Micro-XRF and FT-IR/ATR analyses of an optically degraded ancient document of the Trieste (Italy) cadastral system (1893): a novel and surprising iron gall ink protective action

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Chemical analysis of an optically degraded ancient document of the Trieste (Italy) cadastral system (1893): a novel and surprising iron gall ink protective action

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Keywords

Ancient paper. Manuscript analysis. Browning process. Iron-gall inks. Age-related optical degradation. Negative mirror effect.

Abstract

This paper aims to identify causes and processes of an undesired age-related optical phenomenon in which two kind of paper – a white paper and a green one – and an iron-gall ink are involved together with unavoidable environmental agents. Documents under examination are dated 1893 and come from the Trieste cadastral system archive (*Ufficio del catasto tavolare di Trieste*). The lignin-containing green paper is a pre-printed payment order used in accounting operations and it is adjacent to a white lignin-free paper. Diffused brown stains appear in the white paper being remained strictly and long in contact with the green one handwritten by an iron-gall ink. The green page induces severe yellowing on the contact side of the white one, except for inked areas. The

manuscript black lines of the lignin-containing page seem to protect the adjacent surface, where a mirror image appears. A particular type of mirror effect, that we propose to call *Negative Mirror Effect*, is clearly evidenced. Micro-XRF (micro-X Ray Fluorescence spectroscopy) and FT-IR ATR (Attenuated Total Reflectance Fourier transform Infrared Spectroscopy) techniques were used to achieve information on both diagnostic organic and inorganic components. By way of our chemical model we can hypothesize the migration of oxidized brown low molecular weight extra-cellulose compounds (from lignin and/or hemicelluloses) from green recto to white verso pages. Browning process is only hindered in sharp correspondence with the areas of the green recto folio written with the iron-gall ink: this ink acts as a physical barrier to the migration or, as second hypothesis, it is able to withhold the mobile organic compounds by way of a specific but until unknown interaction. In the field of scientific research on metal-gall ink corrosion this is a novel, interesting and surprising case of the reverse, in which the ink itself is not the cause of the corrosion, but the unforeseen preventive agent.

1. Introduction

As topic of cultural heritage chemistry, in recent years, manuscript analysis has received increasing attention and support from scientists of diverse disciplines who brought their specific know-how in order to light many fields of action as recovering lost writing, image analysis of visual manuscript features, analysis of writing materials, cutting edge techniques. Particularly, non-invasive, non-destructive or micro-destructive surface analytical techniques [1,2] were specifically developed to achieve diagnostic information on ancient paper of historical and archaeological meaning. Analytical techniques able to detect organic or inorganic elements/groups/compounds are useful in this field, especially in view of determinations regarding the metal-gall inks (iron or copper cations mainly used) [3] widely employed for centuries in ancient manuscripts and drawings of the western civilization. Iron-gall inks (henceforth: IGIs) are currently well known to influence the structure of humidity and acid-sensitive cellulose fibres in a specific way, causing optical and mechanical degradation of the paper. This process is known as *iron-gall ink corrosion*. Furthermore, frequently ancient paper develops brown spots of various nature which constitute a widely studied [4-6] condition of degradation commonly referred as *foxing*. Metal ions (mainly, iron ions) and microorganisms have been considered the main causes of foxing, although other substances (organic) and chemical phenomenon (as hydrolysis or oxidation) have been invoked [6]. Age-related foxing stains in vintage paper was attributed to both chemical and biological (as fungi)

causes, although causes of foxing are not yet neither well nor fully clarified. Apart from biological causes, paper can be foxed due to spots of i) inorganic compounds − as metal ions precipitated as insoluble hydroxide or oxide − or ii) to organic molecules − as low molecular weight degradation products (mainly by oxygen and/or sunlight) of lignin or acid-related hydrolysis (humidity necessary) and oxidation of cellulose [6]. A connection has been found between foxing formation and paper composition, production and storage [7].

Beyond the foxing, other types of age-related paper deterioration include i) degradation (as depolymerisation) of the lignin by sunlight and chemical substances picked up by the atmosphere (natural or polluted), typically causing the paper to become brown at the edges, and ii) acid-related damage, which can promote hydrolysis of bioorganic polymers. In general, the yellowing of paper can be attributed to the presence of chromophores found in some of the products formed from the degradation process of one or more components of the paper [5,8].

