Characterization of Archaeological Metal Remains in Micromorphological Thin Sections Using μXRF Elemental Mapping

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The soil micromorphological examination of thin sections obtained from archaeological profiles is a well-established approach in geoarchaeology. However, it provides only limited information about the nature of metal inclusions (shape and taphonomy but not elemental composition). Laboratory micro-X-ray fluorescence (μXRF) elemental mapping is a non-destructive technique that can be applied directly to the resin-impregnated sediment blocks from which thin sections are made. However, resin blocks may not always compare to the final thin sections, since some material is lost during the fabrication process, affecting the investigation of millimeter-sized features, such as metal fragments or hammerscale, features essential for determining the type of metal working taking place at a particular site. In this study, we investigate the potential of μXRF elemental maps acquired directly from covered thin sections. Our experiment demonstrates that a wide array of elements useful for metal fragment identification (Fe, Cu, Zn, As, Ag, Sn, Au, Pb) are detectable even in coverslipped sections. This conclusion extends the potential of μXRF beyond the resin blocks from which thin sections were made, to metal fragments in the thin sections themselves, enriching the archaeological interpretation and providing information missed by traditional techniques, such as optical microscopy. © 2016 Wiley Periodicals, Inc.

INTRODUCTION

Micromorphology, the study of soils and sediments in thin section using petrographic microscopes, is an important technique in archaeological research. The understanding of a site's stratigraphy is a prerequisite in standard archaeological practice. A reliable interpretation of a site is based on the contextual relationship between artifacts, chronological information, and their exact location, which is fundamentally dependant on the correct identification and interpretation of stratigraphy (Schiffer, 1987). In this respect, micromorphology is an ideal technique to understand complex stratigraphy. Since micromorphological samples are undisturbed (the oriented blocks are removed from the profile in their entirety), this technique allows examination and interpretation of the (micro)stratigraphy of sites in much closer detail than possible by the naked eye (Courty, Goldberg, & Macphail, 1989; Stoops, Marcelino, & Mees, 2010). It provides information about the relationships between features, and allows us to distinguish between in situ deposits and post-depositional alterations (Mallol & Mentzer, 2015). The technique has been successfully applied at sites of all periods, and further advances are being made by its combination with other methods (Canti & Huisman, 2015).

However, since the method relies predominantly on visual information, it is not possible to ascertain the chemical composition of particular features. Chemical studies can be performed on associated bulk samples. The benefits of this approach are illustrated by Milek and Roberts (2013), who have shown that multielement analysis of bulk samples is effective for pinpointing the locations of house activity areas that received inputs of fresh, charred, and/or ashed organic materials. These data
are complementary to micromorphological observations, which improve the interpretation of the sources and deposition of these materials, linking them to human activities and formation processes. Elemental composition data can be even more useful when microcontextualized (Goldberg & Berna, 2010) and correlated directly with the visual information. Two-dimensional (2D) elemental distribution maps can be used to provide composition data while still taking into account the precise location of each feature, depositional processes, and the taphonomy of each component, as identified in thin section. When very specific objects observed in thin section are under investigation—as in the case of metal fragments—a mapping approach ensures that elemental signals are from the features themselves rather than components of the surrounding matrix. Moreover, this additional level of compositional data is especially useful in cases where features share similar optical properties, for instance in characterizing metal fragments (opaque in thin section regardless of composition), or in making the distinction between goethite, iron phosphates, or calcium phosphates (indicative of different formation processes/material inputs).

Micromorphological samples can be in the form of either thin sections, uncovered or with coverslip, or as soil profile blocks impregnated in resin. Traditionally applied mapping techniques, for example, scanning electron microscopy-energy dispersive X-ray spectroscopy, electron probe microanalysis (EPMA), may offer more accurate results in terms of absolute concentrations but the sample preparation required (making sample surface conductive, limitations of sample size) means that they are inapplicable in the case of soil profile blocks. There have been cases where EPMA was applied to micromorphological thin sections (Bisdom, Nauta, & Volbert, 1983; Stoops, 1983) but the thin sections have to be uncovered. Even though examination of uncovered thin sections is preferable this type of material may not always be available, especially when dealing with archived collections.

