Article

The Basics of Fast-scanning XRF Element Mapping for Iron-gall Ink Palimpsests

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Abstract

Synchrotron radiation X-ray fluorescence (srXRF) mapping of elements is a good tool for digitising iron-gall ink handwriting, even if the ink has been covered or erased, as was often the case in the Middle Ages in order to re-use pieces of parchment. In this paper, the influence of the excitation energy on the measuring process and resolution will be discussed, showing that 17 keV of excitation energy and a resolution of more than 100 dpi give the best results. Two typical systems of re-used parchment in book bindings were investigated with mock-up samples in a test, one with written parchment in close contact with wood, the other with leather. The results are discussed here with a special focus on the evaluation of what the minimum requirements of a dedicated set-up would have to be to make this method mobile, using an X-ray tube as the light source instead of a storage ring beam.

1. Introduction

In the Middle Ages, the scribal practice of re-using parchment produced numerous palimpsests, manuscripts that contained a newly written text on top of an erased older one. Iron-gall ink was the predominant choice for producing the historical manuscripts under consideration here, and in many cases, the original text was erased chemically. By removing the gallic acid from the organo-metallic compound responsible for the ink's bluish-black colour,[1] the remaining ink was rendered more or less transparent to visible light. This method left all the metallic compounds (mainly metal sulphates) of the old iron-gall ink in the parchment, making it appear more or less unused. Thus the parchment could be re-used to produce a second manuscript, although oxidation of the remaining iron content of the old ink would frequently lead to the eventual reappearance of the old text in a yellowish-brown tint, sometimes clearly readable, sometimes only as a faint trace. In the 19th century, chemicals were used to enhance the readability of the erased script on many of the remaining manuscripts, yielding some stupendous results in the short term, yet often resulting in damage to both parchment and texts (old and new alike) in the long term. Some less invasive, non-destructive approaches that also provide good results in recovering the older script are the use of UV light (since the early 20th century, both for examination and photography), multispectral imaging[2] and other optical imaging methods. In cases where the use of UV light or multispectral imaging will not provide adequate results or is rendered futile by solid layers of paint on top of the older text, for example, another approach that can be considered non-destructive[3] is the use of X-ray fluorescence spectroscopy employing a monochromatic hard X-ray light source of very high intensity (only available in storage rings today), which has proved to be the perfect tool in digitising and visualising hidden texts written in iron-gall ink.[4] Since the first successful experiments on the Archimedes Palimpsest,[5] erased text in several palimpsests has been deciphered as a result of using the synchrotron radiation XRF method, which always requires the documents to be transported to a storage ring facility. There are still a large range of objects that cannot be investigated, however, including manuscripts that are not available for transport to a storage ring facility, even for the short duration of the measurements, due to considerations relating to manuscript preservation, the manuscript's value or library and archive policies.

The same storage-ring-based XRF method was used for

[1] Krekel 1990.

[2] Easton et al. 2010.

[3] Young 2005.

[4] Bergmann 2011.

[5] Bergmann 2007.

the investigation of hidden paintings and led to similarly spectacular results.[6] As with manuscripts, in these cases the often considerable value of the objects investigated (the under-drawings of most interest to researchers tending to be underneath famous paintings) can be one of several reasons for wishing to avoid transport to a storage ring facility. Given the rather intense signals solid paint layers produce, the use of mobile X-ray-lab-source-based XRF set-ups has proved to be possible.[7] Changing the light source from a storage-ring-based system, which is highly monochromatic and most often linearly polarised, to a non-monochromatic unpolarised X-ray source, as most mobile systems are, the quality of the XRF spectrum recorded is decreased dramatically, especially for trace elements.[8] Hence storage-ring-based XRF images of paintings are still of significantly higher quality, even if the mobile equipment available as a prototype at the University of Antwerp today is perfectly sufficient for most paintings.

However, in the case of the slight traces of the erased inks and thus much weaker XRF signals emitted during the measurement of manuscripts as well as the higher spatial resolution required for the results, it is significantly harder to make use of a mobile set-up. As a first step pertaining to the eventual choice of the most suitable X-ray source, we have investigated the minimal resolution required for such a system as well as the dependence of readability contrast of the element maps produced with srXRF spectroscopy on the excitation energy used during the measurements.

