Case study: **Saint under bell jar (Art & History Museum, European ethnology collection, Brussels)**

Case study image:

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Report date: November 18, 2021

1. Non-invasive analysis

1.1. Methodology

XRF

For the material-technical analyses of a saint under a bell jar, X-ray fluorescence (XRF) analyses were performed. Despite a number of limitations and drawbacks, mobile XRF has been successfully used in the past for the identification of pigments in murals, manuscripts, etc.

XRF is an elemental analysis technique that makes it possible to identify the chemical elements present within the irradiated zone, without taking into account the stratigraphy. The chemical elements can thus be present both in the surface layer and / or in the underlying layer(s) (this depends on the nature of the chemical elements and the thickness of the layers).

A second disadvantage of the technique is that the information obtained is “elementary” information and not molecular information. For example, when lead is detected in a paint layer, this may indicate the white pigment lead white [2 $PbCO_3$.Pb $(OH)_2$], or the red lead red (minium) [2PbO.PbO_2], or the yellow massicot [PbO], or a mixture.

Light chemical elements are not detected (positive identification from potassium) and organic pigments / binders cannot be identified.

This technique thus provides a general overview of the chemical elements present in the analysed zone.

The XRF technique is based on the following principle: a primary x-ray (coming from the x-ray source in the equipment) is aimed at the paint layer. Secondary X-rays, characteristic of the chemical elements present, are generated. Due to the high energy of the incident primary x-rays, secondary x-rays are generated not only in the surface layer but also in the underlying layer(s). This obviously complicates the interpretation of measurement results.

All measurements were performed with a µ-XRF instrument ARTAX (Bruker) with a rhodium (Rh) tube with polycapillary optics, which gives the primary x-ray beam a diameter of approximately 70 µm, which allows to analyse very fine details (Figure 1) . The measurement location can be accurately selected using a CCD colour camera (figure 2).

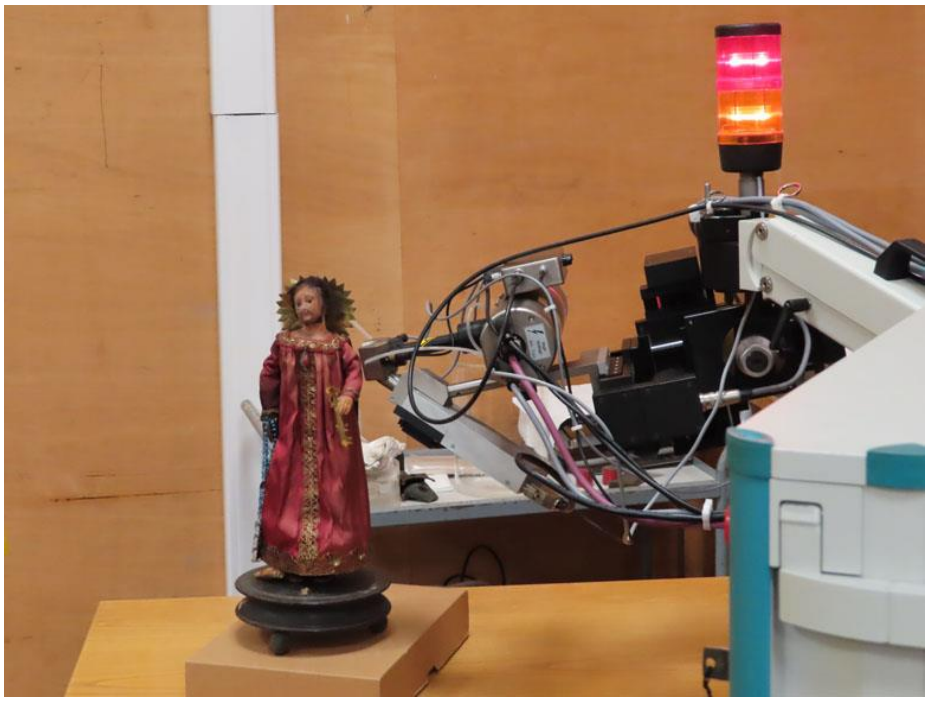


Figure 1: XRF measuring equipment

A typical analysis result is presented in Figure 3.

The following experimental conditions were used in all measurements: Rh tube, 50 kV, 500µA, 120 seconds, no filter.

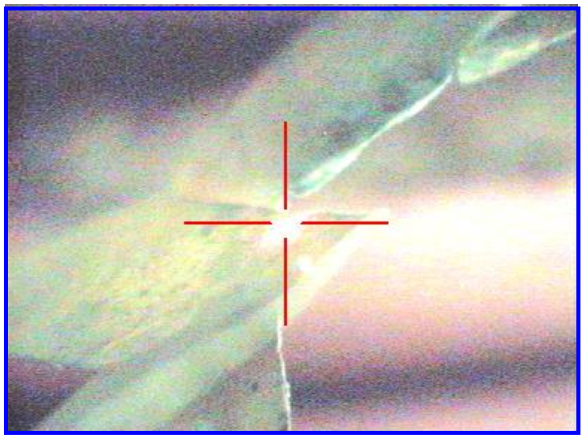


Figure 2: Saint under bell jar (left) and image taken by the camera of the XRF equipment (detail key). The analysed zone (70µm) is in the middle of the cross

All images registered by the XRF-camera (visualisation of the measuring spots) are displayed in this report.

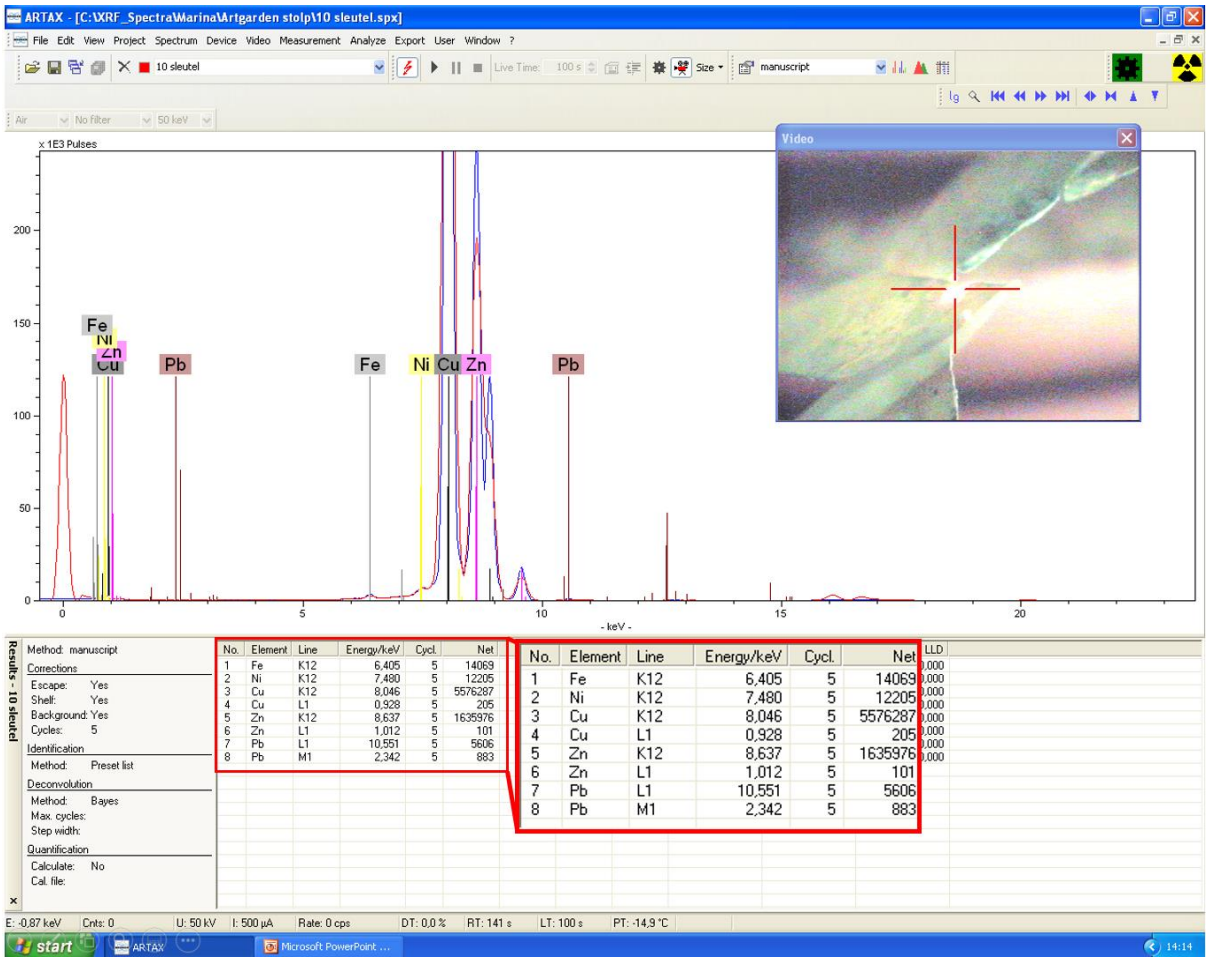


Figure 3: X-ray spectrum and data processing of the analysed spot presented in figure 2 (key)

The interpretation of the spectrum above gives the following result:

The material used to make the key contains mainly copper and zinc. Probably it is brass, a metal alloy of copper and zinc.

