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MICRO-CHEMICAL EVALUATION OF ANCIENT POTSherDS BY μ-LIBS SCANNING ON THIN SECTION NEGATIVES

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ABSTRACT

In the study of ancient pottery, thin section analysis represents the basic approach to study mineralogical and petrographic features in order to obtain preliminary information about the production technology and origin of archaeological ceramics. However, even if thin section analysis allows investigating the textural and structural characteristics of potteries, peculiar features related to clay paste and temper composition, as well as provenance issues, can be detailed addressed only by quantitative mineralogical and chemical studies. In the realization of thin sections, a negative face is always produced, similar to the thin section itself; these remains can be used for additional analyses, such as high spatial resolution micro-chemical studies using, for example, a micro-laser induced breakdown spectroscopy (LIBS) scanner.

LIBS is a spectroscopic technique that, exploiting the laser radiation, is able to bring into the plasma state micrometric portions of the sample, and to analyse its content through the study of the optical emission of the plasma itself. Unlike other techniques, LIBS can detect and quantify also light elements such as aluminium and magnesium. Images produced by the micro-LIBS instrument show the spatial distribution of the chemical elements within a portion of the sample, which may have dimensions from a few hundred microns up to several centimeters. The combination of these images with algorithms derived from image processing techniques may return interesting information and supporting data to in-depth investigate pottery components detected by optical microscopy observations. In this work, we present the results of an experimental study performed on thin-section negatives with different grain size, surface treatments and aggregates, coming from some Neolithic Italian sites, exploring the potential of the LIBS method in micro-chemical studies of ancient potsherds.

KEYWORDS: Elemental mapping, archaeometry, pottery, prehistory, μ-LIBS, PCA, Kohonen SOM
1. INTRODUCTION

Petrographic analysis (Rice, 1987; Quinn, 2013), microstructural analysis by scanning electron microscope SEM coupled with chemical microanalysis, thermal analysis, mineralogical analysis and other spectroscopic techniques (Memmi, 2004; Barone et al., 2014; Teoh et al., 2014; Maritan, 2015; Hunt, 2016; Halperin and Bishop, 2016) are well-established procedures for analysing ancient pottery. However, the possibility to obtain valuable information on ceramics by using new methods requiring no sample preparation and short measurement time are in high demand. Micro-laser induced breakdown spectroscopy (µ-LIBS) has been recently successfully applied on different materials (Schiavo et al., 2016; Pagnotta et al., 2017) for mapping surfaces up to one square centimeter obtaining morphological, compositional and quantitative data, thanks to the advantages offered by the method, namely the detection of light elements (Miziolek et al., 2006), the short time (about half an hour for sample to scan an area of 5 mm$^2$ at lateral resolution of 100 μm) and the low cost of the analysis compared to other techniques (see also, Kouhpar et al., 2017; Javanshah, 2018; Hemeda, 2013).

Among ancient materials, the study of prehistoric pottery is often not straightforward because of the lack of reliable sources able to support hypothesis on production technology and processes. Sometimes, this kind of information appears quite relevant in the reconstruction of social dynamics, as in the transition between phases (Maritan et al., 2017) and manufacture routines (Dal Sasso et al., 2014; Antonelli et al., 2018). A significant example is represented by Neolithic potteries, whose production can be framed in the streamline of the overcoming technological evolution represented by metallurgy; this event shifted the artefacts manufacture from hand-made to specialized production requiring control of the firing processes and a special conditioning of raw materials (Pessina and Radi, 2003). Due to the relevance of this ceramic class, some representative potsherds of Southern Italy Neolithic productions, namely from Abruzzo and Puglia, have been sampled for µ-LIBS analysis. These materials exhibit quite peculiar characteristics: very thin walls, high purified clay paste (with inclusions barely visible to the naked eye) and a glossy black external and internal surface, which sometimes tends to show a metallic aspect (Cremonesi, 1965, 1973; Cremonesi and Tozzi, 1987). The technology for realizing these surfaces is currently of great interest to prehistoric archaeologists (Agostini et al., 2003), interpreting the finishing treatment as an imitative routine of metal prototypes that in the same period began to circulate in the areas of the Near East. In this contribute we therefore explore the potential of µ-LIBS in supporting archaeological investigations on ancient pottery by providing in micro-destructive, fast and short time qualitative chemical maps which interpretation can supply information on bulk mineralogical composition and manufacture of surface finishing.

