

Resumo

A grande experiência do Instituto em análises não-invasivas para a caracterização de pigmentos, tintas de escrever e corantes permite a identificação das paletas utilizadas pelos iluminadores e, por vezes, dos próprios *scriptoria*. Caracterizam-se ainda tratamentos e intervenções passadas bem como se avaliam os métodos e produtos mais adequados para a sua conservação.

Neste trabalho serão apresentados os resultados obtidos, por análise molecular (microRaman) e elementar (XRF e PIXE), no estudo de três manuscritos, o *Pontificale 492* (séc. XIII, Museo Diocesano, Salerno, Italia), a *Bibbia Amiatina* (sêcs VI-VIII, Biblioteca Medicea Laurenziana, Florença, Italia) e o ms *Piana 3.207* (séc. XIII, Biblioteca Malatestiana Cesena, Italia). ●

Abstract

The huge experience of the Institute in non destructive analysis and characterization of pigments, inks, colours and dyes allows to recognize the palettes used by miniaturists, sometimes distinguishing the scriptoria themselves, identify posterior treatments and additions and assess the proper methods and products to be used in conservation.

We present the results obtained by means of non destructive spectroscopic molecular (Micro Raman) and elemental (XRF and α -PIXE) techniques in three case study, the Pontificale 492 (13th century, Museo Diocesano, Salerno, Italy), the Amiatinus Bible (7th-8th century, Biblioteca Medicea Laurenziana, Firenze, Italy) and the ms. Piana 3.207 (13th century, Biblioteca Malatestiana Cesena, Italy). ●

palavras-chave

PIGMENTOS

XRF

RAMAN

PIXE

OURO MUSIVO

key-words

PIGMENTS

XRF

RAMAN

α -PIXE

MOSAIC GOLD

ILLUMINATIONS: SECRETS, ALCHEMY AND CONSERVATION IN THREE CASE STUDIES

MARINA BICCHIERI

Istituto centrale restauro e conservazione patrimonio archivistico e librario, Roma (Italy), Head of Laboratory of Chemistry, marina.bicchieri@beniculturali.it

MICHELA MONTI

Istituto centrale restauro e conservazione patrimonio archivistico e librario, Roma (Italy), Researcher of Laboratory of Chemistry, michela.monti@beniculturali.it

GIOVANNA PIANTANIDA

Istituto centrale restauro e conservazione patrimonio archivistico e librario, Roma (Italy), Researcher of Laboratory of Chemistry, giovanna.piantanida@beniculturali.it

ARMIDA SODO

Istituto centrale restauro e conservazione patrimonio archivistico e librario, Roma (Italy), Researcher of Laboratory of Chemistry, and Università di Roma Tre, Department of Physics, sodo@fis.uniroma3.it

Achieving highly accurate information on miniatures composition allows to customize conservation and restoration strategies aiming at the best preservation with the least impact. Cultural heritage objects represent complex and multifaceted problems and conclusions drawn from observations with the naked eye are likely as faulty as those drawn from limited diagnostics. Moreover, the use of destructive techniques as many traditional methods actually are is to be avoided, since samples are often unique, priceless specimens. In order to work out reliable, unambiguous information from non destructive methods a truly scientific approach, based on multidisciplinary analyses, laboratory simulations and proper statistics, must be combined to the knowledge of history, art and of course alchemy that guide the illuminator's hand.

From the experimental point of view, a rich literature upon the use of elemental (XRF, LIBS, EXAFS, α -PIXE ...) and molecular (ATR-FTIR, DRIFT, FT-Raman, Micro-Raman...) spectroscopies can be found. In the light of previous experiences (Bicchieri et al. 2001, 169), the combination of XRF, α -PIXE and Micro Raman was considered the proper setup choice.

XRF spectrometry is often (Malzer et al. 2004, 229; Cesareo et al. 2004, 703) applied to pigments and dyes analysis: information can be achieved in reasonable times (minutes). Unfortunately, such information is only qualitative on paper and parchment substrates, since elements lighter than Al (Si, in some cases) give a fluorescence response below the detection limit, so it is impossible to detect organic substrates even though the organic matrix contributes to the global spectrum. At the same time, the X-rays penetration depth increases inversely to the atomic weight of the target element and a sheet of paper or parchment is completely crossed. Quantitative XRF analysis requires, in fact, that the thickness of the sample could be considered as

infinite, i.e. greater than the average thickness crossed by the used XRF radiation. Calibration of the measuring arrangement and the use of reliable calibration model that must be representative of the matrix and target element morphology (particle size distribution, heterogeneity and surface condition) and concentration ranges of the sample to be analysed are also necessary.

