"De Colorando Auro" medieval colour surface treatment of silver gilded statuettes decorating the Holy Lady Shrine of Huy (13th century, Belgium) †

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In previous papers, we showed that it is possible to modify the colour of gilding on silver substrate by applying a surface chemical treatment after it has been burnished [Crabbé *et al., Surf. Interface Anal.* 2008 **40** 467; Crabbé *et al. Applied Physics A*, 2013 **111** 39]. These types of techniques are recount in many medieval and older manuscripts [Crabbé *et al., Arch. des Biblio. de Belgique.* 2011 **94** 1581]. They have to be taken into account when applying conservation-restoration cleaning to silver gilded statuette such as the ones from the Holy Lady Shrine from Huy (13th century, Belgium) [Didier *et al., Bull. de L'IRPA* 1970 **12** 5]. Scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX) and synchrotron X-ray absorption spectroscopy (XAS) were carried out both on model and historical samples with the aim of determining if medieval colour treatment have been applied in an efficient way to the silver gilded statuette of shrine. Those results are of first importance to the conservator-restorer responsible for the shrine restoration treatment. They will influence the treatment applied to the shrine but also the interpretation of the art-piece, its final aspect and the art-history of medieval times.

1 Introduction

In ancient history, metal craftsmen were often intrigued by colours and tried to diversify the metals' appearance. Even the colour of gold and gildings can be influenced in many ways, as by changing the composition of the gold alloy or the nature of the substrate on which the gilding is applied. Another, maybe less known technique, is the chemical treatment of the gilded surface itself, *i.e.* after the application and the burnishing of the gilding[1]. Ancient writings from Theophilius[2] (12th century (c.)) and Cellini[3] (15th c.) report some recipes to "colour the gold or the gilding": De Colorando Auro. This chemical treatment was first mentioned by Didier *et al.* in 1970[4] in a restoration context of the Our Holy Lady Shrine of Huy (13th c. Mosan art, Belgium[1]). Our interest in this medieval practise was initiated by the return of the shrine to the metal conservation workshop of the Royal Institute for Cultural Heritage - IRPA (Brussels). Many questions rose concerning its conservation-restoration treatments, which might be facing an artificial colouration of the gildings.

One of the recipes (with acronym RTC*) was previously described by the same research group[6]. It assessed that the tone of a 24 carat gilding on a silver plate becomes warmer after the treatment and that the observed change in colour is due to the presence of iron and oxygen[6]. The question remained whether the detected trace of iron on the surface of the gilded masterpieces is due to a special chemical surface treatment or whether it might come from a cleaning contamination, in particular "rouge à polir".

Following those first promising results and to answer the remaining questions, an extended research was undertaken with the aim to investigate the reactionary (mechanism, kinetics), the technological aspects of the treatment, the effects on the modified gilded silver surfaces due to degradation over time and the impact of different restoration/cleaning methods on model samples (substrate: pure silver, surface: 24 carats fire gilding). These model samples were developed: i) to be as close as possible to the original object and ii) to be easily reproducible. Since the original shrine is ascribed to mediaeval times, our attention is focussed on writings preceding the renaissance period. In particular, the corpus starts in the 3rd c. with the Leyden and Stockholm papyrus[7,8] and finishes in the 15th c. with Cellini's writing[3].

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* In the recipes acronym: *R* = Recipe, *T* = Theophilus and *C* = Cellini. They are related to the historical texts from which the recipes were reinterpreted[5].

In a previous communication, we showed that the X-ray absorption near edge spectrometry (XANES) can be used to distinguish a chemical signature of surface colouring treatment (iron or copper) containing the same element, present on the art-piece via different processes. Indeed, iron traces can come from colouring treatments as well as from left-overs of cleaning/polishing products such as "rouge à polir"[9]. The product analysed in our test is the one used at the IRPA-KIK metal conservation studio. X-ray diffraction shows that it is composed of hydro-haematite ($Fe_{1.83}(OH)_{0.5}O_{2.5}$) being the major constituent along with small amounts of haematite (Fe_2O_3). In the case of copper, another potential origin other than the colouring treatment might be the natural copper trace in gold and silver[10]. We also presented the impact of the colouring treatment on the morphology of the model sample surface[11]. High resolution field emission scanning electron microscope (FE-SEM) images show that the application of the colouring recipes tested on the model samples results in inhomogenious chemical etching of the gilded surface.