The set-up used was not state-of-the-art in synchrotron fast XRF mapping as used in the case of the Archimedes Palimpsest, for example.[9] Today's srXRF upper limit is to measure with a resolution of 600 dpi and illumination times of around 3 ms per spectrum using optimised equipment and a highly brilliant X-ray source with suitable focusing. In principle, it is possible to enhance the readability of the measured data, separating different inks due to their non-iron metal impurities using methods such as principal component analysis or non-negative matrix factorisation.[10] Additionally using XRF detectors on both sides of the illuminated parchment, the nature of the fluorescent light emitted in essentially every direction allows one to separate the signal coming from the front and back of the parchment.[11] This has not been done in the measurements presented in this paper, nor has post-data processing been performed to enhance readability for the data presented in this paper, focusing on the possibilities of the XRF mapping technique itself and the necessary minimal operating parameters for a transportable set-up based on a laboratory X-ray source. The limitations of an X-ray tube to a state-of-the-art beamline at a storage ring facility is in our case mainly in focus, flux, monochromaticity and polarisation. The non-monochromatic flux of modern laboratory X-ray sources is comparable to the monochromatic flux of the bending magnet beamline used for the presented measurements, the focus of those sources is limited to a diameter of roughly 100 µm, hence the resolution achievable with such a beam size was to be analysed. The lack of linear polarisation of light from an X-ray tube would make the otherwise advantageous positioning of the XRF detector at right angles to the light in the polarisation plane useless. The scattered X-rays are minimal in that direction for linear polarised X-ray excitation and energy-dispersive XRF detectors used to perform XRF mapping experiments measure both, hence the background is lowest in this detector geometry. The results obtained with non-monochromatic light[12] show reduced thresholds for trace-element detection – a change from a storage-ring-based source to lab equipment may limit the number of non-iron impurities one may use for analysis to the metallic compounds with sufficient concentration. The latter two effects were not part of the investigation discussed in this paper.

A palimpsest manuscript which we had previously measured fully to identify the erased undertext[13] was available for energy-dependent test measurements. In addition, several mock-up iron-gall ink texts were produced in the lab on modern goatskin parchment, applying the ink with glass ink pens or goose-feather quills. No differences in the XRF maps could be seen as expected between the two ink application methods, with the glass pens being the more convenient to write with and producing thinner lines that were more even, so we stuck to them in the end. Freshly prepared iron-gall

[6] Dik et al. 2008.

[7] Ahlfeld et al. 2011.

[8] Chen et al. 2008.

[9] Bergmann et al. 2012.

[10] Ahlfeld et al. 2014.

[11] Bergmann et al. 2009.

[12] Chen et al. 2008.

[13] Deckers and Glaser 2011.

inks (table 1) were used for our mock-up samples following historical iron-gall ink recipes,[14] but our own sample inks were produced from modern ingredients. To simulate the high impurity of the historic vitriols (containing iron sulphate), we combined the chemically pure compounds, especially various metal sulphates. Iron-gall inks currently in commercial production are based on the essential compounds of the ink, in particular pure iron sulphate, and thus lack the impurities of the vitriol. One modern ink (labelled 'IR' in table 1) was used in comparison. When examining historical inks by methods involving XRF spectroscopy, mapping of these impurities (which sometimes make up more than 50% of the ink's metallic compounds) can often be more interesting than that of the iron signal alone. Using these traces, it is possible to distinguish different inks and/or scribes.[15] To investigate the different points in time at which a document was expanded or revised, for example, this is achieved by determining the minimum number of different inks evident in a specific document. There is always an iron signal to be measured when dealing with iron-gall ink, but the intensities – and sometimes the mere existence (or absence) – of a specific trace element can help one separate the upper from the lower ink, as was the case for calcium in one of our previous investigation, for instance.[16] The words 'upper' and 'lower' in this case refer to the later, fully visible layer of writing and the older, erased one respectively. The gap in production time between the upper and lower layers of text can range from a few centuries to as little as a few decades. As long as the second ink is based on a vitriol of different origin than the one previously used, mapping the non-iron metal impurities will help one to distinguish the upper from the lower text.