As explained, the interpretation of XRF analyses alone is not always unambiguous: only elementary information is obtained and different pigments can at the same time give rise to secondary X-rays. The interpretation is a combination of the obtained element information and, in case of pigments, also on the observed colour. Sometimes multiple interpretations are possible.

A total of 17 measurement points were selected.
All the selected measurement locations are indicated in figure 7.

1.2. Results

Hirox digital microscope images are registrated at areas corresponding to the XRF analysed areas.

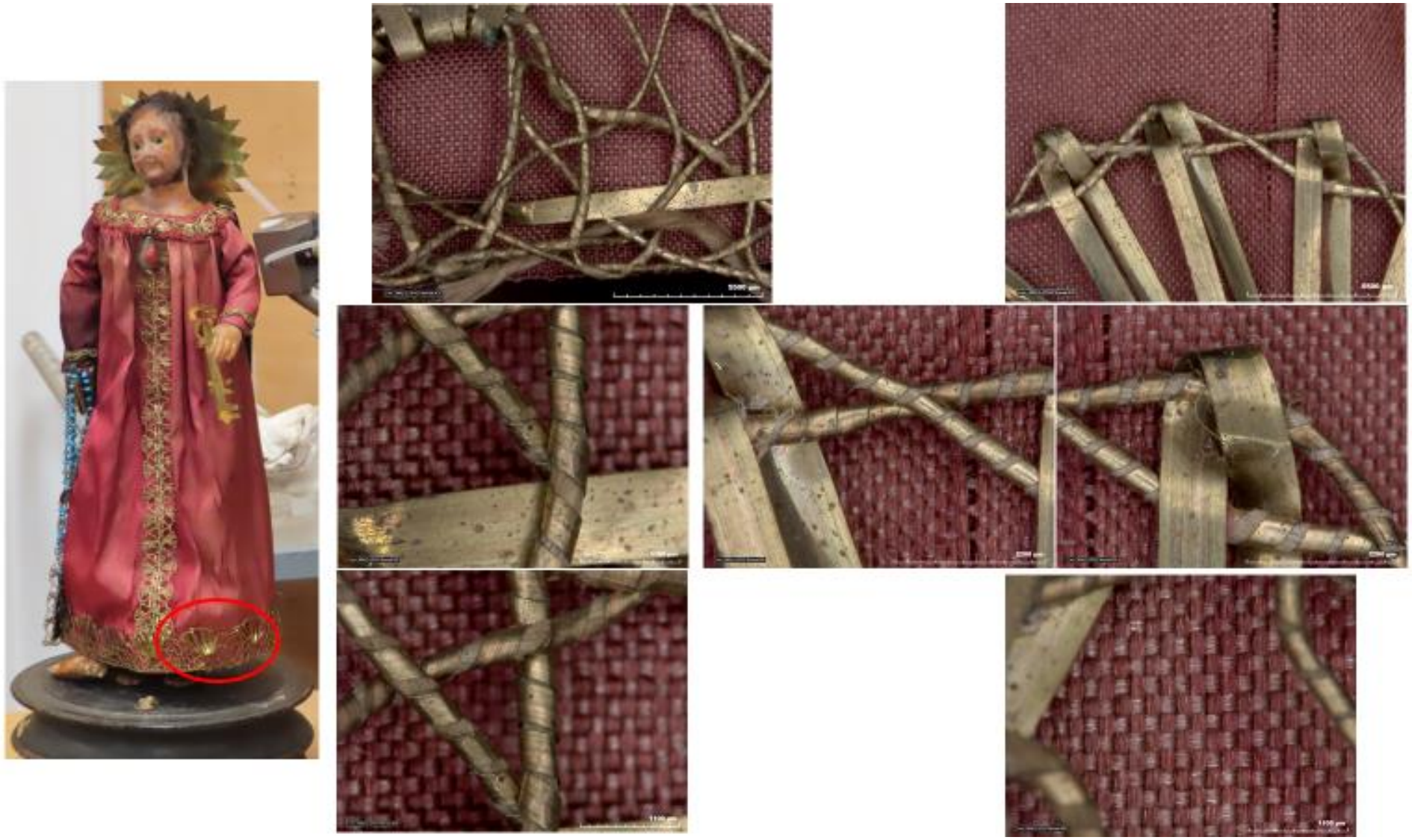


Figure 4: Hirox digital images

Figure 5: Hirox digital images

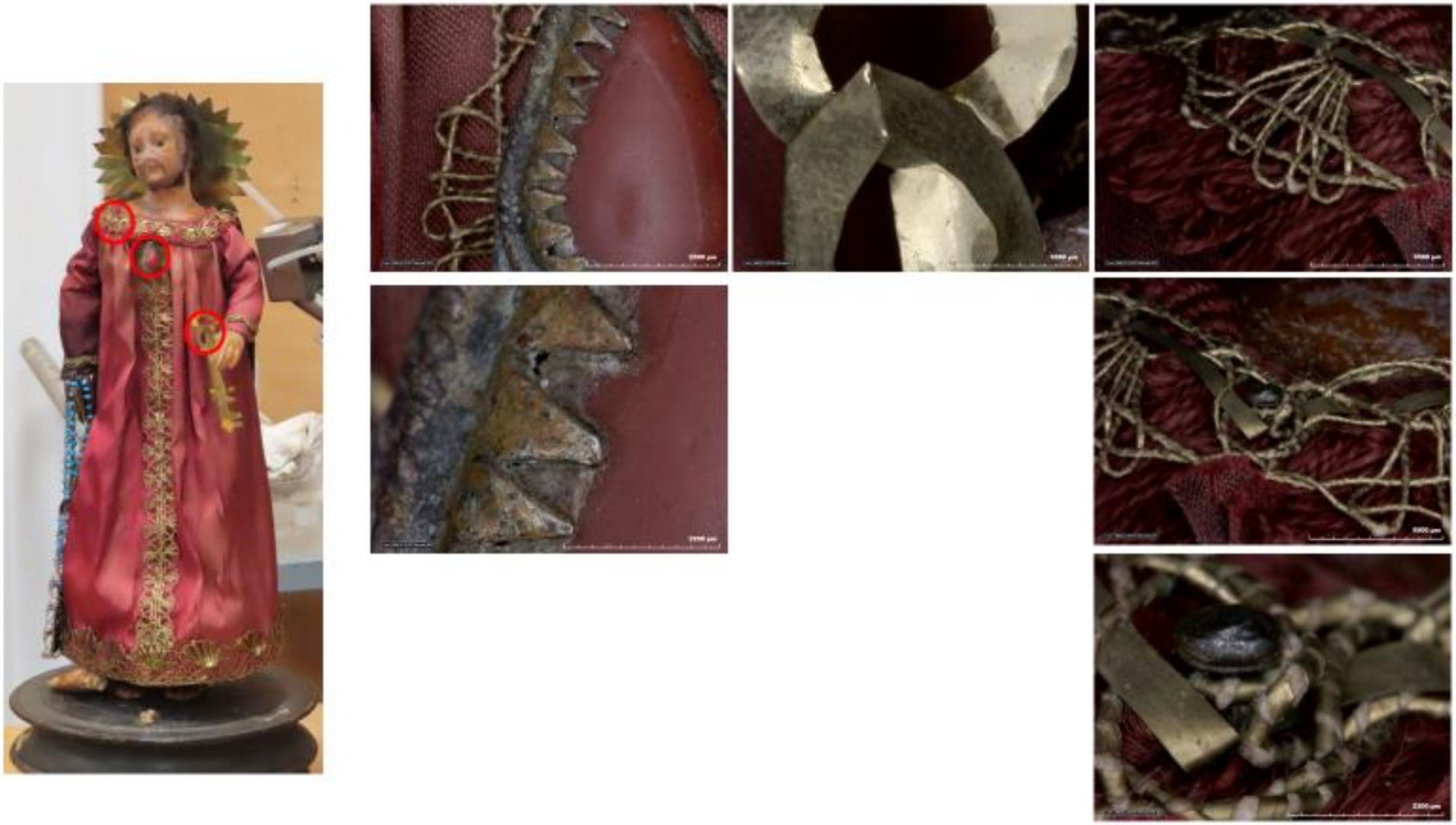


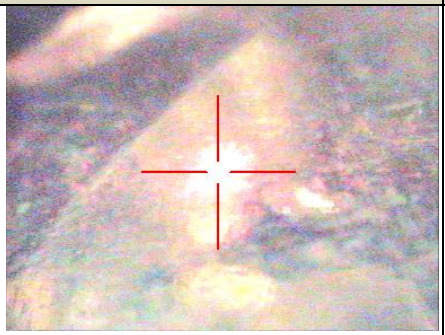
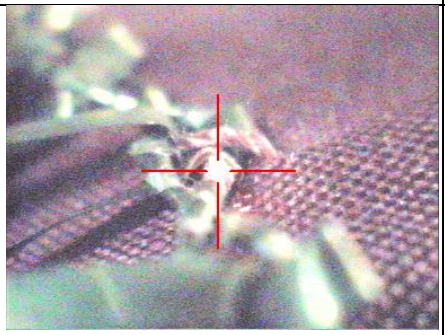
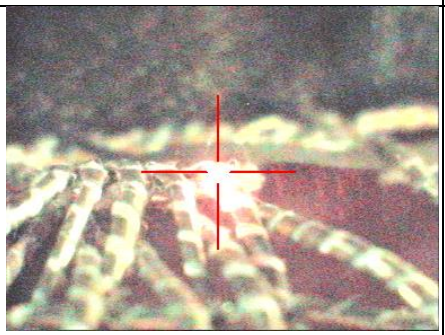
Figure 6: Hirox digital images

