Resumo

A fluorescência de raios-X dispersiva de energias (XRF) foi utilizada na análise de uma Bíblia do séc. XIV proveniente de Nápoles. Este equipamento transportável permite uma análise *in situ* dos materiais presentes nestas luxuosas iluminuras.
Puderam assim ser identificados pigmentos como o vermelho de chumbo (mínio), branco de chumbo, ocre vermelho, vermelhão, azuis e verde de cobre, amarelo de estanho e chumbo em combinação com pigmentos orgânicos ou folha de ouro e prata ou ainda com tinta de estanho. ●

palavras-chave

MANUSCRITOS ILUMINADOS
FLUORESCÊNCIA DE RAIOS-X DISPERSIVA DE ENERGIAS
ANÁLISE *IN SITU*
PIGMENTOS
FOLHAS METÁLICAS

Abstract

X-ray Fluorescence spectroscopy (XRF) has been used to examine a 14th century bible manuscript, originating from Naples. This portable equipment provides a powerful aid to analyse in a non-destructive way the materials of the rich illuminations.
Mineral pigments like red lead, lead white, red ochre, vermilion, copper blue and copper green, lead tin yellow in combination with organic pigments and with gold and silver leaf or with tin paint could be identified. ●

key-words

ILLUMINATED MANUSCRIPT
X-RAY FLUORESCENCE SPECTROSCOPY
NON DESTRUCTIVE ANALYSIS
PIGMENTS
METAL FOILS

ANALYSIS OF THE ANJOU BIBLE

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Introduction to the Bible

The Anjou Bible is a unique bible manuscript originating from the beginning of the fourteenth century. The bible was ordered by Robert I of Anjou, king of Naples and was intended as a present for Andreas of Hungary who was engaged to the granddaughter of Robert of Anjou, Johanna of Naples [1]. When Andreas was murdered in 1345, the Bible came in the hands of Johanna's chancellor Nicoli Alifio, as a present for his diplomatic missions.

The precious manuscript remained in Royal circles and in 1402 the manuscript is described in the inventory of Jean Duc de Berry (1340-1416), brother of the French King Charles V (Avril, 1969; Avril et al, 1984, 2005).

At the end of the 15th century – beginning of the 16th century, the manuscript ended up at the library of the Arras College in Leuven (Belgium) via the Bishop of Arras and there it stood for centuries until finally in 1970, the manuscript was deposited at the Maurits Sabbe Library of the Faculty of Theology of the Catholic University of Leuven [2].

The bible contains almost the complete text of the old en new testament (fig.1). Its size

FIG.1 ANJOU BIBLE, FULL PAGE ILLUMINATIONS
© KIK/IRPA BRUSSELS

1. Born in Naples, Johanna was the daughter of Charles, Duke of Calabria (eldest son of King Robert of Naples) and Marie of Valois (a sister of King Philip VI of France). At the age of seven years (1334), she was betrothed to her six-year-old second cousin Prince Andrew of the Hungarian branch of the House of Anjou, the son of Charles I of Hungary and younger brother of Louis I. On the death in 1343 of her grandfather, Robert of Naples, his will provided that Andrew should be crowned King of Naples in his own right as well as Joan's, Robert having displaced Andrew's father, Charles Robert, from the Neapolitan throne. The Cardinal crowned Joan alone as Queen of Naples at Santa Chiara in Rome in August 1344. After the assassination of Andrew in 1345 (remaining unclear if under her own orders or not), Joan married three more times: with Louis of Taranto, with James IV of Majorca and Prince of Achaea and with Otto, Duke of Brunswick-Grubenhagen.

2. Nicolaus Ruterius founded the college in 1508 as a home for poor students. From then until the 18th century, it was gradually converted into a residential college, with a reception hall, rooms, a library, a chapel, two courtyards and an interior garden. After the French Revolution it was sold,

is 420 by 280 millimeters and it contains 338 folios with two full-page miniatures and more than 160 decorated initial and marginal illuminations leaves. The text has been written by one scribe but the rich illumination is the work of at least three different hands. One of them names himself on folio 308 at the sequence of the Apocalypse: Christophorus di Orimina (fig.2). He was the best-known illuminator in the Neapolitan surroundings in the second quarter of the fourteenth century (Maere 1909, 279 and Maere 1910, 25) (Bräm, 2007).

