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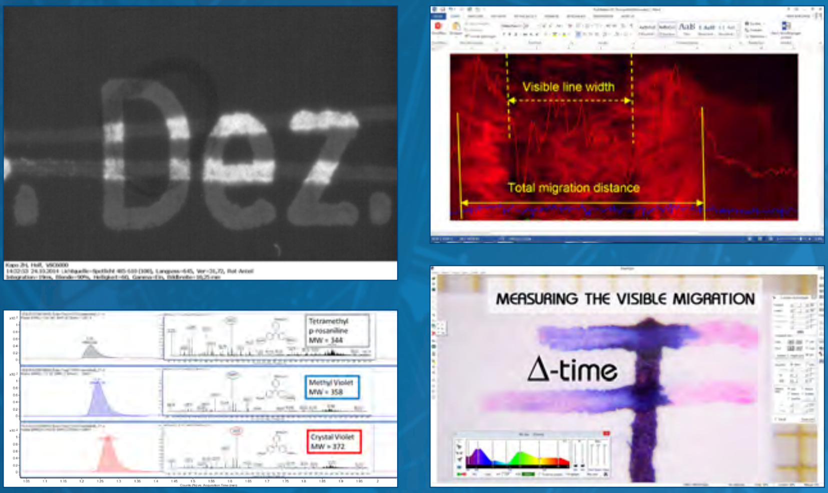
PHYSICAL-CHEMICAL STUDY OF CROSSED LINE INTERSECTION



PHYSICAL-CHEMICAL STUDY OF CROSSED LINE INTERSECTION

November 2016

ACKNOWLEDGEMENTS

The results of the *Physical-Chemical Study of Crossed Line Intersection* were prepared jointly by INTERPOL and the International Academy of Experts in Handwriting and Documents (AIEED).

INTERPOL's Counterfeit Currency and Security Documents Branch (CCSD) and AIEED would like to express their appreciation to all the government forensic experts and academics that participated in this project on the *Physical-Chemical Study of Crossed Line Intersection* which has resulted in the publication of these results.

The Scientific Committee Members established for the project on the *Physical-Chemical Study of Crossed Line Intersection*, and which prepared these results, are as follows:

- Jacqueline BECK, President of AIEED, Handwriting Expert, Court of Appeals of Lyon, France
- José BALBUENA, Director of Research of AIEED, Forensic and Criminal Science Expert for Questioned Documents, Court of Appeals of Versailles, and responsible for Protocol B
- Rolf HOFER, PhD, Scientific Supervisor, Head of the Forensic Chemistry Department, Forensic Science Institute Zurich, Switzerland, and responsible for Protocols A and C
- Daniela DJIDROVSKA, MSc, Chemical Supervisor, Acting Coordinator of CCSD at INTERPOL, and responsible for Protocol D
- Emmanuel BECK, PhD, Academic Advisor of AIEED, Professor at the Jean Moulin University, Lyon, France
- Andrea LEDIĆ, Chemical Advisor, Chief Expert for Handwriting and Documents at the Forensic Science Centre "I. Vucetic", Zagreb, Croatia
- Nathaniel BAKER, PhD candidate, Scientific Advisor of AIEED

In particular, the Scientific Committee Members would like to express their appreciation to Rolf HOFER, PhD, for his invaluable coordination, supervision and commitment to this ambitious scientific project.

We would like to extend a special thank you to José BALBUENA. He initiated this work and directed this scientific study through to completion during a 6-year period, from 2010 to 2016. He has led this study with great skill and a profound commitment demonstrated through scientific means the relation between time and ink.

CCSD greatly appreciates the expertise, knowledge and dedication of José ALMIRALL, PhD, International Forensic Research Institute and Department of Chemistry and Biochemistry, United States.

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- Belgium: Françoise COENRAETS
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- Former Yugoslav Republic of Macedonia: Vesna ANTIKJ and Daniela DJIDROVSKA
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- Spain: Guillermo PUERTO, Jesus BARRON and Juan ORELLANA
- Switzerland: Rolf HOFER
- United States: José ALMIRALL and Rhett WILLIAMSON

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J. Beck

James ANDERSON
Assistant Director
Anti-Corruption and Financial Crimes
INTERPOL

Jacqueline BECK
President of AIEED

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INTRODUCTION

Several forensic instrumental techniques have been tested and used in an effort to determine the time separating the execution of two lines. These techniques have required the use of chemical analysis which is costly, destroys the evidence, and the results are not accurate.

For this reason, INTERPOL's Counterfeit Currency and Security Documents Branch and the International Academy of Experts in Handwriting and Documents proposed a unique non-destructive procedure to address this issue so as to help forensic experts to resolve cases of forgery, for example in identity documents and financial frauds. To carry out their work, experts need to determine when the lines on a questioned document were performed (ink dating) and what is the time separating two or more lines (delta time - Δt).

The advantages of developing a non-destructive technique are two-fold. First, developing a technique that does not physically alter the sample which may need to undergo multiple experiments. This is often necessary in empirical situations where the sample is contested during a trial or when judicial authorities instruct further testing by different parties on the same sample. Second, preserving the sample's validity by using non-destructive experiment techniques would allow for the samples to be stored and archived in a database for crossed line intersections that could be used for future investigations. Such a database would serve document examiners and law enforcement officers as a useful resource and reference tool at national and international levels.

In 2009, AIEED published preliminary research on the physical reactions of inks in crossed line intersections. On the basis of these results, INTERPOL decided in 2010 to conduct a new scientific study in partnership with the AIEED to determine, and prove scientifically, the relationship between time and inks.

This new scientific study has three hypotheses. The first two were studied between 2010 and 2011 and proved that there are physical reactions in crossed line intersections and that in certain cases, the order in which the lines are executed can be determined. These results were approved and validated by the Scientific Committee Members and published by AIEED in 2012.

During the first phase of the project, former INTERPOL staff Mr Carlos VARGAS MERIDA observed the invisible ink migration. As a continuation of his observations, the writing inks of his analysis were also subject of this project. We are thanking him for making available these instruments for our further work.

The study to prove the third hypothesis on the relationship between time and inks (T&I) was conducted between 2013 and 2015. The results of this study, which comprised four protocols, are the subject of this Project.

We wish to share the results of this research on time and inks with the international community, in particular with forensic laboratories and document examiners in preparation of their expert opinions.

We express our gratitude to the 120 forensic document examiners from 54 member countries who have participated in this project. The second phase of the project emphasizes the new approach to determine ink ageing and to identify the luminescence compounds in inks by chemical methods.

The Project on the *Physical-Chemical Study of Crossed Line Intersection* has been guided by principles that are complementary to our mandates and INTERPOL's commitment to support police and law enforcement agencies in its member countries. Gaining a better understanding of the sequencing of line-crossings will help forensic document examiners to identify forged documents thereby assisting criminal investigations and combatting and preventing future crimes.

This publication is divided into four main chapters whereby each explains the purpose of each protocol. Protocol A provides the answer of whether or not invisible ink migration can be used for ink dating. Protocol B addresses the question of whether or not visible ink migration can be used for the determination of Δt. Protocol C answers the question whether or not fading of luminescence can be used to determine Δt. Finally, Protocol D focuses on identifying the chemical compounds of inks, in particular luminescent compound presence.

The annexes of this publication include a glossary of commonly used terms, the list of INTERPOL member countries participating in various workshops organized by INTERPOL and AIEED, and a list of instrumental techniques used by participating countries.

This Study has been edited by Maria-Claudia DRĂGHICI and divided into four main chapters:

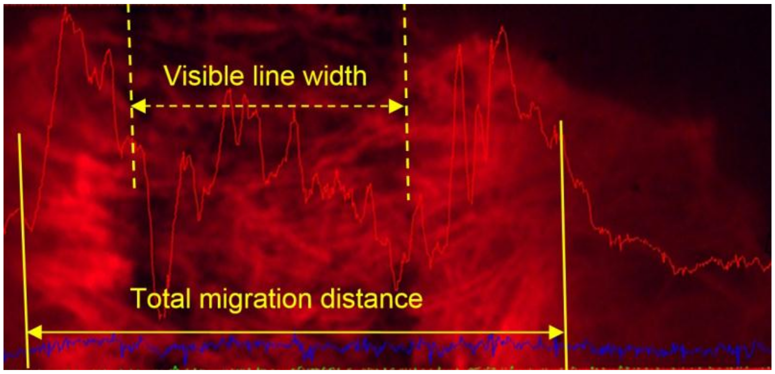
Chapter 1	Protocol A provides the answer of whether or not invisible ink migration can be used for ink dating.
Chapter 2	Protocol B goes through the question of whether or not visible ink migration can be used for the determination of Δt.
Chapter 3	Protocol C answers the question whether or not fading of luminescence can be used to determine Δt.
Chapter 4	Protocol D aims at identifying the chemical compounds of inks, in particular luminescent compound present in inks.

The following three annexes are included in the present publication:

Annex 1	includes a Glossary of commonly used terms in *Physical-Chemical Study of Crossed Line Intersection*.
Annex 2	enlists the countries and participants who regularly attended workshops on the *Physical-Chemical Study of Crossed Line Intersection* at INTERPOL General Secretariat in Lyon, France during the period of 2013-2016.
Annex 3	comprises instrumental techniques used by participating countries.

CHAPTER 1. PROTOCOL A

INK DATING STUDY: MEASURING THE INVISIBLE MIGRATION



1.1 Introduction

We could observe and prove that invisible migration of ink components exist within, and/or outside of intersecting lines. This study shall answer to the question whether or not invisible ink migration can be used for ink dating. A set of samples always include line “ink 1” over line “ink 2” and vice versa.

1.1.1 Participating countries and experts

Latvia: Forensic Service Department of State Police, Inna KUDRJAŠOVA and Marcis SEDLENIEKS
Poland: Forensic Bureau Internal Security Agency, Agata GRABOWSKA
Niger: Forensic Laboratory of Niamey, Abdou Salam YAHAYA BAKO
Switzerland: Forensic Science Institute Zurich, Rolf HOFER

1.1.2 Suggested protocol

Several crossing lines of different writing instrument sets were produced. A set consists of e.g. line of instrument A over line of instrument B and vice versa. The second, intersecting line was applied one minute after the primary one. Pictures were taken with the aid of a document comparator apparatus according the timetable as follows:

1st picture: immediately after the production of the line intersection
2nd picture: 2 hours after the production of the line intersection
3rd picture: 4 hours after the production of the line intersection
4th picture: 1 day after the production of the line intersection
5th picture: 1 week after the production of the line intersection
6th picture: 2 weeks after the production of the line intersection
7th picture: 3 weeks after the production of the line intersection
8th picture: 4 weeks or 1 month after the production of the line intersection
9th picture: 2 months after the production of the line intersection
10th picture: 3 months after the production of the line intersection
11th picture: 4 months after the production of the line intersection
Continuation: one picture per month
Last picture: 12 months after the production of the line intersection

1.1.3 Proposed writing instruments and materials to use

For this dating study, inks were chosen, where migration of ink components has already been observed as well as such inks with unknown behavior. The following writing instruments were used for protocol A:

A: Ballpoint pen, Stabilo, Ref nº 0800M 97 3, blue ink
Stroke dimension: 0.3 mm

B: Ink pad, Troadat, Ref nº 6/4911C, red ink
Stroke dimension: 0.6 mm

C: Felt-tip pen, Paper Mate Flaire, black ink
Stroke dimension: 0.7 mm

I: Ballpoint pen, 80085 CENTRUM Pioneer, blue ink
Stroke dimension: 0.5 mm

J: Ballpoint pen, CARAN d' ACHE, Giant Cartridge "Goliath", 8428.000 medium black, black ink
Stroke dimension: 0.4 mm

Q: Ink pad, Trodat Printy 4822, red ink
Stroke dimension: 0.6 mm

R: Ballpoint pen, CARAN d' ACHE 826, blue ink
Stroke dimension: 0.3 mm

Y: Ballpoint pen, Pilot BPA-10F, black ink
Stroke dimension: 0.3 mm

Z: Ink pad, Sachihata HGN-1, blue ink
Stroke dimension: 0.6 mm

The intersection combinations (sets) thereof were:

A over B	and	B over A
C over I	and	I over C
C over Q	and	Q over C
J over Q	and	Q over J
J over R	and	R over J
Y over Z	and	Z over Y

1.2 Experimental section: methods and materials

Intersections were produced on different paper qualities. Paper was chosen allowing inks to show luminescence (no quenching effect):

a) Non-bleached recycling paper: REFUTURA, Art. Nr. 228 080, 80g/m^2, Switzerland
b) Non-bleached paper: Wrapping paper, 80 g/m^2; Latvia
c) Bleached office paper: CLAIRALFA-CLAIRFONTAINE, A4, 80 g. m2, Ref 1797 3-329680197907 PEFC certified
d) Bleached office paper: XEROX Premier, 80 g/m^2

The following detection instruments were used:

- VSC 5000 with VSC software;
- VSC 6000 with Photoshop;
- VSC 6000/HS with VSC software;
- Projectina 4500 with PIA software;
- Docucenter Nirvis with PIA 7000 Software from Projectina;
- C1 Nicon Eclipse 80i with NIS – Elements.

The setting on the detection unit was optimized for each paper and intersection combination to get adequate luminescence and contrast. These parameters were kept constant during the whole experiment.

Ink combination	Excitation wavelength	Detection wavelength	Magnification	Picture integration time
A over B and vice versa	620 nm	735 nm, long pass	46.20	4 s
C over Q and vice versa	620 nm	735 nm, long pass	46.20	4 s
I over C and vice versa	485 - 590 nm	645 nm, long pass	18.01	53 ms
J over Q and vice versa	485 - 610 nm	645 nm, long pass	31.83	37 ms
R over J and vice versa	485 - 610 nm	645 nm, long pass	31.83	37 ms
Y over Z and vice versa	400 - 420 nm	485 - 590 nm	5	33 ms

Table A1. Examples of sets (ink combinations) and apparatus settings

Pictures were taken with a digital camera (e.g. video comparator system) and the total line width (visible ink line and luminescent zone) was measured from each intersection at each storage time. The measures are presented in real dimension or in arbitrary unit. Depending on the system (microscope with image analysis software or simple measures made on the screen with constant magnification of the intersection), participants measured the migration distance in mm or in number of pixels. The data were transferred in a table and curves were calculated with line width versus age of intersection.

To preserve components from bleaching, the samples were stored at ambient conditions in the dark during the whole experiment.

1.3 Results

Table B1 gives an overview on which laboratory did which CLI set on what paper quality.

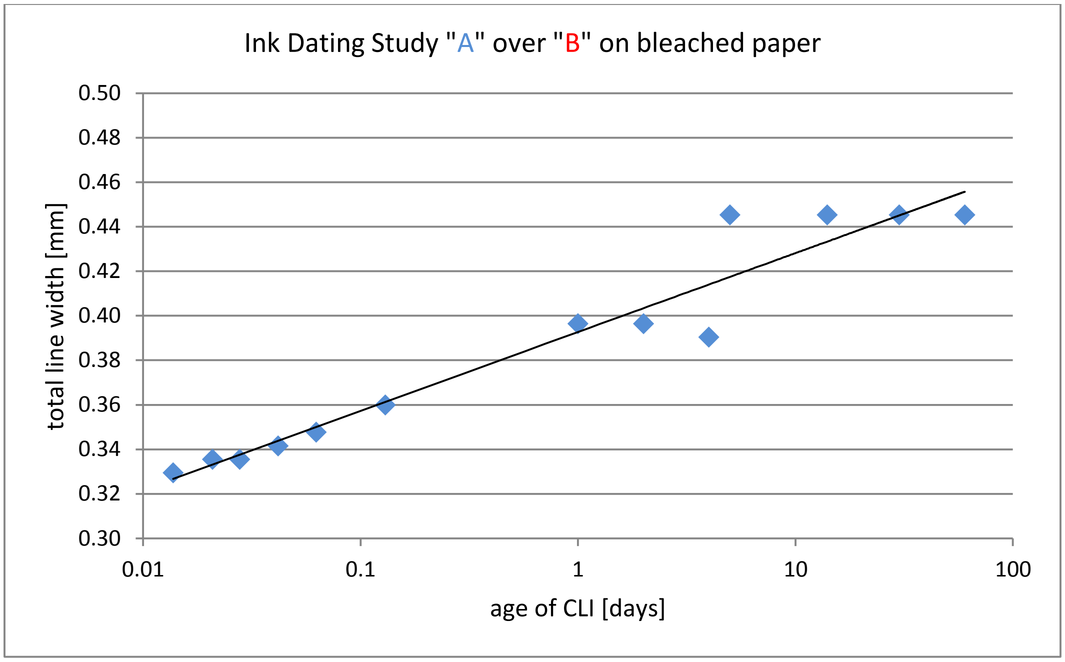
CLI set	Paper brand			Participating country
	a)	b)	c)	
A/B			X	Niger
C/I		X		Latvia
C/Q			X	Niger
J/Q	X		X	Switzerland
J/R	X		X	Switzerland
Y/Z			X	Latvia
Y/Z			X	Poland

Table B1. Overview on sample materials and participants

Paper:	a) Recycling paper of Switzerland
	b) Wrapping paper of Latvia
	c) Bleached paper of Portugal

The migration distance was measured as described above. Four intersection sets (A/B, C/I, C/Q and one set of Y/Z) were observed for the first one to three months; all others for a period of one year.

In the ink combination J/R, the migrating substance showed the same luminescence intensity as the intersecting line ink at any detection setting or one ink absorbed the luminescence of the migrating component(s) of the other. In this intersection set, the migration into the blank paper was measured (R/J, Figure A4 and Figure A5).



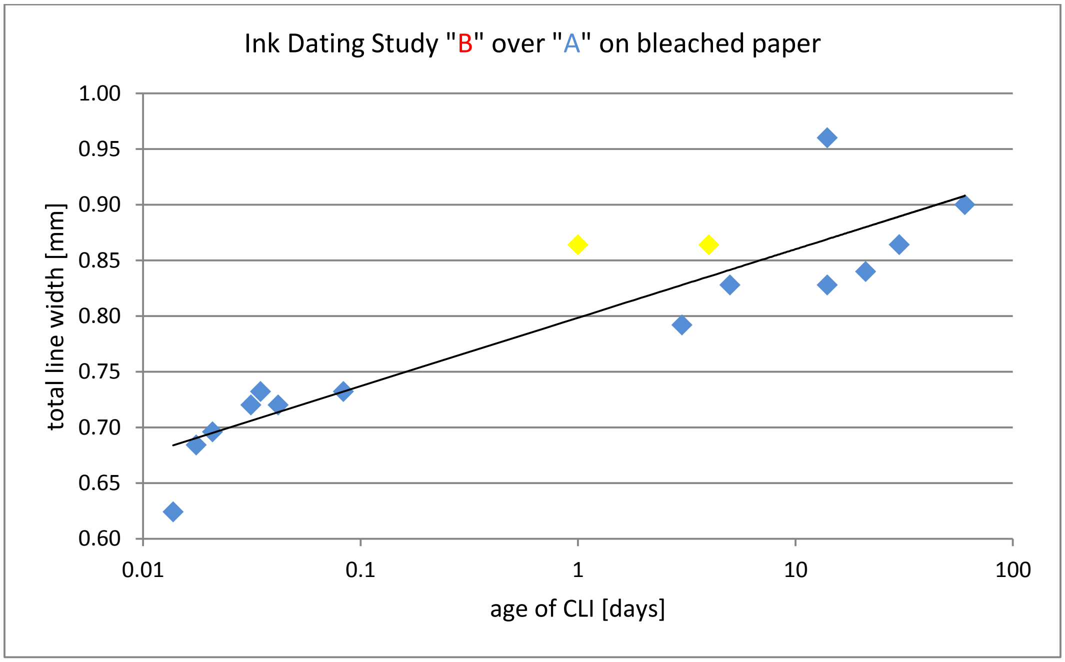
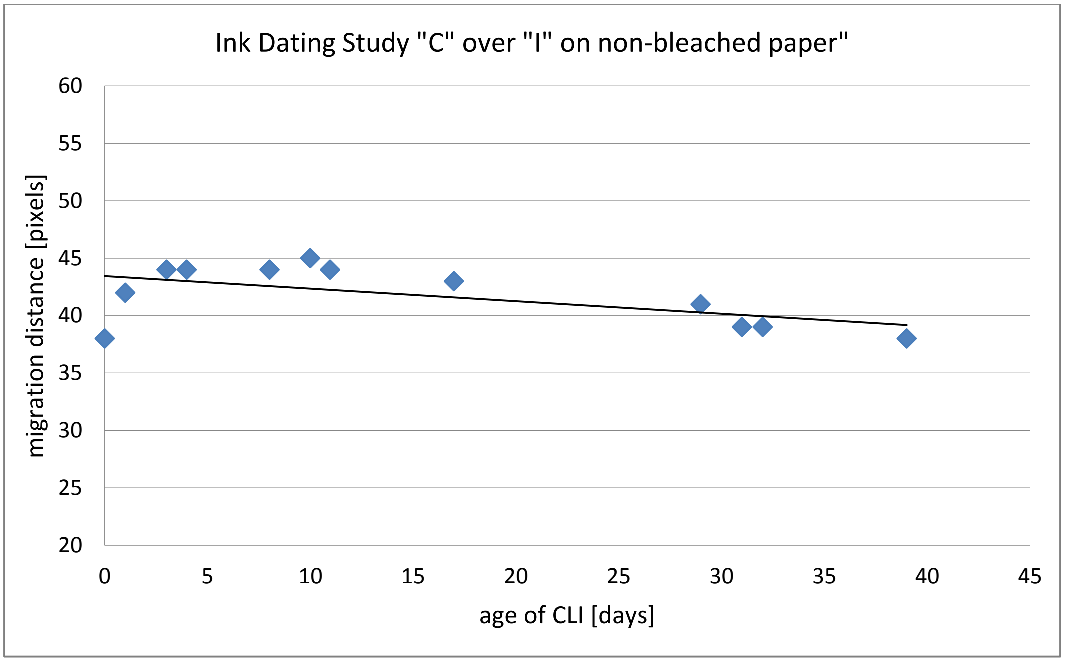


Figure A1. Invisible migration curves of the line intersection of blue ink “A” and red ink “B” on bleached paper c); “A” over “B” (upper curve) and “B” over “A” (lower curve). The real line widths were measured (single measurements). Two measures (yellow dots) were performed with higher integration time on the detection unit. The visible ink line widths is 0.3 mm for “A” and 0.6 mm for “B”.



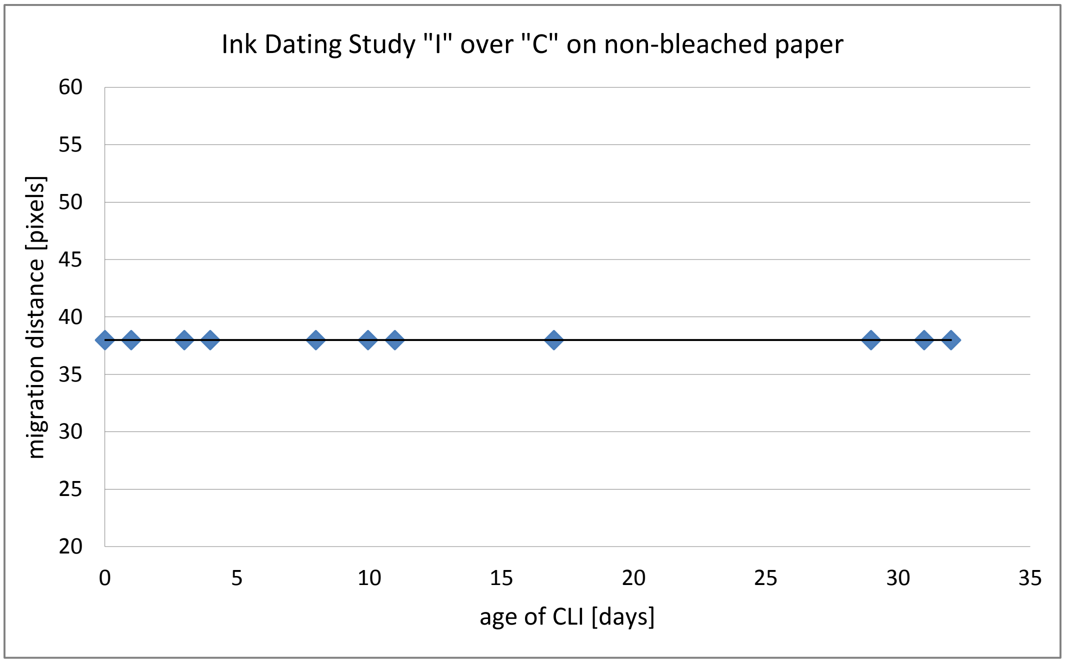
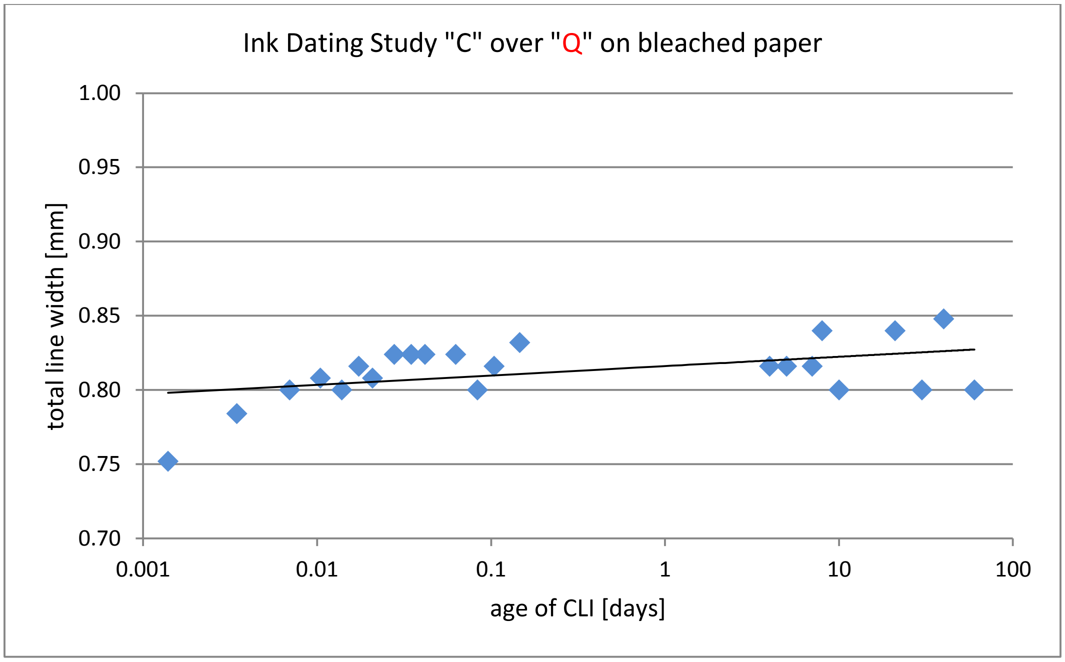


Figure A2. Invisible migration curves from the black inks “C” and blue ink “I” on wrapping paper b). Measures were taken at the border of the intersection; “C” over “I” (upper curve) and “I” over “C” (lower curve). The line widths were measured in pixels (single measurements). 38 pixels correspond to the visible line width for “C” and for “I”.



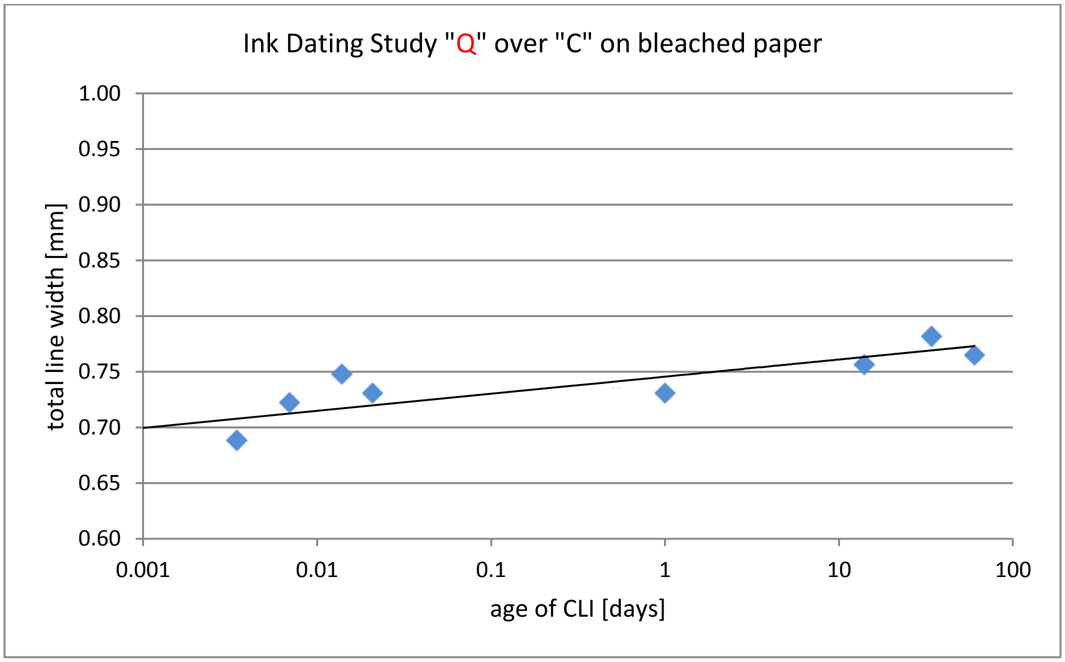
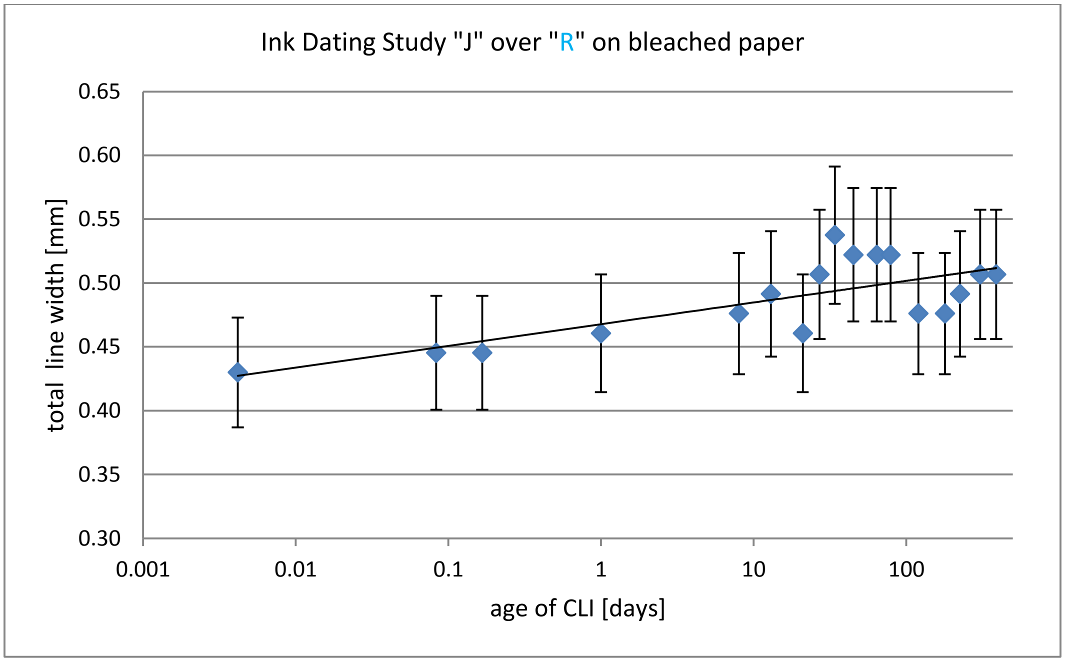


Figure A3. Invisible migration curves of the line intersection of black inks “C” and red ink “Q” on bleached paper c); “C” over “Q” (upper curve) and “Q” over “C” (lower curve). The real line widths were measured (single measurements). The visible ink line widths is 0.7 mm for “C” and 0.6 mm for “Q”.



