

IMPROVING DATA EXPLORATION METHODS FROM MACRO IMAGING TECHNIQUES: *IN SITU* SCANNING MACRO-XRF INVESTIGATION ON A MAJOLICA TILE TABLEAU

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Abstract

A state-of-the-art method for non-invasive visualization of subsurface layers present in works of art is for the first time employed to study an Antwerp majolica tile tableau manufactured in the mid of the 16th century. Scanning macro x-ray fluorescence mapping (MA-XRF), was used to determine the characteristic elements of the renaissance majolica production and the pigments that were used for the colourful painting present on the tableau. Furthermore, the interpretation of the ensuing elemental images, allowed to visualize earlier retouchings and to distinguish original tiles from pieces that were introduced during 19th and 20th century restoration campaigns.

Keywords

Ceramics, MA-XRF, Non-destructive analysis, Tiles.

Introduction

Since the 1980s, when conservation science started to become an internationally recognized discipline within the cultural heritage sector (Townsend, 2006), the analytical characterization of ceramic manufacture processes has been of wide interest (Tite, 2008; Rice, 1996). Therefore, in the last decades, numerous research projects were carried out in this field (Catapano, Affinito, Guerriero, Bisceglia, & Soldovieri, 2016; Bersani *et al.*, 2010).

The application of analytical techniques to the study of majolica artefacts and artworks has led to considerable progress in the knowledge of its production technology (Tite, 2009). Furthermore, these techniques allow us to distinguish between objects that may have a similar appearance, but that was made using different raw materials (Guirao, Pla, & Acosta, 2014). However, to obtain reliable stratigraphic information of majolica objects, invasive techniques are often employed (Alaimo *et al.*, 2004; Padeletti & Fermo, 2003; Pérez-Arantequi, Montull, Resano, & Ortega, 2009).

Instead, in the area of cultural heritage studies, there is a special need for *in situ* non-destructive and mobile techniques, since often ceramic artefacts and artworks cannot be moved (Van de Voorde *et al.*, 2014). The development and the use of such mobile devices are therefore fundamental in ceramic conservation science.

For the aforementioned reasons, in this work, the potential of MA-XRF imaging as a non-invasive tool to characterize flat ceramic objects is assessed through scanning experiments on a 16th century majolica tile tableau. This multi-coloured tableau (Figure 1), part of the MAS (Museum Aan de Stroom) “museum Vleeshuis” collection, Antwerp, Belgium, consists of 98 glazed tiles and depicts an animated biblical scene: “The Conversion of Saul”. The tableau is dated from 1547 and is believed to have been created in the studio of the famous Antwerp majolica maker Guido Andries (Guido di Savino), one of the Italian craftsmen who brought the majolica technique to Antwerp, transforming the city into an important centre for majolica art.

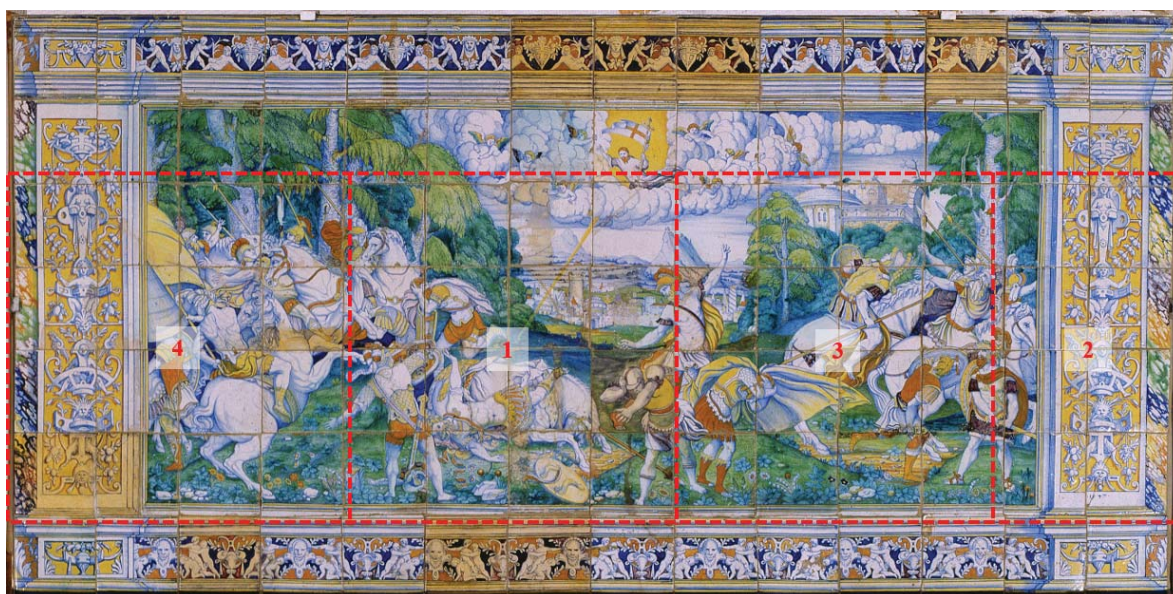


Figure 1 - Photograph of the Tile tableau of “Saul’s Conversion”,
Museum Aan de Stroom – MAS | *Collectie Vleeshuis*, Antwerp (Belgium).
The red shapes indicate the four scanned areas (see below).

During the last centuries, the majolica tile tableau, due to its poor conservation state, underwent different conservation treatments. Some tiles were missing, so the conservators chose to replace them with ones made by synthetic materials. Furthermore, the conservators implemented various other conservation processes aiming to restore the original appearance of the tile tableau (Caignie, 2015). Since the tableau was to be restored in 2016 prior to an international exhibition, a chemical investigation was thought essential in order to better understand what was done in the past and as documentation for the planned treatment.

The penetrative properties of the X-ray beam in combination with the element-specificity of the collected fluorescence signals are used to investigate the majolica tableau, to reveal its multi-layered build-up, to study the glazing techniques employed, and to document which pigments are present in the various coloured areas of the tiles.

In this paper, we also explore to what extent MA-XRF scanning, conducted prior to a full-scale conservation treatment, can help answering research questions such as authentic-

ty issues. Through elaboration and interpretation of the MA-XRF data, we investigate whether it is possible to objectively make a distinction between authentic and non-authentic tiles and to what extent is feasible to classify the tiles with doubtful authenticity.

Materials and Methods

The majolica tiles were fixed in a mortar bed which was supported by a brass frame. This stood on an Al U-profile that was supported by iron hooks (which were connected to other metal parts for wall mounting), as shown in Figure 2.