FIG.2 ANJOU BIBLE, DETAIL OF FOLIO 308 © KIK/IRPA BRUSSELS

The two full-page illuminations in the beginning are clearly made by his hand. The perspective and architectural settings are simple and straightforward and the facial expression isn't very detailed nor expressive, using the profile of King Robert and other royal members.

A second illuminator added decorations when the codex was probably already in possession of chancellor Alifio since he adapted the rich decorations to the new owner. Systematically the imperfection of the edge cuttings in the parchment were camouflaged by a wide range of fantasy birds with long necks and tales, all executed in soft pastel colors (fig.3).

The third hand is probably the best miniaturist and he is responsible for all the marginal work and decoration. Often classical themes and fantasy animals are added to the narrative scenes (fig.4).

Despite the fame and the richness of the manuscript, the bible has almost never been reproduced nor displayed in public.

The conservation state of the manuscript was bad: in the beginning of the 20th century the manuscript was re-bound but the covers were too tight making the manuscript difficult to open; the parchment was folded and pigments and gold leaves were flaking off. Therefore in May 2008, a conservation and preservation project started. The project and the building passed through the hands of a succession of private owners until it was repurchased by the university of Leuven in 1921.

FIG.3 ANJOU BIBLE WITH MARGINAL DECORATION OF A SECOND ILLUMINATOR © KIK/IRPA BRUSSELS

FIG.4 ANJOU BIBLE WITH DECORATIONS OF A THIRD ILLUMINATOR © KIK/IRPA BRUSSELS

3. For generous support and discussion we thank: Jan Van der Stock (K.U.Leuven, Research Center for Medieval Art), Christina Ceulemans (Koninklijk Instituut voor het Kunstpatrimonium), John Lowdon (Courtauld, London), Chris Coppens (K.U.Leuven, Tabularium,); Leo Kenis en Luc Knapen (K.U.Leuven, Library, Faculty of Theology) and Nancy Turner (Senior paper conservator, J.P. Getty Museum, Manuscript Department).

4. Macro photographs (Nikon D 70, AF micro-Nikkor 60 mm) were documenting the techniques and the damage-assessment (Cumulus 5.5©/ digital asset management software). Further infra-red photography and infrared reflectography (InfraCAM SWIR – short-wave infrared – video camera) was combined with highly detailed digital photographs with direct, transmitted and racking light (digital camera MAMIYA RZ 67, Digital back Light Phase I / Nikon D 70 and EOS I D-Mark II, 100 mm macro lens).

is a collaboration between the Department of Art History, K.U.Leuven, the Royal Institute for Cultural Heritage in Brussels and Museum M of Leuven and is funded by the InBev-Baillet Latour Foundation [3].

Experimental

The manuscript is now unbound and the loose folios offer a unique opportunity to examine the manuscript in detail in the laboratory.
It is obvious that the study of such a precious and delicate work of art has to be done using non-destructive techniques. First an extensive series of highly detailed digital photographs with transmitted light and complementary infrared digital photographs were taken [4] (Watteeuw 2009, 168; Watteeuw et al, 2008, 310; Watteeuw and Van Bos, 2010, 147).
Then analyses were performed using X-ray fluorescence spectroscopy (XRF).
This XRF technique offers a multitude of advantages: it is a non destructive technique with a very small spot size of only 70 µm, which is important to be able to analyze small features in a miniature, it offers the possibility to simultaneously analyze multiple chemical elements and it is a fast analysis technique: each measurement only takes 120 seconds.
We used the mobile Arttax equipment (Bruker AXS Microanalysis, Germany) with a Rhodium tube and a built-in color CCD camera (fig.5). The exact location of the measuring spot can be followed (or changed) via the computer screen and also the focusing of the measuring head to the desired position is done via the computer. During the experiments an energy of 50 kV, a current of 500 µA and a Mo 25µm filter were used.

Results for the first full page illumination

The first full page illumination is full of self promotion for the Anjou dynasty. One can read: *Rex Robertus, rex expertus in omnia scientia*. Robert is sitting on a polychrome throne ornate on both sides with gilded lion heads, under a colourful canopy with on the background the gilded lilies of the Anjou dynasty. The King is surrounded by eight cardinal virtues and at the bottom we find seven vices with Diablo.

