Capillary Electrophoresis of Ballpoint Pen Inks

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Two capillary electrophoretic (CE) methods have been designed to differentiate and identify organic and inorganic dyes present in black and blue ballpoint pen inks. CE was chosen because the technique provides chemical information that can provide better discrimination between ink formulations than thin-layer chromatography (TLC) when comparing ink samples during document analysis. One CE buffer was designed to separate and analyze 10 blue ballpoint pen ink formulations. An alternative buffer was designed to separate and analyze 15 black ballpoint pen inks and 2 different inkjet cartridge products from the same manufacturer. The capillary detection method using a photo-diode array (PDA) to acquire absorbance data (190-600 nm) provides lambda max (λ_{max}) and characteristic UV-Vis spectra for analytes. Simultaneous spectral data collection avoids the necessity for densitometry measurements. Mobility values (μ_{ep}) calculated from a migration time replace hand-measured TLC R_f values. The sample electropherograms are reproducible with 2 µg/mL concentration limits of detection, which is superior when compared to TLC separations. Specific chemical identification can be determined based on spectral and mobility value match to reference dye standards. All inks were differentiated from one another in the respective category (blue, black, or inkjet formulation). When possible, chemical compounds were identified in a particular ink to aid characterization. CE offers additional advantages over TLC, including lower reagent consumption, smaller sample requirements, lower detection limits, quantitative analysis, method automation, direct reference comparison, electronic data storage, and searchable spectral libraries. Other complimentary techniques (TLC, positive- and negative-ion mode electrospray-ionization mass spectrometry) can be performed because little sample (20 nL) is consumed for CE analysis. The same CE buffers formulated for ballpoint pen inks have been applied to color inkjet printer formulations, food dyes, gel pen inks, and textile dyes.

Introduction

Determination of ink sources used on different evidentiary materials can be a key priority for forensic document examiners. Inks are complex mixtures containing colorants, vehicles, and additives adjusted in composition to produce the proper writing characteristics (Hunger 2003). Colorants are compounds that give ink the desired color and can include any or all of the following chemical classifications: pigments and/or acidic, basic, azoic, direct, disperse, reactive, and solvent dyes. Colorants are often the focus of ink analysis because of their light absorption and emission properties which can be probed with various analytical methods employing optical detection schemes. Detection of vehicles and/or additives can greatly aid forensic document examiners, but their chemical structures are often a highly guarded secret within ink formulations as are the colorants themselves. Data interpretation to unambiguously identify specific ink components is easier if a chemical separation step precedes detection.

Current typical forensic techniques involve ink extractions from a questioned document followed by TLC separation (ASTM 1996; Tebbett 1991). Investigative knowledge gained from TLC is limited to colored bands that are correlated to a calculated retardation factor (R_f). Reflectance-mode

densitometry can probe the spectral absorbance of a specific band on the TLC slide (Aginsky 1994). TLC is also currently utilized as the forensic chemical examination for inkjet-printed documents (LaPorte 2005). Limited research has been applied to characterize inkjet dyes any further despite significant advances in analytical instrumentation (Mazzella 1999). CE has many desirable characteristics that make this technique suitable for document analysis. CE provides the possibility for minimal sample preparation, fast analysis time, full UV-Vis spectral analysis, electronic data storage, searchable library algorithms, minimal sample and reagent consumption, lower detection limits, and measurable physical and chemical properties.

CE involves the separation and differential analyte migration within a capillary filled with conductive buffer solution during an applied electric field. An analyte's electrophoretic mobility is dependent upon molecular shape-to-charge characteristics. In a normal polarity experiment a small injection volume (~ nLs) is introduced to the buffer-filled capillary. Application of an electric potential causes analyte migration via 2 transport phenomena. The 1st phenomenon involves the attraction and migration of charged species towards the oppositely charged electrode. The 2nd phenomenon allows CE methods to simultaneously detect neutrals, cations, and anions under specific buffer conditions. Electroosmotic flow (EOF) is caused by the inherent internal wall surface charge of fused-silica capillaries (Weinberger 2000). Rapid EOF occurs at high pH buffer conditions and overcomes the anionic migration that could prevent detection. Most organic dyes in ink formulations are charged and make CE a suitable separation technique.

