Science & Justice 62 (2022) 433–447

Contents lists available at ScienceDirect

Science & Justice

journal homepage: www.elsevier.com/locate/scijus

Research Paper

# Profiling and imaging of forensic evidence – A pan-European forensic round robin study part 1: Document forgery

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https://doi.org/10.1016/j.scijus.2022.06.001
Received 3 November 2021; Received in revised form 4 April 2022; Accepted 2 June 2022
Available online 7 June 2022

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ARTICLE INFO

*Keywords:*
Multimodal imaging
Document forgery
Round robin study

ABSTRACT

The forensic scenario, on which the round robin study was based, simulated a suspected intentional manipulation of a real estate rental agreement consisting of a total of three pages. The aims of this study were to (i) establish the amount and reliability of information extractable from a single type of evidence and to (ii) provide suggestions on the most suitable combination of compatible techniques for a multi-modal imaging approach to forgery detection. To address these aims, seventeen laboratories from sixteen countries were invited to answer the following tasks questions: (i) which printing technique was used? (ii) were the three pages printed with the same printer? (iii) were the three pages made from the same paper? (iv) were the three pages originally stapled? (v) were the headings and signatures written with the same ink? and (vi) were headings and signatures of the same age on all pages? The methods used were classified into the following categories: Optical spectroscopy, including multispectral imaging, smartphone mapping, UV-luminescence and LIBS; Infrared spectroscopy, including Raman and FTIR (micro-)spectroscopy; X-ray spectroscopy, including SEM-EDX, PIXE and XPS; Mass spectrometry, including ICPMS, SIMS, MALDI and LDIMS; Electrostatic imaging, as well as non-imaging methods, such as non-multimodal visual inspection, (micro-)spectroscopy, physical testing and thin layer chromatography. The performance of the techniques was evaluated as the proportion of discriminated sample pairs to all possible sample pairs. For the undiscriminated sample pairs, a distinction was made between undecidability and false positive claims. It was found that none of the methods used were able to solve all tasks completely and/or correctly and that certain methods were *a priori* judged unsuitable by the laboratories for some tasks. Correct results were generally achieved for the discrimination of printer toners, whereas incorrect results in the discrimination of inks. For the discrimination of paper, solid state analytical methods proved to be superior to mass spectrometric methods. None of the participating laboratories deemed addressing ink age feasible. It was concluded that correct forensic statements can only be achieved by the complementary application of different methods and that the classical approach of round robin studies to send standardised subsamples to the participants is not feasible for a true multimodal approach if the techniques are not available at one location.

## 1. Introduction

Advances in analytical chemistry continuously bring forth new approaches with forensic significance. In particular, the importance of forensic photography in the production of evidence led to a growing interest in novel imaging techniques. Within the scope of the European COST Action networking scheme [1], a group of European researchers, end users and industry representatives received funding for „MULTImodal Imaging of FOREnsic SciEnce Evidence (MULTI-FORESEE) - tools for Forensic Science“ (Action CA16101) [2,3]. The Action aims to promote innovative, multi-informative, operationally deployable and commercially exploitable solutions/technology to analyse forensic evidence [4].

Traditionally, detection of forgery of documents includes analysis of inks from stamps, pens or printers, printer toners, paper, as well as studies on intersection lines and dating. Various attempts to combine techniques targeting organic and inorganic analytes on the same sample material using Raman spectroscopy, laser induced breakdown spectroscopy (LIBS) [5], Fourier transform infrared microspectroscopy and scanning electron microscope/energy dispersive X-ray mapping or EDX-RF [6], LA-ICP-MS, mass spectrometry [7] and other techniques have been reported in the literature. The reliability of the results could be increased by combining different techniques. An overview of the state of the art of forensic document analysis was given by [8], which distinguished between spectrometric techniques, such as hyperspectral imaging, X-ray spectroscopy, mass spectrometry and infrared or Raman spectroscopy, and separation techniques, such as thin-layer or high-performance liquid chromatography. The rationale for using techniques such as LIBS, ICP-MS, SIMS, MALDI-MS or LDI MS as imaging techniques is to harness the analytical opportunities of imaging based techniques enabling the “anatomical visualisation” of fine physical/molecular features of the evidence, otherwise inaccessible through methods such as chromatography requiring destruction of the sample integrity.

The term multimodal imaging had its origins in medicine and is considered to involve the incorporation of two or more imaging modalities [9], where imaging modalities are often categorized by the method in which images are generated and include techniques like ultrasound, radiation such as x-rays, and MRI [10]. It is of great importance to distinguish between a multimodal approach and multichannel techniques, as each multichannel technique represents only one modality. Hence, an overall statement from a multimodal imaging approach *in sensu strictu* is only possible if the spatial information is identical, i.e. if exactly the same specimen was examined with all techniques. In reality there are two options: 1. Equipment which integrates more than one imaging modalities and the specimen is analysed “on line” by both and 2. Subjecting the same specimen to two or more techniques one after the other “offline”. Taking into account that the highly specialised equipment is not available everywhere, the same type of specimen preparing in multiple identical copies was used, one per lab in the present study.

In forensic science, there is an underlying lack of standardisation underpinning the analytical protocols for the acquisition, processing and reporting of imaging data. Software packages integrated with statistical analysis for processing the imaging data are missing or not specific to the type of evidence investigated. This naturally leads to incomparable data between centres using diverse methodologies and hinders the development of integrated multi-modal imaging platforms [4].

The aims of our study were to a) establish the amount and reliability of information extractable from a single type of evidence and b) on the basis of the results obtained, provide suggestions on the most suitable combination of compatible techniques for a multi-modal imaging approach to forgery detection. In order to recommend workflows that maximise analytical information from the evidence, we do not

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distinguish between spectrometric and separation techniques in our study, but categorise the methods used according to their destructiveness.

The forensic scenario on which the round robin study was based simulated a suspected intentional manipulation of a real estate rental agreement consisting of a total of three pages, which were prepared under controlled conditions at the Portuguese Police Forensic Laboratory. The following research queries were addressed and named tasks T1-T6: (T1) which printing technique was used to print the three pages?; (T2) were the three pages printed with the same printer?; (T3) are the three pages made out of the same paper?; (T4) were the three pages originally stapled?; (T5) were the headings and signatures written with the same ink?; (T6) are the headings and signatures on all pages of the same age? No criteria were set for the selection of the methods at the outset of the exercise, except that at least one method per task should be imaging. The study complies with the "Guidance on the Conduct of Proficiency Tests and Collaborative Exercises within ENFSI" and was designed as collaborative exercise to address method validation or characterization performed on test material supplied to all individual participants for concurrent examination as covert test [11].

The three pages were analysed in seventeen laboratories located in Austria, Belarus, Croatia, the Czech Republic, Germany, Italy, Latvia, Macedonia, the Netherlands, Norway, Poland, Portugal, Slovakia, Spain, Switzerland and the United Kingdom.

The techniques used were classified into the following categories:

### 1.1. Imaging

Broadband multi- and narrowband hyperspectral imaging (MHI [12,13]), smartphone mapping (SM [14–16]), laser induced breakdown spectroscopy (LIBS [5]), scanning electron microscopy coupled to energy dispersive X-ray fluorescence spectroscopy (SEM), laser ablation ICP time-of-flight mass spectrometry (LA-ICP-ToF-MS), secondary ion mass spectrometry (SIMS [17]), matrix assisted laser desorption ionisation spectrometry (MALDI-MS [18]), laser desorption ionization mass spectrometry (LDI MS [19]), electrostatic imaging (ES [20]).

### 1.2. Profiling with imaging capabilities

UV-luminescence (UVL), Fourier transform infrared microscopy (FTIR), Raman microscopy (Raman), particle induced X-ray emission spectroscopy (PIXE), X-ray photoelectron spectroscopy (XPS [21]), (micro-)spectroscopy (UV–VIS).

### 1.3. Other techniques

Physical testing (Phys), visual inspection (VI), thin layer chromatography (TLC).

The category "multi- and hyperspectral imaging" (MHI) includes all imaging techniques using more than three spectral channels of the visible range (typically RGB channels of digital cameras), including all techniques based on monochromatic illumination techniques (like the Foster&Freeman VSC instrument series), based on mounting spectral filters to camera lenses (like RGB-NIR photography), as well as hyperspectral imaging using narrow band imaging sensors. The category "visual inspection" includes all techniques using (non-multimodal in the sense of the given study) RGB imaging, like digital cameras, sensors mounted to optical microscopes, flatbed scanners, single channel imaging techniques (like magneto-optical visualization, metallographic microscopy) as well as RGB image processing. Detailed method specifications are listed in supplementary file mmc2.

A second criterion of classification was destructiveness: while non-destructive methods do not alter the sample at all, microinvasive methods are considered to consume small amounts of the sample, leaving untreated sample areas unchanged. In contrast to these two categories, destructive sampling alters the sample surface in such a way that the sample becomes unsuitable for subsequent analysis, e.g., by gold sputtering in SEM.

## 2. Materials and methods

The forged documents were prepared under identical conditions at the Portuguese Police Forensic Laboratory. The features to be identified are summarized in Table 1. The individual laboratories were given the opportunity to decide which of the tasks they were able to complete and which workflow they deemed it to be most appropriate for it.

The methods employed by the different laboratories to analyse the lease agreement are summarized in Table 2. Each report submitted was given a unique anonymized identifying number. An overview of the instrumentation used for the document forgery study is given in supplementary file mmc1. The individual laboratories detailed in their reports how they had reached their conclusions. We provide the reports as supplementary files mmc3 - mmc20.

Since our study was designed to compare methods but not laboratories, the laboratories were explicitly encouraged to carry out within laboratory method comparisons but not necessarily to use the methods that the investigators considered *a priori* to be the most promising. The participants of the study were from academia, policing and accredited forensic laboratories.