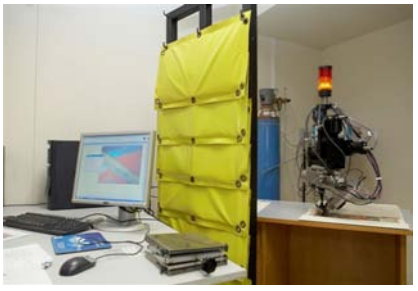

Fig.5 arttax xrf equipment © kik/irpa brussels

The reds

XRF analysis of the orange border (fig.6, XRF 1) results in a spectrum with a large peak for lead (fig.7a and 7b). Although XRF is an 'elemental' analysis technique with no information on the molecular composition of the lead containing pigment, we can assume with high certainty that lead is present as red lead (Pb_3O_4), since we are analyzing an orange-red color. Red lead, an artificial pigment, was already known

Fig.6 Anjou Bible, full page illumination with indication of some of the XRF measuring spots © KIK/IRPA Brussels

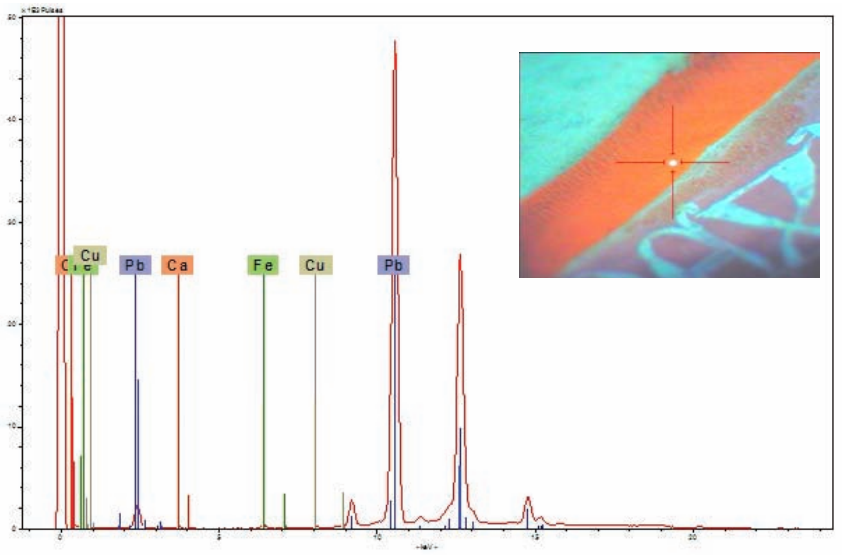

Fig.7a and 7b XRF spectrum of the orange border and ARTTAX image of the measuring area © KIK/IRPA Brussels

for miniature painting and manuscript illumination in Europe since the 8th century on (West Fitzhugh 1986, 109, Munoz Vinas, 1998, 114);

A different result is obtained for the red in the baldachin (see fig.6, XRF 2). XRF measurement results in a large peak for mercury indicating without doubt vermilion (HgS) as vermilion is the only pigment containing mercury (fig.8a and 8b). Although the pigment mercuric sulfide can also be obtained from the mineral cinnabar (HgS), the use of the artificial vermilion, made by heating mercury with sulfur, was already so widespread in the 14th century that nor in '*Il libro dell'Arte*' from Cennino nor in '*De Arte Illuminandi*' (Thompson et al, 1933, Brunello, 1975) a recipe can be found for the preparation of this vermilion.

