Art restoration and archaeological material study are inseparately related to scientific investigation and scientific data processing of the information. This reality makes the mentioned field of the most attractive one and a very generous one for professional development.

The e-proceeding, published by INTEGRA NATURA ET OMNIA - INOE, brings together a large part of the contribution to The Third Balkan Symposium on Archaeometry organized in Bucharest on 29 and 30 October 2012, and is following the close related volume that was published by The Kultur Intitute University from Istanbul. The biennial event gathers scientists, conservators, restorers, architects, companies, decision-makers, professors and students involved in projects on all aspects of archaeometry, the application of modern experimental methods and techniques used in investigation, identification and dating of ancient artifacts, as well as related fields of archaeology and art history. Appreciated researchers from multidisciplinary groups, not only from Balkans, have been invited to contribute with keynote speeches and to support the dissemination of recent results. The event continues the tradition of previous symposiums, the first being held in Ohrid - Republic of Macedonia in 2008 and the second in Istanbul – Turkey in 2010.

Special support for present e-proceeding publishing have been received from Dr. eng. Roxana Savastru – general manager of INOE, who was sustaining all initiatives of the Center for Restoration by Optoelectronical Techniques and who permanently, and who generously offers her experience and professional skills.

The editors wish to remind to all participants to The Third Balkan Symposium on Archaeometry that the devoted specialist and initiator of the Balkan Network on Archaeometry – permanently close to each edition organization- is Prof. Prof. Biljana Minceva-Sukarova from Institute of Chemistry, Faculty of Natural Sciences and Mathematics "SS. Cyril & Methoidius" University, Republic of Macedonia.

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Spectral database of Renaissance fresco pigments by LIBS, LIF and colorimetry

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Abstract: A set of about 70 fresco samples made with pigments and binders typical of the Renaissance period in Rome has been characterized by LIBS, LIF and colorimetric measurements in order to build an as much as possible complete database. Aiming at providing the restorers and art historians with a useful tool for the study of ancient frescoes, the samples have been prepared in agreement with the Cennino Cennini recipes for both materials and procedures. Afterward, the obtained spectral data have been processed by means of multivariate analysis methods in order to find the most significant features that can help in fast characterization and recognition of real unknown specimens.

1 INTRODUCTION

The fast analysis and recognition of fresco pigments by optical methods that are fully non destructive or present a very low invasiveness is an important issue. In fact, the more information on surface materials of a fresco are given to the restorers, the better the restoration works can be carried out. In particular, the used pigments, the followed procedure and eventual successive application of consolidants or modern pigments are the most enquired queries that chemists and physicists receive from art historians, archaeologists and restorers for dating, assignment and investigation of ancient artworks.

During the last decade laser techniques, as Laser Induced Breakdown Spectroscopy (LIBS) and Laser Induced Fluorescence (LIF), have been recognized as unique tools for Cultural Heritage study mainly due to the offered advantages relevant to in situ applicability, capability of remote analysis, minimal or absent invasiveness, and as far as LIBS is concerned, possibility to perform stratigraphic analysis with high sensitivity for a very large number of elements, including light atoms [*Osticioli et al 2009, Caneve et al 2010, Colao et al 2007, Colao et al 2008*].

In the present work, a set of about 70 fresco specimens prepared with pigments and binders typical of the Renaissance period in Rome has been characterized by LIBS, LIF and colorimetric measurements in order to build as much as possible a complete database. Aiming at providing the restorers and art historians with a useful tool for the study of ancient frescoes, the samples have been prepared in agreement with the Cennino Cennini recipes for both materials and procedures. In particular, much attention has been paid to the geographic origin and chemical composition of plaster (*intonachino*) and pigment components. LIBS measurements have been carried out at 1064 nm, while LIF ones have been performed using two wavelengths (355 and 266 nm), in order to compare the different induced fluorescence emissions. Afterward, the obtained spectral data have been processed by means of multivariate analysis methods in order to find the most significant features that can help in fast characterization and material recognition of real unknown specimens. The simultaneous use of these various diagnostic techniques is fundamental in order to obtain a sharper interpretation of the results, as for instance, the certain recognition of different pigments related to their chemical classes that a colorimetric response

couldn't definitely give by itself. Moreover, the concurrent optic techniques have given the possibility to extract the various spectral responses either due to the interaction between pigments and binders, or due to the mix of the same pigments at several concentrations.