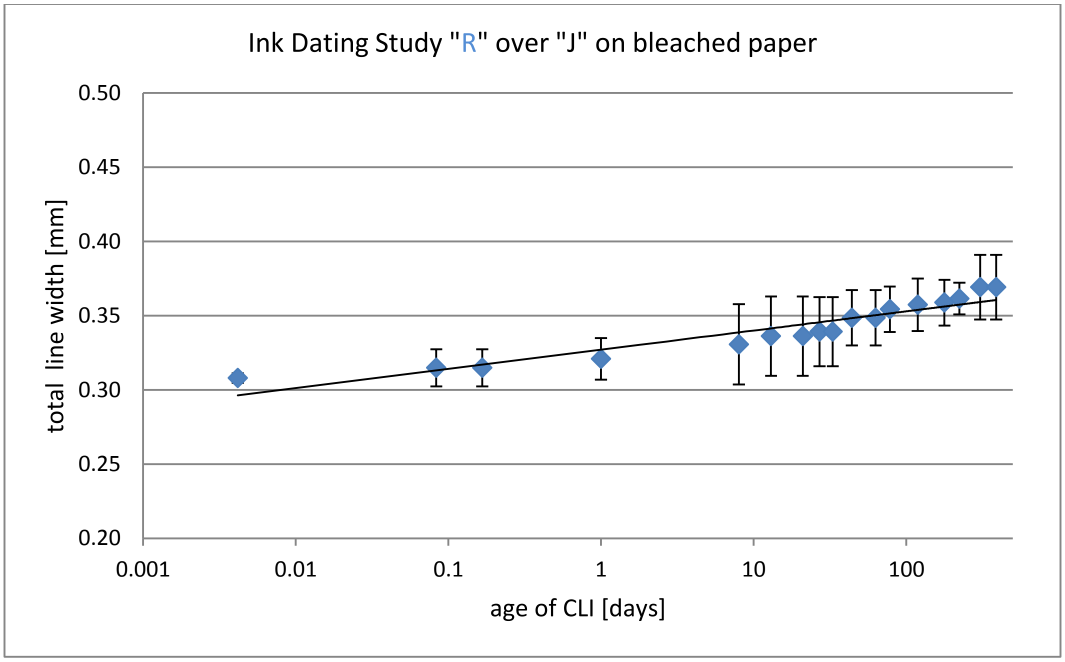
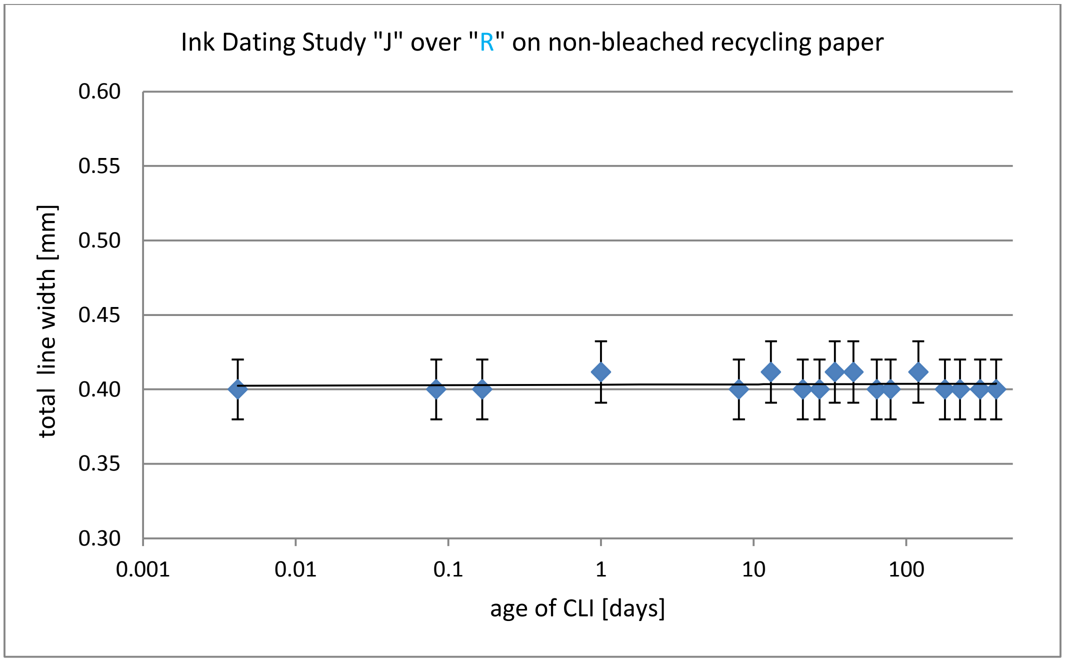


Figure A4. Invisible migration curves of the line intersection of black inks “J” and blue ink “R” on bleached paper c); “J” over “R” (upper curve) and “R” over “J” (lower curve). The real line widths were measured, each interval on three different positions. Migration was measured beside the CLI. The visible ink line widths is 0.4 mm for “J” and 0.3 mm for “R”.



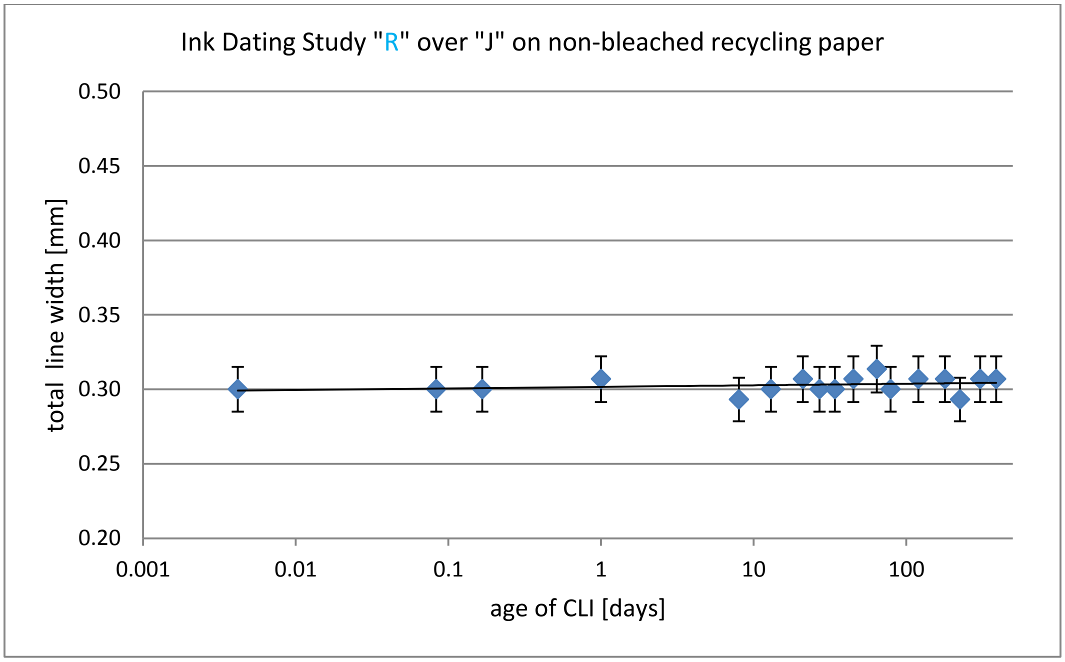
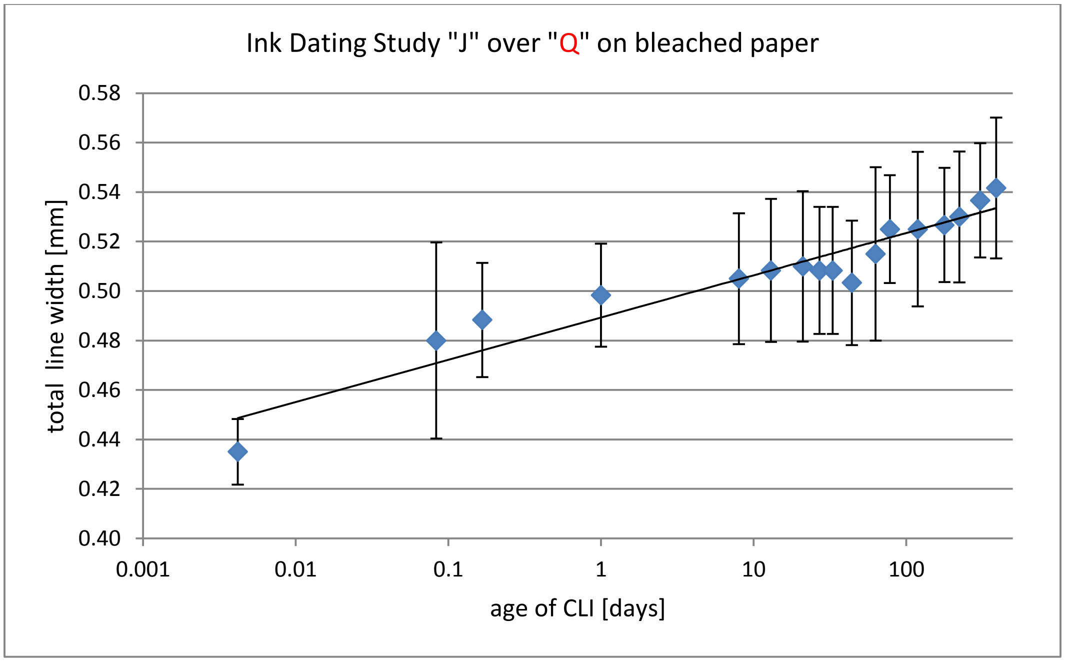


Figure A5. Invisible migration curves of the line intersection of black inks “J” and blue ink “R” on non-bleached recycling paper a); “J” over “R” (upper curve) and “R” over “J” (lower curve). The real line widths were measured, each interval on three different positions. Migration was measured beside the CLI.

The visible ink line widths is 0.4 mm for “J” and 0.3 mm for “R”. Almost no difference between the luminescence of ink “J” and ink “R”. Thus, it was almost impossible to detect the migration.



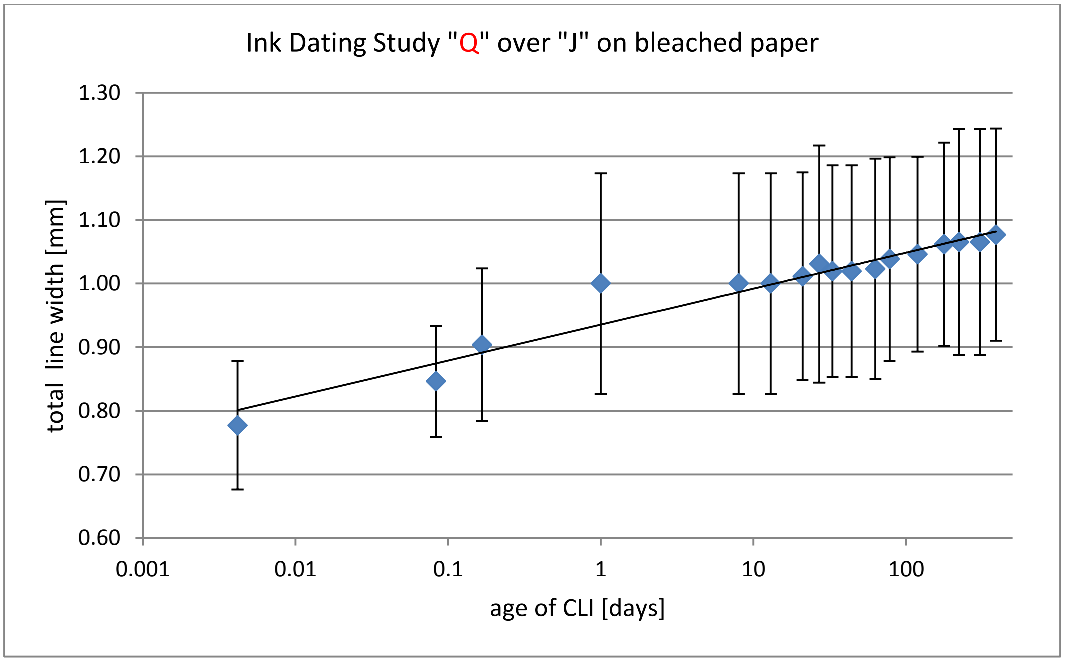
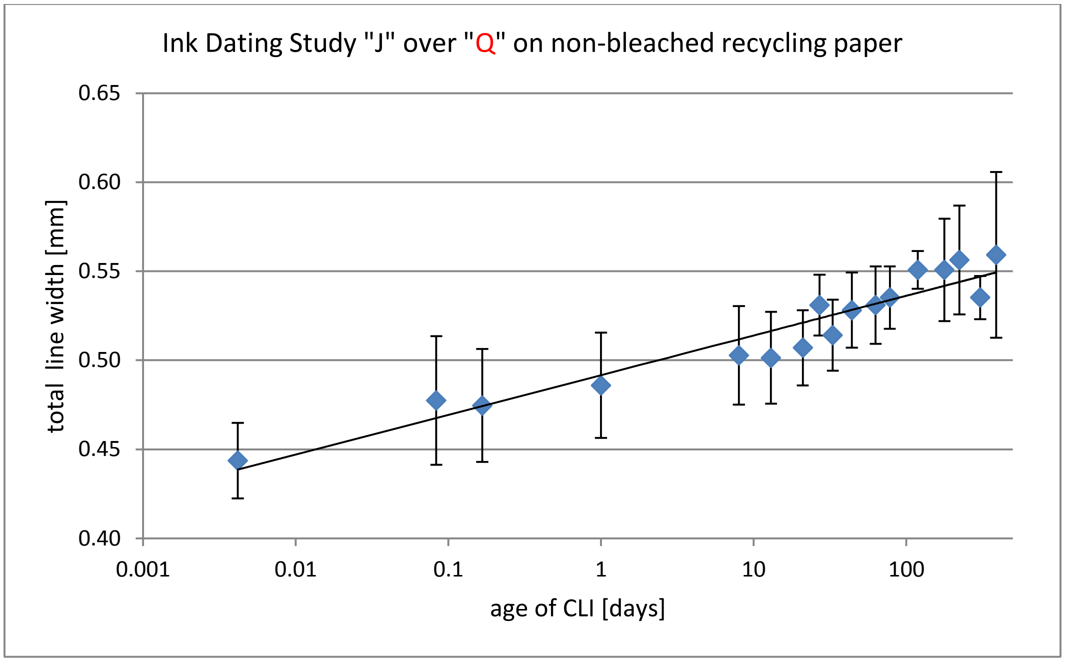


Figure A6. Invisible migration curves of the line intersection of black inks “J” and red ink “Q” on bleached paper c); “J” over “Q” (upper curve) and “Q” over “J” (lower curve). The real line widths were measured, each interval on three different positions. The visible ink line widths is 0.4 mm for “I” and 0.6 mm for “Q”.



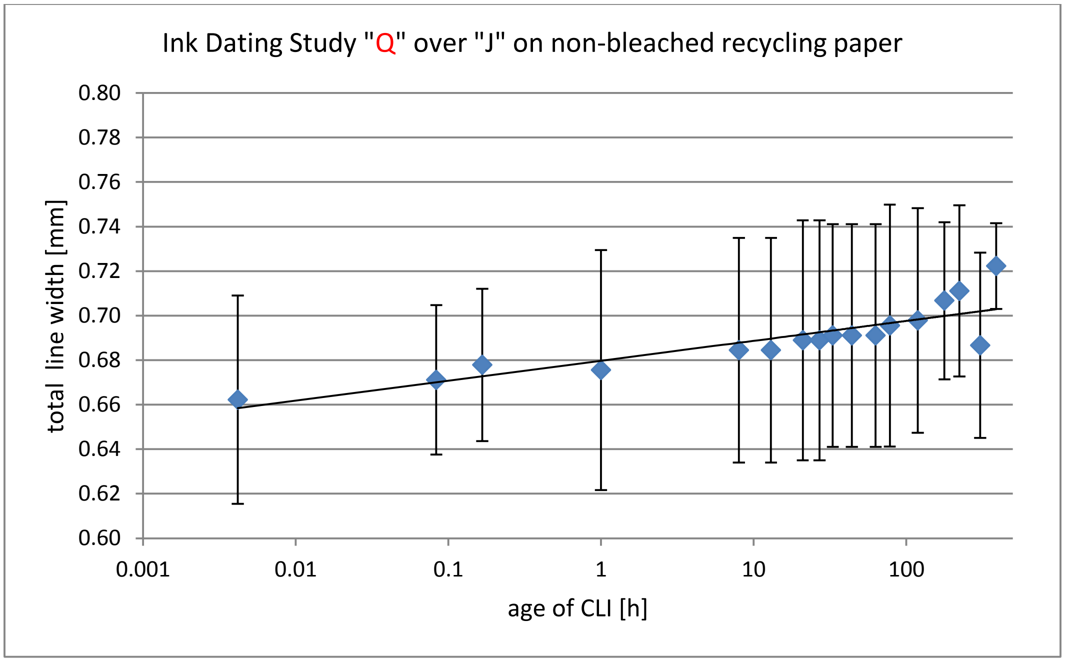
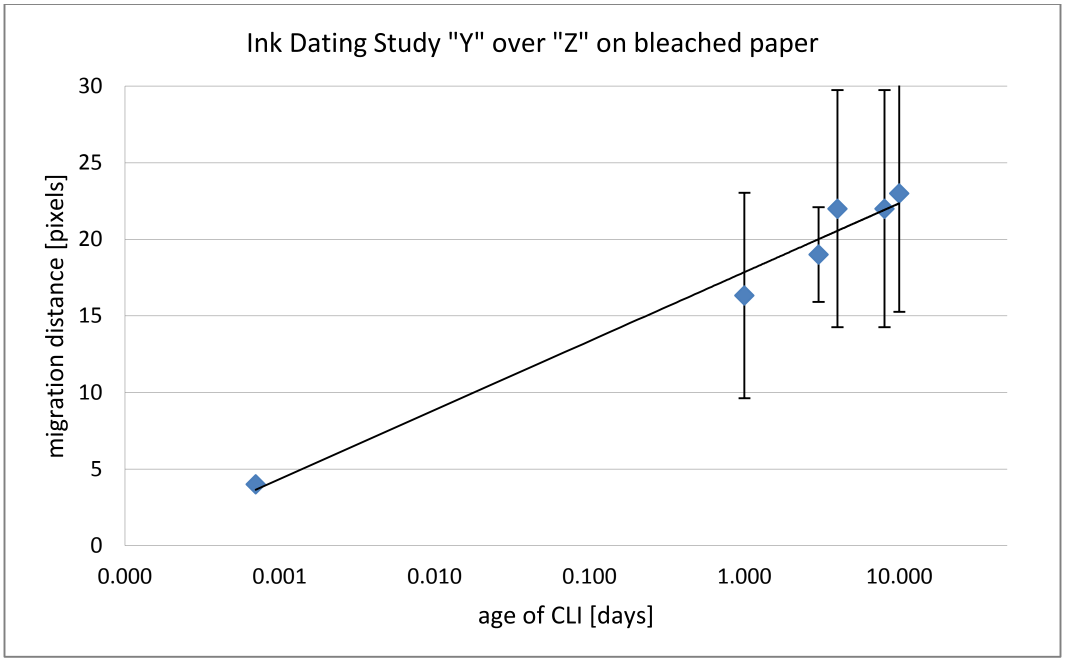


Figure A7. Invisible migration curves of the line intersection of black inks “J” and red ink “Q” on non-bleached recycling paper a); “J” over “Q” (upper curve) and “Q” over “J” (lower curve). The real line widths were measured, each interval on three different positions. The visible ink line widths is 0.4 mm for “J” and 0.6 mm for “Q”.



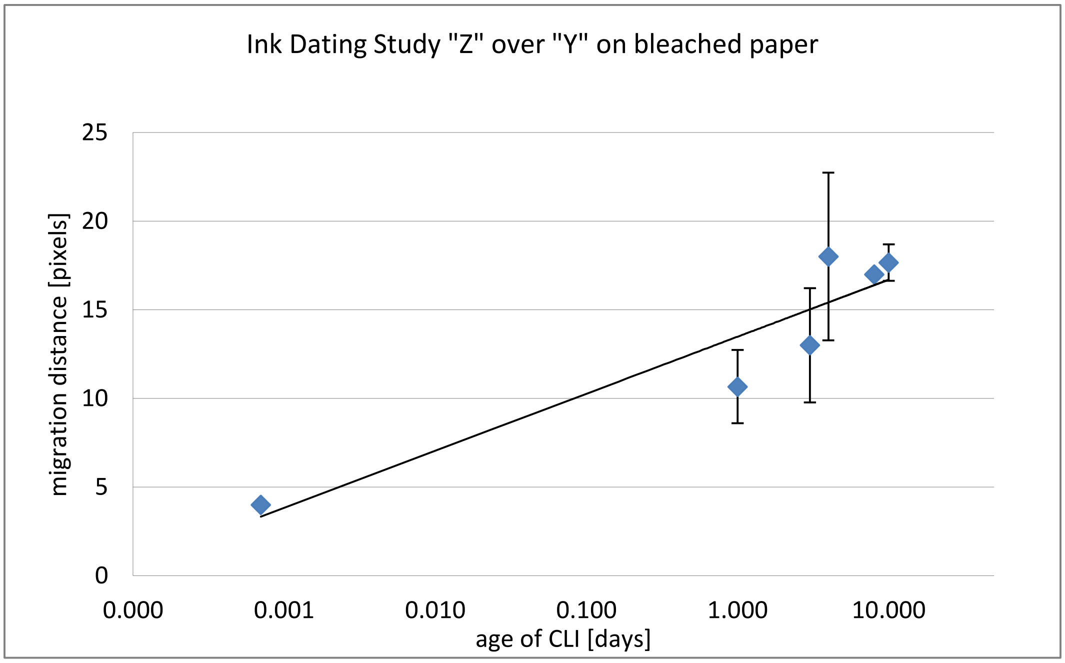
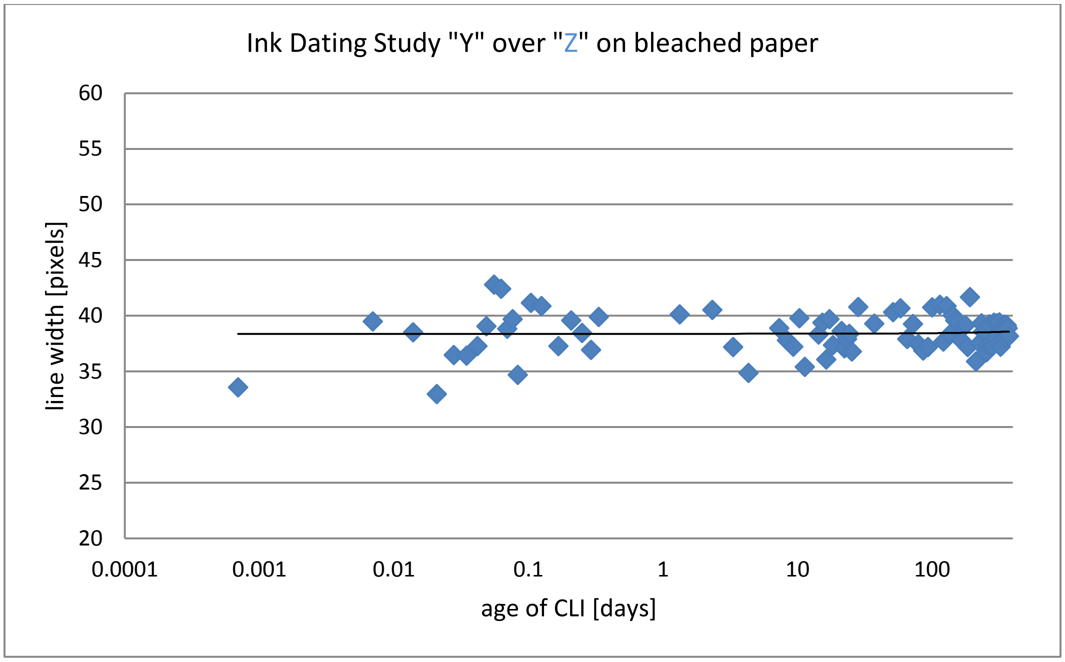


Figure A8. Invisible migration curves of the first ten days from the black inks “Y” and blue ink “Z” on bleached paper c). Measures were taken at the border of the intersection; “Y” over “Z” (upper curve) and “Z” over “Y” (lower curve). The line widths were measured in pixels (three different intersection positions).



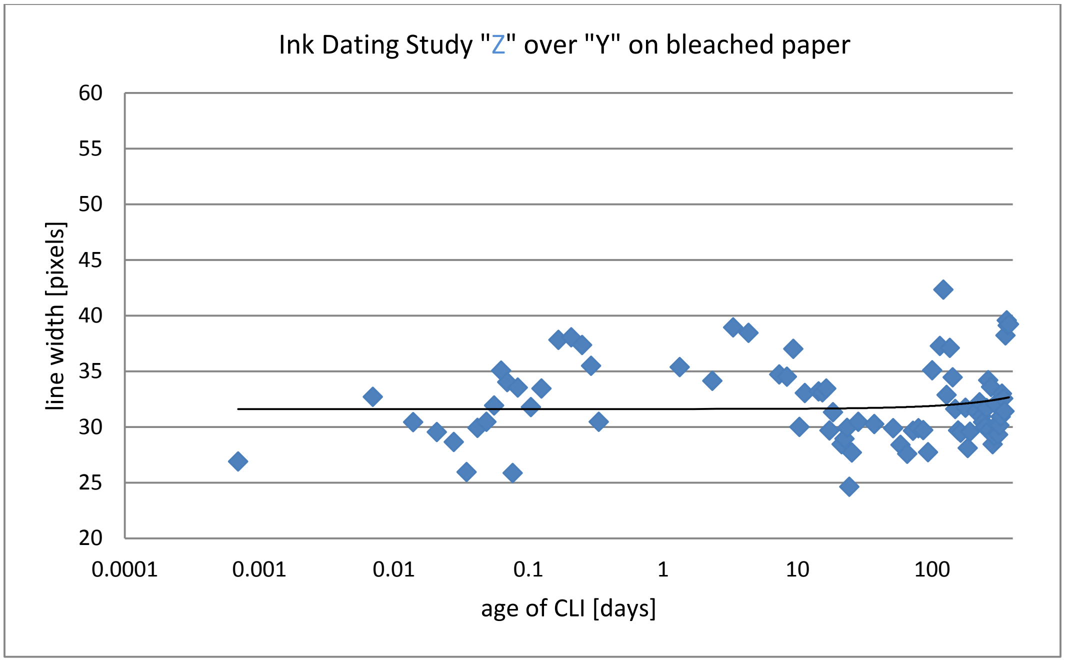


Figure A9. Invisible migration curves from the black inks “Y” and blue ink “Z” on bleached paper d). Measures were taken at the border of the intersection; “Y” over “Z” (upper curve) and “Z” over “Y” (lower curve). The line widths were measured in pixels (single measurements). 38 pixels correspond to the visible line width for Y and 30 pixels for Z.

1.4 Discussions and way forward

As invisible migration strongly depends on the paper structure and chemistry, and therefore on capillary effects, the border of the luminescent zone is not even. To solve this problem, a straight line is drawn along the luminescent zones on both sides of each intersection on the stored pictures. The mean line to line distance corresponds to the mean migration distance of the corresponding ink.

Some intersections show faster invisible migration than others. Again, we believe that the main reason is the capillarity of the paper. Thus, it is important to measure an adequate number of different intersections at each storage time. Single point measurements will result in large error. Nevertheless, data can be used for ink dating (or intersection dating), if the questioned document is measured frequently over a long period.

The measuring time depends on the speed of invisible migration. This reflects in the slope of the migration curve (or ageing curve): The steeper the curve, the shorter measuring time is necessary.

In most cases, invisible migration only takes place from the luminescent substance(s) along the primary intersected line. A reason for this phenomenon is either an improved capillarity of the paper by components of the primary ink, or a reduction of paper inherent quenching effects by components of the primary ink, or secondary fluorescence (or luminescence) effects.

Best curve fit was achieved with a logarithmic trend line.

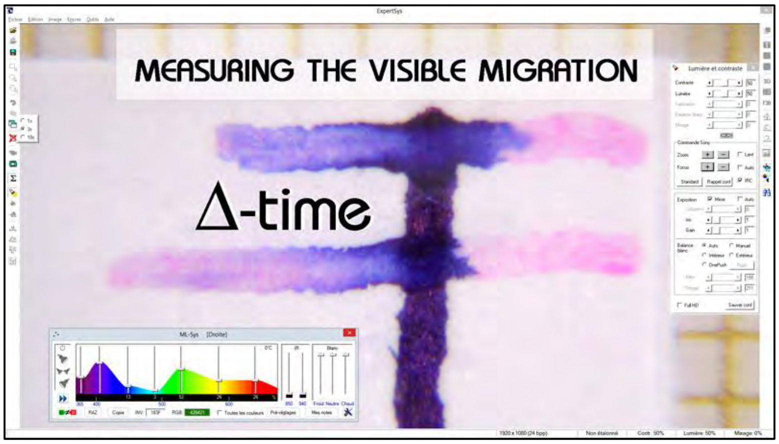
Especially nonpolar inks do not show any invisible migration. If these inks are the primary lines in intersections, they may change the paper in a nonpolar supporting material with strongly reduced capillarity. Luminescent components are soluble in water and, therefore, need a polar stationary phase to migrate.

Whether or not this method can be applied for ink dating (or intersection dating), depends on the inks the ink combination and on the paper. The conditions that have to be fulfilled for a documents that is potentially suitable for ink dating studies are:

- ink must contain at least one luminescent component
- this component must diffuse either into the paper or in the direction of the intersecting line
- the paper must not quench (or absorb) the luminescence of this component
- the paper (or the primary line) must not show the same luminescence as this component. With other words, there must be a setting on the detection unit (excitation and detection wavelengths) producing enough strong luminescence difference between the migrating component(s) and the background.

If invisible migration is observed on a questioned document, it is basically possible to apply this method for ink dating analysis with this method. If invisible migration is observed only beside the Intersection, such cases can be used for ink dating studies anyway (no need of a line intersection).

CHAPTER 2. PROTOCOL B
ΔT STUDY I: MEASURING THE VISIBLE MIGRATION



2.1 Introduction

Visible migration of fresh inks usually results from a combination of diverse phenomena which can be for instance chemical (chemistry of the paper, chemistry of the inks, miscibility of the two inks), or physical (capillary flows in the paper and at the surface resulting from surface tension gradients acting at liquid/solid, liquid/gas and liquid/liquid interfaces). Mechanical effects may also be at play such as ink drag.

This study shall answer the question of whether or not visible ink migration or ink drag can be used to determine the time gap (Δt) between the drawings of two liquid fountain pen inks.

2.1.1 Participating countries and experts

Slovakia: Institute of Forensic Science, Ministry of the Interior, Adriana JABCONOVÁ
Belgium: Court of Appeals of Brussels, Françoise COENRAETS
Georgia: Forensic Criminalistics Department, Ministry of Internal Affairs of Georgia, Tea MIKADZE
Georgia: Forensic Criminalistics Department, Ministry of Internal Affairs of Georgia, Ekaterine KORKOTASHVILI
France: Court of Appeals of Caen, Sandrine LOISEL
France: Court of Appeals of Chambery, Jean Pierre REMBARZ
France: Court of Appeals of Lyon, Jacqueline BECK
France: Court of Appeals of Versailles, José BALBUENA
Spain: Court of Justice, Jesus BARRON
Spain: Court of Justice, Juan F. ORELLANA
Morocco: Court of Justice, Abdelali EL JIRARI

2.1.2 Suggested protocol

An experiment consists of drawing crossing lines using combinations of two instruments from a set of four, hereafter referred to as instruments L, M, O and P. An experiment consists for example of drawing line of instrument L over line of instrument M and vice versa, or line of instrument O over line of instrument P and vice versa. By convention, the primary line is always the vertical one, while the intersecting line is always horizontal and applied after the primary one respecting 15 different time gaps. Crossed line intersections (CLI) were produced and pictures were taken according to the following timetable:

1st CLI: 15 seconds (or as soon as possible after the production of the line intersection)
2nd CLI: $\Delta t = 30$ seconds
3rd CLI: $\Delta t = 45$ seconds
4th CLI: $\Delta t = 1$ minute
5th CLI: $\Delta t = 2$ minutes
6th CLI: $\Delta t = 5$ minutes
7th CLI: $\Delta t = 30$ minutes
8th CLI: $\Delta t = 60$ minutes (Take picture of the first 8 CLI)
9th CLI: $\Delta t = 5$ hours (Take picture after the 9th CLI)
10th CLI: $\Delta t = 1$ day (Take picture after the 10th CLI)
11th CLI: $\Delta t = 1$ week (Take picture after the 11th CLI)
12th CLI: $\Delta t = 2$ weeks (Take picture after the 12th CLI)
13th CLI: $\Delta t = 1$ month (Take picture after the 13th CLI)
14th CLI: $\Delta t = 2$ months (Take picture after the 14th CLI)
15th Last CLI: $\Delta t = 3$ months (Take picture after the 15th CLI)

2.1.3 Proposed writing instruments and materials to use

For this Δt study, inks (L-M) were chosen, where visible migration of ink components has already been observed. The following writing instruments were used by five participating countries and experts:

L: Fountain pen, cartridge Ref.: Pelikan Script 1.0 P52 1.0, black ink
M: Fountain pen, cartridge Ref.: Pelikan Script 1.0 P52 1.0, blue ink

The intersection combinations (sets) were as follows: L over M and M over L

Inks (L-M) used by the following participating four countries: Slovakia, Belgium, Georgia and France.

