

## Resumo

A caracterização das paletas de cor utilizadas na iluminura medieval é tarefa importante de um ponto de vista histórico-artístico, mas árduo numa perspectiva científica: é difícil recolher amostras, não é aconselhável utilizar técnicas que necessitem de contacto (i.e., IR em modo de ATR) nem levar a cabo sessões de análise longas, devido ao stress que se poderá causar aos manuscritos. Por estes motivos, é necessário utilizar técnicas analíticas que sejam não-invasivas e rápidas; para além disso, na maioria dos casos será necessário trabalhar *in situ*, utilizando instrumentação transportável. De entre as técnicas possíveis, a espectroscopia de Raman será a mais informativa, dado o seu potencial de diagnóstico; no entanto, requer tempos de análise longos. A fluorescência de raios-X dispersiva de energias (XRF) é uma alternativa poderosa, mas sendo uma técnica de análise elementar, nalguns casos não permite chegar a conclusões precisas. A espectroscopia de UV-VIS-NIR, em modo de reflectância com fibra óptica (FORS), pode ser considerada uma técnica preliminar promissora, mas apresenta algumas limitações óbvias.

Neste trabalho é proposto um protocolo de análise para a caracterização de iluminuras em manuscritos, de forma não-invasiva, utilizando equipamento transportável e efectuando análises *in situ*. Este protocolo permite a identificação de colorantes através da aplicação sucessiva de técnicas complementares, explorando as vantagens de cada uma delas. Antes de mais, preparou-se uma paleta com os diversos pigmentos que se sabe terem sido utilizados na Idade Média; prepararam-se tintas à base de goma arábica e clara de ovo, seguindo receitas antigas descritas em tratados medievais tais como *De arte illuminandi* by anonymous, *Compositiones ad tingenda musiva* by anonymous and *Il libro dell'arte* by Cennino Cennini. Esta paleta constitui-se como ponto de partida para a construção de uma base de dados para a análise espectroscópica, reproduzindo cenários semelhantes aos encontrados nos manuscritos. É assim importante enfatizar o facto dos espectros obtidos com esta paleta serem mais fiáveis que os obtidos a partir do colorante em pó. O protocolo começa com uma análise global levada a cabo com FORS, sendo adquiridos espectros em todas as áreas pintadas do manuscrito e comparados com a base de dados. Isto permite a identificação de cerca de 60-70% dos colorantes presentes. De seguida, procede-se a uma inspeção visual das cores com uma câmara digital acoplada a um microscópio 10-80x, por forma a obter boas imagens das áreas onde se obtiveram espectros de FORS inconclusivos, i.e., misturas de pigmentos, cores degradadas, etc. Após o que se conduzem as análises de XRF que permite caracterizar os pigmentos metálicos (i.e., pigmentos à base de ouro, prata e cobre), verificar a presença de camadas sobrepostas, identificar mordentes em corantes e lacas, e ainda identificar eventuais produtos secundários que, por sua vez, fornecerão informação útil para estudos de proveniência das matérias-primas. Nesta fase cerca de 90% dos colorantes presentes estarão identificados. Finalmente a espectroscopia de Raman será aplicada a casos que ainda levantem dúvidas. Após a aplicação destas técnicas obtém-se muita informação, causando pouco ou nenhum stress aos manuscritos analisados. ●

## palavras-chave

*IN SITU*  
FORS  
RAMAN  
XRF  
ILUMINURAS



# A PROTOCOL FOR NON-INVASIVE ANALYSIS OF MINIATURE PAINTINGS

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## Introduction

The characterization of palettes used in miniature painting is an important task as a great amount of information can be obtained at the disposal of art historians. It is, though, a hard task since miniatures are among the most precious and fragile artworks. Many problematic aspects must be considered:

- sampling from miniatures is usually not allowed by owners and institutions, so that only *in situ* analysis can be performed;
- it is not possible to use analytical techniques working at contact with the sample, such as ATR-IR;
- while performing analysis sessions, prolonged opening of manuscripts can cause stress to painting layers and to parchment itself, so that after few hours sessions must be closed.

Due to these drawbacks, it is clear that only portable, non invasive and fast analytical techniques must be used.