2 SAMPLES

The knowledge of the materials and the methodologies originally adopted by Michelangelo for the Sistine Chapel frescoes has been necessary to reproduce in laboratory about 70 samples (*Fig. 1*) comparable to real mural paintings belonging to the Renaissance period in Rome.

The mortar constituting the samples has been produced using the slaked lime matured for 48 months, together with the gray pozzolana from Bracciano, in the same Sabatini Volcanic District where Michelangelo provided himself for his frescoes, aimed at the pre-existing tufaceous masonry constituting the Sistine Chapel (Burragato & Gabrielli 1990). The rougher side of a square clay tile, 3 cm long and 0,4 cm thick, has been chosen to prepare the substrate of each sample. The surface has been scratched with a metal file and the entire tile has been wetted to saturation with distilled water. The tile has been covered with the *rinzaffo,* a thin layer that has been made in this case of small splashes of mortar, obtained by mixing 1 part per volume of slaked lime and 3 parts of fine pozzolana, made almost liquid by the addition of distilled water. Afterwards, a layer about 0,5 cm thick, called *arriccio,* has been spread on the dry *rinzaffo*. The *arriccio* has been made of mortar mixed in the proportions of 1 part per volume of slaked lime and 2 parts of pozzolana, characterized approximately by grains of size between 0,5 and 3 mm. Subsequently, the *arriccio,* still humid, has been covered by the ultimate layer, the plaster, originally called *intonachino*, characterized by a thickness of about 5 mm and consisting of 1 part per volume of slaked lime and 2 parts of finer pozzolana, previously sifted until it has reached a final grain size less than 0,5 mm (*Colalucci 1990*).

The chosen pigments include, in addition to the ones laid with successive repaintings, Michelangelo's colour palette, such as: *Bianco San Giovanni* i.e. Lime White; Mars Brown and Yellow; Earth Umbers; Sienna Earths; Yellow and Red Ochres; Green Earths; Ultramarine Natural Blue; Smalt; *Morellone* i.e. ferric oxide; Ivory Black; Vine Black (Gabrielli & Morresi 1990); Cinnabar; Minium (Gabrielli 1994); *Giallolino* i.e. Lead Tin Yellow; Azurite; Red Lake; Malachite (Mancinelli et al. 1992). Most of these pigments, suitable for fresco painting, as the earth pigments, have been dissolved in little distilled water and then spread on the plaster still wet (hence the name of this technique*, a fresco*). Other types of pigment instead, as Minium, Malachite, Copper Resinate (Mancinelli 1994), Flame Black (Conti 1986), Azurite, Red Bole, and Van Dyke Brown require proper binders and have to be spread therefore on dry plaster, previously covered by a layer of the same binder (Cennini 1859; Vasari 1568). Binders used are: linseed oil (Mancinelli et al. 1994); rabbit skin glue (Colalucci 1992); albumen and yolk (Cennini 1859; Vasari 1568).

Both pigments and binders have been prepared in agreement with the Cennino Cennini recipes, proper procedures were followed accordingly. In particular, pigments mix as *Cinabrese*, *Verdaccio* and the preparatory coating for Azurite have been made utilizing the components and the proportions recommended by Cennini (Cennini 1859). Several concentrations have been tested in some cases, as for instance for *Verdaccio*.

