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Identification and dating of the fountain pen ink entries on documents by ion-pairing high-performance liquid chromatography

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ABSTRACT

A novel approach for the identification and dating of the fountain pen ink entries on paper has been established by ion-pairing high-performance liquid chromatography (IP-HPLC). Twelve black and six red fountain inks have been collected, and their ink entries have been prepared by drawing lines on paper. The chromatographic conditions for separation of their dye components after extraction with solvents were optimized. Under the optimized conditions, the 18 fountain pen inks were differentiated individually by comparing the number of detectable main or minor dye components, and the relative peak intensities of each component. The ink entries were artificially and naturally aged, and the analysis results showed that the ink dye components were significantly decomposed when exposed to UV or fluorescent light compare to those of inks stored under natural condition. The changes of the relative peak height for the dye components were linearly related to the aging time, especially under natural aging conditions. The degradation characteristics of the dye components under different aging conditions provide scientific evidences for dating of the suspicious fountain pen ink entries on document.

1. Introduction

In the field of forensic examination of questioned documents, the legitimacy of an ink entry is often an essential question, and the possibility of determining the age of an ink stroke would definitely help to resolve this problem. Fountain pen has been a popular writing instrument for more than a 100 years, and is frequently used to sign formal documents in our social life, such as insurance claims, wills, tax returns, etc. Criminal cases concerning falsified or rewritten documents are often encountered in forensic examination. Therefore, the method for identification and dating of the fountain ink entries on documents play an important role in the field of forensic science.

Systematic approaches for forensic analysis of ballpoint and gel pen ink entries have been developed in previous reports, and they can be divided into destructive and non-destructive methods. The non-destructive techniques were mainly spectroscopic or optical instruments, including UV–Vis microspectrophotometry [1], diffuse reflectance infrared [2], micro-FTIR [3,4] and Raman spectrometry [4–7], surface-enhanced resonance Raman spectroscopy [8], proton-induced X-ray emission spectroscopy and real time mass spectrometry [9,10]. However, such optical and spectrometric methods are useful only for answering the question of whether two or more documents could have the same origin, but they are often insufficient to identify the inks. When more detailed information is required, some form of destructive chemical examination should be used. Thin layer [1,11] or high-performance thin layer chromatography [12] was widely used in the early stage because they do not require special apparatus and have the advantage of simple and direct operation. The limited separation and quantification abilities of these techniques have led to the application of high-performance liquid chromatography (HPLC) [3,13] and capillary electrophoresis [14] to ink analysis. Gas chromatography [15–17] has also been applied to the dating of inks by analysis of the volatile components. Laser/field desorption [18,19] and electrospray ionization mass spectrometries [20] have been used for detecting the dyes of ballpoint ink entries on paper in recent years and chemometrics has also been successfully applied to address the classification problems in ink analysis, such as principal components analysis and linear discriminant analysis [3,21].

Fountain pen inks are a complex mixture of chemical compounds, including colorants (such as acid, basic or direct dyes, organic or inorganic color pigments, iron(II) sulfate) and various additives (surfactants, antioxidants, viscosity adjusters, resins, glycol and glycerol) [22]. There are only a few reports concerning the identification and comparison of fountain pen ink [9,23]. The dye components of the fountain pen inks usually contained sulfonic or

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carboxylic, phenolic and less frequently amino functional groups [9]. They are more sensitive to light and would decompose slowly in natural environment [24], therefore, the analysis of the dye colorants would supply much useful information for ink dating than analysis of other additives did. Ion-pairing high-performance liquid chromatography (IP-HPLC) is a powerful method to separate ionic compounds [25,26], and it would be a potential approach for analysis of the ionic dyes in fountain pen inks.

This study was focused on the degradation of the dye components in fountain pen inks. IP-HPLC analysis was employed to monitor changes in the chemical composition of fountain pen inks of different brands and models after exposure to light and under normal aging conditions. The results would provide scientific evidences for identification and dating of the documents written by black and red fountain pen inks.

2. Materials and methods

2.1. Reagents

HPLC grade acetonitrile was obtained from DIMA Technology (USA). Tributylamine (99%, TBA), tetrabutylammonium bromide (99+%, TBABr) and dihexylamine (99+%, DHA) were supplied by Acros Organics (NJ, USA). Ammonium acetate and triethylamine (TEA) were of analytical grade and purchased from Beijing Yili Fine Chemical (Beijing, China). Other chemicals were of analytical grade and used as supplied. Water for buffer preparation was prepared by Milli-Q filtration system.

