

# Monitoring aging kinetics for forensic document dating: A comparative gas chromatography-mass spectrometry (GC-MS) and chemometric analysis of ballpoint and gel pen inks

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**Abstract:** Determining the age of pen inks plays an important role in the analysis of questioned documents. In this study, a total 40 different pens comprising 20 ballpoint and 20 gel models from various major global and regional brands in blue, black, green, and red colors were analyzed using Gas Chromatography-Mass Spectroscopy to determine the glycol-based solvents in the ink composition, and a time curve between 0–8 months was obtained. The obtained data were evaluated using chemometric methods to assess the effect of pen type and color. The results of this study show that Gas Chromatography-Mass Spectrometry can be used to determine the date of creation of documents produced between 0–8 months by analyzing inks of different brands, models, types, and colors. The novelty of this research lies in providing a comparative aging model that simultaneously evaluates both ballpoint and gel inks using an accessible standard liquid extraction GC-MS method. Furthermore, GC-MS-based RPA tracking offers a promising approach to document creation time estimation, while chemometric methods such as PCA and HCA provide critical classification of the ink type statistically proving that aging kinetics are dependent on the specific interaction of pen type and color.

**Keywords:** Ethylene glycol, GC-MS, document forgery, forensic chemistry

## 1 Introduction

Documents written with gel and ballpoint pen inks frequently appear in many investigations. Therefore, determining the creation dates of documents written with pen inks is of great importance in forensic science. Determining the authenticity of questioned documents is a critical challenge, where the analysis of ink can reveal crucial information regarding document forgery, backdating, and unauthorized alterations (Calcerrada & García-Ruiz, 2015; Weyermann, 2013). The examination of writing media is frequently requested in criminal investigations, civil litigation, and historical manuscript verification (Aginsky, 2008; Weyermann & Techabowornkiat, 2019).

Although there are different types of pens, pen inks are generally a complex mixture containing dye or pigment based colorants, solvents, resins, and many additives (Barker et al., 2016; Cantu, 1995). These chemical formulations vary

significantly between ballpoint pens and gel pens (Aginsky, 2006).

Ink analysis within forensic document examination is typically divided into static and dynamic approaches (Cantú, 2017). Static profiling focuses on characterizing the stable chemical composition of the ink to identify the pen type or match it to a reference database, while dynamic profiling monitors the physical and chemical changes that occur in the ink over time to estimate the absolute or relative age of the document (Aginsky, 2025; Weyermann & Spengler, 2008; Cantú, 2012). Following the deposition of ink on paper, natural aging involves processes such as the fading and degradation of colorants, polymerization of resins, and the evaporation or diffusion of volatile solvents (Andrasko, 2001; Díaz-Santana et al., 2023; Sabater et al., 2021). It is important to note that since the aging process the ink undergoes while stored inside the pen cartridge is negligible compared to the aging process on the paper, researchers generally accept that the ink does not age inside the cartridge; rather, the aging process begins the moment the ink is transferred to the paper (Grim et al., 2002; Andrasko & Kunicki, 2005; Aginsky, 2014).

To monitor these changes, forensic scientists employ a wide array of optical, spectroscopic, and chromatographic techniques. Initial examinations often utilize non-destructive

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or micro-destructive methods such as ultraviolet-visible (UV-Vis) spectrophotometry, Fourier transform infrared (FTIR) spectroscopy, and Raman spectroscopy (Causin et al., 2008; Guo et al., 2025). Furthermore, analytical methods such as thin layer chromatography (TLC), high performance thin layer chromatography (HPTLC), and thermal desorption gas chromatography mass spectrometry (TD-GC-MS) have been extensively used to analyze ballpoint and gel pens (Kravchenko et al., 2024a; Kaur et al., 2025; Radosavljević-Stevanović et al., 2025; Díaz-Santana et al., 2017; Kravchenko et al., 2024b).

In addition to these methods, gas chromatography mass spectrometry (GC-MS) is one of the most frequently preferred methods for ink age analysis due to its accessibility and its ability to measure the concentration of the organic component (Andrasko & Lagesson-Andrasko, 2024; Islek & Cengiz, 2020; Koenig et al., 2015; Bügler et al., 2008). Compared to spectroscopic techniques (e.g., FTIR, Raman, and UV-Vis), which are rapid and non-destructive but often struggle to accurately quantify individual volatile components within complex overlapping matrices, GC-MS provides superior sensitivity, definitive structural identification through mass spectral libraries, and reliable quantitative precision. Furthermore, while techniques like TLC offer cost-effective preliminary screening, GC-MS excels in resolving structurally similar solvents. However, the GC-MS methodology also presents notable limitations. Unlike optical methods, it is a micro-destructive technique that requires physical extraction (micro-punching) from the questioned document. Additionally, it involves higher instrumental and operational costs, necessitates more time-consuming sample preparation, and demands highly specialized personnel for operation and data interpretation (Gin & Imwinkelried, 2018; Hübschmann, 2025). Minimum requirements and standardized protocols have been proposed to ensure the reproducibility of these solvent-based dating methods in casework (Weyermann et al., 2011). Studies have successfully quantified the loss of specific solvents, such as phenoxyethanol, from ballpoint pen ink entries to construct temporal aging curves (Weyermann et al., 2007; Locicero et al., 2004; Carvalho et al., 2019). Furthermore, Li et al. (2014) and Saini and Rathore (2018) examined the volatile components and solvent changes in gel pens; Ni et al. (2020) indicated that age determination could be performed up to 9 months using triethylene glycol analysis.

In studies on ballpoint pens, Koenig et al. (2015) emphasized the reliability of the relative peak area (RPA) value in aging tracking, while Sun et al. (2016) argued for the necessity of combined techniques for accurate differentiation. Díaz-Santana et al. (2023, 2017) developed long term aging models by combining dye and solvent analyses. Today, chemometric methods such as Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA) are indispensable for the objective interpretation of these complex multidimensional datasets, grouping samples effectively and exposing differences in scaling kinetics. Despite these, a significant limitation in the current literature is the lack

of comparative aging models that simultaneously evaluate both ballpoint and gel pen inks using standard, highly accessible liquid extraction GC-MS methods. Many studies focus on isolated ink types or employ specialized desorption techniques that may not be available in all routine forensic laboratories.

To address this gap, the purpose of this study is to establish a comprehensive and comparative aging model for document dating by analyzing glycol-based solvents. Specifically, the procedures performed include the natural aging (0–8 months) of 40 different blue, black, red, and green ballpoint and gel pen inks, followed by standard liquid extraction GC-MS analysis to construct RPA aging curves. Furthermore, descriptive statistics and advanced chemometric models (PCA and HCA) were applied to discriminate pen types and observe effects of formulation and color on aging kinetics.

## 2 Materials and Methods

### 2.1 Pens, Paper and Archive

Forty blue, black, green, and red ballpoint and gel pens were collected from local stationery stores in Türkiye. The sample set was carefully selected to represent a diverse array of 20 ballpoint and 20 gel pens, encompassing popular global manufacturers and regional brands. An ID (e.g., MT1–MT5 for blue ballpoint, MJ1–MJ5 for blue gel) was assigned to each pen. All detailed information regarding the specific brands, models, ink types, colors, and assigned IDs is provided in the Supplementary Material (Table S1). Since the precise manufacturing dates are not provided by manufacturers on retail packaging, all pens were purchased simultaneously and immediately used to create the  $t = 0$  baseline, reflecting realistic conditions in forensic casework. Each month, 40 lines were drawn on paper (80 g/m<sup>2</sup> Copier Bond) using ruler by the same analyst. The lines are approximately 20 cm long and spaced 5 cm apart (the reason for this spacing is to prevent interference due to the horizontal and vertical diffusion of solvents in the ink on the paper surface). A separate sheet of paper was used for each monthly time point (totaling 36 sheets). To minimize the inherent background heterogeneity of the paper matrix, all paper sheets were strictly sourced from the same commercial ream and production lot. The archive was stored at a temperature of 23–25°C and a humidity range of 45–55%.