There have been numerous studies performed on specific compound classifications or ink formulations (Fanali and Schudel 1991; Croft and Lewis 1992; Burkinshaw, Hinks, and Lewis 1993; Jandera, Fischer, Stanek, Kucerove, and Avonicek 1996; Rhodes, McManus, Vogt, and Heineman 1997; Vogt, Vogt, Becker, and Rhode 1997; Rhode, Vogt, and Heineman 1998; Zlotnick and Smith 1998; Vogt, Becker, and Vogt 1999). Recent Federal Bureau of Investigation (FBI) studies have resulted in 2 capillary electrophoretic buffer systems for separating and chemically identifying charged, organic dye compounds utilized in black- and blue-colored ballpoint pen inks (Brewer, Hagan, and Egan 2005; Egan, Hagan, and Brewer 2005). Two characteristic parameters are simultaneously obtained: mobility factor (μ_{ep}) and time-resolved UV-Vis spectra (a PDA detector is required). Together the collected parameters can be utilized to identify the chemical. Chemical reference libraries can be compiled to search against known organic dyes. The excess extraction can be analyzed by further techniques to increase the discrimination power between ink formulations.

Methods and Materials

To devise a CE protocol and enable it to be casework compatible, method development focused on specific procedural requirements:

(1) minimal sample preparation comparable to TLC extractions,

(2) a faster method which would collect more qualitative/quantitative data with respect to TLC,

(3) ease of implementation without using excessive experimental protocols, and

(4) the ability to adapt the technique when new knowledge is gained.

To this end, one buffer was designed to adequately separate cationic dyes (general class of basic dyes), and another buffer was designed to separate anionic dyes (general class of acidic dyes). These buffers were successful in investigating 15 black and 10 blue ballpoint pen inks with specific dye compound identification by comparing electrophoretic mobility (μ_{ep}) and absorbance spectra to standard chemical references. Libraries are currently being compiled that consist of electropherograms, absorbance spectra, digital TLC photographs, and MS data of dye reference standards and extracted ink samples. These libraries could be utilized to compare and characterize unknown samples in the future.

Presented in this study are single examples of ink samples encountered in different questioned document cases. Two unique buffers with differing separation conditions were utilized for ballpoint pen ink CE analysis. Confirmatory TLC experiments were performed in accordance with the ASTM standards using solvent system I (ASTM-E1422-96 1996). Positive- and negative-ion mode electrospray ionization mass spectrometry (ESI-MS) measurements were performed on dilutions of ink solutions removed from pen cartridges. Direct sample infusion into a Thermo-Finnigan LCQ ion-trap MS with an electrospray ionization source was utilized to

collect mass spectra. Different tuning conditions were utilized based on the organic compounds detected in the CE methods. Tuning parameters were optimized on reference standards of dye compounds and instrumental settings differed for each analyte.

A Hewlett Packard/Agilent 3D CE system, equipped with a photo-diode array (PDA) detector, was chosen to perform all inkjet ink separations. Agilent ChemStation software provided instrumental control, data storage, and reference spectra for sample analysis. All black ballpoint pen ink and colored inkjet cartridge samples were separated using a buffer comprised of 25 mM CHES [2-(N-cyclohexylamino)ethanesulfonic acid] (Sigma-Aldrich) and 5 mM β-cyclodextrin (Sigma-Aldrich) and adjusted to a pH of 8.80 with 1.0 M NaOH. Buffer solutions were filtered with 0.45 µm filters (Corning). The effective length (L_d) of the 75 µm i.d. fused silica capillary was 49.5 cm, and the total length was 58.0 cm (L_t). Methanol solutions of extracted and standard samples were hydrodynamically injected in the capillary for 10 s with 25 mbar of pressure. Methanol was utilized for pen ink extractions because pyridine interferes with the PDA detection of dye samples and causes capillary current fluctuations.

