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1 Fast quantitative elemental mapping of highly inhomogeneous materials by
2 micro-Laser-Induced Breakdown Spectroscopy
3

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15 **Abstract**
16

17 In this work, a fast method for obtaining a quantitative elemental mapping of highly inhomogeneous
18 samples by μ -LIBS maps is proposed. The method, transportable and cheap, allows the analysis of
19 large maps through the use of a Self-Organizing Map clustering method coupled to Calibration-Free
20 LIBS for quantification of cluster prototypes. The method proposed has been verified on
21 heterogeneous materials such historical lime mortars but it can be easily applied to a larger class of
22 inhomogeneous materials for very different applications (modern building materials, biological
23 samples, industrial materials, etc.).
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31 **Keywords:** LIBS, Elemental Mapping, Calibration-Free LIBS, Self-Organizing Maps, Mortars
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33

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35 1. Introduction

36

37 Laser-based techniques have attracted a considerable interest in the last decades for their capability
38 of obtaining elemental images of solid samples without specific treatment, with high spatial resolution
39 and at different depths [1-5]. A number of applications have been proposed in several fields, ranging
40 from biomedical, geological and environmental research, to forensic analysis, to industrial
41 diagnostics, to Cultural Heritage study and conservation [6-13].

42 Among these techniques, applications based on the μ -LIBS technique are becoming more and more
43 frequent to scan surfaces and obtain compositional maps, providing interesting results in a number of
44 applications that require qualitative and quantitative analyses [14-22]. The use of μ -LIBS-scan
45 technique has proved to be very advantageous from an economic and experimental point of view with
46 respect to other laser-based techniques such as Laser-Ablation-Inductively Coupled Plasma-Mass
47 Spectrometry (LA-ICP-MS) [23]. The method is, in fact, fast, transportable, relatively cheap and can
48 analyse simultaneously elements with very different ionization energy, a task that can be problematic
49 in LA-ICP-MS [24]. While the qualitative analysis of μ -LIBS elemental maps is a relatively simple
50 task, the quantification of the elemental composition of the sample is much more challenging. In
51 principle, a quantitative analysis based on the use of reference samples of known composition for
52 building linear or non-linear, uni- or multi-variate calibration surfaces is applicable only when the
53 matrix of the sample remains more or less constant in the region of analysis [25]. If the sample is
54 characterized by strong inhomogeneities, with materials of different matrixes, or when suitable
55 reference samples are not available, a possible approach to quantitative elemental mapping would be
56 the use of Calibration-Free approaches [25-27]. An important drawback of the CF-LIBS approach,
57 however, is the time required for the analysis: **the emission lines of the elements in the samples must**
58 **be individuated and their intensities calculated through their fit with a Voigt profile. The electron**
59 **number density must be calculated from the Stark broadening of the hydrogen Balmer alpha line, then**
60 **the electron temperature must be calculated from the Boltzmann or Saha-Boltzmann plot. Finally, the**
61 **sample composition must be calculated. If automated all these operations take at least less than 30**
62 **seconds per spectrum; however, μ -LIBS elemental maps with megapixel spatial resolution have been**
63 **obtained by different groups, and a CF-LIBS approach applied on millions of LIBS spectra is, at the**
64 **moment, unrealistic. D'Andrea et al. [28] have recently proposed a hybrid Artificial Neural Network**
65 **(ANN) – CF-LIBS method that can be very effective in most of the cases, but requires the variations**
66 **in the material matrix to be relatively small for the ANN to work properly.**

67 In this work, we propose a method based on the sequential application of elemental map segmentation
68 (obtained using an automatic classification method based on the use of Self-Organizing Maps, as

69 proposed by the authors in [29]), followed by a CF-LIBS analysis of the prototypal spectra
70 representing the different clusters (materials) in the map. The method is presented and tested for the
71 analysis of ancient mortars. The knowledge developed in the study of this class of highly
72 inhomogeneous materials may have also interesting applications in the analysis and study of modern
73 binding materials and techniques.

