The two illuminated medieval manuscripts selected for the MOLAB application: the Four Gospels Book of Humor and the Four Gospels Anonymous Book from the time of Prince Stephen the Great and Prince Bogdan the Third, preserved at the Monastery of Putna, are considered masterpieces of the Moldavian art, at the end of the 15th century and the beginning of the 16th century, due to their fine artistic and historical value.

The Four Gospels Book of Humor, written by the hieromonk Nicodim from Putna, was ordered by the Moldavian Prince Stephen the Great (1475 – 1504) who offered it in 1473 to the old church of the Humor Monastery (founded before 1415). The manuscript produced in the Scriptorium of Putna Monastery has five miniatures in full illumination (Fig.1) and it is written in Slavonic on 278 parchment sheets in folio. The covers of gilded silver hammered au repoussé technique were made in the Humor Monastery. Book was modelled after the famous Gospel Book written in 1429 at Neamt Monastery by Gavril Uric upon the request of Princess Marina and Prince Alexander the Good, the grandfather of Stephen the Great, now preserved at the Bodleian Library in Oxford1,2.

The Four Gospels Anonymous Book is the last manuscript from the time of Stephen the Great. Abandoned few months before death of the great prince, the work on this book was continued by his son, prince Bogdan the Third. The manuscript was finished completely and bounded in precious metal covers on 5th of May 1507. It
contains four miniatures (Fig.2) and 380 parchment sheets written in Slavonic by an anonymous calligraphist. The covers are made of gilded silver worked *au repoussé*.  

Fig.2 The illuminated miniatures in the Anonymous Gospel Book representing the four Evangelists: Mark and Luke, Matthew and John.

Research on the materials and techniques was carried out using the following MOLAB in-situ techniques: XRF, micro-Raman, fiber-optic Mid FT-IR and NIR (Fig.3). The results obtained permitted identification of almost all the pigments used in the miniatures and decorations. Interesting information on inks composition, on the possible nature of some of the binders in miniatures and on metal cover composition was also obtained.

The main objective of this research was to determine the materials and techniques used in making the manuscripts, to establish the palette of pigments and compare the resulting information with the existing one on pigments reported as present in the European medieval manuscripts.  

94 XRF, 43 Mid FT-IR, 7 NIR and 17 micro-Raman measurements were performed on the Humor Gospel Book (Fig. 4). The pigments identified in the artist’s palette were: gold; silver; white: lead white (PbCO₃xPb(OH)₂), calcite (CaCO₃); red: cinnabar (HgS), bole – iron earth pigment; orange: iron ochre; pink violet: a mixture of lead white and an organic pigment; violet – an organic pigment (possible a lake); violet dark: azurite and an organic pigment; blue: azurite (2CuCO₃xCu(OH)₂); green: malachite (CuCO₃xCu(OH)₂), green earth (hydroxilicate of Fe, K, Mn and Al); brown: ochre; black: carbon black; grey: lead white and carbon black. On the Evangelist Matthew’s page only the lead white applied on the parchment was detected by XRF and confirmed by FT-IR. In the other four miniatures pages and the title pages, calcium in major amounts was detected on parchment by XRF, suggested as calcite by FT-IR.
The metallic covers and the book binder chain buttons analyzed by XRF were determined to be made of gilded silver with varying impurities present: copper in major amounts (detected in the gold consumed areas) and traces of Ni, Fe, Cr. The presence of Hg revealed in all the XRF measurements confirmed that the gilding technique with gold amalgam was employed. The big pink jewels placed on the front cover at its corners, probably semiprecious crystal rock stones, were found to be quartz with Ca, K, Fe, Mn and/or Ni impurities.

Fig.4 The Humor Gospel Book - the back gilded silver cover representing the Assumption of the Virgin, the miniature representing the Evangelist Mark and the votive unfinished miniature representing Prince Stephen the Great. Areas where XRF (in red), micro-Raman (in green), Mid FT-IR (yellow) and NIR (blue) spot analysis were carried out are indicated.

On the Anonymous Gospel Book 34 XRF, 26 Mid FT-IR, 13 NIR and 16 micro-Raman analysis were carried out. The artist’s palette was found to be almost similar as for the Humor Book: gold; white: lead white; red: cinnabar, bole – iron earth pigment; yellow: ochre; pink violet: a mixture of lead white and an organic pigment; blue: azurite; green: malachite; brown: ochre; black: carbon black; grey: lead white and carbon black. In addition to the above mentioned pigments, the white: gypsum (by FT-IR); yellow: orpiment (As$_2$S$_3$); orange: cinnabar and orpiment; pink: lead white and cinnabar, and different shades of green: probably mixtures of azurite and orpiment, and mixtures of malachite, lead white and green earth, were also detected by XRF.

On the gold areas, bands indicative of a proteinaceous binder were revealed by FT-IR on both manuscripts. Evidence of the presence of a gum was found on some illuminated areas. Three colored inks were identified in both manuscripts: gold, red and black. The gold ink used in the title pages of each Gospel was found to be colloidal gold. Identification of Hg (by XRF) in the composition of red ink suggested that a cinnabar-containing ink was employed. Black ink was detected to be an iron gall ink (XRF). It is known that this type of ink could cause deterioration of the parchment or paper support. However, the black written parchment pages in our manuscripts were found to be in a quite good state of preservation. Important amounts of copper, supposedly related to the ink preparation process, were also detected (XRF) in the Humor manuscript only.

In this report some preliminary observations were presented. Further discussion and conclusions are intended to be presented soon into a future paper.

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