Journal of Cultural Heritage xxx (2011) xxx–xxx

Available online at
SciVerse ScienceDirect
www.sciencedirect.com

Elsevier Masson France
EM|consulte
www.em-consulte.com/en

Case study

Diagnostic investigations and statistical validation of EDXRF mapping of the burial monument of Pope Sixtus IV by Antonio Pollaiolo (1493) in the Vatican

Giovanni E. Gigante [a], Stefano Ridolfi [b,*], Daniela Ferro [c]

[a] Dipartimento di Energetica, Sapienza Università di Rome, Via Scarpa 14, 00161 Rome, Italy
[b] Ars Mensurae, Rome, Italy, Via Comparini 101, 00188 Rome, Italy
[c] Istituto Materiali Nanostrutturati, CNR, Vecchio Edificio Chimica, P. le Aldo Moro 5, 00185 Rome, Italy

ARTICLE INFO

Article history:
Received 1st April 2010
Accepted 2 November 2011
Available online xxx

Keywords:
Metal degradation
Portable EDXRF systems
Conservation of metals
Multivariate statistical analysis

ABSTRACT

It has become a common practice to include diagnostics and archaeometric studies during a masterpiece restoration. The advantages and limits of this approach are now topic of discussion in the community of researchers that is growing up quickly. The bronze burial monument of Pope Sixtus IV (1471–84) by Antonio del Pollaiolo, now in the Treasure Museum in the Vatican was intended to be located at the center of a chapel, this explains its apparent asymmetry: lack of height and large base. The restoration of the burial monument started in May 2007, it was carried out by first fulfilling a series of non-invasive analyses using a transportable EDXRF to map the composition of the alloy and evaluate the diagnostic capabilities for deterioration processes of the bronze surface. As a consequence of the first non-invasive diagnostic campaign, a second campaign of micro invasive tests was planned and carried out. The samples were analysed with SEM-EDS and XRF techniques. In this article some of the results of the EDXRF tests will be shown together with the procedures set up to maximize the diagnostic information obtained and minimize the need of microsampling from the artefact. The results and the statistical analysis of data show that a straightforward planning of the measurements can give several, sometimes unexpected, results in the definition of the state of conservation of the monument and also from an archaeometric point of view. With a high amount of data, the use of statistical analysis is necessary, for example in our case, the analysis of the variance confirmed the hypothesis of the use of different alloys for the elements of the panels.

© 2011 Elsevier Masson SAS. All rights reserved.

1. Introduction

In the last decade, it has become common practice to carry out, during restoration, diagnostic exams with conservation finalities and/or archaeometric research. In this article, we discuss the results that can be obtained using a systematic planning of the measures and statistical data analysis. The sector of diagnostics in the Cultural Heritage area is growing up quickly with the development of many techniques and procedures that are now finding a established position in the restoration and maintenance of work of arts. The EDXRF is gaining reputation as a useful technique in the monitoring the state of conservation of metal artefacts, but it is not well established the possibility to detect and follow the degradation processes using non-invasive procedures. In this paper are shown the results it is possible to obtain through a mapping of the surface and a statistical validation of the results.

In the case of metal artefacts, the formation of surface patina is related to the composition and microstructural characteristics of the alloy [1,2]. Therefore, it is more strong the link between the production technologies used in the process and the degradation processes, and the restoration success of the cleaning operation [3]. There are of course other factors determining the deterioration of the surface of a metal artefact, relating to the surrounding environment [4], or the maintenance practices and therefore its ultimate state of conservation. It is not an easy task to determine which may be the main contribution in the degradation process and therefore the most important of them for the artefacts survival [3,5]. Thus, it is of paramount importance to define a minimum set of operations to be fulfilled when practising diagnostic analyses. In the characterisation of alloys and in the identification of the elemental composition of degraded surface the EDXRF technique played an important role for its intrinsic multi-elementary and non-destructive capabilities, together with the low detection limits in a large element range [6]. The *in field* operability added to EDXRF new possibilities that were exploited in the last two decades in the field of Cultural Heritage. The first attempts to use field portable (FP)-EDXRF were in the determination of the alloy composition and homogeneity [7]. It is

* Corresponding author. Tel.: +39 0 63 32 04 31.
E-mail addresses: giovanni.gigante@uniroma1.it (G.E. Gigante), stefano@arsmensurae.it (S. Ridolfi), daniela.ferro@ismn.cnr.it (D. Ferro).