Another important consideration is the following: no analytical technique, when used alone, can yield all information needed to characterize palettes. Several aspects support this statement. Information must be gained either on macroscopic scale (1-3 mm spot) to identify the main components, and on microscopic scale (0.1 - 0.001 mm) to identify single components in a mixture. Mixtures can be apparent (brown ⇔ red + black; pink ⇔ red + white; grey ⇔ white + black) or less evident (green ⇔ blue + yellow; purple ⇔ red + blue). Illuminators used sometimes a mixture of indigo and orpiment called *vergaut* or *vergant*, to obtain a green hue.

Secondly, information must be gained either with surface techniques and with in-depth techniques. Surface techniques (such as Raman spectroscopy) allow identification of colorants in the last pictorial layer, of varnishes and protective layers and of

alteration compounds, while in-depth techniques (such as XRF) allow identification of underlying pictorial layers, information on preparation layers and on grounds. This can be seen from the following example. In the miniature shown in fig.1, taken from a XV century *Book of hours* by Antoine de Lonhy, held in the Museo Civico di Arte Antica in Turin (Italy), the Virgin's robe is painted in blue. XRF analysis on the blue area shows the presence of copper, suggesting the use of azurite; Raman and FORS analysis, though, both show the presence of ultramarine blue in the surface layer, so that we can hypothesize that the author used the *layering* technique, that is the superimposition of different pigments (Aceto et al. 2008).

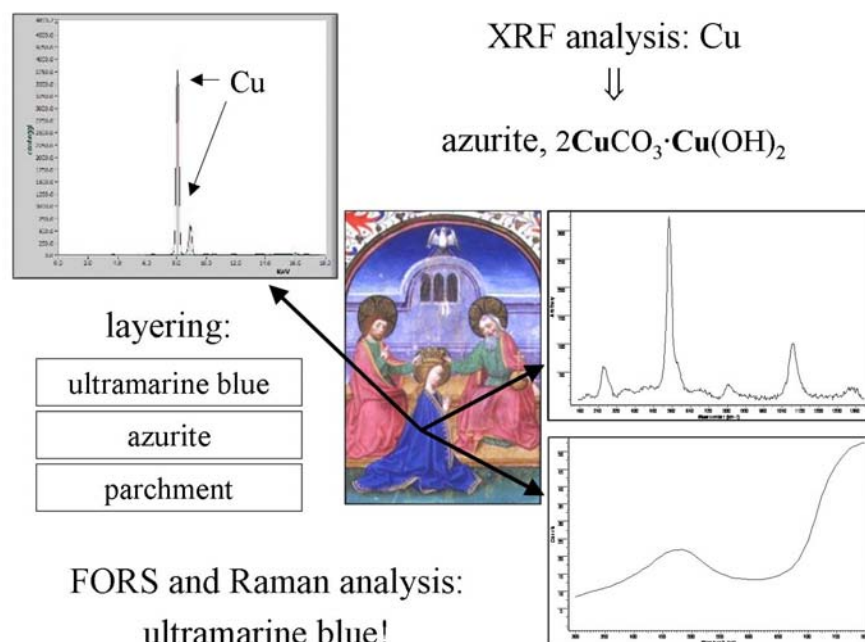


FIG.1 COMPLEMENTARY ANALYSIS ON THE VIRGIN'S ROBE FROM A XV CENTURY MINIATURE

In the analysis of manuscripts, among the techniques available in portable version Raman spectroscopy is with no doubt the one with the best diagnostic power (Aceto et al. 2006; Bersani et al. 2006). It requests, though, lengthy times of analysis. XRF spectrometry has a good diagnostic power (Bruni et al. 2008) but results are sometimes not conclusive, due to the fact that it is an elemental technique; moreover it cannot be used to identify organic compounds. IR spectrophotometry (Bruni et al. 1999) and X-ray Diffraction spectrometry (Duran et al. 2009), though available in portable version, are at present still difficult to be used *in situ* as self-consistent techniques. A good alternative to these powerful but sophisticated techniques is UV-visible diffuse reflectance spectrophotometry, whose acronym is FORS when it is used with fiber optics (Bacci et al. 1997, 28; Bacci 2000). This technique is easy to use, it requests short analysis times and it can be used in all geometrical situations.

