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Non-destructive imaging of fragments of historical beeswax seals using high-contrast X-ray micro-radiography and micro-tomography with large area photon-counting detector array

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ABSTRACT

Historical beeswax seals are unique cultural heritage objects. Unfortunately, a number of historical sealing waxes show a porous structure with a strong tendency to stratification and embrittlement, which makes these objects extremely prone to mechanical damage. The understanding of beeswax degradation processes therefore plays an important role in the preservation and consequent treatment of these objects. Conventional methods applied for the investigation of beeswax materials (e.g. gas chromatography) are of a destructive nature or bring only limited information about the sample surface (microscopic techniques). Considering practical limitations of conventional methods and ethical difficulties connected with the sampling of the historical material, radiation imaging methods such as X-ray micro-tomography presents a promising non-destructive tool for the onward scientific research in this field. In this contribution, we present the application of high-contrast X-ray micro-radiography and micro-tomography for the investigation of beeswax seal fragments. The method is based on the application of the large area photon-counting detector recently developed at our institute. The detector combines the advantages of single-photon counting technology with a large field of view. The method, consequently, enables imaging of relatively large objects with high geometrical magnification. In the reconstructed micro-tomographies of investigated historical beeswax seals, we are able to reveal morphological structures such as stratification, micro-cavities and micro-fractures with spatial resolution down to 5 μm non-destructively and with high imaging quality. The presented work therefore demonstrates that a combination of state-of-the-art hybrid pixel semiconductor detectors and currently available micro-focus x-ray sources makes it possible to apply X-ray micro-radiography and micro-tomography as a valuable non-destructive tool for volumetric beeswax seal morphological studies.

1. Introduction

Historical beeswax seals are not only a historical means of legal authentication of charters to which they are attached, but they are also unique cultural heritage objects. Unfortunately, a number of sealing waxes show a characteristic type of degradation that makes them extremely prone to mechanical damage. The material of many historical seals has a strong tendency to stratification and embrittlement. These changes are accompanied with alterations of optical properties, especially the loss of translucency and change of the color to whitish or light grey-brown (Fig. 1) (Gärtig, 1967; Woods, 1994; Cozzi, 2003; Reifarth, 2003; Peters, 2004). The cause of the described phenomenon has not yet been satisfactorily explained and, therefore, these seals are operationally referred to as “white”, “overdried” or simply “diseased” (Cozzi, 2003).

Some earlier authors were convinced that the embrittlement and porosity are results of microbiological degradation of certain components of the beeswax-based sealing materials (Palm, 1957; Cozzi, 2003). The causal connection between this phenomenon and the activity of microorganisms, however, has never been proven (Clydesdale, 1994; Cozzi 2003). In attempts to shed light on the issue, dedicated analyses of the chemical composition of affected seals were carried out as well (Gärtig, 1967; Woods, 1994; Cozzi, 2003; Reifarth, 2003; Peters, 2004; Bartl et al., 2012). Although the results were not entirely congruent, the historical samples typically contained a lower proportion of low-molecular hydrocarbons

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Fig. 1. Examples of rare historical beeswax seals from 1360 *(left)* and 1487 *(right)* from collections of the National Archive of the Czech Republic. As demonstrated by both images, unfortunately, many beeswax seals have become extremely brittle which presents an issue for their further preservation. Such beeswax seals are consequently suitable only for non-destructive investigation.

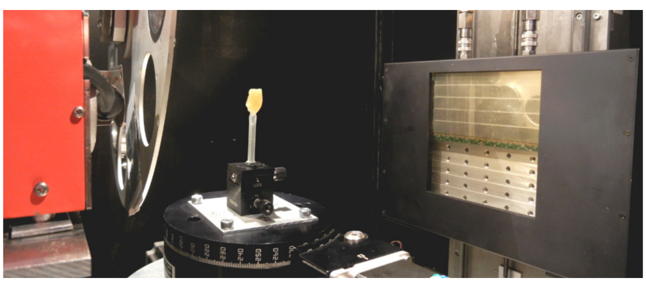

Fig. 2. Setup for X-ray micro-radiography and micro-tomography consisting of a micro-focus X-ray beam source, precise rotation table with positioning sample holder and the large-area photon counting detector array with full sensitive area of $14.3 \times 7.15\,cm^2$.

and wax esters when compared to recent beeswax. The causes and the importance of these changes with respect to the studied phenomenon still need to be verified.

Recent authors, therefore, lean towards the opinion that the primary cause of the phenomenon of seal embrittlement and porosity can lie in the morphological changes of the material (Dernovskova, 1997; Cozzi, 2003). These assumptions are based on the fact that such changes could take place both during the preparation of the material prior to its use and also in the course of its long-term ageing (Cozzi, 2003).

1.1. *Conventional instrumental research methods for beeswax*

The understanding of processes, such as embrittlement and porosity formation, naturally puts strict requirements on the selection and applicability of examination approaches. Conventional methods used for investigation of the chemical composition of beeswax are invasive (gas chromatography, gas chromatography in combination with Fourier transform infrared spectroscopy, gas chromatography coupled with mass spectrometry (GC–MS)) (Regert et al., 2001; Bartl et al., 2012).

Surface imaging is provided by optical microscopes and scanning electron microscopy (SEM). SEM is a valuable tool for surface investigation (surface fractures, crystals) with great spatial resolution down to 50–100 nm, but the method cannot provide any information about internal structures.

For imaging purposes, the method should provide isotropic spatial resolution at the level of a few microns (or even down to the 100 nm range), ideally within the whole seal sample, and show adequate sensitivity for the detection of tiny density and material variation within the beeswax sample. As beeswax seals are often of very rare nature, the non-destructivity of the method is also of key importance.

1.2. *X-ray micro-radiography and micro-tomography*

Considering the practical limitations of conventional methods and ethical difficulties connected with the sampling of the historical material, radiation imaging methods such as X-ray micro-tomography presents a promising non-destructive tool for ongoing scientific research in this field Kruth et al. (2011) and Peyrin et al. (2012). The spatial resolution of X-ray micro-tomography systems is becoming almost comparable to conventional light microscopy (tens of nanometers in the case of synchrotron radiation sources and μm scale in the case of laboratory-scale devices) (Landis and Keane, 2010). Furthermore, the method produces a virtual 3D voxel-based model of the sample with isotropic spatial resolution. The reconstructed volume can be consequently rendered and sliced in any required plane giving many possibilities in the data observation, evaluation and presentation. Thanks to the non-invasive principle, the method can be applied usually without significant risk even for extremely rare samples.

Based on these features, X-ray micro-radiography and micro-tomography have been applied in the last years in cultural heritage studies for a broad range of objects including rare carpets (Karamad et al., 2009), wooden artifacts (Morigi et al., 2010), stone objects (Slavikova et al., 2012). The application of X-ray radiography for wax objects is reported (Gramtorp et al., 2014), but the method was used here only for revealing the presence of an internal metal armature.

1.3. *Photon-counting pixel detectors*

While X-ray micro-radiography and micro-tomography stand as valuable tools for non-destructive observation in various applications, a complication in the application for wax materials is the intrinsic low attenuation contrast of the investigated structures as the sample is formed dominantly by low-Z compounds. This feature can make investigation of beeswax seals by means of X-ray micro-radiography with conventional charge integrating devices such as flat panels, CCDs and CMOS chips with scintillating sensors complicated.