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zur

Archäometrie, Kunsttechnologie und Konservierungswissenschaft



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Looking underneath a glass surface

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*Dedicated to Joseph Salomon**

Abstract

X-ray fluorescence analysis is nowadays widely used for elemental and compositional analysis of cultural heritage objects with great success and benefit. However, special care is needed when these objects consist out of layered structures. The development of x-ray optics has led to three-dimensional x-ray systems, now available for fluorescence analysis. We have applied the two major versions of fluorescence analysis, x-ray induced and particle induced fluorescence, to medieval pieces of stained-glass windows: While gross features could be studied with such a 3-dimensional micro *x-ray fluorescence system* (3d-microXRF) even underneath several micrometers of painted layers on top of the glass body, only the combination of *particle (proton) induced x-ray emission* (PIXE) with *Rutherford backscattering spectroscopy* (RBS) revealed sub-micrometer near-surface changes of the glass due to the incorporation of lead.

1 Introduction

For various analytical purposes in layered structures or in materials with cover layers as e.g. protective means, „looking behind“ such layers is very important without interference from the cover layers. It also applies to paintings with different layers and support structures. The thickness involved is typically in the micro- and sub-micrometer range, in the case of paintings up to tens to even hundreds of micrometers. Since a few years strong efforts were put into the development of micro x-ray fluorescence (XRF) systems and more recently into adding the third dimension in analysing – depth – as well. Based on the development of x-ray focusing and guiding at beam lines of synchrotron facilities using polycapillary lenses (Kanngießer, 2003), three-dimensional micro XRF systems (3d-microXRF) using x-ray tubes are now available in a confocal arrangement of such polycapillary lenses (IFG Institute for Scientific Instruments GmbH) for depth profiling in addition to lateral mapping. Here we present results on glass analysis using the system LouX^{3D}, set up at the Louvre laboratory C2RMF, which was recently used in studies of Louvre Renaissance paintings (Reiche et. al. 2012). The 3d-microXRF study complements analytical work using the ion beam techniques Rutherford backscattering (RBS) and particle induced x-ray emission (PIXE) to test its applicability and limitations. As an illustration of the depth resolution and its applicability for investigations of complicated layered structures we first started with a simple material system. We determined the concentration profile of copper (Cu) in glass which was introduced by ion exchange and diffusion, using the K_{α} -line of Cu. Copper is often used in colored glass. When Cu is introduced into the glass by ion exchange, the resultant concentration is not homogeneous, but a rather pronounced profile may be obtained. Since the K_{α} -line of Cu is near the highest sensitivity

of the micro-XRF system, we consider this glass as an adequate model system for archaeological stained glass windows.

For the conservation and restoration of the large body of stained glass windows originating from medieval and later times, thorough analysis is needed in order to develop procedures for the preservation of this cultural heritage. Various techniques were used in painting on glass, often resulting in layers on top of the glass body which are several micrometers thick, sometimes up to a few hundreds of micrometer. Because of the complexity and heterogeneity of the layers, as they were applied, but also after processing, fired or not-fired, one should seek as much information by many different techniques as possible.

A stained glass window is composed of glass pieces, with or without painting, assembled by lead framing in a lead came structure. One sort of painting often used called „grisaille“ is a mixture of glass and metal oxides (iron oxide, copper oxide...) heated at 630°C. The color of this painting can vary from black to brown, depending on the concentration of the metal oxides and also on the thickness of the drawing line. The thickness of the grisaille is of the order of 100 μm or more. Another kind of painting is called „lavis“, it is a light grisaille with only a small quantity of metal oxides. It looks in reflected light like a light white painting used for the drawing relief. The thickness of lavis is generally less than 20 μm .

The typical thickness of the grisaille paint layers on glass fits well to the depth sensitivity of the 3d-microXRF of up to 200 μm depending on the energy dependent x-ray attenuation as well as to the depth sensitivity up to about 60 μm of the ion beam techniques RBS and PIXE. We have applied both techniques to investigate and analyze two glass pieces, one from the church Saint-Ouen

in Rouen, the other from the cathedral Notre-Dame in Evreux.