Since the studied shrine dates back to the $13^{t}h$ century, the stability through time[12] of the model samples surface after the colouring treatment has also been studied as a function of four ageing factors: Cl contamination (AA_Cl), UV exposition (AA_UV), Temperature/Relative Humidity variation (AA_T/RH) and, most important, S-pollutant (AA_S). For this last case a new set-up was developed[12]. We showed that AA_UV and AA_T/RH alone does not influence the model sample surface. AA_Cl and AA_S have a higher impact on the treated part of the model sample compared to the untreated. This suggests that the colouring treatment seems to induce a weakening of the surface. The XANES iron and copper K-edges are both modified after both artificial ageing tests. In the presence of a sulphur pollutant: i) iron K-edges are very inhomogeneous but seem to indicate the formation of $Fe_2(SO_4)_3$, ii) copper K-edges are very inhomogeneous but tend to indicate a mixture with $Cu_{gilding}$, CuO and $Cu_4SO_4(OH)_6$ as the main compounds, although in very different relative amounts. In the presence of a chlorinated salt spray: i) iron K-edges are more homogeneous and seem to indicate the presence of $FeCl_3$ and $FeOOH$ with variable quantities of Fe_2O_3, ii) copper K-edges are homogeneous and seem to be the same as the Blank signal from the model samples although presenting different copper K-edges when freshly coloured[10].

The aim of this paper is to use the knowledge acquired from previous parts of the research, on historical sources and model samples[1,5,6,9–12], for the study of the historical shrine. This article brings back the research from the theoretical and model sample study to the real historical object, the Holy Lady Shrine of Huy. Indeed, the presented results are acquired on historical samples in the attempt to answer the question at the origin of the project: "Did the silver gilded statuettes of the shrine underwent some chemical colouring surface treat-

ment?"

Scanning Electron Microscope coupled with Energy Dispersive X-ray spectroscopy (SEM-EDX) is used to make the first observation of the samples surface and to evaluate their chemical composition. It allows us to check the presence of potential chemical signatures (iron and copper) and to select the proper candidate for synchrotron analyses.

2 Experimental

2.1 Model samples

The test pieces (3 cm × 6 cm) were cut from a 999 ‰ pure silver plate (1 ‰ mostly copper impurity) and laminated. A professional then gilded the pieces using the mercury amalgam technique (24-carat purity, annealing temperature between 250 and 350 °C[13]). Medieval fire gildings of precious shrine silver decorative parts being usually rather thick (between 10 and 20 μm[14,15]), a gilding of 20 μm thick was obtained by the accumulation of several layers. The surface preparation was completed by burnishing it with agate stone. When colouring the model sample, only two third of its surface was treated with the recipe, leaving untouched the remaining third, referred to as 'Blank'[10]. This allowed us to compare a treated gilding with an untreated one, but that has undergone the same variations in temperature. Indeed Anheuser showed that variations in the temperatures used for fire gilding may influence the final quantity of mercury and the gold-mercury structure of the gilding, which consequently influences its colour[16].
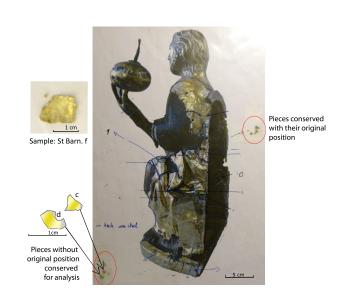
These model samples were used to study the stability in time of the treated gilding from both a morphological point of view and a chemical point of view. The results of these tests and analyses were then used to compare with the results obtained on the historical samples.

