Statistical evaluation of the reproducibility and the influence of paper on the analysis of black gel pen ink using laser desorption ionisation mass spectrometry

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A B S T R A C T

Laser desorption ionisation mass spectrometry (LDI-MS) has demonstrated to be an excellent analytical method for the forensic analysis of inks on a questioned document. The ink can be analysed directly on its substrate (paper) and hence offers a fast method of analysis as sample preparation is kept to a minimum and more importantly, damage to the document is minimised. LDI-MS has also previously been reported to provide a high power of discrimination in the statistical comparison of ink samples and has the potential to be introduced as part of routine ink analysis. This paper looks into the methodology further and evaluates statistically the reproducibility and the influence of paper on black gel pen ink LDI-MS spectra; by comparing spectra of three different black gel pen inks on three different paper substrates. Although generally minimal, the influences of sample homogeneity and paper type were found to be sample dependent. This should be taken into account to avoid the risk of false differentiation of black gel pen ink samples. Other statistical approaches such as principal component analysis (PCA) proved to be a good alternative to correlation coefficients for the comparison of whole mass spectra.

Keywords: Ink Analysis; LDI-MS; Reproducibility; Paper; Gel Pens; Questioned Document

1. Introduction

The analysis of ink entries on a questioned document is an important aspect of forensic document examination as it can provide evidence in a case where a document is alleged to have been tampered with in order to alter its original meaning. The objective generally is to detect the presence of more than one type of ink on the document which can then help support or refute a claim against intent to commit forgery [1]. Practice has generally focused on non-destructive methods i.e., those that avoid/minimise damage to the document, for example: Infra-Red spectroscopy (IR) [2-5], Raman spectroscopy [6-8] and X-Ray Fluorescence (XRF) [5, 9]. However, such optical methods provide a limited amount of information as they generally look at the spectral/luminescent properties of the ink and cannot distinguish between similar functional groups or identify the molecules present in the ink [10]. Destructive methods such as Thin Layer Chromatography (TLC) [11-12], Capillary Electrophoresis (CE) [1, 13-16] and High Performance Liquid Chromatography (HPLC) [17-18] were also proposed. Recently, LDI-MS, a quasi non-destructive technique, has demonstrated a high power of discrimination for inks and was tested successfully in several studies involving samples of dye- and pigment based ball point- and gel pen inks [1, 10, 19 - 29].

LDI-MS has demonstrated to be an ideal analytical method as it is one where fragmentation and degradation of the analyte and document is minimised, sample preparation is kept to a minimum and more importantly it has demonstrated the ability to differentiate inks quickly and effectively, for example, a recent study deduced a discriminatory power (DP) of 85% using 30 black gel pens in comparison to 49% and 75% using Video Spectral Comparator (VSC) and Microspectrophotometry (MSP) respectively [19]. Moreover, as the usage of pigment-based gel pen inks has increased large scale over the last fifteen years, it is more and more common for a forensic scientist to receive exhibits bearing pigment based ink [30] and hence it becomes essential that methods which can analyse both dyes and pigment effectively become incorporated into routine ink analysis.

LDI-MS can be performed on ink samples directly on the substrate i.e. paper without the assistance of a matrix [29]. This is also an advantage as the presence of neutral components found to be in the paper will be difficult to ionise by the laser without the assistance of a matrix, thus minimizing the background noise.

One particular issue which occasionally seems to be problematic with ink analysis using LDI-MS involves sample reproducibility [19]. To further investigate this issue, we proposed a method which involves statistically comparing the LDI-MS measurements of ten replicate samples for each of three different black gel pen inks (analysed previously for differentiation) [19]. In addition, reproducibility of each ink sample will be further assessed on two additional paper types. This comparison step allows one to determine how homogenous the analysis for each ink sample is and hence comment on the reliability of the data obtained with this instrumentation. One can also assess whether a particular paper type has a significant effect on the level of sample reproducibility which may increase the possibility of false differentiation.

Moreover, while studies using ESI-MS, HPTLC and FT-IR have reported that paper can influence data obtained from ink comparison experiments to some extent [31-33], no information about the influence of paper is available for LDI-MS yet. Ideally, one would expect the measurements of a particular type of ink to be consistent and independent of paper type. Hence, an additional aim of this study is to evaluate the influence of paper on black gel pen ink LDI-MS spectra. The proposed method involves comparing LDI-MS spectra of each ink sample on three different paper types. We hypothesise that paper has the potential to introduce interferences in LDI-MS spectra when ink is sampled with paper, and if the interference is significant enough, it may potentially give rise to false differentiation of ink samples.

2. Experimental

2.1. Sample preparation

All three black gel pens used in this study were bought in Switzerland in 2009 and were produced by three different manufacturers (Table 1). The pens were used in a previous study looking at the differentiation of black gel pens [19] and were selected in order to cover very different composition on the basis of Video Spectral Comparison (VSC6000/HS, Foster and Freeman, Evesham, UK) in absorbance mode (Figure 1) and LDI-MS results (Figure 2).

Table 1 – A list and description of the three different gel pens that were used in this study.