1296-2074/$ – see front matter © 2011 Elsevier Masson SAS. All rights reserved.
doi:10.1016/j.culher.2011.11.003

not easy to determine alloy composition because of the presence of the superficial patina and of the complex microscopic structure. The microsampling technique avoids only in part the risk of contamination of the sample with the patina material. The use of a drill in order to remove the patina has become, when possible, a common practice. The analysis of superficial corrosion is also very interesting, mostly to identify the degradation processes but also to identify the external environment for a long time in contact with the artefact.

There is an increasing interest for the study of metal artefacts using several methods, which have been used successfully in archeometallurgical research [8,9]. With this in mind, we studied the magnificent work of Antonio del Pollaiolo: the burial monument of Pope Sixtus IV della Rovere. This monument belongs to a historical period in which the working of metals, often using techniques borrowed from goldsmiths, more evolved and in use for longer period, has seen a rapid evolution.

A more detailed study of an artefact made in a metal alloy which historically represents an important turning point in the history of art is therefore of considerable significance; analysing how it was produced allows us to evaluate to what extent technologies were evolved at the time.

The work, which was originally placed in the Choir Chapel in the Constantine Basilica of San Peter's in the Vatican, is now in the Treasure Museum of the Vatican. The masterpiece was commissioned by the Cardinal Giuliano della Rovere, nephew of Pope Sixtus, and later pope Giulio II.

The work was created between 1484, the year in which the Pope died, and 1493, the date inscribed on the monument together with the artist's signature.

The monument is composed of several pieces melted with a lost wax casting technique. At the base there are ten large panels, forming the basement of a cut pyramid, decorated with acanthus leaves and female images personifying the seven traditional liberal arts to which three new disciplines are added: prospective, philosophy and theology. The upper part is completely dominated by the figure of the Pope laying down and surrounded by the personifications of the seven virtues (Fig. 1); the three theological virtues surround the head of the Pope, with charitable love taking the place of honour while the sides of the figure show the four cardinal virtues. By the feet, a large bronze epigraph in Latin describes the life of the Pope emphasizing his profound knowledge of doctrine, his reputation as a man of culture and patron of the arts.

The monument of Sixtus IV has been undergoing restoration since April 2007. The restoration work has been organised in two distinct lots: the first one contains the ten allegories of the arts and the great acanthus leaves, which surround them; the figure of the Pope and the seven virtues are in the second lot.

2. Materials and methods

2.1. Experimental techniques

The results shown in this paper were obtained with different techniques such as Energy Dispersive X-ray Spectrometry (EDS) and Scanning Electron Microscopy (SEM) with microanalysis.

An portable EDXRF system was assembled using an air-cooled X-ray tube with an active spot of 1.5 mm, working with 38 kV high voltage and 0.2 mA current together with a Peltier cooled SDD (Silicon Drift Detector) detector with an energy resolution of 150 eV at 5.9 keV. A photo of the system at work on the monument is shown in Fig. 2 [10].

Fig. 1. The burial monument of Pope Sixtus IV with the ten large panels of the allegories.

The EDXRF investigations were carried out in two different ways:

- after sponge cleaning with a 20 kV HV tube sufficient to reveal some light elements (S, Cl, Ca, K);
- scratching away a 2 mm diameter of patina, in order to analyse the inside alloy, and with a 38 kV HV tube allowing the detection of tin and antimony.

In the first case, the acquired spectra peaks on the surface, with a low HV, were processed calculating the net area of the most intense peaks of the following elements: S, Cl, Ar, K, Ca, Mn, Fe, Cu. The

Fig. 2. The portable EDXRF equipment in operation during the measurement on the monument in restoration; detail of the probe and operator at work.

Please cite this article in press as: G.E. Gigante, et al., Diagnostic investigations and statistical validation of EDXRF mapping of the burial monument of Pope Sixtus IV by Antonio Pollaiolo (1493) in the Vatican, Journal of Cultural Heritage (2011), doi:10.1016/j.culher.2011.11.003

counts were normalized with the copper peak in order to eliminate, in part, the variability due to the geometrical efficiency and instability of excitation source.

In the second case, the quantitative analysis were obtained using a standard fundamental parameter method using calibration reference samples[7].

For the SEM microanalysis was used a LEO 1450 VP, operating at 20 kV with a variable pressure (65 Pa), and a INCA 300 for the EDS. The samples were observed in back-scattered electrons mode to reveal differences in composition from the grey levels. The microareas of homogenous composition were selected manually to carry out the microanalysis.