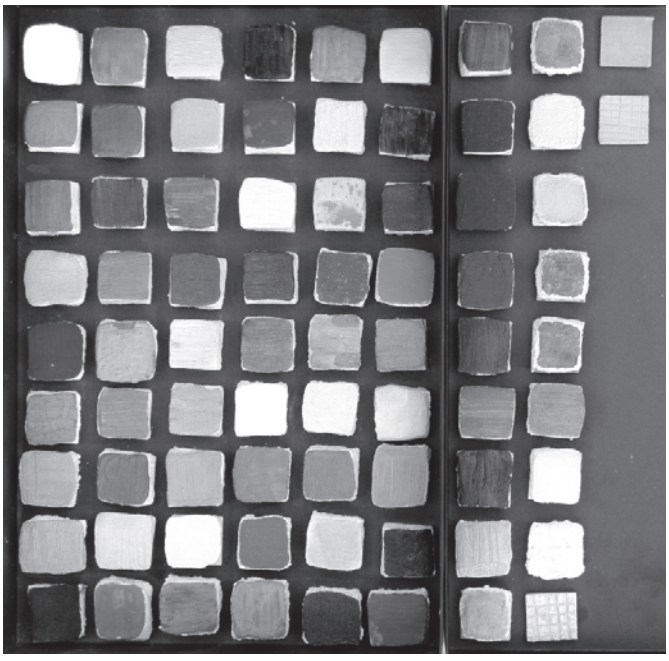

Figure 1: *Fresco samples*

3 EXPERIMENTAL

All samples have been analyzed by LIF, colorimetry and LIBS (LIBS measurements have been carried out after performing other two measure sets). In following sections brief descriptions of the systems used are reported.

3.1 *LIF set up and measurements*

LIF measurements have been carried out with a scanning lidar fluorosensor experimental apparatus developed at the Diagnostic and Metrology Laboratory of the ENEA center of Frascati. The light sources are two compact pulsed, diode pumped, solid state lasers, emitting in the UV @ 355 nm and @266 nm. A set of optics (mirrors, lens and quartz fiber optic) allows to transmit the exciting radiation and to receive the scattering and fluorescence signals from the investigated target.

Two filters (HR @ 355 nm and HR @ 266 nm, respectively) were used to filter out unwanted laser light, nevertheless a portion of the 532 nm still remains in the output laser beam. This residual radiation can be used as an additional channel to evaluate the target reflectance in the green. The coaxial transmitter/receiver scheme was obtained by using a holed mirror, through which the laser beam passes in order to reach the scanning mirror, used also for collecting the radiation emitted by the sample. The latter mirror is actuated by two rotating servo controls operating at high accuracy.

The fluorescence and backscattered radiation is optically driven to a collecting lens and focused at the entrance of a fiber optic, linked to a compact spectrometer. The CCD detector in the spectrometer permits to record the overall spectral emission with 2.5 nm resolution in the range from 200 nm up to 900 nm.

For every sample 16 measurements have been acquired in different points of the surface in order to take into account material and color inhomogeneities. For the acquisition 1 s long, no temporal delay has been applied, while laser energy was set at 1 mJ for the laser at 266 nm, and at 5 mJ for laser at 355 nm.

The measurements have been performed at an average daytime temperature of 26,3°C and relative humidity 50,8 %.

3.2 *Colorimetry measurements*

Colorimetric measurements have been carried out by the ColorLite sph850 spectrophotometer.

The samples have been illuminated with D65 standard illuminant. The measurement geometry was characterized by a circular illumination at 45° and measurement at 0° according to the DIN-Norm 5033. The system has been firstly calibrated with a reference measurement, using the BAM white (certificated by the Federal Institute for Material Research and Testing), in order to determinate the spectral properties of the instrument. The standard spectral properties are subject to change in the course of time, and the results can be hence influenced by strong fluctuating working conditions, as temperature fluctuations. Then, the white calibration has been made at regular intervals during these large series of fresco samples measurements.

The instrument has been furthermore set for performing a single measurement cycle, however repeated 5 times in 5 different surface points, in order to determine the averaged color values of each sample. In order to exactly positioning the probe head onto a chosen point of the sample surface and rotate it during the measurement, the automatic probe head trigger has been also switched off. Moreover, the stray light compensation has been applied, in order to measure any surrounding light in case its head opening was not completely closed due to the sample surface irregularities. Afterwards, the sample of *intonachino* without the ultimate pigment coating has been measured as a standard to be used as reference for every later measurements of the other fresco samples.

The outputs of such measurements consisted in L*a*b* data and in reflectance spectra in the range 400-700 nm with a spectra resolution of 10 nm.

The measurements have been performed at an average daytime temperature of 25,1 °C and a relative humidity of 53,6 %.