Pen	Brand Name	Constituent Ink
1	Pentel Energel BL17-A	Colourant
2	Pilot Frixion Ball	Colourant
3	Uniball Signo Broad	Pigment

The pens were used to draw ten lines for each ink on three different brands of paper (Table 2). The lines were made by using a ruler and applying normal hand pressure. Each sample was prepared by cutting the paper bearing the line of ink which measured approximately 7 x 3 mm (corresponding to 3 x 10 samples). It was then mounted onto a solid steel MALDI sample plate (original MALDI plate from Bruker Daltonics, Bremen, Germany) using an adhesive glue-stick (UHU® stic, Bühl, Switzerland). Blank samples from each of the three types of paper were also prepared in the same way (10 replicates for each type of paper).

Table 2 – A list and description of the three different paper types used in this study.

Paper	Brand Name	Weight
1	MIGROS Recycled (Switzerland)	80g/m2
2	Xerox Business: Multipurpose (Switzerland)	80g/m2
3	HP Premium Inkjet (UK)	120g/m2

2.2. LDI-TOFMS analysis

A Bruker Daltonics AutoFlex matrix assisted laser desorption/ionisation reflector time-of-flight (MALDI-TOF) mass spectrometer equipped with a pulsed nitrogen laser (λ = 337nm) was used (Bremen, Germany). The samples were analysed without the assistance of a matrix in positive mode. Mass detection was set between 20 to 1000 Da and 50 laser pulses were fired along each line of ink with an optimal laser irradiance set at 60%. The laser irradiance value is an important factor to adjust whenever a new set of samples are analysed using LDI-MS and should not be varied during the analyses [24, 25]. Calibration of the instrument was undertaken using blue ballpoint pen ink (BIC Cristal). The dyes in this ink were deduced in earlier studies [27, 28]: the peaks corresponding to 'basic violet 3' (m/z 372.2 and 358.8) and 'basic violet 4' (428.3 and 456.3) were detected. The software running the instrument was 'flexControl – autoflex version 2011'.

2.3. Statistical treatment

The main objective for using a statistical approach was to allow a good way of separating two different populations objectively, i.e., obtain an objective differentiation of analysed ink lines [1, 19]. Approximately 64000 raw data points from each mass spectrum obtained were extracted in the form of text files covering a mass range of 20 to 1000 Da. While previous studies have reported that standardisation is advantageous (i.e., reducing the influence of different absolute scales), this method was not adequate to this study due to the small number of inks studied. Data were therefore directly compared by calculating Pearson correlation coefficients. This statistical comparison method has been previously reported to be very efficient to differentiate gel pen ink samples [1, 19]. Pearson values range from -1 to 1; 1 indicating perfect correlation. Altogether, three sets of Pearson calculations were undertaken to:

- test the reproducibility of the methodology and the homogeneity of the samples (intra-variability): Pearson correlations for comparison of same ink on same paper.

- test the influence of the paper on the results: Pearson correlations for same pen on different paper.

- test the influence of paper and replicate analyses on the differentiation (inter-variability): pearson correlations for different pens on same and different paper.

Data points were further analysed using Microsoft Excel (Microsoft Corporation), Origin 6.0 Professional (OriginLab Corporation) and 'R' software (http://www.r-project-t.org/). Due to the large number of data collected, Cluster dendogram and PCA (Principal Components Analysis) were also used as useful statistical approaches to visualise and determine patterns among samples. This involves compressing and re-adjusting the mean of the data to zero to produce a graph which can highlight the similarities and differences of the data.

3. Results & Discussions

The gel pen inks used in this study were selected because of their very different composition, initially determined through VSC (Figure 1) and LDI-MS (Figure 2) in order to evaluate the reproducibility of analysis and influence of paper on a range of compositions.

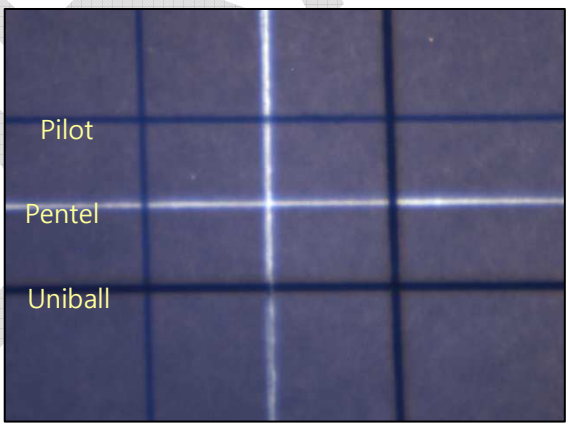


Figure 1 – Video spectral comparator (VSC) photograph of the three black gel pens (620-655nm).

