NUKLEONIKA 2012;57(4):627–631 ORIGINAL PAPER

X-ray techniques in the investigation of a Gothic sculpture: *The risen Christ*

Anna Mikołajska, Małgorzata Walczak, Zofia Kaszowska, Małgorzata Urbańczyk Zawadzka, Robert P. Banyś

Abstract. For over a century, X-ray radiation has played an important role in the area of the conservation and restoration of cultural heritage objects. X-ray techniques are amongst the most fundamental and helpful methods used in the investigation of art works. This paper reviews the application of traditional radiography, X-ray dual source computed tomography (DSCT) and scanning electron microscopy combined with energy dispersed X-ray spectroscopy (SEM-EDX) to the investigation of a wooden, Gothic sculpture, *The risen Christ*. Thanks to the properties of X-ray radiation (different absorption by various materials) first two methods allow the assessment of the preservation state and the observation of the internal structure of an object in 3-D. While SEM-EDX analysis permits the elemental analysis of the polychrome layers. As a result 2-D and 3-D images, permitting the full volume inspection of an object, were taken in a totally non-destructive way. The morphological and physical information about the inner structure of the investigated wooden sculpture was obtained, revealing changes related to previous restorations, as well as ageing effects. Employing the SEM-EDX, painting materials (pigments and filers), were identified. Gained data is essential for restorers to understand the whole structure of the studied object and to decide which further investigation and restoration steps have to be undertaken.

Key words: cultural heritage • X-ray image • X-ray dual source computed tomography (DSCT) • scanning electron microscopy-energy dispersed X-ray spectroscopy (SEM-EDX)

A. Mikołajska✉, M. Walczak, Z. Kaszowska
Faculty of Conservation and Restoration
of Works of Art,
Academy of Fine Arts in Kraków,
27/29 Lea Str., 30-052 Kraków, Poland,
Tel.: +48 12 292 6292 ext. 37, Fax: +48 12 430 1595,
E-mail: amikolajska@asp.krakow.pl

M. Urbańczyk Zawadzka, R. P. Banyś
Center for Diagnosis Prevention and Telemedicine,
John Paul II Hospital,
80 Prądnicka Str., 31-202 Kraków, Poland

Received: 30 November 2011
Accepted: 15 June 2012

Introduction

X-ray radiation, since its discovery in 1895, plays an important role in the field of cultural heritage. X-ray radiography became one of the most popular and commonly used method regarding examination of historical objects, especially paintings and wooden sculptures [2]. The character and number of delivered data made this technique an ideal non-destructive research tool for observing the inner structure of the investigated object as well as localizing metal elements, pieces made of different woods or even the bottom layers of polychrome. It also shows holes caused by woodworms. However, the main disadvantage of this method is that information can be retrieved as two-dimensional (2-D) images and it is hard to define exact position of the observed defects or elements, within the object.

Recently, following the development of technology, computed tomography has been introduced to the diagnostics of cultural heritage objects. In particular, X-ray dual source computed tomography (DSCT) is used for the investigation of different art works, as it preserves the integrity of the object and delivers three-dimensional (3-D) information of its structure [1, 4–6].

The second group of techniques, as scanning electron microscopy combined with energy dispersed X-ray spectroscopy (SEM-EDX), X-ray fluorescence (XRF) or particle induced X-ray emission (PIXE), widely used in the research of historical objects is based on the registration of characteristic radiation [3, 7]. They permit the elemental analysis and so the identification of painting materials (pigments, filers and foils). In case of SEM-EDX, the micro-sized cross sections of paint layers had to be taken due to limited dimensions of vacuum chamber. Whereas it is not necessary to take any sample using two other methods.

In this work we present the results of the analyses performed by the use of X-ray radiography, DSCT and SEM-EDX on the Gothic wooden sculpture *The Risen Christ*. The object (Fig. 1a) originates from a private collection and it has not been investigated before. The original polychrome was found in rather bad preservation state with visible overpainting layers.

Experimental

The X-ray radiography and SEM-EDX analyses were done in Poland at the Academy of Fine Arts, Faculty of Conservation and Restoration of Art Works, Department of Applied Physics (Kraków, Poland). Thanks to collaboration between the Academy of Fine Arts and John Paul II Hospital, X-ray Dual Source Computed Tomography was carried out at the Center for Diagnosis Prevention and Telemedicine (Kraków).