Table 1: The metallic content of the prepared inks as an atomic percentage of the total metallic content of the ink. The ink labelled IR was a modern commercial ink.

Ink	Fe	Cu	Mn	Zn	Sum of Mg, Al, K and Ca
1	95	1	1	1	2
2	90	2	2	2	4
3	85	3	3	3	6
4	80	4	4	4	8
5	75	5	5	5	10
6	50	10	10	10	20
7	40	20	5	25	10
8	30	30	5	25	10
9	20	50	5	15	10
10	60	15	5	5	15
11	50	40	2	2	6
12	40	10	10	10	30
13	60	20	0	10	10
14	60	20	10	0	10
IR	100	0	0	0	0

To further investigate specific configurations of historical manuscript materials that have been considered for future measurements, we also tested the effects that solid pieces of wood and leather have on the XRF signal, simulating the re-use situation of parchment leaves glued to a book's leather or wooden cover. For the tests with wood, we applied different inks on parchment and placed the parchment face down on different kinds of wood (oak, beech, pine and balsa), measuring from the back of the parchment. To test the effect of leather, we covered a text on modern parchment with a 2-mm-thick leather cloth and measured the ink through the leather. The XRF scanning technique works fine, even in the presence of strong matrix effects, as demonstrated with the gold paint cover on leaves of the Archimedes Palimpsest or on paleontological samples such as the Archaeopteryx fossil (Bergmann et al. 2010, Wogelius et al. 2011). In principle, it is possible to use a confocal XRF set-up to minimise the matrix effects of a supporting material, as has been done for single-point measurements on wood (Malzer et al. 2004). For scanning areas of parchment with a confocal setting, the layer of the ink within the fast-moving, uneven parchment sample would have to be kept in the focus of the set-up throughout the measurement. This highly challenging task could be achieved by 3D laser scanning the surface of the parchment in advance and then synchronising a 3D sample stage, compensating for the surface structure throughout the mapping. However, a set-up such as this is not available anywhere at present.

[14] Kolar and Stirlic 2007.

[15] Hahn et al. 2004.

[16] Deckers and Glaser 2010.

2. Data acquisition and analysis

All our measurements were performed at Beamline L of the DORIS III storage ring at DESY in Hamburg, Germany. To preserve the parchment, the experimental hutch was acclimatised to 20°C and a relative humidity of 50%. The beam size was collimated to 100 µm vertically and 70 µm horizontally, while the parchment to be measured was at a 45° horizontal angle to the incident beam, thus producing a 100 µm x 100 µm X-ray footprint on the parchment. The chosen beam size was in the order of the minimal step size planned for the measurements and at the lower end of what is today's limit of focal sizes of laboratory-based high-flux X-ray tubes. A VORTEX EM XRF detector was positioned in reflectance geometry in the plane of the polarisation of the light at angles of 45° to the parchment and 90° to the light (fig. 1) to minimise noise due to the detection of scattered X-rays. The parchment could be scanned continuously in the horizontal plane, while XRF spectra were taken at a photon flux of 10^9 photons/second at 7 Hz, resulting in effective illumination times of 0.13 seconds per point. Most measurements were carried out at a distance of 150 µm between two measured points in the plane of the parchment (~170 dpi), resulting in approximately 4,500 spectra taken within 15 minutes for one square centimetre of mapped parchment. The XRF data was processed using the AXIL code,[17] while the element maps were produced and processed using IDL and Photoshop. The elemental maps were all scaled to use the maximum contrast within the individual element map, but no additional processing such as principal component analysis was used since the actual quality of the measured data of interest in this particular experiment can best be interpreted prior to any further alteration of the data.