3.3 *LIBS set up and measurements*

LIBS experiments have been carried out by a Nd:YAG laser (Handy Quanta System) working at the fundamental wavelength of 1064 nm and a repetition rate of 10 Hz. The pulse duration was of 8

ns for all considered pulses and the total energy was kept below 0.2 J. The plasma emission was collected by suitable receiver optics and the optical signal was carried by an optical fiber to the entrance slit of a 550mm monochromator (Jobin Yvon model TRIAX550) equipped with three different gratings: 3600, 2400, 1200 grooves⁄mm. In the present experiments the 2400 grooves⁄mm was utilized, achieving a resolution of 0.05 nm at 532 nm. A multichannel analyzer based on a gated ICCD, model Insta Spec IV, recorded LIBS spectra; by means of the utilized grating, sections of 10 to 20 nm were acquired depending on the spectral range considered.

The temporal interval for recording emission spectra was selected after measuring kinetic series on a selected pigment sample. Finally, the delay was set at 2000ns and the width at 5000 ns in order to have plasma in LTE conditions. To reduce as much as possible the number of shots on the pigment coatings, only spectral ranges which features interesting to atomic composition have been selected and analyzed. In particular the intervals centered at 235 nm, 253 nm, 286 nm, 326 nm, 354 nm, 388 nm, 399 nm, 501 nm, 535 nm, 604 nm, 611 nm, 692 nm have been chosen. For every sample single shot measurements have been acquired and repeated 15 times in every spectral range selected.

The measurements have been performed at an average daytime temperature of 27,6°C and a relative humidity of 43,8%.

4 DATABASE BUILDING

Thanks to measurements performed by the three techniques presented a spectral database has been built in order to have for every studied pigment as much as possible a complete information on composition and aspect (color). In Table 1 samples studied are listed. For mix the recipe used for the preparation is given. In total 46 pure pigments, 4 binders, 10 mix have been analyzed.

Table 1: *Fresco samples are listed together with specifications on ingredients and preparation. Acronyms used are: LO (linseed oil); RSG (rabbit skin glue); A (albumen); Y (yolk); PPV (part per volume).*

	Sample	Binder	Notes
1	Plaster	-	-
2	Cyprus Ochre	-	-
3	Ultramarine Blue	-	-
4	Cobalt Blue	-	-
5	Egyptian Blue	-	-
6	Brentonico Green Earth	-	-
7	Red Earth	-	-
8	Madder Lake	-	-
9	Raw Sienna Earth	-	-
10	Vine Black	-	-
11	Red Ochre	-	-
12	Preparatory coating for Azurite	-	2 ppv of n. 11 + 1 ppv of n. 10*
13	Morellone	-	-
14	Deep Azurite	RSG	Spread on Morellone coating (see n. 13)
15	Deep Azurite	RSG	Spread on preparatory coating (see n. 12)
16	Lime White paste	-	-
17	Burnt Sienna Earth	-	-
18	Golden Ochre	-	-
19	Ivory Black	-	-
20	Pozzuoli Red	-	-
21	Warm Green Earth	-	-
22	Ultramarine Natural Blue	-	Afghan Lapis Lazuli pigment (first rate quality)
23	Caput Mortuum	-	-
24	Yellow Ochre	-	-
25	English Red	-	-
26	Pale Yellow Ochre	-	-
27	Flame Black	-	-
28	Ercolano Red	-	-
29	Dark Verdaccio Earth	-	-
30	Raw Umber Earth	-	-
31	Lead Tin Yellow	-	-
32	Deep Malachite Green	-	-
33	Mars Black	-	-
34	Mars Yellow	-	-
35	Mars Orange	-	-
36	Mars Red	-	-
37	Mars Brown	-	-
38	Red Bole	A	-
39	Copper Resinate	LO	-
40	Minium	LO	-
41	Van Dyck Brown	LO	-
42	Smalt	-	Spread on preparatory coating composed of 1 ppv slaked lime + 1 ppv smalt
43	Antique Green Earth	-	-
44	Burnt Umber Earth	-	-
45	Natural Sanguine	-	Ground chalk powder
46	Deep Ochre	-	-
47	Deep Cinnabar	-	-
48	Cinabrese	-	2 ppv of n. 11 + 1 ppv of n. 50*
49	Italian Warm Ochre	-	-
50	Lime White powder	-	-
51	Linseed oil	LO	Layer of binder on the plaster
52	Rabbit skin glue	RSG	Layer of binder on the plaster
53	Incarnato	-	1 ppv of n. 11 + 1 ppv of n. 50 + 1 ppv of n. 43