Pigment-coated papers have been used since the beginning of papermaking history for their special properties of gloss and brightness. Kaolin (or china clay) was used as binder/filler in paper making [9] to reduce the porosity and, as a consequence, the water sensitivity starting by the early 19th century. Clay coating made paper whiter, heavier and more correctly receptive to ink. These properties, however, may render coated papers i) more susceptible to certain types of damage, as surface marring, embedding grime and stains, and ii) more reactive to certain conservation treatments.

IGIs are black (due to the stable zero-charged ferric gallate complex), water-insoluble (that contributes to its indelibility) and produced by mixing four basic ingredients:

- galls as source of polymeric hydrolysable gallo-tannin polyphenols,
- iron vitriol (or green vitriol), namely Fe(II) sulphate hydrate,
- gum Arabic, a water-soluble or water-swellable heteropolysaccharides-based exudates of mature Acacia trees or obtained by specific microorganisms [10],
- an aqueous acidic media as beer or wine in antiquity.

It is well known that Fe(II) sulphate can be contaminated with other minor metal ions as those of Cu, Al, Zn, Pb or Mn (green vitriol, the main source of Fe(II) in the IGIs, was obtained from different mines and by various techniques [11]), while impurities of K, Mg and Ca ions are correlated with the organic vegetal components (i.e. gum Arabic) used as thickener. These metal ions are known to be very useful for a classification of different IGIs [12,13] so as to identify degradation processes of the paper. Due to the variety of recipes [11] and to the natural origin of different materials, there is a wide range of components and impurities in historical IGIs. From the

first centuries A.D. until the 19th century most of the manuscripts were written with these inks. The deterioration of paper by IGI − the so-called *iron-gall ink corrosion* − is known since a long time. The excess of iron vitriol with respect to gallate anion from galls can react to iron oxides and sulphuric acid. Other transition metal ions present, especially copper, can also deteriorate the paper by corrosion. Moreover, iron and copper ions catalyse oxidation processes of cellulose, probably being Fe(II) (or Cu(I)) ions the radical forming centre [7], according to a Fenton scheme of reaction. This paper aims to assess a chemical model able to identify causes and processes of an undesired optical phenomenon in which two kind of historical paper – a white paper (of largest size) and a green one (of smallest size), both used in 1893 – and an IGI are involved together with unavoidable environmental agents.

Papers under examination come from the Trieste cadastral system (*Ufficio del catasto tavolare di Trieste*), a particular type of public governmental land registration (aim: census of the land and real estate to allow citizens to be aware on their legal situation as to rights of property) still currently operative in same places of the north-east Italy and inherited from the Austro-Hungarian Empire land management. The green paper, a pre-printed payment order (photo in Fig. 1) used in accounting operations of the Trieste cadastral system (pertaining to a series of documents marked "TERR IX", where "TERR" is the abbreviation used for territory), was found sandwiched inside an envelope-shaped white paper. The originally white paper under study presents itself rusty reddish-brown coloured, except in the precise correspondence of the black IGI used to handwrite on the green paper. The part of the white paper typewritten with printing ink does not show the effect mentioned. Therefore, a particular type of mirror effect, that we propose to call *Negative Mirror Effect* (henceforth: NME), is clearly evidenced (see Fig. 2), since a white trace of writing appears on the rusty brown coloured paper fairly reproducing the text handwritten on the green one. The edges of the blank page, free of contact with the green one, result lightly yellowed-browned only, indicating a core role of some green page component (by paper and/or ink) in determining the optical alteration. The browning alteration is remarkable at the edges of both the type of paper, indicating a significant role of light, humidity and/or molecular oxygen picked up from the atmosphere. All the type of paper here considered is mechanically upright, so a significant extent of an acid-related hydrolysis and oxidation of cellulose can be excluded (the degree of polymerization of the cellulose constituent should not be significantly reduced). In this connection, Ca(II) can have acted as protective alkaline reserve. This allow us to hypothesize a well-balanced in chemical composition of IGI, without particular excess of Fe(II) and hydrogensulphate/sulphate ions with respect to gallate anion binding Fe(III) cation in the complex molecule acting as black pigment.

