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M. Bicchieri, F. Valentini, F. Pascalicchio, M.L. Riccardi, P. Colaizzi, C. Del Re, M. Talamo, *The solution to an unresolved problem: newly synthesised nanocollagen for the preservation of leather*, Journal of Cultural Heritage, <https://doi.org/10.1016/j.culher.2018.03.002>

Abstract

A widespread problem in libraries is related to the preservation of book covers in leather that are often torn, powdery and abraded. The same problem is encountered in the conservation of leather goods. Until now a satisfactory solution to contrast the leather deterioration had not been found and the applied conservation methods offered only temporary solutions, without guaranteeing a real and durable effectiveness. At the Istituto centrale restauro e conservazione patrimonio archivistico e librario (Icrupal) it was decided to research more durable results and to apply nanocollagen solutions to the leather. A new synthesis of nanocollagen was performed in collaboration with Università Tor Vergata, and Fondazione INUIT and the newly synthesised nanocollagen was characterised by different spectroscopic and imaging techniques, then applied to laboratory samples and, at the end of the research, it was used in the restoration of the leather cover of a 18th book. All the measurements performed on the tested leathers did not show any colour change after nanocollagen application, an increase of all mechanical characteristics and, of paramount importance, an increase in the shrinkage temperature of the leather with a partial reconstitution of its lost elasticity and flexibility.

M. Bicchieri *Hard science and history*, Manuscript Cultures 11 (2018), 3-15

Abstract

Books, archival documents and graphic works of art are one amongst the most invaluable patrimony in human history. Each single document is an open window on our history and its preservation is paramount.

Often the value of books is merely evaluated on the basis of their content, either textual or graphical, and it is neglected the history brought by the physical support, the paper used, the kind of ink chosen, their provenience, what are they made of, the fabrication procedures. All of these information, stored between the pages, and somehow hidden to the eye, tell us of the long travel of the paper used, of the technological and scientific discoveries made at the time the book was written or drawn, they tell of the genius of whom invented an ink or a specific paper treatment, they bring with them the evolution of aesthetics and morals and the costumes of the time.

In short terms, they are carriers of our story, of the human history.

This entire incommensurable heritage is unfortunately destined to a slow death.

Supports, media, and binding are subject to ageing and they lose their mechanical characteristics; inks can fade or induce acidity in the support, by damaging it till reaching its complete destruction. The natural aging is a spontaneous and irreversible process; quite slow by itself in absence of other external interferences, such as, for example, the storage in unsuitable places, when other degradation processes -physical, biological or chemical- can take place.

The function of scientists in the field of conservation of Cultural Heritage is manifold. On the one hand by investigating the structure of materials, they can understand the nature and the causes of the degradation and find solutions to prevent a further decay. On the other they can solve some problems or questions related to the manufacturing of the object or to its past life, thus helping scholars in their historical studies. Moreover, each discovery permits, as well, to explore issues of the history of science.

In this paper two case studies -Leonardo da Vinci self-portrait and the Purple *Codex Rossanensis*- will be presented to underline the synergy -positive or negative- between different expertise.

C. Colini, O. Hahn, O. Bonnerot, S. Steger, Z. Cohen, T. Ghigo, T. Christiansen, M. Bicchieri, P. Biocca, M. Krutzsch, and I. Rabin, *The Quest for the Mixed Inks*, Manuscript Cultures 11 (2018), 41-48

Abstract

Analysis of mixed inks obtained by mixing soot or charcoal with tannin extracts or iron-gall ink and comparison with original documents by Raman, Reflectography and XRF.

M. Bicchieri, F. Valentini, A. Calcaterra, M. Talamo, *Newly developed nano-calcium carbonate and nano-calcium propanoate for the deacidification of library and archival materials*, Journal of Analytical Methods in Chemistry Volume 2017, Article ID 2372789, 8 pages, <https://doi.org/10.1155/2017/2372789>

Abstract

Paper-based cultural heritage objects are subject to natural deterioration due to internal and external factors, that is, the presence of heavy metals, incorrect conservation, humidity, exposure of the artifacts to pollutants, light, and high temperatures. To contrast the decay of the original objects, it is necessary to study and apply innovative specific techniques, set up novel preservation methodologies, and implement or synthesize new products. As the nanomaterial science field developed over the last decades, the usage of nanomaterials in cultural heritage gained a prominent role. Such an excitement for the novel materials opened the path for an uncontrolled transfer of nanoparticles developed for different applications to paper restoration, neglecting all their possible interactions with the support or the graphic media. The aim of this work was to synthesize new nanomaterials expressly conceived for the treatment of library materials. To evaluate their possible insertion in the official conservation treatments that are subjected to validation by Istituto Centrale Restauro e Conservazione Patrimonio Archivistico e Librario, the new nanomaterials were tested both on laboratory paper samples and on original documents. This work presents the results of these studies (some of which still preliminary) stressing the positive and extremely promising outcomes of this research.

F. Valentini, M. Bicchieri, A. Calcaterra, M. Talamo, *Raman, X-Ray Fluorescence Spectroscopies and Graphene Oxide Modified Screen Printed Electrodes to Identify the Pigments and Earth Present in Ancient Leather Samples*, DOI: 10.1002/elan.201700457 2 (2017)

Abstract

Micro-Raman and X-Ray Fluorescence combined with electrochemical techniques proved to be suitable for the unambiguous identification of the green pigment in a very deteriorated historical leather. The colouring matter resulted in a mixture of blue and yellow. Raman identified the blue indigo, whereas iron and arsenic were identified by XRF. The redox status of these two elements was investigated by Square Wave Cathodic Stripping Voltammetry (SWCSV). Results demonstrated the presence of As(III), probably As₂S₃ (orpiment), and Fe(III), characterising the red earths. The quantitative results obtained by SWCSV were also confirmed for Fe and As by ICP-MS (Inductively Coupled Plasma Mass spectrometry). Voltammetric techniques, applied here for the identification of the redox status of the elements, contained in pigments, are useful to understand two important aspects: the chemical-physical composition of the colors and the best strategy to be applied for the preservation of the pigments in ancient/deteriorated artwork objects.