### 2.1. Data evaluation

The participating laboratories were invited to provide the methodological specifications together with the results, also all steps of data exploration were requested, i.e. data processing prior to statistical analysis, how was the manufacturer prorpietary software used with respect to data handling and what processing was performed by independent software tools such as Matlab, SPSS, R-programming etc.

The method performance (MP) employed in this work was evaluated according to [22] as:

**Table 1**
Features to be identified of the three pages of the lease agreement.

| | Page 1 | Page 2 | Page 3 |
|---|---|---|---|
| **Task 1** | The printed text was produced by a monochromatic electrophotographic process. | | |
| **Task 2** | Page 2 was printed with a different printer than pages 1 and 3. | | |
| | **Printers** | | |
| | Konica Minolta model bizhub | OKI Model ES8453 MFP223 | Konica Minolta model bizhub |
| **Task 3** | The paper of pages 1 and 3 was identical, the paper of page 2 differed. | | |
| | **Paper** | | |
| | Inacópia office 80 g/m$^2$, 100 µm | Staples 80 g/m$^2$, 100 µm | Inacópia office 80 g/m$^2$, 100 µm |
| **Task 4** | Marks could be observed in the staple area of pages 1 and 3 which were not existing on page 2. | | |
| | Staple marks match with page 3 | Less staple marks than pages 1 and 3 | Staple marks match with page 1 |
| **Task 5** | The writing pen inks used for the headings on page 1 were the same to the respective signatures on page 3. The writing pen inks used for the headings on page 2 are different from the others. | | |
| | Page 1 | Page 2 | Page 3 |
| | *Heading/Signature of the first grantor* | | |
| | Blue Gel pen Mitsubishi uni.ball Signo | Blue Gel pen Mitsubishi uni.ball Signo 0.7 | Blue Gel pen Mitsubishi uni.ball Signo |
| | *Heading/Signature of the second grantor* | | |
| | Black ballpoint pen BIC | Black ballpoint pen Pentel SUPERB | Black ballpoint pen BIC |
| | *Heading/Signature of the third grantor* | | |
| | Blue ballpoint pen 'white label' | Blue ballpoint pen OfficeCover Astro 1.0 | Blue ballpoint pen 'white label' |
| **Task 6** | Signatures on pages 2 were written 5 days after the ones on pages 1 and 3 | | |

**Table 2**
Methods used for the different tasks (T1 to T5) of the document forgery study. Numbers in table indicate report number. Task 6 (ink age) was not conducted by any of the laboratories involved and was omitted here. *without multi-modal imaging capabilities.

| Category | Abbr. | T1 printing technique? | T2 same printer? | T3 same paper? | T4 pages stapled? | T5 same inks? |
|---|---|---|---|---|---|---|
| **Optical** | | | | | | |
| Multispectral imaging | MHI | 2,17 | 2,4,17 | 2,4,17 | 4,17 | 2,4,8,17 |
| Smartphone mapping | SM | | 4 | | | |
| UV luminescence | UVL | | | 9 | | |
| Laser-induced breakdown spectroscopy | LIBS | | 12 | 12 | | 12 |
| **Vibrational spectroscopy** | | | | | | |
| FTIR microscopy | FTIR | 2 | 2,5,7,19 | 2,5,19 | | 2,5,19 |
| Raman microscopy | Raman | | 10 | | | 7,10 |
| **X-ray** | | | | | | |
| SEM-EDX | SEM | 2,3,18,19 | 2,3,18,19 | 2,18 | | 2 |
| microPIXE | PIXE | | 6 | | | |
| X-ray Photoelectron Spectroscopy | XPS | | 20 | 20 | | 20 |
| **Mass spectrometry** | | | | | | |
| LA-ICP-ToF-MS | ICPMS | | 3 | 3 | | 3 |
| ToF-SIMS | SIMS | | 3,6 | 3 | | 3,6 |
| MALDI-MS | MALDI | | 14,15 | 15 | | 14,15 |
| LDI-MSI | LDIMS | | 116 | 16 | | 16 |
| **Single-channel imaging*** | | | | | | |
| Electrostatic imaging | ES | | | | 4 | |
| **Non-imaging*** | | | | | | |
| Visual inspection | VI | 4,7,8,9,14,16 | 4,5,8,9,10 | 7,9,18,19 | 3,5,6,7,8,9,12,14,16,18,19 | 2,4,5,7,9,19 |
| optical spectroscopy | UVVIS | 2 | 2,5 | 2,19 | | 2,5,7,18 |
| Physical testing | Phys | | | 2,9,14,18 | | |
| Thin layer chromatography | TLC | | 9 | 9 | | 9 |

$$MP = 100 \cdot \frac{number\ of\ discriminated\ sample\ pairs}{number\ of\ possible\ sample\ pairs}.$$

However, it is of paramount importance in jurisdiction to distinguish between situations where no decision can be made and false positive claims if no correct answer was given, because these instances can determine the court's decision on the defendant's guilt or innocence. Therefore, undecidability has been calculated as:

$$UD = .100 \cdot \frac{number\ of\ undecidable\ sample\ pairs}{number\ of\ possible\ sample\ pairs}$$ and false positive claims as:

$$FC = 100 \cdot \frac{number\ of\ false\text{–}positive\ sample\ pairs}{number\ of\ possible\ sample\ pairs},$$

with $DP + UD + FC = 100\%$.

Conclusions of the kind: "no decision could be made", "not possible to answer this question", "lack of strong evidence", "the technique does not allow us to distinguish between specimens" or "contradictory results" were treated as undecidability.

## 3. Results

These reports were reviewed by all participants and found to be valid.

### 3.1. Task 1 (printing technique)

Task 1 was addressed using multi- and hyperspectral imaging (2 reports), visual inspection (6 reports), FTIR spectroscopy (1 report), scanning electron microscopy (4 reports), and optical spectroscopy (1 report).

The correct answer, that the printing technique used was a monochromatic electrophotographic process (laser printing) was given by all reports using visual inspection, FTIR spectroscopy and optical spectroscopy. Multi- and hyperspectral imaging failed in 100% of the reports submitted (undecidable in reports #2 and #17, see supplementary files mmc3 and mmc17). Scanning electron microscopy failed in 25% of the reports submitted (pages 1 and 3 falsely claimed as ink printer in report #3, see supplementary file mmc4), and optical spectroscopy failed (undecidable in report #2, see supplementary file mmc3). Example images for successful identification of the printing technique are shown in Fig. 1.

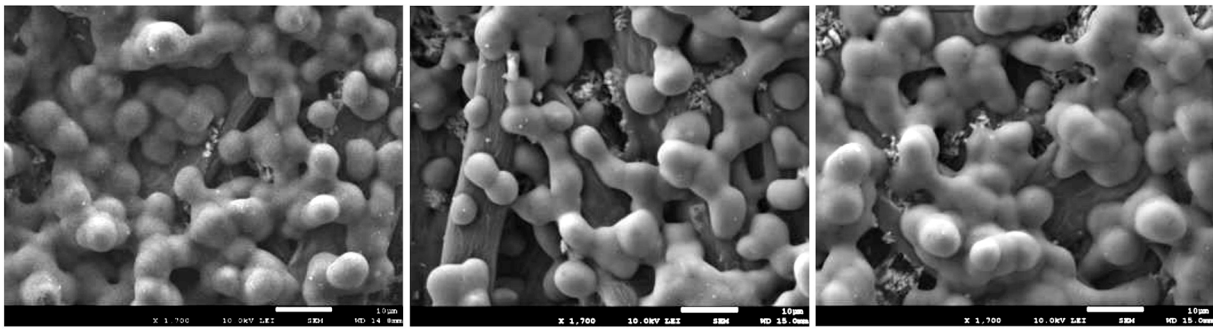
### 3.2. Task 2 (printer discrimination)

Task 2 was addressed using multi- and hyperspectral imaging (3 reports), visual inspection (5 reports), smartphone mapping (1 report), LIBS (1 report), FTIR spectroscopy (4 reports), Raman spectroscopy (1 report), scanning electron microscopy (4 reports), particle induced X-ray emission spectroscopy (1 report), X-ray photoelectron spectroscopy (1 report), LA-ICP-ToF-MS (1 report), SIMS (2 reports), MALDI-MSI (1 report), LDI-MSI (2 reports), optical spectroscopy (2 reports) and thin layer chromatography (1 report).

The correct answer, that page 2 was printed with a different printer than pages 1 and 3, was given by all reports using visual inspection, smartphone mapping, LIBS, FTIR and Raman spectroscopy, scanning electron microscopy, particle induced X-ray emission spectroscopy, X-ray photoelectron spectroscopy, LA-ICP-ToF-MS, SIMS, LDI MSI, optical spectroscopy and thin layer chromatography. Multispectral photography falsely claimed identity in report #2 ("no differences identified", see supplementary file mmc3), and printer discrimination was undecidable with MALDI MSI (report #15, see supplementary file mmc15). Example images for successful printer discrimination are shown in Fig. 2.

### 3.3. Task 3 (paper discrimination)

Task 3 was addressed using multi- and hyperspectral imaging (3 reports), visual inspection (3 reports), UV luminescence (1 report), LIBS (1 report), X-ray photoelectron spectroscopy (1 report), FTIR spectroscopy (3 reports), scanning electron microscopy (2 reports), LA-ICP-ToF-



(a) (b) (c)

**Fig. 1.** SEM-Image of molten toner particles from pages 1 (a), 2 (b) and 3 (c); see Fig. 5 from report #19 in supplementary file mmc19.

