

## Determining malpractice by ink aging method

Dilek Salkim Islek, Esra Isat, Salih Cengiz

*Istanbul University, Institute of Forensic Sciences, Istanbul, Turkey*

Received 15 June 2016; Accepted 02 August 2016

Available online 04.08.2016 with doi: 10.5455/medscience.2016.05.8515

### Abstract

Document forgery is one of the most common crime types. One of the methods for detection of this type of crime is the determination of the age of the ink. The time difference between the suspected articles on the document can be easily detected by the determination of ink age. In our study case the family complained in a court of law with claiming that born of their down syndrome child was a negligence of the doctor. Court demanded us to determine that if notes written by the doctor in "2005" or after the family complained. Ink samples taken from two patient book of records were analysed and ink structures were determined with using High Pressure Liquid Chromatography (HPLC) and aging was determined with using dye ratio technique.

**Keywords:** Ink aging, dye, ratio, crystal violet

### Introduction

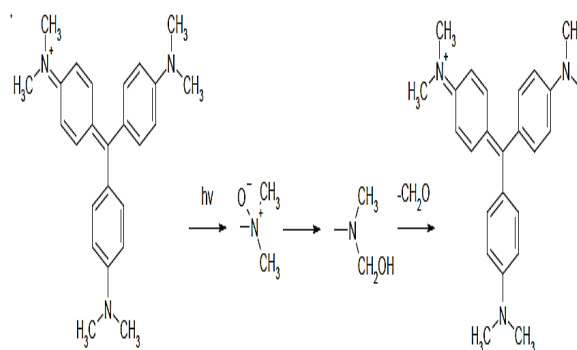
One document forgery detection method is the determination of ink dating. Determination of ink dating is important for forensic science expert. Although there are many studies in this issue, the questions have not been fully answered [1-3].

Composition of ink is divided into 4 groups. 1) Dyes 2) solvents 3) resins 4) additives (surface active agents, corrosion control ingredients, conductivity salts). Dyes used as coloring materials for inks include different classes as defined by the Color Index [1,4]. Crystal violet, methyl violet and Victoria blue are common used to composition of ink.

When ink is applied to paper, composition of ink changes as a function of time. This changes are degradation of dye, polymerization of the resin ve evaporation of the solvents. These changes are determined by analytical methods [5]. This procedure is called ink aging.

In addition to the composition of the dye, fading is also influenced by environmental parameters. Oxygen, moisture, temperature, air contaminants and wavelength of the exposed light are some of the environmental parameters effect the fading process. N-Demethylation is one of the important reactions that occur in photofading. Due to exposure to the light, methyl groups of dyes are replaced by hydrogens and each replacement results in 14 g mass difference [5,6]. This reaction was fig. 1.

As a result of being an easy method for determination of dyes' demethylation with HPLC, HPLC is one of the most choosed method for ink age determination [4,7-8]. In this study dyes of ink samples taken from book of records were analysed with a method which is developed at HPLC and with using the comparisions of dye ratios, ink ages were determined.



**Figure 1.** Demethylation reaction of Crystal violet [1]

### Material Method

Samples were taken and inspected from; "M.P" written patient name and "26 week", "12 W" ilk grosses", "double test, "14 weeks of pregnancy" and "combined double test". Sample locations were shown in Fig. 2,3 and 4.

When their ink samples were analysed it was seen that their ink structures were different, dye ratios 0.94 for "14 weeks of pregnancy", 1.04 for "combined double test" were calculated and their difference is meaningfully 0.1 detected. These two writings were not written at the same time.

\*Corresponding Author: Dilek Salkim Islek, Istanbul University, Institute of Forensic Sciences, Istanbul Turkey  
 E-mail: salkimdilek@gmail.com

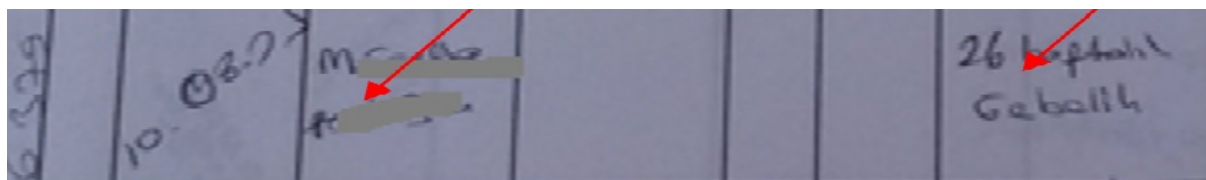


Figure 2. M.P. written patint name and 26 week"

