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PRELIMINARY STUDIES ON IRON GALL INKS COMPOSITION USING AN EXTERNAL ION BEAM

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Abstract

In this work we present and discuss the results obtained by Particle Induced X-ray Emission (PIXE) using an external proton microbeam in documents from the 19th and 20th centuries. Spot analysis and 2D elemental distribution maps were performed in inked and non-inked areas of the documents. Comparison between different types of iron gall inks and paper composition was also made using photography under UV and near IR light. These techniques revealed to be very useful in detecting changes in paper and inks such as corrosion or deterioration. The results showed that besides sulphur and iron, the presence of other metals are helpful to identify different inks in the same document as well as different paper manufacture techniques.

Keywords: *Iron gall ink; External proton beam; PIXE; UV and IR photography.*

Introduction

The application of analytical techniques in arts and archaeological artifacts provides crucial information for historians and art experts in a way that gives information about chemical composition and physical behavior of objects. This knowledge is necessary to test the authenticity or to perform restorations as more and more the ageing phenomenon of cultural heritage is a problem in modern days.

Since 1960s, the need to study archaeological materials stimulated the introduction of many established analytical techniques in this field, like electron beam microscopes and microprobes or mass spectrometry techniques [1]. More recently, techniques based on ion beam analysis (IBA) have been used for the study of ancient artifacts [2].

Concerning to ancient manuscripts, plenty of historical information on the cultural development can be obtained through the study of manufacturing techniques of the support materials for writing on (as papyrus, parchments or papers) and inks or dyes. By allowing the analysis of these documents in a non-invasive and non-destructive way, IBA represent a

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powerful tool to study them [3]. The analytical capabilities of Particle Induced X-ray Emission (PIXE) when using an external proton beam in the specific application to ink analysis have been proven since the pioneering works of the Davis group on Gutenberg Bible [4] and on the Vinland Map [5]. External PIXE has revealed to be ideal for the analysis of inks in valuable documents as it provides a reliable quantitative measurement in a relatively short time and with little risk of damage.

PIXE is an analytical method based on X-ray emission of the sample under study, whose characteristic feature is that the excitation is performed by MeV charged particles (generally protons) generated by an accelerator. The major benefits of PIXE technique using an external beam are that it allows the analysis of documents of any size and shape without any sample preparation and it avoids dehydration problems, reducing the risk of local heating and consequent damage [6, 7].

The purpose of this work was to study the ink composition of different documents from the end of 19th and beginning of the 20th centuries using an external micro-proton beam. Initially, the experimental working conditions, as beam current and deposited charge, were established in order to avoid damages on the cellulose materials such as residual stains. Additionally, the documents were examined using visible (Vis), ultraviolet (UV) and infrared (IR) light.#

For a better understanding of the results exposed one has to describe the standard composition of the inks used in the documents analyzed in this work. In those times documents were written with iron gall inks. These inks, originating from the Roman period, were recurrently used until mid-20th century in Europe, mostly because of its indelibility and easy access to the ingredients [8]. Although there are many recipes, the basic recipe makes use of water (H_2O), Arabic gum, tannin acid extracted from gall nuts, vitriol (iron sulfate $Fe(II)SO_4$) and in some cases additives as wine or vinegar are introduced depending on the recipe. The original resulting color is a deep blue-black, however because of degradation processes it usually turns lighter, dark brown. During the degradation process, iron sulphur can suffer two distinct chemical reactions: oxidation due to Fe(II) and Fe(III) ions and acid hydrolysis. The excess Fe^{2+} ions are oxidized by the oxygen in the atmosphere producing Fe^{3+} ions by reactions known as Fenton reactions. These Fe^{3+} ions are insoluble and so they are constantly recycled in Fe^{2+} ions due to reductive substances in paper and inks. These ions penetrate in the fibers making cellulose chains less hydrophilic with subsequent decrease of mechanical resistance of the paper support. Acid hydrolysis of cellulose causes the break of the cellulose chains through sulphuric acid (H_2SO_4) action. This degradation process tends to worsen with time, spreading along the manuscripts surface [9]. As the name suggests, iron and sulphur are the dominant elements in these inks. Since the vitriol could be obtained from different sources, it is usually contaminated with other metals such as copper, manganese, aluminum or zinc, depending on the place from which it was collected [10]. Due to the high sensitivity of PIXE these metals are possible to be detected. However, it cannot be excluded the possibility of deliberate addition during the ink manufacture. Our results will actually show the presence of copper and zinc in some of the analyzed inks.

