

ORIGINAL ARTICLE

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The structure and age determination of the writings written with ballpoint pen**Dilek Salkim Islek¹, Esra Isat², Salih Cengiz¹**¹*Istanbul University, Institute of Forensic Sciences, natural and applied sciences, Istanbul Turkey*²*Istanbul University, Cerrahpaşa Medical Faculty, metabolism diseases Laboratory, Istanbul Turkey*

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Abstract

Ink age determination is the determination and interpretation of the structure of the ink on a document by using advanced analytical methods. Over time, the dyestuff in the structure of the ink go through demethylation, solvents get evaporated and resins get polymerized. These changes can be determined easily with chromatographic and spectroscopic methods. In this study, five cases that were transferred to the court with the objection of five individuals working in the same firm are examined. Employees claim that the factory made them sign the vacation book on the same day including the retroactive dates although they had not taken their vacation. What the court asked us is whether the writing, numbers and signatures on the pages of the annual paid leave book, which belonged to five individuals, had been written at the same time or at different times. The structures of the inks in the ink samples taken from writings, figures and signatures on the pages of annual paid leave book belonging to five individuals that work in the same company were analyzed by High Pressure Liquid Chromatography analysis. The results were evaluated in terms of age by using dye compound ratio technique.

Keywords: Ink aging, dynamic approach, dye ratio**Introduction**

Forensic document review experts examine who created checks, notes, notebooks, contracts, letters, etc. Aging of document was created is found by examining changes in ink structure with chromatographic and spectroscopic methods. It is possible to divide the structure of ink into 4 main groups. These are dyestuff, resins, solvents and additives [3].

The aging process starts as soon as the ink is transferred to the paper. During this process the dyestuff go through demethylation with the effect of light, solvents get evaporated and resins get polymerized.

Crystal violet, methyl violet and victoria blue are used as dyestuff in the chemistry of ballpoint pen ink. In time, under the influence of light the crystal violet goes through demethylation and it turns into methyl violet. The methyl violet goes through demethylation

and it turns into tetramethyl pararosaniline. This decay is detected by spectroscopic and chromatographic methods [1].

In this study, ballpoint pen structures in the annual paid leave books of factory workers were determined by high pressure liquid chromatography (HPLC) and it was interpreted in terms of ink age.

Material and Methods**Samples**

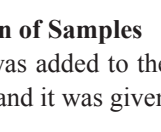
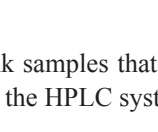
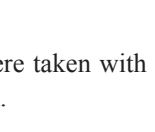
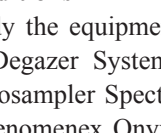
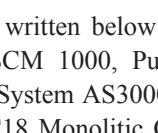
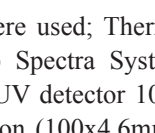
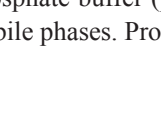
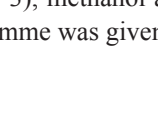
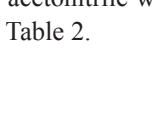
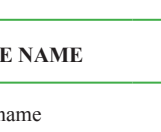
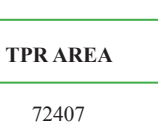
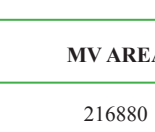
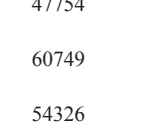
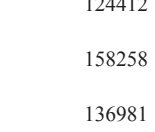
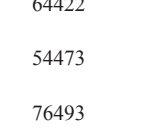
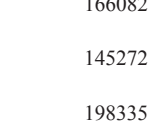
First of all, to find out what kind of pen is used to write on the documents, optical examinations of documents were applied with various wavelengths. As a result of the review, it was found that the writings and signatures of each document were written with wet ink and the documents were original, also writings, numbers and signatures were created with a blue round tip ball-point pen. Table 1 shows the optical ink images of the files 1,2,3,4 and 5.

For the detection of crystal violet, methyl violet and victoria blue ballpoint pen dyes on HPLC, samples of name, date and signatures, which are signed to indicate that they used permission, were taken from the relevant pages of the annual paid leave book via Uni-Core-1.20 model punch .

*Corresponding Author: Dilek Salkim Islek, Istanbul University, Institute of Forensic Sciences, natural and applied sciences, Istanbul Turkey

E-mail: drcanantopcuoglu@gmail.com

Table 1. Optical images that belong to 5 files.

File No.	Optical Image		
1			
			
			
2			
			
			
3			
			
			
4			
			
			
5			

Preparation of Samples

Methanol was added to the ink samples that were taken with the punch tool and it was given to the 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 2.

Table 2. Pump conditions of HPLC

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

Ink composition of tetramethyl pararosaniline (TPR), methyl violet (MV), crystal violet (CV) and victoria blue (VB) was introduced to the device that was worked on and they were defined as follows: Tetramethyl pararosaniline in 5.4 minutes, Methyl violet in 6.3 minutes, Crystal violet in 7.4 minutes and Victoria blue in 10.0 minutes.

