

## Research Article

# Spectroscopic Techniques Applied to the Study of Italian Painted Neolithic Potteries

Lucia Angeli,<sup>1</sup> Claudio Arias,<sup>1</sup> Gabriele Cristoforetti,<sup>2</sup> Cristina Fabbri,<sup>1</sup> Stefano Legnaioli,<sup>2</sup> Vincenzo Palleschi,<sup>2</sup> Giovanna Radi,<sup>1</sup> Azenio Salvetti,<sup>2</sup> and Elisabetta Tognoni<sup>2</sup>

<sup>1</sup>Department of Archaeological Science, University of Pisa, 56126 Pisa, Italy

<sup>2</sup>Institute for Chemical and Physical Processes, National Research Council, 56124 Pisa, Italy

Received 15 September 2006; Revised 6 November 2006; Accepted 6 November 2006

Recommended by Marta Castillejo

In the field of cultural heritage, the study of the materials used by the artist is useful both for the knowledge of the artwork and for conservation and restoring interventions. In this communication, we present results of some decorations analysis obtained by the use of two complementary laser techniques: micro-LIBS and micro-Raman spectroscopy. With both techniques it is possible to operate in a practically nondestructive way on the artwork itself, without sampling or pretreatment. Micro-Raman spectroscopy gives information on the molecular structure of the pigments used, while micro-LIBS can give quantitative information about the elemental composition of the same materials. In this paper, qualitative results are reported obtained on the study of some Neolithic potteries coming from the archaeological site of Trasano (Matera); the fragments show decorations in different colors, red, black, and white. The aim of the study was detecting whether the colored decorations were made by using added pigments or came from the manufacturing process.

Copyright © 2006 Lucia Angeli et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

## 1. INTRODUCTION

The determination of the composition of the pigments used in paintings, frescoes, ceramics, and other painted artworks is useful both for the knowledge of the artwork and for planning for the proper conservation and restoring interventions. In many situations, the information on the materials under study must be obtained *in situ*, in short times and without compromising the integrity of the artwork; these constraints have made interesting the use of laser techniques for the analysis of painted artworks in cultural heritage [1, 2]. The complexity of the problems involved in this kind of applications, linked in particular to the large variety of the materials used and their possible degradation processes does not permit to determine a specific technique or a standard analytical procedure. In this communication, we present some results obtained by the use of two complementary laser techniques: micro-LIBS and micro-Raman spectroscopy; in particular, the micro-Raman analysis can give mainly qualitative information about the material's molecular structure, whilst the LIBS technique permits also quantitative albeit elemental measurements [3–6]. Moreover, the Raman microscopy is very selective, even if the Raman signal is not too high and

in competition with the fluorescence phenomenon, particularly in the case of pigments or organic binding media [7, 8]. In recent years, several groups have proposed the use of laser induced breakdown spectroscopy (LIBS) as a technique capable of giving information on the pigment compositions with minimal damage of the artwork [9–11]. However, until the development of quantitative methods for accurate elemental analysis [9], the LIBS technique was hardly competitive with other methods for quantitative analysis of the samples; a new approach to LIBS spectroscopy, developed by the Applied Laser Spectroscopy Team at IPCF-CNR (Pisa), has re-proposed this technique as a viable technique for the self-calibrated, precise quantitative analysis of pigments used in cultural heritage. Moreover, we have also demonstrated the possibility of obtaining micrometric resolutions ( $\mu$ -LIBS) in LIBS analysis of paintings, reducing the surface damages at minimal levels [12, 13].

## 2. EXPERIMENTAL

The experimental set-up used for the micro-LIBS measurements on the ceramic samples is sketched in Figure 1.