It is not unusual to find different sections of one document written with inks prepared according to different recipes. Thus, it becomes necessary to analyze several spots in the same document to ensure that all the necessary information is collected in order to apply the best restoration techniques. Additionally, the possibilities offered by PIXE mapping technique for the measurement of the migration of some elements around the inscriptions provide a better understanding of ink composition and corrosion processes. This is an advantage since spot analysis does not distinguish between some elements because the difference between inked and non-inked areas is not large enough. Since elemental mapping investigates a large area it may enable us to differentiate between ink's and paper's elemental composition.

Materials and Methods

Samples

The samples selected for this study were two different documents (Document A and B) dated from 1928 and a document dated from 1897 (Document C). They are from Rio de Janeiro (Brazil) and belong to a private collection. Small pieces of paper were used to establish the working experimental conditions.

Methods

PIXE measurements were performed with the external microprobe set-up of the CTN/IST facility, in Portugal. A Van de Graaff accelerator was used to produce the 2 MeV proton beam which is focused by means of set of quadrupole lenses reaching a final beam dimension of 70x70 μm^2. The beam exit window consists on a Si_3N_4 membrane with 100 nm thickness. An X-ray Si-SDD detector is placed at 2.8 cm from the sample at an angle of 45º to the beam direction. It has an active area of 30 mm^2 and 145 eV resolution at 5.9 keV, during measurements a 50 µm foil of Mylar was placed in front of the detector. Documents were placed at 3 mm distance from the exit window with the guidance of two laser beams intersection. More details can be found on [11]. It is also possible to obtain elemental mapping as large as 800x800 μm^2 by scanning the sample with the micro-beam.

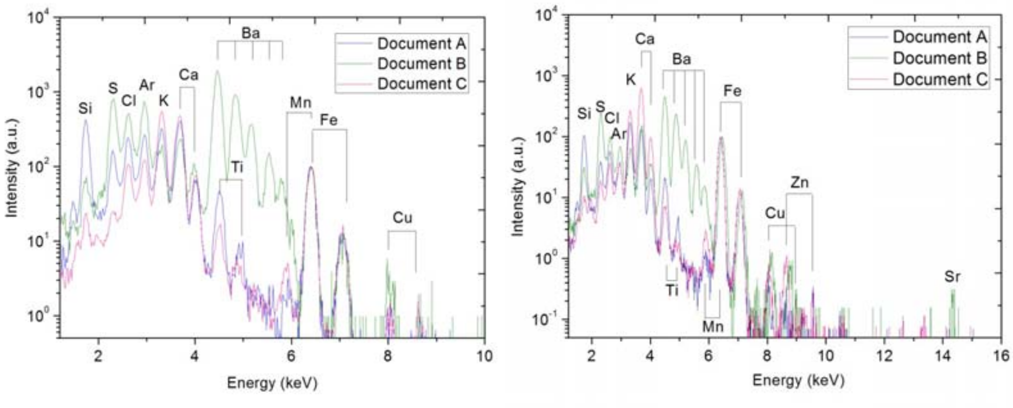
For this work the beam intensity was set at 300 pA and the acquisition time was 15 minutes for each measurement. Measurements were performed in both, bare paper areas and ink regions in order to differentiate the elements from the paper and the ink although some elements can be present in both. Data acquisition and beam control is performed with the OMDAQ V5.2 software package. PIXE spectra evaluation and quantification was done with the GUPIX [12] software. It has to be mentioned that from the PIXE technique, only the elements with atomic number higher than 12 can be detected. During the analysis the samples were assumed as a thick homogeneous target.