2.2. Collection and preparation of fountain pen ink samples

Twelve black and six red pen inks of different manufacturers of various countries were chosen for analysis and labeled as NA1–NA12 and P1–P6. Straight lines were drawn on ordinary A4 print paper for preparing the ink samples. For natural aging, ink entries was drawn and dated every month, then stored at control condition of room temperature in darkness. The paper was not folded and light was prevented from reaching the ink. For artificial aging, the ink entries were either exposed to ultraviolet light with a wavelength of 254 nm, the oven at the temperature of 100 °C or and a fluorescent tube from a short distance (about 10 cm), respectively.

For each sample, 2.5 cm ink line was cut out and extracted by 1 mL 40 mmol/L tetrabutylammonium bromide buffer/acetonitrile (1:1, v/v) for about 12 h at room temperature, and the extract was filtered through a 0.45 μm Millipore filter prior to the HPLC analysis.

2.3. Equipments and HPLC conditions

All HPLC work was carried out on a chromatographic instrument, which consisted of two K-501 pumps, an automatic sampler and a Schnell scannendes Spektralphotometer K-2600 UV detector (LUMTECH, Germany). The software management system used to operate, collect and manipulate data was EastChrom Plus. The column for separation was Inertsil C18 (250 mm × 4.60 mm, 5 μm, Phenomenex, USA). A Cintra-10e UV–Vis spectrophotometer was from GBC (Australia). Ultraviolet analysis apparatus was from Haimen QL-Lab (Jiangsu, China). Basis pH Meter PB-21 was from Sartorius (Goettingen, Germany).

The mobile phase was acetonitrile (Eluent A) and 40 mmol/L tetrabutylammonium bromide (Eluent B, pH 7.0). The eluted condition for black ink was 40–60% A in 18 min, then hold 27 min. And the gradient for red ink was 50–55% A in 15 min, then hold 5 min. The flow rate was both 1.0 mL/min, with the injection volume of 20 μL.

2.4. Experimental reproducibility

In order to confirm the reliability of the experimental method, five experiments with one black and one red fresh ink entries were performed.

A fountain pen ink entry (2.5 cm, aging time = 0 h) was cut out, extracted with the mixture of HPLC mobile phase (Eluent A: Eluent B = 50:50 (v/v)), then analyzed by HPLC with the optimized chromatographic conditions.

The relative standard deviations (R.S.D.) of the RPH for six black ink entries were between 0.97% and 2.35%.

3. Results and discussion

3.1. Chromatographic conditions for separation of the fountain ink dye components

Fountain pen inks often consist of several acid or direct dye components, which are mixed together proportionally to offer the needed colors [22]. These dyes usually contain carboxyl and sulfonic groups and cannot be reserved on routine C18 column, so ion-pairing reagents are usually added to the mobile phases for increasing their retention when carrying out HPLC analysis [27].

The retention of the analytes in IP-HPLC depends on a variety of parameters. Among these interdependent parameters, the ion-pairing reagent is an important factor. On the base of our previous work [25,26], various ion-pairing reagents were tested and tetrabutylammonium bromide was selected for IP-HPLC analysis of the black and red fountain pen ink dye components. The concentrations of TBABr between 10 and 80 mmol/L (10, 20, 40 and 80 mmol/L), and the pH value (5.0, 7.0 and 9.0) of the buffer solutions were evaluated individually. Considering the separation, selectivity and retention time of the dye components in the fountain pen inks, the mobile phase was determined as following: 40 mmol/L TBABr buffer solution (pH 7.0) with acetonitrile as organic modifier and a gradient proportion of the buffer and acetonitrile at the flow rate of 1.0 mL/min was used in the following studies.

The maximum UV absorption bands of the fountain pen inks were situated between 500 and 700 nm, and most of the dye components have maximum absorption nearing 590 nm for black inks and 520 nm for red inks, so the wavelength of detection was set to 590 and 520 nm, respectively. The fluorescent brighteners on paper have no absorption at the above wavelengths.

