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Separation and Comparison of Fountain Pen Inks by Capillary Zone Electrophoresis

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ABSTRACT: The analysis of inks as part of the detection of fraudulent documents is a small but important part in the operation of a forensic laboratory. Apart from optical methods, multiple thin layer chromatography (TLC) is used to separate, compare and distinguish inks based on their dye composition.

Capillary electrophoresis (CE), a relatively young separation technique with very high resolution power, was used for the analysis of water soluble fountain pen inks. Inks are complex mixtures of synthetic organic and inorganic dyes, surfactants, resins and other components. The study focused on the optimization of the separation of 10% aqueous solutions of commercially available inks with respect to resolution and analysis time. During the method development process different buffers, organic modifiers and surfactants were tested. Good results were obtained with a 100 mM borate buffer at pH 8.0 containing 20% methanol. The separations were reproducible and led to baseline resolution of almost all components of blue and black fountain pen inks. Electropherograms of 15 inks of various manufacturers and countries of origin showed patterns which were in the most cases distinctly different from each other. Initial studies of the separation of extracts of inks from paper were successful and are reported here as well. Therefore, it was concluded that CE is a powerful tool for the identification of water soluble writing inks.

KEYWORDS: forensic science, questioned documents, inks, separation, identification, capillary zone electrophoresis, method development

Analytical methodology for the detection of fraudulent documents takes up only a small yet very important part in the operation of a forensic laboratory (1–5). The objects under investigation may range from counterfeit banknotes, tax returns, wills and insurance claims to ransom and threatening notes (which usually have significant financial implications). By utilizing physical and chemical methods, the goal of the investigation is to determine the origin or date of the documents or to detect any additions or alterations to them. Although equally important, the analysis of the substrate material, usually paper, will not be discussed here; attention is focused on the investigations of inks.

In the static approach, the identity of an ink is established by comparing analytical data of the sample with that of genuine ink samples. A standard collection of inks manufactured in the US and of some inks of foreign manufacture has been established with the US Secret Service (USSS) and the Internal Revenue Service (IRS). In the dynamic approach, the dating of the document is attempted (6–12). Methods have been developed to characterize inks and determine their date of initial production. This can sometimes prove that a document has been backdated. The determination of the actual age of ink on a document is challenging. Based on changes in the solubility of inks deposited on paper with time, good results on the determination of the age of a written document have been achieved by the development of various solvent extraction techniques using spectrophotometry or thin layer chromatography with densitometry. Other attempts have involved methods such as gas chromatography and infrared spectroscopy for the analysis of ink extracts.

Inks are complex mixtures of a number of different chemical compounds. Depending on the color and writing or printing instrument, a wide variety of different formulations can be encountered. Although the exact composition of inks is in the most cases proprietary, modern inks contain synthetic acid or base dyes, inorganic and organic color pigments, surfactants, antioxidants, resins, viscosity adjusters, lubricants, glycol and glycerol, all in varying amounts. Formulations of water soluble inks may also contain very fine pigment dispersions and salts of synthetic acid dyes. The composition of stamp pad and toner inks along with those of writing inks used in ball point pens, fountain pens, felt tip and Hi-tec point pens will therefore vary widely.

Although the analysis of inks is largely reduced to the analysis of dried inks, their complex composition remains a challenge to the forensic scientist. Among available analytical techniques, physical and chemical methods can be distinguished. Physical methods are preferred for the investigation of documents since they are nondestructive to the evidence in most cases. Comparisons of inks with genuine samples which may aid in the identification of the questioned material can be achieved using optical microscopy, microspectrophotometry and various modes of IR and UV/Vis spectroscopy (13–17). Chemical tests, in contrast, are semidestructive to the pieces of evidence. Chemical spot tests for Cu, Cr and V as well as scanning electron microscopy and X-ray fluorescence spectroscopy provide information on the elemental profile of the inks. Chromatographic techniques which involve the removal of a small amount of ink from a document and the separation and subsequent comparison of the chromatogram to those of standards are very useful. Each ink is expected to give a distinct pattern. Thin layer chromatography (TLC) is the primary analytical technique used for the analysis of inks in the forensic laboratory (1–3,18–24). Over the years this technique has been optimized

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and has become a standard procedure for routine examinations. To characterize different inks based on their composition, a screening chromatogram is developed followed by a high performance thin layer chromatographic separation. Despite these multiple steps, TLC is a relatively fast and simple technique providing sufficient resolution in most cases. It has a number of advantages when compared to other methods such as paper chromatography and electrophoresis (25–27). High performance liquid chromatography (HPLC) has shown to be a more efficient method for the separation of dye stuffs in inks since it provides greater sensitivity and resolution (28). It is even more attractive when coupled with a diode array detector. This detector is capable of gathering spectra at any point during the separation. With this additional spectral information, components of the colored as well as the noncolored fraction of inks can be identified.