Modern laboratory-based micro-X-ray fluorescence (μXRF) instruments, with appropriate microfocus optics and a moving sample stage, constitute an alternative for the acquisition of high-resolution 2D elemental maps directly from profiles embedded in resin or thin sections. Several published studies describe the use of μXRF in the analysis of resin-impregnated soils (Voegelin, Weber, & Kretzschmar, 2007; Thorne, Herrington, & Roberts, 2009), resin-impregnated lacustrine sediments (Shanahan et al., 2008), and archaeometric samples (Kanngießer, Malzer, & Reiche, 2003). As of yet, however, applications in archaeological micromorphology are not widespread (e.g., Adderley et al., 2007; the work on impregnated sediment blocks by Mentzer & Quade, 2013), and applications on covered thin sections are not reported.

It has already been shown that, for qualitative assessment, μXRF measurements on resin embedded soil blocks are equivalent to those from bulk soil (Mentzer & Quade, 2013). However, this approach may not be applicable to millimeter-sized metal fragments, since, during the cutting and grinding processes, at least 1 cm of material is lost. This means that visually the thin section may not necessarily be comparable to the remaining resin block anymore. For this reason, or in cases where the remainder resin blocks are not available, the application of μXRF on thin sections containing metal fragments should be further investigated.

In the case of thin sections, several problems need to be considered: (1) the small thickness of sample (30 μm), (2) secondary excitation of the sample from fluorescence of the substrate, since X-rays will not be fully attenuated in the sample, (3) elemental interferences from the coverslip, and (4) absorption of outgoing sample radiation by the coverslip. Due to these reasons, μXRF mapping of thin sections is absent from literature and is generally dismissed in advance as inappropriate (Mentzer & Quade, 2013). The only reported examples from geological contexts are in Tagle (2015) and Caja et al. (2014), but in both cases thin sections were uncovered.

In this work, we will demonstrate that, for certain applications, μXRF elemental mapping of covered thin sections can provide useful qualitative results. More specifically, we demonstrate that μXRF can be used to identify the elemental composition of suspected metal fragments in coverslipped thin sections as a wide array of elements are still detectable (in the current case Fe, Cu, Zn, As, Ag, Au, Pb, and potentially Sn). As an example, we use a thin section from the Viking-age settlement site of Hedeby in Germany. μXRF elemental mapping was performed and the fragments were identified as silver alloys. This information could not have been acquired through microscopic observation or using another elemental analysis technique, since the section was coverslipped.

**MATERIALS AND METHODS**

**Sample Selection**

On the Viking-age site of Hedeby, several rows of square geomagnetic anomalies had been observed during geophysical study (Hilberg, 2009: 89). Located along the main road, these were interpreted as possible (metal) workshops from the younger, less well-known phase of the settlement (late 9th–11th centuries A.D.) which has to a large part been disturbed by agricultural activity and erosion (Schultze, 2008: 235–254). Two cores were
drilled (depth 3 m; diameter 4.5 cm) in July 2014 to compare this type of magnetic anomaly with a zone outside of it. For this study, one undisturbed sample from this core, HP_502, was selected from a depth of 50–100 cm, corresponding to the level of the geomagnetic anomaly. The thin section (4.5 cm × 7.5 cm) was fabricated to a thickness of 30 μm at the Laboratory for Mineralogy and Petrology of the University of Ghent in Belgium using their standard protocol. The glass slide is a soda-lime glass and the coverslip a borosilicate glass of 60 μm thickness.

