A database for historical pigments through handheld instrumentation

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Abstract – **Portable instrumentation is largely used in archaeometry for in-field measurements at museums and archaeological sites. The historic evolution of pigments is closely related to the technology developments in past cultures and provides relevant clues regarding their knowledge advancement. Here, a systematic study of 26 historical powdered pigments was carried out through a combined handheld instrumentation for X-ray Fluorescence. Chemical identification was carried out through a set of instrumentation produced by different manufacturers. Their performances are compared on the same set of samples to identify best practices for the study of historical pigments. A database of organic and inorganic pigments studied by additional techniques such as Fiber optics Reflectance spectra (FORS), Raman and Fourier Transform Infrared spectroscopy (FT-IR) is under development with the aim to use it further for the interpretation of the results of real case studies.**

I. INTRODUCTION

Pigment identification has an additional value for archaeologists, conservation scientists and art historians. Analysis of pigments can help to act on a painted surface altered over time even give indications on how an artwork is to be conserved, and to identify the ancient materials from those due to fakes and forgeries or associated with past restorations [1].

The energy dispersive X-ray fluorescence (XRF) spectroscopy analysis is a non-destructive technique widely used in Archaeometry, specially devoted to investigate the elemental composition, and can be used for in situ and real-time elemental mapping of historical paintings [2-3]. This technique is based is based on the measurement of the energy and intensity of X-rays emitted during the irradiation of the sample by a primary X-ray beam, causes emission of fluorescent X-rays with discrete energies characteristic of the elements present in the sample [4]. Here, the XRF measurements on a set of 26 ancient powdered pigments by Zecchi store collection [5] are investigated using two different portable handheld XRF spectrometers through two different instrument set-ups. To observe the high discriminating capability of each one instrument to identify the benchmark/chromophores of these historical pigments, a Principal Component Analyses has been used. In the next future, the Fiber optics Reflectance spectra (FORS), the Raman and the Fourier Transform Infrared spectroscopy (FT-IR) will be implemented to design a data base for historical pigments by non-destructive techniques spread the analysis to the entire original data set, composed by a 46 pigments. Each pigment will be characterising by a series of spectroscopic techniques for the foundation of a database accessible to the scientific community. In literature there are similar cases [6] but no chemometric approach has been used to finalise the method.

II. SET-UPS XRF PORTABLE MEASUREMENTS

A set of 26 powered pigments (Table 1), including inorganic (21) and organic (5) ones, from Zecchi store [5] has been analysed by two different portable XRF instrumentations, XRaman spectrometer (XGLab Bruker [7]) and by Tracer III SD Bruker AXS portable spectrometer [8].

Both the XRF spectrometers are characterised by the same target irradiation: a Rhodium Target X-Ray tube but operating at 40 kV and 11 mA (Tracer III), 50 kV and 200 mA (XGLab). Each spectrometer has acquired the spectra in two different ways: for 30 s (Tracer III), 50 s (XGLab tuning the frames at 30 kV and laser power at 20 µA). The detection of fluorescence X-rays is obtained by a 10 mm^2

silicon drift X-Flash detector, allowed the detection of elements with atomic number Z > 11 (Tracer III), large area Silicon Drift X-ray Detector (SDD) with an active area 25 mm^2 and energy resolution <135 eV measured on MnK$_\alpha$ line (5.890eV) for XGLab.

Table 1. Pigment list analysed by XRF instruments.

Pigment	Formula	ID
BLUE		
Azurite	$Cu_3(CO_3)_2(OH)_2$	BLA_T BLA_XG
Indigo	$C_{16}H_{10}N_2O_2$	BLI_T BLI_XG
Lapislazuli	$Na_{8-10}Al_6Si_6O_{24}S_{2-4}$	BLL_T BLL_XG
Smalt	SiO_2,K_2O,Al_2O_3,CoO	BLS_T BLS_XG
WHITE		
White lead	$(PbCO_3)_2{\cdot}Pb(OH)_2$	WL_T WL_XG
White "San Giovanni"	$CaCO_3$	WSG_T WSG_XG
White bone	$Ca_3(PO_4)_2{\cdot}CaCO_3$	WB_T WB_XG
RED		
Cinnabar	HgS	RCR_T RCR_XG
Red Jasper	SiO_2 (+ Fe, O, H, S)	RJ_T RJ_XG
Hematite	Fe_2O_3	RH_T RH_XG
Red coral	$CaCO3 + Fe$	RC_T RC_XG
Red Ercolano	Fe_2O_3	RE_T RE_XG
YELLOW		
Naples Yellow	$Pb_3(SbO_4)_2$	YN_T YN_XG
Giallorino	Pb_2SnO_4 o $PbSn_2\ SiO_7$	YG_T YG_XG
Yellow ochre	$FeO(OH)$	YO_T YO_XG
Schist Earth	$Fe_2O_3 + MnO_2 + nH_2O +$	ES_T

