

# CHARACTERIZATION OF WRITING MATERIALS OF BOOKS OF GREAT HISTORICAL-ARTISTIC VALUE BY FT-IR AND MICRO-RAMAN SPECTROSCOPY

**Vito Librando, Zelica Minniti**

Dipartimento di chimica  
Università degli Studi di Catania, Italy

*Keywords:* spectroscopy, infrared, Raman, cellulose, ink

## 1. Introduction

### 1.1 State of the art

Due to its non-destructive approach, infrared spectroscopy represents great potential for the characterization of the surface of different materials [1]. Many authors have applied this spectroscopic technique to paper characterization. Calvini and colleagues (2006) studied the composition of old and modern Japanese papers [2]. Hon (1986) demonstrated the effectiveness of FTIR in analyzing and determining acid impurities distributed on the surface of paper documents produced from 1790 to 1983 [1]. In one study by Mossini (1990), some naturally aged papers were subjected to FTIR analysis [3]. In a study by Zotti and colleagues (2008) the main surface components of bio-deteriorated papers from the XVIII century were characterized by FTIR spectroscopy; the author also referred to the presence of gelatin, wood pulp, calcium carbonate, gypsum, hemicelluloses and glue in the composition of the paper, as indicated by the characteristic FTIR absorption bands [4].

Raman spectroscopy has been applied to different types of artworks too. On paper artifacts, the presence of additives in the cellulose can be detected; Raman analysis of a map from the XVII century showed that gypsum was used as an additive in the cellulose [5]. Bicchieri and colleagues (2006) examined degraded papers using several non-destructive spectroscopic techniques, including Raman spectroscopy [6]. The cellulose subjected to accelerated hydrothermal ageing gives rise to a characteristic pattern of carbonyl groups; their vibrational modes were observed in Raman spectra by Lojewska and colleagues (2007) [7].

### 1.2 Paper structure

Paper mainly consists of bonded cellulose fibres that are linear polymers of glucose monomers linked by  $\beta$ -1.4-glycosidic bonds [8]. All chemical reactions occur at the level of the hemiacetal bond (glycosidic linkage) and/or hydroxyl groups. Cellulose chains

---

• Corresponding author: vlibrando@unict.it

are held together by strong intramolecular hydrogen bonds. 80% of these chains are ordered (crystalline forms), the remainder of the chains, are unordered (amorphous form) [9]. In addition to cellulose fibres, paper contains hemicellulose (wood polyoses), lignin and a certain amount of additives. The presence of acidic substances results in the hydrolysis of cellulose that appears in the shortening of its chain, along with a reduction in content of the crystalline form [10-11]. Progressive fragmentation of the chains makes the paper brittle, leading to increased oxidation and yellowing.

As a consequence of the aging process, oxidized groups (carbonyl and carboxyl groups) are formed on the cellulose chains. As there is a synergy between hydrolysis and oxidation, study of the alterations is very difficult [12].

### **1.3 Ink composition.**

Inks can be described as liquid, semi-liquid or solid preparations, which can be used to draw graphic signs on a support. The aging of inks is one of the major causes for corrosion of paper, the mechanism of which depends on the nature of the components and their interaction with paper. Different inks age differently: the literature focuses in particular on iron gall ink, which has been shown to be the principal cause of paper penetration. This is either due to the acid hydrolysis of cellulose (caused by an excess of sulphuric acid in the ink recipe) or to iron (II) ion oxidation reactions (caused by an excess of iron ions) [13-14]. Conversely, carbon black inks are stable due to their chemical inertia, but become more opaque with age. Other modern synthetic inks do not cause paper corrosion, but they are very photosensitive [15].

### **1.4 Aim of the work.**

In this work, FTIR and Raman spectroscopic techniques were used to characterize the cellulose on paper samples from books of great historical and artistic value and to identify inks on ancient samples of paper and parchment.

## **2. Experimental section.**

### **2.1 Methods.**

In order to characterize samples of the papers and the inks used on them, the two spectroscopic methods were used on both printed and non-printed areas of the pages of the books.