Measurement of the red used for the arm of the throne (see fig.6, XRF 3) gave again a different result: a spectrum with different peaks indicating a mixture of pigments: mercury (indicating vermilion), lead (lead white or red lead) and than a very large peak for iron (fig.9a and 9b) . This suggests that also red earth (containing hematite Fe_2O_3) is present here. Associated with the large iron peak is the small peak for

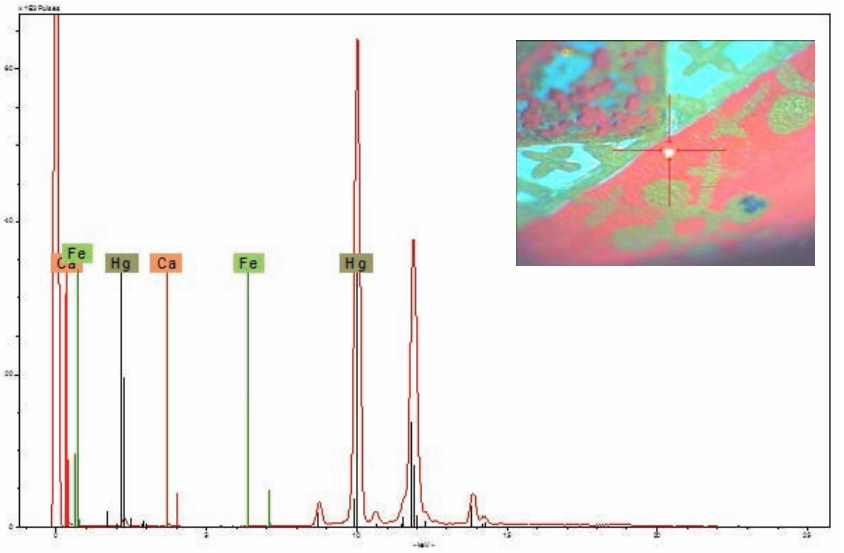

FIG.8A AND 8B XRF SPECTRUM OF THE RED USED IN THE BALDACHIN AND ARTTAX IMAGE OF THE MEASURING AREA © KIK/IRPA BRUSSELS

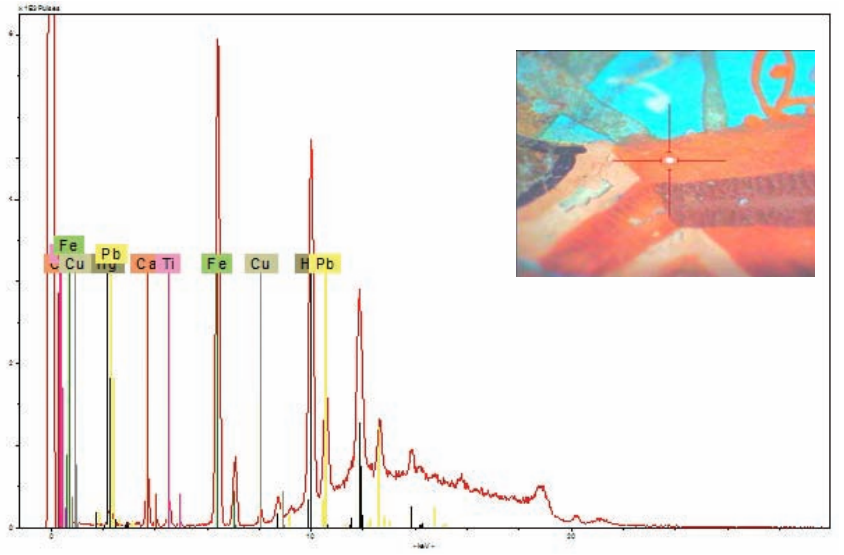

FIG.9A AND 9B XRF SPECTRUM OF THE RED USED FOR THE ARM OF THE THRONE AND ARTTAX IMAGE OF THE MEASURING AREA © KIK/IRPA BRUSSELS

titanium probably indicating the mineral ilmenite ($FeTiO_3$) present in the naturally found red ochre's (Eastaugh, 2004, 320)

A bright red can be found on the border of the miniature (see fig.6, XRF 4).

XRF measurement gives only a weak response with a mayor peak for calcium (fig.10). This spectrum corresponds well with the spectrum obtained for the parchment itself. As organic reds are known for manuscript illumination, it is likely that an organic red, which can not be verified by XRF measurement, is responsible for the bright red color.