The scanner used is an advanced version of the instrument B described by Alfeld, Janssens, Dik, De Nolf, & Van der Snickt (2011). It consists of a measurement head mounted on a software-controlled X-Y motor stage with an ESP 301 3-Axis Motion Controller (Newport Corporation, Irvine, CA, USA) with a maximum travel range of 57 x 60 cm (h x v). The measurement head consists of a compact 10W Rh anode transmission tube (Moxtek, UT, USA) operated at 45 kV and 200 μ A and a Vortex EX-90 Silicon Drift Detector (SDD) with a 50 mm² active area (SII, Northridge, CA, USA) positioned close to the incident X-ray beam. The diameter of the diverging primary beam is reduced by means of a 0.8-mm lead pinhole collimator, yielding a beam size of ca. 1.2 mm at the surface of the majolica tile tableau.

MA-XRF scans were performed by sweeping the measuring head systematically over the tableau surface (Figure 2) (Da Silva *et al.*, 2017). Careful positioning and alignment of the

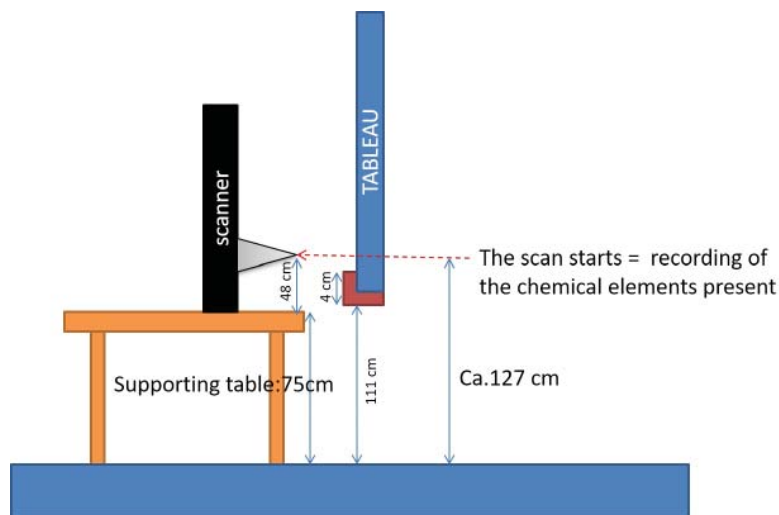


Figure 2 - a) Positioning of the MA-XRF scanner with respect to the tableau.

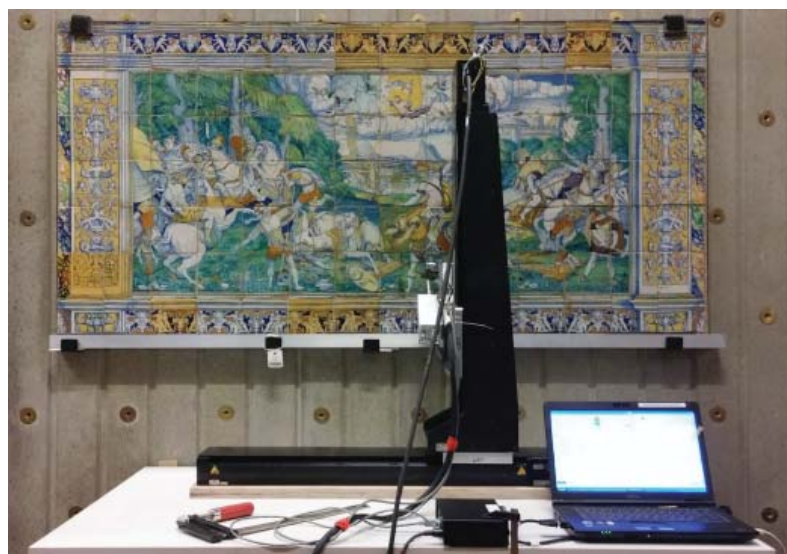


Figure 2 - b) MA-XRF analysis of the tile tableau "Saul's conversion".

scanner ensured a stable distance of ca.1.5 cm in between the snout and the tableau. The alignment was obtained by manually adjusting the distance between the X motor stage and the tableau surface while moving the measuring head along the X-axis. To do so, the position of the X-motor was adjusted, while the majolica tile tableau remained immobile. During the movement, XRF spectra were recorded every 700 μm (step size) with a dwell time of 350 ms (real time) for each spectrum, using a DXP-XMAP multi-channel analyser (XIA LLC, Hayward, CA, USA). The majolica tile tableau was not scanned in its entirety; instead four meaningful sections were chosen to be scanned one at the time in a total scanning time of 9 days. The acquired spectra were processed using PyMCA (Solé, Papillon, Cotte, Walter, & Susini, 2007) and the in-house developed Datamuncher software (Alfeld & Janssens, 2015). In all images shown in this document, a higher brightness indicates a stronger signal. For all images, the minimum and maximum intensity values were selected in order to enhance their readability and highlight the features being discussed.

