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RESEARCH ARTICLE

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Analysis of roller pen inks by capillary zone electrophoresis

Abstract The analysis of roller pen inks has become more and more important in fraudulent document examination because of the extensive use of roller pens in financial documents. Capillary electrophoresis with powerful resolution was applied for the analysis of roller pen inks. The experiment focused on the optimization of the separation of the extract from commercially available roller pen entries. A better separation electropherogram was obtained when a 20 mM borate buffer at pH 8.5 and a fused silica capillary with an inner diameter of 100 μm with a total length of 47 (40 cm to the detector window) were used. Five inks from roller pens of different manufacturers and countries were analyzed, and their electropherograms showed that most patterns are distinctly different from each other. Capillary with inner diameter of 100 μm increased the intensity of determination; therefore, color dyes were identified in the visible range and were able to provide more information for comparing types of roller pen inks.

Keywords document examination, roller pen, inks, capillary zone electrophoresis

Analysis of inks is very important in the identification of questionable documents. Any alterations to documents can lead to significant financial dissension. Currently, more and more forensic examiners determine different types of inks by chemical and physical methods. Inks are complex mixtures of a number of different chemical compounds, including synthetic acid or base dyes, inorganic and organic color pigments, glycol and glycerol. Most roller pen inks are water-soluble and may contain some salts of synthetic acid dyes. Chromatography has been extensively applied to separate inks since the 1980s, to characterize different inks based on their composition. Capillary electrophoresis (CE) is a powerful separation technique and has been applied to many areas of forensic science. Several papers have been published on the separation of different color fountain pen inks [1–3] with diode array detector or UV detector, but they were detected at 214 nm. In this study, we aim to detect dyes of inks in the visible wavelength.

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1 Materials and methods

A capillary electrophresis instrument by Beckman, model P/ACE 5510, was used for the separation. This instrument can provide the highest voltage of 30 kV and is equipped with a diode array detector that can perform scanning between 190 and 600 nm. The instrument's special software P/ACE station 1.1 was used for data acquisition and management. Fused silica capillaries (purchased from Yongnian Company, China) with an inner diameter of 100 μm and with a total length of 47 (40 cm to the detector window). Borax for the borate buffer (pH 8.5), oxalium for the extract and phosphate buffer (pH 5.0); all solutions were prepared with distilled water. The roller pen investigated was numbered from 1 to 100.

The separation was performed in 20-mmol/L borate buffer at pH 8–9 and a voltage of 15 kV, pressure injection was 5 s. Each run was rinsed with 1 mol/L NaOH, 1 mol/L HCl, distilled water in turn, and then the run buffer. Ink samples were diluted with 0.5% solution of oxalium. Ink entry on a paper, i.e, writing on paper using the investigated pen, was cut about 1 cm, and extracted for 15 min in a vial with 0.5% solution of oxalium. 0.1% solutions of ink and extracts of ink entry were run in the same CE condition.

2 Results and discussion

2.1 Optimization of the separation conditions

In acidic or alkaline conditions, the ink's different components are charged, and they could migrate in the electric field of an electrophoresis separation system. Capillary zone

electrophoresis is performed in uncoated fused silica capillary. Separation in acidic buffers (phosphate) did not provide a good resolution of all the ink's components, because most dyes remained together. On the contrary, good separation was achieved in alkaline buffer. In this study, 20 mM borate pH 8.5 can provide good resolution of inks and the separation was finished in 20 min using this buffer. Different components in the roller pen ink can ionize well, and electroosmotic flows in the borate buffer assure simultaneous detection of both anionic and cationic components.