μXRF Instrument

For this study, we used a Bruker M4 Tornado μXRF instrument and the proprietary Bruker M4 software. This is a laboratory-based system, with microfocus capabilities and a moving stage, not to be confused with hand-held portable XRF instruments, which would be inappropriate for this application. The instrument has a 30W Rh-anode X-ray source with a Be side-window. The X-rays are focused using a polycapillary lens achieving a spot size of 25 μm (for Mo Kα). The instrument is equipped with two Silicon Drift Detector spectrometers, with sensitive areas of 30 mm², energy range of 40 keV, and energy resolution of 145 eV for Mn Kα. The two detectors are placed symmetrically in reference to the X-ray spot so that they can be used simultaneously during a measurement. Measurements were performed under vacuum at 20 mbar. The sample chamber is equipped with a motorized sample stage allowing the acquisition of 2D elemental distribution maps. The pixel size for the mappings can be as low as 4 μm but this corresponds only to the binning of the spectral data—the actual X-ray spot size relates to (and is limited by) the polycapillary optics.

Optimization of Measurement Conditions

The four parameters that need to be optimized are the working voltage (V, kV), working current (I, μA), pixel size (d, μm) and residence time per pixel (t, ms/pix). The first two relate to the quality of the acquired spectral information: voltage relates to the elemental range detected as well as to the maximum X-ray penetration depth while current relates to the intensity of the elemental peaks and, therefore, to the detection limits for lower concentration elements (Haschke, 2014). On the other hand, pixel size and residence time relate more to the visual quality (resolution) of the acquired map and to the overall acquisition time.

The voltage could be adjusted to ensure that the X-rays will be attenuated within the sample itself and not the glass substrate (Figure 1b). X-ray intensity decreases exponentially as they traverse matter, according to the Beer-Lambert law:

\[ \frac{I}{I_0} = e^{-\mu_l x} \]

where \( \frac{I}{I_0} \) is the ratio of transmitted intensity to initial intensity, \( \mu_l \) (cm⁻¹) the linear attenuation coefficient, and \( x \) (cm) the thickness of the material. For 85% absorption (\( \frac{I}{I_0} = 0.15 \)), the equivalent path length is equal to \( x_{85\%} = \frac{1.89}{\mu_l} \), and therefore \( x \) depends on the energy (\( E, \text{keV} \)) of incident radiation. To calculate \( \mu_l \) for the range between 0.1 and 50 keV, we used the online tool provided by the NIST Electron Effective-Attenuation-Length Database (NIST, 2014), considering a silicate material with a density of \( \rho = 2.51 \text{ g cm}^{-3} \) (approximating in this case a mean of all the layers of the thin section: glass slide, soil layer, and coverslip).

From the resulting \( E - x \) plot (Figure 1b), we deduce that in order not to exceed a penetration depth of 100 μm the excitation voltage should be adjusted to 6.5 kV. However, in this case elements heavier than Fe would not be excited and detected. Since we are interested primarily in metal fragments we would be missing many potentially interesting elements (Zn, As, Ag, Sn, Au, Pb; refer to Table I for more details). Moreover, excitation of the substrate would only result in secondary excitation of the sample layer. Since the glass slide is a colorless soda-lime glass and does not contain any elements of interest for metal fragment identification, there would be no elemental interferences, even if this radiation was not attenuated by the overlying layers. Therefore, we chose to use the maximum excitation voltage, 50 kV, to increase the detectable elemental range.

Current values between 200 and 600 μA were tested. Higher current values result in higher photon counts and in turn increased dead time of the detectors or even over-saturation (in the case of high fluorescence yield matrices such as metals). Moreover, our tests showed that higher current values did not significantly improve the signal to noise rations for the elements of interest. Therefore, a value of \( I = 200 \text{ μA} \) was selected, for which the observed count rate (on average: 35–40 kcps) was well within the limits of the detector modules (maximum: 130 kcps) and dead time was very low (5–8%).