Figure 7: The saint with indication of XRF measuring spots

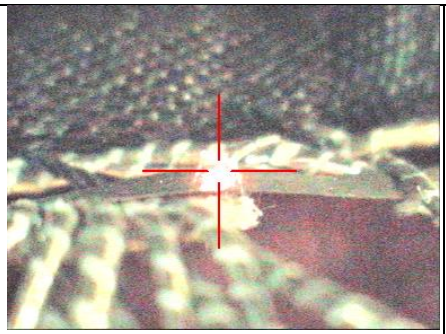
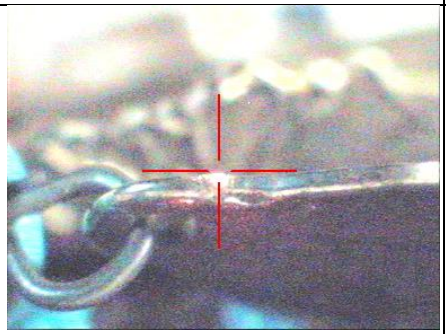
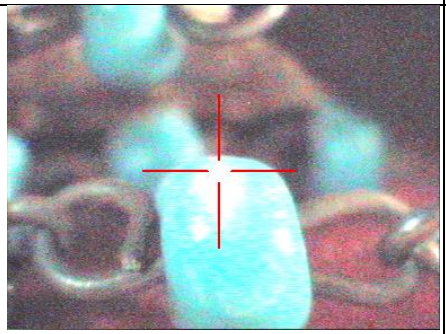
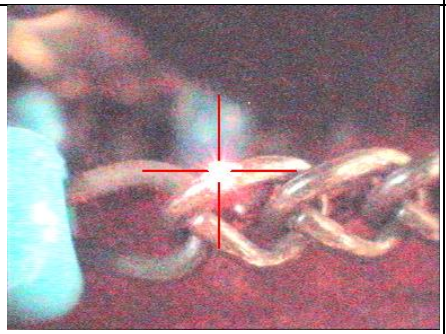
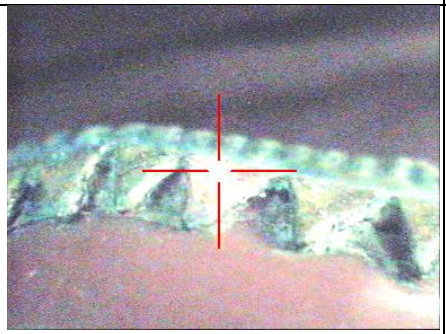
The results of the analyses are summarized in table 1.

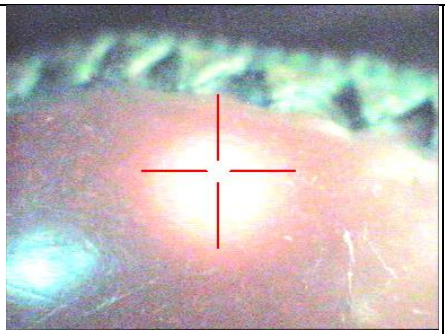
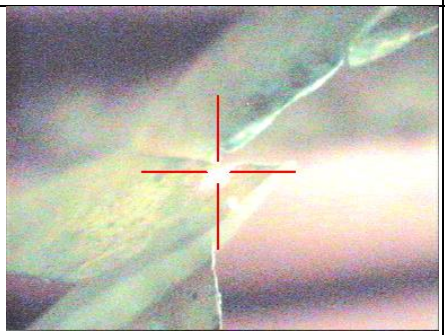
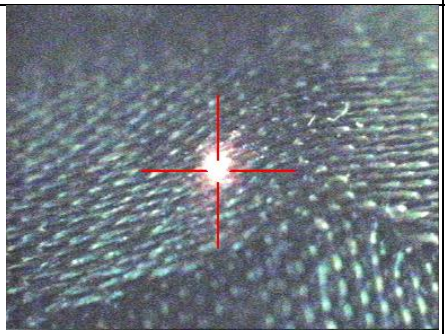
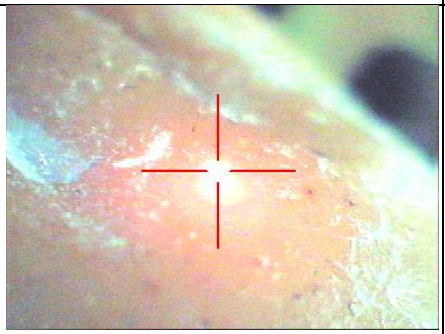
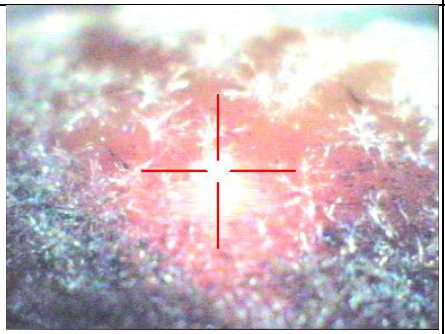
Table 1: description of the analysed zones and results of analyses: chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), strontium (Sr), silver (Ag), barium (Ba), mercury (Hg), lead (Pb)

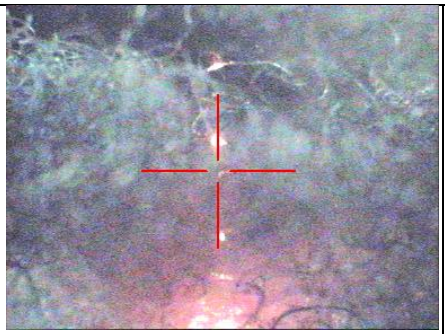
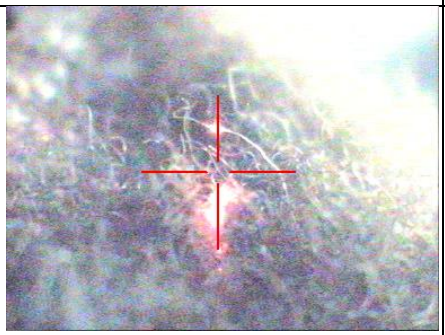
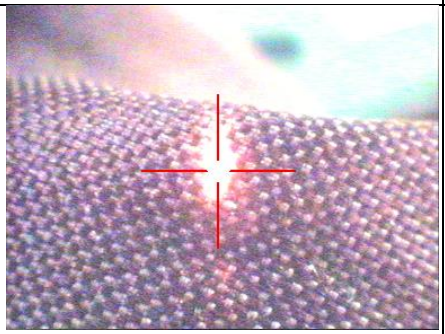
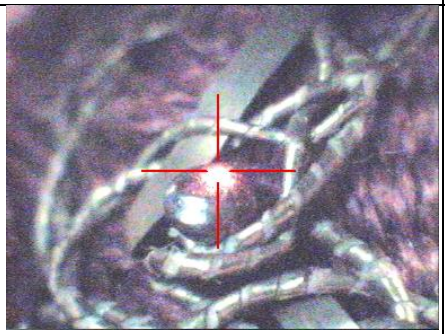
Elements present in low concentrations are in parentheses [1]

N°	Measuring place (image Artax-camera)	Description	Results of XRF-analyses	Interpretation
XRF 1		halo	**Cu**, **Zn**, Fe, Ni, (Pb)	Copper zinc alloy (brass)
XRF 2		Metal wire at the bottom	**Cu**, Zn, Fe, Ca, (K)	Copper with minor amounts of zinc : brass
XRF 3		Metal wire upright collar	**Cu**, Zn, (Fe)	Copper with minor amounts of zinc : brass