Although pyridine can extract certain organic dyes more effectively than methanol, the increased PDA sensitivity, when compared to visual color observation, overcomes the solvent extraction efficiency difference. Water was utilized for the inkjet samples because aqueous extraction of printed documents worked more effectively than methanol extraction. Voltage was applied in normal mode (with the outlet electrode negative with respect to the inlet electrode) at 25 kV and resulted in currents of approximately 19 µA (430 V/cm). Capillary temperature was maintained at 30 °C with heated air utilizing the HP Chemstation software package. Full separation runs were completed in less than 10 minutes. Prior to injection, rinse solutions were used to regenerate and cleanse the capillary for subsequent runs. These rinsing steps included a 1-minute flush with 1.0 % bleach (Clorox), 2-minute flush cycles with 0.1 M NaOH and water, and then a 2-minute capillary fill with the separation buffer. UV-Vis spectra were collected from 190-600 nm, and data channels were utilized to monitor real-time absorbance at 214 nm and the electrical current trace.

All blue ballpoint pen inks were extracted identically to the method used for the black ink and inkjet cartridges. The CE setup was different because the dyes utilized in blue inks are primarily cationic. A Beckman Coulter P/ACE MDQ CE system, equipped with a PDA detector, was chosen to perform all blue ink samples. The separation buffer was comprised of 70/30 (volume/volume) mixture of sodium acetate buffer/methanol titrated to pH = 4.40 with concentrated glacial acetic acid (Fisher Scientific). The sodium acetate buffer was comprised of 25 mM sodium acetate (Fisher Scientific), 25 mM glacial acetic acid, and 10 mM CTAB (hexadecyltrimethylammonium bromide, Sigma Aldrich). The effective length (L_d) of the 75 µm i.d. fused silica capillary was 30.0 cm, and the total length was 40.0 cm (L_t). Methanol solutions were hydrodynamically injected in the capillary for 5 s at 0.3 psi. Voltage was applied in reverse mode at – 25 kV and resulted in currents of approximately – 42 µA. Capillary temperature was maintained at 30 °C utilizing the Beckman software package. Full separation runs were completed in less than 10 minutes. CE separations of printer cartridges were performed with the anionic buffer with pH 8.80 because of the prevalence of anionic dyes encountered in inkjet formulations. Unlike the ballpoint ink samples that were extracted with methanol, CE injections were performed with inkjet cartridge samples diluted in the CE analysis buffer.

Results and Discussion

Black Ballpoint Pen Ink Analysis

Data was collected from an extracted black ink sample from Whatman filter paper (Figure 1). TLC experiments from the same black pen used for the electropherogram indicated 4 colored bands with different retardation factors. Two of the 4 bands are purple, 1 band is yellow, and the final band is blue when observed with the naked eye. From the simple TLC analysis, there is very little definitive chemical knowledge that can be discerned. Without further analytical methods, no measurable λ_{max} spectral absorption and quantitative information can be determined. The 2 purple bands are crystal violet and its demethylation product, methyl violet. The yellow band is metanil yellow, and the blue band is tentatively assigned to a copper phthalocyanine pigment. None of these chemical assignments was based on TLC. Instead, they were determined after comparison to reference standards based on the CE data presented below.

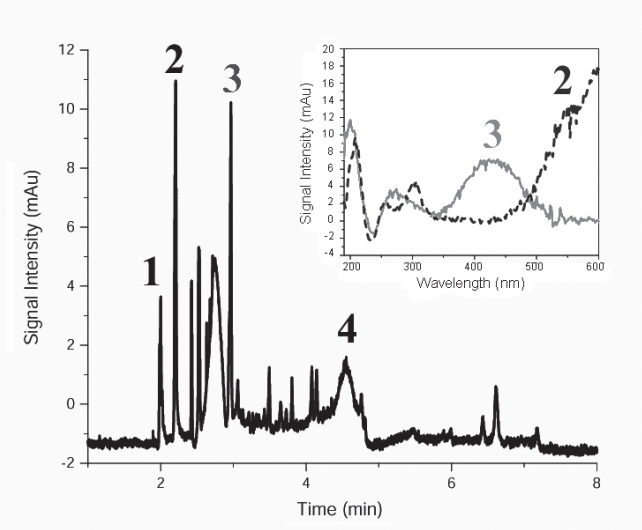

Figure 1. Data example of an electropherogram collected from an extracted black ballpoint ink from Whatman filter paper that was measured at 214 nm and contained multiple resolved peaks. The spectral inset containing PDA data represents absorbance data for resolved peaks labeled 2 and 3 in the electropherogram.

