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Deciphering a removed text on a 16th c. centrepiece: The benefits of using AGLAEMap and AXSIA to process PIXE maps

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Abstract

In the field of archaeometry, it is not uncommon to be presented with art objects that contain inscriptions, signatures and other writings that are nearly impossible to read. Scanned microbeam PIXE offers an attractive approach to attack this problem, but even then the distribution of characteristic X-rays of the element(s) used in these writings can remain illegible. We show in this paper that two methods were used to reveal the inscription: first the use of a GUPIXWin, TRAUPIXE and AGLAEMap software suite enables to make quantitative analysis of each pixel, to visualize the results and to select X-ray peaks that could enable to distinguish letters. Then, the Automated eXpert Spectral Image Analysis (AXSIA) program developed at Sandia, which analyzes the x-ray intensity vs. Energy and (X, Y) position “datacubes”, was used to factor the datacube into 1) principle component spectral shapes and 2) the weighting images of these components.

The specimen selected for this study was a silver plaque representing a scroll from the so-called “MerkelscheTafelaufsatz,” a centrepiece made by the Nuremberg goldsmith Wenzel Jamnitzer in 1549. X-ray radiography of the plaque shows lines of different silver thicknesses, meaning that a text has been removed. The PIXE analysis used a 3-MeV proton beam focused to 50µm and scanned across the sample on different areas of interest of several cm². This analysis showed major elements of Cu and Ag, and minor elements such as Pb, Au, Hg. X-ray intensity maps were then made by setting windows on the various x-ray peaks but the writing on the centrepiece was not revealed even if the map of Cu after data treatment at AGLAE enabled to distinguish some letters. The AXSIA program enabled to factor two main spectral shapes from the datacube that were quite similar and involved virtually all of the X-rays being generated. Nevertheless, small differences between these factors were observed for the Cu K X-rays, Pb, Bi and Au L X-rays. The plot of the factor with the highest Au signal gave also information on the shape of some letters. The comparison of the results obtained by the two methods shows that they both drastically improve the resolution and contrast of such writings and that each of the method can also bring different information on the composition and thus the techniques used for the writing.

Key-words: PIXE, mapping, silver, AGLAEMap, AXSIA, multivariate

1. Introduction

The so-called “MerkelscheTafelaufsatz” is a centrepiece made by the Nuremberg goldsmith Wenzel Jamnitzer in 1549. It is one of the most famous masterpieces in goldsmithing from the sixteenth century. The centrepiece (Figure 1) is approximately one meter tall, made entirely out of partially gilded silver, and well-known for its lifecasts, real plants and animals casted in silver. It undertook during the past two years a large conservation process at the metal conservation department of the Rijksmuseum Amsterdam.

During the process, a 9-cm silver plaque (Figure 2) fixed to the bottom of the centrepiece was investigated because a text scroll could be seen on it, albeit without text. Careful examination of the plaque shows that there might have been text present. Using raking light, horizontal ridges were visible on the surface at regular intervals, which might indicate the presence of characters. Retrieving this text could shed new light on the history of this piece.

The two most common techniques for leaving text on an object of metal at the time were etching or engraving. Any text was probably later removed by abrasion. Looking at other eight smaller plaques of the object, the most probable option was that the letters were etched rather than engraved. The procedure for etching a scene or a text in silver has been in use for centuries. The characters or the design that is meant to decorate the silver are scratched in a wax layer, or built up in wax. The scene is covered with an acid that will dissolve the silver alloy. When the desired depth is reached, the etchant is removed, and the silver is rinsed in clean water. The acid preferably removes the less-noble metal, leaving an enriched silver surface. In manuscripts from the sixteenth century and earlier, "strong water" is mentioned, which normally stands for nitric acid.

Different techniques, available at the Rijksmuseum, were employed to research the plaque. Raking light observation, X-ray radiography and XRF analyses were used showing that horizontal bands of different thickness and difference in copper/silver (Cu/Ag) were visible. These patterns could not be associated clearly with any writing.

PIXE has been extensively used for characterization of silver coins and is known to be sensitive to surface Ag enrichment [Weber 2000, Beck 2004, Beck 2008]. What turns to be a disadvantage for the quantification of bulk materials turned to be an asset for this study. The new scanning system installed at the AGLAE facility allows high-resolution mapping (down to 10µm pixel size) and has a good sensitivity for trace elements. It has already been successfully used for determining chemical composition of solders and inclusions in ancient Egypt gold [Lemasson 2015], for retrieving traces of the lost polychromy and gilding of the Neo-Assyrian ivories [Alberic 2014] or for characterizing the lapis lazuli from the Egyptian treasure [Calligaro 2015]. The system was used to get a qualitative and quantitative distribution of the constituents of the silver alloy on the surface of the plaque.