The spectroscopic analyses were carried out at ambient temperature and humidity; the spectra were acquired on a Thermo-Nicolet 6700 FTIR spectrometer with an Attenuated Total Reflectance (ATR) sampling tool (Diamond Crystal window). FTIR spectral analyses were performed at a resolution of  $4\text{ cm}^{-1}$  in the range of  $4000\text{--}550\text{ cm}^{-1}$  by iterating 32 scans for each analysis; the Raman spectra were recorded on a Thermo Dispersive Raman DXR spectrometer equipped with a 780 nm excitation laser and full range grating coupled to a micro-probe (CCD detector). 10x, 50x and 100x magnifying lenses are mounted on the head of the micro-probe. Neutral density filters implemented in the system were used to attenuate the laser power on the samples (between 1 and 14 mW).

## 2.2 Samples.

The samples, provided by the Public Library of Syracuse (Italy), come from the following books:

- book A - *Histoire naturelle, générale et particulière*, Volume 13, published in Paris in 1789<sup>1</sup>;
- book B - *Tractatus in Quinque Ecclesiae Praecepta*, published in Lyon in 1626<sup>2</sup>.
- Some fragments of paper and parchment belonging to the following books were also analysed;
- book C - *Augustini Eugubini In psalmum XVIII et CXXXVIII interpretatio. Epistola Erasmi Roterodami ad Augustinum Eugubinum. Augustini Eugubini ad Erasmus responsio, super his quae ab eo dicta sunt super Pentateuchum*, published in Lyon in 1533<sup>3</sup>;
- book D - *Officia Propria Sanctorum Jussu Syracusarum Episcopi*, published in Syracuse in 1794.

These fragments were found glued to the back plates of the listed books. Gluing paper fragments from old books was a common practice used to reinforce book covers. For this reason, these fragments are not datable, but they were also characterized and the findings discussed.

## 3. Results and discussion.

### 3.1 Paper characterization.

The FTIR analysis carried out on samples of paper from the three ancient books, A, B and C, show absorption bands typical of calcium stearate (shoulders at 2835\* and 1541\*  $\text{cm}^{-1}$ ) and the presence of gypsum (peaks at 661\*\* and 595\*\*  $\text{cm}^{-1}$ ) (Figure 1) [16]. The most interesting peaks are observed at frequencies of 1425 and 1316  $\text{cm}^{-1}$  and two smaller ones at 1335 and 1370  $\text{cm}^{-1}$ , these bands are very sensitive to the aging process of paper (Table 1) [17-23]. The rearrangement in hydrogen bonds due to oxidative reactions, causes changes in the vibrational pattern of these bands (Figure 1): the band at 1425  $\text{cm}^{-1}$  which is mainly due to H-C-H and O-H-C in plane bending vibrations [17-23] gains intensity with the accelerated aging of cellulose, while the band at 1316  $\text{cm}^{-1}$ , due to C-O-H and H-C-C bending vibrations, loses its intensity. Smaller changes in intensity are observed for the 1335 and 1370  $\text{cm}^{-1}$  bands that are similar to the 1316  $\text{cm}^{-1}$  band, assigned to the bending vibrations of C-O-H and H-C-C [17-23].

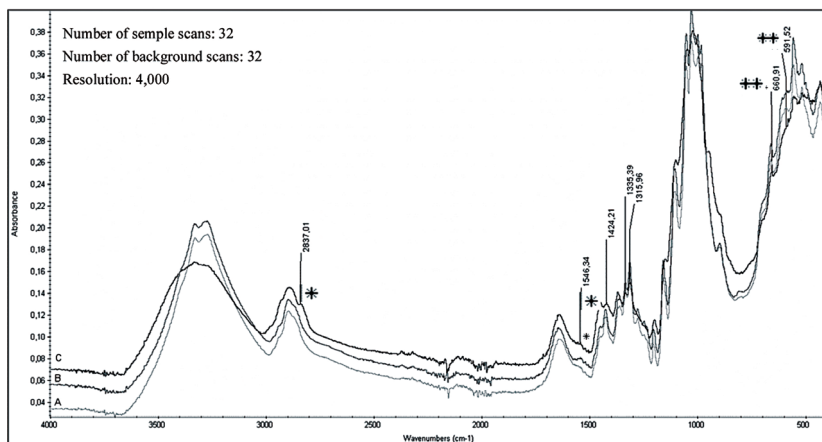


Figure 1. FTIR spectra of paper samples from books A, B and C. The bands at 1425, 1316, 1335 and 1370  $\text{cm}^{-1}$  are very sensitive to the paper aging process.  
\*bands due to calcium stearate;  
\*\*bands due to gypsum.

These changes in vibrational pattern are less marked in the ancient paper samples analysed. In fact, comparing the spectra of paper samples from book A (yr.1789) and book B (yr.1626), with recently produced paper (P-yr.2010) or with one from the last century (P-yr.1955) (16), the oldest samples show a much less marked degree of oxidation (Figure 2).