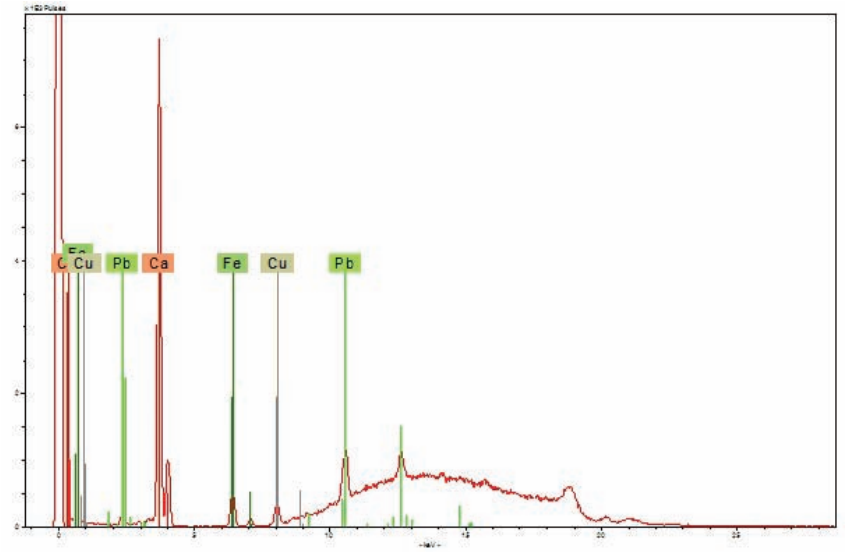

Fig.10 XRF spectrum of the bright red border © KIK/IRPA Brussels

The blue

All blue areas in the full page illumination, ranging from dark blue to light blue or from architectural decoration to the clothes of the King or one of the cardinal Virtues gave all a comparable result after XRF analysis: a large peak corresponding to copper, probably indicating azurite as blue pigment (fig.11). Azurite, a basic copper carbonate ($2CuCO_3.Cu(OH)_2$) is prepared by grinding and washing of the mineral which was occurring in copper deposits in Italy, Spain and particularly Germany (‘*azurium de Alamania*’).

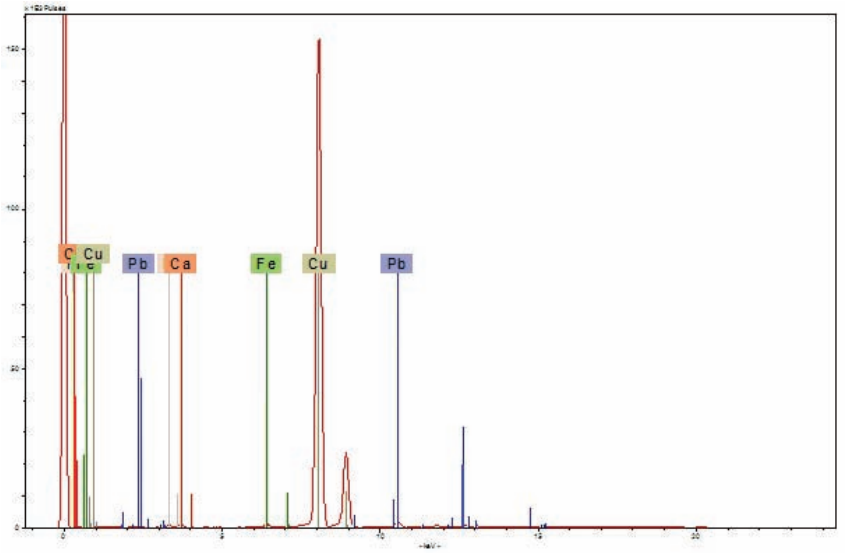

Fig.11 XRF spectrum of a blue area © KIK/IRPA Brussels

The green

XRF analysis of the green socle of the throne (see fig.6, XRF 5) resulted in a spectrum with peaks for lead, copper and tin. Although the exact interpretation of this result in terms of composition ànd paint layer built-up can not be given, it is likely that a mixture of pigments is used here: lead white, a copper green or copper blue and a lead tin yellow (fig.12). Different relative amounts of these pigments, as shown by different peak heights of lead and copper, give different color intensities: 'more' copper for the darker green areas. The mixture of malachite ($CuCO_3.Cu(OH)_2$) with *giallorino* (an artificial made lead-tin yellow) was described by Cennino.
On top of this green layer, occasionally a transparent organic layer is applied to brighten the color.

