

EVALUATION OF POTSHERDS FEATURES USING HYPERSENSPECTRAL MAPS GENERATED BY μ -LIBS SCANNER

Stefano Pagnotta^{1,2,3*}, Marco Lezzerini^{1,2}, Asia Botto⁴,
Beatrice Campanella², Stefano Legnaioli², Giulia Lorenzetti²,
Vincenzo Palleschi², Francesco Poggialini^{2,5}

¹ Department of Earth Sciences, University of Pisa (Italy)

² Applied and Laser Spectroscopy Laboratory, Institute of Chemistry of Organometallic Compounds, Research Area of National Research Council, Pisa (Italy)

³ Department of Civilization and Form of Knowledge,
University of Pisa, Pisa (Italy);

⁴ Dipartimento di Chimica e Chimica Industriale, Università di Pisa (Italy);

⁵ Scuola Normale Superiore di Pisa (Italy)

Abstract

The micro-laser induced breakdown spectroscopy (μ -LIBS) technique allows performing fast elemental analyses, without sample preparation and thus making it specifically useful in the analysis of the composition of ancient potsherd. The μ -LIBS instrument is equipped with a microscope and a scanning system allowing to realize small craters (about $\varnothing = 25 \mu\text{m}$) in order to obtain detailed hyperspectral surfaces maps (up to a maximum size of one square centimeter). The data are processed by Self-Organizing Maps (SOMs) method to visualize in 2D representations allowing significant information on the technological features of ceramic samples.

Keywords

Archaeometry, Micro-Laser-Induced Breakdown Spectroscopy, Self-Organizing Maps, Pottery analysis.

Introduction

Hyperspectral imaging technique has been largely applied for remote sensing applications in the agro-alimentary food industry evaluating the food quality or in medical field for the analysis of tumoral tissue (Dale *et al.*, 2013; El Masry, Kamruzzaman, Sun, & Allen, 2012; Grahn & Geladi, 2007; Lorente *et al.*, 2012; Manolakis & Shaw, 2002; Panasyuk, Freeman, & Panasyuk, 2018). The appearance on the market of new and more performing tools that allow to create elementary maps regardless of the type of samples renewed the interest of the technique spreading its application to the several fields (Moncayo *et al.*, 2018). Big data is generally both visually and computationally hard to manage, new methods for dimensional reduction, as artificial neural networks (ANN) approach, can be successfully used for this purpose.

Our goal is to use the SOM, a type of ANN, to treat data collected with a μ -LIBS-scan to realize hyperspectral elemental maps of pottery samples belonging to an advanced Neolithic culture, in order to evaluate and discuss its most significant technical features: such as particular elementary associations, located in small areas of the maps, that could be due to the presence of certain types of skeletal fragments.

Material and Methods

The experimental setup consists of a Modi smart LIBS system (Bertolini *et al.*, 2006) manufactured by Marwan Technology (Pisa) equipped with a Zeiss A1 microscope. The laser ($\lambda=1064\text{nm}$) is focused on the sample surface through a proper 10X objective. The movement of the sample is ensured by two motorized slides produced by Thorlabs that guarantee translation along the X and Y axis, while the Z axis is manually controlled for the preliminary focusing of the sample. The plasma light is collected by a spherical lens and sent to the spectrometer by means of an optical fiber (Figure 1). The entire scanning system is synchronized using a homemade script in LabVIEW 8.5. All data processing was performed through Matlab scripting.

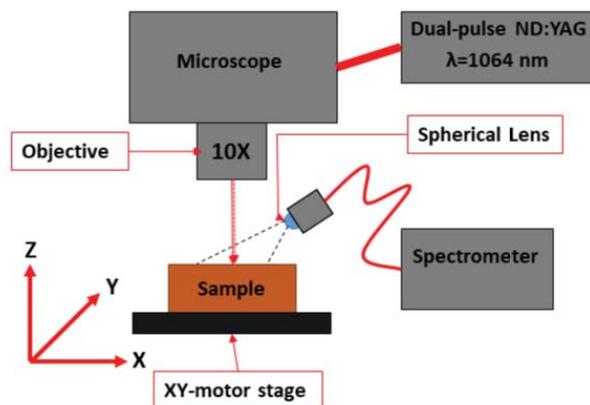


Figure 1 - Experimental setup. The reference system indicates: x=movement of sample from left to right; y=movement from upper to down side; z=focusing distance from the objective lens.