Mapping was conducted at two scales: an exploratory mapping of the entire thin section (Figure 2) and a more detailed mapping of the two major metal inclusions (Figure 3). In the first case, pixel size was set to \( d = 50 \text{ μm} \), residence time to \( t = 1 \text{ ms/pix} \), and only one acquisition cycle was performed to reduce the time of the mapping. In the second case, since only smaller areas were chosen, the parameters could be adjusted for higher visual
μXRF ELEMENTAL MAPPING OF ARCHAEOLOGICAL METALS

RESULTS AND DISCUSSION

Figure 2 demonstrates that certain elements relevant to metal fragment identification (in this case Fe, Cu, Ag) are detected and fully visible even in the presence of a coverslip. On the contrary, the radiation from elements lighter than Fe is fully absorbed by the coverslip layer and they, therefore, present a very homogeneous distribution. Zn is a special case as it is detected (elemental peak present) but its distribution is homogeneous for the area of the coverslip. To determine its source we acquired spectra from areas of the thin section corresponding only to the glass slide and to the full coverslip-epoxy-glass slide stratigraphy (Figure 2a). Comparing these spectra (Figure 2c) reveals that Zn is present primarily in the coverslip, which indeed is the case for some coverslip glass materials.

These results are in full accordance with the fundamental theoretical principles demonstrated in Figure 1c. Outgoing X-rays need to be of sufficient energy in order to be transmitted through the coverslip layer and detected. By examining the $E - x$ diagram it is evident that for a layer of 70 μm (coverslip + epoxy) this condition is fulfilled for all elements of interest in metal fragment identification. Lighter elements, on the other hand, cannot be successfully detected, rendering investigation of the soil matrix impossible. To better illustrate the effect of the coverslip on the resulting elemental maps and spectra we conducted comparative mappings on the surface of the resin block from which the thin section derived. These results are detailed in Supporting Information Document S1.

quality: $d = 4 \mu m$, $t = 1 ms/pix$, and three acquisition cycles were chosen.
Table I: Peak energies and attenuation length for elements of interest in metal fragment identification.

<table>
<thead>
<tr>
<th>Element</th>
<th>Z</th>
<th>Kα1 (keV)</th>
<th>Kβ1 (keV)</th>
<th>Lα1 (keV)</th>
<th>Lβ1 (keV)</th>
<th>L-Series Interferences</th>
<th>Attenuation Length (μm) for Kα or Lα (Where Applicable)</th>
<th>Calculated for Glass Matrix and 85% Absorption.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>26</td>
<td>6.403</td>
<td>7.057</td>
<td>0.705</td>
<td>0.718</td>
<td>Poor resolution</td>
<td>115</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>28</td>
<td>7.478</td>
<td>8.264</td>
<td>0.851</td>
<td>0.868</td>
<td>Poor resolution</td>
<td>170</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>29</td>
<td>8.047</td>
<td>8.905</td>
<td>0.929</td>
<td>0.949</td>
<td>Poor resolution</td>
<td>230</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>30</td>
<td>8.638</td>
<td>9.572</td>
<td>1.011</td>
<td>1.034</td>
<td>Na Kα</td>
<td>285</td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>33</td>
<td>10.543</td>
<td>11.726</td>
<td>1.282</td>
<td>1.317</td>
<td>Mg Kα</td>
<td>470</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>47</td>
<td>22.162</td>
<td>24.942</td>
<td>2.984</td>
<td>3.15</td>
<td>Rh L lines, K Kα, Cr Kα</td>
<td>3970</td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>50</td>
<td>25.271</td>
<td>18.486</td>
<td>3.443</td>
<td>3.662</td>
<td>K Kα and Kβ, Ca Kα and Kβ</td>
<td>5670</td>
<td></td>
</tr>
<tr>
<td>Au</td>
<td>79</td>
<td>68.803a</td>
<td>66.989a</td>
<td>9.713</td>
<td>11.442</td>
<td>Zn Kβ (for Au Lα)</td>
<td>360</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>82</td>
<td>74.969a</td>
<td>84.936a</td>
<td>10.551</td>
<td>12.613</td>
<td>As Kα (for Pb Lα)</td>
<td>470</td>
<td></td>
</tr>
</tbody>
</table>

aLines outside the detection range of the instrument.

The values in bold represent the X-ray emission lines used for elemental identification by our system.