M.C. Sclocchi, L. Kraková, F. Pinzari, P. Colaizzi, M. Bicchieri, N. Šaková, D. Pangallo, *Microbial Life and Death in a Foxing Stain: a Suggested Mechanism of Photographic Prints Defacement*, Microb. Ecology, DOI 10.1007/s00248-016-0913-7 (2016).

Abstract

The gelatin-silver halide black and white prints represent an enormous photography heritage with a great value. Unaesthetic phenomena, the foxing stains that are caused by microbial growth on

surface, have been described in stamps, drawings, books, and tissues but, until now, scarcely for photo-graphic materials. In this study, a combination of various techniques, including culture-dependent and culture-independent approaches (RNA and DNA analysis), scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) and μ -Raman spectroscopy supported by X-ray fluorescence analysis (XRF), permitted to describe the microbial contamination dynamics of foxing stains present on the surface of two gelatin-silver halide photographs. The investigation provided also information on the effects of microbial activity on the materials' chemistry of the two prints. The action of microbial community resulted locally in either (a) formation of mixed aluminum-iron-potassium phosphate compounds that could be attributed to the hydrolytic activity of bacteria, (b) leaching of barite, (c) precipitation of a mixture of oxides, and (d) a change in the barium sulfate chemical structures.

M. Bicchieri, A. Sodo, *Alcoholic deacidification and simultaneous deacidification-reduction of paper evaluated after artificial and natural aging*, Journal of Cultural Heritage, doi:10.1016/j.culher.2016.02.008.

Abstract

Cellulose oxidative and hydrolytical degradation is one of the greatest problems for the conservation of paper supports. To contrast these degradation processes, both deacidification and reduction of the oxidized functions are needed. Dealing with original documents, it is often impossible to perform the two mentioned treatments in aqueous solutions and in a distinct subsequent way, because of the fragility of the artifacts. After studying, in a separate way, an effective deacidifier (calcium propionate) soluble in ethyl alcohol and many reducers (boron complexes), able to act in different non-aqueous solvents, it was decided to test a simultaneous method of deacidification and reduction in ethanol. This paper presents the chemical-physical results obtained by applying simple deacidification and simultaneous deacidification-reduction on laboratory paper samples that were artificially aged and then re-measured after 10 and 15 years of natural aging. Results show that all alcoholic treatments are very effective: papers are stable also after a long period of both artificial and natural aging.

M. Bicchieri, M. Monti, G. Piantanida, A. Sodo, *Effects of gamma irradiation on deteriorated paper*, Radiation Physics and Chemistry Volume 125, August 2016, Pages 21–26; doi:10.1016/j.radphyschem.2016.03.005.

Abstract

Even though gamma radiation application, also at the minimum dosage required for disinfection, causes depolymerization and degradation of the paper substrate, recently published papers seemed, instead, to suggest that γ -rays application could be envisaged in some conditions for Cultural Heritage original documents and books. In some of the published papers, the possible application of γ -rays was evaluated mainly by using mechanical tests that scarcely reflect the chemical modifications induced in the cellulosic support. In the present article the effect of low dosage γ -irradiation on cellulosic substrates was studied and monitored applying different techniques: colorimetry, spectroscopic measurements, carbonyl content and average viscometric degree of polymerization. Two different papers were investigated, a non-sized, non-filled cotton paper, and a commercial permanent paper. To simulate a real deteriorated document, which could need γ -rays irradiation, some samples were submitted to a hydrolysis treatment. We developed a treatment based on the exposition of paper to hydrochloric acid vapours, avoiding any contact of the samples with water. This method induces a degradation similar to that observed on original documents.

M. Bicchieri, F. Pinzari, *Discoveries and oddities in library materials*, *Microchemical Journal* 124 (2016) 568-577

Abstract

Surprising discoveries can happen while analyzing library materials.

This paper presents four case studies focusing on four artifacts of different age and provenance, all analyzed and studied at the Icrepal.

The first case deals with two parchment codices that have been found in 2008 during a fishing expedition in the Canale di Sicilia. At that time a deep-sea fishing boat belonging to the fleet of Mazara del Vallo found, caught in the nets, two artifacts. This was the first discovery of library materials in the deep sea. The SEM and EDS analyses allowed for the creation of a compositional map of the surface of the samples, where several microscopic encrusting sea organisms and biogenic materials were also observed. Almost nothing of the original structure of the parchment (of which the object is presumably made) could be recognized at SEM. The absence of the typical collagen features was confirmed by Raman analyses: only spectra of an isoprenic-type polymer of putative biogenic origin were collected.

The second case deals with fragments of medieval manuscripts that were found in 2007 buried in the walls of the Great Mosque of Sana'a in Yemen. An outstanding discovery regarded the dark brown inks used on a Quranic fragment attributed to the 10th century. SEM micrographs disclosed the presence of red blood cells mixed to inks components. The inks were also investigated with Raman spectroscopy.

The third case study is the book "Libretto di appunti e memorie del Padre Francesco Zazzera", dated 17th century that presented a peculiar modification of the black ink that appeared to be faded and turned to a white-yellowish color. Raman and SEM analyses recognized and documented a biogenic formation of jarosite on top of the ink. It was possible to remove the jarosite layer and to recover the original black ink, thus allowing an easier reading of the text.

The fourth and last case analyzed and presented in this paper consists on the measurements on the invaluable 6th century Codex Purpureus Rossanensis. The analyses allowed, through Raman spectroscopy, to demonstrate the use of an elderberry lake to obtain a mauve color. This is the first experimental evidence of the use of that particular dye in a so ancient illuminated manuscript.

A sort of archeological discovery was also done on the Codex Purpureus Rossanensis respect to the past misfortunes occurred to it, just observing some traces that support some intriguing hypothesis on its history and vicissitudes.