3. Results and discussion

To optimise scanning times and estimate the spot size for which a laboratory X-ray source should preferably be optimised, the same areas of prepared parchment were measured repeatedly with different step sizes between the measured spectra. The test parchment for this verification was inscribed using a glass ink pen and our home-made ink no. 10. Lines, waves, dots and circles were applied to simulate different abstract parts of writing characters, choosing a line distance in a range proportional to the thickness of the ink strokes. The resulting test object was created to represent manuscript handwriting with character sizes between 3 and 6 mm, a suitable average, even if some small, densely written manuscripts can sometimes exhibit characters with a height as small as 2 mm. The measurement was performed with 17.4 keV of photon energy to record the X-ray fluorescence of all the non-iron metal impurities in the ink. As shown in fig. 2, fair readability is achieved for step sizes of 200 µm and below, while the contrast is insufficient for step sizes of 400 µm and above. The region in between is reasonable for the main metallic compound in the ink (iron), but mostly insufficient where the secondary metallic compound (copper) is concerned. For writing with larger or very simple characters, 300 µm steps (equivalent to approx. 85 dpi) may be sufficient, while for smaller or ornamented characters, the use of 150 µm (or smaller) steps seems more suitable and was used for most of our other measurements.

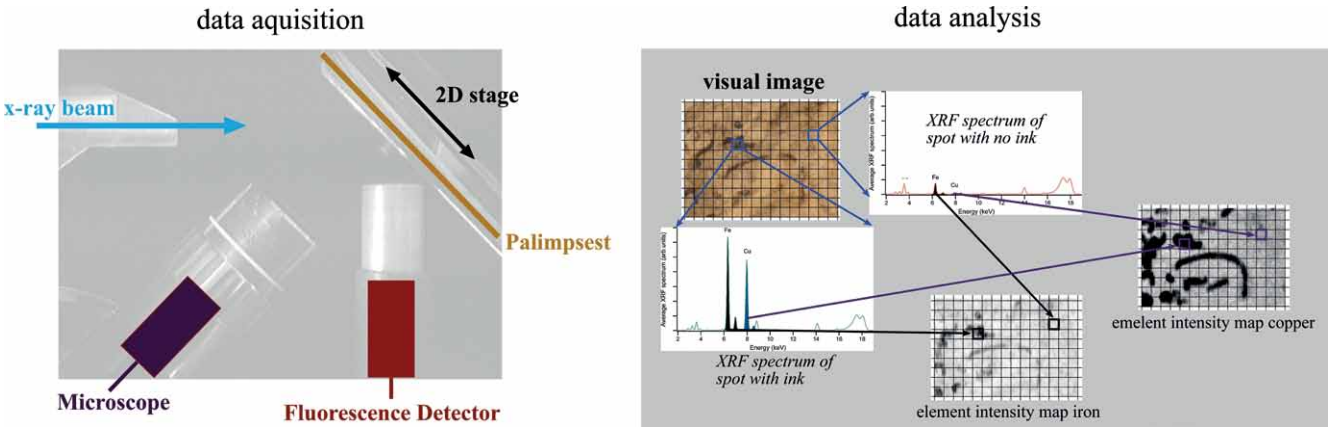

Fig. 1: Experimental set-up on the left-hand side and a schematic description of the analytical steps from image to elemental maps on the right.

[17] Vekemans et al. 1994.

