

# Raman characterization of XIV–XVI centuries Sardinian documents: Inks, papers and parchments



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## ABSTRACT

Raman spectroscopy has been utilized to study ancient documents conserved at the University Library of Cagliari (Italy) with the aim to give an exhaustive scenario about the employment of inks, pigments and supporting materials (papers and parchments) related to specific historical periods (XIV–XV centuries). The samples studied are selected between the most prestigious texts present in the collection: two accounting books of sixteenth and fifteenth centuries, a mathematical text of the sixteenth century, a navigation text of the same period, a copy of the most important Sardinian medieval constitutional text “Carta De Logu”, a medieval copy of the famous Italian poem: “La Divina Commedia”. Finally we characterized a declared false of the nineteenth century reproducing a famous document of the XIII century.

The present study gives fundamental knowledge on the history of different inks used in the manuscripts and also on the conservation as well degradation of supporting materials. In addition we focused our characterization on different techniques and materials applied in previous restorations. Finally, we certified with modern techniques the presence of deliberate falsification processes of some specimens.

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## 1. Introduction

Chemically specific analysis of ancient texts by non-destructive and non-invasive means is a topical issue in the field of Cultural Heritage. This capability, especially if a portable instrument is used, can be fulfilled by Raman microscopy [1–3]. Numerous papers could be cited for the use of Raman spectroscopy applied in papers and parchments, in particular for the identification of inks and pigments used in ancient texts and their conservation state is already ascertained [4–6].

The use of Micro Raman systems especially those operating *in situ* renew particular interest when the dimensions of artifact frustrates the analysis of the sample cause of it cannot be moved in a specific lab [7–18]. In addition the possibility of varying the focal plane of the analysed point could improve the data collection increasing the number of information deriving from the samples.

This is the case of the ancient texts, where the common interest of scientists and archaeologists concerning analyses of ancient inks and support (paper or parchment) is mainly related to the identification of their composition and chemical features. The

aim is to answer questions about the chemical composition of books/documents and inks, as well as to explore the technological aspects (realization procedures and redox state at the environment atmosphere), and to define the nature and the provenance of raw materials.

Beyond the importance of non-destructive characterization on these class of samples, this paper aims to provide a general characterization of ancient documents, pointing out the physical-chemical effects related to the conservation process. Raman spectra from modern samples of papers and parchments were collected and the difference with ancient samples were discussed. Finally, the study was expanded to inks on parchments of the XIX century (*Falsi d'Arborea*) reproducing false manuscripts of the XIII century. The analysis of the Raman spectra gives new further scientific insight on this famous class of forgery samples.

## 2. Experimental

### 2.1. Instrumentation and analysis

Micro-Raman scattering measurements were carried out in back scattering geometry with the 1064 nm line of an Nd:YAG laser. Measurements were performed in air at room temperature

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with a compact spectrometer BWTEK i-Raman Ex integrated system with a spectral resolution of less than  $8\text{ cm}^{-1}$  coupled with a BWTEK BAC 151 B microscope. The spectra were collected with very low power (5 mW) in a spot of  $1\text{ mm}^2$  to avoid heating effect in the sample.

## 2.2. Historical samples

We focused our analysis on different books and documents conserved at the “Biblioteca Universitaria di Cagliari” (BUC). The texts can be considered having fundamental importance in the panorama of Sardinian cultural heritage treasures. The BUC was founded in 1764, during the reign of Charles Emmanuel III of Sardinia. Count Gianbattista Lorenzo Bogino, Minister of Sardinia affairs, promoted the library establishment with the promulgation of a specific act directed to the University of Cagliari. The intent of this measure, initially seen as a restoration act, was aimed by the strengthening and qualification of the entire University which was heavily impoverished in terms of educational and cultural prestige.

The Library conserves nowadays a wealth of texts: 700,000 printed volumes, 238 Incunabula, 5260 Cinquecentine, 5227 periodical Publications and magazines, 6500 Drawings, Prints and Maps. This patrimony designates BUC as one of the most important Italian libraries, as well as the largest in Sardinia, which fairly documents, in its entirety, the unfolding of Sardinian cultural life.

In this work we presented a selection of the most important texts present in the library, having the presumption to represent the historical period where the passage from parchment to paper and from amanuensis operations to printed text was ascertained. The mentioned period ranges from the middle age (1300 AD.) to the early modern age (1540 AD.), with the exclusion of a false text produced in the nineteenth century. The purpose of this choice addressed to study the changes in the application of inks/pigments and relative supporting materials over the centuries, especially during the above mentioned transition phases.

We described below the objects under the present investigation:

- “*Condaghe di San Martino*” is a paper manuscript, dated 1462 AD., considered as an administrative book belonging to the convent of San Martino of Oristano. It was lightly restored (light restoration: washed with distilled water, de-acidification with a basic substance). The analysis was concentrated on a restricted area both on the paper and on letters of the manuscript probing in this way the conservation grade of the support and the used inks. The measurements were performed in a central page of the book (page 40–row 10). More information about this text could be found in Refs. [19] and [20]
- “*Nova Scientia*” written by the mathematician Niccolo' Tartaglia (Nicolo Tartalea), dated 1537 AD., is a printed book with figures and realized on paper. It doesn't present any sign of restoration. The measurement was focused on a restricted area whether on the paper or on letters, also in a part of a figure (page 1 and page 2–row 10). In this text was treated, for the first time, the theoretical ballistics; the curvature in the trajectory of a bullet was recognized. The text represents one of the main books of the Italian mathematician N. Fontana, known as N. Tartaglia [21].
- “*Carta de Logu*”, known as “Code of Eleonora di Arborea”, dated 1400–1500 AD., represents the first collection of laws, written in Sardinian language, entirely dedicated to the Sardinian Giudicati (medieval Regional States ruled by Judges). The most notable and famous version was promulgated, in its first version, by Mariano IV of Arborea. At a later time it was updated and expanded by the children Hugh III and then by Eleanor in the fourteenth century. It remained in force until the promulgation of the Feliciano Code

in 1827 AD. It was written in the vernacular Sardinian language, especially in the Arborea variant, so that everyone was able to completely understand it in each part [22,23]. The sample consist in a restored paper manuscript: washed with distilled water, de-acidificated with a basic substance with the addition of parts of new paper. The study were focused on a restricted area especially on the original paper, on a letter of the main text and on a letter of the side note (pag.89).

- “*Condaxi cabrevalu*”, is a paper manuscript, dated 1533 AD., and represents an administrative book also related to the convent of San Martino of Oristano. This accounting text owes his particular name “Cabrevalu” to the recording operations (“capibreviazione”) reported in its pages [20,24]. The manuscript was lightly restored and the analysis was concentrated on a restricted area especially on the original paper and on a letter of the main text (page 1).
- “*Compasso da navigare*” consist in a paper manuscript, dated 1440 AD., and represents a taxes and transaction code used by mariner merchants. It is also considered a *portolanum* (latin) or *portolano* (italian) i.e. a reference book for navigation. The pilot books were technical texts destined for the practical use of mariners. This text reported all the essential data serviceable to the navigation in particular areas of the sea. The contained information referred to the coasts, the frontiers and the commercial routes. *Portolana* were considered official documents, written with essential style, always plain to reading. They were accompanied by explanatory drawings of the coast morphology and conspicuous points, ranked systematically, constantly updated [25]. The sample was lightly restored and our study was focused on a restricted area either on the paper and on two letters (one red, one black) of the manuscript probing in this way both the state of conservation of the paper and of employed ink(s). The measure were performed in page 2 – row 10 and in the last two pages.
- “*Divina Commedia*”, amanuensis copy dated at the end of 1300 AD., is a parchment manuscript with miniatures. *La Comedia*, better known as the “Divine Comedy” or “Comedy” is a poem composed by Dante Alighieri, written in vernacular Florentine with the structure of triplets chained to eleven-syllable verses. Composed according to critics between 1304 AD. and 1321 AD., the Comedy is the most famous work accomplished by Dante, as well as one of the most important examples of medieval civilization; it was known and studied all over the world and then considered one of the greatest works of literature ever composed [26]. Almost certainly a light restoration were applied in this text. We addressed our attention on the miniature reported in page 30 because of a good diversification of colour tonalities. In particular the analysis was concentrated on three restricted areas consisting of different colours: red, green and light blue.
- “*Falsi di Arborea*”, known as “*Fake documents from Arborea*” or “*The Arborea Cards*”, are parchment manuscripts, produced by a voluntary modification of original manuscripts. They were initially dated 1200 AD. These manuscripts were diffused into the market since 1845 by a priest, Cosimo Manca from Pattada (Nuoro). Among the *Cards* we enumerate documents, chronicles, legal texts, poems in Latin, Italian and a fantastic idiom: the Medieval Sardinian Language. The manuscripts, exhibited as scrolls, were not hailing from Arborea, but they came from Cagliari where they were artificially created in the middle of XIX century by the archivist Ignatius Pillito. In Fact in 1870 a scientific commission of the Berlin Academy of Sciences, chaired by Theodor Mommsen, ascertained their total falsity by means of philological study [27]. In this case we analysed the scroll n° 1–piece n°1 and we concentrated the measurements in order to analyse the parchment and the inks.