M. Bicchieri, *The purple Codex Rossanensis: spectroscopic characterization and first evidence of the use of the elderberry lake in a 6th century manuscript*, *Environmental Science and Pollution Research*, 2014, DOI: 10.1007/s11356-014-3341-6; Volume 21, Issue 24 (2014), 14146-14157

Abstract

This paper presents the results obtained during the measurements campaign started in June 2012 and ended in November 2013 on the invaluable purple Codex Rossanensis, sixth century, one of the oldest surviving illuminated manuscripts of the New Testament. The tasks of the chemistry laboratory were to answer a variety of questions posed both by historians and restorers, concerning the materials used in a previous restoration, the composition of the pictorial palette and the different inks and to determine which colouring material had been applied to dye the parchment support. It was also requested to determine the state of preservation of the manuscript, as a result of its interactions with the environment in which the manuscript had been stored and the vicissitudes experienced during its life (fire, previous restoration, exhibition). The spectroscopic analyses performed by micro-Raman, micro-Fourier transform infrared and X-ray fluorescence allowed to fill a gap in the knowledge of the pictorial materials used in the Early Middle Ages. The pictorial palette, the inks, the dye applied to obtain the purple parchments, the support and the materials used in the previous restoration treatment executed in 1917-19 were fully characterised. Moreover, to the author's

knowledge, the article shows the first experimental evidence of the use of the elderberry lake in a sixth century-illuminated manuscript. The lake was characterised by Raman spectroscopy.

M. Bučková, A. Puškárová, M.C. Sclocchi, M. Bicchieri, P. Colaizzi, F. Pinzari, D. Pangallo, *Co-occurrence of bacteria and fungi and spatial partitioning during photographic materials biodeterioration*, Polymer Degradation and Stability 108 (2014), 1-11. DOI 10.1016/j.polymdegradstab.2014.05.025

Abstract

The microbial spoilage and correlated surface changes of a cellulose nitrate negative film, a gelatine–silver positive print, a cardboard frame and a cellulosic envelope dated back to 1938–1940 was assessed by means of molecular methods and scanning electron microscopy (SEM). Materials characterisation was obtained with Raman, Infrared and Electronic dispersion spectroscopies. DNA was extracted from bacteria and fungi, amplified through PCR oriented to bacterial 16S rRNA gene and fungal internal transcribed spacer (ITS), and clone libraries were constructed for each investigated material. The ITS fungal cloning was able to detect a bigger spectrum of species respect to bacterial one. Correspondence between molecular results and SEM observations was used to address the cause of biodeterioration to single species, and to map the presence of different organisms in separate niches. This investigation highlighted a co-occurrence of both bacteria and fungi on most of the substrata, and a spatial partitioning according to the different photographic materials. Moreover, for the first time, the effects of a biological attack on glassine paper were documented.

F. Pinzari, J. Tate, M. Bicchieri, Young Joon Rhee and G. M. Gadd, *Biodegradation of ivory (natural apatite): possible involvement of fungal activity in biodeterioration of the Lewis Chessmen* (2013) Environmental Microbiology 15(4), 1050–1062

Abstract

Fungal biodeterioration of ivory was investigated with in vitro inoculation of samples obtained from boar and walrus tusks with the fungi *Aspergillus niger* and *Serpula himantoides*, species of known geoactive abilities. A combination of light and scanning electron microscopy together with associated analytical techniques was used to characterize fungal interactions with the ivory, including changes in ivory composition, dissolution and tunnelling, and the formation of new biominerals. The research was aimed at providing further understanding of the potential roles of fungi in the colonization and deterioration of ivory in terrestrial environments, but also contributes to our knowledge regarding the possible origins of the surface damage observed on early medieval sculptures made largely from walrus tusks, referred to as 'the Lewis hoard of gaming pieces', that were presumably produced for playing chess. The experiments have shown that the possibility of damage to ivory being caused by fungi is realistic. Scanning electron microscopy revealed penetration of fungal hyphae within cracks in the walrus tusk that showed also widespread tunnelling by fungal hyphae as well as 'fungal footprints' where the surface was etched as a consequence of mycelial colonization. Similar phenomena were observed with boar tusk ivory, while production of metabolites could lead to complete dissolution of the sample. Colonization of ivory and/or exposure to fungal activity lead to extensive secondary biomineral formation, and this was identified as calcium oxalate, mainly as the monohydrate, whewellite.

G. Piantanida, E. Menart, M. Bicchieri, M. Strlič, *Non-destructive classification of iron-based ink by means of micro-Raman Spectroscopy* (2013) J. of Raman Spectroscopy 44, 1299–1305

Abstract

In this work, multivariate data analysis methods were applied to the analysis and interpretation of micro-Raman spectra, collected from a broad set of historical iron-based ink samples, previously

characterised for the content of organic acids (gallic acid, ellagic acid and protocatechuic acid). The proposed method relies on principal component analysis of the noisy spectra typically obtained on original, degraded, organic samples, where fluorescence could affect the Raman signal. The signal components could be distinguished from the noise components and then used to build a linear discriminant analysis (LDA) model, achieving separation of the spectra into three classes. Selection of pure signal factors also improved effectiveness and performances of partial least square regression (PLS) algorithms, allowing quantification of condensed tannic acid residuals. Application of multivariate methods to discriminate signal from noise removes the need for spectral data manipulation (filtering, smoothing and differentiating). The obtained classification method for discrimination of historic inks and the regression method for determination of condensed tannic acid residuals supports the use of Raman analysis of fluorescing organic materials, and may provide information to scholars on ink composition and potentially on its provenance.

M. Bicchieri, M. Monti, G. Piantanida, A. Sodo, *Non-destructive spectroscopic investigation on historic Yemenite scriptorial fragments: evidence of different degradation and recipes for iron tannic inks* (2013) *Analytical Bioanalytical Chemistry* - 405 (8), 2713-2721

Abstract

Six fragments of different Yemenite manuscripts (three on parchment and three on paper) were analyzed by means of attenuated total reflectance Fourier transform infrared, micro-Raman and X-ray fluorescence spectroscopies. The combination of molecular and elemental techniques allowed the characterization of the conservation state of all the fragments, the identification of sizing agents and salts on the supports and the identification of the composition all red and black writing media. In particular, analysis of black inks provided interesting insights: independent of the substrate, all inks seemed to have identical composition, corresponding to rather well preserved high-quality iron tannic inks to which carbon black had not been added. However, in some samples, the most intense Raman peak of the ink was clearly shifted with respect to the typical bands of iron gall ink. Starting from the hypothesis that the shift could have been produced by the use of sources of tannin other than gallnuts, research was undertaken by preparing and characterizing seven different tannic inks. The experimental results confirmed the hypothesis of different tannin sources.