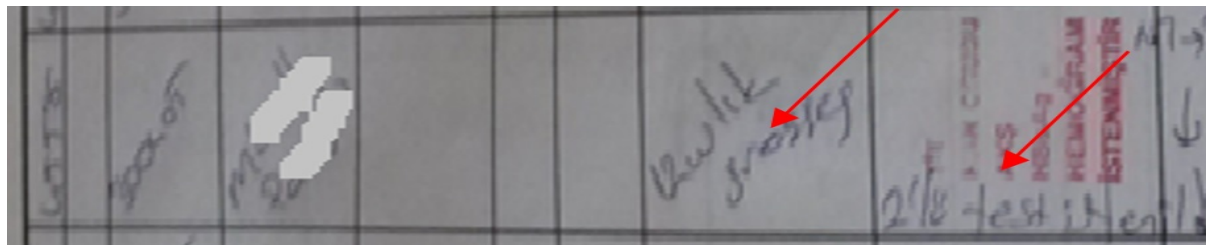


Figure 3. 12 W'lik grosses and double test

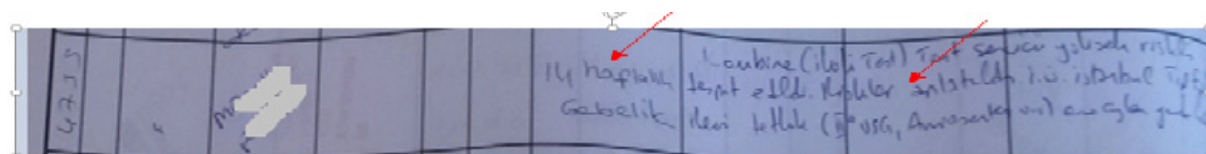


Figure 4. 14 weeks of pregnancy and combined double test

### Sample Preparation

2 samples were taken from the patient records of notebook by 1,2 mm punch. 100  $\mu$ l methanol added then after mixing with vortex inspected in HPLC system.

### HPLC Conditions

In this study the equipments 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). 0,05 M phosphate buffer (pH=3), methanol and acetonitrile were used as mobile phases. Programme was given in Table 1.

Table 1: Pump Conditions

| Time(min.) | Mobile Phase A | Mobile Phase B | Mobile Phase C | Flow rate (mL/min) |
|------------|----------------|----------------|----------------|--------------------|
| 0          | 50             | 30             | 20             | 3                  |
| 0.2        | 50             | 30             | 20             | 3.5                |
| 8          | 30             | 40             | 30             | 3.5                |
| 10         | 50             | 30             | 20             | 3                  |

### Results And Discussion

In this case samples were taken from doctor writings about patient informations from books of records, and analysed in HPLC to determine if they were written with the same pen and writing date with using transformation ratios. Results of samples taken from patient records of notebook were given in Table 2.

It had been detected that, when "M.P." and "26 weeks" writings' inks on the same page and on the same line were analysed CV, MV, TPR and VB were detected as dyes. When looked to dye ratios (CV/MV), respectively 2.83 for "M.P.", 2.79 for "26 weeks" were calculated.

Because of the very small difference as 0.04 between two dye ratios, both writings were written on the same time.

When "Double Test" and "12 W' lik grosses" writings' inks on the line were analysed with HPLC it has seen that they were in the same structure. When looked to dye ratios, 2.84 for "Double Test", 0.88 for "12 W' lik grosses" were calculated, it was determined that inks were at the same structure accoring to HPLC and written at the same time according to dye ratios.

"14 weeks of pregnancy" and "combined double test" writings were written on the same page and same line.

Table 2. Results of samples taken from books of records

| Sample                | TPR Area | MV area | CV Area | Total Area | CV/MV Ratio |
|-----------------------|----------|---------|---------|------------|-------------|
| "M.P."                | 509      | 4531    | 12866   | 17906      | 2.83        |
| "26 week"             | 1324     | 7686    | 21462   | 30472      | 2.79        |
| Double test           | 4738     | 10368   | 8745    | 23851      | 0.84        |
| 12W'lik grosses       | 8672     | 20170   | 17793   | 46635      | 0.88        |
| 14 weeks of pregnancy | 7401     | 14597   | 13760   | 35758      | 0.94        |
| Combined double test  | 3316     | 11437   | 11937   | 26690      | 1.04        |

## Conclusion

Determination of demethylation of dyes with chromatographic methods is one of the most used methods for ink aging. In this situation there were dye transformations and in order to not to affect the results by ink amount and minimize failures mostly ratios were used. As a result of our studies it is seen that CV/MV ratio can be used for determination of ink aging.

## Acknowledgements

The study was financially supported by the Research Fund of Istanbul University (project no. 56198).

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