2.2 Historical samples

The historical samples, used for the study reported in this article, are small fragments detached from the gilded statuettes. Fig. 1 presents one of the working documents used during the Christ's statuette restoration. These documents are pictures of the artefacts and are used to indicate the position of the different pieces and fragments that were detached from the statuette during the removal of the old restorations (black wax used for filling the gaps and coating the statuettes surface or glued doublers from 1969). These schemes allow the restorer to place the pieces back at the right position afterwards.

By the time the picture of the document presented on Fig. 1 was taken, most of the fragments have already been detached from it to be glued back on the statuette. Only very small ones remained. Some of them (bottom left of the picture) do

Fig. 1 Picture of a working document used during the Christ's statuette restoration with indication of the fragments Christ c and Christ d, as well as a picture of the St Barn. f sample, all analysed in this paper.

not have their original position indicated. They were retrieved on the restoration desk after the cleaning of the statuette, so they certainly belong to it but it is not possible to find exactly where they come from. From these fragments, seven of them were available for further investigations, four from the Christ statuette (a to d) and three from the St Barnabas statuette (e to g). On Fig. 1, the samples *Christ c* and *Christ d* are indicated.

These seven samples were first analysed with SEM-EDX to verify i) the presence of a gilding at their surface and ii) the presence of the potential colouration chemical signatures (iron and copper). Then, the gilded samples were analysed with XANES to identify the chemical states of iron and copper. These results were compared with those obtained previously on model samples.

2.3 Chemical element composition using Scanning Electron Microscope coupled with Energy Dispersive X-ray spectroscopy (SEM-EDX)

The elemental analyses were performed using a Scanning Electron Microscope (JSM6300, JEOL, Japan) equipped with an Energy Dispersive X-ray detection system (INCA II, Oxford Instruments, UK) (SEM-EDX). A primary electron beam energy of 20 kV was used together with a current of 10^{-10} A (Working Distance (WD) 15 mm and life time (LT) of 100 s).

2.4 Characterising the chemical atomic environment with hard X-rays

X-ray Absorption Spectroscopy (XAS) was performed on the hard X-ray DiffAbs beamline at SOLEIL Synchrotron. K-edge spectroscopy measurements were done in fluorescence mode using a 4 elements silicon drift detector (Vortex-ME4®, Hitachi). The beam footprint on the sample (*i.e.* probed area) is approximately round and has a size of about 300 μm full width at half maximum (FWHM). Using a Si(111) double crystal monochromator, the X-ray absorption near-edge spectroscopy (XANES) spectra were acquired from 7.05 to 7.30 keV (for iron) and from 8.96 to 9.05 keV (for copper) with 0.70 eV energy steps, 10s of integration time by step. The energy was calibrated using two spectra collected on an iron metallic foil (expected inflection point at 7.112 keV) and a copper metallic foil (expected inflection point at 8.979 keV). The XAS spectra were normalised with the Athena software [17], by removing the pre-edge background and the absorption background [18].

XANES spectra of several iron and copper reference compounds were measured in transmission mode for comparison. The linear combination fitting (LCF) technique was used to further analyse the XANES spectra. The fitting of the normalised $\mu(E)$ results were obtained from the normalised XANES spectrum range: i) from 7093 eV (= -30 eV with respect to the first inflection point of the white band (*i.e.* E_0)) to 7203 eV (=E_0 +80 eV) for iron, ii) from 8949 eV (=E_0 -30 eV) to 9029 eV (=E_0 +50 eV) for copper. LCF was carried out using up to 4 spectra recorded on reference compounds. The smallest relative agreement R-factor and reduced χ^2 values from all available combinations were chosen as best fit.

3 Measurements and discussion

3.1 SEM-EDX characterisation

In Didier *et al.* paper published in 1970 [4], the number of microchemical analyses as well as their position are not specified. It was needed to check the presence of iron and to determine its distribution on the statuette. This was presented in a previous paper [6]. The iron is present all over the statuette surface and is well distributed, but in different concentration, depending on the damage of the surface.