74

75 **2. Materials and methods**

76

77 To assess the analytical capability of the method proposed, two mortar fragments from the Norman
78 Adrano Castle (Catania, Sicily) were selected as test samples. The two samples (labelled with the
79 inventory numbers N2-2 and S2-3) have been analysed with the permission of the *Soprintendenza*
80 *per i Beni culturali e Ambientali di Catania*. They consist of polished thin sections consolidated by
81 epoxy resin; the mortars are characterized by a heterogeneous binder with the presence of aggregates
82 due to volcanic ash, with a large variation in grain size (figure 1).

83 The analysis of ancient mortars is one of the main topics of Earth Sciences disciplines applied to
84 Cultural Heritages. Usually, ancient mortars are classified in two main categories, lime-aerial mortars
85 and hydraulic lime mortars. The latter ones were often obtained by adding to the mixtures volcanic
86 materials ("pozzolana"), and crushed ceramic fragments ("cocciopesto"). In both cases, the final
87 product is a mixture characterised by a relatively homogeneous paste, embedding inside clasts of
88 various dimension. The ability of pozzolanic materials to provide hydraulic proprieties to the mortars
89 is due to the presence of reactive constituents like aluminates and silicates [30]. A quantitative
90 elemental mapping could thus give information about the typology of analyzed mortars (aerial vs.
91 hydraulic) and well as the degree of hydraulicity (Vicat formula [31]). Usually, the characterization
92 of ancient mortars is achieved by optical microscopy (OM), X-ray fluorescence (XRF), X-ray
93 diffraction (XRD), scanning electron microscope (SEM-EDS), termogravimetric methods [32] and
94 inductively coupled plasma mass spectrometry (ICP-MS) [33]. However, from an analytical point of
95 view, the heterogeneity proper of these kind of materials and the presence of low crystalline CSH
96 (Calcium-Silicate-Hydrated) phases [34,35] represent, sometimes, a limit for the complete
97 characterization of mortars, especially considering the difficult to delineate the spatial distribution
98 and the occurrence of CSH with respect to binder and aggregates.

99 An interesting method based on semi-automated algorithm working on elementary maps obtained by
100 SEM-EDS data has recently been proposed by Belfiore et al. [36].

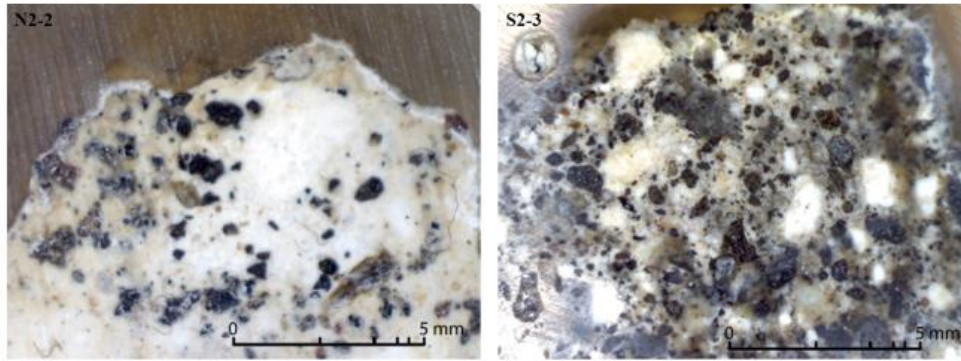


Figure 1. Microphotography of the two mortar samples.

3. Experimental procedure

A μ -Modi double-pulse instrument [37], equipped with a collinear double-pulse Nd:YAG Laser ($\lambda=1064$ nm) coupled with a Zeiss Axio Plan A1 microscope with 10X objective was used for the mapping of the samples. The energy of the two pulses was set to 20 mJ and 30 mJ, respectively, in 20 ns FWHM [38]. The delay between the laser pulses was set at 1 μ s. The LIBS signal was collected using an optical fiber, placed at 45° with respect to the laser direction, at a distance of about 1 cm from the sample. A ball lens in front of the fiber guarantees the optimal collection of the LIBS signal from the whole plasma. The μ -Modi instrument uses an Avantes double spectrometer (AvaSpec-2048-2), covering the spectral region from 190 to 900 nm (0.1 nm resolution from 190 to 450 nm, 0.3 nm resolution from 450 to 900 nm). The spectra were acquired 250 ns after the second laser pulse. The acquisition time of the spectrometer is of about 2 ms (time-integrated measurements). The samples were placed on a motorized X-Y sample holder, synchronized with the laser and spectrometer through a LabVIEW® dedicated software. The element maps were acquired on a 50x50 matrix (2500 LIBS spectra) with a lateral resolution of 100 μ m, for a total scanned area of 25 mm², with the laser operating at 1 Hz repetition rate. The diameter of the laser crater at the sample surface was about 20 μ m [29].

