RESTORATION OF THE FUNERAL MONUMENT OF POPE SIXTUS IV BY ANTONIO POLLAIOLO (1493) IN THE VATICAN BASILICA: NON INVASIVE AND MICRODESTRUCTIVE ANALYSIS – AN OPERATION PROTOCOL

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ABSTRACT

The bronze funeral monument for Pope Sixtus IV (1471-84) by Antonio del Pollaiolo, now in the Museum of the Vatican Basilica was designed to be located at the center of a chapel, which explains its' apparent asymmetry: lack of height and large base. The complex composition of this masterpiece of bronze sculpture, places the Pope at the center of an inner ring with the personification of the virtues and an outer one with ten allegories of Art and Science. The restoration of the funeral monument started in May 2007 and has to be concluded in December 2008. The restoration was carried out by first making a series of non invasive readings using a transportable EDXRF and a portable Raman system, then mapping the deterioration processes that had altered 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 analyzed with SEM-EDS, NMR and XRD techniques. In this article some of the results of the tests will be shown together with the protocol of the procedures implemented to maximize the diagnostic information gathered and minimize the micro-sampling on works of art.

In recent years it has become a common practice to use the event of the restoration of a masterpiece to unite the diagnostic process and the archaeometric study.

INTRODUCTION

In the last decade it has become common practice to use a restoration project to simultaneously carry out the diagnostic process for conservation purposes, and an archaeometric study. There are certainly many practical reasons for doing this and it is certainly not opportune to discuss on these in this article, it is instead worth analysing the results obtained and the risks which may occur, especially where these are linked to an inefficient planning of the various diagnostic methods.

In the case of metal artefacts the formation of a patina is related to the composition and microstructural characteristics of the alloy. In this case there is a closer link between the technologies used in the production process and the outcome of the restoration work. This means that the archaeometric study and conservation diagnostics are more closely related. There are of course other factors determining the deterioration of the surface of a metal artefact, relating to the surrounding environment, or maintenance practices or the uses which the artefact is put to, and therefore its ultimate state of conservation. It is not an easy task to determine which may be the main contributor in the degradation process and therefore the most important for the artefacts survival.

We generally attribute a greater durability to a metal artefact, and therefore it is considered more suitable to outdoor environments, in comparison to works made of other materials. The

exception being works in stone which share, in this sense, several similarities with works in metal.

Experts are increasingly interested in the archaeometrics of metal artefacts and they have experimented with several methods which have been used successfully in archaeometallogical research. In ancient times the treatment of metals, and the different metals mined fulfilled an important role of cultural heritage. Often the capacity to work metals in a technologically evolved manner has been one the factors which determines whether a greater or lesser significance is attached to an ancient civilization. This is true even in more recent times, the production of the first works in bronze of the Renaissance signal a significant change in respect of the earlier period during which a great part of the ability to employ complex techniques known in the classical age had been forgotten and lost.

To some extent also the use of metal in the construction of buildings and bridges in the course of the XIX century meant a significant change, and identifies such works with the modern era.

It is in the light of this that we should consider the study of the magnificent work of Antonio del Pollaiolo; the funeral monument of Pope Sixtus IV della Rovere. This monument belongs to a historical period in which the working of metals, often used techniques borrowed from goldsmiths, which were more evolved and had been in use for longer, bringing with it all the difficulties which the change in scale from small to a large metal artefact would imply.

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 preserved in the Museo del Tesoro, (the Treasures Museum). The work was commissioned by the Cardinal Giuliano della Rovere, nephew of Pope Sixtus, himself a future pope later known as 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 artists signature.