Capillary electrophoresis (CE) is a separation technique which has shown to give separations with efficiencies superior to those achievable by HPLC. It was introduced in the early eighties and has been developed and applied to separation problems of many different areas including that of forensic science (29–31). The separations are carried out in buffer filled capillaries with inner diameters between 10 and 100 μm. Under the influence of an electric field applied across the capillary, charged analytes are separated based on differences in their specific electrophoretic mobilities. Due to the generated electroosmotic flow, cationic and anionic species can be separated very efficiently in a single run. The introduction of pseudostationary phases and gels allows for the separation of neutral species and biomolecules. Electrophoretic separations in capillaries are fast, highly efficient, reproducible and require only minute volumes of reagents and samples.

Our studies were aimed to test the applicability of CE to the analysis of inks for forensic purposes. Thereby we focused on the method development for the separation of water-soluble fountain pen inks. Included also are the results of preliminary studies on the separation of ink components which were extracted from dried ink samples on paper. Only one paper has been published so far on the successful separation of red and black fiber-tip pen inks by CE (32), although separations of dyestuffs by CE have been reported more frequently (33,34). This study is intended to further extend the use of this powerful separation technique in forensic laboratories. Excellent results for the analysis of drugs, gunshot and organic explosive residues as well as DNA have already proven CE to be a powerful and flexible tool of choice, and its admissibility for use in expert testimony in the civil and criminal justice system is under discussion (35).

Experimental

Instrumentation

To record the composite spectra of the inks, a Hewlett Packard 8452A Diode Array Spectrophotometer (Palo Alto, CA) was used. It has the capability to scan the wavelength range between 190 and 820 nm. For the separation, a capillary electrophoresis instrument by Beckman (Palo Alto, CA), model P/ACE 5510, was available. This instrument provides voltages of up to 30 kV and is equipped with a single wavelength UV/Vis detector as well as with a diode array detector capable of scanning between 190 and 650 nm. The instrument specific software System Gold version 8.1 was used for data acquisition and management. Fused silica capillaries with an inner diameter of 50 μm were purchased from Polymicro Technologies (Phoenix, AZ). Capillaries with a total length of 37 and 57 (30 and 50 cm, respectively, to the detector window) were cut and fitted into the capillary cartridge of the P/ACE 5510 instrument. For the extraction of ink from paper an ultrasonic bath model FS3 from Fisher (Fair Lawn, NJ) was used.

Chemicals

The chemicals used for the buffer solutions were obtained from Fisher (Fair Lawn, NJ) p.a. grade. $NaH_2PO_4 \cdot 2H_2O$ was used to prepare phosphate buffers pH 3.0 and pH 7.0, H_3BO_3 for borate buffer pH 8.0, $CH_3COONa \cdot 3H_2O$ for acetate buffer pH 5.0, $Na_3C_6H_5O_7 \cdot 2H_2O$ for citrate buffer pH 5.0 and $C_4H_4Na_2O_4 \cdot 6H_2O$ for succinate buffer pH 5.5. To adjust the pH of the buffers, concentrated solutions of NaOH or the respective acids, all from Fisher, were utilized. Methanol, added to the background electrolyte in some of the separations, was of HPLC grade from Fisher with a UV cutoff at 205 nm. Ethanol used in the extraction of dried inks from paper was obtained from Sigma-Aldrich (St. Louis, MO, Milwaukee, WI). For the investigative studies of the separation of ink components by micellar electrokinetic chromatography (MEKC), surfactants such as sodium dodecyl sulfate (SDS, $C_{12}H_{25}NaO_4S$), Brij 35 and hexadecyltrimethylammonium bromide (CTAB, $C_{19}H_{42}BrN$) by Fluka (Buchs, Switzerland) were used.

All solutions were prepared with distilled water from a Barnstead NANOpure system. The water-soluble fountain pen inks investigated are numbered and listed in Table 1. They were purchased in office supply stores as refill cartridges for the specific brands of fountain pens. Solutions of them were prepared by diluting them with distilled water (or buffers if noted) to the desired concentration.

Results and Discussion

Method Development

First, a spectral analysis of inks 1–5 (Table 1) was performed. The UV/Vis absorption in the range between 190 and 820 nm of 0.1% aqueous solutions was recorded. The composite spectra of the blue and black inks were distinctly different. In general it was found that all inks have different absorption maxima in the visible region. Between the blue inks 3 and 4 by Parker only subtle differences were observed. Since all of the tested inks absorb sufficiently in the lower 200 nm region, the monitoring wavelength of the CE instrument was set to 214 nm. The detector was also

TABLE 1—*Listing of fountain pen inks investigated.*

Ink #	Color	Manufacturer	Country of Origin
1	Blue	Cross	USA
2	Black	Cross	USA
3	Blue-black	Parker	USA
4	Washable blue	Parker	USA
5	Permanent black	Parker	USA
6	Royal blue washable	Parker	France
7	Permanent blue	Parker	France
8	Blue	Pilot	Japan
9	Black	Pilot	Japan
10	Blue	Lamy	Germany
11	Black	Lamy	Germany
12	Royal blue	Pelikan	Germany
13	Brilliant black	Pelikan	Germany
14	Royal blue	Geha	Germany
15	Brilliant black	Geha	Germany

set to scan the region between 190 and 598 nm continuously with a data acquisition rate of 8 Hz.