A series of solvents and mixed solvents with different polarities were applied to extract the dye components from the ink entries on paper. Chromatograms of ink extracts and diluted original inks of the same sample have been compared, and it has been found that the dye components can be efficiently extracted with a mixture of 40 mmol/L TBABr buffer solution (pH 7.0) and acetonitrile (1:1, v/v).

3.2. Identification of the fountain pen ink entries on paper

3.2.1. Identification of the black fountain ink entries

Twelve of dye-based black fountain pen ink entries on paper were satisfactorily separated by IP-HPLC using the above optimum conditions (Fig. 1). The ink entries can be identified by the numbers and kinds of their main dye components. As shown in Fig. 1, some inks contained three main dye components (Fig. 1B), and some inks had two components (Fig. 1C and D), but their retention times were not identical.

For those ink entries on paper, which have the same main dye components, they can be further distinguished by the differences of their minor elements. Fig. 2 shows the chromatograms of the ink entries that have only one main dye component, but the differences could be obviously seen from their fingerprints. The minor components eluted between 15 and 30 min reflected that the two ink entries were different and could be identified.

3.2.2. Identification of the red fountain ink entries

Fig. 3 shows the representative chromatograms of the red ink entries on the detection wavelength of 520 nm. As those of the black ink entries, the red ink entries can also be distinguished from the numbers of their main dye components. From the chromatograms, it could be seen that most of red inks contained three kinds of dyes, and their retention time was 7.9, 8.8 and 12.5 min (see Fig. 3A–D), respectively.

3.3. Dating of the fountain pen ink entries

The fountain ink dyes are usually organic compounds containing conjugated aromatic rings and are sensitive to light. Some dye components in an ink formulation might undergo degradation

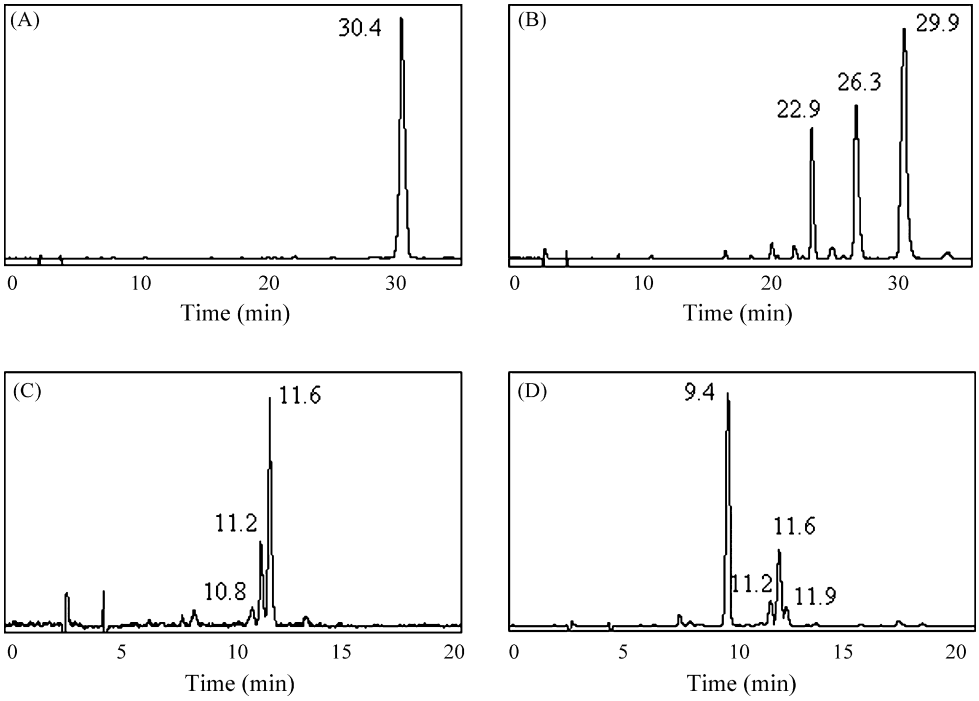

Fig. 1. Representative chromatograms of black fountain pen inks of NA1 (A), NA7 (B), NA11 (C) and NA12 (D).