The monument which in several parts is melted with a lost wax casting technique is made up of a large cut off pyramidal base decorated with acanthus leaves and ten 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 laid down and surrounded by the personifications of the seven virtues; the three theological virtues surround the head of the Pope, with charitable love taking the place of honour whilst the four cardinal virtues are set out by the sides of the figure. By the feet, a large bronze epigraph in Latin sets out 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 and it is expected to be completed in March 2009. The restoration work has been organised in order to divide the great artefact into two distinct lots: the first lot which is made up of the work on the ten allegories to the arts and the great acanthus leaves which surround them, is still in progress; the second lot is made up of the figure of the Pope and the seven virtues and work will be commenced during April 2008. The possibility of dismantling the monument in order to check the state of preservation of the internal surfaces is currently under study. The

scientific observations and investigations that follow therefore all refer to the surfaces of the great base with the ten panels and the foliage like decorations.

MATERIALS AND METHODS

We have analysed the wet swabs used for the surface removal of soil residue, and samples of patinas which were removed from the monument mechanically. All 30 samples have been taken from areas featuring particular characteristics or abnormalities, for example differently coloured patinas. All the materials analyzed are representative of the most external layer of the surface and of particular areas where welding and or plastering had been carried out.

With SEM-EDS micro-fragments of metal which had naturally detached from the surface were studied.

The EDXRF investigations were carried out in two different ways;
- Without any removal of the patina, but after cleaning to remove the layer of wax, with a tube HV sufficient to reveal some light elements (S, Cl, Ca, K)
- By taking away a layer of patina of 2mm, in order to study the uncorroded alloy, and with the instrument set up so it would pick up also on tin and antimony.

On some areas of the bronze panels 2,3,4, examined in the first way, some control measurements were taken after cleaning with water and EDTA.

With the first method 101 areas were examined (which were quite well distributed over all the panels) and nine control measurements were taken after a further cleaning.

Finally, 33 quantitative analysis were carried out on some of the parts put together to built the panels.

In order to reveal the presence of organic and inorganic elements, we used NMR spectroscopy, and energy dispersion x ray (EDS) micro-analysis together with analysis through a scanning electron microscope (SEM).

The ^{1}H-NMR analysis was carried out on the solution obtained by extracting the substances trapped in the fibre of the swabs with the use of deuterochloroform. The analysis were carried out with a Mercury 300 MHz spectrometer. The technique of spin decoupling was also used in order to highlight the relationship between the various proton groups.

The swabs, which were dark in colour, were treated separately, with approx 0,5 cm³ of deuterated chloroform. Solutions containing a black dust were obtained and were filtered, and used for an additional microprobe study.

The black patina was suspended in deuterochloroform and the solution obtained was filtered in order to remove the insoluble particles. The proton spectra of the swabs gave practically identical results, demonstrating that the treatment with the swab had removed only a thin layer of the wax mixed with the insoluble black pigment.

In order to validate and integrate the results obtained, the SEM-EDS technique for the elementary quality/quantity analysis, using a LEO1450VP INCA300 instrument was used. The SEM-EDS micro analysis used the observation of the samples in back-scattered electrons to reveal differences in composition from the grey levels. In this way it was possible to select micro areas of homogenous composition, although it was not possible to obtain a perfect

correlation between all samples. Furthermore, the extremely small dimensions of the layers did not always allow the identification of the single compound present.