The radiographic analysis was carried out using a Baltospot BL 100/5 X-ray tube with a beryllium window, cooled anode with oil and voltage up to 100 kV. X-ray images were taken on a radiographic film, specially cut for this purpose and packed in a special cover to avoid overexposure of the film. After each exposure, the film was developed automatically. Three X-ray images were

a b

Fig. 1. Comparison of photographs in visible light (a) and an X-ray image (b) of the sculpture.

taken, two of dimensions of 110 × 43 cm and one of 30 × 40 cm. The first radiographic test was performed with an X-ray tube voltage of 60 kV, while the exposure time was 5.5 min at a tube-object distance of 180 cm. The second test was performed with an X-ray tube voltage of 80 kV and an exposure time of 6 min at the same distance from the tube to the object. The third test was performed using a voltage of 70 kV and an exposure time of 1.5 min at a distance of 120 cm from the tube to the object. The tube current was 5 mA in all cases.

Computed tomography scans were performed using a dual source CT scanner with a 0.33 s rotation time (Somatom Definition, Siemens, Germany, Forcheim). Scanning was performed using the following parameters: X-ray tube potential 120 kV, effective tube current 78 mA, slice collimation 16 × 0.3 mm, slice thickness 0.6 mm. For each image, 246 slices of the sculpture were acquired. Image analysis was performed using Leonardo Workstation (Forcheim, Siemens, Germany). For object assessment, the following reconstructions were used: cross-sectional multiplanar reconstructions (MPRs), maximal intensity projections 5 mm and 3-D volume rendered.

For chemical analysis, eleven microsamples were taken from different parts of the wooden sculpture in order to prepare cross-sections of the polychrome layers. They were embedded in epoxy resin and polished manually using an abrasive paper of various grain size up to 2500. Such a method of sample preparation may cause cross-contamination within sample layers, however, in the present study it has not been observed. First, colour microphotographs were taken using an optical microscope (Carl Zeiss, Neophot) with a coupled digital camera (Canon EOS 450D). Then, SEM-EDX analysis was performed. Prior to the SEM imaging, all cross-sections were covered with a thin carbon layer to avoid charging of the sample surface. Samples were introduced to the microscope chamber (JOEL 5550). The imaging was performed with a 20 keV electron beam. The EDX silicon detector cooled down to the liquid nitrogen temperature (IXRF Systems) was used for analyzing the elemental composition of the samples. Due to the heterogeneity of investigated samples and in order to obtain the representative results of pigment distribution, the EDX analysis was performed in two or three areas of each layer. Also the single pigment grains were analyzed.

Results and discussion

X-ray images

Figure 1b shows one of the larger X-ray images. It demonstrates that the sculpture is made up of one piece of wood. The range of the original ground can be observed (first of all on the Christ's face and hand). Damage, cracks, deterioration and areas of loss of the original ground (head and incarnates) are also visible. The radiographs provide evidence that in the secondary layer there is a highly absorbent material. The measurements performed with SEM-EDX (these results are shown in the last subsection of this section) revealed that this pigment is lead white. Figure 1b shows all the metallic elements, such as nails and wooden tenons added during previous conservations. On the chest, there are, not visible to the naked eye, strange contours, similar to flowers. There are no holes caused by woodworms.

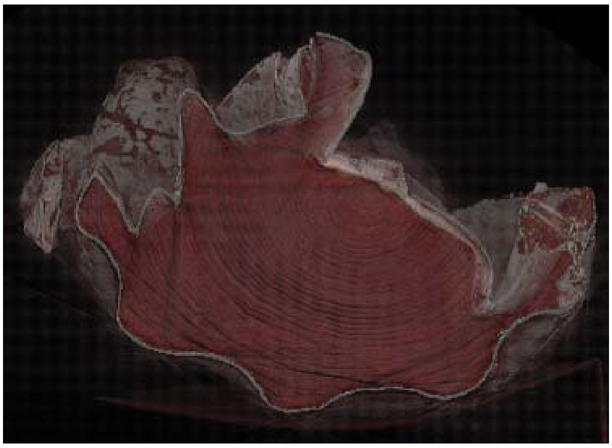

Fig. 2. Presentation of a 3-D volume rendered image.

