ADLİ TIP DERGİSİ
TURKISH JOURNAL OF FORENSIC MEDICINE

Evaluation of Ink Age Determination by GC-MS Method in an Environment Allowing Diffusion Among Paper Documents Stacked After Being Handwritten and Signed

Elle Yazılıp İmzalandıktan Sonra İstiflenen Kağıt Belgeler Arasında Difüzyona İzin Veren Bir Ortamda GC-MS Yöntemiyle Mürekkep Yaşı Tayininin Değerlendirilmesi

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Öz

Amaç: Adli belge incelemesinin önemli bir unsuru olan adli belge sahteciliği kapsamında, bu araştırma belgelerdeki mürekkebin yaşını belirlemeyi amaçlamaktadır. Araştırma, özellikle mavi, kırmızı ve siyah tükenmez kalemlerle elle yazılmış ve imzalanmış, ardından istiflenmiş ve kağıtlar arası yayılımı kolaylaştıran bir ortam oluşturulmuş belgeleri incelemektedir.

Yöntem: Her ay, aynı kişi aynı marka mavi, kırmızı ve siyah tükenmez kalemleri kullanarak aynı metni tutarlı kalitedeki kağıtlara yazmıştır. Eş zamanlı olarak, her belge ıslak mürekkeple imzalanmış ve buna göre tarih atılmıştır. Hazırlanan belgeler daha sonra sırayla istiflenmiş ve her yeni belge daha önce hazırlanan belgenin üzerine yerleştirilmiştir. Bu istifler kapalı bir karton kutuda saklanmış ve homojen ortam koşullarında doğal yaşlanmaya bırakılmıştır. Daha sonra, mürekkebin uçucu bir bileşeni olan fenoksietanol konsantrasyonu, Gaz Kromatografisi-Kütle Spektrometrisi (GC-MS) sistemi kullanılarak numunelerde belirlenmiştir.

Bulgular ve Sonuç: Analizler sonucunda, her üç renkteki tükenmez kalem mürekkebiyle yazılmış belgeler karşılaştırıldığında, 1 gün ve 1 ay sonra fenoksietanol seviyelerinde bir düşüş gözlemlenmiştir. Ancak, 4 aylık örneklerde 3 aylık örneklere, 6 aylık örneklerde ise 5 aylık örneklere kıyasla fenoksietanol seviyelerinde beklenmedik bir artış tespit edilmiştir. Aynı ortamda saklanan birden fazla el yazısı ve imzalı belge arasında yayılma potansiyeli göz önüne alındığında, bu tür yazıtların tarihlendirilmesine yönelik daha bilimsel ve titiz bir yaklaşım, yazılara ve imzalara kesin bir tarih atamak yerine, belgeleri kronolojik olarak karşılaştırmalı olarak analiz edip sıralayarak bir tarih aralığı belirlemeyi içerir.

Anahtar Kelimeler: Adli Belge İncelemesi, Adli Bilimler, Mürekkep Yaşı, Doğal Yaşlandırma, Fenoksietanol

Abstract

Aim: Within the scope of forensic document forgery, a key aspect of forensic document examination, this research aims to determine ink age in documents. The investigation specifically evaluates documents that were handwritten and signed with blue, red, and black ballpoint pens and then stored stacked, creating an environment that facilitates inter-paper diffusion.

Methods: Each month, the same individual inscribed identical text onto paper of consistent quality using the same brand of blue, red, and black ballpoint pens. Simultaneously, each document was signed with wet ink and dated accordingly. The prepared documents were then stacked sequentially, with each new document placed atop the previously prepared one. These stacks were stored in a closed cardboard box and allowed to undergo natural aging under uniform environmental conditions. Subsequently, the concentration of phenoxyethanol, a volatile component of the ink, was determined in the samples using a Gas Chromatography-Mass Spectrometry (GC-MS) system

Results and Conclusion: As a result of the analyses, a decrease in phenoxyethanol levels was observed when comparing documents written with ballpoint pen ink in all three colors after 1 day and 1 month. However, an unexpected increase in phenoxyethanol levels was detected in 4-month-old samples compared to 3-month-old samples and in 6-month-old samples compared to 5-month-old samples. Considering the potential for diffusion between multiple handwritten and signed documents stored in the same environment, a more scientifically rigorous approach to dating such inscriptions involves establishing a date range by comparatively analyzing and sequencing the documents chronologically, rather than assigning an exact date to the writings and signatures.

