Comparison of optical techniques and MeV SIMS in determining deposition order between optically distinguishable and indistinguishable writing tools

Abstract

In the forensic investigation of questioned documents, it is often very important to know the deposition order of two different writing tools at their intersection on a paper. In the present work, intersections of several writing tools were studied using optical techniques that are standardly applied for questioned documents examination in a forensic laboratory, and an accelerator-based Ion Beam Analysis (IBA) technique called Secondary Ion Mass Spectrometry using MeV ions (MeV SIMS) that is applied in an accelerator facility. MeV SIMS provides molecular information about the studied writing tools, which is an added value and can be also applied for determination of deposition order but was so far relatively rarely used in forensic studies. Aim of this paper is to compare performance of optical techniques and MeV SIMS for several combinations of intersecting lines. Cases were divided into those in which optical techniques can distinguish used writing tools and those which are optically completely indistinguishable. In the latter cases, we show that although mass spectra of used writing tools (blue ballpoint pens) had extremely small differences, these in combination with advanced and most importantly objective multivariate algorithms could be very beneficial in resolving the deposition order at the intersection of optically indistinguishable writing tools.

Keywords:

forensic document examination, crossing ink lines, optical techniques, MeV SIMS

1. Introduction

Today, most of the official documents, such as contracts or testaments, which are often the subject of counterfeiting, are produced with commercially available printers. On such documents, a stamp impression or signatures using different types of pens are also applied. The places where such writing tools intersect may reveal if the document is original or was modified in any way after the moment it was produced. Various techniques have been introduced in the forensic work to solve the problem of intersecting lines. Recently, a comprehensive review of different methods that were used so far was given in the work of e Brito et al.[1] In their work, all the techniques ranging from optical methods, introduced in the ’60s and ’70s, over lifting techniques, electronic microscopy, chemical and surface analysis, introduced at the beginning of this century, and finally hyperspectral imaging and chemometrics, introduced in the last decade, were critically assessed. The advantages and limitations of all the techniques, as well as their efficiency in revealing proper deposition order were also discussed. It was emphasized that optical methods that are non-destructive, fast, and easy to apply will probably remain prevalent in the daily forensic work and that the need for other analytical techniques, which are more expensive and complicated to perform, sometimes destructive and time consuming would appear in more complex cases where the information obtained from optical methods is inconclusive and not sufficient to give a proper answer.

The forensic laboratory in which the analysis of intersections is conducted is the only specialized institution for forensic examination in the Republic of Croatia. Handwriting and document examination has been conducted ever since the very establishment in 1953. In 1998, handwriting and document experts became full members of handwriting and document expert working groups within the European Network of Forensic Science Institutes (ENFSI).[2] In 2010, the Centre formally became an accredited laboratory in accordance with the international standard ISO 17025. The Laboratory for forensic handwriting and document examination is equipped with state-of-the-art instruments. Document forensic experts are conducting analyses of questioned documents on a daily basis. From a total number of questioned document cases, only about 10% of the cases involve determination of chronological sequence of two or more writing tools, i.e. intersecting lines. The examination procedures depend on the nature of the intersection areas and no technique is known which is applicable to the whole range of cases with intersecting lines.[3] The examination is most often conducted by using non-destructive techniques, but in some cases, semi-destructive techniques such as Raman spectroscopy may also be applied. Standard non-destructive examinations, including optical microscopic techniques and IR absorption/luminescence, are performed first. The forensic document and handwriting experts at the forensic laboratory conduct examination of intersecting lines mainly using non-destructive optical methods, but these are not sufficient in some real-life cases. The purpose of this paper was to seek another reliable method to help resolve such cases, specifically the ones that involve inks with very similar composition.

Time-of-flight Secondary Ion Mass Spectrometry (TOF-SIMS) using keV ions is a surface technique that provides chemical information from the uppermost few monolayers with superior lateral resolution and was applied for the first time to determine deposition order on intersecting lines for different ballpoint and fountain pens by He et al.[4] In combination with attenuated total reflectance-Fourier transform infrared imaging (ATR-FTIR), TOF-SIMS was used to analyze inks, toners, and stamp inks[5, 6]. Also, sequences of intersections made with black ballpoint pens were studied recently by Goacher et al.[7] Those studies have shown high potential of the technique in analyzing intersecting lines, but also introduced a problem in solving cases that involve writing tools that penetrate deeper into the paper. For the last ten years, several laboratories around the world, among them the accelerator facility in which the analysis of intersections is performed, have started to use MeV ions for desorption of secondary molecular ions from the sample surface, the so-called MeV Secondary Ion Mass Spectrometry (MeV SIMS) technique. In case when MeV ions are used instead of keV ions, higher secondary molecular ion yields are expected as well as less fragmentation of large molecules, since the dominant mechanism of interaction of MeV ions with the sample surface is electronic instead of nuclear stopping, which dominates when keV ions are used. Concerning forensic examination of questioned documents, the technique has demonstrated success in determining deposition order of fingerprints and inks on paper[8]. In the case of intersecting lines made by blue ballpoint pens[9], deposition order of all studied combinations was determined with success. The situation was not so clear in some cases when deposition order of laser toners, inkjet inks and ballpoint pens was studied[10]. The cases including laser toner and ballpoint pen were solved successfully using only MeV SIMS technique, but the problem to reveal deposition order in cases where inkjet ink was present remained unsolved. Some of the problematic cases were further resolved by combining MeV SIMS with Particle Induced X-Ray Emission (PIXE) technique which, contrary to surface-sensitive MeV SIMS, provides information from deeper layers. The cases left unsolved concern a lack of presence of unique characteristic X-rays for either the inkjet ink or the other writing tool. The use of MeV SIMS requires access to an ion beam accelerator facility, which is not always available to the members of the forensic community.

In the present work, intersections of several different writing tools (ballpoint pens, a fountain pen, and a stamp) that can be divided into two groups - optically distinguishable and optically indistinguishable, were studied using standard forensic optical techniques, which include microscopic and infrared luminescence techniques, and MeV SIMS. In MeV SIMS, molecules are desorbed from the uppermost layers of the sample thus ensuring the technique is surface sensitive. Obtained results were compared and discussed.