X-ray dual source computed tomography (DSCT)

The DSCT investigation reveals the statue's good structural condition: the wood is healthy – there are no holes caused by woodworms and tree rings are clearly visible (Figs. 2 and 3). The DSCT scans confirm that the sculpture is made up of one piece of wood. Each DSCT

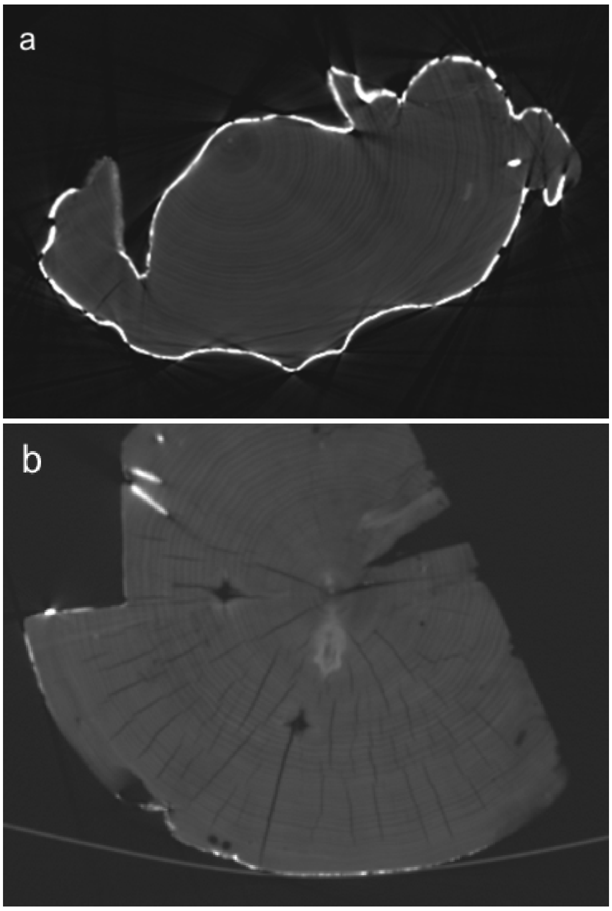

Fig. 3. Presentation of two DSCT – cross-sectional MPRs: one with a thin contour around the sculpture of lead white (a) and the second with clearly visible metallic elements (b).

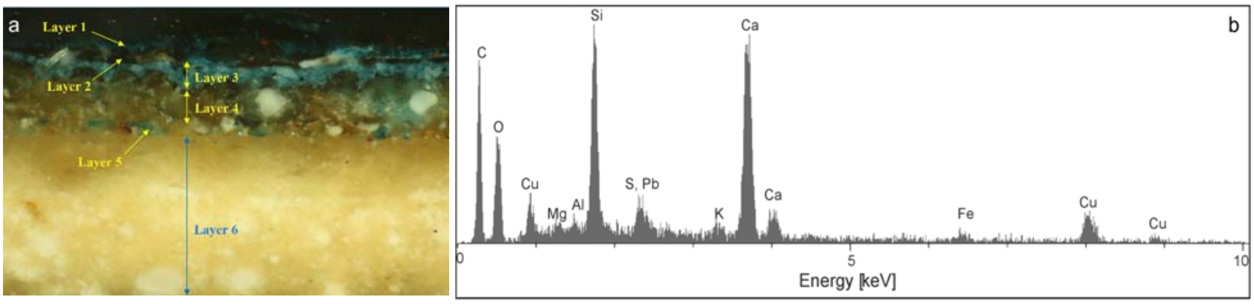

Fig. 4. The optical microscope image of the sample taken from the blue coat (a). The EDX spectrum of layer 5 (b).

image displays a thin contour around the sculpture of highly absorbent material (Fig. 3a), which, as we already know from SEM-EDX analysis, is lead white. It was also possible to assess the depth of the cracks visible on the surface. The most important element in this investigation is that it was possible to accurately localize all the metallic elements such as nails and wooden tenons added during previous conservations (Fig. 3b). On the other hand, creating three-dimensional images it is possible to observe, e.g. the polychrome layer (Fig. 2). 3-D images have also a great value for conservatory documentation.