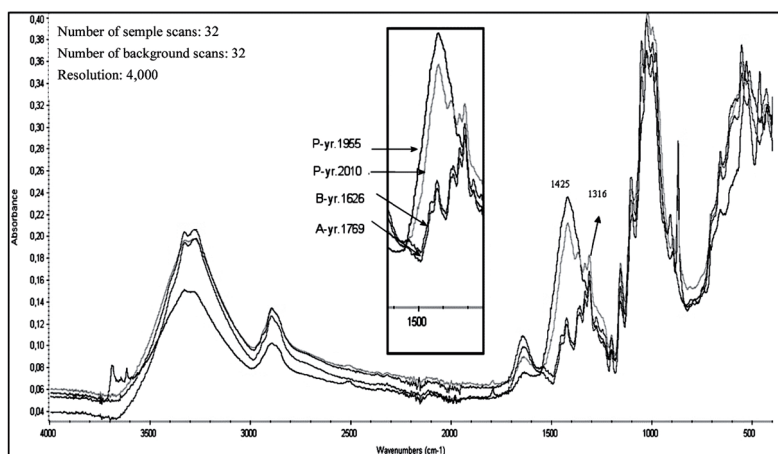


Figure 2. FTIR spectra of paper samples from ancient books A (yr. 1769) and B (yr. 1626) compared with recently produced paper (P-yr.2010) and with that produced last century (P-yr.1955): the band at 1425  $\text{cm}^{-1}$  gains intensity with accelerated aging of cellulose, while the 1316  $\text{cm}^{-1}$  band lowers its intensity



It is very difficult at this point to clearly interpret the data. However, it seems more likely that hydrolysis of the glycosidic bonds at this level of “destruction” causes changes in polymer structure mainly by forcing rearrangement in hydrogen bonding (changing from a crystalline to an amorphous form) which in turn changes the pattern of the CCH, COH, OCH and HCH bending vibration mode.

### 3.2 Characterization of the ink

Spectroscopic analysis revealed important information about the type of ink used in the samples from books A and B. In both samples there are the typical oxalate absorption bands at 1637 and 1315  $\text{cm}^{-1}$  but, without more specific analyses, it is difficult to state whether these signals come from the degradation of the ink or are typical of an iron-tannin complex. The weak peak at 821  $\text{cm}^{-1}$  in both samples suggests the presence of iron(II) oxalate [24] (Figure 3).

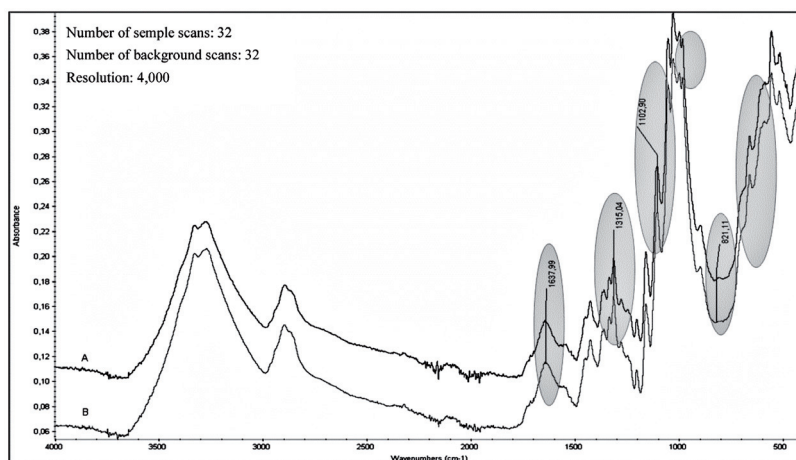


Figure 3. FTIR ink spectra from books A and B: the grey regions are very sensitive to the presence of oxalate, sulphate and carboxylic groups

One of the main problems of FTIR analysis is the presence of hidden bands, due to other components (e.g., calcium oxalate, iron-oxycellulose complexes, copper oxalate, aluminium oxalate) that absorb at approximately the same frequencies as iron oxalates and modify both the shape and the relative heights of the main peaks. The signal at about 1100  $\text{cm}^{-1}$  indicates the presence of sulphates, but the uncertainty regarding the nature of the sulphates (i.e. calcium, iron or sodium sulphate) makes it difficult to perform a thorough analysis of degraded iron gall inks [25]. By comparing the spectrum of the ink with the respective paper one, it is possible to note the increase in intensity of the characteristic absorption bands due to the stretching vibrations in  $\text{SO}_4^{2-}$  (strong in the range between 1120-1040  $\text{cm}^{-1}$  and 645-570  $\text{cm}^{-1}$ , and weak at 976  $\text{cm}^{-1}$ ) and in CO-OH (strong between 1700-1650  $\text{cm}^{-1}$  and 1350-1340  $\text{cm}^{-1}$  and medium between 950 and 825  $\text{cm}^{-1}$ ) [26] (Figures 4-5).