Keywords: Forensic Document examination, Forensic Sciences, Ink age, Natural aging, phenoxyethanol

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INTRODUCTION

Crimes involving the falsification or forgery of documents have significant implications for transnational crime and terrorism (1). A primary forensic approach in such cases is the examination of alterations in the documents, including erasures, insertions, and deletions. The forensic analysis of questioned documents provides critical information that supports criminal investigations (2). One of the major challenges in document examination is the determination of the document's age (3). Establishing the chronological sequence of events is a crucial phase in the investigative process, particularly when a document contains multiple entries recorded at different times. Investigators may question whether a specific entry was made at the time it is claimed to have been. Expert analysis of such documents, which seeks to determine the date of ink deposition, is inherently complex and typically relies on advanced chemical and physical techniques (3–5). The basis of ink age determination lies in detecting time-dependent changes in the ink's chemical composition. Although efforts are made to identify physico-chemical changes in ink components over time, it is not yet possible to determine a precise date of writing. However, such analyses can provide an estimated age range for the ink (6,7).

The degradation of ink is a complex process involving multiple mechanisms. It is influenced by the natural aging of the paper, the chemical composition of the ink, and the ink's potential to undergo various chemical reactions. These reactions, ranging from simple processes such as solvent evaporation to more complex ones like the polymerization or hardening of ink resins on the paper surface, are significantly affected by environmental and storage conditions. The aging of paper begins during its manufacturing process, whereas ink degradation commences upon contact and adhesion to the paper. Inks stored in closed systems, such as pen cartridges or ink bottles, experience negligible aging compared to the degradation that occurs once the ink is deposited onto paper (open system) (8).

Spectrometric and chromatographic methods used to analyze ink composition are highly effective in estimating the age of documents. Ink formulations commonly include a variety of components such as dyes, solvents, resins, lubricants, corrosion inhibitors, emulsifying agents, and buffers (5). Among writing instruments, ballpoint pens are widely preferred due to their affordability and accessibility. Common colorants used in ballpoint pen inks include crystal violet (CV), methyl violet (MV), and Victoria blue (VB), while solvents such as phenoxyethanol (PE), phenoxyethoxyethanol (PEE), and dipropylene glycol (DG) are frequently present in their formulations (5,9).

Ink dating through dye behavior characterization has recently emerged as a complementary, non-destructive analytical approach. Techniques such as Raman spectroscopy (10) and Digital Color Analysis (11) have been applied to examine the natural and artificial aging of writing inks on paper. Solvent-based ink aging approaches rely on destructive analytical techniques, including GC-MS, GC-FID, FTIR, SPME, SPME-GC-MS, HS-GC-FID, and DART-MS, which provide valuable information by tracking changes in the evaporation profiles of volatile ink components (6,12,13).

The objective of this study is to chemically distinguish the ink age in blue, red, and black ballpoint pen writings and wet signatures on naturally aged paper documents, while also highlighting the significance of ink diffusion between stacked documents.

MATERIALS AND METHODS

Ethical approval for this study was obtained from the Ethics Committee of Zonguldak Bülent Ecevit University (Approval Date: 29.05.2014; Protocol No: 2014/08-13). All laboratory investigations were conducted in the Analytical Chemistry Laboratory of the Department of Chemistry, Faculty of Arts and Sciences, Zonguldak Bülent Ecevit University.

In this study, the same brand of blue, red, and black ballpoint pens was used by a single individual to ensure consistency. Between April 15 and October 15, 2018, on the 15th day of each month, identical text was written and wet signatures were affixed, dated accordingly, on identical paper types. Each newly prepared document was placed on top of the previous month's documents and stored under uniform conditions in a closed cardboard box to undergo natural aging. Following the completion of the sample collection period, the volatile solvent phenoxyethanol, present in the ink formulations, was analyzed using gas chromatography–mass spectrometry (GC-MS). Since phenoxyethanol is present in low concentration, splitless injection was used in the analysis to transfer the volatile component to the system as much as possible. Technical information such as the device, column, temperature program, injection volume, etc. used in the analysis are shown in Table 1.