Truly portable instruments are available on the market. Its major drawback is that results are hard to interpret in case of mixtures and when varnishes or patinas are present, being a surface technique. Moreover, due to the present performances of probes, it is not fit to analyze short painted areas (< 3 mm). It must be considered, though, that in miniature painting the range of colorants is usually narrow and known according to age and geographic zone, and that usually varnishes are not present. The range of information available from the cited techniques is the following:

- Raman and IR can yield information on compounds present, such as colorants, ligands and varnishes;
- UV-Visible FORS can yield information on compounds present in the surface layer;
- XRF can yield information on elements present in colorants as key-elements, in order to identify the colorants, and as impurities, in order to have information on the origin or raw materials.

To resume, it is clear the need to operate with more techniques, due to fact that these must be non invasive and portable, fast and with minimal impact on the object being examined, to be executed on macro and micro scale, on surface and in-depth. As said before, no analytical technique can fulfill all these requirements when used alone.

### *Analytical protocol*

In order to address these issues, we propose the development of an analytical protocol to optimize the number and type of analysis needed in the characterization of miniature paintings. The protocol is composed by the following steps.

- preliminary analysis with UV-visible FORS
- chemometric treatment of spectral data
- visual inspection with digital camera
- XRF analysis
- Raman analysis

As it is obvious, the application of the protocol must be preceded by a proper knowledge of bibliographic sources, in order to build spectral databases in proper conditions. This is because it is much better to compare analytical results from unknown samples with analytical standards prepared in similar conditions. A palette of colorants on parchment was therefore prepared, choosing colorants among those used by medieval artists and following recipes of medieval technical treatises such as *De Arte Illuminandi* (Brunello 1971a), *Compositiones ad tingenda musiva* also known as *Manoscritto di Lucca* (Caffaro 2000) and *Il libro dell'arte* (Brunello 1971b). To simulate the painting techniques used by ancient illuminators, paints were prepared either in egg tempera and in gum Arabic. In fig.2 the resulting palette on parchment is shown.

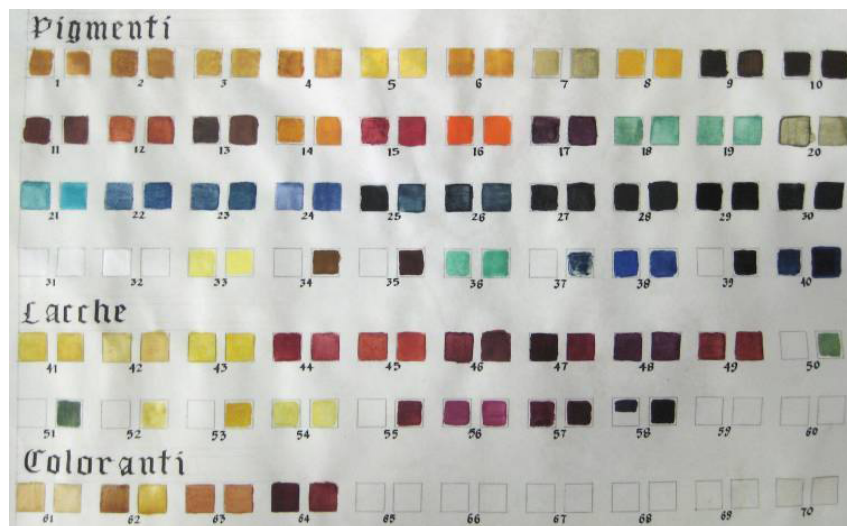


FIG.2 THE COMPLETE PALETTE OF COLORANTS ON PARCHMENT

### 1<sup>st</sup> stage

In the preliminary stage, FORS analysis is executed on all painted areas of a manuscript (fig.3). Identification of colored colorants (i.e. all but black, white and grey) is performed according to their spectral features: reflectance or absorbance maxima for blue, green and purple colorants, inflexion points for yellow, red and orange colorants (fig.4).