It has been determined that the main ingredients of the inks used in the tested documents are Victoria blue, Crystal Violet, Methyl Violet and tetramethyl pararosaniline.

The areas of chromatograms of dye components, which can be converted into each other in time, total dye area and the dye rate conversion rate, which is the first step in the conversion reaction, are shown in Tables 3, 4, 5, 6 and 7 below.

It was found that the writings that appear to be written in different years were written at the same time because there was no significant difference between the minimum and maximum values of 0.97 and 1.05, respectively when the dye ratios of the samples were compared.

It was found that the writings that appear to be written in different years were written at the same time because there was no significant difference between the minimum and maximum values of 1,07 and 1,16 respectively when the dye ratios of the samples were compared.

Table 3: Area, total area, percent area and dye ratio of the document that belongs to Case 1.

SAMPLE NAME	TPR AREA	MV AREA	CV AREA	TOTAL AREA	CV/MV RATIO
Surname	72407	216880	233853	523140	1.07
Signature of 2006	47754	124412	138598	310764	1.11
Signature of 2007	60749	158258	183371	402378	1.16
Signature of 2008	54326	136981	151621	342928	1.11
Signature of 2009	64422	166082	176684	406991	1.06
Signature of 2010	54473	145272	168858	368603	1.16
Signature of 2011	76493	198335	216555	491383	1.09

Table 4. Area, total area, percent area and dye ratio of the document that belongs to Case 2

SAMPLE NAME	TPR AREA	MV AREA	CV AREA	TOTAL AREA	Dye Ratio
Surname part	72760	194218	190284	457262	0.97
Signature of 2005	28158	84728	86189	199075	1.01
Signature of 2006	59306	187715	183752	430773	0.97
Signature of 2007	44628	132480	139799	316907	1.05
Signature of 2008	80994	232177	226777	539948	0.97
Signature of 2009	39804	106190	107266	253260	1.01
Signature of 2010	90322	246974	245790	583086	0.99
Signature of 2012	62815	178381	174049	415245	0.97

Table 5. Area, total area, percent area and dye ratio of the document that belongs to Case 3

SAMPLE NAME	TPR AREA	MV AREA	CV AREA	TOTAL AREA	CV/MV RATIO
Surname:	67696	173196	162859	403751	0.94
Signature of 2010	46925	121127	124875	292927	1.03
Signature of 2012	34139	88745	84480	207364	0.95

It was found that the writings that appear to be written in different years were written at the same time because there was no significant difference between the minimum and maximum values of 0,94 and 1,03 respectively when the dye ratios of the samples were compared.

It was found that the writings that appear to be written in different years were written at the same time because there was no significant difference between the minimum and maximum values of 1,00 and 1,13 respectively when the dye ratios of the samples were compared.

Table 6. Area, total area, percent area and dye ratio of the document that belongs to Case 4

SAMPLE NAME	TPR AREA	MV AREA	CV AREA	TOTAL AREA	CV/MV RATIO
Surname part	65070	201614	216558	483242	1.07
Signature of 2008	17695	51241	51760	120696	1.01
Signature of 2009	31596	103982	111190	246768	1.06
Signature of 2010	31859	110639	110958	253456	1.00
Signature of 2011	27680	100581	103023	231284	1.02
Signature of 2012	22667	60874	69338	132479	1.13

Table 7. Area, total area, percent area and dye ratio of the document that belongs to Case 5

SAMPLE NAME	TPR AREA	MV AREA	CV AREA	TOTAL AREA	CV/MV RATIO
Surname	54353	123578	105696	283627	0.85
Signature of 2006	60308	135221	116774	312303	0.86
Signature of 2007	63545	137325	114177	315047	0.83
Signature of 2008	52028	112065	98218	262311	0.87
Signature of 2009	53645	115265	96879	265789	0.84
Signature of 2010	55556	117229	103429	276214	0.88
Signature of 2011	57260	119649	97579	274488	0.81

It was found that the writings that appear to be written in different years were written at the same time because there was no significant difference between the minimum and maximum values of 0,81 and 0,87 respectively when the dye ratios of the samples were compared.

Conclusion

Ink age determination is a process that starts with the acceptance of the document by the laboratory ends with the reporting. While examining the dates of the arrangement of paid annual leave in 5 separate files, which had come from the court, the deterioration period of the luminescent materials was determined after the evaporation period of the ink solvent was completely exhausted. In order to do this each ink sample was analyzed by HPLC and evaluated in regard of age by using the dye ratio technique. It was

found that the signatures of each case were signed at the same time, not at different times because there was no significant difference between the minimum and maximum values of the dye ratios when each case was evaluated in itself.

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