Forensic Analysis of Unknown Materials: a different vision of questioned documents

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Abstract
One of the biggest challenges in forensic analysis is the correct identification in terms of class characteristics of unknown materials found in a crime scene or crime scene related. Not only in several cases there is nothing to compare to and establish individualization, but also the mere identification of these class characteristics may allow prosecuting new lines of investigation.

Forensic document analysis comprises the characterization, identification and differentiation of various materials such as inks, paper, glues, coatings, laminates, waxes, among others for which it is necessary to use advanced analytical methodologies.

In the present work, some unknown materials were correctly identified and characterized using techniques such as Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy with Energy Dispersive X-Ray Spectroscopy (SEM / EDX) and High Performance Liquid Chromatography (HPLC), as well as morphology characterization and other physical and chemical characteristics inherent to the suspicious material under study.

Based on some case studies, the significant contribution of this kind of identification to the criminal investigation will be demonstrated.

Keywords:
Questioned documents, forensic analysis, HPLC, FTIR, SEM/EDX

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Introduction

Forensic analysis of questioned documents usually aims to evaluate issues related to the authenticity or falsity of the document. The analysis of security features and the analysis of stamp impressions or embossing stamps for the purpose of confirmation of the issuing entity are among the most common performed tasks. Also, the evaluation of tampering, identification and restoration of original inscriptions can be performed so that the alteration of the original text or even the attempt to conceal information can be revealed.

A document is something that attests certain information and therefore, questioned document analysis is not limited to identification or travel documents. It also includes the analysis of numerous different media containing information such as wills, debt statements, employment contracts, show tickets, lottery tickets, and beverage labels, among many others. Given this wide scope, the answer to other types of questions becomes imperative.

Also, if on one side the digital age in which we live makes questioned documents more difficult to counterfeit, on the other it allows criminals an easy access to means that enable the manipulation or production of documents with a very acceptable quality.

Thus, forensic document analysis also aims to answer questions related to the various components used in their production. For this purpose it is necessary to characterize and identify the class characteristics of several materials such as writing inks, printing inks, papers, fibers, glues and polymer materials.

The Questioned Documents section from the Scientific Police Laboratory of the Portuguese Judiciary Police receives an average of several hundred requests for forensic expert examination per year each of which may include one or more documents and/or comparison materials. Only approximately ten percent of these involve the analysis of document components but these may comprise a much more significant number of items than their statistical weight. Due to documents ubiquity, actions like searches and seizures at the suspect’s home or the dismantling of illegal print shops usually produce large amounts of comparison material (see Figure 1).
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Figure 1 — Number of analyzed documents/materials per year in the Questioned Documents section from the Scientific Police Laboratory of the Portuguese Judiciary Police, which include the analysis of inks, printing devices, papers, among others.

These analyses may provide a direct correlation between the document and the place where it was produced or altered. The complexity and degree of difficulty of these analyses rises when the correlation to the suspect or the crime scene is carried out through the characterization and or identification of materials. The main purpose of this paper is to illustrate two of these cases in which advanced analytical techniques were used to achieve the intended result.

EXPERIMENTAL

Instrumentation

The samples were optically examined using a Zeiss Discovery.V12 microscope to identify any significant morphological characteristics. The Foster+Freeman Video Spectral Comparator (VSC) 5000 was used to study the absorbance/fluorescence reaction from suspicious material.

A high-pressure gradient system was used, consisting of an Agilent 1100 liquid chromatograph with diode array detector and manual injection system equipped with a 20 µl loop. Separation was performed on a C18 Alltima column (7 × 53 mm i.d., 3 µm) protected by a 7.5 × 4.6 mm i.d. guard column. The mobile phase, consisting of a mixture of aqueous
phase (containing tetrabutylammonium hydrogen sulfate (TBAHS) and citric acid-1-hy- drate) and acetonitrile, was delivered at a flow rate of 2.0 mL min$^{-1}$. ChemStation for LC 3D systems software was used for data acquisition and processing.