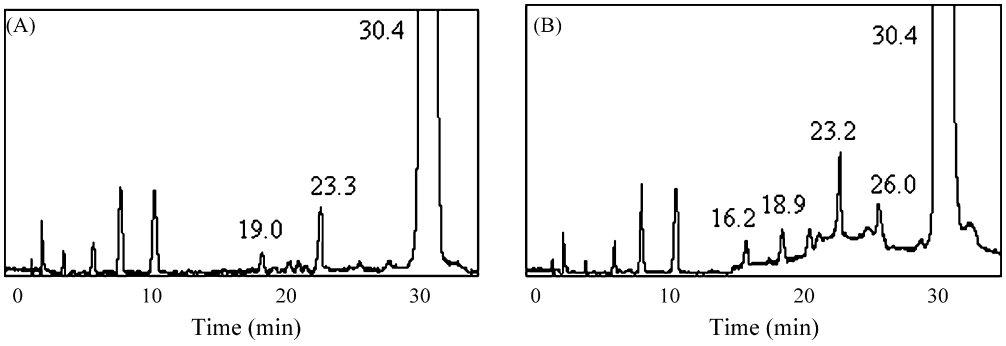

Fig. 2. Chromatograms of fountain inks of NA2 (A) and NA4 (B).

during storage [20]. Exploring the decomposing characteristics of the ink entries under light and normal storage conditions would offer scientific evidences for determination and dating of them on suspicious documents [20,28]. The black and red fountain pen ink entries, which contained three main dye components, were selected to observe their dying behaviors under various conditions.

3.3.1. Aging and dating of the black fountain ink entries

3.3.1.1. Artificial aging of the black ink entries. The compositions of the ink entries would change when exposed to light or heat, especially the dye components [29,30]. The compositional changes of the dyes can be reflected on their chromatograms. Fig. 4A shows the chromatograms of the black ink entries exposed to UV light for 0, 106 and 224 h, respectively. From Fig. 4A, it can be seen that the relative intensities of the three main dye components (labeled as peaks 1–3) have been changed, and meanwhile, the intensities of some minor components (labeled as peaks 4 and 5), which were near peaks 1 and 2, significantly increased with prolonging the aging time.

In order to quantify the changes of these dye components with aging time, the relative peak height (RPH) parameter was defined.

$$\mathrm{RPH}_i = \frac{H_i}{H_{\mathrm{tot}}} 100\%$$

where H_i is the peak height of a component, and H_{tot} is the total height of all the main peaks of the dyes. Mean standard deviations of the RPA values were calculated and were used as error bars in the graphics.

The change tendencies of the relative peak height versus aging time for each component of the ink entries under exposure to UV light were shown in Fig. 4B and C. It can be seen from Fig. 4B that the RPH of peaks 1 and 2 decreased linearly with the aging time, while the RPH of peak 3 correspondingly increased. In fact, by comparing with controlled sample, the actual height of peak 3 also presented reduction after the ink entries were exposed to UV light, and the increase of its relative peak height illustrated that component 3 was relatively stable and its decomposing rate was lower than those of peaks 1 and 2.