A. Sodo, M. Bicchieri, M. Guiso, M. A. Ricci, G. Ricci, *Raman investigations on marker pen inks*, *Journal of Raman Spectroscopy* (2012) DOI: 10.1002/jrs.4070

Abstract

Characterization and conservation of materials used in contemporary art are a big challenge for scientists and restorers because of the huge variability and the large heterogeneity of their use and compositions. The aim of this work is to contribute to the knowledge of the composition of new materials extensively applied in contemporary artworks, namely the marker pen inks. Marker pen inks represent a serious problem for restorers as they fade in a few years, changing colour and shade. Moreover, they are often soluble in the commonly used solvents. This research is performed in collaboration with the Fondazione Federico Fellini, owner of more than 500 original drawings of the famous movie director -most of them realised by marker pens. In this work, we report, for the first time, Raman spectra of marker pen original and 'laboratory' drawings. Studies of the 'laboratory' samples have been complemented by thin layer chromatography in order to separate the complex colouring mixture into its individual components. Raman spectra of yellow, orange and red standard samples of two consumer and two professional brands have been recorded and identified. A comparison among old and new marker pen inks composition is discussed, and inferences are drawn about the brand likely used in the two originals. Interestingly, we notice that food additives are often used as colour agents in marker pen inks and report here their standard Raman spectra. This study puts into evidence the need for a reliable standard database of pigments and dyes.

M. Bicchieri, M. Monti, G. Piantanida, F. Pinzari, S. Iannuccelli, S. Sotgiu, L. Tireni, *The Indian drawings of the poet Cesare Pascarella. Non destructive analyses and conservation treatments*, Analytical and Bioanalytical Chemistry: Volume 402, Issue 4 (2012), 1517-1528, DOI 10.1007/s00216-011-5229-3 ISSN 1618-2642

Abstract

The Italian dialect poet Cesare Pascarella travelled all around the world, noting down in notebooks his keen and caustic observations, and drawing sketches that are a visual reportage of his journeys. The sketches were mounted as a random collage over acidic cardboards that were exposed to direct sunlight in his studio. Their poor state of conservation is related to the use of modern paper: chemical instability of raw materials caused acidification and strong oxidation of the support, with intense yellowing of the surfaces and brittleness of the paper. To ensure future preservation of the drawings, chemical stabilisation with simultaneous alcoholic treatment by deacidification (calcium propionate) and reduction (borane tert-butylamine complex) appeared necessary. To verify its applicability, it was indispensable to characterise the support and identify the nature of all the graphic media. The use of Raman, Infrared, X-ray fluorescence spectroscopies and scanning electron microscopy coupled with X-ray microanalysis allowed us to clear the problems related to the different penetration depth of each analytical technique and the different responses of pigments/dyes to each spectroscopy. The palette, how it varied along the journeys, the different supports used and preparations were completely identified showing a choice of colours compatible with the reduction treatment.

F. Pinzari, M. Bicchieri, *Variable pressure scanning electron microscopy applied in the study of ancient manuscripts and inks*. In: *Historical Technology, Materials and Conservation. SEM and Microanalysis*. N. Meeks, C. Cartwright, A. Meek, A. Mongiatti (eds). London (2012), Archetype Publications Ltd., 188-189. Abstract

Variable pressure (VP) scanning electron microscopy (SEM) represents a micro-invasive methodology that can be successfully applied in the study of ancient manuscripts, inks, illuminated parchments and other writing supports. This method makes it possible to analyse degradation phenomena, study constituent materials and manufacturing processes, evaluate restoration practices, and describe the microscopic effects of chemical treatments.

M. Bicchieri, M. Monti, G. Piantanida, F. Pinzari, A. Sodo, *Non-destructive spectroscopic characterization of parchment documents*, Vib. Spectrosc. (2011) 55, 267-272

Abstract

Membranaceous substrates – widely found in library heritage – are truly challenging, due to the variety of manufacturing traditions, the intrinsic variability of the animal's skin and the different degradation patterns affecting documents along ageing. Moreover, when dealing with unique and delicate objects as cultural heritage specimens, sampling is never recommended and often explicitly forbidden. Aim of the research presented in this work is to achieve correct protocols for unambiguous characterization of the document's materials chemical structure and of the possible surface treatments. Experimental results allow us to evidence that the chosen non-destructive techniques (Raman, ATR-FTIR and SEM/EDS) provide a good differentiation between parchment manufacturing procedures, western with lime and eastern with enzymatic treatment. Incrustations of salts on the surface as well as superficial treatment with tannin can be clearly detected. Origin of tannin – from the surface or in ink – can also be distinguished. Choice of the better technique is sample-dependent, since preparation methods, degradation, presence of incrustations, amount of tannin, dehairing method can differently affect the spectral features. For instance, Raman appears to be the most effective molecular technique on western parchment, whereas ATR-FTIR allows distinguishing the enzymatic dehairing procedure from the chemical one.

M. Bicchieri, M. Monti, G. Piantanida, A. Sodo, *Applied research and critical approach: the proper way to deal with “real” library heritage*. In *New Approaches to Book and Paper Conservation - Restoration*, P. Engel, J. Schirò, R. Larsen, E. Moussakova and I. Kecskeméti (eds.) (2011) Verlag Berger Horn/Wien, 617-628

Abstract

Characterization of manuscripts and books presents several challenges related to the wide amount of involved materials and to the complexity of their possible interactions. In this presentation we want to stress how collecting data -and correctly interpreting them- requires a thorough research work: at the state of the art, diagnostics on cultural heritage cannot be limited to routine tests. Knowledge of materials superimposition, interactions and degradation patterns is necessary to choose, from time to time, the techniques to be used, the way to compare data and, when appropriate, to prepare ad hoc standards. Along decades of conservation science, in fact, a number of specific problems related to documents deterioration (cellulose oxidation and hydrolysis, iron gall inks degradation...) have been deeply investigated and -in some cases- even theoretically modelled. Nevertheless, “real” objects are hardly constituted by ideal materials, showing a single, well-defined degradation pattern. Paper is not just “cellulose” or “cellulose and lignin”, it is sized -in order to be written- and minerally charged, occasionally it can be also treated or bleached. Then, it is written, decorated, illuminated: all materials involved in such processes interact and degrade as well as the constituting fibres.

Last but not least, in case of real artworks' analysis, non-destructivity is mandatory.