Figure 1 demonstrates the separation of diluted original ink 48 and its extract from paper in the 0.5% solution of

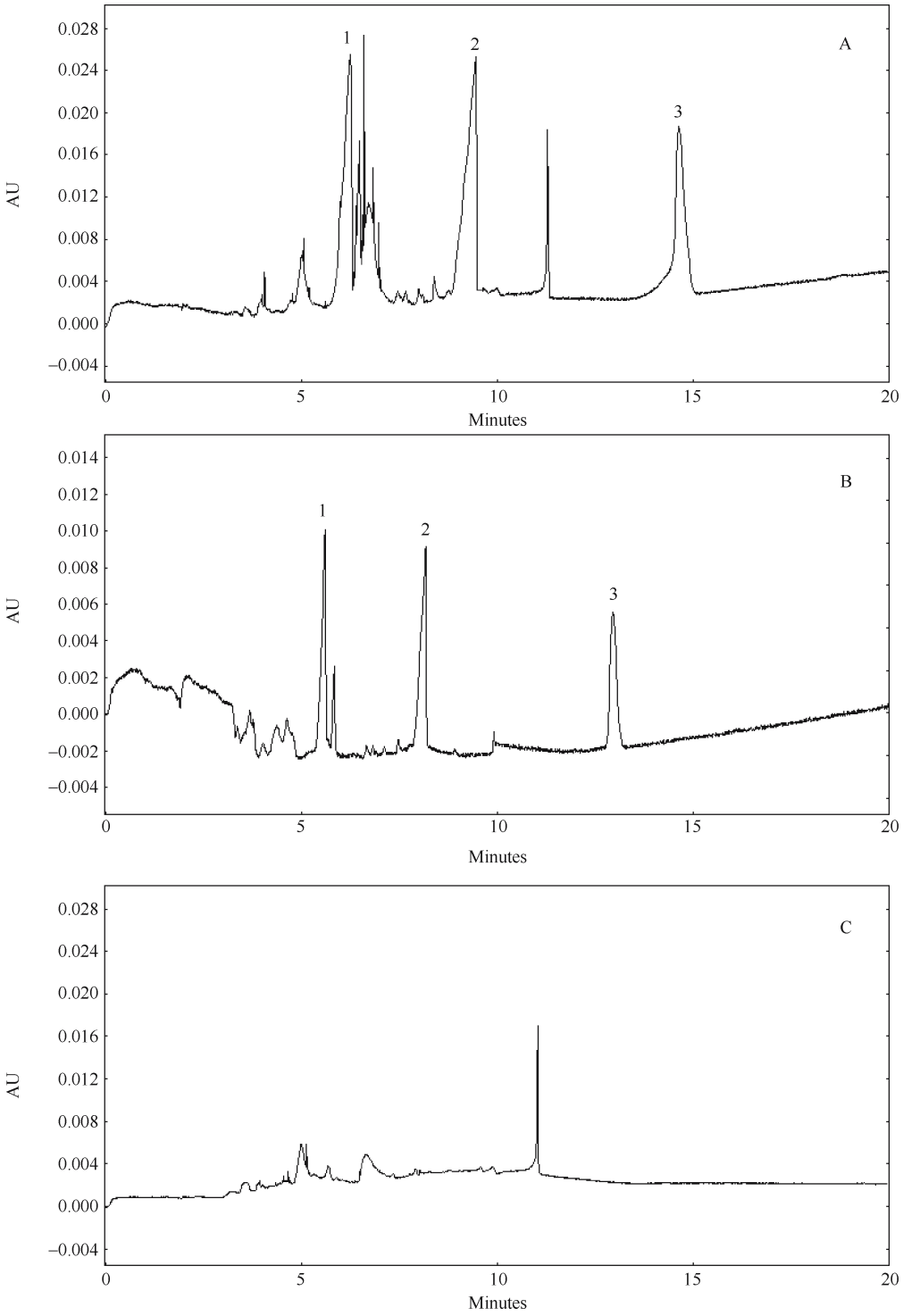

Fig. 1 Electropherograms of different black roller pen ink and paper, detection at 214 nm
Separation in borate buffer 20 mmol/L pH 8.5, capillary length 47/40 cm; A) Ink 48 extract; B) Diluted original of ink 48; C) Extract of paper.

oxalium, signals in both elctropherograms have similar migration time for peak 1, peak 2, and peak 3, respectively. They are the main ingredients of roller pen ink 1. Extracts of paper have no interference to ink analysis in this CE condition. But the migration time could be a little different from run to run, because electroosmotic flow changes with the ionic strength of the buffer. Different roller pen inks were analyzed and compared in the same CE condition.

