Resumo

Guido di Pietro, mais conhecido por Fra Angelico ou Frei Giovanni de Fiesole (c. 1400-1455), foi um dos mais importantes artistas do séc. XV. Exceleu tanto em pintura mural e de cavalete como nas artes da iluminura. O seu talento foi celebrado em 2007-08 no Museu de São Marco em Florença, por ocasião da exposição *Fra Giovanni Angelico. Pittore miniatore o miniatore pittore*, no âmbito da qual se levou a cabo um estudo comparativo dos materiais e técnicas que o artista utilizou na iluminura e na pintura sobre tábua. Este centrou-se nos materiais – pigmentos e corantes – utilizados por Angelico em manuscritos, em particular, numa das suas obras mais belas, que integra a colecção permanente do Museu: o *Graduale n. 558*. Tendo em conta que se tratam de obras em pergaminho, são de preferir métodos de análise que permitam uma identificação *in situ*. Para além disso, técnicas não invasivas são consideradas as mais adequadas, uma vez que é difícil recolher amostras ou micro-amostras. De facto, as camadas cromáticas são tipicamente muita finas quando comparadas com a pintura de cavalete. Acresce que, normalmente, as decorações cobrem áreas pequenas. Este artigo descreve o uso da fluorescência de raios-X dispersiva de energias (XRF) em conjunto com a reflectografia de UV-VIS-NIR por fibra óptica (UV-Vis-NIR FORS), que foram seleccionadas de entre as possíveis técnicas não-invasivas e de aplicação in situ, para o estudo dos materiais utilizados no *Graduale n. 558* de Beato Angelico. ●

palavras-chave

MANUSCRITOS ILUMINADOS
FLUORESCÊNCIA DE RAIOS-X DISPERSIVA DE ENERGIAS (XRF)
REFLECTOGRAFIA DE UV-VIS-NIR COM FIBRA ÓPTICA (FORS)
FRA ANGELICO
GRADUALE N. 558

Abstract

Guido di Pietro, better known as Beato Angelico or Fra Giovanni da Fiesole (c. 1400-1455), was one of the most important artists of the 15th century. He excelled in wall- and panel-paintings as well as manuscripts and illuminations. His talent was celebrated in 2007-08 at the San Marco Museum in Florence with a special exhibition Fra Giovanni Angelico. Pittore miniatore o miniatore pittore? *in which the technique and materials used by the artist in making manuscripts and panel paintings were investigated and compared between these two different forms of art. The focus of the study in the context of the exhibition was on the materials – pigments and dyes – used by Angelico to produce manuscripts and, in particular, one of his most beautiful pieces located in the permanent collection of the San Marco Museum: the* Graduale n. 558. *Due to the fragility of parchment-based artworks, the application of* in situ *non-invasive analytical techniques is strongly recommended for analyzing the materials used by artists in making the manuscripts. Moreover, non-invasive analytical methodologies are usually considered to be the most suitable techniques for the investigation of manuscripts since taking samples, or even micro-samples, from such delicate art objects is generally considered unacceptable. Indeed, the manuscript paint layers are typically very thin compared to those of wall and panel paintings. Also, painted decorations usually cover relatively small areas. This report illustrates the effective use of X-ray fluorescence (XRF) and ultraviolet, visible, and near infrared fiber optic reflectance spectroscopy (UV-Vis-NIR FORS), selected from the available* in situ *non-invasive techniques, to identify the materials used in making the* Graduale n. 558 *by Beato Angelico.* ●

key-words

ILLUMINATED MANUSCRIPTS
X-RAY FLUORESCENCE (XRF)
FIBER OPTIC REFLECTANCE SPECTROSCOPY (FORS)
BEATO ANGELICO
GRADUALE N. 558