SEM-EDX analysis

Eleven samples were taken from different parts of the sculpture. All cross-sections were analysed with SEM-EDX. The identification of the mineral pigments present in the painting layers of the investigated sculpture was done by comparison of the detected elemental composition with optical microscope images (the layers colour) and the basic chemical and conservatory knowledge. The following pigments, both in original and overpainted layers, were identified: the lead white ($2PbCO_3 \cdot Pb(OH)_2$), orpiment (As_2S_3) or realgar (As_4S_4), the chrome yellow ($PbCrO_4$ or $PbCrO_4 \cdot PbO$), yellow or red ochres (iron oxides, clay, silica), azurite ($2CuCO_3 \cdot Cu(OH)_2$) and smalt (potassium glass tinted with cobalt oxides). Also the presence of alumino-silicate compounds was revealed. The high contents of lead in some of the studied layers, may be related to the possible presence of lead oxides, like: minium (Pb_3O_4), litharge (PbO) or massicot (PbO). The filer of the original ground is chalk ($CaCO_3$), however, the presence of alumino-silicate and lead compound (probably the lead white) is also observed. In two samples the gold foil, placed on the red bole base with Fe_2O_3 tinted clay, was detected.

The results obtained for three, most significant samples, were chosen to be presented in this paper in detail. Figures 4–6 show the optical microscope images of the cross-sections with exemplary EDX spectra (one spectrum for each sample).

The first sample (Fig. 4a) was taken from the blue coat and consists of six layers. First four layers are overpaintings. Blue, outer layer consists of lead white and probably of organic pigment (indigo), due to the absence of any elements characteristic for blue mineral pigments. The second layer is created by organic compounds, containing calcium and lead. The third layer is similar to the first one with the white lead pigment and probably indigo. The next layer is generally transparent but possesses a few blue grains. The interpretation of the results is not unambiguous. No element responsible for the blue colour has been detected. However, due to the high concentrations of silicon and the presence of elements such as potassium and calcium, smalt is considerated as the main material of the layer. It is also known that concentration of cobalt in degraded smalt is often below the detection limit of the common EDX analyzers [8]. This layer also includes a lead compound (pigment or siccative). In the fifth layer (Fig. 4b) the blue pigment-azurite and lead compound (again pigment or siccative) were found. The ground layer reveals chalk and alumino-silicate.

The next sample (Fig. 5a), taken from the red coat, consists of nine layers. In the first and second layer earth pigments with lead compounds prevail. In the next three layers lead is the dominant element. The colour of layers 3 and 5 suggests that there is probably lead white, while in the fourth one, lead origins probably from siccative. Layers 6, 7 and 9 are typical chalk ground layers, crossed by bole (eighth layer), suggesting the use of gliding technique. In the original ground layer besides calcium the addition of alumino-silicate and lead compounds was found (Fig. 5b).

Finally, Figure 6a presents the cross-section of paint layers taken from the golden coat edge (trimming). It has eight layers. In the outer layer lead and calcium was found. Next, the yellow layer contains a small amount

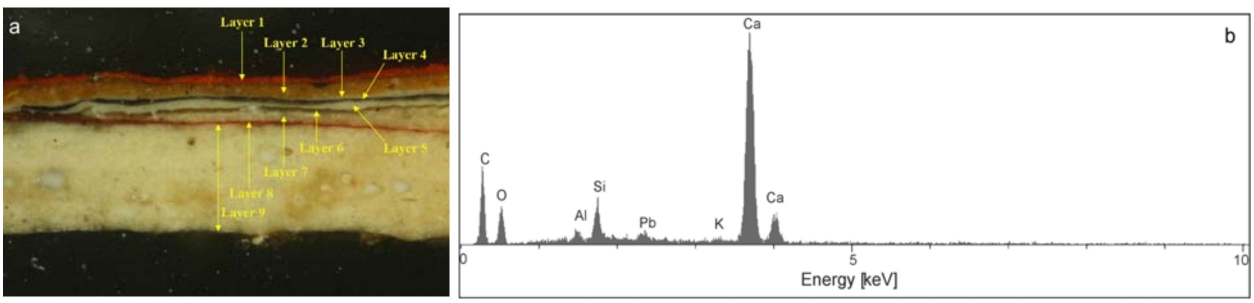

Fig. 5. The optical microscope image of the sample taken from the red coat (a). The EDX spectrum of layer 9 (b).

