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Optical spectroscopy of ancient paper and textiles

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Summary. — Ancient paper and textiles represent a striking example of optically inhomogenous materials whose optical responses are strongly governed by scattering effects. In order to recover the absorption coefficient from non-invasive and non-destructive reflectance measurements a specific approach based on Kubelka-Munk two-flux theory must be applied. In this way quantitative chemical information, such as chromophores concentration, can be obtained, as well as quantitative spectra of additional substances such as pigments or dyes. Results on a *folio* of the Codex on the Flight of Birds by Leonardo da Vinci and a linen cloth dated back to 1653 and called the Shroud of Arquata, a copy of the Shroud of Turin, will be presented.

1. – Introduction

Natural fibres produced by plants are employed since the ancient times as a convenient raw material for manufacturing of several artefacts. In particular, cellulose has played an important role in human civilization because it has been widely used for the production of paper and textile.

The development of textile and clothing manufacture dates back to prehistory. The earliest known woven textiles appeared in the Middle East during the late stone age [1]. Textiles are mostly made of spun fibres woven to make fabrics. Weaving is a method of textile production in which two distinct sets of yarns or threads are interlaced to form a fabric or cloth. The longitudinal threads are called the warp and the lateral threads are the weft. The method in which these threads are interwoven affects the characteristics of the cloth [2]. From the ancient times to the present day, methods of textile production have continually evolved.

The inventor of paper was probably the Chinese court dignitary Ts'ai Lun who began making paper using plant fibres and rags in 105 A.D. [3]. For over 700 years the secret of paper making was jealously stored in the Celestial Empire. Only after many centuries the

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paper making technique spread to Europe, through Arabia, Egypt, Spain and Italy [4]. Production of paper in Spain appeared before 1150 and in Italy before 1230, gradually replacing the more expensive parchment as a material to write on. Some legal documents attest the presence of the first Fabriano (Italy) paper-makers as early as 1283. In France, paper mills settled mainly in Champagne and Lorraine from the mid-fourteenth century. In German-speaking regions, the first mill was probably the Gleismühl of Ulman Stromer in Nuremberg, founded in 1390 [4].

Paper is obtained from a dilute suspension of cellulose fibres in water, that are then drained through a sieve, pressed and dried, to obtain a self-sustaining sheet composed of a network of randomly interwoven fibres. Additional compounds varies depending on the production period and technology employed. In the 15th century in Europe paper was made up of pure cellulose fibres (more than 90% in weight) from cotton, linen or hemp, usually obtained from rags with the addition of animal glue as a sizing agent (about 5% in weight) [5]. Besides cellulose, most of modern paper also contains a relevant quantity of lignin and fillers.

The optical properties of paper and textiles can be properly understood by the combined knowledge of the chemical nature of cellulose molecules and their supermolecular arrangement at different scales. From a chemical point of view cellulose is a linear homopolymer composed of β-D-glucopyranose units $(C_6H_{10}O_5)_n$, which are linked together by β-(1,4)-glycosidic bonds up to form chains with n ranging from $\approx 10^2$ to $\approx 10^4$ elements [6]. The cellulose chains aggregate through an extended network of both intra and intermolecular hydrogen bonds. As a consequence slender bundles of cellulose polymers (2–4 nm in cross section) are formed, called elemental fibrils, which in turn are made up of an assembly of ordered (crystalline) domains and disordered (amorphous-like) regions. In cotton, the crystalline domains are about 100 nm in length [7, 8]. Elemental fibrils aggregate to form microfibrils and then fibres with typical dimensions of about 10 μm in cross section and 1 mm in length. Bonding between single fibres establishes the coherent paper sheet structure (fig. 1).

A system of pores and voids, non-uniform in sizes and shapes, is contained in paper and textiles structure. Their size distributions span from pores diameters of approximately 1 nm when they are fully confined in the amorphous regions of cellulose elemental fibrils, to tens of microns among fibres. Arrangement and distribution of pores and voids within the structure strongly influence external agents accessibility as well as mechanical and optical properties [7, 9, 10].

Degradation of cellulose artefacts depends on the environmental conditions to which they have been subjected [11]. At a macroscopic scale, degradation appears as weakening of the mechanical properties and as discoloration of the substratum. From a microscopic perspective cellulose degradation can be modeled as due to the combination of two most important processes: hydrolysis of β-(1,4)-glycosidic bonds (chiefly affecting the mechanical properties of the artefacts), and oxidation of the β-D-glucopyranose units [11-14].