Table 1. Technical information

System Parameters	System Model and Specifications
GC–MS System	Thermo-Finnigan MAT 4500
Column	ZB-5 MS, 30 m length, 0.25 mm inner diameter, 0.25 µm film thickness
GC Temperature Program	50°C (6 min), ramp 10°C/min to 300°C, hold 5 min
Injector Block Temperature	230°C
Transfer Line Temperature	300°C
Ion Source Temperature	230°C
Scan Mode / Mass Range	Full scan, 50–650 m/z
Ionization Mode	Electron Impact (EI)
Ionization Voltage / Current	70 eV and 350 µA
Carrier Gas / Flow Rate	Helium, 1 mL/min
Software	Xcalibur 3.0
Injection Mode / Volume	Splitless, 1 µL

Chemicals and Equipment

Analytical-grade phenoxyethanol (Fluka) and methanol (Merck) were used as reagents in this study. A BioSan MPS-1 vortex mixer was employed during the sample preparation phase, and chromatographic analyses were performed using a GC-MS instrument.

Pen and Paper Samples

In this study, Mopak Rekort Laser brand paper (A4/80gr/m2 210x297 mm), commercially available on the market, was used. The ballpoint pens utilized were 1425 Faber-Castell models in blue, red, and black ink.

Archiving

Each monthly paper document was placed on top of the previous one, and the entire stack was subjected to natural aging under consistent conditions, i.e., stored in a closed cardboard box at room temperature and protected from light (Figure 1).

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Figure 1. Closed and open versions of a cardboard box in which written paper documents are stacked and stored

A total of 21 paper documents were sampled, with ages ranging from 1 day to 6 months. These documents contained handwritten text and signatures. Phenoxyethanol was analyzed using GC-MS to determine the chronological order of writing among the samples. The first document, dated April 15, 2018, features handwriting and a signature in blue ink, as shown in Figure 2.
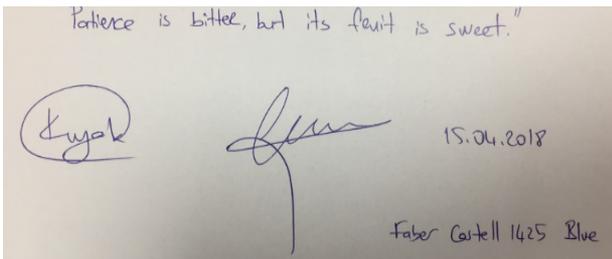

Figure 2. Sample paper document created with the blue ink pen used in the study

Preparation of Paper Documents for Analysis

Circular sections with a diameter of 3 mm were taken from the naturally aged wet signature areas using a biopsy punch (Figure 3). Each sectioned sample was placed into a 2 mL vial, followed by the addition of 20 μL of methanol. The vial was then vortexed at 2500 rpm for 5 minutes using a vortex mixer. Subsequently, a 1 μL aliquot of the resulting extract was collected using a microinjector and subjected to GC-MS analysis.
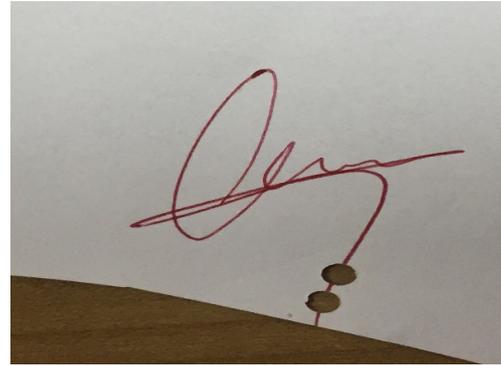

Figure 3. View of the signature after sampling

Calibration of GC-MS System for Phenoxyethanol Analysis

Phenoxyethanol calibration standards with concentrations of 0.5 μg/mL, 0.1 μg/mL, 0.05 μg/mL, 0.01 μg/mL, and 0.005 μg/mL were prepared by serial dilution of a 10 μg/mL stock solution.
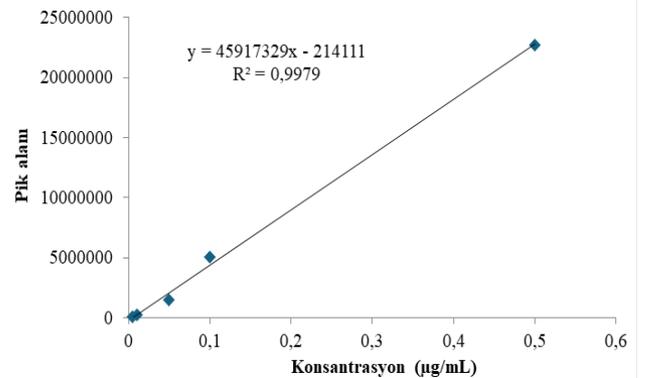