NON-INVASIVE XRF AND UV-VIS-NIR REFLECTANCE SPECTROSCOPIC

ANALYSIS OF MATERIALS USED BY BEATO ANGELICO IN THE MANUSCRIPT *GRADUALE N. 558*

M. PICOLLO
IFAC-CNR, Firenze (Italy)

A. ALDROVANDI
Opificio delle Pietre Dure, Firenze (Italy)

A. MIGLIORI
Dipartimento di Fisica e INFN , Firenze (Italy)

S. GIACOMELLI
Società Internazionale per lo Studio del Medioevo Latino, Firenze (Italy)

M. SCUDIERI
Museo di San Marco, Firenze (Italy)

Introduction

In the study of artworks the application of more than one analytical technique permits one to better identify the materials and the techniques used by the artists (Clarke 2001, Ricciardi *et al.* 2009). These techniques are grouped in two main categories: non-invasive and invasive. Among the first group of techniques both X-ray fluorescence (XRF) and optical fiber reflectance spectroscopy (FORS) provide conservators and curators with useful information about works of art (Bacci *et al.* 2009, Dran *et al.* 2009). Their non-invasiveness enables these light and compact devices to acquire a large amount of data *in situ*.

In some cases, it may be necessary to integrate the data obtained with some non-invasive methods with other non-invasive or micro-invasive analytical techniques. For example, FORS and XRF can also be very useful tools, in conjunction with other techniques, for locating areas for micro-sampling and for extending local data from micro-analyses to a broader scale, thus reducing the extent of micro-sampling. However, the small size of the illuminates and the presence of very fine details prohibit, in most cases, the use of the precise analytical chemical methods typically used on paintings, because of the sample size limitation.

In this case, XRF and ultraviolet (UV), visible (Vis), and near infrared (NIR) FORS were selected from the available *in situ* non-invasive techniques and applied to identify the materials used in making the *Graduale n. 558* by Beato Angelico. Guido di Pietro, better known as Beato Angelico or Fra Giovanni da Fiesole (c. 1400-1455), was one of the most important artists of the 15th century. He excelled in wall – and panel – paintings as well as manuscripts and illuminates. His talent was celebrated in 2007-08 at the San Marco Museum in Florence with a special exhibition *Fra Giovanni Angelico. Pittore miniatore o miniatore pittore?* There, the technique and materials used by the artist in making manuscripts and in making panel paintings were investigated and compared. The focus of the study, in the context of the exhibition, was on the materials – pigments and dyes – used by Angelico to produce manuscripts and, in particular, one of his most beautiful pieces of the permanent collection of the San Marco Museum: the *Graduale n. 558*.

Methodology

The artwork

The *Graduale n. 558* represents one of the most famous illuminate masterpieces of Angelico's young production and was made for the church of San Domenico in Fiesole where the artist lived at the beginning of his monastic life. Fra Angelico was a versatile artist who excelled in the fresco, illuminate, and panel paintings techniques. The *Graduale n. 558* was probably made in two different periods: in 1424-1425 and in 1428-1430. Consequently, the illustrations present some different stylistic characteristics, which make it possible to group the miniatures in four groups by their chromatic, stylistic, and decorative features. This choir book is constituted of 260 folios written in «*Testualis*» with text and music. These folios were bound together probably when the Graduale was added in the *Leopoldo II di Lorena* Collection in the 19th century. The illustrations are composed of 986 watermarked letters, 30 miniatures, and seven decorated letters.

Analytical techniques

FORS was performed using two spectroanalyzers: Zeiss model MSC501 and MCS511 NIR 1.7 operating in the 200-1700 nm range. The approximate spectral resolution was less than 3 nm in the 200-1000 nm range (MCS501) and 10 nm in the 900-1700 nm range (MCS511 NIR 1.7). An internal tungsten lamp (Zeiss model CLH500) was used for the final operative range (350-1700 nm). The sampled area was smaller than the approximate 2 mm diameter, and the acquisition time for each spectrum was less than one second. The spectrometers were calibrated using a white Spectralon® 99% reflectance standard. A 0°/45°/45° reflectance configuration was adopted to avoid specular reflectance. The identification of the pigments was accomplished by comparing the acquired unknown spectra with spectral databases (http://fors.ifac.cnr.it). Assignments were made using both the primary and first derivative spectra. Given the thinness of the paint layers and the presence of overtone bands in the NIR associated with the vellum substrate, the assignment of peaks to pigments required particular care. The NIR region was, however, found to be particularly useful for the identification of some pigments as well as gypsum.