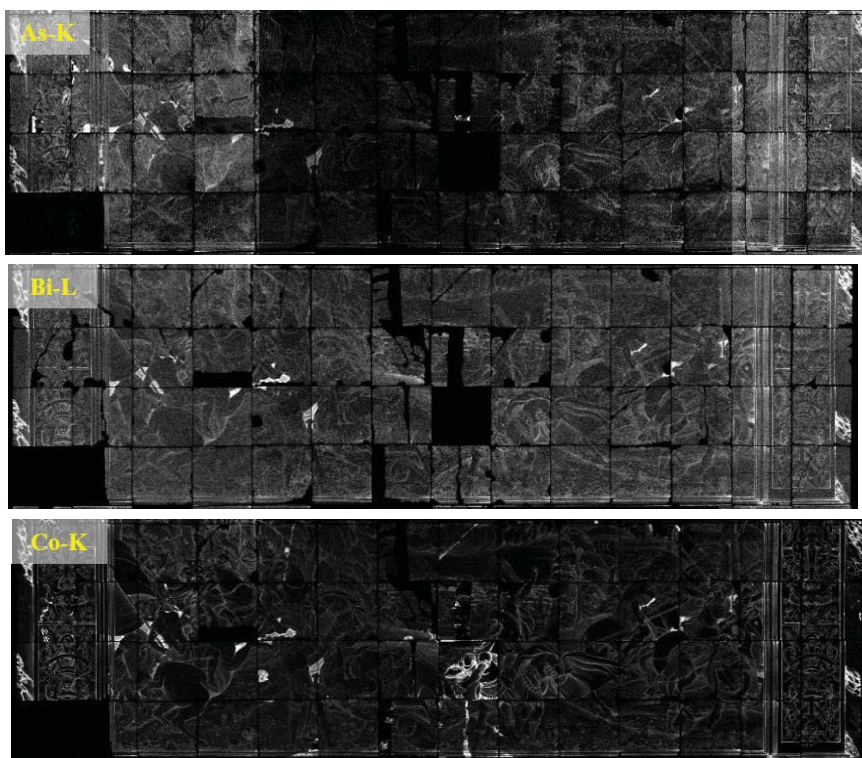
Results and Discussion

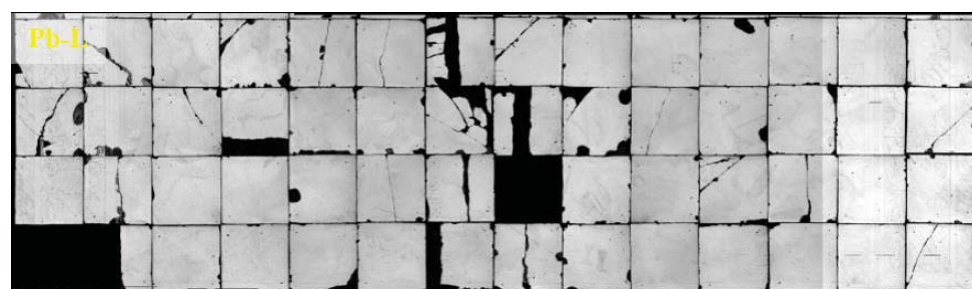
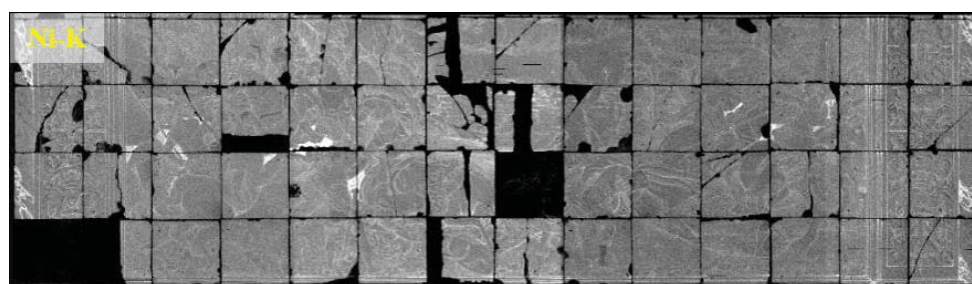
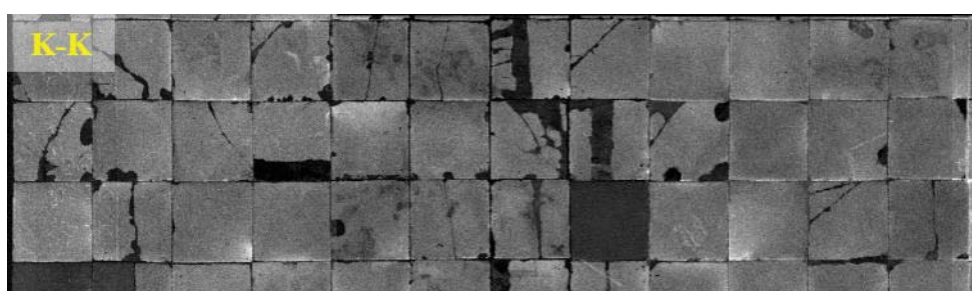
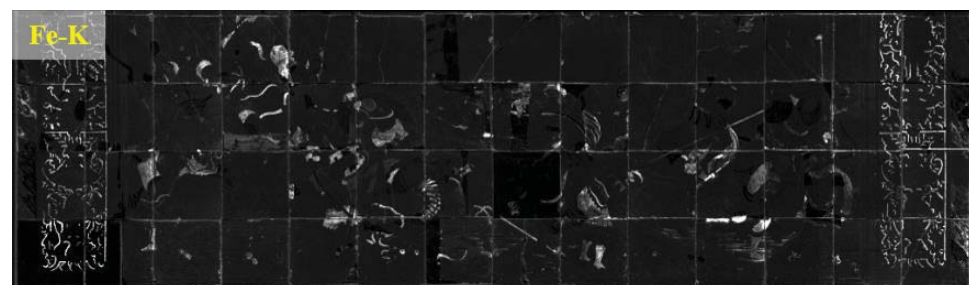
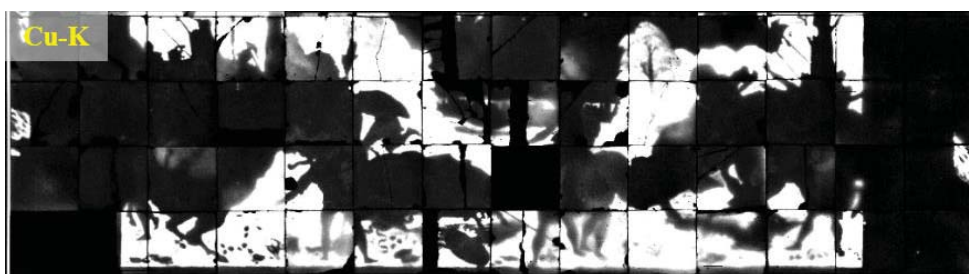
Original Areas

Figure 3 shows the stitched distribution maps that characterize the majolica tile tableau. The elements visible in the distribution images presented can be related to the different production stages of the tableau.

If we look at the distribution images of the elements K, Sn, Pb and Si, their presence is consistent with the typical glazed ceramics composition until the 19th century, consisting of (a) a ceramic biscuit and (b) a white glaze (Figure 4).

The white glaze contains lead and silicon as primary components (Tite *et al.*, 1998; Roldán, Coll, & Ferrero, 2006), which can be deduced from the relative uniform detection of lead over the tiles in the Pb-L map (local absorption to pigments not calculated).





