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Dating the writing age of black roller and gel inks by gas chromatography and UV–vis spectrophotometer

Yuanyuan Xu [a,*], Jinghan Wang [b], Lijuan Yao [b]

[a] Guangdong Police College, Department of Investigation, 500 Binjiangdong Street, Guangzhou, Guangdong 510232, PR China
[b] China Criminal Police College, Department of Forensic Medicine, P.O. Box 755, 83 Tawan Street, Shenyang, Liaoning 110035, PR China

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Abstract

The relative and absolute age of roller and gel ink entries determined by gas chromatography (GC) and UV–vis methods are presented in this paper. The relative age of ink entries is concluded by the comparison of solvent amount between questioned and known dated entries. Absolute age of ink entries is estimated through the changing ratio of solvent components between heated and unheated samples without known samples for comparison. The methods are accurate and reliable.

Keywords: Roller inks; Gel inks; Relative age; Absolute age; Dating; Gas chromatography; UV–vis spectrophotometer

The analysis of roller pen and gel inks is more and more necessary with the extensive use of roller and gel pens in fraudulent documents. So dating the writing age of roller and gel ink is very important for forensic scientists. At present classes tested is in progress by using optical and chemical techniques, such as Raman spectroscopy, microspectrophotometry [1], GC/MS [2–5] and HPCE [6], but dating the writing age of black roller pen and gel inks have not been reported.

So some forensic scientists pay attention to the approaches determining the dynamic characteristics of roller pen ink age.

When the samples known writing age compared with the questioned ink are usable, relative writing age is estimated by using GC and UV–vis. When known samples are not been had, absolute writing age is estimated through solvent changing ratio between heated and unheated samples. The six black roller and gel inks are identified by qualitative and quantitative analysis of the solvent components and dye components using the methods of GC and UV–vis.

1. The relative writing age of black roller pen inks

1.1. Experiment

1.1.1. Materials and methods

1.1.1.1. Samples. The experimental inks are listed in Table 1.

Lines of the six black roller pen and gel inks have been written on white papers for notes put into a drawer.

1.1.1.2. Instruments. A Hewlett-Packand Model 6890 gas chromatography equipped with a flame ionization detector (FID); A Shimadzu Model 250 UV-VIS Spectrophotometer.

GC Condition: column: DB-FFAP, 30 m × 320 μm ID × 0.25 μm; carrier: nitrogen, 2.5 mL/min; oven program: 60 °C (1 min) 10 °C/min 135 °C 15 °C/min 220 °C (4 min); injection: 2 μL, splitless, $T = 240$ °C; detector: FID, $T = 280$ °C, hydrogen, 35 mL/min, air; 350 mL/min.

1.1.1.3. Procedure 1. A 2 cm in length samples of entries written are cut out with a sharp scalpel and analyzed by using GC and UV–vis methods as follows.

Every sample is extracted in a vial with 1 mL methanol containing ethyl benzoate (ethyl benzoate is used as external comparative matter) for 20 min to maximize the amount of all

* Corresponding author.
E-mail address: xyy0123@163.com (Y. Xu).

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Table 1
Samples of experimental inks

Number	Brand	Manufacturer
1	ZEBRA Be-pen (R-100)	Japan
2	ZEBRA Be-pen (Be-109)	Japan
3	SCHENIDER TOP BALL 861 03	Germany
4	STAEDTLER NORIS Pen 333	Germany
5	Rollerball refill MONT BLANC	Germany
6	SCHENIDER TOP LINER 967	Germany

