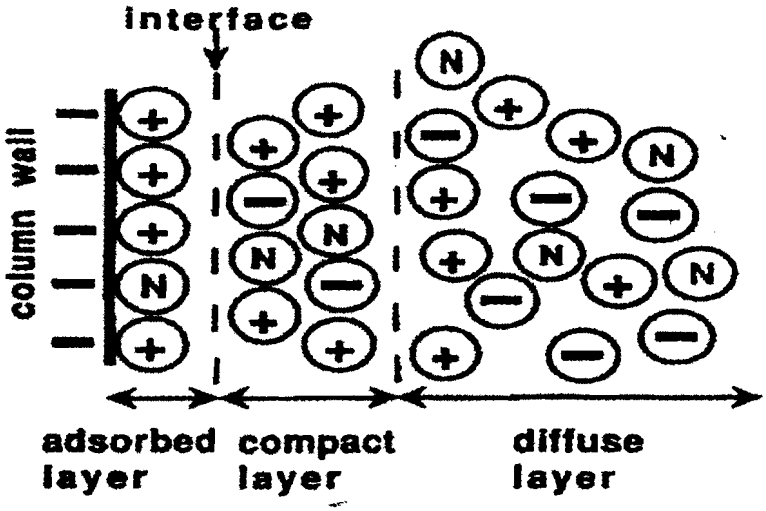


Figure 2. Illustration of the electrical double layer due to the charge of the capillary column wall.

Occasionally additives such as surfactants are incorporated into the buffer system to further control the EOF. Surfactants are molecules that contain long hydrophobic tails and polar head groups producing a heterogeneous environment or 'pseudophase'. The surfactants interact with the solute and organize into aggregates called micelles. A solute's migration time is retarded when it is partitioned into a micellar aggregate, due to its bulky nature. Thus, the addition of surfactants can actually reverse the expected elution order of the solute molecules.

Materials and Methods.

To carry out the separation of ink samples, an Agilent G1600A Capillary Electrophoresis System from Agilent Technologies, Palo Alto, CA was used. The instrument provided voltages up to 30kV, and was equipped with a real time UV/Vis diode array detector with a prealigned deuterium lamp capable of scanning wavelengths from 190-600nm. A voltage of +30kV was maintained throughout each run and the temperature was maintained at 25°C. Samples were injected by pressure at 50.0mbar for 15sec, and were scanned at 214nm. Current was monitored to ensure electrical contact for the duration of the run.

CE standard capillaries of fused silica were purchased from Agilent Technologies with an inner diameter of 50μm and a 72cm effective length. New capillaries were preconditioned using four consecutive 10 minute flushes by pressure of 1.0M NaOH, 0.1M NaOH, HPCE high purity H_2O, and run buffer, respectively. Capillaries were stored overnight after a 10 minute flush by pressure of high purity water, with ends immersed in vials containing the water. All fluids introduced into the capillary were

loaded from 1mL polypropylene vials with crimp/snap caps. At all times, an inlet and outlet vial was present at the beginning and end of the capillary, respectively, to ensure electrical contact. NaOH, H_2O, and vials were all obtained from Agilent technologies.

ChemStation software, common to most Agilent instrumentation, was used to acquire and manage data. Integration of the chromatograms was controlled by integration events in the ChemStation software. Slope sensitivity- 7.8357, peak width- 0.0693, and area reject- 0.3315, were left at default values, while height reject was manually set at 10.

Two run buffers were used throughout the experiment: a 50mM borate buffer, pH 9.3, with 30mM sodium dodecyl sulfate (SDS) and 25% acetonitrile, as well as a 50mM borate buffer, pH 9.3, with 20% methanol. Borate buffers with and without SDS were obtained from Agilent Technologies. HPLC grade acetonitrile was manufactured by Merck KgaA of Darmstadt, Germany, while HPLC grade methanol was manufactured by Burdick and Jackson, Muskegon, MI.

Ink samples were extracted from plugs cut from paper using two methods corresponding to the run buffer used. Samples run in the 50mM borate buffer with 30mM SDS and 25% acetonitrile were extracted with a mixture of 1:1 run buffer and pure acetonitrile. A 1:1 mixture of ethanol and water was used for extracting samples run in the 50mM borate buffer with 20% methanol. Plugs and extraction mixture were placed into a vial and ultrasonicated for 15minutes in a beaker containing water using a Bransonic 3, (117 volts, 50/60Hz, 0.5amps) manufactured by Branson, Shelton, CT. Ink extract was then placed into a clean 1mL vial and filled the rest of the way with buffer.

Nine ink samples were analyzed: 5 ball point pens of black, blue, and red ink, and 4 felt tip markers of black, blue, red, and green ink, see Table 1. An attempt was made to separate each ink with both buffers. The run buffer was replaced after every 3 sample runs to maintain the pH of the system.

Table I. Pen type and color of ink samples analyzed.

Assigned Number	Color	Pen type
#0	Black	Ball point
#1	Blue	Ball point (Bic)
#2	Black	Ball point (Bic)
#3	Black	Ball point (Papermate)
#4	Blue	Ball point
#5	Red	Ball point (Bic)
#6	Blue	Felt tip (Sharpie)
#7	Black	Felt tip (Sharpie)
#8	Red	Felt tip (Sharpie)
#9	Green	Felt tip (Sharpie)

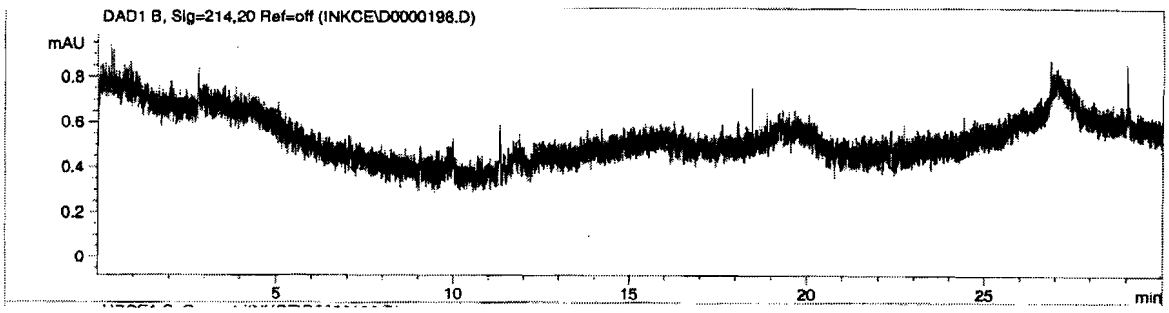
Results and Discussion.