The portable EDXRF system is composed of an air cooled low power tube (35kV and 0,2 mA) plus a SDD (Silicon Drift Detector) detector with 150 eV energy resolution at the iron K line. The tube worked with a 2 mm aluminium filter for the quantitative analysis on the bronze alloy while it worked without filter for the analysis on the patina. In Figure 1 we see the panel named "the Music" with indicated, in black, the spots where non destructive analyses availing of a portable EDXRF system were fulfilled. In Figure 2 a moment of the analysis.
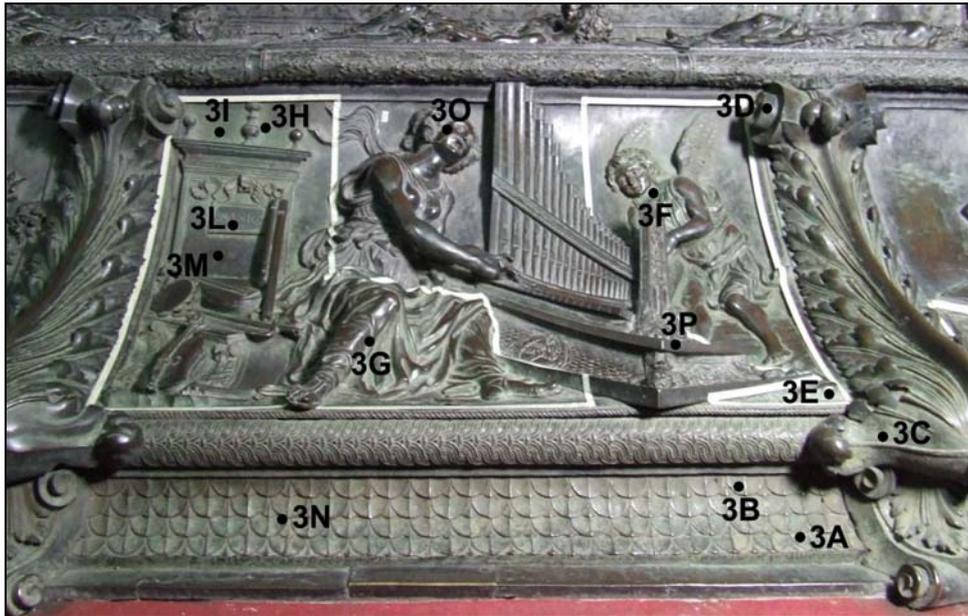
Fig. 1: panel "the Music" and in black the spots where EDXRF non destructive analyses were fulfilled
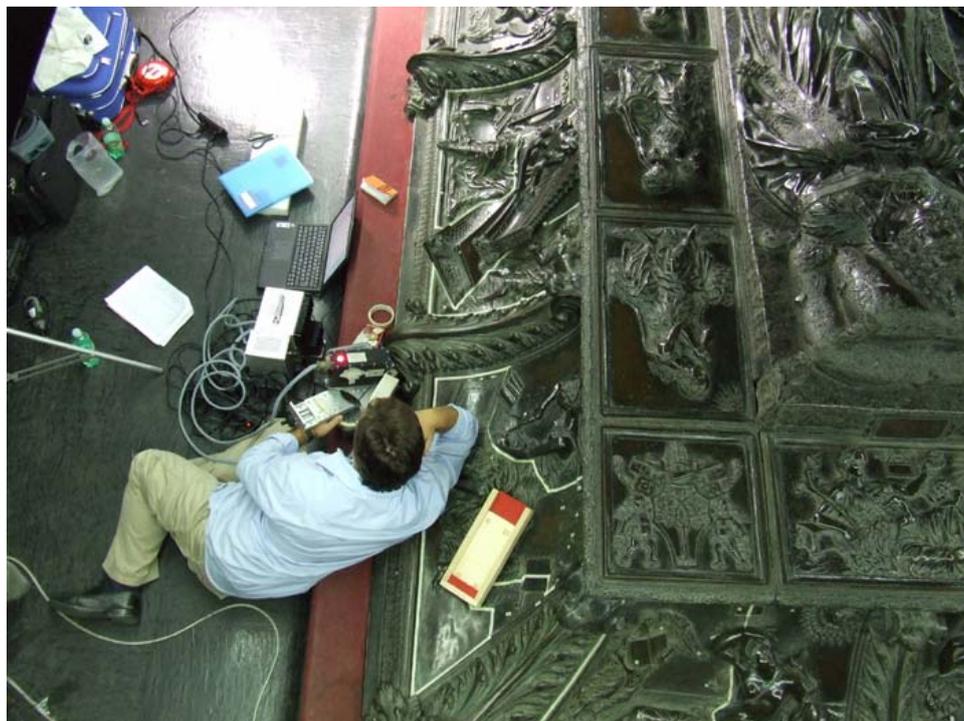
*Fig. 2: portable EDXRF analysis on the panel "the Music"*

RESULTS AND DISCUSSION
The State of the Surface
The surface colour look to be an anomalous from the outset, insomuch to require a diagnostic study so as to better understand its characteristics.