Contrariwise, α -PIXE allows controlling the penetration into the sample and quantitative elemental information even on trace and lighter elements (above Na) can be obtained. The simultaneous use of XRF and α -PIXE gives an almost complete characterization of the elemental composition of the sample (Pappalardo et al. 2005, 114). Raman spectroscopy is a technique sensitive to vibrational states of matter, that actually constitute a «fingerprint» of the material. Raman spectroscopy can be used (Colthup et al. 1990, 60) to identify the molecular composition or even the different state of aggregation of the species in the sample under investigation. The advantages of Raman spectroscopy consist in the short measurement time (seconds-minutes) and in the high sensitivity to inorganic compounds. The main problem with Raman applications is that fluorescence is excited together with the molecular states and sometimes «screens» the measurement, making it impossible to extract data.

As far as measurements on the *Pontificale 492* and *Bibbia Amiatina* are concerned, the portable α -PIXE and XRF spectrometers were entirely designed and developed at LNS/INFN laboratory and the portable micro-Raman spectrometer was a custom-made instrument developed at Physics Dpt, Roma Tre University.

Measurements on the ms. *Piana 3.207* were performed with the Assing Lithos 3000 portable XRF spectrometer and the Renishaw In-Via Reflex Raman microscope currently owned by the Institute (Bicchieri et al. 2008, 1074).

The full sets of analyses on *Bibbia Amiatina* and *Pontificale 492*, including the instruments and their specifications, are fully described in dedicated articles. (Bicchieri et al. 2001, 169; Pappalardo et al. 2008, 466). They will be only synthetically reviewed in present work, whereas a major focus will be given to the investigation campaign on the ms. *Piana 3.207* and the related experimental work on pigments analysis and simulation of mosaic gold.

The *Bibbia Amiatina*, Codex Amiatinus, ms. Laur. Amiat. 1, is the last surviving out of three copies of the Bible produced in Ceolfrith's scriptorium in the area of the twin monasteries of Wearmouth Jarrow in Northumbria between the end of the 7th century and the beginning of the 8th. It is composed of 1029 parchment sheets, measures 345 mm x 540 mm and weighs around 50 kg. The manuscript is the most ancient and complete witness to the Vulgate Latin Bible and it is also a great example of English uncial writing and of illuminations in anglo-saxon style, influenced by the Mediterranean-Bizantine one. Therefore its historical interest is inestimable.

The first goal of the analyses laid in the establishment of the original arrangement of the sheets present in the first booklet. Some pigments, in fact, left offsets on the adjacent sheet that were analyzed under ultraviolet light of two different wavelengths (253 nm and 365 nm). It should be underlined that the ordering of the sheets coming out from such a method did not necessarily correspond to the original one, but rather

represented the sequence that the pages had likely followed for the bulk of the document's lifetime. However, scholars agreed to adopt it when re-assembling the book. For a complete characterization of the precious manuscript all illuminations were analyzed coupling Raman, XRF and α -PIXE and have been recognized and classified (Table 1).

Colour	Composition
White	calcite; white lead
Red	red lead; organic lakes; earths
Blue	not yet identified pigment, copper-based pigments sometimes mixed with earths
Brown	earths (iron and sometime copper) often mixed with orpiment or with gold
Yellow	orpiment, organic lakes, earths
Green	blue and yellow (orpiment) mixtures; verdigris mixed with an unidentified organic compound
Gray	white (sometime calcite, sometime white lead) mixed with blue and carbon black. Silicates containing copper and iron were also used
Metallic inks	mixture with variable composition of copper, lead, silver, gold and sometime added with orpiment (arsenic) and earths (iron)

TABLE 1 THE BIBBIA AMIATINA PALETTE

The ms. 492 *Pontificale* of Museo Diocesano di Salerno is dated back to a period from the end of 13th century and the incoming of the 14th. The manuscript consists of 349 parchment sheets each having dimensions 400 x 285 mm. The miniatures of excellent quality, ascribed to anonymous illuminators working in the Bologna area, were not always completed: in some cases only the preliminary design was present, in other cases the preparation was not covered by the gold-leaf. These circumstances gave the unique opportunity to investigate the different techniques used by the miniaturists and in particular the composition of the gold preparations and their comparison with the medieval recipes. Using the different penetration depth of the three applied techniques it was possible to carry out a completely non-destructive stratigraphy. Resulting palette is summarized in Table 2 .