Some oxidation products are responsible for the changes of the optical properties of cellulose artefacts during aging. In fact, pristine cellulose does not absorb light below about 6 eV (above about 200 nm) [11, 12]. Degraded cellulose, instead, shows an optical absorption spectrum with a broad peak or a shoulder around 4.8 eV (about 260 nm), and a long absorption tail towards lower energies with an additional shoulder at about 3.6 eV (about 340 nm). The yellow color seen in aged cellulose artefacts is mainly due to this absorption tail extending to the violet and blue spectral regions of visible (Vis) range. Yellow and red portions, instead, are largely scattered thereby producing the characteristic yellow-brown hue [12, 15, 16].

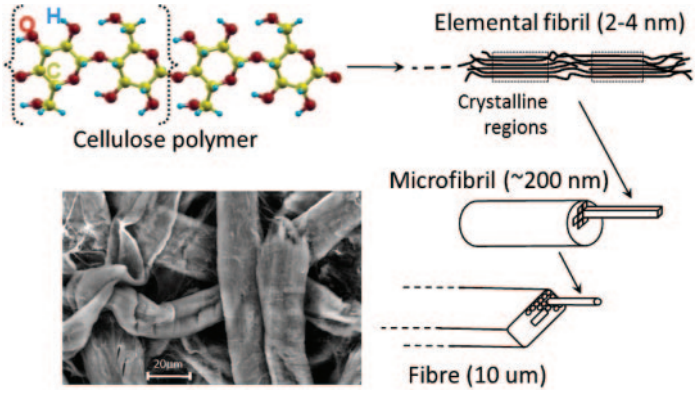

Fig. 1. – Schematic view of the supermolecular structure of cellulose polymers within a fibre and image of Whatman no. 1 paper sample, without prior preparation, obtained by using a Zeiss EVO40 variable pressure electron microscope.

The complicated inner structure of paper and textiles, composed of fibres and pores determines how light propagates inside the artefacts. Indeed, paper and textiles represent striking examples of optically inhomogeneous materials characterized by the presence of elastic light scattering (random media made of random scatterers) which affects their optical response and produces relevant effects on reflected or transmitted light [17]. For example, the white appearance of non-degraded and non-coloured paper or textiles is due to light scattering [18]. In the presence of scattering, the reflectivity of materials is commonly referred to as diffuse reflectance [19].

In the Vis and ultraviolet (UV) region scattered light exceeds absorption so greatly that it is not longer possible to obtain a useful transmission spectrum of paper and textiles without taking account of scattering. On the other hand absorption spectra measured over the UV-Vis range of wavelengths give direct information on the nature and chemistry of the chromophores that contribute to the colour of the artefacts made of cellulose.

Obtaining the absorption spectrum from the measured transmittance or diffuse reflectance of a simultaneously scattering and absorbing material is of great practical importance for the characterization of industrial products of all kind (pigments, textiles, paper, paints, plastics, etc.). To this goal, a number of theories have been developed [19]. The most successful approach is the Kubelka-Munk (K-M) theory [19,20], a two-flux approach to the general radiation transfer theory, describing the propagation through a medium that absorbs, emits, and scatters light. Recently, the K-M model has been extended to accommodate a wider range of optical absorption [17,21]. By this models it is possible to obtain quantitative spectroscopy and analysis of inhomogeneous materials.

In this paper the approach for recovering scattering and absorption coefficients from non-invasive and non-destructive reflectance measurements of ancient paper and textiles is presented. In this way, the optical properties can be obtained up to the UV region where degraded artefacts show strong chromophores' absorption. This knowledge allows chemical information at the molecular level to be extracted. In addition it is possible to discriminate the spectroscopic change due to aging with respect to other agents able to change the colour of the cellulose-based materials, like pigments or dyes.

2. – Methods

2˙1. *Wave propagation and scattering in random media.* – Analytical theories and transport theories are the general approaches to the problem of wave propagation in random media in the multiple-scattering regime [18]. In analytical theories statistical quantities are obtained by introducing the scattering and absorption characteristics of the medium in basic differential equations such as the Maxwell equations or the wave equation. In transport theories the basic differential equation is called the equation of transfer and is equivalent to Boltzmann's equation used in the kinetic theory of gases and in neutron transport. This formulation is capable of treating many physical phenomena.