Emission line energies follow Kortright and Thompson (2009).

The detailed maps of the metal inclusions (Figure 3a and b) reveal a more complicated picture. Sum spectra from the areas of the fragments (Figure 3c) as well as the detailed peak deconvolution for a selection of elements (Figure 3d and e) are provided to demonstrate that the elements discussed are actually present in the fragments. Regarding Fragment 1, Cu is present only in the central part whereas Ag is present throughout the fragment. This is a blend commonly found in Viking-age silver bullion, which was most often derived from medieval coins debased with copper, or Arabic dirhams, containing between 5% and 35% copper depending on the period of minting (Kilger, 2011: 268–270). A thin layer of Br is also observed on parts of the fragment’s surface. The presence of Br as a result of surface alteration has been noted on Viking-age artifacts before (Graham-Campbell, 2008) and can be explained by corrosion related to its burial environment (Hedges, 1976; Marchand et al., 2014). The nonhomogeneous elemental distribution of the inclusion reveals the need for 2D mapping and not just acquisition of point measurements. Even a significant amount of point measurements might not be able to reveal the exact spatial distribution of the different elements. Fragment 2 comprises Ag and a detectable amount of Au. The presence of Au is proved by the deconvolution of the spectral data (Figure 3b). Even though the Au Kα line overlaps with the Zn Kβ, the Au Lβ line is evident and well deconvoluted. For this reason, the Au data in Figure 3a correspond to a map of the Au Lβ line instead of the Lα. The presence or absence of minor elements, such as Au, Bi, or Pb, can also yield information about the coins’ (precise) provenance, as well as that of ingots and hacksilver (Kruse & Tate, 1992; Merkel et al., 2014).

From an archaeological perspective, the discovery of a silver fragment in its original context confirms the presence of a metal workshop at this particular location, as hypothesized by the geophysical study, and provides more information about the types of metals that were treated there. Most importantly, by using micromorphology the silver droplet can be considered in its relation with other metal hammerscale fragments (Fe) and fired clay in the same context, the latter likely derived from ovens or crucibles. This is significant as it suggests that similar magnetic anomalies on the site may also have been workshops where metals were treated. This would indicate that the spatial layout and use of the settlement during its younger phases (beginning in the late 9th century A.D.) differed significantly from previous phases, which in this area of the site contained large houses with mixed occupation/craft activity giving out onto the main street (Schultze, 2008).

CONCLUSIONS

We have successfully demonstrated that μXRF elemental mapping is a viable option for the qualitative examination of thin sections to determine the nature of metal fragments. This holds true even in the case of covered thin sections since a wide array of elements are detectable (Fe, Cu, Ag, Au, Pb in our case; potentially Sn; Zn if not present in the coverslip). This can prove a very useful approach since micromorphological/microscopic examination alone cannot determine the nature of such fragments, and the presence of a coverslip prevents other types of elemental analysis. Even this type of qualitative data enrich the archaeological interpretation on a micro-scale, and provide significant information that is not possible to detect by traditional microscopy techniques. Moreover, our contribution shows that the potential of this technique is not limited to the
The remainder of the resin-impregnated blocks from which thin sections were made, but extends to the thin sections themselves, even coverslipped ones. This not only makes elemental mapping faster, easier, and more accessible, it also opens up possibilities for the vast archives of existing archaeological thin sections containing metallurgical components that could not be studied in the past, either because the block was no longer available, or because they were coverslipped so that it was not possible to use other techniques. This allows for sites studied in the past to be easily re-examined using this non-destructive method on both coverslipped and uncoverslipped thin sections.

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Figure 3  (a) Composite elemental map for Fragment 1. (b) Composite elemental map for Fragment 2. (c) Spectral comparison of Fragments 1 and 2 (coverslip spectrum is used as reference). (d, e) Peak deconvolution for elements between Cu and Ag for Fragments 1 and 2, respectively. Spectral background is shown in gray, the measured spectrum in black and the peak areas in the color of the respective elements.

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REFERENCES