The main elements present in the mortars are reported in table I, along with the central wavelength of the emission line used for building the compositional images from the LIBS spectra. Given the qualitative nature of the analysis, at this stage, the use of self-absorbed resonant lines is tolerable.

126 Table I - Selected elements and central wavelength of the line considered

Element	Ion.	$\lambda(\text{nm})$
C	I	247.8
Na	I	589.0
Mg	II	279.4
Al	I	309.3
Si	I	288.2
Fe	I	372.0
Ca	I	445.2

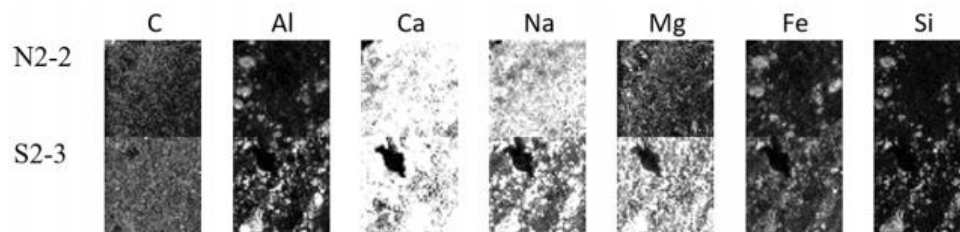
127
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129 4. Results

130

131 Based on the intensity of the lines identified, a series of elementary maps constituting the starting
132 point for the subsequent clusterization (or segmentation) processing were obtained, as shown in [figure](#)
133 [2](#).

134



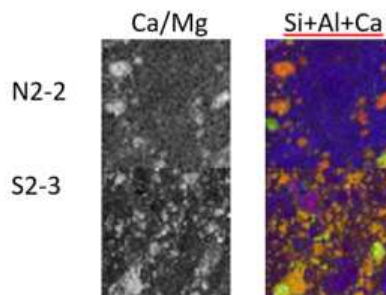
135

136 Figure 2. The elemental maps obtained by μ -LIBS scan

137

138 Following the method described in ref. [29], for the qualitative characterization of the spatial
139 relationship between aggregate and binder we realized for both the samples a grayscale map of the
140 Ca/Mg line intensity ratio and a false-color map of the distribution of Si (red), Al (green) and Ca
141 (blue) line intensity (see [figure 3](#)).

142 The Ca/Mg ratio maps allow us to easily discriminate the distribution of binder (dark areas) and
143 aggregates present in mortar (bright areas). The Si-Al-Ca false-color maps evidence further the high
144 inhomogeneity of the samples.



145

146 Figure 3. At the left, the map representing the Ca/Mg line intensity ratio. At the right, the false-color map
147 representing the distribution of Si (red), Al (green) and Ca (blue) line intensity.

148

149 Although clear from a qualitative point of view, the differences in the sample matrix from point to
150 point prevent the possibility of using a unique calibration strategy based on the construction of
151 univariate calibration curves or multivariate linear (Partial Least Square Analysis, for example) or
152 non-linear (Artificial Neural Networks) approaches.

153 The first step of our proposed analytical strategy is thus the automatic segmentation of the elemental
154 images using a Self-Organizing Map neural network [39], with the purpose of detecting and
155 separating the different components in the samples.

156 The SOM network is an unsupervised neural network that consists of neurons organized in a low-
157 dimensional network. Each neuron is represented by an n-dimensional weight vector where n is the
158 number of dimensions of the input vectors (in our case, $n=7$, corresponding to the peak intensity of
159 the lines reported in table I). The input vectors are normalized to have unit length. The samples (in
160 our case, the set of LIBS spectra defining the 'pixels' of the image) are assigned to the nodes whose
161 weights are 'closer' to their LIBS spectra. The different neurons adjust their weights in order to get
162 the largest possible number of samples, in a competitive way.