Thus, a step behind is required and an approach must be followed that, though taking advantage of a solid theoretical background, keeps an eye well fixed on practical aspects. Moreover, scientific analysis of artworks can and therefore must accomplish much more than a diagnostic useful to restoration and preservation purposes: insight can be achieved on manufacturing methods, on colours technology evolution, on peculiarities that make even more unique a single object, thus completing and enriching the historical and artistic knowledge upon which conservation is based.

The research here presented addresses some major issues in the practice of non-destructive analysis of paper and parchment manuscripts: methods applied in manuscripts analysis are demonstrated through laboratory experiments. Micro Raman, ATR FTIR and XRF, for instance, are verified to be suitable for the complete characterization of many and mixed-up substrates, graphic media and treatments. Occasionally, when micro sampling is allowed -as in some cases of stains, residuals, adhesives, frames used in former restorations et cetera- the results obtained by means of destructive analyses can be related and correlated.

Applications to conservation practice is presented by means of some diagnostics campaigns case studies.

G. Piantanida, A. Sodo, M. Monti, M. Bicchieri, *“Reading between the lines” of ancient manuscripts*. In *YOCOCU contribute and role of youth in conservation of cultural heritage*, A. Macchia, E. Greco, B.A. Chiarandà, N. Barbabietola (eds), Roma (2011), De Vittoria s.r.l., 33-38

Abstract

Non-destructive analysis and characterization of manuscripts present several challenges related to the variety of involved materials and to the complexity of their possible interactions. Laboratory research is presented, demonstrating some phenomena to be encountered, together with a case study.

M. Bicchieri, M. Monti, G. Piantanida, A. Sodo *Illuminations: secrets, alchemy and conservation in three case studies*, *Revista de História da Arte*, N° 1 Série W 2011, 175-181, ISSN 2182-3294, <http://revistadehistoriadaarte.wordpress.com/>

Abstract

The huge experience of the Institute in non-destructive analysis and characterization of pigments, inks, colours and dyes allows to recognize the palettes used by miniaturists, sometimes

distinguishing the scriptoria themselves, identify posterior treatments and additions and assess the proper methods and products to be used in conservation. We present the results obtained by means of non-destructive spectroscopic molecular (Micro Raman) and elemental (XRF and α -PIXE) techniques in three case study, the Pontificale 492 (13th c. Museo Diocesano, Salerno, Italy), the Amiatina Bible (6-8th c. Biblioteca Medicea Laurenziana, Firenze, Italy) and the ms Piana 3.207 (13th c., Biblioteca Malatestiana Cesena, Italia).

M. Bicchieri, *Paper*. In *Scientific Methods and Cultural Heritage*, G. Artioli (ed) New York (2010), Oxford University Press Inc., Chapter 3.7.3, 384-395

The paper covers the different aspects of paper degradation and analysis.

M. Bicchieri, M. Monti, G. Piantanida, A. Sodo, *Library materials preservation: a review, Preservation and Access of the monuments of culture and history. Modern approaches, Saint-Petersburg* (2010), Russian National Library, 197-207

Abstract

Analysis on cultural heritage objects is concerned with artefacts -mostly unique masterpieces- that are subjected to a superposition of spontaneous and non-reversible interactions with internal and external degradation factors. Conservation science is actually an applied science related to the understanding of chemical, physical, morphological and biological features responsible for the deterioration phenomena and focused on the reduction and -whenever possible- prevention of degradation effects. Studies in this field are strongly aimed at the development and improvement of non-destructive or micro-destructive techniques, in order to detect ageing and degradation markers. Some of the most significant results accomplished in our laboratory will be shortly reviewed in this paper.

C. Sanna, A. Sodo, G. Laguzzi, G. Mancini, M. Bicchieri, *Tert-butyl amine borane complex: An unusual application of a reducing agent on model molecules of cellulose based materials, Journal of Cultural Heritage* (2009) 10 (3), 356-361

Abstract

The need to preserve cultural heritage on paper requires the setting up of methods and treatments that can be applied to original documents. The cellulose main degradation processes are hydrolysis and oxidation. Only the first one has been widely investigated. The Istituto Centrale per la Patologia del Libro (ICPL) focused its attention on oxidation phenomena and studied a particular class of reducing agents, namely the borane-amine complexes. During the investigation it was found that the borane tert-butylamine complex, besides being the most promising reducing agent, was also able to react with carboxylic functions. In the present study ¹H and ¹³C NMR, Pulsed field gradient NMR spectroscopy as well as Raman spectroscopy were used as analytical tools to disclose the mechanism of the interaction between the borane tert-butylamine complex and the carboxylic functions. Given the complexity of the paper/environment interactions and the subsequent degradation phenomena, we worked on simplified models based on small carbohydrate molecules in order to reproduce the behavior of degraded paper after reductive restoration. Modified D-glucose and D-cellobiose were used in this first step in order to set up the analytical methods before approaching more complex systems such as microcrystalline cellulose and paper. Our results give the experimental evidence that borane tert-butylamine complex is also able to neutralize acidic functions. This finding has important perspectives in paper restoration.

M. Bicchieri, M. Monti, G. Piantanida, A. Sodo. *La raccolta "Sport Italia". Problemi di conservazione dei giornali.* In "Scienza e ricerca per i beni culturali. Microscopia elettronica a scansione e microanalisi", Collana "Quaderni" Istituto Centrale per la Patologia del Libro, F. Pinzari Ed., Gangemi Editore, Roma (2008), pagg. 67-72. ISBN 978-88-492-1431-4

Abstract

Presso la sede di Milano della SISAL S.p.A. è conservata l'intera collezione del giornale sportivo Sport Italia, che è stato pubblicato nel periodo che va dal 1946 (anno di costituzione della SISAL stessa) al 1997 ed ha accolto sulle sue pagine gli scritti delle più grandi firme del giornalismo sportivo.

In vista del recupero della collezione l'Istituto è stato chiamato a verificare lo stato di conservazione dei giornali e a fornire il necessario supporto scientifico e tecnico nel corso del restauro conservativo che la SISAL vuole effettuare per tutelare la memoria storica della sua attività editoriale.