2.2 Analysis of roller pen inks

Elctropherograms at different wavelengths from 190 to 600 nm were acquired by diode array detector. In the same buffer, if a capillary with 75 or 50 µm inner diameter was used, electropherogram in the visible range cannot be achieved. UV-Visible absorption is connected with the ray path, which is the diameter of the capillary in the CE detector. If the length of the ray path is too short, absorption strength will decrease. Capillary with 100 µm inner diameter increases the length of the ray path, so the high intensity of determination was achieved. Figure 2 shows the maximum absorption of the three ingredients at 200 nm, 460 nm, 595 nm as seen in the UV-Visible range in the three dimension (3D) electropherogram of the three inks. In the visible range, color dyes were identified that can provide more information for comparing the types of roller pen inks.

Extracts of 100 roller pen entries on paper from different manufacturers were separated using the optimized condition discussed in this paper. Most inks were baseline separated into their ingredients within 20 min. The electropherograms demonstrate enough distinct difference and can help in the qualitative analysis of the different roller pen ink extracts. The main components of the different roller pen inks have some differences, i.e., with different ingredients and different additives, so entries of different roller pens could be identified by CE separation.

The reproducibility of the above analysis was tested on a run to run basis with three replications for each ink extract. The relative standard deviation of migration time and peak area of the main components was below 4% if each run was followed by a capillary rinse with NaOH, HCl, distilled water, and run buffer.

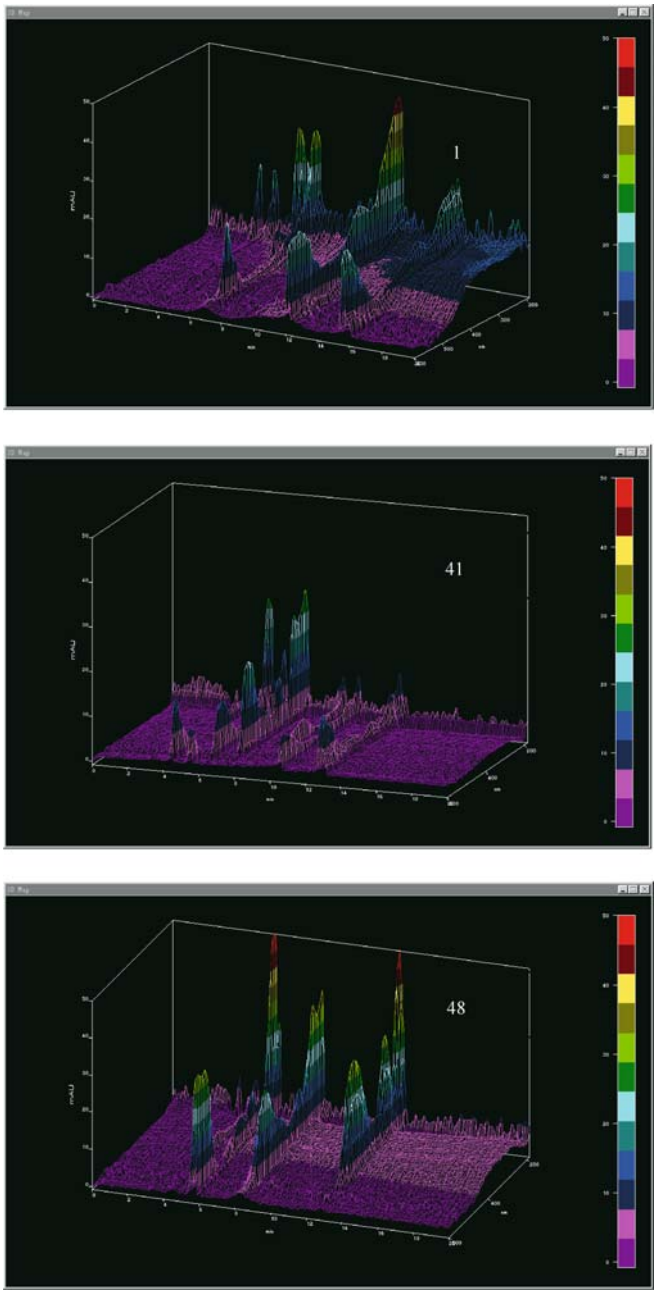

Fig. 2 3D electropherogram of ink 1, ink 41, ink 48
X: Migration time; Y: Absorbance intensity; Z: Absorbance wavelength from 190 to 600 nm.