Initial separations were performed in 50 mM borate buffer at pH 8.0 and under an applied potential of +25 kV. Due to the 200-times shorter optical pathlength of the detection cell in the CE instrument the 0.1% ink samples used in the spectrophotometric studies gave only signals of very low intensity. Therefore a concentration study of the analyte was performed starting with 100% ink and testing 10-fold aqueous dilutions down to 0.1% ink. For the purpose of the method development process, 10% solutions of ink were found to be suitable. They were pressure injected for 4 s. The injection time corresponds to an injection volume of roughly 4 nL of ink solution, i.e., 400 pL of pure ink. However, due to the instrument design a minimal sample amount of 10 μL is required to assure reproducible injections. It was observed that all of the 5 inks tested exhibit qualitatively different separation patterns in their electropherograms. For the optimization of the separation parameters, ink 1 (Cross blue) and ink 2 (Cross black) were chosen since their composition seemed to be most complex. In the electropherogram mainly negatively charged species were observed, which eluted later than a neutral marker (acetone). Under the given conditions (pH 8.0) the electroosmotic flow (EOF) within the capillary is sufficiently strong to transport negatively charged analyte components against the direction of their electrophoretic mobility towards the cathodic end of the capillary and past the detector window.

Ink is composed of compounds which can be divided into two fractions: colored and noncolored. By means of the diode array detector the separation was not only monitored at $\lambda = 214$ nm but UV/Vis spectra were accumulated over the time of the separation as well. From the absorbance pattern in the visible region of several of the numerous peaks, the separated compounds can be assigned to either one of these fractions.

In a buffer study a number of different buffers were tested for their suitability to separate writing inks. In addition to borate buffer (pH 8.0), phosphate buffers (pH 3.0 and 7.0), acetate buffer (pH 5.0), citrate buffer (pH 5.0) and succinate buffer (pH 5.5) were prepared. The two latter ones have a high self absorbance in the lower UV region and provided only poor separations under both positive and negative potential. With acetate buffer we failed to achieve good separations for water-soluble writing inks although Fanali and Schudel (26) reported similar conditions to be optimal for the separation of black and red inks from felt-tip pens by CE. The EOF in the pH regions covered by these three buffer systems can change significantly with only slight changes in the pH of the buffer solution. This can cause some of the irreproducibilities of the migration times observed. Under both positive and negative polarity, species were separated and detected. This implies that in the region of pH $\leq$ 6, some of the formerly negative components become neutral or positively charged. This also explains why in the electropherogram with phosphate buffer at pH 3.0, within reasonable analysis time, fewer components were observed than in a separation with phosphate buffer pH 7.0. From this initial study borate buffer pH 8.0 and phosphate buffer pH 7.0 were determined to be suitable as background electrolytes (BGE).

Each of the two buffers provides a condition which results in a different separation for inks 1 and 2. A 100 mM borate buffer generates a current of ca 30 μA with an applied potential of +25 kV. The majority of peaks of ink 1 will have migration times of less than 10 min. Three major groups of unresolved peaks are observed. For ink 2 all species pass the detector in under 5 min migration time (Fig. 1A). Two major unresolved peaks with many sharp shoulders are observed. In 50 mM phosphate buffer of pH 7.0, a current of ca 80 μA is observed and all species migrate slower. For ink 1 the analysis time exceeds 15 min. Peaks are spread out but not resolved. This is analogous to ink 2. In phosphate buffer the analysis time extends to 7 min. The prolonged separation does not provide for base line separation of the components.

Assuming the presence of small amounts of synthetic azo-dyes or other nonpolar components in the inks, we expected the utilization of micelles as a pseudostationary phase to facilitate the separation. Negatively charged (SDS), neutral (Brij 35) and positively charged (CTAB) surfactants were dissolved in the BGE at concentrations above their critical micellar concentrations. Neither the different micellar solutions alone nor mixed micellar solutions (SDS and Brij 35) in either buffer brought a significant enhancement in the resolution. It was therefore concluded that the components of blue and black inks interact with the tested micellar systems to only a very limited extent.