2. Materials and methods

Optical methods. Optical non-destructive techniques used for determination of deposition order at intersecting lines were performed using existing equipment for questioned document examination in the forensic science laboratory. Firstly, the intersections were examined microscopically to determine the nature of the intersecting material, particularly the type of the inks involved. Physical characteristics at the point of intersections were observed under Leica M205C stereo microscope from accompanying Video Spectral Comparator VSC6000/HS workstation (Foster + Freeman, UK), which has multi-angle LED illumination modules. Images were captured at magnification of 30x and were transferred to a computer with VSC6000HS imaging software. The intersections were examined with Olympus BX51 optical microscope from accompanying SENTERRA dispersive Raman spectrometer (Bruker, USA). Images were taken at magnification of 500x with objective 50x, NA=0.90, wd:0.3mm. The images represent an area of 150 x 62 μm^2. At least three different regions at the intersection were examined. The intersections were also examined using the spot infra-red light source with a VSC6000/HS workstation (Foster + Freeman, UK). It should be noted that by using a spot infra-red light source it was possible to determine the sequence of lines only if ink dyes have the property of infrared luminescence and hence the inks containing these dyes show infrared luminescence. This light source is a high-intensity source that is filtered to provide the user with a choice of excitation wavebands of light. In these cases, a 645 nm camera filter with a 485-500 nm green spot filter has been automatically selected. Samples were viewed and captured at 30x digital magnification in autofocus mode.

MeV TOF SIMS. MeV SIMS measurements were performed in a vacuum using a heavy ion microprobe available at the accelerator facility. The setup with the time-of-flight spectrometer described in detail in Tadic et al[11] was used. An 8 MeV Si^{4+} beam focused to approximately 5 × 5 μm^2 was employed to extract the secondary molecular ions. First, a mass spectrum of each writing tool was measured by scanning smaller areas (100 × 100 μm^2) at the sample, far from the intersection region. After that, the intersection region of up to 1400 × 1400 μm^2 was scanned for imaging, and 2D molecular maps of intersections were created. The beam current in pulsed mode was about 0.2 fA. The sample holder was set at +5 kV to accelerate secondary molecular ions toward a TOF extractor. A multi-stop time-to-digital converter (TDC) data acquisition system in heavy-ion-deflection start-mode was used with 100 µs between the ion pulses of 4 ns duration.

Data analysis. An in-house built data acquisition system SPECTOR[12] was used to control all parameters and data acquisition during the experiment. Basic spectra inspection was carried out using mMass[13]. Principal component analysis (PCA) was employed on molecular images using MATLAB tool simsMVA[14] to enhance the contrast between different chemical compositions of each pixel. All images were binned by a factor of 2 (resulting in 64 x 64 pixels from the original 128 x 128 pixels), due to small number of counts per pixel. It is important to mention that some images were cropped due to scattering recorded on the edges of the scan area and appear in different sizes, but all maps contain the whole intersection area and a part of the surrounding region for context. MeV SIMS images were pre-processed using Poisson scaling (or in some cases square root scaling) with mean centering, and 2D Gaussian smoothing with varying standard deviation, as appropriate. Additionally, the score matrices were standardized for contrast enhancement (to have a mean of zero and standard deviation of one). K-means clustering was performed on the most informative principal components to produce the final image with a predetermined number of three clusters (two writing tools and the paper), having the highest silhouette score. In the case of the last two combinations from Table 2, t-distributed stochastic neighbor embedding (t-SNE) algorithm was employed within Orange software[15] on normalized, binned, Poisson scaled and mean-centered data, and 2D Gaussian smoothed with SD = 0.8.

Sample preparation. The intersections were prepared in a way that the first line deposited was left to dry out on a blank white A4 paper for about 1 hour before the deposition of the second line with a different writing tool. In order to perform MeV SIMS analysis, it is necessary to cut out a small portion of the sample which includes the intersection as well as a bit of the surrounding individual ink. Then, the sample is put inside a vacuum chamber, where the analysis is conducted under a pressure of around 10-6 mbar. Hence, this is a destructive process and is meant to be carried out, if necessary, as a last resort. However, in the sense of chemical consistency of the sample, MeV SIMS is not considered destructive, since the achieved primary ion beam dose is well below the so-called static limit of 1012 ions/cm2. The list of all writing tools studied in the present work is given in Table 1. There are two different types of writing tools present. The first type involves oil-based inks such as ballpoint pens, which leave a trace at the surface of the paper. The second type are fountain pen and stamp, which are water-based and penetrate deeper into the paper. Pairs of samples have been produced from these writing tools; each pair is comprised of two combinations with respect to deposition order of the writing tools present. Not all writing tools have been paired. Deposition order of each combination is emphasized in all figures. The studied pairs of samples are given in Table 2. The last two combinations were impossible to distinguish using optical techniques available at the forensic laboratory, hence these cases are deemed especially interesting.

Table 1. Writing tools manufacturers and models.

Writing tool	Manufacturer	Model	Color of ink
Ballpoint pen	Pilot	unknown	blue
Ballpoint pen	BIC	unknown	black
Fountain pen	unknown	unknown	blue
Stamp	Trodat Printy	4912	blue
Ballpoint pen (BP1)	unknown	unknown	blue
Ballpoint pen (BP4)	unknown	unknown	blue
Ballpoint pen (BP2)	unknown	unknown	blue
Ballpoint pen (BP5)	unknown	unknown	blue

Table 2. List of studied combinations of writing tools.

Pair no.	Combination
	Optically distinguishable
1	Fountain pen & BIC
2	Pilot & BIC
3	Trodat Printy & Pilot
4	Trodat Printy & Fountain pen
	Optically indistinguishable
5	BP1 & BP4
6	BP2 & BP5

3. Results and discussion

During image inspection, MeV SIMS, being a surface technique, should yield a discontinued trace from an ink deposited first, with a break located at the point of an intersection of two writing tools. The trace from an ink deposited second should appear continuous. As shown in our previous work, this is the case if oil based ballpoint pens are used[10], while situation is not so simple if water-based writing tools are used[11].