2.2. Sampling procedures

The core of the diagnostic procedure to study an ancient metal artefact is the definition of the sampling plan. We tested, in this work, several concepts we put together in the recent years of work on big outdoor and indoor metal artefacts [11]. The finalities in the sampling of the surface were:

- look for correlations of low Z elements and visual alterations, due to surface processes;
- detect the presence of superficial layers;
- evaluate the depth of penetration of the transformation processes;
- study the inner alloy with the aim to correlate the composition to the technology of production, homogeneity obtained in the casting and difference between pieces belonging to the same artefact.

In the planning of the sampling, it had to be taken into account the time needed in order to perform a single measure and the schedule of the restoration in which it is necessary to include the diagnostic procedures.

2.2.1. Sampling of the surface

To perform a effective sampling of the surface of the statue it is a helpful method to start from as visual inspection looking for points in which the typology of alterations look similar. In order to do so, we asked the help of restores and museum curators. For a satisfactory sampling of all panels and visible alterations it was necessary to scheduled 111 measures. The identification of the points was performed in a way in which the colours, in the first case, can be used to classify the detected typologies. For each point, together with a picture of the sampled area and the XRF spectrum, it was added a short text describing the surface morphology.

The execution of the whole program of measures required more than three day of work of a small group of researchers. The equipment was recalibrated several times during the day and its stability was systematically verified. On the panels 2, 3 and 4 nine additional measurements were done, after several consecutive cleaning, in order to verify the depth and total removal of sulphur and chlorine to help the restoration activity.

Finally, with the EDS, were analysed fragments of metals accidentally detached from the panels.

2.2.2. Sampling of the alloys

The number of the points sampled to analyse the alloy composition was necessarily small. The measurements were performed after a careful scratching of the patina in a small area of about 2 mm of diameter, using mechanical tools. Same measurements were carried out before and after the patina removal. The choice of the point was done to minimise the visible damage.

With a visual inspection, it was easy to find out that each panel was constructed using different pieces (a typical goldsmith technique); the background of the panels are surrounded by acanthus leaves and on the base of them there are decoration obtained with thin foils of bronze. In order to do a satisfactory sampling, it was established to sample each of the different pieces (background, foils and leaves). To fulfil quantitative analyses 33 measures were performed, from two to four measures for each panel.

Fig. 3. Photo documentation of the position of the analysed spots.

The position of the measuring points was documented by pictures with the clear indication of the position of the point (Fig. 3).

3. Results and discussion

3.1. The state of the surface

The systematic low energy EDXRF mapping allowed us to determine that potassium, calcium, manganese and iron are elements involved in a surface treatment. In fact, the very good correlation between such elements in all panels point out as these elements were used together. In Fig. 4 is shown the scatter plot of calcium with potassium and iron, it can be observed that the correlations are very good (0.97 and 0.98 respectively).

A plausible hypothesis is a generalized surface treatment with waxes coloured with pigments, perhaps earths, containing iron oxides and/or manganese that can produce the very characteristic dark black colour. In addition the EDS analysis on a small fragment show that phosphorous and calcium are in stoichiometric ratios suggesting the presence of calcium phosphate (Fig. 5). Some NMR measurements on residues of cleaning confirmed the use of wax.

This practice was very common in the past but also in nineteen century, it is not possible to determine when this treatment was applied. It is plausible to suppose that it was carried out when the first signs of surface alterations became apparent, in order to make uniform the surface colour. During the last documented restoration in the seventies of the 20th century, the surface was covered with a thick wax layer removed in the first steps of restoration, before our measurements.

The possibility to have large number of sampled points suggests the idea to verify if the differences in the chlorine and sulphur counts (directly correlated to their surface concentration) can be significant. This could open the way to the use a EDXRF mapping in the detection and verification of the different surface processes.

Please cite this article in press as: G.E. Gigante, et al., Diagnostic investigations and statistical validation of EDXRF mapping of the burial monument of Pope Sixtus IV by Antonio Pollaiolo (1493) in the Vatican, Journal of Cultural Heritage (2011), doi:10.1016/j.culher.2011.11.003