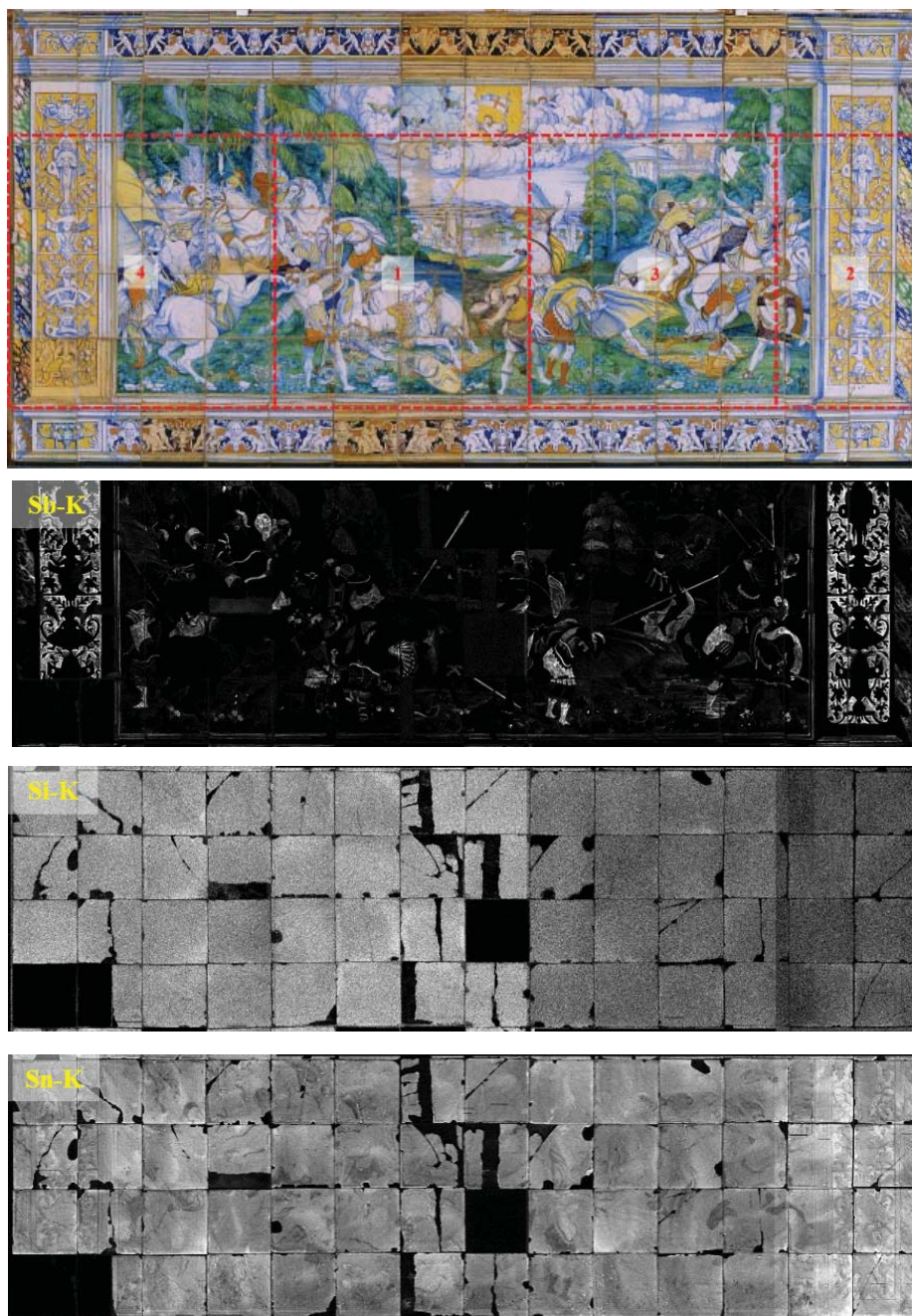


Figure 3 - Tile tableau of "Saul's Conversion", *Museum aan de Stroom – MAS | Collectie Vleeshuis*, Antwerp (Belgium). Photograph and elemental distribution images of K-K, Sn-K, Pb-L, Si-K, Sb-K, Fe-K, Mn-K, Co-K, Bi-L, Ni-K, As-K and Cu-K. The red shapes in the photograph indicate the four scanned areas. Data processed with in-house written software Datamuncher.

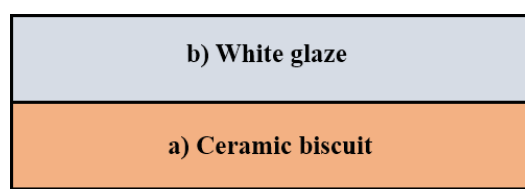


Figure 4 - Schematic of layering of typical glazed ceramics composition until the 19th century.

Furthermore, the lead distribution allows us to readily distinguish between original tiles (presence of lead; brighter tone) and inauthentic ones (where lead is not present; darker tone).

In the original Pb based glaze, tin was added to opacify it. In addition, the potassium map looks similar to the tin map, due to the presence of potassium dispersed in the glaze.

A final thin “coperta” of transparent glaze (Pb+Si+K) may have been sprinkled over the surface, as it was addressed by Mimoso (2012) in a paper on Flemish tiles.

The blue decorations are characterized by the presence of cobalt, suggesting the use of smalt (PbO-SiO₂-K₂O-CoO + associate elements). Although cobalt was only recognized as a separate chemical element in the 18th century, its use (in the form of compounds or ores) as pigment has been known for thousands of years. Even at low concentration levels, it produces a noticeable blue shade in enamel. As reported by Mimoso (2015), the concomitant presence of arsenic, nickel, bismuth and iron in the blue decorations is due to the fact that during the 16th century the blue pigment originated from the cobalt ores of the Erzgebirge, showing a characteristic association of Co, As, Ni and Fe. Eventually, it may also contain different amounts of bismuth, (Fares reports 2012), as in the case under examination, suggesting that the pigment was processed at a relatively low temperature. This correlation of elements agrees with the fact that the traditional chromophore used for ceramic pigments with a blue tint is the cobalt ion incorporated into different crystalline structures (silicate, aluminate, stannate, chromite, etc.) (Orecchio, 2013; Sendova, Kaiser, Scalerac, & Zhelyaskova, 2010).

From the elemental distribution images of antimony and iron in Figure 3, it is clear that they are elements characteristic for both the yellow and orange decorations. This evidence can be associated with the use of Naples Yellow (Pb₂Sb₂O₇) and iron oxides. The explanation is consistent with the introduction of the yellow lead antimonate pigment in the majolica palette from the first half of the 15th century onwards, and with the fact that many times it has been found mixed together with different amounts of iron oxides (Cartechini *et al.*, 2011; Chiarantini *et al.*, 2015).

The purplish brown decorations show the presence of manganese, indicating the use of manganese-rich minerals (e.g., MnO₂) (Schalm *et al.*, 2009). Manganese exists in various oxidation states and can incur in several colours. The tone of these colours in the decorations can be modified by the kiln atmosphere. In a non-reducing kiln conditions, the colour of manganese-containing glass is pink. If present from 5 to 10%, manganese produces shades of purplish brown (Karasu & Turan, 2002; Cultrone, Rodriguez-Navarro, Sebastian, Cazalla, & Jose De La Torre, 2001).

Black motifs are recognized and associated with mixtures of iron (Fe₂O₃, Fe₃O₄ etc.), cobalt (CoO) and manganese (e.g. MnO₂) oxides, as suggested by Coentro *et al.* (2012).

The green decorations appear to have been prepared on the basis of a copper-based pigment, for example, copper oxide (Padilla, Schalm, Janssens, Arrazcaeta, & Van Espen, 2005).

Earlier Retouchings

In order to gain further knowledge of the elements that characterize the earlier retouchings in the tableau, two different sub-areas, labelled as A and B, were investigated (Figure 5).

