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Case Report

Determination of ink aging by two different methods

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Abstract

Ink age determination; based on the detection of changes in the structure of the ink on the document over time. These changes are degradation of dyes, evaporation of solvents and polymerization of resins. The time for these changes to ocur varies according to the structure of the ink and the environment in which the document stored. In this study, the age of the document was determined by analyzing the dyes and solvents in the structure of the ink that document was sent by the court in 2017. The phenoxyethanol was which found in the structure of the ink was detected by thermal desorption –gas chromatography-mass spectrometer while the determination of the dyes (crystal violet, methyl violet, tetramethyl pararosanil and Victoria blue) were determined by high pressure liquid chromatography-ultraviolet detector. Dye and relative solvent ratios were calculated and compared in age determination. It was discovered that the signature was produced after the writings by examining the ratio of CV/MV for the signature and personal name. Additionally, the presence of contamination from a different document was detected through phenoxyethanol analysis. The age of the document was determined using the V%-time curve, revealing that the signature was created between 3-7 months from the date of analysis.

Keywords: Ink aging, questioned document, case report, GC-MS

INTRODUCTION

Forensic document experts works on the detection of document forgery. Experts analyze the document by dividing it into three parts. These are paper, writing instruments and ink. Ink age is determined according to changes in the ink structure over time by analytical methods[1]. There are many studies from past to present regarding ink age determination. Most of these studies based on at detecting either the degradation of colorants or the evaporation of their solvents by chromatographic or spectroscopic methods [2-13]. The reason for using ratio in studies on age determination is to eliminate changes in the amount of ink caused by ink print. In this study, the age of suspicious writings was determined by analyzing both the colorants with high pressure liquid chromatography-ultraviolet detector (HPLC-UV) and the phenoxyethanol with thermal desorption –gas chromatography-mass spectrometer (TD-GC/MS). In this study, both dye ratio(Crystal Violet peak area/ Methyl Violet peak area) and the relative solvent ratio (V %) were used.

CASE

Creditor A.D. and Debtor H.U. issue a promissory note in 10/10/2014. The promissory note also bears the signature of the debtor. According to Debtor H.U, Creditor A.D. changed the amount section on the signed promissory note and increased the amount that Debtor H.U. should pay. In 2017, when it came to us, the court requested a report on whether the ink structures of the writing, numbers and signatures on the deed are the same, whether

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there is an age difference between them, and whether they are issued on a new date and shown as old. Samples taken from name and signature shown in Figure 1.

Figure 1. Samples taken from name, numbers and signature in promissory note (Note: No.1 and 2 were taken for dye analysis. No.3 and 4 were taken for solvent analysis)

MATERIAL AND METHOD

Analytical Methods

To perform the HPLC analysis for crystal violet (CV), methyl violet (MV), tetramethyl pararosanil (TPR), and Victoria blue (VB), the Thermo Scientific Degasser System SCM 1000, Pump Spectra System P1000, Autosampler Spectra System AS3000, and UV detector 1000 system were utilized. The Phenomenex Onyx C18 Monolithic Column (100×4.6 mm) was used. For the analysis of phenoxyethanol, the Unity Thermal Desorber Agilent HP 6890N GC 5975B MS (Agilent Technologies, Palo Alto, CA) was used. The column used was a DBVR-X (60m×0.25 mm; thickness 1.4 µm), and a Tenax tube with activated carbon removal was used. Method validation and experimental steps are described elsewhere [3].

Sample Preparation

To prepare samples for analyzing dye content, two samples were taken from the suspicious writings using a 1.2 mm punch. These samples were mixed with 200 µL of methanol and vigorously mixed for 5 minutes using a vortex. The resulting mixture was then subjected to analysis using HPLC.

To analyze phenoxyethanol content, samples were taken from the signature, text, and non-ink parts of the paper using a 5 mm punch. This was done because solvents tend to diffuse both horizontally and vertically from the moment ink is transferred to paper. Placing a newly written paper on top of a promissory note can cause solvent migration and contamination. The samples were then analyzed using TD-GC/MS.

RESULTS and DISCUSSION

HPLC and TD-GC/MS are commonly used together for ink ageing analysis because they are complementary analytical techniques that allow for the detection and quantification of a wide range of ink components. HPLC is used for the separation and identification of dyes and pigments in ink samples, while TD-GC/MS is used for the identification and quantification of volatile organic compounds (VOCs) in the same sample. By using both techniques together, it is possible to analyze both non-volatile and volatile components in the ink sample, providing a more complete picture of its composition. TD-GC-MS is used for documents requiring short-term age determination, while HPLC is used for documents requiring long-term age determination. Phenoxyethanol analysis by TD-GC-MS is used to determine the time of suspicious writings for 0-24 months old documents. If phenoxyethanol analysis cannot be used to determine the time of suspicious writings, i.e. if the allegation in the document is older than 24 months and it is thought that there is a difference of at least 4 years between the creation times of suspicious writings, dyestuff analysis by HPLC is used.