For our study, we used potsherds belonging to a conclusive phase of the Italian Final Neolithic (Figure 2). All the analyzed samples come from archeological sites in Abruzzo (Italy) which are coherent from a cultural and chronological point of view. The fragments come from a homogeneous fine-texture pottery class that has black gloss surfaces, sometimes with a metallic appearance. From a technological point of view, these classes testify an important passage from domestic to increasingly specialized productions attesting a precise knowledge of materials and manufacturing techniques. For the analysis of the negatives of the thin sections were used, and the scans were carried out on the side-face of the ceramic slices.

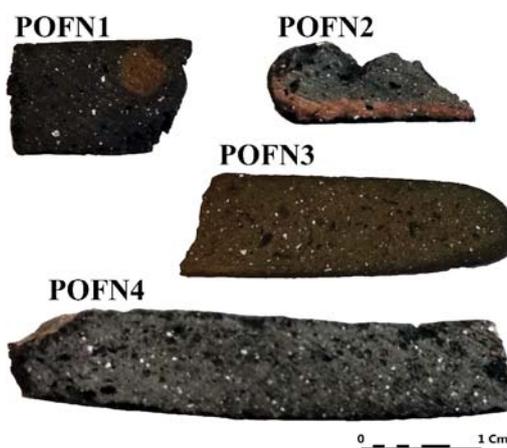
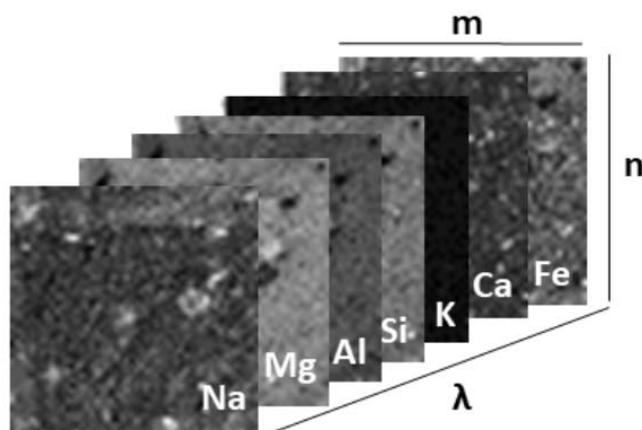


Figure 2 - Analyzed samples.

The micro-LIBS maps acquisition procedure has been described previously (Bertolini *et al.*, 2006; Pagnotta *et al.*, 2017; Pagnotta, Legnaioli, *et al.*, 2018; Pagnotta, Lezzerini, *et al.*, 2018; Schiavo *et al.*, 2016). Four spectral datasets, one for each sample, have been prepared. Each one represents a hyperspectral cube ($m \times n \times z$), where m and n are the number of the single LIBS shots along the sample surface, and z is related to the 3533 values of the LIBS signal intensity at different wavelengths. To reduce the data size, only the lines associated with the elements of interest have been selected: Na, Mg, Al, Si, K, Ca and Fe (Figure 3).



Na	Mg	Al	Si	K	Ca	Fe
819.48nm	279.55nm	309.24nm	288.16nm	766.5nm	422.68nm	538.72nm

Figure 3 - 2D maps of the elements selected for the analyses (Na, Mg, Al, Si, K, Ca and Fe).

The reduced cubes belong to a dimensional space still too large (R^7) to be easily reproduced. The main drawback is the possibility to use the 3 color channels (Figure 4). The basic approach is building a false color image representing the three most representative elements for the analysis.