2 Experimental

Some characteristics of the techniques applied should be summarized to emphasize the applicability and validity as well as limitations of the obtained results of the analyses. The 3-dimensional XRF system of the C2RMF installed in a joint program with the Technische Universität (TU) Berlin and the IFG was first tested by measuring diffusion profiles on a micrometer scale before studying pieces of stained glass windows. It operates with a Rh anode and uses a polycapillary lens for the excitation and a polycapillary conical collimator (PCCC) for the detection of the fluorescence in a confocal geometry. This technique yields a sensitive volume for analysis in the order of $40 \times 40 \times 40 \mu\text{m}^3$ which is dependent on energy and decreases with increasing energy. It is operated at a working distance to the sample of about 6 mm with a spot size of the x-ray beam of about $50 \mu\text{m}$. Stepping motors in all three directions allow 3-dimensional profiling with micrometer accuracy. A sketch of the system is presented in Fig. 1. Especially valuable is to look into the bulk material underneath a surface layer without perturbing fluorescence radiation from the surface layer. The applicability of such a system, however, is limited by the energy characteristic of the multi capillary „lenses“, cutting off at low energies as well as at high energies leaving a usable energy window between 3 and 20 keV. A detailed description on performances of such systems can be found in ref. (Mantouvalou et. al., 2010). Due to absorption in the material the application is limited in the case of glass to a total thickness of roughly 1 mm, depending on the constitution and the energy of the x-rays to be measured (see the table available on the webpage (see the table available on the webpage: <http://henke.lbl.gov>).

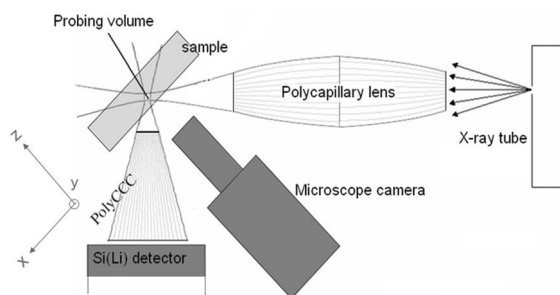


Figure 1: Sketch of the 3d-microXRF system. For depth information, the sample is moved along the z-direction.

The ion-beam analyzing techniques RBS and PIXE were performed with the external 3-MeV proton beam of AGLAE, the objects being positioned closely to the exit window (Si_3N_4) of the beam line (vacuum). The space between the window and the object was flushed with He gas to reduce absorption of low energy x-rays. With this arrangement, elements as low in their elemental number Z as sodium (Na) could be detected.

Because of the limited proton range in the material under investigation as well as the finite absorption length of the emitted x-rays, the analytical results can be obtained only for the near surface region (less than about $35 \mu\text{m}$ for RBS and $60 \mu\text{m}$ for PIXE), for further details on PIXE (Calligaro, 2008). As spatial resolution (lateral resolution), approximately $50 \times 50 \mu\text{m}^2$ are feasible. Typical ion beam currents are of the order of 1 nA, with typical measuring times of 200 s. The way the excitation and detection is achieved, practically no depth information is obtained in PIXE, while the depth resolution in RBS is approximately 100 nm near the surface.

For an illustration of the depth resolution of the 3d-micro-XRF we have analyzed the diffusion of Cu introduced into borosilicate glass, type flat panel glass Schott D263, with a thickness of $100 \mu\text{m}$, compatible with the attenuation length of x-rays in this energy range. The nominal composition is given in weight percent as follows: SiO_2 64.1; B_2O_3 8.4; Al_2O_3 4.2; Na_2O 6.4; K_2O 6.9; ZnO 5.9; TiO_2 4.0; Sb_2O_3 0.1 with a total density of 2.51 g/cm^3 . By dipping the glass into a melt of Cu(I)Cl , Cu ions exchange with the Na ions in the glass and diffuse into the glass platelet from both sides.