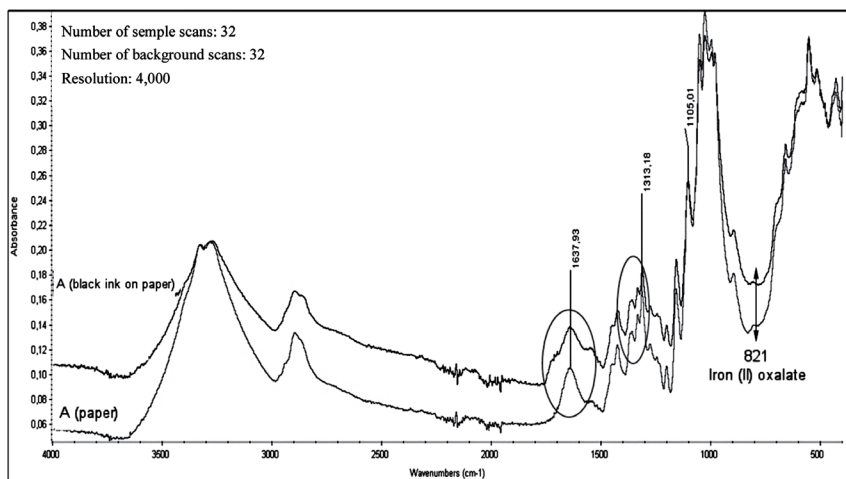


Figure 4. Ink sample from book A: comparison between the ink FTIR spectrum and the respective paper one, it is possible to notice the increase in intensity of the characteristic  $\text{SO}_4^{2-}$  absorption bands (in the 1120-1040 and 645-570  $\text{cm}^{-1}$  ranges); in the circles the oxalate and carboxylic groups bands (in the 1700-1650 and 1350-1340  $\text{cm}^{-1}$  regions) typical of metal-gall inks

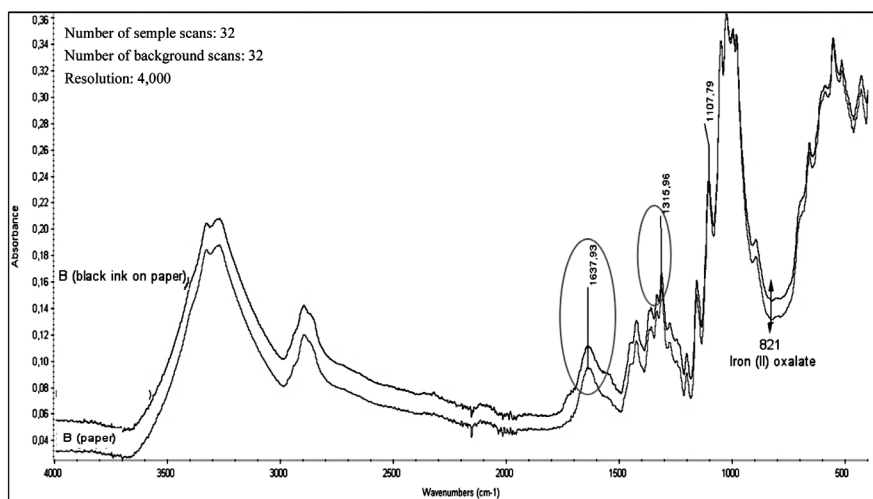


Figure 5. Ink sample from book B: comparison between the ink FTIR spectrum and respective paper one, it is possible to notice the increase in intensity of the characteristic  $\text{SO}_4^{2-}$  absorption bands (in the 1120-1040 and 645-570  $\text{cm}^{-1}$  ranges); in the circles the oxalate and carboxylic groups bands (in the 1700-1650 and 1350-1340  $\text{cm}^{-1}$  regions) typical of metal-gall inks