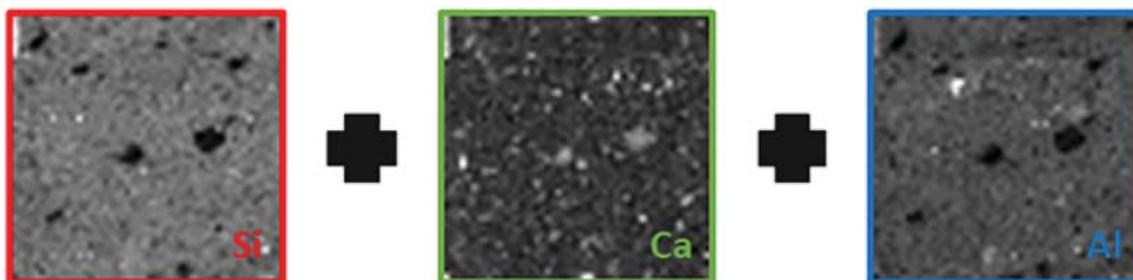


Figure 4 - Elemental RGB maps set-up (sample POFN2).

In Figure 5 different approaches are shown regarding the specific mineral species to be identified: from bottom to up, the first row shows the main chemical elements indicating the presence of plagioclases (Na = red, Al = green and Ca = blue); the second one refers to the chemical elements useful to individuate the presence of spinel phases (Mg/Al) and carbonate phases (Mg = red, Al = green and Ca = blue) and, the last ones, the characteristic elements of the clayey material (Si = red, Al = green, Ca = blue).

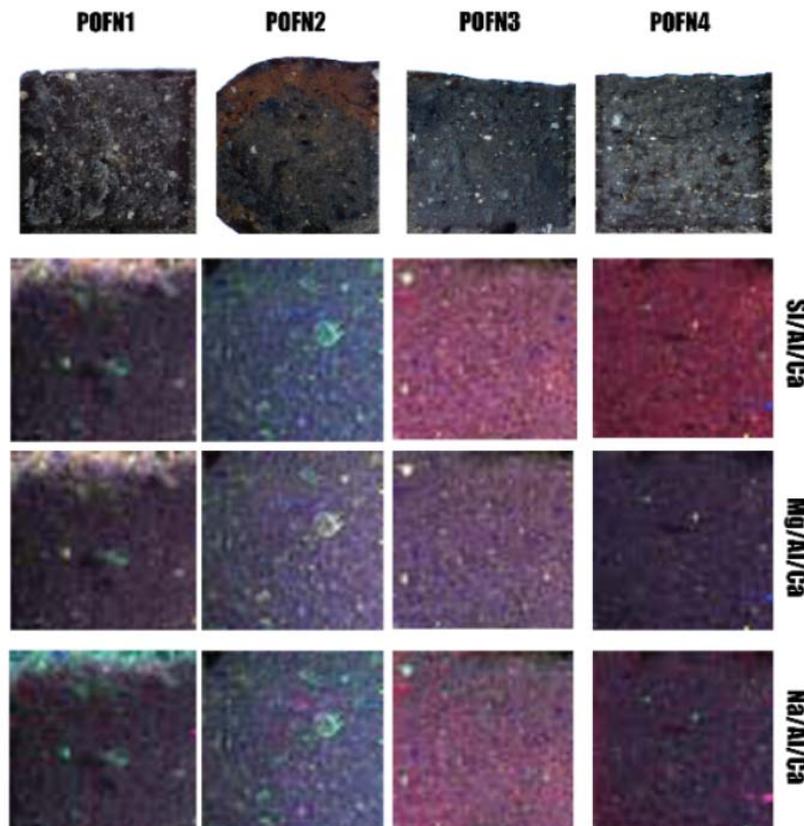


Figure 5 - False color maps realized with a different group of three elements according to the specific mineralogical information to point out.