I. *Methods Development*

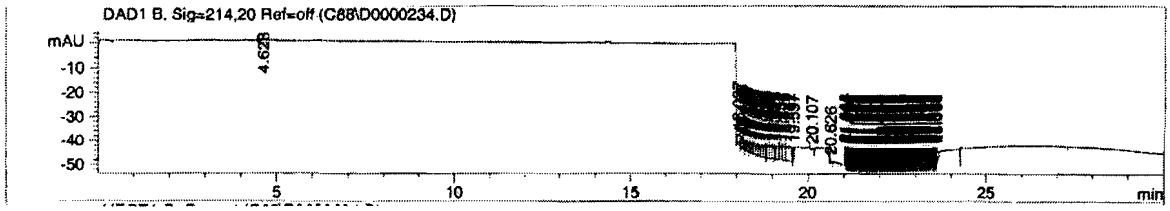
Based on two previous studies of ink analysis using capillary electrophoresis, a wavelength of 214nm, and buffers of 50mM borate buffer, pH 9.3, with 30mM SDS and 25% acetonitrile, as well as a 50mM borate buffer, pH 9.3, with 20% methanol were chosen to carry out analysis (2, 3).

In the initial extraction of the ink sample from paper, approximately 10 plugs, each 1mm^2, were placed in a solution of 25μL of the first run buffer containing SDS and 25μL acetonitrile, followed by sonication. The CE analysis of this extraction produced

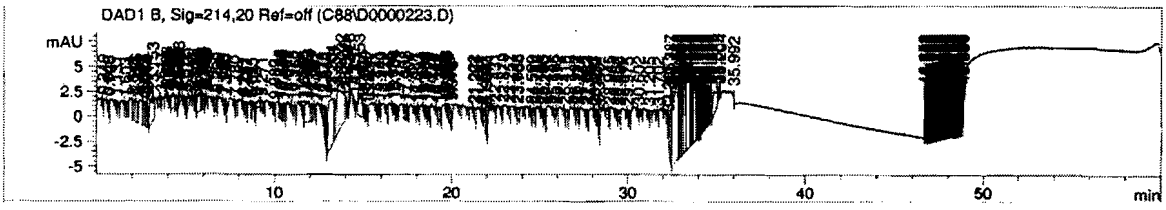
electropherograms ranging from no peaks detected, to a very large number of peaks detected as seen in Figure 3.



(a)



(b)



(c)

Figure 3. Initial CE electropherograms of black ballpoint pen ink #0 extracted from 10 plugs in 25µL run buffer and 25µL acetonitrile and run in 50mM borate buffer, pH 9.3, with 30mM SDS and 25% acetonitrile; (a) no peaks found, (b) one group of peaks found, (c) numerous peaks detected.

Due to the number of electropherograms that produced a large number of detected peaks, several blank runs were conducted to ensure the buffer was not responsible for any of these peaks. As in the initial electropherograms of the ink samples, irreproducible

results were obtained, ranging from no peaks found, to a large number of peaks (see Figure 4.

