

Energy-Filtered Secondary Electron Imaging for the Study of Degradation Processes in Paintings

Filip Mika¹, Silvie Švarcová², Cornelia Rodenburg³, Zuzana Pokorná¹, David Hradil²

¹ Institute of Scientific Instruments of the Czech Academy of Sciences, Czech Republic, ² Institute of Inorganic Chemistry of the Czech Academy of Sciences, Czech Republic, ³ The University of Sheffield, UK

Energy-Filtered Secondary Electron Imaging (EFSE) is complementary to scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS), two techniques that are well-established for cultural heritage analysis and routinely used. EFSE shows the sample only in a very narrow secondary electron energy window at a time and the variations in signal can reveal minute differences in chemical composition [1]. Compared to EDS it is about a hundred times faster and better spatially resolved. We have developed a miniaturized EFSE device that can be inserted inside a SEM chamber onto the sample holder [2]. It has a 0.5 mm entrance slit, 0.02% energy resolution for input angles $\pm 6^\circ$, good S/N ratio.

EFSE was used in a study of the degradation of arsenic-based pigments in wall paintings with the aim to explain the origin of mimetite $Pb_5(AsO_4)_3Cl$ as the corrosion product resulting from originally used arsenic- and lead-based pigments. Unusual mimetite was found on valuable Gothic wall paintings uncovered in the St. Gallus church in Kuřívody, Northern Bohemia [3]. A series of model samples imitating the possible composition of original paint layers was exposed to various corrosive agents (rising moisture, salt solutions, oxalic acid or their combinations). Samples in which the presence of mimetite was detected by XRD were then submitted for a detailed study by SEM, EDS and EFSE. Fig.1 shows an SEM image of a one such microsample, in which EDS analysis verified the prevalent presence of As in the smooth area and Pb in the rough area.

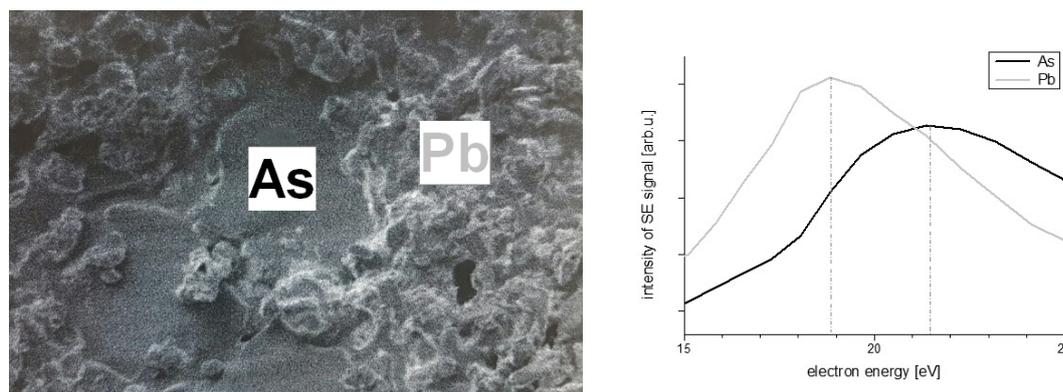


Fig.1 – On the left, SEM image of a sample (area $70 \times 50 \mu m$) containing mimetite. On the right, EFSE analysis of the area at 2 keV primary energy shows a marked difference between the peaks of the most probable secondary electron energies of the two respective areas, by as much as 1.5 eV.

[1] Abrams, Kerry J., et al.: *Making Sense of Complex Carbon and Metal/Carbon Systems by Secondary Electron Hyperspectral Imaging*. Advanced Science (2019): 1900719.

[2] Mika, F.; Pokorna, Z.; Konvalina, I.; et al. (2018). Possibilities of a Secondary Electron Bandpass Filter for Standard SEM. *Proceedings of the 16th Seminar on Recent Trends in Charged Particle Optics and Surface Physics Instrumentation, 2018*, pp.46-48.

[3] Hradil D., Hradilová J., Bezdička P., Švarcová S., Čermáková Z., Košařová V., Němec I.: *Crocoite $PbCrO_4$ and mimetite $Pb_5(AsO_4)_3Cl$: rare minerals in highly degraded mediaeval murals in Northern Bohemia*. J. Raman. Spectrosc. 45 (2014) 848-858

This research was supported by Strategy AV21, Diagnostic Methods and Techniques.