FTIR spectra were collected in transmission mode using a ThermoNicolet FTIR spectrophotometer (standard resolution 0.5 cm$^{-1}$) coupled to a Nicolet Continum model microscope with a MCT (mercury–cadmium–telluride) detector (spectral range 11700-600 cm$^{-1}$, D* 4.7E10, Ry 750V/W). Under an optical microscope some particles were removed from the suspect material, using a scalpel. In order to obtain a suitable thickness the samples were placed into a Thermo Spectra-Tech compression micro-cell with a 1.8 x 1.8 mm diamond window working area. The IR spectra were obtained in the absorbance format at 8 cm$^{-1}$ resolution and 75 scans in the range of 4000–650 cm$^{-1}$. ThermoNicolet OMNIC software was used for data acquisition and processing.

SEM-EDX analyses were performed with a Zeiss EVO 50 coupled with an IncaX-sight EDX system from Oxford Instruments. The EVO 50 is a thermionic emission SEM (0-30keV) with a tungsten filament and is equipped with both SE and BSE detectors. The EDX system uses a SiLi detector with a resolution of 133eV at 5,9keV. Samples were carbon coated.

**Reagents**

All solvents and chemicals used were analytical grade: methanol (≥ 99.9 % - gradient grade for liquid chromatography) from Merck, water for chromatography from Merck, acetone p.a. (≥99.8 %) from Merck, acetonitrile (≥99.9 % - gradient grade for liquid chromatography) from Merck, Crystal Violet certified (dye content 91 %) from Aldrich, tetra-n-butylammonium hydrogen sulfate for synthesis (≥98 %) from Merck and citric acid monohydrate p.a. (99.5-100.5 %) from Merck.

**Results and discussion**

**Case 1 — Determination if a certain object can be used to erase / delete / tamper data documents / checks.**

During the criminal investigation of a documents’ falsification case, a gypsum object with traces of an unknown blue substance was found in the house of a bank checks counterfeiting suspect.
The characteristics of the seized items suggested that they probably could belong to a set of molding tools. The tip of one of the objects showed traces of a blue colored substance, resembling ink (see Figures 2-4).

Taking in account the observed morphology, it was necessary to use a chemical analysis technique that allowed the correct identification of the class characteristics of the substance in question.

Despite the scarcity of the traces under analysis, high-performance liquid chromatographic (HPLC) method has been used. The suspicious sample was dissolved in a methanol/acetone solution and analyzed by ion pair chromatography using standard reversed phase columns.

This technique was selected considering the probability that the sample included widely different components (mixtures of acidic and basic analytes). The mobile phase consisted...
in a buffer solution, to which an ion pair reagent (tetrabutylammoniumhydrogensulfate and Citric acid-1-hydrate) was added at low concentration. The obtained chromatogram was compared with our library (see Figure 5) allowing us to conclude that the blue colored substance deposited on the object in question had similar class characteristics to some components usually present in ballpoint pen inks.

Figure 5 — Chromatograms of some blue ballpoint inks brands existing in the Portuguese market (Mitsubishi – red line, Reynolds – green line, Bic – blue line, Pentel – pink line).

These type of inks are generally constituted by dyes (eg. Crystal Violet- see Figure 6, Victoria Blue B- see Figure 6, Phtalocyanine, Methyl Blue, Methylene Blue Trihydrate, Acid Blue 1) dissolved or in suspension in solvents (eg. fenoxiethanol) and resins (eg. polyvinyl acetate - PVA and polyvinyl chloride - PVC).

Figure 6 — Hexamethyl-para-rosaniline chloride (Crystal Violet) and Victoria Blue B dyes structures.
In order to obtain a more robust result, the peaks within the chromatogram needed to be assigned to a known component so, in this case, we injected one dye and assigned the peaks in the chromatogram based on the retention time of this standard. The analysis was performed with a selective detector, diode-array (spectral range 11700-600 cm\(^{-1}\), D* 4.7E10, Ry 750V/W), which assists in identification by producing UV-VIS spectra, using Crystal Violet dye (see Figure 7).

**Figure 7** — Chromatogram of the standard dye (red line) and the suspicious sample (blue line) and the UV-VIS spectra of Crystal Violet dye.

A qualitative identification of the component hexamethyl-para-rosalnine (Crystal Violet) was possible and, therefore, the analytical results allowed us to conclude that this substance had similar class characteristics to a ballpoint blue ink.