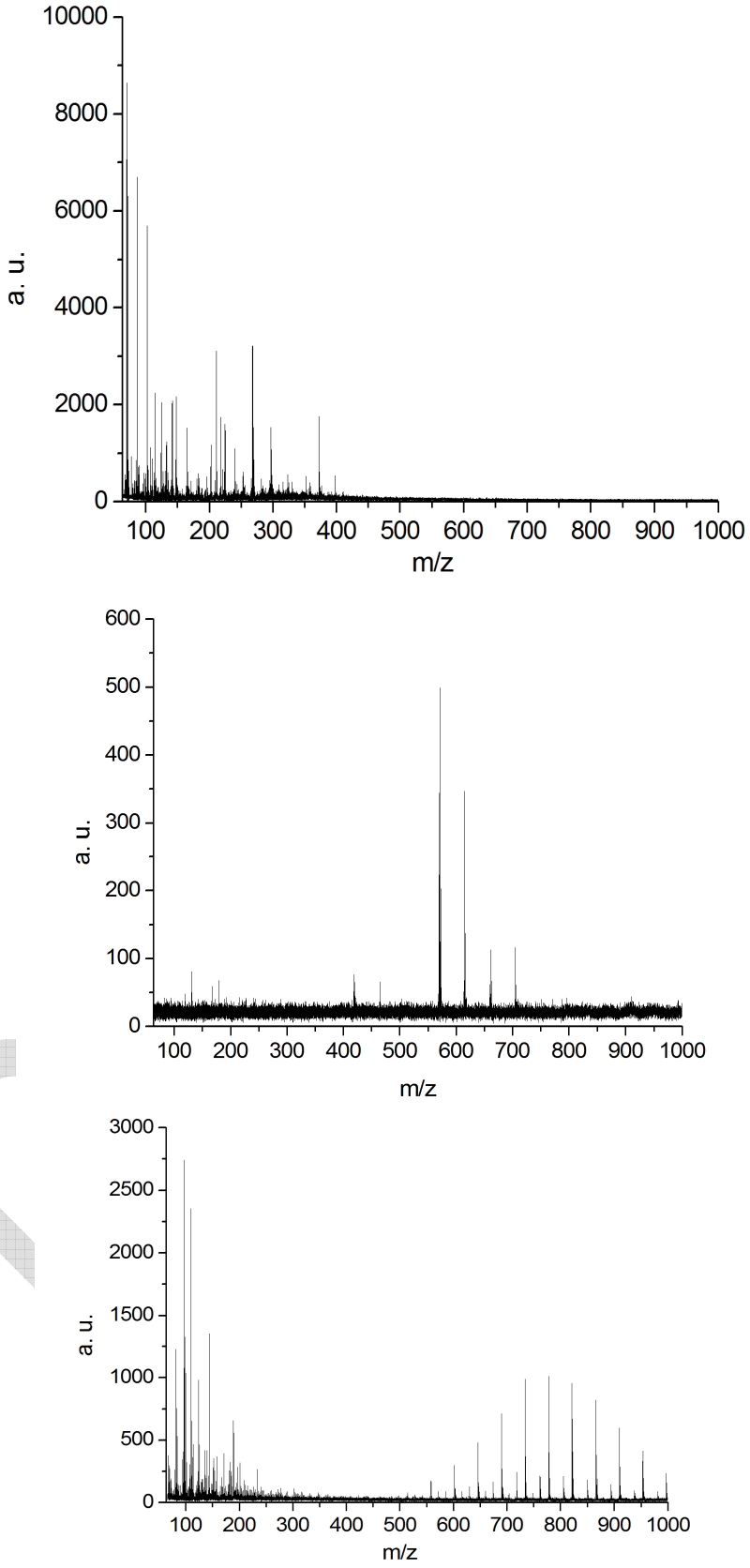


Figure 2 – LDI-MS Spectra of gel pen inks: Pentel, Pilot and Uniball on paper 2 (Xerox).

3.1 Reproducibility

As with every type of sample, it is important to determine how homogeneous the replicate samples are in order to accurately evaluate its repeatability and to eliminate potential outliers. In this particular case, it is essential that homogeneity of ink on one paper is achieved so that false differentiation of ink is avoided. The reproducibility of analysis must also be tested for that particular purpose (LDI-MS is not a quantitative methodology and comparison of relative peak areas may be irreproducible). So we analysed the homogeneity of each of the 3 types of gel pen ink samples that were used in this study on the different paper types (= 3 papers x 3 inks x 10 replicate). Including 10 replicates for each blank analysis of papers, altogether 120 LDI-MS spectra were obtained. The first observations showed that the issue of calibration must be carefully considered when evaluating different strokes of the same ink. Indeed an m/z shift was observed in the results within spectra of the same pen (see figure 3a). For a given ink, the shift was always highest on paper 1. This shift may be due to a problem in the laser focalisation due to small depth difference in the paper. In order to compensate that, m/z values were corrected using common unidentified peaks in the spectra (see figure 3b). Ideally the calibration ink lines should be drawn next to the analysed line to avoid this problem earlier in the analysis; however this would mean altering the questioned document and is not always possible.