L'ambito di intervento è molto interessante non solo dal punto di vista del restauro - le carte moderne sono finora poco studiate - ma anche da quello dello storico della scienza, della carta e della comunicazione: avere a disposizione una collezione completa di un giornale, che copre più di 50 anni a partire dall'immediato dopoguerra, può permettere uno studio approfondito sull'evoluzione storica degli impasti fibrosi impiegati nella fabbricazione della carta giornale, sui metodi e i caratteri di stampa, in funzione dell'evoluzione della tecnologia e del gusto del pubblico, sulle eventuali variazioni nelle retinature e negli inchiostri, in funzione dell'evoluzione delle macchine di stampa e, anche, sull'impatto della pubblicità in funzione dell'epoca di pubblicazione.

M. Bicchieri, M. Monti, G. Piantanida, A. Sodo. *Colori e segreti: le miniature del codice Piana 3.207.* In "Per giusta causa. Il restauro del Decretum Gratiani (Ms. Piana 3.207) della Biblioteca Malatestiana di Cesena", Daniela Savoia Ed., Edizioni Nova Charta, 2008, pagg. 103-115.

Abstract

Un aspetto importante della conservazione di un manoscritto riguarda la caratterizzazione dei materiali che lo compongono. In tale ottica, contemporaneamente all'intervento di restauro, il codice Piana 3.207 è stato sottoposto ad analisi non distruttive per valutarne lo stato di conservazione e per identificare la tavolozza dei colori impiegati dai miniaturisti. Particolare attenzione è stata dedicata alle tredici carte che erano state oggetto di furto.

Le tecniche di analisi utilizzate sono tra loro complementari: la spettroscopia Raman fornisce indicazioni sulla composizione molecolare dei pigmenti, mentre la fluorescenza X rivela gli elementi presenti nel colore analizzato.

M. Bicchieri, M. Monti, G. Piantanida, A. Sodo, *All that is iron-ink is not always iron-gall!, J. of Raman Spectr. , V. 39 (2008); 1074-1078*

Abstract

A number of different inks were used, with the type and precise composition depending on geographical area and historical period. China, iron-gall and logwood were the most widespread, although a number of other graphic media were also used at particular times and places. Because of a problem encountered while planning the restoration of a manuscript apparently written with different media, we have carried out a systematic characterization of the inks involved. The manuscript (Francesco Maria da Ponticelli, 'Nova Rhetorica', 18th century) showed alternately, sometimes in the same page, dark-black well-defined inks and reddish-brown smudged ones. The latter ones were very difficult to be read and historians identified it as an iron-gall. Our first investigations of the document revealed that the ink had variable composition, but it always showed some typical features of logwood ink. To obtain a better understanding, we prepared, following ancient recipes, logwood inks with the addition of various metallic (Fe, Cr and Cu) salts or amorphous carbon. Iron-gall ink was also used for comparison and in order to obtain an

unambiguous and full characterization of the most widespread inks used in manuscripts. Raman and infrared spectroscopies allowed us to identify the characteristic vibrational features of each prepared medium. These techniques, together with X-ray fluorescence (XRF) and multispectral investigations of the original document led us to hypothesize that iron salts were periodically added to the original logwood ink. These sequences of ink quality can be ascribed to a shortage of ink during the writing of the manuscript. A small amount of iron salt immediately darkens the logwood extract, allowing its prolonged use. The presence of iron complexes produces a reddish-brown coloration and causes ink migration in the paper. Combining all the information, we were able to suggest an appropriate restoration treatment and to choose infrared illumination to maximize the readability of the text.

C. Coluzza, M. Bicchieri, M. Monti, G. Piantanida, A. Sodo: *Atomic force microscopy application for degradation diagnostics in library heritage*. Surf. Interface Anal., V.40 (2008); 1248-1253

Abstract

Atomic Force Microscopy was used on pure cotton cellulose paper to characterize the relationship between surface topographies and cellulose degradation patterns. Whatman N.1 chromatography paper and Fabriano Umbria paper artificially aged with different procedures and then naturally aged-were evaluated together with a sample from an original book. Evidence is found of a clear distinction between surface heights distribution of chiefly oxidised samples with respect to those where hydrolysis is the dominant process. In both cases, deteriorated paper shows surface features well different from the paper in good preservation state, in agreement to results from previous experiments. This is a first step that could open the way to AFM application as a qualitative diagnostic tool for library materials. The only way to achieve such a goal is to extend the experimentation to a wider population of paper samples, so to improve the statistical evaluation.

G. Piantanida, A. Sodo, M. Monti, F. Pinzari and M. Bicchieri, *High-resolution imaging techniques in characterization of paper damage: SEM-EDS and AFM use in stains classification*. In YOCOCU, YOUTH in CONSERVATION OF CULTURAL HERITAGE - PROCEEDINGS. A. Macchia, E. Borrelli, L. Campanella (eds), Roma (2008), Centro Stampa De Vittoria srl; 127-132

Abstract

Library materials – archival documents, books and artistic works – can undergo many kind of alteration processes along their lifetime. Among these, a challenging issue is the appearance of differently coloured and shaped spots and stains on cellulose-based writing media. This phenomenon has been classified as “foxing” for decades, only referring to the aesthetical aspect, without any relation to the chemical and/or biological features.

Since the 1930s, several studies were carried out to get a deep knowledge of this paper alteration and some specific cases have been thoroughly addressed but, until now, the general picture is still incomplete, as stated in the recent review by Choi [1].

In this paper, we report the results of some experiments assessing the contribution given by high-resolved imaging, as from SEM-EDS and AFM analysis. Spots and stains occurring on naturally aged paper and on paper artificially deteriorated were observed at high magnification, in order to individuate the microscopic characteristics of paper fibres, inorganic constituents, impurities, and the deteriorating agents related to the altered areas.

Beside qualitative information, statistical analysis of the topographic datasets has been demonstrated to provide useful insight on the degradation processes at stake (Coluzza et al. [2]), showing that a different surface aspect is found depending on the degradation mechanism. This applies to foxing, as well, helping in stains classification.

Dedicated to the memory of Prof. Carlo Coluzza

M. Placido, L. Residori, D. Ruggiero, L. Botti, M. Bicchieri, G. Guida, *Description of a method of analysis for the characterization of pigments in some paintings from the nineteenth century conserved at the "Museo Nazionale del Compendio Garibaldino di Caprera.* In YOCOCU, YOUTH in CONSERVATION OF CULTURAL HERITAGE - PROCEEDINGS. A. Macchia, E. Borrelli, L. Campanella (eds), Roma (2008), Centro Stampa De Vittoria srl; 259-263

Abstract

The identification of pigments is of importance to conservators and restorers, allowing the most appropriate methods of treatment to be employed.

