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Conservation materials and strategies for stained glass windows: Microtomography results from the CONSTGLASS project

A. Vichi(*)

Dipartimento di Chimica "G. Ciamician", Università di Bologna - Bologna, Italy

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Summary. — The European research project "Conservation Materials for Stained Glass Windows - Assessment of Treatments, Studies on Reversibility, and Performance of Innovative Restoration Strategies and Products" (CONSTGLASS) involved a consortium of 11 partner organisations from 7 countries for a period of three years, beginning in June 2007. This paper provides an overview of results of the project based on the use of synchrotron radiation microtomography. The research activities of the project dealt mainly with the evaluation of conservation treatments performed in the last fifty years on European stained glass windows originating from the mediaeval to the 20th century periods, and taking into account the present state of preservation and/or the potential risks posed by former conservation protocols.

PACS 07.85.Qe – Synchrotron radiation instrumentation.
PACS 87.59.bd – Computed radiography.

1. – Introduction

In the framework of the CONSTGLASS project, studies are underway to document the degradation behaviour of conservation materials (in particular coatings, consolidants and adhesives) and to analyse the glass substrates for any changes in form or appearance which are associated with the treatments [1]. The investigation of stained glass windows treated with some conservation materials from the cathedrals of Cologne, Canterbury, Chartres, Le Mans and Bourges is being complemented by studies of glass in museum and other locations. Advanced analytical and imaging techniques have being combined with visual examination and the results are presently being integrated into a newly developed documentation scheme. Microscopic damage and deterioration effects have been investigated by nano-computed tomography (CT), phase-contrast CT, Raman

(*) E-mail: alessandra.vichi@gmail.com

spectroscopy, infrared spectroscopy and other methods. Reversibility and re-treatability trials on polymeric materials have been undertaken. In addition, the impact of microbial threats to glass and, especially, conservation materials has been assessed. The scope for the introduction of advanced conservation materials is being explored by the preparation and evaluation of new inorganic consolidants for stabilisation of internally fractured glass or fragile glass paint.

2. – Morphological analysis of historical glass

Glass is a material which has inspired artists for more than four thousand years. Ancient glass objects belong to the masterpieces of arts and crafts in Europe, and stained glass windows cover the period from the Middle Ages until contemporary times. Glass pieces from different origins exhibit special degradation phenomena [2-4], and the reason for degradation is connected to its composition and the interaction with the environment. Moreover, treatment of stained glass with natural and synthetic polymers as surface coatings, paint consolidants and adhesives has been performed for more than 50 years to preserve the integrity of objects and in their original architectural surrounding. Various materials have been propagated and applied for the conservation of stained glass, including epoxy resins, acrylates and polyurethanes with different brand names. For all conservation materials on stained glass there is a substantial lack of assessment of treatments after several decades of natural weathering. This project responds to the urgent need to carry out an assessment of the sustainability of former conservation procedures, their reversibility and re-treatability.

Since most of the applied materials cause problems nowadays, the introduction of innovative and promising new preservation strategies and materials is also necessary. A full morphological characterization of stained glass, before and after treatment (or removal of a previous treatment), is one of the major points in the study of restoration and conservation of these precious artifacts.

Conservators and scientists frequently use optical microscopy as a simple tool for characterising the external structure of objects of cultural and historical interest. For more accurate investigations with higher magnifications, scanning electron microscopy (SEM) is applied for evaluating morphological parameters. If a sample needs to be evaluated in the SEM, the sample itself needs to be embedded, cut and polished, implying a destructive procedure with respect to the original material. Moreover, this method is time-consuming and delivers images from only one single cut, which might not be representative for inhomogeneous fragments. Additionally, for the characterisation of samples treated for consolidation purposes, the presence of a consolidant in the microcracks of the sample needs to be controlled in order to guarantee suitable adhesion between the polymer and the exposed surface of the object. The presence of new cracks and holes caused by a possible induced stress needs also to be evaluated. For this problem no adequate method was available until the last decade.

