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Micro-invasive study of a 15th century Armenian manuscript: first identification of lac dye by means of HPLC-MS

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The possibility of analyzing small samples taken from paintings allows obtaining interesting information that could not be gained by means of non-invasive techniques. This is particularly true for illuminated manuscripts which are fragile and precious artworks, for whom sampling is therefore usually not allowed. On such cases the knowledge of the colourants used for the miniatures is forcedly confined to the results yielded by the a poorly selective non-invasive analytical approach.

In the present case a 15th century Armenian illuminated manuscript held in the collection of Matenadaran ancient manuscripts Museum, in Yerevan (Armenia). The manuscript was made in a scriptorium at Aghtamar Island, in the Vaspurakan region of historic Armenia and the present investigation represent one of the very few performed on Armenian ancient manuscripts. A selection was carried out in order to obtain samples from all hues present in the miniatures and 15 micro samples (mostly < 1 mm²) were obtained. The size of the samples was suitable for performing non-destructive measurements with UV-Visible diffuse reflectance spectrophotometry with optic fibres (FORS), in order to obtain preliminary information useful for addressing further analyses. After that, Raman spectroscopy, Surface Enhanced Raman Spectroscopy (SERS), SEM-EDX and HPLC-MS were used for a complete characterization of the samples.

The combination of molecular (Raman, SERS, FORS, HPLC-MS) and elemental (SEM-EDX) techniques allowed the identification of all the pigments used in the miniatures. Natural ultramarine, indigo, cinnabar, minium and orpiment were the main pigments identified. Green hues were obtained with a mixture of indigo and orpiment, the so-called *vergaut*. Of particular interest was the identification of iron-gall ink, which in this case has been used as a pigment in the black areas of the paintings.

As to red-pink areas, preliminary FORS analysis suggested the presence of dyes from scale insects such as Kermes, Armenian cochineal, Polish cochineal or lac dye (Indian lac), whereas Mexican cochineal was excluded for historical reasons. Despite the extremely tiny size of the sample, upon hydrolysis with formic acid and HPLC-MS analysis it was possible to identify lac dye through the identification of laccaic acid A and B. Lac dye is obtained from *Kerria lacca*, a species native of Southeastern Asian countries, therefore its presence - and not that of Armenian cochineal - might seems unusual from the geographic point of view. The exhaustive molecular characterization obtained here for the organic dyes is relevant as miniature paintings are very rarely analysed with invasive techniques and such information is therefore almost totally lacking.

Interesting information was also obtained with concern to later interventions on the miniatures. Raman analysis highlighted the presence of 20th century pigments such as phthalocyanine blue and Naphthol Red, clearly indicating contemporary restorations.