### 3. Results and discussion

#### 3.1. Paper

Paper composition is ascribed to mostly treated and bonded cellulose fibres constituting by linear polymers of glucose ( $\beta$ -D-glucopyranose) monomers linked by  $\beta$ -1,4-glycosidic bonds. Molecular chains are held together by strong intermolecular hydrogen bonds having an important role in the aggregation of single chains into highly oriented structure. The aggregates are ordered up to even 80% ("crystalline" forms). The rest, considered disordered, is called "amorphous" form. Fig. 1A shows the Raman spectrum of modern paper. As indicated by Proniewicz et al. [2] the presence of the  $900\text{ cm}^{-1}$  band is very sensitive to the amount of crystalline versus amorphous structure of cellulose. This band is assigned to the angle around the  $\beta$ -glycosidic linkages and hydrogen bond rearrangement and then it depends on the deformation of COC, CCO, CCH and stretching vibrations of C5 and C6 atoms. The  $1000\text{--}1300\text{ cm}^{-1}$  range involves mainly C–C stretching and COH and CCH deformation vibrations. The  $1425\text{ cm}^{-1}$  band is assigned to H–C–H and O–C–H in plane bending vibrations, while the  $1316\text{ cm}^{-1}$  band is due to C–O–H and H–C–C bending vibrations [3]. The bands at  $1370\text{ cm}^{-1}$  and  $1335\text{ cm}^{-1}$  are also correlated to the same vibrations but they are weakly sensible to the structure variations. The band centred at  $1600\text{ cm}^{-1}$  is typically assigned to the presence of lignin in the composition of the paper, responsible of the principal degradation processes due to its photo-oxidation properties [3].

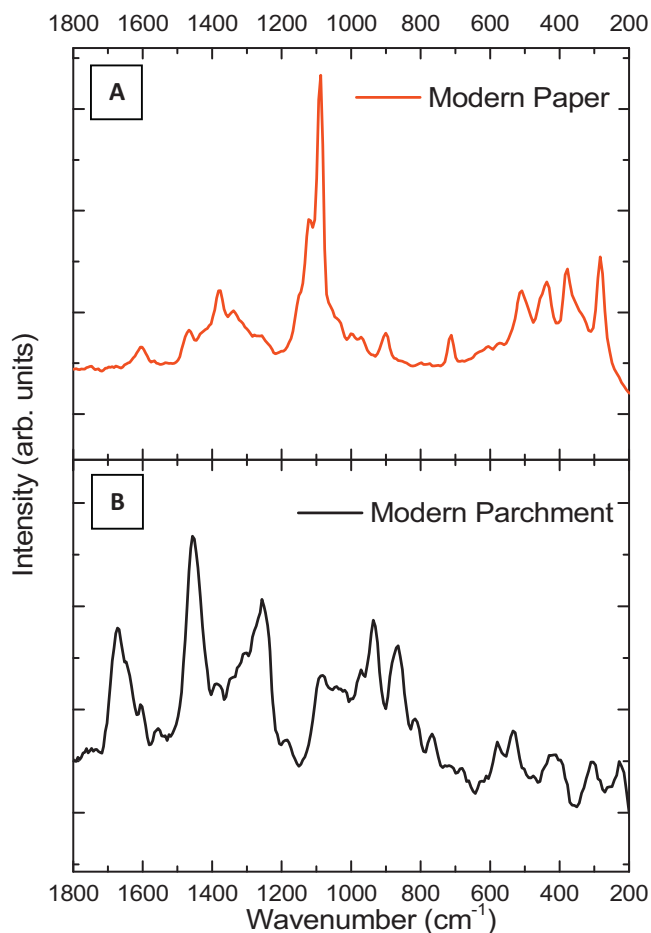


Fig. 1. Raman spectrum of modern Paper (A) and Parchment (B).

Although it is well known that since the 19th century the use of wood pulp introduced a great amount of lignin in the industrial production of paper, in the middle age it was also possible to find products containing lignin especially if the paper derived by linen, hemp or jute rags production [28]. In fact, as indicated by many historical sources, papermakers from important Italian producer, in Genoa and Fabriano in particular, tried to improve the Arab technique. They still used linen or hemp rags to obtain pulp, but improved the process especially for what concerns the beating. Water power was used to drive heavy stamping mills, huge oak trunks comprising four to six large troughs with three or four heavy wooden stampers each beating the rags in fresh circulating water. The rags were transferred in the circular motion every six hours to improve the degree of refining. Further production innovations consisted in the wooden molds with inlaid copper or brass wire, heavy screw presses, and the replacement of starch by animal glue in sizing procedure. In addition to different sizes, three main typologies of paper were produced: writing paper (for letter and chancery use), printing paper (mostly unsized) and cheap wrapping paper (also broke, screenings), used also for drafts [29].

#### 3.2. Parchment

Parchment is the result of tanning process of animal skins from sheep or goats; vellum, with finer quality, is derived from the skin of kids, lambs, pigs and calves. For what concerns the chemical point of view, parchment major component is collagen: this protein is constituted principally of three amino acids (~33% glycine, 20–30% of proline and hydroxyproline) [1,6]. A triple-helix constitutes the collagen basic unit: helices are arranged in fibrils and, at an upper hierarchical level, fibrils are arranged into the final collagen fibres. Degradation of ancient parchment is a complex process which involves the chemical oxidative deterioration of the amino acid chains producing conformational changes from helical to  $\beta$ -sheet or  $\beta$ -turn structures. Many Raman studies analysed the vibrational spectra of parchments and studied the problem of degradation processes [1]. Bacteriological modifications are superimposed on chemical changes and are focused on the C–S–S–C disulfide bridges in cysteine residues, which have characteristic conformational fingerprint near  $500\text{ cm}^{-1}$  in the Raman spectrum (see for example the Raman spectrum of modern parchment – Fig. 1B). Changes in environmental conditions, especially in the humidity and in air pollution, can introduce variations in the residues remaining from the preparation and treatment of the animal skin: sulfur dioxide and carbon dioxide, for example, react with hydrated lime or calcium hydroxide residues ( $700\text{ cm}^{-1}$  and  $780\text{ cm}^{-1}$  in the Raman spectra) to produce calcium sulfate and calcium carbonate, respectively [8]. Edwards et al. assign in the Raman spectrum the molecular vibration associated to the –CONH– bond and nearby groups such as –CH<sub>2</sub>– in the collagen chain. For the amide I the ranges  $1660\text{--}1645\text{ cm}^{-1}$ ,  $1680\text{--}1665\text{ cm}^{-1}$  and  $1670\text{--}1660$  are assigned to  $\alpha$ -Helix,  $\beta$ -Pleated sheet and Random coil respectively. For The Amide II the ranges  $1310\text{--}1260\text{ cm}^{-1}$ ,  $1240\text{--}1225\text{ cm}^{-1}$  and  $1260\text{--}1240$  are assigned to  $\alpha$ -Helix,  $\beta$ -Pleated sheet and Random coil respectively. For the Skeletal C–C the ranges  $950\text{--}885\text{ cm}^{-1}$ ,  $1010\text{--}1000\text{ cm}^{-1}$  and  $960\text{--}950$  are assigned to  $\alpha$ -Helix,  $\beta$ -Pleated sheet and Random coil respectively. The band at  $1450\text{ cm}^{-1}$  is due to a N–H deformation in the amide III structure. Shifts in the amide I bands, which is predominantly  $\nu(\text{C}=\text{O})$  stretching, can be attributed to secondary structural changes in the proteins, and then are considered key molecular biomarkers for the initial stages of biodegradation. As a principal conclusion of the study conducted by Edwards et al. the bands in the collagen are sharp and well defined. The  $\nu(\text{S}–\text{S})$  mode indicates a preferred *trans-trans-gauche* conformation. In the ancient parchment the totally absence of this bands reflects the