It is likely that they are metal gall inks. Through Raman analyses it was possible to characterise the red and black inks found on a sample of very deteriorated paper from book C (Figures 6-7). In particular, the strongest peak in the Raman spectrum at  $244\text{ cm}^{-1}$  (Figure 6) is typical of vermilion red ink ( $\text{HgS}$ , mercury sulphide of a natural mineral) [27]. The Raman absorption bands of black ink in the  $1350\text{-}1380$  and  $1580\text{-}1600\text{ cm}^{-1}$  range, are typical of amorphous carbon, known as “lampblack” or carbon black, which has been used since ancient times. In the spectrum of the paper fragment from book C, two bands are located at  $1365$  and  $1578\text{ cm}^{-1}$  (Figure 7) [28-29].

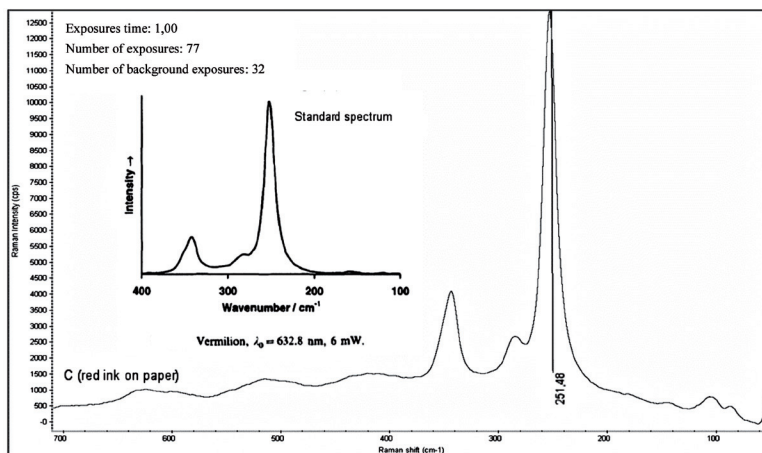


Figure 6. Red ink on fragments from book C; characteristic Raman spectrum of vermilion ( $251\text{ cm}^{-1}$  absorption band of mercury sulphide  $\text{HgS}$ )

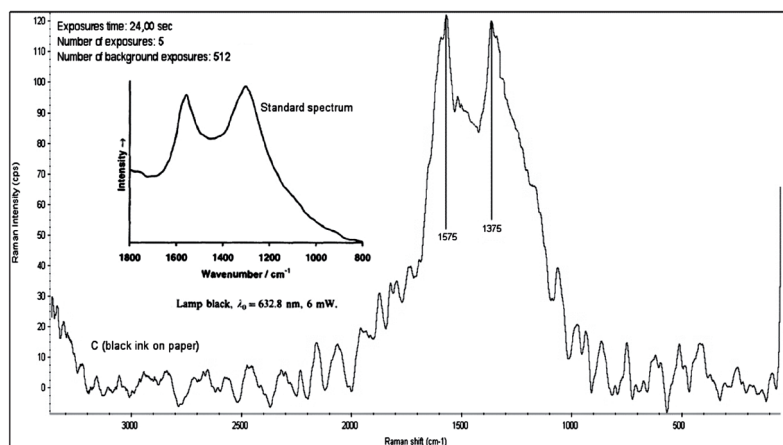


Figure 7. Black ink on fragments from book C; characteristic Raman spectrum of Lamp black ( $1575$  and  $1365\text{ cm}^{-1}$  absorption bands of amorphous carbon)

Raman analysis also made it possible to characterize the ink found on the samples of parchment fragments from book D (Figure 8). In particular the very strong band at  $1474\text{ cm}^{-1}$  is typical of iron gall ink and the broad band at about  $580\text{ cm}^{-1}$  may be related to the presence of metal salts. The absorption bands around  $1334$  and  $1588\text{ cm}^{-1}$  are probably due to the presence of a certain amount of amorphous carbon in the ink mixture. At times amorphous carbon (carbon black) was added to a metal gall ink (which was transparent immediately after preparation) in order to make it immediately usable. The other absorption bands are probably independent of the ink composition and may be related to organic iron complexes [27].