Different spectroscopic methods and imaging techniques are employed in this study to identify pigments of some nineteenth century paintings, conserved in the "Museo Nazionale del Compendio Garibaldino di Caprera - Soprintendenza Beni Ambientali, Architettonici, Artistici e Storici di Sassari".

Due to the complexity of composition of the different pictorial layers, the use of different methods of analysis, e.g. FORS, XRF, Raman, FTIR-ATR and false color reflectography, thus proves necessary. The combination of these different non-destructive techniques thus provides an exhaustive spectroscopic characterization of the pigment observed. These applications allow us to monitor color change in some pigments, pigment identification and detection of alteration products. A suitable methodology has been described in order to make the measurements accurate and reliable.

M. Bicchieri, M. Monti, G. Piantanida, A. Sodo, *Diagnostica? No, ricerca. La riduzione ... 10 anni dopo.* In *Il restauro in Italia e oltre i confini MiBAC*, a cura di MiBAC-Direzione generale per l'innovazione tecnologica e la promozione, Mirabilia, 2007, 17.

Riassunto

Si presentano i risultati chimico-fisici ottenuti sulla carta in laboratorio con la sola deacidificazione con propionato di calcio alcolico e la deacidificazione-riduzione simultanea (riduzione con *t*-butilammino borano), verificati sia dopo invecchiamento accelerato sia dopo dieci anni di invecchiamento naturale. Sono inoltre mostrati i risultati ottenuti su documenti originali. Le carte sono state caratterizzate tramite misure di grado di polimerizzazione, contenuto in carbonili, pH, coordinate di colore, carico di rottura, spettroscopie Raman e UV-Visibile-NIR, e microscopia a Forza Atomica. I risultati mostrano che tutti i trattamenti alcolici sono altamente efficaci e stabili nel medio-lungo termine.

M. Monti, M. Bicchieri, G. Piantanida, A. Sodo, *Il laboratorio alchemico.* In *Il restauro in Italia e oltre i confini MiBAC*, a cura di MiBAC-Direzione generale per l'innovazione tecnologica e la promozione, Mirabilia, 2007, 18.

Riassunto

In questo lavoro si ripercorre il viaggio effettuato sulle tracce dei maestri del colore per riscoprire i segreti della fabbricazione dell'oro musivo, a partire dalla scoperta della presenza nelle miniature di un antico manoscritto di "...un colore simile all'oro, il quale è buono in carta di questi miniatori..." (Tratto da: Cennino Cennini, "Il libro dell'arte"), fino alla sua identificazione.

M. Bicchieri, M. Monti, G. Piantanida, A. Sodo, P. Fleres, *L'abito non fa il ferro-gallotannico.* In *Il restauro in Italia e oltre i confini MiBAC*, a cura di MiBAC-D.G. per l'innovazione tecnologica e la promozione, Mirabilia, 2007, 19.

Riassunto

Prendendo le mosse da un problema di restauro di un manoscritto (Francesco Maria da Ponticelli, "Nova Rhetorica", XVIII sec.) apparentemente scritto con due differenti, abbiamo intrapreso una ricerca volta alla caratterizzazione non distruttiva degli inchiostri da manoscritto.

Il documento originale mostrava l'alternarsi - talvolta nella medesima pagina - di due mediazioni grafiche diverse: una di colore nero intenso, molto nitido, l'altra marrone-rossiccio con bordi sfumati era penetrata nel corpo della carta ed era di difficile lettura. Quest'ultima sembrava presentare le medesime caratteristiche visive di un ferrogallotannico.

Le nostre indagini hanno evidenziato che nell'intero manoscritto non era stato impiegato un ferrogallotannico, ma un unico inchiostro a base di legno di campeggio mescolato con nerofumo e con periodiche aggiunte di ferro, responsabile della penetrazione dell'inchiostro nel corpo della carta.

G. Piantanida, M. Bicchieri, M. Monti, F. Pinzari, *Fitati, non fidatevi*. In *Il restauro in Italia e oltre i confini MiBAC*, a cura di MiBAC-Direzione generale per l'innovazione tecnologica e la promozione, *Mirabilia*, 2007, 18.

Riassunto

L'Istituto ha svolto un accurato progetto di ricerca, volto a verificare l'efficacia e le condizioni di applicazione dei fitati, come complessanti del Fe^{2+} , nel restauro e nella conservazione della carta.

I risultati ottenuti fino ad oggi mostrano come l'azione dei fitati sugli ossidi di ferro sia sì efficace, ma non più degli altri trattamenti in uso. Il positivo effetto visivo e colorimetrico rilevato da molti autori, infatti, è dovuto soltanto al rilascio di composti del fosforo sul supporto cartaceo; questi provocano fosforescenza e quindi uno sbiancamento apparente, ma creano anche dei complessi con il supporto stesso. Tali complessi alterano la struttura della carta, e nel medio-lungo termine queste alterazioni diventano macroscopiche, rendendola più rigida e ruvida al tatto

M. Bicchieri, *Stampa*. In *Libri e Documenti. Le scienze per la conservazione ed il restauro*, a cura di M. Plossi, A. Zappalà, Gorizia (2007), Edizioni della Laguna, 393-418.

Riassunto

Vengono trattati i metodi di stampa, l'evoluzione dei caratteri da stampa, i loro tratti costitutivi e gli inchiostri.

M. Bicchieri, *Deacidificazione e riduzione delle carte*. In *Libri e Documenti. Le scienze per la conservazione ed il restauro*, a cura di M. Plossi, A. Zappalà, Gorizia (2007), Edizioni della Laguna, pp. 625-638.

Riassunto

Sono presentati i metodi di deacidificazione e di riduzione messi a punto dal laboratorio di chimica dell'Istituto.

M. Bicchieri, *Chimica della cellulosa e metodi di studio della sua degradazione*. In *Libri e Documenti. Le scienze per la conservazione ed il restauro*, a cura di M. Plossi, A. Zappalà, Gorizia (2007), Edizioni della Laguna, 197-218.

Riassunto

Sono presentati i metodi di studio -chimici e spettroscopici- sia della cellulosa, sia della carta, in funzione della sua degradazione.