Figure 4. Calibration Graph for Phenoxyethanol

These standards were analyzed by GC-MS, and the resulting phenoxyethanol peak area values were plotted against their respective concentrations to generate a calibration curve. The calibration graph for phenoxyethanol is presented in Figure 4, and its corresponding mass spectrum is shown in Figure 5
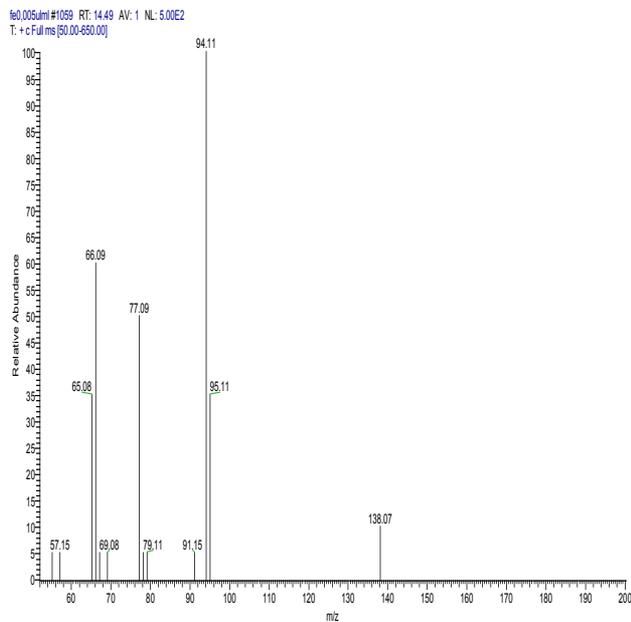

Figure 5. Mass spectrum for Phenoxyethanol

Analysis of Blank Paper Document Sample in GC-MS System

A control sample was taken from a blank sheet of paper containing no writing. The sample was prepared following the same protocol and analyzed using GC-MS. As expected, no peak was observed in the 14–15 minute retention time range, where phenoxyethanol typically appears, indicating that there was no contamination from the blank paper (Figure 6). The peaks observed at approximately 19, 20, and 22 minutes are unrelated to phenoxyethanol. If contamination had occurred on the blank paper sample, either from ink residues or from the blank paper itself, GC-MS analysis would have revealed a peak at 14–15 minutes

corresponding to phenoxyethanol, with a molecular ion at m/z 138.1, as shown in Figure 5.
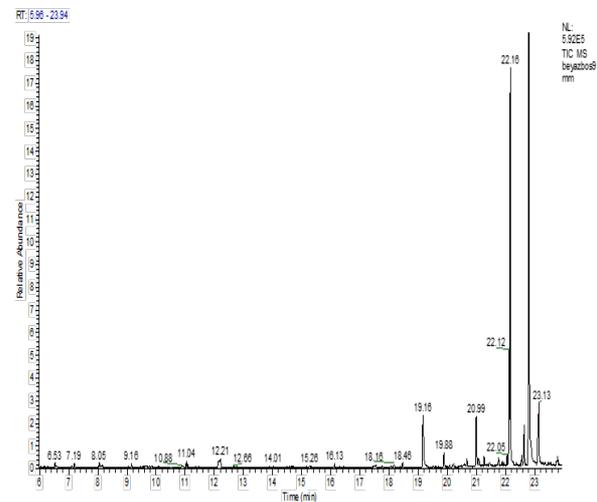

Figure 6. Chromatogram of a sample taken from a blank paper document

Limit of Detection (LOD) and Limit of Quantification (LOQ) of the GC-MS System for Phenoxyethanol