[1] > 100.000 counts in bold, >10.000 in normal letters, >1000 in parentheses

XRF 4		Flat metal wire	**Cu**, **Zn**, Fe	Copper with minor amounts of zinc : brass
XRF 5		Metal lover	**Fe**, Mn, (Cu), (Pb), (Zn)	Iron metal
XRF 6		Blue bead	**Pb**, **As**, **Cu**, Fe, (Ca), (Mn), (K)	Artificial gemstone? Turquoise?
XRF 7		Chain of blue beads	**Fe**, Cu, Mn, (Pb), (Hg)	Iron metal
XRF 8		Metal around red bead	**Cu**, **Ni**, **Zn**, Ag, Fe, (Co)	« Nickel silver ? », a copper alloy containing zinc and nickel, with an attractive silvery appearance

XRF 9		Red bead	**Zn**, Ba, Pb, Ca, (Cu), (Sr), (Hg), (Fe), (K)	Artificial gemstone? Traces of vermilion
XRF 10		Key	**Cu**, **Zn**, Fe, Ni, (Pb)	Copper zinc alloy (brass)
XRF 11		Dark cape	**Fe**, Cu, (Ca), (Pb)	Black dying using vitriol?
XRF 12		Wax hand	**Pb**, Hg, (Ba)	Wax opacified/coloured with lead white and vermilion?
XRF 13		White haze	**Pb**, Hg, (Ba), (Ca)	Idem XRF12

XRF 14		Beard	**Pb**, (Fe), (Hg)	Organic material? Detected elements are from the wax?
XRF 15		Beard	Fe, Pb, (Cu), (Ca), (Zn)	Organic material?
XRF 16		Red sleeve	(Ca), (Fe), (Cu), (Pb)	Organic colorant (see further)
XRF 17		Nail	**Fe**, Cu, Mn, (Pb), (Cr)	Iron metal

2. Invasive analysis

2.1. Wax

2.1.1. Methodology

In order to understand the white efflorescence on the head or the hand of the Saint, a small sample was withdrawn and analysed by infrared spectroscopy (FT-IR, Hyperion 3000 microscope coupled to a Vertex 70 spectrometer, both from Bruker). The sample was pressed between 2 diamond windows of a SpectraTech compression cell in order to obtain a transparent layer of the material to be analysed. The spectrum was recorded in transmission mode, in the range 4000 – 650 cm^{-1}, with 64 scans and 4 cm^{-1} resolution.

2.1.2. Results

Both the head and the hand of the Saint show the same surface phenomenon: on the surface, a white layer (or bloom) is present that is visually very disturbing (figure 8).

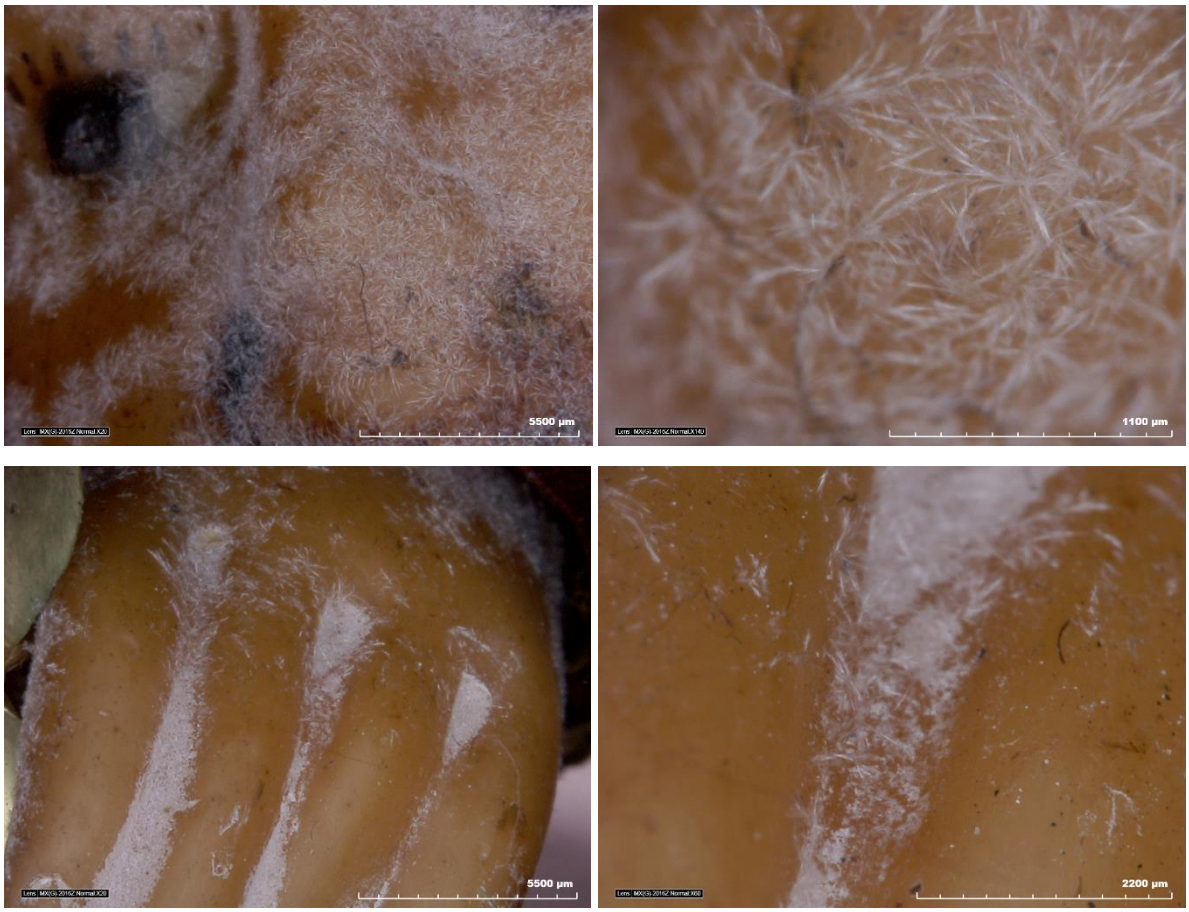


Figure 8: Hirox digital images of the head (top) and the hand (bottom)

A sample of both the white layer and of the 'original' (non-altered surface) material was withdrawn with a needle and analysed by FT-IR. Both spectra are shown in figure 9.

The 'original' material of the head is <u>beeswax</u>.

Beeswax is a natural wax of animal origin. The use of wax, especially beeswax, which has always been the most commonly used wax, dates back to ancient times.

Wax figures, based on beeswax have already been used by the ancient Egyptians during funeral rites.

Beeswax can easily be cut and shaped, it melts at a relatively low temperature (melting point 64°C), it can be mixed with colorants/pigments to change the tint or the texture, hence its use as material for sculptures is not surprisingly[2].

Chemically, beeswax is a mixture of hydrocarbons, free acids and esters.

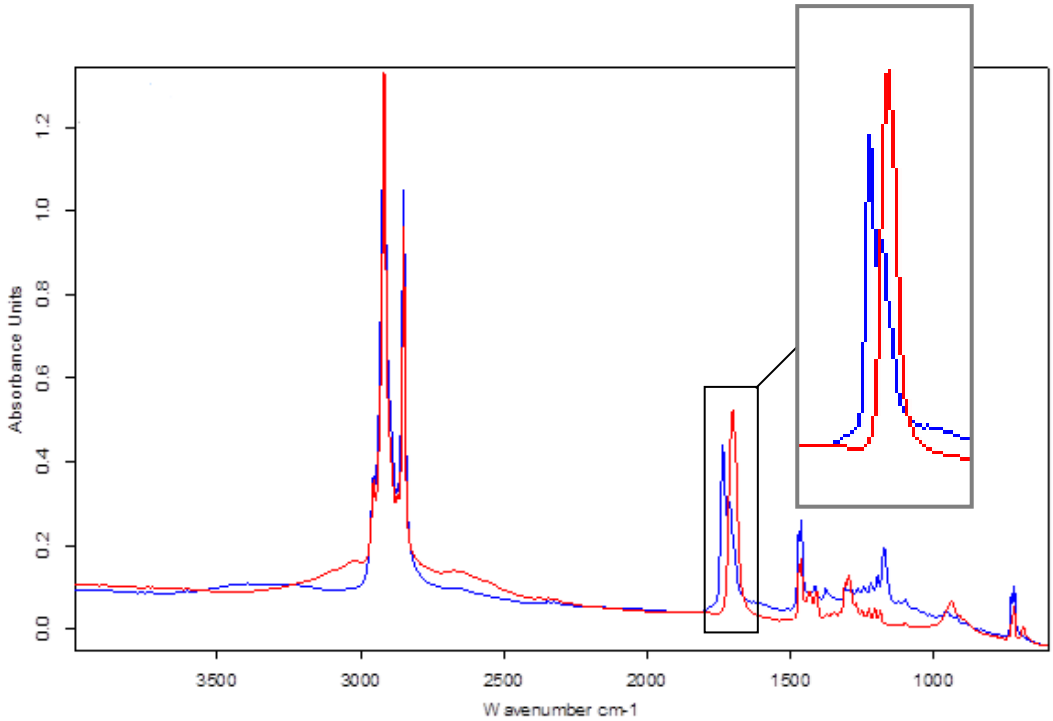


Figure 9: FT-IR spectrum of the original material (spectrum in blue) and of the white surface material (spectrum in red)

The mayor differences in the FT-IR spectra of figure 10 can be observed in the 1750 – 1650 cm $^{-1}$ region: the original material shows 2 peaks (1735 cm^{-1} and 1708 cm^{-1}); the white surface material shows only the peak at 1708 cm^{-1}.