The concentrations of both phosphate and borate buffer were varied to find an optimum. For borate buffer, improved resolution was obtained when its concentration was increased from 20 to 200 mM. A higher ionic strength of the buffer system results in a decrease of the EOF which then leads to the improved resolution observed. Lower concentrated buffers created lower currents and very short analysis times, but also limited resolution. In phosphate buffer systems, increasing concentrations caused increased baseline noise levels and analysis times without significantly improving the resolution. Mixed background electrolytes composed of borate and phosphate buffer in varying ratios were tested to find a compromise for a buffer system providing a stable base line, reasonable analysis time and maximal resolution for all ink components. A BGE composed of 3 parts 50 mM phosphate buffer pH 7.0 and 1 part 100 mM borate buffer pH 8.0 was found to be the optimum in this study.

The result of an electrophoretic separation can be effectively controlled via variations in the hydrophobicity of the BGE. The addition of organic solvents will result in an increased hydrophobic character of the buffer system resulting in a decrease of the EOF and frequently in the induction of changes in the hydration sphere of analytes. For the separation of water soluble inks, increasing amounts of methanol (MeOH) added to the BGE have shown to be decisive. Phosphate buffer, borate buffer and the mixed buffer systems provided improved separations when 10, 20 and 30% of methanol were added, respectively. The BGE composed of equal parts of 50 mM phosphate buffer and 100 mM borate buffer with 10% MeOH allowed for complete resolution of almost all components although the peak shapes were not perfect and the analysis time exceeded 15 min. A 100 mM borate buffer with 20% MeOH gave very promising separations for both inks within 10 min. The separation of ink 2 in this buffer system is shown in Fig. 1B. To achieve an even better resolution using this buffer the length of the capillary was extended from 37/30 cm to 57/50 cm. An increase in the distance for the separation usually leads to separations with improved resolutions but also increased analysis times. Within 30 min all the components of both inks 1 and 2 (Fig. 1C) were almost baseline separated. Furthermore it was found that the use of ink samples dissolved in 4 mM borate buffer instead of in water contributed to enhanced resolution and peak shape. This phenomenon has been discussed and utilized in sample stacking procedures for the analysis of samples of very low concentrations (36).

Therefore all further studies of blue and black fountain pen inks were carried out in 57/50 cm long capillaries filled with a 100 mM borate buffer at pH 8.0 containing 20% MeOH.