163 The use of SOM networks is suitable for detecting the topology of samples [40-41] and, at the same
164 time, operating in a multidimensional parameters space without reducing the dimensionality of the
165 system [42]. Since the number of different materials in the mortars is not known a priori, we chose a
166 5-neuron SOM which will select a maximum of 5 independent clusters (figure 4). These clusters
167 should well represent the inhomogeneity of the sample. Given the unavoidable slight experimental
168 differences between the two acquisitions, each sample was segmented independently on the other.

169

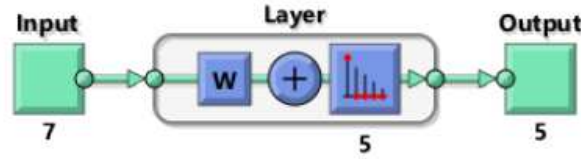


Figure 4. The network scheme: 7 inputs (peak line intensities), 5 segments as output.

Five segments for each sample was therefore obtained (figure 5). Each image obtained from SOM segmentation represents materials with similar composition/matrix [29].

	Seg. 1	Seg.2	Seg.3	Seg.4	Seg.5
N2-2					
pixel	238	309	20	744	1189
S2-3					
pixel	523	677	682	455	163

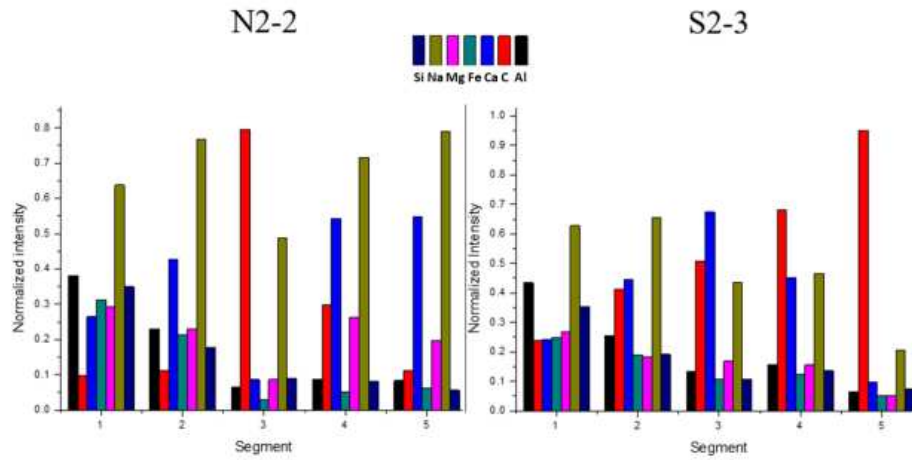
Figure 5. Image segmentation produced by the SOM neural network with the number of pixels represented.

In both the mortar samples studied, the SOM segmentation reproduces similar patterns, although not corresponding to the same cluster number. For example, the regions of the samples where the epoxy resin used for consolidating the samples is exposed are clearly evidenced in segment 3 for sample N2-2 and segment 5 for sample S2-3.

As an interesting by-product of this classification, the area covered by each material can be estimated by the ratio between the pixel associated with a given cluster and the total number of pixels of the map. While the surface exposed in sample N2-2 is negligible (20 pixels over 2500 = 0.8 %), the corresponding exposed surface on sample S2-3 corresponds to 163 pixels over 2500 = 6.5 %.

It is evident that averaging the LIBS spectra over the whole map would give unreliable results, that would be strongly affected by the amount of clasts, the exposed epoxy resin, etc., in the scanning area. Thus, the quantitative determination of the composition of the samples must be done separately for the different clusters/materials evidenced by the SOM classification. As discussed in [29], the SOM segmentation gives the 'coordinates' (normalized peak line intensities, since the input vectors are normalized to have unit length) of the centroids of the clusters (see figure 6). However, the centroids of the clusters do not necessarily coincide with the coordinates of a 'pixel' of the image. In

195 other words, the corresponding intensities does not match any physical LIBS spectrum, so this
 196 information cannot be used for a Calibration-Free quantitative analysis.



197
 198 Figure 6 – Normalized intensities corresponding to the centroid of the distribution.

199
 200 On the other hand, the materials corresponding to each cluster have a homogeneous distribution
 201 within the cluster, therefore we can average the spectra corresponding to each cluster and apply the
 202 CF-LIBS method to these spectra only, obtaining the quantitative composition of the materials in the
 203 sample.

