ANALYSIS OF ART OBJECTS AND OTHER DELICATE SAMPLES: IS XRF REALLY NON-DESTRUCTIVE?

Michael Mantler and Jan Klikovits

Institute of Solid State Physics
Vienna University of Technology, Vienna, Austria

ABSTRACT

XRF is generally considered a non-destructive analytical method in the sense that a specimen is not altered by the analytical procedure. This study is related to paintings and illuminated manuscripts, where the analytes are often inorganic pigments embedded into organic matrices such as fabrics (canvases), paper or parchment, binders, and varnish. We found that a typical measurement cycle with conventional tubes and energy dispersive systems (e.g. 100s, 100W tube-power) causes no visible harm. However, 3kW radiative power for several minutes and more (as often required for wide angle scans as well as for the analysis of light elements or traces in a wavelength dispersive spectrometer) can leave visible traces of permanent yellowing, brittleness, and even mechanical decomposition. In such cases SEM-images indicate permanent alteration of the cellulose fibers and, in paper, of the binder. Employment of modern X-ray optical devices which focus the photons of a wide beam onto a small spot may also leave visible (and invisible) traces of destruction.

INTRODUCTION

Analysis of art objects is not different from the analysis of any other objects except for the fact that the objects are often unique and irreplaceable and non-destructiveness is a main concern of the owner or a curator. “Non-destructiveness” is generally defined as "no alteration of the object by the analytical process" and seen as the main advantage of XRF over the consumptive methods of UV/vis spectroscopy, where sample material is atomized in a flame, spark/arc, plasma, or by sputtering. Nevertheless and non-withstanding, XRF may require the analyst to take a suitable sample from a larger object (e.g., a splinter of paint) or shape, cut, clean, or polish the object, whereby a valuable piece may be considerably affected or even ruined.

This paper is concerned with radiation damage by the analytical process. Most sensitive are organic materials, such as fabrics, parchment and paper, binders and varnishes, dyes and inorganic pigments. Inorganic pigments, which are often the final target in the investigation of historic objects, are largely unaffected by X-rays, but since they are usually embedded in organic materials, analysis may be destructive for the whole object.

Conventional EDXRF with filtered primary (tube) radiation has been widely used over many years and is apparently unproblematic. Slow wide angle scans with high powered wavelength dispersive spectrometers, employment of X-ray optical devices which are capable of focusing a wide beam onto a small spot and thereby enhance the physical intensity by a factor of several thousand, as well as intense synchrotron radiation (particularly in combination with X-ray optics) may, however, raise some concerns.
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EXPERIMENTS

We analyzed several types of fabrics, papers, and samples of paintings with varying intensities, tube voltages, and filters. Single sheets were investigated with and without backing material (amplifying the dose by backscattered and fluorescent radiation). Stacks of sheets were used to make the shielding effects and penetration depths visible.

Instrumentation. A Siemens SRS 303AS wavelength dispersive spectrometer with Rh-end window tube (76µm Be window, 20-30kV, up to 100mA.) was used for irradiating the specimens and operated in air unless otherwise indicated. Irradiation times ranged up to 120 minutes and are indicated in the figures below. For some measurements a 150µm Al-filter was inserted into the primary beam. An Olympus MX65 optical microscope with a CCD-camera was used for a few color measurements. The SEM images were obtained with a Philips ESEM XL30.

Sample preparation. All materials were cut to disk-shaped pieces of around 40mm diameter in order to fit into standard Siemens SRS specimen holders, and inserted in stacks of 20-50 pieces. The term "top of stack" (see Figure 1) indicates the sheet closest to the X-ray tube. Altogether about 400 sheets were used.

EXPERIMENTAL RESULTS

Irradiation causes yellowing and brittleness. White paper and fabrics exhibited discoloring (yellowing) and became brittle after intense irradiation of 10-120min (Figure 2). The effect is well known since early (mainly medical) radiography and was sometimes used for dose estimates. We found the first clearly visible traces of yellowing after approximately 10 minutes of irradiation (20kV, 100mA, no filter). Yellowing and brittleness were strongest at regular office paper (material 1), followed by paper of material 2 (chlorine-free paper), and cotton. It was much less for silk.

The discoloring is not homogeneous. One reason is that the primary beam is divergent and not perpendicular to the surface of the specimen; the beam intensity at the nearer side of the tube is therefore higher and a resulting gradient towards the far side is clearly visible (Figure 2b-d). The magnification of the exposed area shows a pattern of speckles rather than an even discoloring (Figure 2d). The reason is unknown; a possible explanation is that certain fillings or additives on the surface are not homogeneously distributed. This effect was observed on (flat) paper but could not be verified with fabrics due to their textured surface.
(Figure 2). (a) Irradiated samples (material 1). The six topmost sheets of four stacks are shown in each row from left to right (The 2nd sample in row 1 was partially damaged during handling). All topmost sheets show cracks, and pieces of the material fall off during normal handling. Row 1: 120 min, 80 mA, 30 kV. Row 2: 120 min, 80 mA, 20 kV. Row 3: 80 min, 80 mA, 30 kV. Row 4: 40 min, 80 mA, 20 kV. (b) Magnified center area of sample in row 1/column 1. (c) Magnified center area of irradiated silk (material 3), 20 kV, 80 mA, 40 min. (d) Magnified center area of sample in row 2/column 2, in high contrast mode to enhance speckled structure.