FIG.3 ANALYSIS OF MINIATURES BY FORS

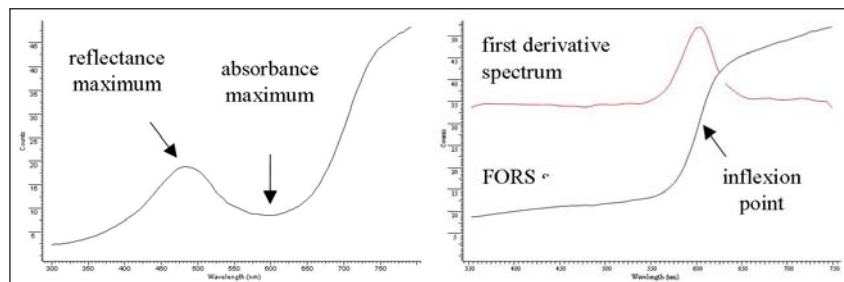


FIG.4 SPECTRAL FEATURES IN THE FORS SPECTRUM

### 2<sup>nd</sup> stage

Multivariate analysis is performed on FORS spectra in order to identify painted areas obtained with similar pigments. Among unsupervised pattern recognition techniques, Hierarchical Cluster Analysis (HCA) or Principal Components Analysis (PCA) can be used. Upon classification of FORS spectra into different classes, identification performed on a single painted area can be extended to all items, i.e. all painted areas belonging to the same class. It must be noted that classification must be performed

separately on painted areas of a single hue: if all hues were classified simultaneously, the differences among hues would be stronger than the differences among pigments of the similar hue.

In fig.5 a dendrogram is shown resulting from cluster analysis on blue painted areas taken from a XII century Italian manuscript: painted areas are clearly grouped into three classes, respectively made of azurite, indigo and ultramarine blue. In fig.6 a similar result is obtained by red painted areas from a XV century Italian manuscript: again, it is apparent the classification in distinct groups, in this case made of minium and cinnabar.