In the chromatograms, irregular fluctuations near the baseline that do not form distinct peaks are considered instrumental noise. For phenoxyethanol, the Limit of Detection (LOD) of the GC-MS system was determined based on the ability of the system to detect a signal three times greater than the noise level. Similarly, the Limit of Quantification (LOQ) was calculated using a signal-to-noise (S/N) ratio of 10. To calculate these values, the S/N ratios obtained from the analysis of a standard phenoxyethanol solution at a concentration of 0.01 µg/mL were used, as this concentration approximates the lower detection range and is commonly used in previous studies. For example, the analysis of the 0.01 µg/mL standard solution yielded an S/N ratio of 105. Using this value, the LOD and LOQ were calculated as follows:

- LOD = 0,01 µg/mLx3/105 = 0,00029 µg/mL

- LOQ = 0,01 µg/mLx10/105 = 0,00095 µg/mL

These results indicate the GC-MS system's sensitivity in detecting and quantifying trace amounts of phenoxyethanol.

RESULTS

In the present study, the phenoxyethanol content of written documents prepared using red, blue, and black ballpoint pen ink was analyzed over different aging periods. A comparison between 1-day-old and 1-month-old samples revealed a reduction in phenoxyethanol content of 5.4% in red ink (0.12905803ng/cm), 32.26% in blue ink (0.112814342ng/cm), and 2.5% in black ink (0.007381382ng/cm) in 1-month-old samples. When comparing 3-month-old and 4-month-old documents, a slight increase in the phenoxyethanol content of 4-month-old samples was observed: 0.27% (0.000479 ng/cm) in red, 1.25% (0.002129 ng/cm) in blue, and 0.036% (0.000062431 ng/cm) in black. Between 5-month-old and 6-month-old documents, a decrease was noted in all inks in 6-month-old samples: 4.25% (0.0020217 ng/cm) in red, 5.9% (0.007418 ng/cm) in blue, and 1.1% (0.00131686 ng/cm) in black. Notably, when comparing the phenoxyethanol content of 1-day-old and 6-month-old documents, a significant decrease was detected in 6-month-old documents: 52.5% (0.124942419 ng/cm) in red, 66.5% (0.232727433 ng/cm) in blue, and 60.1% (0.176727273 ng/cm) in black (Figures 7, 8, and 9).
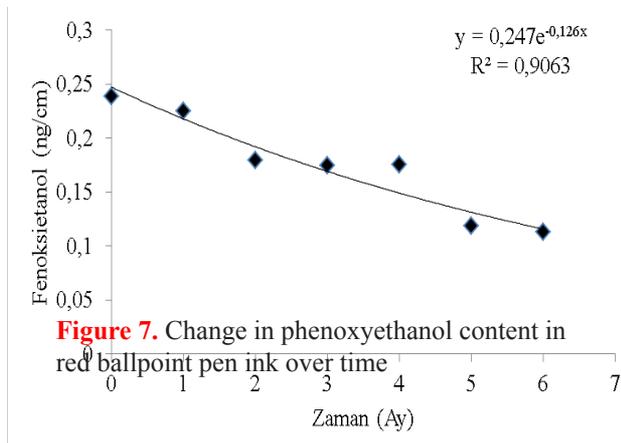

$$y = 0,247e^{-0,126x}$$
$$R^2 = 0,9063$$

Figure 7. Change in phenoxyethanol content in red ballpoint pen ink over time

$$y = 0,3077e^{-0,17x}$$
$$R^2 = 0,9414$$
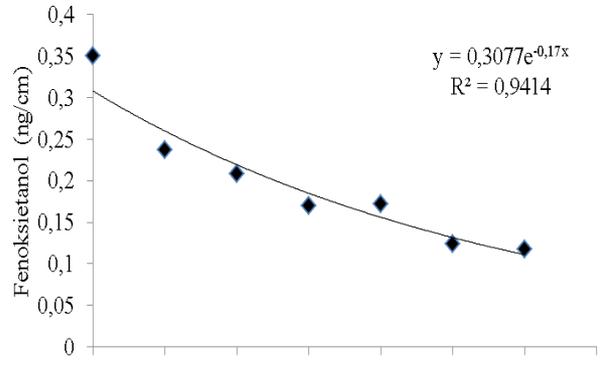
Figure 8. Change in phenoxyethanol content in blue ballpoint pen ink over time