(Figure 3). Left: Comparison of applied tube voltages, $V$, at equal settings of the anode current, $I$. Note that the photon-number per wavelength-interval in Bremsstrahlung for constant $I$ is proportional to $V^2$. Right: Bleaching after 3 days. A few measurements have been made in vacuum.
Measurement and documentation of the yellowing effect as a function of irradiation time was tried by two methods: Visually by finding the deepest sheet in a stack which exhibited still a faint darkening distinguishable from the pure white, and, secondly, by investigating all sheets by a video-system through an optical microscope and obtaining the RGB/gray-values electronically. The simple visual classification proved to be more reproducible, easier to apply, and faster, probably due to temperature stabilization problems of the involved electronics, lamps, and the influence of external illumination. An important reason could also be the inhomogeneous structure of the discoloring which is averaged by the eye, but registered by the microscope with comparably high resolution (even at low magnification) at randomly distributed spots with varying yellowness. The “bleaching effect” (see below) was "measured" by the same method.

**Effect of filters.** Insertion of an Al-filter drastically reduces damages, indicating that long wavelengths are most relevant for the absorbed dose. As can be seen from the irradiated samples in Figure 2, the filter-equivalence of a few paper sheets is already very effective. Use of filters is therefore strongly advised unless very light elements must be analyzed.

**Yellowing bleaches out.** A bleaching effect was observed after irradiation, which partially reverses the yellowing and may possibly be supported (but perhaps not solely caused), by impregnation of the paper by special resins (modern papers and other materials are often coated with “radiation curable resins” which makes the material appear white after UV-irradiation [1, 2]. It is not known, if the investigated sample materials have been treated in that way.).

**Bleaching is not healing.** SEM-images show that visible alterations of the irradiated area in paper or fabrics are not "cured" or reversed by waiting. The radiation damages (yellowing) may become less visible after some time but the destroyed or altered chemical bonds and electronic states are not reconstituted.

(Figure 4). **SEM-Images taken from the topmost sheets (maximum absorbed dose) of cotton (top) and paper (bottom), before (left) and after (right) irradiation.**

The images of cotton show individual interwoven fibers of cellulose of around 15µm thickness, which are partially broken and decomposed after irradiation. Paper consists of cellulose fibers as well as of binders (starch/glue, resins) and fillers (e.g., CaCO₃, clay, or titania in grains of 0.2 to 5 µm). Irradiation apparently affects the binder as well.
CONCLUSIONS

Several scenarios of modern analytical XRF-applications make it advisable to consider radiation damage of delicate specimens possible:

Modern X-ray optical devices (poly-capillaries) focus a divergent primary beam into a small spot of a few tens of micrometers and can increase the local (physical) intensity by a factor of 5000-6000 compared to an unfocused beam. Even if low-power tubes are used, this can be harmful for delicate specimens.

Synchrotron radiation is by its nature most intense and its combination with X-ray optical devices should be applied with caution. Delivered doses in the order of Mega-Gray have been reported.

In inhomogeneous specimens, where enclosures of elements with different absorption properties exist, local minima and/or maxima of deposited energy (dose) exist. In the context of this paper, pigments containing heavy elements such as Fe, Ni, Pb, or Hg in an organic matrix may be capable of absorbing the incident radiation much more efficiently than the light matrix elements and cause enhanced dose effects in their neighborhood by spreading the energy by photo-electrons and Auger-electrons. Because of the short range of electrons, radiation damage is confined to a small area in the vicinity (typically a few micrometers) of the heavy absorber and may be invisible to the naked eye, but nevertheless exists. Monte-Carlo methods can be used to study such effects.

Wavelength dispersive XRF has several advantages over EDXRF, but their disadvantages are that

- Most likely the primary beam intensity is much higher in order to compensate for the small allowed divergence of the collimated beam and the loss by the diffraction process.
- The scanning time for qualitative analysis is much longer, particularly for traces of light elements. Qualitative and quantitative analysis of trace elements in cotton has been destructive in the authors’ experience.

In EDXRF the large solid angle of fluorescent radiation accepted by the detector, the fact that no reflection by crystals is required, and the much shorter measurement times due to the simultaneous acquisition of spectra rather than scanning over possibly large ranges of diffraction angles are obviously an advantage in terms of power requirement and delivered dose.

REFERENCES