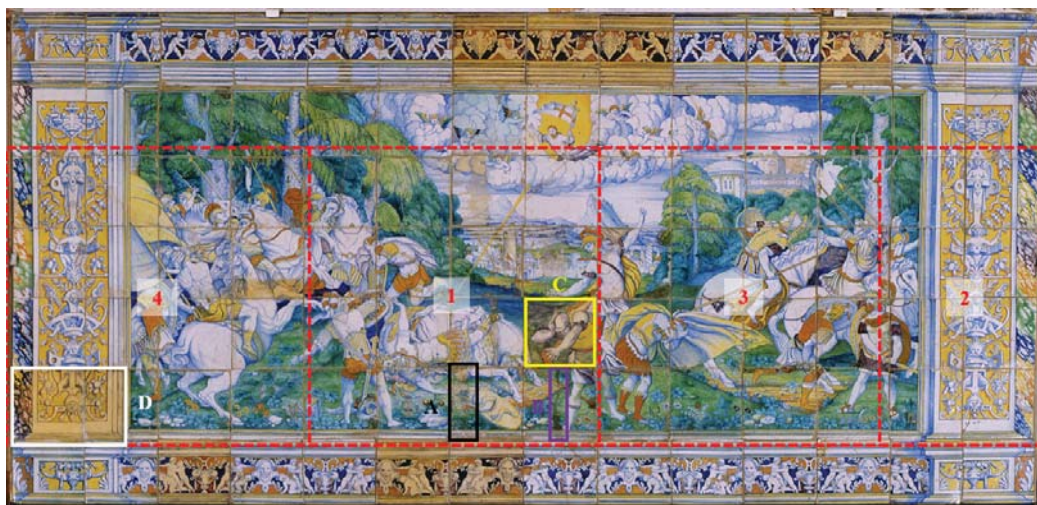


Figure 5 - Photograph of the Tile tableau of "Saul's Conversion", *Museum aan de Stroom* – MAS | *Collectie Vleeshuis*, Antwerp (Belgium). The red shapes indicate the four scanned areas, instead the black, purple, yellow and white rectangles indicate the areas A, B, C, D being discussed.

The most relevant elemental distribution images of areas A and B are discussed below. Although the elements are often correlated to colours that are not easily discernible due to the limited resolution of the detail photograph, it was possible to explore the complex mixtures used during past restoration treatments.

Sub-area A

Figure 6 shows the most relevant distribution images for the sub-area A marked with a black rectangle in Figure 5. This area was chosen because of its singular combination of elements.

The elemental distribution map of chromium shows its correlation to the green colour, suggesting the possible usage of green chromium oxide (Cr_2O_3). This was first synthesized in the 19th century and therefore the material in a chromium green area should be of recent date.

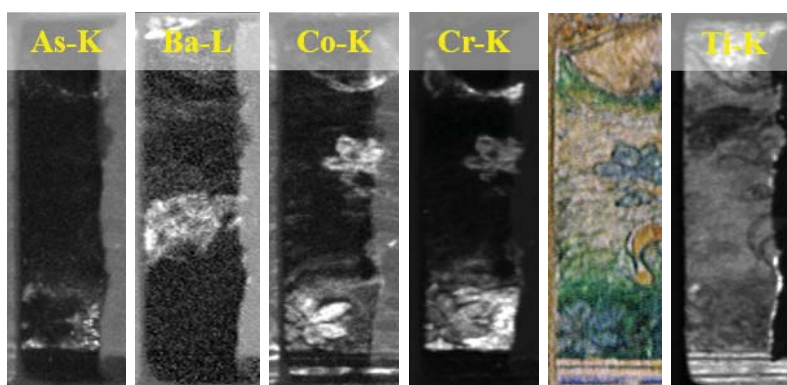


Figure 6 - Detail photograph and corresponding elemental distribution images of Co-K, Cr-K, As-K, Ba-L, and Ti-K of the area (A) indicated in Figure 5 marked with a black rectangle.

Data processed with in-house written software Datamuncher.

The presence of cobalt mainly in the two blue flowers suggests the use of a cobalt rich pigment with arsenic found as an associated element.

Titanium dioxide (TiO₂) is likely to have been used to obtain the desired pastel shades during the restorations, or as an opacifier. The deliberate use of TiO₂ indicates a decoration from at least the 20th century.

Barium, as suggested by Orecchio (2013), may have been used to obtain the desired hue during the retouching phase (e.g. blanc fixe aka permanent white, BaSO₄). The presence of barium confirms the hypothesized dating (20th century) for the retouchings present in sub-area A.

Sub-area B

Figure 7 shows the distribution images of Zn-K and Sr-K for the sub-area B marked with a purple rectangle in Figure 5.

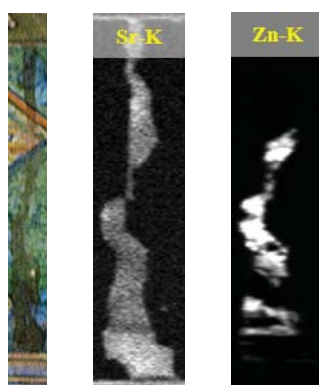


Figure 7 - Detail photograph and corresponding elemental distribution images of Zn-K and Sr-K of the area (B) indicated in Figure 5 marked with a purple rectangle.
Data processed with in-house written software Datamuncher.

Zinc Oxide might have been used during the retouching phase to obtain the desired hue as suggested by Orecchio (2013) and strontium is likely part of the filling material used during past restorations treatments.

Later Additions

During the restoration treatments carried out by KIK-IRPA (Royal Institute for Cultural Heritage, Brussels, Belgium) between 1960-1965, due to the poor conservation state, Caignie (2015) reports that some of the original tiles of the tableau were replaced by polyester replicas. In order to gain further knowledge of the elements that characterize the replicas present in the tableau, two different sub-areas labelled as C and D, were investigated (Figure 5).

The most relevant elemental distribution images of the areas C and D are discussed below. Since the tiles in the areas C and D are polyester replicas their elemental composition significantly differs from that of the original tiles. Furthermore, the replicas are discoloured due to aging and probably UV light effects. Discerning these tiles is therefore relatively easily (see Figure 3) and the contrast in the elemental distribution images presented below highlights this.

Sub-area C

Figure 8 shows the distribution images of Co-K, Fe-K, Cr-K and Ni-K for the sub-area C marked with a yellow rectangle in Figure 5.