The SEM-EDX analyses performed on the seven historical samples (*Christ a* to *d* and *St Barn. e* to *g*) show that only three of them present a gilding at their surface: *Christ c*, *Christ d* and *St Barn. f*. Fig. 2 shows the SEM-EDX surveys acquired on these three samples as well as two SEM images showing the surface of the historical gilding. Each chemical survey is acquired at a different position on the samples sur-

face. A $200 \times 200 \ \mu m^2$ surface area was scanned to acquire the spectra from the *St Barn. f* and *Christ c* samples as presented here. The position and area analysed on the *Christ d* sample are marked on the SEM image (Fig. 2). These last six spectra (three on areas with gilding and three on areas where the gilding is clearly missing) shows the relation between the presence of a thick gilding and the presence of iron.

Fig. 2 SEM-EDX chemical surveys acquired on the three samples presenting a gilding at their surface. Various areas of each sample are analysed.

All of spectra presenting a important gilding signal contain detectable amounts of iron (Fe K_α and K_β lines, respectively at 6.4 and 7.1 keV and Fe L_α at 0.7 keV) and copper (Cu K_α line at 8.1 keV and Cu L_α line at 0.9 keV). Their signal intensity varies depending on the measuring spot. Silver (Ag L_α and L_β lines at 3.0 and 3.4 keV respectively) is also present

in different amounts on the surface.

Magnesium (Mg K_α at 1.2 keV), aluminium (Al K_α at 1.5 keV), silicon (Si K_α at 1.7 keV) and calcium (Ca K_α at 3.6 keV) are present in most of the surveys. These elements are commonly present in dust produced by stones and earth material [19] as well as in cleaning powders used on goldsmith art-pieces for centuries [20]. A chlorine peak (Cl K_α at 2.6 keV) is visible in most of the surveys. Its origin may be the environment pollutant as well as a colouring surface treatment. The presence of sulphur could not be determined. If present, its signal (S K_α and K_β line at 2.3 and 2.5 keV respectively) is hidden by the peaks of silver.

From all acquired SEM-EDX data, no iron is detected when no gilding is present. Copper is present whenever gold or silver signals are present on the survey. Copper is a chemical element of the substrate and the gilding while iron is linked to the gilding only. It diminishes the probability that the iron present in these measurements has for origin "rouge à polir" contamination.
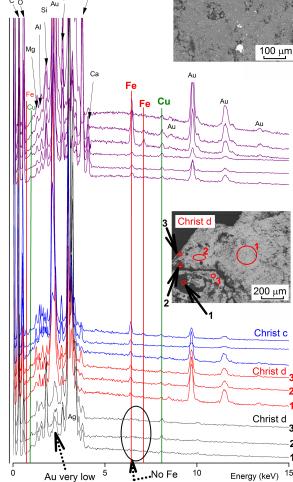
3.2 Chemical signatures

As demonstrated on model samples, XANES measurements performed at DiffAbs beamline proved to be an adequate technique for establishing the chemical state of iron [9] and copper [10] on a gilded surface. The analysis of these potential colouring chemical signatures on the historical samples are of major importance. Indeed they investigate the possible use of one of the ancient colouring treatments. The iron K-edge signal will also allow us to definitively determine if the iron present on the shrine originates from left over of "rouge à polir" cleaning material.

The measurements are performed on the three historical samples presenting a gilding at their surface (*Christ c*, *Christ d* and *St Barn. f*).