			**
54	Incarnato	-	1 ppv of n. 11 + 1 ppv of n. 50 + 1 ppv of n. 29 **
55	Incarnato	-	1 ppv of n. 11 + 2 ppv of n. 50 + 1 ppv of n. 43 **
56	Incarnato	-	1 ppv of n. 11 + 2 ppv of n. 50 + 1 ppv of n. 29 **
57	Verdaccio	-	1 ppv of n. 46 + 1 ppv of n. 50 + hint of n. 10 + hint of n. 48 *
58	Verdaccio	-	1 ppv of n. 46 + 2 ppv of n. 50 + hint of n. 10 + hint of n. 48
59	Incarnato	-	2 ppv of n. 11 + 6 ppv of n. 50 + 3 ppv of n. 43 **
60	Incarnato	-	1 ppv of n. 11 + 6 ppv of n. 50 + 2 ppv of n. 43 **
61	Albumen	A	Layer of binder on the plaster
62	Deep Malachite Green	A	-
63	Yolk	Y	Layer of binder on the plaster
64	Flame Black	Y	-
65	Flame Black	RSG	-
66	Red Bole	LO	-
67	Smalt	-	Spread on the plaster consisting of a different slaked lime
68	Red Bole	RSG	-
69	Verdaccio	-	1 ppv of n. 46 + 1 ppv of n. 50 + hint of n. 10 + hint of n. 48 *, spread on the plaster consisting of a different slaked lime
70	Red Ochre	-	4 coatings on the plaster

**(Cennini 1859)*
***(Gabrielli 1994)*

For every sample the database is composed by:

- *LIF*: averaged spectrum normalized on the background intensity picked in a range free from emission bands.
- *Colorimetry*: averaged reflectance spectrum, L*a*b* data and XYZ values.
- *LIBS*: presence/absence of the selected emission lines (reported in table 2) as a file containing 0 (absence) and 1 (presence). Intensity values of these lines normalized by background intensity picked in a range free from emission lines.

All data are in ASCII format, easy to consult and to handle. An example is presented below.

```
red ochre  sample id
 0           binder  (0 none, 1 linseed
oil, 2 rabbit glue, 3 albumen, 4 yolk)
   7           number of blocks
   3         channels block 1 (XYZ)
   5         average on block 1
   3         channels block 2 (L*a*b*)
   5         average on block 2
   31        channels      block      3
(reflectance 400-700/10 nm)
   5         average on block 3
   278       channels block 4 (LIF 266
nm 200-890/2.5 nm)
   16        average on block 4
   278       channels block 5 (LIF 355
nm 200-890/2.5 nm)
   16        average on block 5
   -999      channels      block      6
(presence  atomic  lines  0  absence,  1
presence)
   15        average on block 6
   -999      channels      block      7
(intensity atomic lines/bck)
   15        average on block 7
START
13.7512
10.3532
4.1424
ALT
START
38.454
27.922
26.398
ALT
START
3.718
3.724
3.844
3.512
3.622
3.828
3.944
3.916
4.274
…
ALT
```

Table 2: *Database of lines free from overlapping and self-absorbing for LIBS analysis.*

Fe II	26	2343.50	Ca	20	3933.66
Fe II	26	2348.12	Al	13	3944.01
As	33	2349.84	Ti	22	3948.67
Cd	48	2508.91	Al	13	3961.52
Mn	25	2572.76	Ca	20	3968.47
Cd	48	2580.11	Mn	25	4030.76
Sn	50	2863.32	Mn	25	4033.07
Si	14	2881.57	Mn	25	4034.49
Co	27	2886.44	Ti	22	4991.07
Ni	28	2907.45	Ti	22	4999.51

Cu	29	3247.54	Cr	24	5345.81
Sb	51	3267.51	K	19	5359.57
Zn	30	3302.60	Cr	24	5409.79
Cu	29	3524.23	S	16	6052.66
Pb	82	3572.73	Ba	56	6142.10
Mg	12	3832.30	Hg	80	6934.00
Mg	12	3838.29			

5 RESULTS AND DISCUSSION

A very large amount of data is present in the database built. Several interesting information can be extracted from row data. However it has to be noticed that the most important results can be obtained only comparing the three techniques. In fact, for example, LIF spectra give information mainly on used binders. As it is possible to see in figure 2, thanks to the LIF analysis at 2 different wavelengths, rabbit glue, albumen, yolk, linseed oil, can clearly distinguished.