The systematic low energy EDXRF measurements allowed us to individualize elements which are part of the surface treatment. These are: potassium, calcium, manganese and iron. With the 111 surface areas studied on the ten panels it has in fact been possible to demonstrate a good correlation between such elements.

Figure 3 shows the calculations (normalised to copper peaks) for calcium and iron; and as shown in figure the correlation is 0.953. Tests on the other elements also gave analogous results; for example, the correlation for calcium and potassium is 0.942, and for iron and magnesium 0.911.
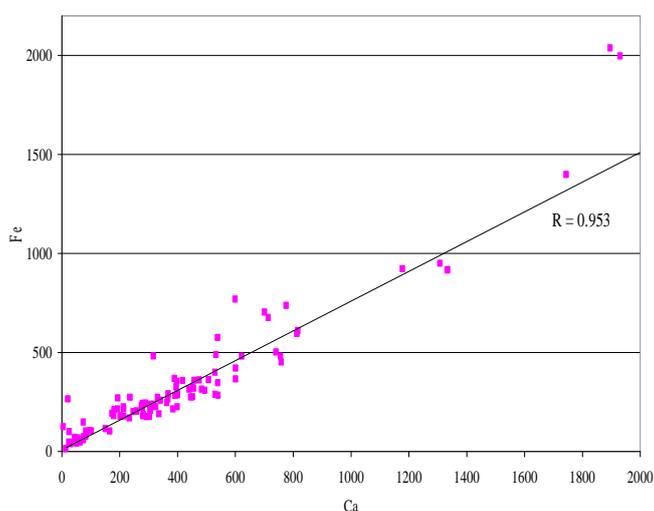
Fig. 3: scatterplot for calcium and iron (the correlation is 0.953)

The swabs and patina ^{1}H-NMR spectra differ by the presence, in the swabs, of signals of an unsaturated waxy or oily substance, as well as signals relating to the use of a cleaning product. All however contain signals attributable to geminal protons with hydroxylic or ethereal function. Figure 4 shows how in the spectrum of the black patina taken from panel 2 appear the characteristic peaks of esterified primary alcoholic functions of the waxes (4.04 ppm), along with those of the adjacent methylene group to carboxylic function (2.30 ppm), as well as signals of other protons of the aliphatic chains.
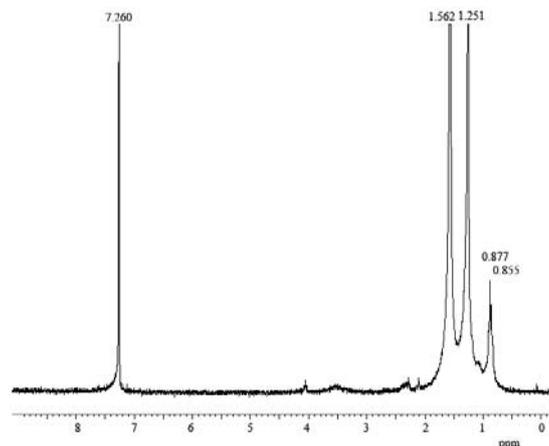
Fig. 4: ^{1}H-NMR Spectrum in CDCl$_3$ of the black patina.

The presence on all of the panels of the aforementioned elements agree with a generalized surface treatment with coloured waxes and pigments such as bone black, (given that in the EDS test on the swabs residual powder the phosphorous and calcium were found in stoichiometric ratios suggesting the presence of calcium phosphate) and soils containing iron oxides and/or manganese which confer the characteristic dark colour. It is not realistic to answer the question when this treatment was carried out, it is plausible to suppose however that when the first signs of surface alterations became apparent the treatment was carried out to unify the colour of the surface.

Several visible alterations of colour were studied in the surface samples: green, black, grey, yellow, white.