XRF analyses were performed with an Assing LITHOS 3000 portable spectrometer equipped with a molybdenum tube and a Peltier cooled Si-PIN detector with a sensitive area of 7 mm^2, thickness of 0.5 mm and a berillium (Be) window 12.5 μm thick. The resolution was of approximately 165 eV at 5.9 keV. For the measurements on the *Graduale* the X-ray tube voltage was 24 kV, the current was 300 μA, and the acquisition time was 100 seconds (in case of intense X-ray counting rate the current was reduced and the acquisition time was increased). Also, a 1 mm collimator was used for an investigated area of approximately 2 mm in diameter.

The distance between the investigated area and the detector was about 2.8 cm. The X-ray sending and collecting angles were approximately 45° and 50°, respectively. Due to the intrinsic limitation of XRF, which does not yield results spatially resolved in depth; and, in order to avoid confusing results, the areas for analysis were chosen, whenever possible, so that no decoration was present in the corresponding area on the verso of the manuscript leaf.

Results and discussion

On the *Graduale* approximately 130 FORS and 50 XRF spectra distributed on about 30 pages were acquired. Pigment identification was achieved by combining FORS and XRF spectral data. From the XRF measurements the preparation of the parchment was found to be made with calcium carbonate as calcium, with a small amount of arsenic, were the only chemical elements recorded. However, the calcium element could have been related to the presence of calcinated animal bones (Brunello 1975). FORS measurements in the presently available operative range were not able to better specify the materials used to prepare the parchment (Fig. 1). FORS data, on

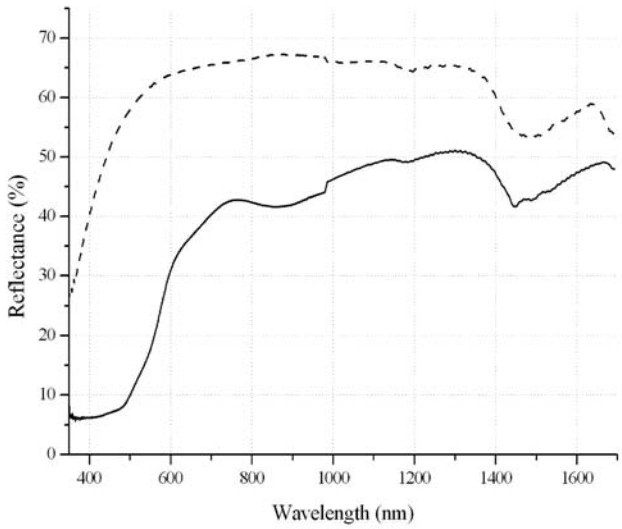

FIG.1 FORS SPECTRA OF THE PARCHMENT (DASHED LINE) AND OF THE GYPSUM WITH IRON OXIDE (HEMATITE) IN THE PREPARATORY LAYER FOR THE APPLICATION OF THE GOLD LEAVES (*F.* 33V)

the other hand, made it possible to exclude the use of calcium sulfate bi-hydrated (gypsum) or calcium sulfate hemi-hydrated (plaster of Paris) in the ground layer (Bacci et al. 2007). This information was also confirmed by XRF because no sulfur was found in the preparation of the parchment. The gypsum was present only as a preparatory layer for the application of the gold leaves (c.33v, c.86v, c.124r) in mixture with iron oxide (hematite) based pigments (Fig. 1). In one case, XRF also found the presence of mercury, together with iron, in the preparatory layer. This was due to the presence of cinnabar, which gave a reddish tint to the layer. The gold leaves, which were extensively used in the *Graduale* for background and aureole areas, were made with pure gold. The XRF analysis did not show the presence of impurities such as silver, tin, lead, or copper (c.9r, c.21r, Fig. 2).