### 2.2 Chemicals

In this study, Ethylene Glycol (EG, Reagent Grade, ≥99%), 1,5-Pentanediol (PD, ≥97%), 2-Pyrrolidone (PYR, ≥99%), 1,6-Hexanediol (HD, 99%), Diethylene Glycol Monobutyl Ether (DGME, 99%) (Sigma Aldrich, Germany), Phenoxyethanol (PE, ≥99.5 %) (Tekkim Kimya, Türkiye), and Phenoxyethoxyethanol (PEE, >98.5%) (TCI, Japan) standards were used. N-Butanol (IS, HPLC Grade) (Sigma Aldrich, Germany) was used as the internal standard, and the solutions were prepared in methanol (Sigma Aldrich, Germany). These specific solvents were selected as targets because they are the most frequently utilized volatile

**Table 1.** Temperature program of GC-MS oven

|        | Rate<br>(°C/min.) | Temp. (°C) | Hold<br>(min.) | Total<br>(min.) |
|--------|-------------------|------------|----------------|-----------------|
| Start  |                   | 50         | 1              |                 |
| Ramp-1 | 10                | 80         | –              | 15              |
| Ramp-2 | 15                | 150        | –              |                 |
| Ramp-3 | 5                 | 180        | –              |                 |

vehicle components in commercial ballpoint and gel ink formulations.

### 2.3 Instrumentation

The analyses were performed on an Agilent (Agilent Technologies, USA) Gas Chromatography-Mass Spectrometer 7820A/5977E Mass Selective Detector (MSD) device. An Agilent (Agilent Technologies, USA) HP 5MS capillary column (30 m × 0.25 mm × 0.25 μm) was used in the study. Helium was used as the carrier gas, and the gas flow was set at 1 mL/min. The sample was injected in splitless mode, and the injector temperature was maintained at 250°C. The analyses were performed in scan mode and lasted a total of 15 min. The GC-MS oven program is given in Table 1.

For the mass spectrometer (MS) parameters, the system was operated in Electron Impact (EI) ionization mode with an electron energy of 70 eV. The transfer temperature was set to 280°C, the ion source temperature was set to 230°C, and the quadrupole temperature was maintained at 150°C. Data acquisition was performed in full scan mode and a solvent delay of 5 minutes was applied. Peak areas were integrated automatically using the instrument's analytical software.

### 2.4 Preparation of Solutions

Mixture solutions at concentrations of 1, 5, 10, 15, 20, 25, and 30 μg/mL with include each analyte were prepared from standard analytes using methanol. Solutions were stored at +4°C until analysis to prevent solvent loss due to the evaporation. Specificity, selectivity, Limit of Detection (LOD), and Limit of Quantitation (LOQ) calibration, and repeatability analyses were performed. LOD and LOQ were determined experimentally based on Signal-to-Noise (S/N) ratios of 3:1 and 10:1, respectively. The upper limit of linearity for the calibration curves was established at 30 μg/mL.

### 2.5 Archived Sample Preparation

Five sample disk were extracted using a 5 mm micro punch. The extraction was performed by adding 500 μL of methanol containing the Internal Standard (N-Butanol) at a concentration of 10 μg/mL. The samples were vigorously vortexed at 2500 rpm for 5 minutes to facilitate initial solvent release, followed by extraction in an ultrasonic water bath at 70°C for 10 minutes to maximize solvent recovery.

### 2.6 Statistical Analysis

All statistical analyses and graphical representations of the data obtained within the scope of the study were performed

using OriginPro 2025b (OriginLab Corporation, Northampton, MA, USA) software.

#### 2.6.1 Descriptive Statistics

To determine the general distribution characteristics of the data set, descriptive statistical analyses were performed, including the mean, standard deviation, median, minimum-maximum values, skewness, and kurtosis coefficients.

#### 2.6.2 Normality Test

The normality of the data distribution was checked using the Shapiro-Wilk test, and it was examined whether the data met the assumptions of parametric tests.

#### 2.6.3 Three-Way ANOVA

A Three-Way Analysis of Variance (ANOVA) was used to examine the main effects of independent variables (e.g., pen type, ink color, and time) on the dependent variable (RPA) and the interaction effects between these variables. To determine the source of the differences found to be significant in the variance analysis, the Tukey's Honestly Significant Difference (HSD) test was applied from multiple comparison tests, and the statistical significance level was accepted as  $p < 0.05$ .

#### 2.6.4 Principal Component Analysis (PCA)

Principal Component Analysis was performed to reduce the number of dimensions in the multivariate data set, explain the relationships between variables, and visualize clustering tendencies between samples. The PCA analysis was based on the correlation matrix so that the variables would not be affected by differences in scale, and the principal components explaining the highest variance were interpreted. The input variables for the PCA model were the quantitative RPA values measured at each monthly interval (0 to 8 months) for all samples.

#### 2.6.5 Hierarchical Cluster Analysis (HCA)

Hierarchical Cluster Analysis (HCA) was applied to determine the solvent loss kinetics and pattern similarity of ink samples during their 0–8 month aging processes. The input variables for the PCA model were the quantitative RPA values measured at each monthly interval (0 to 8 months) for all samples. In the analysis, the Ward linkage method was preferred, which forms compact groups by minimizing the variance between clusters. As a distance measure, the Cosine distance metric was used, which focuses on the orientation and curve shape of the change vectors over time rather than the absolute RPA values of the samples. This metric demonstrates superior performance in grouping inks that exhibit similar aging behavior, even if they have different initial concentrations. Variable standardization was not applied, and the analysis was performed under the assumption of two clusters ( $k = 2$ ) to test ink type discrimination.

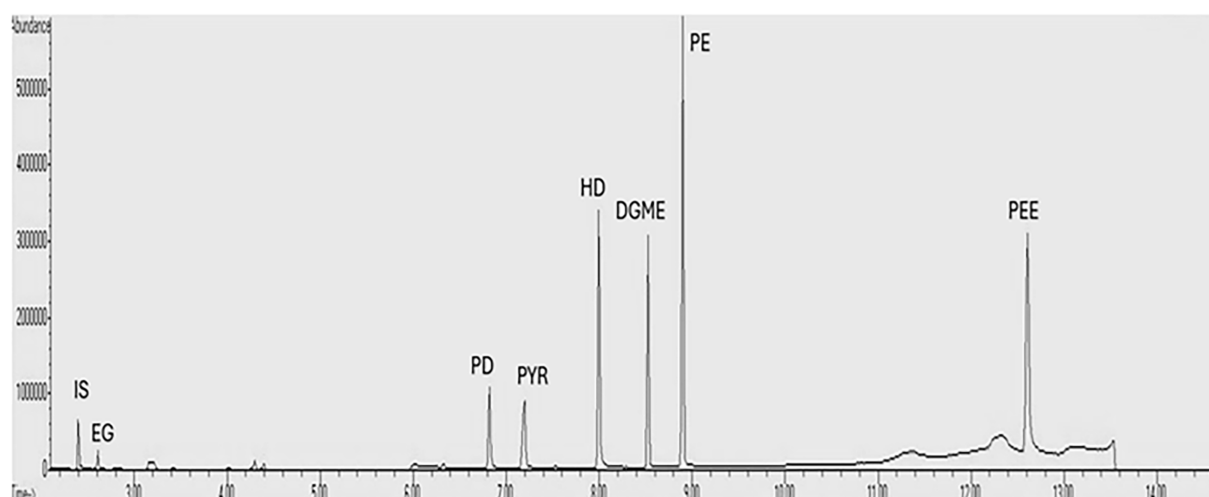


**Figure 1.** Chromatogram of 30 µg/mL mix solution

### 3 Results

#### 3.1 Validation Parameters

Specificity and selectivity were confirmed by analyzing blank paper extracts and ensuring the absence of matrix interferences at the specific retention times of the target analytes (2.61 min for EG, 6.815 min for PD, 7.195 min for PYR, 7.998 min for HD, 8.523 min for DGME, 8.899 min for PE, and 12.608 min for PEE, Table S2). Specificity and selectivity were verified by analyzing blank paper extracts and confirming the absence of interfering peaks at the retention times of the target analytes (Figure S8). Analyte identification was confirmed by matching retention times and mass spectra with library databases and pure standards. The representative chromatogram of the 30 µg/mL mix solution is shown in Figure 1.