The presence of chlorine and sulphur in all the points tested suggests that these elements are involved in the degradation processes. In particular their distribution is not uniform, as shown by the low correlation between these elements and the other elements used in the surface treatment. In particular the presence of chorine in the green patina was confirmed with SEM-EDS.

Figure 5 shows a false colours mapping of the distribution of the elements detected with EDS.
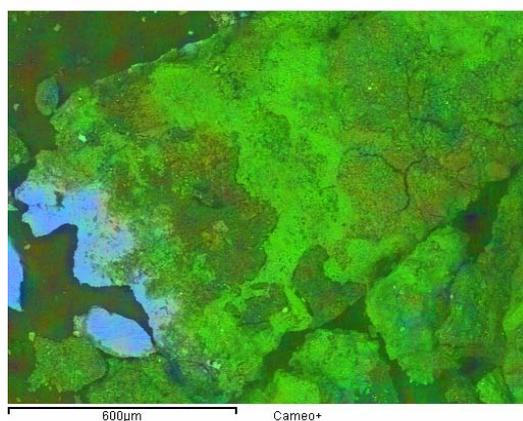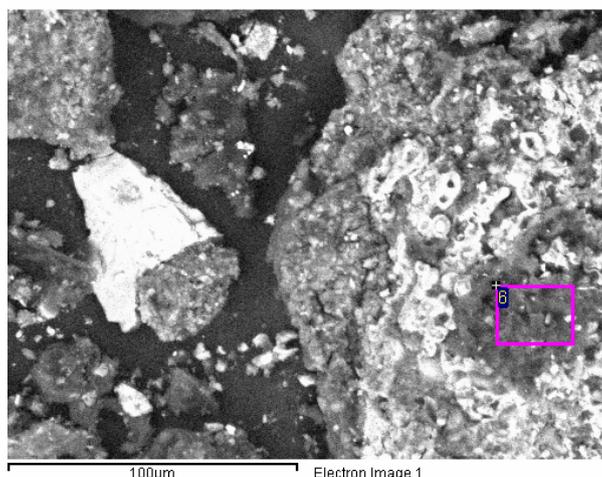

Fig. 5 An image in false colours of elemental mapping
with EDS of copper (blue); chlorine, (green) phosphorous (red)

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In nearly all the quantitative analyses the chlorine and copper was found in concentrations often attributable to the co-presence of $CuCl$ and $CuCl_2$. Fig. 6 shows the characteristic morphology of copper chlorides.

Fig.6: A back-scattering electron image where the characteristic morphology of copper chloride is highlighted.

A more careful observation of the results on the green areas has revealed how, in respect of the observed mean values there is a significant increase in the green areas of chlorine (Student test t passed with $p<0.005$) and a significant decrease in the levels of the other elements. Table I shows a comparison between the mean values of the normalized counts for the green and all others sample areas. The chlorine counts difference is significant, such as the systematic reduction of the counts of the elements involved in the surface treatment. The presence of copper chlorides causes a diminution of thickness of the protective patina.

	S	Cl	K	Ca	Mn	Fe
mean $\pm\ \sigma_{mean}$	2.3±0.2	28.7±1.8	13.4±1.3	247.4±25.4	7.2±0.7	194.3±17.0
All analysed surface points						
mean $\pm\ \sigma_{mean}$	3.7±0.2	17.3±1.1	22.0±2.0	490.9±64.2	10.5±1.1	366.3±39.6

Table I Composition of the green surface points (EDXRF analyses)

With regard to the black areas on the other hand we notice a diminution in the level of chlorine and a small increase in the levels of sulphur. The protective patina seems though to be substantially unaltered.

This agree with the hypothesis that the black areas are not greatly involved in the degradation processes. Other considerations may be made regarding other areas like the yellow incrustations which present evident alterations in the relationship between the elements.
The possibility to study the surface after cleaning confirmed the hypothesis that the presence of chlorine and sulphur is superficial, in fact there is a reduction of more than 20 % of the counts related to such elements in the control areas examined on the metal panels.