204 The emission lines considered for the quantitative analysis are reported, with the corresponding
 205 spectral parameters, in table II. The lines were chosen trying to avoid strong self-absorbed emissions,
 206 whenever possible.

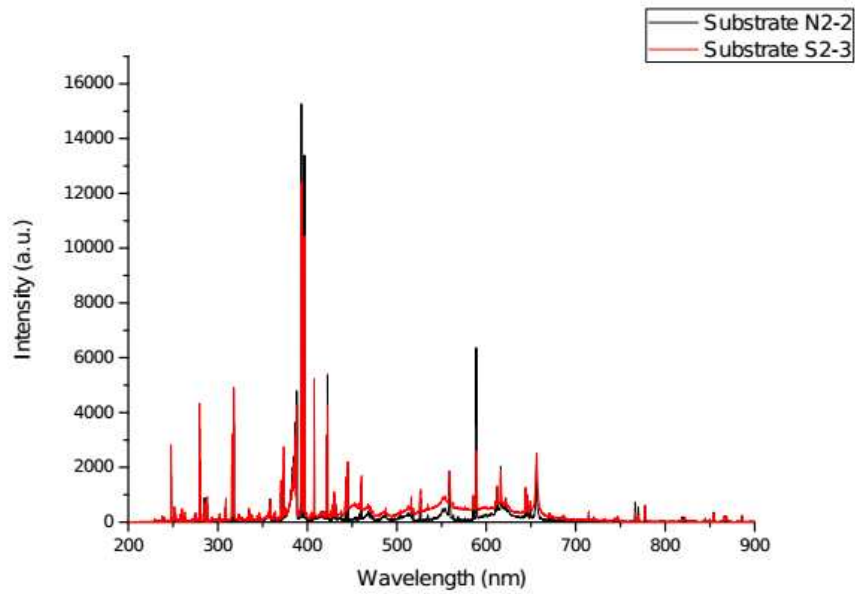
207
 208 Table II - Emission lines used for the CF-LIBS analysis and their relevant spectral parameters

Element	Ion.	Wavelength (nm)	E_k ($\times 10^{-4}$ cm $^{-1}$)	A_{ki} ($\times 10^{-8}$ s $^{-1}$)	g_k
Al	I	237.31	4.22	0.81	6
Fe	II	238.20	4.2	3.8	12
Fe	II	239.56	4.21	2.5	10
Fe	II	239.92	4.23	1.4	6
C	I	247.85	6.2	0.18	3
Si	I	250.69	4.0	0.47	5
Si	I	251.61	4.0	1.21	5
Si	I	251.92	3.98	0.46	3
Si	I	252.41	3.97	1.82	1
Si	I	252.85	3.98	0.77	3
Fe	II	258.58	3.87	0.81	8

Fe	II	259.94	3.85	2.2	10
Fe	II	260.65	7.46	1.8	6
Mg	I	285.21	3.51	4.91	3
Si	I	288.15	4.1	1.89	3
Al	I	308.21	3.24	0.63	4
Al	I	309.27	3.24	0.74	6
Ca	II	315.88	5.68	3.1	4
Ca	II	317.93	5.69	3.6	6
Ti	II	336.12	3.0	1.1	10
Ti	II	337.28	2.97	1.11	8
Sr	II	346.44	5.34	2.84	6
Ca	II	370.60	5.22	0.88	2
Ca	II	373.69	5.22	1.7	2
Fe	I	385.99	2.59	0.1	9
Sr	II	407.77	2.45	1.47	4
Sr	II	421.55	2.37	1.34	2
Ca	I	422.67	2.37	2.18	3
Ca	I	442.54	3.77	0.5	3
Ti	I	498.17	2.69	0.66	13
Ti	I	499.10	2.68	0.54	11
Ti	I	499.95	2.67	0.53	9
Ti	I	500.72	2.66	0.49	7

210

211 The analysis evidences that the LIBS spectra of the epoxy resin (segment 3 in sample N2-2 and
212 segment 5 in sample S2-3) are very similar in the two samples, and the corresponding elemental
213 composition obtained by the CF-LIBS analysis is very similar, as well (figures 7 and 8)