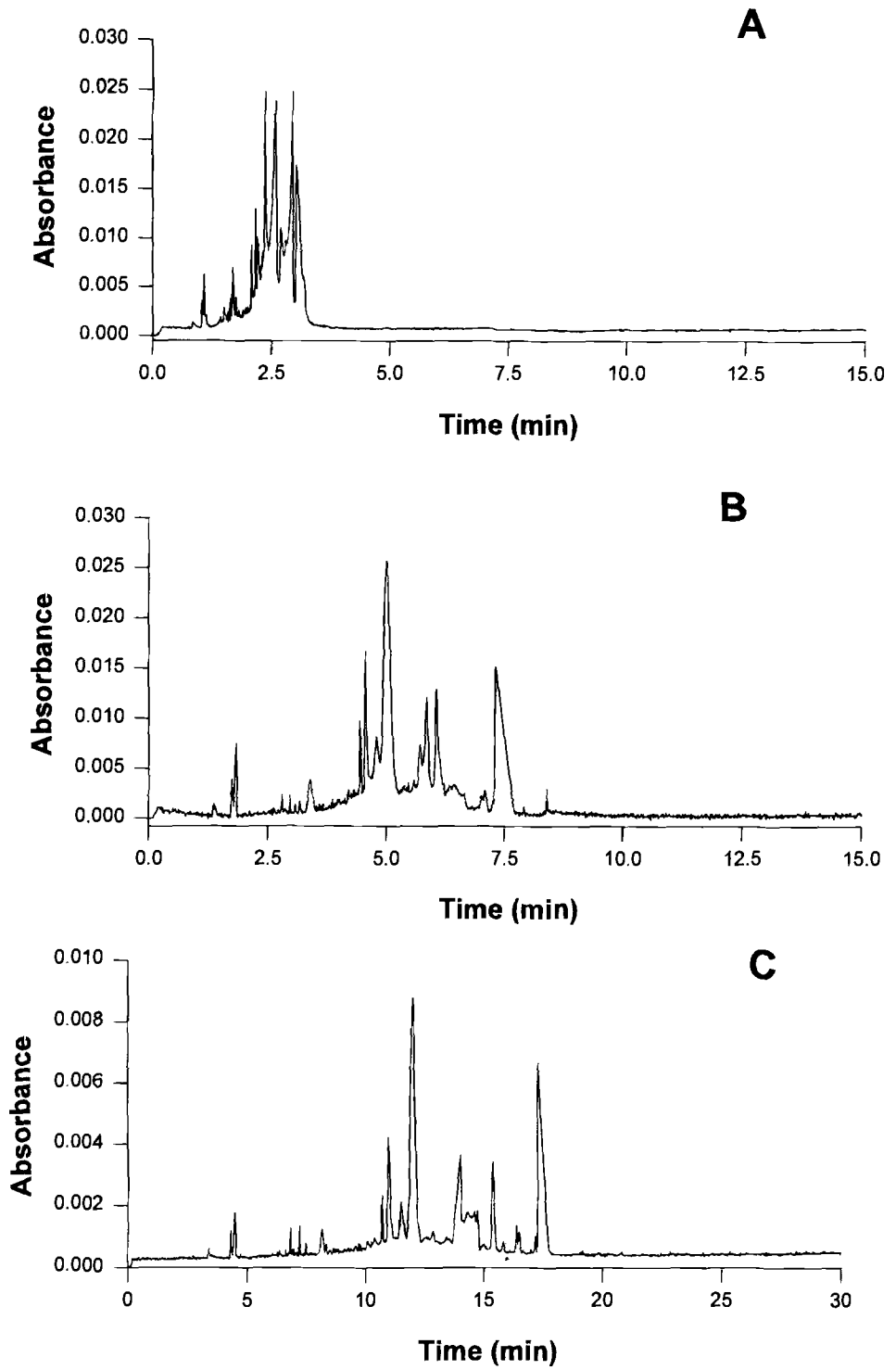

FIG. 1—*Electropherograms of ink 2 (Cross black, USA) during different stages of the method development process, detection at* $\lambda = 214$ *nm. A. Separation in borate buffer 100 mM pH 8.0, B. Separation in borate buffer 100 mM pH 8.0 and 20% MeOH, capillary length 37/30 cm, and C. Separation in the same buffer system as B., capillary length 57/50 cm.*

Comparison of Inks

Under these optimized conditions, 15 ink samples of different manufacturers and/or manufacturing countries were separated. Almost all inks were baseline separated into their components within 30 min. Apart from the obvious differences of the sample color, the electropherograms show enough evidence to qualitatively distinguish among different blue and different black inks. A few interesting observations were made.

Blue inks differ either in the migration time of various tall peaks, in the lack of peaks in certain regions or in the exhibition of distinctively different "fingerprint" patterns. Three electropherograms of blue inks are shown in Fig. 2. The electropherogram of ink 4 (Parker washable blue, USA) (Fig. 2A) is characterized by