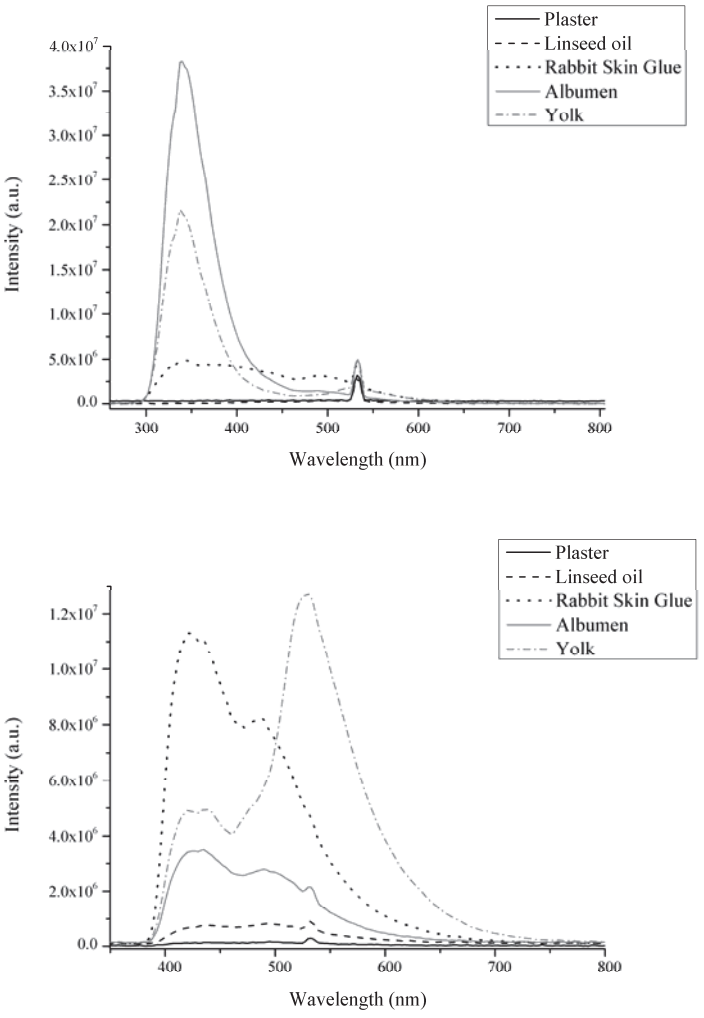

Figure 2: *LIF spectra for plaster and binders on plaster at 266 nm (above) and at 355 nm (below).*

Instead, colorimetric measurements cannot help to this purpose, as well shown in figure 3 for the case of flame dark, while are obviously useful in the classification of the pigments depending on their color Moreover colorimetry can give some interesting information on the used technique, as presented for the flame black in figure 3 and revealed also for other pigments, the reemission intensity is quite different if a pigment has been spread "a fresco" or with a undetermined binder.

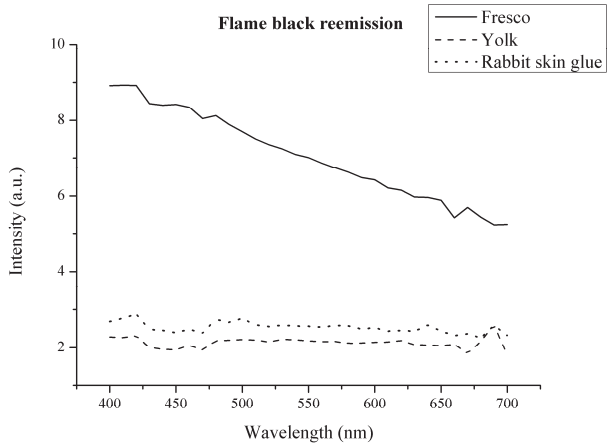

Figure 3: *Reemission spectra by colorimetric measurements on flame black pigment.*

Besides, with LIBS measurements, the pigment recognition can be improved thanks to its ability to perform an elemental analysis of the surface material.