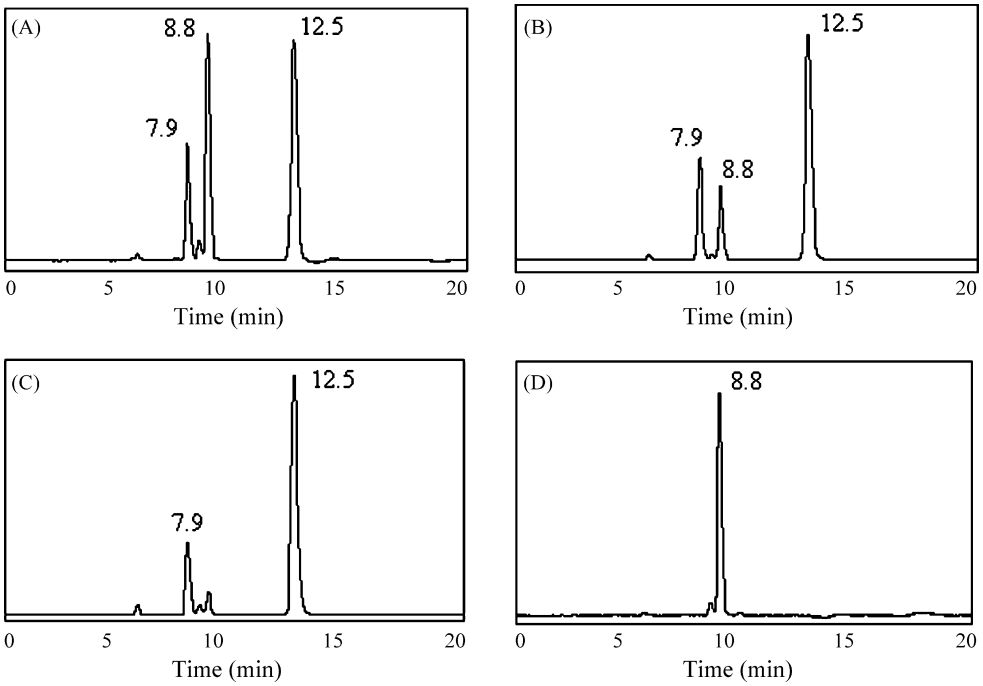

Fig. 3. Chromatograms of red fountain inks of P1 (A), P2 (B), P3 (C) and P4 (D).

It was interesting to note from Fig. 4C that the RPH of the two minor peaks (components 4 and 5) obviously enhanced with the increase of aging time (the RPH of peaks 4 and 5 were relatively low and the figure was drawn individually for clarity). From above results, it can be proposed that components 4 and 5 may originate from the degradation of components 1 and 2, respectively.

Through the changing tendencies of RPH for the three main dye components versus the aging time under fluorescent lamp, it can be seen that the decomposing characteristics of the ink entries exposed to fluorescent lamp were similar to those exposed to UV light condition, but the decomposing rates of the dye components were relatively gentle. It seems reasonable because the ultraviolet light has a stronger energy compared to the fluorescence light.

No obvious difference was observed for the RPH of the three main dye components after the fountain ink entries were stored in an oven at 100 °C for 50 h. It was demonstrated that the dye components were insensitive to heat, which was consistent with our previous observations [26].

3.3.1.2. Natural aging of the black ink entries. The dye components of the black ink entries on documents would undergo degradation or decomposition in natural storage conditions and their decomposing characteristics can be related to the dating of the documents [31]. The ink entries on paper stored in dark at room temperature over 2 years were extracted and analyzed by IP-HPLC. Fig. 5A shows the representative chromatograms after the ink

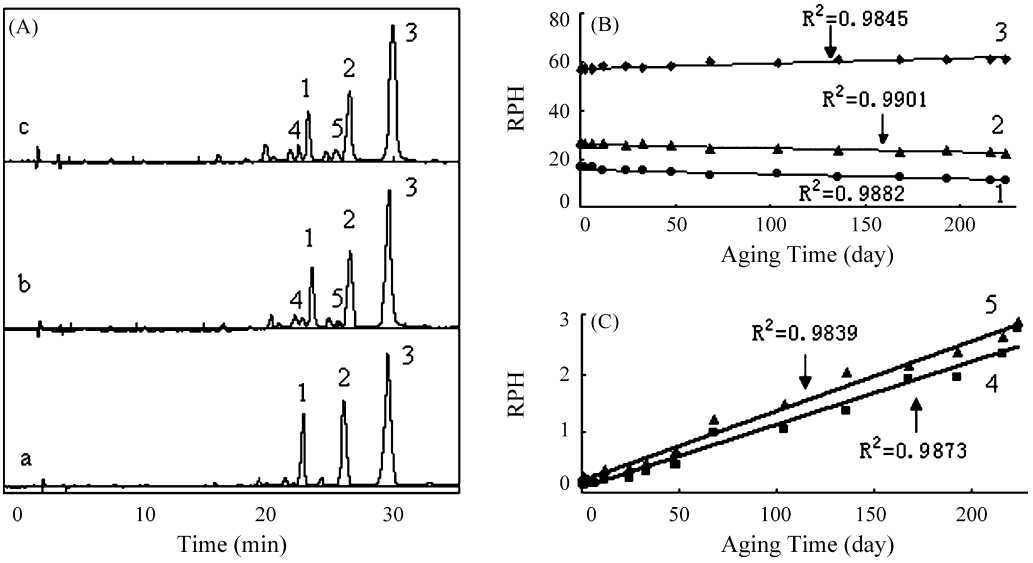

Fig. 4. (A) Chromatograms of the NA7 ink entries on paper after exposure to UV light for 0 h (a), 106 h (b) and 224 h (c); (B and C) aging curve of NA7 fountain ink under UV light condition.

