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µXRF ANALYSIS OF DECORATION MOTIFS 0N MAJOLICA POTTERY.

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ABSTRACT

µXRF analysis of decoration motifs in fragments corresponding to several Majolica types was carried out using an spectrometer comprising a low power Mo x-ray tube and a elliptic-shape concentrating lens with a 60 µm spot. Both surface scanning and spot measurements were carried out, allowing the qualitative identification of the inorganic pigments used for the surface painting decoration. The absence of interference signal arising from the excitation of the underlying paste when analysing thin-lead glazing was evaluated, allowing to ensure the suitability of the analytical procedures. A distinction was found between different types of Majolica by the presence of other elements in the blue and black.

INTRODUCTION.

Large museum collections of pottery from the colonial period witness the intense trade and cultural activity that the city of San Cristóbal de la Habana played during the XVII and the XVIII centuries, as an important stop-over port for most of the ships traveling between the Old and New Worlds. The archaeological researches conducted since 1968 during the restoration of the historic center of Havana (Old Havana) have revealed a marked presence of Majolica pottery in the excavations performed in the associated colonial contexts.

Majolica is a distinctively Hispanic category of glazed, wheel-thrown ceramics, distinguished by its soft earthenware paste covered by an opaque vitreous enamel or glaze. The addition of tin oxide to the lead glaze produced an opacity which is also found on the technically related French faience and English and Dutch delftware. The establishment of Spanish potters in the American colonies leaded to the manufacture of Majolica in the new world, being Mexico city and Puebla their major production centers.

The findings of Majolica pottery have been stated in sites covering practically all the period of Spanish presence in Cuba *[1]*, even in those corresponding to the earlier XVI century *[2, 3]*. Different researchers have identified ceramic artifacts in Havana *[1]* and other major Cuban cities *[4, 5]* with the distinctive features described for the Majolica types found in America and the Caribbean basin *[6 ,7],* such as *Isabela Polícromo*, *Santo Domingo Azul sobre Blanco*, *Columbia Simple*, *Yayal Azul sobre Blanco*, *Abó Polícromo*, *San Juan Polícromo*, *Caparra Azul*, *Ichtuknee Blue on White*, *Catalana Azul sobre Blanco*, *Puebla Polícromo*, *Puebla Azul sobre Blanco,* among others.

The study and the classification of ceramic artifacts related with different archaeological researches conducted in Cuba has comprised mainly the analysis of their morphology, style features, and techniques of elaboration, texture or other properties.

The application during the last decade of several micro and trace analytical techniques has proved to bring useful information for solving different research questions when analyzing goods of the cultural heritage. The less invasive, or in some cases even non-destructive performance of some

of these techniques have fulfilled the main restriction imposed to the analysis of extremely valuable or unique objects. The classification of some types of Spanish and Puebla Majolica was reinforced as the result of a research involving the Instrumental Neutron Activation Analysis (INAA) of the paste in about hundred fragments [*8*].

The study of ceramic decoration is an important tool not only for its classification but also for revealing the possible procedures of its manufacture. During the last years, several spectrochemical methods have been used for pigment analysis, such as INAA, atomic absorption spectrometry (AAS), inductively coupled plasma mass spectrometry (ICP-MS), electron probe X-ray microanalysis (EPMA) and X-ray fluorescence spectrometry (XRF). Many of these above mentioned methods either require the dissolution of the paint samples prior to analysis (AAS, ICP-MS) or the removal of a certain amount of sample (INAA, EPMA, conventional XRF).

The application of different X-ray emission techniques has allowed the non-destructive analysis of valuable goods [*9*, *10*]. The development of X-ray spectrometers using specially constructed devices to focus X-ray beams in to relative small areas has been introduced in the practice for non-destructive analysis of art collections by several research teams [*11*, *12*, *13*]. However, the deeper penetration of X-rays in to the matter, and therefore the excitation of several different layers constituting the structure of paintings or other decorated artefacts, imposes the need of a careful interpretation of the measured spectra.