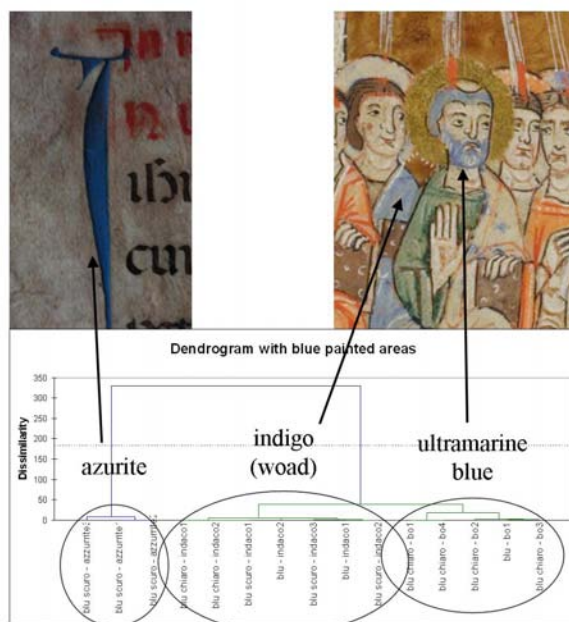


FIG.5 DENDROGRAM FROM CLUSTER ANALYSIS ON BLUE PAINTED AREAS FROM XII CENTURY ITALIAN MANUSCRIPT

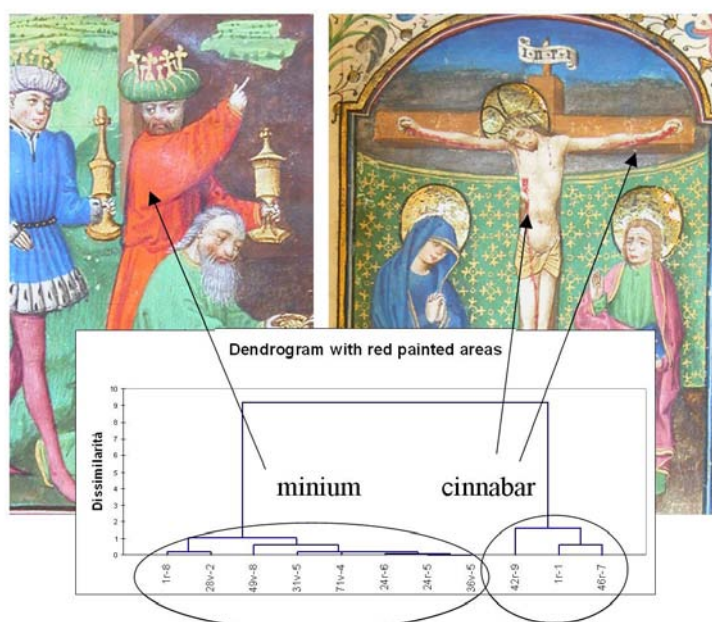


FIG.6 DENDROGRAM FROM CLUSTER ANALYSIS ON RED PAINTED AREAS FROM A XV CENTURY ITALIAN MANUSCRIPT



FIG.7 VISUAL INSPECTION ON A MANUSCRIPT WITH A DIGITAL CAMERA AND A ZOOM LENS

### 3<sup>rd</sup> stage

After performing FORS analysis, it is useful to carry out a visual inspection of painted areas in order to better understand the result of FORS analysis. This can be made through a digital camera connected with a zoom lens (in the present case a 10x-80x zoom, fig.7), in order to have a look under the microscopic scale. Visual inspection can yield useful information concerning the identification of mixtures, which can help tuning the interpretation of FORS spectra; moreover identification of altered areas and of particular features can be obtained. In the following figures some examples are shown, taken from inspection on a XII century Italian manuscript called *Liber Evangeliorum*, held in the Archive and Chapter Library of Vercelli (Italy).

In fig.8 a blue initial is shown. The corresponding FORS spectrum, shown in fig.9, suggests the presence of azurite but we must note that the reflectance maximum is red-shifted. An image at 80x magnification (fig.10) allows to clarify this behavior: little red particles, later identified as made of cinnabar, are present that cause the red shift in the spectrum; as a consequence we must think that the blue initial was painted with a mixture of azurite and cinnabar, possibly due to a dirty brush.

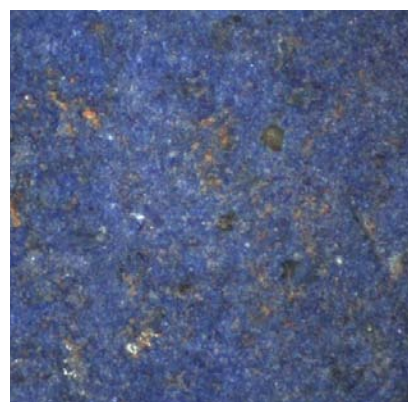
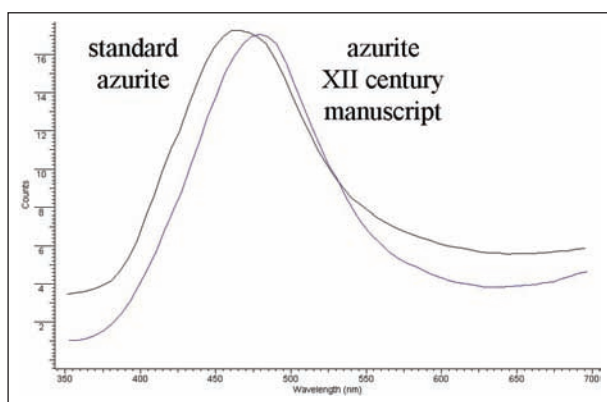


FIG.8 A BLUE INITIAL FROM A XII CENTURY ITALIAN MANUSCRIPT

FIG.9 FORS SPECTRA OF THE BLUE INITIAL (BLUE LINE) AND OF A STANDARD OF AZURITE (BLACK LINE)

FIG.10 MAGNIFIED IMAGE (80X) OF THE BLUE INITIAL

In fig.11 the miniature shows the Virgin's and Saint John's robes painted in a very weak blue hue. The image at 80x magnification (fig.12) put into evidence that residual particles of ultramarine blue are present: most probably both robes were painted in blue but the painted areas were later subjected to a phenomenon known as *ultramarine sickness*, in which ultramarine loses its color as a consequence of interaction with acidic agents.

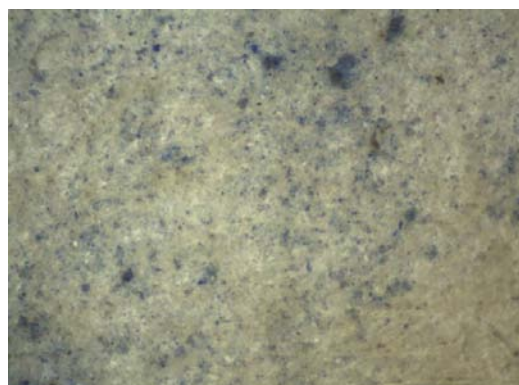


FIG.11 A HIGHLY DEGRADED MINIATURE FROM A XII CENTURY ITALIAN MANUSCRIPT

FIG.12 MAGNIFIED IMAGE (80X) OF THE BLUE PAINT ON THE VIRGIN'S ROBE



In fig.13 it is possible, at high magnification, to see the preparation layer underlying a gold foil and to hypothesize that the preparation be of the *flat gilding* type, that is with glue.