A high-resolution camera with a digital sensor (Nikon 5700) was used to record images under visible and UV light. The UV source is composed by 4 lamps of long wave UV light at 350 nm, they were oriented at 45º with the documents. Near-IR images were recorded with a Sony camera with a Carl Zeiss® Vario-Tessar lens.

Results and Discussions

Representative X-ray spectra from the 3 documents are shown in figure 1, obtained in uncovered paper and in ink covered regions. Comparing the spectra it is obvious that elements as Si, S, Cl, K, Ca, Ti and Fe are present in all three documents. Regarding the non-inked areas (Fig. 1a) the concentration of these elements is usually higher than for the inked areas (Fig. 1b). Despite being a characteristic of iron gall inks, sulphur and iron exist in most everything in nature, so it is not surprising to find these elements in high concentration in paper. In general, chlorine concentration is invariably smaller in ink spots than adjacent paper. This effect has been observed systematically in the three documents. However, whatever reason lies behind this, the chlorine concentration is not relevant for differentiating between different inks. The concentration of calcium and potassium have to be interpreted with a certain precaution since these elements are not expected from the basic ingredients of iron gall inks composition although can be used as fillers in paper manufacture and they are usually natural contaminants. The concentrations of these two elements are always very similar in all documents, giving the impression that they could be part of some common ingredient. It is possible to attribute their existence to the use of a gum as a binding medium when existing in significant amount but there are still some discussion around this subject [13, 14]. Following these considerations, in this work we will mainly focus on the relative concentration of the heavier metallic elements as a tool for discrimination.

Concerning the composition of the papers analyzed (Fig. 1a), some differences were detected among them, even between the documents from the same year. In all of them Ti was detected which can be attributed to titanium dioxide (TiO_2), widely used as a white pigment or bleaching agent in paper [15]. In document B, the PIXE spectrum in figure 1a shows the presence of barium as one of the elements with higher concentration. Barium is an indicator of industrial paper manufacture [16]. For instance, non-inked areas have higher amount of this element than inked areas where concentrations can vary due to the thickness of the ink. All three documents show the presence of manganese in paper composition in low concentration.



a b

Fig. 1. X-ray energy spectra obtained from non-inked areas (a) and inked areas (b) in documents A, B and C. The signal is normalized to the Fe-Kα line.

Additional studies should be done to understand its provenance and discard some kind of contamination. Figure 2 shows an UV photography of all the documents, where the difference in paper color and appearance is clearly seen. In general the three documents fluoresces faintly whitish, being the document A the one with the highest glow signal. Document B appears to be darkish than the other two documents under UV light, probably as a result of the barium in its composition. Under UV illumination it was also possible to recognize foxing and some water stains, particularly on the edges of the Document C.

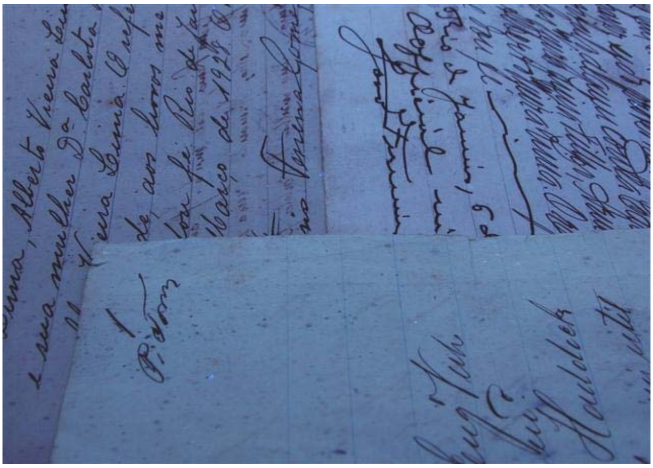
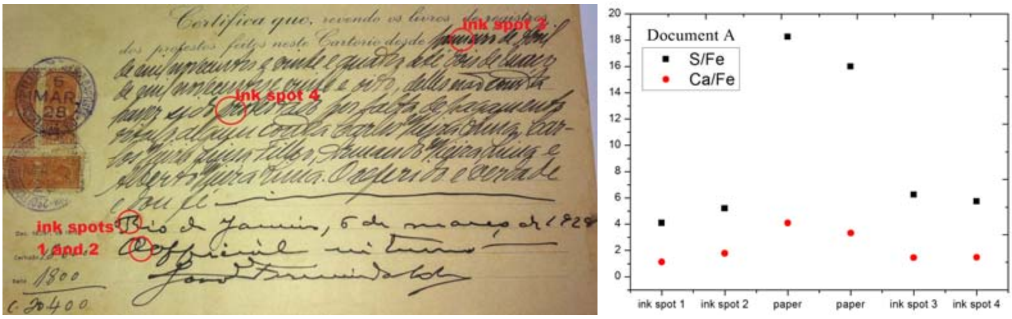