The aim of our work consisted in the study of the pigments used for the decoration motifs in several types of Majolica pottery from Old Havana museum collections. The μXRF analysis was carried out using a spectrometer comprising a low power Mo X-ray tube and a XOL concentrating lens with a 60 μm spot. A full description of the spectrometer features is provided in [*14*].

The adequacy of interpreting the measured spectra, as resulting only from the glaze layer, was theoretically evaluated for assessing its possible composition variations.

Both, surface scanning and spot measurements were carried out, allowing the qualitative identification of the inorganic pigments used for the surface painting decoration. The qualitative analysis of pigment composition in the blue and black decorations allowed establishing subtle distinction between different types of Majolica.

MATERIALS AND METHODS.

Analyzed samples:

Table 1 summarizes the characteristics of the analyzed fragments, belonging to ceramic vessels from different Majolica types, most of them from Spain or Puebla. The selection of samples comprises several of the color motifs among the rich variety of decorations found in Majolica pottery. The thickness of the glaze was approximately evaluated by registering the sudden drop of the fluorescence intensity from lead while performing a 60 μm step scan of the cross section of the analyzed fragments.

The use of blue decoration over the white-opaque background, as the result of the influence of the spreading through the world of the Chinese porcelain, inspired the masters manufacturing Majolica in Spain and Puebla. The import from Chinese porcelain through the Pacific Ocean arrived to Acapulco, and after crossing the Mexican isthmus was reshipped to Spain from the port of Veracruz. The addition of other colors to the decorations is also common for the Mexican baroque during the XVII-XVIII centuries, as well as the use of wide traces to reinforce the decoration. The presence of Puebla pottery in the colonies evidences that it displaced the Spanish concurrence not only due to the lowest costs and availability, but also due to the high quality performance achieved by the masters [*15*].

Two samples of Italian origin were also included in the analysis. The trace element composition of the paste of these fragments, which were initially classified as Sevilla Azul sobre Azul due to its similarity to this style, suggested an Italian origin [*8*]. Two samples of pre-Columbian

Mexican pottery were also analyzed, trying to corroborate the hypothesis about the clay nature of its red painting.

ID	Type	Origin	Dated period	Ground glaze type	Color decoration	Glaze thickness (μm)
S05	Liguria Azul sobre Azul	Italy	1550–1650	Light blue	DB	200 – 250
S07	Liguria Azul sobre Azul	Italy	1550–1650	Light blue	DB	300
S11	Sto. Domingo Azul s/blanco	Spain	1550-1630	White	DB	250 – 300
S06	Sevilla Azul sobre Azul	Spain	1580-1650	Light blue	DB	250 – 300
S17	Catalana Azul s/blanco	Spain	1700-1800	White	LB	250 –300
S01	SV Polícromo	Spain	1780-1825	White	DB, LB, O	300 – 400
S02	SV Polícromo		1780-1825	White	DB, Y, BR	200 – 250
S08	San Juan Polícromo	Valley of Mexico or Puebla	1550-1630	White	DB	300 – 400
S09	San Juan Polícromo		1550-1630	White	DB, LB, O	250 – 300
S10	San Juan Polícromo		1550-1630	White	DB, LB	500
S15	Abó Polícromo	Puebla	1600-1725	White	DB, LB, O, B	100
S16	Abó Polícromo		1600-1725	White	DB, LB, Y, G, B	200 – 250
S18	San Luis Polícromo	Puebla	1630-1725	White	G, B	150
S19	San Luis Polícromo		1630-1725	White	G, B	100
S20	San Luis Polícromo		1630-1725	White	G-B, B	350
S03	Puebla Polícromo	Puebla	1650– 1725	White	DB, B	200 – 300
S04	Puebla Polícromo		1650– 1725	White	DB, B	400 – 600
S12	Puebla Azul s/blanco		1680-1820	White	DB	200 - 250
S13	Puebla Azul s/blanco		1680-1820	White	DB	350
S14	Puebla Azul s/blanco		1680-1820	White	DB	350
S21	Mexico Red	Mexico		Red paint	None	< 50
S22	Mexico Red			Red paint	None	< 50