Computed X-ray tomography (CT) is an imaging technique with major potential applications in the cultural heritage domain. For the detailed analysis of the integrity of a glass sample resolution on the 10 micrometer-scale is obligatory. The potential of laboratory CT for this class of samples has been explored in several projects, but for the detection of polymers it turned out that the sufficient contrast between the original material and the organic polymers could not be achieved [5].

3. – X-ray microtomography with synchrotron radiation

The possibilities offered by the last generation synchrotron sources have increased interest in X-ray microtomography (μCT) [6-8]. The main characteristics of synchrotron radiation are the continuous spectrum, extending from infrared to hard X-rays, the high intensity and the high spatial coherence of the X-ray beam. These features allow one to obtain fast exposure times, to tune the photon energy as a function of the sample characteristics and to use digital subtraction techniques [9]. Monochromaticity and high collimation of the beam, moreover, allow data analysis with reduced artefacts and better quality. Furthermore, phase-sensitive imaging techniques using highly coherent hard X-rays from third-generation synchrotron sources have the additional advantage of allowing imaging of samples with very low absorption contrast, such as light-element glues and consolidants [10, 11]. These measurements can be performed in a completely non-invasive way in monitored environments, where temperature and humidity can be carefully controlled.

3˙1. *Phase-contrast microtomography.* – In conventional radiology, image formation relies on the X-ray absorption properties of the sample and can be expressed by means of geometrical optics. The image contrast originates from a variation of density, composition or thickness of the sample and is based exclusively on the detection of intensity variations of the transmitted X-rays. Information about the phase of the X-rays is not taken into account. The main limitation of this technique is the poor inherent contrast in samples of low-atomic-number composition: indeed this is the case of "soft matter" which is considered, in the common sense, as transparent to X-rays. Contrary to absorption radiography, phase-contrast imaging techniques are based on the observation of the phase shifts produced by the object of the incoming wave. They are described by means of wave optics. Absorption and phase shifts are effects occurring for X-rays crossing any kind of material. Their relationship is described by the material's complex index of refraction n, which in the X-ray region differs only slightly from unity: $n = 1 - \delta + i\beta$, where δ is real and related to the refractive properties and β determines the absorption. In the energy range between 15 and 25 keV, the phase shift term δ (of the order of 10^{-7}) can be up to 1000 times greater than the absorption term β (of the order of 10^{-10}), so that it is possible to reveal phase effects even if the absorption is negligible (phase objects). The observation of the local variations in the optical path-length, determined by variations of δ, is related to Fresnel diffraction. In general, phase information can be accessed if the X-ray source has a high spatial coherence as in the case of synchrotron light sources [10-12] like Elettra or the ESRF.

4. – Experimental results

In the following we will show some examples of applications of synchrotron-radiation microtomography to different samples from the CONSTGLASS project, showing the advantages of the phase-contrast approach.

4˙1. *Viacryl resins detection in Chartres and Bourges Cathedrals, France.* – Viacryl, a polyurethane resin mixture of 80% acrylic resin and 20% aliphatic isocyanate, was the most used organic coating on stained glass windows in France and in Austria during the 1979s to consolidate the pigment layers applied as decoration on glass, named "grisailles". The promising *in situ* results at Santa Maria am Gestate, in Austria (1970), led to a significant campaign of application in France and specially in Le Mans (1974),