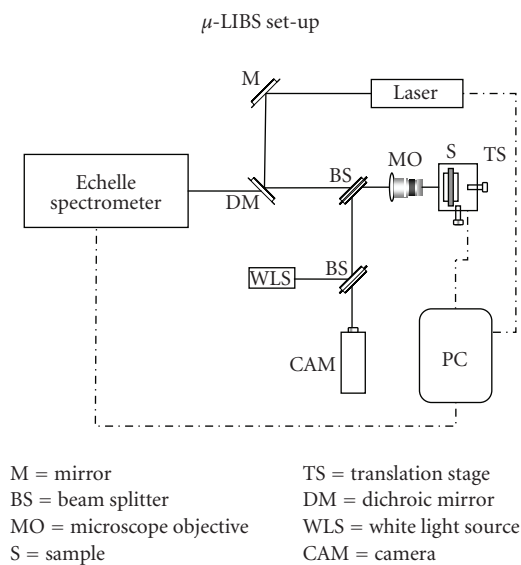
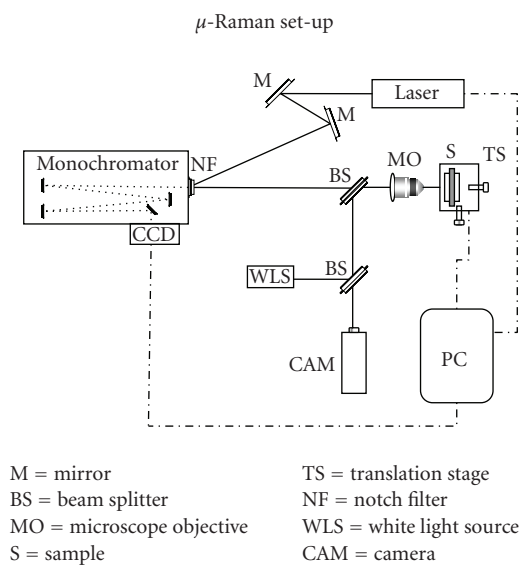
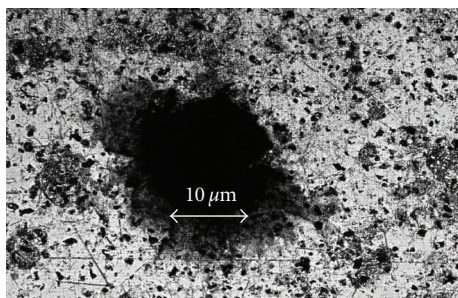
FIGURE 1:  $\mu$ -LIBS experimental setup.FIGURE 3:  $\mu$ -Raman experimental setup.

FIGURE 2: Computer-enhanced enlargement of the crater produced by the laser on the surface.

The laser beam is focussed on the sample surface using a microscope objective, and the signal is taken on axis through the same objective. An optical digital microscope allows for the visual inspection during the measurement; the sample is mounted on a three-axis motorized stage, controlled by a personal computer, for adjustment of the focusing position. The laser source is an Nd : YAG pulsed laser, operating at 1064 nm, which delivers about 10 mJ on the sample surface, in 8 nanoseconds. The spatial lateral resolution of the LIBS measurements corresponds to the dimensions of the microcrater left by the laser on the sample surface. The same dimensions are also a measurement of the damage induced on the pigment. A computer-enhanced enlargement of a typical laser crater is shown in Figure 2; its diameter does not exceed 10 microns, which makes it practically invisible at naked eye. The reduced size of the crater also allows for a high spatial resolution of the LIBS analysis.

The LIBS spectral signal is detected using an Echelle spectrometer + iCCD camera, which provides the whole time-resolved NUV-NIR spectrum in a single laser shot. A com-

puter controls the whole measurement process; dedicated software allows to perform surface scanning, spectral averages, and acquisition of the spectra. In typical experimental conditions, the micro-LIBS spectra are taken in a single laser shot, from 300 nanoseconds to 2 microseconds after the laser pulse and using a measuring gate ranging from a few ns to 1 or 2 microseconds, depending on the laser characteristics (e.g., a faster signal decrease using a UV instead of a near IR exciting laser) [14]. The LIBS spectra are analyzed with proprietary software, developed at IPCF, which implements the Calibration-free LIBS procedure (CF-LIBS) and allows the precise quantitative determination of the elemental composition of the material without any reference sample or calibration curve. The software also automatically implements the corrections for plasma self-absorption recently developed by the IPCF group; a more detailed discussion on the CF-LIBS technique and self-absorption correction has been given in [4]. In typical experimental conditions, the complete characterization of the material is performed in less than five minutes, with practically no damage of the decorated surface.

The experimental set-up used for micro-Raman measurements shown in Figure 3 is essentially identical to the one used for the micro-LIBS analysis. In this case, the laser beam (generated by either a multimode Ar<sup>+</sup> laser working at the 514.5 nm wavelength or an He-Ne laser operating at 632.8 nm) is reflected by a notch filter, which, in a first phase, behaves exactly as a mirror, then is focused on the sample by a 50X microscope objective. The diffused light goes back to the notch filter, which does not transmit the laser wavelength. The light is collected onto the entrance slit of a spectrometer (Jobin Yvon THR1000) with a 600 lines/mm grating, flat field, and long focal length (1000 mm), allowing a spectral resolution of about 1 cm<sup>-1</sup>. The spectral signal is detected by a cooled CCD (KAF-1001E, produced by DTA scientific instrument) and then analyzed with appropriate software.