The dataset produced by the analysis has been processed by two different programs, the AGLAE software package (AGLAEMap, TrauPIXE) [Pichon 2015] and the AXSIA software that has already used for PIXE mapping processing [Doyle 2006]. The issue of this work is to compare the results obtained through these two data treatments.

2. Materials and methods

The imaging of the silver plaque has been done thanks to the PIXE elemental imaging capabilities of the AGLAE facility at the C2RMF [Pichon 2014]. The 3-MeV proton beam was focused to 50-µm on the target. The scanning system combining a vertical magnetic scan of the beam over 640 µm with a horizontal and vertical target translation allowed to quickly acquire elemental maps. The central area of the plaque was mapped on a 1.8x4.4 cm² area with a pixel size of 80 µm.

Four 50 mm² SDD X-ray detectors were used to produce PIXE spectra. Three of them were screened with 50 µm Al absorbers and are combined to create a single spectrum dedicated to the major and high-Z trace elements. One detector flushed with helium gas and protected from backscattered protons by a magnetic deflector is dedicated to measure low-Z elements.

With a beam intensity of 20 nA, the counting rates were 90-120 k counts/s total in the trace detectors and 10 k counts/s in the low energy detector for a total acquisition time up to 100 min. The whole scanning took approximately six hours for a total area of 4 x 4.4 cm². The charge was monitored by recording silicon X-rays emitted by the Si_3N_4 exit window with a dedicated SDD detector.

The raw data recorded in list mode was afterward converted into a datacube in ESRF Data Format (EDF). The comparison between the two data treatments was carried out on the most significant part of the plaque, i.e. the central area. In-house AGLAEMap program was used to visualize the distribution of major (Ag and Cu) and trace elements (Au, Bi, Hg, Pb and Fe) by defining region of interest (ROI) in spectra. Some areas were drawned and their corresponding PIXE spectra were extracted for further quantitative processing using TRAUPIXE [Pichon 2010], a home-made program based upon GUPIXWin engine [Campbell 2010]. This software also allowed calculating pixel by pixel the PIXE dataset to produce quantitative maps [Pichon 2015].

Then, the Automated eXpert Spectral Image Analysis (AXSIA) program developed at Sandia, which analyzes the x-ray intensity vs. Energy and (X,Y) position "datacubes", was used to factor the datacube into 1) principle component spectral shapes and 2) the weighting images of these components. Data were first converted in Matlab and scaled for non-uniform noise [Keenan 2004, Kotula 2003]. Factor analysis was performed to produce a spatially-simple representation of the data [Keenan 2009]. Inverse scaling for non-uniform noise was then performed.

3. Results

Data processing with AGLAE software package

The maps of the elemental distribution made by AGLAEMap show a pattern drawn by clear differences in the metal compositions, especially in the main alloy composition. The high-energy detectors enabled the exposure of several elements of the alloy such as Ag, Cu, Pb, Hg, Au, Bi and Fe on the overall spectrum. Not all of the elements seemed to follow the pattern (Figure 3).

It appeared that Cu, Ag and Au showed correlated pattern behaviour. These elements were present in different amounts in specific areas. Where the Ag counts were high, the Cu was relatively low, and the Au was relatively high. In the main time, Fe map tends to only show patterns that could be related to scrapping. The maps of the three other elements, Bi, Pb and Hg do not present well defined patterns.

Three different alloy compositions in the large plaque can be discriminated (Table 1). One corresponds to what can be called the background of the pattern, while a second corresponds to the supposed letters. A third alloy composition can be found in some areas of the background. Average compositions have been calculated by selecting large amount of pixels (over 1000) from the different areas and treating the corresponding spectra with GUPIXWin. The overall spectrum (the sum of all pixels) gave an average composition of the plaque. These compositions confirm that Au and Ag are linked, Hg also increase as the same time. They show also that Pb and Bi should present the same pattern as Cu since they decreased as the same time.

Quantitative maps of the major elements (Ag, Cu) were calculated with TrauPIXE and generated with homemade software called DataImaging. Quantitative map of Cu is shown in Figure 4. Nevertheless, statistics was not sufficient to give quantitative mappings of trace elements.