214

215 Figure 7 – Average LIBS spectra of the epoxy resin in samples N2-2 and S2-3

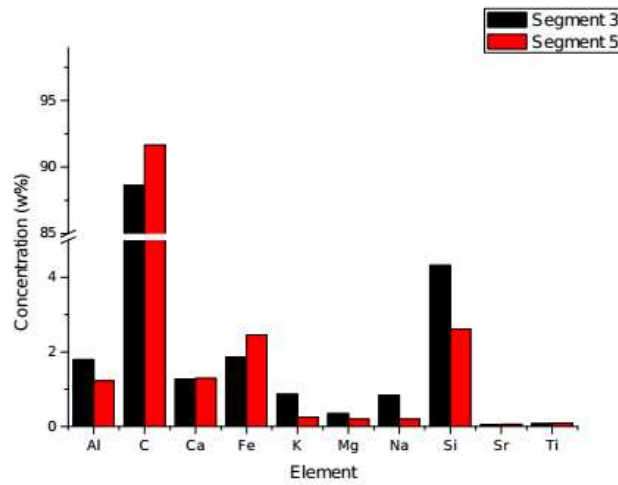


Figure 8 – Composition of the epoxy resin as determined by CF-LIBS in samples N2-2 (segment 3) and S2-3 (segment 5)

The composition of the other clusters is shown in figure 9, for the two mortar samples.

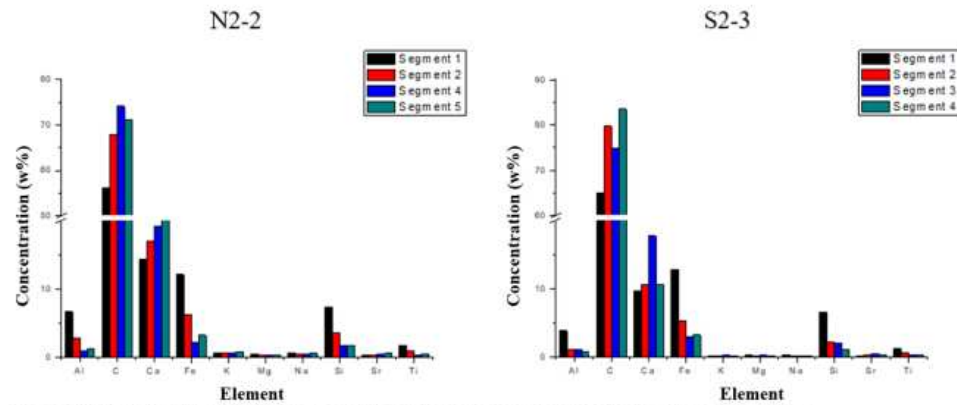


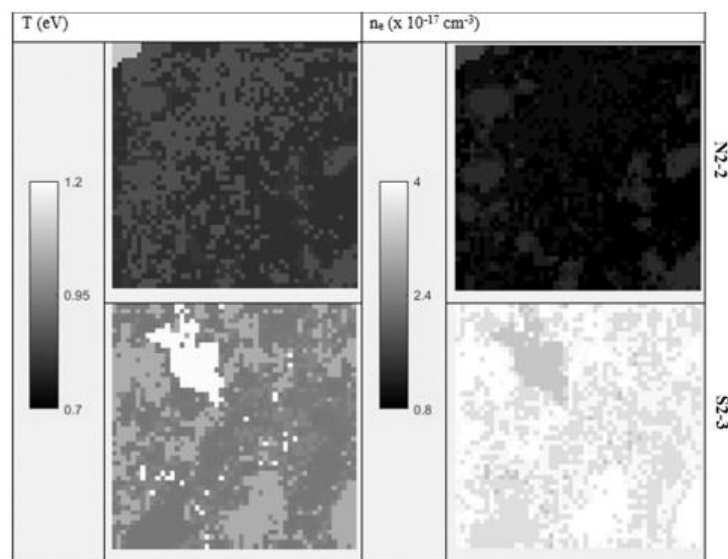
Figure 9. Results of CF-LIBS obtained for each segmented area (excluding the epoxy resin).