From the single maps, it is clear that the samples exhibit a strong inhomogeneity. In order to better display all the possible information, the method already proposed by Pagnotta *et al.* (Pagnotta, Lezzerini, *et al.*, 2018) appears particularly suitable. A Kohonen SOM network (Kohonen, 1990, 1998) was built using the seven elementary maps as input; the optimized procedure allowed for four outputs, called segments (Figure 6).

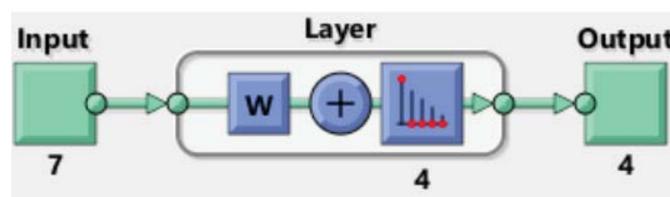


Figure 6 - Structure of the Self-Organized Map for the analyzed samples as provided by the MATLAB ANN tool.

In Table 1 the obtained four outputs for each sample are shown. Each segment may be associated with a specific mineralogical class. In this way it is also possible to carry out quantitative analysis based on standard-less methods such as the Calibration-Free (CF-LIBS) [11]–[13], in order to define its composition. The spectra relative to each segment were extracted and averaged. Since each SOM network is trained on a single sample, it is not possible to directly compare the results between different samples, so Seg. 1 for sample 1 has a different meaning with respect of Seg. 1 for, for instance, sample 2 or 3, etc...

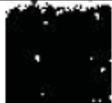
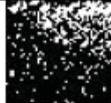
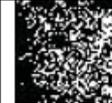
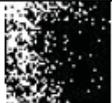
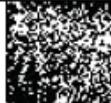
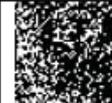
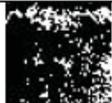
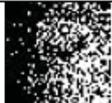
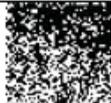
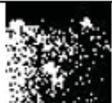
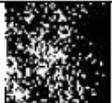
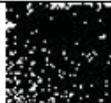
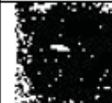
	POFN1	POFN2	POFN3	POFN4
Seg.1				
	10.04%	18.64%	13.8%	30.16%
Seg.2				
	43.96%	25.12%	36%	30.68%
Seg.3				
	18.2%	32.64%	40.44%	26.56%
Seg.4				
	27.8%	23.6%	9.76%	12.6%

Table 1 - SOM segments for each analyzed sample, with a relative percentage of the area in respect to the total scanned area.

Results and Discussion

The study of the false colors maps allows to easily identify the skeletal fraction and the matrix of the individual potsherds. The fraction probably containing carbonate phases is widespread with different size and angled edges in all fragments.

In the POFN1 sample, it is possible to distinguish a thin superficial layer probably constituted by the same clayey material of the bulk, differing from it only for a greater purification (something that we can identify as “chamotte”). In the other samples, where a metallic black gloss surfaces are still present (due to the similar surface aspect to the other), this layer is not detectable in the maps. The Si/Al/Ca maps of POFN3 and POFN4 appear particularly reddish testifying a widespread presence of silicates. In the Mg/Al/Ca maps, instead, the shade tends to magenta (red + blue) showing the dispersion of the carbonates inside the ceramic body, while the presence of small yellowish spots may indicate the presence of spinels. Similarly, small yellow dots in the Na/Al/Ca maps may highlight the existence of plagioclases, while the cyan areas (blue + green) confirm the presence of an enrichment in silico-aluminates.

The quantitative analysis confirms the qualitatively observations (Table 2, Table 3, Table 4, Table 5). Assuming that the segment with the greater percentage (in bold) represents the matrix of the ceramic, samples POFN3 and POFN4 are quite similar, while POFN2 is substantially different, POFN1 seems to be a mixture, although macroscopically all of them show the same features of the other fragments. The results of these preliminary analyses carried out on a limited number of samples show that for a ceramic class of similar appearance, there are still different ways of realization, starting from different “recipes”, due to a not yet standardized production process that will be typical of the subsequent Neolithic phase.