Mass spectra of all writing tools involved in the study are shown in Figure 1. For simplicity, the spectra are ordered according to Table 1. The data were normalized to the total number of counts. The most discriminating features for each spectrum are pointed out. Some of the writing tools contain prominent peaks at high masses (most often dyes and pigments) which make their identification in images easier. On the other hand, fountain pen does not contain any heavy compounds and instead yields sodium with intensities quite different than the other writing tool in the sample, which is then used for separation. It should be noted that the success in separating writing tools in an image largely depends on the combination of writing tools in the sample (i.e. similarity of their compositions). On that note, the last two combinations from Table 2, which are indistinguishable by optical methods, involve two pairs of ballpoint pens having very similar, almost identical mass spectra. Here, all four ballpoint pens possess Basic Violet 3 and Basic Blue 7, common dye components present in most blue and black ballpoint pens.

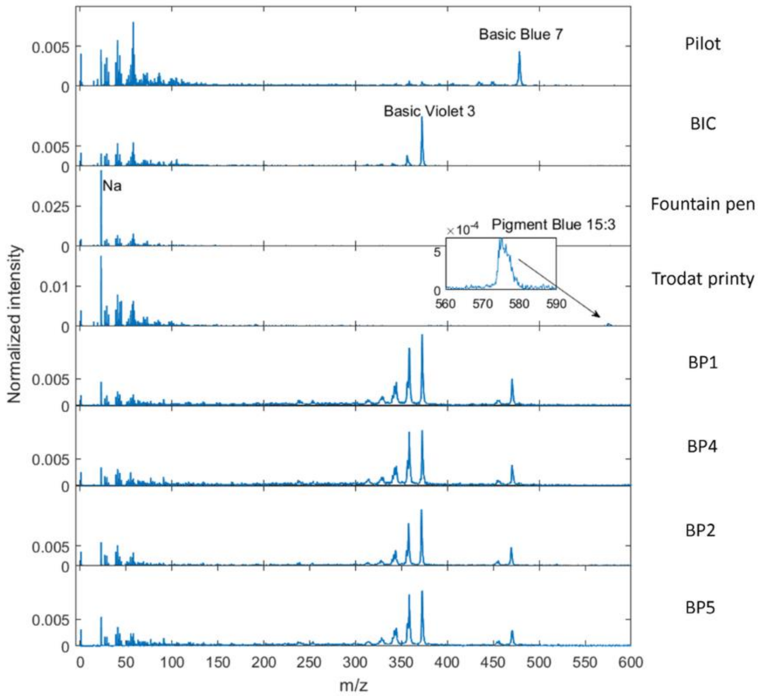

Figure 1. MeV SIMS spectra of individual writing tools ordered from top to bottom according to Table 1.

Non-destructive optical techniques could be applied to determine the sequence of intersecting lines and are routinely employed in the area of forged document forensics. According to the ENFSI-EDEWG Methods[2], it should be noted that in real cases it is often useful to be able to replicate the intersection to be studied under a variety of conditions prior to the examination. If the writing tool involved in the creation of an intersection is available, or the type of the writing tool can be determined, it is desirable to recreate the intersections, or, if not available, with the same types of inks and pigments. Test intersections should represent both line sequences (line 1 on top of line 2; line 2 on top of line 1). Conditions in the test intersection should replicate conditions in the questioned document as much as possible. For instance, the quantity of ink should correspond to the ink quantity of the questioned lines, as well as the applied pressure. Also, the test intersection should be produced under different degrees of ink drying, as the time that the first ink was on the surface before the second one was applied will affect the appearance of the intersection. Test intersection should be made on a paper similar to or the same as the paper containing the intersection to be examined. The examination results obtained from these test intersections are compared to the ones from the unknown intersections. A variety of techniques can be employed to inspect an intersection and the choice of the technique will depend on the type of writing tools involved in the intersection.

Caution has to be taken when one of the inks involved in the intersection is aqueous-based (e.g. fountain pen inks, fiber tip pen inks, highlighter inks, stamp inks, and some inkjet inks) because these inks tend to diffuse into the paper fibers (often no ink deposition occurs on the paper surface, depending on the paper quality), making determination of the sequence difficult and often extremely risky. Therefore, many examinations of intersecting lines result in an inconclusive opinion, particularly if the same ink type and color are involved. The examination of a line intersection problem requires knowledge of inks and their behavior once on a paper surface. Determination of the

type of ink is important so that the appropriate test intersections can be made. Thus, a forensic document expert possessing a great deal of practical experience plays a key role in successful determination of intersecting lines.
In the current study, IR luminescence proved to be especially efficient when one of the two writing tools involved appeared IR-luminescent. Under the optical microscope, the ink colors are clearly different from the colors seen by the stereo microscope. For instance, in a blue vs. black system, the blue ink appears blue and the black ink appears reddish.
It should be noted that the expert examining optical images draws a subjective conclusion based on previous experience, as well. The images presented in this study may not be entirely representative of the actual images examined at the time of analysis directly on the instruments, i.e. some conclusions may not be as obvious as to the examiner during the analysis.

3.1. Intersections of optically distinguishable writing tools

Fountain pen and black ballpoint pen (BIC). Both combinations of deposition order of fountain pen and ballpoint pen are shown in Figure 2, along with the results from both the optical techniques and MeV SIMS. Based on the optical methods, it was found that the fountain pen was deposited above the ballpoint pen in Figure 2.a. Under the stereo microscope, it is visible that the fountain pen pulled the black ballpoint pen ink a bit downwards, leaving a trace of black ballpoint pen ink over the blue fountain pen ink line. Under the optical microscope, it can be seen that the blue color of the fountain pen ink predominates. Fountain pen ink spreading and diffusion phenomena[16, 17] over the ballpoint pen ink line is visible under the spot infra-red light at the intersection area. This is due to the fact that fountain ink is liquid-based with high tendency for being absorbed into the paper fibers, while ballpoint pen ink is oil-based ink with a very small tendency for being absorbed. Hence, most of the ballpoint pen ink stays adherent to the paper surface. Consequently, when the fountain pen crosses over the ballpoint pen ink line, it immediately reacts in contact with ballpoint pen ink by spilling to the sides. In Figure 2.b the situation is reversed - under the spot infra-red light there is no visible reaction when the ballpoint pen crossed over the fountain ink line, and there is no difference in the ink line latitude. The black ballpoint pen ink line is over the blue fountain pen ink line and it is also visible from the colors under the optical microscope.
K-means clustering of MeV SIMS images produced a discontinued trace for a line deposited second with a fountain pen (Figure 2.a) when it should have been continuous. It also assigned an area just outside of the intersection region to the line deposited first with a ballpoint pen, indicating that diffusion of ballpoint pen ink occurred on neighboring paper fibers before the deposition of a fountain pen on top of it. This can also be seen from the stereo microscope image. The combination in Figure 2.b correctly showed deposition order. Nevertheless, there was not enough information to draw an absolute conclusion. Details on multivariate analysis of MeV SIMS images for fountain pen over BIC case can be seen in Figures S-1 (PCA) and S-2 (k-means), and for BIC over fountain pen case in Figures S-3 (PCA) and S-4 (k-means).