Fig. 2. UV photography of Document A (right side), Document B (left side) and Document C (down in the picture).

As described in the introduction, iron gall inks are characterized by the presence of vitriols, nominally iron sulphates, but may also contain other metal sulphates as impurities such as manganese, nickel, zinc, copper or lead [14]. However, they may come from deliberate additions to the recipes. In our results we have detected in the inks elements besides S and Fe, in concentrations that validate this supposition.

Concerning to Document A, figure 3 shows the S/Fe and Ca/Fe ratios obtained for different inked areas (the values for the bare paper are also showed for a better comparison). From this figure 3 it is observed that the non-inked areas have higher ratio of S/Fe than the other analyzed areas, and also that the Ca/Fe ratio is higher for the paper, although not so significantly. On the other hand, the inks present slightly different values among them. According with figure 3 it seems to be two distinctive groups of inked areas with similar ratios of S/Fe. Traces of copper can be found in all spots.



a b

Fig. 3 Image of the document with the analyzed areas marked (a) and S/Fe and Ca/Fe ratios obtained (b). The amount of sulphur is much higher in non-inked areas while calcium does not differ that much from inked to non-inked areas.

Through IR and UV illumination of the inks in this document A (Fig. 4) it is possible to confirm that the ink (ink 1) used to write the text (spot 3 and spot 4) appears different (almost transparent to the IR radiation) from the ink (ink 2) used to sign the document (spot 1 and 2). Also UV light reveals some ink migration to the surrounding areas especially in the type 2 ink, due to the degradation processes of the ink [17].

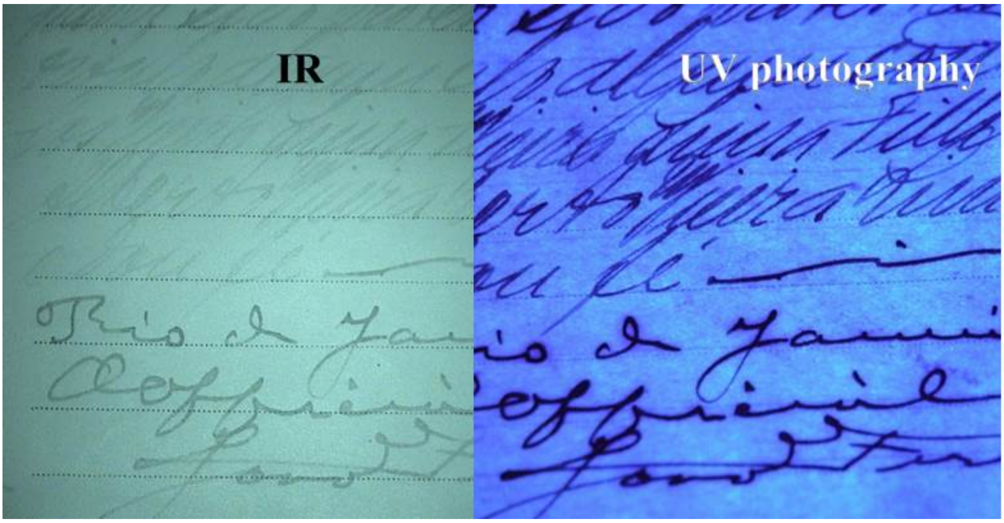


Fig. 4. Detail of the IR and UV photography of Document A.