In fig.14 another gilding shows the presence of gold and silver foils overlapped (the so-called *oro di mistà*).

Finally, in fig.15 a translucent layer of iron-rich paint is shown, which was later identified as iron-gall ink used as pigment.

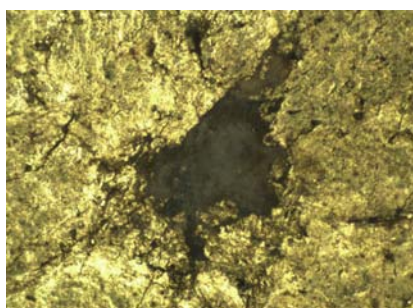


FIG.13 MAGNIFIED IMAGE (80X) OF A GILDING

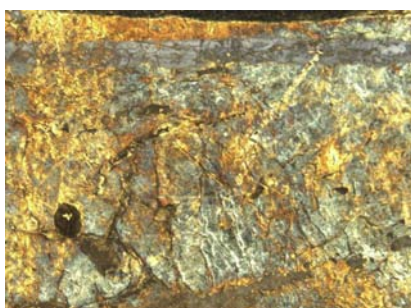


FIG.14 MAGNIFIED IMAGE (80X) OF A ORO DI MISTÀ GILDING



FIG.15 MAGNIFIED IMAGE (80X) OF A PAINT MADE FROM IRON-GALL INK



FIG.16 ANALYSIS OF MINIATURES BY XRF SPECTROMETRY

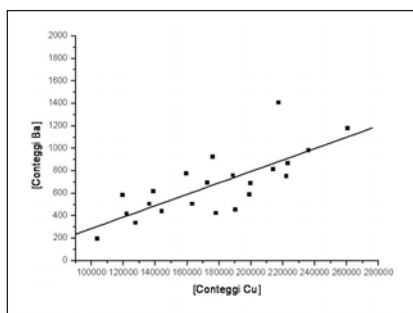


FIG.17 RELATIONSHIP AMONG COPPER AND BARIUM IN BLUE PAINTS

#### 4<sup>th</sup> stage

After FORS analysis, identification of colorants is followed by XRF analysis (fig.16). Application of XRF is mandatory to address the following issues that cannot be fulfilled by other techniques:

- characterization of metal pigments such as gold, silver, tin, etc. either in foil or in powder form;
- characterization of uncolored colorants, i.e. white, black and grey pigments that cannot be identified by FORS;
- identification of overlapping layers;
- identification of mordants used with dyes and lakes;
- identification of impurities in pigments, useful to yield information on the provenance of raw materials.

The last issue is exemplified in fig.17 which shows the relationship among copper and barium as determined by XRF on blue painted areas laid with azurite on a XV century Italian manuscript. It is apparent the good correlation among copper (chromophore in azurite) and barium (impurity in azurite). Same result is obtained for copper and zinc in green areas laid with malachite. These results suggest a link among the pigments and the minerals from which they were obtained: if large enough information is available, the geographical origin of the minerals used can be determined.

*5<sup>th</sup> stage*

At this stage almost 80-90% of the colorants is already identified. Raman analysis (fig.18), which is together the most sophisticated and the most cumbersome of the cited techniques, can be used as far as uncertain cases are left and to confirm previous identifications. Its spatial resolution helps in fine-tuning identification.

Finally, to illustrate the application of the proposed protocol, results from characterization of the palette of a manuscript are described. The manuscript is the already cited Book of hours by Antoine de Lonhy, held in the Museo Civico di Arte Antica in Turin (Italy) and dating to the XV century. The whole palette is reported in tab.1.