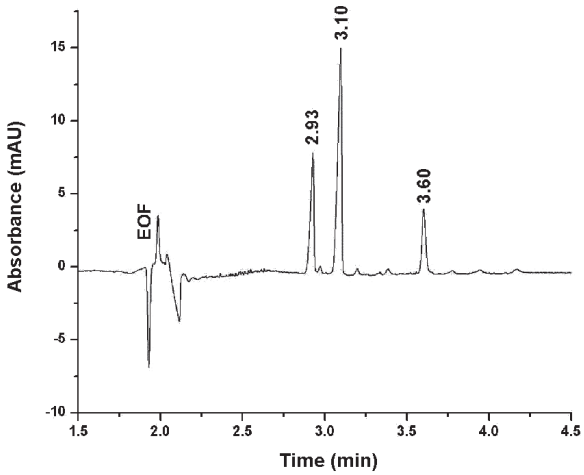

Figure 2. Three peaks are observed at 214 nm in the electropherogram of a blue ballpoint pen using the cationic dye method.

Sample analysis using CE illustrates the increased information obtained from a single sample injection. Evidence of all TLC bands is observed in an electropherogram (Figure 1). Peaks labeled 1 and 2 are positively charged compounds because the peaks appear prior to the electroosmotic flow (EOF) and neutral indicators that are detected between 2.40-3.00 minutes. Peak 2 is identified as crystal violet (t_m = 2.21 min; μ_{ep} = +0.83 x 10^{-4} $cm^2 \bullet V^{-1} \bullet s^{-1}$) and is ubiquitous in both black and blue ballpoint pen inks. The characteristic spectrum was searched against a reference standard database, and the μ_{ep} was also compared and appeared to match the crystal violet reference [μ_{ep} = (+0.78 ± 0.02) x 10^{-4} $cm^2 \bullet V^{-1} \bullet s^{-1}$]. There is no separate CE peak for methyl violet utilizing this buffer because of the short migration time, but positive-ion ESI-MS detected peaks at *m/z* 372 and 358 representing crystal violet and methyl violet, respectively. Peaks 1 and 4 are attributed to the blue TLC spot. Peak 1 is a series of 3 or 4 peaks that have been assigned to various diarylguanidine compounds. These guanidine compounds are known for their formulation inclusion to allow greater aqueous solubility of copper phthalocyanine pigments. Peak 4, a broad and weak intensity peak, has been tentatively assigned to the copper phthalocyanine pigments that are fairly insoluble in the CE buffer. Peak 3 is identified as metanil yellow (t_m = 2.96 min; μ_{ep} = -1.52 x 10^{-4} $cm^2 \bullet V^{-1} \bullet s^{-1}$) because of the similarity to the reference [μ_{ep} = (-1.49 ± 0.03) x 10^{-4} $cm^2 \bullet V^{-1} \bullet s^{-1}$]. Other peaks are present in the electropherogram yet have not been identified. These unidentified peaks are indicative of other chemicals utilized in the particular ink composition. None of the unassigned peaks exhibit visible absorbance and are probably not due to organic dye molecules. Additional black ballpoint pen inks were studied with CE and led to discrimination of all 15 black pen inks that were investigated (Egan, Hagan, Brewer 2005).

Blue Ballpoint Pen Ink Analysis

In the electropherogram (Figure 2) obtained for a blue ballpoint pen using the CE buffer with high resolution for cationic (positively charged ions) dye compounds, 3 peaks are observed with migration times of 2.93, 3.10, and 3.60 minutes. Based on the EOF migration time (labeled EOF in Figure 2), the μ_{ep}'s of the species were calculated to be -1.41, -1.56 and -1.92 x 10^{-4} $cm^2 \bullet V^{-1} \bullet s^{-1}$, listed in order of increasing migration time, where the negative sign indicates a mobility vector opposing the EOF direction. In addition to μ_{ep} values, the UV-Vis spectrum for each peak was