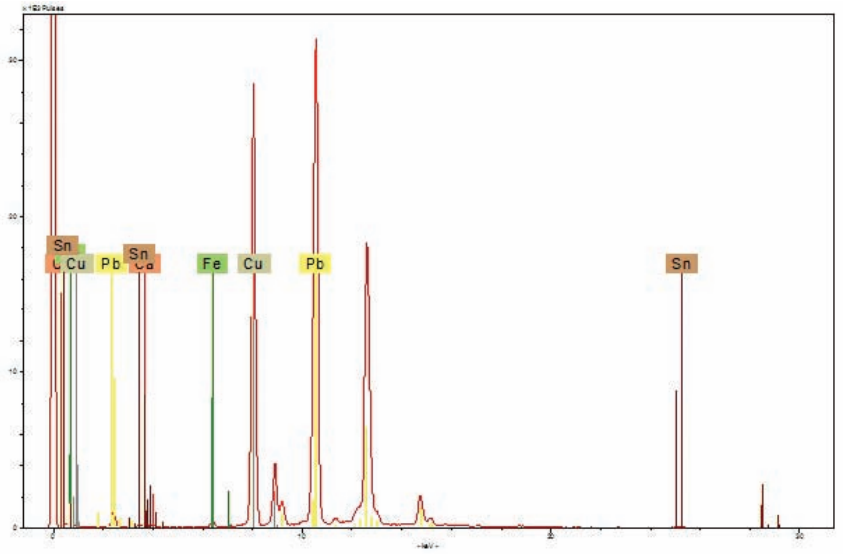

FIG.12 XRF SPECTRUM OF A GREEN AREA IN THE SOCLE OF THE THRONE © KIK/IRPA BRUSSELS

The white

The white inscription on top of the illumination is based on lead white as evidenced by the large lead peak in the XRF spectrum. Lead white, the basic lead carbonate ($2PbCO_3.Pb(OH)_2$), made by reaction of vinegar to lead strips, is described in the *Arte Illuminandi* as the only white color suitable for illuminating practice.

Metal: paint and foil

Gold leaf is used for the scepter hold by the King or for the decoration in the baldachin. This gold leaf is either applied on a grayish ground layer or on a bright red under layer.

A grey ground, based on gesso, is frequently observed in the gold size used in medieval manuscripts. XRF measurement of this layer indicates only calcium which is not surprisingly as with this XRF equipment only elements higher than sodium can be detected and the sulfur associated with the calcium can not be detected.
As the gold leaf can be very thin, using a red under layer gives a warmer color to the gold compared to the same gold leaf applied on a grey under layer. This red under layer is often based on Armenian Bole (clay pigmented with iron oxides), following the recipes of the *Arte Illuminandi* or *Il Libro dell'Arte*.
XRF measurement of the bright red under layer shows however the presence of vermilion as shown by the large mercury peak in the resulting XRF spectrum.
To further embellish the gilding, an orange glacis layer is occasionally applied on top of it as can be seen for the belt of the King (fig.13). However, using our XRF analysis method, no information about the composition of this layer is obtained.
Silver leaf is used as well: XRF measurement of part of the decoration in the socle of the King's throne (see fig.6, XRF 6) shows the presence of silver (fig.14a and 14b). The silver leaf could be applied using the same size as for gold leaf.

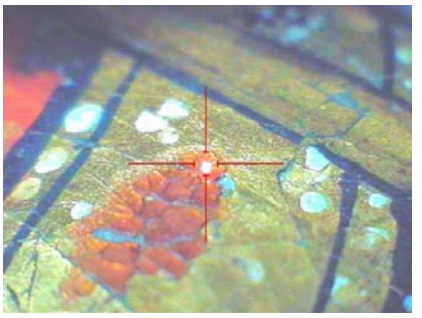

Fig.13 arttax image of the decoration on the belt of the king © kik/irpa brussels