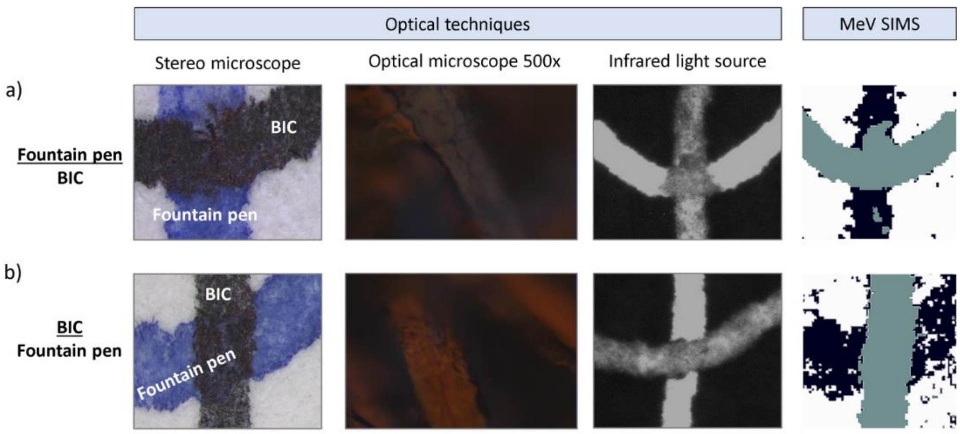

*Figure 2. **Fountain pen and BIC**. The first column shows microscopic images of samples. The next two columns show results from optical techniques. The last columns show results from MeV SIMS.*

Blue ballpoint pen (Pilot) and black ballpoint pen (BIC). Both combinations of deposition order of blue and black ballpoint pens are shown in Figure 3, along with the results from both the optical techniques and MeV SIMS. Under the stereo microscope in this case in both combinations the deposition order cannot be determined, but under the optical microscope it is possible – in Figure 3.a the color of Pilot ballpoint pen ink predominates (blue effect) and in Figure 3.b the BIC ballpoint pen ink predominates at the intersection (reddish effect). Also, in Figure 3.a under the spot infra-red light it can be seen that the Pilot ballpoint pen ink partially attenuates the IR luminescence of the BIC ballpoint pen ink line, indicated by the Pilot ballpoint pen ink line latitude difference before and after the intersection. Hence, it was concluded that the Pilot ballpoint pen ink is deposited above the BIC ballpoint pen ink. In Figure 3.b the situation is reversed and it was concluded that the BIC ballpoint pen ink is deposited over the Pilot ballpoint pen ink.

In MeV SIMS images, it looks as though the black ballpoint pen is deposited second in both combinations, which is not the case. K-means clustering produced a discontinued trace for a line deposited second with the blue ballpoint pen (Figure 3.a), although it does show a small area of Pilot ballpoint pen ink inside the intersection, also visible in the IR image. The combination in Figure 3.b correctly showed deposition order. Details on multivariate analysis of MeV SIMS images for BIC over Pilot case can be seen in Figures S-5 (PCA) and S-6 (k-means), and for Pilot over BIC case in Figures S-7 (PCA) and S-8 (k-means).

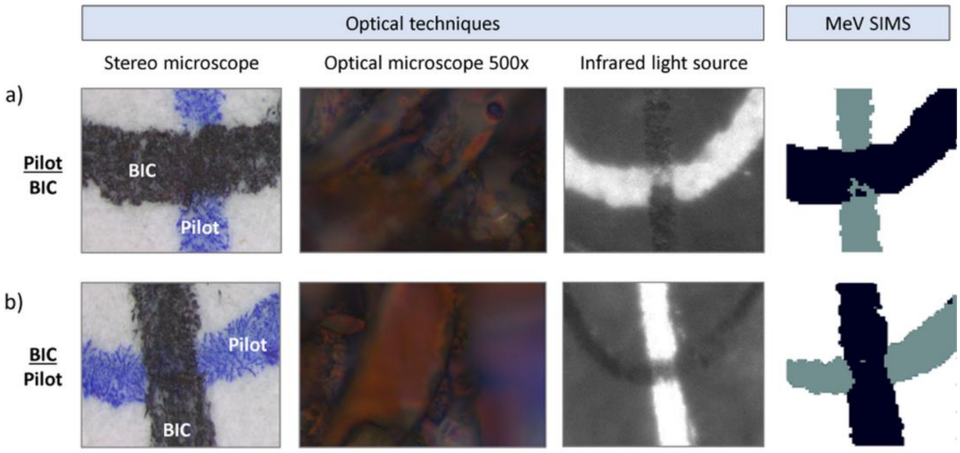

*Figure 3. **Pilot and BIC**. The first column shows microscopic images of samples. The next two columns show results from optical techniques. The last columns show results from MEV SIMS.*

Stamp (Trodat Printy) and blue ballpoint pen (Pilot). Both combinations of deposition order of Pilot and BIC are shown in Figure 4, along with the results from both the optical techniques and MeV SIMS. In this case, it was not possible to determine deposition order of intersecting lines using optical methods. Under the optical microscope and especially under the spot infra-red light, it seems that the stamp ink is deposited over ballpoint pen ink (Figure 4.a), while in Figure 4.b it seems that ballpoint pen ink is deposited over stamp ink, which is incorrect.