This very huge and etherogeneous quantity of information collected in the database requires, therefore, techniques of data mining to extract useful information and allow unambiguous material recognition. In the last past years the Principal Component Analysis (PCA) has been applied with good and encouraging results to solve problems related to the analysis of complex data sets deriving from many different optical experimental systems [*Baumgartner et al 2000, Sarmiento et al 2011*].

On a selected set of pigments a test of the performance of multivariate analysis has been carried out. In particular PCA has been applied on data relevant to presence/absence of the database lines in LIBS spectra. The first results show the capability of such approach to group the pigments in agreement with their origin (mineral pigments, earths, synthetic, …), and not with similar colors.

In fact, as shown in *Figure 4*, in the plane

individuated by PC1 and PC2, starting from the axes origin, it is possible to notice directions along which groups of pigments with common features are distributed. In the plane individuated by PC2 and PC3 artificial chemical based pigments are even better grouped and isolated. Moreover, in this plane, it can be observed a disposition of the points depending on the importance of the substrate contribution to the relative experimental spectra (presence of mixes, thick or thin pigment layers).

This interesting result confirms the choice of combining in the database the colorimetric measurements and the LIBS data, that seems to be complementary. Finally the database is completed by the presence of LIF spectra, that provide, instead, information on binders and media, not achievable from LIBS and colorimetry.

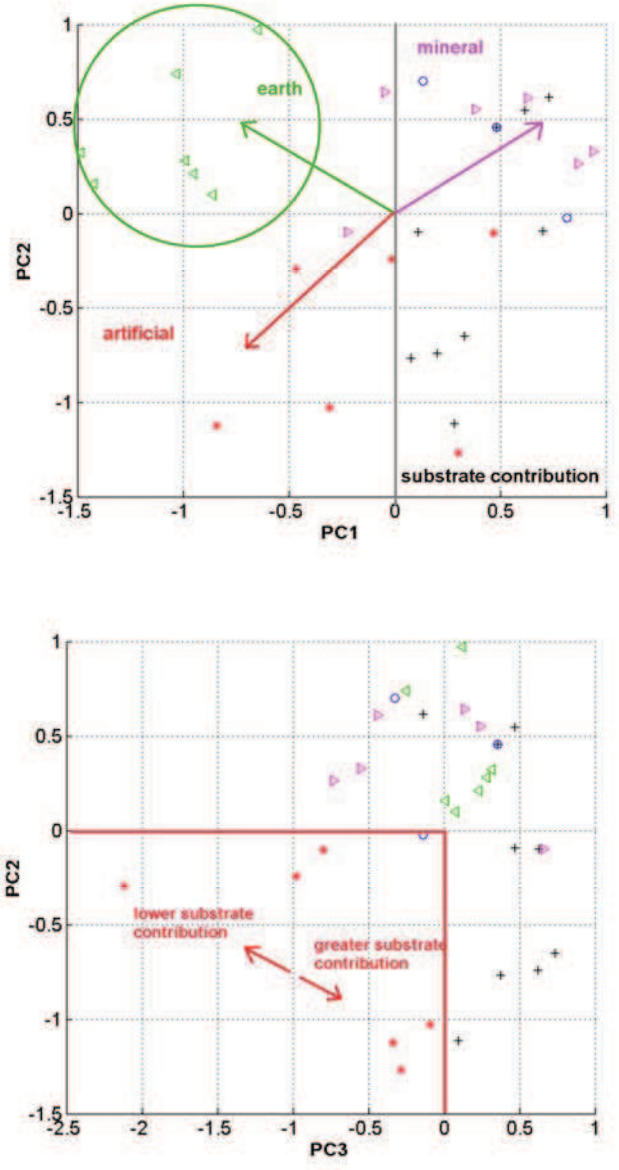

Figure 4: *above PC1 vs PC2, below PC3 vs PC2.*

6 CONCLUSIONS

The results obtained support the choice of combining in the database colorimetric measurements, LIBS data and LIF spectra at two different excitation wavelengths. Such data, in fact, are demonstrated to be complementary among them. Moreover, the results found on applying a multivariate analysis method on data extracted from LIBS spectra prove the necessity and the utility to use multivariate analysis method to correctly interpret experimental data and to find out from these the most important features for clustering and material characterization. In particular these outcomes suggest to use statistical approaches in the analysis of all the acquired data of the database for a smart and quick characterization, that can help in on field analysis of historical frescoes.

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