	$Si + Al_2O_3$	ES_XG
Rubia	$C_6H_4\ (CO)_2C_6H_2(OH)_2$	LG_T LG_XG
Shellac	$C_{30}H_{50}O_{11}$	LGU_T LGU_XG
BLACK		
Ivory black	$C, Ca_3(PO4)_2$	BI_T BI_XG
Graphite	C	BG_T BG_XG
Bitumem	$C_{28}H_{16}Cl_8O_8$	BB_T BB_XG
GREEN		
Verdigris	$Cu(CH_3COO)_2$	GCU_T GCU_XG
Green jasper	SiO_2 (+ Fe, O, H, S)	GJ_T GJ_XG
Malachite	$CuCO_3 \cdot Cu(OH)_2$	GM_T GM_XG
Verzino	$C_{16}H_{14}O_5$	GV_T GV_XG
Chrysocolla	$(Cu_{2-x}Al_x)H_2{-}xSi_2O_5(OH)_4{\cdot}nH_2O$	GC_T GC_XG

The pigments are listed according their groping's' colour: "BL" stands for blues, "W" for whites, "R" reds, "Y" for Yellows, "E" for Earth, "L" for lacquers, "B" for blacks, finally "G" for the greens ones. The successive capital letter indicates the name of the pigments. "XG" label stands for XGLab Bruker while "T" for TRACER III spectrometer. Each new ID, reported in the last column, with the capital letter stands for the class of colour belonging.

III. XRF DATA TREATMENT

A total of 23 elements have been identified. Beyond the characteristics 18 benchmarks of a typical colour (Al, Si, P, S, K, Ca, Ti, Mn, Fe, Co, Cu, Zn, As, Sr, As/Pb, Pb, Sn, Cr, of which just Fe, Co, Cu, As, Pb, Sn and Cr are chromophores), there are some elements considered "fixed signal", such as the Ni (Kα 7.46 keV) or Pd (green jasper, verzino, shellac and rubia), or "contaminant signals" or artefacts" found in some pigments. The Ni peak is characteristic of the 17/23 pigments investigated by Tracer III SD Bruker AXS portable spectrometer, as well the signal at 21.2 (Pd). The latter are attributable to internal instrument components. There are also some extra-peaks at 4.4 keV or at 9.2 keV. The XGLab Bruker, at the contrary, even if presents spectra with no signal coming from collimator or other internal part of the instrument

(Fig. 2), is blind to the K spectral features between the 25-28 keV energy range. Indeed, the Kα lines belonging to *Giallorino* (Sn) and Naples Yellow (Sb – see Fig. 1) are absent. On the other hand, the $L\alpha_1$, $L\alpha_2$, $L\beta_1$, $L\beta_2$ and even the $L\gamma$ of the above cited elements are present.
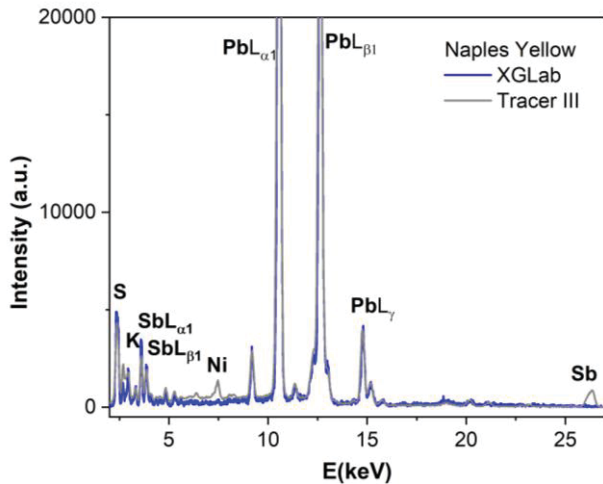

