Analytical Diagnostic with X-ray Spectroscopy of Cultural Artifacts

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1. Introduction
X-radiation is the light for going into the depth. It has the appropriate energy to explore matter on the macroscopic as well as on the atomic scale. On the other hand, X-rays having wavelength in the nano-meter regime are best suited for structure investigation and manipulation of matter on the micro- and nano-meter scale. The latter is only possible since the advent of efficient X-ray optics and the use of synchrotron radiation. X-ray Fluorescence Spectroscopy facilitates not only non-destructive elemental analysis but also elemental imaging inside a sample and chemical speciation when carried out at a synchrotron source. Due to its non-destructiveness it is very well suited for diagnostics of cultural artifacts. Some characteristic examples of investigations on cultural artifacts, like manuscripts, parchments, paintings and glass objects, will be shown and discussed.

2. Experimental
Micro X-Ray Fluorescence Analysis (Micro-XRF) is one of the newest branches of XRF. It has been developed very rapidly in the past ten years which is mainly due to the use of synchrotron radiation. With the advent of new X-ray optics, elemental microanalysis became a real analytical tool – in particular due to the technological development of polycapillary lenses. Micro-XRF utilizes a focusing X-ray optic in the excitation channel in order to make lateral micro imaging possible. Lateral resolutions of less than 100 µm have become feasible even with X-ray tube excitation, thus, facilitating routine investigations on a micrometer scale [1]. At synchrotron sources Micro-XRF can be combined with micro X-ray absorption near edge structure spectroscopy (Micro-XANES) for the determination of the oxidation state and the chemical environment of the elements of interest. If Micro-XANES is carried out in fluorescence mode, i.e. detecting the intensity change of a characteristic fluorescence line with varying excitation energy, thick samples may be investigated as well.
Depth resolution can be achieved, when utilizing a second X-ray lens in the detection channel. The relatively new method of three-dimensional micro-X-ray fluorescence spectroscopy (3D Micro-XRF) delivers for the first time non-destructive, non-integral measurements for the elemental analysis of a wide variety of samples. The technique is based on the use of two polycapillary optics in a confocal arrangement. The overlap of the foci of the two X-ray optics forms a probing volume from which fluorescence and scattered radiation is exclusively derived. The achievable information depth depends strongly on the matrix of the sample. For a glass matrix the usual information depth for transition elements is up to 100 µm [2]. Through the development of a full quantification for stratified samples, 3D Micro-XRF with synchrotron radiation has in recent years turned into a true analytical tool [3]. 3D Micro-XRF with X-ray tube excitation on the other hand can only be used as a qualitative method up until now, as quantification for polychromatic excitation is still a research topic.

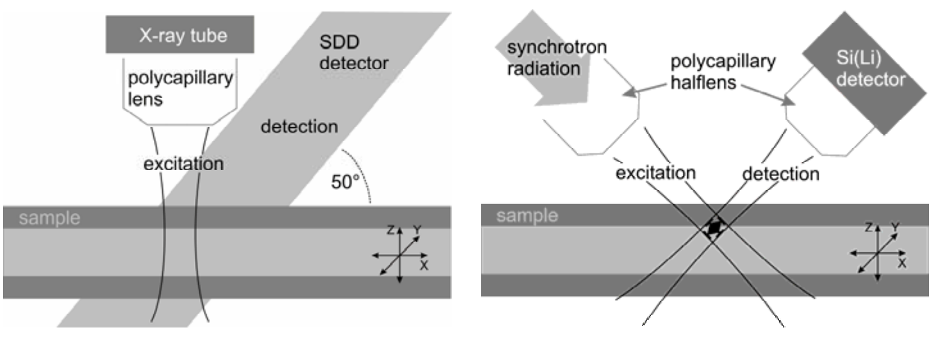

Figure 1: Left: Scheme of Micro-XRF: Radiation is focused with a polycapillary lens onto a sample; emitted radiation is collected with an energy-dispersive detector. The use of the X-ray optic enables lateral microanalysis. Right: Scheme of 3D Micro-XRF: the overlap of the foci of two polycapillary optics forms a probing volume from which information is exclusively collected. Three-dimensional elemental maps can be obtained.

3. Application Examples

With a combination of Micro-XRF and Micro-XANES the oxidation and migration processes of inorganic compounds in ink-corroded manuscripts was studied. Elemental mapping on iron gall inks by micro-XRF shows the correlation of the minor elements in the ink to the major element Fe. Along concentration profiles of Fe, Micro-XANES measurements were carried out in order to determine the oxidation state and the local environment. With the help of model inks, we could show that Cu is a further important element in the paper degradation process due to iron gall ink corrosion [4].

With a combination of Micro-XRF and 3D Micro XRF we studied corrosion processes in reverse-glass paintings [5] and in parchments [6]. To elucidate the mechanism of corrosion processes taking place in the objects depth profiles of mobile elements are of interest. In case of the parchment investigations, the elemental depth profiles could reveal marker elements for provenance studies.

As a last example, the applicability of a new 3D Micro-XRF laboratory spectrometer for the investigation of historical glass objects is demonstrated. Although absorption and resolution effects complicate qualitative analysis of the data, layered structures can be distinguished from homogeneous samples without the need for full quantification. The manufacturing technique could be determined for the investigated historical glass object [7].

4. Conclusions

X-ray spectroscopy has developed into a versatile tool for elemental analysis and chemical speciation for many kinds of cultural heritage objects. Its non-destructiveness in combination with the possibility to obtain three-dimensionally resolved information about the sample exhibits a valuable feature for the analytical diagnostics of these objects. Especially stratified objects like paintings, tiles, parchments and glass objects can be investigated with this technique as the density of these samples is not too high, preventing high absorption of radiation, and the layer thicknesses are in the μm regime.

In general the combined use of Micro-XRF and 3D Micro-XRF constitutes a very helpful strategy for quantitative analysis. The broader elemental range on Micro-XRF can supply valuable information for the quantification of 3D Micro-XRF depth scans. 3D Micro-XRF can be used for answering specific questions like finding marker elements or identifying elemental migration in corrosion processes, while Micro-XRF is a tool for routine measurements.

A new spectrometer renders routine 3D Micro-XRF measurements in the laboratory possible. The presented application example proves the applicability of the spectrometer to investigate stratified objects. The application field, though, is by no means limited to glass objects, but can easily be extended to easel paintings, wood icons, bones, ceramics etc. Thus, confocal measurements with transportable spectrometers become feasible for specific applications. Even though there is not a quantitative evaluation available for polychromatic excitation in a confocal setup, yet, a careful qualitative evaluation may very often lead to valuable and reliable information.

5. References

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