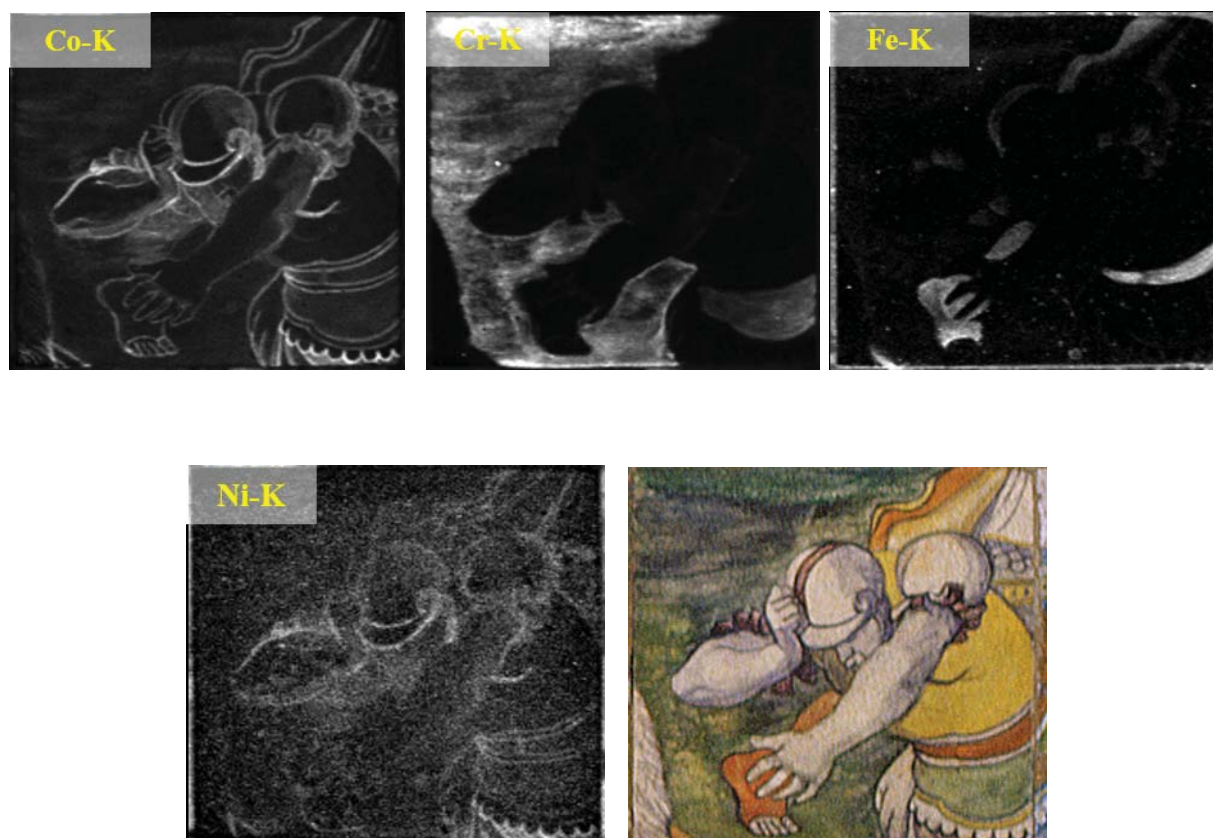


Figure 8 - Detail photograph and corresponding elemental distribution images of Co-K, Fe-K, Cr-K and Ni-K of the area (C) indicated in Figure 5 marked with a yellow rectangle. Data processed with in-house written software Datamuncher.

The cobalt distribution map suggests the presence of a blue based pigment with nickel found as an associate element.

The orange decorations present in the belt of the soldier, in the foot and leg on the back of the soldier and in the vest on the upper part of the soldier, are likely to be correlated with the use of mixtures containing different amounts of iron oxides (Fe_2O_3 , Fe_3O_4 etc.). It is worth noting that the orange decoration present in the vest on the upper part of the soldier has a lower amount of iron than the other orange decorations previously mentioned. The last assumption was confirmed by the ROI imaging tool in PyMCA. Two local sum XRF spectra were obtained representing the orange decoration in correspondence of the belt of the soldier (point A) and the orange decoration of the vest in the upper part of the soldier (point B), as shown in Figure 9.

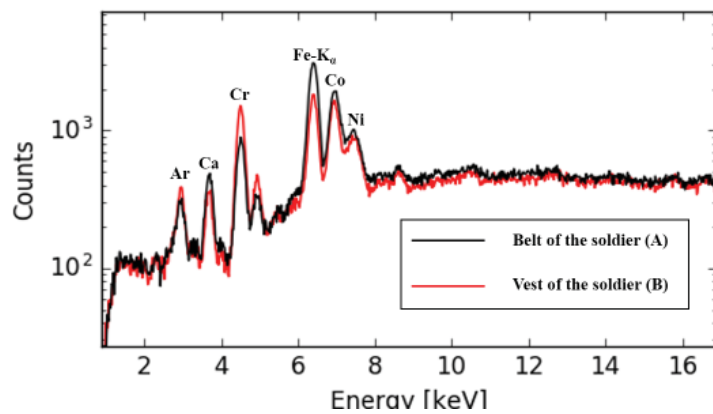
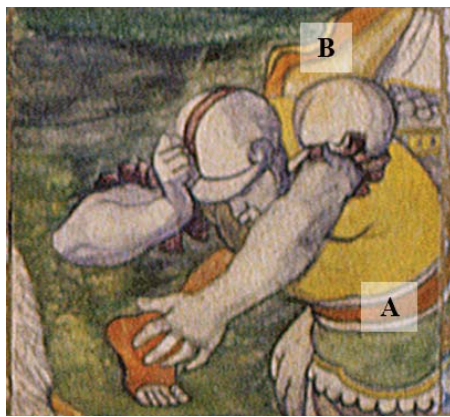


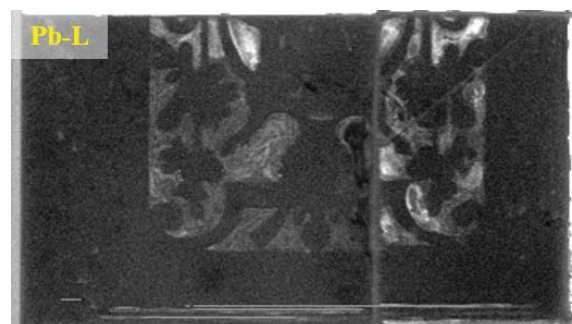
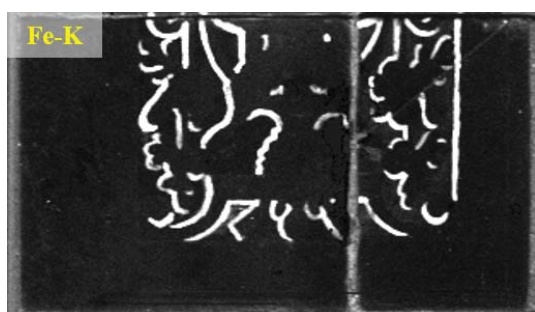
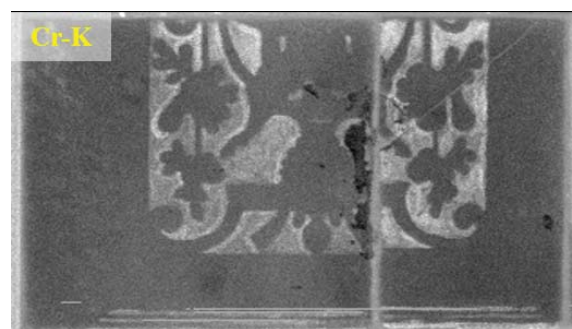
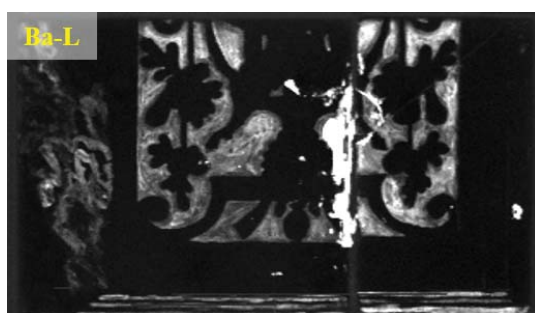
Figure 9 - Photograph of the area (C) indicated in Figure 5 marked with a yellow rectangle, together with the points (A) and (B) from where two local sum XRF spectra were obtained. The counts under the Fe-K α peak are clearly different between the two local sum spectra.