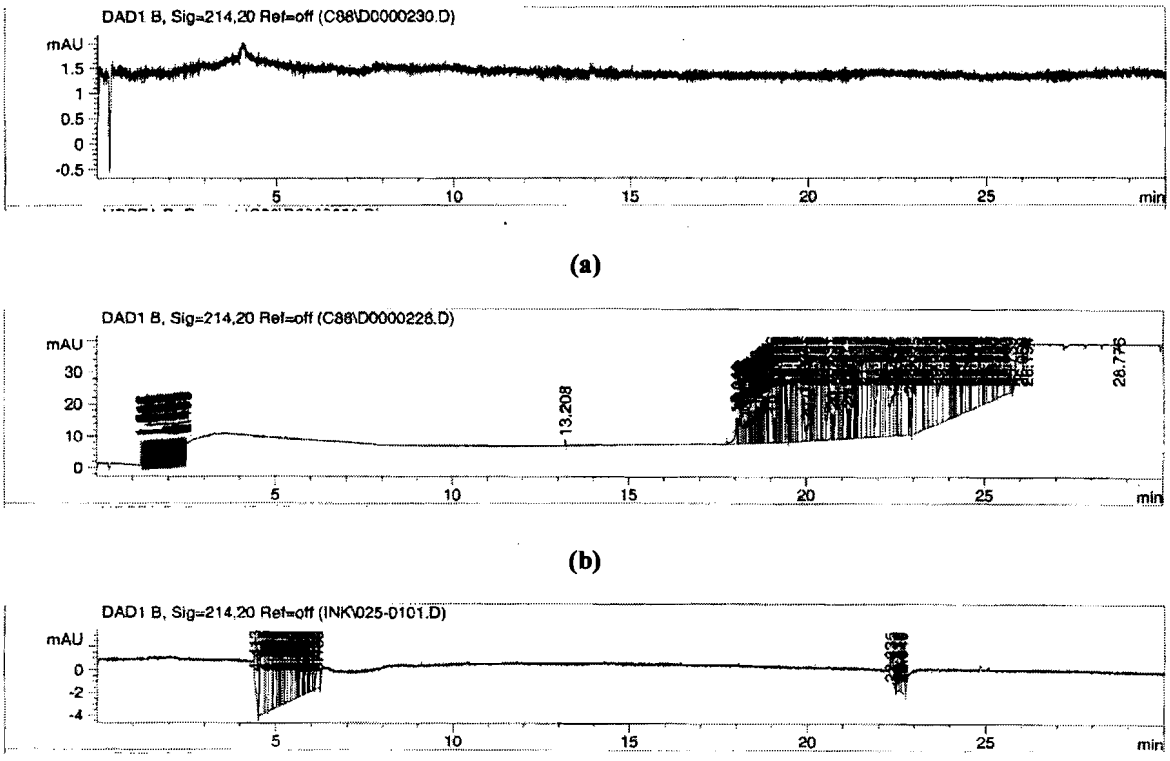


Figure 4. CE electropherograms of run buffer, 50mM borate buffer, pH 9.3, with 30mM SDS and 25% acetonitrile; (a) no peaks found, (b) numerous peaks detected, (c) a few peaks detected.

Based on these results, it was concluded that the initial ink extraction was not concentrated enough to be above the CE system's limits of detection. Therefore, the concentration and amount of extracted ink was increased to 20 plugs in 50μL run buffer and 50μL acetonitrile, 100 plugs in 50μL run buffer and 50μL acetonitrile, and finally 400 plugs in 200μL run buffer and 200μL acetonitrile. At this concentration, some reproducible peaks began to emerge from the baseline noise, and were identified using the auto-integrate option in the ChemStation software (see Figure 5).

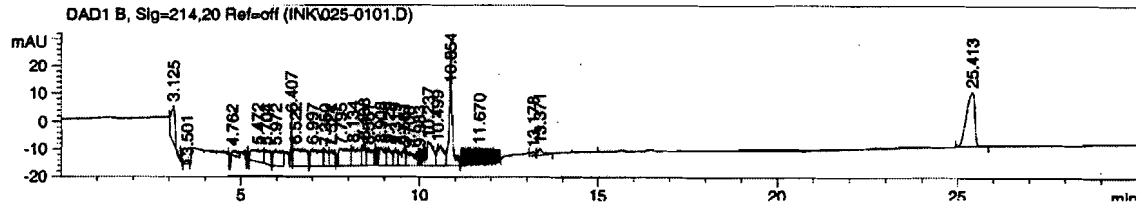


Figure 5. CE electropherogram of black ball point pen ink #0 extracted from 400 plugs in 200μL SDS buffer and 200μL acetonitrile and run in 50mM borate buffer, pH 9.3, with 30mM SDS and 25% acetonitrile, after an auto-integration of the peaks by ChemStation software.

To further distinguish the peaks from the baseline noise, the peaks were integrated manually by adjusting the peak height reject setting in the integration events. Since the major peaks that were being consistently produced maintained heights of at least 10, the minimum peak height allowed to be expressed in the chromatograms was set to 10. This manual integration produced a clean electropherogram with easily visible, prominent peaks, as in Figure 6.

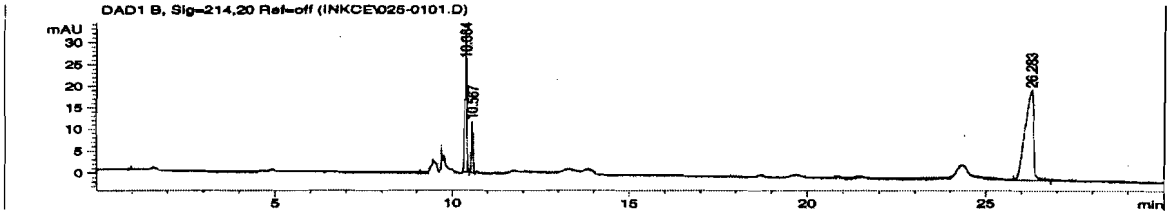


Figure 6. Manually integrated CE electropherograms of black ballpoint pen ink #0 extracted from 400 plugs in 200μL SDS buffer and 200μL acetonitrile and run in 50mM borate buffer, pH 9.3, with 30mM SDS and 25% acetonitrile.

II. *Comparison of ink samples in Borate Buffer w/SDS and Acetonitrile*

Once reproducible results were obtained with the initial ink sample, several other brands and colors of inks were analyzed to determine if this method could distinguish between them. While three electropherograms of each sample were completed to ensure reproducibility, only one will be shown. All successive electropherograms were manually integrated as above. Figures 7-11 illustrate the results of the analysis of ballpoint pen ink samples 1-5.

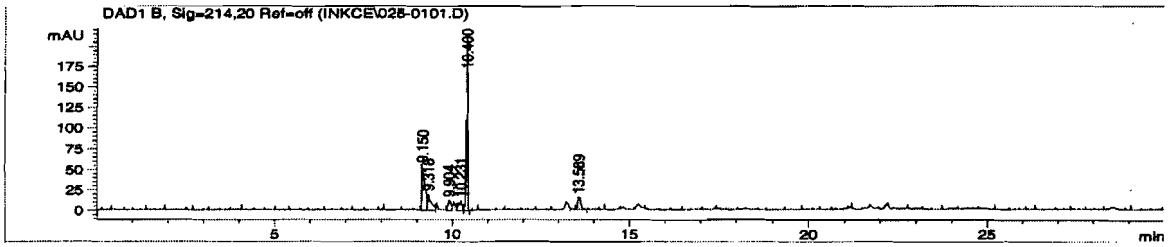


Figure 7. CE electropherograms of ink #1 extracted from 400 plugs in 200µL run buffer and 200µL acetonitrile and run in 50mM borate buffer, pH 9.3, with 30mM SDS and 25% acetonitrile.