	Seg.1	Seg.2	Seg.3	Seg.4
Al	25.7	25.7	25.3	24.2
Ca	5.7	9.4	8.3	10.3
Na	0.3	0.6	0.5	0.6
Mg	0.8	0.8	0.8	0.8
Fe	35.8	32.1	35.6	39.2
K	1.4	2.7	2.2	3.1
Si	30.3	28.1	27.3	24.2

Table 2 - Elemental chemical composition (wt.%) of the four segments in sample POFN1 map.

	Seg.1	Seg.2	Seg.3	Seg.4
Al	12.4	12.5	12.8	11.5
Ca	4.8	4.6	5.1	5
Na	0.2	0.3	0.2	0.2
Mg	0.3	0.2	0.3	0.2
Fe	68	67.7	67.8	70.2
K	0.7	0.9	0.8	0.9
Si	15.5	13.8	13	12

Table 3 - Elemental chemical composition (wt.%) of the four segments in sample POFN2 map.

	<i>Seg.1</i>	<i>Seg.2</i>	<i>Seg.3</i>	<i>Seg.4</i>
<i>Al</i>	<i>24.7</i>	<i>32.1</i>	<i>35.5</i>	<i>31</i>
<i>Ca</i>	<i>6.2</i>	<i>8.2</i>	<i>9</i>	<i>9.8</i>
<i>Na</i>	<i>0.23</i>	<i>0.4</i>	<i>0.4</i>	<i>0.5</i>
<i>Mg</i>	<i>0.9</i>	<i>1.2</i>	<i>1.2</i>	<i>1.2</i>
<i>Fe</i>	<i>36.4</i>	<i>15.9</i>	<i>11.6</i>	<i>15.7</i>
<i>K</i>	<i>1</i>	<i>1.4</i>	<i>1.7</i>	<i>1.8</i>
<i>Si</i>	<i>30.5</i>	<i>40.8</i>	<i>40.6</i>	<i>39.9</i>

Table 4 - Elemental chemical composition (wt.%) of the four segments in sample POFN3 map.

	<i>Seg.1</i>	<i>Seg.2</i>	<i>Seg.3</i>	<i>Seg.4</i>
<i>Al</i>	<i>30.7</i>	<i>30.3</i>	<i>25.9</i>	<i>33.7</i>
<i>Ca</i>	<i>6.9</i>	<i>7.4</i>	<i>6</i>	<i>11</i>
<i>Na</i>	<i>0.3</i>	<i>0.3</i>	<i>0.3</i>	<i>0.5</i>
<i>Mg</i>	<i>1.1</i>	<i>1</i>	<i>0.9</i>	<i>1.2</i>
<i>Fe</i>	<i>21.1</i>	<i>23.7</i>	<i>32.4</i>	<i>10</i>
<i>K</i>	<i>1.1</i>	<i>1.3</i>	<i>1</i>	<i>1.8</i>
<i>Si</i>	<i>39.2</i>	<i>35.8</i>	<i>33.4</i>	<i>41.8</i>

Table 5 - Elemental chemical composition (wt.%) of the four segments in sample POFN4 map.

Although macroscopically all the ceramic fragments belong to the same archeological class (fine ceramics with glossy black surfaces), only in the sample-POFN1 is clearly detectable the presence of a surface layer of purified clay which, once cooked, confers this characteristic aspect. Moreover, the LIBS analyses reveal that the composition of the ceramic matrix is not the same.

Conclusion

The elemental maps obtained from a scanning micro-LIBS system and processed by Self-Organizing Maps (SOMs) method can provide valuable results with inhomogeneous matrices. In the case of ceramic materials, this approach allows to identify features that can provide important information about the manufacturing technology. We can automatically calculate the percentage of the scanned area occupied by a single cluster and identify the chemical composition. The segmentation of the scanned surfaces reduces the dimension of the data set offering the possibility to conduct also quantitative analysis for each recognized cluster. In this particular case it has been possible to understand that even in the case of a homogeneous class of artifacts with similar macroscopic characteristics, the "recipes" of realization are very different in accordance with the tendency of the final phases of the Neolithic in which there is a tendency to maintain an identity, probably at a domestic level, in the creation of objects with a very standardized appearance.