A careful investigation of the chemical composition of both IGI and papers is then necessary trying to understand the phenomenon under study. Spot-specific non-destructive contactless measurements were then conducted. Micro-XRF (X-Ray Fluorescence) is a very suitable analytical technique for the elemental qualitative characterization of both ink and paper. Fourier transform infrared microscopy (FT-IR ATR, Attenuated Reflectance Mode) was used to investigate the presence of substances (as cellulose, lignin, sulphate, fillers and pigments) or functional groups in the complex paper matrix.

2. Materials and methods

2.1 Sample preparation

No treatment sample was required for both spectrometric analyses, XRF and FT-IR ATR.

2.2 Micro-XRF measurements.

Micro-X-Ray Fluorescence elemental analysis was carried out on an ArtTAX 200 micro-X-Ray Fluorescence (micro-XRF) spectrometer (supplied by Bruker Nano GmbH).

This instruments is a portable XRF-spectrometer built to meet the specific requirements of non-destructive in-situ elemental analysis. It consists of an air-cooled Mo X-ray fine focus tube (max. 50 kV, 1 mA, 40 W) controlled by a compact high voltage generator unit and with a polycapillary X-ray optic (minimum spot size: 100 micrometers). It is equipped with a Peltier cooled XFlash® silicon drift detector (10 mm² of active area and energy resolution <150 eV for Mn-Ka at 100 kcps) and a colour CCD camera (500 x 582 pixels) for sample positioning. The focal spot is 1.2 x 0.1 mm^2, 0.2 mm lateral resolution and 100 µm beryllium window.

An ARTAX control semi-quantitative XRF software is employed for hardware control and analytical data evaluation. Data are plotted as counts versus energy (KeV).

For our analyses the instrument was set up with the following test parameters: X-ray tube, 30 W, Mo target U = 45 KV, I = 600 µA, acquisition time: 40 s (live time), collimator: 650 μm (air environment).

It is well known that the matrix effect makes problematic a quantitative analysis of the elements present in examined samples, but it is possible to compare the data obtained at two different points by normalizing the results of the detected radiation counts in relation to a reference element, usually chosen between the major elements present in the sample (i.e. Fe for iron gall inks). It is also

suggested to report counts of two elements on x-y graphs and check the consistency of the relationship in order to draw useful quantitative considerations.

In this study the examined elements were: Fe (line: Kalfa1 6.4052 KeV), Cu (line: Kalfa1 8.0463 KeV), K (line: Kalfa1 3.3138 KeV), S (line: Kalfa1 2.3095 KeV), Ti (line: Kalfa1 4.5122 KeV) and Ca (line: Kalfa1 3.6923 KeV).

2.3 FT-IR ATR measurements

The infrared analysis was carried out by means of a Perkin-Elmer Spectrum 100 FT-IR equipped with an Universal Attenuated Total Reflectance (ATR) sampling accessory (ZnSe cell) and diamond window (about 2 mm of diameter). Spectral analyses were performed at a resolution of 4 cm^{-1} in the range of 4000-550 cm^{-1}, scanned 8 times, at room temperature and humidity. The paper samples were set down on the surface of the sample holder and were subjected to some pressure in order to assure the contact with the diamond beam window. The FT-IR data were normalised between 0 and 1 (absorbance mode) and the FT-IR plots, were shifted onto the vertical axis to permit convenient comparisons.

By means of FT-IR ATR technique it is possible to detect in paper samples the presence of inorganic compound such as filler materials (carbonates, sulphates, etc.) and coating agents (kaolin, talc, etc.) [14-15]. For example, carbonates give strong signals around 1400 and 870 cm^{-1}, while sulphates (e.g. $CaSO_4$) often have a characteristic corrugated absorption bands in the range about 3600-3300 cm^{-1} and a typical signal at about 1620 cm^{-1} [16-18].

In addition to the cellulose and non-cellulosic materials, it is sometimes possible to identify signals indicating the presence of degradation (oxidation, biological contamination, etc.) [19]. For example, the oxidation products (as carboxyl/carboxylate, conjugated and unconjugated carbonyl groups) in a degraded paper [20] can be detected by the presence of absorption bands within the restricted range from 1750 to 1600 cm^{-1} [21-22].