destruction of the S—S bonds. Moreover the amide I band at  $1667\text{ cm}^{-1}$  is characteristic of an  $\alpha$ -helical structure and the broadening of this bands towards lower Raman shifts is attributable to a structural change towards a  $\beta$ -sheet/random coil configuration.

### 3.3. Typical ancient writing inks: Iron Gall

Since the late Middle Ages, until the early part of last century, Iron Gall inks were extensively used. They were black, indelible inks and they constituted an organometallic compound. From the late Middle Age until the early part of the last century, they were the most commonly used black inks in the Western World [4,30]. The ink is essentially a solution of iron (II) sulfate with tannins (tannic or gallic acids either from plant gall extract or in later years as pure compounds) in various portions. These compounds were combined in water with the tannins breaking down to gallic or digallic acid to give rise the ink complex. The resulting compound responsible for the black ink is obtained once written on the support and exposed to oxygen in the air: this iron (II) complex oxidizes becoming 1:1 iron(III)-pyrogallin or 1:1 iron(III)-gallic acid complexes. Related spectra present Raman bands at  $1575, 1470$  (strong)  $\text{cm}^{-1}$ ,  $1425, 1315$  (strong),  $1230, 1095$  (weak),  $960, 815, 710$  (weak),  $620\text{--}500$  (broad due to multiple peaks),  $400$  and  $255\text{ cm}^{-1}$ .

The majority of conservation problems, associated to iron gall inks, are due to their corrosive nature and the tendency to undergo colour change from black to brown or red, often fading quite significantly. Numerous documents, manuscripts and artworks now stand in danger of severe deterioration, while others are in excellent condition. The corrosive properties take place when residual iron sulfate in the ink reacts with the water present in the air and the consequent formation of iron oxides (especially  $\text{Fe}_2\text{O}_3$  with typical red colour) and sulfuric acid [4,31].

### 3.4. Samples analysis and assignation

Table 1 summarizes the assignation of the main Raman bands of pigments and compounds in each sample. Corresponding symbols used in Table 1 has been reported in the experimental spectra only for trace compounds and in the main frequencies used for the

assignation. The analysis is based on the comparison with the main Raman frequencies reported in Table 2.

### 3.5. Samples written on paper support

#### 3.5.1. Condaghe di San Martino

The Fig. 2 shows an illustration of the sample “Condaghe di San Martino” and the representative points where Raman spectra have been collected: black “ink” corresponds to the main written text in the sample and black “light ink” refers to a different coloured characters. In relation to the representative areas called “ink”, the principal modes are at the frequencies  $336$  (medium),  $403$  (strong),  $1230$  (strong),  $1315$  (strong),  $1470$  (strong) and  $1575$  (strong)  $\text{cm}^{-1}$  corresponding to the raman spectrum of Iron Gall ink. However the relative intensity of mentioned Raman bands, especially at  $1575\text{ cm}^{-1}$  and  $336\text{--}403\text{ cm}^{-1}$ , suggests to consider an altered composition of Iron Gall ink. A comparison between the collected spectrum and literature works indicates the presence of the gallic acid (strong modes at  $1580\text{ cm}^{-1}$  and  $340\text{ cm}^{-1}$ ) and, from the comparison of the ratio of these modes, it seems in higher concentration with respect to compounds analysed in literature [4,30,31]. Moreover the broadening of the spectrum in the range  $1250\text{--}1700\text{ cm}^{-1}$  suggests the presence of an additional compound used to obtain the ink. By means of bands deconvolution, Fig. 3 reveals the presence of two broad bands characteristic for graphite-like compounds ( $1300\text{ cm}^{-1}$  and  $1590\text{ cm}^{-1}$ ) ascribing, in the case of historical inks, to the Carbon-based pigment [32].

In the case of “light ink” area we identified once again the iron gall ink. In analogy with the previous analysis, the low intensity of the bands in the range  $1200\text{--}1600\text{ cm}^{-1}$ , implies only the presence of tannic acid or gallic acid in the ink. The just enunciated result suggests a different composition of this compound with respect to the previous analysed area (see the point identified as “ink”) [30,31].

#### 3.5.2. Nuova Scientia – Tartaglia

The Fig. 4 shows an illustration and raman spectra of the sample “Nuova Scientia – Tartaglia” where the investigated areas concern the paper and the ink. The areas indicated as “paper” confirm the presence of cellulose in their composition [2], whereas the “ink” areas could be univocally and easily identified as Carbon-based

**Table 1**  
Pigments and compounds detected in the samples..

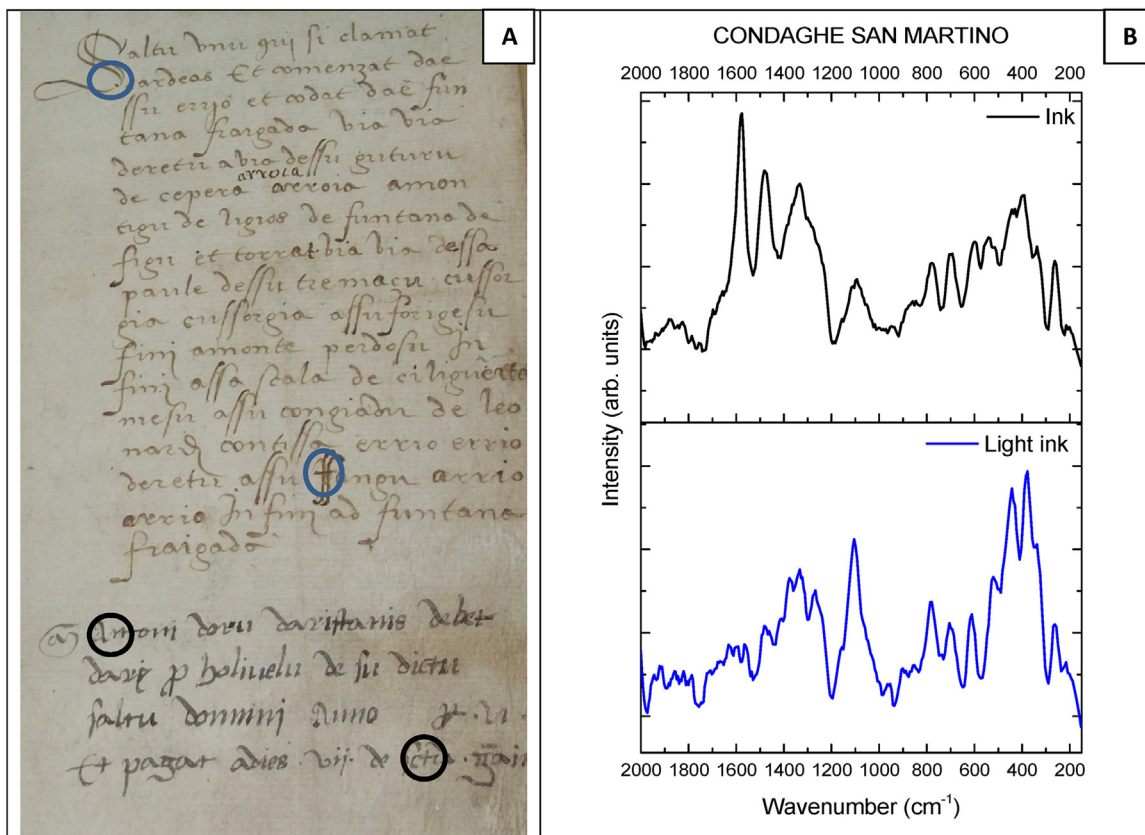
Sample		Writing Support				Pigment/Ink												
		Cell.	Lig.	CaOH	Par.	IGall	A-Carb.	B-Cin.	Ver.	Pyr.	R-Lead	Hem.	Mal.	Az	TiO <sub>2</sub>	Mars-Y	Chrys	
<b>S. Martino</b>	Light ink	●				x												
	Ink	●				x	○											
<b>Tartaglia</b>	Ink	●					○											
	Paper	●																
<b>Carta de Logu</b>	Paper	●	+	◇														
	Note Ink	●		◇		x			▲									
	Near Text	●	+	◇														
	New Paper	●	+	◇														
<b>Condaxi Cabreavadu</b>	Black ink	●		◇		x												
	Paper	●																
	Ink	●				x												
<b>Compasso Navigare</b>	Red Ink	●		◇					▲									
	Paper	●		◇														
	Black Ink	●		◇				#										
	Black Ink (last)	●				x				◆		♥	*					
<b>Divina Commedia</b>	Red Ink			◇	■													
	Black Ink				■	x		#										
	Green Ink			◇	■								♣	♠				
	Blue ink			◇	■			#					♣					
<b>Falsi Arborea</b>	Blue ink			◇	■			#					♣					
	Ink			◇	■										□	△	†	