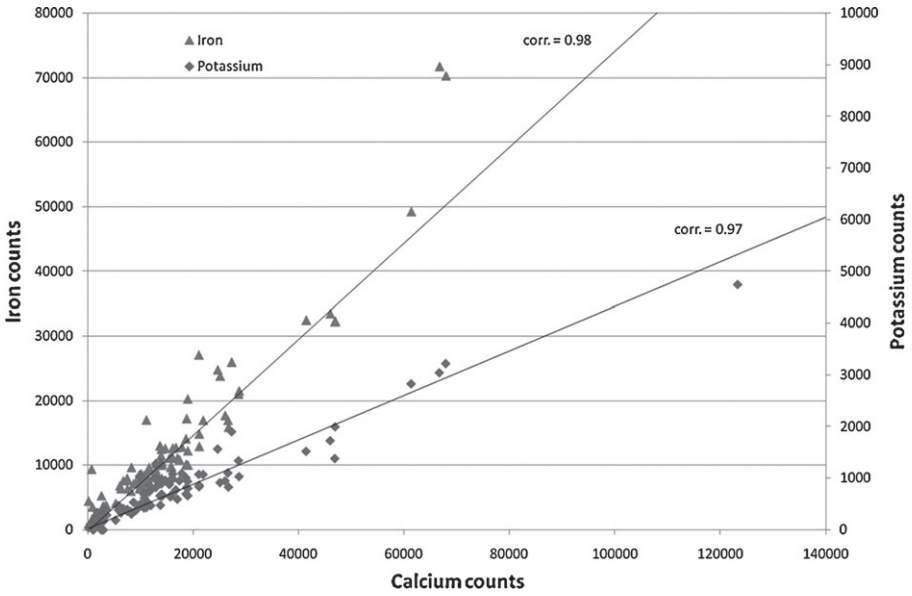

Fig. 4. Scatter plot of normalized counts of calcium, potassium and iron K_α lines. In the figure are shown the results of the calculation of correlation.

A careful study of the surface of the nine panels showed several typologies of alteration characterised also by a visible change of colour. Therefore, we synthetically classified these detected typologies through their colour:

- Green (32);
- Black (16);
- Grey (12);
- Yellow (15);
- White (10).

In parenthesis are indicated the number of sampled point for each typology. The chlorine and sulphur are involved in many degradation processes of copper alloys although those elements can also be included in many artificial patination formulations, as reported in the literature [1,2]. Their presence in a metropolitan outdoor environment, due to marine (chlorine) and urban/industrial (sulphur) atmospheres, is practically out of doubt [12], it is not so sure in a restricted area. In our case, the conservative history of artefact is very complex, also in a recent period before its transfer to the Treasure Museum in the Vatican Basilica. The basilica from the beginning can be regarded as an open space because of the continuous exchange of air between the interior and the outside due to the incessant flux of a huge amount of people with contaminated cloths through the constant open doors of the basilica itself. Another element to be taken into account is the continuous maintenance of artefacts performed with not scientifically based technique, with cleaning products. The low correlation between chlorine and sulphur demonstrated they are not uniformly distributed in the surface, therefore we put the focus on the fact that these two elements could be possible indicators of degradation process [13,14]. In Table 1 are shown the calculated mean values, and their standard deviations (s.d.), of sulphur and chlorine normalised counts for each visually detected typology. The results of one way analysis of variance (between the five degradation typologies) in the case of chlorine led to a value of F of 43 with 84 degrees of freedoms, that is very significant (Fig. 6). Also in the case of sulphur the differences were significant with a F value of 2.57 and a $P < 0.05$. Thus, it is possible to use a surface sampling, driven by a careful observation of degradation typologies, to detect significant changes of chlorine and sulphur in the analysed spots.

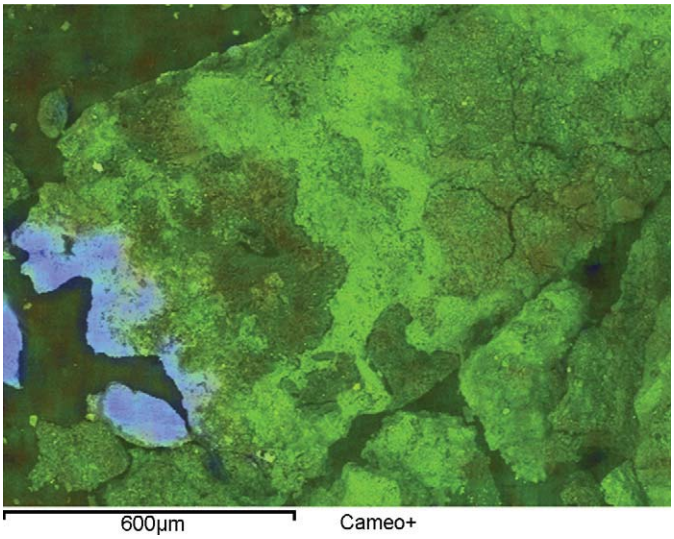

Fig. 5. An image in false colours of elemental mapping with EDS of copper (blue); chlorine, (green) phosphorous (red) on a sliver.

