A PROTOCOL FOR NON-INVASIVE ANALYSIS OF MINIATURE PAINTINGS

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The characterisation of palettes used in medieval manuscript illumination is an important task from the historical-artistic point of view, but a hard one from the scientific point of view: miniatures cannot be sampled, it is unsuitable to use techniques operating in contact (i.e. IR in ATR mode) and to perform long-lasting analytical sessions, due to the stress that can be inferred to manuscripts. For these reasons it is necessary to use analytical techniques either non-invasive and fast; moreover, in most of cases it is necessary to work *in situ* with portable instruments Among available techniques working in portable versions, Raman spectroscopy is the most informative, due to its diagnostic power; it requires, though, long time of analysis. XRF spectrometry is a powerful alternative but being an elemental technique, in some cases it does not yield accurate results. UV-visible-NIR spectrophotometry in reflectance mode with fibre optics (FORS) can be promising as preliminary technique with some apparent limits.

In this work a protocol of analysis is proposed for characterisation of miniature paintings on manuscripts in non-invasive way, using only portable techniques and performing *in situ* analysis. The protocol allows identification of colorants by successive application of complementary techniques, exploiting the advantages of each technique. First of all a palette with several pigments, dyes and lakes on parchment has been prepared with colorants that were in use in Middle Ages; paints have been prepared in gum Arabic and in egg white, according to ancient recipes described in medieval textbooks such as *De arte illuminandi* by anonymous, *Compositiones ad tingenda musiva* by anonymous and *Il libro dell'arte* by Cennino Cennini. This palette is the base on which to build a database of spectroscopic analysis, reproducing a situation similar to the one present on manuscripts. It is important, therefore, to stress out the fact that spectra collected from this palette are more reliable that spectra obtained from analysis of colorants in powder. Protocol is started with an overall investigation with FORS, collecting spectra from all painted areas of the manuscript and comparing them with the database. This allows to identify almost 60-70 % of the colorants present. Then visual inspection of the paintings is performed with a digital camera connected with a 10-80x microscope, in order to have a clear image of areas that show uncertain FORS spectra, i.e. mixtures of pigments, altered paints, etc. Then XRF spectrometry is performed in order to characterise metal pigments (i.e. gold, silver and copper pigments), to verify the presence of overlapping layers, to identify mordants for dyes and lakes and to identify contaminants in pigments yielding information useful to study the provenance of raw materials for colorants. At this stage almost 90% of colorants can be identified. Finally Raman spectroscopy is used for the most uncertain cases. After application of these techniques a wealth of information is obtained, causing little or no stress at all to the manuscripts under analysis.