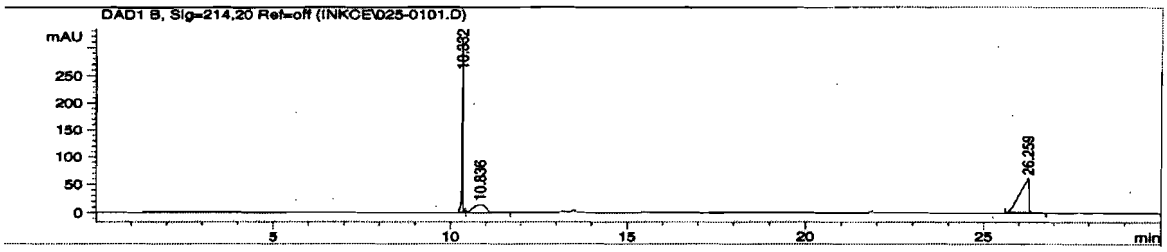


Figure 8. CE electropherograms of ink #2 extracted from 400 plugs in 200µL run buffer and 200µL acetonitrile and run in 50mM borate buffer, pH 9.3, with 30mM SDS and 25% acetonitrile.

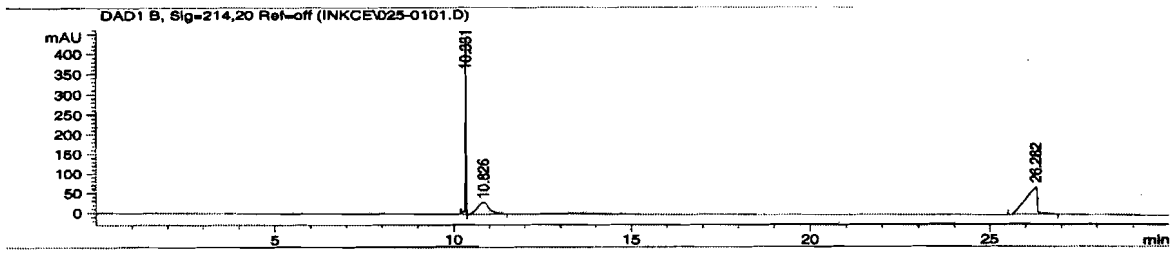


Figure 9. CE electropherogram of ink #3 extracted from 400 plugs in 200µL run buffer and 200µL acetonitrile and run in 50mM borate buffer, pH 9.3, with 30mM SDS and 25% acetonitrile.

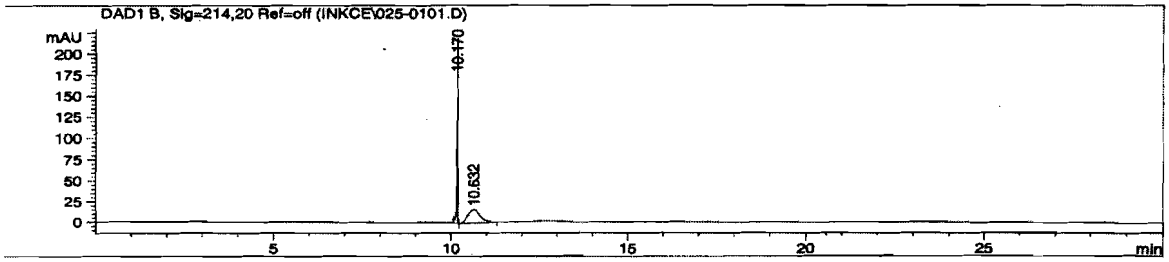


Figure 10. CE electropherogram of ink #4 extracted from 400 plugs in 200µL run buffer and 200µL acetonitrile and run in 50mM borate buffer, pH 9.3, with 30mM SDS and 25% acetonitrile.

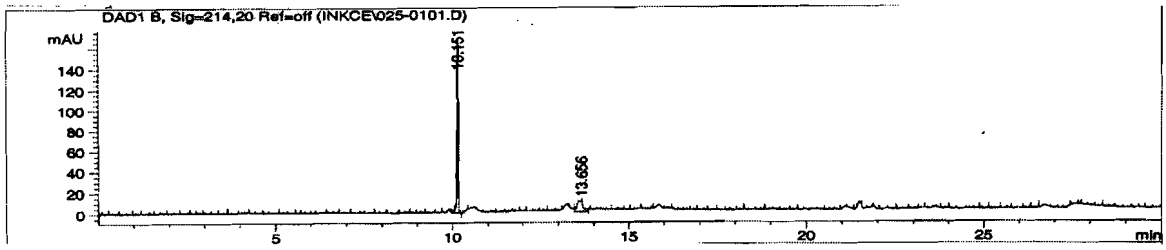


Figure 11. CE electropherogram of ink #5 extracted from 400 plugs in 200µL run buffer and 200µL acetonitrile and run in 50mM borate buffer, pH 9.3, with 30mM SDS and 25% acetonitrile.

The borate buffer with acetonitrile was successful in providing a separation of each ballpoint pen ink analyzed, with prominent peaks present in each electropherogram. Each of the colors analyzed produced a unique electropherogram, discernable from the electropherograms produced from the other ink sample colors. The following table summarizes each sample and its migration times.

Table II. Summary of ballpoint pen ink samples and their migration times.

Sample	Migration times (min)
0	10.3, 10.5, 26.2
1	9.0-9.9, 10.4, 13.5
2	10.3, 10.8, 26.2
3	10.3, 10.8, 24.4
4	10.1, 10.6
5	10.2, 13.7

The three black ball point pen inks, shown in Figures 6, 8, and 9, all produced similar electropherograms, with comparable peak migration times, suggesting that the black inks found in these three different pens consist of the some of the same components. However, slight differences in migration times of the peaks suggest a distinction between the three black inks. For example, while the tallest peak in all three inks occurs at a migration time of 10.3min, the second, shorter peak occurs at 10.5min for ink #0, but at 10.8min for both inks #2 and #3. In addition, the final large peak in inks #0 and #2 occurs at a migration time of 26.2min, while ink #3 occurs at 24.4min. These small variations in the electropherograms provide a unique fingerprint for each ink, sufficient in distinguishing between several black ballpoint pen inks.