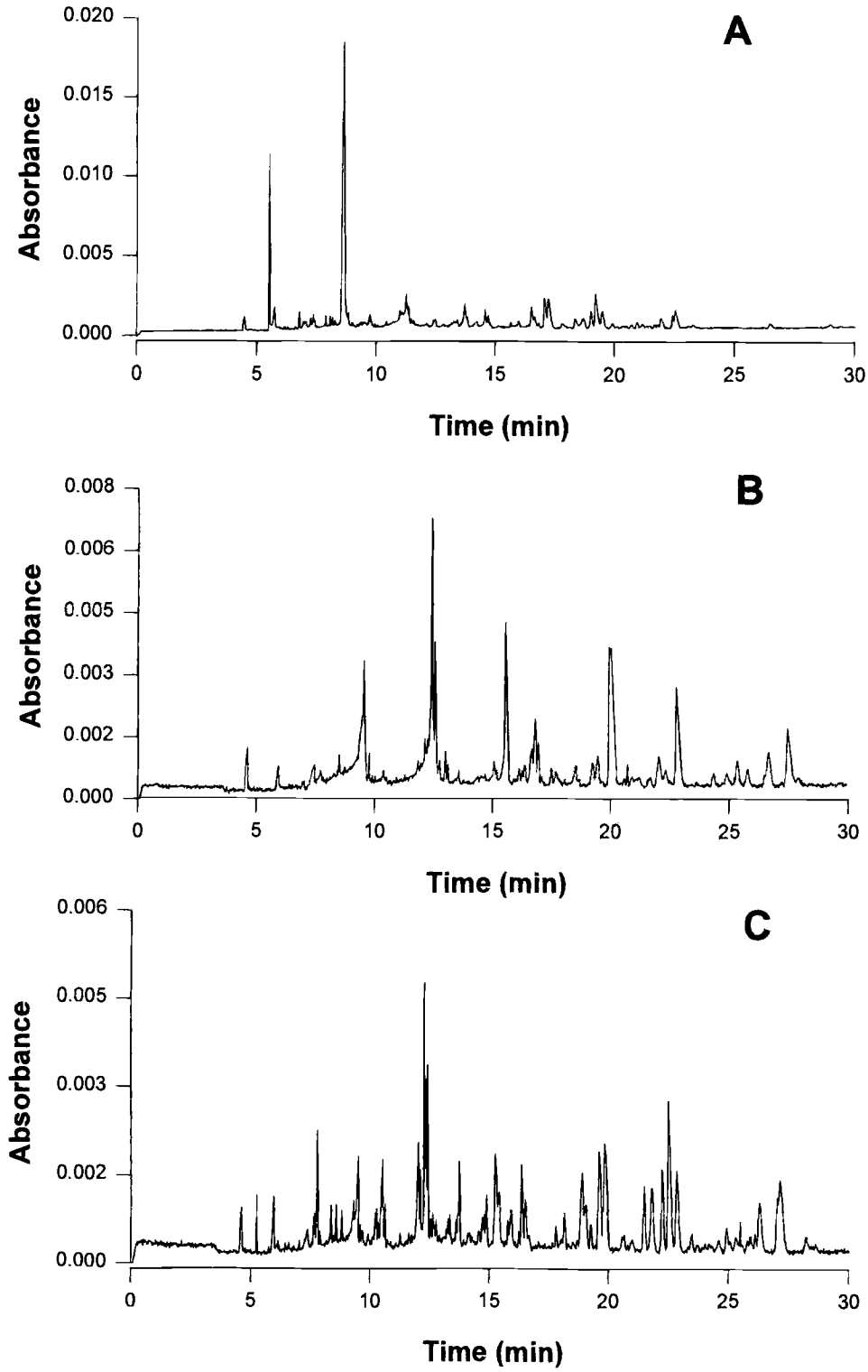

FIG. 2—*Electropherograms of various blue inks obtained under optimal separation conditions, detection at* $\lambda = 214$ *nm. A. Ink 4 (Parker washable blue, USA), B. Ink 10 (Lamy blue, Germany), and C. Ink 14 (Geha royal blue, Germany).*

a peak of high intensity with a migration time of 8.6 min. Ink 10 (Lamy blue, Germany) (Fig. 2B) and ink 14 (Geha, royal blue, Germany) (Fig. 2C) exhibit very complex electropherograms with the most prominent peak at 12.4 min. Although very similar at first glance the separation patterns differ sufficiently to distinguish between these two inks. It also was found that the migration times of peaks in electropherograms of ink 4 (Parker washable blue, USA) and ink 6 (Parker royal blue washable, France) are almost identical. For late eluting peaks the migration times differ only by 30 s. The spectra of major peaks at 6.8 min, 12.0 min and 17.1 min are identical (correlation between normalized spectra > 0.99). Consequently it is assumed that both inks are of the same composition.

Electropherograms obtained from black inks can also differ

distinctly. Ink 9 (Pilot black, Japan) (Fig. 3A) gives a very simple and completely different separation pattern from the other black inks. A brief glance at the electropherograms of ink 11 (Lamy black, Germany) (Fig. 3B) and ink 13 (Pelikan brilliant black, Germany) (Fig. 3C) may create the impression that the composition of these two inks is identical. Careful observation reveals a difference in peak height for a peak with a migration time of 19.5 min found in both electropherograms. Furthermore subtle differences in the peak heights of two minor peaks with migration times of 15.3 min and 15.4 min and in the general peak pattern between