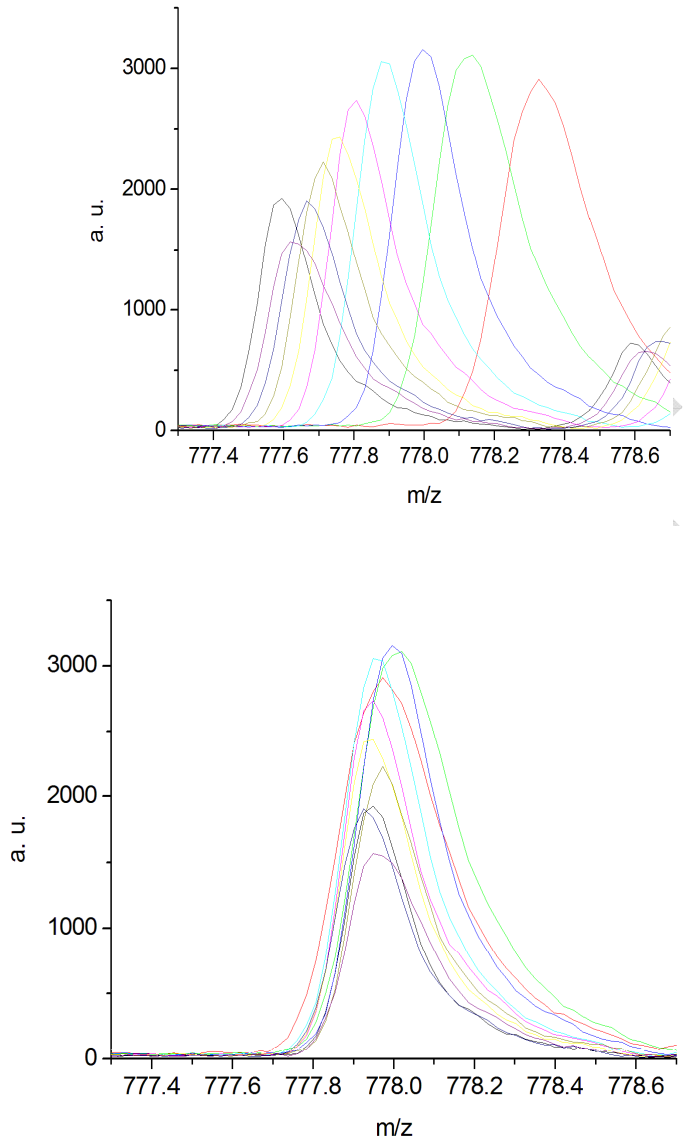


Figure 3 – 10 replicate LDI-MS spectra of Uniball ink lines on paper 3: (a) shift in the m/z spectra between ink specimens (b) recalibrated data.

Then to ensure there is no human bias and that decisions are made objectively when comparing spectra, Pearson correlation coefficient values were calculated and the distribution of the data were represented in box charts (Figure 4A). The expected values for a given sample type (same ink on same paper) should be close to 1 in order to show good reproducibility. While the Pearson coefficient values were relatively high for both Pentel and Uniball inks (median of 0.85 and 0.93 respectively), the values obtained for the Pilot ink was quite low (median of 0.32). This seems to be partly due to the very small number of peak and peak intensities obtained for this pen at a laser intensity of 60%, as well as considerable differences in the relative peak intensities (see Figure 5). It is therefore really important to

assess several replicates in order to detect outliers (i.e., very large Pearson values should be obtained for same ink comparison to be able to compare it to other entries).

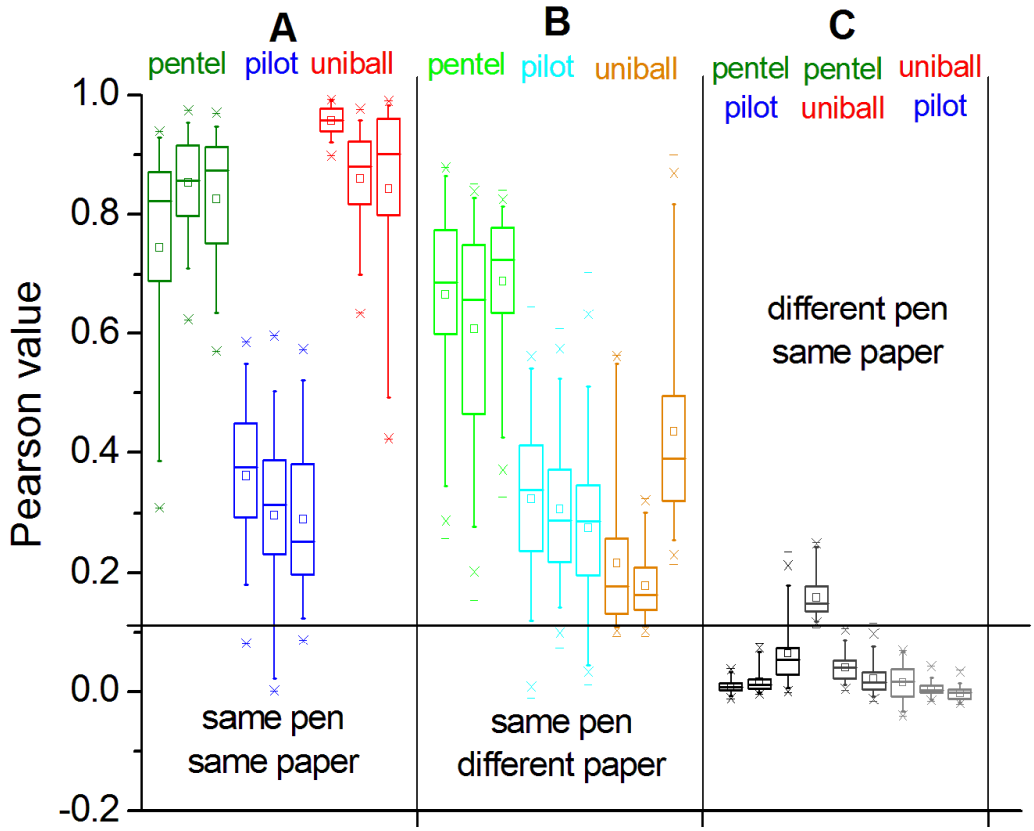


Figure 4 - Box charts showing the distribution of Pearson correlation coefficient values for the comparison of ink samples: (A) same pen on same paper (each set of three boxplots representing within paper 1, 2 and 3 respectively), (B) same pen on different paper (each set of three boxplots representing comparison between paper 1&2, 1&3 and 2&3 respectively), and (C) different pen on the three different paper types (each set of three boxplots representing within paper 1, 2 and 3 respectively).