To verify Δt results with inks, where visible migration has already been observed two other inks (O-P) where visible migration has never been observed, were studied.

O: Waterman blue ink Ref: 50110950
P: Waterman rouge ink Ref: 50110970

The intersection combinations (sets) with these inks (O over P and P over O) have been used by the expert from Spain.

Intersections were produced on two different paper qualities: bleached regular office paper and non-bleached-recycling paper.

Slovakia:	Reference bleached paper: A4, 80 g/m^2, natural paper, 100% Elementary Chlorine Free, acid free with alkaline, Long Life (ISO 9706), for laser, inkjet, fax Reference A4 non-bleached recycling paper: 80 g/m^2
France:	Reference bleached paper: CLAIRALFA-CLAIRFONTAINE, A4, 80 g/m^2, Ref 1797 3-329680197907 PEFC certified Reference non-bleached recycling paper: Every copy Label "Blue Angel", A4, Whiteness Index CIE 95. Great opacity. Reference bleached paper: CLAIREALFA-1979, A4, 80 g/m^2. Reference non-bleached recycling paper: PLEIN-CIEL, multifunction naturel, A4, 80 g/m^2
Belgium:	Reference bleached paper: HEMA-Ultrawhite, A4 210X297mm, 80 g/m^2. Reference non-bleached recycling paper: Draft paper, A4 210X297mm, 80 g/m ^{2}
Georgia:	Reference bleached paper: PREMIUM A4, Double A paper 80 g/m^2. 210X297mm Reference non-bleached recycling paper: A4. 45g/m^2. 210X297mm. Produced in Georgia
Spain:	Reference bleached paper: GREENING, DIN-A4 210x297mm, 80 g/m^2 Reference non-bleached recycling paper: INAPA TECNO, DIN-A4 210x297mm, 80 g/m^2

The following instruments were used:

- Stereo microscope LEICA, MW75 with imaging source HD camera, 1/2.5 inch Micron CMOS sensor (MT9P031)-M;
- Stereo microscope LEICA, MZ 16 + Digital camera JVC-KY-F75U (3×CCD ½ -inch);
- Metameric light source, with ML-Sys Software, EXP00146;
- LUMINISYS Tr TR-ACL® HD120x USB3, with ExpertSys Software;
- LUMINISYS-STM, Exp-217, with ExpertSys Software;
- VSC 5000 with VSC software;
- VSC 6000 with VSC software;
- Δt was tested with a timed device;
- Horizontal star desiccator was used for monitoring humidity at 0% or 100% humidity;
- To control the temperature at 0 ° C, 25 ° C and 45 ° C POL-EKO-APARATURA, Type SLW53STD, was used.

The settings of capturing devices were optimized for each ink intersection to get optimal brightness and contrast of inks.

To measure the visible ink migratory characteristics, measurement software and a millimetre scale was used. The following measuring software was used:

- Measuring Photoshop Software (mm);
- Measuring ExpertSys Software (mm).

2.1.4 Working conditions

LUMINISYS-TR and LUMINISYS-STM with ExpertSys software

Ink combination	Instrument	Metameric light	Detection wavelength	Magnification X
L over M and vice versa	Stereo microscope Leica, + Digital camera	0000FF+CW	FREE	30x-141x
L over M and vice versa	Stereo microscope Leica, + Digital camera	63196B+CW	400-490>630	30x-141x
L over M and vice versa	Stereo microscope Leica, + Digital camera	BD5A00+CW	400-490>630	30x-141x
O over P and vice versa	Stereo microscope Leica, + Digital camera	63B595+CW	FREE	30x-141x
O over P and vice versa	Stereo microscope Leica, + Digital camera	001919+CW+NW	FREE	30x-141x

VSC 5000 AND 6000 with VSC software

Ink combination	White Light	Detection wavelength	Magnification
L over M and vice versa	Brightness: 60, Iris: 70, Integration : 16 ms	FREE	30x – 141x

Stereo microscope

Ink combination	Instrument	Source of light	Detection wavelength	Magnification
L over M and vice versa	Stereo microscope Leica, MW75 + HD digital camera	White light.	FREE	30-141x
L over M and vice versa	Stereo microscope Leica, MZ 16 Leica, + HD digital camera	Metameric light source, + ML-Sys Software	FREE	30x-50x

Table B1. Examples of sets (ink combinations and apparatus settings).

Pictures of visible ink migration were taken with a digital camera (e.g. video comparator system or stereomicroscope with imaging source HD camera). The visible migration (vertical/horizontal) was measured from each intersection at the end of the experiments.

The measures are presented in real dimension or in arbitrary unit. Depending on the system (microscope with image analysis software or simple measures made on the screen with constant magnification of the intersection), participants measured the migration distance in mm.

The data were transferred in to a table and curves were calculated with visible migration distance versus time gap (Δt) between the two line drawings of the intersection.

Special sample storage

Experiment 1, Normal conditions: one set for normal conditions (Set N). 25° C, in the dark or at least not in direct irradiation with any light source.

Experiment 2, Humid conditions: two sets for low humidity at 0% (set LH) and high humidity at 100% (set HH), respectively.

Experiment 3, High/Low temperature conditions: two sets for low temperature 0° C (set LT) and high temperature 45° C (set HT), respectively.

Samples have been stored in the above mentioned conditions for three months.

2.2. Experimental section: methods and materials

In this chapter, we have the following orders of magnitude:

- Very short Δt: from seconds to minutes (up to one hour);
- Short Δt: from hours to days;
- Long Δt: from weeks to months (studied up to three months).

During the analysis of liquid inks, by using a stereo microscope, equipped with white and metameric lights, we have observed different phenomena: creating a groove and humid ink path (G/HP) or a groove and dry ink path (G/DP), ink dissolution, mechanic transport of compound and visible migration (diffusion). A groove is created in the paper by the metallic point of the fountain pen. All liquid substance will fill it.

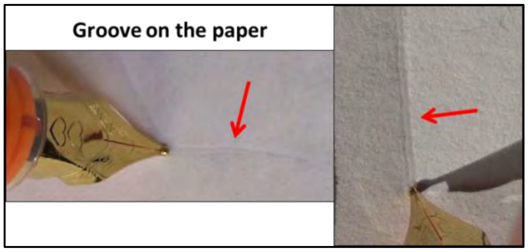


Image B1.

The groove with liquid inks create a humid ink path (G/HP) on the paper. Paper is a porous medium where capillary flows occur in the paper and/or its surface which results due to surface tension gradients acting at liquid/solid, liquid/gas and liquid/liquid interfaces. These flows take place at the micro scale (~ 100µm thickness) (Image B2).

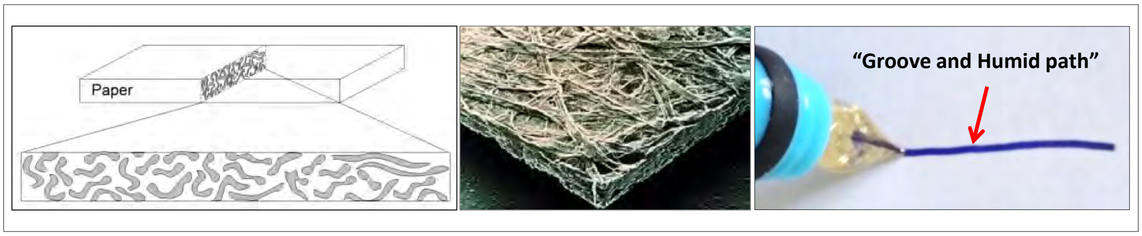


Image B2.

The 2nd liquid ink spreads further and faster (fluid dynamics) along a G/HP (produced by the 1st line) than on the dry paper surface or dry path (Image B3).

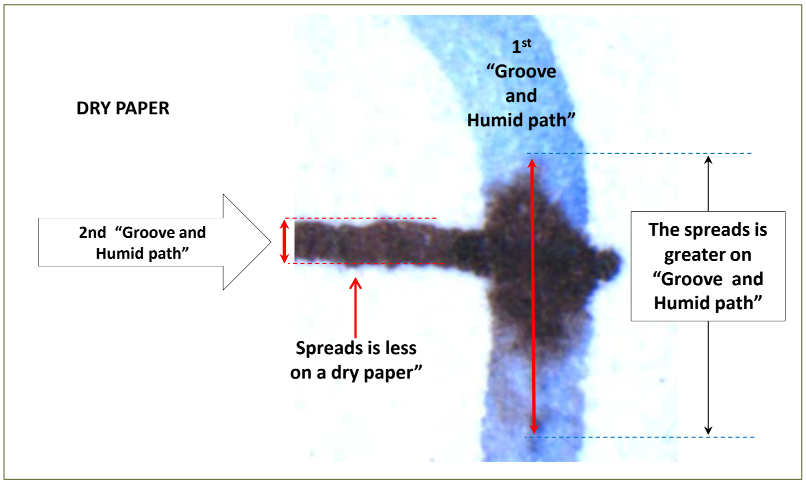


Image B3.

Dilution occurs when the colour of the primary ink is in contact with the solvent from the secondary ink. When two fluids of different concentration meet, a gradient of surface tension is introduced (Image B4).

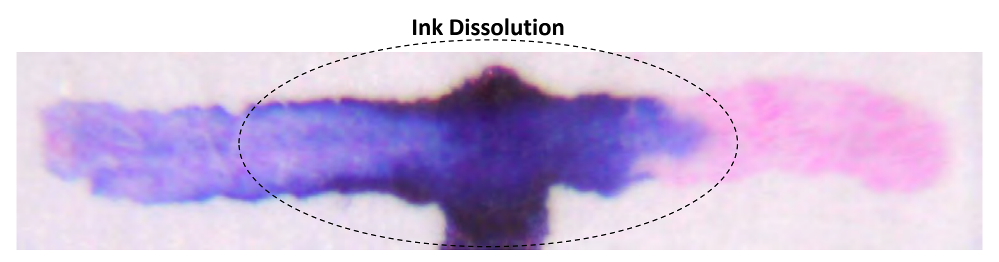


Image B4.

“Ink drag” is produced by the mechanical dragging of the components of the 1st liquid ink line by the mechanical movement of the 2nd writing instrument. Ink drag is useful to determine the sequence of two intersecting lines (Image B5).

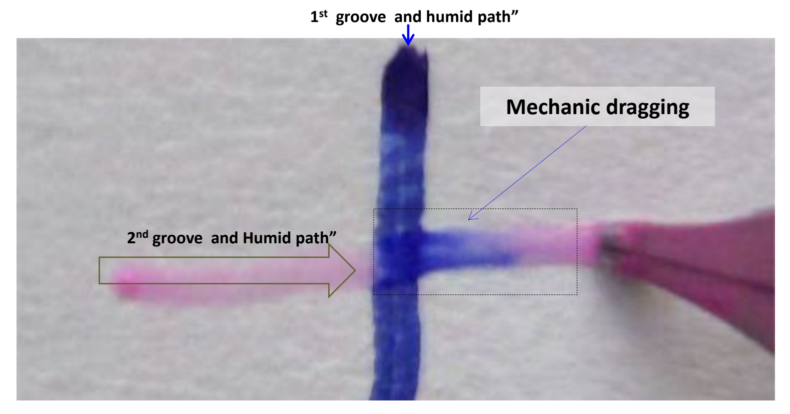


Image B5.

There are several possibilities for an ink to spread: into the paper material and/or along the G/HP and/or along the G/DP. Capillarity acts by triggering a flow inside the porous paper, or by introducing a capillary flow at the surface of the G/HP (Marangoni effect). In all cases, capillary effects can go in all directions and are independent of the mechanical movement of the writing instrument (Image B6).

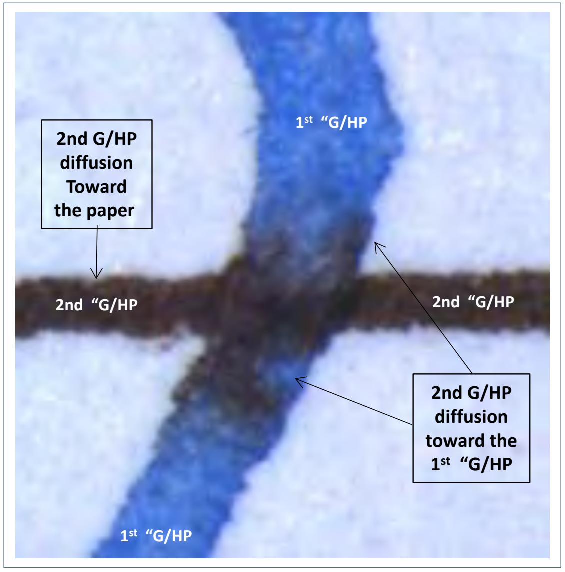


Image B6.

In cases of normal storage conditions, visible migration characteristics may occur either by ink drag or dissolution or dilution or capillarity or a combination thereof. This is not applicable to CLI in high humid condition cases (Image B7).

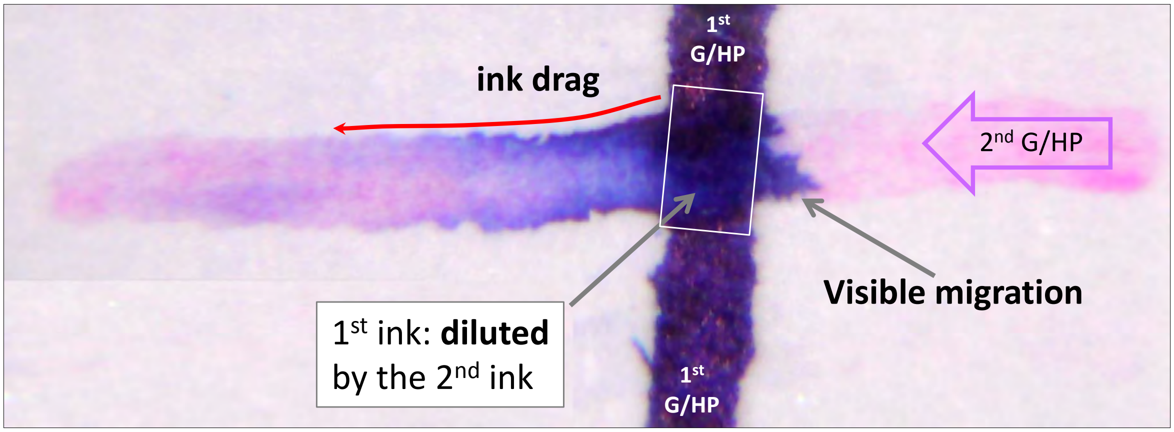


Image B7.

The visible migration characteristics change according to work conditions:

- Low/high temperature influences (G/DP) drying process of the ink, and processes of dissolution and dilution.
- Low/high humidity influences how long the G/HP will remain wet. As a consequence, dissolution produces low/high propagation.
- In high humidity, visible migration could spread the whole length of the line or the quenching effect of the paper is influenced by humidity (Image B8).

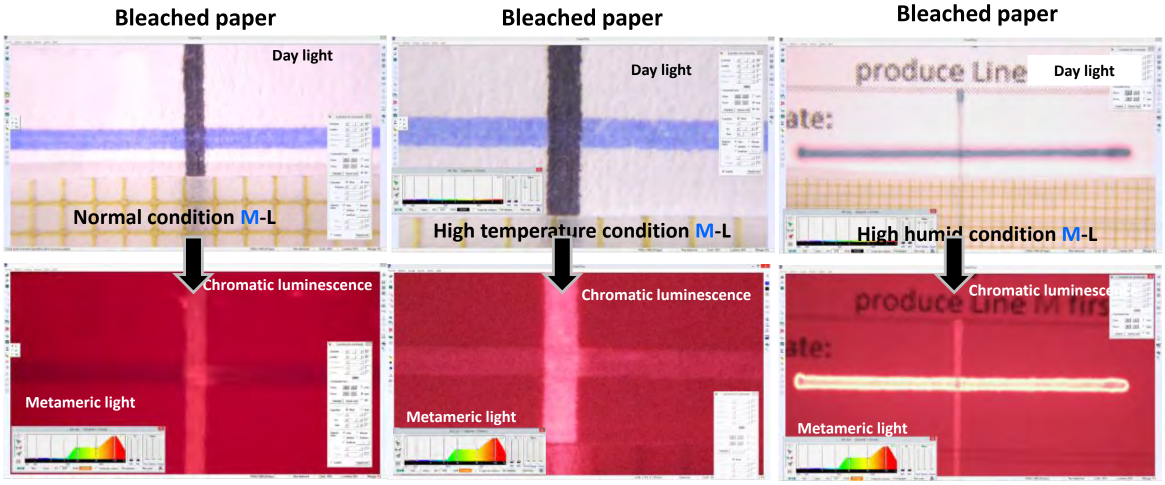


Image B8.

GROOVE/HUMID PATH - GROOVE/DRY PATH

1. At normal conditions we have observed: humidity effects in G/HP are visible up to Δt of 60 min.
2. At normal conditions we have observed: G/HP progressively turns to G/DP in storage time of two weeks.
3. At both low and high temperature storage conditions we have observed: 1st G/HP is still wet 5 minutes after line execution.
4. At high temperature storage conditions we have observed: G/HP progressively turns to G/DP in storage time of one week.
5. At humid conditions we have observed: humidity effects in G/HP are visible up to Δt of one month.

DILUTION/CAPILLARY EFFECTS

1. At all storage conditions, we have observed: strong dilution/capillarity, when 2nd ink is applied over G/HP in a very short Δt: 1 to 5 minutes after the execution of the 1st ink. The ink of the 2nd line will spread and follow the 1st G/HP. A strong ink drag will follow the direction of the 2nd fountain pen.

2. At normal storage conditions, we have observed: dilution/capillarity, when 2nd ink is applied over G/HP in a very short Δt: (30 to 60 minutes after the execution of the 1st ink). The effects of dilution and capillarity will be visible along the 1st G/HP.

3. At normal storage conditions, we have observed: decrease of dilution/capillarity effects when 2nd ink is applied over the 1st G/DP in a Δt of two weeks. The ink spread still follows the 1st groove. Only limited ink drag can be seen in the direction of the 2nd fountain pen.

4. At humid storage conditions we have observed: strong dilution/capillarity effects, when 2nd ink is applied over the 1st G/HP with a Δt between 1 minute and 1 hour.

5. At very high humid storage conditions we have observed after one month an intense change in the aspect of migratory characteristics.

6. At high temperature storage conditions we have observed: strong dilution/diffusion/ink drag when 2nd ink is applied over the 1st G/HP, in a very short Δt: 1 to 5 minute after 1st ink. The dilution/ capillarity characteristics will extend and will follow the 1st G/HP.
7. At high temperature storage conditions, we have observed: a change in the aspect of migratory characteristics (diminution in dilution/capillarity/ink drag) when the 2nd ink is applied over the 1st G/DP with a Δt of about two weeks. Only small ink spread will follow the 1st groove of the ink.

INK DRAG

1. A strong ink drag appears at all storage conditions and on all different papers, when 2nd ink is applied over the 1st G/HP with a Δt of 1 to 60 minutes after 1st ink line execution. Ink drag always follows the direction of the 2nd writing instrument.
2. Strong ink drag at normal storage conditions when the 2nd ink is applied over the 1st G/HP with a Δt of 30 to 60 minutes after the execution of the 1st ink line.
3. Ink drag diminution at normal storage conditions, when 2nd ink is applied over the 1st G/DP with Δt of about two weeks and after the execution of the 1st ink line.
4. Long and strong ink drag at humid storage conditions, when 2nd ink is applied over the 1st G/HP with Δt of 1 minute to 1 hour after the execution of the 1st ink line.
5. Strong diminution in length of ink drag at humid storage conditions, when the 2nd ink is applied over the 1st G/DP with Δt of about one month.
6. Strong ink drag at high temperature storage conditions, when 2nd ink is applied over the 1st G/HP with Δt of 1 to 5 minutes after the execution of the 1st ink line.
7. Migratory characteristics changes presenting very short ink drag at high temperature storage conditions, when 2nd ink is applied over the 1st G/DP with a Δt of about three weeks.

The experiments realised at all storage conditions using non-bleached-recycling paper show stronger visible migration effects than those using bleached paper. Indeed, the former is more porous and hence, capillary effects are more prominent.

OBSERVATION AND MEASUREMENT OF MIGRATION DATA

The observation of visible migratory characteristics in CLI is easier to distinguish when two light ink colours are used (for instance light red and light blue ink). The colour reflection in both inks helps observation. In these cases, a stereo microscope equipped with white light source and measurement software could be enough (Image B9).

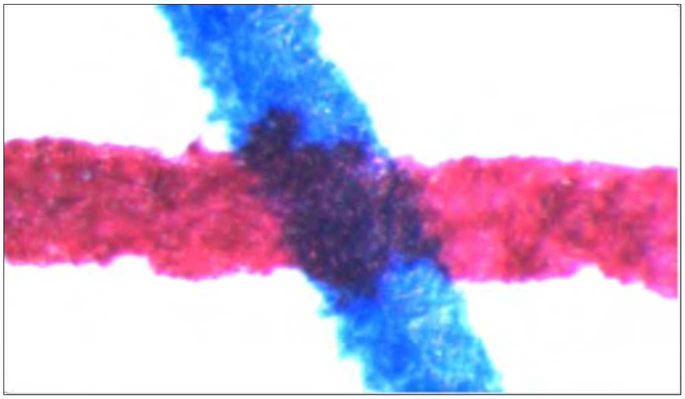


Image B9.

The observation of migratory characteristics in CLI using dark and light colour inks (for instance, black and light blue inks) is less obvious. The colour absorption of the darker ink makes observations more difficult. In these cases, a stereo microscope equipped with white light source is not sufficient. Metameric light source is useful to enhance the chromatic diagram of the light beam by increasing the contrast of reflected colours, thus enhancing the observation of visible migration (Image B10).

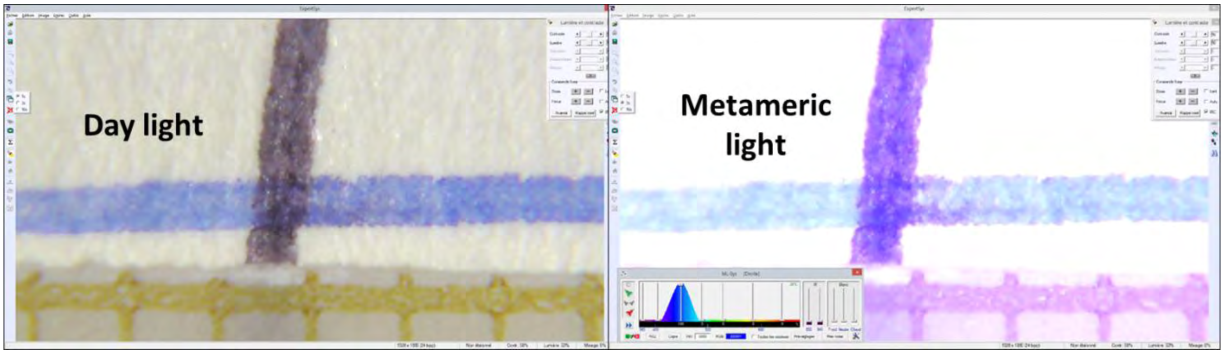


Image B10.

The observation of visible migratory characteristics in CLI is always difficult when black ink is applied. In cases when black inks are used, the method is only suitable when ink contains luminescent components (Image B11).

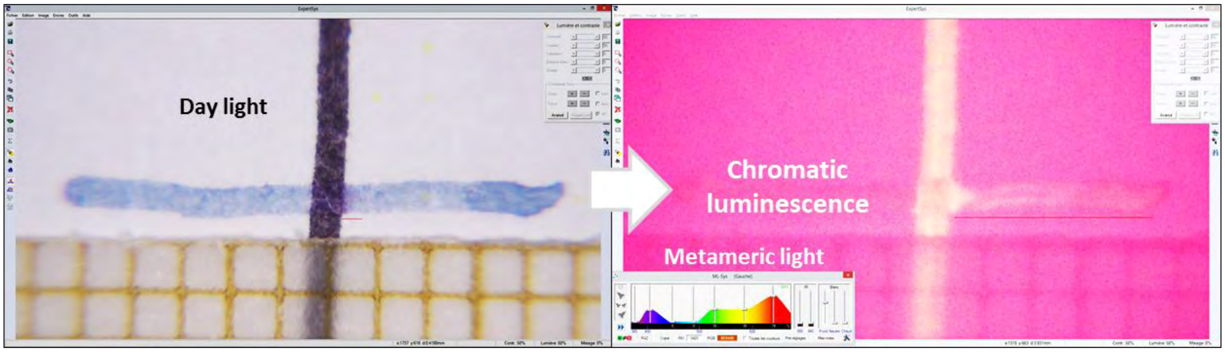


Image B11.

2.3 Results

CLI set	Paper brand		Special conditions			Participating country
	a)	b)	N	T	H	
L over M and vice versa	X		X	X	X	Georgia
L over M and vice versa		X	X	X	X	Georgia
L over M and vice versa	X		X			Slovakia
L over M and vice versa	X	X			X	Belgium
L over M and vice versa	X	X	X		X	France
O over P and vice versa	X	X	X			Spain
O over P and vice versa	X	X	X			France

Table A2: Overview of type of paper, special conditions and country participants, a) bleached paper, b) non-bleached-recycling paper, N) Normal condition, T) Law/High temperature, H) humidity

Following the performance of the first nine CLI, pictures of the samples were taken. The next six CLI (10 – 15) have been then performed and pictures have been taken at the end of this process. After the above mentioned 15 CLI, samples had been stored for 15 to 30 days during which measurements were regularly performed.

RESULTS FROM GEORGIA

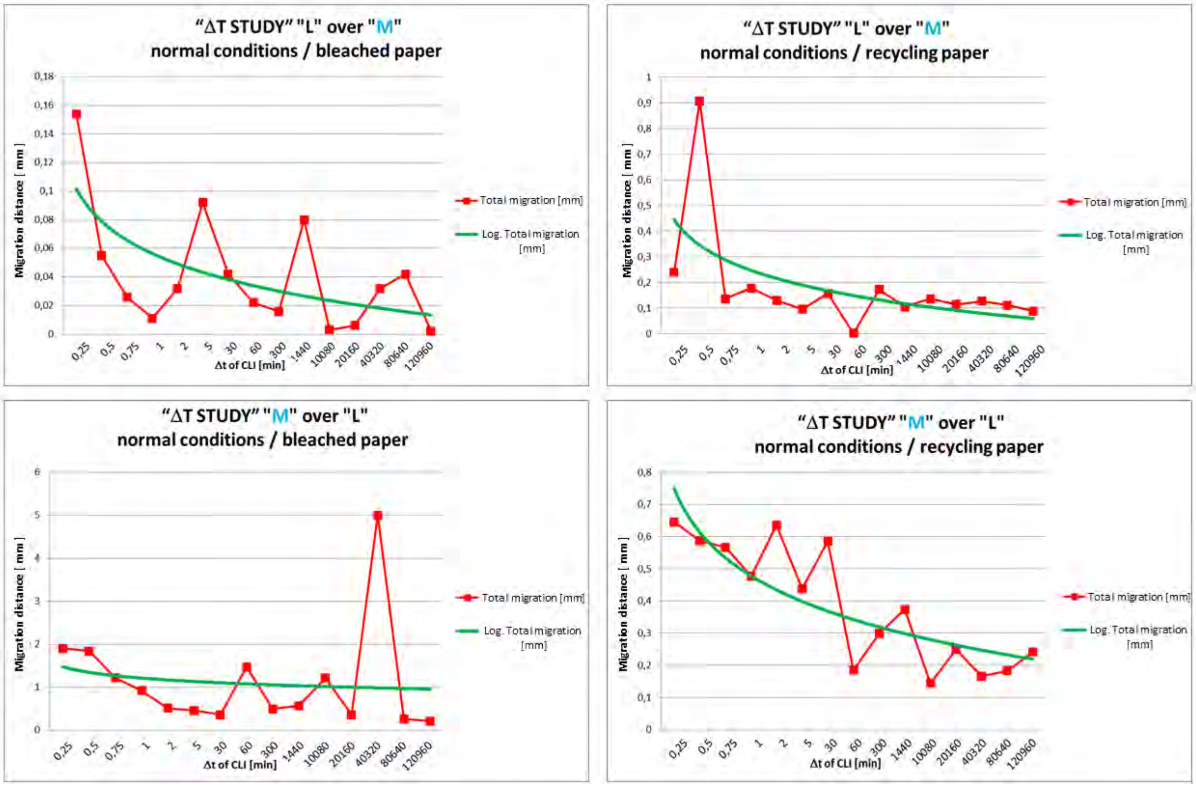


Figure B1. NORMAL CONDITIONS, “L” over “M” (upper graphics) and “M” over “L” (lower graphics).

In Figure B1, the red lines show total visible migration distance and the green lines show the logarithmic trend. Fifteen different intersections were measured for each Δt sample. The green curves show that there is a stronger migration at short Δt than long Δt.

RESULTS FROM GEORGIA

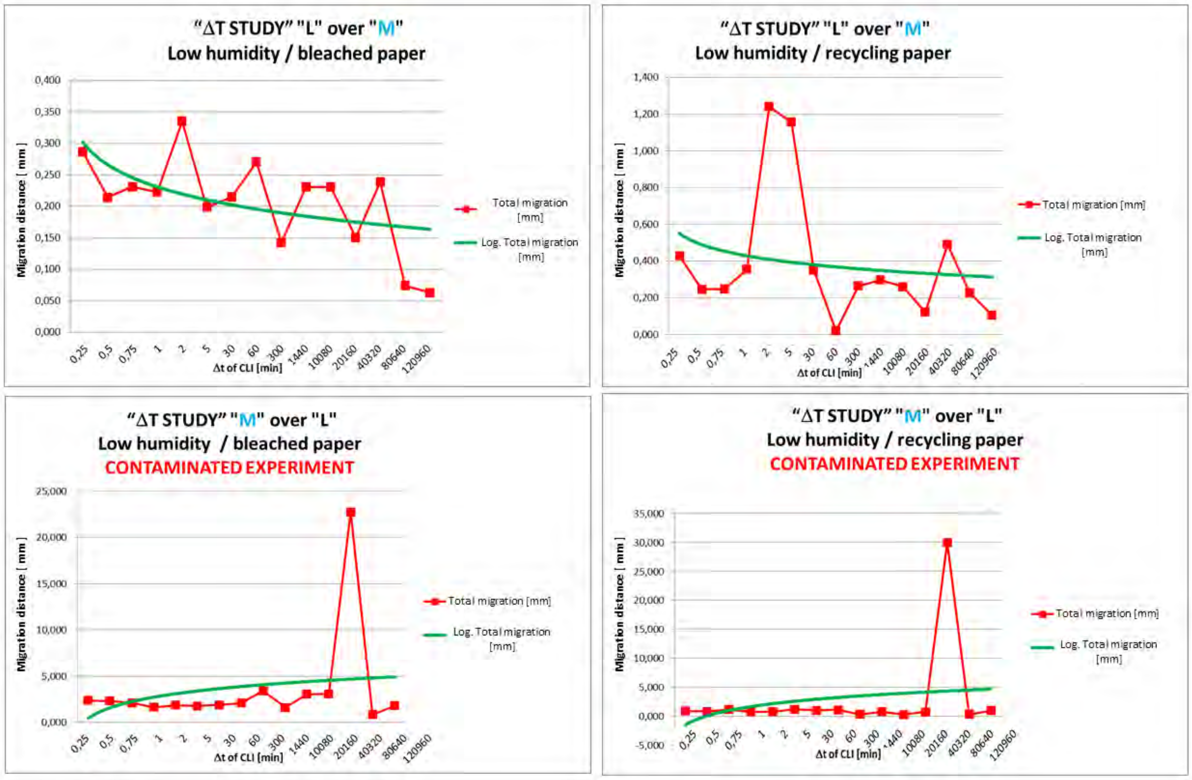


Figure B2. LOW HUMIDITY CONDITIONS, "**L**" over "M" (upper graphics) and "M" over "L" (lower graphics).