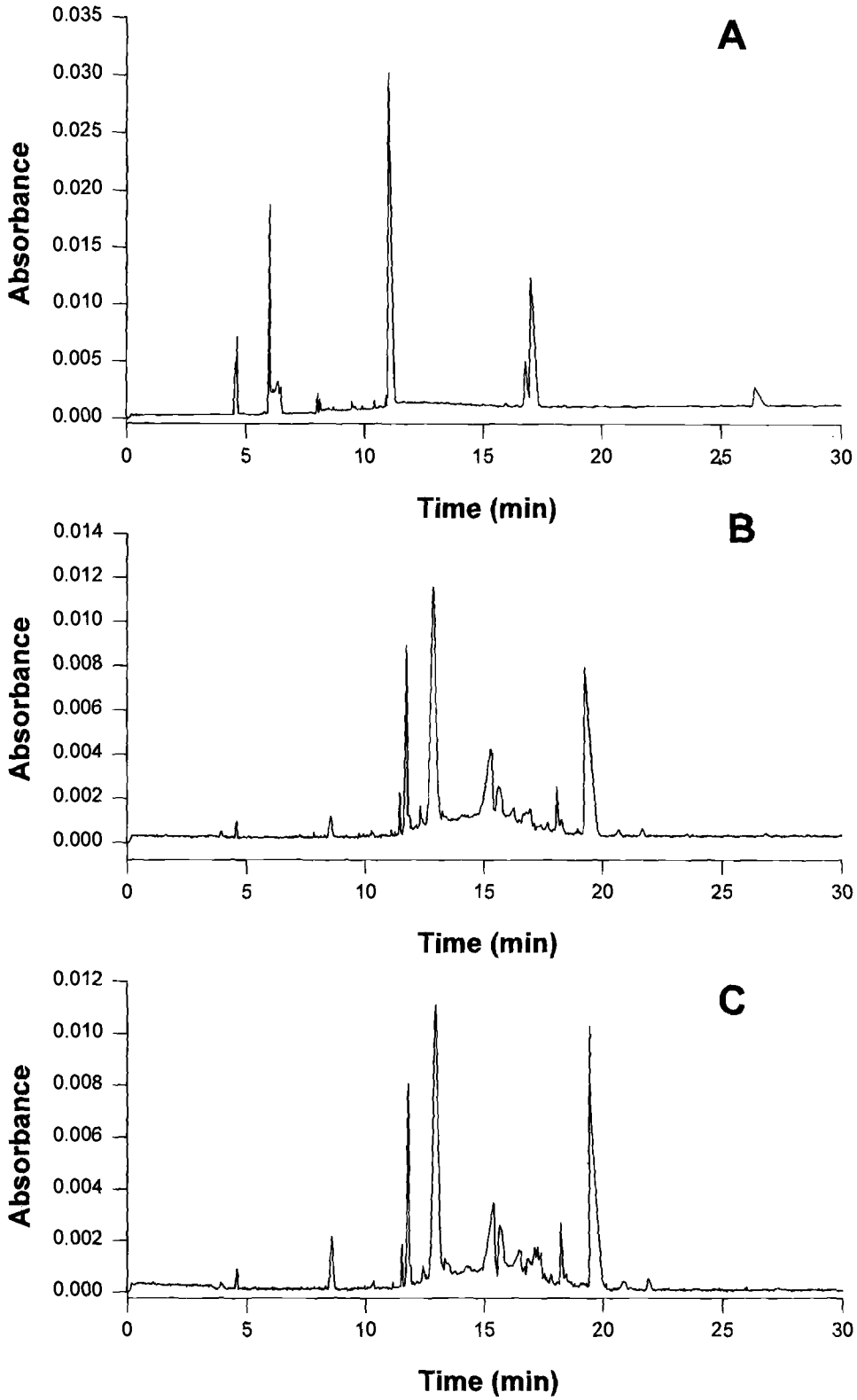

FIG. 3—*Electropherograms of various black inks obtained under optimal separation conditions, detection at λ = 214 nm. A. Ink 9 (Pilot black, Japan), B. Ink 11 (Lamy black, Germany), and C. Ink 13 (Pelikan brilliant black, Germany).*

the major peaks at 12.8 and 19.5 min indicate that these inks are not identical. Spectra of separated compounds in this region did not correlate as well (coefficients of 0.92–0.94).

The reproducibility of these separations was tested on a run-to-run basis and day-to-day basis with 5 replications each. The relative standard deviation with respect to migration time and peak area of the main components in consecutive runs was below 2% if each separation was followed by a capillary rinse with NaOH and SDS containing buffers at elevated temperatures (40°C). The same was true for separations performed on consecutive days using the same capillary. Electrophoresis of ink solutions in capillaries of different batches or manufacturers were found to be of lower reproducibility due to the high variability of the surface characteristics of fused silica. The use of standards may be advised in those situations.

Electrophoresis of Inks Extracted from Paper

Preliminary studies on the separation of ink components extracted from paper by CE were carried out. Samples of dried handwriting with some of the previously investigated inks on white Hammermill Tidal®DP printer paper were investigated. The extraction procedure included the removal of 6 circular pieces of paper with a 14 gage blunt syringe needle. This corresponds to a total expunged area of 12.1 mm^2. Due to the rather large diameter of the punching device (1.6 mm) the entire area of the sample pieces was not covered with dried ink and hence less ink was analyzed. The same amount of substrate material was removed for a blank study. The sample pieces were placed in an Eppendorf tube and 50 μL of the extraction solvent was added. Earlier, pyridine, ethyl acetate, acetone, ethanol (EtOH), MeOH and mixtures of the latter solvents with water of varying ratios were tested to determine the best solvent for the removal of ink from paper. Among those solvents of varying polarity, a mixture of EtOH and H_2O 1:1 was found to extract most efficiently based on visual evaluation of the extract. These findings agree with recommendations made by Brunelle et al. for the extraction of water-soluble non-ball point inks (10). To improve the extraction process, the sample was placed in an ultrasonic bath for 15 min.

The ink extract (25–30 μL) was transferred to a microvial and subjected to separation by CE. In the electropherogram distinctly different separation patterns among blue and black inks were observed. The separation of the blank extract did not yield any signals when the absorbance was monitored at 214 nm. The electropherogram of an extract of handwriting using ink 11 (Lamy black, Germany) is shown in Fig. 4. Compared to the electropherogram of a solution of neat ink 11, the separation pattern was found to be different, presumably due to variations in the degree of extractability of the various ink components.