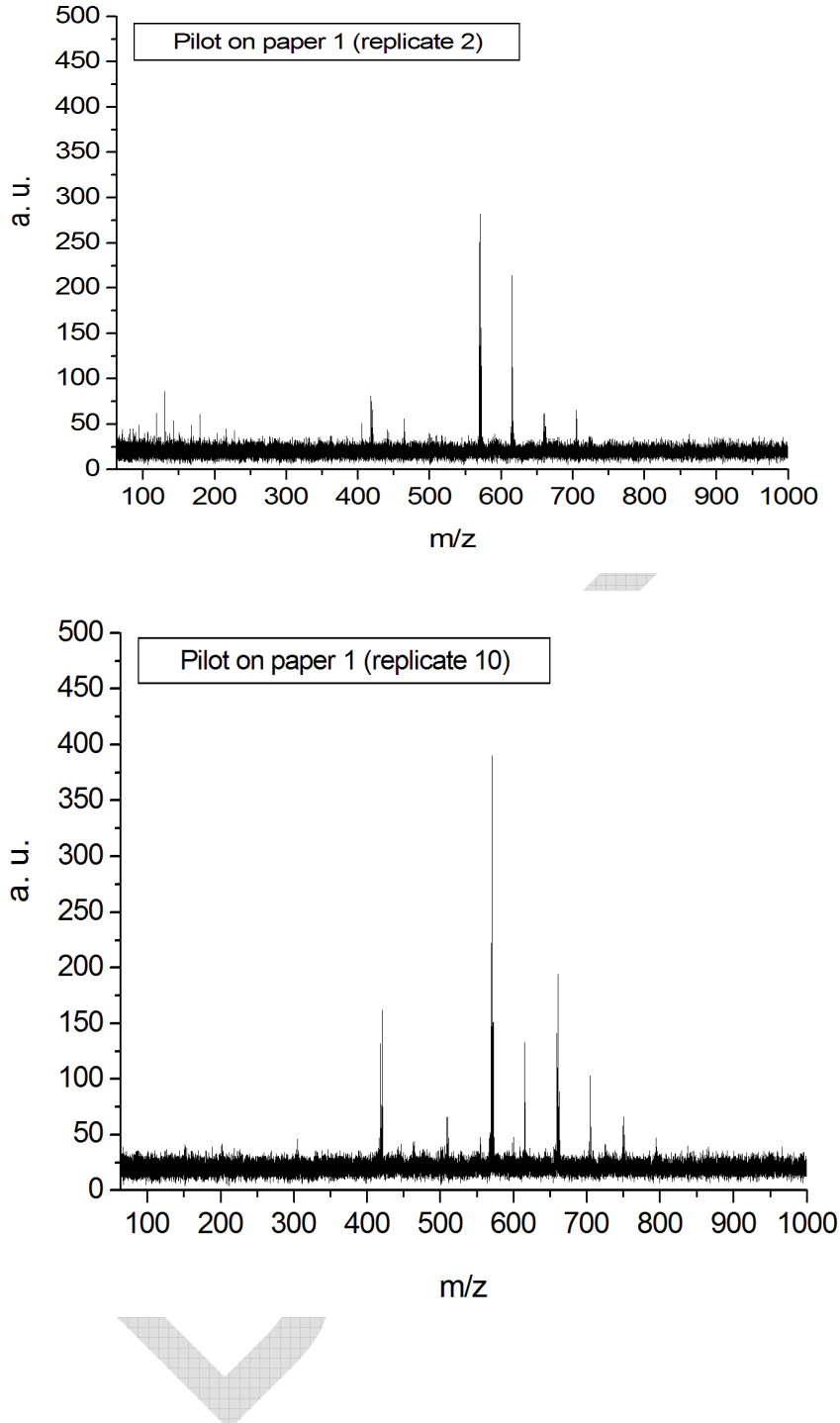
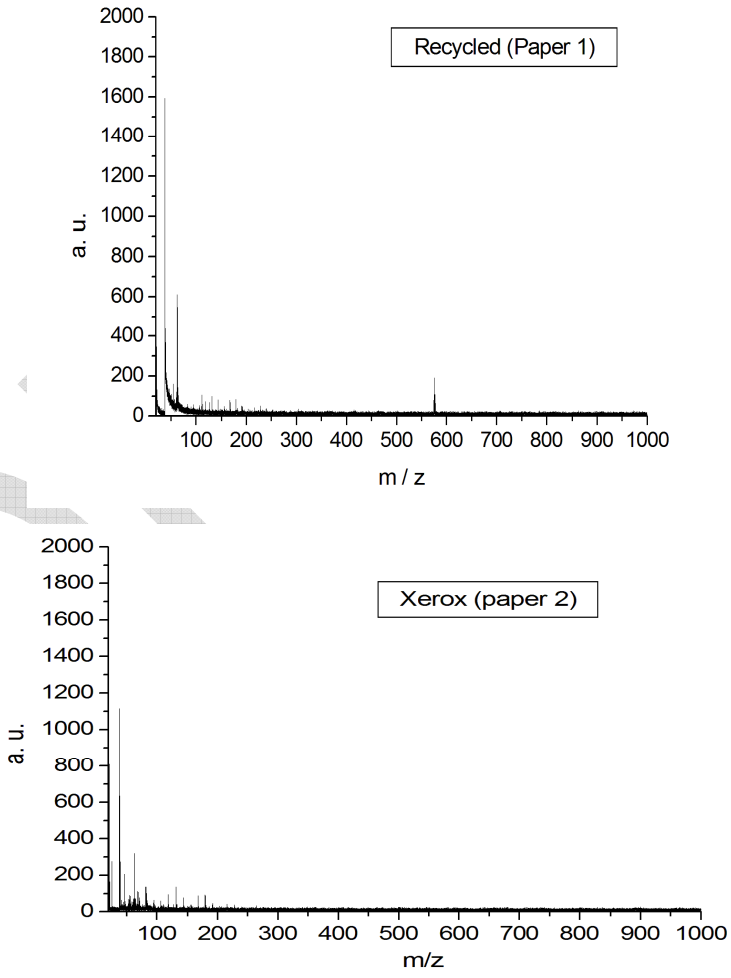


