

## Instrumental Neutron Activation Analysis (INAA) of Glass Paintings (Hinterglasmalereien)

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The purpose of this study is to analyze glass paintings which were produced between 1700 and 1900 in Austria, Bavaria, Bohemia and neighbouring areas, and distributed in Upper Bavaria, East of Bavaria/Austria, Augsburg and South Tyrol. Specifically, there have been analyzed samples from Oberammergau, Seehausen and Murnau in Southern Bavaria, Sandl in Austria, Raimundsreut in Eastern Bavaria, Buchers in Bohemia and from Silesia.

The samples were collected by Prof. Dr. Josef Riederer who suggested that the glasses should be analyzed using INAA because neither the origin area nor the date could be determined by the type of pictures, due to the fact that often glass painters went from one region to another. To receive these information, it is necessary to determine the content of a large number of elements with good accuracy and precision. This study is focused on examination of the composition of the samples. The analysis of glasses is a possible way to find out the origin by local producers. A total of thirty-two samples were collected and ten of them have been analyzed until now using the INAA at the Institute für Kernchemie in Mainz to determine the parts per million of each element in samples. The results show many different compositions and also different concentrations.

### Sample Collection and Preparation

One sample of each glass painting - each with a mass of 20-100 mg - was taken carefully to prevent damage of the samples. As they were painted, first of all the paint should be removed due to the fact that paint elements could interfere in the analysis, i.e. Hg of cinnabar, Cu of azurite. To remove the paint and also surface contaminations, the glass samples were carefully washed with Isopropanol during 1h and then washed with Millipore water. After that, the samples were treated with HNO<sub>3</sub> for 50 min and washed with Millipore water. Finally they were washed with acetone during 1h and dried overnight. Before irradiation, the surface of the samples was checked again using the microscope. Ten samples without paint were taken for the analysis.

Irradiation of the samples with short and long irradiation times was executed to receive

an overview about the main and trace elements of the samples. The short irradiation is carried out in the rabbit system with a neutron flux of  $1,7 \cdot 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$  and the long irradiation in the Rotary specimen rack with a neutron flux of  $7 \cdot 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$ , in the research reactor TRIGA Mainz.

After the irradiations gamma-spectrometric measurements were carried out with HPGe semiconductor detectors using the program "Genie 200 V 2.1 A" of the company Canberra Eurisys GmbH. For short irradiation times 3 samples of every glass were taken, each one with a mass of approx. 10 mg, irradiated for 1min and measured immediately after that 10 and 30min. Hence it was possible to analyze the elements Na, K, Mg, Mn, Ti and V, (by the nuclide <sup>24</sup>Na, <sup>42</sup>K, <sup>27</sup>Mg, <sup>56</sup>Mn, <sup>51</sup>Ti, <sup>52</sup>V) which have half life times of few minutes or hours. Aluminium can not be used for the analysis since the Silicon amount in the samples (Al is produced by a (n,p)-reaction from Si). For long irradiation time 3 samples of every glass, each one with a mass of approx. 100 mg, were irradiated for 6h and measured 1h and 8h after waiting ~3 days / 15-20 days respectively. The elements with longer half life time as Sc, La, Sm, Cr, Zr, Zn, Fe, Co, Rb, Sb, Ba, Cs, Ce, Eu, Ta, Tb, Lu, Hf, Pa, and Yb (by the nuclide <sup>46</sup>Sc, <sup>140</sup>La, <sup>153</sup>Sm, <sup>47</sup>Ca, <sup>51</sup>Cr, <sup>95</sup>Zr, <sup>65</sup>Zn, <sup>59</sup>Fe, <sup>60</sup>Co, <sup>86</sup>Rb, <sup>124</sup>Sb, <sup>130</sup>Ba, <sup>134</sup>Cs, <sup>141</sup>Ce, <sup>152</sup>Eu, <sup>182</sup>Ta, <sup>160</sup>Tb, <sup>177</sup>Lu, <sup>181</sup>Hf, <sup>233</sup>Pa, <sup>169</sup>Yb) are determined.

### Results

To define the real concentration in each sample, a comparison with reference standard liquids of the detected elements were done. The following main and trace elements in the samples were found, considering main element when its concentration is higher than 1000 ppm. In short irradiation time the main elements were Mg, Mn, K and Na, and the trace elements were Ti, V. In long irradiation time the main element was only Fe, and the trace elements were Sc, Cr, Co, Zn, Sb, Ba, Sm, La, Eu, Ce, Yb, Hf and Ta.

The most interesting elements for the interpretation of the results are specifically Mg, Ti, Zn, Rb, Sb or Yb, because of they are not present in all samples or their concentration is so different in each one.