The electropherograms obtained from the blue ball point pen inks #1 and #4 in Figures 7 and 10, respectively, produced similar, but not identical electropherograms. Both blue inks produced electropherograms lacking the large peak at a migration time of approximately 26min, which was predominant in the black ballpoint pen ink electropherograms. These results were effective in distinguishing between the blue and black inks.

In addition, the slight differences in the electropherograms also allow one to distinguish between the two blue ink samples, and the two pens from which they were taken. Both blue ink samples produce a very tall peak, at 10.4min and 10.1min, for ink #1 and #4, respectively. The electropherograms for ink #1 also contains several smaller peaks ranging in migration times from 9.0 to 9.9min, while there are no such peaks present for ink #4. The last peak is located at 13.5min for ink #1, and 10.6min for ink #4. These differences allow for distinction between the two blue ballpoint pen ink samples.

Capillary electrophoresis also provides a unique and efficient separation of ink components in a red ballpoint pen ink to distinguish it from other colors in Figure 11, and in addition, distinguishes between various felt tip pens. Electropherograms for the felt tip inks are found in Figures 12-15.

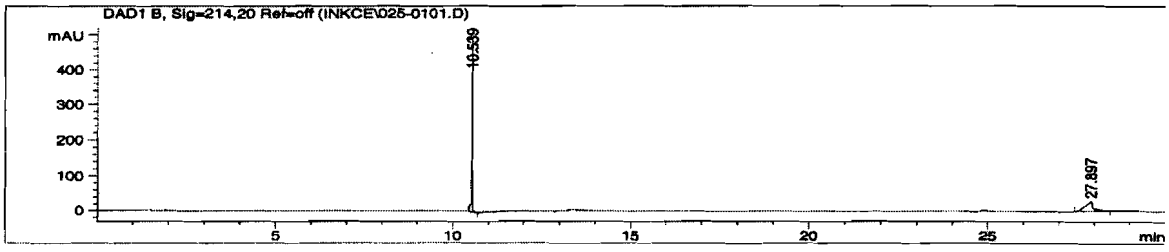


Figure 12. CE electropherogram of ink #6 extracted from 400 plugs in 200µL run buffer and 200µL acetonitrile and run in 50mM borate buffer, pH 9.3, with 30mM SDS and 25% acetonitrile.

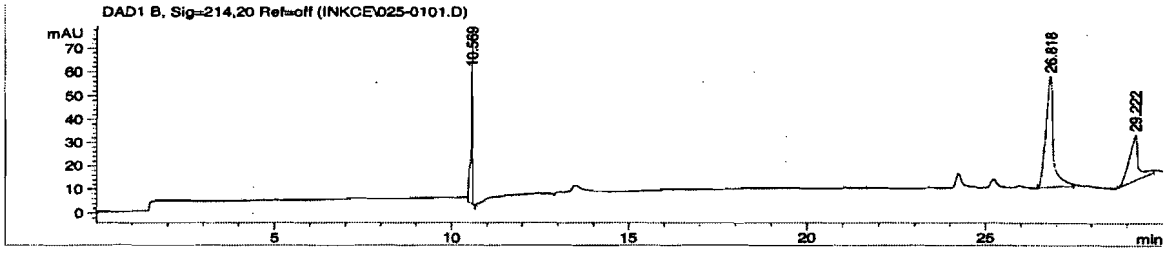


Figure 13. CE electropherograms of ink #7 extracted from 400 plugs in 200µL run buffer and 200µL acetonitrile and run in 50mM borate buffer, pH 9.3, with 30mM SDS and 25% acetonitrile.

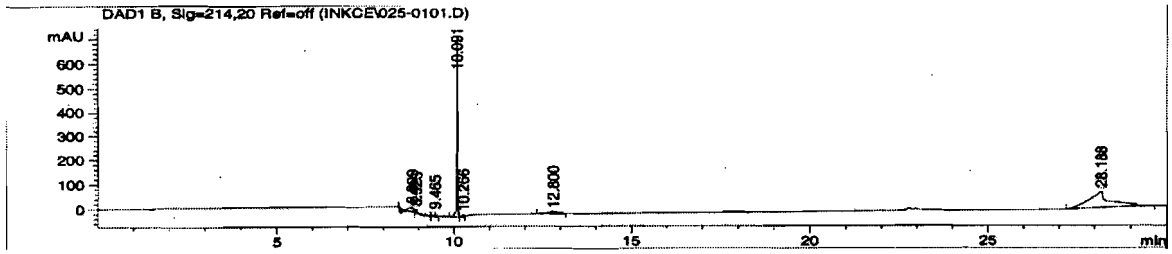


Figure 14. CE electropherogram of ink #8 extracted from 400 plugs in 200µL SDS buffer and 200µL acetonitrile and run in 50mM borate buffer, pH 9.3, with 30mM SDS and 25% acetonitrile.

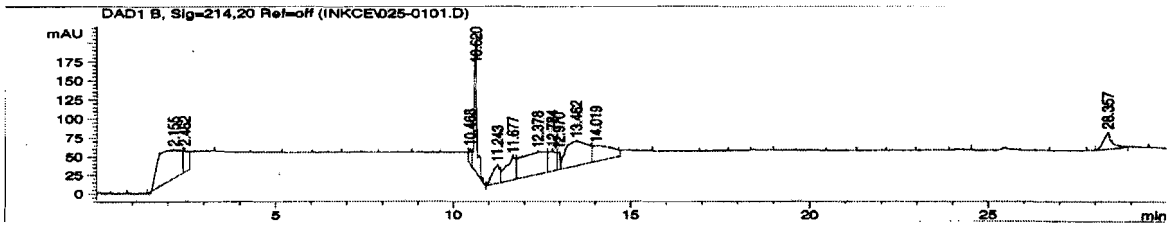


Figure 15. CE electropherogram of ink #9 extracted from 400 plugs in 200µL run buffer and 200µL acetonitrile and run in 50mM borate buffer, pH 9.3, with 30mM SDS and 25% acetonitrile.

