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## Further investigation on the characterisation of the ancient *folium* dye

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The folium dye, extracted from *Chrozophora tinctoria* (L.) A. Juss., is cited in several ancient treatises as a pictorial material to obtain blue-purple hues [2-3]. Therefore its use in painting art must have been common, in particular with main to miniature painting. Nevertheless this dye has been rarely identified on artworks [4] possibly due to the lack of diagnostic information. In addition, at present it is almost entirely missing the comprehension of the chemical nature of the dye. For this purpose, in a recent work an improvement of the spectroscopic information concerning folium has been proposed [1], allowing to evidence its presence on some Western European manuscripts. The same authors started a study in order to characterise the chemical behaviour of folium and to gain information on the structure of the molecules composing it. A relevant feature, always cited in the description of folium in ancient treatises, is the behaviour of the dye in relation to pH but this was shown to be incorrect information as the only difference in colour is actually given by the maturation state of *Chrozophora* fruits, and upon addition of transition metallic ions to folium. Another feature is the behaviour of folium, both hydrophilic, being very soluble in water, and hydrophobic, as the coloured fraction of an aqueous extract can be completely adsorbed on a reversed phase resin. Most probably its molecules have an amphiphilic nature, containing both polar and nonpolar functional groups. Instrumental analysis was performed with different techniques (HPLC-MS, SERS-Raman, MALDI-ToF-MS, NMR) in order to define the structure of the dye. For simplifying the matrix, a first purification step on a C18 resin was carried out and an hydrolysis with a pectolytic enzyme was then attempted, in order to remove the hydrophilic part of the molecule which is made of oligosaccharides. Works are in progress in order to hypothesise chemical structures of the molecules present in the different fractions.

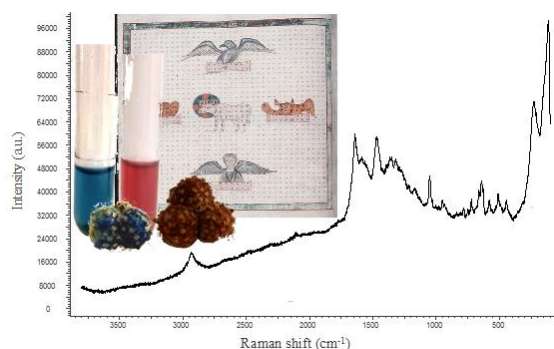


Figure 1: SERS spectrum, fruit extract and artworks containing Folium

[1] Aceto M., Arrais A., Marsano F., Agostino A., Fenoglio G., Idone A., Gulmini M., A diagnostic study on folium and orchil dyes with non-invasive and micro-destructive methods, *Spectrochimica Acta A* 142 (2015) 159-168.

[2] Brunello F., *De arte illuminandi* (1971) Neri Pozza, Vicenza.

[3] Dodwell C.R., *Theophilus: the various arts* (1961) Nelson, London.

[4] Guineau B., Le folium des enlumineurs, une couleur aujourd'hui disparue, *Revue d'archéologie medievale*, 26 (1996) 23-44.