In Figure B2, In the graphics "L" over "M", the red lines show total visible migration distance and the green lines show the logarithmic trend which shows that there is stronger migration at short Δt than long Δt.

In the graphics "M" over "L", the green curves show a significant disruption in the extension of the visible migration. The experiments are contaminated by a fluorescent substance. No correlation between Δt and the length of the migration is possible.

RESULTS FROM GEORGIA

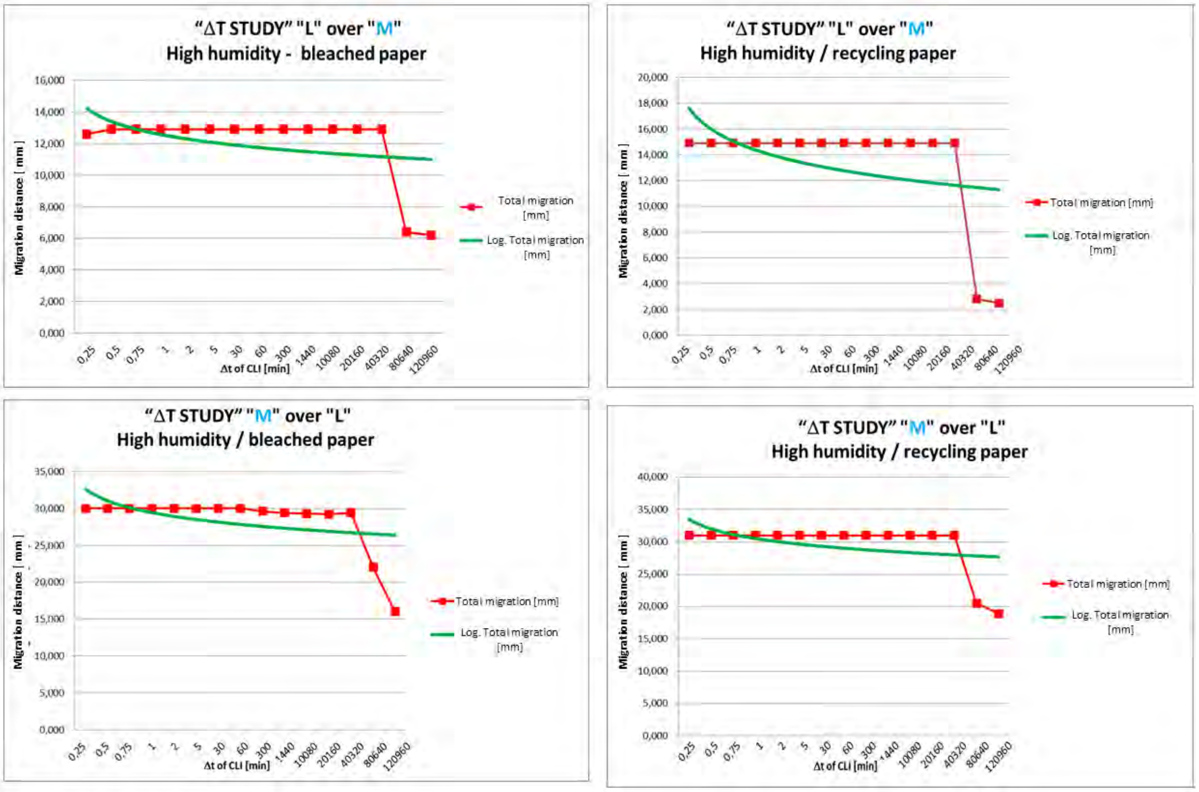
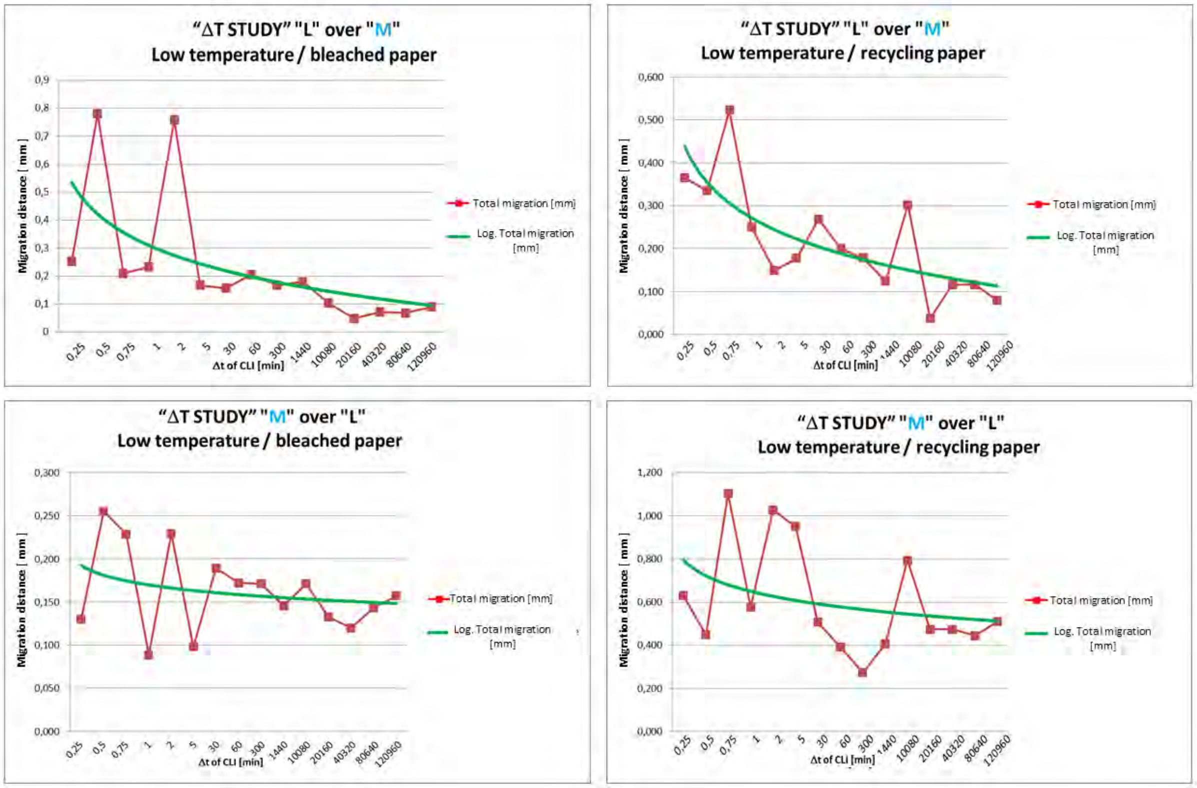


Figure B3. HIGH HUMIDITY, “L” over “M” (upper graphics) and “M” over “L” (lower graphics).

In Figure B3, the green curves show that high humidity has had strong influence in the extension of visible migration. Until the end of the 1st month visible migration has almost the same extension. Short Δt is not sufficient for Δt studies in humid conditions. Only in the last two measurements (2nd and 3rd months), visible migration is significantly reduced.

RESULTS FROM GEORGIA



"ΔT STUDY" "L" over "M"
Low temperature / bleached paper

"ΔT STUDY" "L" over "M"
Low temperature / recycling paper

"ΔT STUDY" "M" over "L"
Low temperature / bleached paper

"ΔT STUDY" "M" over "L"
Low temperature / recycling paper

Figure B4. LOW TEMPERATURE CONDITIONS, "L" over "M" (upper graphics) and "M" over "L" (lower graphics).

In Figure B4, the red lines show total visible migration distance and the green lines show the logarithmic trend. Fifteen different intersections were measured for each Δt sample. The green curves show that there is stronger visible migration in short Δt than long Δt.

RESULTS FROM GEORGIA

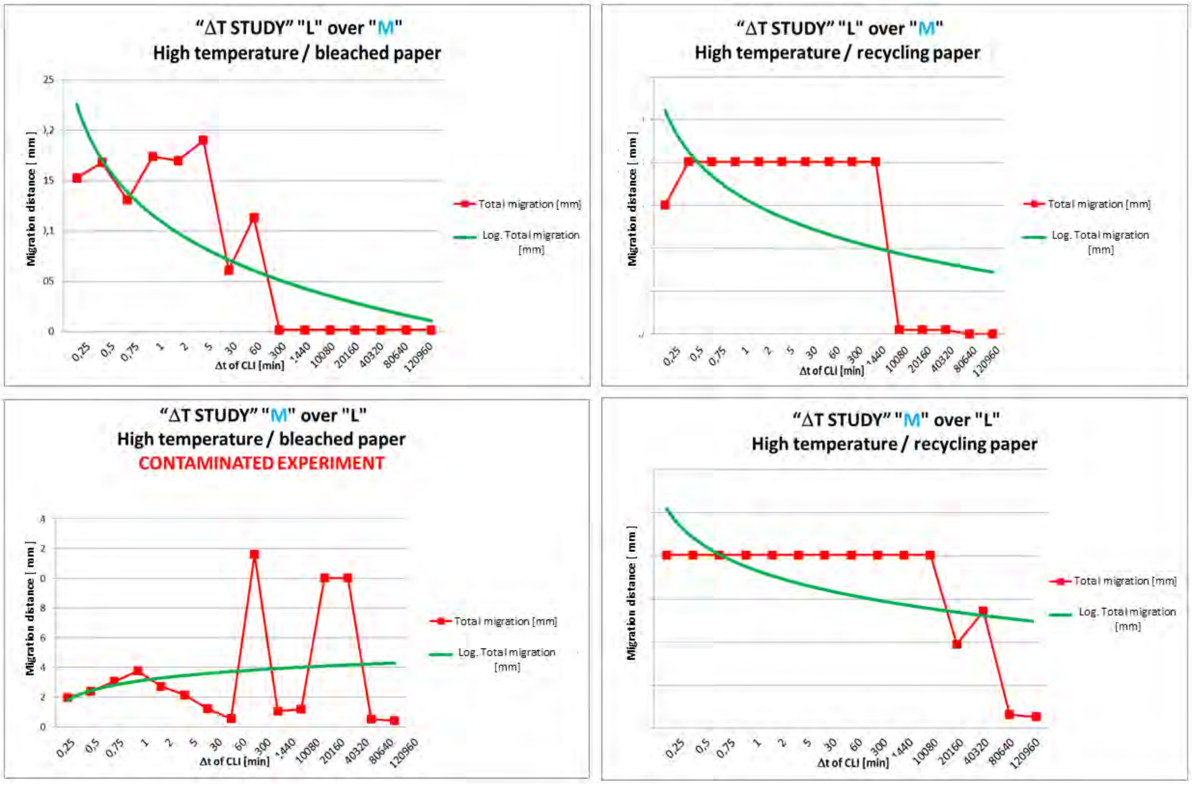


Figure B5. HIGH TEMPERATURE CONDITIONS, “L” over “M” (upper graphics) and “M” over “L” (lower graphics).

In Figure B5, the red lines show total visible migration distance and the green lines show the logarithmic trend. Fifteen different intersections were measured for each Δt sample. The green curves show that there is stronger migration in short Δt than long Δt.

“M” over “L” High temperature, bleached paper (lower graphics). The green curves show an opposite trend due to contamination by a fluorescent substance (from fingerprints) in samples 9, 11 and 12. No correlation between Δt and the length of the migration is possible.

RESULTS FROM SLOVAKIA

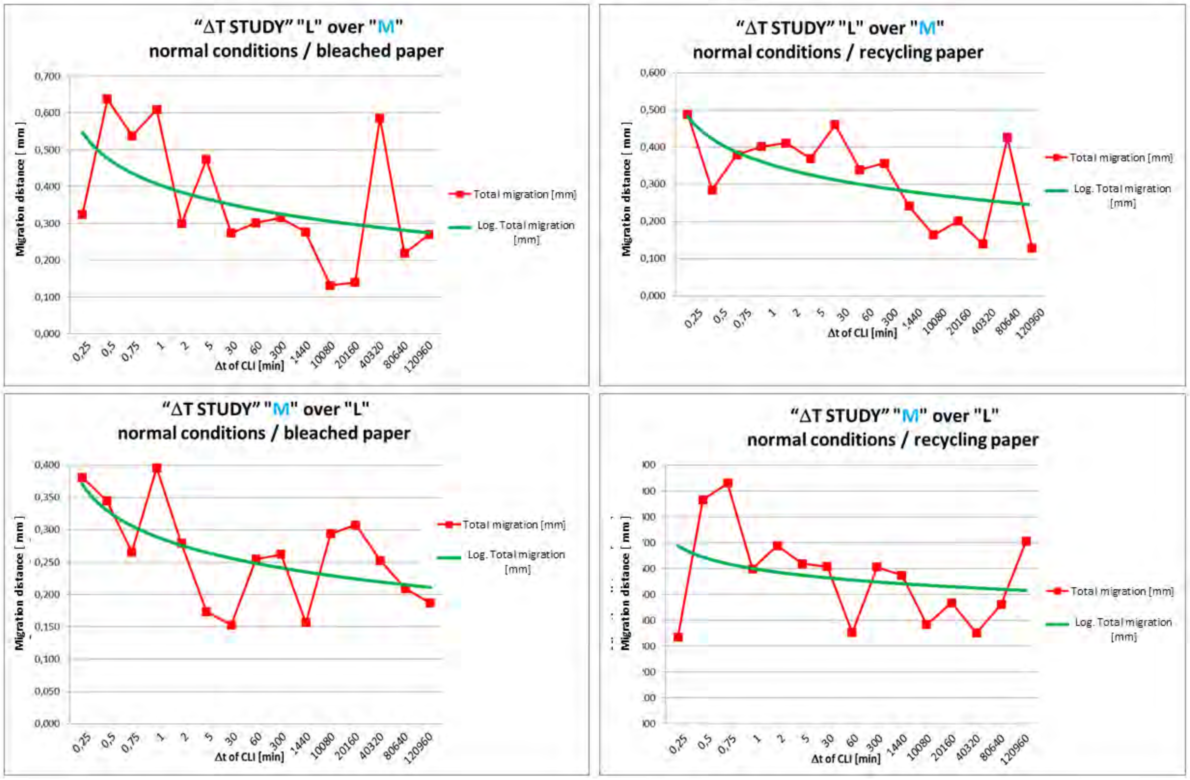


Figure B6: NORMAL CONDITIONS, “L” over “M” (upper graphics) and “M” over “L” (lower graphics).

In Figure B6, the red lines show total visible migration distance and the green lines show the logarithmic trend. Fifteen different intersections were measured for each Δt sample. The green curves show that there is stronger migration at short Δt than long Δt.

RESULTS FROM BELGIUM

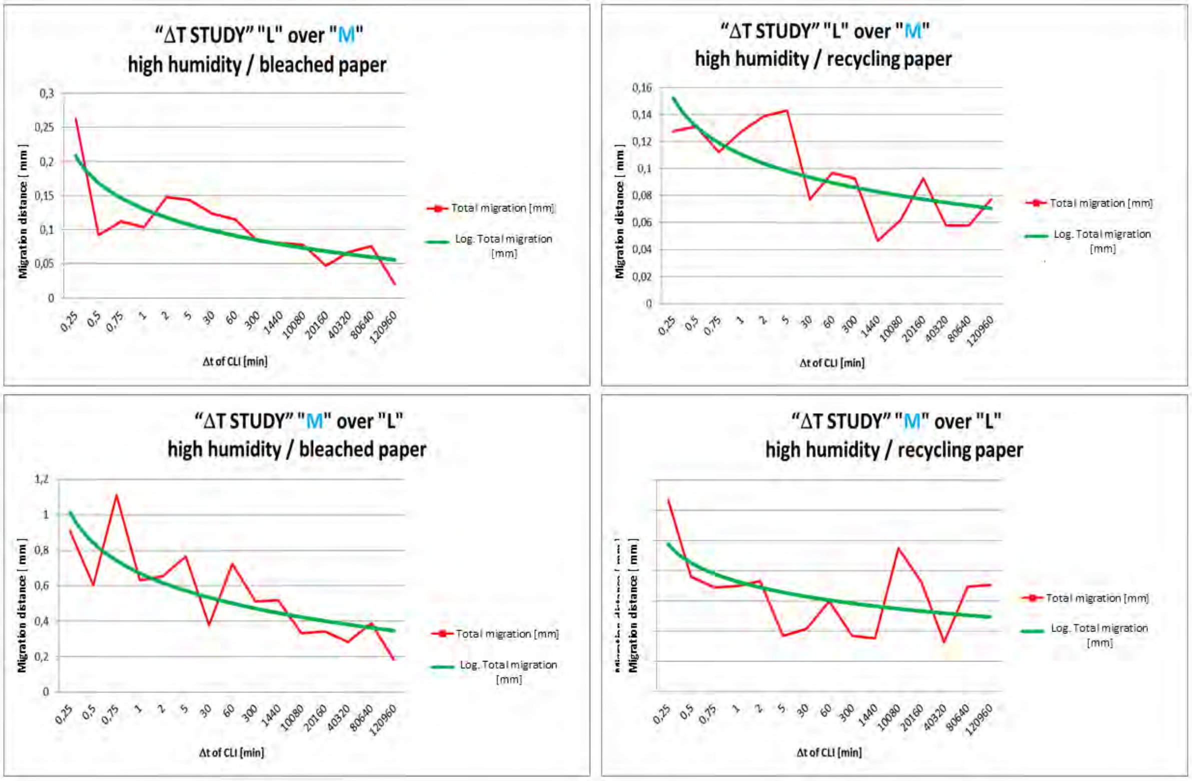


Figure B7. HIGH HUMIDITY CONDITIONS "L" over "M" (upper graphics) and "M" over "L" (lower graphics).

In Figure B7, the red lines show total visible migration distance and the green lines show the logarithmic trend. Fifteen different intersections were measured for each Δt sample. The green curves show that there is stronger migration at short Δt than long Δt.

RESULTS FROM BELGIUM

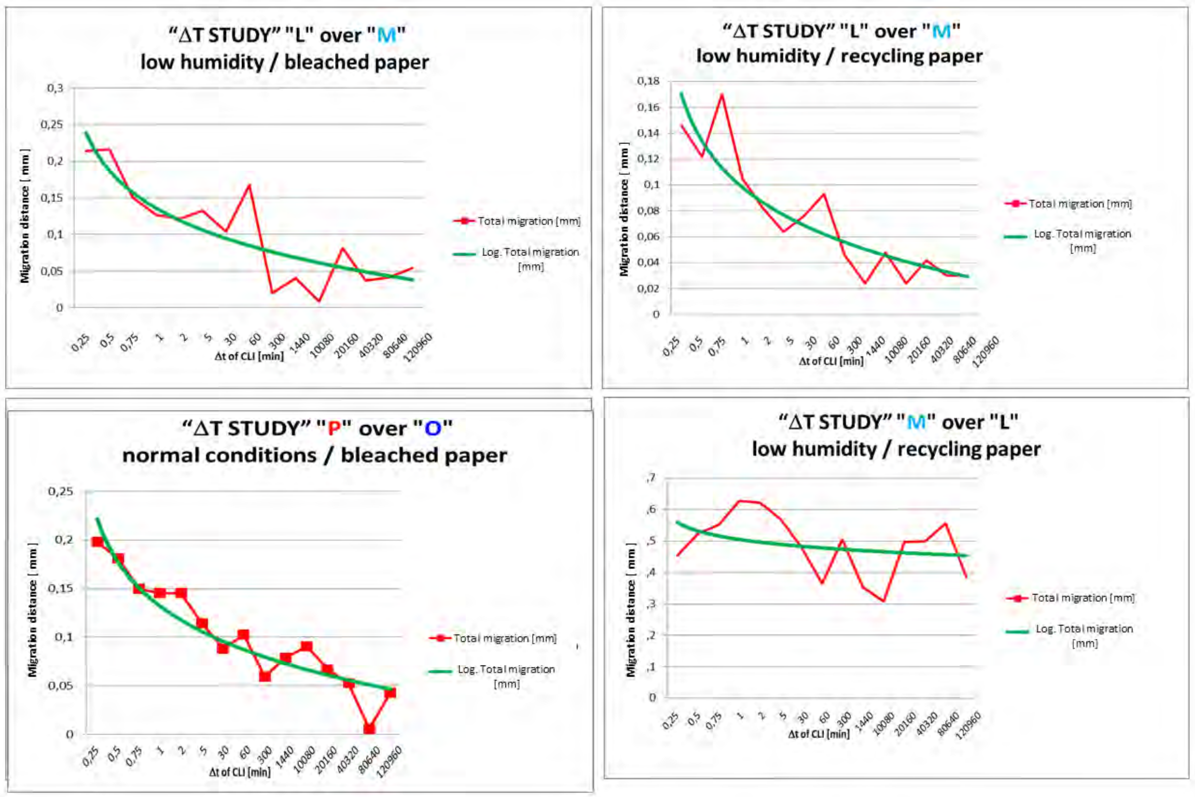


Figure B8: LOW HUMIDITY CONDITIONS "L" over "M" (upper graphics) and "M" over "L" (lower graphics).

In Figure B8, the red lines show total visible migration distance and the green lines show the logarithmic trend. Fifteen different intersections were measured for each Δt sample. The green curves show that there is stronger migration at short Δt than long Δt.

RESULTS FROM FRANCE

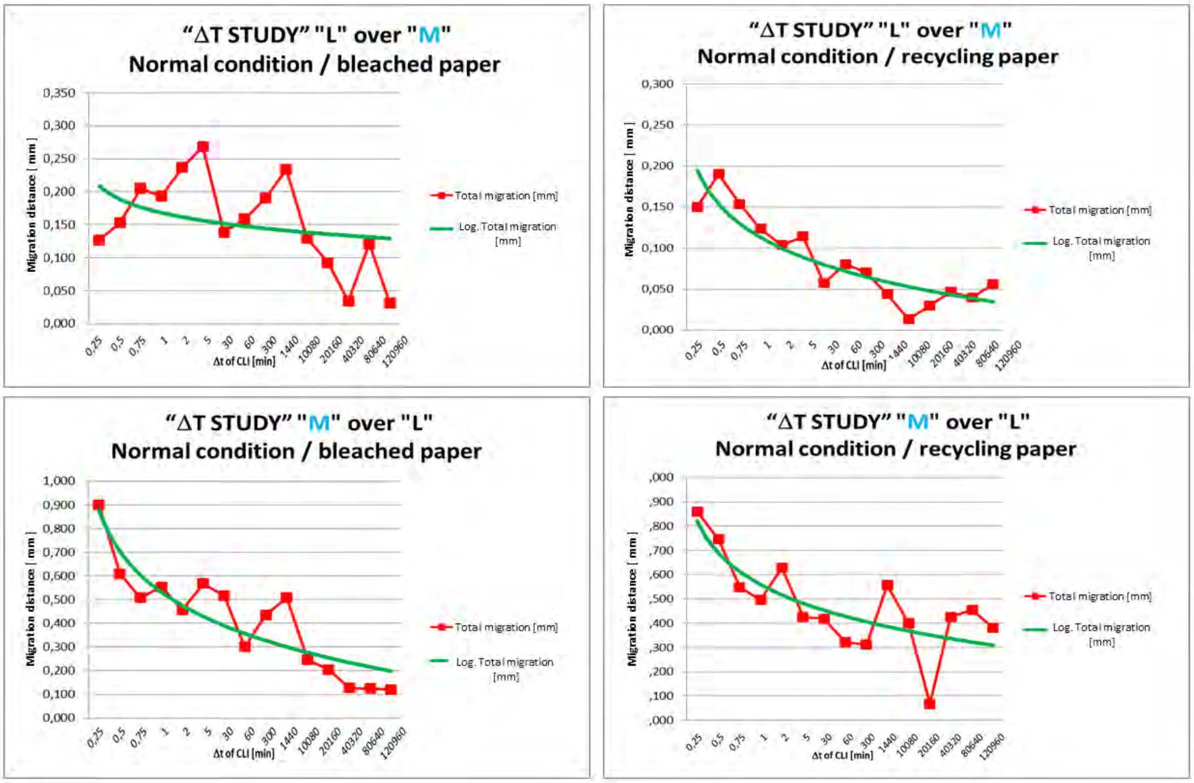


Figure B9. FRANCE: NORMAL CONDITIONS “L” over “M” (upper graphics) and “M” over “L” (lower graphics).

In Figure B9, the red lines show total visible migration distance and the green lines show the logarithmic trend. Fifteen different intersections were measured for each Δt sample. The green curves show that there is stronger migration at short Δt than long Δt.

An additional expert has been requested to perform similar experiment by using liquid inks other than "L" over "M". Mr Jesus BARRON from Spain repeated the same experiment by using blue and red inks, as follows:

O: Waterman blue ink Ref: 50110950;
P: Waterman red ink Ref: 50110970.

RESULTS FROM SPAIN

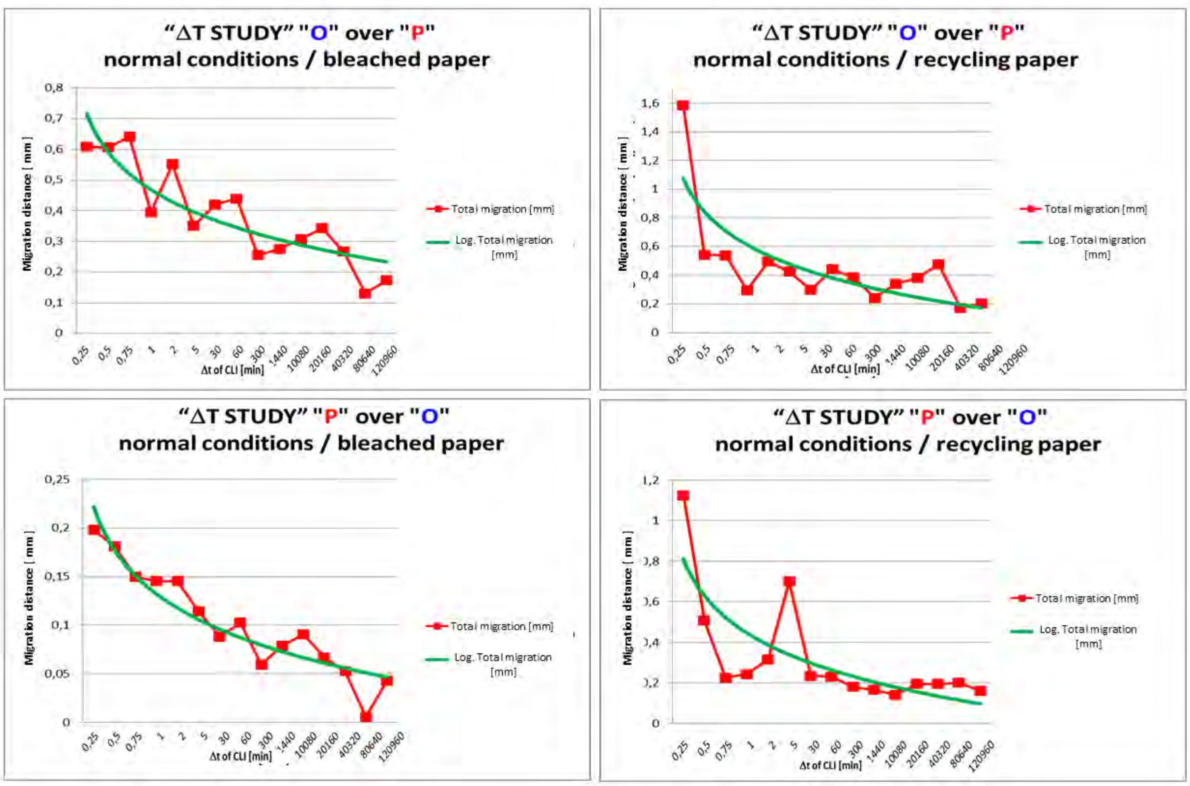


Figure B10. NORMAL CONDITIONS, "O" over "P" (upper curve) and "P" over "O" (lower graphics).

In Figure B10, the red lines show total visible migration distance and the green lines show the logarithmic trend. Fifteen different intersections were measured for each Δt sample. The green curves show that there is stronger migration at short Δt than long Δ

2.4 Discussions and way forward

In this study (Protocol B) we aimed to verify if it is possible to determine the time gap (Δt) between the drawing of the 1st liquid ink “L” and the 2nd liquid ink “M”.

At normal storage conditions, using coated (bleached) and uncoated (recycling) paper, the experimental curves (LM/ML) show a correlation between a short Δt and stronger visible migratory phenomena. Visible migration decreases as Δt increases.

At controlled temperature conditions, using coated (bleached) and uncoated (recycling) paper, the experimental curves (LM/ML) show a correlation between short Δt and stronger visible migratory phenomena. Visible migration decreases as Δt increases.

At high humid conditions, using bleached and non-bleached paper, the experimental curves (LM/ML) show a strong increase in visible migratory phenomena towards the 2nd line and towards the paper until the end of the 1st month. Visible migration strongly decreases from the 2nd month onwards. In humid conditions the Δt must be longer than one month to observe a decrease in visible migration.

Temperature/humidity of environment and the characteristics of the paper fibres have important influence on the magnitude of the visible migration.

Concerning the storage humidity conditions, the general rule is that the higher the humidity, the stronger the visible migration.

An additional experiment has been performed using bleached and non-bleached paper with inks O-P (the visible migration behaviour is unknown). At normal storage conditions the experiment curves (OP/PO) confirmed a correlation between a short Δt and stronger visible migratory phenomena. Visible migratory phenomena decreases with long Δt.

At normal, low and high temperature storage conditions, measuring the characteristics of visible ink migration can be used to determine short and long Δt between the 1st and the 2nd line.

CHAPTER 3. PROTOCOL C
ΔT STUDY II: MEASURING THE LUMINESCENCE INTENSITY IN CLI

3.1 Introduction

This study shall answer to the question whether or not fading of luminescence can be used to determine the production time gap (Δt) between two intersecting lines. This study does not take into account ink migration. Therefore, measurements were exclusively performed within the crossing line intersection area.

A set of samples always include line “ink 1” over line “ink 2” and vice versa.

Fading of luminescence with time in an ink line or a CLI occurs due to many unknown factors such as the chemistry of the paper (e.g. quenching effect), the chemistry of the inks (e.g. quenching effect or secondary luminescence), the miscibility of the two intersecting inks, the storage conditions, the sequence of two inks (1/2 or 2/1) and the light fastness of the luminescent agent.

3.1.1 Participating countries and experts

Spain: Comisaría General de Policía Científica, Guillermo PUERTO
Slovakia: Institute of Forensic Science, Adriana JABCONOVÁ and Alena UVÁČKOVÁ
Switzerland: Forensic Science Institute Zurich, Rolf HOFER

3.1.2 Suggested protocol

A series of 13 lines was produced of each ink. Line intersections with the corresponding ink (second ink building a set) were produced as described in the following table:

1st intersections (with the 1st line): Δt = 1 minute
2nd intersections (with the 2nd line): Δt = 1 month
3rd intersections (with the 3rd line): Δt = 2 months
4th intersections (with the 4th line): Δt = 3 months
5th intersections (with the5th line): Δt = 4 months
6th intersections (with the 6th line): Δt = 5 months
7th intersections (with the 7th line): Δt = 6 months
8th intersections (with the 8th line): Δt = 7 months
9th intersections (with the 9th line): Δt = 8 months
10th intersections (with the 10th line): Δt = 9 months
11th intersections (with the 11th line): Δt = 10 months
12th intersections (with the 12th line): Δt = 11 months
13th intersections (with the 13th line): Δt = 12 months

3.1.3 Proposed writing instruments and materials to use

For this study, inks are chosen where luminescence fading has already been observed.