These absorption bands can be attributed to free fatty acids and glycerol bound fatty acid esters (peaks at 1708 and 1735 cm^{-1} respectively) meaning that the surface white material can be identified as a migration of components (free fatty acids) originating from the beeswax composition. The white deposit is an alteration of the beeswax itself, whereby one or more components from the wax itself migrate to the surface. This phenomenon is described/investigated in literature[3] .

Storage of the wax at an appropriate temperature (16°C is considered as a minimum temperature) is recommended in order to avoid the surface crystallization.

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[2] Britannica, The Editors of Encyclopaedia. "Wax sculpture". Encyclopedia Britannica, 4 Apr. 2013, https://www.britannica.com/art/wax-sculpture.

[3] « Surface Crystallisation on Beeswax Seals ». P. Novotna and J. Dernovskova, Restaurator, (2002), 23(4), 256-269

« Analysis of efflorescence on surface of beeswax seals ». J. Bartl et al. Journal of Cultural heritage 12 (2012), 275-284

« Efflorescence on the surface of beeswax seals : a calorimetric study ». J. Bartl et al. Thermochimica Acta 566 (2013), 292-297

« Wax bloom' on beeswax cultural heritage objects : exploring the causes of the phenomenon ». J. Bartl et al. Magn. Reson. Chem (2015), 53, 509-513

2.2. Textile

Sample Description

Not much is known about this 19th century object. The bell jar in glass from this shape has been popular since the 18th century.[4] This object was examined because of the various degradation phenomena occurring. Here, two fabrics will be studied, the red dress, and the black cape (figure 10).

Figure 10: Red dress and black cape with indication of the sample location

[4] According to Lieve Watteeuw (KUL), the shape of a bell jar was cylindrical with a cover before the 18th century. The use of a glass bell jar became popular in the 18th century. Its use can be associated with the food industry. It was used for food preservation and, as a result, a bell jar began to be used for the preservation/protection of objects of value.

Red silk dress

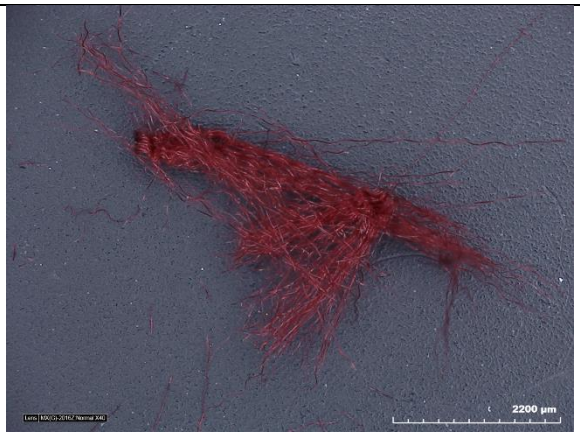
The red dress is made of silk, which seems quite well in shape though locally degradation is visible. On the front side the textile is locally torn in vertical direction. At that location, it is however not possible to take a sample without visual damage. A fragment of the red textile (/k01) with warp and weft threads is taken at the border of the dress on back side (figure 10). From this fragment, two samples are taken for dye (/k01a-b) and SEM-EDX analysis.

To study the fibre degradation, another sample (/v01) is taken from a more degraded area in the opening under the left arm (figure 10).

Black cape

The black cape is made of a damask weave with black and brown silk. The cape seems in good state, which makes sampling not obvious. It was only possible to take a very small sample of brown/black yarns at a side of the fragment (/k02) to identify the dyes (figure 10).

Table 2: Overview of the samples with indication of the object, sample description and image, KIK sample code and type of analyses

Object	Sample description	Image + KIK/IRPA code (images©KIK-IRPA Textile Lab)	Analysis / Technique(s)
Red silk dress	Red yarn	 14426c/k01a	Dye identification (HPLC-DAD, SEM-EDX)
	(faded) red yarn	14426c/k01b	Dye identification (HPLC-DAD, SEM-EDX)
	Degraded red silk	14426c/v01	Silk degradation (HPLC-FL, FT-IR, MRS)
Black silk	Black silk	No image was taken, sample too small 14426c/k02	Dye identification (HPLC-DAD)

2.2.1. Methodology

HPLC-DAD

The identification of the organic colorants is performed by High Performance Liquid Chromatography and photo diode array detection system (HPLC-DAD) with Alliance HPLC equipment (Waters, USA). The analyses are interpreted using the Empower software system from Waters. A detailed description of the analytical protocol was published before (Vanden Berghe et al. 2009). The colorants are recovered from the fibres using acidic extraction with hydrochloric acid (HCl)[5]. Hydrochloric acid extraction was preferred to extract the dyes, as to identify a very wide range of organic dyes, either natural or (half) synthetic, by comparison with spectra from the in-house developed textile colorant reference database. Preliminary to the analysis, the samples are examined under binocular in order to avoid any visible surface contamination.

The result of the HPLC-DAD analyses of the extract is listed in Table 3. The first column comprises the code of the sample given by KIK-IRPA, followed by the sample colour in the next column. The type of extract analysed and the analysis code are mentioned in the third and fourth columns. The results of the chromatographic analyses are given in the following two columns. The dye composition mentioned in column five is expressed as relative proportions of the dye constituents after calculation of their peak area measured at the wavelength (nm) mentioned in column six.

SEM-EDX

The elementary composition is studied by SEM-EDX (scanning electron microscopy coupled with energy dispersion X-ray spectroscopy, Zeiss EVO LS15 and detector of Oxford Instruments). Prior to analysis the samples were coated with a thin layer of carbon. The secondary electron images of the samples with indication of the analysed zones, as well as the corresponding spectra, are shown in figures 15 to 18.

[5] Extraction in 250 µL water/methanol/37% HCl (1/1/2, v/v/v) for 10 minutes at 105°C - vacuum evaporation - dissolving the residue in 30/30 µL methanol/water from which 20 µL is injected

2.2.2. Results

Red silk dress

The Hirox images (figure 11) show that the silk dress is made from yarns with different hues in warp and weft direction. The vertical silk yarns are red, while the horizontal yarns are pale (faded or undyed?). Therefore, it is decided to investigate the dyes from the red and paler yarns separately.

In addition, the gaps and the cracks in this fabric are mainly due to broken horizontal yarns suggesting severe fibre degradation of the pale horizonal yarns in contrary to the vertical yarns.

Figure 11: Hirox images of the red dress with details of the ripped areas of the textile

The red silk yarns (/k01a) are mainly dyed with synthetic dyes. A combination of monoazo dyes were detected: Acid red 88 (Fast red AV) as the main dyestuff, combined with acid yellow 11 (Flavazine L). In addition, another spectrum was detected similar to the one obtained from Azoflavine S in the BASF reference book from 1902.

Apart from synthetic dyestuffs, a small amount of luteolin and apigenin are detected, referring to the presence of weld (*Reseda luteola* L.) or an equivalent dye source. At last, also ellagic acid is identified, indicating the use of ellagitannin as mordant and/weighting agent.

In the currently 'uncoloured/pale' yarns (/k01b), only a trace is detected of both acid red 88 and yellow 11. This likely indicates that these yarns were not dyed originally and the dyes detected the result of cross-contamination from the red yarns.

The detection of the synthetic dyes implied a *post quem* dating of this textile. Acid red 88, Fast red AV, was discovered in 1877 by H. Caro and Z. Roussin while Acid yellow 11, Flavazine L, in 1892 by C. Möllenhoff. From Azoflavin S it is known to derive from Orange 5 (acid orange IV, discovered in 1876-77) (1991; Cain 1922).

Table 3. Result HPLC-DAD analyses. Detected dye composition

KIKIRPA code	Colour	Extr.	Analysis n°	Dye composition	λ (nm)
14426c/ k01	Red + faded red	HCl	02/210208/15	5 phb, 42 ellagic acid, 5 acid yellow 11, 48 acid red 88	255
				3 luteolin, 11 BASF-3A-S (Azoflavine S), 3 apigenin, 19 acid yellow 11, 63 acid red 88	350
14426c/ k01a	Red	HCl	02/210208/14	1 mphb, 54 ellagic acid, 1 BASF-3A-S (Azoflavine S), 5 acid yellow 11, + BASF-3A-S (Azoflavine S), 37 acid red 88	255
				32 ellagic acid, 3 luteolin, 11 BASF-3A-S (Azoflavine S), 3 apigenin, 14 acid yellow 11, 6 BASF-3A-S (Azoflavine S), 38 acid red 88	350
14426c/ k01b	Faded red	HCl	02/210208/13	-	255
				Trace of acid yellow 11 and acid red 88	350

The elemental composition of the silk filaments in both directions as well as of particles on the fibre surface is analysed with SEM-EDX. The analysis was done on the sample taken at the border from the back side of the red dress (figure 13).