These results and the abrasive properties of the object lead to conclusion that the object in question could in fact have been used to erase data in bank checks. This kind of tampering is very common and involves the superimposition and/or addition of features, obliteration and insertion of new entries or signatures not only of bank checks (see Figure 8) but also in other various types of documents such as invoices and contracts.
Case 2 — Suspicious material found in a fire. In this particular case it was important to find out if it is part of a newspaper.

Some partially charred material of suspicious origin was found at the fire starting point in a burned forest area. In the course of the investigation a person admitted to have been responsible for starting the fire and confessed to have done it with a newspaper. However, other elements pointed that this confession was not genuine. Thus, it was important to determine if the material had indeed or not class characteristics that could correlated to newspapers. The material was properly packed and sent for analysis (see Figure 9, 10).
Figure 10 — Enlarged images obtained with natural light, where the various constituent fragments of the material in question (A, B, C, D and E) are visible.

The partially charred material was humidified in a specific camera so that the various constituent parts could be separated. Different structures were observed corresponding to different types of materials (see Figure 11).
Figure 11 — Image magnified 5x and obtained with white light, where the fragments A, D and F are visible, after the material has been humidified and disaggregated. F1 and F2 belong fragment F.

The observed morphology led to the suspicion that the pattern of stripes and numbers observed in fragment A could have been a barcode (see Figures 12-13).

Figure 12 — Image of fragment A magnified 18x and obtained with white light, after the material has been humidified and disaggregated, in which traces of numbering are visible.
Due to the condition of the sample it was not possible to restore the original characters or reading of the code. Once traces of characters in some of the fragments were found, the absorption and fluorescence reactions were studied by illuminating these materials with different light sources: UV, IR and visible light in an attempt to find more traces of the original characters (see as an example, Figure 14 where traces of printed characters are displayed).

**Figure 14** — Image of fragment F1 magnified 15x and obtained with green light (bandpass: 445-590 nm and longpass: 648 nm).
The analysed material was compared with several Portuguese newspapers, including Expresso, Diário de Notícias, Diário Económico, Público, Record, Correio da Manhã and Le Monde Diplomatique (Portuguese edition). The measurement of the barcodes height revealed that the observed barcode height was different from the height of the barcodes in the mentioned newspapers (see Figure 15 and Table 1) so further analyses needed to be performed.

Table 1
Maximum height of barcodes contained in some of the major newspapers existing on the Portuguese market

<table>
<thead>
<tr>
<th>Newspaper</th>
<th>Barcode maximum height (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Correio da Manhã</td>
<td>1.2 ± 0.1</td>
</tr>
<tr>
<td>Record</td>
<td>1.5 ± 0.1</td>
</tr>
<tr>
<td>Expresso</td>
<td>0.8 ± 0.1</td>
</tr>
<tr>
<td>Público</td>
<td>0.8 ± 0.1</td>
</tr>
<tr>
<td>Diário Económico</td>
<td>0.8 ± 0.1</td>
</tr>
<tr>
<td>Diário de Notícias</td>
<td>1.6 ± 0.1</td>
</tr>
<tr>
<td>Le Monde Diplomatique (portuguese edition)</td>
<td>1.0 ± 0.1</td>
</tr>
</tbody>
</table>

A controlled burn of Expresso, Diário de Notícias, Diário Económico, Público, Record and Correio da Manhã newspapers was carried out. Analysis of the burned papers and the charred material was performed by Fourier Transform Infrared Spectroscopy (FTIR). The infrared spectra of the observed materials and the ones for comparison, obtained by transmittance using a diamond cell, were compared with those contained in the available databases (Sprouse Polymers by Transmission, Coatings Technology, Aldrich polymers, Aldrich
Condensed Phase, Polymer Additives and Plasticizers, Rubber Compounding Materials, Commercial Materials Polypropylene Additives, Commercial Materials Painter Minerals, Synthetic Fibers Library e Hummel Polymer and Additives). Using these infrared spectral libraries, as well as standard structural diagnosis techniques, the type of material was assigned to the different fragments in analysis. Nevertheless, we should mention that IR analysis just gives an indication of the material present in the samples.

The fibers observed in fragment A presented similar spectral class characteristics to cellulose (see Figures 16 and 17).

