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The Book of Kells: A non-invasive MOLAB investigation by complementary spectroscopic techniques

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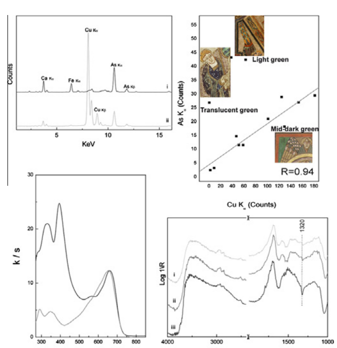
HIGHLIGHTS

- The Book of Kells is assessed by non-invasive in situ portable spectroscopy.
- Complementary techniques highlight the intentional use of anhydrite.
- Rare identification of the organic lichen dye, orchil in a manuscript.
- Alteration of organic black giving rise to calcium carboxylate and calcium oxalate.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper highlights the efficacy of non-invasive portable spectroscopy for assessing the execution technique and constituent materials in one of the most important medieval manuscripts, the Book of Kells. An aimed campaign of in situ measurements by the MObile LABoratory (MOLAB) has analyzed its elemental composition and vibrational and electronic molecular properties. The ample analytical toolbox has afforded complementary diagnostic information of the pigment palette permitting the characterization of both inorganic and organic materials as pigments and dyes in the white, purple, blue, red, orange, green and black areas. In particular, the novel widespread use of calcinated gypsum (anhydrite) as both a white pigment and in correlation to the organic dyes in this manuscript has been noted. The non-invasive identification of the organic dye orchil is significant considering its rare non invasive detection in medieval manuscripts. Finally the occurrence of particular alterations of the organic black areas giving rise to calcium carboxylate and calcium oxalate has been specifically highlighted. Importantly, this work elaborates complex aspects of the employed painting materials which have given rise to numerous significant points of interest for a more elaborate understanding of this Irish treasure.

Introduction

Recent advances afforded to the development of analytical techniques have aided the introduction and routine use of portable instrumentations which enable valuable investigations to be carried out in a non-invasive manner. This strategy has become

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particularly important for analyses in the field of cultural heritage as this advantage eliminates the necessity to sample the artworks under study and can be supported by the rich array of literature of non-invasive studies applied to a variety of objects. In particular for the examination of manuscripts, recent non-invasive protocols have been shown to be notably adapt where a multi-analytical approach is capable of supplying information regarding both the elemental and structural composition of the object. Such information is diagnostic of constituting materials (support, pigments, binders, etc.) of these often fragile artworks that can lead to considerations concerning the overall state of conservation and eventual restoration methodologies [1–3]. Moreover, access to MOLAB combines a sophisticated toolbox of state of the art non-invasive portable analytical instruments for point and image analyses in multi-geometrical situations with a unique capability to carry out all examinations in situ (i.e. where the artwork is exhibited or conserved) [4]. It is through data collected during the MOLAB intervention that this work is fruit of interpretation of one of Ireland's treasures, the Book of Kells housed at Trinity College Dublin.

The Book of Kells, a calfskin-parchment manuscript, dating from around 800 CE, is a surviving example of medieval Christian art of the gospel by Matthew, Mark, Luke and John [5,6]. Surrounding the text, are elaborately decorated symbols and portraits of varying sizes and complexity. Only a limited number of investigations have been performed on the Book of Kells, and were carried out principally by light microscopy from the 1960s and hypothesised a creative yet restrictive color palette [7]. A more recent in situ examination by Micro Raman spectroscopy has permitted an important evaluation of the pigment palette [8]. The role of MOLAB has been to complement the earlier investigations by implementing a multi-analytical protocol to characterize even further, the main inorganic and organic materials present in the colored decorations of the white, purple, blue, red, orange, green and black areas.

A preliminary elemental study of numerous folios and zones of particular interest was carried out by X-ray fluorescence (XRF). UV–VIS spectroscopy in reflection (FORS, fibre optic reflectance spectroscopy) and in emission (RF, reflectance fluorimetry) and TC-SPC, time correlated single photon counting technique, was used to gain information leading to the possible identification of natural organic dyes used as pigments. Furthermore, vibrational spectroscopy in the medium (mid-FTIR) Infrared region was utilized to obtain information concerning the molecular nature of the organic and inorganic compounds relative to the fundamental materials of the painting layers and/or altered products as an indicator of their state of conservation. As a result of this non-invasive study, numerous new complex aspects of the painting materials and execution techniques utilized have been highlighted and researched to obtain a further understanding of the highly prized Irish Gospel book.

