



## Case Study

# Ink aging by dye ratio: case study

İslek Salkım D.<sup>1\*</sup>, İřat E.<sup>2</sup> and Cengiz S.<sup>1</sup>

<sup>1</sup>Institute of Forensic Science, Istanbul University, Cerrahpasa Medicine Faculty Fatih Campus, Istanbul, Turkey

<sup>2</sup>Cerrahpasa Medicine Faculty, Istanbul University, Cerrahpasa Medicine Faculty Fatih Campus, Istanbul, Turkey  
salkimdilek@gmail.com

Available online at: [www.isca.in](http://www.isca.in), [www.isca.me](http://www.isca.me)

Received 8<sup>th</sup> February 2018, revised 16<sup>th</sup> May 2018, accepted 25<sup>th</sup> June 2018

## Abstract

*Ink age determination; Changes in the structure of the ink (demethylation of the stain, evaporation of the solvents and polymerization of the resins) on the document are determined by chromatographic and spectroscopic methods. The dyes that are generally used are crystal violet, methyl violet and Victoria blue. Due to light exposure, in time crystal violet transforms in to methyl violet and methyl violet in to tetra methyl pararosaniline. Detection of this change can be easily determined by chromatographic methods. In this study, in order to determine whether the texts, signatures and figures on the same bond were written at the same time, the ink age of crystal violet, methyl violet and Victoria blue dyes were determined by using high pressure liquid chromatography and a dye ratio technique. The detection range of the method used is 0.02-0.6 ng. The statistical evaluation of these methods were examined performing intra day (n=6) and inter day calibration (n=6) which were found to be satisfactory, with highly accurate and precise results. This phenomenon came to us in 2015. The arrangement date written on the bond is 16/05/2007 and the date of payment is written as 14/06/2007. What was asked of us was to determine whether there is a date difference between the signature on the bond and the writing in the address section and also if the date has been edited to display an older date rather than a newer date. Therefore, the ink samples were taken from the writing on the bond and analyzed using high pressure liquid chromatography, dye ratios were compared and evaluated by age.*

**Keywords:** Ink aging, crystal violet, methyl violet, dye ratio, HPLC.

## Introduction

One of the most important areas of judicial document examination is age determination. There are three main approaches to age determination. These are static approach, dynamic approach and relative dynamic approach. Interpreting by determining the change of the dye matter, solvents and resins in the ink, forms the basis of this dynamic and relative dynamic approach. The dyeing elements used in ballpoint pen ink consist of crystal violet, methyl violet, and Victoria blue<sup>1-4</sup>.

As soon as ink is transferred to paper, the aging process begins. The main factors affecting this process are light, oxygen and so on. It is the demethylation of crystal violet which is easily detected in aging process detection. In this reaction, depending on the exposure to light, the methyl groups of the dye are in replaced by hydrogen one after the other. In each of these displacements the molecular weight is reduced by 14g. As a result of exposing the crystal violet to oxygen is that the central C-phenyl bonds are split. Therefore as a result of this reaction, phenols and benzophenones are formed. Triaryl methane dyes have been proven to produce single oxygen upon exposure to light on paper. It has also been shown that OH radicals formed from single oxygen in the water also causes the bonds to be separated.

The final reaction is when the alerted dye cation is converted to a colorless leuco dye form, as a result of electron attachment or photochemical hydrogenation<sup>4</sup>.

In this age determination study, the structure of the ink and the effect of environmental factors on the structure of the ink were determined by chromatographic methods. However, since these methods damage the document, spectroscopic methods that do not damage the document have been preferred recently, but chromatographic methods are still used<sup>4-8</sup>.