References

- Bertolini, A., Carelli, G., Francesconi, F., Francesconi, M., Marchesini, L., Marsili, P., ... Salvetti, A. (2006). Modi: A new mobile instrument for in situ double-pulse LIBS analysis. In *Analytical and Bioanalytical Chemistry* (Vol. 385, pp. 240–247). <https://doi.org/10.1007/s00216-006-0413-6>
- Dale, L. M., Thewis, A., Boudry, C., Rotar, I., Dardenne, P., Baeten, V., & Pierna, J. A. F. (2013). Hyperspectral imaging applications in agriculture and agro-food product quality and safety control: a review. *Applied Spectroscopy Reviews*, 48(2), 142–159.
- El Masry, G., Kamruzzaman, M., Sun, D.-W., & Allen, P. (2012). Principles and applications of hyperspectral imaging in quality evaluation of agro-food products: a review. *Critical Reviews in Food Science and Nutrition*, 52(11), 999–1023.
- Grahn, H., & Geladi, P. (2007). *Techniques and applications of hyperspectral image analysis*. John Wiley & Sons.
- Kohonen, T. (1990). The self-organizing map. *Proceedings of the IEEE*, 78(9), 1464–1480.
- Kohonen, T. (1998). The self-organizing map. *Neurocomputing*, 21(1), 1–6.
- Lorente, D., Aleixos, N., Gómez-Sanchis, J., Cubero, S., García-Navarrete, O. L., & Blasco, J. (2012). Recent advances and applications of hyperspectral imaging for fruit and vegetable quality assessment. *Food and Bioprocess Technology*, 5(4), 1121–1142.
- Manolakis, D., & Shaw, G. (2002). Detection algorithms for hyperspectral imaging applications. *IEEE Signal Processing Magazine*, 19(1), 29–43.
- Moncayo, S., Duponchel, L., Panczer, G., Trichard, F., Bousquet, B., Pelascini, F., & Motto-Ros, V. (2018). Exploration of megapixel hyperspectral LIBS images using Principal Component Analysis. *Journal of Analytical Atomic Spectrometry*.
- Pagnotta, S., Legnaioli, S., Campanella, B., Grifoni, E., Lezzerini, M., Lorenzetti, G., ... Raneri, S. (2018). Micro-chemical evaluation of ancient potsherds by μ -LIBS scanning on thin section negatives. *Mediterranean Archaeology and Archaeometry*, 18(5), 171–178. <https://doi.org/10.5281/zenodo.1285906>

Pagnotta, S., Lezzerini, M., Campanella, B., Gallelo, G., Grifoni, E., Legnaioli, S., ... Palleschi, V. (2018). Fast quantitative elemental mapping of highly inhomogeneous materials by micro-Laser-Induced Breakdown Spectroscopy. *Spectrochimica Acta - Part B Atomic Spectroscopy*, 146. <https://doi.org/10.1016/j.sab.2018.04.018>

Pagnotta, S., Lezzerini, M., Ripoll-Seguer, L., Hidalgo, M., Grifoni, E., Legnaioli, S., ... Palleschi, V. (2017). Micro-Laser-Induced Breakdown Spectroscopy (Micro-LIBS) Study on Ancient Roman Mortars. *Applied Spectroscopy*, 71(4), 721–727.

Panasyuk, S. V, Freeman, J., & Panasyuk, A. (2018, May 3). Medical hyperspectral imaging for evaluation of tissue and tumor. Google Patents.

Schiavo, C., Menichetti, L., Grifoni, E., Legnaioli, S., Lorenzetti, G., Poggialini, F., ... Palleschi, V. (2016). High-resolution three-dimensional compositional imaging by double-pulse laser-induced breakdown spectroscopy. *Journal of Instrumentation*, 11(08), C08002.