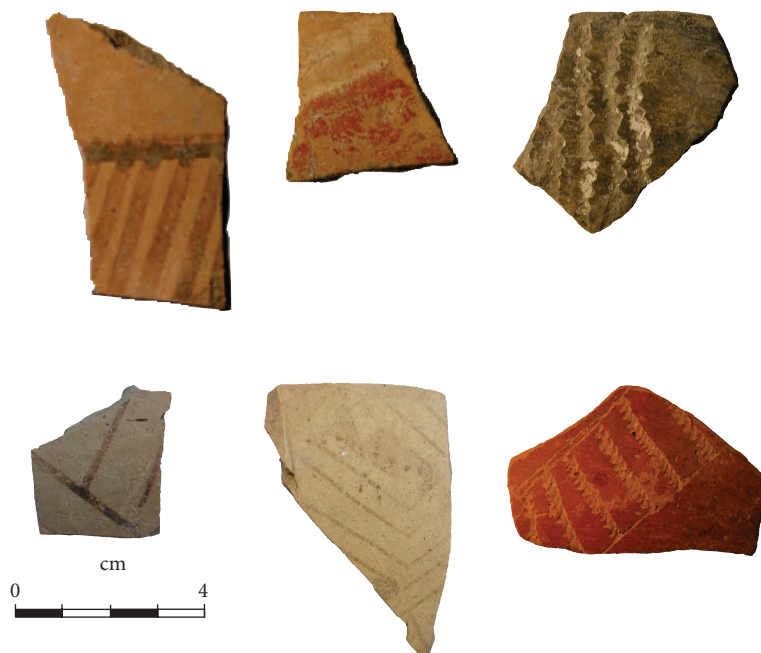


FIGURE 4: Some of the pottery fragments analyzed (clockwise TR06-TR13-TR03-TR05-TR15-TR09).

The sample is mounted on a three-axis motorized stage, controlled by a personal computer, for adjustment of the focusing position. Moreover, a camera allows the visualization of the examining zone, assuring a perfect focusing of the position.

### 3. RESULTS AND DISCUSSION

Fifteen samples of decorated pottery coming from the Trasano site have been analyzed. The Trasano site is located near Masseria Trasano (Matera, Italy) and it has been systematically excavated from 1984 to 1991 [15]. The area involved in the study is particularly wide with a very rich stratigraphic series that covers a long chronologic period: from the early Neolithic age (V Century BC), characterized by stamped pottery (phases I, II, III), to the middle Neolithic age (IV Century BC) with bicolored painted pottery (phase IV) and finally to the late Neolithic age (phase V) [16]. In particular, the samples analyzed belong only to the III, IV, and V phases and have the following typological characterizations:

- (1) colored pottery with a purified dough and graffiti, (TR03-TR04-TR06-TR11-TR12-TR13-TR14);
- (2) “figulina” type pottery painted with red stripes, (TR01-TR02-TR05-TR07-TR08-TR10);
- (3) “figulina” type pottery referring to “Serra d’Alto Culture,” (TR09-TR15).

Some of the samples analyzed are shown in Figure 4. They present external glossy surfaces with dark or red color, often decorated with graffiti or stripes.

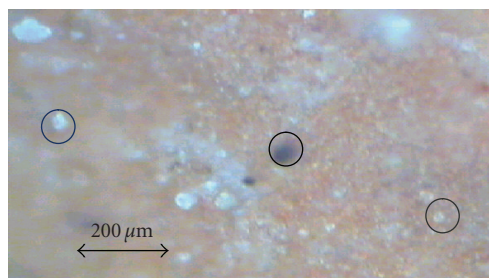


FIGURE 5: Microscope image of sample TR01.

#### 3.1. Raman analysis

The 15 samples were analyzed by the Raman technique, using an Argon ion laser source operating in CW mode and selecting the 514.5 nm component. The power of the beam on the surface was a few mW. The laser beam was focused onto the sample’s surface with a 50X microscope objective, so that the laser spot was a few micrometers in diameter. Figure 5 shows the microscope image of sample TR01. The surface is red, but it reveals also the presence of some impurities like quartz, rutile (silver spot-blue circle), amorphous carbon (dark spot-dark circle) and calcium (white spot-grey circle). The same minerals were present also in the other samples analyzed.

All the Raman spectra were taken with an acquisition time of 150 s. In Figure 6, a spectrum obtained from the red region is shown. All the spectra have been compared with the database of known minerals edited by the Chemistry Department of University College of London (UCL) [17].

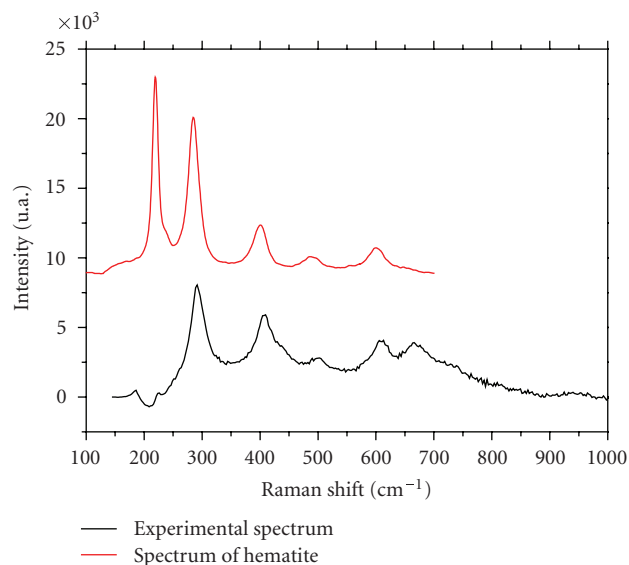


FIGURE 6: Raman spectrum of the red region (sample TR01).