3.2.1 Iron

Fig. 3 presents the iron K-edge signals acquired on the historical samples and their first derivatives. Four measurements are recorded on different areas of sample *St Barn. f* and two measurements are recorded on different areas of each of the Christ samples.
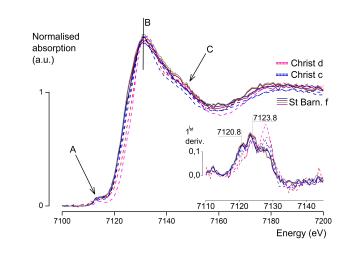
The iron K-edge signals acquired on the historical samples are very similar. On St Barnabas sample, they are very similar while the Christ ones present some differences concerning the energy value at which the first inflection point is detected (here after referred as the first inflection point). The first derivatives show that the first inflection points energy is positioned at 7120.8 eV for most of them except for one of the Christ's measurement, positioned at 7123.8 eV. All the K-edge spectra present a pre-edge feature (A) positioned around 7114.3 eV. Depending on the area analysed, its intensity varies. No shoulder is visible on the up slope of the white line. One shoulder
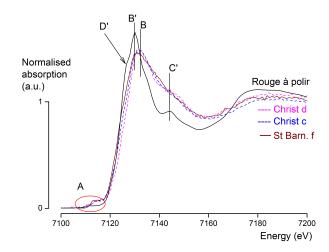
Fig. 3 Iron K-edges acquired on the historical samples accompanied of the first derivative (inset) pointing out the inflection point of the edges.

might be present after the edge crests (C) on some spectra. The edge crests (B) are positioned between 7130.8 (all St Barnabas measurements) and 7132.7 eV (two of the Christ).

Fig. 4 compares the XANES iron K-edge signals acquired on the historical samples with the one acquired on the "rouge à polir" reference.
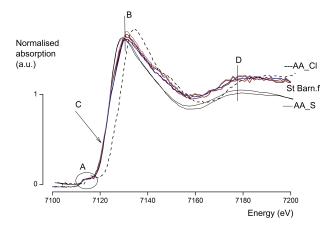

Fig. 4 Comparison of the iron K-edge signals acquired on the historical samples and the "rouge à polir" reference.

The signals close to the iron K-edge acquired on both statuettes' samples are very different from the signal measured on the "rouge à polir" reference, which shows a pre-edge feature positioned much lower in energy (A). The crest edge (B') is positioned lower in energy than any of the ones measured on the historical samples (B). It presents a shoulder on the upslop of the white line (D') and the shoulder after the edge crest

(C') is above 1740 eV. This confirms that the iron present on the statuettes is not due to left-overs of the cleaning material. Consequently, it is possible that its presence is due to some meaningful historical surface colouring treatment.

St Barnabas statuette:
The iron K-edge XANES spectra acquired on St Barnabas are compared to the iron K-edge measured on i) model samples freshly coloured and ii) model samples coloured and artificially aged by exposing to S and Cl (see later on in the text). The iron K-edge signals from the historical samples are different from the signals acquired on the freshly coloured model samples (not shown here). Fig 5 compares the iron K-edge signals acquired on St Barnabas sample, one acquired on the coloured model samples artificially aged in chlorine polluted atmosphere and two of the ones acquired on the model samples artificially aged in sulphur polluted atmosphere. The XANES resulting from the sulphur artificial ageing vary slightly. The two XANES signals shown on the graph are the ones exhibiting a lower energy position for the K-edge [10].

Fig. 5 Comparison of the spectra in the vicinity of iron K-edges acquired on St Barnabas sample, one of the AA_Cl model sample and two of the AA_S model sample (the ones exhibiting a lower energy for the K-edge).

It is observed that the iron K-edge signals acquired on St Barnabas sample are very different from the iron K-edge measured on the model sample artificially aged in chlorine polluted environment. On the other hand they match quite well these acquired on the AA_S model samples. Their first inflection point (C), pre-edge features (A) and first oscillation (D) after the edge crest have the same position in energy. There is a slight difference at the edge crest (B). These AA_S XANES are the only two of the inhomogeneous iron K-edge acquired on the AA_S model samples.

LCF is performed to interpret further the iron K-edge acquired on St. Barnabas sample. Table 1 presents the LCF

Table 1 LCF results for XANES signals recorded in the vicinity of the iron K-edge acquired on St Barnabas sample. Corresponding R-factor and reduced χ^2 are also shown.