Calibration curves were plotted for solutions at concentrations of 5, 10, 15, 20, 25, and 30 µg/mL (Figure S1). The calibration parameters, including linear ranges, regression equations, correlation coefficients ( $r$ ), and determination coefficients ( $R^2$ ) for all target analytes are summarized in Table S4. Examining the calibration curves, it is observed that the  $R^2$  values are greater than 0.98, indicating that the calibrations are linear (Figure S9). LOD and LOQ were experimentally determined based on Signal-to-Noise (S/N) ratios of 3:1 and 10:1, respectively, using low concentration spiked samples. Accuracy and repeatability were assessed by analyzing six independent replicates of the low, medium and high concentration with respectively 5, 15 and 30 µg/mL mixture. The most conservative LOD and LOQ values across all target analytes for this method were determined to be 1 µg/mL and 5 µg/mL, respectively, ensuring a uniform reporting baseline. All archive sample measurements remained within the established linear range of the calibration curves. A 5, 15 and 30 µg/mL mixture solutions were prepared by the same analyst on the same day and introduced into the system in six consecutive replicates. The mean, standard deviation (SD), and relative standard deviation (%RSD) values are given in Table 2.

The precision at the highest concentration remained exceptionally high, with %RSD values between 0.3% and 0.4% across all compounds. Crucially, the methodology also demonstrated precision at the lower limits (5 µg/mL) the %RSD values ranged from 2.3% (PEE) to 6.7% (DGME). Furthermore, the intermediate concentration yielded highly reproducible results, with %RSDs consistently at or below 2.4%. Consequently, these validation parameters conclusively demonstrate that the developed GC-MS procedure is reliable, accurate, and reproducible.

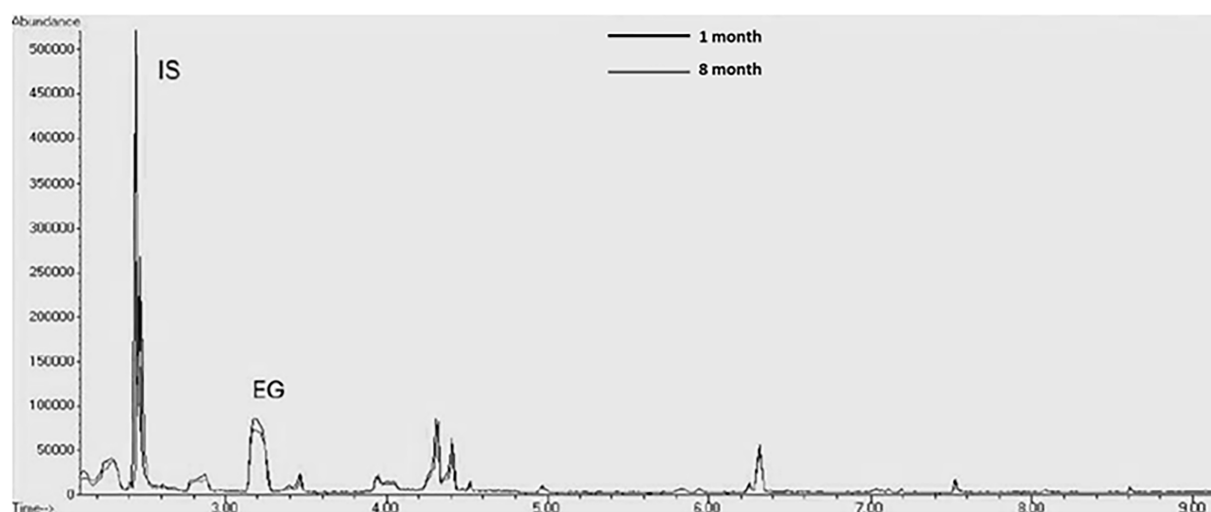
#### 3.2 Archive Analysis and Aging Curve

Analysis of the 0–8 month archives revealed that EG was detected in all pens, while PYR were predominantly detected in gel pens (in 16 out of 20 pens). The solvents PD, HD and DGME could not be quantified because their concentrations remained below the LOD when working in scan mode. On the other hand, while PE and PEE solvents were detected qualitatively, they could not be detected quantitatively as they were not suitable for quantitative determination. To systematically characterize the ink compositions, the qualitative presence of the target glycol-based solvents across all 40 ballpoint and gel pens is summarized in Table S3. To demonstrate the aging phenomenon, representative sample has been selected. Figure 2 shows that the overlaid chromatograms of a black gel (SJ-1) pen at the 1-month and 8-month archiving intervals.

Although it is known that the ratio of the solvent peak area to the internal standard decreases over time in chromatograms, it has been observed that this change is influenced not only by volatility but also by the total solvent mass, which is related to the width and thickness of the ink trace. To eliminate this variation caused by the amount of extracted material, Koenig proposed comparing the volatile solvent peak area to the peak area of a nonvolatile or stable component within the ink. RPA calculated using this method becomes independent of the amount extracted and theoretically exhibits an exponential decrease over time (Koenig

**Table 2.** Validation of GC-MS in terms of repeatability

| Analyte | Concentration (µg/mL) | Mean (n = 6) | SD  | %RSD |
|---------|-----------------------|--------------|-----|------|
| EG      | 5                     | 5.1          | 0.3 | 5.5  |
|         | 15                    | 15.0         | 0.2 | 1.3  |
|         | 30                    | 30.0         | 0.1 | 0.3  |
| PD      | 5                     | 4.9          | 0.2 | 4.6  |
|         | 15                    | 15.2         | 0.1 | 0.5  |
|         | 30                    | 30.1         | 0.1 | 0.4  |
| PYR     | 5                     | 5.1          | 0.3 | 5.0  |
|         | 15                    | 15.2         | 0.3 | 1.8  |
|         | 30                    | 29.9         | 0.1 | 0.4  |
| HD      | 5                     | 5.2          | 0.2 | 4.4  |
|         | 15                    | 15.1         | 0.3 | 1.8  |
|         | 30                    | 29.9         | 0.1 | 0.3  |
| DGME    | 5                     | 5.0          | 0.3 | 6.7  |
|         | 15                    | 15.2         | 0.4 | 2.3  |
|         | 30                    | 30.1         | 0.1 | 0.3  |
| PE      | 5                     | 5.0          | 0.2 | 3.3  |
|         | 15                    | 15.1         | 0.2 | 1.0  |
|         | 30                    | 29.9         | 0.1 | 0.3  |
| PEE     | 5                     | 5.1          | 0.1 | 2.3  |
|         | 15                    | 15.0         | 0.4 | 2.4  |
|         | 30                    | 29.9         | 0.1 | 0.3  |

**Figure 2.** Overlaid chromatograms of a black gel (SJ-1) pen at the 1-month and 8-month

et al., 2015). Although seven solvents were initially screened and calibrated, Ethylene Glycol (EG) was selected as the primary target analyte for the RPA aging calculations. This decision was based on its ubiquitous presence across the tested ink samples and its consistent, measurable solvent loss profile over the 8-month period. For the archives analyzed, the age curve for ethylene glycol, which is suitable for ink age detection, was calculated according to the RPA equation (Eq. (1)).