$$y = 0,3012e^{-0,166x}$$
$$R^2 = 0,9345$$

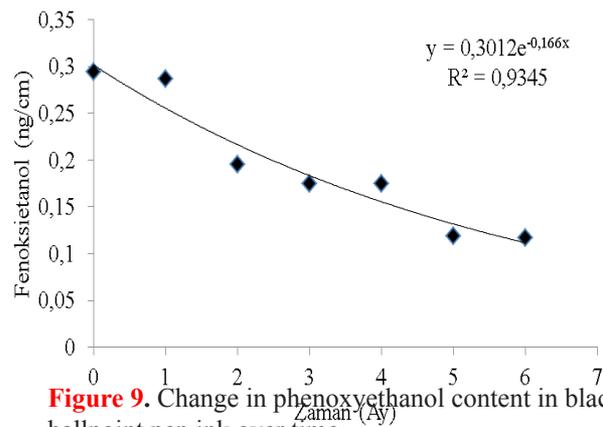**Figure 9.** Change in phenoxyethanol content in black ballpoint pen ink over time

It was observed that the phenoxyethanol concentrations in 6-month-old documents written with red, blue, and black ballpoint pens were relatively similar, with values of 0.11318 ng/cm, 0.117016 ng/cm, and 0.117263401 ng/cm, respectively.

DISCUSSION

In forensic document examination, determining the time at which handwriting or a signature was made is often possible by analyzing the chemical properties of the ink on the paper (2, 4). Over the years, various methods have been developed to estimate ink age based on temporal changes in the composition of dyes, resins, and volatile components within the ink (2, 4, 13, 14). Among these

components, phenoxyethanol, a highly volatile solvent, has been extensively studied for its decreasing concentration over time, which serves as a potential indicator of ink aging (6, 7, 8, 13, 15). In the present study, phenoxyethanol was selected as the focus of analysis to investigate not only its degradation over time but also the possibility of diffusion between inked paper surfaces and, if present, the extent to which such diffusion occurs.

A chronological review of key studies on volatile components in ink used for ink age determination includes the work of Stewart (1982), Humecki (1985), Cantu (1988), Aginsky (1993), Brazeau et al. (2000, 2002), Lociciro et al. (2004), Weyermann (2007), Ezcurra et al. (2010), Cantu (2012, 2017), and Leal et al. (2023) (2, 5, 16–22).

Utilizing gas chromatography (GC) in combination with mass spectrometry (MS), Aginsky demonstrated that the ratio of volatile to dye components in ink can vary over time, indicating a time-dependent relationship in the aging process (20). Through the use of accelerated aging techniques via GC, Aginsky further examined the extraction of volatile components from ink on paper, confirming that this process may also be time-dependent (5, 20). More recently, Leal et al. (2) enhanced the reliability and accuracy of ink dating methods by converting phenoxyethanol (PE) into its trimethylsilyl derivative, thereby increasing its volatility and making it more amenable to GC-MS detection. In the present study, phenoxyethanol, a key volatile compound, was similarly analyzed using GC-MS. However, unlike previous studies, we focused solely on naturally aged documents and did not employ artificial or accelerated aging techniques. This decision reflects real-world forensic scenarios, where document examiners frequently deal with naturally aged materials. Furthermore, our investigation uniquely addresses the potential diffusion of phenoxyethanol between stacked paper documents, an aspect often encountered in practical examinations but rarely explored in the literature.

Brazeau and Gaudreau quantified volatile components in ballpoint pen ink directly on paper without the use of solvents, employing solid-phase microextraction (SPME) in conjunction with gas chromatography (GC) (15). In contrast, the present study utilized a GC-MS system to determine the amount of phenoxyethanol, a key volatile component, in written documents. Unlike Brazeau and Gaudreau's solvent-free approach, methanol was used as the extraction solvent in our methodology.

Brazeau and Gaudreau introduced the volatile loss rate method using a dynamic approximation model to estimate the age of ink. This same model was employed in the present study. After analyzing 63 ballpoint pen ink samples, Brazeau and Gaudreau identified phenoxyethanol as one of the most prevalent solvents and, consequently, selected it as the primary target compound for ink dating. Following their rationale, phenoxyethanol, recognized as the most common volatile component in ballpoint inks, was also selected for analysis in our study. In the studies conducted, based on Brazeau and Gaudreau's method, phenoxyethanol exhibits a high rate of evaporation during the first 6–8 months, continues to evaporate at a slower rate up to 18 months, and significantly ceases to evaporate after approximately two years (17, 22). In our study, we monitored phenoxyethanol levels in documents over a 6-month natural aging period, with particular emphasis on assessing the impact of diffusion between paper surfaces. The observed reduction in phenoxyethanol content between 1-day and 6-month-old documents, 52.5% for red ink, 66.5% for blue ink, and 60.1% for black ink, aligns with the evaporation patterns reported by Brazeau and Gaudreau, thereby supporting the underlying principles of their model.