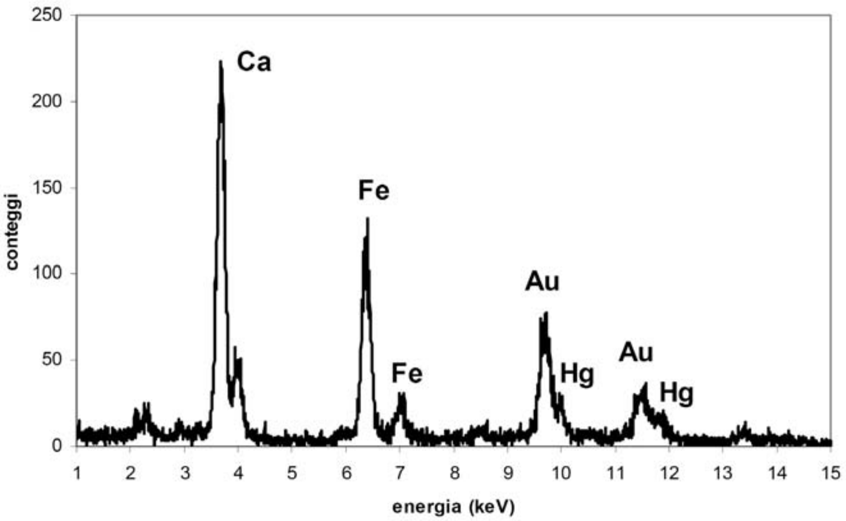

FIG.2 XRF SPECTRUM OF A GOLD LEAF, MADE WITH PURE GOLD. FROM THE XRF DATA THE GOLD LEAVES DID NOT SHOW THE PRESENCE OF IMPURITIES SUCH AS SILVER, TIN, LEAD, OR COPPER (F.9R)

As found by FORS spectra on about 30 different areas of the *Graduale* the painted blue areas were made with ultramarine blue (*lapis lazuli*). Ultramarine blue was also used in mixture with a red pigment, red lake mainly, at different concentrations to depict violet-purple details (Figs. 3 and 4). Azurite was used only for the watermarked letters. This second blue pigment was positively identified by the two analytical techniques.

A copper based green pigment, such as malachite, mainly, created the green zones. This pigment was used to depict both the cloths of the characters and the landscapes. Also, as illustrated by FORS measurements on 12 areas of the illuminated manuscript, it was used to make frames and decorations surrounding the painted scenes. Another green pigment, green earth, was only applied to paint complexion (flesh tones) areas in mixture with lead white, iron oxide and hydroxide (yellow and brown ochre or earth pigments) pigments, and cinnabar. In this *Graduale* the artist

FIG.3 DETAIL OF THE *FOLIUM* 33V WITH REPORTED SOME XRF AND FORS MEASUREMENT

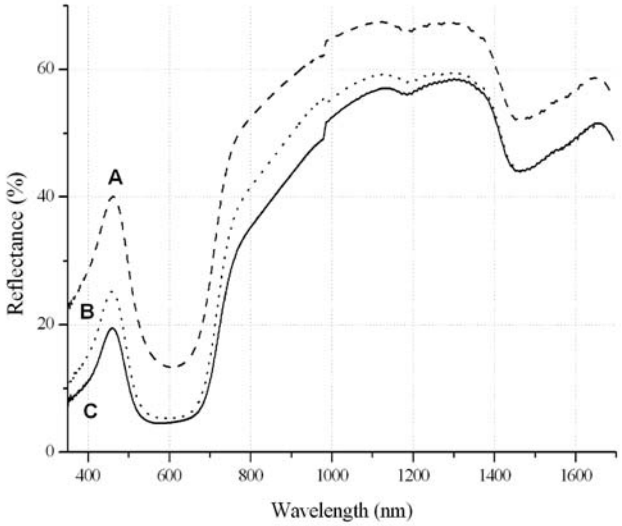

FIG.4 FORS SPECTRA FROM BLUE AREAS MADE WITH ULTRAMARINE BLUE (*LAPIS LAZULI*). SPECTRUM A FROM *FOLIUM* 33V; SPECTRUM B FROM F*OLIUM* 60V; SPECTRUM C FROM *FOLIUM* 93R

did not use mixtures of blue (azurite, indigo, *lapis lazuli*) and yellow (lead-tin yellow, orpiment) pigments to produce green hues/shades. In one case only, the FORS acquired spectrum resembled a mixture of ultramarine and lead-tin yellow pigments; but here the yellow pigment was painted as a glaze on the blue sky.