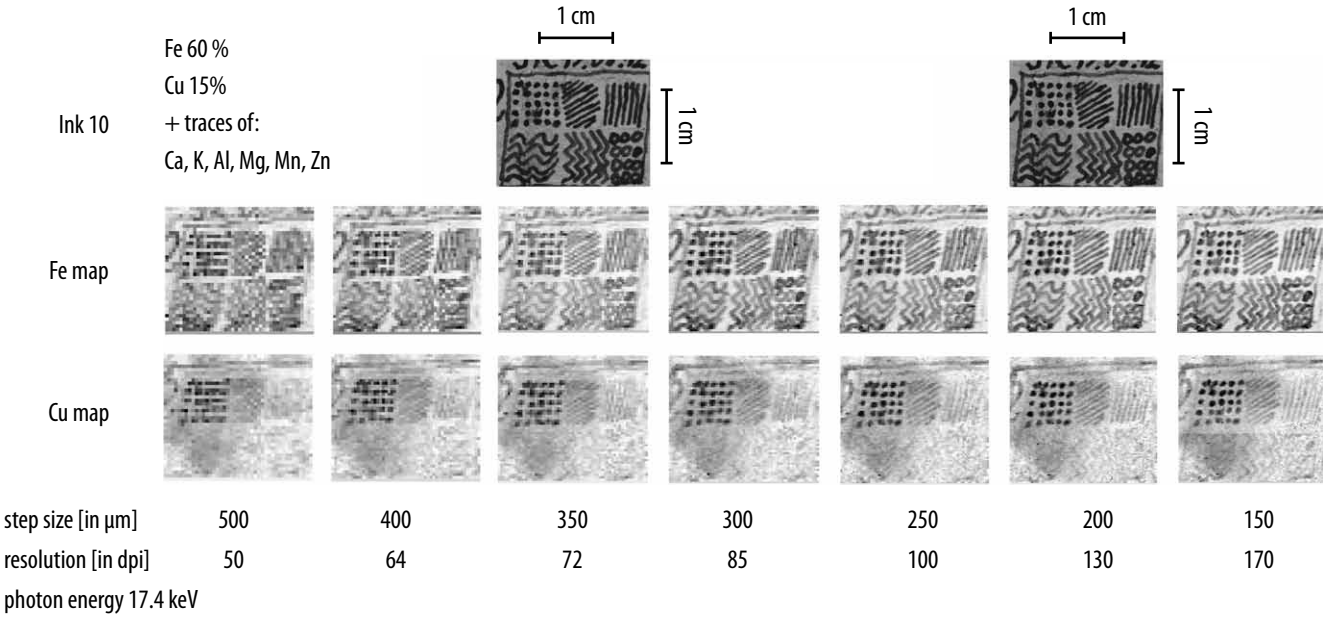

Fig. 2: Simulating a typical sample of handwriting with characters 3 to 6 mm in size, the test sample was prepared on modern thick parchment using circles, dots, lines and zigzags instead of actual letters. Good-quality mapping of the primary metallic ink component (iron) and the main secondary metallic component (copper) can be achieved with sampling steps of 150 to 200 µm, while insufficient contrast is achieved when using steps above 350 µm, even for the main component.

The usual expectation in X-ray absorption spectroscopy is that the signal of a specific element will be enhanced when exciting above but close to the corresponding absorption edges, hence we chose several energies above the iron K-edge, above the copper and zinc K-edges, above the lead M-edges and above the silver K-edge (7.15 / 10 / 17.4 / 31.6 keV). The energy above the silver K-edge was included even though there is no silver in iron-gall ink, as some historical drawings were done using silver-point pens. This was to investigate how much the quality of the iron-gall ink element maps would deteriorate when measuring at an energy level high enough to possibly excite silver-pen lines on the parchment. It was unclear whether the effects of the matrix from the parchment measured would change significantly from lower to higher excitation energies, but due to the chemical composition of parchment we expected to see decreasing effects (less noise) towards higher excitation energies.

As shown in fig. 3, the elemental contrast is quite good for iron when exciting with an energy slightly above the K-absorption edge, but with that energy being too low to

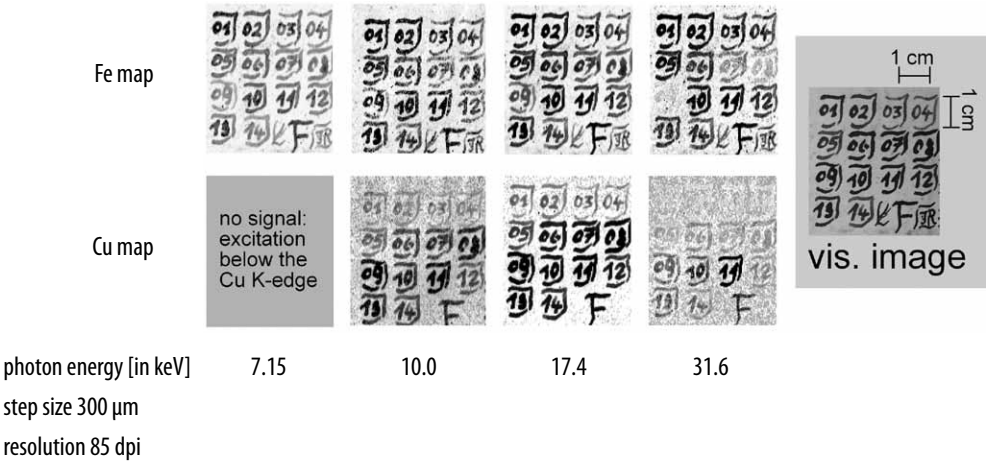

Fig. 3: The elemental contrast is increasing due to the reduced noise from the parchment towards higher photon energies, but when increasing the energy too much, the reduced absorption cross-section of the elements of interest lead to a decrease in contrast, especially for those of the ink's elements only present in low concentrations.