Moreover, lignin that is characterised by its aromatic structure, can be easily identified with the FTIR analysis. It is known [23-24] that the aromatic ring absorbs at ~1510 and ~1605 cm^{-1}. Among these bands, the signal at 1510 cm^{-1} is a clear marker of the presence of lignin in paper [21].

3. Results and discussion

3.1 Micro-XRF results on D179 and D180 folios

Figure 3 shows the EDRXF spectra and the analyses of the peaks of the relevant elements are given in Table 1.

Strong XRF signals attributable to iron, potassium and sulphur confirm the presence of an IGI for the handwriting. Very low XRF signals attributable to iron, potassium and sulphur are recorded in ink-free spots.

A sharp peak attributable to titanium was also revealed by micro-XRF technique (see Table 1) measuring spots of the green paper with and without ink (similar intensities were found). Titanium impurities were detected with a certain regularity in many earths and ochres, included kaolin rock [25-27], coherently with the presence of titanium in many natural clay-based minerals. The presence of titanium (and of iron in areas not written) can then be related to the kaolin. Finally, calcium significant micro-XRF signals were detected.

3.2 FT-IR data on D179 and D180 folios

It can be assumed that the green paper D180 was manufactured using mechanical pulp and coated with kaolin. In fact, FT-IR analysis of the green paper D180 *recto* highlights, in addition to the cellulose absorption bands, strong signals due to the presence of lignin. The comparison with the reference spectrum of hardwood pulp shows a close correspondence in the range between 1800 and 1500 cm^{-1} (in particular, the absorption bands at 1643, 1592 and 1508 cm^{-1}) [28-29] The signal at 1732 cm^{-1} indicates the presence of carboxylic groups, probably resulting from oxidation of lignin [30] and/or from the presence of hemicelluloses [31-33]. Beyond that, it can be easily identified the characteristic absorption bands (3689, 3620, 1004, 937, 912, 788 and 750 cm^{-1}) due to the presence of the kaolin probably used as coating agent and filler material (Fig.4) [34-36]. Evident signals of degradation in the same paper is observed at the edges which are strongly browned, probably due to greater exposure to the external environment with respect to the internal areas of the sheet [37-38]. FT-IR analysis of the yellowed-browned edge shows the changes related to signs of degradation of the lignin in the range between 1800 and 1500 cm^{-1} compared to clear area. It known [30, 39] that the oxidation of this polymer leads to a lowering of the intensity of the signal at 1508 cm^{-1} and an increase in absorbance in the area between 1750 and 1600 cm^{-1}, with shoulders at 1721, 1670 and 1594 cm^{-1}, relative to the presence of oxidized compounds (Fig. 5).

FT-IR spectrum of the white paper D179 *recto* shows, all over the range 4000-550 cm^{-1}, a close correspondence with the reference spectrum of a pure cellulose paper (Whatman N[o]. 1 grade chr) and weak signals, at 3693, 3620, 1004 and 912 cm^{-1}, related to kaolin (Fig. 6).

The originally white paper D179 *verso*, remained very probably for long time in contact with the green D180 *recto* one, presents itself rusty reddish-brown coloured, except in the sharp correspondence of the black ink used to handwrite on the green paper and in the edges that were not in contact with the paper D180 *recto*. FT-IR data of the clear areas of the paper D179 *verso* shows the same composition as that of the paper D179 *recto* (Fig 6).

FT-IR peaks at 1721, 1677 and 1594 cm^{-1}, attributable to oxidation of lignin and/or hemicelluloses, are present on both the reddish-brown coloured areas of the D179 *verso* and on the green D180 *recto* papers (Fig. 7).

The same phenomenon described above was also observed for the cards to D181 *verso* and D182 *recto*. The paper D181 *verso*, with high lignin content and kaolin (spectra omitted for brevity), has led to strong browning to paper 182 *recto*, in areas that were in contact with the exception of the areas protected by the IGI.