The yellow and brown colors were obtained by using lead-tin yellow pigment for lighter areas and iron oxide and hydroxide pigments for darker and less saturated hues. The first pigment was identified by the presence of contemporary lead and tin in the XRF spectra (Fig. 5) and from its reflectance spectral shape (FORS); the second pigments showed typical FORS, in which the characteristic absorption bands

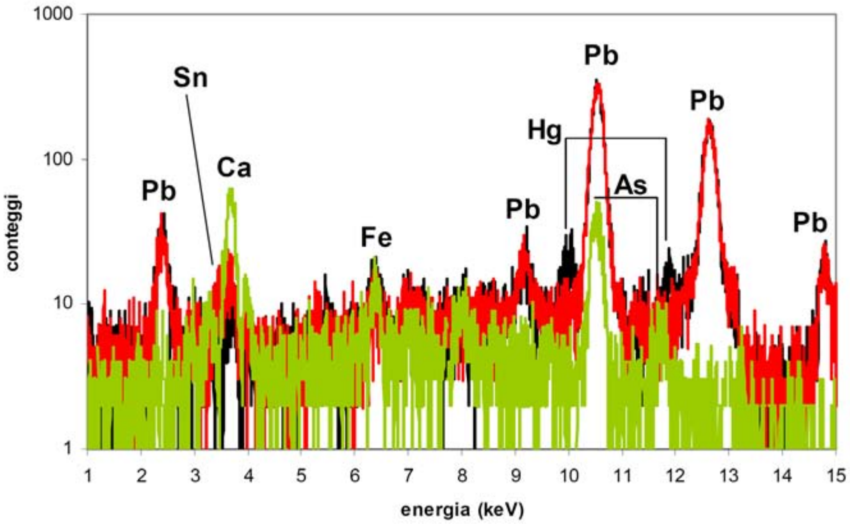

FIG.5 XRF SPECTRA OF YELLOW AND BROWN AREAS OBTAINED BY USING LEAD-TIN YELLOW PIGMENT (RED CURVE, *F.* 93R), IRON OXIDE AND HYDROXIDE PIGMENTS (SIENNA EARTH, BLACK CURVE, *F.* 21R), AND ORPIMENT (GREEN CURVE, *F.* 60V)

of trivalent iron are easily detected, and XRF spectra. In the case of XRF data, the presence of iron is usually linked to manganese, which usually is related to the occurrence of Sienna and, more typically, of umber earths.
In the folium 60v the dark yellow mantle of San Peter was depicted using orpiment (Fig. 6). This material was only identified in this area of the *Graduale* by the presence of arsenic in XRF spectrum and by its FORS spectrum, even though the reflectance spectra of most of the yellow pigments could be easily modified when mixed together or with red pigments (Fig. 5).

FIG.6 DETAIL OF THE THE *FOLIUM* 60V WITH THE DARK YELLOW MANTLE OF SAN PETER DEPICTED USING ORPIMENT (XRF MEASUREMENT N. 92)

The red areas were created primarily by use of cinnabar and red lakes. In certain cases red lead (minium) was found, even if most of the time it was associated with cinnabar (Fig. 7). Cinnabar is easily detected by XRF due to the presence of mercury in the paint layer. This pigment was extensively used for the main scenes, the decorations, and the watermarked letters. The red lake, instead, was mainly used to paint the purple-violet glazes and to produce hues from pink to purple. This pigment is not seen by XRF, and its identification by means of FORS is certain only when red lakes are used as glaze on a light substrate or in a mixture with a white pigment, such as lead white. To date, to the best of the authors' knowledge, there have been no systematic studies to determine how preparation, ageing, and type of lake affect the reflectance spectra. Many of the absorption features can vary depending on the preparation of the dye into a lake (Bacci et al. 2001) as well as the preparation of the paint (Bisulca et al. 2008). In some cases characteristic features are less intense