A summary of each felt tip pen ink, in the borate buffer with SDS and acetonitrile, and its migration time for comparison, is organized in Table 3.

Table III. Summary of felt tip pen ink samples and their migration times.

Sample	Migration times (min)
6	10.5, 27.9
7	10.5, 26.8, 29.2
8	10.1, 28.2
9	10.6, 28.4

Three of the four electropherograms contained two main peaks; however, the electropherogram of green ink #9 contained two groups of several other peaks ranging from 2.0 to 2.4 and 11.2 to 14.0.

It can be concluded from the preceding results that CE is a sufficient method for the separation of ballpoint pen and felt tip pen ink samples in a 50mM borate buffer, pH 9.3, with 30mM SDS and 25% acetonitrile. All separations were efficient in providing a unique fingerprint for each ink, allowing one to distinguish between different colored samples, as well as various inks of the same color.

III. *Comparison of ink samples in Borate Buffer w/ Methanol*

In addition to the borate buffer with SDS and acetonitrile, a 50mM borate buffer, pH 9.3, with 20% methanol was used to analyze the same ink samples referred to in Sections I. and II. Samples were extracted in 200µL ethanol and 200µL water. This second buffer system was tested to determine if the choice of buffer system had an effect on the efficiency of separation. Electropherograms for ballpoint pen ink samples are shown in Figures 16-21.

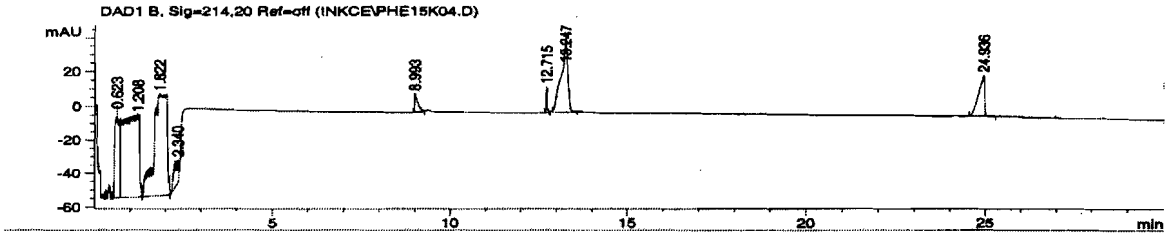


Figure 16. CE electropherogram of ink #0 extracted from 400 plugs in 200µL ethanol and 200µL water and run in 50mM borate buffer, pH 9.3, with 20% methanol.

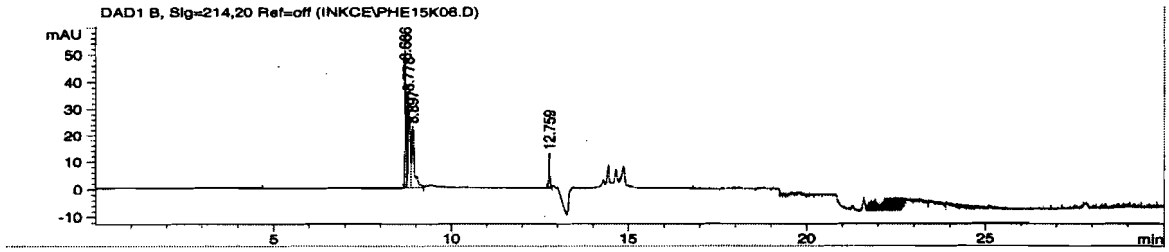


Figure 17. CE electropherogram of ink #1 extracted from 400 plugs in 200μL ethanol and 200μL water and run in 50mM borate buffer, pH 9.3, with 20% methanol.

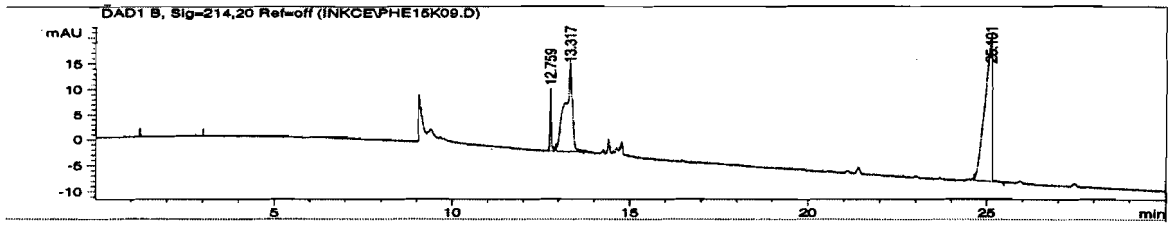


Figure 18. CE electropherogram of ink #2 extracted from 400 plugs in 200μL ethanol and 200μL water and run in 50mM borate buffer, pH 9.3, with 20% methanol.

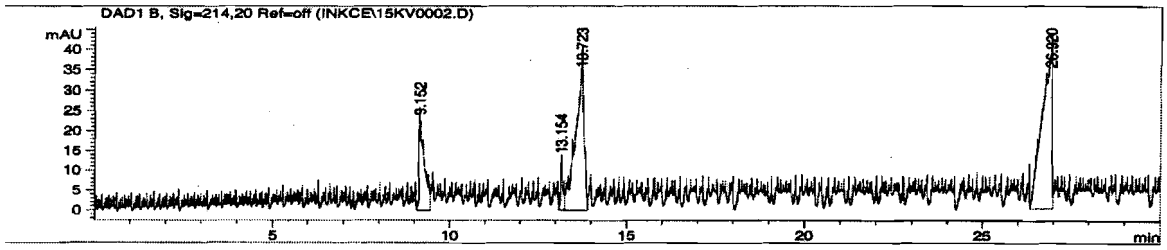


Figure 19. CE electropherogram of ink #3 extracted from 400 plugs in 200μL ethanol and 200μL water and run in 50mM borate buffer, pH 9.3, with 20% methanol.