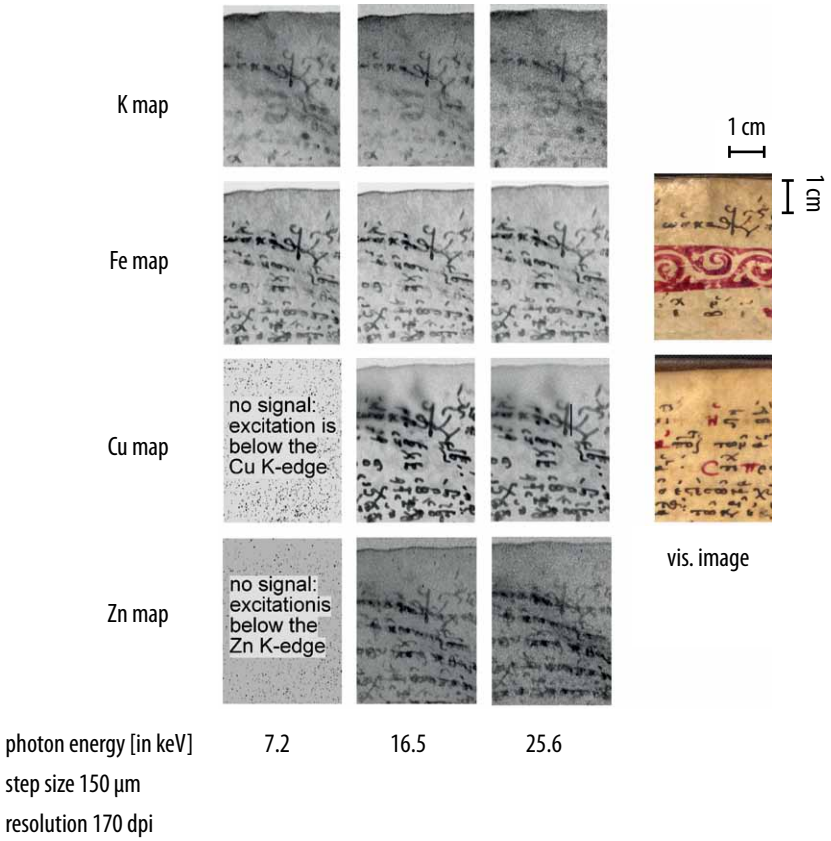

Fig. 4: The readability is quite good at 16.5 keV of excitation energy, even for light elements such as potassium, while contrast decreases for all elements if the excitation energy is too high. The red ink only shows up in the mercury elemental map, but it does not contain any potassium, iron, copper or zinc.

stimulate XRF of heavier elements (such as copper), it is not ideal for historic ink mapping experiments. The matrix effects of the parchment decrease with increasing photon energy, thus producing nicely readable elemental maps at 17.4 keV of photon energy. When using a rather high excitation energy such as 31.6 keV, it is obvious that the quality of the elemental maps decreases and inks with little metallic content (e.g. ink 9 in the Fe map or inks 1–5 in the Cu map) no longer show up in the results. If only one scan of the parchment can be performed (especially if a light source without or of limited tunability is to be used), it therefore seems a good default practice to use monochromatic X-ray photons whose energy is close to 17 keV. Note that for XRF measurements far above the excitation thresholds of the elements, as in the case of iron-gall ink, and excitation energy above 14 keV, slight changes in the excitation energy are not reflected very much in the resulting spectra, hence the excitation energy of 16.5 keV and 17.4 keV can be considered equal in this context. Using a real palimpsest from Leipzig University Library, the energy-dependent investigation was able to be reproduced. Some of the results are shown in fig. 4.