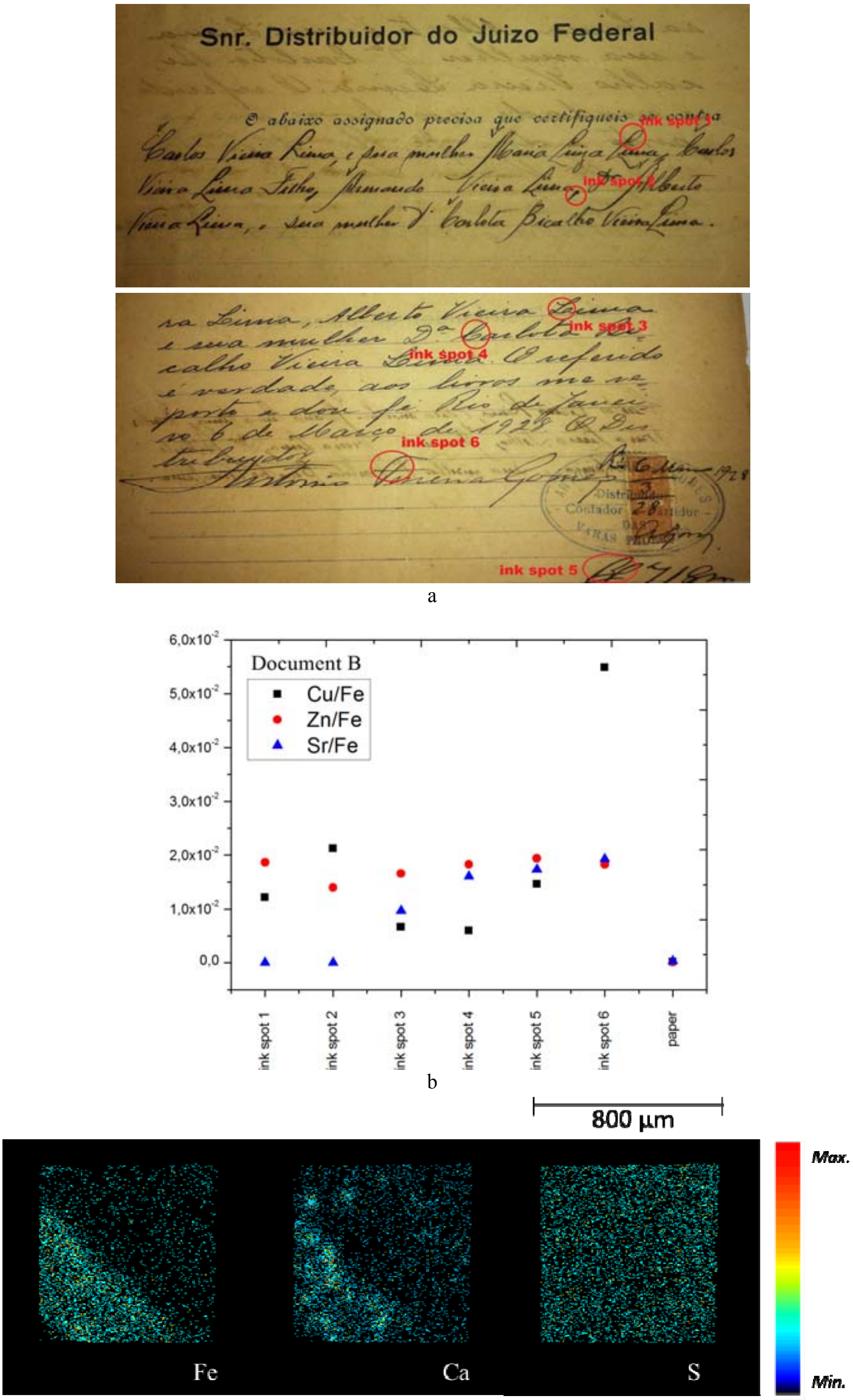


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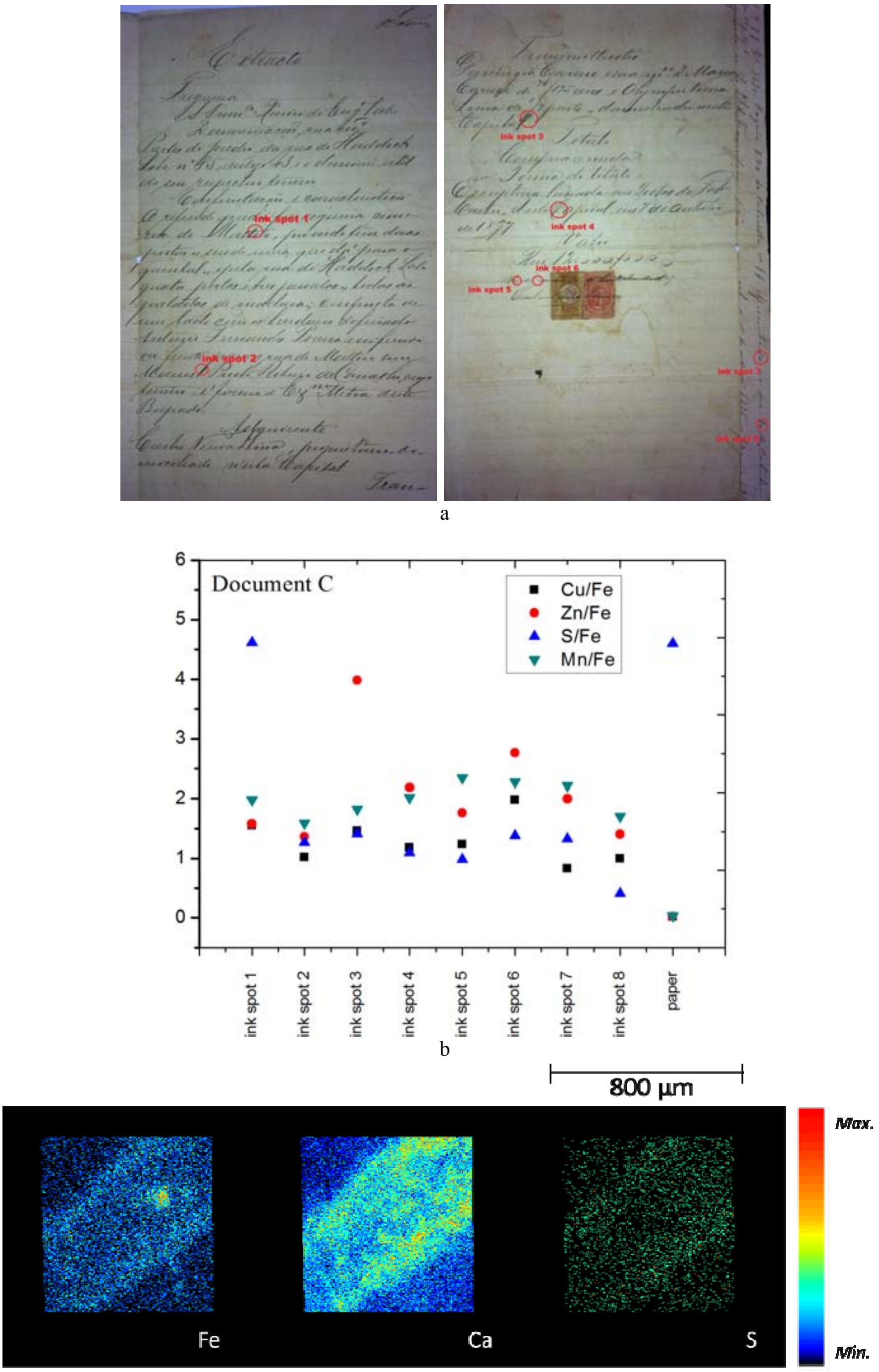
Fig. 5. Image of the document with the analyzed spots (a); Cu/Fe, Zn/Fe and Sr/Fe ratios for the spots analyzed in Document B (b).; 2D elemental maps for Fe and Ca obtained for Document B. (800x800 µm^2) (c).



a

b

c

Fig. 6. Image of the document with the analyzed spots (a); Ratios of some elements present in the ink spots analyzed in Document C (Cu/Fe, Zn/Fe and Mn/Fe ratios are multiplied by 100) (b). Elemental maps of ink spot 3 of Document C (800x800 μm^2) (c).