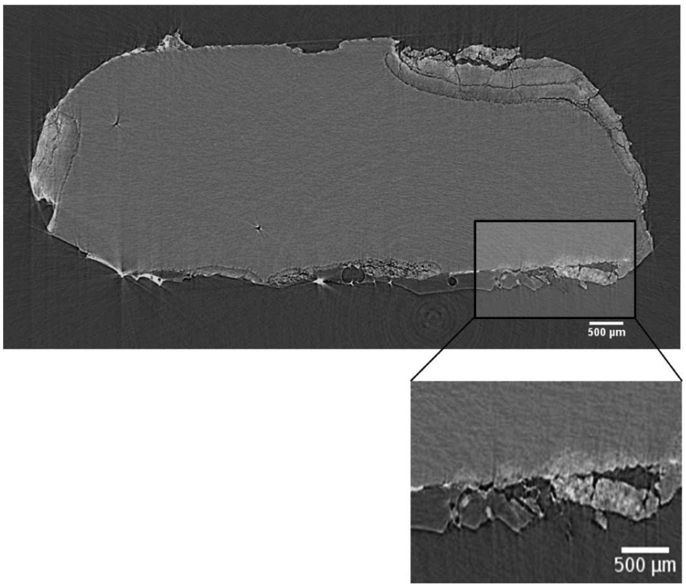

Fig. 1. – SR-micro-CT acquisition on glass sample with "grisailles" decoration from Chartres Cathedral (cha_b37p16i_v2_slice 259), treated with Viacryl polymer located in the interior part of the object. The selected zone shows how Viacryl is detaching from the substrate and fragments of the original decoration have not been consolidated. Moreover, there is visible alteration of the glass in gel layers in the external surface.

in Chartres (1988) and in Bourges (1981) Cathedrals [13, 14]. Today, it is important to assess the evolution of this Viacryl application. Questions to be answered concern a better understanding of alteration processes of the Viacryl which started detaching spontaneously, a more precise knowledge of the impact of this coating on the glass and "grisailles" substrates and the choice of the relevant and possible cleaning solvent. Nowadays, the only method to control the penetration of a coating or a consolidant into the micro-cracks of the corrosion layers of the original substrate is based on phase-contrast tomographic experiments. Therefore, we need to observe the penetration of the Viacryl into the gel layer of the glass. We need to characterize treated samples after conservation and weathering in order to explain the adherence between the polymer and the surface of the decorations.

Several samples from Chartres and Bourges Cathedrals have been analyzed with phase-contrast microtomography to describe the interaction between the glass structure (and its paintings) and the consolidant (fig. 1).

One of the most interesting results comes from the analysis of some Viacryl flakes fallen from a Bourges window without any human intervention. Some selected flakes were inserted in a polyethylene vial and examined with phase-contrast microtomography (fig. 2).

It is evident from a simple analysis of the densities that the Viacryl flakes have removed some original decorative "grisailles" fragments from the glass, and that extreme care must be used, when removing this kind of consolidants, in order to reduce further damage to the window (fig. 3).

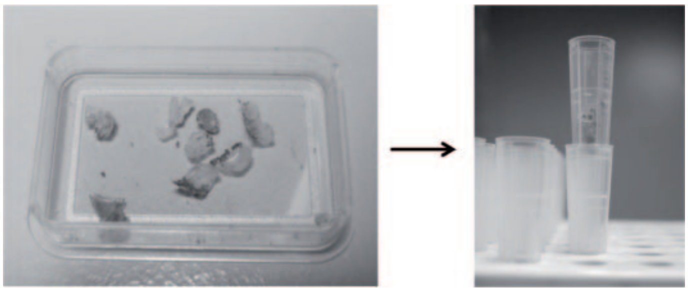

Fig. 2. – Viacryl flakes from Bourges Cathedral: phase-contrast micro-CT analyses at Elettra Synchrotron were performed after placing some flakes in a polyethylene vial.

Fig. 3. – SR-micro-CT results on Viacryl flakes from Bourges Cathedral: it is evident how Viacryl, which spontaneously detached, removed a fragment, probably of the original support.

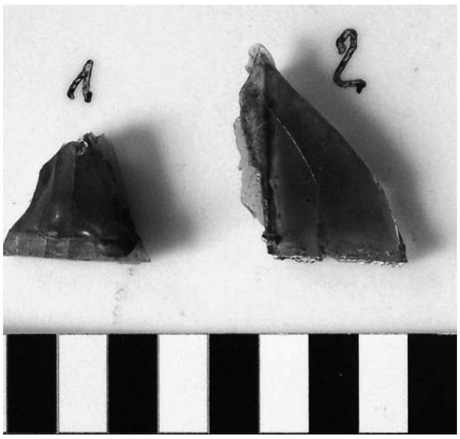

Fig. 4. – Samples 1 and 2 from window of the Academy of Fine Art in Krakow (Art Nouveau, beginning of 20th century).