MeV SIMS image correctly reveals deposition order for the case in Figure 4.a (Pilot trace is continuous, while stamp ink shows a break), but for the case in Figure 4.b, it shows the Pilot trace as deposited second, which is not the case. Details on multivariate analysis of MeV SIMS images for Pilot over Trodat Printy case can be seen in Figures S-9 (PCA) and S-10 (k-means), and for Trodat Printy over Pilot case in Figures S-11 (PCA) and S-12 (k-means).

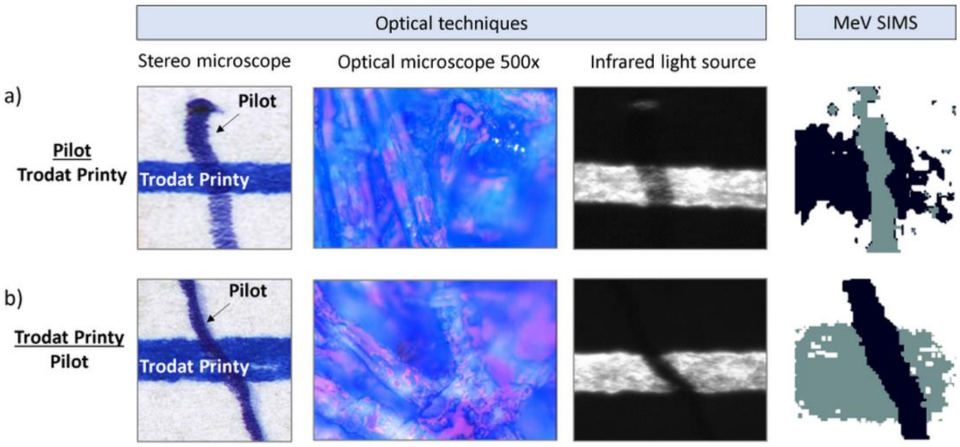

*Figure 4. **Trodat Printy and Pilot**. The first column shows microscopic images of samples. The next two columns show results from optical techniques. The last columns show results from MeV SIMS.*

Fountain pen and stamp (Trodat Printy). Both combinations of deposition order of fountain pen and stamp (Trodat Printy) are shown in Figure 5, along with the results from both the optical techniques and MeV SIMS. The results of optical methods correctly showed deposition order in both combinations and they are very similar to the results from the case involving fountain pen and black ballpoint pen (BIC). In Figure 5.a, it is clearly visible that the fountain pen is deposited over the stamp - the blue color of the fountain pen ink predominates under the optical microscope, ink spreading and diffusion phenomena are evident under spot infra-red light. In Figure 5.b the situation is reversed, the stamp is deposited over the fountain pen – the blue color of the stamp predominates, the stamp ink attenuates the IR luminescence of fountain pen ink with no visible ink diffusion.

After k-means clustering, MeV SIMS images correctly revealed deposition order in both cases, that is, the line deposited first yields a trace with a break, and the line deposited second yields a continuous trace. Details on multivariate analysis of MeV SIMS images for fountain pen over Trodat Printy case can be seen in Figures S-13 (PCA) and S-14 (k-means), and for Trodat Printy over fountain pen case in Figures S-15 (PCA) and S-16 (k-means).

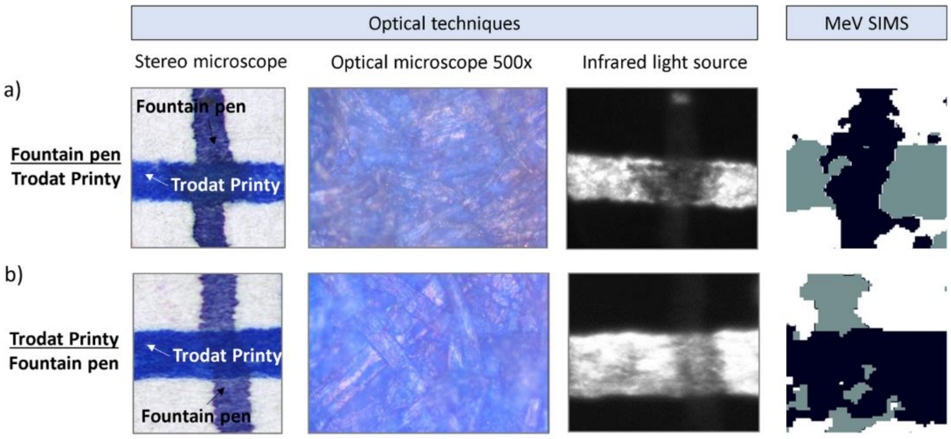

*Figure 5. **Fountain pen and Trodat Printy**. The first column shows microscopic images of samples. The middle columns show results from optical techniques. The last column shows results from MeV SIMS.*

3.2. Intersections of optically indistinguishable writing tools

Four different blue ballpoint pens marked as BP1, BP2, BP4 and BP5 of unknown producer were obtained from the forensic laboratory, as it was not possible to conclude anything about the deposition order for combinations BP1 & BP4 and BP2 & BP5 using standard optical methods.

BP1 and BP4. Both combinations of deposition order of BP1 and BP4 are shown in Figure 6, along with the results from both the optical techniques and MeV SIMS. It is evident from Figure 6 that neither optical nor IR images can distinguish these two very similar ballpoint pens. Also, it can be concluded from the mass spectra in Figure 1 that ballpoint pens BP1 and BP4 are also chemically very similar and not easy to distinguish through mass peaks belonging to binders (in the lower mass region) or mass peaks belonging to pigments (in the high mass region). In such cases involving a combination of very similar pens, PCA analysis sometimes could not distinguish two pens and would characterize both deposited lines (including the intersection) as one type of pen. Therefore, t-SNE algorithm[18] was attempted to try to differentiate the two pens, on the assumption that the linearity constraint of PCA may limit its sensitivity to subtle differences throughout the sample. T-SNE uses non-linear embeddings of high-dimensional spectral information (input dataset) to form clusters in a single 2D map representation, preserving both local detail and the global data structure. Unlike PCA, which is only an orthogonal transformation of correlated variables to a set of uncorrelated variables while preserving global structure, t-SNE tries to preserve the local structure of the data by minimizing the Kullback-Leibler divergence between the two probability distributions (original, high-dimensional, and embedded, low-dimensional) with respect to the locations of the points in the map. The perplexity parameter for t-SNE was conditioned by combining two different perplexity values (50 and 500) to try to preserve both the local and global structure. Clustering of pixels represented in t-SNE space was performed using DBSCAN code, within Orange software, which is a density-based clustering algorithm. The optimal number of clusters was defined by selecting the neighborhood distance parameter to the value in the first "valley", as suggested by the authors of the algorithm[19]. Hence, the final MeV SIMS images are presented in the form of pixels colored according to clusters in the resulting t-SNE space. As can be seen from MeV SIMS results in Figure 6, BP1 and BP4 are successfully distinguished and the deposition order is correctly identified in both combinations. Additionally, the DBSCAN clustering algorithm recognized trace edges (marked in orange) as a transient region of pixels between paper and pens in t-SNE space (Figure 7). Details on t-SNE clustering results for the BP1 over BP4 case can be found in Figure S-17.