Notes: DB – dark blue, LB – light blue, G – green, O – orange, Y – yellow, B – Black, BR – Brown

Table 1 Description of the analyzed samples

Qualitative and quantitative analysis:

The analysis of surface decorations in pottery is in general constrained by the non-homogeneity of the irradiated volume. The penetration of X rays varies depending on matrix composition, and as far as in the more general case a decorated surface can be thought as composed by several layers of painting, enamel, glaze or other kind of materials, the measured signal can comprise the contribution due to the fluorescence of the elements present in several layers. Although several methods have been developed with the aim to achieve quantitative analysis in multi-layered samples [*16*, *17*, *18*], the fact that there are more unknowns than measurable experimental variables limits solving the problem in the absence of additional information about the sample structure and composition. That constraint has lead most of the researchers to limit their work to perform only qualitative analysis of the measured X-ray spectra. Spectra from the interested spots are compared with the spectra from the "background" areas, and inferences about the pigment composition are made on the basis of the observed differences.

X-rays scanning of surfaces have been carried out using different μXRF spectrometers, providing maps of elemental composition with a spatial resolution in the sub-mm range. The identification

of the pigments used for each decoration is eased by the comparison with the visual observed decoration motifs. In most of the cases the informative signal in automatic scanning consists of the integral counts registered within the energy interval comprising each interference-free X-ray peak. The outstanding feature of this approach lies in an express performance, when compared to the choice of peak areas resulting from spectrum fitting procedures. However, the limitations of such method are set by the impossibility to reveal some elements that are significant in pigment identification. For instance, the Sb-L lines of antimony are strongly interfered by the Ca-K lines; Co-K_α is hampered by the almost higher intensity Fe-K_β peak, among other examples.

To avoid these limitations we performed the spectra fitting of the scanning spectra, using a batch utility developed for that purpose based on an algorithm developed for the Canberra WinAxil package and saving the peak areas resulting from the fitting in an MS Excel file. The data was further converted to a three dimensional matrix (X-pixels, Y-pixels, N-elements) and plotted in intensity readouts graphs using MatLab 6.1.

In the case of performing nondestructive microanalysis of the surface of decorated pottery, major concern shall be paid to assessing the possible contribution to the measured spectra from the ceramic paste body. The well-known Sherman equation formulates the relation between the measured fluorescent radiation intensity $\boldsymbol{R_i}$ from an element $\boldsymbol{i}$ in a sample with thickness $\boldsymbol{T}$ when it is irradiated by an X ray beam with spectral distribution $\boldsymbol{I_0(E_0)}$:

$$R_i d\Omega_1 d\Omega_2 = d\Omega_1 \frac{d\Omega_2}{4\pi} \frac{\varepsilon(E_i)}{\sin(\psi_1)} \int_{E_0=\phi_{K/L}}^{E_{\max}} W_i \tau_i(E_0) \frac{r_{K/L}-1}{r_{K/L}} \omega_{K/L} f \int_{X=0}^{T} \exp\left[\frac{-\mu(E_0)\rho X}{\sin(\psi_1)}\right] \exp\left[\frac{-\mu(E_i)\rho X}{\sin(\psi_2)}\right] \rho dx I_0(E_0) dE_0 \quad (1)$$

where all of the employed symbols complain the commonly accepted meaning (for reference see he list provided in the X-Ray Spectrometry Journal website).

Expression (1) is integrated by from X=0 to T along the thickness layer and for both solid angles, and can be rewritten as

$$R_i = G \frac{\varepsilon(E_i)}{\sin(\psi_1)} \int_{E_0=\phi_{K/L}}^{E_{\max}} Q_{if}(E_0) \left[\frac{1-\exp(-\rho T\left[\mu(E_0)/\sin(\psi_1) + \mu(E_1)/\sin(\psi_2)\right])}{\mu(E_0)/\sin(\psi_1) + \mu(E_1)/\sin(\psi_2)} \right] I_0(E_0) dE_0 \quad (2)$$

where, $Q_{i,f}(E_0) = W_i \tau_i(E_0) \frac{r_{K/L}-1}{r_{K/L}} \omega_{K/L} f$

and G is a proportional factor taking into account the geometry of the instrumental arrangement.