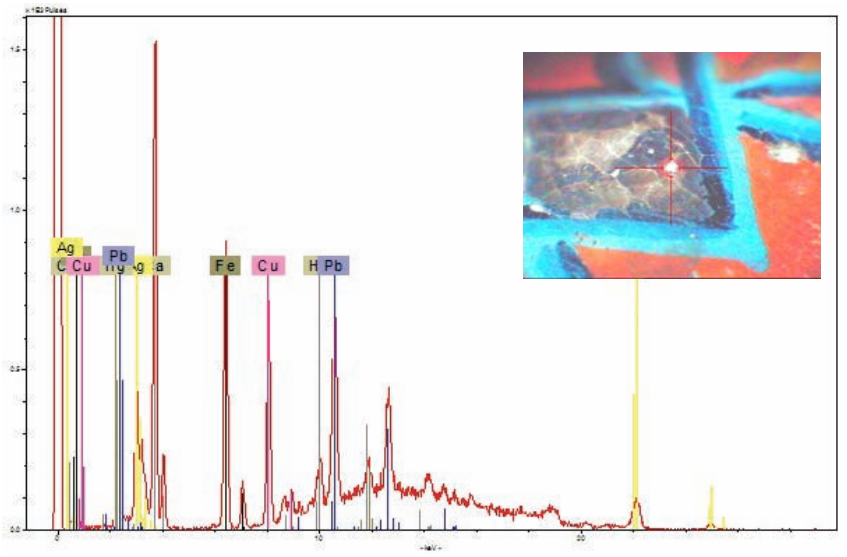

Fig.14a and 14b xrf spectrum of decoration in the socle of the throne and arttax image of the measuring area © kik/irpa brussels

A surprising result was obtained when analyzing the quadrofold in the canopy or the lilies in the baldachin (see fig.6, XRF 7). Although these decorations look like gold, XRF analysis reveals the presence of tin. Since the lilies are painted on top of the blue ground, a large copper peak is present as well in the resulting XRF spectrum (fig.15a and 15b). In this spectrum also a relative small peak corresponding to mercury is present. This result could point to the use of Mosaic Gold. In the *Arte*

Illuminandi mosaic gold (stannic sulfide SnS2) is described as an imitation gold color. The preparation of this mosaic gold starts with: «*take one part of tin and melt it, and throw upon it one part of pure quicksilver*». Mosaic gold could replace the costly true gold powder but did not show the same full brilliance of gold. Therefore it was recommended to model it up with gold powder.

Analysis of the decoration with small crosses in the baldachin shows this mixture of gold and tin applied as paint (no metal leaf) on top of the lead white layer, pointing out towards the use of mosaic gold. [5]

5. Also Theolfilus describes the use of tinpaint in his chapter: *How paintings in Books are Embellished with Tin and Saffron/ If you have neither of these [i.e., gold or silver] and still want to embellish your work in some way, take pure tin, scrape it very fine, mill it, and wash it as you did the gold. Then, with the same glue, apply it on letters or other places that you wanted to ornament with gold or silver. After polishing it with a tooth, take some of the saffron with which silk is dyed, pour glair without water over it, and let it stand overnight. On the following day cover with a pencil [dipped in this medium] those places you wanted to gild; leave the rest [of the tin bare] to take the place of silver. Then, using a quill, draw fine lines with minium around the letters, foliage, scrollwork, materials of robes, and the other places to be ornamented.* Theophilus 37

