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## Determining the relative age of blue ballpoint ink by gas chromatography

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**Abstract** A method for identifying the writing age of blue ballpoint pen ink has been established due to the imperative demand in forensic laboratories. The content of the volatile components in blue ballpoint pen ink were determined by gas chromatography (GC). The absorbance of dye in blue ballpoint pen ink was measured by UV–Vis spectrometry. A writing age curve of the ink was established using the ratio of the content of the volatile components to the dye, based on the identification of 74 kinds of blue ballpoint pen ink of domestic and international origins. The change of benzene alcohol or phenoxetol with the writing age was also tested. Different kinds of blue ballpoint pen ink were detected and the repeatability of the experiment was investigated. The results indicate that the method is reliable, sensitive, systematic and is especially suitable for practical use.

**Keywords** gas chromatography, ultraviolet–visible spectrum, blue ballpoint pen ink, Ethylene phenyl, Benzyl alcohol, age

### 1 Introduction

The determination of the relative age of ballpoint pen ink used on questionable files with data, invoices, IOUs, common seals, etc. has often been required in the detection and uncovering of criminal cases. Local and foreign forensic experts have made extensive efforts on the problem for a number of years. Extensive physical and chemical studies using spectra [1], chromatogram [2], etc. have been conducted abroad. Aginsky et al. [3] ascertained the relative age of ballpoint pen ink by the volatility of certain ingredients in the ink. However, the ink components were

different between specimens. Local researchers have studied the buildup time problem of ballpoint pen ink by gas chromatography (GC) [4, 5], but it was confined to a few local samples and not systematic and definitive enough to be of value. We have previously ascertained the relative age of ballpoint pen ink by the variation with time of the volatile components—phenoxetol and benzyl alcohol—but it was not applied to all specimens [6]. Based on previous results, the dye inside the ballpoint pen was used as the reference substance. By utilizing the ratio of the volatile component content (peak area), measured by GC, and dye absorbance value, measured by UV–Vis spectrum, with 2-cresol as the standard substance (expressed as the chromatogram peak area), a writing age curve of the blue ballpoint pen ink was established. In this paper, using appropriate GC conditions, a natural aging time curve of a common blue ballpoint pen ink was created based on a previous experiment that detected the benzyl alcohol and phenoxetol component of 74 kinds of blue ballpoint pen ink [7]. Favorable experimental results were obtained. In addition, the repeatability of the experiment was investigated. From this study, a very reliable, sensitive, and systematic method was set up for inferring writing age, which is especially suitable for practical cases.

### 2 Experimental

#### 2.1 Laboratory apparatus, reagents and specimen

Laboratory apparatus: HP6890 type gas chromatograph equipped with a hydrogen flame ionization detector (FID).

Reagent: acetonitrile (superfine chromatograph-grade alcohol), phenoxetol, benzyl alcohol (Shanghai Pen Core Plant, China).

Specimen: 1<sup>#</sup>: ZEBRA JANMEE RB-100 (Japan), 2<sup>#</sup>: HOUDLY 198KB, 3<sup>#</sup>: KOREA PIONEER 602 0.38 blue ballpoint ink (Mirae Co. J-203, Korea).

#### 2.2 Chromatographic conditions

Chromatographic column: FFAP, high-inertia cross linkage

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elastic quartz capillary column (30 m×0.25 mm, i.d.×0.3 μm), column temperature: 60 °C (1 min), 8 °C/min 220 °C (10 min), detector temperature: 280 °C, vapourizing chamber temperature: 240 °C, carrier gas (N<sub>2</sub>) flowing velocity: 2.0 ml/min, H<sub>2</sub> velocity of flow: 35.0 ml/min, air flowing velocity: 350 ml/min, tail wind drift velocity: 2.0 ml/min, sample size: 2 μl.

### 2.3 Selection of the inside reference substance

Seven positions on the same stroke and on a different stroke were sampled separately from Specimen 1<sup>#</sup>. A 2-cm length stroke was taken per position and placed in an extraction solution of 1 ml methanol for 10 minutes. Extraction was determined by ultraviolet spectra.

### 2.4 Selection of the chromatogram standard substance

p-Cresol and 2-cresol (1 μl each) were added separately to 500 ml acetonitrile to make two different solutions. The stroke samples obtained in Sect. 2.3 above were broken down and placed in two test tubes, then 100 μl of the above solutions were added to determine which cresol could be used as the chromatogram standard substance. The crucial component of the stroke specimen solution was distilled for 30 minutes, then the extracted solution was analyzed by GC.