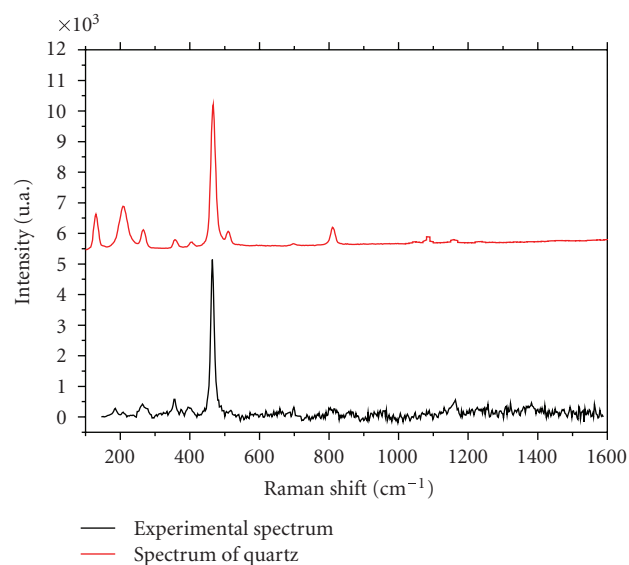


FIGURE 7: Raman spectrum of quartz (sample TR01).

It can be noted that there is a good correspondence between the experimental spectrum and the one from the UCL database corresponding to hematite: the lines at  $291\text{ cm}^{-1}$ ,  $407\text{ cm}^{-1}$ ,  $610\text{ cm}^{-1}$  correspond quite well, whereas the first peak at  $224\text{ cm}^{-1}$  is not visible, because the notch filter tends to cut off this wavelength region. In Figure 7, instead, the spectrum obtained for one of the silver spots (blue circle) present on the surface is shown: the line at  $465\text{ cm}^{-1}$ , typical of the quartz Raman signal, is evident. The presence of this mineral, together with others like titanium oxide is characteristic of the red ochre. This is an inorganic pigment of mineral origin, composed by a clay-based body rich in hy-

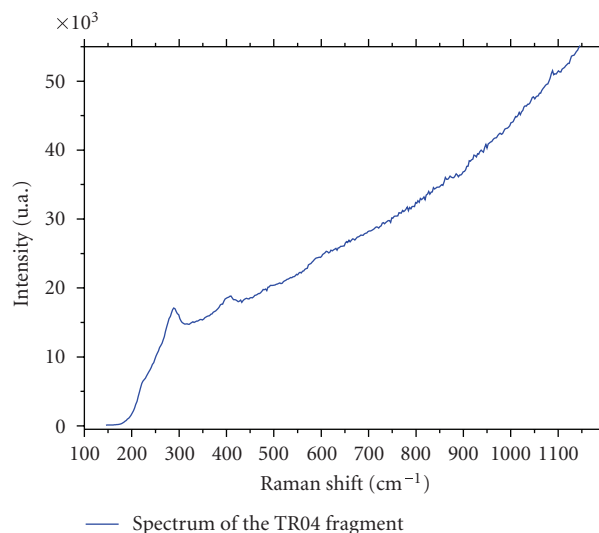


FIGURE 8: Raman spectrum of the red region (sample TR04).

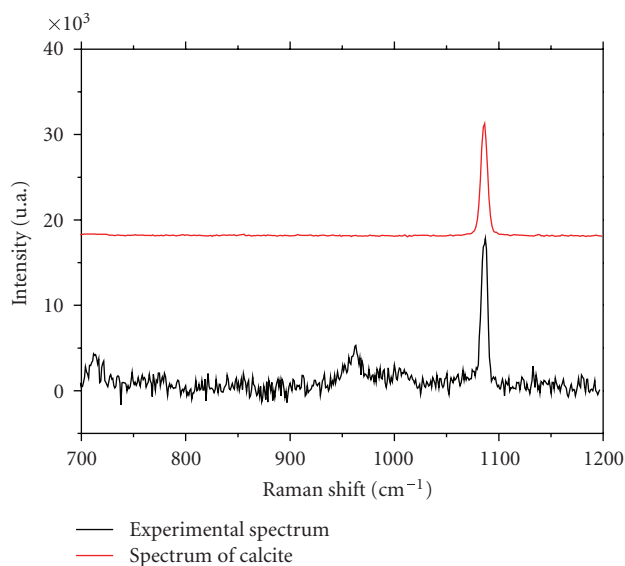


FIGURE 9: Raman spectrum of calcite (sample TR06).

drated iron oxides (hematite) and precipitated aluminium ( $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O} + \text{Al}_2\text{O}_3$ ).