3.3 Colour of the green paper

Starting by the atomic and molecular spectroscopic data recorded, we can hypothesize that the green paper is coloured with a common mineral pigment, the green earth (also known in art as *terre verte*). An organic green pigment specifically added during the manufacturing can be reasonably excluded, since no significant FT-IR bands remain to be attributed to unknown chemical groups. Green earth consists in a mixture of phyllosilicates including celadonite and/or glauconite with Fe, K and Al ions. Such a peculiar clay was found chiefly in small deposits (mainly celadonite) in rocks in the area of Monte Baldo, Verona, north-east Italy, near enough to Trieste. Moreover, a sharp peak attributable to titanium was revealed by micro-XRF technique measuring spots of the green paper. Titanium impurities were detected with a certain regularity in many earths and ochers, coherently with the presence of titanium in many natural clay minerals. This fact is also verified for the green earth [39] and confirmed by our micro-XRF measurements on a test sample of this pigment and might confirm the chemical nature of the pigment chosen to colour the green paper under investigation, although titanium could also be present in kaolin rock. The presence of titanium also could draw the attention on an its specific mineral, the green titanite ($CaTiSiO_5$, a nesosilicate used as industrial source of titanium dioxide), whose uses in art, nevertheless, is currently unknown.

4. Conclusions

Joining these two non-destructive analytical techniques enabled us to identify the probable substances involved in the curious phenomenon under study. From the whole of the data we can formulate a chemical model hypothesizing the migration of oxidized brown low molecular weight extra-cellulose compounds from green D180 recto to white D179 verso pages, promoted by strict and long contact. The very small amount of water in papers is enough to carry small molecules throughout the lignin-rich paper and towards the lignin-free adjacent sheet. The chemical model under construction is enriched excluding that inorganic compounds − as metal ions precipitated as insoluble hydroxide or oxide − are the cause of the phenomenon, since brown stains are absent in the correspondence of the areas in contact with the cation-rich IGI.

Browning process of the D179 *verso* folio is only hindered in sharp correspondence with the areas of the green D180 *recto* page handwritten with IGI: this ink acts as a physical barrier to the migration, and/or it is able to withhold, the mobile light organic compounds − formed from alteration of lignin – by way of a specific interaction inhibiting their movements through the paper's capillaries. Fe(II) ion, even out of the context of ink, is known to promote cellulose degradation. Nevertheless, this IGI could also protect the extra-cellulose components of the green paper from the degradation: as a hypothesis, since gallate anion can form stable complexes with transition metal ions, it seems reliable that oxidation is slowed under IGI due to unavailability of free (unbound) metal cations acting as catalysts. All the data reinforce our hypothesis of a well-balanced chemical composition of the IGI used (a recipe for a well-stable ink), particularly because we are here assisting to a chemical prevention of staining ascribed to IGI, in counter tendency with the typical iron-gall behaviour leading to the well-known *iron-gall ink corrosion* according to which acidity coming from IGI composition destabilizes constituent organic fibres of the paper causing structural damaging, really absent in the papers under investigation, which is structurally healthy. There is so much scientific research on metal-gall inks damaging paper of various centuries, while this under current observation is a novel, interesting and surprising case of the reverse, in which the ink itself is not the cause of the corrosion, as in many other investigated cases, but the unforeseen preventive agent.

Acknowledgements

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FIGURE and TABLE CAPTION LIST

Figure 1: Photos of the samples under study pages D179 and D180.

Figure 2: Detail of the "Negative Mirror Effect".

Figure 3: ED-XRF spectra recorded on three different areas: a) paper D180, iron gall ink ; b) paper D179 verso, reddish-brown edge; c) paper D180 recto, clear zone.