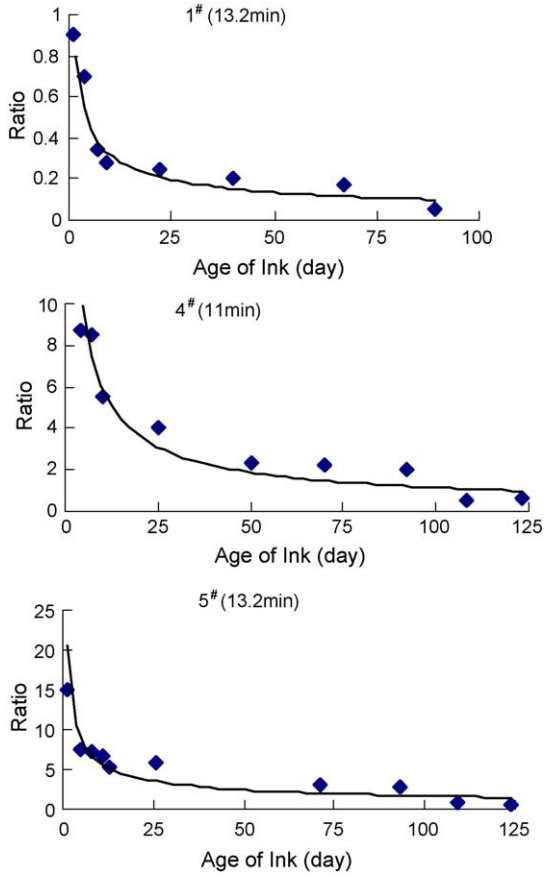

Fig. 1. Natural aging curve of the Ratio of known dated samples decreasing with the time.

available volatile components of ink. After extraction, 2 μL of every sample is removed and analyzed by GC.

The residual solution of extraction is extracted secondarily with 0.9 mL DMF for 20 min to maximize the amount of all available dye components of ink. The solvent of extraction is analyzed by UV–vis and the absorption spectra of the colored extracts obtained are recorded. The absorbance measured at the absorption maximum of a dye presented in the ink analyzed is read for every sample.

The aging parameters can be ascertained: the Ratio is determined by the peak area of solvent to the peak area of external comparative matter to the absorbance of dye:

$$\text{ratio} = \frac{\text{peak area (solvent)}}{[\text{peak area of external comparative matter} \times \text{peak area (dye)}]} \quad (1)$$

Then aging curve (see Fig. 1) for known writing age of ink can be obtained from these ratios plotted versus actual age. Throughout the aging curves, the writing age of the questioned entries can be evaluated from the ratio.

2. Results and discussions

If the ink sampling has at least two solvent components, two or more aging curves can be obtained. Then the writing aging of the questioned entries can be evaluated from more ratios and it is more accurate. The results can be verified one another.

Fig. 2 shows that two chromatographic peak areas of solvent components in no. 5 decrease with the time. Because the solvent components have special volatility, the contents decrease with the time.

The content of external comparative matter is almost unvarying. The physical and chemical reactions of dye components in the ink nearly do not happen in initial 3 months, so the ratios decrease.

The roller and gel inks are complex mixtures. They are composed of solvents (volatile components), dyes, synthetic resins and other organic compounds that begin changing or evaporating as soon as the ink is placed on a paper. The rates of these processes are significantly different. The evaporation of the solvent components is very intensive initially and it

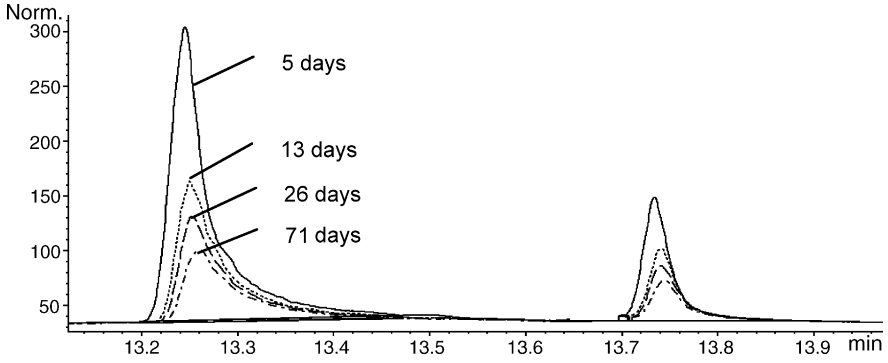

Fig. 2. Graphical presentation of two chromatographic peak areas of no. 5 decreasing with the time.