The calculations are given in Table S5–S6. The graphs obtained as a result of the calculations are shown in Figures 3 and 4. Also, individual graphs for each pen group were provided in Figure S10–S17.

$$\text{RPA} = \text{Peak Area of EG} / \text{Peak Area of IS} \quad (1)$$

In all analyzed ink types and colors, it was found that RPA values decreased over time. The degradation kinetics varied

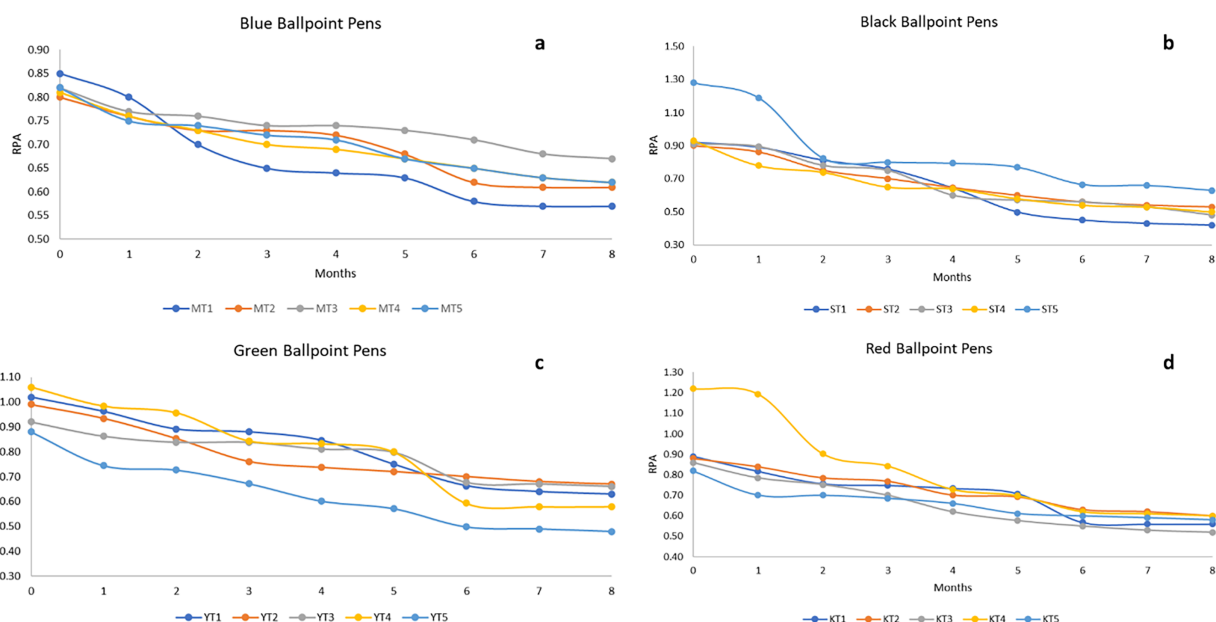


Figure 3. (a) Blue ballpoint pen, (b) black ballpoint pen, (c) green ballpoint pen, and (d) red ballpoint pen RPA-time graph

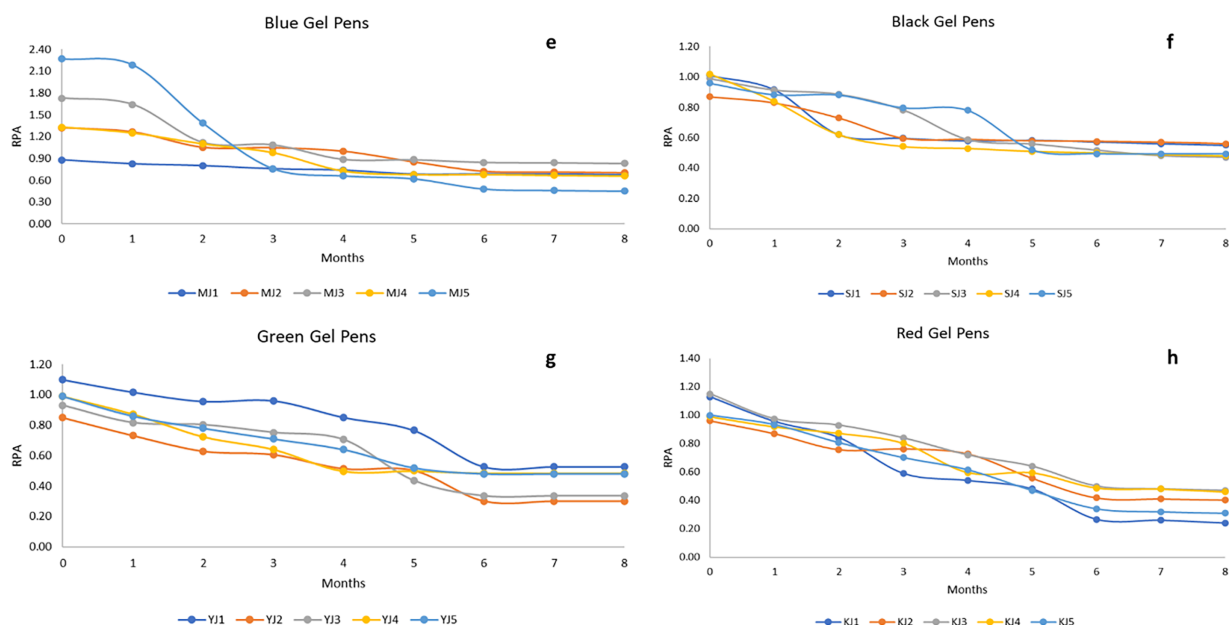


Figure 4. (e) Blue gel, (f) black gel, (g) green gel, and (h) red gel pen RPA-time graph

significantly depending on the formulation; while some samples (e.g., red gel and certain black ballpoint pens) showed a rapid decline within the first 1–2 months, others exhibited a more gradual and stable decrease over the 8-month period. This finding indicates that a volatile component such as EG rapidly disappears in the early stages of archiving. Gel pen inks generally exhibited higher initial RPA values and lower RPA values at 8 months compared to ballpoint pen inks. This situation reveals that gel ink formulations are less stable than ballpoint inks in terms of the EG component under archival conditions and that these types of inks exhibit more complex solvent loss kinetics in studies determining ink age in the

context of forensic science. The effect of pen type and color on the time dependent change in EG was evaluated in detail using statistical methods.

Although other solvents such as PD, HD, and DGME were evaluated during the initial screening, their concentrations in most ink formulations proved inherently low. As a result, their levels rapidly decreased below the LOD shortly after deposition, precluding continuous quantitative tracking. To effectively mitigate the statistical variance introduced by these sub-LOD values, a targeted analytical selection was crucial. For these reasons, all statistical models and aging curves in this study were constructed exclusively utilizing EG.

### 3.3 Statistical Analysis

#### 3.3.1 Descriptive Analysis

In this study, descriptive statistical analysis was performed on measurements taken from  $t = 0$  to  $t = 8$  for four different colors (blue, black, green, red) of permanent and gel pen inks. The sample size  $N = 5$  was kept constant for each group. The analysis results were evaluated based on the mean, standard deviation (SD), and distribution parameters (Skewness, Kurtosis) (Table S7). In this context, skewness was utilized to evaluate the asymmetry of the data distribution around its mean, which helps in identifying whether the solvent evaporation kinetics exhibit disproportionate shifts (e.g., instantaneous changes in fresh samples causing positive deviation). Kurtosis was evaluated to measure the tailedness of the probability distribution, providing a quantifiable metric to identify the presence of extreme outliers or heavy tails, particularly in the highly variable initial drying stages of the inks. The mean RPA value of blue ballpoint pens was  $0.82 (\pm 0.01)$  at the beginning ( $t = 0$ ) and decreased steadily to  $0.61 (\pm 0.03)$  at the end of the 8th month. The low standard deviation values throughout the process ( $0.01\text{--}0.03$ ) indicate that the blue ballpoint pen measurements are repeatable. The initial value for black ink pens is higher ( $0.98 \pm 0.16$ ). However, with the aging process, a much sharper decline occurred, reaching a value of  $0.51 (\pm 0.07)$  at  $t = 8$ . In particular, the high values of Kurtosis (4.90) and Skewness (2.21) at  $t = 0$  indicate that the data in fresh samples deviated from normal distribution and contained outliers. Both color groups exhibited similar aging kinetics. Green ink decreased from  $0.97 (\pm 0.07)$  to  $0.60 (\pm 0.07)$ , while red ink decreased from  $0.93 (\pm 0.16)$  to  $0.57 (\pm 0.03)$ . It is noteworthy that the initial ( $t = 0$ ) variation of red inks ( $SD = 0.16$ ) is higher than that of green inks ( $SD = 0.07$ ). As shown in Figure 3 (see Figure S9–12 for a detail) samples ST5 and KT4 presented a notable deviation. This demonstrated ST5 and KT4 significantly higher initial RPA value and experienced a rapid, sharp decline within the first 2 to 3 months. This unique behavior of ST5 and KT4 in the stages of aging indicates a potential variation in their chemical formulation, such as a higher initial concentration of the volatile solvent which facilitates a faster evaporation rate immediately upon deposition.