Due to the relatively short optical pathlength in CE, the sensitivity of the detection is limited. An increase in the sample amount injected can improve signal intensity, but is usually accompanied

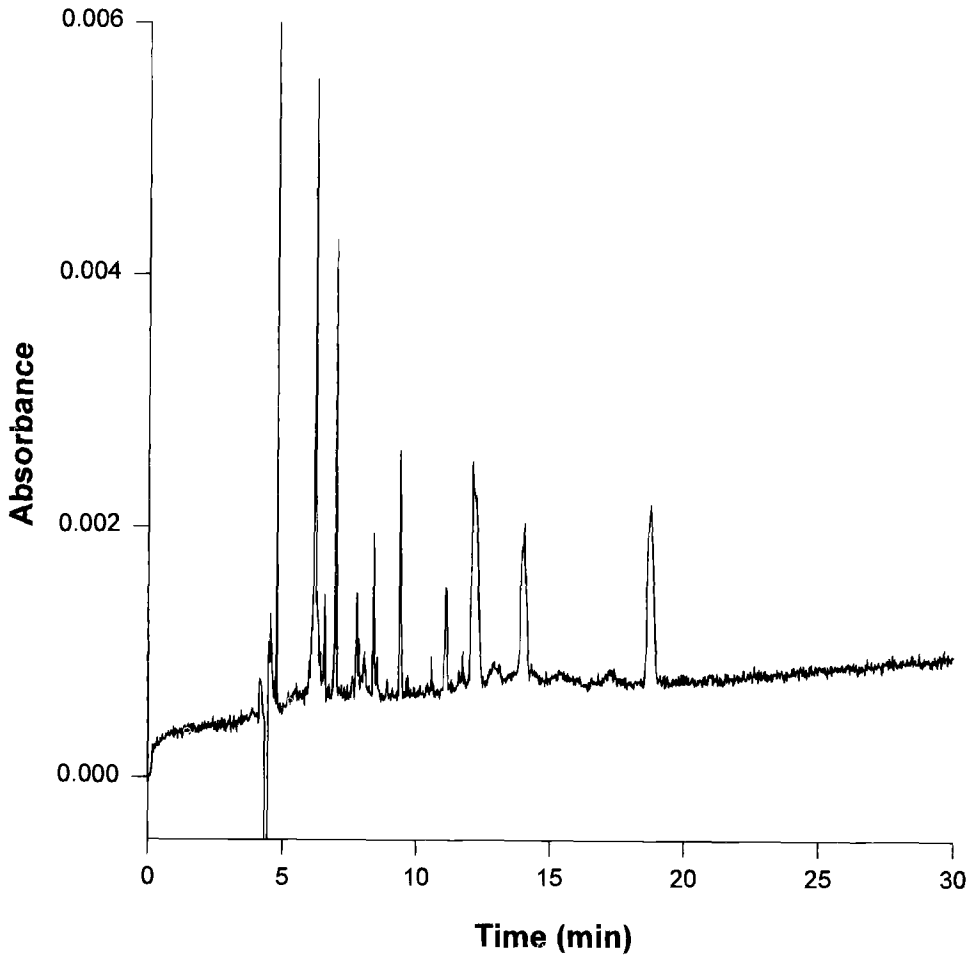

FIG. 4—*Electropherogram of an extract of ink 11 (Lamy black, Germany) from paper obtained under optimal separation conditions, detection at* $\lambda = 214$ *nm,* $t_i = 16$ *s.*

with a loss of resolution. In a systematic study it was found that injection times of t_i = 32 s (i.e., $V_i \approx$ 33 nL) for blue inks and t_i = 16 s (i.e., V_i = 16.5 nL) for black ink extracts represent a good compromise with respect to signal intensity and resolution. Future studies will address possibilities of on-line preconcentration procedures as well as systematic evaluations of extraction parameters including the reproducibility of the procedure.

Conclusions

With the analysis of 15 blue and black ink samples of different manufacturers by capillary electrophoresis, it was shown that, under optimal separation conditions, baseline resolution for almost all components of each ink can be achieved and a qualitative distinction between different blue and black inks can be made. Separations have been shown to be reproducible from run-to-run and from day-to-day. The developed method allows the efficient separation of water-soluble inks within reasonable analysis times and with minimal reagent and sample volume requirements. Due to the resolution power of this technique, the obtained electropherograms can be used as a basis for the identification and differentiation between inks from different manufacturers. Based on these results and those of our preliminary study of dried inks extracted from paper, capillary electrophoresis has the potential to be used as an efficient analytical technique for the analysis of inks in a forensic laboratory.

In future studies methods will be developed to increase the sensitivity of the analysis by CE. Preconcentration steps may be needed along with more sensitive detection schemes such as laser induced fluorescence (LIF).

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