Experimental

The portable instrumentations are part of MOLAB which were accessed for measurements through the EU-ARTECH project (Access, Research and Technology for the conservation of the European Cultural Heritage). This project at the time of writing this work has become CHARISMA (Cultural Heritage Advance Research Infrastructures Synergy for a Multidisciplinary Approach to Conservation/Restoration) [9–11].

X-ray fluorescence (XRF)

XRF spectra were recorded using portable equipment made with a miniaturized X-ray generator EIS P/N 9910, equipped with a tungsten anode and a silicon drift detector (SDD) cooled with a Peltier element. The SDD has a resolution of about 160 eV at 5.9 keV. The portable instrument allows the detection of elements with atomic number higher than silicon ($Z > 14$). The excitation parameters used during the investigations were: voltage of 38 kV and current of 0.05 mA. The acquisition time was 120 s. The distance sample-detector was fixed at 2 cm. The beam diameter under these conditions was 4 mm. A PyMCA 4.2.1 fitting has been employed for calculating the areas of each element in order to obtain a semi-quantitative response for the most important fluorescent lines. The resulting areas have been further standardized by the presence of Zr in each spectrum and the data are expressed by dividing the fitted area by the acquisition time (120 s).

Reflection mid-Infrared (mid-FTIR)

Spectra were recorded using a portable JASCO VIR 9500 spectrophotometer equipped with a Remspec mid-Infrared fiber optic sampling probe. The bench is made up of a Midac Illuminator IR radiation source, a Michelson interferometer and a liquid nitrogen cooled MCT (Mercury Cadmium Telluride) detector. The fiber optic probe is a bifurcated cable containing 19 chalcogenide glass fibers that allow the collection of spectra in the range 4000–900 cm^{-1} at a resolution of 4 cm^{-1}. The width of the investigated area is determined by the probe diameter which is about 4 mm. The total reflectivity, R, due to the combined diffuse and specular components, is measured using the spectrum from an aluminum mirror plate as background. The spectrum intensity was defined as the pseudo absorbance A′ where $A' = \log(1/R)$.

Fiber optics reflectance spectroscopy (FORS)

UV–VIS reflectance spectra were collected using a portable spectrophotometer assembled using the following components: a deuterium halogen lamp, an Avantes CCD spectrometer (sensitivity 86 photons/counting) in the 250–850 nm range, a bifurcated bundle of quartz fibers and a 45° probe-head. The spot size is about 12 mm^2; each spectrum is collected using 800 ms integration time and the final output consists in 5 averaged spectra.

Reflectance fluorimetry (RF)

The portable fluorimeter was assembled at the University of Perugia [12] using separate components: the light source (175 W Cermax Xenon lamp) is focused on a H-10 Jobin Yvon UV-monochromator (linear dispersion 8 nm/mm) for selecting the excitation wavelength. A silica-fused fibre-optic cable directs the exciting light on the sample. The emitted light is convoyed by another fibre-optic cable to a high sensitivity (86 photons/counting, 2048 pixels, 200–1100 nm range) Avantes CCD spectrometer. A large number of short band-pass and long-pass filters, suitable to avoid scattered and higher harmonic excitation light, are also available to be used in on-line filter holders both in excitation and emission.

Portable single photon counting apparatus (TC-SPC)

The instrument was assembled at the University of Perugia [13] and is composed by a pulsed source with interchangeable diodes and LEDs (two diodes, emitting at 375 and 650 nm, picosecond time scale, and one LED at 455 nm, nanosecond time scale), a photocathode detector working in the 350–850 nm range suitable for the detection of emissions of all organic colorants; a FluoroHub electronic device containing the TAC (time–amplitude converter) and a PC which fully controls the system of data acquisition and elaboration. A fibre optic sampling system, composed by a 400 mm single silica fused fibers, transfers the excitation light to whichever point on a surface. A co-axial crown, constituted by 6