In Fig. 6, the normalized counts in the chlorine peak were plotted for the five typologies of degradation. The most evident changes are in the green areas with the maximum for chlorine and the lowest values for calcium and iron. These areas are probably affected by a severe deterioration with the complete depletion of the superficial wax layer. The involvement of chlorine in the deterioration of the surface is witnessed also by the large number of green areas in which the selective action of this element is evident. The origin of such element in a indoor environment is matter for more accurate investigations, but a possibility is its presence in some product used in the past for treatment of the surface (as, for example, the wax itself) or for cleaning.

The sulphur in the detected alteration typologies has a less evident behaviour but is extremely significant that it increases, firstly, in the black area and, secondly, in the white areas with the strong

Please cite this article in press as: G.E. Gigante, et al., Diagnostic investigations and statistical validation of EDXRF mapping of the burial monument of Pope Sixtus IV by Antonio Pollaiolo (1493) in the Vatican, Journal of Cultural Heritage (2011), doi:10.1016/j.culher.2011.11.003

Table 1
Statistical analysis on the set of points synthetically grouped based on colour.

Points	S	Cl	K	Ca	Mn	Fe
Green	96 ± 10	1160 ± 71	543 ± 51	10113 ± 1016	293 ± 27	8241 ± 774
Black	177 ± 17	410 ± 45	860 ± 100	15333 ± 2342	307 ± 47	11234 ± 1749
Gray	129 ± 23	363 ± 52	896 ± 90	19897 ± 2502	423 ± 43	14587 ± 2014
Yellow	153 ± 26	232 ± 52	1153 ± 141	26048 ± 2924	634 ± 121	20595 ± 1978
White	216 ± 82	232 ± 46	1636 ± 988	52580 ± 31941	676 ± 384	31565 ± 19756
All points	227 ± 56	641 ± 44	1777 ± 557	40774 ± 12553	979 ± 331	30009 ± 9563

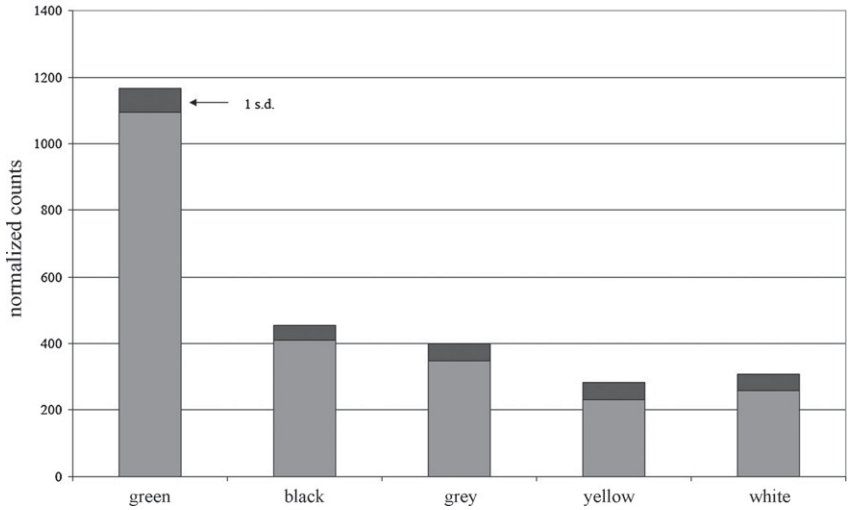

Fig. 6. Normalized counts in the chlorine peak for the five colours of surface patina.

increment of calcium counts supporting the hypothesis of the formation of gypsum.

Finally in Fig. 7, the slight and simultaneous increment of the counts of the three elements involved in the superficial treatment shows as the thickness of the artificial patina depletes in correspondence to the areas rich in chlorine.

Some control areas were analysed by EDXRF before, during and after restoration cleaning. The presence of chlorine and sulphur was deeply reduced after the cleaning operations therefore confirming the superficial presence of these elements.

3.2. The archeaometric characterization of the alloy

The quantitative analysis on the areas where the patina has been removed lead to the determination of the core bronze alloy composition. Table 2 shows the results of the quantitative analysis on 33 areas of the panels. It is useful to underline that the panels were probably produced in successive phases and welded together at the end of the process.