Figure 5 – LDI-MS Spectra of gel pens ink Pilot on paper 1: replicate analyses 2 and 10 yielded significantly different spectra (resulting in a low Pearson correlation value of 0.07 for the comparison),

3.2 Influence of Paper

The blank paper spectra showed several peaks in the beginning of the spectra between m/z 20 and 64 u (Figure 6). The Pearson correlation coefficients were indeed larger when the statistical comparison was performed on a data set starting at m/z 64 u. (instead of 20 u.). Both recycled and HP paper additionally yielded a peak at 575 u., probably from low quantities of pigment blue 15 (PG15) present in the paper [20]. While Pilot ink also contains this pigment, it also showed the usual derivatives of PG15 [25]. However, the paper PG15 peak did not seem to actually significantly influence the results (i.e., the mean relative intensities were not different between paper 1, 2 & 3).



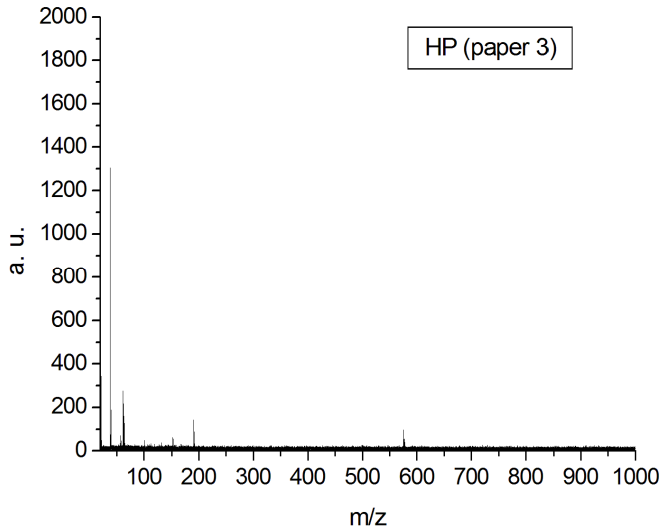
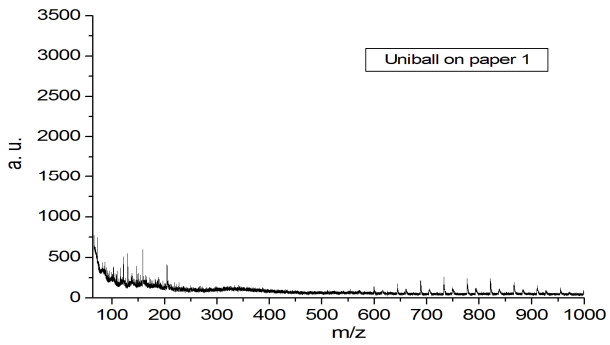


Figure 6 – LDI-MS Spectra of blank paper 1 (recycled), 2 (Xerox) and 3 (HP).

The homogeneity of ink samples was thus analysed by comparing Pearson values of the same ink on different papers (Figure 4B). Obtained Pearson coefficients values were generally lower, indicating a significant influence of paper on the results. While the influence was relatively low for Pentel and Pilot inks (median values showing a decrease of 0.17 and 0.02 respectively), Uniball ink proved to be the least homogenous on different paper yielding much lower Pearson values (median showing a decrease of 0.71). For this ink, the differences between papers came essentially from the beginning of the spectra and were particularly visible for paper 1 that yielded much less intense MS spectra (Figure 7). The influence of the paper did not seem to come from additional peaks from the paper actually disturbing the statistical comparison, but from differences within the ink signals (mainly repression or decrease of signals and large differences in relative intensities).