2. SAMPLES AND TECHNIQUES

Five samples of black gloss ceramics from Fucino - Paterno (Abruzzo region, central-eastern Italy) and one from S. Anna di Oria (Puglia region, south-eastern Italy) have been analysed in this study (Fig. 1).
The samples were selected on the basis of the statistical representativeness of this particular ceramic class. Details about samples are provided in Table 1.

<table>
<thead>
<tr>
<th>Id.</th>
<th>Provenance</th>
<th>Shape</th>
<th>paste</th>
<th>Finishing</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAOFN1</td>
<td>S. Anna di Oria (Puglia)</td>
<td>Tronco-conical vessel</td>
<td>Semi-depurated</td>
<td>Black-gloss</td>
</tr>
<tr>
<td>POFN1</td>
<td>Paterno (Abruzzo)</td>
<td>Tronco-conical vessel</td>
<td>Semi-depurated</td>
<td>Black-gloss</td>
</tr>
<tr>
<td>POFN2</td>
<td>Paterno (Abruzzo)</td>
<td>Tronco-conical vessel</td>
<td>Semi-depurated</td>
<td>Black-gloss</td>
</tr>
<tr>
<td>POFN3</td>
<td>Paterno (Abruzzo)</td>
<td>Tronco-conical vessel</td>
<td>Semi-depurated</td>
<td>Black-gloss</td>
</tr>
<tr>
<td>POFN4</td>
<td>Paterno (Abruzzo)</td>
<td>Tronco-conical vessel</td>
<td>Semi-depurated</td>
<td>Black-gloss</td>
</tr>
<tr>
<td>POFN5</td>
<td>Paterno (Abruzzo)</td>
<td>Tronco-conical vessel</td>
<td>Semi-depurated</td>
<td>Black-gloss</td>
</tr>
</tbody>
</table>

Data were acquired using a Modi smart LIBS system (Bertolini et al., 2006) equipped with a Zeiss Axioplan A1 microscope and a Thorlabs’s XY stage. The Modi Smart was equipped with an Nd:YAG Laser (λ=1064nm), focused on the sample through a dedicated 10X microscope objective (Figure).

The plasma light was focused with a ball lens and sent through an optic fibre to an AvaSpec Dual Spectrometer, covering a spectral range from 200 nm to 900 nm (resolution of 0.1 nm in the UV and 0.3 in the VIS-IR region). A double pulse laser (first pulse= 5.4 mJ; second pulse= 8.7 mJ with 1 ms retard between them) was used to realize raster of 50x50 shots at a lateral resolution (pixel dimension) of 100 μm for the acquisition of compositional data on a 5 mm².

In order to synchronize the laser pulses with the motorized sample holder, a dedicated software developed with the NI LabVIEW 8.5 was used.

Collected data were processed by an in-house routine on MATLAB®, able to select the intensity lines of interest for each detected element (Al, Si, Ca, Mg, Fe, Na, K) in the square matrix associated to the scanned surface. At the same time, the software performed a normalization procedure point-by-point based on the total intensity of the LIBS spectrum (Figure), to minimize effects caused by changes in the focusing of the laser beam.

![Figure 2. Scheme of the Micro-Modi system.](image)

![Figure 3. A typical LIBS spectrum of a potsherd.](image)
Table 2. Elements of interest for this study and their wavelength.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>819.48</td>
</tr>
<tr>
<td>Mg</td>
<td>279.55</td>
</tr>
<tr>
<td>Al</td>
<td>309.24</td>
</tr>
<tr>
<td>Si</td>
<td>288.16</td>
</tr>
<tr>
<td>K</td>
<td>766.5</td>
</tr>
<tr>
<td>Ca</td>
<td>422.68</td>
</tr>
<tr>
<td>Fe</td>
<td>538.72</td>
</tr>
</tbody>
</table>

Starting from the intensity matrix based on the µ-LIBS spectral lines, gray-scale elemental maps were therefore obtained each of them accounting the distribution of a specific element over the wavelength interval 200 - 900 nm. The treatment of elementary maps as multi-spectral images allows to obtain a multispectral “cube” in which the contribute of detected elements can be simultaneously visualised (Figure).