The Raman analysis has been repeated for the other fragments showing a red coloring (TR02-TR04-TR07-TR08-TR10-TR13-TR14); also in these cases the presence of red ochre has been detected. In particular, for the TR04 sample the main Raman peaks look wider and less intense with respect to the ones found in the others spectra; moreover, the fluorescence background is dominating (see Figure 8). A possible interpretation of this effect can be related to the different kind of clay used as body for the pottery.

The TR03 and TR06 samples present white strips in the decoration; the measurement on the TR06 surface produced

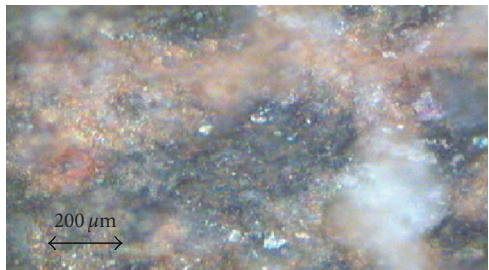


FIGURE 10: Microscope image of the sample TR03.

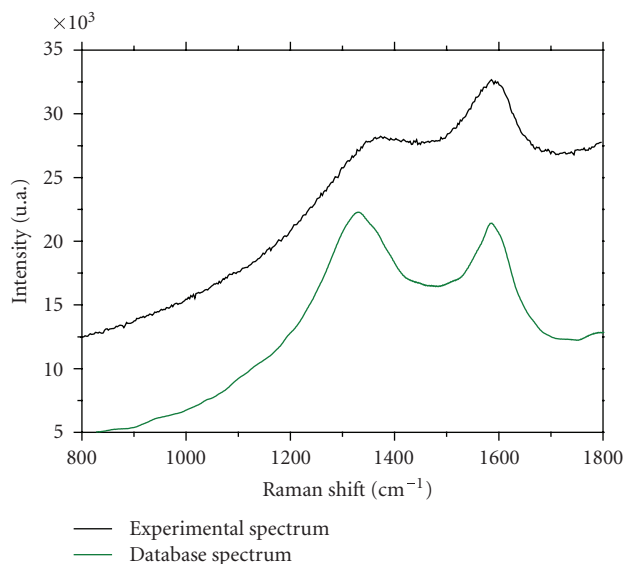


FIGURE 11: Raman spectrum of the dark region (sample TR03).

the spectrum shown in Figure 9, where a good agreement with the spectrum of calcite is obtained: in fact, the characteristic line around  $1088\text{ cm}^{-1}$ , corresponding to the symmetric stretching of the carbonate, is well visible.

The Raman analyses have been also performed on the samples with a dark surface (TR03-TR05-TR06-TR09-TR11-TR12-TR15). In Figure 10, a microscope image of one of the studied surfaces is shown. Some of the spectra obtained are reported in Figures 11 and 12.

In the first spectrum, the typical bands of carbon black at  $1325\text{ cm}^{-1}$  and  $1580\text{ cm}^{-1}$  are present; while in the spectrum of the TR05 sample, the characteristic magnetite Raman line at  $652\text{ cm}^{-1}$ , together with a large band at higher values of the Raman shift, is evident. Actually, according to the literature [18], also the Raman spectrum of lepidocrocite ( $\gamma\text{-FeOOH}$ ) exhibits a broad band about  $1322\text{ cm}^{-1}$ , therefore the presence of some iron oxyhydroxides on the surface of the sample cannot be excluded. While the carbon black is essentially composed by amorphous carbon and is obtained for partial combustion of wood, magnetite ( $\text{Fe}_3\text{O}_4$ ) is an inorganic pigment with natural origin.

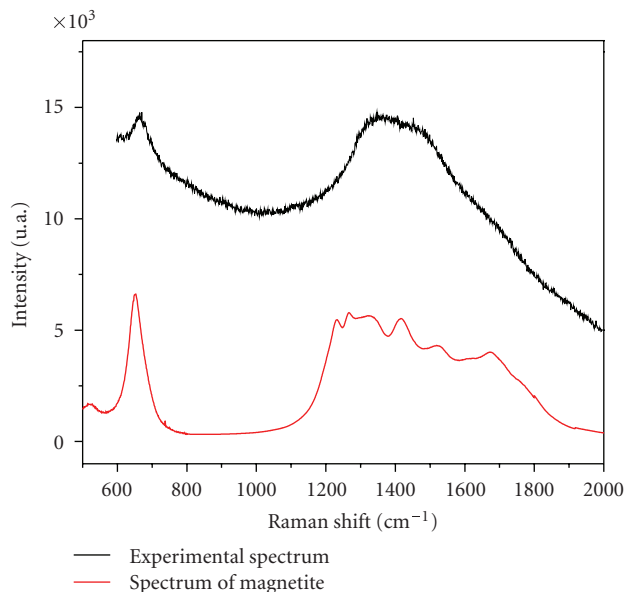


FIGURE 12: Raman spectrum of the dark region (sample TR05).