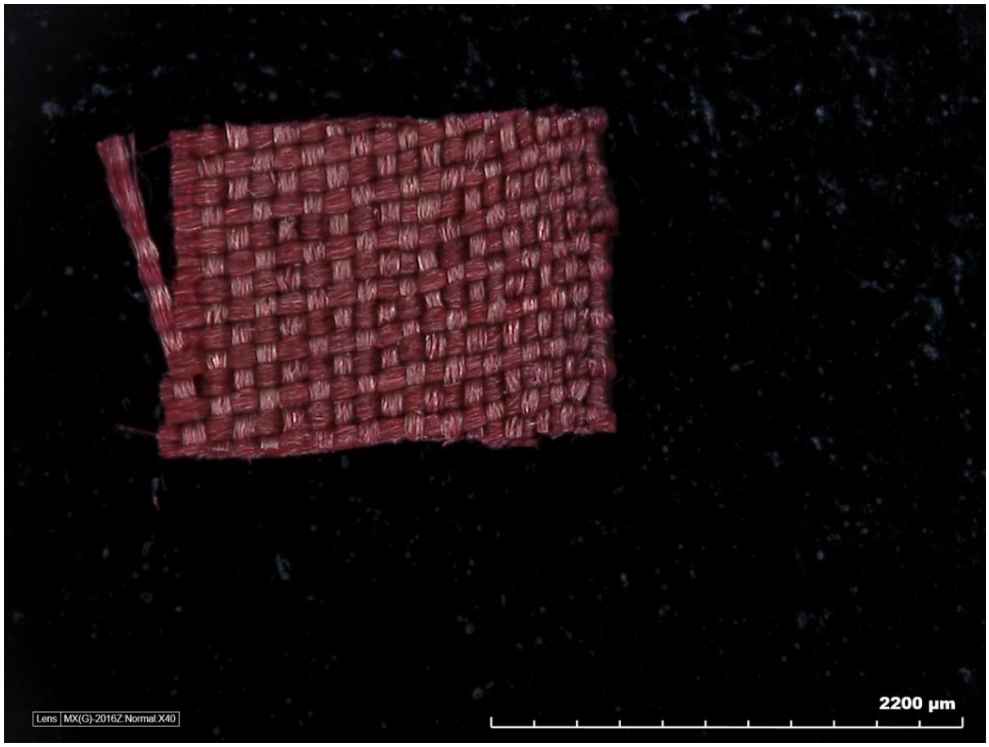


Figure 13: Hirox image of sample 14426c/k01, used for SEM-EDX analysis

The secondary electron image of the samples doesn't show any particular fibre degradation in the fragment of the red silk (figure 14). (It has to be noticed however that this doesn't concern a sample taken at a particular degraded area).

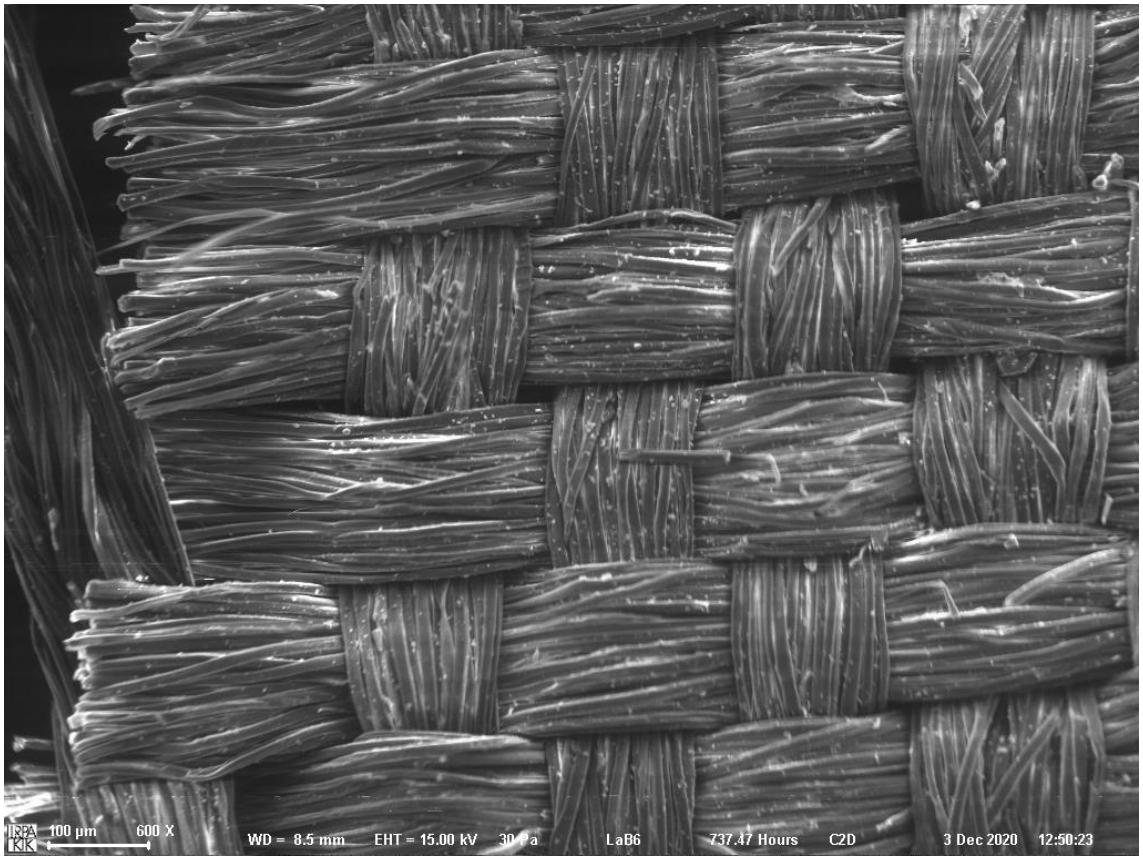


Figure 14: Secondary electron image of sample 14426c/k01

The silk yarns contain, apart from carbon (C) (partly from the carbon coating) and oxygen (O), a high amount of sulphur (S), as well as some calcium (Ca), silicon (Si), sodium (Na), aluminium (Al), chlore (Cl) and potassium (K) (figures 15-16).

No specific difference is found between the red and undyed yarns.

The high sulphur amount present indicates a sulphur bleaching treatment of the fabric.

Surface particles are detected on the fibres containing a high amount of aluminium (Al), silicon (Si), sulphur (S), potassium (K), calcium (Ca) and some iron (Fe), while other particles contain lead (Pb) or copper (Cu) and zinc (Zn) (figure 17). Zinc chlorides were used in the second half of the 19th century for silk weighting while also lead salts, especially lead acetate have been employed in the beginning of the 20th century (Hacke 2008). Aluminium sulphate and sodium silicates are known as additives in the silk weighting procedures in that period.

Out of the elemental analysis, it can be concluded that the red silk has undergone sulphur bleaching and has been heavily weighted with metal salts.