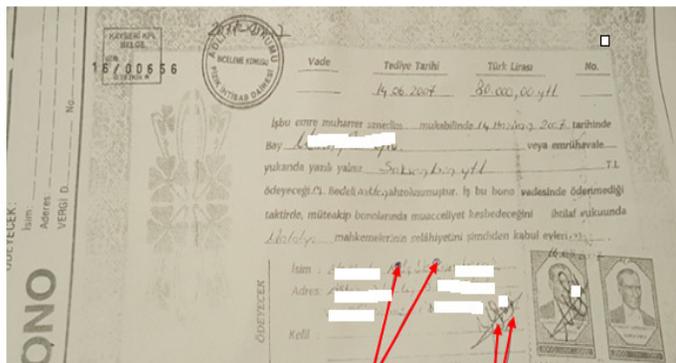
In this study, the dyes in the ink on the document were analyzed by HPLC, whereas in other studies the age was determined using the dye ratio.

## Case

In 2015 we were sent a 16/05/2007 dated bond with a payment date of 14/06/2007 to determine whether it was written at a different date and also if the date had been edited to display an older date rather than a newer date. The image of the bond is shown in Figure-1.

Since this method was developed for the detection of ball-point dye components (crystal violet, methyl violet, Victoria blue),

studies were initially made under various light sources in order to determine whether the bond was written with a ball-point pen or not. Images of the writing under various light sources are shown in Figure-2.



**Figure-1:** The image of the bond and the areas of examples given (Some ethical principles have been taken into consideration; therefore a section of the ID information on this document has been electronically deleted by us so that it will not decipher these individuals).

Ink samples were taken from this section because it was claimed that there may be an age difference between the signature on the document and the text on the address line.

## Materials and methods

**Chemicals and reagents:** Methanol (HPLC grade), acetonitrile (HPLC grade), acetic acid and phosphoric acid (concentration 85%) were purchased from Merck (Germany).

**Sample preparation:** Two paper samples were taken from the sections where the signature and address were written with a hole puncher. 100µl of methanol was added to the samples they were then put in a HPLC system and vortexed at high-speed.

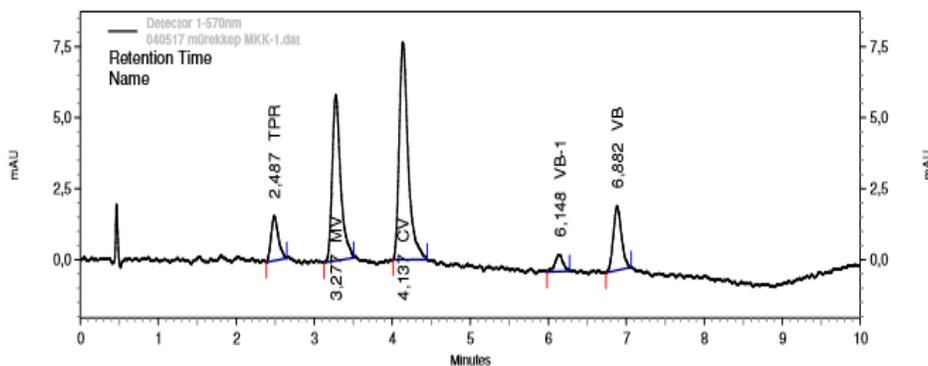
**HPLC Conditions:** In this study the equipment written below were used; Thermo Scientific Degazer System SCM 1000, Pump Spectra System P1000, Autosampler Spectra System AS3000, UV detector 1000 system, Phenomenex Onyx C18 Monolithic Colon (100x4,6mm). 0,05M phosphate buffer (pH=3). Mobile phases components were A: 0.05M Phosphate buffer, B: 100% Methanol and C: 100% Acetonitrile, % ratios found of the mobile phases were A: 50%, B: 30% and C: 20%.

