A. Bergomi [1,*], V. Comite [1], C. Della Pina [1], P.M. Carmona-Quiroga [2], L. Maestro-Guijarro [2], M. Oujja [2], A. Crespo [3], C.A. Lombardi [1], M. Borelli [1], M. Castillejo [2], P. Fermo [1].

Elemental analysis of black crusts using Laser Induced Breakdown Spectroscopy for the determination of pollutant sources

1 *Department of Chemistry, University of Milan, Via Golgi 19, 20133 Milan, Italy*
2 *Physical Chemistry Institute Blas Cabrera, IQF-CSIC, C/Serrano 119, 28006 Madrid, Spain*
3 *Institute for the Structure of Matter, IEM-CSIC, C/Serrano 121, 28006 Madrid, Spain*
* ***andrea.bergomi@unimi.it***

Black crusts represent one of the most widespread degradation phenomena on stone surfaces exposed to the outdoor environment and protected from washout. The metal-rich carbonaceous particles which compose particulate matter (one of the major air pollutants) play a key role in the formation of these dark patinas by catalyzing the sulphation of the calcareous substrate leading to the formation of gypsum. Numerous source apportionment studies carried out on particulate matter highlight the possibility of determining the pollutant sources based on the elemental composition of the particles [1]. For this reason, elemental analysis on black crusts has been carried out throughout the years to determine the main pollutant sources of the surrounding areas and put forward targeted mitigation strategies for the protection of cultural heritage.
However, the most employed analytical technique for these studies is Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) [2], which requires extensive sample preparation, including the need to retrieve part of the black crust from the monument. In this context, Laser-Induced Breakdown Spectroscopy (LIBS) may represent a valid alternative, due to its micro-destructive nature and the potential for *in-situ* applications. Another advantage of LIBS is the possibility of performing stratigraphic analyses to determine the in-depth distribution of metals and other elements. To date, few studies have been performed on black crusts using LIBS [3,4] and none of them assess the ability of this technique in recognizing the main pollutant sources by evaluating the presence of tracer elements.
In this study, black crust samples were collected from the Monumental Cemetery of Milan (Italy) in order to assess the ability of LIBS in recognizing the main pollutant sources of the surrounding area (surface analysis) and their variation throughout the years (stratigraphic analysis). Indeed, Milan is one of the most polluted European cities and the sampling area is located less than 1 km way from the second main railroad of the city, as well as being at the center of numerous heavily trafficked arterial roads. Therefore, railroad and vehicular traffic represent two significant pollutant sources, which are characterized by several tracer elements (markers). Only previously detached samples were taken for analysis from funerary monuments, enabling precise dating of the crust and of the years of pollutant accumulation.
LIBS surface analysis proved successful in identifying the main tracer elements of railroad traffic (Fe, Mn) and vehicular traffic (Ti, Zn, Cu, Cr, Ba). Also, using CaF molecular bands it was possible to identify the presence of fluorine for the first time in black crust sample analysis. This element is used as a flux in the production of steel, which is the main component of train wheels and rails. Moreover, stratigraphic analysis of the four elements found in all samples (Fe, Mn, Ti, Ba) showed a decrease in concentration from the surface towards the bulk of the crust, giving interesting insight into the variation of the impact of pollutant sources throughout the years.

References

[1] Manousakas M., Furger M., Daellenbach K.R., Canonaco F., Chen G., Tobler A., Rai P., Qi L., Green D., Hueglin C., Slowik J.G., El Haddad I., Prevot A.S.H., Source identification of the elemental fraction of particulate matter using size segregated, highly time resolved data and an optimized source apportionment approach, Atmos. Environ. X, vol.14 (2022), No.100165.
[2] Barca D., Comite V., Belfiore C.M., Bonazza A., La Russa M.F., Ruffolo S.A., Crisci G.M., Pezzino A., Sabbioni C., Impact of air pollution in deterioration of carbonate building materials in Italian urban environments, vol.48 (2014) pp.122-131.
[3] Botto A., Campanella B., Legnaioli S., Lezzerini M., Lorenzetti G., Pagnotta S., Poggialini F., Palleschi V., Applications of Laser-Induced Breakdown Spectroscopy to Cultural Heritage and Archaeology: a critical review, Spectrochimica Acta Part B: At. Spectr., vol. 56 (2001), pp. 887-903.
[4] Senesi G.S., Carrara I., Nicolodelli G., Milori D.M.B.P., De Pascale O., Laser cleaning and laser induced breakdown spectroscopy applied in removing and characterizing black crusts from limestones of Castello Svevo, Bari, Italy: A case study, Microchem. J., vol. 124 (2016), pp.296-305.