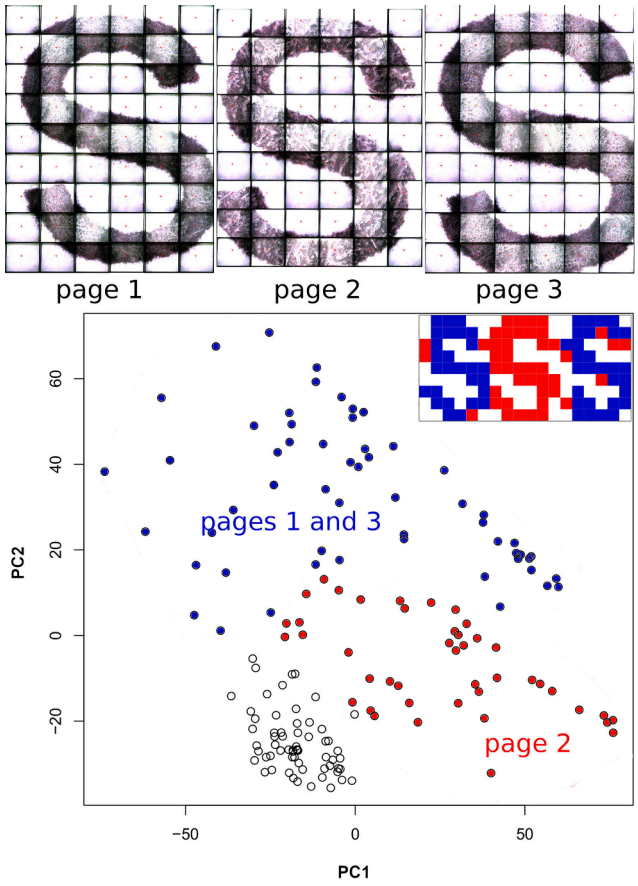



**Fig. 2.** Result of PCA classification of microscopic FTIR spectra of the letter "s" from pages 1, 2 and 3. In the upper section, composite images of the examined letters of individual 300 µm × 300 µm recordings in diffuse reflectance mode (DRIFTS) are shown. The upper right part of the ordination plot maps cluster membership. The spectra of the toner of page 2 (coloured in red) cluster apart from the spectra of the toner of pages 1 and 3 (coloured in blue) in a PCA ordination plot. (report #2, see supplementary file mmc3). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

MS (1 report), SIMS imaging (1 report), MALDI-MSI (1 report), LDI-MSI (2 reports), optical spectroscopy (3 reports), physical testing (4 reports) and thin layer chromatography (1 report).

The correct answer, that the paper of pages 1 and 3 was identical, whereas the paper of page 2 differed was given by all reports using visual inspection, UV luminescence, LIBS, scanning electron microscopy, optical spectroscopy, physical testing and thin layer chromatography. Example images for successful identification of the printing technique are shown in Figs. 3 and 4.

While SIMS imaging resulted in a false positive claim in report #3 (supplementary file mmc4), multi- and hyperspectral imaging, FTIR spectroscopy, X-ray photoelectron spectroscopy, LA-ICP-ToF-MS, LDI-MSI, and MALDI-MSI claimed undecidability in reports #17 (supplementary file mmc17), #5 (supplementary file mmc6), #20 (supplementary file mmc20), #3 (supplementary file mmc4), #16 (supplementary file mmc16) and #15 (supplementary file mmc15), respectively.

### 3.4. Task 4 (pages stapled)

Task 4 was addressed using multi- and hyperspectral imaging (2 reports), visual inspection (11 reports) and electrostatic imaging (1 report). The performance of visual inspection amounted to 91%, because report #14 (supplementary file mmc14) identified multiple staple marks at page 2 and single staple marks at pages 1 and 3, which was documented photographically. Electrostatic imaging produced the correct result that multiple marks could be observed in the staple area of pages 1 and 3 which were not existing on page 2, whereas multi- and hyperspectral imaging and visual inspection failed in report #17 (supplementary file mmc17) but succeeded in report #4 (supplementary file mmc5). An example image for successful identification of staple marks is shown in Fig. 5.

### 3.5. Task 5 (comparison of inks)

Task 5 was addressed using multi- and hyperspectral imaging (4 reports), visual inspection (3 reports), LIBS (1 report), FTIR spectroscopy (2 reports), Raman microscopy (2 reports), scanning electron microscopy (1 reports), X-ray photoelectron spectroscopy (1 report), LA-ICP-ToF-MS (1 report), SIMS imaging (2 reports), MALDI-MSI (1 report), LDI-MSI (2 reports), stereomicroscopy (3 reports) and thin layer chromatography (1 report).

Task 5 was subdivided into independent comparisons of the signatures of each signer between the three pages. Scanning electron and Raman microscopy, LA-ICP-ToF-MS, SIMS imaging and LDI-MSI failed the task. The correct answer for signature 1 (João Oliveira Martins) was given by visual inspection (reports #8 and #19, supplementary files mmc9 and mmc19), optical imaging (report #5, supplementary file mmc6) and thin layer chromatography (report #9, supplementary file mmc10); the correct answer for signature 2 (Sonia Alexandra Sousa Marques Figueira) was given by optical spectroscopy (report #18, supplementary file mmc18) and by MALDI-MSI; the correct answer for signature 3 (Pedro Miguel Sousa Marques) was given by FTIR spectroscopy (report #19, supplementary file mmc19), MALDI-MSI (report #15, see supplementary file mmc15), optical spectroscopy (report #18, supplementary file mmc18) and thin layer chromatography (report #9,

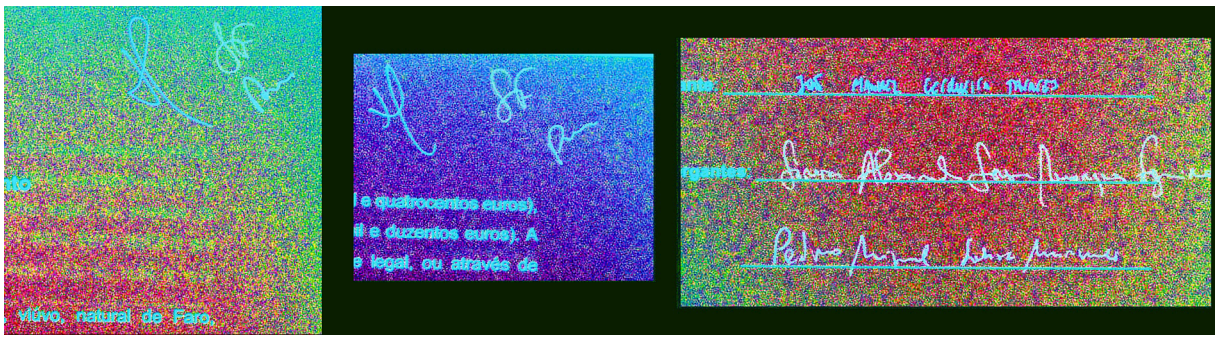


**Fig. 3.** Self-organized map clustering of RGB-NIR image (using the GERBIL hyperspectral imaging tool [23], 4 spectral channels, cluster membership is depicted in different colours); Page 2 (depicted in blue) clustered differently from pages 1 and 3 (appearing in red and green, depending on intensity of illumination; see Fig. 1 from report #2 in supplementary file mmc3). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

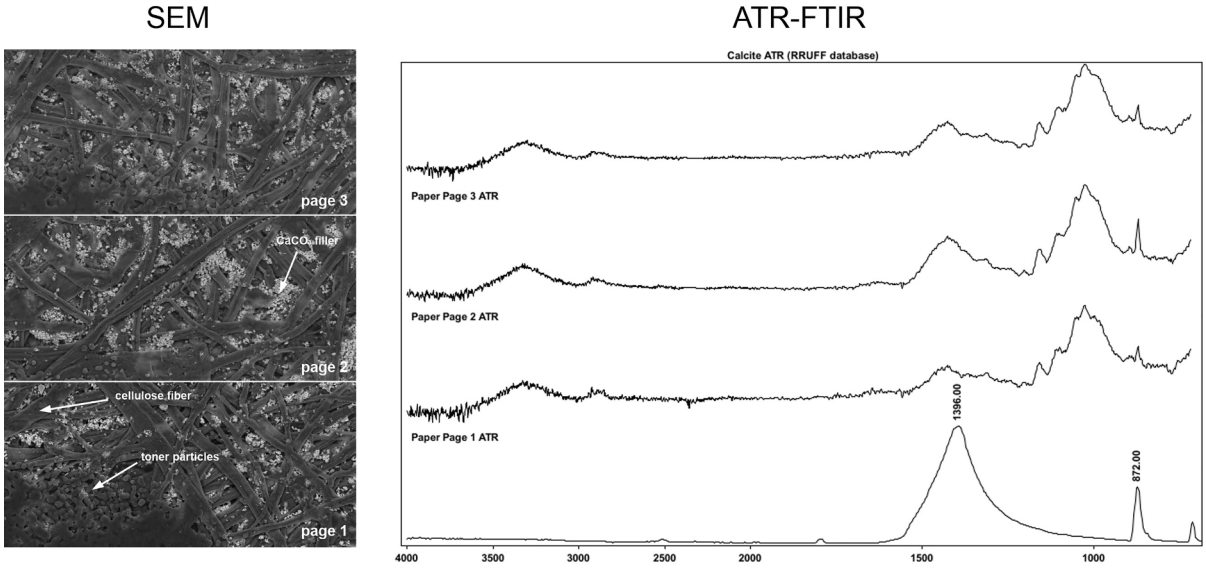



**Fig. 4.** SEM images (left) and ATR spectra (right, calcite shown as reference) of the paper of pages 1, 2 and 3. Higher intensities of peaks at 1396 cm-1 and 872 cm-1 indicate higher amount of filler in the paper of page 2. Higher amounts of Ca in the paper of page 2 were confirmed by elemental analysis (supplementary file mmc3).