A: Ball point pen, Stabilo Ref nº 0800M 97 3, blue ink
B: Ink pad, Troadat ref: 6/4911C, red ink
C: Felt-tip pen, Paper Mate Flaire, black ink
J: CARAN d' ACHE, Giant Cartridge "Goliath", 8428.000 medium black, black ink
R: Ballpoint pen, CARAN d' ACHE 826, blue ink
S: Felt-tip pen, Stabilo point 88 0.4

The intersection combinations (sets) thereof were:

A over B	and	B over A
B over C	and	C over B
B over S	and	S over B
R over J	and	J over R

3.2 Experimental section: methods and materials

Intersections were produced on different paper qualities. Paper was chosen allowing inks to show luminescence (no quenching effect):

a) Non-bleached recycling paper: REFUTURA, Art. Nr. 228 080, 80g/m^2, Switzerland
c) Bleached office paper: CLAIRALFA-CLAIRFONTAINE, A4, 80 g. m2, Ref 1797 3-329680197907 PEFC certified

The following detection instrument has been used: VSC 6000

The setting on the detection unit was optimized for each paper and intersection combination to get adequate luminescence and contrast. The pixel saturation at the highest luminescence stall not be higher than 90%. Luminescence intensities (pixel saturation) were measured at the same time and at constant parameters on all samples.

Inks combination	Excitation wavelength	Detection wavelength	Magnification	Picture integration time
A over B and vice versa	515 - 640 nm	695 nm long pass	31.83	9 ms
A over B and vice versa	485 - 590 nm	645 nm long pass	18,01	53 ms
R over J and vice versa	485 - 610 nm	645 nm long pass	31.83	11 ms
B over C and vice versa on bleached paper	400 - 610 nm	665 nm long pass	17.93	750 ms
B over C and vice versa on recycling paper	445 - 640 nm	725 nm long pass	17.93	250 ms
B over C and vice versa	515 - 640 nm	695 nm long pass	44.39	88 ms (B over C)/

				149 ms (C over B)
B over C and vice versa	400 - 640 nm	695 nm long pass	22.27	44 ms (B over C)/ 53 ms (C over B)
B over S and vice versa on both papers	400-640 nm	630 nm long pass	17.93	125 ms

Table C1. Examples of sets (ink combinations) and apparatus settings

The data were transferred in a table and curves were calculated with luminescence intensity (% pixel saturation) versus production time gap between the two intersecting lines (Δt).

3.3 Results

Table C1 gives an overview on which lab did which CLI set on what paper quality.

Paper: a) Recycling paper of Switzerland
c) Bleached paper of France[1]

CLI set	Paper brand		Participating country
	a)	c)	
A/B	X	X	Switzerland
B/C		X	Slovakia
B/C	X	X	Spain
B/S	X	X	Spain
J/R	X	X	Switzerland

Tab. C1: Overview on sample materials and participants

Samples were produced as described above. All intersections were analyzed after the drawing of the last intersection; thus, all samples were analyzed at the same time.

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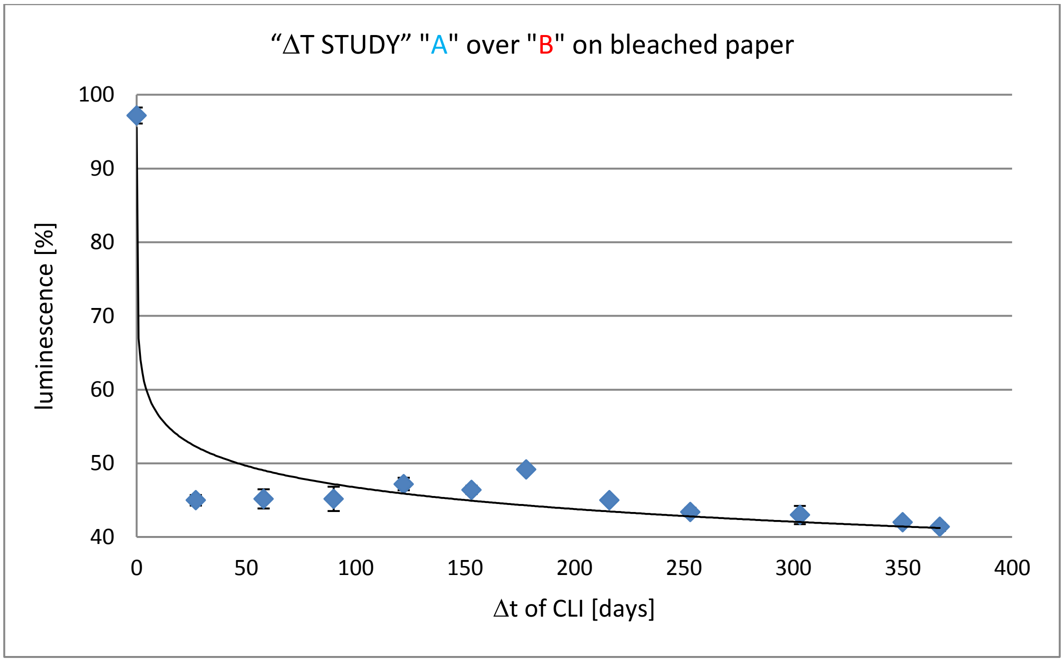
[1] Please see reference as Protocol A.



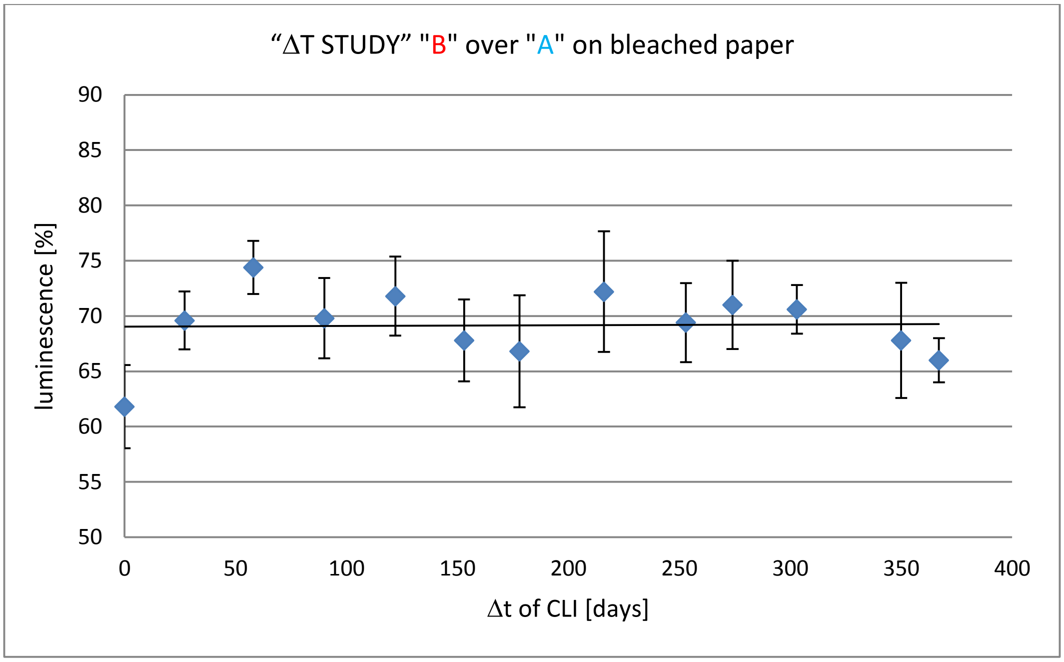
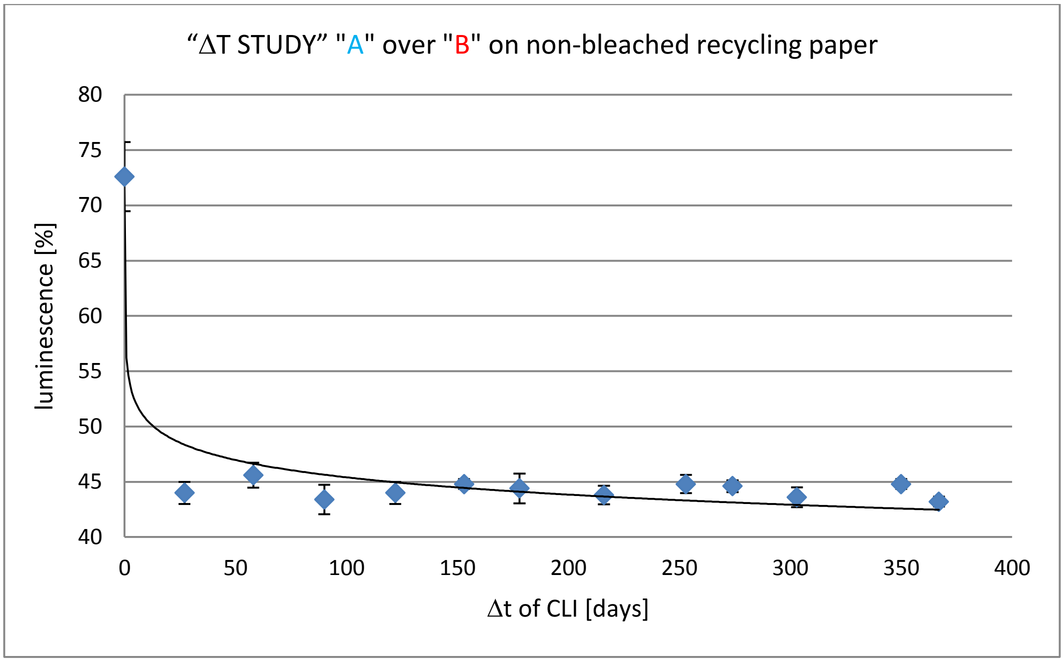


Figure C1. Luminescence intensity measures within crossing line intersections of blue ink “A” and red ink “B” on bleached paper c); “A” over “B” (upper curve) and “B” over “A” (lower curve). Five different intersections were measured of each Δt sample. A logarithmic trend line is introduced.



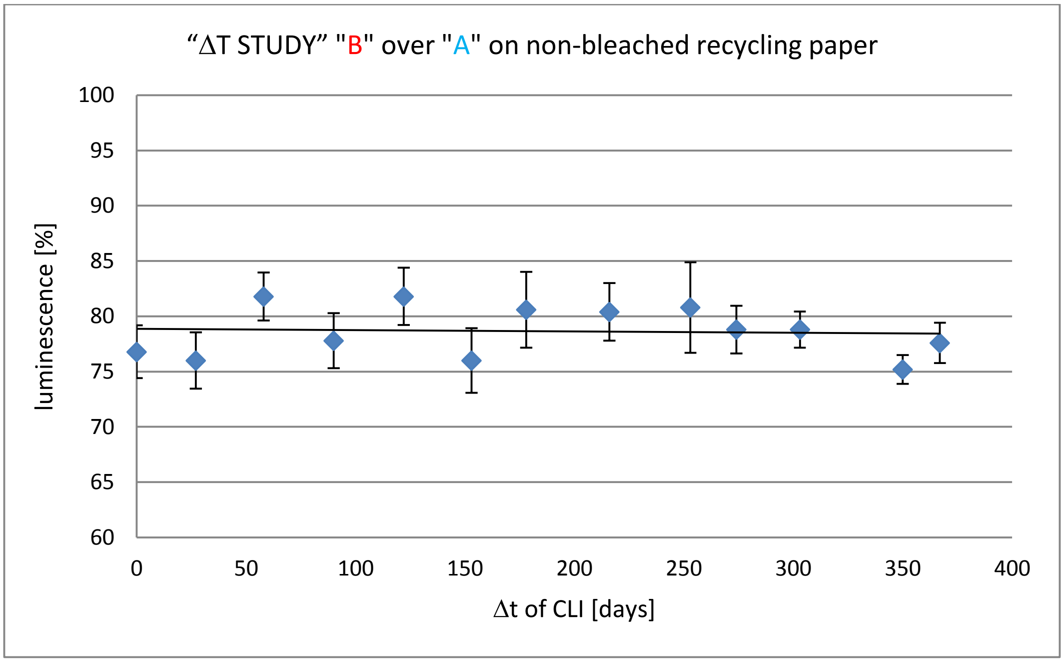


Figure C2: Luminescence intensity measures within crossing line intersections of blue ink “A” and red ink “B” on non-bleached recycling paper a); “A” over “B” (upper curve) and “B” over “A” (lower curve). Five different intersections were measured of each Δt sample. A logarithmic trend line is introduced on the “A” over “B” curve and a linear trend line on the “B” over “A” curve.

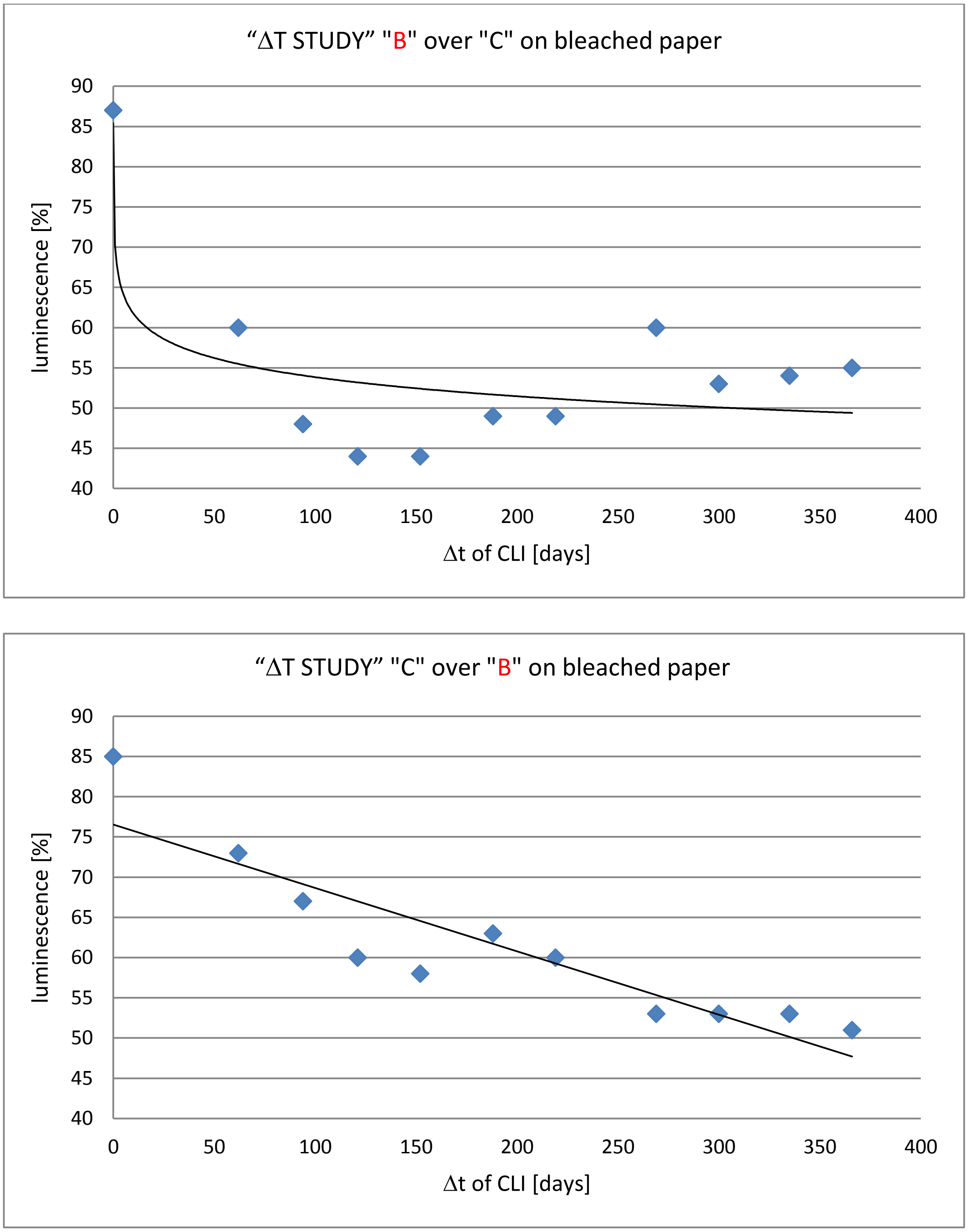
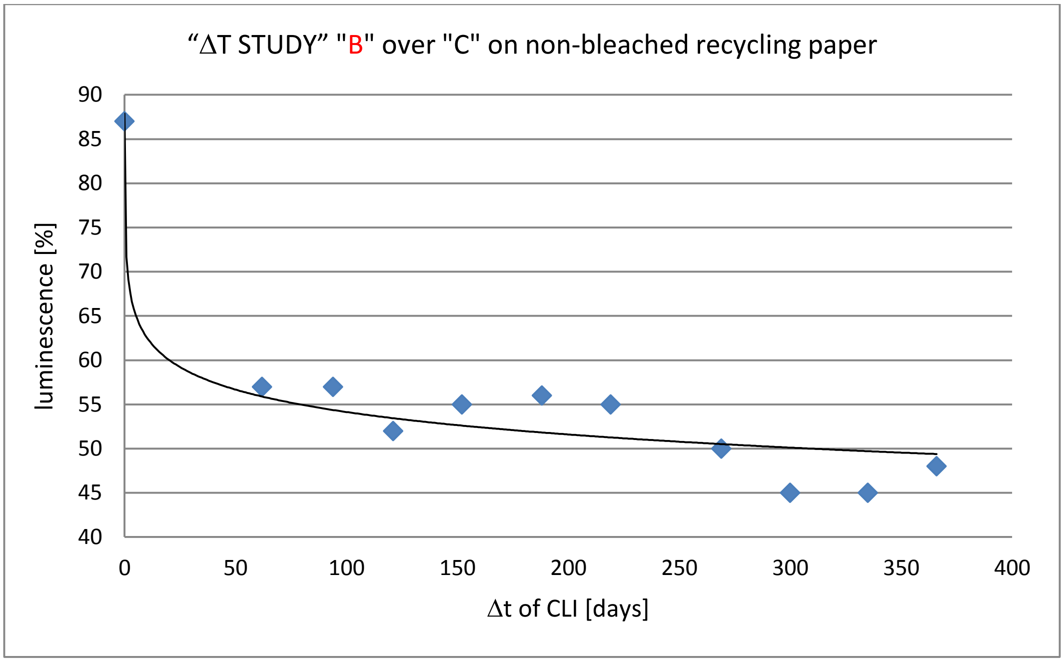


Figure C3: Luminescence intensity measures within crossing line intersections of red ink “B” and black ink “C” on bleached paper c); “B” over “C” (upper curve) and “C” over “B” (lower curve). Only one intersection was measured of each Δt sample. A logarithmic trend line is introduced on the upper curve and a linear one on the lower.



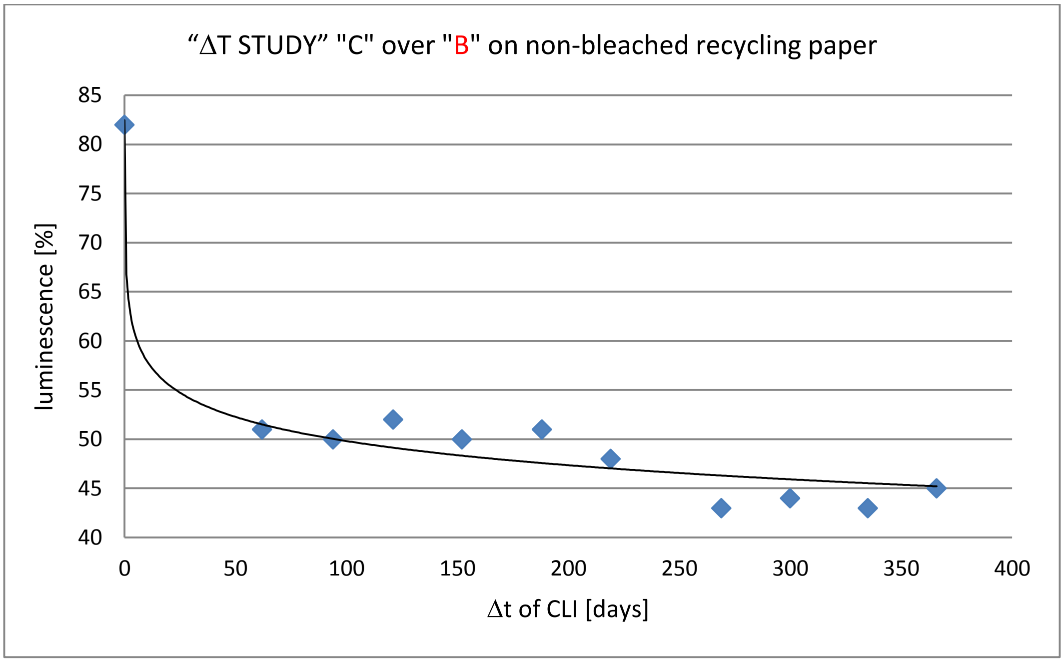
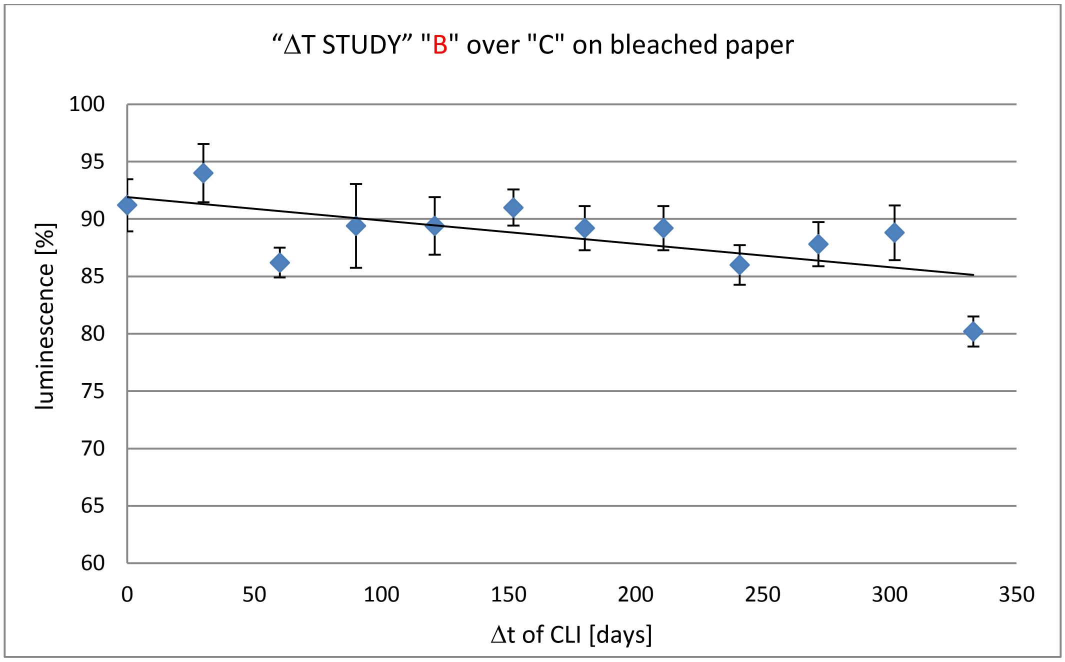


Figure C4: Luminescence intensity measures within crossing line intersections of red ink "B" and black ink "C" on non-bleached paper a); "B" over "C" (upper curve) and "C" over "B" (lower curve). Five different intersections were measured of each Δt sample. A linear trend line is introduced on both curves.



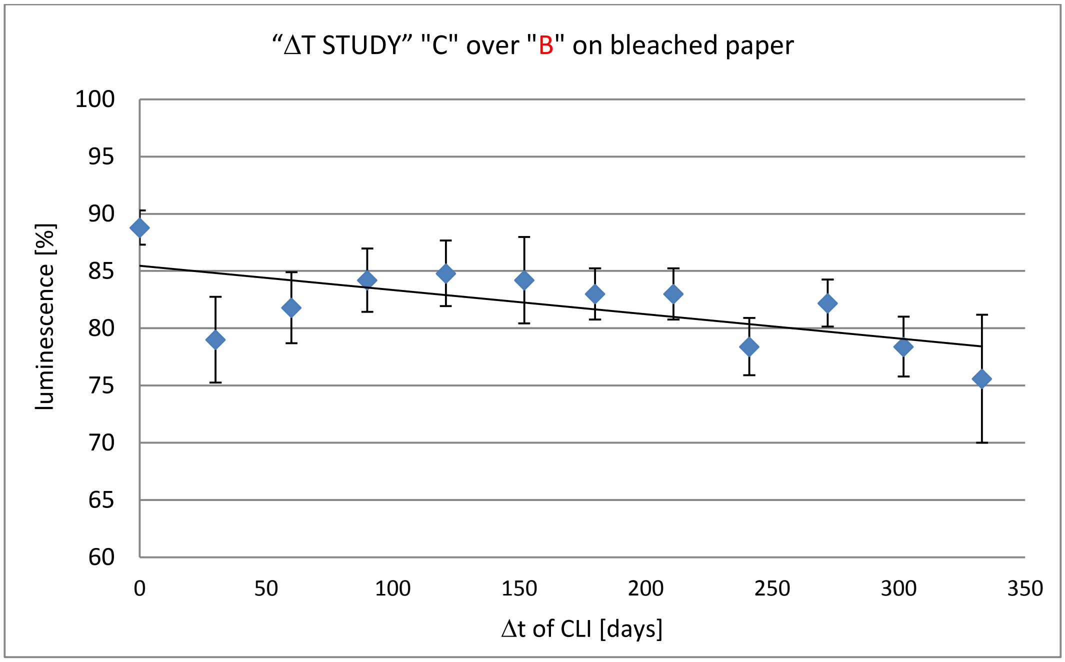
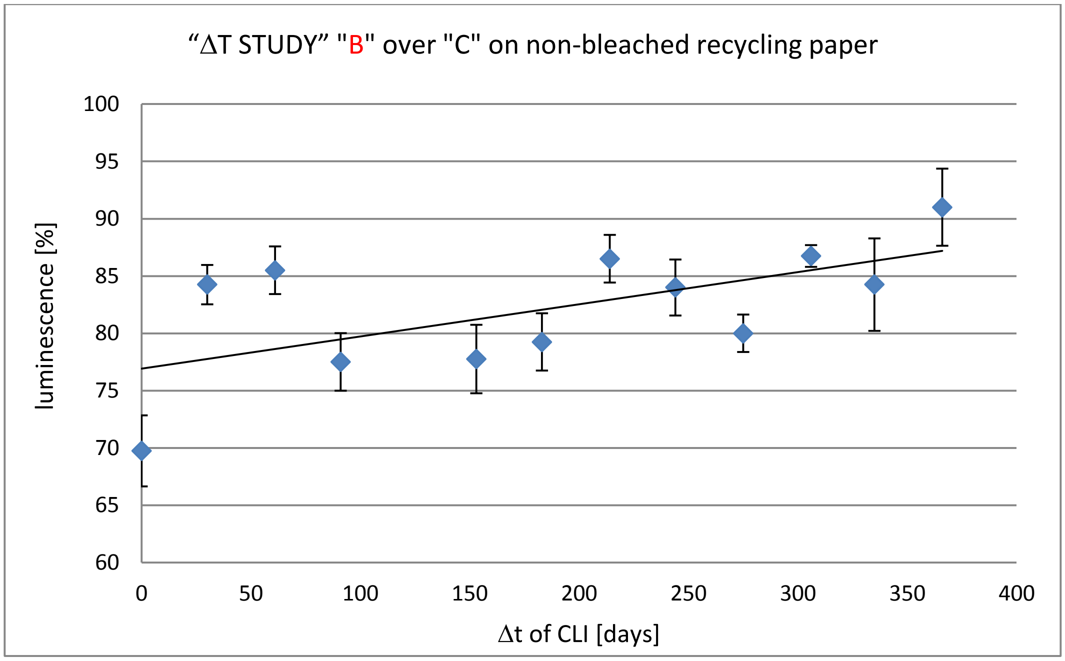


Figure C5: Luminescence intensity measures within crossing line intersections of red ink “B” and black ink “C” on bleached paper c); “B” over “C” (upper curve) and “C” over “B” (lower curve). Five different intersections were measured of each Δt sample. A linear trend line is introduced on both curves.



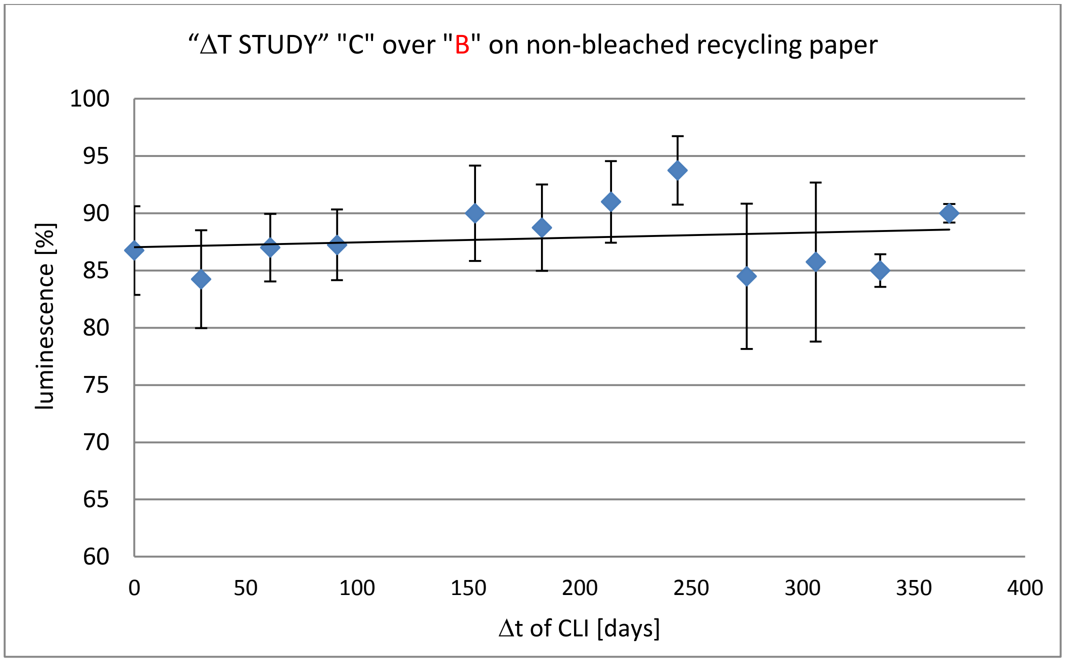
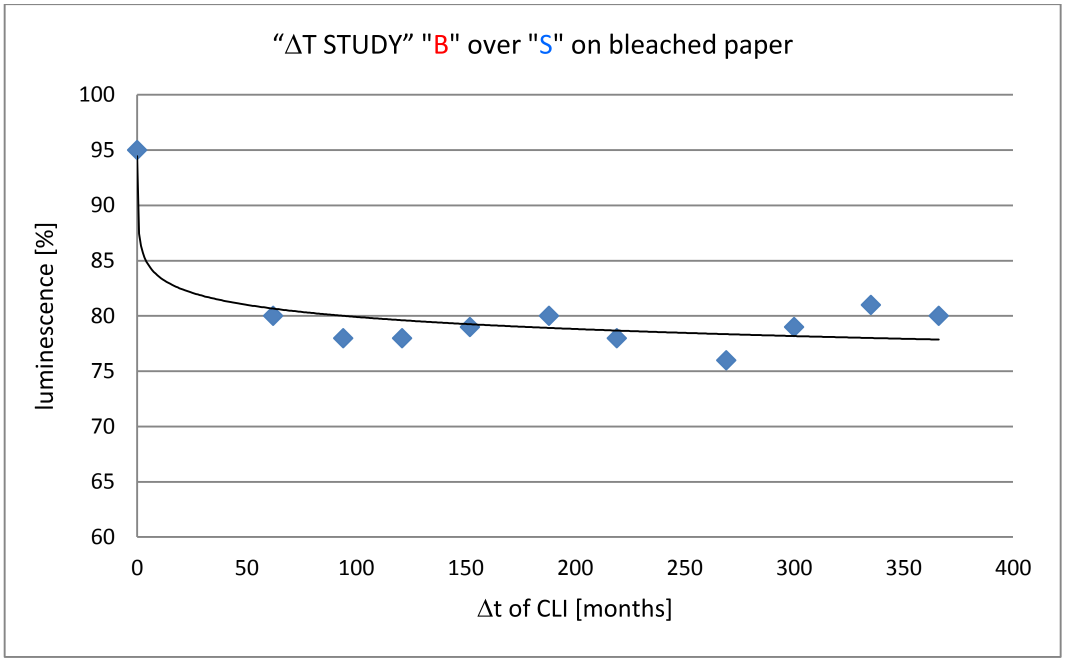


Figure C6: Luminescence intensity measures within crossing line intersections of red ink “B” and black ink “C” on non-bleached recycling paper a); “B” over “C” (upper curve) and “C” over “B” (lower curve). Only one intersection was measured of each Δt sample. A logarithmic trend line is introduced on both curves.