3 Conclusions

The ideal separation was obtained with 20 mM borate buffer at pH 8.5 and fused silica capillaries with an inner diameter of 100 µm with a total length of 47 cm. One hundred inks of roller pens from different manufacturers and countries were analyzed, and their electropherograms showed that most patterns are distinctly different from each other. Capillary with inner diameter 100 µm increases intensity of determination; therefore, color dyes were identified in the visible range and were able to provide more information to compare types of roller pen inks.

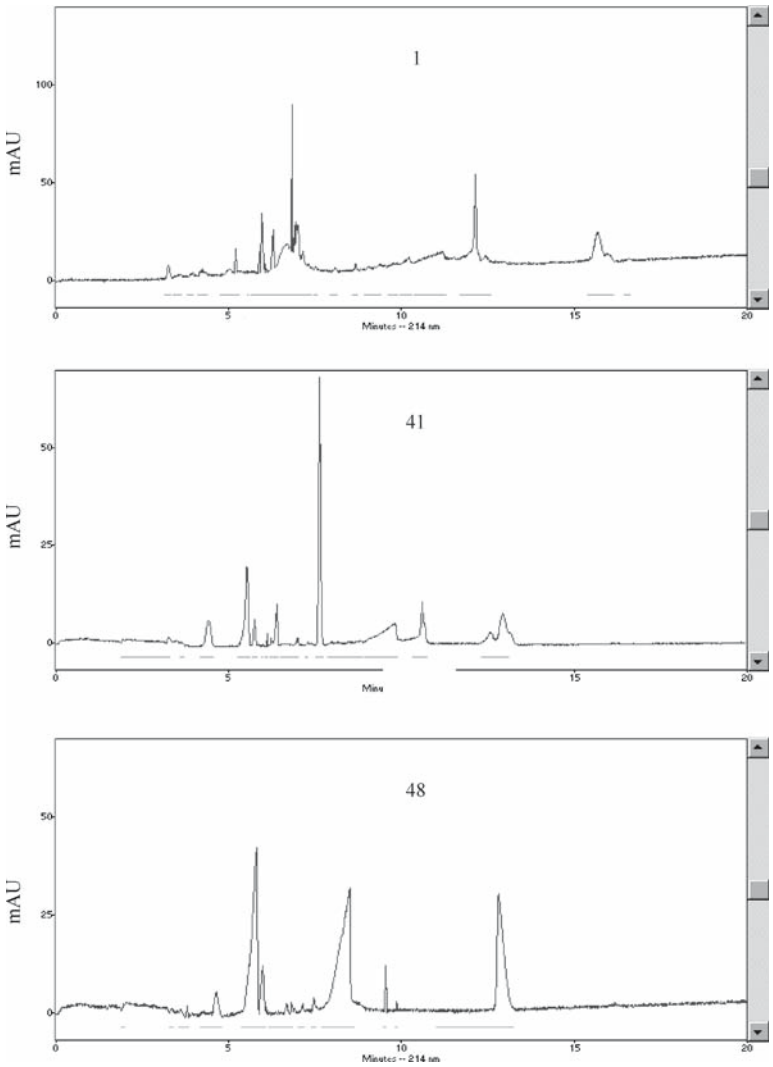

Fig. 3 Elctropherograms of different black roller pen ink extracts.
Ink 1, ink 41, ink 48, detection at 214 nm; Separation in borate buffer 20 mmol/L pH 8.5, capillary length 47/40 cm

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