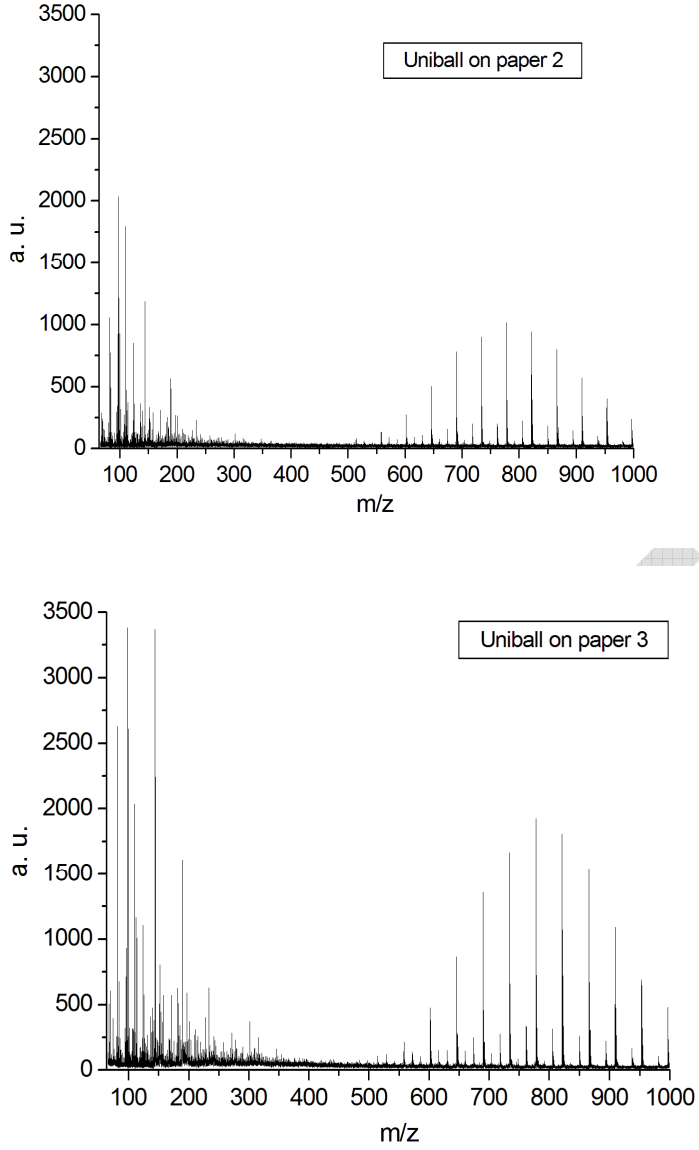


Figure 7– LDI-MS Spectra of Uniball on three papers (recycled), 2 (Xerox) and 3 (HP).

3.3 Ink discrimination

In addition, the results were evaluated to determine whether it was possible to discriminate between 2 different samples of ink without taking into account the paper type (Figure 4C and Figure 8).

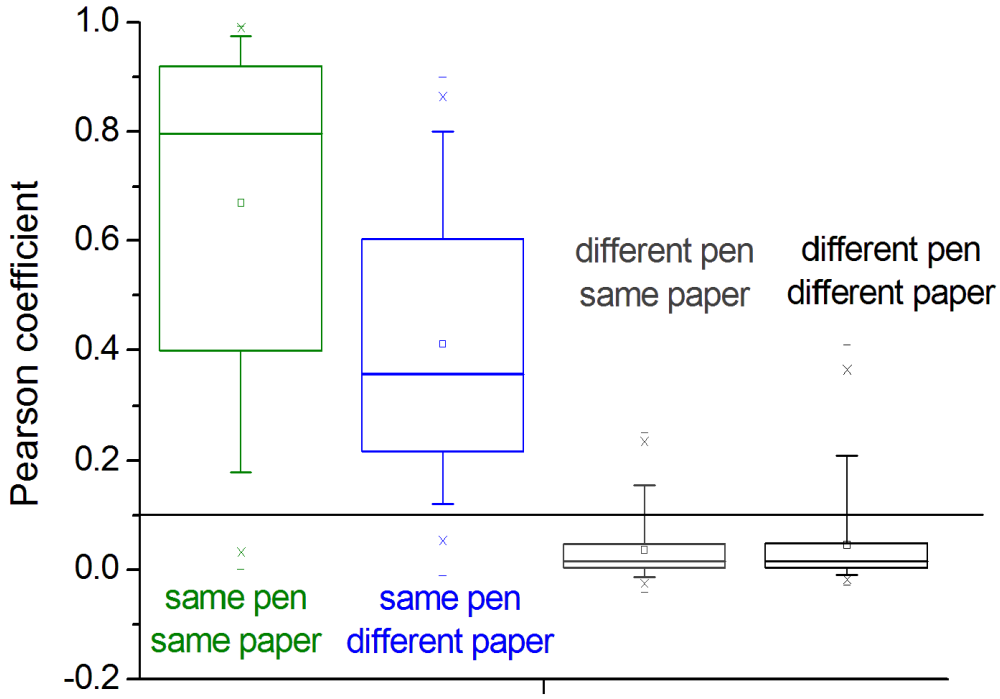


Figure 8 - Box charts showing the distribution of Pearson correlation coefficient values for the comparison of ink samples between specimens of: (1) same pen on same paper specimen, (2) same pen on different paper, (3) different pen on same paper and (4) different pen on different paper.