In the Table 3, the mean compositions and the standard deviations for the three typologies of element and for all the analysed

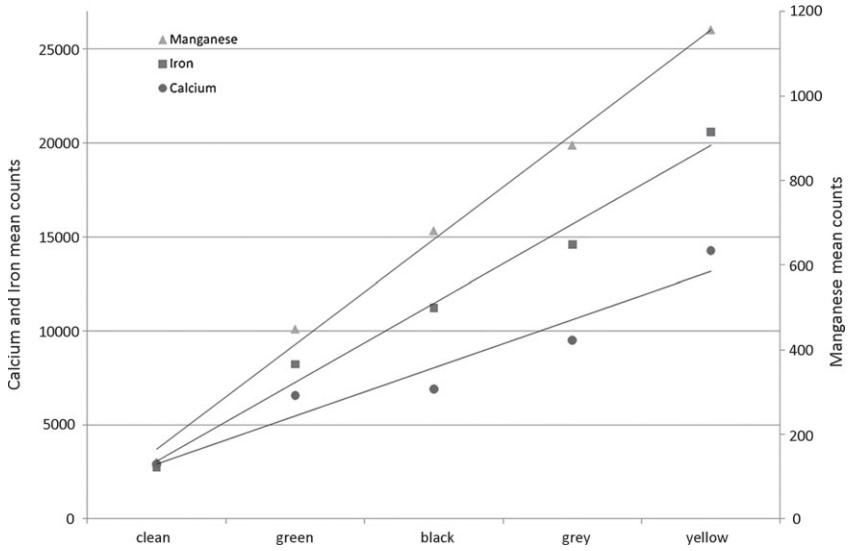

Fig. 7. Plot of the mean counts of calcium, manganese and iron K_α lines versus the visual colour of the analysed spot.

Please cite this article in press as: G.E. Gigante, et al., Diagnostic investigations and statistical validation of EDXRF mapping of the burial monument of Pope Sixtus IV by Antonio Pollaiolo (1493) in the Vatican, Journal of Cultural Heritage (2011), doi:10.1016/j.culher.2011.11.003

Table 2
Results of quantitative analysis done on the panels (in %).

		Cu	Sn	Pb	Ag	Sb	Fe	Ni	Zn	As
Panel 1	foil	86.7	9.1	2.4	0.1	1.4	0.3	N/D	N/D	N/D
	body	85.9	11.7	2.3	0.1	N/D	N/D	N/D	N/D	N/D
	leaf	88.0	9.4	2.5	0.1	N/D	N/D	N/D	N/D	N/D
Panel 2	leaf	87.7	8.7	2.7	0.1	0.2	0.5	N/D	N/D	N/D
	foil	82.2	13.1	1.9	0.1	2.3	0.4	N/D	N/D	N/D
	foil	83.5	3.0	3.2	0.1	N/D	0.4	3.3	6.4	N/D
	body	86.0	11.5	2.5	N/D	N/D	N/D	N/D	N/D	N/D
Panel 3	leaf	86.4	9.9	2.5	0.1	0.6	0.4	N/D	N/D	N/D
	foil	80.9	13.0	2.8	0.1	3.2	N/D	N/D	N/D	N/D
	body	86.8	9.9	2.2	0.1	0.9	N/D	N/D	N/D	N/D
	body	87.7	9.2	2.4	N/D	0.7	N/D	N/D	N/D	N/D
Panel 4	leaf	88.4	8.7	2.6	0.2	0.1	N/D	N/D	N/D	N/D
	foil	79.0	13.9	2.6	0.1	3.9	0.4	N/D	N/D	N/D
	body	84.1	11.5	2.8	0.1	1.5	N/D	N/D	N/D	N/D
Panel 5	foil	84.6	10.1	1.6	0.1	3.3	N/D	N/D	N/D	0.3
	body	81.0	14.3	2.4	0.1	1.7	0.4	N/D	N/D	N/D
Panel 6	leaf	87.9	5.9	4.1	0.1	1.9	N/D	N/D	N/D	N/D
	foil	87.5	8.0	1.5	0.1	2.5	N/D	N/D	N/D	0.5
	body	90.2	7.9	1.8	N/D	0.1	N/D	N/D	N/D	N/D
	leaf	89.5	7.5	2.7	0.2	0.1	N/D	N/D	N/D	N/D
Panel 7	foil	86.4	8.5	2.3	0.1	2.6	N/D	N/D	N/D	N/D
	body	87.8	9.9	2.3	N/D	N/D	N/D	N/D	N/D	N/D
	leaf	90.9	6.6	2.3	0.2	N/D	N/D	N/D	N/D	N/D
Panel 8	foil	86.4	9.0	2.5	0.1	2.1	N/D	N/D	N/D	N/D
	body	88.1	9.8	2.0	0.1	N/D	N/D	N/D	N/D	N/D
Panel 9	leaf	89.3	8.3	2.2	0.2	N/D	N/D	N/D	N/D	N/D
	foil	87.9	8.5	2.3	0.1	1.2	N/D	N/D	N/D	N/D
	leaf	87.0	7.8	3.2	0.1	1.4	0.5	N/D	N/D	N/D
	body	86.6	9.3	2.5	0.2	1.1	0.3	N/D	N/D	N/D
	body	89.0	8.2	1.7	0.1	1.0	N/D	N/D	N/D	N/D
Panel 10	foil	86.4	8.5	4.0	0.1	0.6	0.4	N/D	N/D	N/D
	body	88.5	9.4	2.0	0.1	N/D	N/D	N/D	N/D	N/D
	leaf	90.6	7.0	2.2	0.2	N/D	N/D	N/D	N/D	N/D