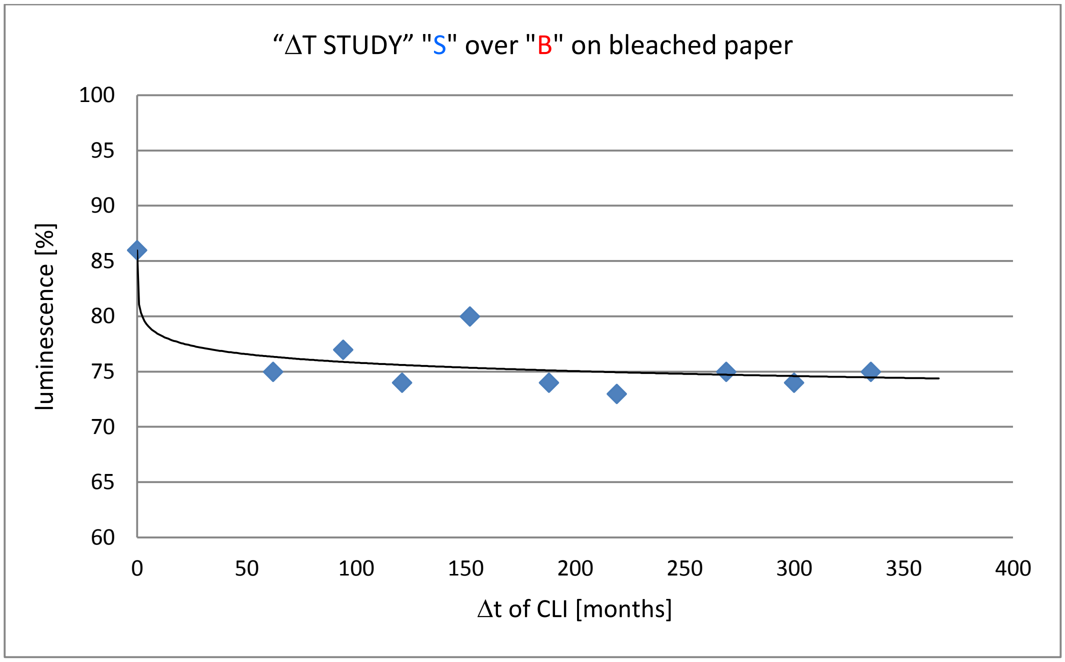
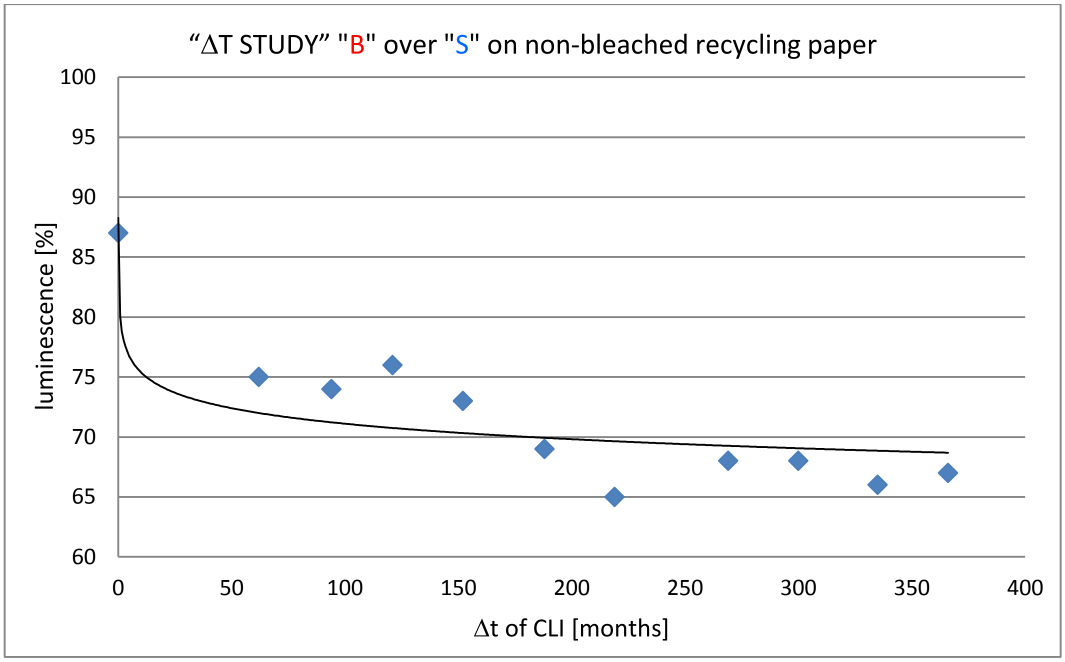


Figure C7: Luminescence intensity measures within crossing line intersections of red ink “B” and blue ink “S” on bleached paper c); “B” over “S” (upper curve) and “S” over “B” (lower curve). Only one intersection was measured of each Δt sample. A logarithmic trend line is introduced.



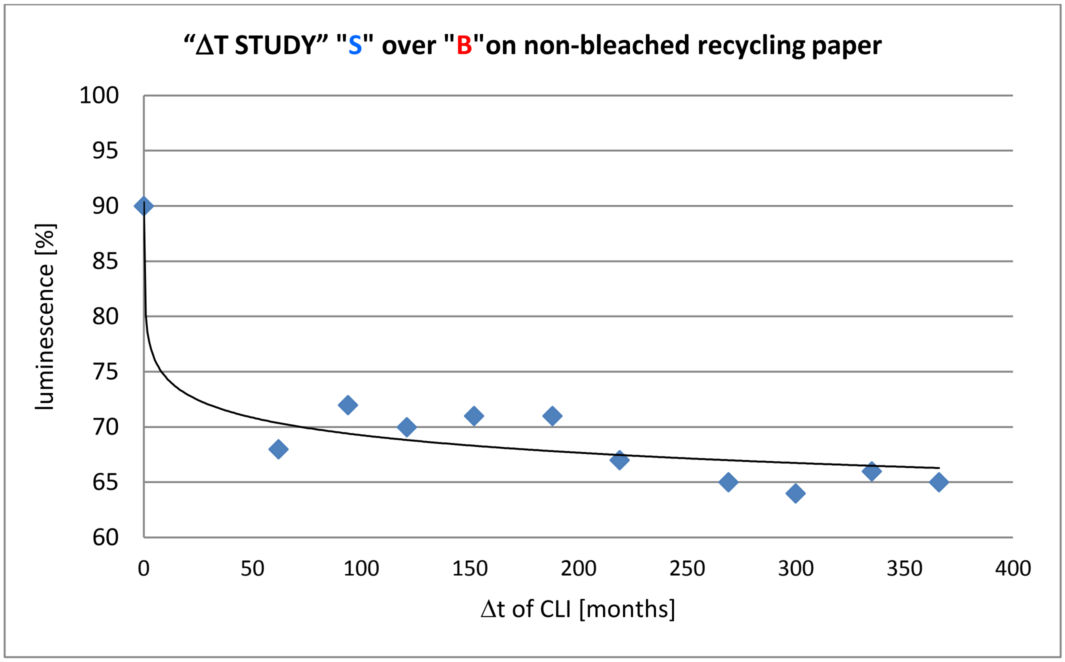
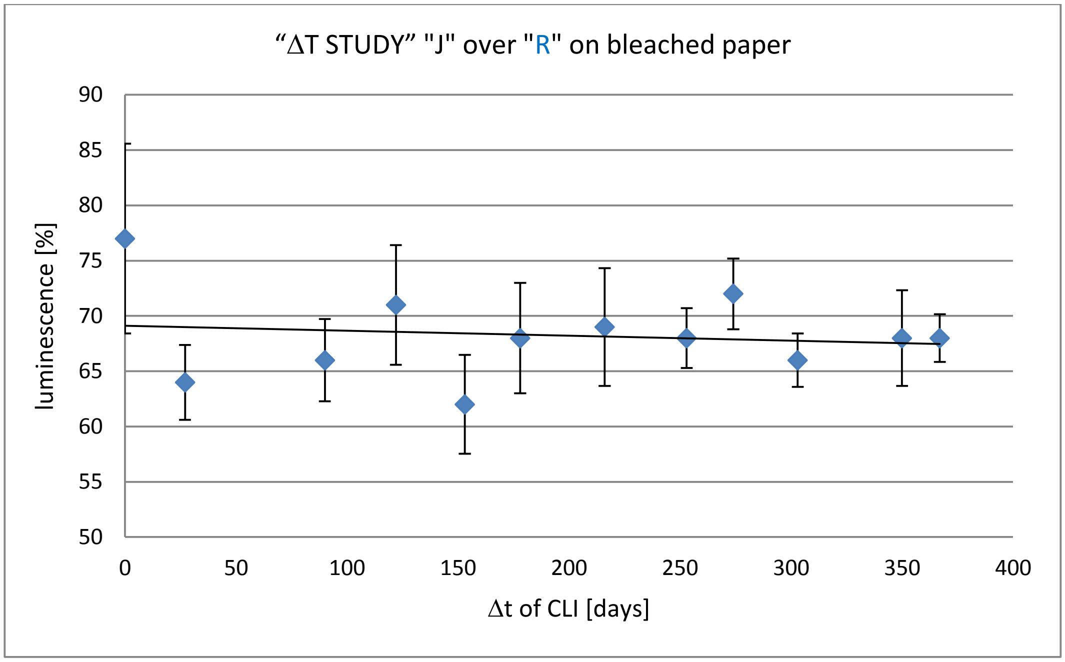


Figure C8: Luminescence intensity measures within crossing line intersections of red ink “B” and blue ink “S” on non-bleached recycling paper a); “A” over “B” (upper curve) and “B” over “A” (lower curve). Only one intersection was measured of each Δt sample. A logarithmic trend line is introduced.



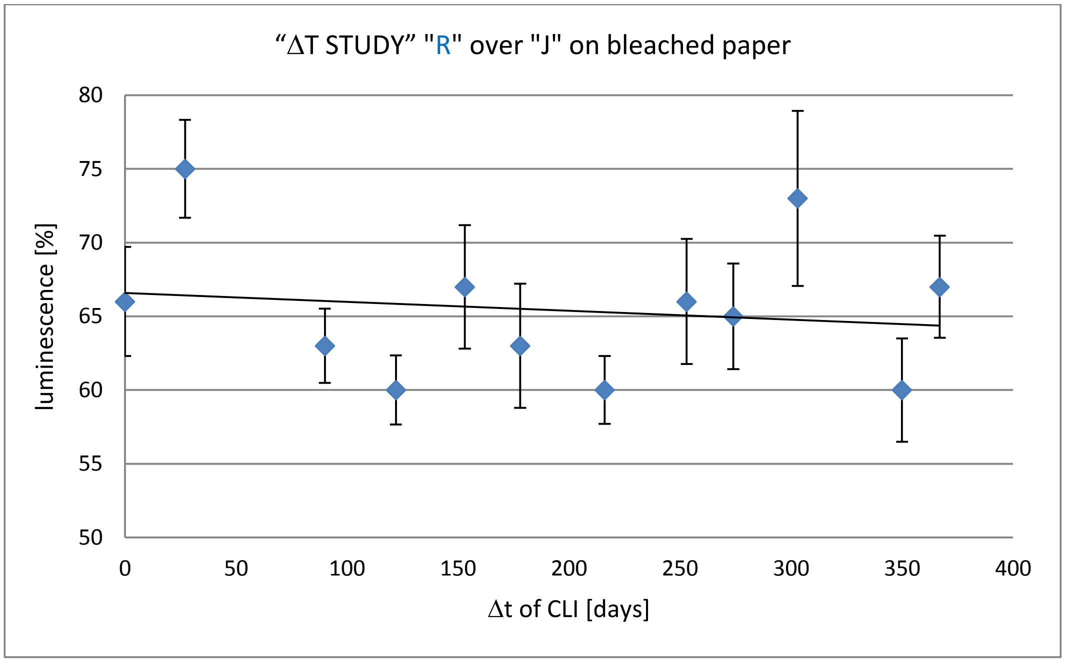
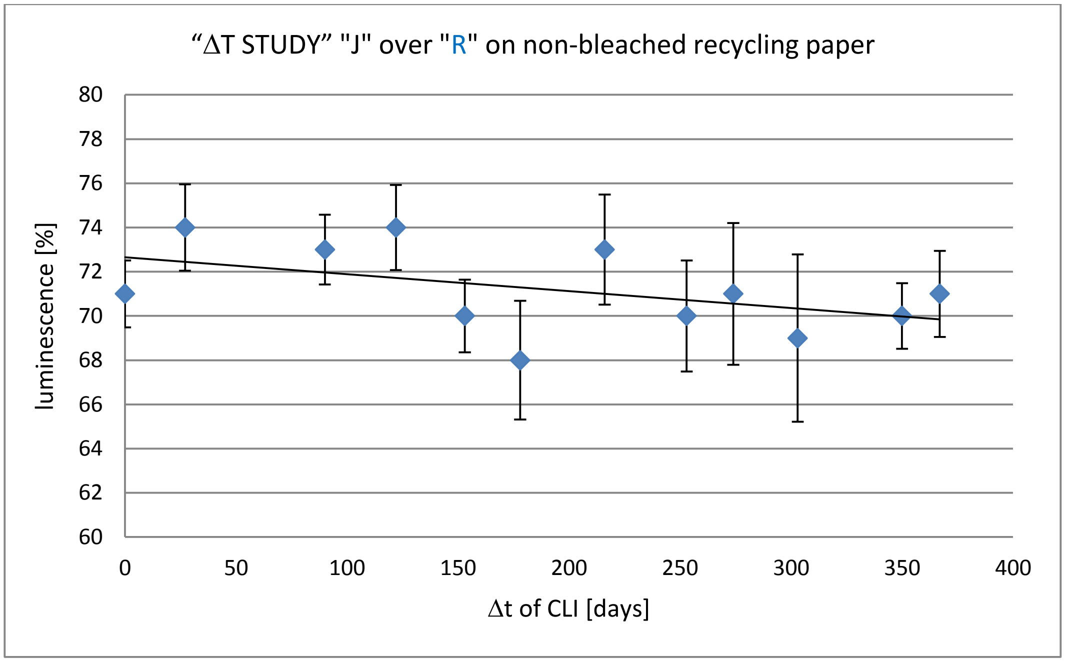


Figure C9: Luminescence intensity measures within crossing line intersections of black ink “J” and blue ink “R” on bleached paper c); “J” over “R” (upper curve) and “R” over “J” (lower curve). Five different intersections were measured of each Δt sample. A linear trend line is introduced.



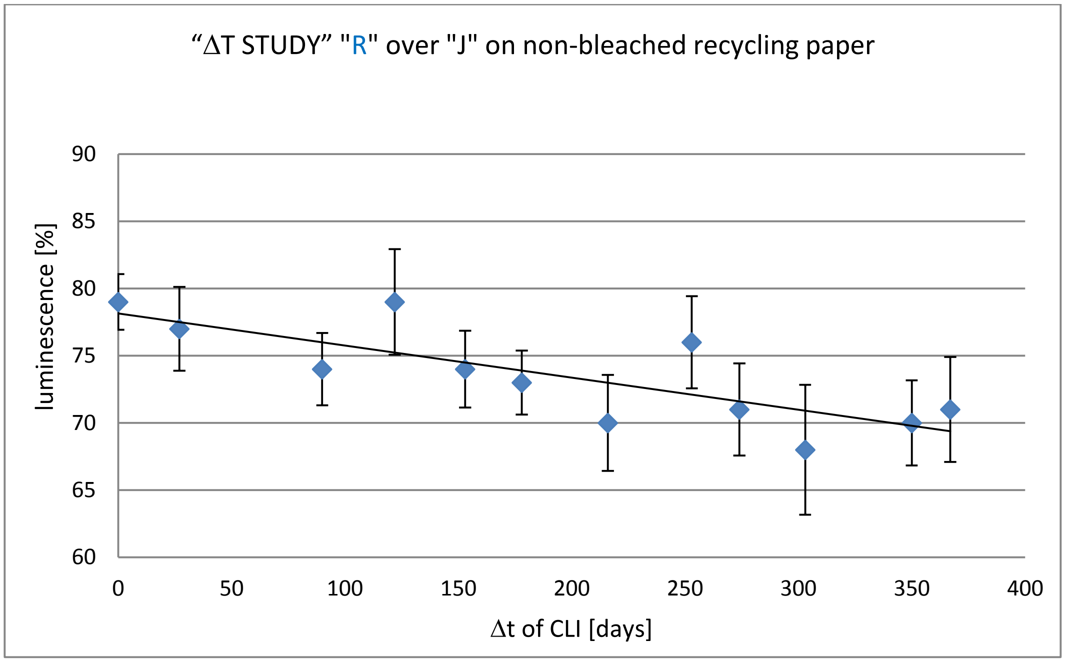


Figure C10: Luminescence intensity measures within crossing line intersections of black ink “J” and blue ink “R” on non-bleached recycling paper a); “J” over “R” (upper curve) and “R” over “J” (lower curve). Five different intersections were measured of each Δt sample. A linear trend line is introduced.

3.4 Discussions and way forward

It is important to keep in mind, that this study does not discuss any ink ageing processes.

The results of the Δt study showed a trend of decreasing luminescence with increasing Δt in most cases (fading of luminescence). Some of the combinations gave the best curve fit with a logarithmic and some with a linear trend line.

Usually, the luminescence intensity decreases with higher Δt. In some cases, the CLI of the first sample (intersection immediately produced on fresh first line) showed a strong luminescence, but, from the second to the last sample almost constant, very weak luminescence was measured. In some ink combinations, the optical behavior changed dramatically with the paper quality.

An interesting ink combination is “B”/“C”. Using bleached and non-bleached recycling paper, three series of “B” over “C” and vice versa were produced and completely different curves have been observed.

Different physical (or chemical) processes can be the reason for this optical behavior. As there is no sufficient evidence for a specific process, only the following hypotheses could be discussed at the moment:

- Quenching effect of the paper (hypothesis): Components from the first line saturate quenching components within the paper. Luminescence of the second, intersecting ink is visible.
- Miscibility of inks: First ink is wet when it is applied on the paper and dries slowly with time. The more solvent left in the primary ink stroke, the higher its miscibility with the second ink. Colors absorb the luminescence: If the primary ink zone is still wet, colors from the second ink may diffuse toward/into the paper and the luminescent components stay or even concentrate at the surface. → higher luminescence, when fresh
- Chemical reaction: Components from one ink my react with components from the other. This may be neutralization (change of pH), ligand exchange or complex building effects. → higher or lower luminescence, when fresh
- Secondary luminescence: components of the one ink has a fluorescence/luminescence. The emitted light acts as excitation wavelength for luminescent components of the second ink component.

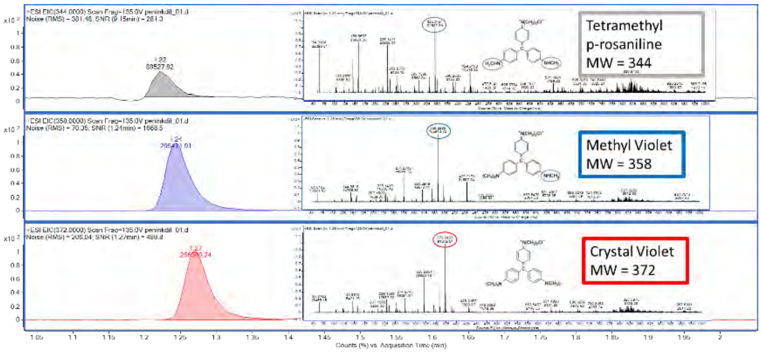
The reason for the observed behavior may be a combination of the hypotheses or another effect, we still do not know.

The paper had an influence on the intensity of the luminescence, but not on the general luminescence intensity trend of the ink set.

In real criminalistics cases, the used inks are usually unknown. As the curves are quite different from ink to ink, and as short Δt may be lower or higher than long Δt, standard samples have to be produced with identic material. Therefore, it will almost be impossible to determine Δt of unknown intersections.

CHAPTER 4. PROTOCOL D

CHEMICAL STUDY: CHEMICAL ANALYSIS OF INK COMPONENTS



4.1 Introduction

In questioned document examination, it is useful to be able to determine the sequence of deposition of ink and/or markings on a substrate. This is most commonly explored in fraud investigations involving official documents, checks, or other documents of interest. Though optical examination and electron microscopy have been most widely applied, there is no universally accepted method to determine the sequence of ink deposition undisputedly (1). The composition of each component ink of a crossed line intersection (CLI) and how the multiple inks interact with one another affect the ability to determine sequence of deposition (2).

Additional techniques that have been applied to the analysis of line crossings with varying degrees of success including atomic force microscopy (AFM), attenuated total reflectance Fourier transform infrared spectral imaging (AFM-FTIR), 3D laser profilometry, and scanning electron microscopy energy dispersive x-ray spectroscopy (SEM-EDX) (1, 3-5).

Characterizing the fluorescent components of inks, most commonly dyes, is very useful in document examination for association, discrimination, and intelligence purposes. Optical methods such as fluorescence, infrared luminescence, and spectroscopic methods such as Fourier transform infrared spectroscopy and UV/Vis spectroscopy rely on these properties, and useful information is derived. In addition, chromatographic, spectroscopic, and mass spectrometric techniques such as High Performance Liquid Chromatography (HPLC), Gas Chromatography (GC), paper chromatography, nuclear magnetic resonance (NMR) spectroscopy, liquid chromatography mass spectrometry (LC-MS), and gas chromatography mass spectrometry (GC/MS) have been applied to analysis of dyes and pigments over the past 100 years (6). Matrix Assisted Laser Desorption—Mass Spectrometry (MALDI-MS) is another attractive method for ink analysis in that it is considered a soft ionization technique which allows for the ionization of intact molecular ions with limited fragmentation as compared to traditional electron impact ionization (7-9). In recent years, laser desorption has been applied to the analysis of inks, with success in characterizing both the dye, pigment, and more limitedly the polymeric content of the inks on paper in combination with other techniques such as TLC and Raman spectroscopy (8, 10).

After conducting non-destructive optical examinations, the chemical analysis of the ink (e.g ballpoint pen inks, felttip pen inks, ink pad inks) is useful for the identification and separation of mixtures of organic compounds, including luminescent components.

The project described here was performed in collaboration with three laboratories (Croatia, Former Yugoslav Republic of Macedonia and United States) in an attempt to establish a standard and reliable method for questioned document ink analysis. The specific objective of this protocol "D" was to identify the compounds contained within the inks. In particular, there was an interest to identify the luminescent compounds within the inks in order to better understand the migration effects of these compounds that were observed at the interfaces of the line-crossing sites. The analysis of multiple inks by different laboratories has also provided some insight into the chemical composition of the inks as well as demonstrated the forensic utility and complementarity of each of the analytical methods for the chemical analysis of inks. This information will help to establish a standard protocol that could be used in forensic ink analysis such as differentiation of inks, questioned document dating, and the determination of sequence in crossed line intersections in the future.

4.1.1 Participating countries and experts

Former Yugoslav Republic of Macedonia:	Ministry of Interior of the Former Yugoslav Republic of Macedonia, Forensic Chemistry Department, Vesna ANTIKJ and Daniela DJIDROVSKA
Croatia:	Forensic Science Centre "I. Vucetic", Andrea LEDIĆ and Stjepan BRZICA
United States:	International Forensic Research Institute and Department of Chemistry and Biochemistry, José ALMIRALL and Rhett WILLIAMSON

4.1.2 Suggested protocol, proposed writing instruments and materials

A total of eight different inks, including two ballpoint pens, two fountain pens, three ink pads, and one felt tip pen were analyzed. A part of this study and their descriptions below, and the analysis performed on each writing instrument can be seen in Table D1.

Writing Instrument A:	Ballpoint pen, Stabilo, Ref nº 0800M 97 3, blue ink
Stroke dimension:	0.3 mm
Writing Instrument B:	Ink pad, Troadat, Ref nº 6/4911C, red ink
Stroke dimension:	0.6 mm
Writing Instrument C:	Felt-tip pen, Paper Mate Flaire, black ink
Stroke dimension:	0.7 mm
Writing Instrument L:	Fountain pen, Pelikan Script, black ink
Stroke dimension:	0.3 mm
Writing Instrument M:	Fountain pen, Pelikan Script, blue ink
Stroke dimension:	0.3 mm
Writing Instrument Q:	Ink pad, Trodat Printy 4822, red ink
Stroke dimension:	0.6 mm
Writing Instrument Y:	Ballpoint pen, Pilot BPA-10F, black ink
Stroke dimension:	0.3 mm
Writing Instrument Z:	Ink pad, Sachihata HGN-1, blue ink
Stroke dimension:	0.6 mm

It has been suggested to use the paper allowing inks to show luminescence (no quenching effects). Suggested paper to use was the following:

- FABRIANO, Fabriano Paper Copy2, A4, 80g/m^2, 41021297, Natural paper.
- Height whiteness produced with 100% pure ECF (Elemental chlorine Free) cellulose.
- Acid Free with alcaline to guarantee long permanence – Long liv(f)e (ISO 9706) Copy 2 performance.

4.2 Experimental section: methods and materials

Several chemical methods were used by participating countries including: Thin Layer Chromatography (TLC), Gas Chromatography Mass Spectrometry (GCMS), High Performance Liquid Chromatography (HPLC), Matrix Assisted Laser Desorption Ionization – Time-Of-Flight – Mass Spectrometry (MALDI-TOF-MS), Direct Analysis in Real Time – Quadrupole Time-Of-Flight – Mass Spectrometry (DART-QTOF-MS), and Liquid Chromatography – Mass Spectrometry (LC-MS).

To identify the luminescent compounds in inks, forensic examiners from the participating countries were able to use the following instrumental techniques:

- Former Yugoslav Republic of Macedonia – TLC and GC/MS;
- Croatia – HPLC;
- United States – MALDI-MS, TLC, LC-MS, DART-MS.

Countries	Chemical analysis	Writing instruments
Forensic Chemistry Department, Ministry of Interior of the Former Yugoslav Republic of Macedonia	TLC	L,M and traces of A, B, C, Q, Y, Z
	GC/MS	L, M
Forensic Science Center “I.Vucetic”, Zagreb, Croatia	HPLC	Y, Z and traces of A, B, L, M
International Forensic Research Institute and Department of Chemistry and Biochemistry, Florida International University, Miami, Florida, United States	MALDI-TOF-MS, DART-QTOF-MS, TLC, LC-MS	Y, Z

Table D1. Chemical Analysis of each ink independently by laboratory in each country institution.

GC/MS and TLC Analysis by the Forensic Chemistry Laboratory, Ministry of Interior of the Former Yugoslav Republic of Macedonia

A 10 mm long ink line was cut out and put into a micro-vial with 1 ml of methanol around 15 minutes. Different solvent systems were used to develop chromatograms as follows: ethyl acetate, ethanol, water (26:13:11); 1-butanol, ethanol, water (50:10:15) and ethanol (100). The TLC plates were activated at 60° C for 20 min. After cooling, small amounts (2 to 10 µl) of the extracts were spot onto the TLC plate at a distance of about 10 mm from the bottom edge with the aid of a micro-pipette. The TLC plates were developed in a horizontal developing chamber. Chromatographic development of the plates was performed at room temperature for 30 min. The TLC plate was placed upright and the solvent system allowed to migrate for about 6 cm. The plate was removed from the chamber and dried in cold air stream. Strokes of writing instruments L and M were exposed to three separate conditions for three days prior to separation by TLC: 1) in dark ambient conditions at 25° C, 2) in complete darkness at 25° C, and 3) under direct sunlight.

Each of the components of the Fountain black and blue ink samples, resolved by TLC and observed under IR -Infra red light and spot light source 440-580 nm VSC2000/HR were scraped off the pure luminescent zone of the plate, and extracted with methanol in an Eppendorf tube using an ultrasonic bath for 6 minutes.

The extract was analyzed by GC/MS and its components were identified. GC/MS analyses were conducted using a GC/MS -QP 2010 Shimadzu (Columbia, MD, USA), software package version CCSS-5000 Equipped with a ZB-5 column (Supelco, Bellefonte, PA, USA) 30 m, liner diameter 0.25mm, thick film of stationary phase 0.25 µm, injection temperature 270°C, injection volume 1 µL, split ratio 20:1, split flow 19.9 mL/min, pressure- 7.32 Psi, controlled linear velocity 36 cm/sec, total flow 23.8 mL/min, carrier gas He, column flow 1.0 mL/min, Oven initial temperature: 45° C, hold 3.70 min, Rate 10° C/min, Final temperature: 295° C, hold 10 min, total run time 38.70 min.

HPLC Analysis by the Forensic Science Center "I. Vucetic" in Croatia

HPLC analyses were conducted using LC 1200 (Agilent: Santa Clara, CA, USA) with Waters symmetry column, C18 3.5 µm, 4.6 x 100 mm (Waters: Milford, MA, USA), T_{column} = 40° C, flow rate: 1.0 mL/min, eluent A (acetonitrile [ACN]), eluent B (H_2O:TFA), Program: Start - 40% A, 60% B, 29 min. - 95% A, 5% B, 30 min. - 40% A, 60% B, injection volume = 20 µL, λ_1= 591.0 nm (Ref. 360 100), λ_2= 591.0 nm (Ref. 360 100) Run time = 30 min + 3 min stabilization. Crystal violet in methanol was used as a standard. Ink samples were analyzed by extracting from paper with methanol. Only samples that exhibited luminescent properties after visualization in VSC were analyzed with HPLC.

MALDI-TOF-MS, DART-QTOF-MS, TLC, LC-MS Analysis by the International Forensic Research Institute and Department of Chemistry and Biochemistry, Florida International University, United States

MALDI-TOF-MS analyses were conducted on a Voyager DE Pro TOF mass spectrometer (Applied Biosystems: Carlsbad, CA USA). Sample preparation involved cutting a ~2x2 mm portion of the ink on whatman 42 paper (Whatman: Maidstone, UK) and attached to a 100 well stainless steel target (JBI Scientific: Huntsville, TX, USA). The matrix used was 9-aminoacridine (9AA: Aldrich: St. Louis, MO, USA) dissolved in 70% methanol: water (5mg/mL). 0.5 µL of the matrix solution was spotted on top of the sample on the target. Instrumental parameters were as follows: 337 nm Nitrogen laser, 3ns pulses, 2Hz, 50 shots per sample, negative and positive mode, mass range m/z 100-1000. Data Analysis was performed using Data Explorer TM software (v 4.0.0.0: Applied Biosystems, Carlsbad, CA, USA). Samples analyzed by MALDI-TOF-MS include writing instrument Y, writing instrument Z, and crossed line intersections with writing instrument Y on top, and writing instrument Y on bottom.

The LC-MS analyses were conducted using a zorbax column coupled to a 6530 Q-TOF-MS (Agilent: Santa Clara, CA, USA). Chromatography parameters were as follows: 1.0µL injection volume, T_{column} = 40° C, flow rate: 0.400 mL/min, eluent A: water, ammonium formiate pH 4.0 (adjusted with formic acid); eluent B: acetonitrile (ANC), 0.1% formic acid, program: start - 5 min 95.00% A, 5.00% B, 25 min. 5.00% A, 95.00% B, 30.0 min total runtime total. Electrospray ionization and mass spectrometer parameters:

heater gas at 350° C, drying gas flow at 7 L/min, nebulizer at 35 Psi, sheath gas at 375 C, sheath gas flow at 11 L/min, cap voltage at 4000V, fragmentor voltage at 135 V, skimmer voltage 65V, and mass range of 50-1000 amu. Mass Chromatogram, mass spectra, and data acquisition were achieved using MassHunter Workstation Software LC/MS Data Acquisition for the 6200 series TOF/6500 series Q-TOF (v B.05.00: Agilent: Santa Clara, CA, USA). Samples were extracted from paper with 0.1 mL methanol (HPLC grade, Thermo Fisher Scientific: Waltham, MA, USA). Samples analyzed include methanol blank, whatman paper blank, writing instrument Y extract diluted 1:10, and writing instrument Z extract.