Colour	Composition
Gold	pure gold leaf, only rarely added with silver
Yellow	mosaic gold; yellow-ochre
White	lead white
Red	red lead, cinnabar
Blue	lapis-lazuri, azurite
Brown	ochre, earths
Pink	organic lake mixed with lead white
Preparations for gold	armenian bole + gypsum; armenian bole + gypsum + white lead; gypsum + white lead

TABLE 2 THE PONTIFICALE PALETTE.

The experimental results also allowed to prepare laboratory reproductions of the original illuminations, that were artificially aged and deteriorated in order to test different adhesives on them and to choose the best and less invasive preservation treatment. The Decretum Gratiani, ms. *Piana 3.207* (13th-14th c.), also known as *Concordantia discordantium canonum* is a collection of Canon law. The code consists of 329 parchment sheets (455 mm x 280 mm) and is preserved at the Biblioteca Malatestiana in Cesena, Italy. The restoration of ms. *Piana 3.207* was the topic of project *Salviamo un codice 2nd edition*, an initiative of Alumina – Nova Charta press – with the High Patronage of the President of the Italian Republic (Savoia 2008). Ms. *Piana 3.207* had been preserved in a very good condition up to the '80s, when it was dramatically maimed: thirteen pages were torn off, damaging the sewing of the binding, and stolen. In the following years, the law enforcement retrieved all the missing pages but one (c.107) which is now considered lost. ICPL (now Icpal), the institutional authority appointed for library materials preservation, was responsible for the thorough scientific analysis of the manuscript and for the subsequent restoration.

XRF and Raman measurements allowed us to characterize the palette (Table 3).

Colour	Composition
Gold	pure gold leaf, only rarely with traces of copper; mosaic gold
Yellow	not fully reacted mosaic gold; yellow-ochre
White	lead white
Red	red lead, cinnabar, earths
Blue	indigo, azurite
Brown	ochre, earths
Green	not fully reacted mosaic gold mixed with indigo
Black	carbon black (for inks, contour lines and shadows)
Other colours	mixture of the previously described pigments for other colours and tones
Preparations for gold	white lead

TABLE 3 THE MS. *PIANA* PALETTE.

Very interesting was the discovery that gilded miniatures had been realised either with pure gold or with mosaic gold (tin IV sulphide; Fig.1 and 2). The latter pigment, a yellow crystalline powder that closely resemble gold, was widely used in Europe in the Middle Age and in the Renaissance and in ms. *Piana* was applied not as gold-imitation but in order to obtain particular hues.

To confirm the presence of mosaic gold, a standard Raman spectrum was necessary. Due to the fact that modern preparation of stannic sulphide differs from the ancient methods and that Raman spectra from literature (Edwards et al. 2003, 2291) had been obtained from the modern compound, we decided to prepare mosaic gold following ancient recipes. Many texts were consulted, but the most detailed recipe was found in *De Arte Illuminandi*¹. Concerning amounts of reagents, not cited in

1. Handbook of technical recipes, written in Latin by anonymous authors in the 14th century and currently kept at the Biblioteca Nazionale di Napoli (Napoli, Italy).

2. Sulphur and Mercury are the alchemic pair. They are transported into the «labyrinth of the transformation of matter» by the external fire. In the Temple (crucible, Ed.) their marriage is celebrated and is only possible with the help of the arcane fire of salt – the alchemic Priest – able to transform the metals. In chemical terms, amalgam increases the reactivity of tin; mercury reduces sulphur to sulphide. In meantime elemental tin is oxidized to tin IV. Ammonium chloride decreases the reaction temperature, allowing the formation of stannic sulphide.

the recipe, we decided to use the proportions suggested by *Villavecchia: Dizionario di Merceologia e di Chimica Applicata* (Villavecchia 1932).

The procedure foresees many steps: preparation of Hg-Sn amalgam, addition of sulphur and ammonium chloride and heating for a long time, choosing the temperature in order to obtain the desired hue. In this process we can recognize the two first steps of the alchemic *Opus Magnum*, the *nigredo* (mixing amalgam and the two others compounds the mixture becomes black) and the *albedo* (during heating, dense white fumes rise)². When no more fumes appear, heating is stopped and a gold-coloured powder is found in the crucible: this is mosaic gold.