### 2.5 Measurement of the specimen

The three specimens were used separately to make strokes of equal lengths on paper with out fluorescence. The strokes were then allowed to age naturally under indoor lighting conditions. Sampling of each specimen was conducted every other half-month for ten months. Each stroke was sampled by pricking them with a syringe needle. From each specimen, 20 samples were taken and placed in a test tube and extracted for 30 minutes with 100 μl acetonitrile (containing 2-cresol), the extracted solution was then used for GC analysis. Pure methanol (900 μl) was added into the test tube and extraction was conducted for 10 minutes, the highest absorbency at 665 nm (for copper phthalocyanine) and/or 580 nm (for three fragrant methane genera dye) was measured and recorded using the ultraviolet spectrophotometer. At the same time, the extracted solution from the same paper was also used as a UV reference solution.

### 2.6 Repeatability of the experiment

Based on the experimental procedure in Sect. 2.5, five experiments could be conducted on four specimen strokes for three different time frames in order to confirm the repeatability of the result.

## 3 Results and discussion

### 3.1 Ascertaining the basis of ballpoint ink buildup time change law

Ballpoint pen ink contain a highly volatile solvent, which primarily dissolves resin to maintain the flow of the ink. In ballpoint pen ink that has been on paper for a period of time, the solvent would continue to be volatile and eventually disappear. From this, we can establish a curve based on the decrease in volatility of the solvent and thus determine the writing age of the ballpoint pen ink. In order to eliminate the effect of writing force, writing thickness difference, pen oil pump capacity difference, etc. on writing age, there is a need to select the proper reference substance. At the same time, to eliminate sample size and instrumental operation error, a proper standard substance should also be selected.

#### 3.1.1 Selection of the reference substance

The ink in ballpoint pen cartridges contains both dye and solvent and are stable under measurement conditions. The dye of the ballpoint pen ink was then selected as the reference substance. The essential component of blue ballpoint pen ink dye is either copper phthalocyanine or three fragrant methane genera dye. Some dyes do not contain copper phthalocyanine, but contain three fragrant methane genera dye only. Previous experiments [6] indicate that copper phthalocyanine and three fragrant methane genera dye can be used as reference substance .

#### 3.1.2 Selection of the chromatogram standard substance

Both the molecular weight and boiling point values of the chromatogram standard substance and reference substance should be close with similar structures, and the holding time of the standard substance and the analyte should also be close, but distinguishable. The experiment results indicated that p-cresol and phenoxetol cannot be separated, but the retention time of 2-cresol is between that of the holding time of benzyl alcohol and phenoxetol (see Ref. [6] for chromatogram). When 1 μl of 2-cresol is added to 500 ml acetonitrile, its response value and the response value of benzyl alcohol or phenoxetol in fresh ink were close. The amount of chromatogram standard substance was 0.2 μl after 0.5 hours and its response value and the response value of benzyl alcohol or phenoxetol in ink remained close. Therefore, 2-cresol is a better chromatogram standard substance than p-cresol.

### 3.2 Determining the relative age of blue ballpoint pen ink

The solvent component in ballpoint pen ink made by various ballpoint pen manufacturers is different. It is also

different for every brand—benzyl alcohol, phenoxetol, glycol, diatomic alcohol content, etc. At present, both benzyl alcohol and phenoxetol are used in China. We have been able to identify 74 kinds of blue ballpoint pen ink [7] and placed them in 3 categories based on the different contents of the solvent. Their buildup time law is discussed below.

### 3.2.1 First category specimen writing age variance law

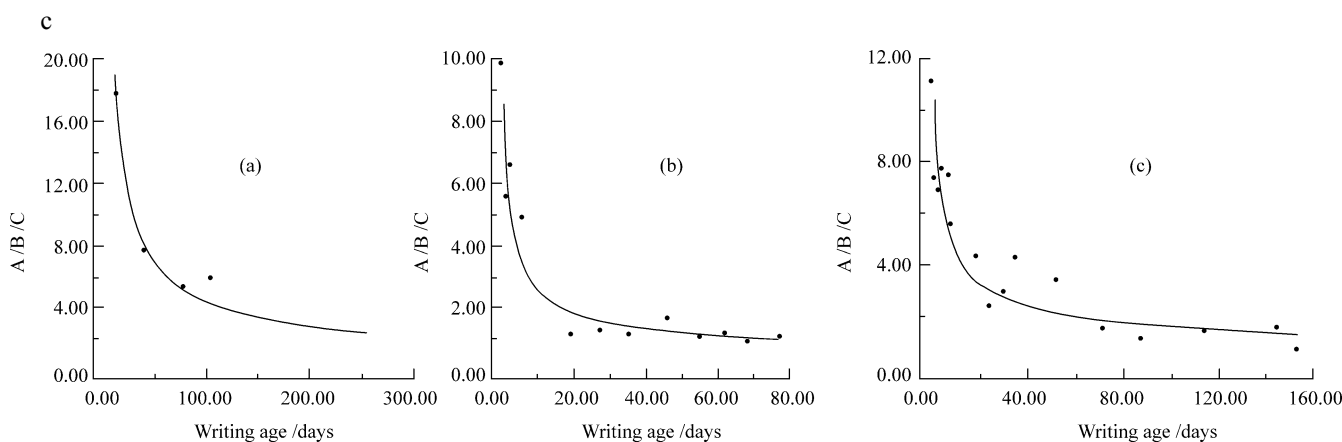
All solvents in the first category of ballpoint pen ink contain both benzyl alcohol and phenoxetol, but the phenoxetol component is greater than benzyl alcohol. Sample 1 belongs to this category. Table 1 shows the peak areas of phenoxyethyl