Table 3
Mean values and standard deviations for the three typologies parts of the panels.

		Cu	Sn	Pb	Ag	Sb	Fe	Ni	Zn	As
Thin foils in the base	Mean	84.68	9.52	2.46	0.10	2.10	0.17	0.30	0.58	0.07
	Standard deviation	2.92	3.05	0.71	–[a]	1.20	0.20	0.99	1.93	0.17
Body of the panel	Mean	86.83	10.34	2.22	0.06	0.50	0.04	N/D	N/D	N/D
	Standard deviation	2.69	1.93	0.34	0.05	0.68	0.13	N/D	N/D	N/D
Acanthus leaves	Mean	88.57	7.98	2.70	0.15	0.43	0.14	N/D	N/D	N/D
	Standard deviation	1.48	1.26	0.57	0.05	0.68	0.23	N/D	N/D	N/D
All analysed points	Mean	86.6	9.3	2.5	0.1	1.0	0.1	N/D	N/D	N/D
	Standard deviation	2.8	2.3	0.6	0.06	1.1	0.2	N/D	N/D	N/D

[a] All Ag values are 0.10.

point are reported. The composition is typical of a bronze of the 16th century.

In the analysis of Table 2 we can follow two criteria:

- detect, if anyone, the difference in composition between the panels;
- answer to the question if there are different compositions for the decorative leaves around the panels, the decoration with thin foils on the base and the panel itself.

We made use of the analysis of variance to work with the data collected.

The two criteria (panels and typology) give rise to two different reorganisation of the table. The two-way analysis of the variance for the four principal elements (copper, tin, lead, and antimony) allowed us to demonstrate that there are significant differences in the alloy composition either between the different typology of objects as between the panels. It is evident that the difference in composition between the different pieces belonging to a same panel is more interesting, from a archaeometric point of view, rather than the difference between the panels, that is a mere confirmation of the fact that the panels were sculptured in different phases.

For the copper, we found that the value of the F(Fisher ratio) between typologies (leaves, body of panels and thin foils) is 9.067 with two degrees of freedom so the hypothesis that there are significant copper differences is verified with a probability less than 0.002. In addition, the hypothesis of significant differences between panels is verified with an F of 2.773 and nine degrees of freedom, with a probability $P = 0.031$ which is lower than the

Please cite this article in press as: G.E. Gigante, et al., Diagnostic investigations and statistical validation of EDXRF mapping of the burial monument of Pope Sixtus IV by Antonio Pollaiolo (1493) in the Vatican, Journal of Cultural Heritage (2011), doi:10.1016/j.culher.2011.11.003

critical threshold of 0.05. In the case of tin, we found similar results (as it is obvious being the only other major element of the alloy, apart lead) with an F of 17.324 between typologies that is significant with a $P = 0.006$ (i.e. very significant). In the case of lead, the differences between panels and typologies are not significant. Finally for antimony, an F of 30.568 between typologies and $F = 3.302$ between panels give a very good level of significance in the first case ($P < 0.001$) and a $P = 0.015$ in the second. Therefore, also in this case, the analysis shows that it is possible to hypothesize a different alloy for the three typologies of elements of the panels. If we observe the Table 2, we can see that the only spot on a foil that has no presence of antimony is also the only one with nickel and zinc, we can therefore hypothesize we are dealing with a reparation.

In order to summarize the results in Table 3, the mean values and standard deviation for the three typologies are shown.

4. Conclusions

The possibility to use the capabilities of low energy element detection with portable EDXRF systems, that is, to detect elements such as sulphur, chlorine, potassium and calcium can increase significantly the surface information that non-invasive portable systems can give.