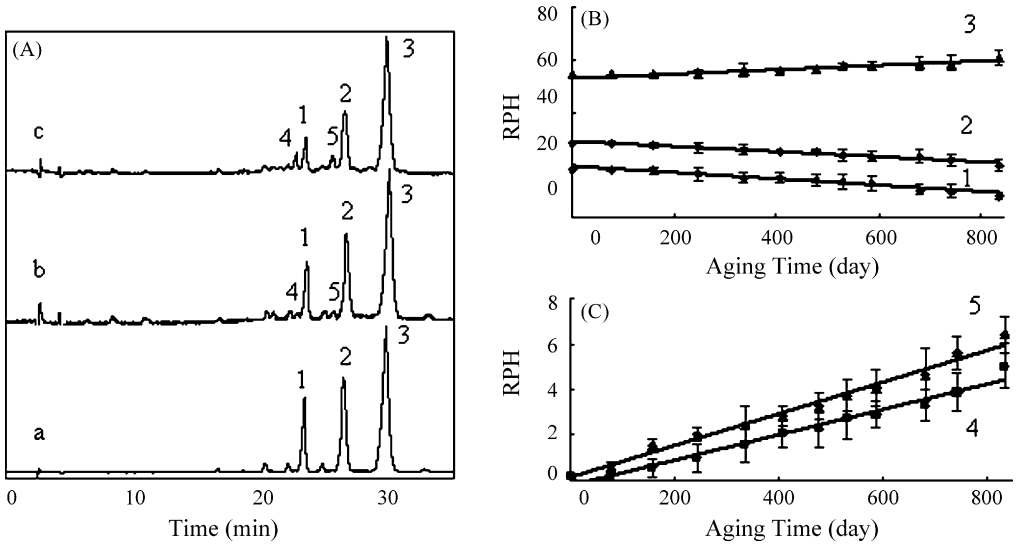

Fig. 5. (A) Chromatograms of NA7 ink entries on paper stored in natural conditions for 0 day (a), 326 days (b) and 863 days (c); (B and C) natural aging curve of NA7 fountain pen ink.

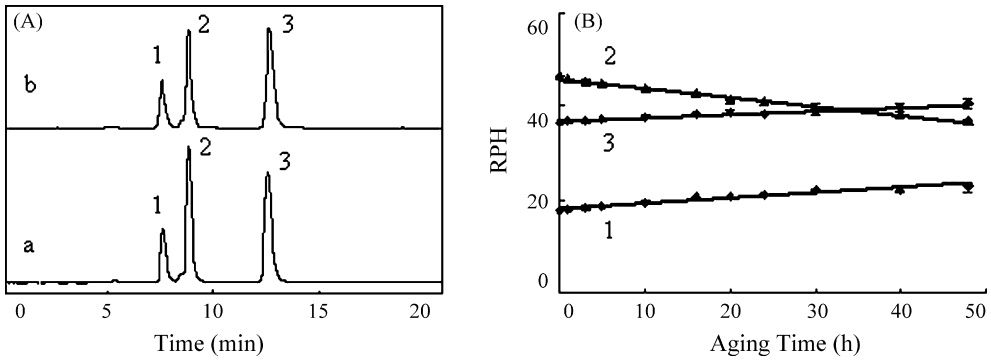

Fig. 6. (A) Chromatograms of the P1 ink entries on paper after exposed to UV light for 0 h (a, control sample) and 48 h (b). (B) Aging curve of P1 fountain pen ink under UV light condition.

entries stored in dark for 0, 326 and 863 days, respectively. It can be obviously noted from Fig. 5A that the relative intensities of the dye components have been obviously changed with the natural aging time.