The two pieces of white glass (transparent glass), 3 mm thick, maximum extension approximately 6 cm, from Rouen and from Evreux are from the 14th century, and on the pictures we observe the indoor face being covered with brown painting (grisaille) as identified in reflected light. The glass piece from Rouen appears to be a little more greenish than the piece from Evreux indicating a higher content of iron oxide. Both pieces seem to have been assembled in a Pb came structure along the edges, but not at all edges. The Evreux piece was freshly broken (in modern times), its edge showing no signs of chemical attack. Therefore an analysis on such edges may be considered as representative for the glass body.

3 Results and discussion

3.1 Depth-resolution – Diffusion profile of copper

An illustration of the depth resolution is presented in Fig. 2 with the depth profile of Cu determined by metering the intensity of the K_α -line of Cu. In the as-measured profile the Cu intensity peak from the in-diffusion from the back face is strongly reduced due to x-ray absorption. Applying a simple correction for the exponential attenuation by using the attenuation length as found e.g. in Calligaro, 2008, the depth profile over the whole thickness of the plate becomes symmetric. The procedure was checked on the energetically nearby K_α -line of Zn present in the original glass. When applied to Zn, a uniform concentration profile is obtained over the whole depth with a fall-off according to the resolution of the system of roughly $30 \mu\text{m}$. The Cu, in contrast to the Zn profile, shows a deep concentration minimum in the center of the plate due to the limited diffusion. This proves without further quantification that the depth resolution at the Cu K_α -line of 8 keV is well below $50 \mu\text{m}$ in accordance with (Reiche, 2012; Mantouvalou, 2010).

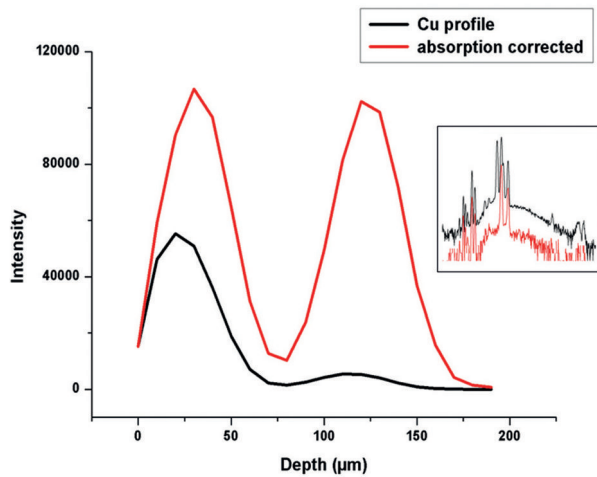


Figure 2: Cu intensity depth distribution after Cu incorporation by ion-exchange and diffusion into a 100- μm thick borosilicate glass platelet. Insert: XRF-spectrum of glass without Cu (bottom, in red) and with Cu incorporated by ion exchange and diffusion (top, in black).

3.2 Surface layer of lead

When trying to determine the composition of the bulk glass of the painted glass pieces a 3-MeV proton beam for a PIXE analysis was directed onto glass edges near the center of the 3-mm thick glass. Fig. 3 illustrates the significant difference in the two glass pieces: While the Evreux glass shows a negligible intensity in the Pb-L-fluorescence, a remarkable Pb „concentration“ of approximately 0.4 % seems to be part of the Rouen glass. The RBS spectra taken simultaneously on the same spots revealed that the Pb contribution in the Rouen glass results from a rather thin layer at the surface and not from bulk glass (see Fig. 4). Although the width of the Pb layer seems to be comparable to a 23 nm Au layer shown for comparison, presently, due to the limited sensitivity of

the proton RBS, only an upper limit of 400 nm can be given for the thickness of this Pb layer.

An illustration for the depth profiling potential and limitations of the 3d-microXRF is presented in Fig. 5. The spot called „Rouen dot 04“ (left part of Fig. 5) is located within the uncovered unpainted glass region on the painted face near the arrow marking the spot for the “bulk” analysis. While the contribution from the small fraction of Zn within the glass decreases as expected due to increasing absorption with greater depth, the Pb-L-line intensities decrease rather rapidly. This intensity fall-off is in accordance with an RBS spectrum taken additional on a nearby spot, which looks like the one presented in Fig. 4 for the bulk taken at the edge. In contrast to the glass spot, the grisaille spot analyzed (right part of Fig. 5) shows a quite regularly changing intensity for Pb as well as for Fe due to the absorption of the material.