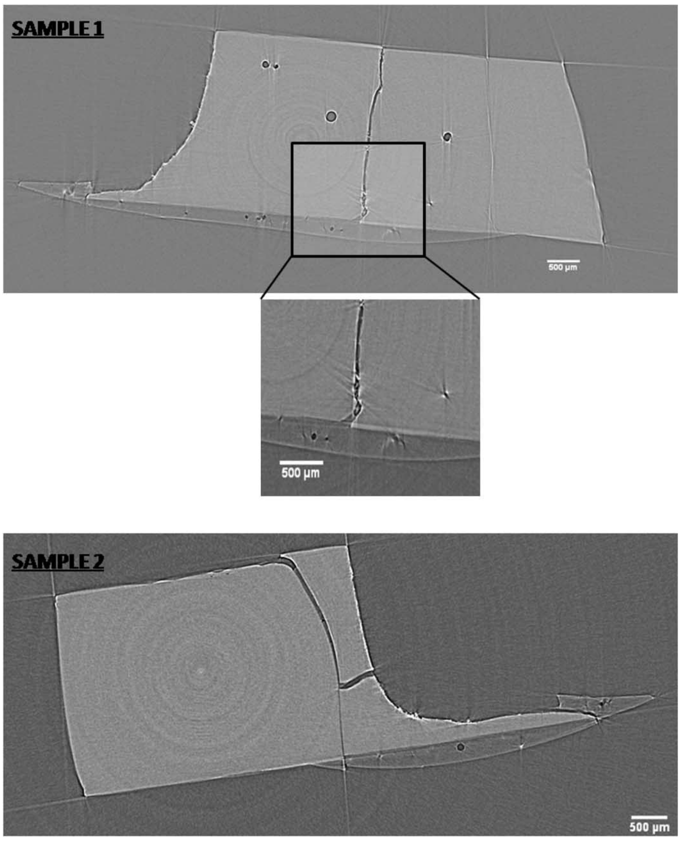

Fig. 5. – SR-micro-CT results from sample 1 and 2 from the Academy of Fine Art window in Krakow: thanks to the high resolution achievable, sample 1 shows how the epoxy resin has not penetrated into the fracture; sample 2 shows instead how the adhesive has perfectly penetrated.

4·2. *Epoxy resin detection in treated samples from Krakow, Poland.* – We show here some results from samples all taken from the same window at the Academy of Fine Arts in Krakow (beginning of the 20th century). Sample 1 has been bonded with an epoxy resin (Epidian 53) about 30 years ago from the interior, without glass dismantling. Sample 2 has been recently bonded with same material. Both samples have been analysed with the same experimental parameters and two slices have been selected to describe the internal structure of the samples (fig. 4).

Sample 1 shows a thick layer of resin on the glass surface and only a slight penetration of resin into the break, which is contaminated by external pollution. As a result, the bonding is rather weak. Sample 2 shows that penetration of the adhesive resin is complete, and the bonding is satisfactory (fig. 5). Conventional X-ray tomographic analyses are not able to detect the difference between empty spaces and resin.

4·3. *Araldite treated samples from Burgdorf Parish Church, Switzerland.* – The following sample comes from the vestry on the south side of the choir of the Burgdorf Parish Church (15-16th century). The choir windows were probably destroyed in 1707, and fragments were found in 1968 and mounted in panels in 1971. The Araldite polymer used

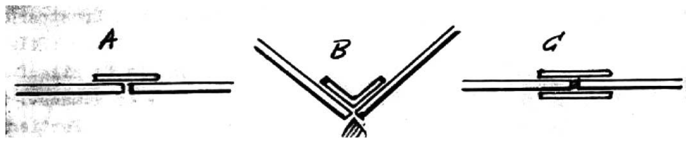

Fig. 6. – Schematic of the double method used to consolidate fragments of the choir windows of the Burgdorf Parish Church destroyed in 1707 and remounted in 1971.