Figure 16 — Image magnified 30x and obtained with white light, in which some constituent fibers of fragment A material are visible.

Figure 17 — Transmittance spectrum of the constituent fibers of fragment A
Fragments B and C presented similar spectral class characteristics to the resins and oil bases usually present in plastics, for e.g., dimethylnaphthalene formaldehyde resin.

**Figure 18** — Transmittance spectrum of the constituent material of fragments B and C

Fragment D had the spectral class characteristics of some minerals and pigments, such as iron oxide and aluminum silicate. Fragments F1 and F2 had similar spectral class characteristics to those of aluminum silicate. These compounds have a wide range of applications, in particular widely as components of ink systems, due to their electrical and optical properties and can be used as an additive to titanium dioxide white pigment. The back of fragment A had spectral class characteristics similar to those of certain acrylic polymers used in adhesives, coatings and inks, such as the poly(2-ethylhexyl acrylate).
Based on the optical and spectroscopic analysis, it was concluded that the fragments of the suspicious material had different morphological and spectral class characteristics from the newspapers burned for comparison (Record, Correio da Manhã, Diário de Notícias and Expresso).

In order to obtain more information to characterize these fragments we also used Scanning Electron Microscopy with Energy Dispersive X-ray Spectrometry (SEM-EDX). This is one of the most powerful tools a forensic scientist can use to classify and discriminate evidence material due to its ability to simultaneously examine the morphology and the elemental composition of objects. Also, by the variation of the accelerating voltage, in-depth elemental composition information can be obtained.

The analysis was performed at 25kV using a beam current of 707pA (EDX detector resolution 133eV at 5.9keV) and revealed that fragment A had a different elemental composition from the newspapers burned for comparison (Record, Correio da Manhã, Diário de Notícias and Expresso). While this fragment was mainly composed by aluminum (Al), silicon (Si), chlorine (Cl), calcium (Ca) and titanium (Ti), the burned newspapers’ samples included essentially aluminum (Al), silicon (Si) and calcium (Ca) (see Table 2). Due to matrix nature of the samples, no quantitative analyses were performed.
Table 2
Elemental analysis of suspect and comparison materials obtained by SEM-EDX

<table>
<thead>
<tr>
<th>Samples</th>
<th>Element Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suspect material (coating)</td>
<td>✓ ✓ ✓ ✓ ✓</td>
</tr>
<tr>
<td>Suspect material (fibrous zone)</td>
<td>✓ ✓</td>
</tr>
<tr>
<td>Diário de Notícias Newspaper</td>
<td>✓ ✓</td>
</tr>
<tr>
<td>Expresso Newspaper</td>
<td>✓ ✓</td>
</tr>
<tr>
<td>Record Newspaper</td>
<td>✓ ✓</td>
</tr>
<tr>
<td>Correio da Manhã Newspaper</td>
<td>✓ ✓</td>
</tr>
</tbody>
</table>

Figure 20 – Image magnified 40x and obtained with white light, showing the coating of the material from fragment A

Titanium can be produced in the form of titanium oxide and is used as a white pigment in the production of inks and paper. This molecule is quite resistant due to the oxide which acts as a protective layer on the titanium surface, allowing it to support high temperatures.
Considering all the above results, it was concluded that the partially charred material in question consisted essentially of paper fragments and polymeric material fragments. The performed observations and analysis suggests that at least some of the type of material found at the fire starting point, had class characteristics that could be correlated to adhesive tag(s) and also that they were different from what would have been the result of the burning of newspapers.

**Conclusions**

The justice system acts directly on the crime prevention and fight, therefore it requires the unequivocal discovery of the material truth of the facts, the identification of the offenders and their relationship to crime. Based on this need, it is necessary to apply all available means to ascertain this material truth. Forensic science acts accordingly. In western judicial systems, the technical and scientific conclusions of a forensic expert analysis provide evidence to the court.

The analytical results obtained in both cases described herein show the added value that a forensic expert analysis can have in criminal investigation. In the first case, it allowed to correlate the materials seized from the suspect to the crime of forgery of checks. In the second case, the possible characterization of the charred materials, in conjunction with other evidence, led to the investigation of the real arson’s suspect.

**References**