The DART-TOF-MS analyses were conducted using a 6530 Q-TOF-MS (Agilent, Santa Clara, CA) coupled to a DART SVP (IonSense, Saugus, MA) ambient ionization source. The experimental parameters were as follows: positive ion mode with a DART helium gas at 350° C, Q-TOF heater gas at 350° C, drying gas flow at 0.2 L/min, fragmentor voltage of 175 V, skimmer voltage 65 V, and a mass range of 100-1000 amu. A 5ppm solution of polyethylene glycol 600 (Emerald Biosystems, Bainbridge Island, WA) in 50:50 water:methanol (Thermo Fisher Scientific, Waltham, MA) was used as a quality control standard and internal mass calibrant. DART ion source control was achieved using DART SVP software (v 3.0.x: IonSense, Saugus, MA). Mass spectra and data acquisition were achieved using MassHunter Workstation Software LC/MS Data Acquisition for the 6200 series TOF/6500 series Q-TOF (v B.05.00: Agilent, Santa Clara, CA). Samples were analyzed directly from paper substrate. Samples analyzed include paper blank, writing instrument Y, and writing instrument Z.

The TLC separation were performed using silica gel plates heated at 60° C for 20 min. with mobile phase: ethyl acetate/ethanol/distilled water (70:35:30, v/v/v). Ink was extracted from paper using 0.1mL pyridine and spotted using tube capillary 1.5-1.8 x 90mm (Kimble Chase: Vineland, NJ, USA). VSC observations were made using the VSC-200 (Foster and Freeman, UK) under spot light source (white light) with 440-580 nm filter. Samples separated via TLC include writing instrument Y, writing instrument Z, paper blank, and pyridine blank.

4.3 Results

GC/MS and TLC Analysis Performed at the Forensic Chemistry Department, Ministry of Interior of the Former Yugoslav Republic of Macedonia

Separation of pen inks was achieved, at varying degrees of success, utilizing three different solvent systems. The visual results of the separation can be seen in Figure D1.

The TLC separation of writing instruments M and L in the 1-butanol, ethanol, water (50:20:30) solvent system can be seen in Figure D2 and under spot light source (440-580nm filter). The luminescent spots of writing instruments M and L can only be visualized under these light conditions. The TLC separation of writing instruments A and Y in the same solvent system can be seen in Figure D3, and under infrared and spot (440-580 nm) light sources. The luminescent spots can only be visualized under these conditions. The separation of writing instruments B, Q and C under spot (440-580 nm) light source can be seen in Figure D4. Only one component of writing instrument B was luminescent, with little separation overall.

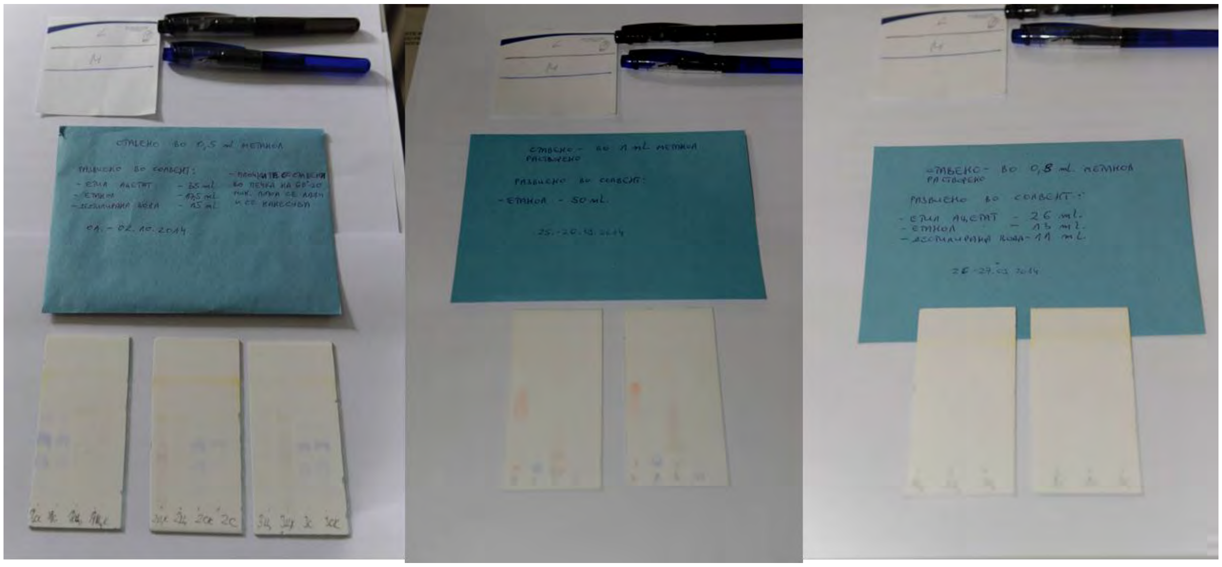


Figure D1. Same writing instruments analyzed via TLC utilizing different solvent systems.

The gas chromatogram of the luminescent zone of writing instruments L and M can be seen in Figure D5 in which four distinct elution peaks were separated at retention times (RT) of 11.075 minutes, 11.102 minutes, 12.135 minutes, and 25.77 minutes. The mass spectra of each individual peak can be seen in Figure D6, in which degradation products of crystal violet were confirmed with the NIST standard reference database.

Figure D2. Writing instruments M and L separated via TLC: (left) separation visualized in ambient conditions, (right) TLC plate visualized in VSC under spot light (440-580nm) exhibiting luminescent spots that are invisible to the naked eye (colorless).

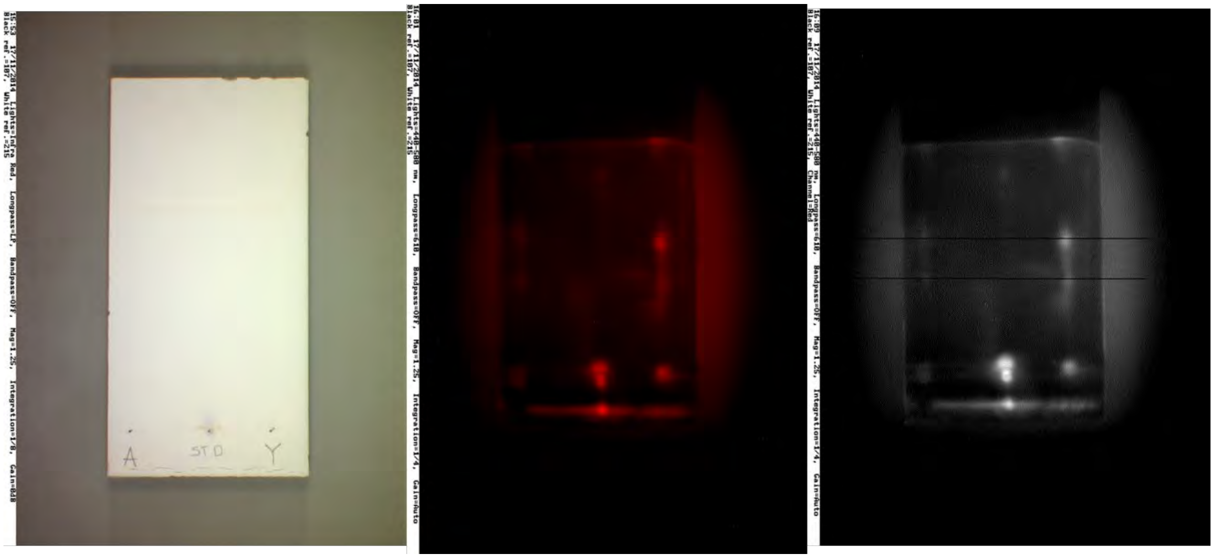


Figure D3. Writing instruments A and Y separated via TLC: (left) separation visualized in ambient conditions, (middle) TLC plate visualized in VSC under IR light, and (right) TLC plate visualized in VSC under spot light (440-580nm) exhibiting luminescent spots that are invisible to the naked eye (colorless).

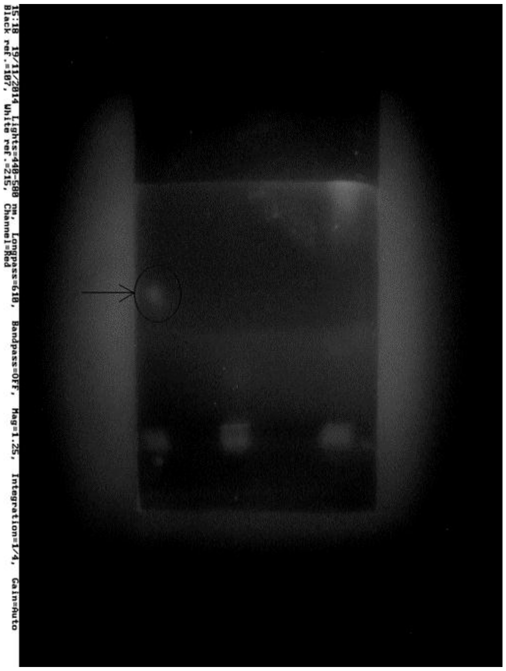


Figure D4. Writing instruments B, Q and C separated via TLC visualized in VSC under spot light (440-580nm) exhibiting lack of luminescence with the exception of one spot for instrument B.

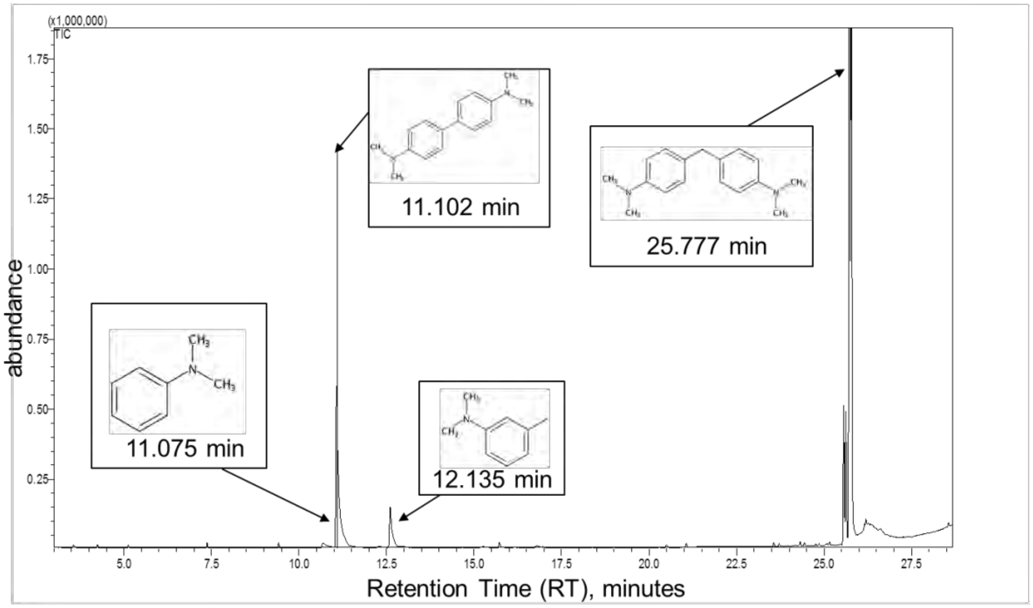


Figure D5. Total Ion Gas Chromatogram for fountain pen ink extract exhibiting four distinct peaks which correspond to Crystal Violet degradation products.

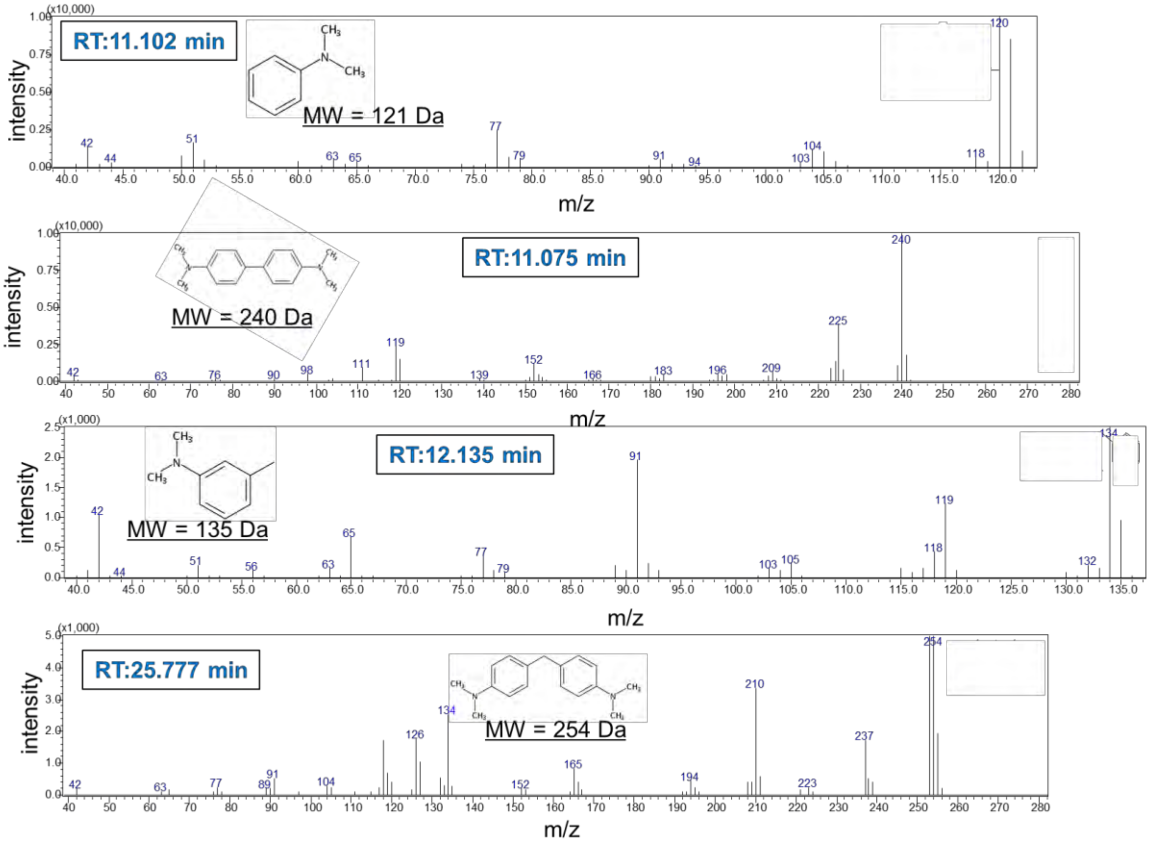


Figure D6. Electron Impact (EI) Mass Spectra for chromatographic peaks, corresponding to degradation products of Crystal Violet and confirmed with NIST Standard Reference Database.

HPLC Analysis Performed at the Forensic Science Center "I. Vucetic", Croatia

Prior to HPLC analysis, all inks were visualized in the VSC under IR and spot (580-725 nm filter) light sources to confirm luminescence. An image of the fluorescent visualization of writing instrument A can be seen in Figure D7. Invisible migration was observed in writing instruments Y and Z, with a luminescent area surround the ink on paper, which can be seen in Figure D8. The liquid chromatogram of the standard crystal violet can be seen in Figure D9. The chromatogram for instrument A (Figure D9) shows the presence of crystal violet, with similar peaks at the same elution times. The chromatogram for writing instrument Z did not reveal any useful information as to the identity of the compound causing the luminescent migration region, but the chromatogram for writing instrument Y can be seen in Figure D10 and contains peaks with elution times that are consistent with crystal violet.

Figure D7. VSC image of writing instrument A under spot light source (580-720nm) exhibiting luminescent properties.

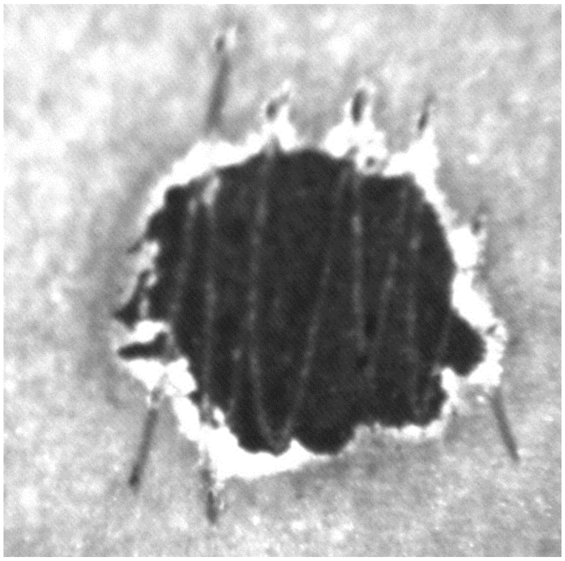


Figure D8. Invisible (colorless) migration observed for writing instruments Y and Z in VSC under spot light source.

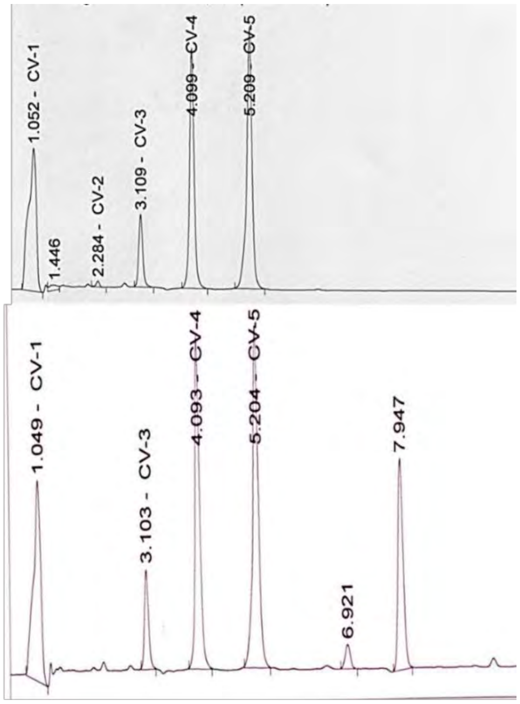


Figure D9. Liquid chromatograms of (top) standard Crystal violet and (bottom) writing instrument A, exhibiting presence of crystal violet and another (6.9 and 7.9 min) blue colorant in the formulation of writing instrument A.

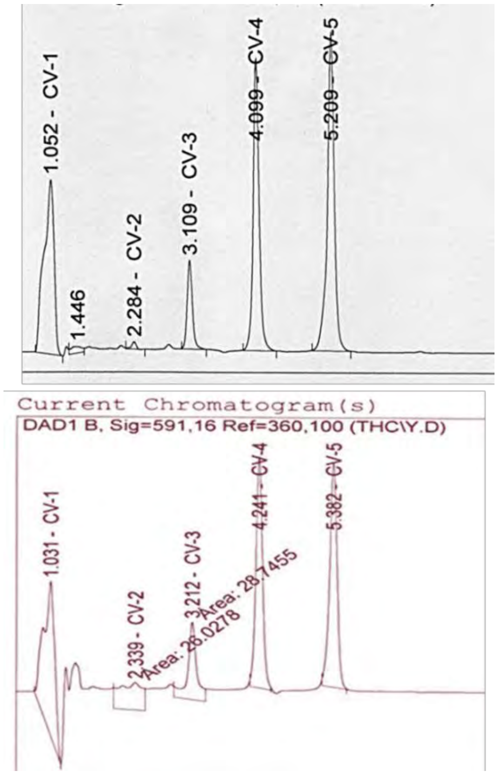


Figure D10. Liquid chromatograms of (top) standard crystal violet and (bottom) luminescent invisible (colorless) migration area of writing instrument Y, exhibiting presence of crystal violet in writing instrument Y formulation.

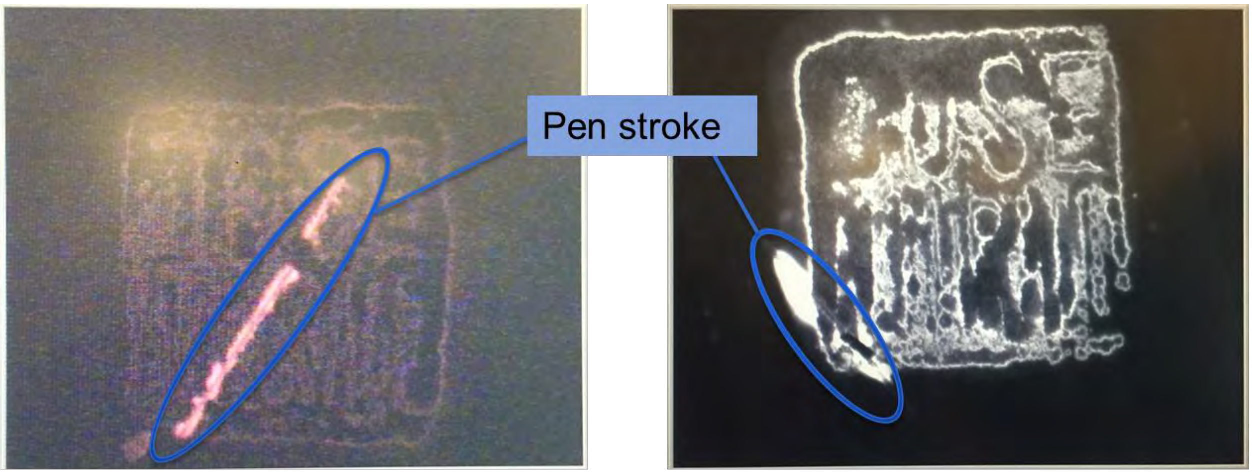


Figure D11. Cross line intersections of writing instruments Y and Z visualized in VSC exhibiting invisible migration (colorless) under spot light source (480-620nm) in color mode (left), and black and white image mode (right).

MALDI-TOF-MS, DART-QTOF-MS, TLC, LC-MS Analysis Performed by the International Forensic Research Institute and Department of Chemistry and Biochemistry, Florida International University, United States:

A colorless, therefore invisible migration band was observed at the interface of the paper and the visible inks when writing instruments Y and Z were viewed in the VSC under spot light source (480-620 nm filter), as illustrated in Figure D11. The MALDI-TOF-MS spectrum obtained of writing instrument Y contains molecular ions that correspond to multiple dyes present in the formulation of the ink (Figure D12 and Figure D13).

The series of molecular ions present in positive mode at m/z 344, 358, and 372 correspond to methyl violet minus a chlorine atom and its degradation products, which preferentially ionize in the positive model. It has also been reported that the m/z values at 358 and 344 actually correspond to distinct crystal violet molecules with less than six methyl groups, with the m/z 358 containing five methyl groups and the m/z 344 containing four methyl groups. The intact molecule does not exist in ionized form in the mass spectrum, but the molecule plus a sodium molecule does form a molecular ion which is present at m/z 429.

The presence of methyl violet was confirmed by analyzing an extract of the ink via LC-MS, with the same ions present (Figure D18). In negative mode, the dominant ions present at m/z 712 correspond to Acid Violet 49, which is also present in the formulation of the pen ink, and preferentially ionizes in the negative mode. Acid Violet 49 is also present as a mixture with other dyes that are analogues of the molecule, substituted with additional sulfonated benzene groups. The ion at m/z 925 refers to an Acid Violet 49 analogue (structure seen in Figure D13) and is present in all replicate measurements of the pen ink in negative mode.

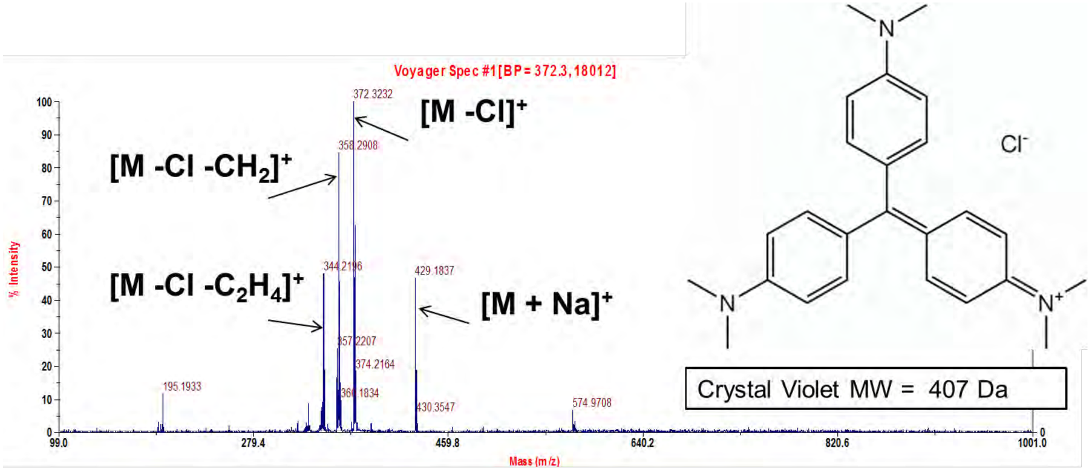


Figure D12. Positive mode MALDI-MS spectrum of pen ink Instrument Y containing Crystal Violet.

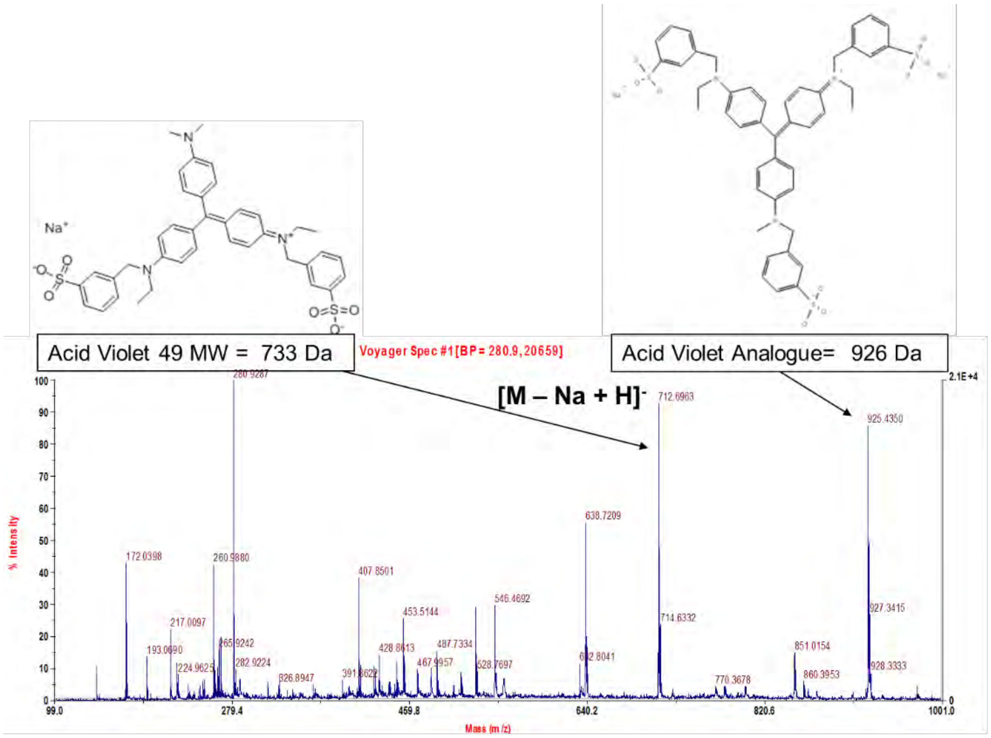


Figure D13. Negative mode MALDI-MS spectrum of pen ink Instrument Y containing Acid Violet 49.

In the positive ion spectra obtained of writing instrument Z (Figure D14), the prominent ionic species present at m/z 575 corresponds to copper phthalocyanine.

In the negative mode, the ions present at m/z 653 and 733 correspond to sulfonated copper phthalocyanine species, which are ionized preferentially in the negative mode, due to the anionic nature of the molecules. These molecular ions give insight into the presence of three distinct copper phthalocyanine pigments used in this ink formulation, one disulfonated pigment, one monosulfonated pigment, and one with no substitutions. Manufacturers often include these sulfonated pigments to increase solubility and thus can be used as a point of chemical characterization.

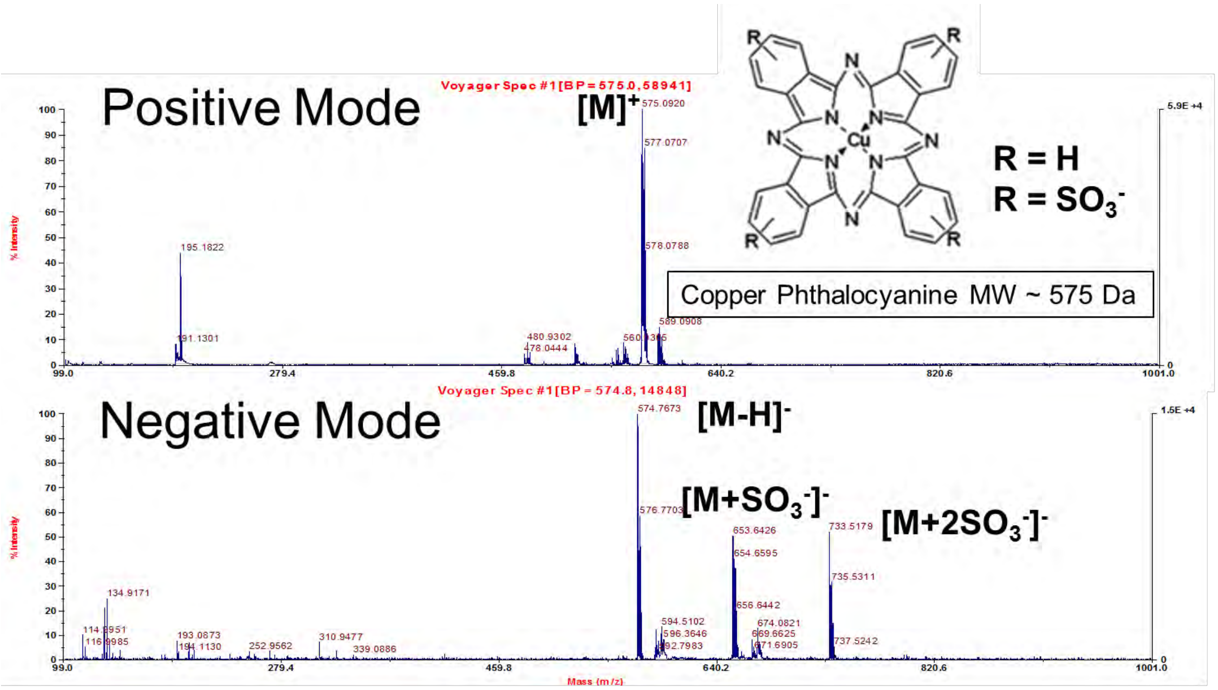


Figure D14. (top) Positive mode and (bottom) negative mode MALDI-MS spectra of stamp ink Instrument Z containing sulfonated Copper Phthalocyanine.

The positive ion mode spectra of the crossed line intersections (both with pen on bottom and on top of stamp ink) contained molecular ions corresponding to both writing instrument Y and writing instrument Z, with the series of m/z 429, 372, 358, 344 originating from the methyl violet present in the pen ink instrument Y, and the peak at m/z 575 originating from the copper phthalocyanine present in the stamp ink instrument Z (Figure D15).

The negative ion mode spectra of the crossed line intersections (Figure D16) also contained molecular ions corresponding to both inks, with the molecular ions at m/z 925 and 712 originating from the acid violet 49 and analogue present in the pen ink writing instrument Y and the peak at 575 originating from the copper phthalocyanine present in the stamp ink writing instrument Z.