Analysis of Dyes

Crystal violet and methyl violet dyestuffs were detected in the inks taken from both signature and writing samples. Chromatograms were given in Figure 2 and 3. Results were given in Table 1.

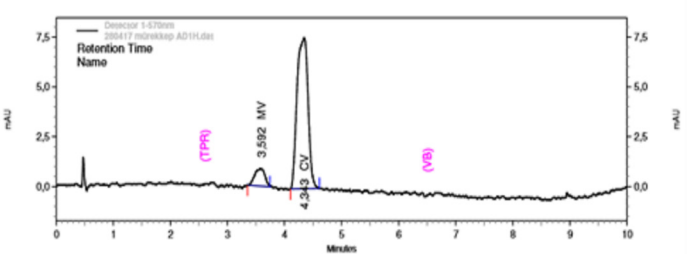

Figure 2. Analysis result of the sample taken from the personel name

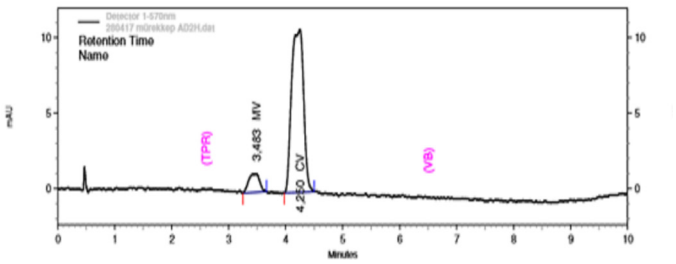

Figure 3. Analysis chromatogram of the sample taken from signature

Table 1. Analysis results of personal name and signature

Sample	TPR Peak area	MV Peak area	CV Peak area	Total area	CV Peak area/ MV Peak area
Personal name	-	10880	101549	112429	9.3
Signature	-	16459	158390	174849	9.6

When the CV peak area/MV peak area ratios of two suspicious texts on the same document are compared, three situations will emerge.

These :

Ratio A < Ratio B: A is written before B

Ratio A = Ratio B: Both articles were written at the same time

Ratio A> Ratio B: A is written after B

When the obtained rates were evaluated, it was determined that there was no significant difference and no interpretation could be made. In order for there to be a significant difference between the rates, there must be at least 4 years between the writing time of the suspicious articles.

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Analysis of Phenoxyethanol

The relative phenoxyethanol ratios (V%) of the analyzed samples were calculated. Results were given in Table 2.

Table 2. The relative phenoxyethanol ratios

Sample	90°C peak Area	200°C Peak Area	%V
2.000.000 £	835	10933	7
Signature	2310	4791	33

$\%V=M_{90°C} /(M_{90°C} + M_{200°C})$

$M_{90°C}$ = Phenoxyethanol Peak Area (Thermal Desorption 90°C)

$M_{200°C}$= Phenoxyethanol Peak Area (Thermal Desorption 200°C)

In order to determine whether there is phenoxyethanol contamination in the document from another document, a sample was taken from the non-ink part of the suspect document and analyzed in TD-GC/MS as mentioned in the analytical methods section. We used V%-time(month) curve for V% values obtained from suspicious articles. V%-time curve was used from our previous study as the age curve. When we compare the V% values we obtained from suspicious articles with the curve, the signature was made within 3-7 months from the date of analysis but 2.000.000£ was not evaluated because the V% value was below 10. Since the curve starts to flatten below 10 in the V%-time(month) curve, there is no comment for this value and below.

CONCLUSION

In conclusion, the analysis of the suspicious promissory note aimed to determine whether the writing on it was done in 2014 or on a later date. Two analytical methods, dye analysis and phenoxyethanol analysis, were utilized to provide evidence for the court. Samples were taken from the ink and non-ink parts of the document and analyzed using HPLC and TD-GC/MS, respectively.The phenoxyethanol analysis also provided evidence of contamination from another document. The V%-time curve was used to determine the age of the document, and it was found that the signature was made within 3-7 months from the date of analysis. Therefore, the document could not have been issued in 2014 as alleged.

Consequently, the use of analytical methods in forensic science plays a critical role in providing evidence in legal cases. The combination of different techniques allows for a comprehensive evaluation of the samples and provides strong evidence that can be used in court. In this particular case, the use of HPLC and TD-GC/MS allowed for the determination of the age of the document and provided evidence that the document was not written in 2014 but at a later date. This study demonstrates the importance of analytical methods in forensic science and their potential to contribute to the resolution of legal cases.

Conflict of interests
The authors declare that there is no conflict of interest in the study.

Financial Disclosure
The authors declare that they have received no financial support for the study.

Ethical approval
Ethics committee approval is not required.

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