The occurrence of a Pb surface layer on uncovered parts of the glass, and the lack of such a Pb layer in freshly broken glass edges confirmed by the 3d-microXRF leads to the speculation of weathering influence (chemical processes with the Pb came metal due to condensed water with non-neutral pH-value).

4 Summary – conclusion

In the context of glass analysis, the presently performed analyses on two examples of glass pieces of stained glass windows have shown the need for depth sensitivity in XRF to distinguish surface contamination from bulk properties. The presented example of glass study also illustrates both, the potential and the limitations in applying the 3d-microXRF as compared to ion-beam analysis. With higher sophistication in the analysis and a better quantification, as e.g. used in ref. [4], complicated layered structures such as several layers of grisailles of different compositions may be distinguished if the layers are not too thick (less than 100 μm in total, beyond

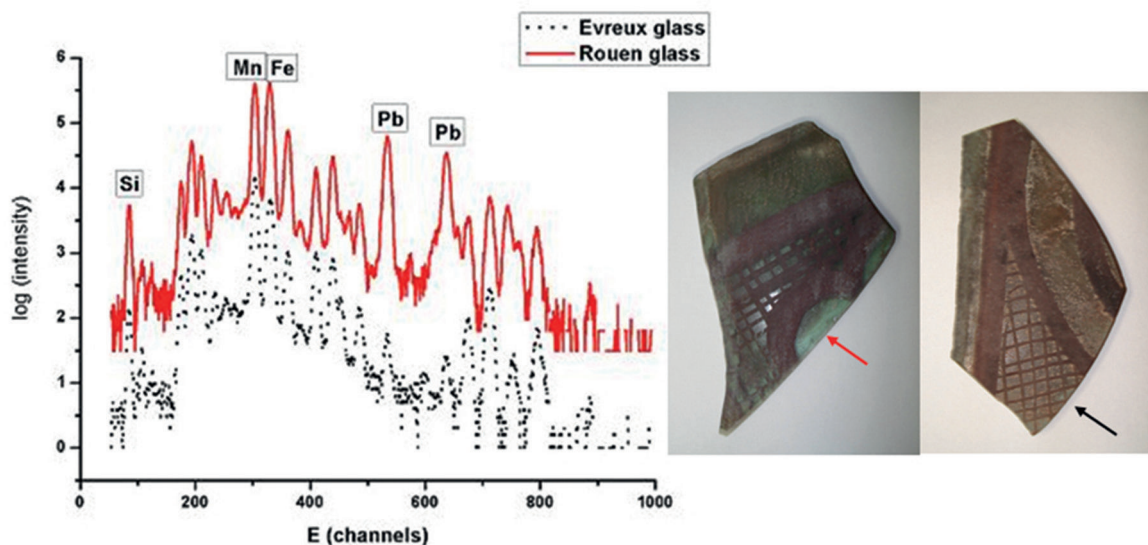


Figure 3: PIXE spectra for the two shown glass pieces taken on the glass edges as indicated by the arrows. The Evreux glass (photograph to the right) was analyzed on a freshly broken edge (dashed line in black, lower curve), the Rouen glass (photograph to the left) was analyzed with an edge originally in contact with the Pb came metal for framing (solid line in red, upper curve).