On the monument's surface, the relation among the visual green colour and the presence of chlorine together with the absence of the elements found with the coloured layer suggest the fact the we are in presence of a degradation process.

The high number of analyses that it is possible to fulfil with a non-invasive method, such as FP-EDXRF, can balance the limitations that the technique inherently has. This high number of results must be data-mined with statistical analysis to deploy all the right information.

In addition, the 33 quantitative analysis of the alloys, obtained removing the patina, lead to useful results. The particular technique of production used by Pollaiolo, more typical of a goldsmith rather than of a sculptor, opens the question if he used different alloys to produce the various elements of the masterpiece. In this case a correct sampling and a straightforward use of statistical methods allow us to answerer positively to the question.

Acknowledgments

The authors are very grateful to Dr. N. Gabrielli and P. Zander of the "Fabbrica di San Pietro" for the collaboration in the work and useful discussion. The collaboration of Dr. M. Guiso was very important in the clarification of the products used in the superficial treatment. The authors are indebted with the restores for the assistance during the phase of sampling and the useful discussions. The work was possible for the permission of the responsible of the "Museo del Tesoro di San Pietro" in the San Peter Basilica in Vatican.

References

[1] L. Robbiola, J.M. Blengino, C. Fiaud, Morphology and mechanisms of formation of natural patinas on archaeological Cu - Sn alloys, Corrosion Science 40 (1998) 2083–2111.
[2] J. Wang Chunchun Xu, L.V. Guocheng, Formation processes of CuCl and regenerated Cu crystals on bronze surfaces in neutral and acidic media, PR China Applied Surface Science 252 (18) (2006) 6294–6303.
[3] M. Wadsak, I. Constantinides, G. Vittiglio, A. Adriaens, K. Janssens, M. Schreiner, et al., Multianalytical study of patina formed on archaeological metal objects from Bliesbruck-Reinheim, Microchim Acta 133 (2000) 159–164.
[4] L. Robbiola, R. Portier, A global approach to the authentication of ancient bronzes based on the characterization of the alloy-patina-environmental system, Journal of Cultural Heritage 7 (2006) 1–12.
[5] I. Constantinides, A. Adriaens, F. Adams, Surface characterization of artificial corrosion layers on copper alloy reference materials, Applied Surface Science 189 (2002) 90–101.
[6] G.E. Gigante, S. Ridolfi, P. Ricciardi, M. Colapietro, Cultural heritage conservation and environmental impact assessment by non-destructive test and microanalysis, Taylor & Francis group, London, 2005.
[7] G.E. Gigante, R. Cesareo, Non destructive analysis of ancient metal alloys by in situ EDXRF transportable equipment, Rad Phys and Chem 51 (4) (1998) 689–700.
[8] B. Pichler, A. Vendl, Recent Advances in the conservation and analysis of artefacts, Summer Schools Press, University of London, 1987.
[9] D. Attanasio, G. Bultrini, G.M. Ingo, The possibility of provenancing a series of bronze Punic coins found at Tharros, (western Sardinia) using the literature lead isotope database, Archaeometry 43 (4) (2001) 529–547.
[10] M. Diana, N. Gabrielli, S. Ridolfi, Sulfur determination on stone monuments with a transportable EDXRF system, X-Ray Spectrom 36 (2007) 424–428.
[11] R. Cesareo, S. Ridolfi, M. Marabelli, A. Castellano, G. Buccolieri, M. Donativi, et al., Portable X-Ray fluorescence spectrometry: capabilities for in situ analysis, The Royal Society of Chemistry, London, 2008.
[12] M. Marabelli, M.L. Tabasso, Il degrade dei Monumenti in Roma in rapporto all'inquinamento atmosferico, BetaGamma, 1992.
[13] L.S. Selwyn, N.E. Binnie, J. Poitras, M.E. Laver, D.A. Downham, Outdoor bronze statues: analysis of metal and surface samples, Studies in Conservation 41 (1996) 205–228.
[14] H. Strandberg, Perspective on bronze sculpture conservation, Avdelningen foer Oorganik Kemi, Goeteborgs Universitet, 1997.

Please cite this article in press as: G.E. Gigante, et al., Diagnostic investigations and statistical validation of EDXRF mapping of the burial monument of Pope Sixtus IV by Antonio Pollaiolo (1493) in the Vatican, Journal of Cultural Heritage (2011), doi:10.1016/j.culher.2011.11.003