Figure 4. Iper-spectral “cube”, composed by the elemental maps.

To process to the compositional maps generated by the µ-LIBS system, the typical multispectral imaging approach has been used (Legnaioli et al., 2013).

The recombination of some elementary maps, relevant in the analysis of archaeological ceramics, allows thus to obtain false color images describing specific compositional variation into a sample; in this case, RGB images accounting the detection of Si (Red), Al (Blue) and Ca (Green) were processed.

Moreover, a self-organized map (SOM) of Kohonen with four neurons were provided to evaluate the potential of unsupervised segmentation process in assisting the interpretation of chemical data. The use of SOM network allows to reduce the dimensionality of the classification problem, preserving the topology of the training set (inputs).

The kohonen algorithm, starting from each input image, generates a random centroid for each output neuron. The randomly generated centroid updates with the weights of the pixels most similar to that centroid, reaching a mean value after several iterations (generally 1000). At the end of the learning process the images will be segmented into areas with similar properties. In this case, the process started from a seven-dimensional space (inputs), consisting of the maps of all the analysed elements, and was reduced to a maximum 4-dimensional (output neurons) space (Figure). The four output segments can be therefore recombined in a final image able to describe the contribute of the obtained segments, by assigning to each of them one channel in a CMYK color space (Cyan-Magenta-Yellow-Black).

Figure 5. Structure of the SOM network utilized.

3. RESULTS

The interpretation of RGB colour maps, based on the normalized intensities (a.u.) of Si (Red), Al (Blue) and Ca (Green) (Figure), can provide information on the possible differences in chemical composition between clay paste and surface layers.

First of all, it can be observed that almost all the samples tend to a purple colour; only the sample POFN4 tends to a reddish colour, suggesting higher level in Si-rich phases. Green areas account Ca-rich phases, mainly attributed to minerals phases containing calcium; blue areas, on the contrary, delineate the distribution of minerals phases enriched in aluminium.

In the case of studied samples, it is interesting to note that in some specimens (SAOFN1, POFN1 and POFN3) the upper part of the scanned area (that corresponds to the surface of the potsherds) turns from purple/magenta to lighter or darker colour, due to different proportion of aluminium and silica content (Figure). This result could support the hypothesis on composition as well as technology employed to make the surface finishing. In fact, a homogenous composition between ceramic body and surface should indicate a simple lustre of the surface. Alternatively, a different composition should possibly suggest the application of high-depurated layers of clays to obtain black gloss.
In order to overcome interpretation based only on three elements and obtain information based on the overall chemical composition, SOM approach has been applied. The use of the SOM network generated (as results of training stage) different segmented images for each sample (Figure), with black and white areas accounting the different weights related to each input element (Figure).

![Figure 6. Micro-photographs of the scanned area of about 5 mm² (top) for the analysed samples; composed RGB colour maps of distribution of Si (Red), Ca (Green) and Al (Blue) (bottom).](image)

![Figure 7. Binary images showing the distribution of the various segments obtained for each of the analysed samples.](image)
A simpler visualization of the segmented images have been therefore obtained recombining them in the CMYK space, and specifically attributing segment 1, segment 2, segment 3 and segment 4 to C, M, Y and K, respectively (Figure 1).

The resulting images give back interesting qualitative information, complementing data obtained from the simple elemental distribution. Particularly, two main aspects can be investigated. The first concerns the distribution of inclusions within the ceramic body; the second concerns the minerals compositing then inclusions that may belong to (i) aplastic mineral and rock fragments naturally occurring in the clayey sediment, (ii) added temper, or (iii) secondary mineral phases precipitated for post-depositional processes.