FIG.7 DETAIL OF THE *FOLIUM* 13V WHERE RED LEAD (MINIUM) AND CINNABAR WERE FOUND

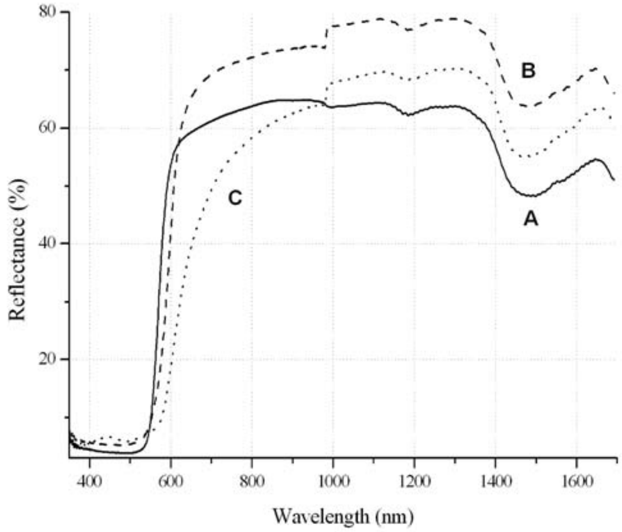

FIG.8 FORS SPECTRA OF RED LEAD (SOLID LINE - A, *F.* 13V), CINNABAR (DASHED LINE – B, *F.* 13V), AND RED LAKE (DOTTED LINE – C, *F.* 93R)

or absent altogether, which can cause misleading results in interpretation of spectra. While it is sometimes possible to distinguish between these dyes or to broadly classify them as of animal or insect in origin, in the analysis of real paintings identification is complicated by the presence of other pigments, the nature of their application, and the effects of natural ageing. These factors can mask or alter characteristic features in UV-Vis-NIR reflectance spectra (Fig. 8).

Finally, it was noteworthy to report that sometimes, such as in the folium 85v, the ring shape bronze/light brown decorations of the letter were made by using mosaic gold, a very fine powder made with tin and copper, as revealed by XRF (Fig. 9).

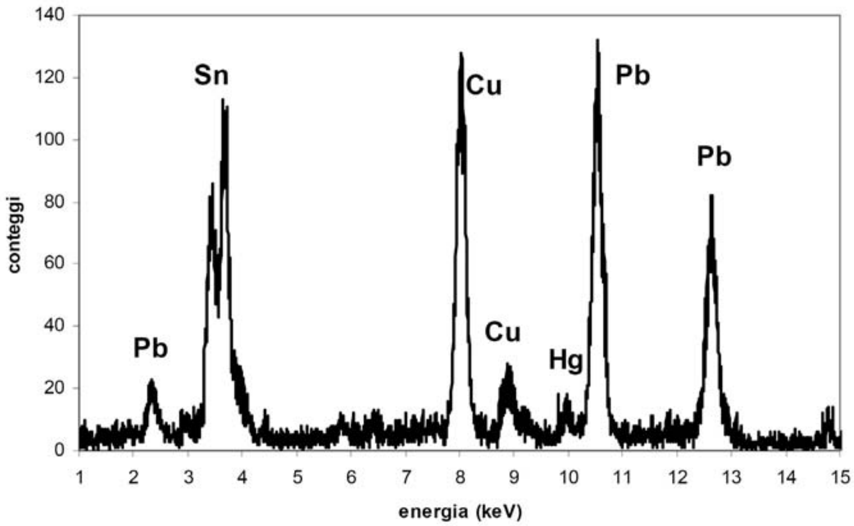

FIG.9 XRF SPECTRUM FROM THE RING SHAPE BRONZE/LIGHT BROWN DECORATIONS OF THE LETTER OF *FOLIUM* 85V MADE BY USING MOSAIC GOLD, A VERY FINE POWDER MADE WITH TIN AND COPPER