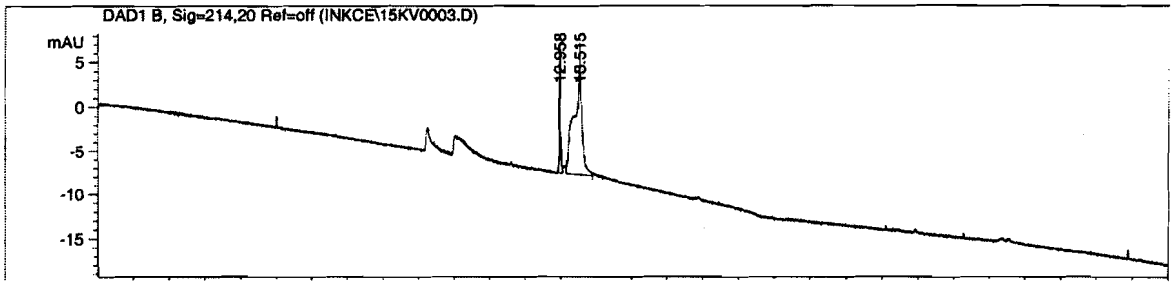


Figure 20. CE electropherogram of ink #4 extracted from 400 plugs in 200μL ethanol and 200μL water and run in 50mM borate buffer, pH 9.3, with 20% methanol.

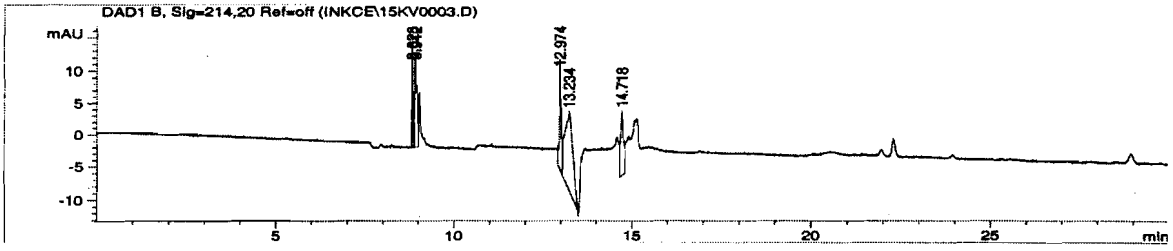


Figure 21. CE electropherogram of ink #5 extracted from 400 plugs in 200μL ethanol and 200μL water and run in 50mM borate buffer, pH 9.3, with 20% methanol.

A summary of each ballpoint pen ink, in the borate buffer with methanol, and its migration time for comparison is organized in Table 4.

Table IV. Summary of ballpoint pen ink samples and their migration times.

Sample	Migration times (min)
0	9.0, 12.7, 13.3, 25.0
1	8.6-8.9, 12.8
2	9.0, 12.7, 13.3, 25.0
3	9.1, 13.2, 13.7, 26.9
4	13.0, 13.5
5	8.9, 12.9, 13.2, 14.7

The borate buffer with methanol was also successful in providing a separation of each ballpoint pen ink analyzed, with prominent peaks present in each electropherogram. It also maintains the ability to distinguish between some, but not all of the different brands of the same color ink, as did the borate buffer with acetonitrile. As seen in Figures 16 and 18, the black ballpoint pen inks #0 and #2, share migration times of all four peaks: 9.0, 12.7, 13.3, and 25.0min. Ink #3, as shown in Figure 19, has a similar electropherogram, but with two of the peaks shifted slightly to 13.7 and 26.9min.

The separation of blue ballpoint pen inks #1 and #4 by the borate buffer w/methanol are shown in Figures 17 and 20. As with the borate buffer with acetonitrile, these electropherograms lack the large peak at a migration time near 26min that is characteristic in the black inks. In addition, each blue ink has a unique electropherogram, allowing for discrimination between the two different brands of blue pens. Ink #1 includes a group of peaks between 8.6 and 8.9min, and another peak at 12.8min, while ink #4 includes a peak at 13.0 and 13.5min.

The red ballpoint pen ink #5 was also successfully separated with a unique electropherogram from that of the other ballpoint pen ink color samples as shown in Figure 21.

The four felt tip pens were also analyzed using the borate buffer with methanol. Again, CE provided a sufficient separation to distinguish between the varying colors of each ink sample. These results are displayed in Figures 22-25. Both blue ink #6 and #7 were separated into two main peaks, but with different migration times: 9.9 and 12.7min for blue #6 and 12.9 and 21.1min for black #7 (see Figures 22 & 23). The

electropherogram of red ink #8 also produced two peaks, but with migration times of 9.3 and 13.0min in Figure 24. Green ink #9 depicts only one peak at 13.1min(Figure 25).

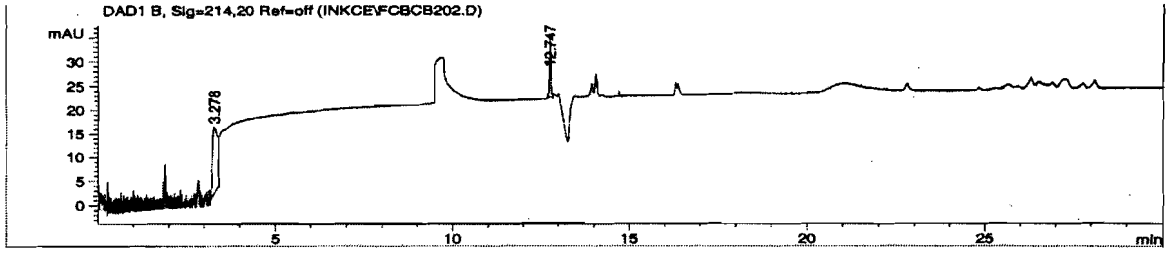


Figure 22. CE electropherogram of ink #6 extracted from 400 plugs in 200μL ethanol and 200μL water and run in 50mM borate buffer, pH 9.3, with 20% methanol.