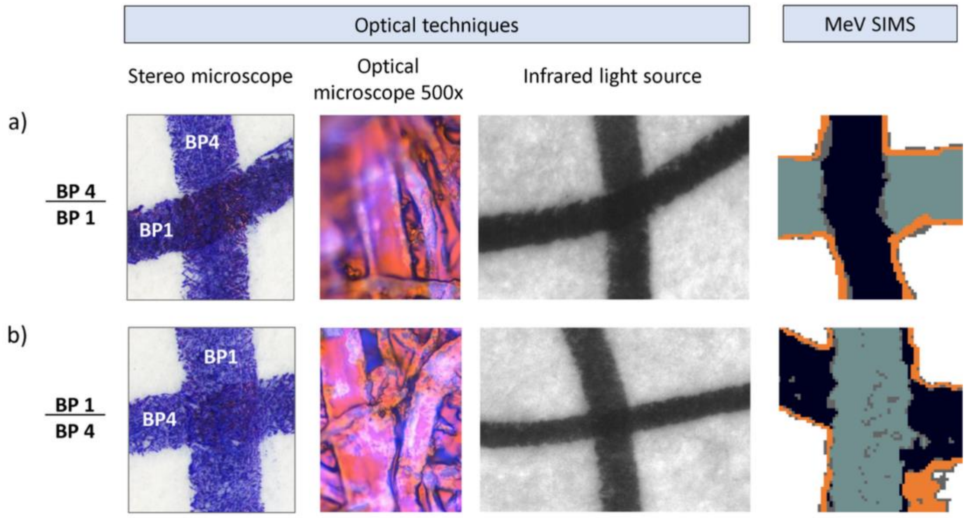

*Figure 6. **BP1 and BP4**. The first column shows microscopic images of samples. The middle columns show results from optical techniques. The last column shows the results from t-SNE performed on MeV SIMS dataset.*

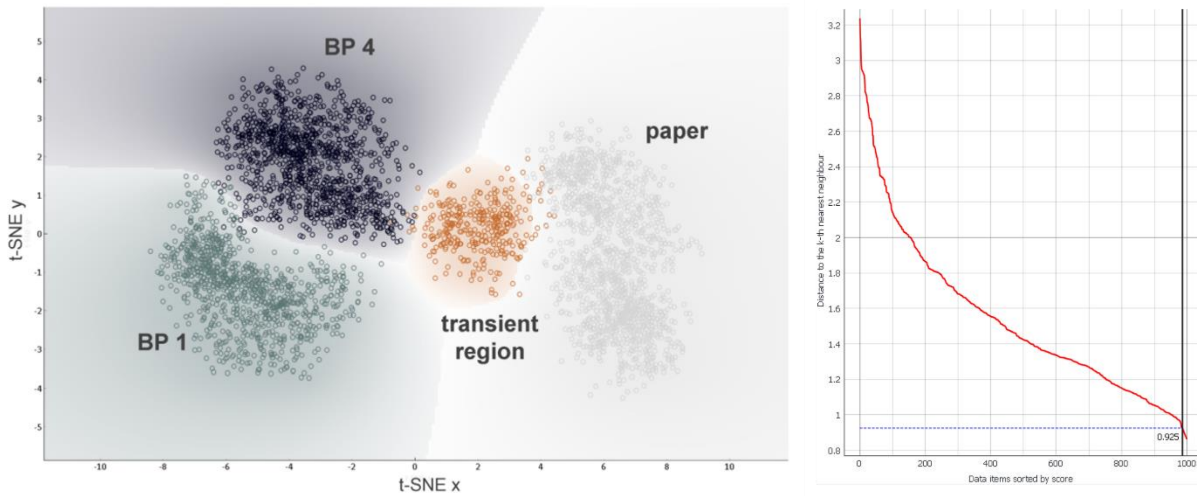

Figure 7. BP4 over BP1 combination. Clustered pixels originating from BP1, BP4, paper, and a transient region, represented in t-SNE space(left). Optimal number of clusters is defined by DBSCAN, by selecting the neighborhood distance parameter to the value in the first "valley" (right).

Moreover, average pixel spectra of BP1 and BP4 from both samples (combinations) were derived from clusters in t-SNE space, shown in Figure 8. Upon simple manual inspection, subtle differences in several peaks or groups of peaks are evident. For example, BP4 has a small unknown peak at m/z 123, which BP1 does not have. Also, Basic Violet 3 seems to be slightly lower in BP4 than in BP1. All perceived differences are not pronounced enough for a standard manual RGB representation of ink intersections. Yet, t-SNE takes all this information at once into account and is able to represent a clear picture of the intersection.

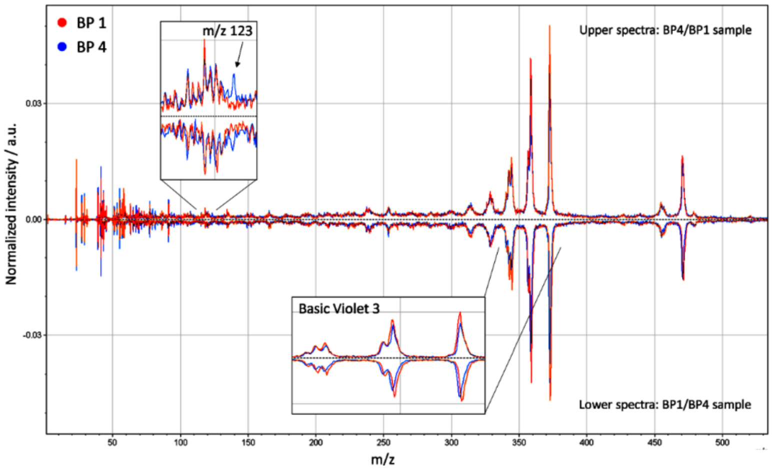

Figure 8. Average pixel spectra derived from clusters in t-SNE space; BP1 (orange), BP4 (blue). Upper and lower spectra are acquired from BP4 over BP1 sample and BP1 over BP4 sample, respectively.