(●)Cell. = Cellulose; (+)Lig. = Lignin; (◇)CaOH = Calcium Hydroxide; (■)Par. = Parchment; (x)IGall = Iron Gall; (○)A-Carb. = Amorphous Carbon; (#)B-Cin. = Black Cinnabar; (▲)Ver. = Vermilion (Cinnabar); (◆)Pyr. = Pyrolusite; (♥)R-Lead = Red Lead; (\*)Hem. = Hematite; (♣)Mal. = Malachite; (♠)Az = Azurite; (□)TiO<sub>2</sub> = Anatase/Rutile; (△)Mars-Y = Mars Yellow; (†) Chrys. = Chrysocolla.

**Table 2**  
Main frequencies used as reference.

Material	Band Raman Shift (cm <sup>-1</sup> )															
<b>Cellulose</b>	285	379	437	512	715	903	968	1001	1085	1119	1290	1336	1379	1425	1469	1602
	s	s	s	s	m	m	w	w	vs	vs	m	s	s	m (sh)	m	m
<b>Lignin</b>	1290	1602														
	s	vs														
<b>Calcium Hydroxide</b>	700	780														
	s(br)	s(br)														
<b>Parchment</b>	1028	1080	1165	1239	1340	1432	1532	1659								
	s	s	m	s	s	s	m	s								
<b>Collagen</b>	1235	1445	1457	1535	1542	1555	1570	1630	1650	1660	1675					
<b>Iron Gall</b>	255	400	620–500	710	815	960	1095	1230	1315	1425	1470	1575				
	w	m		w	w	w	w	m	s	m	s	m				
<b>Amorphous Carbon</b>	1300	1580														
	s(br)	s(br)														
<b>Black Cinnabar</b>	252 (s)	282	343													
<b>Vermilion</b>	252	282	343													
	vs	w(sh)	m													
<b>Pyrolusite</b>	238	536	663													
<b>Red Lead</b>	122	149	223	313	340	390	480	548								
	vs	m	w	s	vw	w	vw	vs								
<b>Hematite</b>	220	286	402	491	601											
	vs	vs	s	w	w											
<b>Malachite</b>	155	178	217	268	354	433	509	553	558	757	1051	1085	1492			
	s	s	m	m	m	vs	m	s	w	vw	m	m	vs			
<b>Azurite</b>	145	180	250	284	335	403	545	746	767	839	940	1098	1432	1459	1580	1623
	w	w	m	w	m	vs	w	w	w (sh)	m	m	w	m	w	m	vw
<b>Anatase/Rutile</b>	145 a	198 a	235 r	399 a	445 r	516 a	610 r	640 a								
<b>Mars Yellow</b>	245	299	387	480	549											
	w	m	s	w	w											
<b>Chrysocolla</b>	124	193	337	407	490	677 vs	844	1045	1093m							
	w	w	s	s	s		s	m								

vs = very strong; s = strong; m = medium; w = weak; vw = very weak; br = broad; sh = shoulder; a = Anatase; r = Rutile.



**Fig. 2.** Condaghe di San Martino: written text (A) and collected spectra (B).

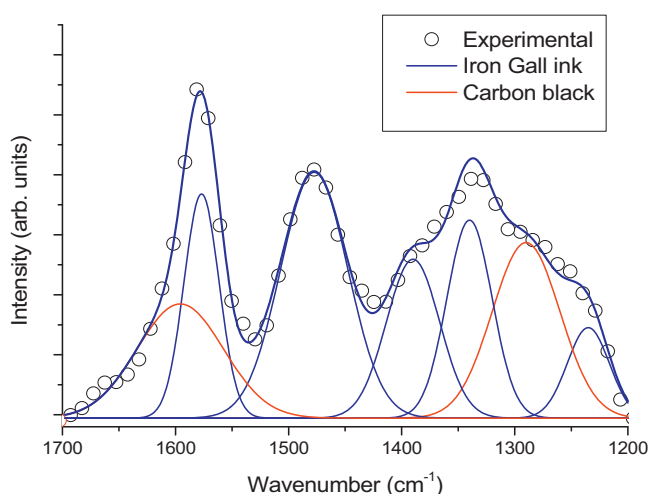


Fig. 3. Deconvolution of Raman spectrum in the region 1200–1700  $\text{cm}^{-1}$ .

pigment [32]. These assignments are confirmed by the historical information in which graphite inks were used as writing compound since the 1500 [33].

### 3.5.3. Carta de Logu

In Fig. 5 we reported the raman spectra collected in the sample “Carta de Logu”. The identified areas are relative to the black ink used in the main text, the ink used in the notes, and the supports used to writing (paper) and or in the restoration phases (new paper). In some reported spectra we identified the weak bands associated to the Calcium Hydroxide ( $700\text{--}780\text{ cm}^{-1}$ ) [1,8], probably used in the restoration procedures. These bands are not present in the sections “New Paper” and “Black ink”. Furthermore the presence of typical bands assigned to the cellulose molecule were found in the region  $1100\text{--}1500\text{ cm}^{-1}$

[1]. The intense bands at  $255\text{ cm}^{-1}$  and  $338\text{ cm}^{-1}$ , found in the black-brown “note ink” zones, could be assigned to a particular phase of Cinnabar used not only for red pigments, but sometimes used in black inks in the concentrated version “Black Vermilion” or “Black Cinnabar” [34–36]. Mercury sulphide ( $\text{HgS}$ ), known as Cinnabar, can be found in different crystallographic phases: the common trigonal structure which presents red colour (used in the production of “Red Vermilion” pigment) and the cubic structure having black colour (used in the production of rare “Black Cinnabar” or “Black Vermilion” pigment) [35]. Although the colour of the ink suggests the presence of “Black Cinnabar”, this assignation appears quite strange. Due to the rare use of “Black Cinnabar” in the past, we are prone to consider the well-known phenomenon of darkening related to the “Red Vermilion”. In any case the use of “Cinnabar” in the writing inks, mixed with iron gall, is quite rare and could suggest a particular technique of inks production. For what concerns the paper support some considerations should have been conducted in relation to this ancient manuscript. At this purpose a comparison between the original paper and new paper, used for the restoration, is possible by analysing either Fig. 5B and what we discussed in the introduction. In the Raman spectrum of the original paper we observed the presence of the band assigned to the lignin molecule ( $1580\text{--}1620\text{ cm}^{-1}$ ) and the total absence of the band centred at  $900\text{ cm}^{-1}$  ascribed to the crystallinity of the cellulose structure. This condition reveals a possible use of paper with a significant content of lignin (as discussed in the introduction it was not so rare especially if jute or linen rags were used in the production of the paper), normally considered as the principal responsible for the paper degradation. The total absence of the band at  $900\text{ cm}^{-1}$  indicates an important degradation state of the manuscript which justifies the restoration procedure. We underline the successful choice of the new paper used in the restoration which presents not only a low content of lignin but also a high grade of crystallinity as indicated in the spectrum (Fig. 5B).