Figure 1. Naples Yellow XRF spectra. The plot shows the YN pigment measured by XGlab (blue line) and Tracer III (grey line) spectrometer.
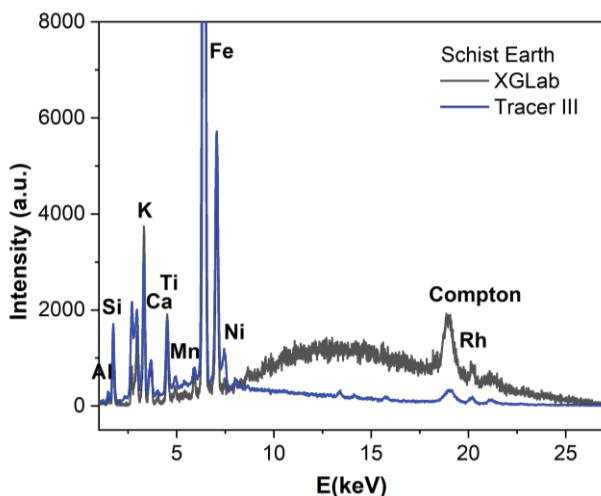

Figure 2. Schist Earth spectra. The plot shows the YN pigment measured by XGlab (blue line) and Tracer III (grey line) spectrometer. The XGlab is able to see Mn fundamental for this type of pigment identification.

Moreover, the XGLab instrument shows the $Mn_{K\alpha}$ peak (Fig. 2), fundamental for the identification of the Schist Earth pigment.

The Compton profile is present for the organic pigments (bitumen, graphite, indigo, both the lacquers and verzino) in both such kind of instruments, a part some exceptions for the XGLab spectrometer (see Fig. 2). The contribute of the Compton, if present has been subtracted to the peak

areas from elements with atomic number Z > 19.

The normalised counts were obtained selecting the net counts of Kα line of each element detected taking into account all the elements detected by both the spectrometers, including the "contaminant signals", except Ar contribute (at 2.96 keV), detected by both the instruments. This to try to understand the difference of the instrument behaviours in terms of sensitivity. Finally, a baseline subtraction has been applied on all raw data.

IV. PRINCIPAL COMPONENT ANALYSIS

A data set matrix was built to import it to the Unscrabler X software (CamoAnalytics [9]) for the multivariate analyses (Algorithm used: SVD, Validation method: Cross validation, Cross validation method: Random with 20 segments). The data set consists of a 52x24 matrix (52 pigments in rows x 23 elements in columns) where for each one pigments the normalised net area peaks are calculated.

The Figure 3 shows the Bi-plot, used to interpret sample properties, a two-dimensional scatter plot or map of scores for two specified components (PCs), with the X-loadings displayed on the same plot. It enables one to interpret sample properties and variable relationships simultaneously. In this case is carried out to observe the distributional correlation analysis of the element with the correspondent elements. The PCA shows two principal components with a 78% and 13% respectively, explaining a 91% of the total explained variance. The majority of the pigments are closed together in the first left quadrant (positive PC2) where the pigments analysed with each one spectrometer well are grouped according to the benchmark leader: Pb for "WL" and "YG", Cu for "GM, "GCU" and "GC", Fe for "RH" and "YO", Ca for "WSG" and "RC" or in case of organic pigments according to the similar chemical structure i.e. ("GV" and "BB"). "RJ" and "RE", analysed by TRACER III, represent an interesting grouping, not only because Fe is involved. This would suggest another hidden variable implied.
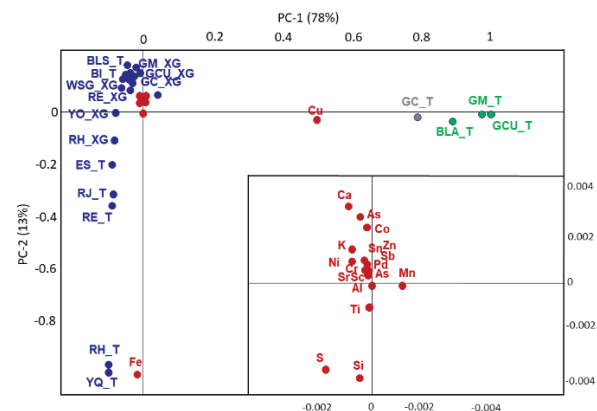

Figure 3. Bi-Plot (point measurements vs. elements reported in red colour) and Sample Grouping Clustering

Analysis on point measurements (reported in green, grey and blue) of the total XRF measurements.