In the presence of an additional layer covering the sample (figure 1) the expression for the signal arising from a given element $\boldsymbol{i}$ present in the substrate is:

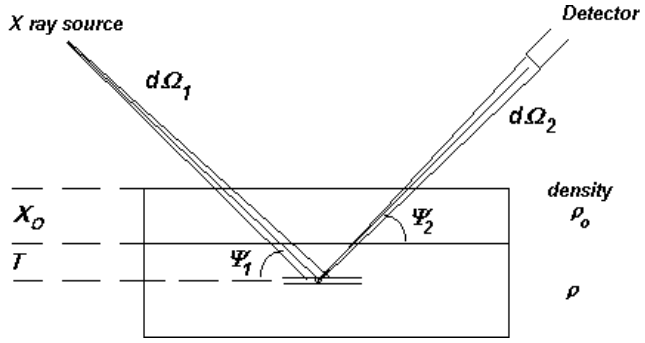

Figure 1. Illustration of the two-layered sample geometry

$$R_i^{und} = G\frac{\varepsilon(E_i)}{\sin(\psi_1)}\int_{E_0=\phi_K}^{E_{\max}} Q_{ij}(E_0)A_{und}A_oI_0(E_0)dE_0 \qquad (3)$$

where

$$A_{und} = \int_{X1=0}^{T} \exp\left[\frac{-\mu(E_0)\rho X_1}{\sin(\psi_1)}\right]\exp\left[\frac{-\mu(E_i)\rho X_1}{\sin(\psi_2)}\right]\rho dX_1 = \left[\frac{1-\exp(-\rho T\left[\mu(E_0)/\sin(\psi_1)+\mu(E_1)/\sin(\psi_2)\right]}{\mu(E_0)/\sin(\psi_1)+\mu(E_1)/\sin(\psi_2)}\right] \quad (4)$$

$$A_o = \exp\left[-\rho_o X_o\left(\mu_o(E_0)/\sin(\psi_1)+\mu_o(E_1)/\sin(\psi_2)\right)\right] \quad (5)$$

The additional term A_o accounts for the attenuation of both the excitation (E_0) and fluorescent radiation (E_i) when traveling across the outer layer with density ρ_o and thickness X_o. Although the expression (3) does not take into account the enhancement of fluorescence radiation i by the fluorescence arising from the outer layer, the coefficient (4) serves to assess its attenuation by the outer layer in a simple way. It is enough to demonstrate whether the fluorescence signal with the largest excited energy arising from the layer beneath the surface is completely absorbed or non significant by evaluating A_o for the maximal possible excitation and fluorescence energies. If $A_o \cong 0$, the measured signal comprises only the contribution of the glaze layer.

In qualitative analysis, pigments were identified by the presence in the measured spectra of high intensity fluorescent peaks corresponding to their main constituent elements. We also explored the spectra measured at different colour spots in an attempt to reveal differences in regard to other elements associated to the main pigment. Several metals were found to be present in cobalt glass pigments [*19*] and to be potential indicators of differences in pigment provenance.

As far as the decoration were done by applying additional coloured layers over the main glaze base, the contribution of the later to the measured spectra from coloured spots was excluded by direct subtracting of counting intensities for each element. Although such procedure is only fair for a qualitative interpretation, the resulting net data are indeed interference free. Further, the fitted areas for accompanying elements were normalized to the major constituent element in the identified pigment, in an attempt to avoid the differences conditioned by uneven amounts of pigment material. The dimensionality of the data sets was reduced by principal component analysis with the aim to reveal the major sources of variability and to simplify the interpretation of the results.