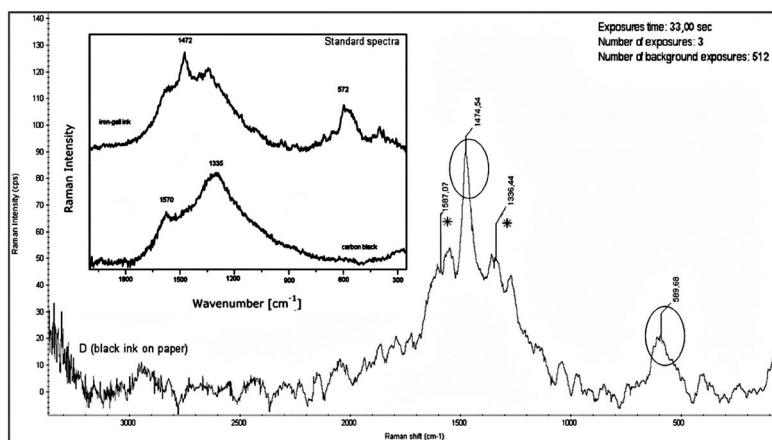


Figure 8. Black ink on fragments from book D: in the circles the typical absorption bands of iron-gall inks; absorption bands probably due to the presence of amorphous carbon in the ink mixture. In the box the standard spectra of iron-gall and lamp-black inks

#### 4. Conclusion.

In this study, FTIR and Raman techniques applied on original writing materials gave important information about paper composition and conservation state and enabled the type of ink used on them to be identified. Several samples of ancient paper were compared with each other and with modern paper samples in order to highlight differences between the more recent and the older paper. Analysis of the old paper revealed the presence of additives in lesser quantities than in present-day paper or that of the last century. Furthermore, the amount of amorphous cellulose in the ancient paper is lower than that in the samples of contemporary paper. These facts can be explained by the significantly higher quality of the materials constituting the older paper. Since ancient paper is essentially made of long chain cellulose derived from cotton rags used in old mills, it has better withstood the attacks of external agents and has been affected less by hydrolysis and oxidation processes.

The identification of metal-gall inks or organic inks from books A and B was rather difficult, since the ink absorption bands were covered by the cellulose band: indeed, cellulose is the main component of the sample and only small discrepancies were observed between the spectra of the inked paper and the spectra of the uninked paper

area. The interpretation of these small discrepancies measured on these ancient samples remains difficult due to the degradation processes in the ink and paper.

Raman spectroscopy has proved to be a very sensitive instrument for the identification of inks on parchment and paper samples. This technique allowed us to identify the red and black inks from paper fragments belonging to book C (as shown by the characteristic Raman spectrum of vermilion and lamp black) and the black ink on fragments belonging to book D. The spectrum of this black ink, in particular, showed a very strong band at  $1474\text{ cm}^{-1}$  typical of iron-gall ink, and two absorption bands around  $1334$  and  $1588\text{ cm}^{-1}$  that are probably due to the presence of a certain amount of amorphous carbon in the ink mixture.

### Acknowledgements

The authors wish to thank the MIUR (Ministry for Education, University and Research), PRIN 2009, for the financial support.

### Notes

- <sup>1</sup> Georges Louis Leclerc de Buffon (Montbard, 1707-Paris, 1788) was an eighteenth-century French naturalist. Buffon developed his interest in natural history after being appointed by Louis XV in 1739 as director of the Jardin du Roi (Royal Gardens and Natural History Collections) in Paris. He was ambitious and produced a collection of books about natural history (animals, plants, and minerals). In 1749 he published (along with a set of co-workers) the first three volumes of his famous *Histoire naturelle, générale et particulière* that ultimately comprised thirty-six volumes published over a period of fifty years. The *Histoire Naturelle* was an enormous success and became one of the most widely read books of the century. Buffon also included a number of theoretical essays in his *Histoire Naturelle* that were historically important for the theory about the evolution of life and on the concept of species.
- <sup>2</sup> The Jesuit, Tommaso Tamburino (Caltanissetta, 1591 – Palermo, 1675) was a dominant figure in the production of Italian casuistry which had developed in Sicily in the seventeenth century following that of Spain (School of Salamanca). Tamburino's works, thanks to the efforts of the Jesuits, spread throughout Europe from the mid-seventeenth century. His writings on moral theology, collected in "Opera Omnia", were published several times in Italy and abroad and were used as reference books in Europe for a century, even after his death.
- <sup>3</sup> Agostino Steuco (in Latin Steuchus or Eugubinus) (Gubbio, 1497 – Venezia, 1548), an Italian humanist, Old Testament scholar, a counter reformation polemicist and antiquarian, was born in Gubbio, in Umbria. Over several years (1529-33) Steuco wrote a series of controversial works against Luther and Erasmus, the latter of whom he accused of helping to foment the Protestant revolt against the Church. These works show Steuco's staunch support of the traditions and practices of the church, including a strident defence of papal authority. Part of his output during this period included an important set of annotations on the Pentateuch.