The sample grouping is also obtained to predict the classes belonging amongst pigments. The Sample grouping has been evaluating for 7 number of groups to separate the cluster till three groups. Indeed, it is possible to find three classes of pigments: 15.4% of the pigments (chrysocolla, verdegris, malachite and azurite measured by Tracer spectrometer, respectively grey and green colours) (grey and green colour), spread over the whole region resulting very different from the rest (blue). These pigments are characterized by the Cu chromophore. Among them, there is another distinction: the chrysocolla, the 3.8% of the set total, is a distinct class.

Among the blue group, in the lower quadrant (negative PC2 - Fig. 4), one red and one yellow are grouped together by Fe benchmark. It is interesting to see how "RE" is keeping out from this group even if has the "same" elemental composition specially with the hematite one. Actually the composition of the pigment is unknown because the Zecchi store does not report the formula for all the pigments.

Two additional statistical analyses have been performed: Influence Analysis and Sample Residual. The first one represents two different kinds of outliers. The residual statistics on the ordinate axis describe the sample distance to model, whereas the Leverage and Hotelling's T^2 describe how well the sample (ID) is described by the model.

The Influence (Fig. 4 upper panel) shows two pigments," GJ" and "BLS" (both measured by TRACER III instrument) that are poorly described by the model. However, caution is required that the additional components are predictive and not modelling noise.

The Sample Residuals (Fig. 4 below panel) useful for detecting outlying sample or variable combinations, shows: "GCU_T", "GM_T", "BLA_T", "GC_T", and YO_T, as those with major sample residuals (the list is in decreasing order).
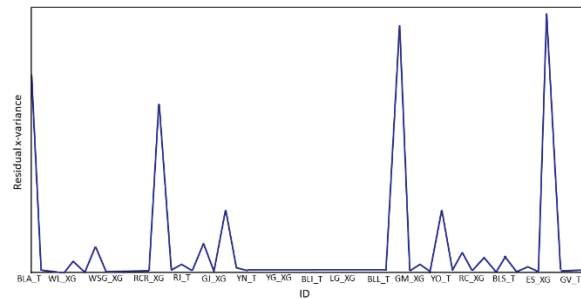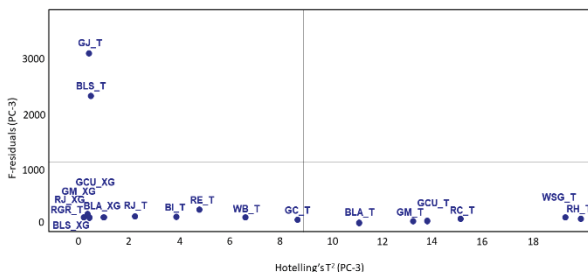

Figure 4. Influence (upper panel) and Sample Residuals (below panel). The first one plot shows the F-residuals vs. Leverage or Hotelling's T^2 statistics. The second one gives information about residuals for all the ID.

An additional PCA has been carried out (with size 52 samples, 18 variables) keeping out all the contribute signals not characteristics (Ni, Pd, Ga, Sc, Sb, Sn) of the pigments under investigation and no changes in the data distribution has been obtained. The influence and the Sample Residuals give also the same contributes.

V. CONCLUSIONS

A database for historical pigments through handheld instrumentations is under development for interpretation of spectra from archaeological and cultural heritage objects. A systematic study of 26 historical powdered pigments has been carried out through two different setups for handheld X-ray Fluorescence. Their performances are compared on the same set of samples to identify best practices for the study of historical pigments.

By comparison of the spectra collected by XGLab and TRACER III spectrometers it has been possible to distinguish the behaviour and the instrumental sensitivity of each instrument. This assumes a particular importance in the study of inorganic and organic pigments composed by a wide range of different elements.

An XRF-PCA combined approach has highlighted how with a systematic approach is possible to develop a procedure useful for the next database developing.

The PCA has revealed some interesting differences in the TRACER III spectrometer in which the there are some hidden information that have to be more investigated. Indeed, two clusters show an additional distinction from the entire dataset do no link with only the benchmark.

The Sample Grouping Analysis shows an additional hidden variable that must be investigate considering the entire data set (46 pigments), together with the others spectroscopic techniques.

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