The Archeaometric Characterisation of the Alloy

The quantitative analysis on the areas where the patina had been removed lead to determination of the bronze alloy composition. Table II shows the results of the quantitative analysis on 33 areas of the various panels. It worth to note that the panels, probably produced in successive phases, were put together with pieces welded together individually.

		Cu	Sn	Pb	Ag	Sb	Fe	Ni	Zn	As
panel 1	*foil*	86.7	9.1	2.4	0.1	1.4	0.3	-	-	-
	leaf	85.9	12	2.3	0.1	-	-	-	-	-
	body	88	9.4	2.5	0.1	-	-	-	-	-
panel 2	*body*	87.7	8.7	2.7	0.1	0.2	0.5	-	-	-
	foil	82.2	13	1.9	0.1	2.3	0.4	-	-	-
	foil	83.5	3	3.2	0.1	-	0.4	3	6	-
	leaf	86	12	2.5	-	-	-	-	-	-
panel 3	*body*	86.4	9.9	2.5	0.1	0.6	0.4	-	-	-
	foil	8-.9	13	2.8	0.1	3.2	-	-	-	-
	leaf	86.8	9.9	2.2	0.1	0.9	-	-	-	-
	leaf	87.7	9.2	2.4	-	0.7	-	-	-	-
panel 4	*body*	88.4	8.7	2.6	0.2	0.1	-	-	-	-
	foil	79	14	2.6	0.1	3.9	0.4	-	-	-
	leaf	84.1	12	2.8	0.1	1.5	-	-	-	-
panel 5	*foil*	84.6	10	1.6	0.1	3.3	-	-	-	-
	leaf	81	14	2.4	0.1	1.7	0.4	-	-	-
panel 6	*body*	87.9	5.9	4.1	0.1	1.9	-	-	-	-
	foil	87.5	8	1.5	0.1	2.5	-	-	-	1
	leaf	9-.2	7.9	1.8	-	0.1	-	-	-	-
	body	89.5	7.5	2.7	0.2	0.1	-	-	-	-
panel 7	*foil*	86.4	8.5	2.3	0.1	2.6	-	-	-	-
	leaf	87.8	9.9	2.3	-	-	-	-	-	-
	body	9-.9	6.6	2.3	0.2	-	-	-	-	-
panel 8	*foil*	86.4	9	2.5	0.1	2.1	-	-	-	-
	leaf	88.1	9.8	2	0.1	-	-	-	-	-
panel 9	*body*	89.3	8.3	2.2	0.2	-	-	-	-	-
	Foil	87.9	8.5	2.3	0.1	1.2	-	-	-	-
	body	87	7.8	3.2	0.1	1.4	0.5	-	-	-
	leaf	86.6	9.3	2.5	0.2	1.1	0.3	-	-	-
	leaf	89	8.2	1.7	0.1	1	-	-	-	-
panel 10	*foil*	86.4	8.5	4	0.1	0.6	0.4	-	-	-
	leaf	88.5	9.4	2	0.1	-	-	-	-	-
	body	9-.6	7	2.2	0.2	-	-	-	-	-
	mean	86.63	9.31	2.45	0.11	1.04	0.12			
	s.dev	2.80	2.30	0.57	0.06	1.14	0.19			

Table II Composition of the different panels (EDXRF analyses)

In the last two rows of the table are reported the mean composition and the standard deviation of the measurements. The composition is typical of a bronze from that period.

The analysis of the individual elements gathered in the table allow us to verify whether Pollaiolo used alloys with different composition. The analysis of the variance for the four principle elements (copper, tin, lead, and antimony) has permitted us to demonstrate that the differences in composition of the alloys used to create the body of the masterpiece, in respect of those used for the panels and the floral decorations are significant.

In fact with regards to copper, it was calculated a value of the Fisher ratio F of 6.68 with 28 degrees of freedom, then the hypothesis that we are dealing with different groups is verified with a $p < 0.0045$, and thereby it is highly significant; in the case of tin F= 2.91 with $p < 0.073$ and therefore the significance is not very high; and finally for antimony F=10.41 with $p < 0.0005$ and therefore highly significant the difference between groups.