## References

- [1] HON D., 1986, *Fourier-Transform IR Spectroscopy and Electron-Spectroscopy for Chemical Analysis — Use in the Study of Paper Documents*, Advances in Chemistry Series, 212, pp. 349 - 361.
- [2] CALVINI P., GORASSINI A., CHIGGIATO R., 2006, *Fourier Transform Infrared Analysis of some Japanese Papers*, Restaurator, 27, pp. 81 - 89.
- [3] MOSSINI V., CALVINI P., MATTOGNO G., RIGHINI G., 1990, Derivative Infrared Spectroscopy and Electron Spectroscopy for Chemical Analysis of Ancient Paper Documents, Cellulose Chemistry and Technology, 24, pp. 263 - 272.
- [4] ZOTTI M., FERRONI A., CALVINI P., 2008, *Microfungal Biodeterioration of Historic Paper: Preliminary FTIR and Microbiological Analyses*, International Biodeterioration & Biodegradation, 62, pp. 186 - 194.
- [5] CASTRO K., PESSANHA S., PROIETTI N., PRINCI E., CAPITANI D., CARVALHO M.L., MADARIAGA J.M., 2008, *Noninvasive and Nondestructive NMR, Raman and XRF Analysis of a Blaeu Coloured Map from the Seventeenth Century*, Analytical and Bioanalytical Chemistry, 391, pp. 433 - 441.
- [6] BICCHIERI M., SODO A., PIANTANIDA G., COLUZZA C., 2006, *Analysis of Degraded Papers by non-Destructive Spectroscopic Techniques*, Journal of Raman Spectroscopy, 37, pp. 1186 - 1192.
- [7] LOJEWSKA J., MISSORI M., LUBANSKA A., GRIMALDI P., ZIEBA K., PRONIEWICZ L.M., CCONGIU CASTELLANO A., 2007, *Carbonyl Groups Development on Degraded Cellulose. Correlation between Spectroscopic and Chemical Results*, Applied Physics A - Materials Science & Processing, 89, pp. 883 - 887.
- [8] PRONIEWICZ L. M., PALUSZKIEWICZ C., WESELUCHA-BIRCZYNSKA A., MAJCHERCZYK H., BARANSKI A., KONIECZNA A., 2001, *FT-IR and FT-Raman Study of Hydrothermally Degradated Cellulose*, Journal of Molecular Structure, 596, pp. 163 - 169.
- [9] FENGEL D., WEGENER G., 1989, *Wood Chemistry, Ultrastructure, Reaction*, Walter de Gruyter. Berlin.
- [10] BROWING B. L., 1977, *Analysis of Paper*, Marcell-Dekker, New York.
- [11] WILSON K. W., PARKS E. J., 1979, *An Analysis of the Aging of Paper: Possible Reactions and their Effects on Measurable Properties*, Restaurator, 3, pp. 1 - 2.
- [12] CSEFALVAYOVÁ L., HAVLÍNOVÁ B., ČEPPAN M., 2006, *Monitoring of Corrosive Effect of Iron-Gall Ink on Paper*, In Pre-Conference Proceedings The Final MIP Conference/2nd International Iron Gall Meeting, Newcastle upon Tyne (UK), pp. 24 - 26.
- [13] CALVINI P., 2001, *Organic Chemistry: Chemical Processes which Foster Degradation Agents, Conservation of Paper Materials and Books in Central and Eastern Europe*, TVM, Mestre.
- [14] REIßLAND B., HOFENK DE GRAAFF J., 2001, *Conditioning Rating for Paper Objects with Iron-Gall Ink*, ICN-Information, 1, pp. 1 - 4.
- [15] MARAVAL M., FLIEDER F., 1993, *The Stability of Printing Inks*, Restaurator, 14, pp. 141 - 150.
- [16] LIBRANDO V., LORUSSO S., MINNITI Z., 2011, *Ancient and Modern Paper Characterization by FTIR and Micro-Raman Spectroscopy*, Conservation Science in Cultural Heritage, 11, 249 - 268.
- [17] VASCO P.D., BLACKWELL J., KOENIG J.L., 1972, *Infrared and Raman Spectroscopy of Carbohydrates. Part II: Normal Coordinate Analysis of Glucose*, Carbohydrate Research, 23, pp. 407 - 416.
- [18] LIN-VIEN D., COLTHUP N.B., FATELY W.G., GRASELLI J.G., 1991, *The Hand-*