Even when observed at the microscope, the similarity between the mosaic gold prepared in the lab and the pigment used on the ms. *Piana 3.207* is total and Raman spectroscopy demonstrates that the two compounds had the same structure.

The effectiveness of the presented techniques in analysis of such invaluable manuscripts, the related scientific advance and the more than positive feedback from restorers who take advantage from the obtained information, confirmed once more the Institute choice of pioneering and always pursuing multidisciplinary based on strictly non-destructive methods. ●

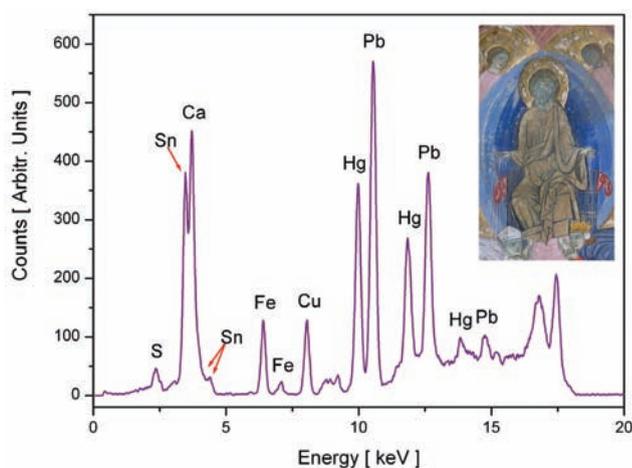


FIG.1 X SPECTRUM OF MOSAIC GOLD FROM THE ORIGINAL (CHRIST ROBES). X RAY SOURCE ^{96}Mo ; COLLIMATOR 0.5 mm DIAMETER, ACQUISITION TIME 600 s, X TUBE TENSION 25 kV, CURRENT 0.300 mA, ESD SILICON DETECTOR, RESOLUTION 160 eV AT 5.9 keV

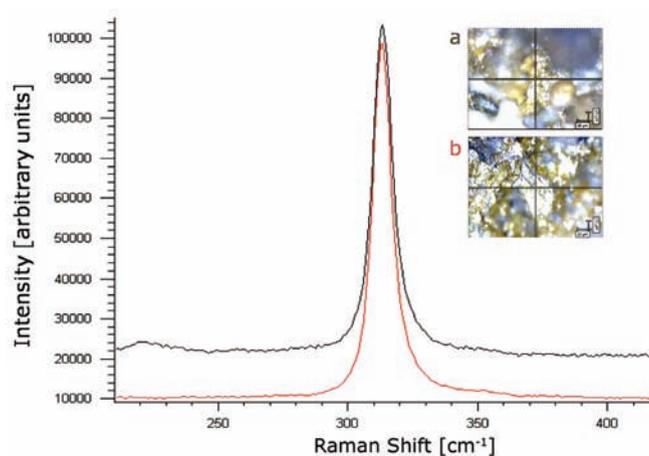


FIG.2 COMPARISON BETWEEN THE RAMAN SPECTRA OF MOSAIC GOLD LABORATORY SAMPLE (BLACK LINE, MICROSCOPE IMAGE «A») AND OF THE ORIGINAL PIGMENT (RED LINE, MICROSCOPE IMAGE «B»). EXCITATION $\lambda = 785 \text{ nm}$

Bibliography

Bicchieri, Marina, Francesco Paolo Romano, Lighea Pappalardo, Luigi Cosentino, Michele Nardone, Armida Sodo. 2001. «Non-destructive Analysis of the Bibbia Amiatina by XRF, PIXE- α and Raman.» *Qvinio: International Journal on the History and Conservation of the Book* 3: 169-79.

Bicchieri, Marina, Michela Monti, Giovanna Piantanida and Armida Sodo. 2008. «All that is iron ink is not always an iron-gall!» *Journal of Raman Spectroscopy* 39, no 8: 1074-78.

Cesareo, Roberto, Alfredo Castellano, Giovanni Buccolieri, Stefano Quarta, Maurizio Marabelli, Paola Santopadre, Marcella Leole, Antonio Brunetti. 2004. «Portable equipment for energy dispersive X-ray fluorescence analysis of Giotto's frescoes in the Chapel of the Scrovegni.» *Nuclear Instruments and Methods in Physics Research B* 213: 703-06.