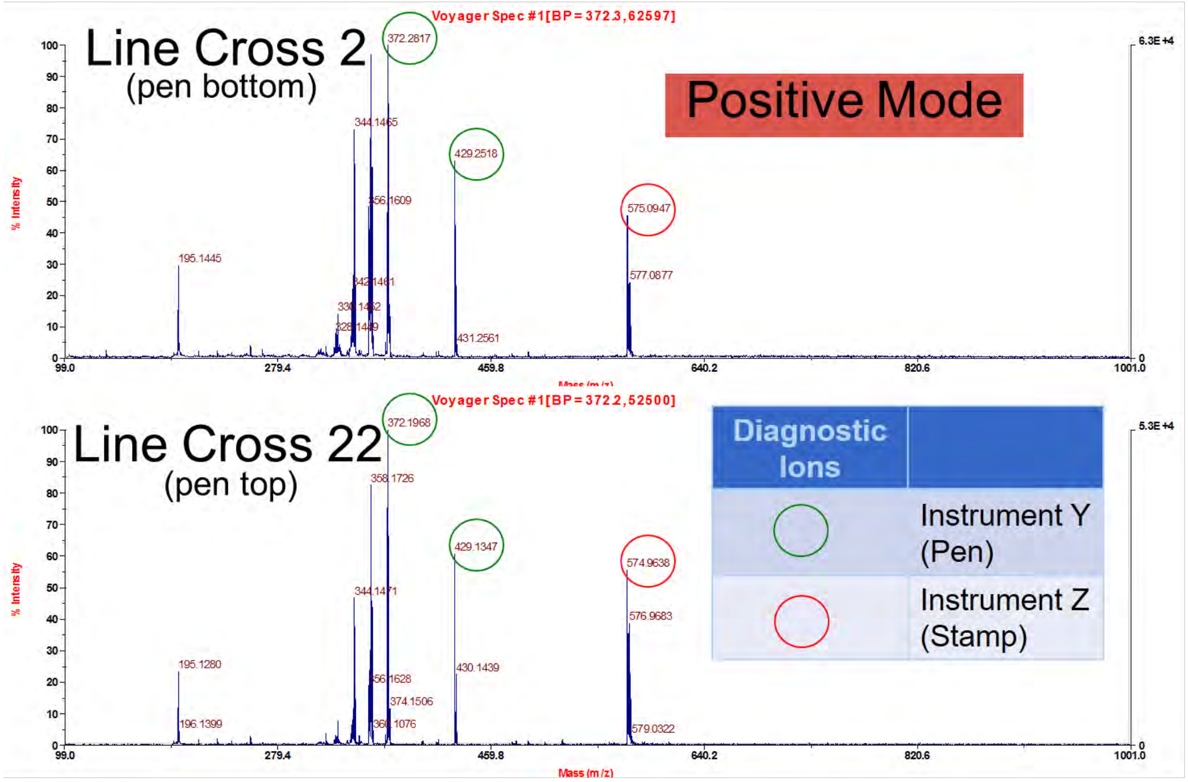


Figure D15. Positive mode MALDI-MS spectra of line crosses containing pen and stamp ink.

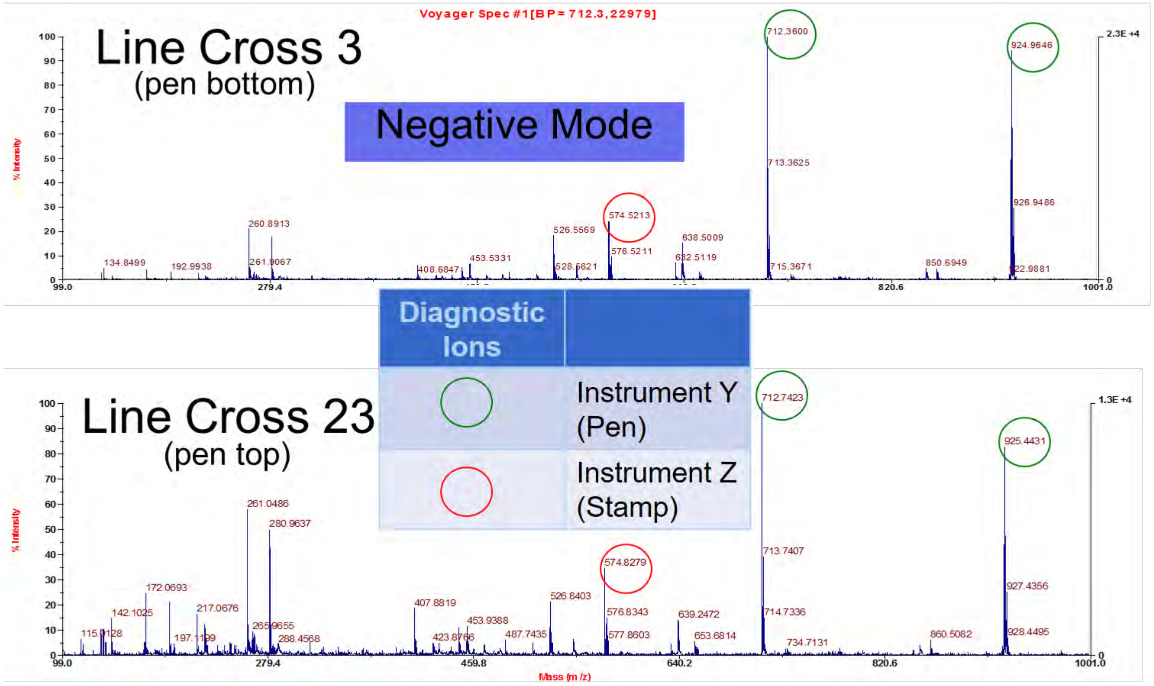


Figure D16. Negative mode MALDI-MS spectra of line crosses containing pen and stamp ink.

The TLC analyses of writing instrument Y revealed the presence of three fluorescent bands visible under spot light source and filter of 400-480 nm (Figure D17). The TLC of instrument Z did not reveal any separation or luminescent visualization. It was confirmed with LC-MS analyses that the fluorescent component of the pen ink is crystal violet, methyl violet and tetramethyl pararosaniline (Figure D18).

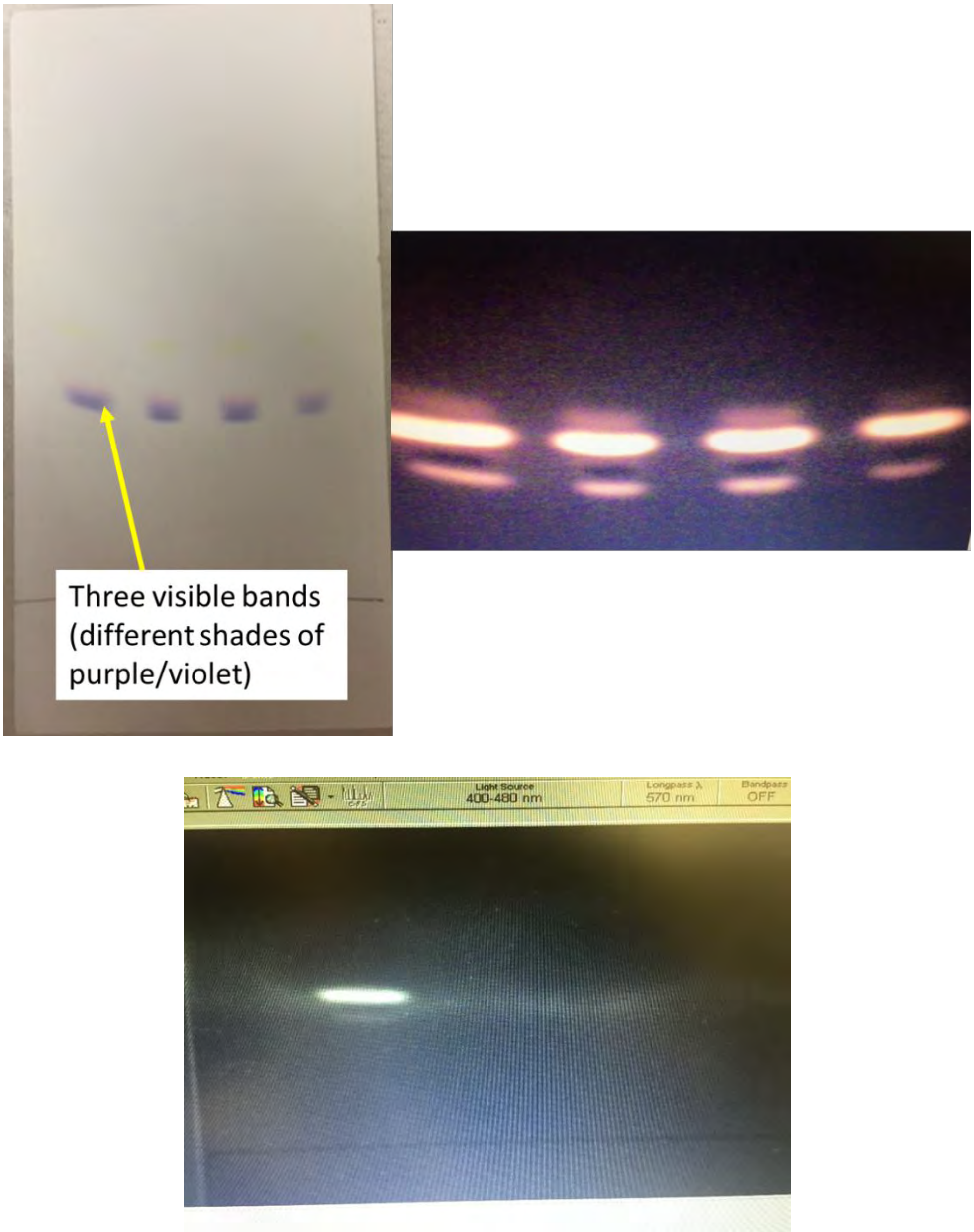


Figure D17. (left) Writing instrument Y separated via TLC with three bands separated and (right) luminescent components of writing instrument Y visualized in VSC under spot light source (400-480nm).

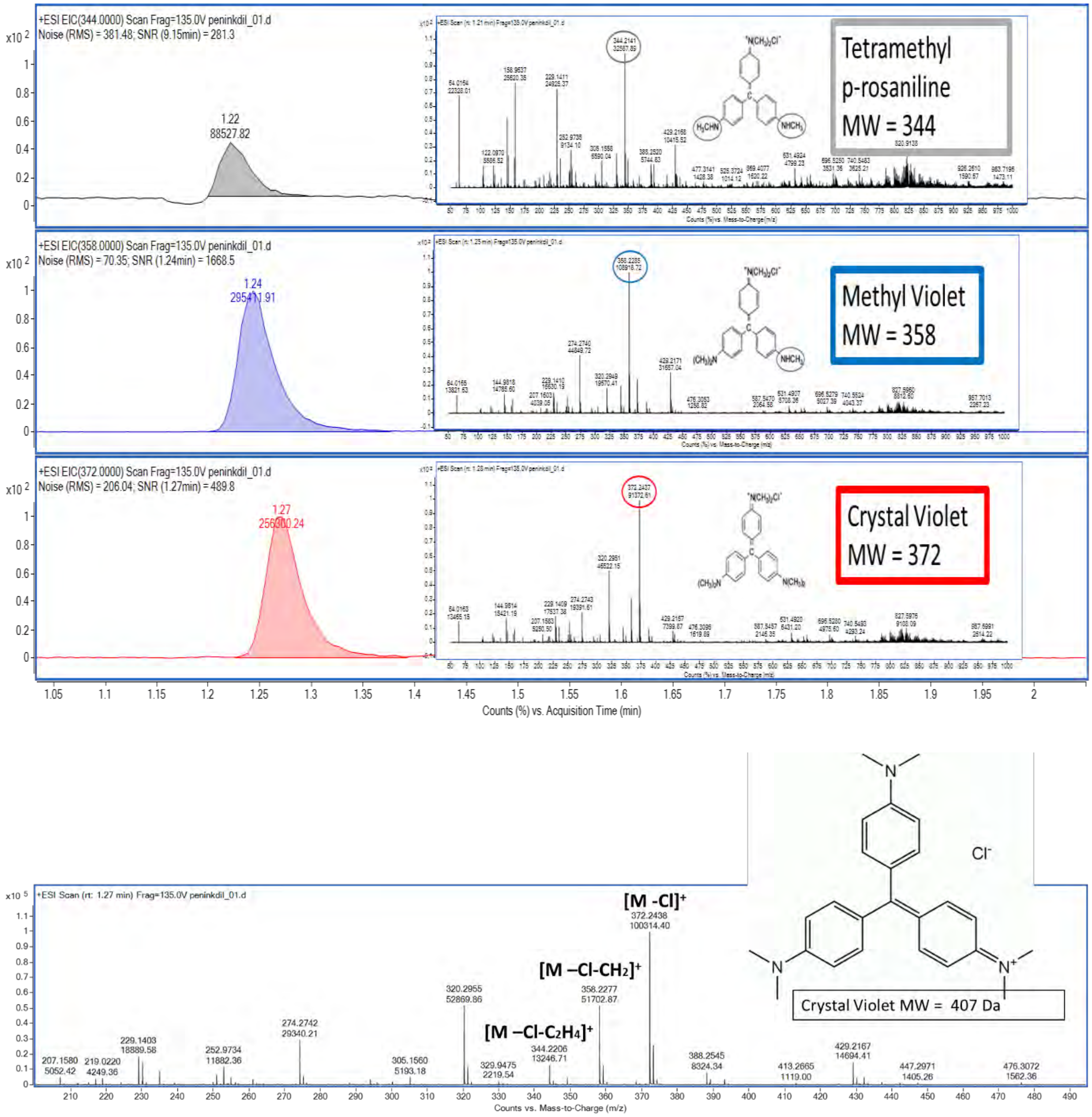


Figure D18. Liquid chromatogram and Positive mode LC-MS spectrum of writing instrument Y pen ink exhibiting three distinct molecules tetramethyl p-rosaniline, methyl violet and crystal violet.

The DART-MS results did not characterize any colorant molecules, though revealed the presence of both polypropylene glycol (PPG) and polyethylene glycol (PEG) polymeric fragments in the pen ink, as seen in Figure D19.

The direct DART-MS analysis of the luminescent bands for instrument Y did not contain any ions that did not come from the blank TLC plate. DART-MS analysis of writing instrument Z also showed the presence of polymeric content. The LC-MS of writing instrument Z corroborated to the presence of the liquid polymeric vehicle component.

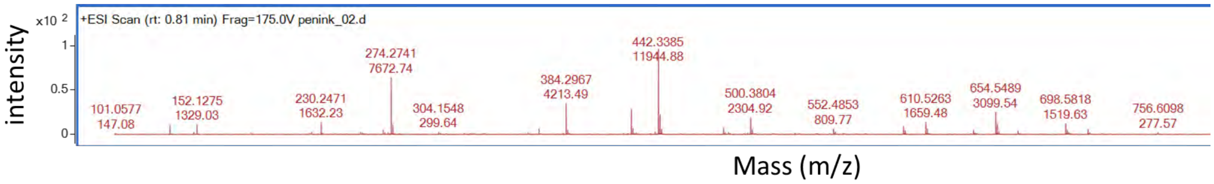


Figure D19. DART-MS spectrum of writing instrument Y exhibiting series of mass fragments that correspond to polyethylene glycol (PEG) at m/z 610, 654, 698 which are 44 units apart and polypropylene glycol (PPG) at m/z 384, 442, 500 which are 58 units apart.

4.4 Discussions and way forward

Table D2 contains a list of the chemical components of interest that were identified by each of the analytical techniques employed by the laboratories in this study.

By placing the TLC plates in VSC 2000 under IR (Infra red light) and a spot light source, the luminescent components in ink samples were visualized. The most intense colours of the spots were developed in the solvent system: ethyl acetate, ethanol, water and plates activated at 60° C for 20 min. This solvent system was utilized by two separate labs and produced the best separation of the inks into luminescent components. Reliable results were not obtained when the mobile phase consisted of only ethanol**.**

Dyes are aromatic, organic components that absorb electromagnetic radiation including visible light with wavelengths of 350-700 nm. Fluorescence generally refers to re-emission in the visible region of the spectrum of 400 nm-700nm, UV Fluorescence or UV excited visible fluorescence is referred to in ink analysis as infrared luminescence or visible – excited infrared luminescence. The properties of these molecules allows for visualization in the VSC under the spot light source.

Characterization of ink samples with GC/MS is important for many reasons, including determination for quality assurance and cases where the age of a document is in question. GC/MS also differentiates and characterizes intermediates of the degradation process of the crystal violet. There was a series of demethylated compounds, including the mono- to penta-demethylated derivatives of crystal violet, which correspond to the luminescent regions separated by TLC, which were invisible to the naked eye.

An invisible migration band may be the result of and/or influenced by the chemistry of the paper (such as additives), the chemistry of the inks (such as solvents), the chemistry of the luminescent agent, and the stability of the components (solvent evaporation rate). It was shown that the components present in this invisible migration region are crystal violet and degradation products, as exhibited and corroborated by HPLC, MALDI-MS, and LC-MS analyses. Two separate labs were able to confirm, independently, that three colorless component of the ink, in this case writing instrument Y, contained crystal violet and degradation productions, which are luminescent compounds. The dyes themselves are not, in fact, colorless, but because they exist at such low concentrations, they are not visible to the naked eye.

Identification of these luminescent compounds was achieved via HPLC analysis of the ink extract and confirmation with a crystal violet standard, and separately, LC-MS analysis of the luminescent bands of the ink, which produced mass spectra corresponding to crystal violet and demethylated derivatives. These compounds are demethylated derivatives of the triaryl methane dye crystal violet, which are methyl violet and trimethyl pararosaniline. The dyes are known to be present in a mixture in the formulation of writing inks. Additionally, it has been reported that crystal violet naturally demethylates over time, thus a solution of crystal violet or an ink containing crystal violet will always have a mixture of dyes present. The HPLC of the crystal violet standard shows multiple peaks, and these peaks can be associated to the demethylated derivatives of crystal violet.

The LC-MS data confirms this, as three distinct peaks were resolved, and the mass spectra of each of those peaks correspond to crystal violet, methyl violet (one less methyl group), and trimethyl pararosaniline (two less methyl groups). The three visible bands in the VSC of writing instrument Y also confirm the presence of three distinct luminescent compounds. The VSC of writing instrument Y also shows a non-luminescent band. This corresponds to a black, non-luminescent dye that is present in the formulation of the ink. The inclusion of a non-luminescent black dye has been reported in the formulation of black pen inks, similar to writing instrument Y. For that reason, the ink itself does not seem to luminesce, but when it is separated into components via TLC, the luminescent dyes are no longer inhibited by the non-luminescent black dye and luminescence is observed.

When inks interact in crossed line intersections, invisible migration may occur, as illustrated in Figure D11. This migration is a result of the interaction of the liquid inks with one another, causing a solvation effect. This causes the luminescent compounds, in this case crystal violet and derivatives, to leach out of the ink marking. Once this occurs, the quenching effect of the non-luminescent black dye is inhibited, and the crystal violet dyes are able to luminesce. This seems like an invisible migration, probably due to the concentration of the violet dyes which is too low that the color is not visible to the naked eye. That being said, the identification of the luminescent compounds in these crossed line intersections does not give insight as to the sequence of deposition of the inks, as this migratory effect occurs regardless of which ink is deposited first.

While HPLC by itself provides minimally useful information unless a comprehensive set of chemical standards representative of ink substituents is available, LC-MS is a preferred method which allows for both separation of ink components and confirmation with mass spectrometric analyses. The HPLC analyses conducted as a part of this study, however, provided complimentary results to the other analytical techniques and allowed for the identification of crystal violet and derivatives in the ink samples.

MALDI-MS is an effective tool for the characterization of inks directly on paper and it could be minimally destructive to the sample. Positive and negative modes of MALDI can provide complimentary chemical information. The addition of a MALDI matrix improves the spectral quality and reduces the background. Inks in layers/crossed line intersections can be characterized using MALDI-MS, allowing for the identification of the separate inks in a mixture but the layer/line sequence cannot be determined using MALDI-MS. MALDI-MS, as compared to the other combination of chromatographic and mass spectrometric techniques included in this study, allows for the instantaneous characterization of multiple components present in ink, such as the crystal violet, acid violet 49, and copper phthalocyanine molecules identified in this study.

Separation of ink components via TLC prior to further analysis by GC/MS, HPLC, and/or LC-MS allows for isolation and confirmatory characterization of the luminescent component(s) of inks, useful in document examination and intelligence purposes. GC/MS is useful in determining the degradation products of luminescent compounds. HPLC can confirm the presence of a compound if a reference standard is available. LC-MS also allows for identification of luminescent compounds and dyes present in ink formulations. DART-MS is useful when characterizing the semi-volatile solvent and/or polymeric vehicle components of inks. MALDI-MS is a useful technique for the rapid analysis of inks directly on paper that allows for instantaneous characterization of multiple colorant and/or luminescent components that may be present in inks. Overall, this study demonstrates the utility of a protocol involving VSC observation, TLC separation, and subsequent analysis by GC/MS, HPLC, LC-MS, DART-MS, MALDI-MS and/or a combination of these methods for the identification and isolation of luminescent compounds present in the composition of inks for implementation in document examination.

Countries/Labs	Chemical analysis	Components of Interest Identified
Forensic Chemistry Department, Ministry of Interior of the Former Yugoslav Republic of Macedonia	GC/MS, TLC	Crystal violet, degradation products
Forensic Science Center "I. Vucetic", Zagreb, Croatia	HPLC	Crystal violet
International Forensic Research Institute and Department of Chemistry and Biochemistry, Florida International University, Miami, FL USA	MALDI-TOF-MS, DART-QTOF-MS, TLC, LC-MS	Crystal violet, demethylated derivatives (methyl violet, tetramethyl and trimethyl pararosaniline); acid violet 49 and analogue, copper phthalocyanine and sulfonated analogues; polypropylene glycol, polyethylene glycol

Table D2. Summary of components of interest identified in inks via each of the corresponding analytical techniques.

CONCLUSIONS AND MAIN RESULTS

In this work, we studied different behaviors on crossing lines intersection such as ink drag, visible and invisible migration.

We worked on the following hypotheses:

1. Visible ink migration can be used for sequencing of crossing line intersection;
2. Ink migration within CLI can be used for estimating the time gap between the 1st and the 2nd line (Δt);
3. Invisible migration can be used for ink dating;
4. Decreasing luminescence intensity within crossing line intersection can be used to estimate Δt;
5. We are able to identify migrating luminescent ink components;

1. Visible ink migration can be used for sequencing of crossing line intersection

General conclusions – We were able to observe that the humidity and temperature of the working environment have an important influence on the diffusion. Based on project experiments, we concluded that the higher the humidity, the greater the diffusion. Depending on the environmental conditions the appearance of crossed line intersection is different. It is also important to mention that the visible migration is terminated within a certain period of time (within seconds) except at very high humidity.

Methodological results – any kind of stereo microscope and stereo microscope equipped with metameric light are suitable for this methodology.

Limitations – a limited number of liquid inks and paper have been tested.

Future orientations – Further analysis using different liquid inks and writing instruments such as ink-jet printer, felt-tip pen, Ink-pad, liquid ball point pen, should be applied. Additionally, experts should be trained to recognise migratory characteristics before using the method.

2. Ink migration within CLI can be used for estimating the time gap between the 1st and the 2nd line (Δt);

General conclusions – based on experiments outlined in Protocol B, we were able to conclude that under normal conditions there is a correlation between Δt and visible migratory phenomena (visible migration decreases while Δt increases). Under different humidity conditions, experts were able to observe a decrease of visible migration when Δt is longer than one month.

Methodological results – any kind of stereo microscope and stereo microscope equipped with metameric light are suitable for this methodology.

Limitations – a limited number of liquid inks and paper have been tested.

Future orientations – Additional experiments should be conducted in order to understand the interaction of ink and paper and/or ink to ink.

3. Invisible migration can be used for ink dating

General conclusion – we could show that if invisible migration is observed on a questioned document, it is basically possible to apply this method for ink dating analysis.

Methodological results – any kind of fluorescence microscopy is suitable for this methodology.

Limitations – we are aware that only for a few inks invisible migration can be observed. Thus, these type of questioned documents cannot be used for ink dating purposes with this method.

Ink invisible migration is a very slow process: time-consuming and one will not be able to observe this phenomenon in old questioned documents anymore.

Future orientation – more detection unit such as metameric light (chromatic luminescence) and new detection filters have to be tested at a larger scale. More questioned documents (inks and paper) in different environmental conditions should be tested in order to prove the effectiveness of this method.

4. Luminescence intensity within crossing line intersection can be used to estimate Δt;

General conclusion – we could show that luminescence intensity within crossed line intersections depends on the time gap between the 1st and the 2nd line.

Methodological results – any kind of fluorescence microscopy is suitable for this methodology.

Limitations – fluorescence intensity drops very fast in the time gap is more than a few weeks. Therefore, this method can only be used to distinguish between very short Δt and Δt more than a few weeks.

Future orientation – the time length of fluorescence degradation has to be tested with more questioned documents (inks and paper) in different environmental conditions.

5. We are able to identify migrating luminescent ink components;

General conclusion – We were able to identify the components present in both visible and invisible migration such as crystal violet and its degradation products.

Methodological results – all mass-spectroscopic methods (except LCMS) were suitable.

Limitations – some of the migrating substances could not be identified by liquid chromatography.

Future orientation – we should combine separating and detecting methods (e.g. TLC, GCMS and MALDI-TOF) to be able to get pure single components for the identification of the luminescent components**.**

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ANNEX 1. GLOSSARY

Anti-Stokes Luminescence: Luminescent materials which are capable of emitting in the visible light range (380-780 nm) when excited with infrared (IR) radiation.

Capillarity: is the ability of a liquid to flow in narrow spaces without the assistance of, or even in opposition to, external forces like gravity.

Chromatic Luminescence: when using metameric light or a visible light excitation without UV/IR, the emission is observed in the visible spectrum (380-780 nm).

CLI: Crossed line intersection. It is the intersection between the 1st and 2nd inks.

ΔT (Delta Time): is the time gap between drawing of the 1st ink and drawing of the 2nd ink in a CLI.

Diffusion: spread effect of components of the ink towards the paper or towards another ink.

Dilution: The action of making a liquid ink less concentrated.

G/HP: Groove and humid ink path, meaning that ink is still wet.

G/DP: Groove and dry ink path, meaning that ink is dry.

Hydrophobic ink: ink not diluted by water.

Hydrophilic ink: ink tends to be dissolved by water.

Immiscible inks: when two inks do not dissolve in one another (e.g. hydrophilic and hydrophobic ink).

Ink drag: is produced by the mechanical dragging of the visible/invisible components of the 1st liquid ink line by the mechanical movement of the 2nd writing instrument.

Ink dating: processes to determine when one or several ink lines were performed.

Invisible migration: it is an ink migration not visible to the naked eye. An appropriate instrument is necessary to observe it.

IR Luminescence: excitation in visible light and emission observed in a shift against infra-red wavelength.

Liquid ink: Water based inks.

Metameric light: Visible light in which the intensities of RGB can be modified.

T&I: relation between Time & Inks.

UV fluorescence: excitation in UV light (254 and/or 366 nm) and emission observed in the visible wavelength.

Visible migration: is the visible diffusion of ink components (dyes) towards the paper or towards another ink.

ANNEX 2. LIST OF INTERPOL PARTICIPATING MEMBER COUNTRIES*[2]

1	Algeria	Redjah Hakim
2	Argentina	Borghi Josefina
3	Azerbaijan	Malikov Ali, Abbasov Nail
4	Bahrain	Alsaeedi Mohamed Khaled Mahmood, Daraj Isa Hamad Othman
5	Bangladesh	Patwary Javed
6	Belgium	Coenraets Françoise
7	Bosnia and Herzegovina	Radović-Rajević Gordana, Rašidović Muhidin
8	Canada	Binette Julie
9	Comoros	Ibrahim Mohamed
10	Croatia	Ledić Andrea
11	Egypt	Abdelrhman Ahmed, Elshandidi Medehat Mohamed
12	Finland	Syrjänen Taru
13	Former Yugoslav Republic of Macedonia	Popovska Sofia, Antikj Vesna, Djidrovska Daniela
14	France	Beck Jaqueline, Beck Emmanuel, Balbuena José, Balbuena Jaime, Baker Nathaniel, Oriol Florence, Campserveux Sylvie, Tixier Celine, Guillier-Sahuque Dominique, Bourgeois Jean-Michel, Luca Mayor Jacqueline, Theismann Valerie, Rembarz Jean-Pierre, Badufle Christel, Carliez Sophie, Dolbeau Christophe, Georges Jean-Luc
15	Georgia	Korkotashvili Ekaterine, Mikadze Tea
16	Germany	Fabich Markus

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[2] List of participants who regularly attended workshops on the *Physical-Chemical Study of Crossed Line Intersection* at INTERPOL General Secretariat in Lyon, France during the period of 2013-2016.

17	Ghana	Asiedu Ampomah Michael
18	Greece	Tousi Christina
19	Hungary	Karoly Istvanne Agnes
20	India	Vinod Kumar, Saha Sujay, Handa Deepak Raj, Shri Ravi
21	Indonesia	Erzyanto Yukama, Eri Hermansyah Eri
22	Iran	Jalali Hamid Reza, Mohammadi Goudarzi Ahmad, Boragh Mohammad, Mobarakpour Hamzeh, Serkani Rouhollah, Ardi Esmaeil
23	Iraq	Al Saedi Omar Sabah Jasim
24	Italy	Dellavalle Francesco, Candeo Graziamo
25	Kenya	Kimani John Muinde
26	Kuwait	Alshammeri Salah, Alsahlawi Abdullah
27	Latvia	Kudrjašova Inna, Freidenfelds Vitālijs
28	Lebanon	Mhanna Ghaleb, Assaf Hassan, Beaini Camile, Al Annan Mahmoud, Korresly Nazih
29	Lithuania	Bartkeviciene Diana
30	Luxembourg	Lucius Chloé
31	Macao, China	Lao Chi Keong
32	Malaysia	Othman Huzaini, Tan Yan Thian
33	Mexico	Miguel Oscar Aguilar
34	Morocco	El Jirari Abdelali
35	Niger	Yahaya Bako Abdou Salam
36	Nigeria	Etim Cornelius
37	Norway	Sletten Marianne, Isager Gunhild
38	Oman	Al Kalbani Abdullah, Al Mashikhi Ahmed

39	Peru	Vargas Merida Carlos
40	Poland	Konarowska Urszula, Czerniawski Wojciech, Lasinska Anna
41	Russia	Mokrousov Alexey, Toropova Marina
42	Serbia	Dabetic Kirst Natasa, Georgiev Dunja
43	Slovakia	Jabconová Adriana, Uvačková Alena, Antalová Mariana
44	Spain	Curto Garcia Ruben, Baron Martin Jesus, Fernandez Salmeron Vicente, Alonso Dominguzz Javier, Julio Saez Martinez, Vicente Ayra Daniel, Venzal Placido Pedro
45	Sri Lanka	Jayasundara Ranbanda, Kalupage Kumudu Apsara
46	Sudan	Hamdo Abdelkareem, Zeinalabdeen Mahir
47	Switzerland	Hofer Rolf
48	Tanzania	Kitandala Chrisantus, Waryoba Lilian Benjamin
49	Timor-Leste	Da Costa Mario Vitor
50	Tunisia	Chafchar Nabil, Chafchar Nabil
51	Turkey	Sertce Selahattin, Aydogmus Bulent, Aksoy Cagdas, Kocabey Hakki, Çağdaş Aksoy
52	Uganda	Sebuwufu Erisa
53	United States	Joseph Stephens, Watts Gabriel, Almirall José
54	Zimbabwe	Gombakomba Clara

ANNEX 3. INSTRUMENTAL TECHNIQUES

EQUIPMENT LABORATORIES	VSC	LUMINISYS	PROJECTINA DOCUCENTER	MICROSCOPY	TLC	HPLC	GC-MS	MALDI-MS	OTHER
Belgium		*X*		*X*					
Croatia	*X*				*X*	*X*	*X*		
Former Yugoslav Republic of Macedonia	*X*			*X*	*X*		*X*		*SEM*
France		*X*		*X*					
Georgia				*X*					
Latvia	*X*			*X*					
Niger			*X*						
Poland	*X*			*X*					*SEM*
Slovakia	*X*			*X*					
Spain	*X*	*X*		*X*					
Switzerland	*X*			*X*	*X*	*X*	*X*		
United States	*X*				*X*	*X*	*X*	*X*	

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