If we observe the table we can see that the only area on a foil that has no presence of antimony is foil 10. It is also the only one with nickel and zinc, we can therefore hypothesize that we are dealing with a reparation. In the case of lead the differences between the groups are not significant, as shown in Table III where the mean values for the three groups are reported.

	Cu	Sn	Pb	Ag	Sb	Fe
body	88,63	7,82	2,72	0,16	0,48	0,16
leaf	84,48	9,56	2,47	0,10	2,17	0,16
metal foil	86,68	10,27	2,29	0,07	0,60	0,07

Table III mean values for the alloy elements (EDXRF analyses)

The increased concentration of tin is easily explained by the necessity to give more fluidity to the fusion of the more elaborate decorative elements. The increased presence of antimony in the leaves does not, however, have an immediate significance, it may have been added involuntarily through the increase in the concentration of tin, or it may be due to the use of re-melting materials. It may also have a technological significance.

During the restoration operations we concentrated on a small area of the decoration representing an acanthus leaf, it had a yellow, brown and green colour and a consistency which was different from the other bronze material.

Again under SEM back-scattered electrons observation, punctual analysis were made as is indicated in Fig. 7 the values obtained are shown in Table IV.
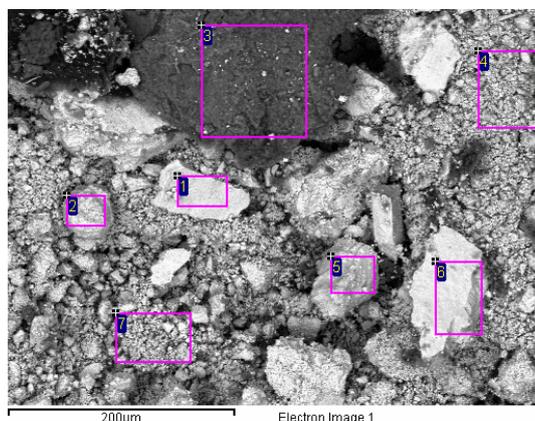

Fig. 7: SEM image of one of the samples where the analysed areas are highlighted, the values of this composition are set out in Table IV.

Spectrum	C	N	O	Mg	Al	Si	P	S	Cl	K	Ca	Fe	Co	Cu	Sn
1	7.45	-	6.56	0.03	0.98	0.29	0.25	0.06	0.06	-	1.16	--	30.14	0.26	55.35
2	13.00	-	11.59	0.06	0.53	0.14	0.09	-	0.19	-	0.80	-	22.83	0.31	51.19
3	23.32	4.42	44.34	0.50	1.31	4.12	3.05	1.02	0.26	0.88	12.65	0.48	0.21	3.46	0.47
4	17.20	-	13.71	0.03	0.82	0.19	0.09	-	0.15	-	0.79	-	24.09	0.49	49.45
5	12.66	2.53	9.15	0.09	0.55	0.32	-	0.04	0.04	-	0.44	0.02	23.24	0.45	50.87
6	7.43	-	8.03	-	1.03	0.16	0.03	0.03	0.10	0.10	0.80	0.04	26.33	0.25	55.57
7	12.65	-	7.56	0.14	0.75	0.22	-	0.24	-	-	0.52	-	26.04	0.07	52.45

Table IV EDS composition in elements in percentages and in weight (error $\pm 0.2\%$)

In the table several elements have been added in order to check for their presence, even though in traces. From data analysis a high presence of tin emerges, which may refer to a zone of welding by low temperature braizing, but above all the presence of cobalt is considerable. The latter appears in a constant relationship with tin in many of the measurements carried out, this indicates a correlation between the two elements. Stoichiometric calculations have indicated that the ratio agree with $CoSnO_3$ which is a pigment with a blue colour. The presence of pigment may be an attempt to cover up a welding vein by simulating the colour of the bronze.

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