BP2 and BP5. Both combinations of deposition order of BP2 and BP5 are shown in Figure 9, along with the results from both the optical techniques and MeV SIMS. As with the previous case, it is evident from Figure 9 that neither optical nor IR images can distinguish these two very similar ballpoint pens. Mass spectra of BP2 and BP5 pens are also chemically very similar, as seen on Figure 1. MeV SIMS analysis was done in the same way as in the previous case, resulting in correct determination of deposition order in case where BP5 was deposited on BP2 (Figure 9.a), but failing in the opposite combination (Figure 9.b). T-SNE algorithm recognized the intersection in Figure 9.b as different from both inks (marked as red). It should be noted that the deposition of BP5 ink was difficult due to dryness, even after minutes of restarting the ink flow, this being a potential cause of partially unsuccessful MeV SIMS results. A slight difference in deposition intensity between BP2 and BP5 can be observed on a stereo microscope in both combinations, as well. Details on t-SNE clustering results of MeV SIMS images for BP5 over BP2 case can be seen in Figure S-18, and for BP2 over BP5 case in Figure S-19.

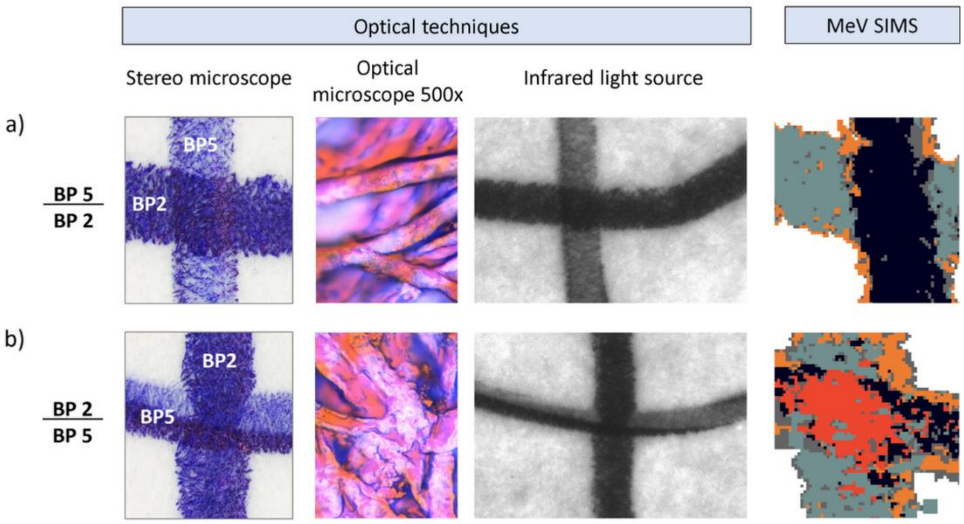

*Figure 9. **BP2 and BP5**. The first column shows microscopic images of samples. The middle columns show results from optical techniques. The last column shows the results from t-SNE performed on MeV SIMS dataset.*

A summary of results from all presented cases obtained from optical methods and MeV SIMS is given in

Table 3. The first four rows show cases where optical methods are able to distinguish writing tools in question, while the last two rows concern cases where no optical method available at the forensic laboratory can distinguish the two writing tools. MeV SIMS in combination with PCA image processing slightly underperforms in comparison to optical methods for the first four pairs of intersecting lines but was

definitely superior to optical methods for the last two pairs after employing t-SNE. For the last pair, even though MeV SIMS managed to correctly reveal the deposition order in one combination, the result was incorrect for the other combination, thus this case is generally unresolvable. Nevertheless, it is worth to mention that although BP2 and BP5 are optically identical, MeV SIMS still managed to identify independent parts of inks (away from the intersection) as of different origin.

As mentioned in the introduction, water-based writing tools (in this case fountain pen and stamp) tend to be problematic for MeV SIMS when they are deposited on top of another writing tool, since the deposition is often not as effective as on a paper. In the current study, PIXE that was very useful in some previous cases[11] could not reveal any additional information for unresolved cases because at least one writing tool per case did not yield any unique characteristic X-rays. On the other hand, results from optical methods marked with asterisk in Table 3 indicate that the conclusion is partially based on analyst's previous experience with fountain pen behavior under IR light source – while optical microscope shows predominance of the ink above, there was no clear attenuation of IR luminescence.

Table 3. A summary of all results obtained by optical methods and MeV SIMS.

Pair no.	Combination	Order	Optical methods		MeV SIMS	
			Success	Deposition order differentiable	Success	Deposition order differentiable
			Optically distinguishable cases			
1	Fountain pen & BIC	Fountain pen /	✓*	✓*	✗	✗
		BIC / Fountain	✓*		✓	
2	Pilot & BIC	Pilot / BIC	✓	✓	✗	✗
		BIC / Pilot	✓		✓	
3	Trodat Printy & Pilot	Stamp / Pilot	✗	✗	✗	✗
		Pilot / stamp	✗		✓	
4	Trodat Printy & Fountain pen	Stamp /	✓*	✓*	✓	✓
		Fountain pen /	✓*		✓	
			Optically indistinguishable cases			
5	BP 1 & BP 4	BP 4 / BP 1	✗	✗	✓	✓
		BP 1 / BP 4	✗		✓	
6	BP 2 & BP 5	BP 5 / BP 2	✗	✗	✓	✗
		BP 2 / BP 5	✗		✗	