The transport theory describes the propagation of intensities in randomly inhomogeneous media in terms of the specific intensity $I(\mathbf{r}, \hat{s})$, which is in general a function of position $\mathbf{r}$ and direction $\hat{s}$ in three-dimensional space. However, even for simple geometry, such as parallel-plane random medium illuminated by a plane wave normally incident upon it, no closed-form solution has been found for a general arbitrary phase function [18]. Approximate methods called two-flux and four-flux theories based on simple algebraic operations have been found to give reasonably good agreement with experimental data. Two-flux theory adequately describes the experimental results if the illumination is diffused. Collimated beams should be handled by the four-flux theory.

2˙2. *Optical spectroscopy of random media.* – K-M theory is based on a model of two light fluxes traveling in the forward and backward directions [19, 20]. Let us consider diffuse radiation fluxes $I(z)$ and $J(z)$ traveling in the positive and negative z-directions, respectively (fig. 2). Let us designate the absorption coefficient and the scattering coefficient per centimeter of the medium for diffuse radiation by k and σ respectively. Then, within the layer $\mathrm{d}z$ the fraction $kI2\mathrm{d}z$ will be absorbed, and the fraction $\sigma I2\mathrm{d}z$ will be lost by back scattering. Factor 2 takes into account that the mean path length of completely diffuse radiation is twice the geometrical layer thickness [19]. The radiation flux J from below will itself give the fraction $\sigma J2\mathrm{d}z$ through the scattering in the positive z-direction. Overall, the intensity change from I in the layer element $\mathrm{d}z$ is made up of three parts $\mathrm{d}I = -(k+\sigma)2I\mathrm{d}z + \sigma J2\mathrm{d}z$. Similarly, we obtain the intensity reduction of J in the negative z-direction $\mathrm{d}J = (k+\sigma)2J\mathrm{d}z - \sigma J2\mathrm{d}z$.

If we designate $2k \equiv K$ and $2s \equiv S$ we obtain the two coupled differential equations

$$\begin{aligned} \frac{\mathrm{d}I(z)}{\mathrm{d}z} &= -(K+S)I(z) + SJ(z), \\ \frac{\mathrm{d}J(z)}{\mathrm{d}z} &= (K+S)J(z) - SJ(z). \end{aligned} \tag{1}$$

Solutions to eq. (1) with the appropriate boundary conditions provide expressions for the diffuse reflectance $R = J(0)/I(0)$ and transmittance $T = I(t)/I(0)$ of the optical inhomogeneous layer of thickness t in terms of S and K parameters [18, 19].

When the randomly inhomogeneous layer is of infinite thickness (or infinite optical thickness) then the reflectance R_∞ depends exclusively on the ratio of the absorption and scattering coefficients K and S

$$A_{KM} = \frac{K}{S} = \frac{(1-R_\infty)^2}{2R_\infty}, \tag{2}$$

where A_{KM} is the so-called K-M pseudo-absorption or remission function [19], which can be readily recovered from the experiments once the absolute reflectance of a reference

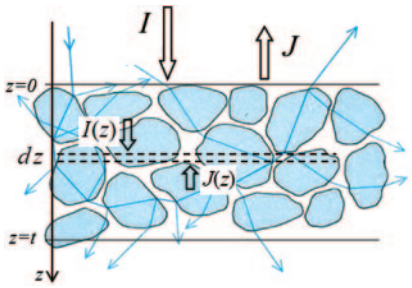

Fig. 2. – Positive (I) and negative (J) flowing fluxes in an inhomogeneous layer of thickness t. The random propagation of a single light ray subjected to multiple refractions and reflections is also sketched (cyan lines).

material is known (for example, Spectralon®, Labsphere, Inc., USA, with $R \cong 1$ in a wide wavelength range).

The relationship between the concentration, c, of a specific compound within the random medium and R_∞ is given by $A_{KM} = \frac{K}{S} = \frac{\epsilon c}{S}$, where ϵ is its molar absorptivity. For quantitative purposes, a calibration procedure by using reference standards of known concentration is necessary.