The quantitative analysis of the ground white glaze composition may reveal differences allowing to differentiate the provenance of samples even in an inter-regional scale. Two quantitative methods can be followed to derive the composition of the glaze enamel: a) by experimental determination of the geometric proportionality factor G via measurement of suitable reference materials (Fundamental Parameter Approach) or; b) by normalizing the measured intensities to the intensity of the element with higher concentration (n-1 equations), and assuming that the residual matrix consists of a known element. In both cases, the need of integration over all of the energy distribution of the excitation spectrum $I_0(E_0)$ is of major concern when using X-ray condensing lenses, which substantially modify the original distribution of a conventional X-ray tube.

If the analyzed sample is considered as of being of “infinite thickness” the expression (2) becomes

$$R_i = G\frac{\varepsilon(E_i)}{\sin(\psi_1)} W_i \frac{r_{K/L}-1}{r_{K/L}} \omega_{K/L} f \int_{E_0=\phi_{K/L}}^{E_{max}} \left[\frac{\tau_i(E_0)}{\mu(E_0)/\sin(\psi_1) + \mu(E_1)/\sin(\psi_2)} \right] I_0(E_0) dE_0 \qquad (6)$$

For ***n*** unknown elements, ***(n-1)*** equations can be written normalizing to the equation corresponding to the largest constituent in the sample [W_{max} = max (W_i)].

$$\frac{R_i}{R_{max}} = \frac{\varepsilon(E_i) W_i}{\varepsilon(E_{max}) W_{max}} \frac{(r_{K/L}-1)^j}{(r_{K/L})^j} \frac{(r_{K/L})^{max}}{(r_{K/L}-1)^{max}} \frac{\omega^j_{K/L}}{\omega^{max}_{K/L}} \frac{f_i}{f_{max}} \frac{\int_{E_0=\phi_{K/L}}^{E_{max}} \left[\frac{\tau_i(E_0)}{\mu(E_0)/\sin(\psi_1) + \mu(E_1)/\sin(\psi_2)} \right] I_0(E_0) dE_0}{\int_{E_0=\phi_{K/L}}^{E_{max}} \left[\frac{\tau_{max}(E_0)}{\mu(E_0)/\sin(\psi_1) + \mu(E_{max})/\sin(\psi_2)} \right] I_0(E_0) dE_0} \qquad (7.1)$$

The last needed equation to solve the system is the condition of establishing the total concentration of fluorescent elements:

$$\sum_i W_i = W_F \qquad (7.2)$$

The system of equation is solved by an iterative procedure, starting from an initial set of concentrations defined by the ratio of measured intensities. The quantification of ground glaze composition is still in progress, and the results will be published in a forthcoming paper.

RESULTS.

Evaluation of attenuation correction for the glaze layer.

The Majolica glaze is distinguished by the use of lead oxide to improve the fusion of the glaze and achieving a soft melting at moderate temperatures, and by the addition of tin oxide to produce an opacity and transparence that improved its esthetic value. The proportion of these two components, as well as the type of clay or sand used to conform the glaze paste is supposed to be inherent to each manufacturing center, and was even fixed by guilt regulations and policy. A study of several exponents from the kilns of Manises and Paterna carried out by Olin & Myers [*20*], reported values ranging from 0,7 % to 8,4 % for SnO_2 and from 30,6% to 41,5% for PbO.

A value of the "infinite thickness" ($A_0 \leq 0{,}001$) was calculated for a wide range of concentrations of PbO and SnO_2 (see figure 2), and assuming the residual matrix as being composed solely from SiO_2. The density of the glaze was calculated by simple additive estimation (*21*) and the values for elemental mass attenuation coefficients were taken from Thinh-Leroux tables (*22*). For concentrations of PbO and SnO_2 exceeding 20 % and 1,5 % respectively even a glaze layer as thin as 100 microns will absorb all of the fluorescence that might arise from the underlying ceramic paste. Considering the measured thickness of the analyzed samples (see table 1) it is safe to infer that the measured spectra for all Majolica samples contain information only about the glaze layer.