LaPorte et al. (23) expanded upon the work of Brazeau and Gaudreau (15) by analyzing 633 ballpoint

pen inks using GC-MS to determine the prevalence of phenoxyethanol in ink formulations. Their study revealed the presence of phenoxyethanol in 85% of black ink pens and 83% of blue ink pens (23). In our study, three different colors of ballpoint pens, blue, black, and red, were used, and phenoxyethanol was detected in the ink transferred to the paper from all three colors by scanning with the GC-MS system.

In 2007, Weyermann et al. analyzed phenoxyethanol, ethoxyethanol, dipropylene glycol, and phenoxyethoxyethanol in 1.5-year-old documents using GC-MS to investigate the relationship between solvent evaporation and document age. In our study, 6-month-old documents were analyzed using GC-MS to similarly explore the temporal evaporation pattern of phenoxyethanol. Weyermann et al. reported that minor solvents other than the primary components evaporated rapidly following ink application, with ethoxyethanol levels stabilizing within 10 days, and significant reductions in dipropylene glycol, phenoxyethanol, and phenoxyethoxyethanol occurring within the first two weeks (5, 22). Unlike their study, in the present study, only phenoxyethanol was examined, and other solvents present in the ink composition were not analyzed. Additionally, since the written documents analyzed in our study were created on a monthly basis, 2-week-old samples were not included. However, the rapid decrease in phenoxyethanol levels within two weeks, as reported by Weyermann et al., was not found to be consistent with the decrease observed between 1-day and 1-month-old samples prepared with red and black ballpoint pens in our study (5.4% for red, 2.5% for black). In contrast, the decrease observed in documents written with blue ballpoint pens over the same period (32.26%) was interpreted as being consistent with the early-phase evaporation pattern reported by Weyermann et al.

Weyermann et al. found that phenoxyethanol, ethoxyethanol, and dipropylene glycol can diffuse and migrate from the ink-containing paper to adjacent sheets when documents are stored in direct contact (5, 22). In our study, although a progressive decrease in phenoxyethanol content was expected with document aging, the results showed no reduction between 3- and 4-month-old documents; in fact, a slight increase was observed. Similarly, when comparing 5- and 6-month-old documents, the anticipated decline was minimal, with the values remaining relatively close. This phenomenon was primarily attributed to the diffusion of phenoxyethanol between overlapping documents written by the same individual and stored under identical conditions. This result supports the view presented in the study by Weyermann et al. (22) that phenoxyethanol can diffuse from one document to another when documents are stored in close contact. However, unlike their study, where such diffusion was one of several factors contributing to unexpected variations in phenoxyethanol levels, our findings showed that, although a decrease over time was anticipated, this decrease was not statistically significant. This was interpreted as being influenced not only by the storage conditions, ink, and paper properties, but also by the fact that the documents were stacked on top of each other in a closed container.

Weyermann et al. reported that phenoxyethanol could be detected in documents aged up to 562 days when using a relative peak area–time curve, and that it was present in more than 90% of the samples analyzed (5, 22). In the present study, phenoxyethanol was successfully detected in documents aged up to 180 days, and a phenoxyethanol concentration (ng/cm)–time curve was employed. Weyermann et al. also noted that the aging process of ink is influenced by factors such as the storage conditions, as well as the type of ink and paper. Based on their findings, they concluded that while precise ink dating is not feasible, it is possible to establish approximate age ranges and to compare whether inks are relatively new, old, or older (5,

22). Similarly, the results of the present study suggest that when there is a marked difference in phenoxyethanol levels among documents written by the same individual and stored under identical conditions, a relative ranking of document age may be possible. However, definitive dating remains unattainable. These findings are therefore consistent with those reported by Weyermann et al.