However, calibration procedures are impossible to realize on actual cultural heritage samples made of paper or textiles. Therefore, it is necessary to recover K and S individually from reflectance measurements. A suitable method for cultural heritage is as follows. The reflectance spectra, R_b and R_w, of a single sheet of paper or textile placed, respectively, over a poor-reflecting (black) and a good-reflecting (white) backgrounds are recorded. Reflectance of black and white backgrounds, R_{bb} and R_{wb} respectively, are also recorded. The reflectance R_∞ that would have an infinite layer of the same sample can be calculated from equations [19]

$$R_\infty = a - \sqrt{a^2 - 1}, \tag{3}$$

where

$$a = \frac{(R_{wb} - R_{bb})(1 + R_w R_b) - (R_w - R_b)(1 + R_{wb} R_{bb})}{2(R_b R_{wb} - R_w R_{bb})}. \tag{4}$$

Once R_∞ is determined, it is possible to recover the S and K coefficients by

$$S = \frac{1}{t(\frac{1}{R_\infty} - R_\infty)} \ln \frac{(1 - R_b R_\infty)(R_\infty - R_{bb})}{(1 - R_\infty R_{bb})(R_\infty - R_b)}, \tag{5}$$

$$K = \frac{S(1 - R_\infty)^2}{2R_\infty}. \tag{6}$$

The constants K and S are assumed dependent on the intrinsic absorption and scattering properties of the medium. However, experiments demonstrated an inherent nonlinear relationship between K and S and the physical intrinsic optical properties of the materials, represented by the absorption and scattering probabilities, α and s, respectively. In 2005, the K-M model has been extended by Yang and Miklavcic (Y-M) in order to face

these problems [21]. In this approach, the effect of photon scattering on the path length of light propagating into an absorbing and scattering medium is taken into account. The essential point is that the scattering that takes place within the random medium has an influence on the final probability of a photon being absorbed. This leads to new analytical relationships between the K-M phenomenological scattering S and absorption K coefficients and the intrinsic scattering s and absorption α coefficients of a material:

$$\alpha = \frac{K}{2\mu}, \quad s = \frac{S}{\mu}, \tag{7}$$

where $\mu = \sqrt{2SD}$,

$$D = \frac{1}{A}\frac{1 - 2Ate^{(-At)} - e^{(-2At)}}{1 - 2e^{(-At)} + e^{(-2At)}} \tag{8}$$

and $A = \sqrt{K^2 + 2KS}$. All variables depend on the wavelength λ of incident radiation. The quantity $\mu = \mu(s, a)$ is the scattering-induced path variation (SIPV) factor [21]. It describes the influence of light scattering on the total path length and is nonlinearly dependent on both the absorption and scattering properties of the medium. D represents the average depth of photons that undergo reflection and exit the upper surface of the paper sheet [21].

If samples are optically thick, R_w and R_b assume the same value, and singularities in the K-M equation for S (eq. (5)) appear, because of the vanishing denominator in the argument of the logarithm ($R_\infty = R_b$). Therefore, in order to estimate α, a different approach to estimate S in the wavelength region where samples are optically thick is needed. This was recently obtained by considering that the portion of radiation scattered throughout the solid angle by a layer of an inhomogeneous medium, in a given time interval, can be expressed as [17]

$$s_\infty(\lambda) \propto tT(\lambda)\sigma(\lambda) \propto D(\lambda)T(\lambda) \propto \left[\frac{e^{-\frac{1}{\sqrt{1+\frac{2}{A_{KM}}}}}}{[4(A_{KM}^2 + 2A_{KM})]^{\frac{1}{4}}}\right]^{\frac{1}{2}}, \tag{9}$$

where t is the layer thickness, T is the layer transmission coefficient and $\sigma(\lambda)$ is the total scattering cross-section per unit volume. t depends on the penetration depth of photons for the incident radiation and can be approximated with D. The sample transmission coefficient T can be expressed as a function of A_{KM} according to the results of the K-M theory valid for $K > S$ equivalent to $\alpha > s/2$ [17]. For materials like paper or textiles, which are made of a collection of non-uniformly sized rough-surfaced fibres, the total scattering cross-section $\sigma(\lambda)$ per unit volume varies smoothly with the wavelength and can be considered constant [18]. s_∞ of eq. (9) has the same physical meaning of s and its physical dimensions are the inverse of a length. s_∞ represents the scattering coefficient estimated for photon energies for which the layer is optically thick and eq. (5) diverges. The expression (valid for $K > S$ equivalent to $\alpha > s/2$) on the right side of eq. (9) can be easily calculated from the measured reflectance spectra even in case of optically thick samples. This equation allows the extension of the experimental measurements of the optical properties of actual artefacts made of paper or textiles to the UV region.

3. – Materials

The Codex on the Flight of Birds (CFB) is a relatively short codex by Leonardo da Vinci dated back to about 1505. The name given to the CFB puts the focus on its principal topic, but other subjects are addressed as well. It is constituted of 18 *folios* (sheets) of approximately 21×15 centimetres in size and approximately $200\,\mu$m in thickness. The CFB is held at the Royal Library of Turin, Italy. In 2013, the CFB was made available for the purpose of carrying out diagnostic investigations. This privileged access enabled us to quantify its current level of optical degradation.