Data processing with AXSIA

Principle component spectral shapes exhibit several factors, some minor factor that are surface particles or localized impurities and two main factors. The two factors are composed by the X-Rays of all the elements detected in the plaque but are characterized, for a same amount of Ag, by, on one hand, higher content in Cu, Pb, Bi and in the other hand Au, Hg and maybe Fe enrichment (Figure 5).

The spatial representation of the distribution of the Au enriched factor (Figure 6) gives slightly the same results as the Cu map determined by AGLAEMap. The visualization of the remnants of the past inscription is clear and seems to show more details than the only representation of the region of interest.

4. Discussion and perspectives

The representation of the data either by AGLAEMap or AXSIA shows that there are areas in the plaque where there are differences in chemical composition and that these differences are drawing a pattern that can be related to letters. This is a simple case with only two main factors shown by AXSIA that corresponds to the two mains components of the silver alloy. Therefore, the overall picture of the remaining text is giving nearly identically by the two programs. For the AGLAE software package, better contrast was achieved with quantitative maps than with only ROI maps.

The Cu map enables the best visualization of the remnants of the past inscription induced by the differences in concentration within the plaque. This result was to be expected, since Ag and Cu are the major elements of the alloy, and Cu being the less-noble metal, would be the marker metal in terms of whether it had been etched away or not. The black lines where the Cu concentration is relatively low seem to form the outlines of letters. Horizontal zones with letters did show up clearly. Some letters could be identified, like an “a” and a “Q” (Figure 7). These letters are of the same font as the type used on the smaller plaques present on the centrepiece, as can be seen with the “Q” with its typical long tail.

These results make it very probable that the text could be from the same time period as Jamnitzer's and probably was even made by him or his workshop. Nevertheless, it was unexpected to see the outlines of letters instead of complete, full letters. One would expect the areas between the letters to be Cu-poor, and the areas under the filed away letters to be Cu-rich. A theory was developed to explain this phenomenon and was presented in a precedent article [Van Bennekom 2014] implying that the background has been evened out by abrasion living only the edges of letters to be Cu-poor.

Both approaches also gave complementary results on the manufacturing process of the plaque. First, the quantitative composition of the alloy achieved through AGLAEMap coupled with TrauPIXE is 11.7% of Cu for 87.8% of Ag in the main area of the plaque. In 1540, the Nuremburg City Council decreed that silverware needed a purity of fourteen lots, with a tolerance of one quint (i.e. 87.5% Ag and 12.5% Cu) [Timann 2007]. The silver alloy employed for the manufacturing matches the purity standards set by the Nuremburg City Council.

A correlation between two groups of elements can be brought out from the calculated average composition of silver appears and appears clearly with the principal component factors: on one hand, Cu, Pb and Bi and on the other hand Au, Hg and Ag. The written characters have lower contents in the Cu-linked elements. That is consistent with the hypothesis of an etched text.

These trace elements were also giving clue on the process used for etching. Mercury was found on the surface of the plaque with the PIXE analysis, but in very small quantities, and in all areas in similar concentration, a bit higher in the Cu-poor areas. In case of mercury Hg-based etching, one would expect Hg to be present in higher concentrations in the areas where the etchant was spilled which is the case. Still, Hg can also be a contaminant in silver, especially since it can consist of remelted and/or scrap silver, along with parts of gilded silver done via the fire-gilding method [Untracht 1982]. Etching with mercury would also have left higher amount of Hg. Etching with mercury was therefore found to be less likely and it is most probable than citric acid or nitric acid has been used.

These findings are very significant in the study of the Merkel centrepiece. Until now it was thought that the surface had been without text. This study made possible to understand the way the text was made and latter erased even if mystery upon the history of the object was not unveiled since the text is still unreadable. AXSIA showed the links between the different elements of the plaque (Ag/Au on one side and Cu/Bi/Pb on the other side) quite easily whereas with AGLAEMap, be it with ROI imaging or quantitative imaging, only the major elements and traces in a sufficient amount could be correlated to the writing because not enough statistics were available. Nevertheless, it allowed getting a quantitative alloy composition for the core alloy and the Cu-poor areas confirming the links between the elements seen with AXSIA.

These two programs appear to be complementary. AXSIA can give fast information even with low statistics to determine the areas of interest within the mapping while AGLAEMap allows going deeper in the data treatment, especially allowing quantification of the differences. This approach would be interesting to be tested on the data processing of more complex structures, for example to separate mineral phases in rocks. The multivariate analysis could also be performed on datacube containing other spectra, either from PIXE with different absorbing filters but also from other IBA techniques such as IBIL, RBS or PIGE.