As we can objectively see, the net area below the Fe-K α peak is different between the two local sum spectra, confirming that a mixture poorer in iron oxides was likely employed for the orange decoration of the vest on the upper part of the soldier than for the belt.

The green decoration presents in the background of the scene is well correlated to the distribution map of chromium suggesting the possible usage of green chromium oxide (Cr $2O_3$).

Sub-area D

Figure 10 shows the most relevant distribution maps for the sub-area D marked with a white rectangle in Figure 5.



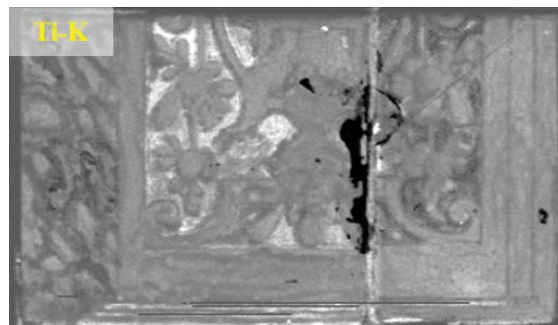


Figure 10 - Detail photograph and corresponding elemental distribution images of Fe-K, Cr-K, Ti-K, Ba-L and Pb-L of the area (D) indicated in Figure 5 marked with a white rectangle.
Data processed with in-house written software Datamuncher.

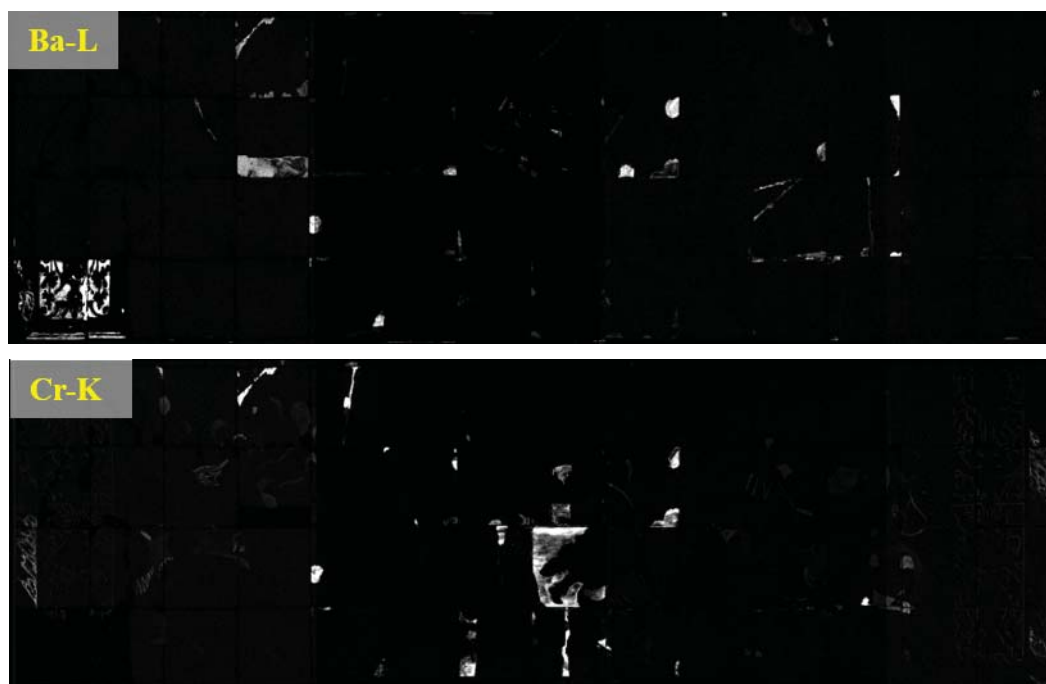
Titanium dioxide (TiO_2) appears to have been used to obtain the desired pastel shades during the restorations, or as an opacifier.

If we carefully look at the iron elemental distribution image, the presence of Fe is evident in the orange contours of the white motifs, probably present in the form of iron oxides (Fe_2O_3 , Fe_3O_4 etc.). In order to imitate the orange pattern of the authentic tiles, to some extent similar raw materials were employed.

However, also pigments clearly not present in the authentic tiles were employed. For example, chromium is present in the yellow pattern together with lead, strontium and barium suggesting the use of Chrome yellow (PbCrO_4), Strontium yellow (SrCrO_4) and Barium Chromate (BaCrO_4).

Stitched Distribution Maps of the Elements that Characterize the Restored Areas

In Figure 11 the overall presence on the tableau of the elements that characterize the non-authentic areas (earlier retouchings and later additions), is shown by means of the Ti-K, Zn-K, Ba-L, Cr-K and Sr-K distribution maps of the entire tableau.