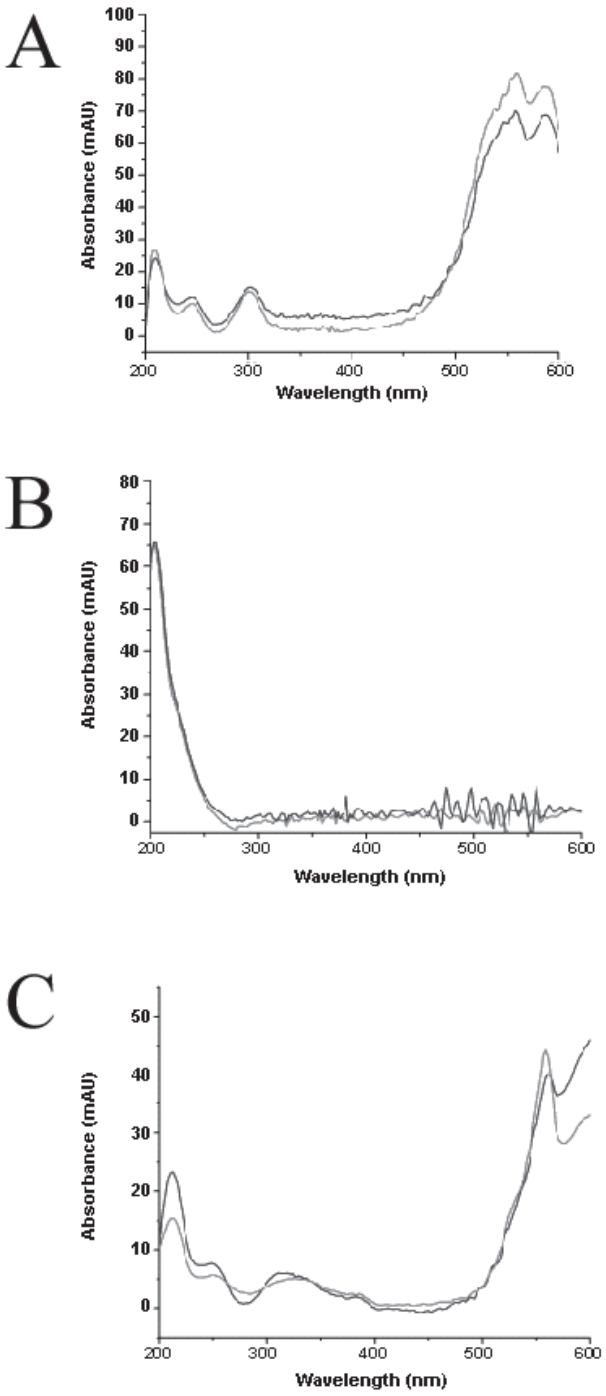

Figure 3. UV-Vis spectra of the peaks presented in Figure 2 are overlaid with the UV-Vis spectra for the best match from spectral library searches: (A) 2.93 minutes, best match—crystal violet, "calculated similarity value" = 0.9988; (B) 3.10 minutes, best match—diaryl-guanidine, "similarity" = 0.9693; (C) 3.60 minutes, Victoria pure blue BO (nearly identical matches were obtained with Victoria Blue B and Victoria Blue R), "similarity" = 0.9779.

recorded (Figure 3). UV-Vis spectral library searches provided the best match data reported. The first peak (2.93 minutes) is assigned to crystal violet based on the UV-Vis spectrum similarity of 0.9988 and the μ_{ep} value being a close match to the independently measured μ_{ep} of crystal violet = (-1.45 ± .03) x 10^{-4} $cm^2 \bullet V^{-1} \bullet s^{-1}$. Additional assignment verification was provided by positive-ion mode ESI-MS, which resulted in a peak at *m/z* 372.7 indicative of crystal violet upon loss of a chloride counter-ion ($[M\text{-}Cl]^+$). Another peak present at *m/z* 358.7 indicates presence of pentamethylpararosaniline upon loss of a chloride ion (also known as methyl violet). Methyl violet is a common degradation product of crystal violet that is formed by demethylation initiated by ultraviolet radiation absorption (Grim, Siegel, and Allison 2002). Ink manufacturers do not purchase dyes in pure form, and it is common to observe impurities such as methyl violet in inks. In fact, multiple methyl violet structures (penta- and tetra-methylpararosaniline) were also observed with CE and ESI-MS in the purchased crystal violet dye standard (Sigma-Aldrich, ≥ 90% pure) used in this study.