Blue gel pens have the highest initial average ( $1.506 \pm 0.52$ ) in the study. However, the most notable finding in this group is the very high standard deviation at  $t = 0$  and  $t = 1$  ( $SD \approx 0.52$ ). The difference between the median (1.33) and the mean, along with the wide range (Min: 0.88, Max: 2.27), indicates that the fresh blue gel samples are not homogeneous or that they show significant variation in the early stages of the drying process. At the end of the process, the value decreased to  $0.66 (\pm 0.13)$  and the variation decreased. The generally low standard deviations in black gel pens ( $0.97 \pm 0.03\text{--}0.51 \pm 0.06$ ) indicate that the measurement stability of black gel ink is much higher than that of blue gel ink. Red gel pens showed one of the most dramatic declines in the study. The average value, which was  $1.04 (\pm 0.08)$  at  $t = 0$ , declined to  $0.37 (\pm 0.09)$  at  $t = 8$ . In this case, it is thought that red gel pens have a higher fading rate over time than other colors due to differences in their formulations.

In fresh samples ( $t = 0$ ,  $t = 1$ ), some groups (e.g., Ballpoint Black  $t = 0$ , Skewness: 2.21) are observed to deviate positively from the normal distribution. This situation may be due to the evaporation of solvents in fresh inks causing instantaneous changes, resulting in unexpectedly high peak areas in some samples. Over time ( $t = 5$  and beyond), it was observed that the Skewness values of most groups approached zero and the distribution became more symmetrical. This indicates that the chemical structure of the ink transitioned to a more stable phase over time. Permanent pens exhibit a more consistent aging profile with lower standard deviations, while gel pens (especially blue) show high variation in the initial phase but exhibit a faster degradation/decline trend. Red colored inks (both gel and ballpoint) were identified as the group experiencing the highest proportional value loss compared to other colors.

#### 3.3.2 Normality Test

To ensure the reliability of statistical analyses and determine the type of hypothesis tests to be applied, the normality of the data set was examined using the Shapiro-Wilk test. The Shapiro-Wilk test is a statistical method utilized to evaluate whether a continuous variable follows a normal distribution. Its primary usefulness in this experimental design lies in its high sensitivity and statistical power for relatively small sample sizes ( $N = 5$  per subgroup). Establishing normality is a crucial mathematical prerequisite to ensure that subsequent parametric methods (e.g., Three-Way ANOVA), which offer superior statistical power for evaluating interactions between variables, yield valid and unbiased results. Therefore, the normality of the data distribution was systematically checked using the Shapiro-Wilk test to examine whether the data met the fundamental assumptions of these parametric tests. The analyses were performed separately for each subgroup created according to the parameters of pen type, color, and time, and the statistical significance level was set at  $\alpha = 0.05$ . The analysis results are given in Table S8, and the box chart is given in Figure 5.

When examining the Shapiro-Wilk test results, it was observed that the calculated  $p$ -values were greater than 0.05 ( $p > 0.05$ ) in the vast majority of experimental groups. This indicates that the null hypothesis ( $H_0$ ), that the data of the relevant groups follow a normal distribution cannot be rejected, thus confirming that the data conform to a normal distribution. Deviations from normal distribution were detected in the black ballpoint pen ( $t = 0$ ,  $p = 0.001$  and  $t = 4$   $p = 0.039$ ), red ballpoint pen ( $t = 0$ ,  $p = 0.012$ ), black gel pen ( $t = 4$ ,  $p = 0.037$ ), and green gel pen ( $t = 5$ ,  $p = 0.044$ ) deviate from normal distribution. Normality was achieved at a 93% rate, and it was concluded that the general distribution characteristics of the data set meet the assumptions of parametric tests. Therefore, it was decided to use parametric methods for intergroup comparisons.

#### 3.3.3 Three-Way ANOVA

A three-way ANOVA was conducted to determine the main effects of ink type, color, and aging time (months) on the

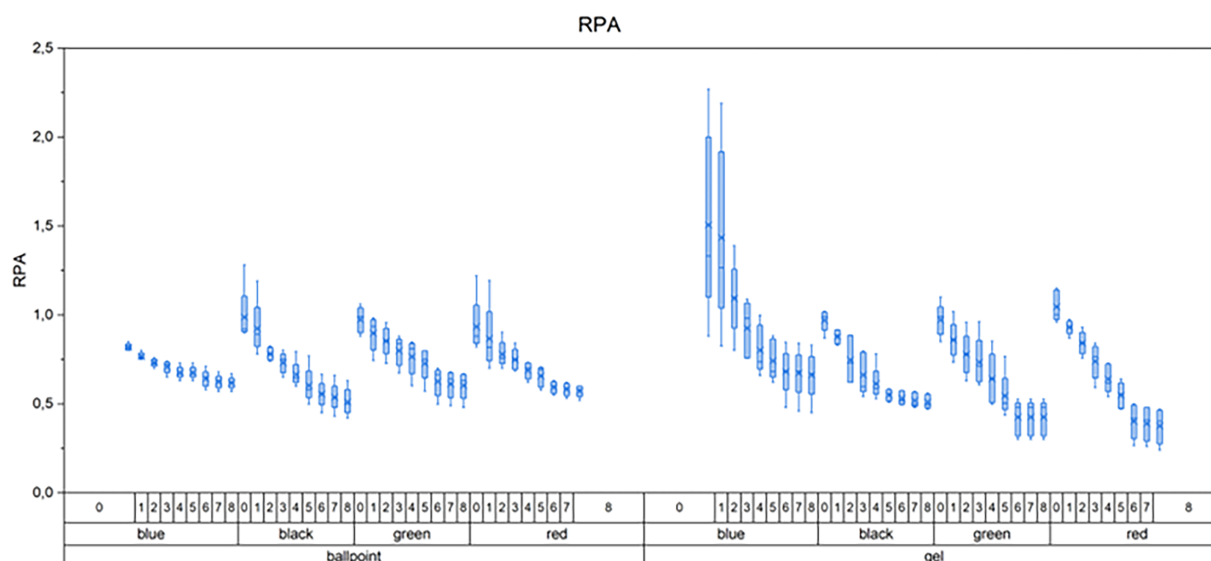


Figure 5. Box chart of normality test

Table 3. Overall ANOVA

|                      | DF  | Sum of squares | Mean square | F Value | P Value |
|----------------------|-----|----------------|-------------|---------|---------|
| Type                 | 1   | 0.01           | 0.01        | 0.62    | 0.42    |
| Color                | 3   | 1.18           | 0.39        | 24.07   | <0.0001 |
| Month                | 8   | 10.27          | 1.28        | 78.62   | <0.0001 |
| Type * Color         | 3   | 1.80           | 0.60        | 36.91   | <0.0001 |
| Type * Month         | 8   | 0.98           | 0.12        | 7.50    | <0.0001 |
| Color * Month        | 24  | 0.21           | 0.01        | 0.53    | 0.96    |
| Type * Color * Month | 24  | 0.81           | 0.03        | 2.07    | 0.002   |
| Model                | 71  | 15.28          | 0.21        | 13.17   | <0.0001 |
| Error                | 288 | 4.70           | 0.01        |         |         |

RPA, as well as the interactions between these factors. The overall model was found to have high explanatory power ( $F(71, 288) = 13.18$ ,  $p < 0.001$ ). The complete results of the analysis are summarized in Table 3.