To investigate the effect of wood and leather upon the readability of the measured ink signals, two objects were produced using our 14 inks and the one commercial ink. The measurements with 17.4 keV of photon energy and a step size of 150 µm between two points (fig. 5) clearly show that the contrasts of the used inks are most visible in different elemental maps. The logo in the middle sketched with the commercial ink completely disappears in all but the iron elemental map, while ink no. 12 with a manganese content of only 10% exhibits the best contrast in the Mn element map, and even ink no. 10 with only 15% of copper (and containing four times more iron) is most readable in the Cu element map. It is quite obvious that the parchment used for our test objects contains a high amount of zinc, hence the Zn element map in these examples is not

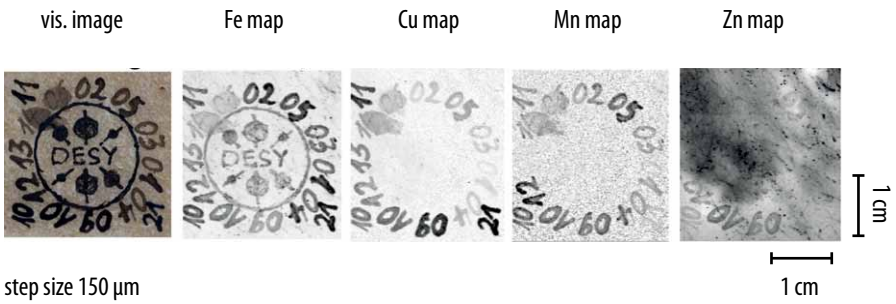

Fig. 5: A test with several differently prepared iron-gall inks (cf. table 1) shows that better contrast can be achieved for some inks from other metallic componentsthan iron. In this case, the modern parchment has a high zinc content, whereas historical texts (in those cases where the ink contains zinc) tend to yield a very good contrast between the writing and parchment in the zinc map.

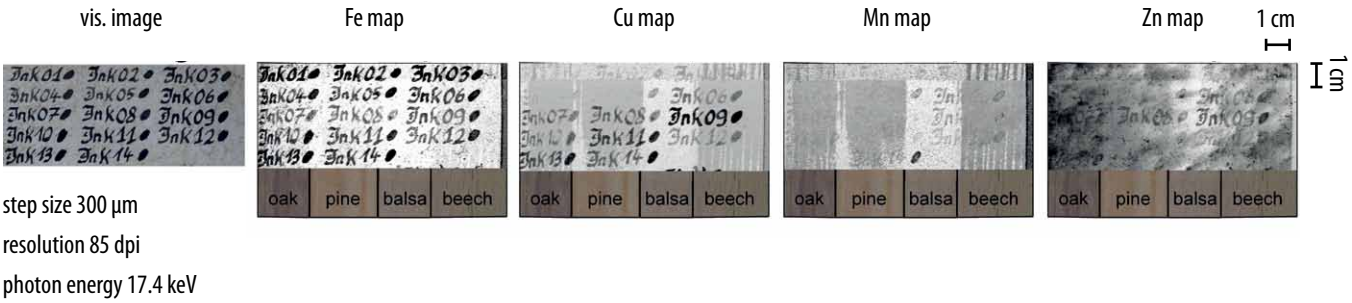

Fig. 6: Testing the method using iron-gall ink writing on modern thick parchment which was put face down onto different types of wood. The results show that the iron and copper maps are quite readable in all cases. The manganese and zinc maps from this test are rather illegible, with the zinc mostly showing the signal from the modern parchment rather than from the structure of the wood.

as useful as that in measurements of writing on historical parchment which typically contains less zinc.

For the test objects with parchment on wood, relatively large letters were used due to the use of a goose-feather quills instead of the glass ink pen employed for the other samples, hence the step size was increased to 300 µm, while all the other parameters were kept the same as before. The structure of typical European wood samples has a strong effect on the elemental maps of copper and manganese (fig. 6), while the balsa wood of tropical origin with little structure and no annual rings only adds a very small amount of noise. Due to the rather low iron content in wood, these effects are minimal in the Fe elemental map.