The 2nd peak (3.10 minutes) is not a dye because there is no detectable absorption for visible wavelengths (Figure 3B). The μ_{ep} value (-1.56 x 10^{-4} $cm^2 \bullet V^{-1} \bullet s^{-1}$) is a match with a diarylguanidine component [μ_{ep} = (-1.56 ± .02) x 10^{-4} $cm^2 \bullet V^{-1} \bullet s^{-1}$] stored in the database that was observed for several dye standards. Diarylguanidines are used by the dye industry to form salts with acidic dyes or pigments that would be otherwise water insoluble. A positive-ion mode ESI-MS peak at *m/z* 240.5 suggested the diarylguanidine present in the blue ink is ditolylguanidine, which would result in a $[M+H]^+$ peak at *m/z* 240.3. It is suspected that 1,3 ditolylguanidine is used by one particular manufacturer to form salts with sulfonated copper phthalocyanine pigments (Green 1990). Evidence of copper phthalocyanine was provided by negative-ion mode ESI-MS of the same ink extraction.

The presence of multiple sulfonated copper phthalocyanines was indicated by peaks of *m/z* 814.3, trisulfonated copper phthalocyanine $[M\text{-}3Na+2H]^-$ (Conneely, McClean, Smyth, and McMullan 2001), and 734.3, disulfonated copper phthalocyanine $[M\text{-}2Na+H]^-$ (Ng, Lafontaine and Brazzeau 2002). Each blue-colored pen that was observed to contain diarylguanidine(s) also possessed copper phthalocyanine pigments as reflected by the *m/z* 734 and 814 peaks in the

negative-ion mode ESI-MS spectra. The copper phthalocyanine sulfonation process leads to multiple sulfonate groups at different ring locations, which explains the observation of multiple peaks (Green 1990). In addition, a weak UV-Vis absorption spectrum tentatively assigned to copper phthalocyanine has been observed with the anionic CE method in many pens containing diarylguanidines. However, the electrophoretic peak is often broad with low absorption intensities because of the insoluble nature of copper phthalocyanine in the buffers used and the multiple sulfonated species present. The developed CE methods alone are not enough to unambiguously characterize this pigment. This is a good example of ESI-MS as a complementary method.

The UV-Vis spectrum (Figure 3C) and μ_{ep} (-1.92 x 10^{-4} $cm^2 \bullet V^{-1} \bullet s^{-1}$) for the 3.60-minute peak exhibited the characteristics for a Victoria blue dye, but this data was not sufficient to distinguish between Victoria blue B and Victoria pure blue BO. However, a *m/z* 478.7 peak in the positive-ion mode ESI-MS allowed an assignment for Victoria pure blue BO, based on loss of a chloride ion ($[M\text{-}Cl]^+$).

Based on the data collected, the blue ballpoint pen ink was determined to consist of crystal violet and Victoria pure blue BO dyes. In addition, the ink contained ditolylguanidine and sulfonated copper phthalocyanine. The same analyses were conducted on other blue ballpoint pen inks and have been discussed elsewhere in further detail (Brewer, Hagan, and Egan 2005). The identification of 5 components was sufficient to distinguish the 10 pens investigated. Three pen inks contained more than 1 diarylguanidine compound, which aided in formula differentiation. A study conducted by Ng, Lafontaine, and Brazeau (2002) indicated similar findings. The amount of different diarylguanidines used in a dye formulation appears to be manufacturer specific. The type and quantity of diarylguanidines in an ink sample provides another aspect of formula differentiation, which could be particularly useful if comparing pens that contain the same dye formulations, but originate from different raw dye components.

Printer Inkjet Cartridge

Success with ballpoint pen ink CE analysis led to testing additional ink types used for document production. Preliminary results obtained on colored inkjet cartridges resulted in understanding that inkjet formulations contained exclusively negatively charged organic dyes. The high pH buffer utilized for black ballpoint pen inks (described above in the black ballpoint pen ink subsection) was determined to be sufficient for differentiating major inkjet manufacturers' products from each other. TLC is also capable of providing enough resolution to differentiate manufacturers' cartridges, but cannot provide the chemical detail CE has illustrated. Further data compilation on inkjet cartridges is currently underway to compile a detailed database containing analytical measurements consisting of TLC, CE, and MS results to aid questioned document examiners in either identifying the correct inkjet cartridge utilized or eliminate potential product candidates.