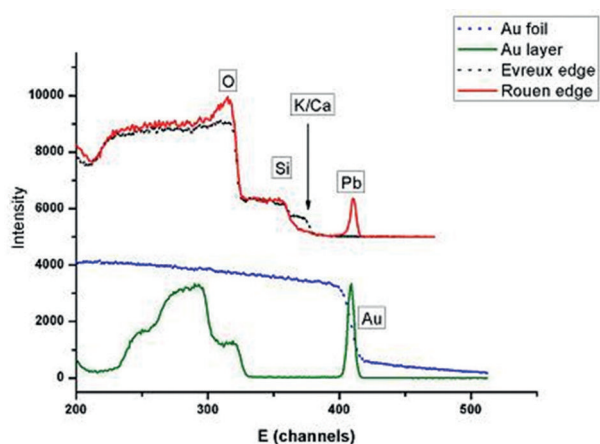


Figure 4: RBS spectra on the same spots of the glasses shown in Fig.2 (top) compared with Au spectra (bottom): to illustrate the thickness of the Pb surface layer, RBS spectra for a thin Au layer ($46\mu\text{g}/\text{cm}^2$ corresponding to 23 nm) and a thick Au foil are also shown. The RBS spectra for the glass pieces are offset for better illustration.

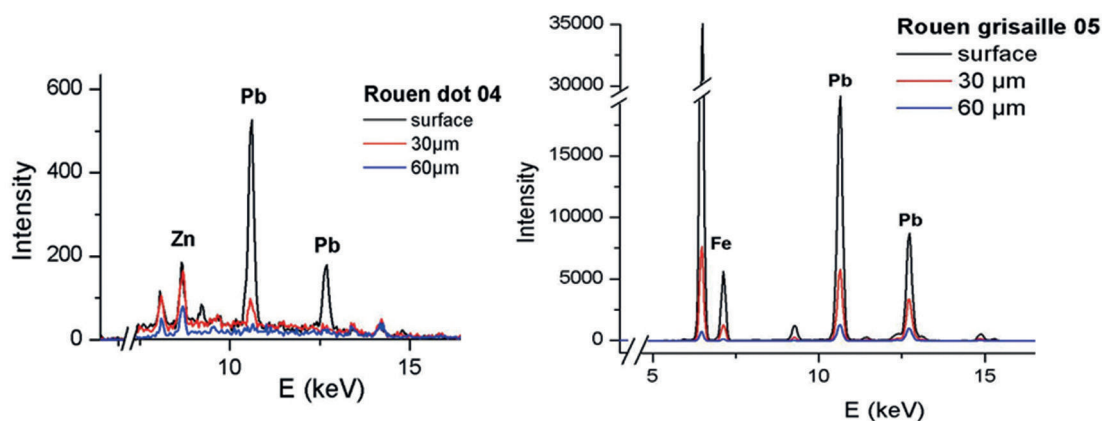


Figure 5: XRF spectra taken at various depth sensitive positions with the 3d-microXRF on a glass surface spot (left) and on a grisaille spot (right) on the Rouen glass piece. On the glass surface spot, Pb is only a contamination layer on the surface, while the grisaille contains Pb throughout the whole depth (note that the reduction in intensity is due to absorption).

Acknowledgement

H.-E.M. is very grateful for the warm hospitality he experienced during his time at the C2RMF. Special thanks go to M. Menu who made the visit at the C2RMF possible and to L. Pichon and B. Moignard operating the AGLAE facility. We thank M. Haschke (IFG) and B. Kanngießer, D. Grötzsch and team (TU Berlin) for the help during the installation and running-in of the 3d-microXRF system. We also very much appreciate the skilful help by P. Szimkowiak from the HZB preparing the Cu ion exchanged glass sample.

* In the course of the early part of this research our colleague Joseph Salomon passed away on February 3, 2009. We not only miss his skills on accelerators and ion beam techniques, but beyond that we miss him as a friend and colleague.

that the attenuation by absorption becomes too high). In cases where only thin layers of a few μm were applied („lavis“ layers), a look „behind“ is easily feasible simply with 3d-microXRD presently available. For even thinner layers („surface contaminations“ or cover layers) the 3d-microXRF can easily analyze structures of different composition underneath such a cover layer. However, for a more precise determination of the thickness and structure and for detailed studies on the formation process, other methods have to be applied, such as e.g. RBS. To reveal the main features of the chemical process of surface contamination or reactions, the 3d-microXRF may be the method of choice because it is now easily available as a laboratory system and easier in handling as compared to an accelerator needed for ion beam analysis such as RBS with nanometer resolution.

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