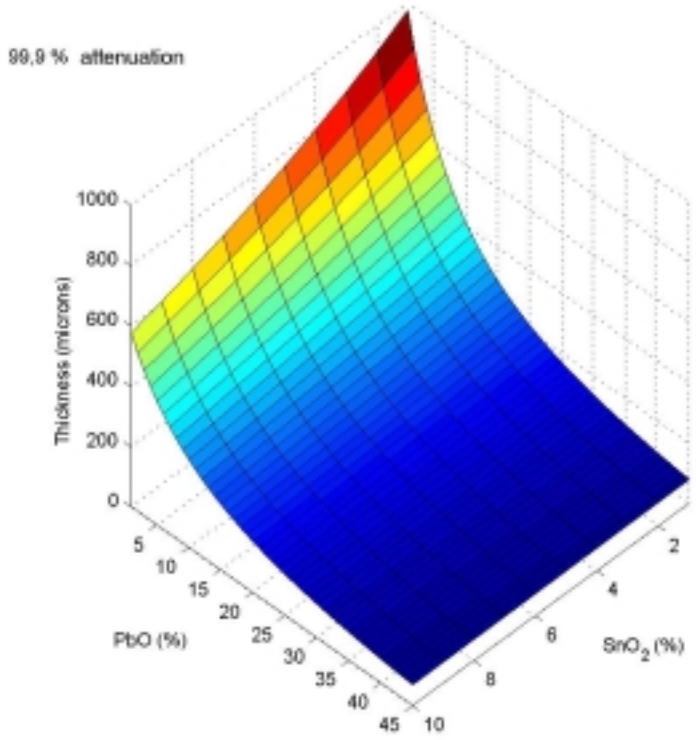

Figure 2 “Infinite” glaze thickness

Qualitative identification of pigments:

The colorful decorations of ceramic artifacts were achieved by the use of different metal oxides, which melt during the firing and changed their hues in a wide diapason of hues. Sometimes, the use of natural minerals and clays was also included in the manufacture practice of different artisans.

Both, surface scanning and spot measurements were carried out, allowing the qualitative identification of the inorganic pigments used for the surface decoration. The spectra were collected during 30 seconds and with a step of 200 microns in automatic scans. Sharp images of the distribution of the elements were obtained, and an example showing the results obtained for a sample of the type Abó Polícromo, decorated with several colours, is given in figure 3.

In general, the blue motifs were identified as resulting from the use of cobalt pigments (cobalt blue or smalt). Principal component analysis of the normalized data resulting from spot measurements showed the main differences between the blue decorations in the analysed Majolica types to be conditioned mainly by the proportion of Fe-K and Ca (see figure 4 and table 2). Higher amounts of Ca were found in the Spanish, Italian and Valley of Mexico types, whereas a larger proportion of Fe, and K differentiated the samples of Puebla. This result corroborate the hypothesis raised by Lister and Lister [*23*] about the probable use of local Co-containing materials by the Puebla potters.

Although black motifs were present only in 6 of the analysed samples and all of them were identified as being prepared with mixtures of black iron and manganese oxides, a sharp distinction was found between the Puebla Polícromo and San Luis Polícromo samples. The figure 5 shows the ordination of the samples in the resulting PC space accounting for 98 % of the variability in the data set.