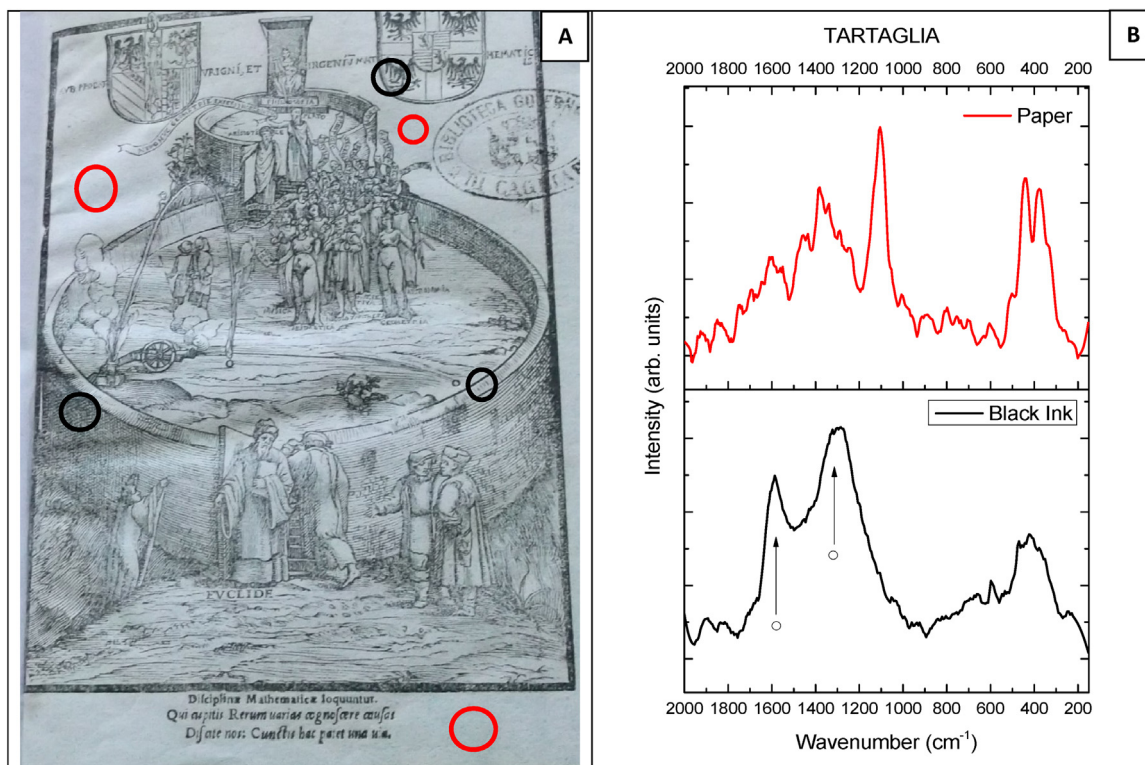


Fig. 4. Nova Scientia: printed text (A) and collected spectra (B):  $\circ$  = Amorphous Carbon.

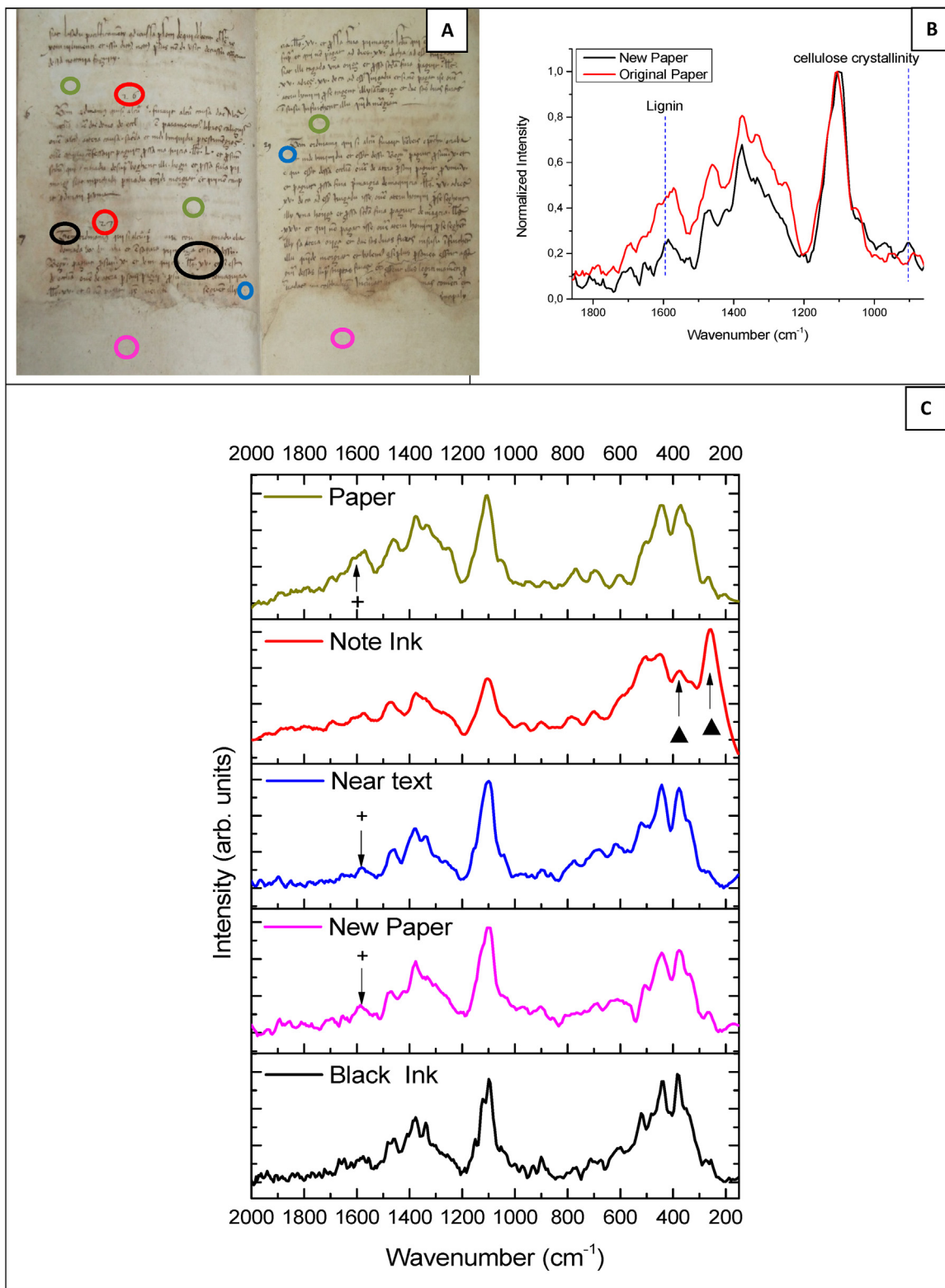


Fig. 5. Carta de Logu: written text (A), comparison between Original paper and New paper (B) and collected spectra (C): ▲ = Red Vermillion (darkening); + = Lignin.

### 3.5.4. Condaxi Cabrevadu

The raman spectra collected in the sample “Condaxi Cabrevadu” (Fig. 6) refer to the areas “paper” and “black ink”. As pointed out in the Table 1, the ink present in the sample corresponds to the iron gall ink, confirming the use of this typical compound in that particular historical period [5]. On the same basis of previous discussion, concerning a typical degraded sample, we interpreted

the presence of a medium band at 900 cm<sup>-1</sup>, in addition to a less content of lignin, as a better conservation of the paper support related to this manuscript.