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Figure 1: Merkel Centerpiece, 1549, Wenzel Jamnitzer, Rijksmuseum Amsterdam, BK-17040-A.

Figure 2: Plaque screwed to the backside of the foot of the centrepiece (9cm width).

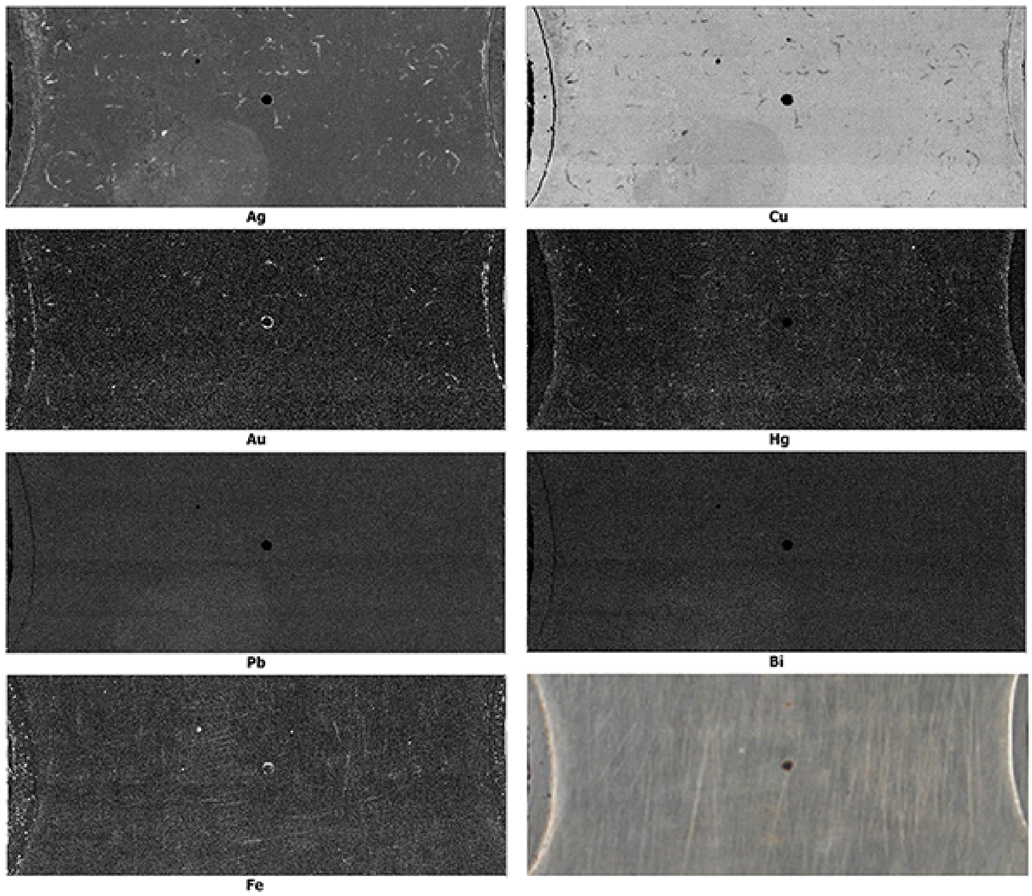

Figure 3: Elemental distribution in greyscale of Ag, Cu, Pb, Hg, Au, Bi and Fe on the central part of the plaque obtained by AGLAEMap (1.8x4.4 cm², pixel size 80x80 µm²).

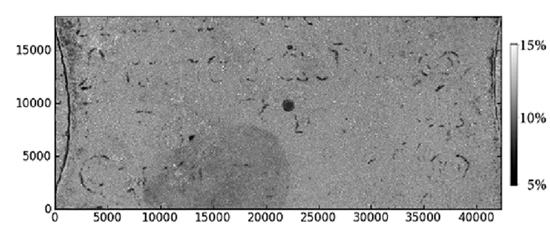

Figure 4: Quantitative mapping of Cu on the central part of the plaque obtained by TrauPIXE (1.8x4.4 cm², pixel size 80x80 µm²).