Although the method presented is independent on the specific instrument used for the acquisition of the LIBS spectra, is worth to stress that, in our case, the LIBS spectra were acquired using a time-integrated spectrometer. Since the CF-LIBS method relies on the fundamental hypothesis of having the plasma close to Local Thermal Equilibrium [43], and this condition occurs in LIBS plasma only in a limited time interval, it might seem inappropriate its application to spectra which were acquired during the whole lifetime of the plasma. However, the authors have recently demonstrated that, due

231 to the fast decay of the LIBS signal in time, the acquired spectra are in fact dominated by the emission
 232 of the plasma in a time window of about 1 μs [44]. In the time interval considered, typically the LIBS
 233 plasmas are close to LTE conditions, and this consideration gives us confidence that the results
 234 obtained are, indeed, meaningful.

235 The calculate electron temperature and number density are shown on top of the compositional map,
 236 in figure 10. We see that the parts of the map where the epoxy resin was exposed are characterized
 237 by hotter plasmas. This is a further occasion to note that whatever analytical method, applied to the
 238 whole map, would have probably suffered the large differences in the matrix that characterize our
 239 samples.

240



241

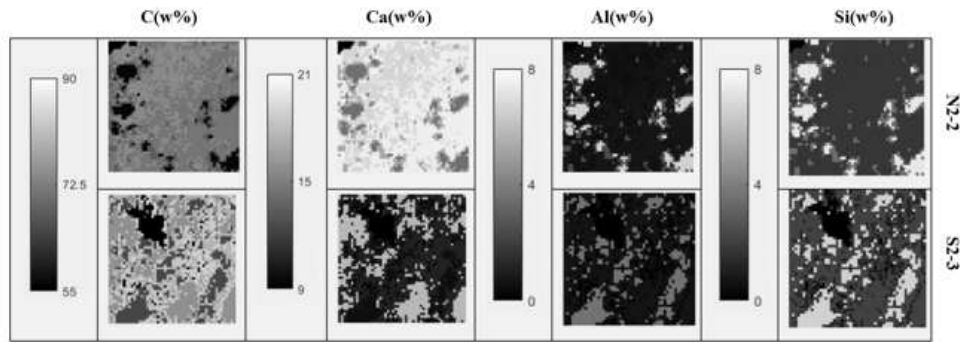
242 Figure 10 – Electron temperature and number density as calculated by CF-LIBS

243

244 From the data reported in figure 9, the quantitative compositional maps of the mortars can be obtained.

245 The most significant are shown in figure 11 (the epoxy resin was not considered).

246



247

248 Figure 11 – Quantitative compositional maps of the two mortar samples (top: N2-2, bottom: S2-3)

249

250 The inspection of **figure 11 shows** that the method proposed in this paper, although not able to assess
 251 the fine compositional variations inside the different groups, provides results that reproduce well the
 252 texture of the samples. The comparison of the compositional maps obtained confirms quantitatively
 253 the differences between the two mortars that were already qualitatively evident from the visual
 254 inspection. **The composition of the constituents of the sample can be obtained with a reasonable**
 255 **precision, typical of CF-LIBS analysis [45], of about $\pm 1\%$ on the major elements and proportionally**
 256 **higher on the minor and trace elements, as evidenced in figure 8, where the same material (epoxy**
 257 **resin) was analysed in the two samples.** We would like to stress once again that the high
 258 inhomogeneity of the samples would have made difficult any other quantitative approach based on
 259 global averages or comparison with reference samples. The CF-LIBS analysis has evidenced, in fact,
 260 large variations in the plasma parameters (electron temperature and number density, **figure 10**) within
 261 the same sample and between the two samples that can only be efficiently dealt with using a
 262 Calibration-Free approach.

263

264 4. Conclusions

265 We have proposed a fast method for the quantitative analysis of μ -LIBS elemental images, based on
 266 the application of the SOM method for the determination of the different classes of materials in the
 267 samples, followed by CF-LIBS analysis of the average representative spectra.

268 In this way, large variation of the sample matrix can be dealt with, and the textural features of the
 269 material can be obtained. The technique proposed is transportable, rapid and cheap. It has been
 270 presented and tested for the realization of compositional maps of historical mortar samples, but it
 271 could be easily applied to in situ analysis on modern building materials as well as, in general, to the
 272 analysis of highly inhomogeneous materials.

273

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