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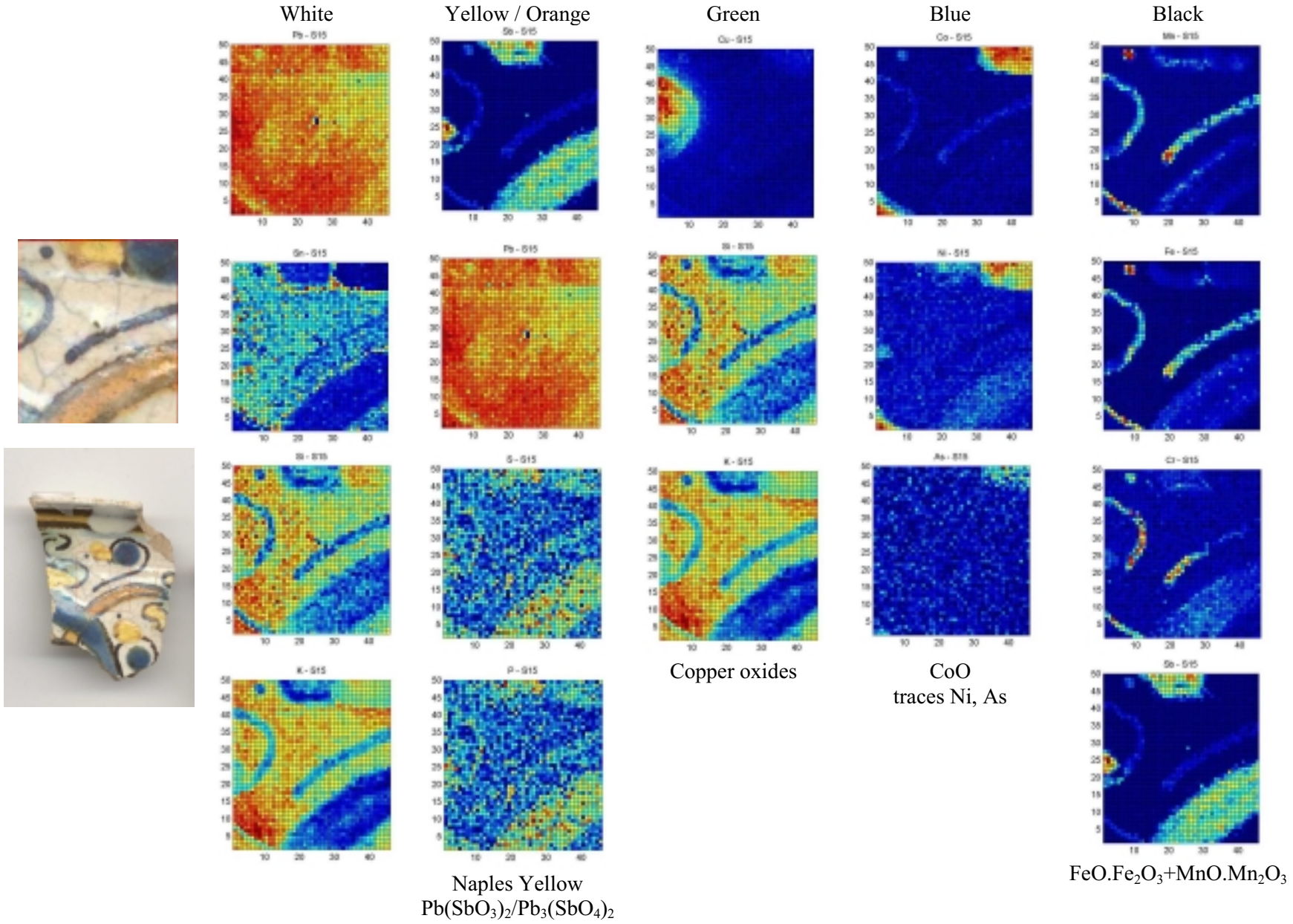

Figure 3. Identification of pigments in a sample of Abó Polícromo

Table 2. Rotated Component Matrix

	Raw Component		Rescaled Component	
	1	2	1	2
FE_NOR	1,433	-0,041	0,997	-0,029
K_NOR	0,678	0,254	0,887	0,333
AS_NOR	0,162	0,034	0,332	0,069
TI_NOR	0,014	0,005	0,260	0,088
CA_NOR	0,173	0,867	0,196	0,978
NI_NOR	-0,040	-0,048	-0,227	-0,273
MN_NOR	-0,005	-0,067	-0,013	-0,184

Notes: Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.