### 3.5.5. Compasso da Navigare

The raman spectra collected in the sample “Compasso da Navigare” are reported in Fig. 7 and divided in different points

of interest: “Red ink” (first pages); “Black ink” (first pages); “Black ink (last pages)”; Other spectra were collected in the paper support. As a first analysis of gathered data, we can evidence a procedure of paper deacidification due to the presence of Calcium Hydroxide ( $700\text{--}800\text{ cm}^{-1}$  broad band in the Raman spectrum). Referring to Table 1, we found the compound Red Vermilion for the “Red Ink” region (mercury sulphide  $\text{HgS}$ ) [34]. We also identified the “Cinnabar” used for the “Black ink” of the first pages [34,36]. In analogy with the case of previous sample “Carta de Logu” this point deserves particular attention especially in the composition of the analysed ink. We are in presence of a black ink, not composed by the typical iron gall, but only with “Cinnabar” very similar to the “Red ink” identified with the compound Red Vermillion. Even though red vermilion darkening could be invoked also in this case, it seem quite anomalous that the darkening affected only the area “Black ink” and not the region “Red ink”. For that reason we can only suppose the effective use of “black cinnabar”, but this hypothesis must have confirmed with further analysis. The “Black ink” of the last pages were identified as Iron gall ink [5] with the probable addition of pyrolusite pigment ( $238$  and  $622\text{ cm}^{-1}$ ) [34,37]. Pyrolusite, with chemical formula  $\text{MnO}_2$ , is a mineral used not only as a brown-black pigment, but also to remove iron and manganese salts in aqueous solutions. The presence of this compound, considered as an additive of iron gall ink, remain until now undefined at this step of analysis: the use could be ascribed not only to aesthetic colouration of the ink, but also as a component to remove the excess of iron sulfate salts in the iron gall composition. In fact, the latter compound is the first responsible for the oxidative reaction with the air humidity and the consequent formation of sulphuric acid (typical iron gall corrosion process) [5,38].

### 3.6. Samples written on parchment support

#### 3.6.1. Divina Commedia

Fig. 8 shows the raman spectra collected in the sample “Divina Commedia”, written in parchment support, in which different colour areas are delineated: “Green ink” (miniature); “Black ink” (in the miniature and also in the text); “Red ink” (miniature); “Blue ink” (miniature). We detected the presence of Calcium hydroxide for each one spectrum according to the application of this compound in the technique of vellum treatment. The “Red ink” zone is compounded by a blend of different red pigments such as Red Lead and Hematite. The strong band at  $255\text{ cm}^{-1}$  in the “Black ink” were assigned to Black Cinnabar pigment in analogy with the previous samples. In addition, the bands in the region  $1275\text{--}1600$  could be easily assigned to Iron Gall ink. The “Green ink” and “Blue ink” are characterized respectively for the presence of Malachite + Azurite pigments ( $250\text{--}560\text{ cm}^{-1}$  region) and Malachite + Black Cinnabar and Iron Gall mixture [9–12,33]. For what concerns the support, Fig. 8B presents the raman spectrum of the parchment in the region of major interest. As above discussed in the introduction we remarked in the spectrum a broadening and a shift of the bands assigned to the amide I in a  $\beta$ -sheet/random coil configuration ( $1584\text{ cm}^{-1}$ ) which corresponds to an initial stage of biodegradation. Moreover, about the amide II and amide III structure ( $1250\text{ cm}^{-1}$  and  $1450\text{ cm}^{-1}$ ), we observed a weak broadening with respect to the raman spectrum of modern parchment, prelude to a deformation of the structure. The presence of  $1340\text{ cm}^{-1}$  band were ascribed to the  $\delta(\text{CH}_2)$  vibrational mode of collagen, as usual weakly present in modern parchment, in accordance with Edwards et al. In addition the presence of the  $1086\text{ cm}^{-1}$  band in the spectrum evidences the carbonation process Calcium Hydroxide occurring in the parchment.

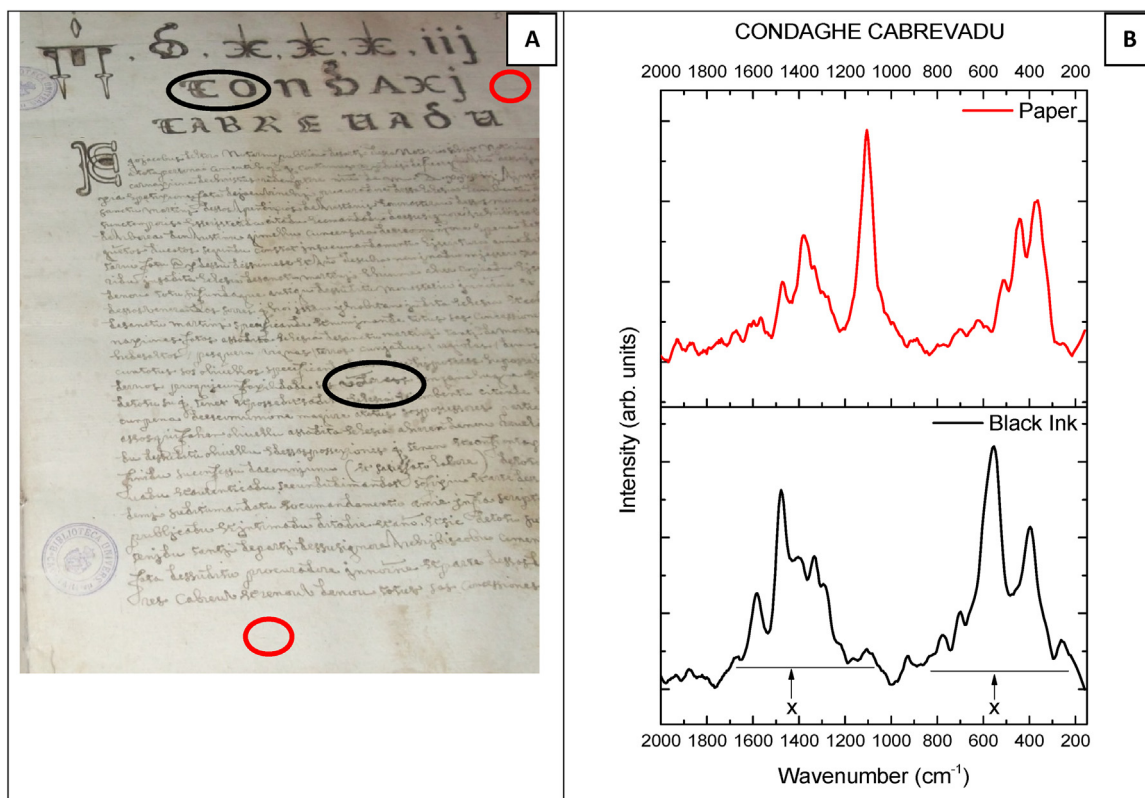


Fig. 6. Condaxi Cabrevadu: written text (A) and collected spectra (B): x = Iron Gall.