Median Pearson values for discrimination (i.e., different ink comparison) were generally much lower than for same ink comparison (Figure 4C). Median values were 0.016 and 0.017 for discrimination on same paper and on different papers respectively (Figure 8). However comparison of Pentel and Uniball inks on paper 1 yielded higher correlation values than expected for different pens due to the influence of paper on Uniball results (median of 0.14 in figure 4A). This may actually disturb the comparison into a non-differentiation (i.e. a false positive) which is however not as problematic as false negatives (i.e. false differentiation) [17]. However, this must be taken into account when comparing inks which are more similar in composition, because the issue of paper may then be more pronounced.

However, using PCA it was clearly possible to classify the three inks in different groups (Figure 9). Larger distributions were observed when considering replicate analyses on all types of papers (see Figure 9A). It was also interesting to see that the Pilot ink showed less

variation using PCA than Pentel or Uniball, contrary to the results obtained when comparing two samples using Pearson correlation coefficient. This may indicate that better approaches to statistically differentiate inks using whole LDI-MS spectra may yield more promising results. Our results seem to indicate that background noise may cause most of the differences when comparing inks that actually yielded lower signals using Pearson correlation. In fact, the Pilot and Uniball ink spectra on recycled paper (paper 1) were visually differentiable (see figure 5 and 7 for mass spectra), indicating the unsuitability of the proposed comparison using Pearson correlation for such mass spectra.

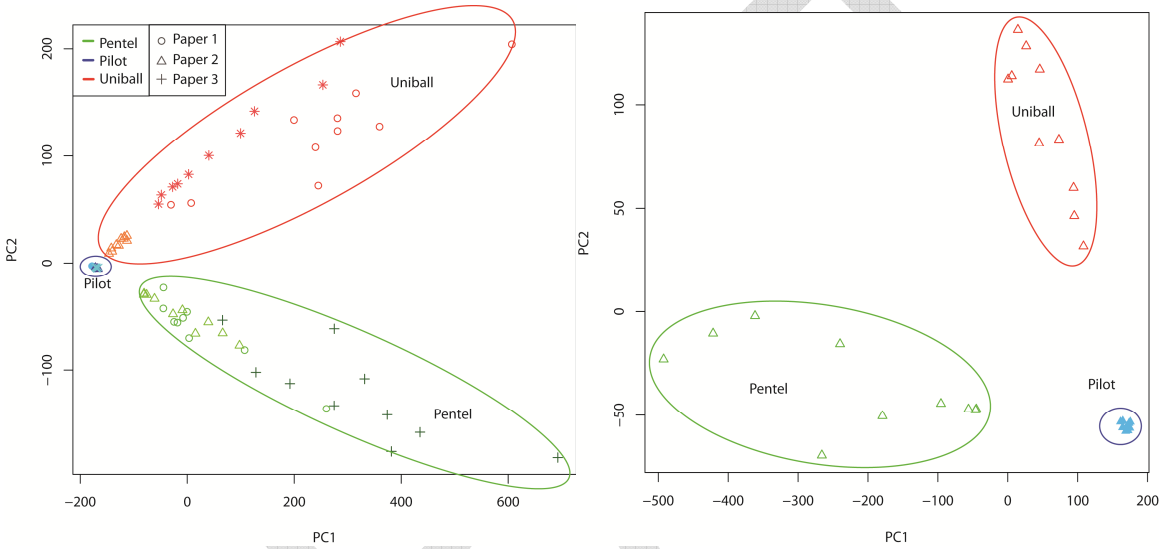


Figure 9 – PCA distribution of raw data for: (A) All pens on all papers (PC1 and 2 explained 83% of the variance) and (B) All pens on paper 2 (PC1 and 2 explained 75% of the variance).

4. Conclusion

This study has introduced a new understanding to the field of ink analysis using LDI-MS in terms of reproducibility of the analysis and potential interferences in spectra produced by the paper.

Firstly, when evaluating reproducibility, we observed that the mass spectra of each of the sample replicates (different strokes of the same ink) demonstrated slight calibration irregularities probably due to paper irregularities. It is essential that these m/z shifts are corrected early prior to data comparison thus enhancing data reliability. Our results thus

demonstrated that homogeneity for replicate ink sample was generally satisfying (i.e., large Pearson correlation values were obtained). However, it was to some extent sample dependent and the comparison of Pilot ink samples showed large variations (i.e., low Pearson values). The homogeneity was generally more problematic for inks yielding small peak intensities. It is therefore crucial to test the sample homogeneity before comparing it to other ink samples using correlation coefficients. If the ink is proven to be inhomogeneous, analysis should cease using this method.

It was also observed that paper had to some extent a significant influence on the mass spectra as a decline in Pearson values was observed for the same ink tested on different paper types. The largest paper influence was observed for Uniball ink on recycled paper. Interestingly, the paper influence was never due to additional peaks appearing in the spectra. It was mainly due to a change in the intensity of the ink mass spectra. For this reason, it is also important to ensure that the sample of paper bearing the ink is the same or does not significantly influence the results for the inks under question.

When trying to discriminate between two different inks (without taking into account the paper type) using Pearson's Correlation, inks yielding small signals were not always well discriminated (e.g., Pentel and Uniball on recycled paper). However, the spectra were easily differentiable visually. Thus PCA statistics were used as an interesting alternative to differentiate the three different inks independently of the paper type.

Future research should endeavour to focus on more suitable objective comparison of the mass spectra than correlation coefficients calculated on the whole spectra.

5. Acknowledgements

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