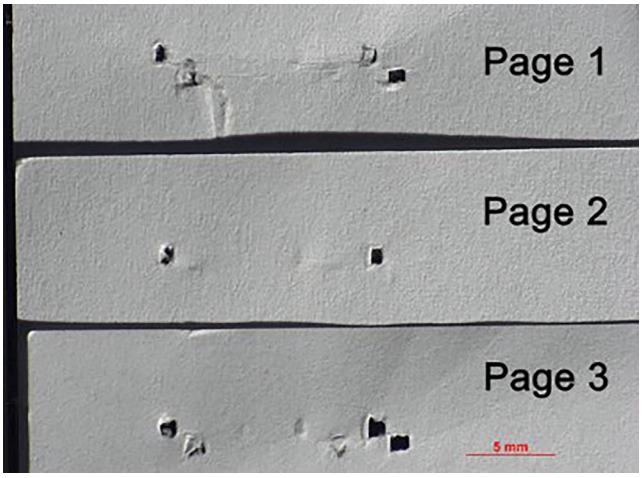



**Fig. 5.** Visual inspection was used to examine staple marks. While pages 1 and 3 were staples twice, page 2 was stapled only once (Fig. 2 of report #8 in supplementary file mmc9).

supplementary file mmc10). LIBS and X-ray photoelectron spectroscopy fully succeeded in task 5. Table 3 details the statements in each report of how participants justified their conclusions for task 5. Example spectra for the successful discrimination of inks are shown in Fig. 6.

### 3.6. Task 6 (age of signature)

The age of the signature can be used as an additional feature to detect a forgery. For example, it can be assumed that the signatures on subsequently replaced pages must be newer than the original signatures. However, task 6 was not addressed in any of the reports submitted as currently there is no workable framework or operational protocols to address this forensic question.

## 4. Discussion

The method performance, false positive claims and undecidability for each method category and task are summarized in Fig. 7.

### 4.1. Tasks 1 (printing technique) and 2 (printer discrimination)

Toner is a dry powder that contains organic polymers (binders) in addition to the colorant which melt by heat when an image is fixed to

**Table 3**
Correct answers, false claims and undecidability of ink comparison (task 5). The signatures of João Oliveira Martins (bright blue), Sonia Alexandra Sousa Marques Figueira (black) and Pedro Miguel Sousa Marques (dark blue) are denominated as signatures 1, 2 and 3, respectively. N/A - no conclusion made, answer provided by organizer of study, HPLC - high performance liquid chromatography with diode array detection, [#]individual differences not indicated, [§]thickness of the pen-point at page 2 differs from pages 1 and 3; For detailed method specifications see supplementary file mmc2.

| Method used | Result | Report No. | Conclusion |
|---|---|---|---|
| MHI | undec. | 2 | Results contradictive depending on algorithm. |
| | | 8 | The optical examinations (VSC) cannot discriminate the inks. |
| | false claim | 4 | Each signature on all pages most likely is written with the same ink; slight differences of blue ink signatures on 1st and 2nd pages were observed. |
| | success | 17 | Not with the same ink: this could be classified very easily.[#] |
| VI | false claim | 2 | Different signature 1 on page 3. |
| | | 8 | Signatures 2 and 3: The signature/heading on pages 1 and 3 have been produced with a ballpoint pen using a black ink. The same is true for the page 2. |
| | undec. | 4 | Metallographic microscopy: We cannot claim that the used inks are different as the traces may look differently depending on how hard writer pushes the pen to paper, which paper is used, etc. |
| | | 19 | Signature 2: There is variability in all observed pages since all the signatures slightly vary. |
| | success | 8 | Signature 1: different stroke morphology. |
| | | 19 | Signature 1: Continuity of signature 1 on page 2 differs from pages 1 and 3. Signature 1 on page 2 has differences in colour through line thickness. |
| LIBS | success | 12 | light blue signatures: The signature at page 2 is different because it contains also barium and manganese impurity.<br>dark blue signatures: The ink at page 2 is different as it has about twice higher Zn content than at pages 1 and 3, and it also contains iron, which was not observed at pages 1 and 3 [5].<br>black signatures: Page 2 is different but when dealing with very low discriminatory signals as here (from Pb and Zn) and with single point measurements, such difference is weakly supported [5]. |
| XPS | success | 20 | Signature 1: Different atomic composition at pages 1 and 3 and at page 2. Atomic concentration of C, O and Cu averaged to 78.2, 10.2 and 1.5%, respectively, at pages 1 and 3 and to 69.8, 22.1 and 0.9%, respectively, at page 2. The C 1 s core level spectra used at pages 1 and 3 were identical but clearly differed from page 2, showing a band at 287.2 eV, assigned to > C = O functional groups.<br>Signature 2: Different atomic composition at pages 1 and 3 and at page 2. P atomic concentration below limit of detection at pages 1 and 3 and 0.60% at page 2.<br>Signature 3: Different atomic composition at pages 1 and 3 and at page 2. Atomic concentration of C, O, Cu and S averaged to 76.2, 20.6, 0.18 and 0.35%, respectively, at pages 1 and 3 and to 72.9, 22.6, 0.48 and 0.70%, respectively, at page 2. |
| FTIR | false claim | 2 | No differences identified, significant interference with spectra from paper. |
| | | 19 | Signature 2: No differences between FTIR spectra which indicate that the same pen/ink was used to sign all three pages. |
| | undec. | 19 | Signature 1 on page 2 shows slight difference in spectra but it is not possible to clearly confirm differences between used pen inks due to significant spectra from paper. |
| | success | | Signature 3: Page 2 was signed by different pen/ink and person. |
| Raman | undec. | 7 | This technique doesn't allow us to distinguish the chemical formulation of the ink pairs with the same characteristics. |
| | false claim | 10 | Yes, the signatures and headings have been produced with the same ink. |
| SEM | false claim | 2 | Different signature 3 on page 3, signatures 1 and 2 identical at all pages. |
| ICPMS | undec. | 3 | Lack of strong evidence that signature samples on each page of the document may originate from various inks. |
| SIMS | false claim | 3 | The same pigments are present in the studied inks on each page of the document. The composition of each studied ink on each paper page is very similar. |
| | | 6 | Yes, the signatures and headings have been produced with the same ink. |
| MALDI-MSI | false claim | 14 | It looks like the signatures have been produced with the same ink. |
| | | 15 | Headings and signature 1 (bright blue): appears to be made using the same ink on pages 1 and 2 (very characteristic signal at *m/z* 574.6), indication that the third signature is made with a different ink (shoulder peak at *m/z* 253.0 seems to be present in all 3 signatures but not in the third corresponding heading). |
| | success | | Headings and signature 2 (black): Seems to have been produced using the same ink for both page 1 and page 2 (peak signal at *m/z* 184.0 and a signal prevalent in this heading than in the 2nd but of similar ratio at *m/z* 558.8 and very strong signal at *m/z* 372.0 on both pages). For the first signature no mass spectral differences with the corresponding headings have been found (still present the characteristic peak at *m/z* 184.0). However the signal at m/z 302.0 is only visible in the header and signature of the same person on page 1 and 3 respectively suggesting that the heading on page 2 was made in a different ink.<br>Headings and signature 3 (dark blue): Page 2 differs from page 1 (discriminate at *m/z* 315.8), the signature appears to be made with the same ink as that used for page 1 to produce the corresponding heading (through the signals at *m/z* 315.8 and 302.0). |
| LDI-MSI | false claim | 16 | All the signatures and headings have been produced with the same ink. The mass spectra of all three signatures throughout the three pages are identical, hence no forgery could be detected in this regard. |
| UVVIS | N/A | 7 | In this case, microspectrophotometry/VIS-MSP didn't allow us to distinguish the chemical formulation of the ink pairs with the same characteristics. HPLC is preferred technique. |
| | false claim | 2 | Headings and signatures at all three pages differ |
| | | 5 | Signature 2: all signatures (headings) were signed with the same ink.<br>Signature 3: all signatures (headings) were signed with the same ink. |
| | | 18 | Signature 1: identical spectral characteristics.[§] |
| | success | 5 | Signature 1: the signature (heading) at the second page was most probably written with different ink in comparison with signatures on the first and third page. |
| | | 18 | Signatures 2 and 3: The reflectance features of the inks of the Signature PEDRO and Signature SONIA on Page #2 are vividly different from the corresponding signatures on Page #1 and Page #3. |

(*continued on next page*)

**Table 3** (*continued*)

| Method used | Result | Report No. | Conclusion |
|---|---|---|---|
| TLC | success | 9 | Signature 1: At page 2 written with ballpoint pen, at pages 1 and 3 written with gel pen. Signature 3: Differs on pages 1 and 3 from page 2. |
| | false claim | | Signature 2: No difference in characteristics obtained with method used. |

paper in the fuser. Typical binders include polymers like styrene, epoxy resins, or methacrylate, sometimes cured with other organic components. For monochromatic laser printing as used in the present study, the colorant typically consists of iron oxide or graphite particles with additional elements that depend on the manufacturing process. Traditionally, laser printing is distinguished from other printing techniques using stereomicroscopy [24], because the border of the letters is much more distinct if the document is printed by a laser printer and because, on occasion, single toner particles can be identified on the paper (Fig. 1). Analysis of photocopies often starts with determination of class characteristics such as paper type, toner type, toner application, fusion method, and magnetic properties [25]. Besides, both elemental composition [25,26] as well as type of polymer binder [27,28] have been used in the literature to discriminate between toners.