The Shroud of Arquata (SA), a copy of the Shroud of Turin, is a linen cloth which dates back to 1653. It is 4.8 m long and 1.1 m wide and it is folded at the extremities to have an apparent length of 4.4 m [22]. The linen cloth is a plane weave, warp (2.6/mm) perpendicular to weft (2.7/mm) and the average filling factor of the texture is 83%. The average thickness of the cloth is $270\,\mu$m. The most peculiar feature of the SA is the front and back body impressions that do not show perceptible drawings or painting.

3˙1. *Experimental set-up.* – R measurements in the UV, Vis and NIR wavelength regions were obtained by a set-up from Avantes BV, The Netherlands. It consists of a combined deuterium-halogen source that generates a continuous emission of radiation in the spectral range from UV to NIR. The radiation is sent by an optical fibre to a 30 mm diameter integrating sphere coated with Spectralon. The integrating sphere is used to illuminate the sample and to collect radiation remitted from the sample surface over all angles. The sphere has a sampling port of 6 mm diameter and is connected through another optical fibre to a spectrometer with a CCD detector. The set-up possesses a spectral coverage from 248 to 1050 nm with a resolution of 2.4 nm [16, 17].

4. – Results

The method described in subsect. **2**˙2 was applied to some paper sheets belonging to the CFB. In fig. 3 the experimental absolute diffuse reflectance spectra obtained on the *folio* 11 *verso* (11th sheet, back side) is shown. Measurements were performed in the lower part of the sheet, in a spot approximately 5 cm from the left edge and 2.5 cm from the bottom edge.

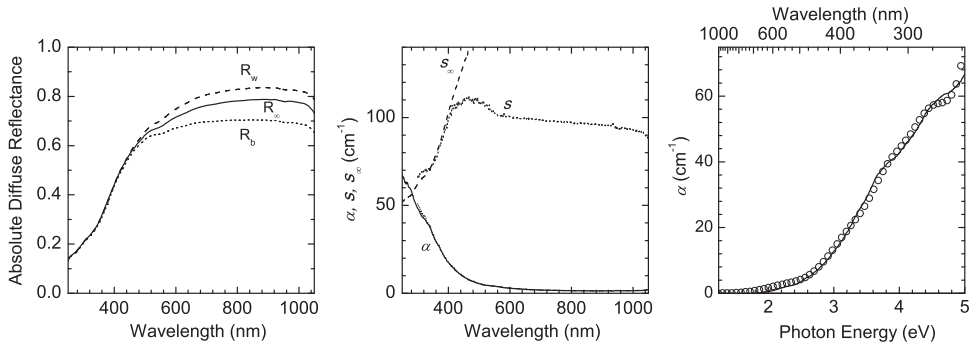

Fig. 3. – R_w, R_b and R_∞ spectra of the *folio* 11 *verso* of the CFB (left panel). α (measured and estimated below 350 nm by using eq. (9)), s and s_∞ (central panel). The experimental and theoretical absorption coefficients of cellulose fibres in the measured spot (right panel).

Results for measured R_w and R_b as well as for R_∞ calculated from eqs. (3) and (4) are shown in the left panel of fig. 3. In the NIR and Vis range, R_w shows higher values with respect to R_∞, which, in turn, is higher than R_b. This behavior is true up to a certain wavelength (around 350 nm) from which the three spectra become indistinguishable within the measurement error. This is caused by the increasing absorption of paper in the higher-energy side of the visible spectrum and in the UV due to the presence of chromophores in the cellulose fibres. Due to the relatively higher values of thickness, sheet optical transmission is negligible.

Once R_∞ is determined, it is possible to recover the S and K coefficients by using eqs. (5) and (6) of the original K-M theory. From the knowledge of S and K, and by using the Y-M eq. (7), the intrinsic absorption α and scattering s coefficients of paper can be recovered [21].

In order to estimate α in the wavelength region where the sample is optically thick eq. (9) is needed. The spectral behavior of α, s, s_∞ and the estimated absorption coefficient below 350 nm are represented in the central panel of fig. 3. In the right panel of fig. 3 the experimental and theoretical absorption coefficient of cellulose fibres in the measured spot in the *folio* 11 *verso* of CFB are shown. The theoretical optical absorption spectra were simulated by using an *ab initio* method and considering only the oxidized groups showing optical absorption below 4.96 eV by A. Mosca Conte *et al.* [15, 17]. The agreement between experiment and theory is excellent and allows calculating the concentrations of optically active chromophores to be 1.73 mmoles per 100 g of cellulose. This value is below what is normally found in ancient paper of comparable age and indicate a good conservation state of this sheet of the CFB of Leonardo da Vinci.