Regarding the main effects at the 0.05 significance level, the aging time factor was the variable that produced the most statistically significant variance in RPA values ( $F(8, 288) = 78.62$ ,  $p < 0.001$ ). This finding confirms the hypothesis that the RPA parameter is a reliable indicator for determining ink age. Similarly, a significant main effect of ink color on RPA was detected ( $F(3, 288) = 24.08$ ,  $p < 0.001$ ). In contrast, the main effect of pen type alone did not produce a statistically significant difference in the population means of RPA ( $F(1, 288) = 0.63$ ,  $p = 0.429$ ). However, this does not imply that pen type has no influence; rather, its effect is masked by strong interactions with the other variables.

When examining the two-way interactions, the Type  $\times$  Color interaction was highly significant ( $F(3, 288) = 36.92$ ,  $p < 0.001$ ). This demonstrates that the variation in RPA values based on pen type differs depending on the color (e.g., the comparative behavior of blue gel versus blue ballpoint differs from that of red gel versus red ballpoint). Furthermore, the Type  $\times$  Month interaction was also

significant ( $F(8, 288) = 7.50$ ,  $p < 0.001$ ), indicating that the aging kinetics of gel and ballpoint pens exhibit distinctly different profiles over time. Interestingly, the Color  $\times$  Month interaction was not statistically significant ( $F(24, 288) = 0.54$ ,  $p = 0.964$ ). This suggests that, regardless of pen type, the time dependent degradation trends of the different colors follow parallel trajectories.

Ultimately, the most striking finding of the study is the statistically significant three-way interaction between Type  $\times$  Color  $\times$  Month ( $F(24, 288) = 2.08$ ,  $p = 0.003$ ). This result definitively shows that the ink aging process cannot be generalized by a single model. Each pen type (gel/ballpoint) combined with a specific color possesses unique aging characteristics. Therefore, these statistical outcomes prove that accurate ink dating requires the use of specific, individual aging curves for each ink type and color combination, rather than relying on a generalized aging formula.

To provide a clearer understanding of the variance in RPA values, the calculated F-ratios ( $F_{cal}$ ) for the main effects and their interactions were compared with their respective critical F-values ( $F_{crit}$ ) at the  $\alpha = 0.05$  significance level, as detailed in Table 4.

**Table 4.** Comparison of calculated F-values versus critical F-values ( $\alpha = 0.05$ ) across all main effects and interactions

| Source               | DF1 | DF2 | Calculated F-Value ( $F_{cal}$ ) | Critical F-Value ( $F_{crit}$ ) | Significance                 |
|----------------------|-----|-----|----------------------------------|---------------------------------|------------------------------|
| Type                 | 1   | 288 | 0.62                             | 3.87                            | No ( $F_{cal} < F_{crit}$ )  |
| Color                | 3   | 288 | 24.07                            | 2.63                            | Yes ( $F_{cal} > F_{crit}$ ) |
| Month                | 8   | 288 | 78.62                            | 1.97                            | Yes ( $F_{cal} > F_{crit}$ ) |
| Type * Color         | 3   | 288 | 36.91                            | 2.63                            | Yes ( $F_{cal} > F_{crit}$ ) |
| Type * Month         | 8   | 288 | 7.50                             | 1.97                            | Yes ( $F_{cal} > F_{crit}$ ) |
| Color * Month        | 24  | 288 | 0.53                             | 1.55                            | No ( $F_{cal} < F_{crit}$ )  |
| Type * Color * Month | 24  | 288 | 2.07                             | 1.55                            | Yes ( $F_{cal} > F_{crit}$ ) |

The F-statistic serves as a fundamental metric in ANOVA, representing the ratio of the mean square (the variance explained by the specific factor) to the mean square of the residual error (the unexplained variance or background noise). A statistically significant variance is established mathematically when the variance attributed to the tested factor sufficiently exceeds the residual error, which occurs when ( $F_{cal} > F_{crit}$ ). It is critical to emphasize that the  $F_{crit}$  threshold is not a singular, static value applied uniformly across the entire analytical model. Rather, the critical boundary is dynamically governed by the specific degrees of freedom associated with each independent variable or interaction. The  $F_{crit}$  values presented in Table 4 were calculated using the inverse cumulative probability distribution function in OriginPro software. This calculation accurately derives the precise critical limit by utilizing a 95% confidence interval, the specific numerator degrees of freedom for the evaluated effect (DF 1), and the constant denominator degrees of freedom representing the residual error of the population (DF 2 = 288). An indepth analysis of the F-ratios reveals the robust statistical power of the primary variables. The main effect of the aging period (Month) yielded the highest variance ratio ( $F_{cal} = 78.62$ ), far exceeding its specific critical threshold ( $F_{crit} = 1.97$ ). This mathematically confirms that the intra sample variance caused by time dependent degradation is vastly greater than the inter sample background noise, solidifying the RPA parameter's reliability as an age indicator. Similarly, the main effect of ink color demonstrated profound significance ( $F_{cal} = 24.07 > F_{crit} 2.63$ ). Conversely, the isolated main effect of pen type did not reach the critical threshold ( $F_{cal} = 0.62 < F_{crit} = 3.87$ ), indicating that pen mechanics (gel versus ballpoint) alone do not uniformly dictate the RPA value across the entire dataset without considering color and time. However, the true complexity of the ink degradation kinetics is elucidated by the interaction terms. The highly significant two-way interactions, specifically Type  $\times$  Color ( $F_{cal} = 36.91 > 2.63$ ) and Type  $\times$  Month ( $F_{cal} = 7.50 > F_{crit} = 1.97$ ), demonstrate that the influence of pen type is not absent, but rather highly conditional upon the specific dye formulations (color) and the duration of environmental exposure. Most importantly, the F-statistic evaluation definitively validates the three-way interaction of Type  $\times$  Color  $\times$  Month. Despite having a lower absolute  $F_{cal}$  (2.07) compared to the primary main effects, this value strictly exceeds its respective, precise critical threshold of

$F_{crit} = 1.55$ . Because the calculated F-value surpasses the critical region boundary, the resulting probability value remains statistically significant ( $p = 0.002$ ). This outcome mathematically proves that the intra sample variance among specific combinations of pen type, color, and aging month cannot be attributed to random residual error.

Therefore, when analyzing ink aging, related aging curves for ink type and color should be considered. This highlights a critical in forensic document examination: an unknown ink must first be accurately classified into its specific structural subgroup (ballpoint or gel, colour) before a reliable aging model can be applied.

### 3.3.4 Principal Component Analysis (PCA)

Principal Component Analysis (PCA) was applied to compare the solvent profiles (RPA) of ink from different brands and models of ballpoint and gel pens during their 0–8 month aging process and to determine characteristic differences between types. The data matrix was structured such that each aging interval (Months 0 through 8) for every individual sample was treated as an independent observation (data point) rather than being aggregated into a single temporal average. Prior to extracting the principal components, the raw RPA values were preprocessed by calculating their standardized scores, and the model was built utilizing a covariance matrix to capture the underlying time dependent data structure. When examining the eigenvalues obtained from the analysis, it is seen that the first two principal components (PC1: 69.71% and PC2: 23.02%) explain 92.73% of the total variance in the data set (Figure 6). This high variance explanation rate proves that the multidimensional data belonging to the nine month time series was successfully modeled in a two-dimensional space with minimal information loss. From a chemometric perspective regarding variance contribution, the predominant variance captured by PC1 is primarily associated with the overall magnitude of the relative solvent content across the samples, effectively distinguishing between ink matrices with inherently high and low solvent bases. Conversely, PC2 captures the secondary variances, which are indicative of the subtle, brand-specific temporal evaporation dynamics during the aging process.