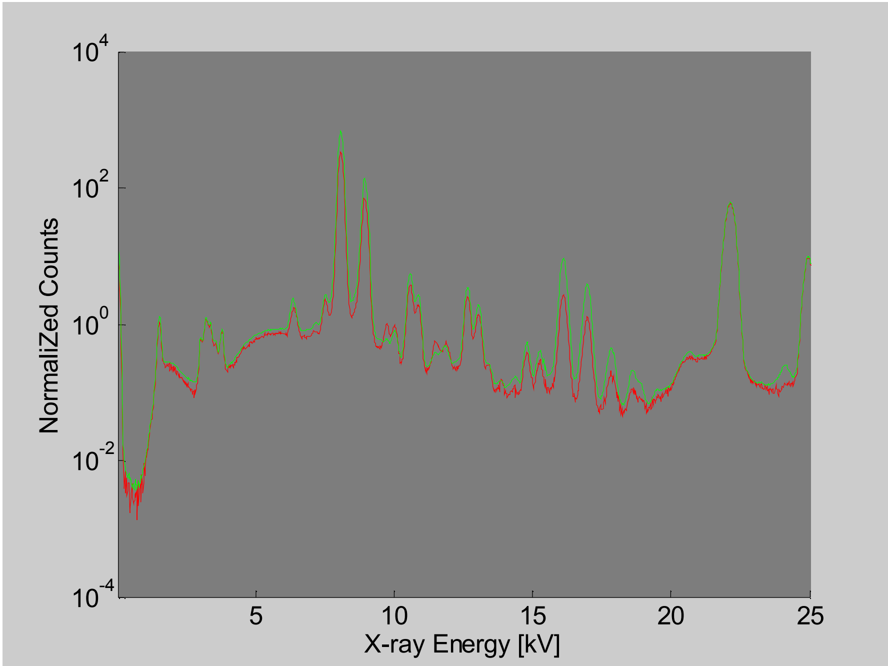

Figure 5: Main principle component spectral shapes factors calculated by AXSIA.

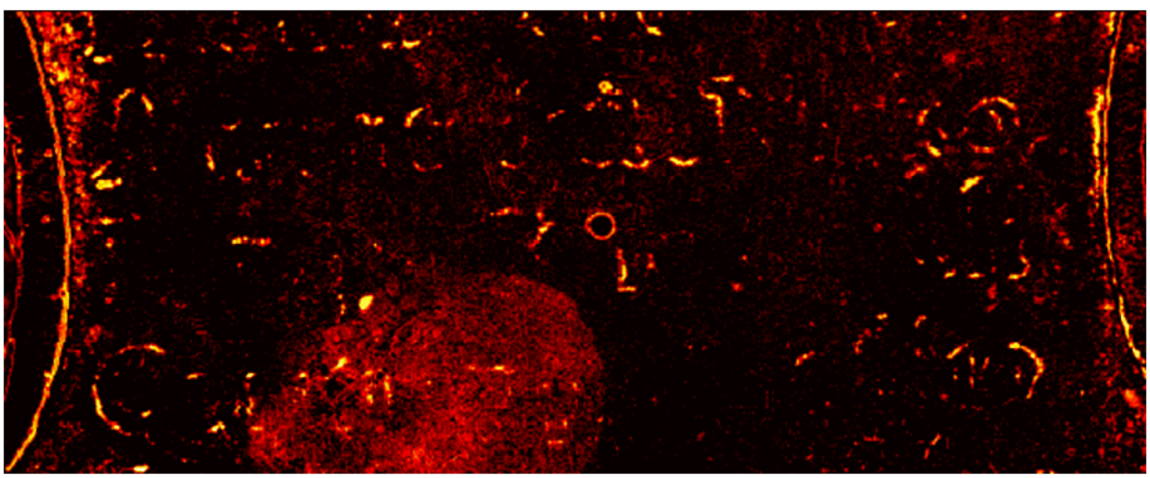

Figure 6: Weighting image of the Au-enriched factor.

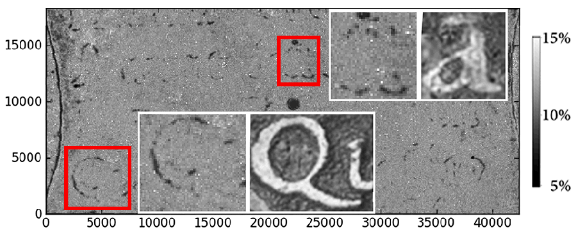

Figure 7: Particular pattern from the Cu mapping compared to some letters found on the smaller plaques of the centrepiece.

	Cu (%)	Ag (%)	Fe (ppm)	Au (ppm)	Hg (ppm)	Pb (ppm)	Bi (ppm)
Black area	9.6	89.7	130	260	390	3,900	1,900
Dark-gray area	10.4	89.1	90	140	360	4,600	2,300
Light-gray area	11.7	87.8	100	130	340	4,600	2,300
Average	11.5	87.7	80	140	380	4,800	2,400

Table 1: Alloy composition of the different areas seen in the mapping.

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