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Investigation of multilayer painting by means of molecular spectroscopy

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Abstract. The study of paintings' layer structure under microscope was implemented in the early XX century; since that time method of cross-section preparation as well as composition of embedded materials changed and capabilities of optical microscopy broadened. Nevertheless, until recently cross-sections were prepared only for analysis of paintings' layer-specific structure, morphological and technological features, tracks of restoration treatments. Examination of chemical composition required additional sampling as well as division of these samples layer by layer in order to determine pigments and binding media; these procedures didn't always lead to proper results. Micro-Raman and micro-FTIR spectroscopy allow carrying out investigation of painting cross-sections without any additional preliminary sampling; this is shown on example of investigation of a number of paintings.

For the first time painting stratigraphy issue attracted investigators' attention in the early XX century, when in 1914 paintings' structure was studied under microscope on a picture and on painting samples put on edge. Later, while technology advanced the method improved, different variants of embedded materials for cross-sections preparation were suggested and capabilities of optical spectroscopy developed [1]. But the procedure of cross-section preparation remains the same and consists in the following: painting sample of 1-1.5 mm size which contains as many layers as possible (ground, paint layers and varnish) is placed in an embedded material at 90° angle.

Until recently microscopic investigation of painting cross-sections allowed determining only the technological features of a picture: paint layer structure, quantity, colour and thickness of layers, presence of imprimatura and underpainting, tracks of restoration interventions. Determination of pigment and binding media composition in painting is a difficult issue because components of each layer should be investigated using different analytical methods including optical microscopy, X-ray fluorescence analysis, electronic microscopy, molecular spectroscopy, gas chromatography etc. [2, 3]. For example, thanks to investigation of cross-sections from different parts of the picture of unknown artist (F. Budkin, "Portrait of M. Lermontov") three primers were revealed, which is a rare occurrence. Also, study of icon "Hagiography of St. Parthenius, Bishop of Lampsacus" (Uspenskiy

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Cathedral, Smolensk) established that latter restoration wispy paint layer drawn above the original painting in fact has an underlying calcium carbonate ground.

Most conventional FTIR spectroscopy methods are invasive and require relatively large amount of sample. For a good absorbance spectrum an additional sampling is needed: it consists in mixing of a sample and potassium bromide with further grinding and pressing into pellets. ATR spectroscopy also have serious drawbacks: samples can not be used in further investigations due to changing of their layer structure after contact with ATR crystal and the method provide the information regarding only the upper layer. Unlike methods described above, micro-Raman and micro-FTIR spectroscopy allow examining paint layer composition directly from a cross-section. That spares a sample and makes it possible to use it in further investigation.

One of the advantages of micro-FTIR technique is capability of collecting spectra in different modes, among which the most suitable for cross-sections investigation is ATR mode. It requires small amount of a material, minimal sample preparation process and is able to achieve higher spatial resolution (about 10 μm) due to higher refractive index of the ATR crystal (Ge). It is possible to obtain high-quality IR spectra of most of paint layers with thickness no less than 10 μm. In case of investigation of thinner layers precision of analysis can be maintained by changing the configuration and aperture size. Micro-Raman spectroscopy which has higher spatial resolution (about 1 μm) allows obtaining spectra from separate grains of pigments and minerals, determining structural features of different pigments, for example, defining crystal system of titan white (TiO_2).

Complementary nature of Raman and IR spectroscopy can be illustrated by analysis of a cross-section from Titian painting. Verdigris was found in the paint layer by means of micro-ATR-FTIR spectroscopy, and lead-tin yellow type I was found with the help of micro-Raman spectroscopy.

Raman and ATR-FTIR micro-spectroscopy are valuable analytical techniques for analysis of paint cross-sections. Both methods require minimal sample preparation and have high spatial resolution. Besides, the technique allows performing chemical mapping – generation of visual images depicting the distribution of components of paint layers, variations of molecular structure including the result of paint layers degradation.

References

1. M.J. Wachowiak, JAIC **43**, 205 (2004)
2. J.S. Tsang, JAIC **30**, 163 (1991)
3. B. Singer, T.E. Aslaksby, B. Topalova-Casadiego, Stud. Conserv. **55**, 274 (2010)