Even in the case of the SA the application of the method described above is the most suitable approach to discriminate the oxidative degradation due to aging with respect to other agents able to change the colour of the cloth, like pigments or dyes [22]. Figure 4 (left panel) shows the spectra R_w, R_b and R_∞ calculated from eqs. (3) and (4) of two areas of the SA (named 2 and 3 in ref. [22]). The area named 2 corresponds to linen outside the body impression while the area named 3 is inside the body impression and corresponds to a blood-like stain on the chest. Indeed the spectral curves appear to be quite different even if they show the common trend to be most intense in the NIR region of the spectrum while they show a decrease in the Vis and UV regions.

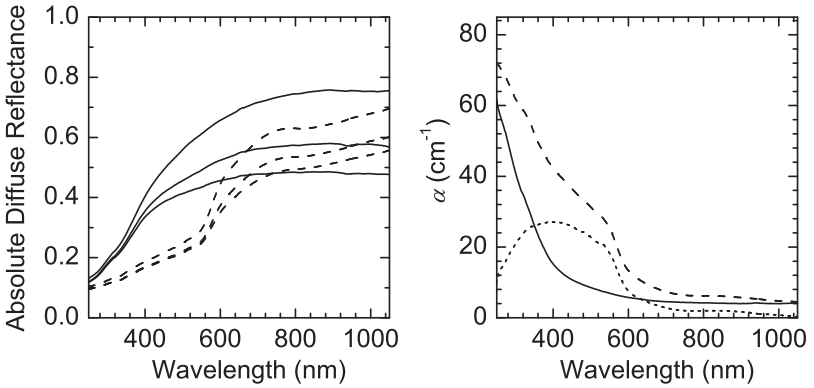

Fig. 4. – R_w, R_b and R_∞ spectra of the area of the SA named 2 (solid lines) and 3 (dashed lines) (left panel) and recovered intrinsic absorption coefficients (right panel). The short-dashed curve is the difference between absorption coefficients of areas 3 and 2.

The recovered intrinsic absorption coefficients (fig. 4, right panel) of the constituent cellulose fibres of the area 2 of SA show a maximum in the UV, a decreases in the Vis and a lower constant level in the NIR with a first inflexion point around 270 nm and a second around 340 nm. These features are those observed in cellulose oxidized by aging. The spectrum of the area 3 shows instead trends which differ from that described above due to structures of different intensities at wavelengths smaller than 600 nm. The absorption spectrum of area 3, corresponding to the blood-like stain on the chest, shows features suggesting the presence of foreign substances such as pigments or dyes, each having different spectral characteristics with respect to aged linen. A better view of these differences can be obtained by subtracting the spectrum of area 3 to that of area 2 (short dashed in the right panel of fig. 4). A broad band peaked at about 400 nm with an absorption coefficient of about $27\,\mathrm{cm}^{-1}$ appears. The methemoglobin, a form of hemoglobin oxidized by aging, has a peculiar spectral behaviour, which is compatible with the peak at 400 nm of the difference spectrum on the right panel of fig. 4 [22]. Therefore, it is possible that the artist has painted the blood-like stains by mixing pigments with blood. Of course, this observation requires a check by specific chemical and immunological tests on a sample of coloured yarn for a confirmation.

5. – Conclusions

This work reports the methodology for quantitative spectroscopic analysis from non-invasive and non-destructive reflectance measurements of ancient paper and textiles. Once the absorption coefficient of cellulose fibres in the UV-Vis-NIR wavelength range is known, *ab initio* simulations can be applied to fit the experimental absorption and extract chemical information at the molecular scale. By using this approach, the concentration of oxidized groups acting as chromophores in the the *folio* 11 *verso* of the Codex on the Flight of Birds by Leonardo da Vinci was obtained. Needless to say, such information is invaluable to restorers and conservators for the evaluation of the evolution of degradation and to assess the conservation strategies. When theoretical simulations are not available absorption spectra can be compared to that of reference materials for pigments or dyes identification. Results for the SA suggest the presence of a mixture of red pigments with blood. This approach, even if developed for cellulose-based materials, like paper and textiles, has a wide range of applications for other inhomogeneous materials of great industrial and cultural interest.

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