#### 4.1.1. *Printing technique*

In the presented study, the methods chosen by the laboratories and method success clearly reflect the literature findings: while stereomicroscopy, which was categorized as non-multimodal visual inspection in this study (supplementary files mmc1 and mmc2, Table S2.2), was the most commonly used technique for successful identification of the printing technique (method performance of 100% for task 1), multi- and

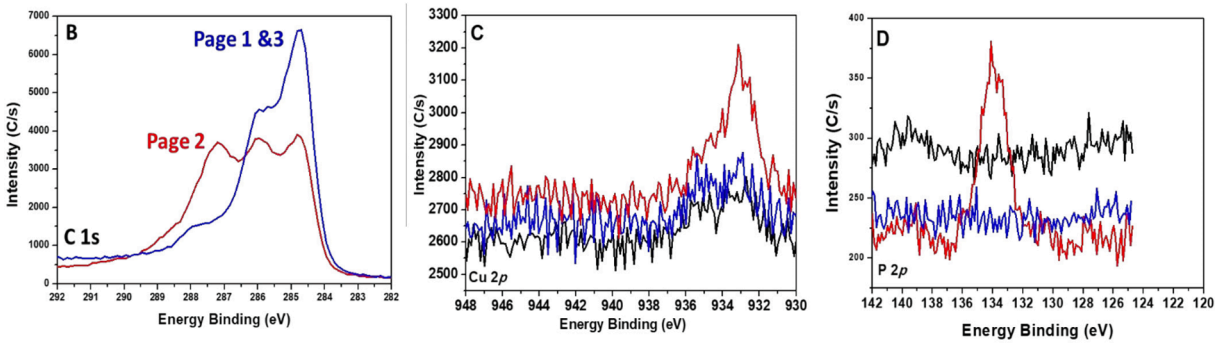



**Fig. 6.** XPS results of ink analysis; (B) C 1s core level of signatures with blue ink (blue P1&3; red P2) (C) Cu 2p3/2 core level spectra of signatures with purple ink (blue and black spectra are P1&3; red P2) and (D) P 2p core level spectra of signatures with black ink (blue and black spectra are P1&3; red P2). Inks at page 2 (red) clearly discriminate from inks at pages 1 and 3, see report #20 in supplementary file mmc20. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

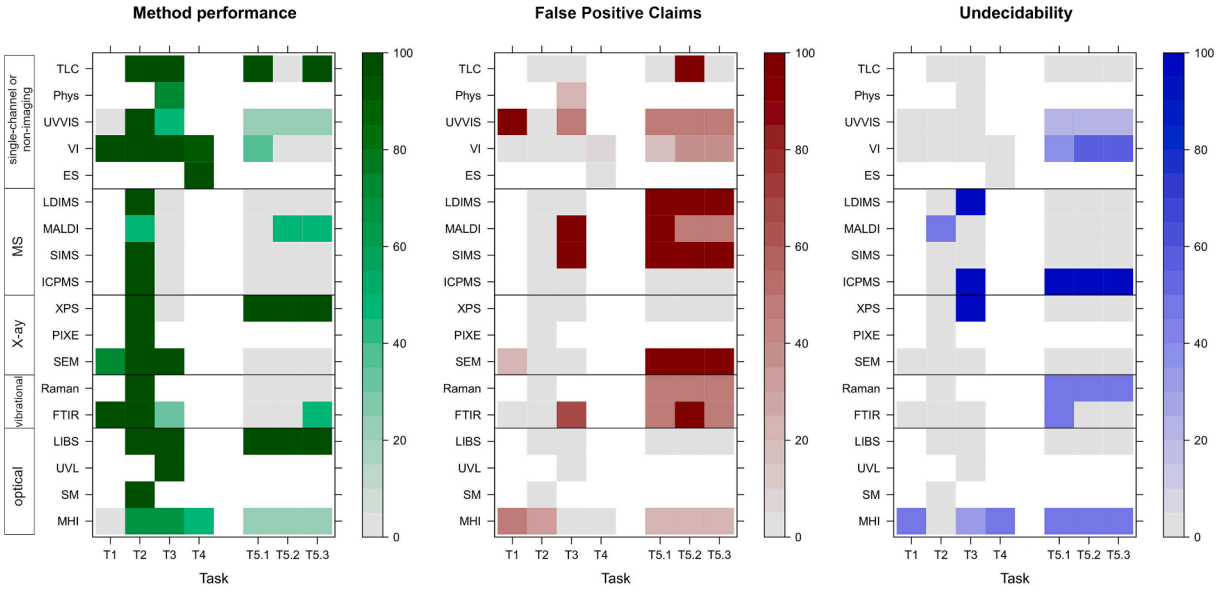



**Fig. 7.** Levelplot of the method performance (green), false positive claims (red) and undecidability (blue) for method categories per task. T5.1, T5.2 and T5.3 denote signatures 1 (bright blue), 2 (black) and 3 (dark blue), respectively. White colour indicates that no results were submitted. Categorization according to Table 2. MHI - multi- and hyperspectral imaging, SM - smartphone mapping, UVL - UV-luminescence, LIBS - laser induced breakdown spectroscopy, FTIR - Fourier transform infrared microscopy, Raman – Raman microscopy, SEM - scanning electron microscopy, coupled to energy dispersive X-ray fluorescence spectroscopy, PIXE- particle induced X-ray emission spectroscopy, XPS - X-ray photoelectron spectroscopy, ICPMS - laser ablation ICP time-of-flight mass spectrometry (LA-ICP-ToF-MS), SIMS - secondary ion mass spectrometry, MALDI - matrix assisted laser desorption ionisation time-of-flight mass spectrometry (MALDI-ToF-MS), LDIMS - laser desorption ionization mass spectrometry, ES - electrostatic imaging, VI - visual inspection (including non-multimodal (micro-)photography), UV–VIS - non-imaging (micro-) spectroscopy, Phys - physical testing, TLC - thin layer chromatography. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

hyperspectral imaging and optical spectroscopy failed when used. In FTIR, highest correlation with library spectra served for printing technique identification, whereas appearance of molten toner particles was used for discrimination in scanning electron microscopy.

The approach that one single letter of printed text per page was randomly selected for SEM did not differ between the reports. The conclusion of report #3 (supplementary file mmc4) that an inkjet printer was used for pages 1 and 3 was based on the finding that the toner stained single fibres of the paper, and that its appearance resembled a printing ink, which was supported by SEM images. It can be assumed that samples were taken from areas where high temperatures caused complete melting of the polymer in report #3 (supplementary file mmc4), causing deep penetration of the toner into the pores of the paper, thus making individual toner particles indistinguishable. We excluded sample preparation as a likely cause of the false positive claim, because the subsamples of each page were placed together on one SEM stub (Fig. 1 of report #3 in supplementary file mmc4), which ensured equal treatment of the samples. Consequently, this finding has two implications: (1) during preparation of the samples by the organizer the pages were printed one after the other using the same printer, thus likely leading to continuing increase of temperature of the fuser or of other printer parts while printing and causing more intense melting of the toner polymer as printing proceeded; (2) well molten text may have been sampled by coincidence. These implications point to the requirement of providing comparable samples in future Round Robin studies and to the necessity of representative sampling (supplementary file mmc3).

#### 4.1.2. Printer discrimination and identification

The printer models were a Konica Minolta model bizhub with original cartridge for pages 1 and 3 and an OKI model ES8453 MFP 223 with original cartridge for page 2 (see Table 1). The literature gives no support of the notion that printer models can be identified using FTIR spectroscopy and that toner brand should be stated instead [27,28]. This is of particular importance when original toner cartridges get refilled by unauthorized dealers or replaced by low-cost substitutes. With the exception of report #7 (supplementary file mmc8), none of the reports attempted to identify printer model nor the toner brand.

There are no reports in the literature covering the use of multi- and hyper-spectral imaging, however, non-imaging UV–Vis spectroscopy has successfully been used to discriminate between toners [29]. While broadband Vis-NIR photography failed in our study (report #2, supplementary file mmc3), narrow band smartphone mapping (report #4, supplementary file mmc5), hyperspectral imaging (reports #4 and #17, supplementary files mmc5 and mmc17) and non-imaging optical spectroscopy (reports #2 and #5, supplementary files mmc3 and mmc6) fully succeeded in toner discrimination. Vis-NIR photography is commonly used in other fields of science, like remote sensing or small-scale vegetation mapping ([12,30]), but we assume that the limited amount of information contained in a little number of broad spectral bands restrains its feasibility for document forgery analysis. LIBS (report #12, supplementary file mmc12) was the only techniques based on optical spectroscopy, which provided correct results for all the tasks worked on.

Report #14 (supplementary files mmc13 and mmc14) clearly identified differences in the mass spectra of the toner between page 2 and pages 1 and 3 at a lateral resolution of 75 μm × 75 μm, however, no decision could be made for toner discrimination at a resolution of 150 μm × 100 μm by MALDI-MSI in report #15 (Table S2.6 in supplementary file mmc2), where higher resolution imaging was suggested. In contrast, a lateral resolution of 125 μm × 125 μm was sufficient to discriminate between toners by LDI-MSI (report #16, supplementary file mmc16). It is suggested that better discrimination with MALDI MSI would have been possible if statistical analysis was performed and suitable databases had been available. The spatial resolution was not high enough the physical features of the printed letters could not be observed with reliability to make a distinction.

It can be concluded for tasks 1 and 2 that toners reliably could be discriminated by conventional non-imaging techniques, as well as techniques with imaging capabilities, such as LIBS, XPS, FTIR and Raman microscopy, scanning electron microscopy, coupled to energy dispersive X-ray fluorescence spectroscopy, particle induced X-ray emission spectroscopy, laser ablation ICP time-of-flight mass spectrometry (LA-ICP-ToF-MS) and secondary ion mass spectrometry (SIMS).

### 4.2. Paper discrimination

X-ray fluorescence analysis used with SEM and LIBS correctly found that page 2 contained higher amounts of Ca, which was specified as elevated amounts of calcite ($CaCO_3$) with FTIR and which served as filler (Fig. 4). In turn, XPS did not allow for discriminations of papers. The performance of non-multimodal visual inspection, which included macroscopic paper and microscopic fibre morphology, UV luminescence, non-imaging optical spectroscopy and thin layer chromatography amounted to 100%.

The FTIR spectra of the paper were interpreted as mixed spectra of cellulose and calcite (reports #2 and #19, supplementary files mmc3 and mmc19), where report #19 (supplementary file mmc19) characterized elevated signals at 1403–1405 cm-1 and 871 cm-1 as different chemical composition, which in combination with the unaligned paper texture in case of pages 1 and 3 and aligned paper texture in case of page 2 lead to the correct conclusion that the paper of page 2 was different. These elevated bands can also be identified in the FTIR spectra shown in report #2 (Fig. 5 in supplementary file mmc3).

