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Characterization and identification of luminescent components in inks using various analytical techniques for the study of crossed-line intersections

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ABSTRACT

Several analytical instrumental techniques have been tested and utilized in an effort to determine the sequencing in crossed-line intersections (CLI) in order to gain insight into the eventual development of a standardized method to determine temporal sequence of line writing. One important facet of this study was to determine the chemical identity of the luminescent compounds present in the formulation of inks to better understand the interaction of different inks in crossed-line intersections. This study involved independent analyses of a number of inks by three laboratories. A combination of Thin Layer Chromatography (TLC), Gas Chromatography Mass Spectrometry (GC/MS), High Performance Liquid Chromatography (HPLC), Matrix-Assisted Laser Desorption Mass Spectrometry (MALDI-MS), Direct Analysis in Real Time Mass Spectrometry (DART-MS), and Liquid Chromatography Mass Spectrometry (LC-MS) were implemented by the three laboratories in order to characterize the luminescent components of inks present in crossed-line intersections. A combination of luminescent compounds including Crystal Violet and Methyl Violet were characterized and identified to be present in mixtures in the ink formulations utilizing each of the analytical techniques included in this study. However, the temporal sequence of deposition of inks present in crossed-line intersections could not be determined. The protocol described here allows for the isolation and characterization of luminescent compounds present in the formulation of inks to varying degrees, and the information presented here can be used in the future establishment of a standard protocol for the identification of luminescent compounds in inks.

1. Introduction

In questioned document examinations, 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 consensus method to determine the temporal sequence of ink deposition [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, attenuated total reflectance Fourier transform infrared spectral imaging, 3D laser profilometry, and scanning electron microscopy energy dispersive X-ray spectroscopy (SEM-EDX) [1,3–6].

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 [14]. In addition, chromatographic, spectroscopic,

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and mass spectrometric techniques such as High Performance Liquid Chromatography (HPLC), Gas Chromatography (GC), paper chromatography, nuclear magnetic resonance (NMR) spectroscopy, and liquid chromatography mass spectrometry (LC-MS), and gas chromatography mass spectrometry (GC/MS) have been applied to analysis of dyes and pigments [7]. 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 characterizes molecular ions with limited fragmentation as compared to traditional electron impact ionization [8–10]. 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 [9,11].

After conducting non-destructive optical examinations, the chemical analysis of the ink (e.g. ballpoint pen inks, felttip pen inks, ink pad) is useful for the identification and separation of mixtures of organic compounds, including luminescent components. For the past 50 years, optically examining documents and inks with infrared light sources to detect luminescent properties has been well established and readily used for the comparison of inks [12]. However, the limitations of solely relying on optical examination has been repeatedly reported, with the majority opinion necessitating that additional examinations and testing be performed before any conclusion is made [13]. Thus, luminescence observation has been readily combined with other techniques such as Thing Layer Chromatography (TLC) to improve the amount of chemical information obtained [14,15]. The biggest obstacle for the utility of optical and luminescence examination for inks is that a majority of inks are mixtures of components, some of which are luminescent and others that are not, and the non-luminescent components have a masking effect and therefore inhibit overall luminescence [16]. Therefore, it is most useful to employ optical examination as a preliminary step in the analysis of inks, and to combine with other techniques that can provide complimentary information [17–19].

The project described here was performed in collaboration with three [3] laboratories (in Croatia, Macedonia and USA) in an attempt to establish a standard and reliable method for the determination of the sequence in crossed-line intersections. The specific objective of this protocol 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 the determination of sequence in crossed-line intersections in the future.

Several chemical methods were used by participating countries including: Thin Layer Chromatography (TLC), Gas Chromatography Mass Spectrometry (GCMS), High Performance Liquid Chromatography (HPLC) and Matrix Assisted Laser Desorption Ionization – Mass Spectrometry (MALDI-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:

- MKD: Republic of Macedonia – Thin Layer Chromatography (TLC), Gas Chromatography—Mass Spectrometry (GC/MS);
- CRO: Croatia – High Performance Liquid Chromatography (HPLC);
- USA: United States of America –Matrix Assisted Laser Desorption Ionization—Mass Spectrometry (MALDI-MS), Thin Layer Chromatography (TLC), Liquid Chromatography—Mass Spectrometry (LC-MS), and Direct Analysis in Real Time—Mass Spectrometry (DART-MS).

2. Experimental section

2.1. Materials and methods

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 1:

Writing Instrument A: Ballpoint pen, Stabilo, Ref n° 0800M 97 3, blue ink
Stroke dimension: 0.3 mm
Writing Instrument B: Ink pad, Troadat, Ref n° 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

2.2. GC/MS and TLC analysis by the MKD laboratory

A 10 mm long ink line was cut out and put into a micro-vial with 1 ml of methanol around 15 min. 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 (2–10 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 into the developing chamber and the solvent system allowed to migrate for about 6 cm. The plate was removed from the chamber and dried in cold

Table 1
Chemical Analysis of each ink independently by laboratory in each country.

Countries	Chemical analysis	Writing instruments
Ministry of the Interior, Forensic Chemistry Department, Skopje, Republic of Macedonia (MKD)	TLC	L, M and traces of A, B, C, Q, Y, Z
	GC/MS	L, M
Forensic Science Centre Ivan Vucetic, Zagreb, Croatia (CRO)	HPLC	Y, Z and traces of A, B, L, M
International Forensic Research Institute and Department of Chemistry and Biochemistry, Florida International University, Miami, FL USA	MALDI-TOF, DART-MS, TLC, LC-MS	Y, Z