When evaluating the Biplot graph obtained in Figure 6, it was determined that the samples separated into two main clusters. The ballpoint pen samples (red dots) are clustered in a narrow area around the origin in the negative left region

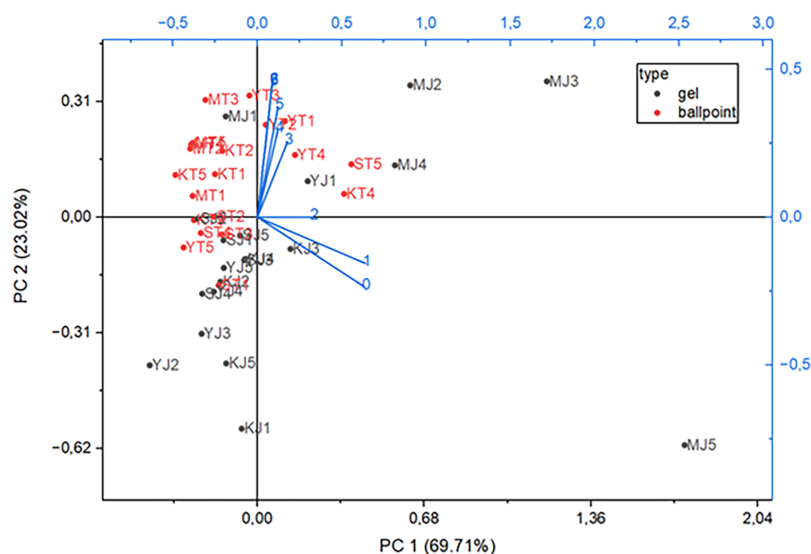


Figure 6. PCA biplot graph of ballpoint and gel pens

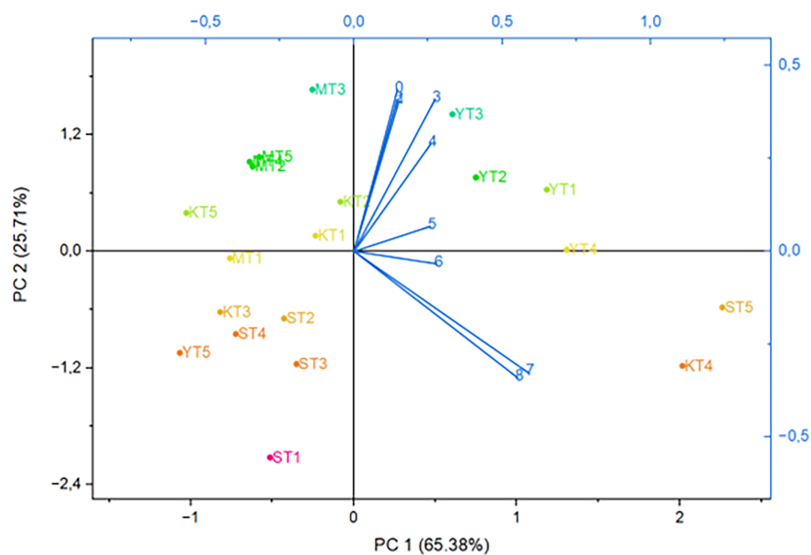


Figure 7. PCA biplot graph of ballpoint pens

of the graph. This compact grouping exhibits a homogeneous chemical composition, indicating that ballpoint pens show low variation between brands and maintain a stable profile during the aging process. In contrast, gel pen samples (black dots) are spread over a fairly wide area. This heterogeneous distribution in the gel group reveals that gel ink formulations contain significant chemical differences depending on the brand and that solvent evaporation kinetics are more variable in nature compared to ballpoint pens. In the PCA biplot, the variable vectors representing the 0–8 month measurements (loadings) indicate the direction of maximum value increase. The directional alignments and magnitudes of these loading vectors reflect the strong correlation between specific temporal aging stages. The observation that all time vectors are oriented towards the spatial quadrant occupied by the gel pen cluster geometrically demonstrates that gel inks maintain

systematically higher RPA scores—and thus a higher relative measurable solvent content—throughout the aging process compared to the ballpoint pen group.

To provide a more accurate evaluation of the multidimensional aging dynamics, and to prevent the inherently high variance of gel inks from masking the subtle temporal trends of ballpoint inks, PCA was applied to the RPA of the two pen types independently. Prior to extracting the principal components, the raw RPA values were preprocessed by calculating their standardized scores, and the models were built utilizing a covariance matrix to capture the underlying time dependent data structure.

For the ballpoint pen model (Figure 7), the first two principal components explained 91.09% of the total variance (PC1: 65.38% and PC2: 25.71%). Similarly, the gel pen model

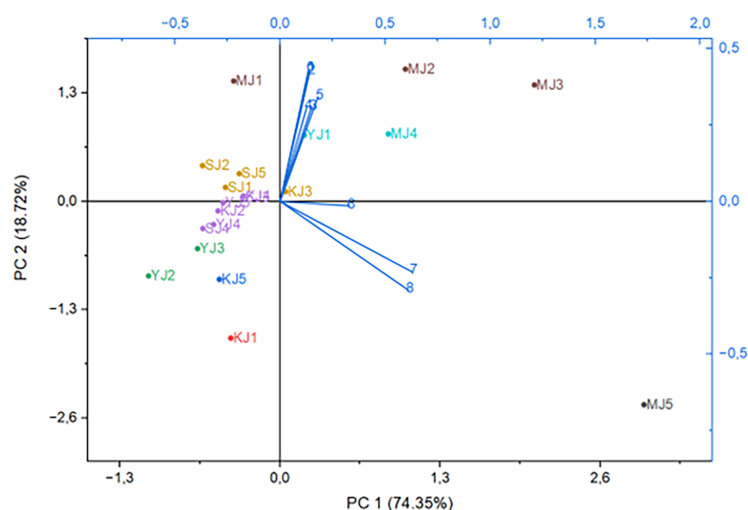


**Figure 8.** PCA biplot graph of gel pens

(Figure 8) captured 93.07% of the total variance within its first two components (PC1: 74.35% and PC2: 18.72%).

When evaluating the biplot graph for the ballpoint pens (Figure 7), separating the data reveals a structured internal variance that was previously obscured. Rather than being tightly clustered without a pattern, the ballpoint samples demonstrate distinct spatial distributions along the principal components. This indicates that while they are chemically more stable compared to gel inks, they still undergo a measurable, systematic solvent loss over time. The loading vectors representing the aging months illustrate a clear temporal trajectory; early to intermediate aging periods (Months 0–5) are primarily oriented towards the positive region of PC2, whereas the later aging periods (Months 6–8) shift downward into the negative region of PC2. This vector transition mathematically demonstrates a progressive and consistent alteration in the solvent profile across the ballpoint samples as the aging process advances. The shift in loading directions along PC2 implies a non-linear rate of solvent depletion, where the initial continuous loss tapers into a distinct, slower stabilization phase in the later months.

For the biplot for the gel pen samples (Figure 8) displays a heterogeneous distribution, confirming that gel ink formulations possess chemical variability and complex evaporation kinetics depending on the brand. Notably, samples from the “MJ” series exhibit dispersion compared to the tightly grouped SJ, YJ, and KJ series located closer to the origin. Sample MJ5, in particular, acts as a distinct outlier situated far into the positive PC1 and negative PC2 quadrant. An analysis of the component loadings provides deeper insight into this distribution: the initial aging months (Months 0–5) exert a strong pull towards the upper right quadrant, heavily influenced by the high initial RPA values of samples like MJ2, MJ3, and MJ4. In contrast, the vectors for the final aging stages (Months 7 and 8) elongate towards the lower right quadrant, aligning strongly with the unique trajectory of MJ5. This distinct loading behavior underscores that the most substantial chemometric variance in gel inks emerges

not uniformly, but predominantly during the late stages of aging, driven by brand-specific matrix retention properties.

### 3.3.5 Hierarchical Clustering Analysis (HCA)

The dendrogram obtained as a result of the Hierarchical Clustering Analysis (Figure 9) shows that the 40 ink samples examined are divided into two main phenotypic groups according to their aging profiles. In the tree structure created based on the cosine distance metric, the majority of gel ink samples (coded MJ, KJ, SJ, YJ) were grouped in the first main cluster (branch shown in red in Figure 9), while the majority of ballpoint pen samples (coded MT, KT, ST, YT) were grouped in the second main cluster (shown in blue in Figure 9).