Figure 4: FT-IR ATR spectra: (a) paper D179 *recto*; (b) paper D179 *verso* (clear edge); (c) Whatman n° 1 paper (reference); (d) Kaolin (reference).
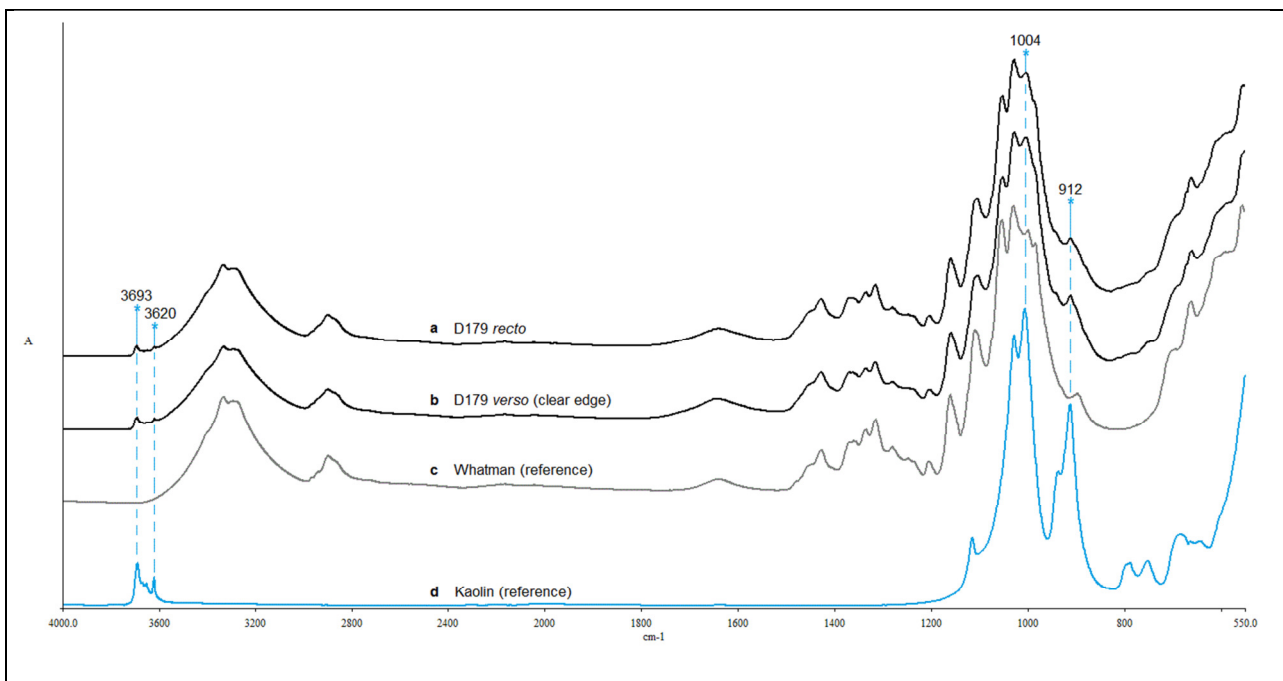
Figure 5: FT-IR ATR spectra: (a) green paper D180 *recto* (clear zone); (b) Hardwood pulp (reference); (c) Kaolin (reference).

Figure 6: FT-IR ATR spectra of green paper D180 *recto*: (**a**) yellowed-browned edge; (**b**) clear zone. The yellow areas show the differences in the oxidation region (1850 - 1500 cm^{-1}) between the yellowed-browned edge and the clear zone of the paper D180.

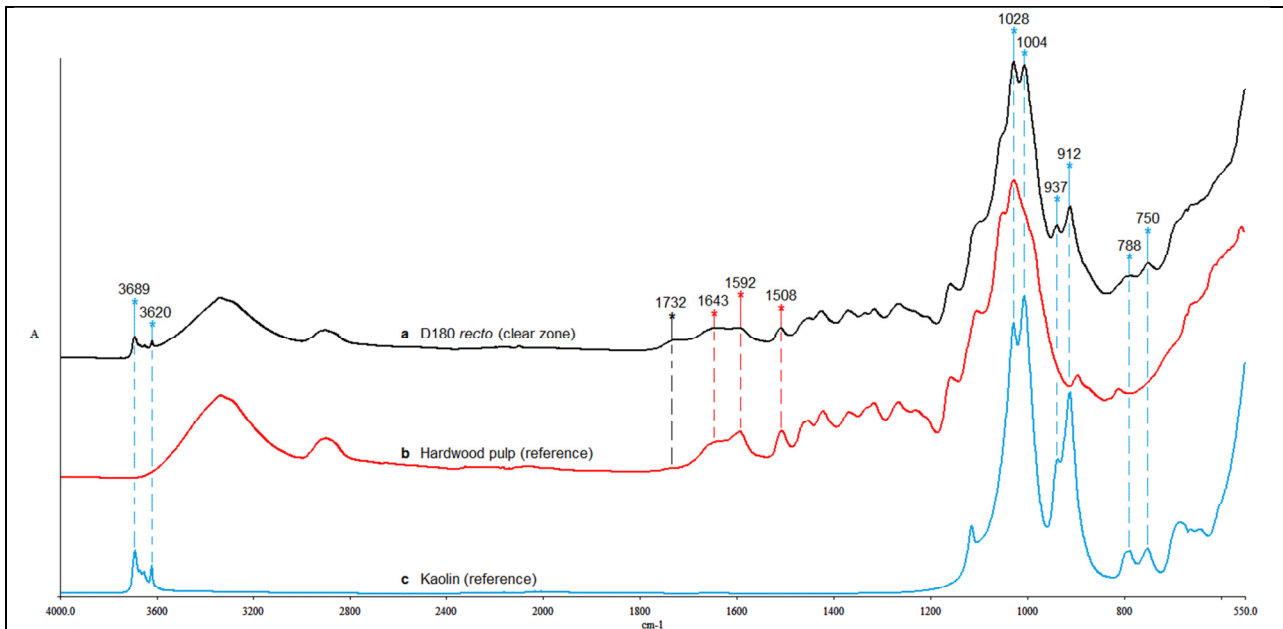**Figure 7**: FTIR-ATR spectra: (**a**) paper D179 *verso* (reddish-brown edge); (**b**) paper D179 *verso* (clear edge); (**c**) green paper D180 *recto* (yellowed-browned edge). The yellow areas show the presence of signals of oxidation in both papers 179 *verso* (reddish-brown edge) and 180 *recto* (yellowed-browned edge).