Figure 5b shows the Cu/Fe, Zn/Fe and Sr/Fe ratios for Document B recorded in different covered areas. The first aspect to be noticed is that ink spots 1 and 2 (text from the front page of the document) correspond probably to the same ink since they are the only ones where Sr was not detected. Similarly, ink spots 3, 4 and 5 may belong to the same ink as their Cu/Fe, Zn/Fe and Sr/Fe ratios are quite similar and they all belong to the main text in the back page of the document. Ink spot 6 seems to correspond to a third different ink since the amount of copper is much higher than in the other ink spots analyzed. The presence of strontium, in very low concentration, in four of the six ink spots examined is not fully understood, and more studies about its origin are needed. In this document copper could be associated to vitriol impurities however it appears with relevant ratios only in the region of the signature (ink spot 6), such that the assumption of a third ink for that signature is not so misplaced. Zinc appears to be an ingredient added to inks since it appears in significant amount only in ink spots. By the UV and IR images obtained in this document it is also possible to obtain slightly differences between the three inks, although the contrast is not so clear as in Document A.

Figure 5c shows the elemental maps for Ca, Fe and S recorded in an area partially marked with ink spot 4 from Document B. Apparently, the iron and calcium signals in inked area are higher than in non-inked area, while the signal for sulphur is mostly uniform in all area. Iron and sulphur content is due to the iron gall ink and calcium presence can be due to a binding medium [13, 14]. Inked areas in this document also contain significant amounts of copper and zinc (figure 1B – X-ray spectra for document B) as seen in figure 5b, but due to the low statistical data the maps are not showed.

Document C dates from 1897, being the oldest of these sets of documents. Figure 6b shows the Cu/Fe, Zn/Fe, Mn/Fe and S/Fe ratios for different marked areas analyzed along this document. In ink spots 3 and 4 the Zn/Fe ratio is significantly higher than in the other ink spots analyzed. This suggests that this element could be purposely introduced as an extra ingredient in the ink or this ink could have a different provenience. This, in addition to the fact that these are the only spots which belong to the main text in the back side of the document, indicates that spots 3 and 4 correspond to a different ink (ink 1). Ink spots 1-2 (current text from the front page) and ink spots 5-8 (annotations in the margin and in the date of the document) appear to have similar ratios of the elements to iron, giving the idea that they correspond to another type of ink (ink 2). It is also important to mention the presence of manganese in this document. This is usually added as a pigment to give a brownish color to ink when incorporated as manganese oxide [10]. However, since its presence was detected in inked and non-inked areas all over the document it is more consistent to assume that this element result from some kind of contamination of paper. Ink spot 1 shows high amount of sulphur when compared to the other ink spots which could be related to some contamination from the atmosphere. The fact that the S/Fe ratio for the other ink spots is approximately about 1:1 proves that these are iron gall inks.

Figure 6c shows elemental mapping of Fe, Ca and S in spot ink 3 where is visible the profile of the hand-writing. In all three maps the concentration of the three elements is higher in inked area than in non-inked area, which is consistent with the assumption that these elements are used in ink fabrication.

Conclusions

With PIXE analysis it is possible to identify most of elements present in iron-gall inks and paper although some attention should be paid to distinguish constituent elements of paper and ink. Although under UV and IR light the inks show differences, by PIXE it was possible to identify more precisely different inks based on the elemental composition. Furthermore, the PIXE elemental maps are useful to study the distribution of the inks over the paper. During these experiments PIXE revealed to be a nondestructive method (low proton beam currents were used) since no structural or visible damages were detected after measurements on the documents. Our results showed that elements other than iron and sulphur (present in all iron-gall inks) as for example zinc, copper and barium, can help us to identify different inks in the same document, or different paper manufacture techniques.

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