Weyermann et al. (2007), in their statement for the European Network of Forensic Science Institutes (ENFSI), proposed that ink age estimation can be categorized into five intervals: within the first 3 months after writing, 3–6 months, 6–9 months, 9–15 months, and documents older than 15 months (5, 22, 24). In the present study, it was observed that the amount of phenoxyethanol in the 4th month was higher than in the 3rd month, and that the amounts measured in the 5th and 6th months were relatively similar. These findings suggest that the classification proposed for the first six months is not fully consistent with the results of our study.

Cantu (16) demonstrated the ink aging curve obtained when phenoxyethanol, the solvent in the ink, was used in place of the volatile solvent, and cellulose from the paper was used in place of the non-volatile solvent. In this method, the initial stage, characterized by a high amount of solvent on the surface and rapid evaporation, is defined as the fast drying phase. As the amount of solvent on the surface decreases and evaporation slows due to the interaction with the cellulose matrix during outward movement or back diffusion toward the surface, this phase is referred to as slow drying. In the present study, the observed decreases in phenoxyethanol levels in documents aged 1 day versus 6 months (red: 52.5%, blue: 66.5%, black: 60.1%) suggest a pattern consistent with the fast drying phase described by Cantu. However, the absence of data from documents older than 6 months limits the extent to which these findings can be generalized to later stages of ink aging.

In another study, Cantu (25) analyzed phenoxyethanol levels in written documents using GC-MS systems and reported an absence of expected decreases; unexpectedly, he observed either stable or even slightly increased phenoxyethanol levels in documents produced at different times. He suggested that this anomalous behavior, despite using the same pen and identical paper, might be attributed to factors such as extraction errors, pressure differences, insufficient paper homogeneity, transfer of ink solvents into the paper matrix, and varying storage or environmental conditions (25). In the present study, it was interpreted that one potential reason for the unexpected phenoxyethanol measurements was diffusion between documents stored in direct contact, which supports Cantu's hypothesis. The documents in our study were allowed to age naturally while stacked, reflecting real-life conditions where written materials are often stored closely together in files or folders. Additionally, in our study, one of the possible reasons for the unexpected behavior observed in phenoxyethanol levels was interpreted as pressure differences that may occur even in documents produced by the same person at different times, potentially affecting the results. This supports the previously reported hypothesis that pressure variation is among the factors contributing to unexpected phenoxyethanol outcomes. Furthermore, we believe that storing documents in a closed container is also an important factor to consider.

In contrast to Cantu's study (25), where paper inhomogeneity was identified as a potential source of unexpected variations in phenoxyethanol levels, this factor was minimized in our study by using commercially available paper of the same brand and model throughout. To address the issue of incomplete extractions raised by Cantu, a standardized extraction procedure was applied consistently across all samples, thereby reducing the likelihood of extraction-related variability. Moreover, environmental conditions, another factor cited by Cantu,

were controlled by storing all samples at room temperature in a light-proof cardboard box under uniform conditions.

Based on the results of our study, it is interpreted that when there are significant differences in phenoxyethanol levels between documents written by the same individual under identical conditions and stored similarly, it may be possible to establish a relative chronological order among the documents. Although precise dating remains unattainable, it may still be feasible to estimate a general time range, albeit with some uncertainty. As noted in the 2015 study by Avcı and Gökçedağ, the creation of an ink databank, achieved by archiving inks with known formulations, along with the development of a formulation system akin to a watermark (commonly used as a security feature in valuable documents), would facilitate ink age estimation. Using ink pens with identifiable formulation codes when writing or signing valuable documents could significantly enhance the accuracy and reliability of forensic ink dating analyses (26).

In practical terms, written documents subject to examination are often stored in files and archives for extended periods, with some documents emerging for review after many years. Given this, further studies on the dyestuffs and resins in ink compositions may be beneficial for improving ink age determination in documents older than two years. This study highlights the significance of diffusion between multiple documents stored in closed boxes, which may impact ink age determination, as well as the application of chemical methods for ink age estimation, which have recently been introduced in Türkiye. It is believed that further research focusing on the analysis of volatile components, dyestuffs, and resins in ink should be conducted. Although the current study has limitations in terms of sample size, we believe that future studies with larger samples and adding secondary markers such as PEE and DPG in addition to PE will make significant

contributions to the literature. Finally, continued research and development in this field could enhance the reliability and accuracy of ink dating methods, contributing to both the administration of justice and the protection of society.

Declarations

Conflict of Interest

Funding

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