In fact, by assuming a possible correspondence between the distribution of chemical elements and mineralogical phases present in ceramics (both tempers and clay paste), the following can be proposed. Segment 1 might describe the occurrence of aluminium and potassium enriched mineral phases (such as feldspars; e.g. KAlSi₃O₈). Segment 2 reveals the greater weights of Fe and K, possibly describing the composition and distribution of the clay paste matrix (phyllosilicates, such as mica); segments 3, accounting mainly Mg and Al, might shows the distribution of secondary minerals due to reactions during firing (such as spinel, MgAl₂O₄). Finally, segment 4 could account the distribution of mineral fragments enriched in Mg. As regard morphology, the edge of the tempers in SAOFN1 and POFN5 shows a sharpened aspect that may suggest that they are voluntary added to the original paste.

4. DISCUSSION AND CONCLUSIONS

The qualitative analysis of elemental maps allow us to obtain both compositional and technical information, as well to highlight interesting differences in term of manufacture techniques among studied potsherds. The differences in grain size and in the chemical properties of the different components of the studied samples, which are reflected in a different laser-matter coupling, can be exploited to the benefit of the use of self-organized SOM networks, possibly providing insights on distribution of minerals in the ceramics; of course, the univocal identification of mineralogical phases by their chemical composition based on multispectral images should include more detailed input data. However, it is out of the scope of this work, mainly finalised to explore the possibility to use µ-LIBS in obtaining preliminary compositional information to discriminate ceramics samples and inspect technical manufacture issues.
First, differences in raw material selection can be assessed based on RGB maps, also among samples coming from the same area and exhibiting quite similar aesthetical features; this concerns especially the temper composition in POFN specimens (from Abruzzo). The sample POFN2 and POFN3 seem to have the same inclusion fraction, as suggested by similarity in RGB maps (green/red areas), with a quite homogeneous distribution and high thickening. The samples POFN4 has inclusion fraction different from the previous two (as revealed by green/red/blue color in RGB maps), the entire surface presents a lot of blue areas mixed with red and green areas with a very homogeneous distribution. The last sample, POFN5, has a different inclusions fraction, as suggested by the diffused red dots, mainly concentrated in the outer part of the section analysed.

The image processing of μ-LIBS maps helps to clarify the technology used to realize the luster surface finishing. The color differences in SOM maps allow us to discriminate almost two different methods: first, the application of a surface layer (possibly a barbotine) with different composition respect to body paste (e.g. in sample SAOFN1, in which the different colors distinguish the body paste and the outer surface layer); second, the simple treatment of a surface characterized by the same body paste composition (e.g.: in sample POFN1, in which an homogeneous color can be observed on the overall section). Moreover, it is interesting to note that in some specimens from Abruzzo (POF2 and POF3) the distribution of inclusions seems to show curved trends that could indicate the use of “colombino” technique (i.e.: application of rolled string of clays), claiming the simultaneous application of two different routines, namely application of barbotine and colombino, in the same chronological time lap.

Finally, information about manufacture technology of body paste can be inferred by segment 4 inspection of SOM maps. In particular, SAOFN1 and POFN5 maps reveals the presence of mineral phases exhibiting large grain size than the other samples and very sharp margins, suggesting an intentional addition of them as tempers, while in the other samples the finer grain size and the quite rounded shape of aplastic inclusions indicate the possible presence of them in the original raw clayey sediments. Moreover, the similar trends in composition between POFN2 and POFN3 show a possible use of the same raw material, as well for POFN4 and POFN5. The sample POFN1 is different from the others, suggesting the employment of a different clay material.

Going to the archeological considerations based on experimental data, we can suggest that the similarity between the technological choices adopted for the SAOFN1 and POFN5 samples would lead to hypothesize an exchange of knowledge between Apulia and Abruzzo for the final phases of the Neolithic, a topic that still remains an open question.

Summarizing, with this work we explored the potential of μ-LIBS in providing compositional and technological information on ancient ceramics. The study carried out allowed us to bring further evidence supporting the thesis sustained by several authors that the realization of black gloss surfaces with metallic aspect is a voluntary operation, carried out through a wealth of highly advanced technical and experiential knowledge. Even if the study has been applied only on few samples to test the methodological routine on thin section negatives, the promising obtained results encourage to applying the method to other cases and extending the potentiality of the technique (with the possibility to study thin sections together) to quantitative studies for the analysis of elemental maps.

REFERENCES