CE and MS data from 2 different sets of colored inkjet products from the same manufacturer can be distinguished through CE analysis (Figure 4). Cyan, magenta, and yellow colors were examined individually to better construct reference data for inclusion into the inkjet database. Mass spectra were collected for further formulation differentiation. Tentative chemical species are discussed when CE peaks suggest specific organic compounds.

According to TLC experiments, the yellow formulations contain multiple yellow dyes, with one dye appearing to be common for both products based on R_f values. Panels A and B in Figure 4 contain electropherograms for all colors of both inkjet cartridges. Inkjet yellow formulation A contains one peak [Y-A1] with a μ_{ep} of -4.82 x 10^{-4} $cm^2 \bullet V^{-1} \bullet s^{-1}$ (t_m = 5.53 min). Inkjet yellow formulation B contains 2 peaks with μ_{ep} of -3.79 x 10^{-4} $cm^2 \bullet V^{-1} \bullet s^{-1}$ (t_m = 3.97 min)[Y-B1] and μ_{ep} of -4.79 x 10^{-4} $cm^2 \bullet V^{-1} \bullet s^{-1}$ (t_m = 5.17 min)[Y-B2]. Y-A1 and Y-B2 are tentatively assigned to the same compound, tartrazine, because of the UV-Vis absorbance spectra and μ_{ep} being similar to the reference chemical. Opposite the electropherogram panels are negative-ion mode ESI-MS of directly infused cartridge samples. The 2 mass spectra exhibit different base peaks. None of the ions directly support the presence of tartrazine, but absence of some expected peaks may be due to: (1) the polysulphonated chemical groups that cause ion signal suppression or (2) multiple polysulphonated dyes in the formulation that also make it difficult to obtain a consistent spray current (Rafols and Barcelo 1997). Further investigation is necessary to analyze the best ionization conditions for these polysulphonated dyes.

TLC experiments on the cyan formulations exhibited similarities in R_f values, but there is a portion of both cyan formulations that remain at

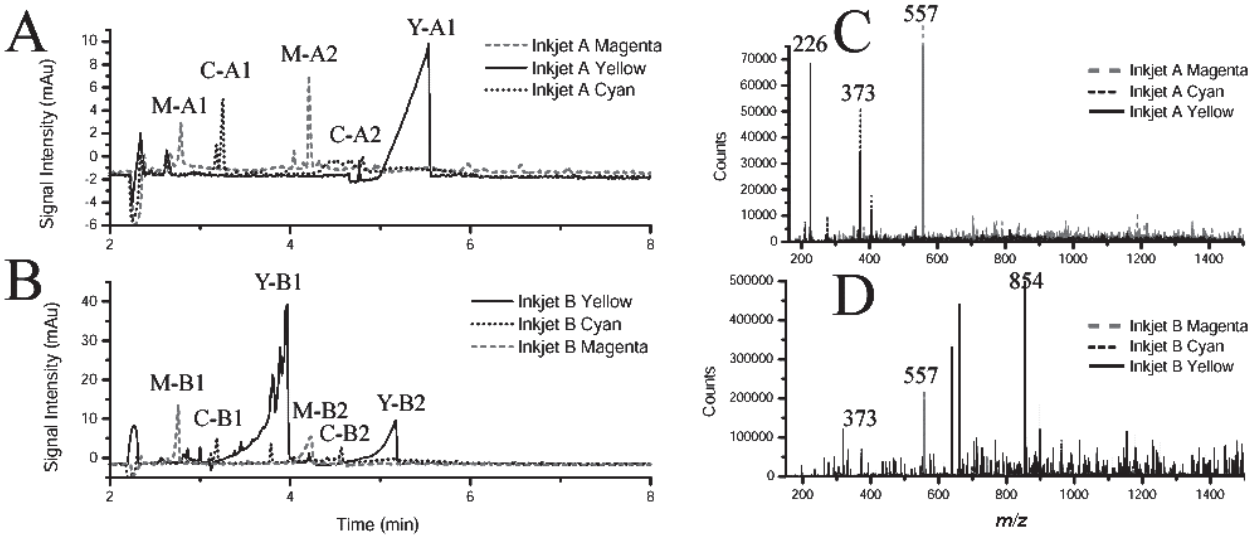

Figure 4. Illustration of different products from the same manufacturer that can be distinguished through CE analysis. Panels A and B contain overlaid individual electropherograms for colored inkjet cartridges from formulation A and B, respectively. Panels C and D contain negative-ion mode ESI-MS data collected by direct infusion of dilute cartridge ink solutions from both inkjet products.