The changing tendency curves of the RPH versus aging time for different dye components were shown in Fig. 5B and C. The curves showed that there is a satisfactory linear relationship between the RPH of the dye components and the aging time, and their linear regression coefficients were about 0.99. It was illustrated that the ink entries (or the documents) can be dated by determination of the RPH of the dye components. It also can be noted from Fig. 5B and C that the RPH of components 1 and 2 decreased with the natural aging time, while those of components 3, 4 and 5 increased, which were similar with the artificial aging results. The similar changing tendencies of dye components RPH were beneficial to prepare the reference ink entries for dating of the documents by artificial aging methods.

3.3.2. Aging and dating of red ink entries

A red ink, which contained three main dye components, was selected as the representative of the currently available red inks. The red ink entries on paper before and after exposure to UV light,

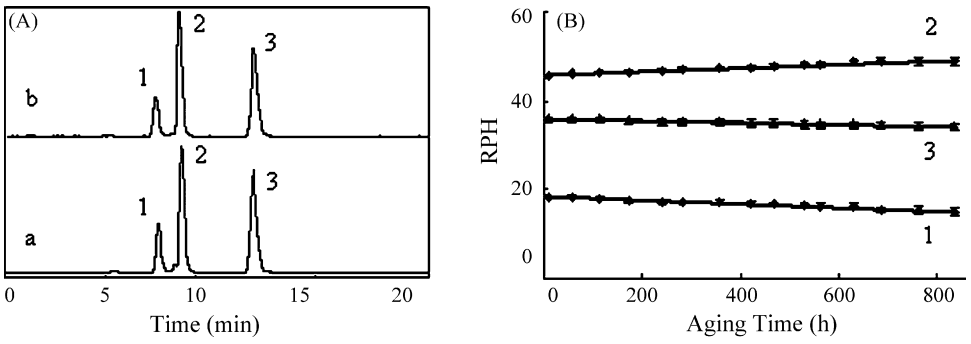

Fig. 7. Natural aging curve of each component in P1 ink entries on paper.

fluorescent lamp, heat and storage in natural conditions were extracted and analyzed by IP-HPLC.

Fig. 6 shows the chromatograms and aging curve of the red ink entries exposed to UV light. It could be seen from Fig. 6A that the relative peak height of component 2 significantly reduced when the red ink entry was exposed to UV light for 48 h, while no obvious new peak was noticed accompanying the degradation of component 2. It was probably because the degradation product could not be detected at the wavelength of 520 nm. The changing tendencies of dye components were clearly reflected in the aging curve (Fig. 6B). The RPH of component 2 decreased with the aging time, while those of components 1 and 3 relatively increased. Comparing with the control ink entries, the actual height of peaks 1 and 3 almost remained unchanged and the enhancement of their relative peak height originated from the reduction of the total peak height.

In fluorescent light tube and oven aging conditions, the composition changes of dyes were minor, and the relative peak height of each component seemed unchanged with the aging time (figure not shown).

The chromatograms and relative peak height of each component versus aging time in natural aging condition was shown in Fig. 7. The RPH of the components 1 and 3 linearly decreased with the aging time, while that of component 2 increased. In fact, the peak height of all the components decreased with increasing the aging time. The phenomenon indicates that the decomposing rate of component 2 was slower than this of other components in the ink entries under natural aging conditions and it was also demonstrated that the dye component 2 was more sensitive to ultraviolet radiation.

It can be noted from above results that the tendencies of compositional changes were obviously different than those under the UV light accelerated aging conditions, especially for component 2. The different degradation behaviors of the dye components would cause a problem for preparing reference sample for determination of the relative age of the document by artificial aging method, but their degradation characteristics could be used to identify whether the ink entries were treated by exposure to light or stored in natural condition. The fine linearity between variations of the component's RPH and the aging time can be used to the dating of the document.

4. Summary and conclusions

Black and red fountain pen inks were collected and their ink entries were extracted and analyzed by IP-HPLC with TBABr as the ion-pairing reagent. The ink entries can be identified individually by their main and minor dye components. The degradation characteristics of the dye components under light and natural conditions was also investigated, and the results showed that the compositional changes of the dye components and the degraded products were linearly related to the artificial or natural aging time.

The degradation of the ink on paper is complex, it may involve reactions with paper components or influence by environmental temperature and humidity, etc., much works should be further investigated for the practical sample. The present experimental results could only supply a feasible method and scientific evidences for identification and dating of the fountain pen ink entries on documents in forensic analysis.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.forsciint.2008.06.008.

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