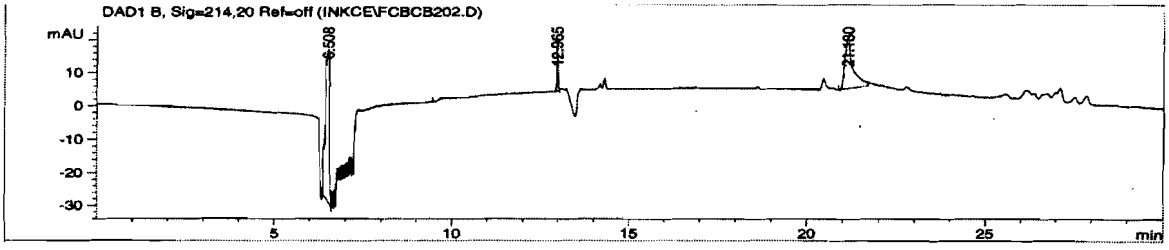


Figure 23. CE electropherogram of ink #7 extracted from 400 plugs in 200μL ethanol and 200μL water and run in 50mM borate buffer, pH 9.3, with 20% methanol.

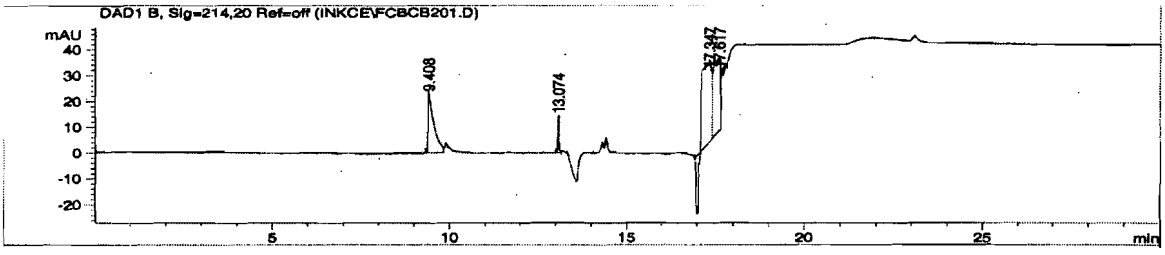


Figure 24. CE electropherogram of ink #8 extracted from 400 plugs in 200μL ethanol and 200μL water and run in 50mM borate buffer, pH 9.3, with 20% methanol.

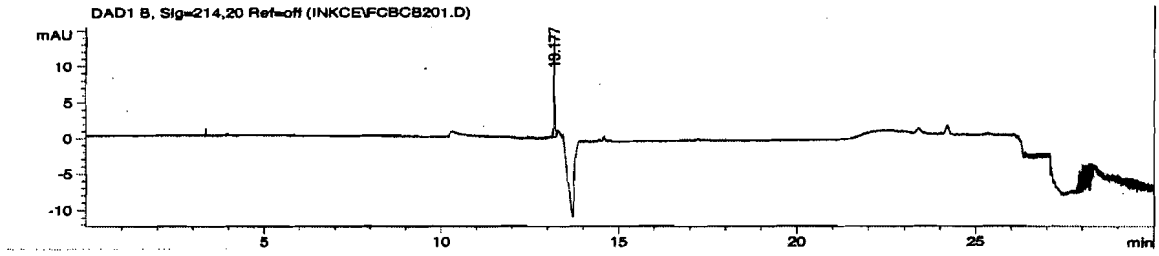


Figure 25. CE electropherogram of ink #9 extracted from 400 plugs in 200μL ethanol and 200μL water and run in 50mM borate buffer, pH 9.3, with 20% methanol.

Results are summarized in the following table with each felt tip sample and its migration times in borate buffer with methanol.

Table V. Summary of felt tip pen ink samples and their migration times.

Sample	Migration times (min)
6	9.9, 12.7
7	12.9, 21.1
8	9.3, 13.0
9	13.1

IV. *Comparison of buffer systems*

Upon comparison of the separation results for ballpoint pen inks for each buffer system, it appears that the borate buffer system with methanol is superior to that with SDS and acetonitrile. Inks #0, #3, and #5 all have increased numbers of peaks with the borate buffer with methanol, and therefore provide better separations. However, this buffer was not able to distinguish between inks #0 and #2, while the borate buffer with SDS and acetonitrile was able to make a distinction.

When considering the separation of the felt tip pen inks, the borate buffer with SDS and acetonitrile appears to be a better buffer system due to its reduced baseline noise

compared to the buffer containing methanol. In addition, this buffer also produced an increased number of peaks per electropherograms, suggesting a better separation.

Conclusion.

Capillary electrophoresis was proven successful in the separation of ballpoint and felt tip pen inks. While both buffer systems used were able to provide separations of all inks samples analyzed, it can be concluded that each system has strengths with a specific type of ink sample. It is possible that the differing extraction methods contributed to this divergence, but further experimentation should be completed in order to determine the actual cause of these differences, and to maximize the separation conditions.

In continuation of this research, repetition of the above outlined analyses should be performed to ensure the reproducibility of the CE system over extended periods of time. An attempt should be made to improve sensitivity of the instrument, while decreasing the baseline noise that was often present. It would be useful to determine the limit of detection, in order to establish the lower limits that peak height reject setting could be adjusted to. Additional adjustment of other integration events may also prove necessary. In order to reduce the amount of sample needed to avoid defacing of documents, an attempt should be made to reduce analysis sample size once sensitivity has increased. Also, due to the length of time required for each run (30 min), it may be beneficial to reduce the effective length of the capillary to reduce run time. Finally, once methodology is overcome, additional types and colors of inks should be analyzed to create a library of chromatograms of numerous ink samples to be used as comparison in future analyses.

References.

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