the spotting origin, possibly indicating a pigment. CE analysis of cyan formulation A (Panel A) indicates one definitive peak with μ_{ep} of -2.36 x 10^{-4} $cm^2 \bullet V^{-1} \bullet s^{-1}$ (t_m = 3.25 min) [C-A1]. A 2nd broader peak [C-A2] is present in the same cyan formulation A and may support the presence of a blue pigment. Inkjet cyan formulation B has 2 peaks with μ_{ep} of -2.32 x 10^{-4} $cm^2 \bullet V^{-1} \bullet s^{-1}$ (t_m = 3.19 min)[C-B1] and μ_{ep} of -4.15 x 10^{-4} $cm^2 \bullet V^{-1} \bullet s^{-1}$ (t_m = 4.57 min)[C-B2]. The absorbance spectra and μ_{ep}'s for the 1st peak in both cyan formulations agree well with the compound erioglaucine. Negative-ion ESI mass spectra of the 2 cyan formulations also contain significant peaks at *m/z* 373 and 769, assigned to erioglaucine charged species $[M-2Na]^{2-}$ and $[M-Na]^-$, respectively. Cyan formulation B has another peak around 3.80 minutes that exhibits no visible absorption and has not been identified at this time. This peak does give further discrimination between the 2 different cyan inks.

Inkjet magenta formulation A and magenta formulation B CE results suggest a common organic dye as a peak appearing with μ_{ep} of -1.23 x 10^{-4} $cm^2 \bullet V^{-1} \bullet s^{-1}$ (t_m = 2.79 min)[M-A1] for magenta formulation A and μ_{ep} of -1.27 x 10^{-4} $cm^2 \bullet V^{-1} \bullet s^{-1}$ (t_m = 2.76 min)[M-B1] for magenta formulation B. These peaks are assigned to sulforhodamine B. Inkjet magenta formulation A also contains a 2nd dye peak with μ_{ep} of -3.57 x 10^{-4} $cm^2 \bullet V^{-1} \bullet s^{-1}$ (t_m = 4.21 min)[M-A2] with a very sharp chromatographic peak. Inkjet magenta formulation B also contains a 2nd dye peak with μ_{ep} of -3.78 x 10^{-4} $cm^2 \bullet V^{-1} \bullet s^{-1}$ (t_m = 4.23 min)[M-B2]. Although the peaks have very similar mobility values, the peaks appear very different from an electrophoretic standpoint and are not attributed to identical chemicals. Mass spectra for both formulations show a base peak at *m/z* 557 for the common constituent, which supports the Sulforhodamine B assignment ($[M-Na]^-$). Only the mass spectrum for inkjet magenta formulation B exhibits intensity for other ions under the electrospray ionization conditions utilized.

The current CE and MS methods allow substantially more data to be collected with the same sample extraction volumes utilized for typical document examinations. Although not all collected data are understood at this time, the information does allow further differentiation of inkjet cartridge formulations. The methods discussed are capable of collecting data that is already contained in ink extractions but not easily observed with TLC alone. The inkjet printer cartridges have multiple colors that can be analyzed either as a mixture or separately. The example in this investigation illustrates that any of the 3 colors could

be used to distinguish between cartridges. Products will not always show this drastic formulation difference but the possibility exists for inkjet cartridge differentiation with a single color.

Conclusion

CE has been shown to be a powerful analytical tool for forensic analysis of dyes contained in ballpoint pen inks, the food and textile industries, and inkjet printer cartridge products. Two unique informational characteristics (UV-Vis spectrum and μ_{ep} value) can be gained and used in ink identification or differentiation. Protocols have been developed to conform to present casework scenarios and the remaining extraction solution can be further analyzed with other complementary techniques. More complete ink and dye reference standard databases will make the CE method more reliable and versatile in total ink characterization.

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