## Results and discussion

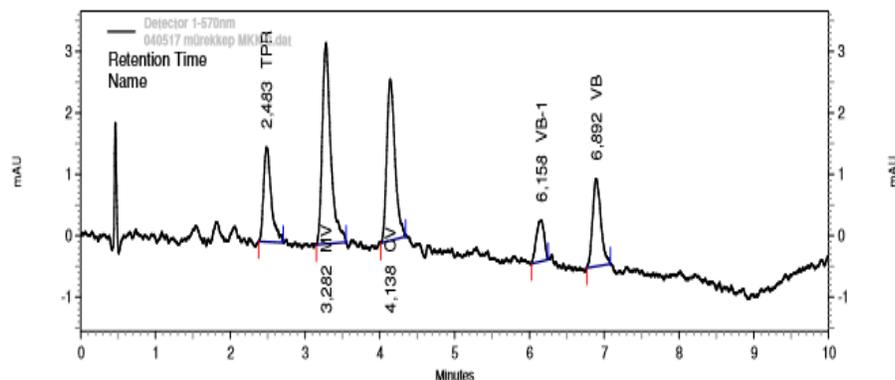
It has been concluded that the main components of the tested inks used on the document are inks made up of Violet Blue, Crystal Violet, Methyl Violet and a material known as pararosaniline, and do not contain any other pigments in their compositions.



**Figure-2:** Images of the document under various light sources.



**Figure-3:** Chromatogram of the ink sample taken from the signature.



**Figure-4:** Chromatogram of the ink sample taken from the address.

The peak areas of the analytes, and the CV/MV conversion ratio being the first step in the conversion reaction are shown in Table-1.

**Table-1:** Peak areas of analytes, CV/MV (Dye ratio).

Sample Name	TPR Area	MV Area	CV Area	Total Area	CV/MV Ratio (Dye ratio)
Signature	10044	43715	60898	114657	1.39
Address	11038	25716	19866	56620	0.77

From the analysis of the samples taken from the signature and the address, CV/MV ratios were calculated to be 0.77 and 1.39.

When the results were evaluated, it was seen that they were formed at different time intervals with ballpoint pens with similar formulations.

### Conclusion

Changes in the structure of the dye, solvents and resins over time occur during ink age determination. A method of analyzing ballpoint pen ink components is developed and validated. The method is applicable for the relative dating of ink entries in

notebooks and other documents where, often, several ink entries are written by the same ink. CV/MV ratio can be used to designate texts written at different times in the same structure on the same document.

### Acknowledgement

The study was financially supported by the Research Fund of Istanbul University (project no. 29341 and 42313).

### References

1. Ezcurra M., Góngora J.M., Maguregui I. and Alonso R. (2010). Analytical methods for dating modern writing instrument inks on paper. *Forensic Science International*, 197(1-3), 1-20.
2. Samandiou V.F., Nikolaidou K.I. and Papadoyannis I.N. (2004). Development and Validation of a Gradient-HPLC-PDAD Method for the Identification of Ballpoint Pen Ink Components: Study of Their Decomposition on Aging for Forensic Science Applications. *J. Liquid Chrom. & Related Tec.*, 27(2), 215-235.
3. Andrasko J. (2001). HPLC analysis of ballpoint pen inks stored at different conditions. *J Forensic Sci.*, 46(1), 21-30.

4. İslak Salkim D. (2015). Structure and Age Determination of Blue ballpoint pen ink of paper. Istanbul University Institute of Forensic Science, Turkey.
5. Lalli P.M., Sanvido G.B., Garcia J.S., Haddad R., Cosso R.G., Maia D.R.J., Zacca J.J., Maldanerc A.O. and Eberlin M.N. (2010). Fingerprinting and aging of ink by easy ambient sonic-spray ionization mass spectrometry. *Analyst*, 135(4), 745-750
6. Grim D.M., Siegel J. and Allison J. (2001). Evaluation of Desorption/Ionization Mass Spectrometric Methods in the Forensic Applications of the Analysis of Inks on Paper. *J.For.Sci.*, 46(6), 1411-1420.
7. Siegel J., Allison J., Mohr D. and Dunn J. (2005). The use of laser desorption/ionization mass spectrometry in the analysis of inks in questioned documents. *Talanta*, 67(2), 425-429.
8. Weyermann C., Kirsch D., Costa-Vera C. and Spengler B. (2006). Photofading of ballpoint dyes studied on paper by LDI and MALDI MS. *Journal of the american society for mass spectrometry*, 17(3), 297-306.