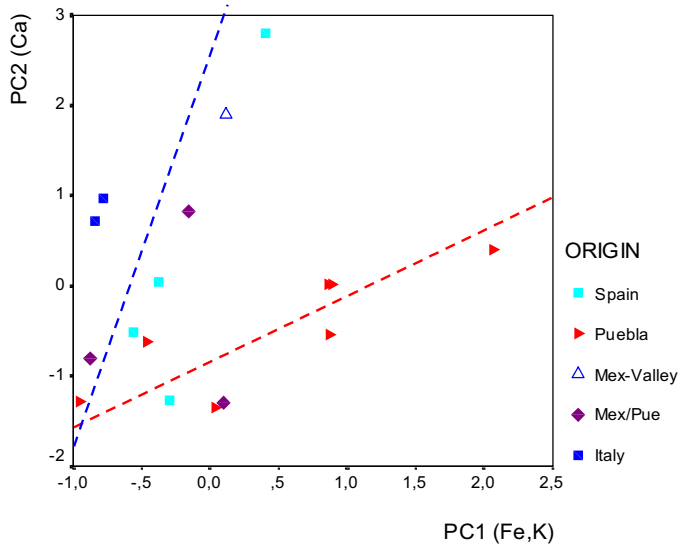

Fig 4 Differences in cobalt blue pigments due to trace elements.

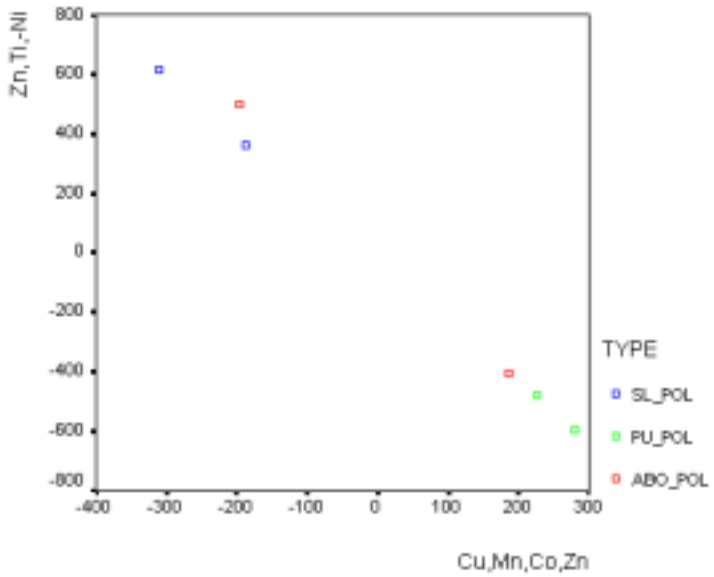

Fig 5 Differences in black pigments due to trace elements.

The green decorations seem to be prepared from Cu oxides. Lighter hue in sample s15 seems achieved by the addition of Zinc and/or Barite, whereas samples s18 and s19 show a more dark hue. Both yellow and orange decorations show the presence of Sb and Pb, and therefore seem to be prepared using Naples Yellow. The preparation of the orange hues was probably performed by the addition of Red Ochre to the Naples Yellow, considering the high intensities of Fe and the presence of other clay-constituent elements in the measured spectra.

CONCLUSIONS:

The work carried out allowed to identify the main materials used for color decoration in several Majolica types. The trace element composition of the blue decoration motifs revealed differences identifying Puebla types. This feature might indicate the use of local or at least different raw materials, when compared to vessels decorated in Spain or Italy. Some differences were also revealed in the composition of the black pigments, showing the presence of Mn containing materials in some cases.

The evaluation of the absorption corrections for a wide range of variations of PbO and SnO_2 proportions in the ground glaze allowed to prove the possibility of a non-destructive quantitative analysis of its composition, which might reveal differences allowing to differentiate the provenance of samples even in an inter-regional scale. The quantification of ground glaze composition is still in progress, and the results will be published in a forthcoming paper.

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