Acknowledgments

The authors thank the Soprintendenza Archeologia, Belle Arti e Paesaggio dell’Abruzzo and the Department of Civilization and Forms of Knowledge of the University of Pisa, chair of Prehistory for the availability of study samples.

This work has been supported by MAECI in the framework of Italian Serbian bilateral project (PGR00793).

Authors' Curriculum Vitae

Stefano Pagnotta

2013 Master Degree in Archaeology at University of Pisa; Ph.D. candidate in Earth Sciences “Regional Program (Tuscany)” University of Florence, Pisa and Siena. “Cultore della Materia” in Archaeology at University of Pisa.

2013-2018 scholarship at ICCOM-CNR in Pisa, actually research grant at ICCOM-CNR in Pisa. Co-author of more than 40 papers on international peer-review journals.

Contact: stefanopagnotta@yahoo.it

Marco Lezzerini

In Earth Sciences (University of Pisa), associate professor at Earth Sciences (University of Pisa). Head of the XRF Laboratory, University of Pisa, Department of Earth Sciences. Head of the Applied Mineralogy Laboratory, University of Pisa, Department of Earth Sciences. He is lecturer in Earth Sciences for Cultural Heritage, Applied Petrology and Environmental Mineralogy at the University of Pisa. Co-author of more than 100 papers on international peer-review journals.

Contact: marco.lezzerini@unipi.it

Asia Botto

2018 Master Degree in Chemistry at University of Pisa. Co-author of 2 papers on international peer-review journals.

Contact: asia.botto@gmail.com

Beatrice Campanella

Master Degree in Chemistry at the University of Pisa in 2013; .Ph.D. Degree in Chemical Sciences at the University of Pisa in 2016.

"Cultore della materia" in analytical Chemistry at University of Pisa. Visiting scientist at National Research Council - Measurement Science and Standards (Ottawa, Canada) from April 2015 to August 2015. "Menzione d'onore" (Cultural Heritage sector) - Conferenza del Dipartimento di Scienze Chimiche e Tecnologie dei Materiali (24-26 settembre, Assisi). Premio Ambrogio Mazzucotelli - Incontri di Spettroscopia Analitica (29 maggio - 1 giugno, Cagliari). Co-author of more than 30 papers on international peer-review journals.

Contact: b.campanella89@gmail.com

Stefano Legnaioli

2002 Degree in Physics at the University of Pisa; 2006 Ph.D. in Chemical Sciences at the University of Florence; 2011 Master degree on Innovation and Knowledge Transfer (MIT) at the School of Management MIP, Politecnico of Milano.

2002-2008 fellow at the IPCF-CNR; 2008-2012 Fixed-term Researcher at ICCOM; since 2012 Researcher at ICCOM (Pisa). Co-author of more than 70 papers in international peer-review journals.

Contact: s.legnaioli@pi.iccom.cnr.it

Lorenzetti Giulia

Master degree in Science for Cultural Heritage at University of Florence, with a thesis on Confocal Raman Spectroscopy. Since February 2009 Ph.D. student in Science of Cultural Heritage Conservation at University of Florence, in collaboration with ICCOM – CNR in Pisa. Co-author of more than 65 papers in international peer-review journals.

Contact: a_lorenzetti@hotmail.com

Vincenzo Palleschi

Physicist, Senior Researcher at the Institute of Chemistry of Organometallic Compounds and Head of the Applied and Laser Spectroscopy Laboratory at Research Area of CNR in Pisa (Italy). Co-author of more than 160 papers in international peer-review journals.

Contact: vincenzo.palleschi@cnr.it

Poggialini Francesco

Master Degree in Chemistry at University of Pisa, Ph.D. student in Chemistry at Scuola Normale Superiore of Pisa. Co-author of more than 15 papers in international peer-review journals.

Contact: francesco.poggialini@gmail.com