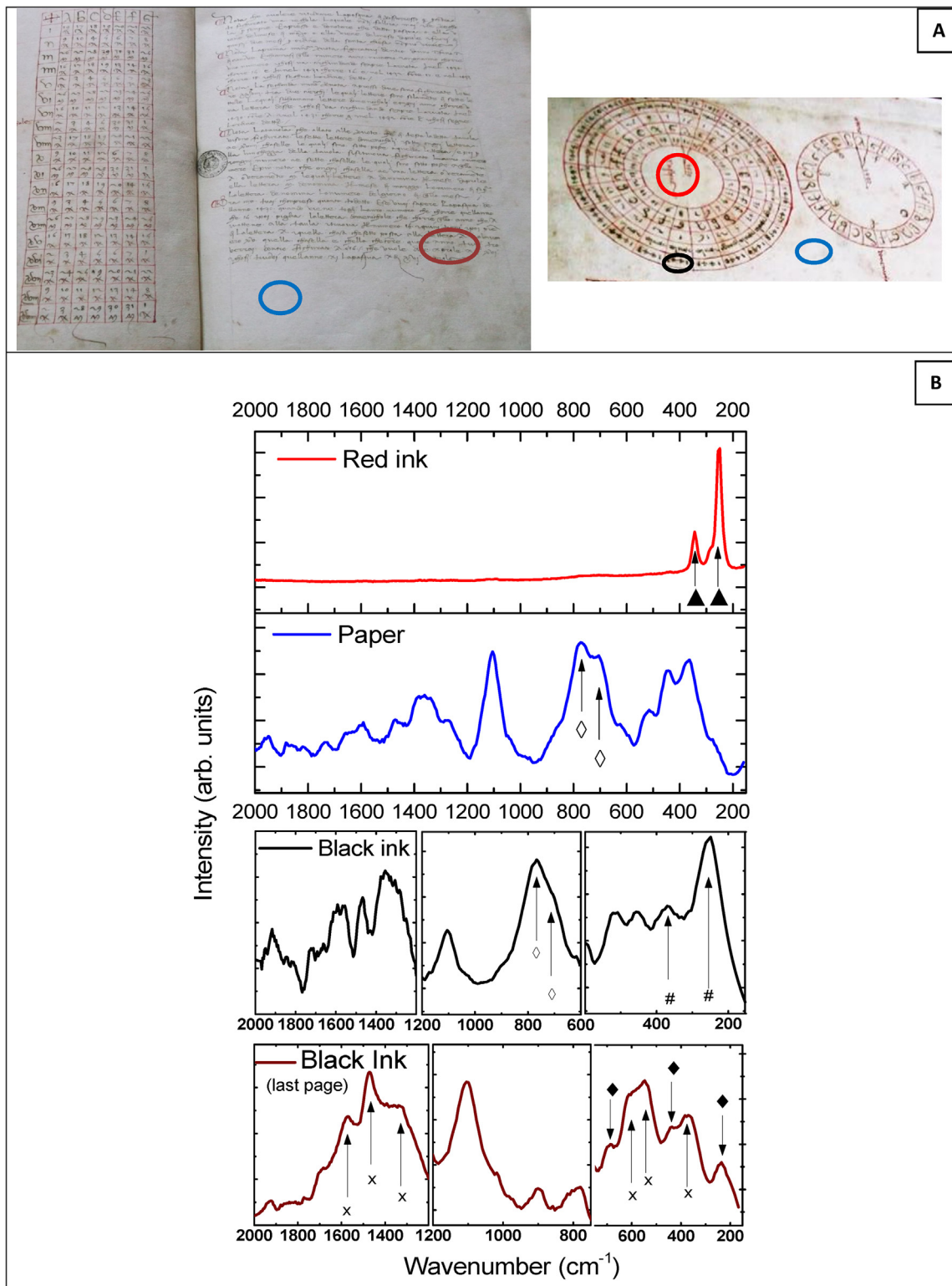
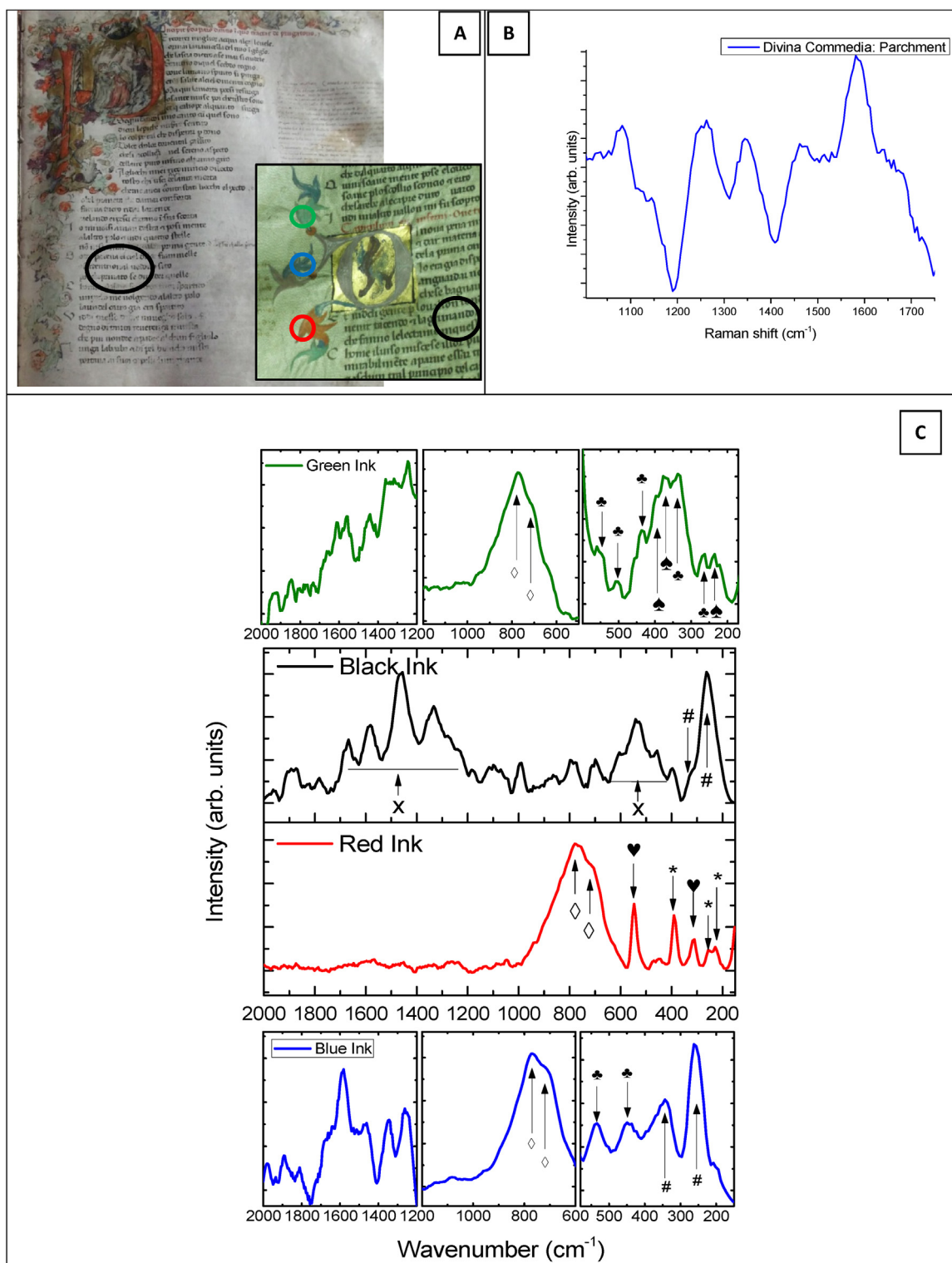


Fig. 7. Compasso del Navigare: written text (A) and collected spectra (B): ◆ = Pyrolusite; x = Iron Gall; # = Black Cinnabar.

### 3.6.2. Falsi di Arborea

Fig. 9 displayed the raman spectra collected in the sample “Falsi di Arborea” where the areas of interest were identified as written “Ink” and the support “parchment”. In the spectra could be easily identified the contribution of bands assigned to the parchment (see region 1200–2000 cm<sup>-1</sup>). In the raman spectrum related to the “Ink” area we evidenced the contribution of the bands at 1043–

1090 cm<sup>-1</sup> and also in the range 250–650 cm<sup>-1</sup> with respect to the same range in the “parchment” spectrum. In particular we identified the pigment Chrysocolla, classical name of various compounds used in the hard soldering of gold, and among these were certain green copper minerals, the basic carbonate, the silicate, etc. The name is now used in pigment production, specifically to indicate natural copper silicate (approx. CuSiO<sub>3</sub>).