- book of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press, San Diego, CA.
- [19] ZHBANKOV R. G., ADRIANOW W.M., RATAJCZAK H., MARCHEWKA M., 1995, *Vibrational Spectra (IR and Raman) and Stereoisomers of Carbohydrates*, Journal of Physical Chemistry, 68, pp. 553 - 558.
- [20] ZHBANKOV R. G., ADRIANOW W. M., RATAJCZAK H., MARCHEWKA M., 1995, *Vibrational Spectra and Stereochemistry of Mono- and Polysaccharides. Anomers of D-Glucose*, Journal of Structural Chemistry, 36, pp. 287 - 294.
- [21] WILEY J. H., ATALLA R. H., 1987, *Band assignments in the Raman-spectra of celluloses*, Carbohydrate Research;160, pp. 113 - 129.
- [22] TU A. T., LEE J., MILANOVICH F. P., 1979, *Laser-Raman Spectroscopic Study of Cyclohexaamylose and Related Compounds; Spectral Analysis and Structural Implications*. Carbohydrate Research, 76, pp. 239 - 244.
- [23] GILBERT C., KOKOT S., MEYER U., 1993, *Application of DRIFT Spectroscopy and Chemometrics for the Comparison of Cotton Fabrics*, Applied Spectroscopy, 47, pp. 741 - 748.
- [24] FERRER N., SISTACH M.C., 2005, *Characterisation by FTIR Spectroscopy of Ink Components in Ancient Manuscripts*, Restaurator, 26, pp. 105 - 117.
- [25] CALVINI P., VASSALLO S., 2007, *Computer-Assisted Infrared Analysis of Heterogeneous Works of Art*, Preservation Science, 4, pp. 13 - 17.
- [26] SENVAITIENĖ J., BEGANSKIENĖ A., SALICKAITĖ-BUNIKIENĖ L., KAREIVA A., 2006, *Analytical Identification of Historical Writing Inks – A new methodological Approach*, Lithuanian Journal of Physics, 46, 1, pp. 109 - 115.
- [27] EDWARDS H. G. M., FARWEL D. W., NEWTON E. M., RULL PEREZ F., JORGE VILLAR S., 2001, *Application of FT-Raman Spectroscopy to the Characterisation of Parchment and Vellum*, Spectrochimica Acta Part A, pp. 1223 - 1234.
- [28] BUGIO L., CIOMARTAN DAN A., CLARK R. J. H., 1997, *Pigment Identification on Medieval Manuscripts, Paintings and other Artefacts By Raman Microscopy: Applications to the Study of Three German Manuscripts*, Journal of Molecular Structure, 405, pp. 1 – 11.
- [29] BELL I.M., CLARK R. J. H., GIBBS P. J., 1997, *Raman Spectroscopic Library of Natural and Synthetic Pigments (pre- 1850 AD)*, Spectrochimica Acta Part A, 53, pp. 2159

### Biographical Notes

**Vito Librando** has a degree in Chemistry, he is Full Professor of Environmental Chemistry and Cultural Heritage at Catania University and he has been Professor of Chemistry of Cultural Heritage, Restoration Chemistry, Laboratory of Chemistry of Cultural Heritage, both in three-year and magisterial degree courses of "Science and Technology of Restoration."

He has been involved in the study of organic inhibitors of the crystallization of mixtures of salts in stone materials, as well as in FT-IR mapping and Raman micro-spectroscopy applied to the Cultural Heritage. He has coordinated national and international research projects, such as Strategic Projects of the NRC, MIUR, INTAS and the Sicilian Region.

He is the author of 110 publications in international scientific journals, mainly in the field of Chemistry of Cultural Heritage and Environmental Chemistry.

**Zelica Minniti** graduated in Biological Science at Catania University in 2004. She did a doctorate in Chemical Science at Catania University with a thesis on advanced characterization methods of organic materials of environmental and historical-artistic relevance through Micro-FTIR Mapping and Raman Microscopy. She has taken part in different environmental chemistry research projects in partnership with different organizations such as: ARPA Sicilia, Consorzio Catania Ricerche e Consorzio COMETA. She is currently working for the research center "CRAM3RA" directed by Prof. Vito Librando.