alcohol (A) and 2-cresol (B), the absorbance of copper phthalocyanine (C), and their ratio (A/B/C) in Sample 1 after several months.

Figure 1a shows the ratio of the peak area of phenoxyethyl alcohol, the peak area of 2-cresol, and the absorbance of copper phthalocyanine on the vertical ordinate, and the writing age on the horizontal ordinate. It can be observed that the writing age law of this category of ballpoint pen ink sample is: as the writing time increases, the ratio of the peak area of phenoxyethyl alcohol, the peak area of 2-cresol, and the absorbance of copper phthalocyanine decreases. At the beginning, the slope of the curve is bigger. This is because resin does not solidify immediately and solvent is highly volatile on the surface.

**Table 1** Peak area of phenoxyethyl alcohol (A), peak area of 2-cresol (B), absorbance of copper phthalocyanine (C) and their ratio (A/B/C) in Sample 1 after several months

Writing age (days)	A	B	C	A/B/C
255	11.5	131.1	0.047	1.87
104	47.9	130.3	0.062	5.93
78	48.4	129.7	0.068	5.49
38	75.9	131.8	0.075	7.68
11	52.1	127.5	0.023	17.77



**Fig. 1** (a) Age curve of Sample 1 (in ink containing greater phenoxetol component). (b) Age curve of Sample 2 (in ink containing greater benzyl alcohol component). (c) Age curve of Sample 3 (in ink containing benzyl alcohol only).

The slope of the curve decreases as time increases, which is due in part to the resin beginning to solidify by this time. The solvent is less volatile or diffuses with more difficulty from a half-solidified membrane. Finally, when the resin and other components have completely solidified, the solvent barely diffuses and escapes, and is kept basically constant.

### 3.2.2 Second category specimen writing age variance law

The solvent in the second category of ballpoint pen ink

contains both benzyl alcohol and phenoxetol, but the benzyl alcohol component is greater than phenoxetol. Sample 2 belongs to this category.

Based on the experiment results, the peak areas of phenoxyethyl alcohol and 2-cresol, and the absorbance of copper phthalocyanine were plotted. Figure 1b shows the ratio of the samples on the vertical ordinate and the writing age on the horizontal ordinate. It can be observed that the writing age law of this category of ballpoint pen ink are basically the same as the first category, but the ratio decreases very quickly. This indicates that the volatilization speed of benzyl alcohol is quicker than that of phenoxetol.

### 3.2.3 Third category specimen writing age variance law

The solvent of the third category ballpoint pen ink contains benzyl alcohol only. Sample 3 belongs to this category. Since the dye of this sample does not contain copper phthalocyanine, three fragrant methane category dye was used as the reference substance. From the experiment results, the ratio of the peak area of benzyl alcohol, the peak area of 2-cresol and the absorbance of three fragrant methane category dye were plotted on the vertical ordinate, and the writing age on the horizontal ordinate (Fig. 1c). It can be observed in Fig. 1c that the writing age law of this category of ballpoint ink is basically the same as the first and second categories of ballpoint ink.

The time curve variance of the third category specimen is basically the same in trend. However, the time for the solvent to reach a constant level is different because the solvent category and content are different, therefore, inflection of the curve is different. At the same time, the experimental results indicate that utilizing solvent component variance to investigate writing age is suitable for determination of handwriting of up to three months. 2.3 experimental repeatability

### 3.3 Experimental repeatability

In order to confirm the reliability of the experimental method,

we performed five experiments with three handwriting samples from Sample 1 to Sample 3 at different writing ages. The experimental results indicate that, since all relative standard deviations are in the range of the allowable error, the repeatability is satisfactory. Table 2 shows the results from Sample 1.

**Table 2** Repeatability results of Sample 1

Writing age (days)	Average value	RSD (%)
97	5.45	6.42
83	5.28	3.62
4	17.25	2.23

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