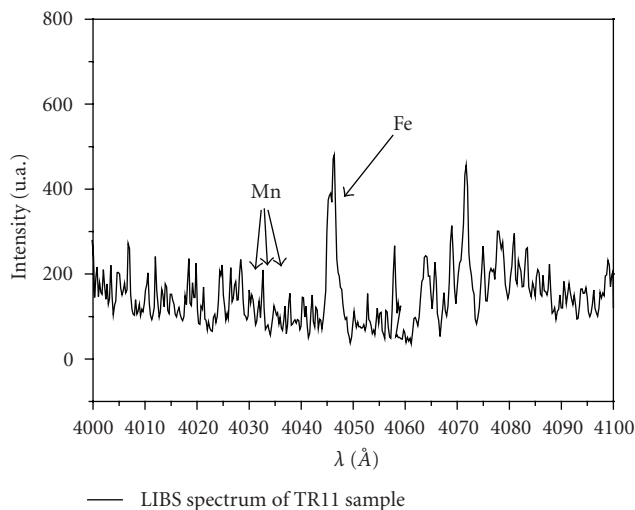


FIGURE 13: LIBS spectrum of the dark region (TR11 sample).

### 3.2. LIBS analysis

All the fragments studied with the Raman technique were also analyzed using the LIBS technique. The LIBS spectra have been acquired by averaging 20 laser shots on the sample surface. Every sample was moved after two shots in order to have a uniform measurement not affected by the development of the laser crater. The time delay and the gate of the acquisition were fixed at 1 and 2 microseconds, respectively. For what concerns the dark surfaces, the presence of manganese has not been revealed from the LIBS spectra for all the fragments belonging to the third typological characterization (Serra d'Alto type potteries). Therefore, one can exclude the use of a dark pigment based on manganese oxide for the first



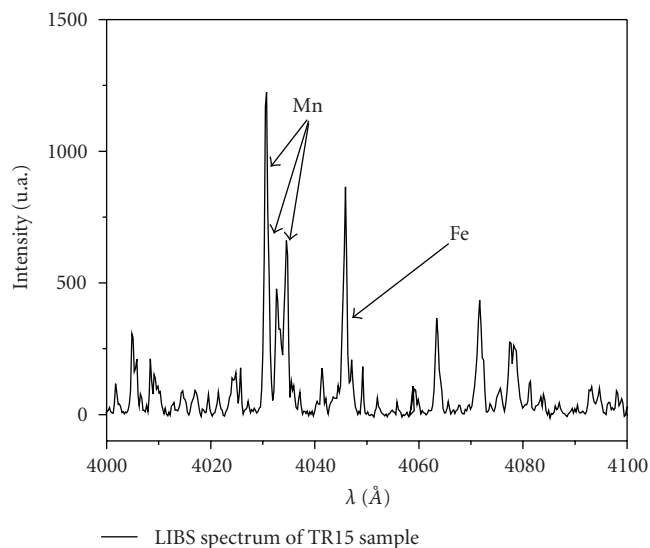


FIGURE 14: LIBS spectrum of the dark region (TR15 sample).

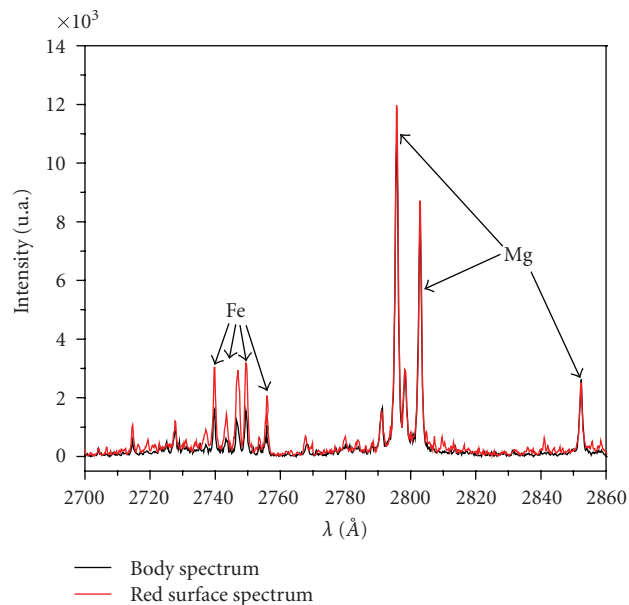


FIGURE 16: LIBS spectrum of the red region (TR04 sample).