Colthup, Norman B., Lawrence H. Daly and Stephen E. Wiberley. 1990. *Introduction to Infrared and Raman spectroscopy*. San Diego: Academic Press Inc.

Edwards, Howell G.M., Emma L. Dixon, Ian J. Scowen, Fernando Rull Perez. 2003. «Lead/tin mirror formation from mixtures of red lead and tin sulphide.» *Spectrochimica Acta Part A* 59: 2291-99.

Malzer, Wolfgang, Oliver Hahn and Birgit Kanngießer. 2004. «A fingerprint model for inhomogeneous ink-paper layer systems measured with micro-x-ray fluorescence analysis.» *X Ray Spectrometry* 33: 229-33.

Pappalardo, Lighea, Andreas G. Karydas, Despina Kotzamani, Giuseppe Pappalardo, Francesco Paolo Romano and Charalambos Zarkadas. 2005. «Complementary use of PIXE-alpha and XRF portable systems for the non-destructive and in situ characterization of gemstones in museums.» *Nuclear Instruments and Methods in Physics Research B* 239:114-21.

Pappalardo, Lighea, Marina Bicchieri, Michele Nardone, Giuseppe Pappalardo, Francesco Paolo Romano, Pio Alfonso Russo, Armida Sodo. 2008. «The LNS portable PIXE-alpha system for the examination of gold preparations in the Salerno 492 code miniatures.» *X-Ray Spectrometry* 37 no 4: 466-69.

Savoia, Daniela, ed. 2008. *Per giusta causa. Il restauro del Decretum Gratiani (Ms. Piana 3.207) della Biblioteca Malatestiana di Cesena*. Padova: Edizioni Nova Charta.

Villavecchia, Vittorio. 1932. *Dizionario di merceologia e di chimica applicata*, vol. 4. Milano: Ulrico Hoepli.

Biographies

Dr. Marina Bicchieri works since 1979 in cultural heritage field and from 2000 she is the director of the chemistry department in Istituto centrale restauro e conservazione del patrimonio archivistico e librario of Rome-Italy (former ICPL). Her research activity is focused on the chemistry of library materials (cellulose, parchment, inks, pigments, charges, adhesives, sizes), the study and set-up of new restoring products and new non-destructive diagnostic methods (μ -Raman, XRF, PIXE- α , μ -IR, AFM, UV-Vis-NIR, SEM) for writing supports and graphic media.

She taught classes in chemistry, conservation and restoration organized by Italian and foreign Universities and Public Institutions, the European Union, and several private institutions.

Michela Monti obtained her Master Degree in chemistry at University of Rome «La Sapienza» in 2000. From 2001 to 2002 she worked as researcher in the field of conservation of cultural heritage at the University of Udine and at the Istituto Centrale per la Patologia del Libro in Rome.

From 2002 to September 2005 she worked as consultant for industrial safety, focusing on the prevention of chemical risk. Since September 2005 she works for the Chemistry Department of the Istituto Centrale il Restauro e la Conservazione del Patrimonio Archivistico e Librario (former Istituto Centrale per la Patologia del Libro), focusing on the application of X-ray fluorescence for the analysis of library materials and carrying out research projects on new methods for restoration and conservation of paper and parchment.

Giovanna Piantanida, after achieving a M. Sc. in Physics (2000), worked for three years in the Italian R&D site of L.M. Ericsson Corporate. She then decided to turn back to research activity and obtained a post-doc position in the Department of Physics, at University of Rome «La Sapienza», co-funded by ICPL, an institution within the Italian Ministry for Cultural Heritage and Activities. The research project was the finalization of diagnostic protocols based on physics methods, in particular Atomic Force Microscope. Currently, she is a fellow researcher at the Laboratory of Chemistry Icpal (former ICPL) and she is pursuing PhD in analytical chemistry at University of Ljubljana.

Armida Sodo is researcher at the Physics Department of University Roma Tre. After the degree in Chemistry (1998), she obtained the PhD in Chemical Physics and then got a post-doc position at ESRF (European Synchrotron Radiation Facility). Her research studies concern principally spectroscopic – principally Raman – investigation on Cultural Heritage; in particular degradation process analyses, material characterisation and development of instruments devoted to Cultural Heritage applications. She gives university courses and is co-author of more than 40 publications on international journals, books and conference proceedings.