4. Conclusions

In the present work, non-destructive optical techniques used in daily forensic work for solving problems related to intersecting lines on questioned documents used in the forensic laboratory were compared with a new and emerging IBA technique MeV SIMS available at the accelerator facility. Several cases of intersecting lines made by combining ballpoint pens, a stamp, and a fountain pen were prepared and examined. The intersecting lines were divided into those that are distinguishable by optical techniques used at the forensic laboratory and those that are not. Optical techniques slightly outperform MeV SIMS in determining the deposition order for intersections of optically distinguishable writing tools where both oil-based and water-based writing tools were used. MeV SIMS proved to be more efficient for oil-based writing tools while difficulties were encountered with water-based ones, similar to optical methods. However, in some cases, the experience of a forensic analyst proved to be important in decision making. The situation was quite different for two combinations of intersecting lines from four very similar blue ballpoint pens which were completely indistinguishable by optical methods. Although their mass spectra were also very similar and had negligible differences, when combined with advanced nonlinear multivariate analysis tools such as t-SNE, which are more objective and independent of the analyst, these differences were sufficient to correctly determine the deposition order in one case and partially in the other. Therefore, MeV SIMS outperforms standard forensic optical techniques in some of these cases. It seems reasonable to conclude that in some cases where standard forensic optical methods fail, MeV SIMS could play an important role and be a method of choice in revealing the deposition order of two very similar ballpoint pens which are optically indistinguishable, by using multivariate analysis tools to extract critical latent information from the obtained hyperspectral molecular data. No matter the ability to determine the deposition order, if the inks involved can be differentiated using MeV SIMS (e.g. BP2 and BP5 pair), such valuable information can be exploited in other cases of official document forgery, such as alteration or addition of letters and numbers, where no overlapping traces are present or relevant.

A logical future direction would be data fusion of several complementary techniques, both conventional and unconventional in forensic sciences, which could undoubtedly strengthen the evidential value in forensics of forged documents.

References

[1] L.R. e Brito, A.R. Martins, A. Braz, A.B. Chaves, J.W. Braga, M.F. Pimentel, Critical review and trends in forensic investigations of crossing ink lines, TrAC Trends in Analytical Chemistry 94 (2017) 54-69.

[2] EDEWG, Examination of Intersecting Lines, ENFSI, September 2004.

[3] K. Saini, R. Kaur, N.C. Sood, Determining the sequence of intersecting gel pen and laser printed strokes — A comparative study, Science & Justice 49(4) (2009) 286-291.

[4] A. He, D. Karpuzov, S. Xu, Ink identification by time-of-flight secondary ion mass spectroscopy, Surface and Interface Analysis 38 (2006) 854-858.

[5] J. Lee, S.H. Kim, Y.-J. Cho, Y.S. Nam, K.-B. Lee, Y. Lee, Characterization and sequence determination of pen inks, red sealing inks, and laser toners by TOF-SIMS and ATR FTIR, Surface and Interface Analysis 46 (2014) 317-321.

[6] J. Lee, Y.S. Nam, J. Min, K.-B. Lee, Y. Lee, TOF-SIMS Analysis of Red Color Inks of Writing and Printing Tools on Questioned Documents, Journal of Forensic Sciences 61 (2016) 815-822.

[7] R.E. Goacher, L.G. DiFonzo, K.C. Lesko, Challenges Determining the Correct Deposition Order of Different Intersecting Black Inks by Time-of-Flight Secondary Ion Mass Spectrometry, Analytical Chemistry 89 (2016) 759-766.

[8] M.J. Bailey, B.N. Jones, S. Hinder, J. Watts, S. Bleay, R.P. Webb, Depth profiling of fingerprint and ink signals by SIMS and MeV SIMS, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 268 (2010) 1929-1932.

[9] M.C. Malloy, I. Bogdanović Radović, Z. Siketić, M. Jakšić, Determination of deposition order of blue ballpoint pen lines by MeV Secondary Ion Mass Spectrometry, Forensic Chemistry 7 (2018) 75-80.

[10] K.L. Moore, M. Barac, M. Brajković, M.J. Bailey, Z. Siketić, I. Bogdanović Radović, Determination of Deposition Order of Toners, Inkjet Inks, and Blue Ballpoint Pen Combining MeV-Secondary Ion Mass Spectrometry and Particle Induced X-ray Emission, Analytical Chemistry 91 (2019) 12997-13005.

[11] T. Tadić, I. Bogdanović Radović, Z. Siketić, D.D. Cosic, N. Skukan, M. Jakšić, J. Matsuo, Development of a TOF SIMS setup at the Zagreb heavy ion microbeam facility, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 332 (2014) 234-237.

[12] D. Cosic, M. Bogovac, M. Jakšić, Data acquisition and control system for an evolving nuclear microprobe, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 451 (2019) 122-126.

[13] M. Strohalm, M. Hassman, B. Košata, M. Kodíček, mMass data miner: an open source alternative for mass spectrometric data analysis, Rapid Communications in Mass Spectrometry 22 (2008) 905-908.

[14] G.F. Trindade, M.-L. Abel, J.F. Watts, simsMVA: A tool for multivariate analysis of ToF-SIMS datasets, Chemometrics and Intelligent Laboratory Systems 182 (2018) 180-187.

[15] J. Demsar, T. Curk, A. Erjavec, C. Gorup, T. Hocevar, M. Milutinovic, M. Mozina, M. Toplak, P. M., M. Toplak, A. Staric, M. Stajdohar, L. Umek, L. Zagar, Z. J., M. Zitnik, Z. B., Orange: Data Mining Toolbox in Python, Journal of Machine Learning Research 14 (2013) 2349-2353.

[16] R. Williamson, D. Djidrovska, A. Ledic, S. Brzica, V. Antikj, R. Hofer, J. Almirall, Characterization and identification of luminescent components in inks using various analytical techniques for the study of crossed-line intersections, Forensic Chemistry 3 (2017) 28-35.

[17] INTERPOL, AIEED, Physical-Chemical Study of Crossed Line Intersection, Lyon, 2016, p. 92.

[18] L. van der Maaten, G. Hinton, Visualizing Data Using t-SNE, Journal of Machine Learning Research 9 (2008) 2579-2605.

[19] M. Ester, H.-P. Kriegel, J. Sander, X. Xu, A Density-Based Algorithm for Discovering Clusters in Large Spatial Databases with Noise, Proc. of 2nd International Conference on Knowledge Discovery and Data Mining, AAAI Press, 1996, pp. 226-231.