Point	$Fe_2(SO_4)_3$		$FeSO_4$		Fe_3O_4		R-factor	Reduced χ^2
1	0.74	±0.03	0.11	±0.01	0.15	±0.05	0.00459	0.00013
2	0.67	±0.04	0.14	±0.01	0.19	±0.04	0.008177	0.0002384
3	0.65	±0.03	0.09	±0.04	0.26	±0.03	0.004011	0.0001137
4	0.69	±0.04	0.16	±0.02	0.14	±0.05	0.00118	0.0003579

values obtained from the fitting of the Fe K-edge measured on the St. Barnabas sample. In order to do so, spectra of reference compounds were recorded at the same beamline as the samples. These compounds were selected because they could be present on the treated model samples at different steps of the research. The main features (energy at inflection points and general shape) of the spectra measured in on our reference compounds are in good agreement with the spectra reported in the literature [21–23].

The normalized fitting $\mu(E)$ is carried out in the normalised XANES spectrum range from 7093 eV (= -30 eV to the E_0) to 7203 eV (= +80 eV to the E_0). Different combinations of all plausible chemical products that can be present during the treatment reaction occurring during the colouration are used. Those references are separately tested against the iron signal from the coloured samples by calculating the combination of 1 to 3 variables. The smallest relative R-factor and reduced χ^2 values from all available combinations represent the best fit. The R-factors and reduced χ^2 shows that our model of combining these results is robust [18]. All the XANES signals can be reproduced by majority $Fe_2(SO_4)_3$ with lower amounts of $FeSO_4$ and Fe_3O_4. This composition from LCF seems in good accordance with the hypotheses stating that the final iron compounds could be mainly $Fe_2(SO_4)_3$ after a much longer residence time in the AA_S test chamber [10,12].
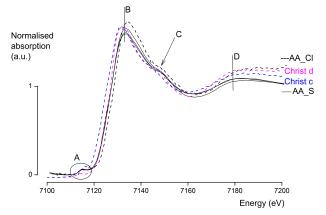
The Christ statuette:
The inhomogeneous iron K-edge signals acquired on different area of the Christ samples are different from the signals acquired on the freshly coloured model samples [9]. Fig 6 compares the iron K-edges acquired on the Christ samples, one of these acquired on the coloured model samples artificially aged in chlorine polluted atmosphere (AA_Cl) and three of these acquired on the model samples artificially aged in sulphur polluted atmosphere (AA_S). In this case, these three AA_S XANES are the ones exhibiting a higher energy position for the K-edge [10].

Comparing the iron K-edge signal acquired on the Christ samples and on the coloured model samples artificially aged in sulphur polluted atmosphere, one can note that the ranges of their main feature (A, B, C and D) are similar on the differ-

Fig. 6 Comparison of the XANES signals in the vicinity of iron K-edge acquired on the Christ samples, one acquired on the AA_Cl model sample and three of these acquired on the AA_S model sample absorption edge exhibiting a higher energy position for the K-edge.

ent spectra. The iron K-edge signals acquired on the coloured model samples artificially aged in sulphur pollutant, the one exhibiting a higher energy position for the K-edge, are also close to the iron K-edge signals acquired on the coloured model samples artificially aged in chlorine polluted atmosphere. No clear link can be made between the Christ samples signals and the ones from the coloured model samples aged artificially. In the attempt to interpret further the iron K-edge signals acquired on the different areas of the Christ samples, LCF is performed. None of them produced satisfying R-factors or reduced χ^2 values.

Interpretation:
We conclude from these data that the iron compounds on the two statuettes are different (see Fig. 3). Since the iron compound on the surface is not left over from "rouge à polir" two hypotheses may be formulated to explain this difference. i) Both statuettes' gilded surfaces were treated in the past but they were differently exposed to atmospheric pollutants. This is not very plausible. Didier *et al.* demonstrated that the shrine has not been modified much through its history and that most
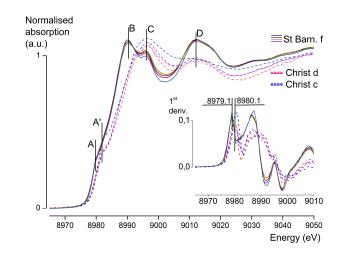
of the statuettes (with a reserve about the Lady) are from the same workshop[4]. ii) The surface treatments of the statuettes were different from the beginning. Since the Christ is one of the two most important figures of the shrine (with the Lady), it is possible that more attention was given to it than to the apostles. To verify this second hypothesis, iron K-edge signals should be recorded on a large corpus of historical samples coming from all statuettes.