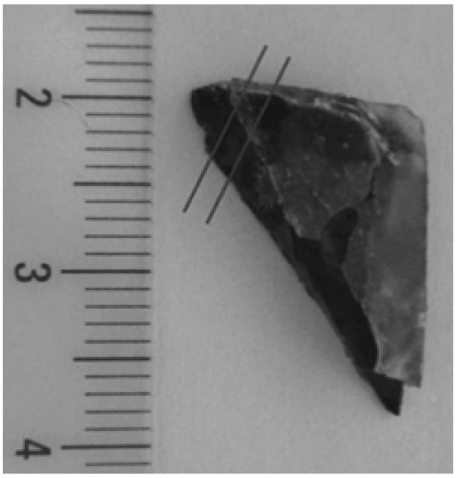

Fig. 7. – Sample CSRIV_01 analysed with SR-micro-CT from the Burgdorf Parish Church: the zone analysed is underlined.

as adhesive shows some alteration phenomena, such as yellowing and loss of adhesion. Where it flakes off, it shows clearly different types of deterioration. Araldite was applied with a double method to consolidate thin fragments with multiple cracks, instead of a simple bond edge (fig. 6).

Araldite was poured on a thin carrier glass, the fragment was put on top and left under pressure (binder AY 103 100 parts, hardener hy951 9 parts). For the sample analysed, the carrier glass was cut along the old crack of the original piece of glass. It was noticed how in this area the Araldite was just sticking to the old glass (fig. 7).

Again, only a phase-contrast approach allowed the characterization of the behaviour of the low-absorbing adhesive. In this case it was possible to verify the good adhesion between the original glass and the Araldite, but also an important effect. The cracks of the consolidant in proximity to sharp features of the glass are due to different thermal expansion of the glass as compared with the Araldite (fig. 8).

4˙4. *Wax/Paraloid B72 treated samples from Canterbury Cathedral, UK*. – In this case we tested the reliability of a technique used in the Canterbury Cathedral Studio in the 1970s. A dummy test sample using a XII/XIII Century dated glass fragment was prepared in order to replicate the condition of the glass surface and the methods used on the original glass during old conservation treatments. A fragment of a medieval green tinted glass with slight surface corrosion was selected for this experiment. A mixture of microcrystalline wax (90%) and polythene A wax (10%) melted together and diluted

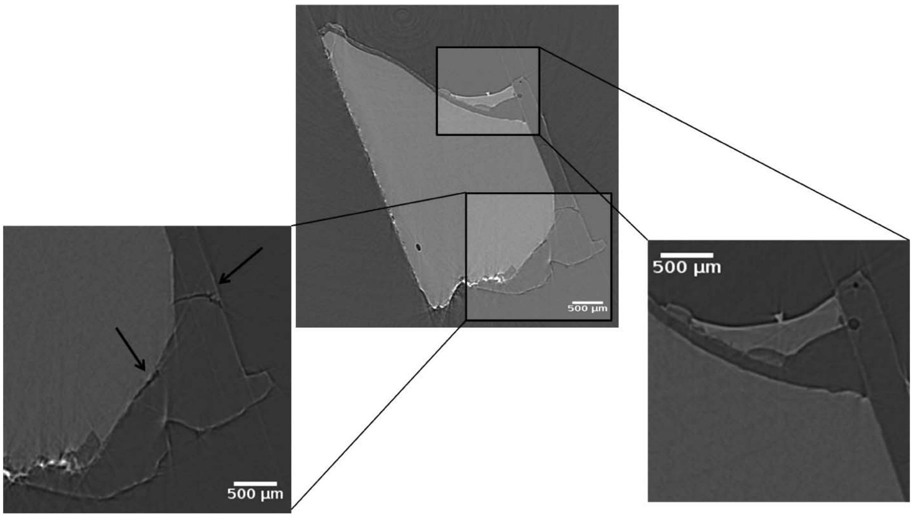

Fig. 8. – SR-micro-CT results from sample CSRIV_01, Burgdorf Parish Church: Araldite adheres perfectly to the support, but fractures in the polymeric layer are evident where the glass surface shows discontinuities.