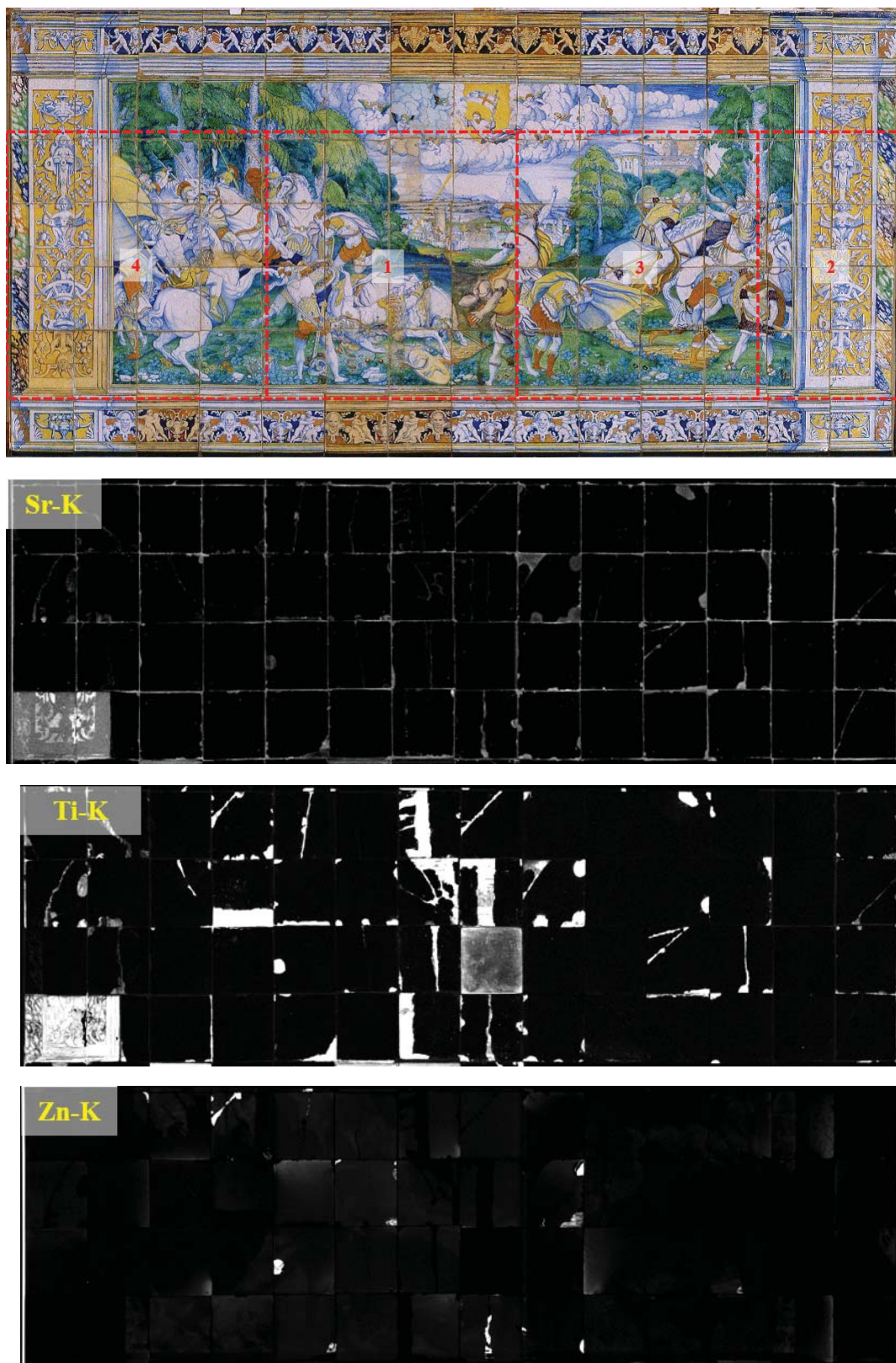


Figure 11 - Tile tableau of "Saul's Conversion", *Museum aan de Stroom – MAS | Collectie Vleeshuis*, Antwerp (Belgium). Photograph and elemental distribution images of Ti-K, Zn-K, Ba-L, Cr-K and Sr-K. The red shapes in the photograph indicate the four scanned areas. Data processed with in-house written software Datamuncher.

Conclusions

Majolica artefacts and artworks can be considered as precious parts of humanity's cultural heritage. Their investigation and preservation for coming generations is supported by scientific investigations.

In this project, a combination of Macroscopic X-ray Fluorescence (MA-XRF) scanning and data exploration methods have been used to study the 16th century Antwerp majolica production.

MA-XRF scanning proved to be highly useful in the study of these ceramic artefacts and artworks. By presenting compositional information from the entire (sub)surface decoration in a visual manner, the elemental distribution images could comprehend a large part of the materials used in the Antwerp Renaissance majolica and the pigments that were used for the colourful motifs present on the majolica tiles. Furthermore, by exploiting the functionalities of the software packages PyMCA and Datamuncher, it was possible to visualize the presence of earlier retouchings and to distinguish original tiles from nineteenth and twentieth century additions.

The use of MA-XRF allowed to identify the main components of the ceramic biscuit, the glaze and the pigments of the Antwerp majolica tiles.

The particular use of tin-opacified, high lead glazes in Antwerp Renaissance majolica is consistent with the technology being introduced from Italy by the Italian craftsman Guido Andries (Guido di Savino); in turn this technology originated from Islamic Spain or North Africa, with the archaeological evidence favouring Spain (Berti, 1995).

From the collected data, in general, we can deduce that most of the decorations associated with one colour had a similar elemental composition and that the different colours could be associated with different colouring elements. Enamelled decorations in Antwerp majolica tiles were varied in tones and chromatic effects, obtained with a limited number of elements such as cobalt, copper, iron, manganese and antimony.

The yellow and orange decorations are present on many analysed majolica tiles and can be identified as a mixture of iron oxides and Naples Yellow. Black motifs were recognized and associated with mixtures of iron, cobalt and manganese oxides. The purplish brown hues appear to have been prepared by different amounts of manganese oxides, aimed to obtain various tonalities. The green decorations, instead, may have been made using copper oxide as starting material. The blue decorations in all the Antwerp majolica tiles are characterized by the presence of cobalt, suggesting the use of smalt with different amounts of associate elements present.

The elements Ti, Zn, Ba, Cr and Sr prove the existence of non-authentic areas in the tableau, due to earlier retouchings and later additions.

From the last example is therefore clear that the elemental distribution images obtained by MA-XRF can provide additional information, helping in the discrimination between authentic and inauthentic tiles. This allows to support conservation treatments.

MA-XRF scanning is a novelty in the field of scientific investigations carried out on ceramic artefacts and artworks. As a matter of fact, chemical elements present in these type of Cul-

tural Heritage objects are most of the times determined locally and invasively. In the first case by investigating a number of locations in a non-destructive manner with a portable XRF instrument, in the second case by sampling the object and preparing a cross section through its stratigraphy for investigation with SEM-EDX. MA-XRF allows to gain insights on the distribution of an element over the entire surface of a ceramic artwork on the one hand, and for a faster investigation without the need to transport the ceramic artwork from the museum to a research facility on the other.

MA-XRF has two fundamental limitations: it only offers elemental, not molecular information and contrast and self-absorption effects can render the detection of light elements in covered layers challenging. Furthermore, the elemental distribution images obtained with MA-XRF are 2-dimensional projections with only limited depth information.

These limitations can be overcome by combining MA-XRF with complementary techniques. This is particularly important since only a multi-technique approach can give a complete description of complex materials.

For all these reasons we foresee the application of MA-XRF in future projects regarding high-profile ceramic objects, especially when a non-contact and non-invasive diagnostic technique is needed.

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Acknowledgments

This work is part of the joint Master thesis in Conservation Science (University of Bologna, University of Antwerp) of M. Colombo. Thesis supervisors were Prof. Dr. Rocco Mazzeo (University of Bologna) and Prof. Dr. Koen Janssens (University of Antwerp). M. Colombo was the recipient of a grant of the Flaminia Foundation (Ravenna, Italy).

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