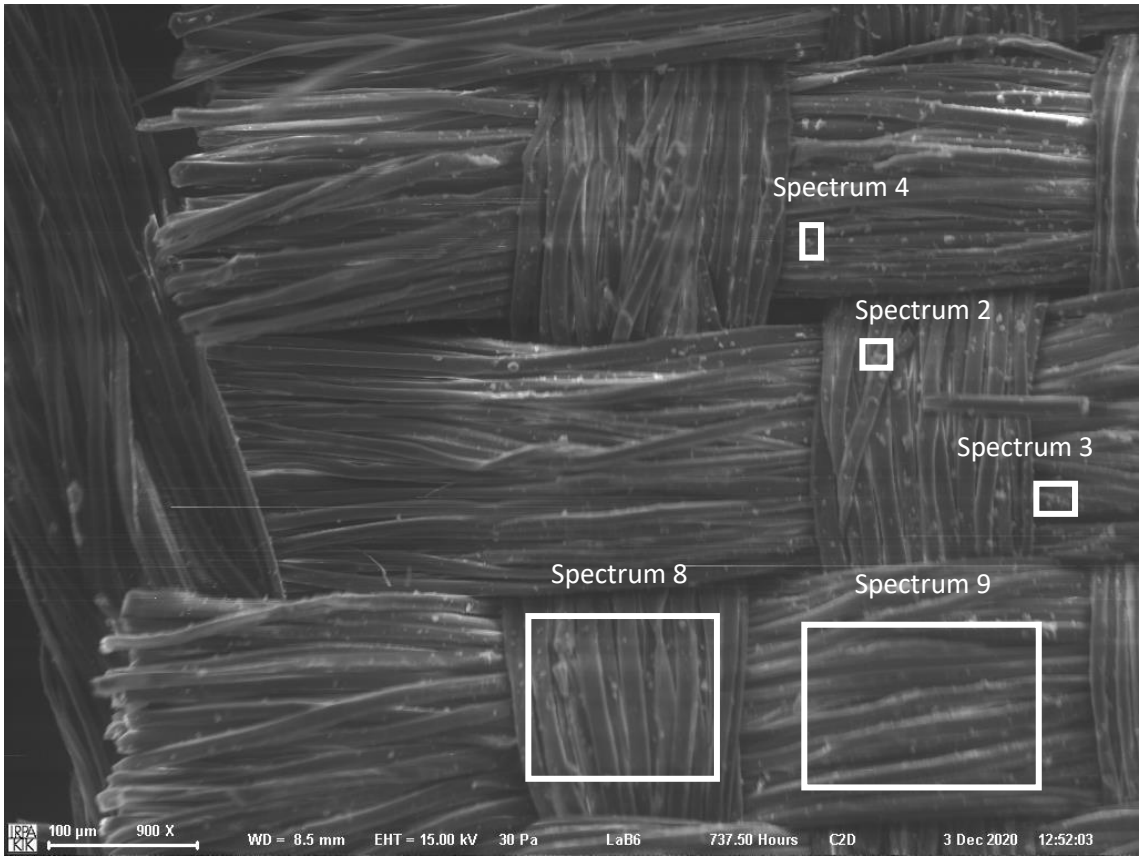


Figure 15: Secondary electron image of sample 14426c/k01 with the indication of the analysed zones in white of the red faded yarns (spectrum 8) and the red yarns (spectrum 9)

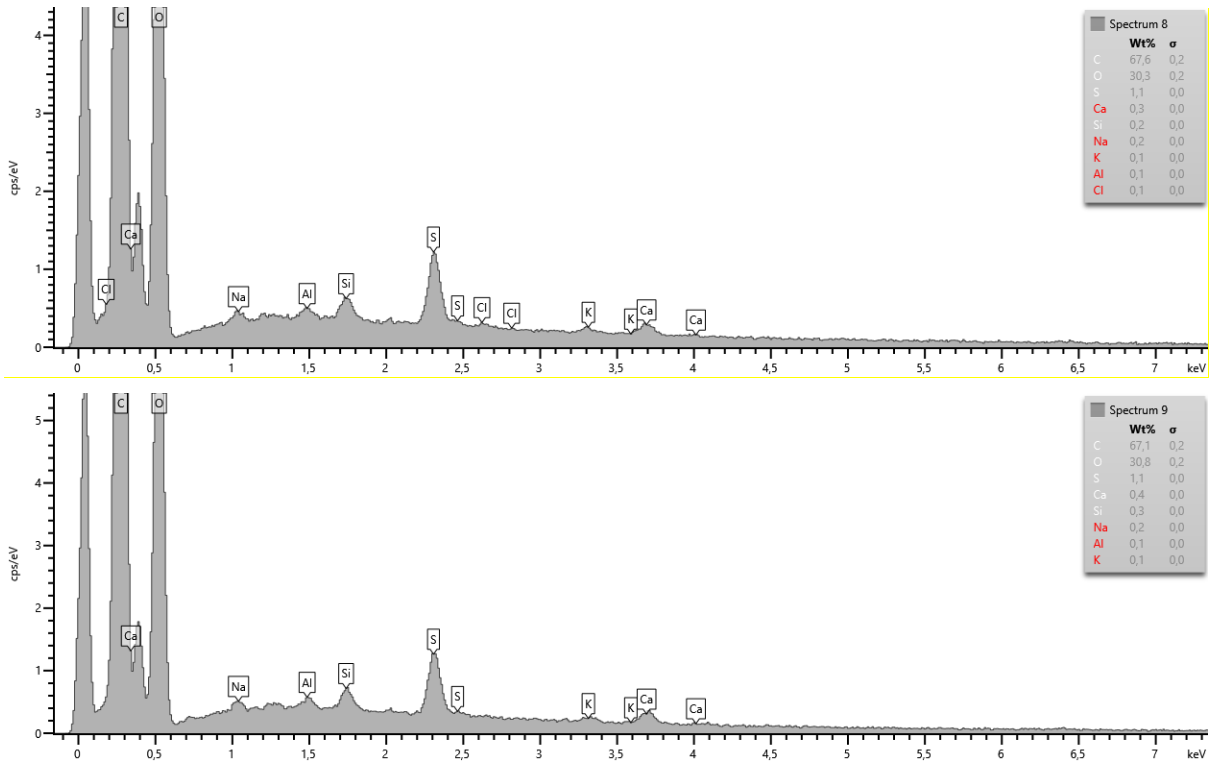


Figure 16: Element spectra of the red faded yarns (spectrum 8, top) and the red yarns (spectrum 9, down)

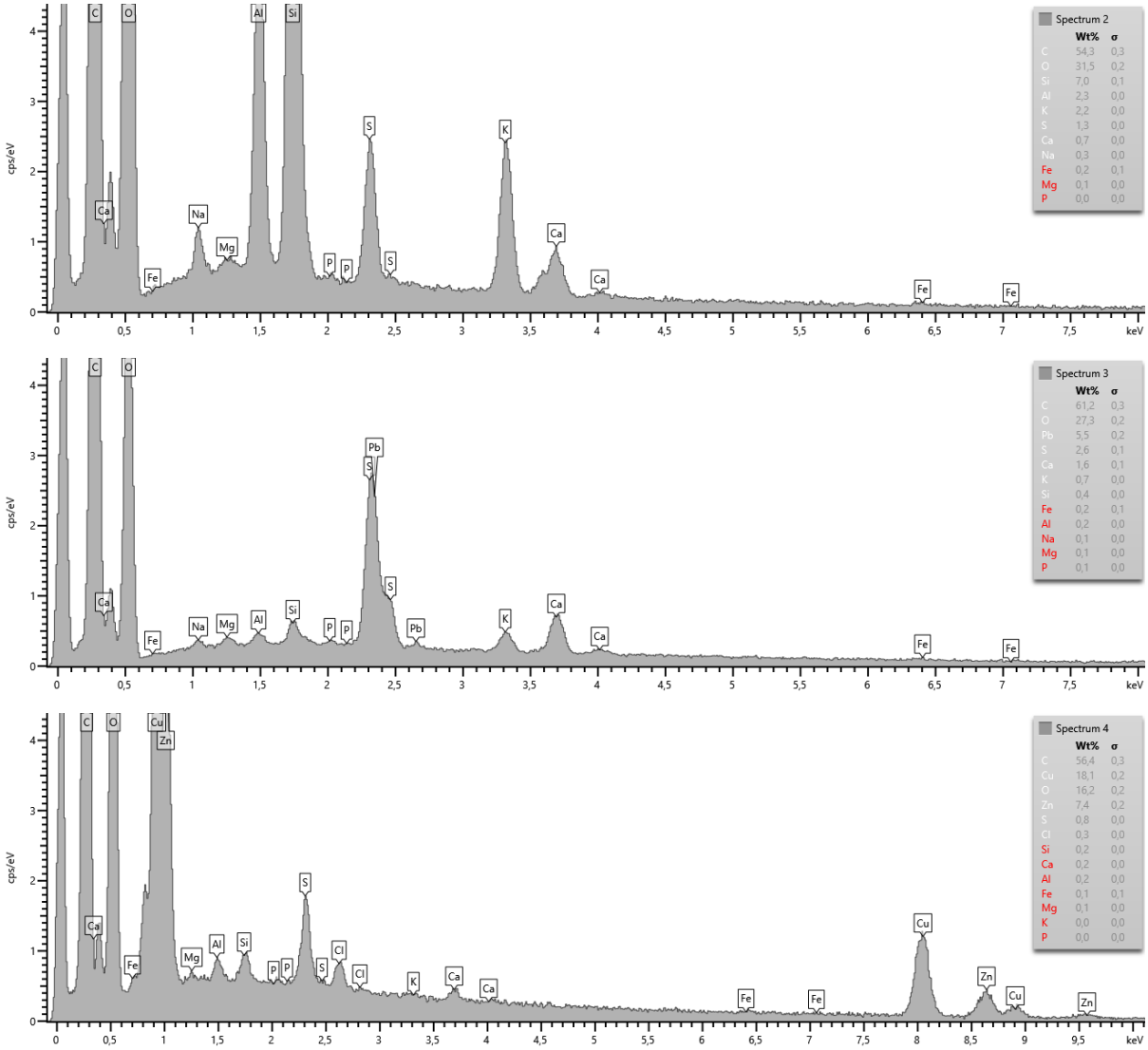


Figure 17: Element spectra of the surface particles (spectra 2, 3, 4)

<u>Black cape</u>

The Hirox images show that the black cape is made in damask weave with black and brown threads (figure 17). HPLC-DAD analysis indicates the presence of ellagic acid (table 4), which refers to the use of ellagitannins, hydrolysable tannins which can derive from a wide range of plant sources (Cardon 2007). Applies on silk yarns, tannins act both as mordant and weighting agent.