with white spirit was painted onto the glass in three separate layers and left for three days. The acrylic polymer Paraloid B72 mixed together with raw umber pure powder pigment was then applied with a small brush on the wax. No traces of net interface were found between the different wax layers and between wax and Paraloid (the air bubbles in the Paraloid are due to the evaporation of the solvent), which is due to a good interdiffusion between the different layers. A sharp interface would have been detected by phase contrast (fig. 9).

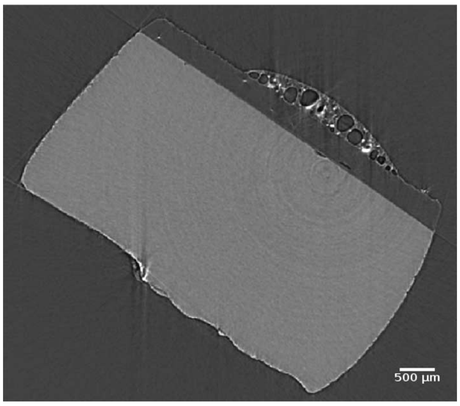

Fig. 9. – SR-micro-CT results from sample Can_1a, Canterbury Cathedral, prepared with XII/XIII century glass and covered with a multiple layers consolidation system: results show how it is not possible to distinguish the two products, without mixing the second with a higher absorbing material (in this case a pigment).

4·5. *Experimental parameters.* – The SYRMEP beamline with its optics based on a double-crystal silicon (111) monochromator, working in an energy range between 8 keV and 35 keV is the right choice for the proposed samples [15]. At a distance of about 20 m from the source, the beamline provided a monochromatic X-ray beam with a maximum area of $(150 \times 6)\,\text{mm}^2$. The detector was a 4008 (H) × 2672 (V) pixel CCD detector (pixel size = $4.5\,\mu$m, field of view $18 \times 12\,\text{mm}^2$) in binning 2×2 configuration. A total of 8 tomograms were recorded after setting suitable parameters for the measurement to 27 keV energy, 720 rotations, and a distance between the sample and the detector of 66 cm. From the mathematical point of view, computed tomography is related to the analysis of the three-dimensional distribution of the real or imaginary part of the refractive index inside an object from transmission images collected at different incident angles. The filtered back-projection algorithm (a computer implementation of the so-called approximate inversion formula [16]) is the most popular reconstruction method. The tomographic projections have been elaborated using *Syrmep_tomo_project*, a software written by F. Montanari and based on this algorithm. In this software a set of routines allows the reconstruction of single slices or volumes; data can then be saved in several formats and subsequently loaded by other applications for visualization and analysis. The computer code is written in the IDL© language (ITT Visual Information Solutions, White Plains, NY, USA). The 3D reconstruction is performed using a filtered back-projection algorithm: for each projection an intensity map is recorded in the xy detector plane, then each intensity map is back projected along the normal to the projection itself. Projections are sub-mitted to filtering procedures to eliminate noise and artefacts and, finally, the intensities are added for all the projections. Then, the reconstructed slices can be visualized as stacks of 2D images, or 3D views of the sample can be obtained by volume rendering procedures.

5. – Conclusions

These preliminary experiments show the potential of phase-contrast microtomography to study corrosion and alteration processes on glasses and conservation materials as demonstrated on original and selected model glasses. The protection of Cultural Heritage is an extremely promising new application field for this X-ray imaging technique providing a non-destructive tool. This method allows the 3D structure of corrosion patterns to be visualized and to detect conservation materials within fragile original objects. The systematic development of conservation materials will be improved by this new non-destructive method to detect the effectiveness of treatments on originals. Therefore, further research is needed to optimise the resolution and to adjust the method for detecting a sequence of treatments for a variety of different fragments.