**Fig. 8.** Divina Commedia: written text with illustrations (A), particular region of interest of the Raman spectrum on parchment (B) and collected spectra in written or drawn points (C): # = Black Cinnabar; ♣ = Malachite; ♠ = Azurite; \* = Hematite ♥ = Red Lead; ◇ = Calcium Hydroxide.

nH<sub>2</sub>O), a green mineral fairly common in secondary copper ore deposits [39]. Moreover in the region ranging from 200 cm<sup>-1</sup> to 650 cm<sup>-1</sup> we identified other two compounds: Mars Yellow (chemical formula Fe(OH)<sub>3</sub>) with the characteristic intense band at 387 cm<sup>-1</sup> [40]; Titanium oxide probably in Anatase and Rutile phases [41]. Despite the famous controversy about the use of titanium dioxide as pigment before the 19th century [42–44], the

tendency is to consider these two compounds, or their combination, as synthetic and developed after the middle of 19th century [45,46]. No traces of Iron Gall ink were detected in this sample. This information lead us to consider the falsity of the writing ink used in the preparation of this sample: the employment of yellow/orange pigment in addition to a green pigment had the purpose to obtain a discoloured ink simulating the degradation process of the famous

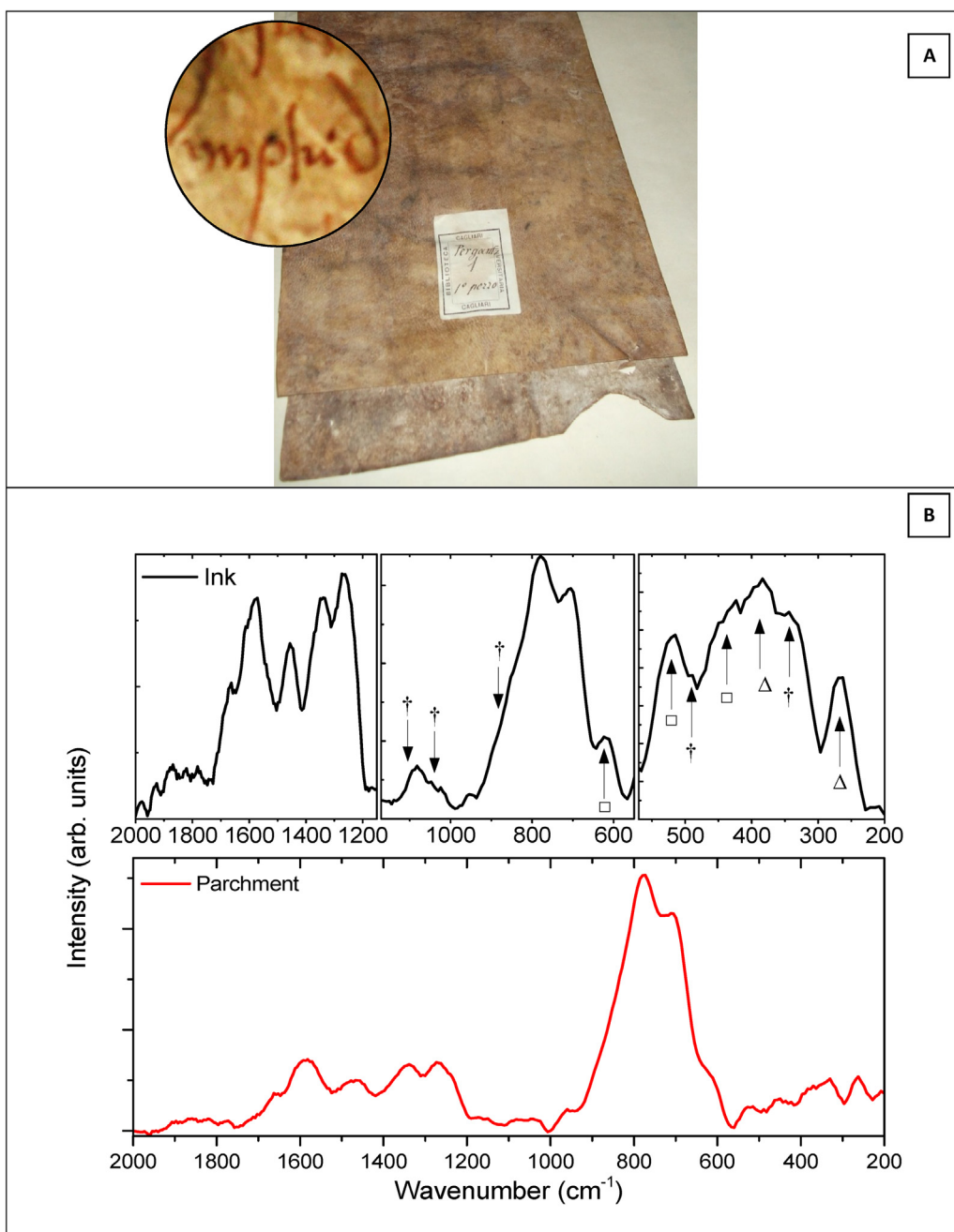


Fig. 9. Falsi di Arborea: written text (A) and collected spectra (B):  $\Delta$  = Mars Yellow;  $\square$  = Titanium oxide;  $\ddagger$  = Chrysocolla.

and most commonly used iron gall ink. It was also known the use of titanium oxide as binder in inks or paints in the 19th century [47]. For what concerns the parchment used for this sample, we found in Fig. 9 a spectrum very similar to the same analysed for the sample “Divina commedia”. As above discussed a broadening and a shift of the bands assigned to the amide I in a  $\beta$ -sheet/random coil configuration ( $1584\text{ cm}^{-1}$ ) corresponds to a biodegradation of this support. Concerning the amide II and amide III structure ( $1250\text{ cm}^{-1}$  and  $1450\text{ cm}^{-1}$ ) we observed a weak broadening with respect to the raman spectrum of modern parchment implying a consequent deformation of the structure. The presence of  $1340\text{ cm}^{-1}$  band was ascribed to the  $\delta(\text{CH}_2)$  vibrational mode of collagen which is weakly present in modern parchment, as suggested by Edwards et al.

Furthermore, the totally absence of the  $\nu(\text{S-S})$  mode ( $400\text{ cm}^{-1}$ ), due to a preferred *trans-trans-gauche* conformation, reflects the destruction of the S-S bonds confirming the ageing of the parchment. This information is important especially for the origin of the support which seems to be original (medieval period), but conveniently treated to realize the fake writing [1].

#### 4. Conclusions

By means of non-destructive NIR Raman spectroscopy (excitation at  $1064\text{ nm}$ ) we analysed for the first time some ancient texts conserved in the Biblioteca Universitaria di Cagliari, Sardinia. The manuscripts were written on paper or parchment support and they are dated in the period XIV–XVI centuries A.D. The analysis aimed

to investigate not only the support (Paper or Parchment) used in the written procedure, but also a characterization of the employed inks.

The applied technique, and in particular the use of the IR excitation, which prevents any possible emission from the chemical species in the visible region, allowed us to investigate the nature of pigments and inks used in the manuscripts: we found a strong diffusion also in Sardinia of iron gall ink as typical medieval compound in the writing procedure substituted by carbon black (graphite) in the printed documents. The raman band at  $900\text{ cm}^{-1}$ , associated to the cellulose crystallinity, were analysed in order to determine the conservation state of the paper support. For what concerns the parchment we studied the presence of the band at  $500\text{ cm}^{-1}$  related to the S-S bond in disulfide bridges and the shift of the band at  $1667\text{ cm}^{-1}$  in order to characterize the conservation state of the parchment. Moreover the detection of pigments dated 19th century, confirms scientifically the falsity of the sample “Falsi di Arborea”.

In conclusion, through the exposed results we contributed to gain original insights about the Sardinia history and with more precision to testify the presence of particular treatments related to some specimens. As a consequence of this study we can speculate about a possible extension of the present results with those related to contemporary texts of other Italian regions (e.g. kind of inks and history or conservation state of paper and parchment). These actions don't exclude the systematic studies, with the same portable and non-destructive techniques, on the state of conservation of all the main treasures of the Biblioteca Universitaria di Cagliari and at the same time on other cultural heritage subjects in Sardinia.

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