The variability of the LA-ICP-ToF-MS results within each paper sample was significant. Moreover, for any of the selected for comparison *m/z* ratios, the signal was considerably different for all studied paper sample, which means that based on the analysis of the whole mass spectra it was not possible to select elements which can be used as a good indicator for sample discrimination. Only some slight differences were noticed for Ca and Al in report #3 (supplementary file mmc4). Contrarily, ToF-SIMS analysis of paper surface from each page of document showed no significant differences among studied samples in the composition and distribution of chosen ions in report #3 supplementary file mmc4). Vis-NIR photography in combination with artificial neural network unsupervised learning and global clustering correctly identified page 2 to be different from pages 1 and 3 (Fig. 3), however, the combination with FTIR and the results of paper density testing yielded an over-discrimination of the paper types in report #2 (supplementary file S3), which stated that the paper of all three pages was different. Paper density was correctly reported to be different for page 2 in reports #14 and #19 (supplementary files S13a and S18).

At a first glance of the average MALDI spectra extracted from each of the 3 pages, there appears to be no difference (report #15, supplementary file mmc15). Zooming into the spectra, the 3 sampling areas present the same mass spectral peaks although those in page 3 seem to be consistently higher. An analysis of the matrix distribution revealed that this could be due to better and higher matrix coverage for page 3. On the other hand, thin layer chromatography after dimethylformamide extraction correctly revealed differences between page 2 and pages 1 and 3 by the chromatographic behaviour of colourless components (likely optical brighteners) - one blue luminescent zone with $R_f = 0$ for pages 1 and 3 and three luminescent zones of blue colour with $R_f = 0$; $R_f = 0.34$; $R_f = 0.47$ for page 2 (report #9, supplementary file mmc10). Apparently, the concentration of components detected by TLC is little compared to the main component cellulose, which is insoluble in dimethylformamide. Calcite is not volatile and almost insoluble in dimethylformamide, so it cannot be expected to be detectable neither by MALDI nor by TLC. LDI-MS was also unable to determine whether or not the three pages of the document consist of the same paper. Three peaks, which can be clearly assigned to paper (*m/z* 130.9. 158.0. 575.0) occur

on each spectrum and the remaining peaks differ strongly (report #16, supplementary file mmc16).

### 4.3. Stapling of pages

Because page stapling produces physical marks, but multimodal imaging addresses chemical properties of the evidence, only two reports used multi- and hyperspectral imaging for task 4, where the main techniques used involved visual inspection, electrostatic imaging and documentation with RGB (micro)photography of stapling marks. Assuming that all three pages were attached together when the agreement were signed, report #4 (supplementary file mmc5) concluded that page 2 was replaced based on missing signature imprints, which again is an interpretation of physical properties. Report #14 (supplementary files mmc13 and mmc14) falsely identified multiple staple marks at page 2 and single staple marks at pages 1 and 3. However, this interpretation is consistent with the photographic documentation, which points to non-conforming sample preparation or uncareful handling.

### 4.4. Comparison of inks

Paper documentation fully or partially hand-written with ink (e.g., certificates, currency notes, wills, passports, loan agreements and other official documents) is often important material for forensic investigations. There are usually several questions to be answered, namely identification of the source of the tested ink, the ink identity on various places of one document or between several documents and the age of ink written text. The determination of correct order of crossing ink lines and discrimination between homogeneous and heterogeneous intersections is extremely important. Such analysis allows the determination of whether entries have been added or altered in the document(s) tested ([31–35]).

Several ink types can be distinguished, based mainly on the characteristics of a colorant (dye or pigment), type of solvent (water or organic one) and consistency (liquid or paste). Many inks contain also additional chemicals including fatty acids, emulsifiers, softeners and polymeric resins, designed to improve their consistency, flow or drying characteristics [36], and also strong adhesion to the substrate. Typical writing instruments comprehend fountain, ballpoint, rollerball, felt-tip, gel, ruling or brush pens.

Many procedures have been already developed for inks identification and comparison, including visual examination, thin layer chromatography (TLC) and high performance thin layer chromatography (HPTLC), high performance liquid chromatography (HPLC), gas chromatography (GC) and spectroscopic techniques (Fourier-transform infrared spectroscopy (FTIR), Raman or UV–VIS spectroscopy and mass spectrometry) [8,33]. The ideal method for ink analysis should provide a very high degree of discrimination between tested documents, should be applied to very small areas, to be non-destructive, requiring minimal or no sample preparation, be rapid, and producing both qualitative and quantitative data [37].

Before advanced ink analysis, preliminary non-destructive examinations are usually performed, including visual observation using a stereomicroscope (to obtain ink lines morphological and colour characteristics), and optical examination using artificial light sources (short and long UV radiation and visible light [33]).

#### 4.4.1. Non-imaging or non-multimodal techniques

*4.4.1.1. TLC.* Separation techniques are most common in ink analysis with TLC playing a predominant role, where digital photography/scanners, or monochromatic illumination (UV, video spectral comparators), occasionally using fluorescent plates, are used for detection. TLC has also successfully been used in forensic chemistry for sample clean-up and preparation, combined with advanced analysis like MS, FTIR or NMR. Since TLC requires solubility testing and extraction before separation can be accomplished, it is at least challenging to retrieve spatially resolved information from forensic specimen, hence, only one laboratory decided to include TLC as non-imaging method into our study (report #9, supplementary file mmc10). The overall performance of TLC was 67% in our study.

*4.4.1.2. Visual inspection.* Visual inspection of inks includes luminescent techniques and, particularly in the case of pigments, stereomicroscopy, which can identify pigments on the basis of their crystalline form and their optical properties [24]. In our study, IR luminescence, visual appearance under the microscope and stroke morphology were used to distinguish the inks. It was noted that it was impossible to claim that the inks used were different, as the traces can look different depending on how hard the writer presses the pen on the paper, what paper is used, and so on (report #4, supplementary file mmc5). Overall, the visual inspection yielded false results in 41% of the findings, and in 41% of all findings no decision could be made.

#### 4.4.2. Techniques with imaging capabilities

*4.4.2.1. Microspectrophotometry.* Imaging techniques can efficiently be used to analyse forensic evidence including inks in questioned documents in a non-destructive way. Microspectrophotometry was used to obtain spectral characteristics of the individual inks and the order of crossing ink lines, based on the assumption that the characteristic "spectra from the point of intersection should correspond to the peak characteristics of pure ink which was executed later. Using spectral reflectance curves, microspectrophotometry was possible to determine whether the ink was above or below the inkpad/stamp-pad ink seals" [32]. This procedure worked well if there was no physical mixing of the two coloured materials and the spectrum of the uppermost coloured material was measured without the interference from the other coloured material [32].

The performance of microspectrophotometry was 25% in our study. While comparison of reflectance spectra of the visible range was partly successful for signature 1 (report #5) and signatures 2 and 3 (report #18) it completely failed for report #7. Extending the spectral range to 2500 nm and applying PCA, report #2 reported an overdiscrimination, which possibly was caused by NIR signals originating not only from ink, but also from the paper or from external influence, like intense absorption bands of hygroscopic humidity (supplementary file mmc3).

*4.4.2.2. FTIR.* Fourier transform infrared (FTIR) spectroscopy and especially microFTIR can be efficiently used to analyse inks on the tested documents in the non-destructive way [38]. Using microFTIR it is possible to obtain spectra of individual inks; in addition to the main dye characterization also other ink components (e.g., natural or synthetic polymers, oils, ethylene glycol, glycerine, styrene etc.) can be determined. The spectrum range of 400–2000 $cm^{-1}$ is informative, reliable and provides quantitative analysis of ink samples [39,40]. In most cases the discrimination is carried-out by visual inspection to decide whether the two samples show the same spectra under the same experimental conditions; the use of chemometric multivariate analysis (e.g., principal component analysis (PCA) and linear discriminant analysis (LDA)) to explore the analytical data efficiently and to enable unbiased decisions about the similarities among the ink samples seems to be necessary [41].

Despite the fact that both diffuse reflectance (DRIFTS, reports #2, supplementary file mmc3) and attenuated total reflectance (micro-ATR, report #19, supplementary file mmc19) techniques were involved in situ in our study, only micro-ATR microscopy successfully discriminated between the inks for the signature of Pedro Miguel Sousa Marques (dark blue). For the other signatures no discrimination could be achieved, so that the overall discriminating power of FTIR microscopy for inks amounted to 17% in our study. Both laboratories reported significant

interference with the signal yielded by the paper. It was reported that diffuse reflectance FTIR successfully distinguished between inks [42]. However, in this case, FTIR was performed after extraction with ethanol and subsequent evaporation of the solvent to dryness. Recently, 57 blue ballpoint pen ink samples were analysed using ATR-FTIR with the paper carrier recorded as background, where visual inspection of the spectra achieved a discriminating power of 97.93 %, while using multivariate analysis the DP value reached 99.69% [39]. The same procedure was used to analyse blue pen ink present in ballpoint, rollerball and gel pens; very high percentage of correct classification was obtained after LDA spectral data editing [41]. The high discriminating power of FTIR for inks reported in the literature contradicts our findings and underline the conclusion of Merrill and Bartick [43] that the additional information provided by the diffuse reflectance FTIR analysis provides enhanced value to the forensic examination of inks when combined with complementary information.