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REFERENCES

[1] Mottner P., Brinkmann U., Pallot-Frossard I., Warscheid T., Seliger L., Caen J., Zanini F., Jacobs P., Tennent N. H., Trümpler S. and Karaszkiewicz P., in *The Art of Collaboration: Stained-Glass Conservation in the 21st Century*, edited by Shepard M., Pilosi L. and Strobl S. (Brepols, Turnhout) 2010, p. 123.

[2] Davison S., *Conservation and restoration of glass* (Butterworth-Heinemann, Oxford) 2003.

[3] Tennent N. H., *The conservation of glass and ceramics* (James & James, London) 1999.

[4] Römich H., in: *Conservation Science – Heritage Materials*, edited by May E. and Jones M. (the Royal Society of Chemistry Publishing, Cambridge) 2006, p. 160.

[5] Römich H., López E., Mees F., Jacobs P., Cornelis E., Van Dyck D. and Doménech Carbó T., in *Proc. 7th International Conference on Non-destructive Testing and Microanalysis for the Diagnostics and Conservation of the Cultural and Environmental Heritage* (University of Antwerp, Antwerp) 2002, p. 1.

[6] Mancini L., Tromba G. and Zanini F., *J. Neutron Res.*, **14** (2006) 75, doi:10.1080/10238160600673300.

[7] Römich H., Zanini F., Wittstadt K., Müller-Weinitschke C. and Sodini N., *Nondestructive Testing Journal*, **13** (2008) 30.

[8] Dreossi D., Favretto S., Fioravanti M., Mancini L., Rigon L., Sodini N., Tromba G. and Zanini F., in *Wood Science for Conservation of Cultural Heritage: State of the Art* (Florence University Press, Florence) 2010, p. 34.

[9] Kaiser J., Reale L., Ritucci A., Tomassetti G., Poma A., Spanò L., Tucci A., Flora F., Lai A., Faenov A., Pikuz T., Mancini L., Tromba G. and Zanini F., *Eur. Phys. J. D*, **32** (2005) 113, doi: 10.1140/epjd/e2004-00183-2.

[10] Snigirev A., Snigireva I., Kohn V., Kuznetsov S. and Schelokov I., *Rev. Sci. Instrum.*, **66** (1995) 5486, doi:10.1063/1.1146073.

[11] Cloetens P., Pateyron-Salomé M., Buffière J. Y., Peix G., Baruchel J., Peyrin F. and Schlenker K., *J. Appl. Phys.*, **81** (1997) 5878, doi:10.1063/1.364374.

[12] Baruchel J., Cloetens P., Härtwig J., Ludwig W., Mancini L., Pernot P. and Schlenker M., *J. Synchrotron Rad.*, **7** (2000) 196, doi:10.1107/S0909049500002995.

[13] Bettembourg J.-M., in *Etude de films de résines synthétiques, in verres et réfractaires*, Vol. **30**, No 1, numéro spécial (Corpus Vitrearum, Paris) 1975, p. 87.

[14] Bettembourg J.-M., in *Colloque international sur la conservation des vitraux de la cathédrale de Bourges* (Corpus Vitrearum, Paris) 1978, p. 12.

[15] Abrami A., Arfelli F., Barroso R. C., Bergamaschi A., Billè F., Bregant P., Brizzi F., Casarin K., Castelli E., Chenda V., Dalla Palma L., Dreossi D., Fava C., Longo R., Mancini L., Menk R.-H., Montanari F., Olivo A., Pani S., Pillon A., Quai E., Rigon L., Rokvic T., Tonutti M., Tromba G., Vascotto A., Venanzi C., Zanconati F., Zanetti A. and Zanini F., *Nucl. Instrum. Methods A*, **548** (2005) 221, doi:10.1016/j.nima.2005.03.093.

[16] Herman G. T., *Image Reconstruction from Projections* (Academic Press, New York-London) 1980.