For the second special use-case examination, we prepared one more mock-up sample with writing and covered it with a 2-mm-thick leather cloth. We recorded the data scanning the ink signals through the leather, simulating the case of a text glued to a leather binding or otherwise obstructed by leather in way that would only allow an examination from the rear side if the structure of the object were to remain unaltered. The leather had a very strong obscuring effect on the contrast of the iron and manganese element maps, but this was not the case for the copper map. The contrast of the elemental distribution in the zinc remained surprisingly high as well, showing those inks with a zinc content of at least 10% quite clearly. It appears that the leather as a cover layer compensates (i.e. absorbs) some of the noise emitted by the modern parchment rich in zinc used for these experiments.

If the parchment is covered with a leather rich in iron and the ink only contains iron, as was the case for the ink used in our experiment for drawing the lines and circles (fig. 7), even a powerful technique such as srXRF has its limits. Fortunately, historical inks are never quite free of non-iron metal impurities, as has been discussed above, and thus far at least two elemental maps in our tests reproduced the inscribed text well.

4. Conclusions

In this paper, we have shown that when measuring iron-gall ink writing with the XRF scanning technique using a highly intense monochromatic source, the best results for element mapping of iron and non-iron metal impurities in examining characters just 3 mm in size can be achieved with

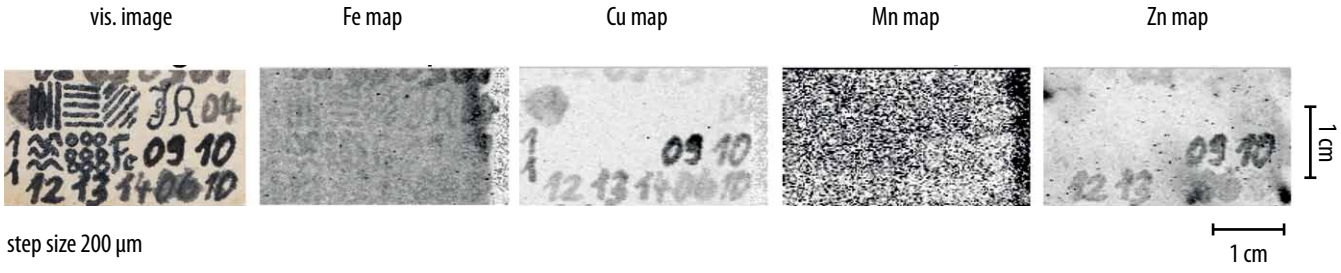

Fig. 7: Testing the method on iron-gall ink writing on modern parchment covered by a 2-mm leather cloth. The high iron and manganese content of the leather produces noise in the corresponding elemental distribution maps, while the copper and zinc channels are mostly undisturbed.

a grid below 200 µm. The best photon energy to use for the experiments is close to 17 keV. If a tunable light source is available, a single map can be improved by re-scanning the entire area for the element in question using a specific photon energy directly above the element's K-shell ionisation threshold (or M-shell threshold for heavier elements), which of course results in doubling the total amount of time for the mapping experiment. It should therefore be avoided if possible. The usefulness of recording further non-iron metal impurities in addition to the iron always present in these inks was demonstrated, showing that the higher-contrast copper and zinc elemental maps are especially valuable in restoring hidden or erased writing. The tests that involved using the scanning methods on a written surface covered by wood or leather proved successful, suggesting that original objects in this condition are suitable for this kind of examination. With respect to the option of using a mobile X-ray source, we have come to the conclusion that the requirements for achieving the best resolution can be met by a mobile source with a focal spot diameter in the order of 100 µm. The most suitable single excitation energy of close to 17 keV for the photons could be achieved using a molybdenum target material. The photon flux needed to scan pages within several days can be produced using at least non-monochromatic laboratory sources. The use of a non-monochromatic photon source that is not linearly polarised in conjunction with the fast-scanning XRF method still remains to be tested; this would enable us to estimate whether the quality of the elemental maps is still good enough to reproduce hidden or erased text. If we tried to keep the measuring time as short as possible, a drop in the quality of the elemental maps would be unavoidable due to changing from a storage-ring-based light source to a mobile X-ray source, but as long as measuring with a non-monochromatised beam of a portable X-ray source is possible, the examination of iron-gall ink writing should yield fairly good results in a dedicated mobile set-up.

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