3.2.2 Copper
Fig. 7 presents the copper K-edges acquired on the three historical samples presenting a gilding at their surface; their first derivatives are shown in the inset.

Fig. 7 XANES signals in the vicinity of copper K-edge acquired on the three historical samples presenting a gilding at their surface accompanied of the first derivative (inset) spotting the inflection point of the edges.

Four measurements are acquired on St Barnabas sample and two on each of the Christ samples. XANES signals in the vicinity of copper K-edges clearly show differences between statuettes. The XANES spectra recorded on different areas of St Barnabas samples are very similar. Their first inflection point is positioned at 8979.1 eV, which seems to indicate the presence of Cu^0. A shoulder (A) is present on the up-slope of the white line at 8979.7 eV. At the top of the edge, two crests are present at 8990 (B) and 8995.9 eV (C) and a first oscillation (D) is clearly marked around 9013 eV.

The measurements acquired on different areas of the Christ samples vary more but their main features positions are reproducible. Their first inflection point is positioned at 8980.1 eV which is between Cu^0 and Cu^+. A shoulder (A') is present on the up-slope of the white line at 8981.8 eV. The edge crest is composed of only one peak (C) positioned at the same energy as the second peak of the *StBarn. f* measured edge crest (8995.9 eV). A first oscillation (D) is also present around

9013 eV.

St Barnabas statuette:
St Barnabas copper K-edge signals are compared with those acquired on the freshly coloured model samples, on the Blank, and on the coloured samples artificially aged with sulphur (AA_S)and chlorine (AA_Cl) pollutants. Fig. 8 shows that they are very different from the copper signals recorded after the treatment by the recipes RCV^* and $RASAa^*$ presenting copper as chemical signature[10]. Their general shapes are close to the ones of the copper signal recorded after the treatment by the recipes RTC^*, $RMC100^*$ and $RMC263b^*$ not containing copper in their reagents and having iron as chemical signature[10] but their first inflection point (A) is not at the same energy.
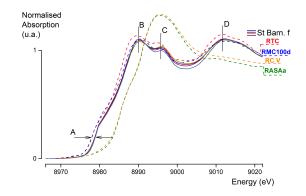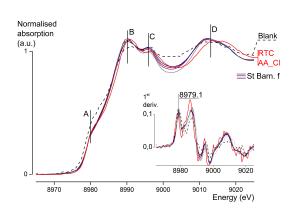

Fig. 8 Comparison of the copper K-edge signal acquired on St Barnabas' samples compared with these acquired on the freshly coloured model samples.

None of the copper K-edge signals measured on the coloured model samples artificially aged in sulphur polluted atmosphere (AA_S) are similar to St Barnabas ones. Fig. 9 presents the copper K-edge signals acquired on St Barnabas, on the Blank of the model samples (non-altered gilding) and on the coloured area of one of the model samples (here RTC as example) artificially aged in chlorine polluted atmosphere (AA_Cl).

The up-slope first inflection points are positioned at the same energy on St Barnabas samples and on the Blank and the coloured sample artificially aged in chlorine atmosphere (AA_Cl). Their up-slope shoulder (A) and the two edge crests (B and C) are positioned at the same energy for all the XANES. But these features relative intensities are slightly different for the copper K-edge signals acquired on the Blank. The first oscillation after the edge crest (D) is higher in energy on the XANES of the artificially aged coloured sample.

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* Reminding from the introduction part, in the recipes acronym: R = Recipe, T = Theophilus, C = Cellini, PL = Papyrus of Leyden, MC = Mappae Clavicula and ASA = Arab Syrian Alchemist.

Fig. 9 Comparison of the XANES signals in vicinity of copper K-edge acquired on St Barnabas' samples compared with the signal of the Blank and one of the coloured samples after artificially aged in chlorine chamber accompanied of the first derivative spotting the inflection point of the edges.

