

Simultaneous LIBS and LA-ICP-MS analysis of wall-paintings cross-sections

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The research was devoted to elemental mapping of multilayered historic samples characterized by a high degree of inhomogeneity using two laser-based instrumental methods: (i) LIBS (laser induced breakdown spectroscopy) and (ii) LA-ICP-MS (laser ablation inductively coupled plasma mass spectrometry).

Samples were analyzed in the form of cross-sections prepared from tiny blue fragments of mediaeval Nubian wall-paintings embedded in resin and polished in such way that every layer of the mural was visible and available for the analysis.

All experiments were performed using a J200 Tandem LA/LIBS instrumentation (Applied Spectra Inc., Fremont, CA) equipped with a 266 nm Nd:YAG laser. For collection and spectroscopic analysis of the radiation emitted by the laser induced plasma a Bruker Aurora Elite spectrometer was employed. Generated aerosol was analyzed using a Thermo iCAP Qc quadrupole ICP-MS (ThermoFisher Scientific, Bremen, Germany). LIBS and LA-ICP-MS analysis were performed from the same sample area simultaneously in the multiline scan mode (n=11).

Both methods enabled to determine two blue pigments used in Nubian wall-paintings only on the basis of their elemental composition. Egyptian blue (CaCuSi₄O₁₀) was identified when Cu, Ca and Si were distributed in the same areas of the analyzed samples. Co-presence of Na, Al and Si indicated the use of lapis lazuli (Na₈-10Al₆Si₆O₂₄S₂-4). Low limits of detection characteristic for LA-ICP-MS permitted to observe the distribution of some mineralogical impurities such as Ag, Sn, Sb, Hg, As, Cl in the thin dark blue painting layer, which led to conclude about the use of natural ultramarine instead of artificial one. LIBS provided the information about lighter elements such as O not accessible by applying only LA-ICP-MS mapping.

The finding of lapis lazuli used as a pigment in Nubian wall-painting was quite surprising, because mediaeval Nubia was supposed to be a rather insignificant artistic centre and the price of natural ultramarine in that times was close to the price of gold.