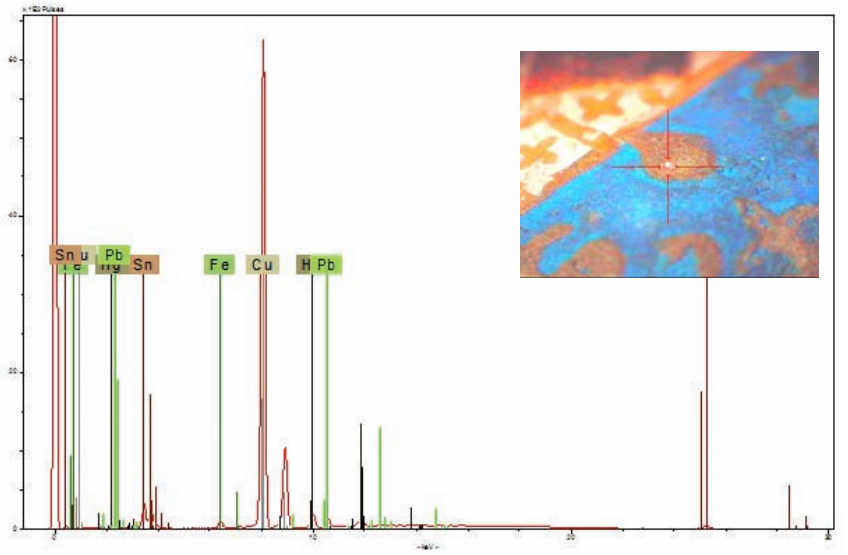

FIG.15A AND 15B XRF SPECTRUM OF LILIES IN THE BALDACHIN AND ARTTAX IMAGE SHOWING THE MEASURING AREA © KIK/IRPA BRUSSELS

FIG.16 ANJOU BIBLE, DETAIL WITH COAT OF ARMS © KIK/IRPA BRUSSELS

The coat of arms

At the bottom of the page, the coat of arms of chancellor Alifio is present (fig.16).

For this coat of arms, the same materials as present in the miniature were identified: Vermilion applied on a white lead layer for the red and white triangles, red lead for the orange border, silver leaf and gold leaf.

A different result was obtained for the golden fess which is a gold paint '*shell gold*' and not a gold leaf.

Another difference was found when analysing the blue ground of the coat of arms. Although it concerns a very intense blue colour, only a relative small amount of copper was detected during the analysis (fig.17). This result could indicate the use of the blue pigment ultramarine ($Na_{8..10}Al_6Si_6O_{24}S_{2..4}$) made from lapis lazuli, a pigment that can not be identified using XRF.

Ultramarine was a very expensive pigment with well known outstanding characteristics.

The coat of arms as present now is not the original coat of arms. Originally, the coat of arms of the first owner of the manuscript, Andreas of Hungary was present. But when Alifio became the new owner, all original coats of arms were removed by abrasion and over painted, as a clear possession mark. In that respect, it is maybe not surprisingly that such an expensive and precious pigment is used. This however has to be confirmed using a complementary analysis technique (like non destructive micro Raman spectroscopy).

The spectrum shows also an important iron peak (red earth) which indicates the underlying original coat of arms.

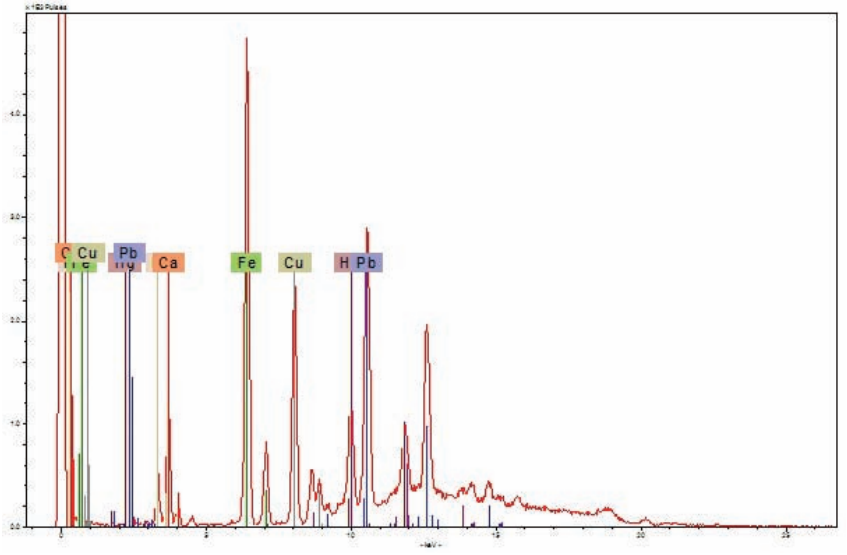

Fig.17 XRF spectrum of the blue ground in the coat of arms © KIK/IRPA Brussels

Conclusion

Although having a long history, the Anjou Bible was now for the first time ever examined in detail.

The combination of highly detailed photographs with transmitted light in combination with the non destructive XRF analysis provides more insight into the craftsmanship of the miniaturist. A very rich pallet of mineral and organic pigments in combination with gold, silver and tin as foil or as paint has been identified.

Although the use of a non destructive technique, like X-Ray fluorescence has its limits, this technique is extremely useful when analyzing very delicate and precious works of art. ●

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