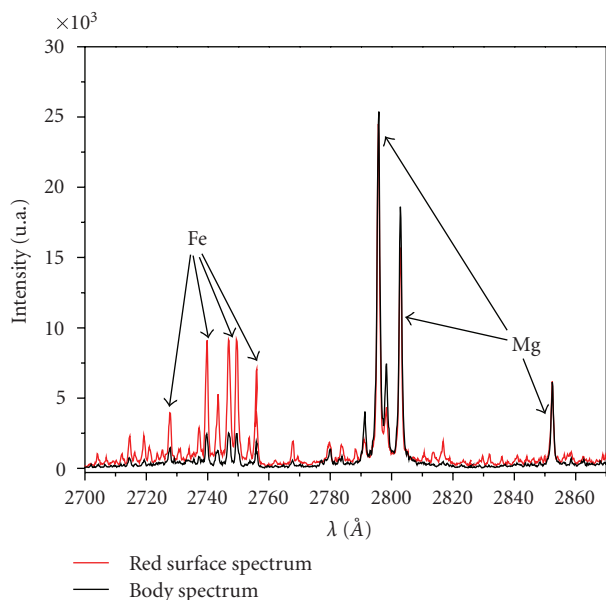


FIGURE 15: LIBS spectrum of the red region (TR13 sample).

two groups. In Figures 13 and 14, the LIBS spectra of TR11 and TR15 samples respectively are shown. The wavelength interval considered (4000–4100 Å) corresponds to the region where the more intense lines of manganese (4030 Å, 4033 Å and 4034.5 Å) should be visible, in the first case it is evident that they are not present, while in the second one they are well detectable.

On the other hand, the LIBS analyses performed on the red colored fragments showed a higher intensity of iron lines with respect to the clay body. Observing Figures 15 and 16, in fact, the increased intensity of the iron lines in the spectrum

relative to the surface is well visible; the two spectra have been normalized to the magnesium lines, which are characteristic of the clay and practically do not change from the surface to the bulk. This phenomenon appears more evident in the TR13 sample and this is in agreement with the hypothesis of the use of a red added pigment for coloring the sample surface.

### 3.3. Discussion of the results

Thanks to the joint use of Raman and LIBS techniques and in agreement with the results obtained with more traditional approaches, a good characterization both of the ceramic dough composition and of the pigments has been possible; at the same time, also useful information about the production of the Trasano site can be carried out. In phase III, very pure clay is used, whereas on the decorations amorphous carbon, calcite, and iron oxide have been recognized. Amorphous carbon has been used both for internal and external surface decoration of the pottery fragments in the painted strip. Calcite is the main component of the white traces inside the graffiti (TR03–TR06). In some cases (TR04–TR08–TR10), it has been very difficult to distinguish between the surface and the body due to the very fine granulometry, the partial vitrification, and the extreme thinness of the surface. In other cases (TR13–TR14), the LIBS analyses revealed the presence of a red pigments; while in samples TR03–TR06–TR11–TR12, the measurements suggest the possible coloring due to the making process together with a repetitive rubbing of the surface (according to a chemical phenomenon called peptidation) [19]. In phase IV, the figulina-type pottery starts to be produced, so the supplying of a different type of clay can be hypothesized. For what concerns the decoration styles, which is also changed with respect to Phase

III pottery, hematite, magnetite, and calcite are present. In particular, hematite is present together with calcite in the painted red stripes of TR01, TR02, and TR07 samples, even if the last fragment appears to be darker than the others; magnetite has been detected only in the TR05 sample. In phase V, the figulina-type pottery production belongs to the Serra d'Alto Culture [20], presenting probably the same mineral composition of the clay, but with the introduction of the use of a dark pigment based on manganese oxide (TR09-TR15).

#### 4. CONCLUSIONS

The results reported show that the joint use of micro-LIBS and micro-Raman spectroscopy allows the complete characterization, both structural and elemental, of the pigments under study. The measurements performed with the two techniques are fast, reliable, and virtually nondestructive. The results obtained are, therefore, encouraging for the realization of an integrated micro-LIBS/micro-Raman prototype for *in situ* analysis of cultural heritage.

