First results of diagnostic investigation on purple dyes from lichens

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Purple lichen dyes were often used as substitutes of Tyrian purple (obtained from Murex) in many applications such as textiles dyeing or for the realisation of illuminated manuscripts since the past 2000 years [1]. The principal lichen species used was *Roccella canariensis*, but in literature it can be easily found evidence that other lichen species from genera such as Ochrolechia and Lasallia were used to produce orchil [2]. Several spectroscopic techniques have been applied in order to improve the possibility of identifying orchil on artworks. After that, the same techniques have been used in order to try to distinguish the lichen species from which orchil was created. Developing a method to distinguish the species of origin in an ancient sample of purple dye could be useful, because it could reveal historical information about the manifacture and the ancient trade route.
Orchil purple dye is primarily composed by orcein-like molecules, obtained from some chemical precursors contained in lichens after extraction and subsequent reaction with ammonia and atmospheric oxygen passing through the intermediate formation or orcinol.
Among others, particularly promising seemed to be the HPLC-MS technique, which was used for this purpose to discriminate orchil samples prepared in laboratory from the species *Roccella canariensis*, *Ochrolechia tartarea* and *Lasallia pustulata*. The samples used in this study were dye powders, parchment dyed with the previous powders and samples of wool and silk textiles dyed with orchil obtained from known species. For HPLC-MS analysis, samples were extracted with an 80% formic acid/water solution, filtered and injected directly in the instrument.
The first results indicate that there are at least four specific masses that seem to be promising for discriminating *Roccella canariensis* samples from *Ochrolechia* and *Lasallia* samples.
As a first application of this study, the purple dye in the parchment of the 6th century *Codex Brixianus* was analysed.

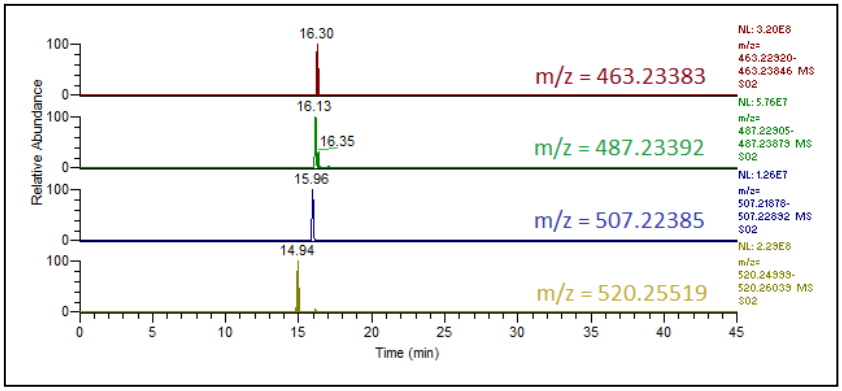

Figure 1 : Masses and retention time of HPLC-MS analisys of textile dyed with Roccella C.

[1] Caley E.R. The Stockholm Papyrus: an English translation with brief notes. *Journal of Chemical Education* 1927; 4: 979-1002.
[2] Kok A. A short history of the orchil dyes, *The Lichenologist* 1966; 3: 248-272.
[3] Martuscelli E. *I coloranti naturali nella tintura della lana, arte, storia, tecnologia e "archeo-materials chemistry"* 2003, Napoli, CAMPEC.