*4.4.2.3. Raman spectroscopy.* Raman spectroscopy is a very useful non-destructive tool for the forensic examination of inks on various documents. This technique can provide the chemical information about the ink rapidly as it does not require any time consuming sample preparation steps and the integrity of the analysed document as a court evidence is preserved. The main advantage of this technique is the rich spectral information, presented as a high number of vibrational bands [44]. Raman spectroscopy has been often used for ink analysis, exhibiting high discrimination power; the extensive reviews about forensic applications of Raman spectroscopy for the in situ analyses of ink pigments and dyes in questioned documents have been published recently [37,44]. However, one of the problems is the presence of fluorescent compounds on the paper surface which can decrease the intensity of the important Raman signal. In general, it is possible to use lasers working in the infrared region, which reduce the undesired effect of fluorescence. Another possibility is to employ Surface Enhanced Raman Spectroscopy (SERS) which enables both the elimination of such types of interference, and the increase of the Raman signal of selected bands, thus increasing the sensitivity of the assay [45].

Several SERS approaches can be used for ink identification [37]. Alyami et al. described identification of the dye content in coloured BIC ballpoint pen inks; SERS analysis was carried out in situ, by deposition of Ag nanopaste (highly concentrated silver nanoparticles suspension) directly on pen coloured paper surfaces. Silver nanoparticles evenly covered large areas of the paper substrate and wrapped uniformly around the paper fibres, forming high density and highly uniform particle areas, necessary to achieve intensive and reproducible SERS signals. As a result, more efficient dye identification was achieved by SERS; however, the drawback of this procedure is associated with the deposition of silver nanoparticles on the analysed surface [46].

Besides the success reported in the literature, identical Raman spectra were obtained from the writing ink of the signature of João Oliveira Martins (bright blue), Sonia Alexandra Sousa Marques Figueira (black) and Pedro Miguel Sousa Marques (dark blue) in both reports submitting Raman spectra for ink comparison (reports #4 and #10, supplementary files mmc5 and mmc11).

*4.4.2.4. LIBS.* LIBS has successfully been used to discriminate papers produced at different time interval, and both LIBS and LA-ICP-MS provide excellent discrimination between different printer sources [47]. A method performance of 83, 82 and 61% could be achieved for 34 samples of blue, 30 of black, and 21 of red writing inks, respectively, which were analysed by LIBS after elimination of elements contained in the paper [48]. In our study, LIBS was the only technique which reached a method performance of 100%.

*4.4.2.5. XPS.* XPS analysis has been found to be useful for the analysis of thin films of different sources deposited in surfaces [21], where inks could be discriminated by means of high resolution spectra of C 1 s and O 1 s core levels and using concentrations of specific trace elements, such as Mg, Na and Si [49]. In our study, C 1 s, C sp2, O 1 s and Si 2p core levels, as well as the Cu, S and P concentrations allowed to successfully discriminate between toners and inks. However, XPS failed to discriminate between papers.

*4.4.2.6. LA–ICP–MS, ToF-SIMS, SEM.* Almirall and Trejos (2016) [50] reported that „laser ablation inductively coupled plasma mass spectrometry (LA–ICP–MS) provides qualitative and quantitative measurements of the elemental and isotopic composition“ of natural and man-made materials of forensic interest, including inks. They further reported that this technique possesses excellent sensitivity, reproducibility, and selectivity, that it is „fast, with virtually no sample preparation and minimal destruction of the sample (<1 Âµg)“, and that laser ablation systems used for ink identification „can be configured to operate at different wavelengths (e.g. 1064 nm, 532 nm, 355 nm, 266 nm, 213 nm, or 193 nm) and at different pulse durations (ns, fs)“. Typical ablation lines never exceed a width of 200 µm, and typically elements analysed in writing inks comprehend Al, Mg, Fe, Mn, Cu, Ba, Ni, Pb, Si, and K [50].

Trejos et al. (2010) [51] analysed the ink of several hundreds of black pens using LA-ICP-MS and LIBS to „determine the variation of the chemical composition of the ink within a single pen, between pens from the same package and between brands of gel inks and ballpoint inks“. They found that „a discrimination of ~ 96–99% was achieved for sets that otherwise would remain inseparable by conventional methods“, where the mass removal did not exceed 15 µg in their study and where the document's substrate was only minimally destroyed [51].

ToF-SIMS was successfully used to differentiate between 13 blue ballpoint pens [52] and 2 red ballpoint/felt tip pens, where the main advantage of ToF-SIMS was the analysis of intersection lines [53]. MeV ToF-SIMS was successfully used to determine chemical composition and deposition order of 6 different blue ballpoint pens [54], and MeV ToF-SIMS in combination with PIXE was successfully applied to address the problem of the deposition order when inkjet ink was included [35]. In our study, both ToF-SIMS and LA-ICP-ToF-MS were able to identify three different dyes for the three signatures, however, it was not possible to discriminate within signatures between pages (report #3, supplementary file mmc4).

As another tool for inorganic analysis, SEM-EDX is well known for element mapping and was successfully used for paper and toner discrimination in our study. It was reported to be an effective tool for inkjet ink discrimination [55] and the greatest degree of differentiation between blue gel inks was achieved when using a combination of SEM-EDX and Raman (method performance > 70%) [6,56] or FTIR techniques (method performance 95%) [40]. Similar to LIBS, LA-ICP-MS and ToF-SIMS, Cu was identified to be characteristic for the blue inks, but unlike LIBS, SEM-EDX, ToF-SIMS and LA-ICP-ToF-MS could identify discriminating impurities in our study.

*4.4.2.7. MALDI and LDI-MSI.* MALDI has successfully been used for ink discrimination, in particular to be complementing or surpassing TLC [57–59]. In our study, it was difficult to measure all signatures under the same conditions, as inks differed in intensity (writing pressure) and matrix coating appeared to be sub-optimal in terms of coverage homogeneity of the different samples. The absence of a mass spectrometric ink database and the lack of use of statistical processing contributed to an underplay of this technique.

*4.4.2.8. Multi- and hyperspectral imaging.* Hyperspectral imaging was successfully used for ink mismatch detection [60] and hyperspectral ink databases are publicly available [61]. However, the method performance (MP) did not exceed 25% in our study.

### 4.5. Ink age

Ink dating is mostly based on the kinetics of solvent evaporation or degradation of ink components. While the direction of these reactions is known, their speed often depends on the type of paper and on unknown conditions in the environment of document storage, like temperature, sunlight or humidity, so that absolute dating is often not possible. Numerous studies showed that relative age could be determined reliably for different brands of inks [8,62,63]. The methods used in the literature also include methods capable of imaging, like LDI MSI, MALDI MSI, FTIR or optical spectroscopy. However, none of the participating laboratories deemed addressing Task 6 feasible as dating forensic evidence, including ink globally remains an unresolved problem [64–66].

#### 4.5.1. Recommendation of methods and preferred workflow

Fig. 8 gives an overview of the analytical targets, destructiveness, performance and false positive claims of the methods used. Our recommendation for prioritized methods and workflows is based on the following considerations:

(1) It was reported that the toner was a non-magnetic black toner (report #4, supplementary file mmc5) manufactured from graphite powder (report #2, supplementary file mmc3) where the polymeric binder was not specified. The paper consisted of cellulose fibres with the mineral calcite as filler (report #2, supplementary file mmc3), and the dyes of the inks were identified as methyl violet (signatures 2 and 3), crystal violet (signatures 2 and 3), basic blue 26 (signature 3), basic blue 7 (signatures 2 and 3) and copper phthalocyanine (signature 1, report #3, supplementary file mmc4). Therefore, it can be stated that each of the specimen contained both inorganic and organic components. Consequently, we hypothesize that maximisation of the intelligence and discrimination can be achieved when methods are combined in such a way to address all of the forensic questions drowing from the individual strengths and molecular targets of the individual techniques (Fig. 8).

(2) Methods targeting organic analytes should be complemented by inorganic methods and vice versa for this reason. While PIXE, ICPMS, LIBS and SEM/EDX were used for inorganic analysis, MALDI, LDIMS, and Raman microscopy were used to analyse organic compounds. All other imaging techniques were used for both organic and inorganic analytes in our study. PIXE and Raman microscopy were not used for paper analysis (task 3). Despite its ability for identification of minerals, Raman microscopy was not used to identify the paper filler in our study. To detect as many sample features as possible, we recommend a combination of PIXE, ICPMS, LIBS and SEM/EDX with MALDI-MSI and LDI-MSI.

(3) All methods can be applied when sufficient amount of sample is available and when subsampling is possible. However, non-destructive methods should precede destructive methods when subsampling is not feasible (Fig. 9). We included into our recommendation only methods which produced no false positive claims, meaning that any positive finding is valid, but forged