Conclusion

The combination of high fidelity site-specific methods (FORS and XRF) proved to be a useful tool for the examination of illuminates and miniatures artists' materials, as already found in easel and mural paintings. Expanding the FORS range of analysis further into the infrared, improving the XRF procedure in the detection of light chemical elements, and adding Raman spectroscopy to the list of applied techniques, would make possible more precise descriptions of the characteristics of the materials found in this kind of artworks, in particular when organic materials, such as binding media, need to be identified. ●

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Biographies

Marcello Picollo, geologist, is a Researcher at the Institute of Applied Physics «Nello Carrara» IFAC-CNR, Florence. He has been working on spectroscopic investigations of works of art since 1991. His main focus is on pigment characterization using non-invasive spectroscopic, imaging and X-ray techniques. Address: *Institute of Applied Physics «Nello Carrara» IFAC-CNR, Via Madonna del Piano 10, 50019 Sesto Fiorentino (Italy)*. E-mail: m.picollo@ifac.cnr.it

Alfredo Aldrovandi received his Master in Science in Physics at the University of Modena. He has been working from 1983 at the Restoration Laboratories of the Opificio delle Pietre Dure in Florence. His main focus is on the development and application of non-invasive diagnostic investigation techniques on artworks. Address: *Opificio delle Pietre Dure, Via degli Alfani 78, 50121 Firenze, Italy*. E-mail: alfredo.aldrovandi@gmail.com

Alessandro Migliori received his Master in Science in Physics in June 2001 and his PhD in «Science for the Conservation of Cultural Heritage» in December 2004, both at University of Florence. He is an expert in techniques for compositional analysis using ion beams (*Ion Beam Analysis* techniques: PIXE, PIGE, RBS, NRA) and X-ray radiation (XRF), mainly in the field of Cultural Heritage. He has worked at CMAM laboratory in Madrid and Opificio delle Pietre Dure in Florence. Presently he is working as researcher at LABEC laboratory of INFN-Florence. Address: *Dipartimento di Fisica e INFN (Florence), Via Sansone 1, 50019 Sesto Fiorentino, Italy*. E-mail: migliori@fi.infn.it

Sara Giacomelli received her Master in Humanities in 2004 with a thesis on History of Ancient Book Illumination. She received a post Master specialization in Art history in 2008 with a thesis on techniques and pigments used in miniatures. She has worked at the Museum of San Marco for the exhibitions «Miniatura in Umbria del Rinascimento. Suggerimenti per un percorso artistico» (2004); «Fra Giovanni Angelico. Pittore miniatore o miniatore pittore?» (2007-2008); «L'Angelico ritrovato. Studi e ricerche per la Pala di San Marco» (2008-2009); «Beato Angelico. L'alba del Rinascimento» (2009). Her publications dealt with Umbrian and Florentine illumination artworks. Address: *Società Internazionale per lo Studio del Medioevo Latino (S.I.S.M.E.L.), Certosa del Galluzzo, Via della Certosa 1, 50124 Firenze, Italy*. E-mail: saragiacomelli@gmail.com

Magnolia Scudieri received her Master in Humanities specializing in Medieval and Modern Art history. She is the Director of both the Museum of San Marco and the Conservation Laboratories of Soprintendenza of the Florentine area. She is actively involved in encouraging and initiating study and research to further the knowledge on the permanent collection of the Museum of San Marco. She is responsible for creating proficient collaboration with prominent institutes dedicated to the investigation of, in particular, the artistic production of Beato Angelico and his followers. She has organized several exhibitions and published works on this topic. Address: *Museo di San Marco, Piazza San Marco, 50100 Firenze, Italy.* E-mail: scudieri@polomuseale.firenze.it