Hue	Colorant	FORS	XRF	Raman
White	lead white	n.i.	Pb	X
Blue	ultramarine blue on azurite	X	Cu	X
	azurite	X	Cu, Ba	X
	phtalocyanine blue	X	Cu, Ti	X
Yellow	gold foil	n.i.	Au	n.i.
	shell gold	n.i.	Au	n.i.
	mosaic gold	n.i.	Sn, S	X
	lead-tin yellow type I	X	Pb, Sn	X
Grey	gold on silver	n.i.	Ag, Au	n.i.
Black	carbon	n.i.	n.i.	X
Red	cinnabar	X	Hg, S	X
	minium	X	Pb	X
Green	malachite	X	Cu, Zn	X
Violet	lake (kermes?) with lead white	n.i.	Pb	n.i.

TABLE 1 PALETTE OF THE BOOK OF HOURS BY ANTOINE DE LONHY (XV CENTURY). X = COLORANT IDENTIFIED BY THE TECHNIQUE; N.I. = COLORANT NOT IDENTIFIED BY THE TECHNIQUE

In fig.19 a miniature taken from the Book of hours shows the presence of four different yellow pigments used by the author in order to obtain different effects. Identification was possible only by complementary application of analytical techniques, following the protocol described.

The miniature in fig.20 shows a peculiar feature. Again, the application of the protocol allowed to put into evidence a later retouch in the background sky, in which the original paint in ultramarine blue was reinforced with phtalocyanine blue laid on titanium white, an intervention made later than 1935 when phtalocyanines were patented. ●



FIG.18 ANALYSIS OF MINIATURES BY RAMAN SPECTROSCOPY

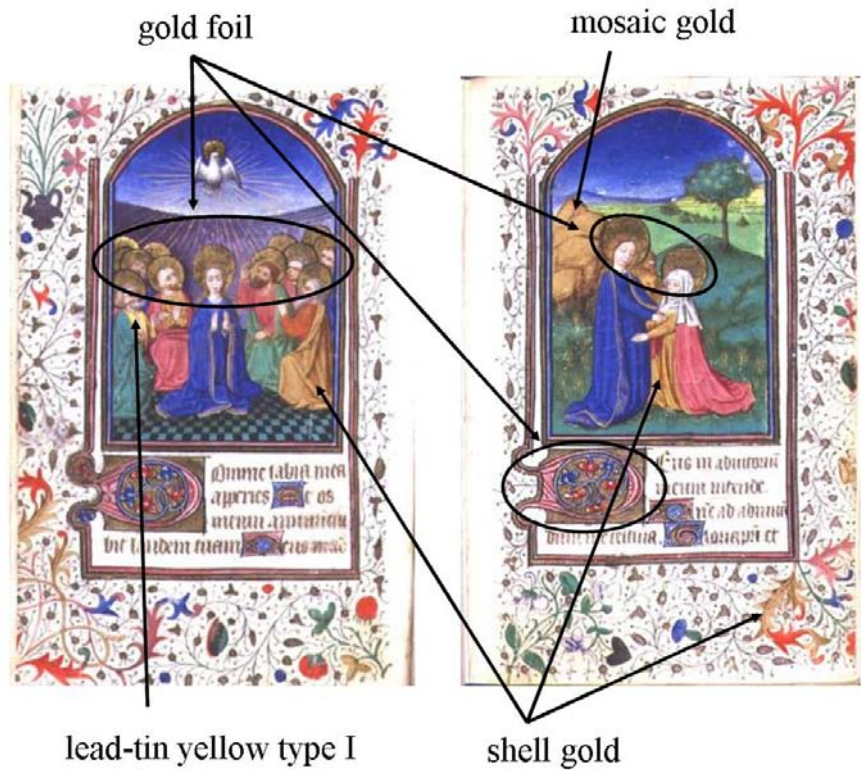
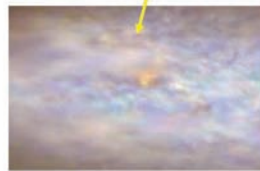


FIG.19 YELLOW PIGMENTS IDENTIFIED ON A XV CENTURY MINIATURE



XRF: evidence of Cu, Ti  
 FORS, Raman: phtalocyanine blue



phtalocyanine blue on titanium white (retouch later than 1935!)



XRF: evidence of Cu  
 FORS, Raman: ultramarine blue



ultramarine blue on azurite

FIG.20 ORIGINAL AND LATER ADDED BLUE PIGMENTS ON A XV CENTURY MINIATURE

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