Table 1: Results of representative elements in the analysis of paper D179 and D180. ~~Data are calculated as average of measurement results in three points.~~ Abbreviations are: 179v_ NB for paper D179 verso clear zone (not browned), 179v_B for paper D179 verso browned, 179v_NME for paper D179 verso "Negative Mirror Effect" area, 180r for paper D180 recto clear zone and 180r_ink for paper D180 inked areas. Data are calculated as average of measurement results in three points (reported here as average and standard deviations)
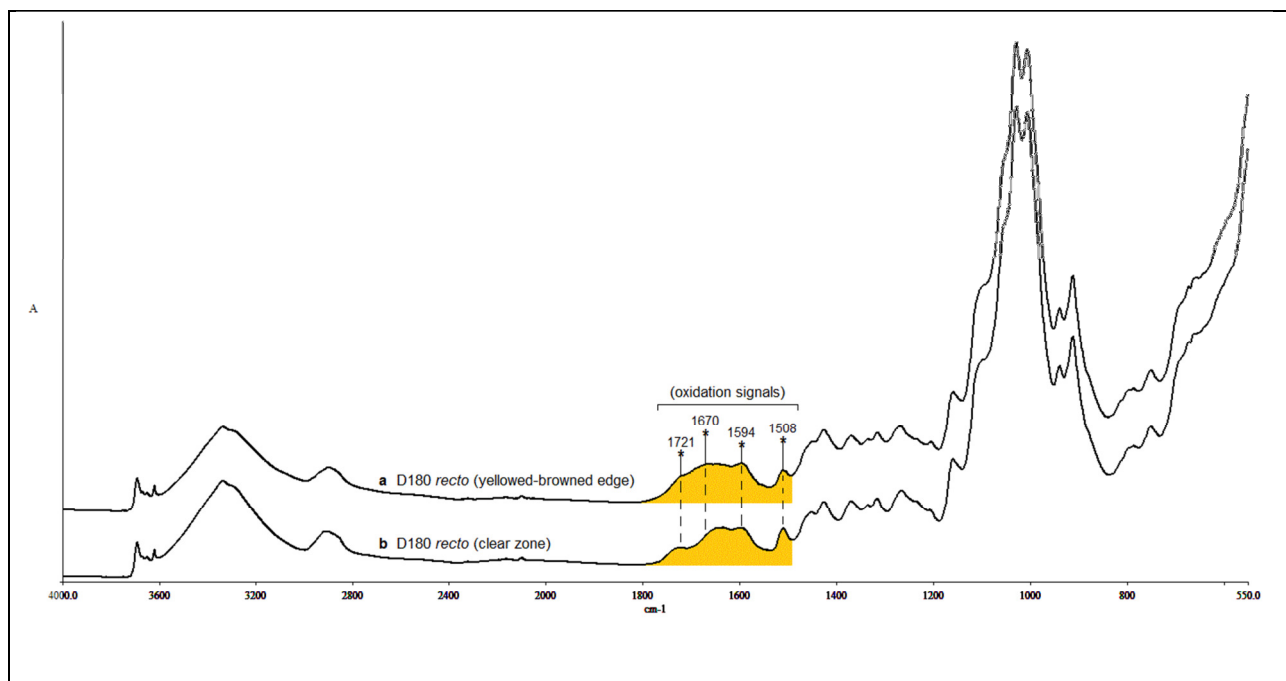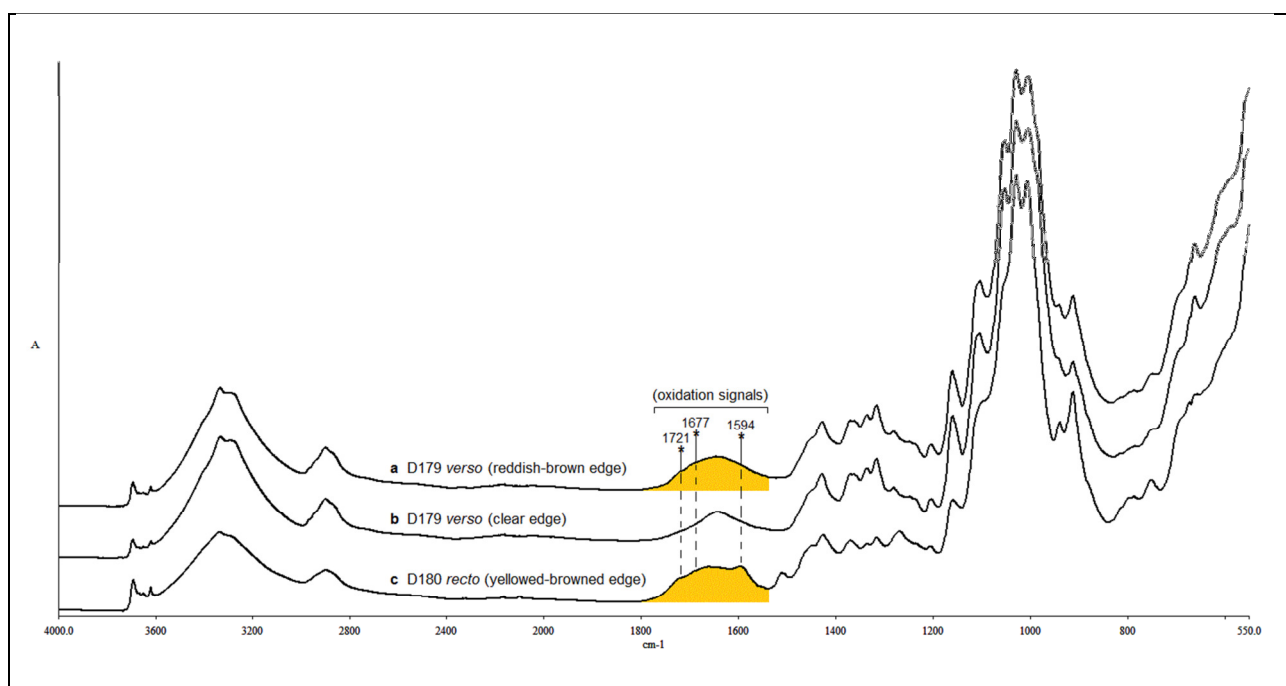
Fig. 54. FT-IR ATR spectra: (**a**) paper D179 *recto*; (**b**) paper D179 *verso* (clear edge); (**c**) Whatman n° 1 paper (reference); (**d**) Kaolin (reference).

Fig. 55. FT-IR ATR spectra: (**a**) green paper D180 *recto* (clear zone); (**b**) Hardwood pulp (reference); (**c**) Kaolin (reference).

Fig. 56. FT-IR ATR spectra of green paper D180 *recto*: (**a**) yellowed-browned edge; (**b**) clear zone. The yellow areas show the differences in the oxidation region (1850 - 1500 cm^{-1}) between the yellowed-browned edge and the clear zone of the paper D180.

Fig. 57. FT-IR ATR spectra: (**a**) paper D179 *verso* (reddish-brown edge); (**b**) paper D179 *verso* (clear edge); (**c**) green paper D180 *recto* (yellowed-browned edge). The yellow areas show the presence of signals of oxidation in both papers 179 *verso* (reddish-brown edge) and 180 *recto* (yellowed-browned edge).