Non-destructive XRF-analysis was performed which confirmed the presence of iron (see above, non-invasive analysis, XRF11).

The use of ellagitannin together with an iron-based mordant, is a well-known procedure for black dyeing of silk.

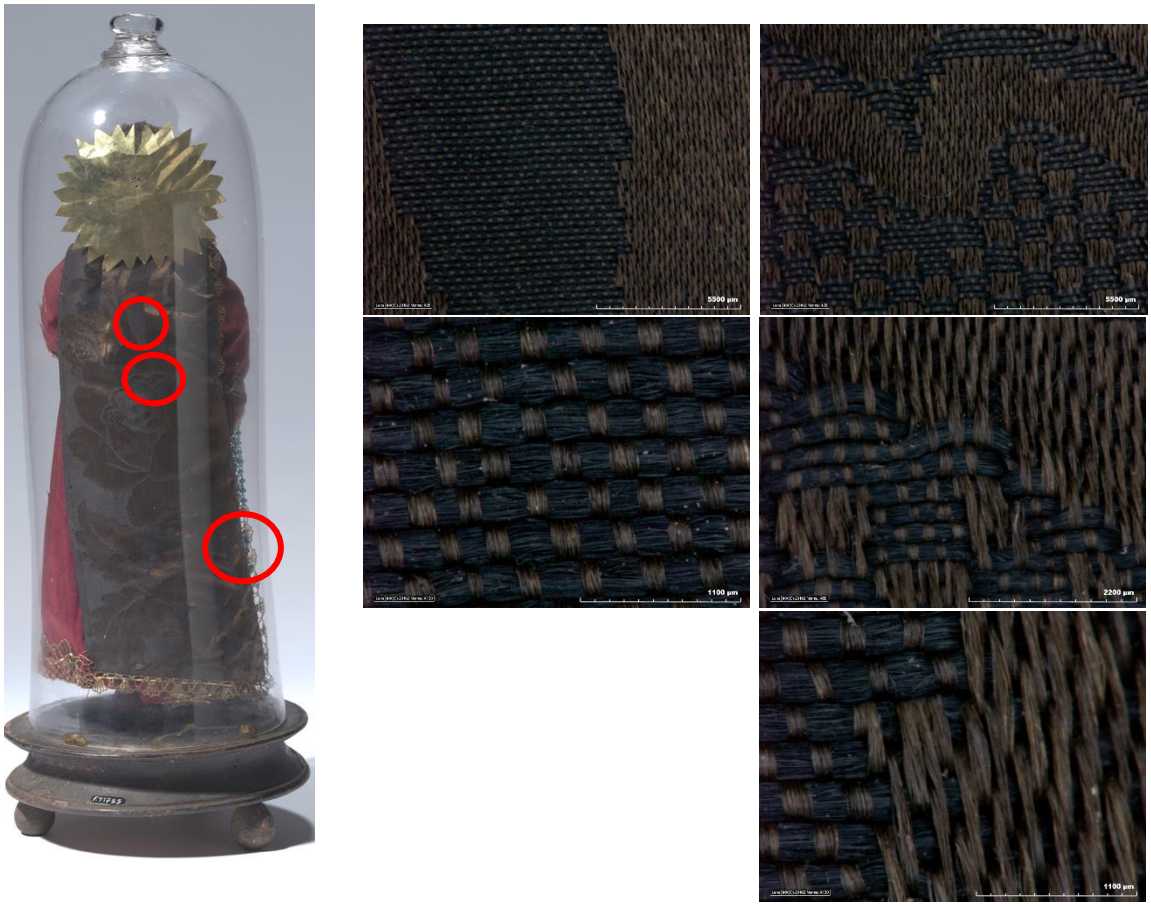


Figure 17: Hirox images of the black cape

Table 4. Result HPLC-DAD analyses. Detected dye composition

KIK/IRPA code	Colour	Extr.	Analysis n°	Dye composition	λ (nm)
14426c/ k02	Black	HCl	01/210308/08	2 phb, 98 ellagic acid	255

3. Conclusion

A combination of non-invasive and invasive analyses were performed on this saint under a bell jar.

Hirox images were made to get an overview of the materials used in the object. XRF-analyses identified the metals used. Both the halo and the key are made of a copper zinc alloy (brass). Also the metal wires are made of brass, but copper with a minor amount of zinc. The metal lover, the chain holding the blue beads together and a nail are made of an iron metal. The metal around the red bead might be “nickel silver”. For the blue and red beads, it’s not clear whether they are artificial or not.

In order to understand the white efflorescence on the head and the hand of the Saint, a small sample was analysed by infrared spectroscopy. The ‘original’ material of the head is beeswax, the dates back to ancient times. It can be mixed with colorants/pigments to change the tint or the texture, XRF-analyses detected lead and mercury what points to the use of white lead and vermilion. Chemically, beeswax is a mixture of hydrocarbons, free acids and esters. The surface white material was identified as a migration of components (free fatty acids) originating from the beeswax composition.

The red dress is made of silk, which seems quite well in shape though locally degradation is visible. The Hirox images show that the silk dress is made from yarns with different hues in warp and weft direction. The vertical silk yarns are red, while the horizontal yarns are pale. The gaps and the cracks in this fabric are mainly due to broken horizontal yarns suggesting severe fibre degradation of the pale horizonal yarns in contrary to the vertical yarns.

The vertical red silk yarns are mainly dyed with synthetic dyes, a combination of monoazo dyes: Acid red 88 (Fast red AV) as the main dyestuff, combined with acid yellow 11 (Flavazine L). In addition, another spectrum similar to the one obtained from Azoflavine S in the BASF reference book from 1902 was detected. Apart from synthetic dyestuffs, a small amount of weld (*Reseda luteola* L.) or an equivalent dye source was detected. At last, also ellagic acid is identified, indicating the use of ellagitannin as mordant and/weighting agent. The currently ‘uncoloured/pale’ yarns were not dyed originally.

The detection of the synthetic dyes implied a *post quem* dating of this textile. Acid red 88, Fast red AV, was discovered in 1877 while Acid yellow 11, Flavazine L, in 1892. From Azoflavin S it is known to derive from Orange 5 (acid orange IV, discovered in 1876-77).

Out of the elemental analysis, it can be concluded that the red silk has undergone sulphur bleaching and has been heavily weighted with metal salts.

The black cape is made in damask weave with black and brown threads. HPLC-DAD analysis detected the use of ellagitannins. Applied on silk yarns, tannins act both as mordant and weighting agent. XRF-analysis confirmed the presence of iron. The use of ellagitannin together with an iron-based mordant, is a well-known procedure for black dyeing of silk.

4. References

(1991) Important early synthetic dyes. Chemistry, constitution, date, properties. Ed. by Mary Ballard. Conservation Analytical Laboratory Smithsonian Institution.

Bartl J. et al., Analysis of efflorescence on surface of beeswax seals, Journal of Cultural heritage 12 (2012), 275-284

Bartl J. et al., Efflorescence on the surface of beeswax seals : a calorimetric study, Thermochimica Acta 566 (2013), 292-297

Bartl J. et al, Wax bloom' on beeswax cultural heritage objects : exploring the causes of the phenomenon, Magn. Reson. Chem (2015), 53, 509-513

Britannica, The Editors of Encyclopaedia. "Wax sculpture". Encyclopedia Britannica, 4 Apr. 2013, https://www.britannica.com/art/wax-sculpture.

Cain, J. C. (1922) The manufacture of dyes, Macmillan and Co. Limited St. Martin's Street, London, 16.

Cardon, D. (2007) Natural dyes. Sources, Tradition, Technology and Science, Archetype Publications, London

Hacke, M. (2008) Weighted silk: history, analysis and conservation. Reviews in conservation 9, 3-15.

Novotna P. and Dernovskova J., Surface Crystallisation on Beeswax Seals, Restaurator, (2002), 23(4), 256-269

Van Bos M., Watteeuw L., "Composition of iron gall inks in Illuminated Manuscripts (11th -16th century). The Use by Scribes and Illuminators", in: Care and conservation of Manuscripts, eds. Gillian Fellows-Jensen and Peter Springborg, The Arnamagnæan Institute, University of Copenhagen, Museum Tusculanum Press, 2014: 365 – 381

Vanden Berghe, I., Gleba, M. and Mannering, U. (2009) Towards the identification of dyestuffs in Early Iron Age Scandinavian peat bog textiles. Journal of Archaeological Science 36, 1910-1921

Watteeuw L., Van Bos M. "A 15th-century Flemish enclosed garden in cuir bouilli. Production, degradation and conservation issues of a small painting on leather". In ICOM-CC 17th Triennial Conference Preprints, Melbourne, 15–19 September 2014