LCF is performed to attempt to further interpret the copper K-edge signals acquired on St. Barnabas sample. None of them produced satisfying R-factors or reduced χ^2 values.

Thus, it seems that the St Barnabas statuette might have undergone some colouring treatment with any of the recipes and then would have been exposed to polluting chlorine spray. This is not in accordance with the iron K-edge measured signals showing an exposure to sulphur pollutant, which is highly more probable. We can formulate the hypothesis that copper signal measured on St Barnabas' statuette is mainly due to the copper from the gilding. To discuss further this point, extra measurements in the vicinity of copper K-edges from the artificially aged Blank are needed.

The Christ statuette:
The signal close to copper K-edges acquired on the Christ statuette samples are compared with those acquired on the freshly coloured model samples, on the Blank, on a coloured sample artificially aged with sulphur (AA_S) and chlorine (AA_Cl) pollutants. They are very different from the copper signals recorded after the treatment by the recipes *RCV* and *RASAa* (chemical signature: copper) as well as by the recipes *RTC*, *RMC*100 and *RMC*263*b* (chemical signature: iron). The copper K-edges measurements on the coloured model samples artificially aged in chlorine polluted atmosphere (AA_Cl) do not present any comparison points.

Some of the copper K-edges shapes measured on the coloured model samples artificially aged in sulphur polluted atmosphere (AA_S) are similar to the ones measured on the Christ statuette. However, they are not reproducible and we cannot interpret them any further without making assumptions difficult to support by experimental data.

None of the LCF attempts procured satisfying R-factors or reduced χ^2 values. Nevertheless, some main trends can be pointed out. The most likely LCF composition is a majority of copper from the gilding (Blank) with variable quantities of Cu_2O and CuO. But the corresponding reduced χ^2 values are very bad. To go further with the data treatment, more copper K-edge measurements from corrosion compound references are needed, especially those containing sulphur as well as the artificially aged Blank.

Interpretation:
Both sets of historical samples present some similarity with the copper K-edge signals acquired on the Blank. This observation is supported by the fact that copper is always present in the gilding layer and silver substrate as a trace element.

The differences in copper K-edge signals between the two sets of historical samples tend to confirm the observation made on the iron K-edge signals. It is likely that the statuettes' gildings have undergone different treatments that might results in different finishing aspects.

4   Conclusion

On all historical samples, iron and copper are detected on the gilding surface. Their signal intensities depend on the measured position on the ample itself (spatial inhomogeneity). The SEM-EDX surveys performed on the small samples from the Christ and St Barnabas statuettes confirm that the presence of iron is linked to the presence of gold (gilding). The probability that the iron presence is due to a cleaning powder contamination is low.

The study of the iron and copper K-edge XANES measurements tends to indicate that the iron present on the statuettes is not due to left-over of cleaning material such as the "rouge à polir". It is thus more probable that its presence is due to some historical surface treatment. This could not be fully confirmed, nor the exact recipe could be identified. More reference measurements are needed, such as XANES measurements in the vicinity of copper K-edges recorded on the the artificially aged Blank and on copper reference compounds containing sulphur as well.

The results shown here have important implications for the practical restoration of the statuettes. Since it is possible that the statuettes gilding might have been colour treated and that iron and copper compounds seem to take important part in the final aspect of the masterpieces, it is important not to change their oxidation state or to remove them. To do so, it is recommended to remove the black coating on the statuette surface using a soft chemical technique such as neutral organic solvent. It is important to avoid using techniques such as Ethylenediaminetetraacetic acid (EDTA) baths, which would drastically reduce the oxidation state of these ions. Techniques

involving too much removal of the surface material should also be avoided.

Acknowledgement

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+/- 130 cm

The Holy Lady Shrine, 13th century, is composed of gilded silver statuettes, waffled plates of gilded copper, niello, "vernis brun", enamels, precious stones...
It is from the Holy Lady collegiate church in Huy, Belgium.

XANES iron K-edge signal

XANES copper K-edge signal