#### REFERENCES

- [1] V. Tornari, V. Zafropoulos, A. Bonarou, N. A. Vainos, and C. Fotakis, "Modern technology in artwork conservation: a laser-based approach for process control and evaluation," *Optics and Lasers in Engineering*, vol. 34, no. 4–6, pp. 309–326, 2000.
- [2] D. Anglos, C. Balas, and C. Fotakis, "Laser spectroscopic and optical imaging techniques in chemical and structural diagnostics of painted artwork," *American Laboratory*, vol. 31, no. 20, pp. 60–67, 1999.
- [3] L. Burgio, K. Melessanaki, M. Doulgeridis, R. J. H. Clark, and D. Anglos, "Pigment identification in paintings employing laser induced breakdown spectroscopy and Raman microscopy," *Spectrochimica Acta Part B: Atomic Spectroscopy*, vol. 56, no. 6, pp. 905–913, 2001.
- [4] M. Bicchieri, M. Nardone, P. A. Russo, et al., "Characterization of azurite and lazurite based pigments by laser induced breakdown spectroscopy and micro-Raman spectroscopy," *Spectrochimica Acta Part B: Atomic Spectroscopy*, vol. 56, no. 6, pp. 915–922, 2001.
- [5] M. Castillejo, M. Martín, D. Silva, et al., "Laser-induced breakdown spectroscopy and Raman microscopy for analysis of pigments in polychromes," *Journal of Cultural Heritage*, vol. 1, supplement 1, pp. S297–S302, 2000.
- [6] L. Bussotti, E. Castellucci, and M. Matteini, "The micro-Raman technique in the studies for the conservation of artworks: identification of lakes in paints," *Science and Technology for Cultural Heritage*, vol. 5, no. 1, pp. 13–19, 1996.
- [7] L. Burgio and R. J. H. Clark, "Library of FT-Raman spectra of pigments, minerals, pigment media and varnishes, and supplement to existing library of Raman spectra of pigments with visible excitation," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 57, no. 7, pp. 1491–1521, 2001.
- [8] C. Lofrumento, A. Zoppi, and E. M. Castellucci, "Micro-Raman spectroscopy of ancient ceramics: a study of French sigillata wares," *Journal of Raman Spectroscopy*, vol. 35, no. 8–9, pp. 650–655, 2004.
- [9] A. W. Miziolek, V. Pallechi, and I. Schecter, *Laser-Induced Breakdown Spectroscopy (LIBS) Fundamentals and Applications*, Cambridge University Press, Cambridge, UK, 2006.
- [10] D. Anglos, S. Couris, and C. Fotakis, "Laser diagnostics of painted artworks: laser-induced breakdown spectroscopy in pigment identification," *Applied Spectroscopy*, vol. 51, no. 7, pp. 1025–1030, 1997.
- [11] V. Pallechi, G. Arca, S. Rastelli, A. Ciucci, and E. Tognoni, "Verso il laser intelligente: applicazione alla pulitura di monumenti," Internal Report B01LS/96, IFAM, Pisa, Italy, 1996.
- [12] A. Ciucci, M. Corsi, V. Pallechi, S. Rastelli, A. Salvetti, and E. Tognoni, "New procedure for quantitative elemental analysis by laser-induced plasma spectroscopy," *Applied Spectroscopy*, vol. 53, no. 8, pp. 960–964, 1999.
- [13] D. Bulajic, M. Corsi, G. Cristoforetti, et al., "A procedure for correcting self-absorption in calibration free-laser induced breakdown spectroscopy," *Spectrochimica Acta Part B: Atomic Spectroscopy*, vol. 57, no. 2, pp. 339–353, 2002.
- [14] A. Ciucci, V. Pallechi, S. Rastelli, et al., "Trace pollutants analysis in soil by a time-resolved laser-induced breakdown spectroscopy technique," *Applied Physics B: Lasers and Optics*, vol. 63, no. 2, pp. 185–190, 1996.
- [15] C. Corrado and E. Ingravallo, "L'insediamento di Masseria Le Fiate (Manduria) nel popolamento neolitico del nord-ovest del Salento," *Stdi di Antichità*, vol. 5, pp. 5–78, 1988.
- [16] J. Guilaine, G. Cremonesi, G. Radi, and J. Coularou, "Trasano e la céramique gravée materane," in *Autour de Jean Arnal*, pp. 123–137, Université des Sciences et Techniques du Languedoc, Montpellier, France, 1990.
- [17] <http://www.chem.ucl.ac.uk/resources/raman/pigfiles/>.
- [18] D. L. A. De Faria, S. Venâncio Silva, and M. T. De Oliveira, "Raman microspectroscopy of some iron oxides and oxyhydroxides," *Journal of Raman Spectroscopy*, vol. 28, no. 11, pp. 873–878, 1997.
- [19] G. Radi, "Trasano Basilicata," in *Le ceramiche impresse nel Neolitico antico in Italia e Mediterraneo*, pp. 695–705, Istituto Poligrafico e Zecca dello Stato, Roma, Italy, 2003.
- [20] T. DiFraia, "Resti di un villaggio della cultura di Serra D'Alto a Saldone presso Metaponto (Lucania)," *Atti della Società Toscana di Scienze Naturali, Memorie, Serie A*, vol. 77, pp. 54–77, 1970.