A clustering rate of 92.5% was achieved between the two main groups, with inter species transition and misclustering observed in three pens (MJ2, SJ2, and MJ1). Because HCA is an unsupervised method, it groups samples based strictly on mathematical distance. The utilization of the cosine distance metric is particularly effective here, as it emphasizes the geometric orientation and overall shape of the temporal aging profiles rather than merely their absolute magnitudes. The instances where gel inks clustered alongside ballpoint inks likely stem from a convergence in their residual EG profiles at later aging stages, where the solvent levels become nearly indistinguishable regardless of the initial ink matrix. At this advanced stage, the evaporative solvent loss results in baseline levels that are dimensionally indistinguishable from the intrinsically low-solvent ballpoint formulations, effectively overriding their initial class characteristics within the clustering algorithm.

## 4 Discussion

In this study, the natural aging processes of ballpoint and gel pen inks (blue, black, green, red) frequently encountered in forensic document examinations were monitored using GC-MS analysis over a 0–8 month period, and the RPA

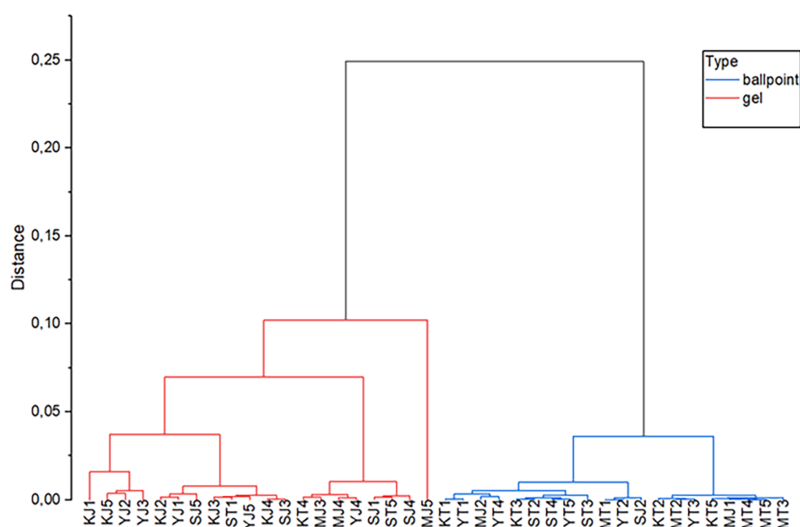


**Figure 9.** Dendrogram for HCA analysis

data obtained were evaluated using statistical methods. This study demonstrates that GC-MS-based RPA tracking offers a systematic approach to document creation time estimation specifically for commercial ink formulations where Ethylene Glycol acts as a quantifiable solvent.

These findings show consistent with upon previous solvent based dating studies in the forensic literature. Mostly TD-GC-MS is use to track the evaporation of solvents such as phenoxyethanol in ballpoint inks (Bügler et al., 2008; Koenig et al., 2015; Weyermann et al., 2007). While TD-GC-MS is highly sensitive, our study demonstrates that standard liquid extraction combined with conventional GC-MS can achieve reproducible tracking efficacy using ethylene glycol. This provides a highly accessible alternative for routine forensic laboratories that may not possess specialized thermal desorption equipment (Weyermann et al., 2011; Carvalho et al., 2019).

Statistical analyses showed that the effect of the time factor on RPA was highly significant ( $p < 0.0001$ ) and that RPA values exhibited a regular decrease over time in all groups. This finding confirms that the change in the amount of glycol-based solvents can be used as a reliable parameter for determining ink age, corroborating earlier methodologies that quantified single-solvent depletion (Locicero et al., 2004). However, whereas previous studies frequently focused on isolated pen types or single colors, the most critical finding of the present study is the significant Type  $\times$  Color  $\times$  Time interaction ( $p = 0.0027$ ) revealed by the Three-Way ANOVA analysis. This result proves that ink aging cannot be explained by a single mathematical model; each color of gel and ballpoint pens (such as the rapid deterioration in red inks and the high initial variation in blue gel pens) has its own unique aging characteristics. Therefore, in forensic ink age analysis, it is imperative to use age curves specific to the ink type and color rather than general formulas.

This complex evaporative behavior is particularly evident in gel inks. Our observations support the findings of Li et al. (2014) and Ni et al. (2020), who documented the

dynamic volatility of gel pen components. Specifically, Ni et al. successfully utilized triethylene glycol for age determination up to 9 months; our 8-month tracking of ethylene glycol across a comparative dataset of both ballpoint and gel matrices validates this temporal framework, while uniquely demonstrating how color interactions inherently alter these kinetic rates.

Principal Component Analysis (PCA) clearly distinguished the chemical profiles of ballpoint and gel pens, explaining 92.73% of the variance in the complex data set. The analyses revealed that ballpoint pens exhibit a more homogeneous and stable structure chemically, while gel pens show a heterogeneous distribution and higher solvent content due to formulation variations depending on the brand. Hierarchical Cluster Analysis (HCA), which focuses on the vector similarity of aging trends, demonstrated a high clustering rate of 92.5%. The analysis using the cosine distance metric, where deviation was observed only in a limited number of samples (MJ1, MJ2, SJ2), demonstrates that the proposed methodology has high sensitivity in distinguishing inks with different chemical formulations. While this study focused on the most commonly encountered traditional ballpoint and gel pen inks in forensic document examinations, future studies should evaluate the aging kinetics of waterbased and emulsion type inks to further expand the applicability of this chemometric approach. The 0–8 month interval evaluated in this study successfully captures the highly dynamic initial phases of solvent evaporation which is particularly crucial for identifying altered documents this relatively short time interval represents a limitation of the current model.

Although environmental conditions critically modulate solvent evaporation, the methodology yields consistent results for entries generated with same inks on the same document under shared storage background. Consequently, variations in environmental exposure, ink composition, or paper porosity should not be regarded as methodological constraints. Rather, these factors establish the essential sample acceptance criteria in routine casework, defining the

prerequisites for valid comparative analysis rather than limiting the analytical method.

Furthermore, although the incorporation of a diverse array of brands and colors substantially bolsters the comparative breadth of this research, the restricted sample size within individual subgroups ( $N = 5$ ) necessitates a degree of interpretive caution. While preliminary normality assessments validated the application of parametric statistical frameworks, subsequent investigations must utilize expanded sample cohorts to augment the statistical power and broader generalizability of the proposed chemometric models.

GC-MS-based RPA tracking offers a systematic and statistically supported approach to document creation time estimation for specific formulations, while chemometric methods such as PCA and HCA provide critical classification of the ink type. While PCA and HCA successfully highlighted the natural variance and clustering tendencies among ink types, future studies will aim to employ supervised techniques such as Partial Least Squares Discriminant Analysis (PLS-DA) for definitive classification modeling. In future studies, expanding the database with different brands and paper types will minimize the margin of error of the model in forensic applications.

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### Author Contributions

Dilek Salkim Islek: Conceptualization, Writing—review & editing, Writing—original draft, Visualization, Validation, Methodology, Investigation, Project administration, Formal analysis, Data curation. Eda Kiris: Writing—review & editing, Writing—original draft, Validation, Methodology, Analysis, Data curation, Investigation, Conceptualization. Halitcan Adas: Validation, Methodology, Analysis, Nazli Holumen: Writing—review & editing, Omer Karatas: Writing—review & editing, Murat Yayla: Investigation, Emel Hulya Yukseloglu: Project administration, Writing—review & editing, Erdogan Kose: Project administration, Writing—review & editing.

### Availability of Data and Materials

The authors declare that the data supporting the findings of this study are available within the paper and its Supplementary Information files. Should any raw data files be needed in another format they are available from the corresponding author upon reasonable request. Source data are provided with this paper.

### Conflicts of Interest

The authors declare that they do not have any conflict of interest.

### Supporting Information

Supporting Information accompanies this paper on <http://www.acgpubs.org/journals/records-of-natural-products>.

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