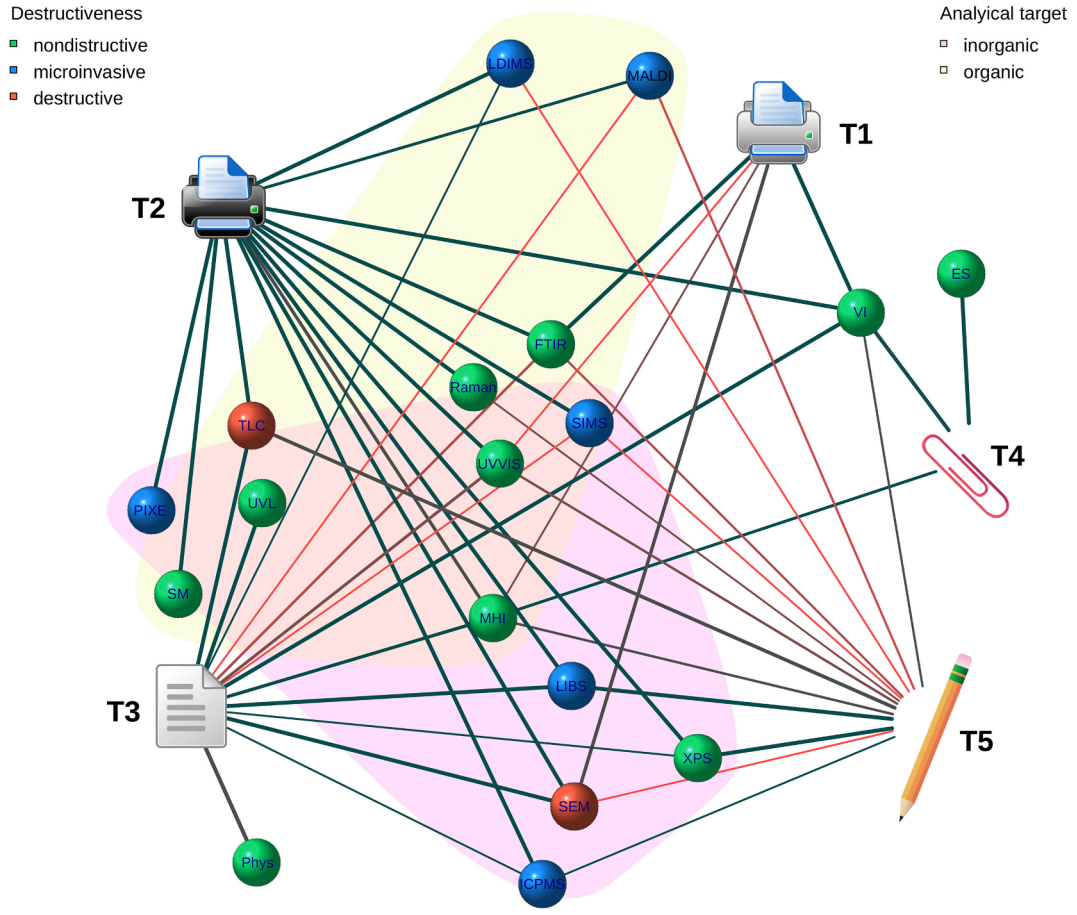



**Fig. 8.** Analytical targets (shaded areas), destructiveness (colour of balls), performance and false positive claims of the methods used for tasks 1 to 5. Methods preferably targeting both inorganic and organic analytes are placed in the intersection of the two areas. Line thickness indicates method performance, red line colour indicates false positive claims. Abbreviation of method names: see legend of Fig. 7. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

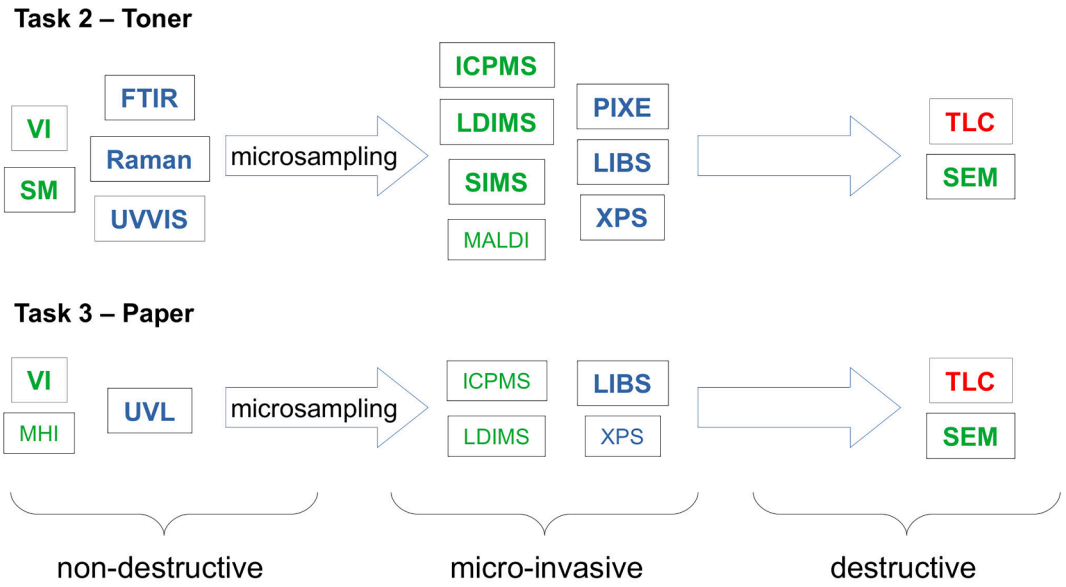



**Fig. 9.** Recommended workflow for identification and discrimination of toner (T2) and paper (T3). Bold text indicates high method performance, text colour indicates category (green – imaging, blue – profiling with imaging capabilities and red – other). T1, T4 and T5 were omitted because the methods used each belonged to only one category of destructiveness. Abbreviation of method names: see legend of Fig. 7. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

pages may remain undetected, depending on method performance. It should be kept in mind that even methods that have only weak performance can increase the overall probability of discrimination, as long as they do not mislead to false positive claims.

Although, for example, methods belonging to multi- and hyperspectral imaging had lesser performance compared to other techniques, they are non-destructive and have the potential to provide complementary information, so that their use can fully be recommended. Several advanced techniques were not combined with complementary methods in our study and answers to the tasks could not be given or were erroneous, either because such methods were unavailable or because they were excluded *a priori* by expertise. For example, MALDI on the one hand or LIBS on the other were not combined with any inorganic or organic techniques, respectively, so that the possibility of a benefit from complementary information was not achieved.

In our study, only a few participants used different techniques but preferred established in their laboratories protocols instead. In addition, advanced imaging techniques, which have not yet been able to establish themselves on a broad scale, were mostly hosted at the academic institutions. When creating the workflow, it should therefore be noted that the microinvasive techniques of this study are not available everywhere and that - also considering their performance in solving the tasks - the hierarchy shown in Fig. 9 is to be expected with a transport of the evidence to specialised laboratories. It is therefore advisable to use microinvasive techniques when all the non-invasive/less destructive methods have been applied first and have not yielded the desired result. Where possible, further consideration could be given to either splitting the samples and examining them in parallel or subject the same specimen to consecutive compatible techniques.

## 5. Conclusions

Although there is a large amount of scientific literature on the investigation of document forgery, procedures are not yet standardised at the level of certifying bodies. With the presented study, especially the methods documented in detail in the supplements, we attempt to make our contribution to closing this gap.

Our study has shown that the reliability of the testimony cannot necessarily be increased by increasing the amount of recorded data and that none of the techniques used can individually solve all tasks completely and/or correctly, thus supporting the advocation of multimodal technology application to this type of evidence. This leads to the conclusion that correct forensic statements can only be achieved by the complementary application of different methods. A multimodal approach which combines information from several modalities should be preferred. We recommend combination of methods targeting inorganic analytes on the one hand and organic on the other, with compatibility achieved through the use of non-destructive and microinvasive methods first and, if still necessary, followed by more destructive techniques.

A particular challenge for all methods turned out to be the discrimination of inks, which was only completely correctly solved by LIBS and XPS. Unexpectedly, even classical microspectroscopy or TLC led to partially incorrect results. Highest performance was achieved by all methods in task 2 (printer used for the three pages). For the discrimination of paper, solid state methods proved to be superior to mass spectrometric methods. Apart from the identification of inks, the performance of classical visual inspection (VI) was good.

In order to enable true multimodality and to go beyond a mere comparison of methods, it should be ensured when planning future round robin studies on multimodal examination that exactly the same samples can be examined by all participants. A sequence of application of non-destructive, then microinvasive and finally destructive methods should be designed and trialed a future round robin study. Thus, the classical approach of round robin studies to send standardised subsamples to the participants is not feasible for a true multimodal approach if the techniques are not available at one location. For this purpose, it is further necessary to identify the available imaging techniques in advance and to plan the workflow on the part of the organiser instead of by each participant individually.

*CRediT authorship contribution statement*

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Investigation, Validation, Project administration. **Ana Cristina Assis:** Conceptualization, Methodology, Resources, Investigation. **Michal Levin Elad:** Conceptualization, Methodology. **Manuel Algarra:** Resources, Investigation, Validation. **Marko Barac:** Resources, Investigation, Validation. **Iva Bogdanovic Radovic:** Resources, Investigation, Validation. **Flavio Cicconi:** Resources, Investigation, Validation. **Britt Claes:** Resources, Investigation, Validation. **Nunzianda Frascione:** Resources, Investigation, Validation. **Sony George:** Resources, Investigation, Validation. **Alexandra Guedes:** Resources, Investigation, Validation. **Cameron Heaton:** Resources, Investigation, Validation. **Ron Heeren:** Resources, Investigation, Validation. **Violeta Lazic:** Resources, Investigation, Validation. **José Luis Lerma:** Resources, Investigation, Validation. **Maria del Valle Martinez de Yuso Garcia:** Resources, Investigation, Validation. **Martin Nosko:** Resources, Investigation, Validation. **John O'Hara:** Resources, Investigation, Validation. **Ilze Oshina:** Resources, Investigation, Validation. **Antonio Palucci:** Resources, Investigation, Validation. **Aleksandra Pawlaczyk:** Resources, Investigation, Validation. **Kristýna Pospíšková:** Resources, Investigation, Validation. **Marcel de Puit:** Resources, Investigation, Validation. **Ksenija Radodic:** Resources, Investigation, Validation. **Māra Rēpele:** Resources, Investigation, Validation. **Mimoza Ristova:** Resources, Investigation, Validation. **Francesco Saverio Romolo:** Resources, Investigation, Validation. **Ivo Šafařík:** Resources, Investigation, Validation. **Zdravko Siketic:** Resources, Investigation, Validation. **Janis Spigulis:** Resources, Investigation, Validation. **Malgorzata Iwona Szynkowska-Jozwik:** Resources, Investigation, Validation. **Andrei Tsiatsiuyeu:** Resources, Investigation, Validation. **Joanna Vella:** Resources, Investigation, Validation. **Lorna Dawson:** Validation, Writing – original draft. **Stefan Rödiger:** Writing – review & editing. **Simona Francese:** Writing – original draft, Writing – review & editing, Resources, Investigation, Validation, Project administration.

## Acknowledgements

This work has been funded in part by the COST action CA16101 "MULTI-modal Imaging of FOREnsic SciEnce Evidence (MULTI-FORESEE)".

## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scijus.2022.06.001.

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