

Archeometric investigations of medieval stained glass panels from Grodziec in Poland

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Stained glass panels were one of the most important and precious features of medieval architecture. During the Middle Ages in Europe glass were generally formed from quartz and ash from beech trunks or from bulk beech trees. Application of such materials were reflected in high amount of silicon, potassium and calcium. Medieval glass technology utilized different materials for gaining specific colour of glass and additional borders, glazings were applied to make impressions on spectators or users of the building.

Information about elemental composition of glass is necessary to determine glass type, technology and provenance of the object. Information about changes in elemental composition due to corrosion processes is usually extremely valuable to settle proper conservation treatment. Many analytical methods can be applied to investigations of glass samples. Scanning Electron Microscope coupled with an Energy Dispersive X-Ray spectrometry (SEM-EDX) enables for measuring content of main elements. Nevertheless information about trace elements content is not accessible for this method. This information usually has significant value for provenance studies of historical glass. One of the methods capable for delivering information about trace elements without sample preparation is Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS).

Investigations were focused on three stained glass panels of Austrian origin, dated on 1425-30. The panels come from Grodziec in Poland and nowadays they belong to the collection of the National Museum in Wrocław. Elemental composition of bulk glass and external layers of glass samples was determined using SEM-EDX and LA-ICP-MS methods. Morphology of the deteriorated glass were investigated through SEM-BSE images of the cross-sections. Also *LA-ICP-MS* longitudinal concentration *profiles were elaborated*. Corning D and NIST 610 glasses were used as reference materials for LA-ICP-MS analysis.

The applied analytical techniques provided valuable information about the structure of glass and external paint layers and gave insight on the manufacture processes. Results show that the stained glass panels reveal characteristic elemental composition of wood ash glass produced from 1000 to 1400 AD. Almost equal proportions of potassium and calcium oxides indicate that high quality beech wood was applied by manufacturers. Main elements content is similar for almost all investigated glass samples, which means that manufacturers follow strictly the assumed recipe during panels production. Common correlations between elements (i.e. Sr – Ca, Rb i Ba – K, Ti – Al) were detected. Especially concentration of titanium (0,1 – 0,15% by weight) and barium (0,3 – 0,4% by weight) were relatively constant and typical of medieval wood ash glass. Some differences in elemental composition were detected for minor or trace elements which are connected to impurities or colour additives. Several stained glass samples exhibit typical composition of modern glass. Such samples were probably used during conservation treatments in the 20th century.

Additionally, considerable differences between the composition of healthy bulk glass and the deteriorated surface of glass were detected though SEM-BSE images and LA-ICP-MS longitudinal concentration *profiles*. High concentrations of lead, copper and iron were also determined in external layers of glass samples. Results can be connected with decorative paint layers and drawings.

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