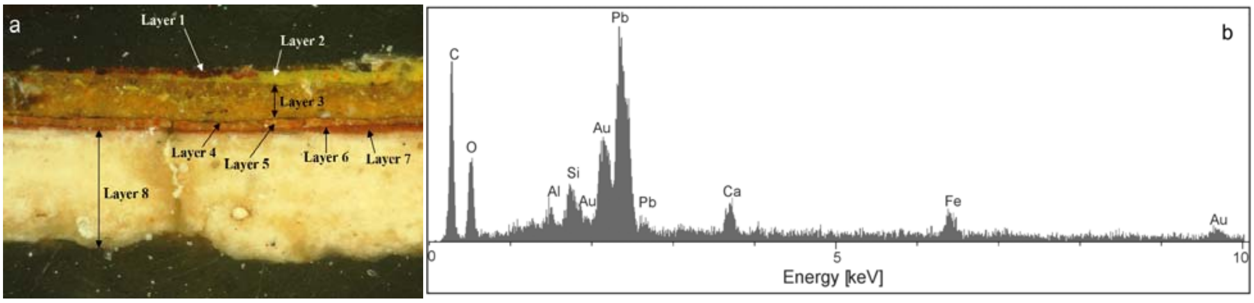

Fig. 6. The optical microscope image of the sample taken from the golden coat edge (a). The EDX spectrum of layer 4 (b).

of earth and chrome pigments and it is characterized by the higher concentration of elements mentioned above. In the third layer (thick yellow-orange) there are earth pigments, orpiment or realgar and lead presence is revealed, too. The high concentration of lead in first three layers evidences the contribution of lead pigments, however, since the colour of those layers is not defining it is difficult to say exactly which lead compounds are present. The next, very thin layer, it is gold (Fig. 6b). The spectrum shows also elements present in the neighbour layer 5: Al, Ca, Fe, Si and Pb, that could be assigned to lead and earth pigments (ochers). The sixth and seventh layers are again golden foil with ground bole of red colour (earth pigment). The last layer is the original ground.

Conclusions

The results presented in this study demonstrate the application of three analytical techniques, based on the properties of X-ray radiation, to the area of art conservation. The 2-D and 3-D images of investigated sculpture, together with chemical information obtained by SEM-EDX contribute to the detailed documentation of the object. Gained data are interesting and combined with the knowledge of museum conservators will be very helpful during future conservation of the sculpture. It should be mentioned that the data presented in this paper are satisfactory when it comes to inorganic pigments. However, for full characterization of the object, also other techniques, such as Fourier transform infrared spectroscopy (FTIR) or Raman spectroscopy suitable for recognition of the organic compounds, should be applied.

Furthermore, the presented data confirm the importance of multidisciplinary approach to conservation science problems. In the restoration process it is essential to integrate various techniques to be able to understand the whole structure and the preservation state of the object investigated.

Acknowledgment. A. Mikołajska wishes to thank MARR (Małopolska Agencja Rozwoju Regionalnego) and EU for the contract which helped to carry out the results presented and also wishes to thank the John Paul II Hospital authorities for collaborative partnership. M. Walczak wishes to thank EU (FP7 Marie Curie Re-integration Grant, PERG04-GA-2008-239318) for a contract.

References

1. Bettuzzi M, Brancaccio R, Casali F *et al*. (2004) Innovative systems for digital radiography and computed tomography: applications for cultural heritage diagnostics. In: Martini M, Milazzo M, Piacentini M (eds) Physics methods in archaeometry. IOS Press, Amsterdam, pp 461–470
2. Gilardoni A, Ascani Orsini R, Taccani S (1977) X-rays in art. Gilardoni S.p.A., Mandello Lario (Como)
3. Janssens V (2004) X-ray based methods of analysis. In: Janssens K, Van Grieken R (eds) Non-destructive microanalysis of cultural heritage materials. Elsevier, Amsterdam, pp 129–226
4. Morigi MP, Casali F, Berdondini A *et al*. (2007) X-ray 3D computed tomography of large objects: investigation of an ancient globe created by Vincenzo Coronelli. In: Fatakis C, Pezzati L, Salimberi R (eds) Optics for arts, architecture, and archaeology. Proceedings of SPIE, vol. 6618
5. Morigi MP, Casali F, Bettuzzi M *et al*. (2007) CT investigation of two paintings on wood tables by Gentile da Fabriano. Nucl Instrum Methods Phys Res A 580:735–738
6. Morigi MP, Casali F, Bettuzzi M *et al*. (2010) Application of X-ray computed tomography to cultural heritage diagnostics. Appl Phys A 100:653–661
7. Schreiner M, Melcher M, Uhlir K (2007) Scanning electron microscopy and energy dispersive analysis – applications in the field of cultural heritage. J Anal Bioanal Chem 387:737–747
8. Sprig M, Higgitt C, Saunders D (2005) Investigation of pigment-medium interaction processes in oil paint containing degraded smalt. National Gallery Technical Bulletin 26:56–70