M. Bicchieri, *Analisi di pigmenti e inchiostri*. In *Libri e Documenti. Le scienze per la conservazione ed il restauro*, a cura di M. Plossi, A. Zappalà, Gorizia (2007), Edizioni della Laguna, pp. 639-654.

Riassunto

Metodi spettroscopici e colorimetrici per la caratterizzazione di pigmenti e inchiostri storici.

M. Bicchieri, M. Monti, Frati & Livi S.r.L.: *La liofilizzazione quale intervento di recupero di volumi danneggiati da catastrofi naturali*, Atti del IV congresso nazionale di archeometria, C. D'Amico Ed. Bologna, Patron (2007). ISBN 978-88-555-2939-6.

Abstract

Books and documents can be damaged by water, mud or other chemical substances during floods or fire. All subsequent restoration treatment must be preceded by a drying treatment that needs to be executed with great care and attention, so as not to further damage material.

The freeze-drying process has often been used employing industrial plants not specifically designed for this purpose. The Frati & Livi and Brizio Basi companies designed and realised a system -the "Book's WIND"- that is capable of drying up to 1,5 cubic meters of wet paper in only 4 or 5 days. The machine is also transportable and its design was studied to allow an easy introduction and removal of volumes after the treatment. The Istituto Centrale per la Patologia del Libro and the Frati & Livi company are cooperating to optimize the experimental conditions in order to set up a damage free treatment. This article reports the results of physical and chemical tests on paper samples subjected to the freeze-drying method. After the treatment with the "Book's WIND" machine the samples didn't show any significant variation on the monitored parameters, confirming that this drying method is innocuous for paper. More studies are in progress on different types of paper and parchment.

G. Piantanida, F. Pinzari, M. Montanari, M. Bicchieri, C. Coluzza: *Atomic Force Microscopy Applied to the Study of Whatman Paper Surface Deteriorated by a Cellulolytic Filamentous Fungus*, Macromol. Symp. V 238 (2006), 92-97

Abstract

In this study AFM technique has been used to observe the degradation of cellulose fibres in paper samples used as substrata for the growth of a filamentous fungus known to be responsible for damage to art works made from or supported on paper. Images obtained from the analysis of artificially deteriorated samples have been used for comparison with topographies obtained by AFM from naturally affected samples. As "control" images, AFM topographies of samples obtained from the same paper quality utilised as substrata for fungal inoculum were considered. The samples that were artificially deteriorated and those naturally affected by biological agents showed, at the molecular level, distinct surface differences when compared with control images. The biodegradation of cellulose fibres that appeared in AFM images can be attributed to the activity of both cellulolytic enzymes and acidic compounds produced by the fungal cells. Further studies using the AFM technique could reveal interesting aspects of paper biodeterioration caused by different microorganisms and might allow for a better description of the different stages of fungal attacks on cellulose fibres.

M. Missori, C. Mondelli, M. De Spirito, C. Castellano, M. Bicchieri, R. Schweins, G. Arcovito, M. Papi, and A. Congiu Castellano, *Modifications of the Mesoscopic Structure of Cellulose in Paper Degradation*, Phys. Rev. Lett. 97, (2006) 238001

Abstract

Paper is the main component of a huge quantity of cultural heritage. It is primarily composed of cellulose that undergoes significant degradation with the passage of time. By using small angle neutron scattering (SANS), we investigated cellulose's supramolecular structure, which allows access to degradation agents, in ancient and modern samples. For the first time, SANS data were interpreted in terms of water-filled pores, with their sizes increasing from 1.61 nm up to 1.97 nm in natural and artificially aged papers. The protective effect of gelatine sizing was also observed.

M. Bicchieri, A. Sodo, G. Piantanida, C. Coluzza, *Analysis of degraded papers by non-destructive spectroscopic techniques*, J. of Raman Spectr. V 37, N 10, (2006) 1186–1192

Abstract

Scientific approach to Cultural Heritage conservation is very important for cultural reasons and also in order to avoid from restoration mistakes.

Acidity and oxidation play a very important role in paper conservation. Deacidification is a widely used method to remove acidity on aged papers, but if a large amount of carbonyl groups is present in the paper a strong deacidification can promote an alkali-catalysed β -alkoxy-elimination, leading to the breaking of the anhydroglucose ring in the cellulose chain.

In this case and also in the case of non-acidic but oxidised papers, a reduction treatment is necessary. Because of the high costs of restoring procedures, it is essential to determine if the reduction treatment is a primary need.

In this work we report a study, based on micron scale space resolved Raman microscopy, Infrared Reflectance spectroscopy and Atomic Force Microscopy, of differently degraded samples of paper. Non-treated, and oxidised samples were investigated as well as original ancient documents.

The aim of this work is to achieve a better understanding of the degradation pattern of historical samples in order to be able to choose the most appropriate restoration treatment, using non-destructive spectroscopic techniques.

Analysis of the samples demonstrates that degradation processes occur mainly on fibrils and on the fibre wall, as shown also by Atomic Force Microscopy measurements.

G. Piantanida, M. Bicchieri, F. Pinzari and C. Coluzza, *Surface roughness of degraded paper*, In Proceedings of MIP 2006

Abstract

This work reports the application of Atomic Force Microscopy (AFM) in detection of paper ageing-markers: aside from topographies, surface roughness parameter (r) was evaluated. Samples non-treated and oxidized were investigated as well as original ancient documents, showing foxing stains.

The considered processes are the chemical reactions induced by an accelerated ageing in climatic chamber (80°C, R.H. 65%), by oxidation with a KIO₄ 0.015M water solution and subsequent ageing, and the effects of a fungal attack reproduced in vitro inoculating paper samples with *Aspergillus terreus* Thom (6000spores/100ml, 27°C, R.H. 100%). Comparison between values along artificial treatments and values related to naturally degraded samples provides evidence of complexity in the natural process.

M. Bicchieri, M.L. Riccardi: *Lezioni di miniatura Alumina* 5, 42-47 (2005).

Riassunto

Il codice 492 datato fine XIII inizio XIV secolo, magnificamente miniato, era in cattivo stato di conservazione e necessitava di un completo intervento di restauro conservativo.

Le analisi non distruttive sono state necessarie sia per connotare il documento, sia per preparare campioni che simulassero l'originale, sui quali eseguire prove di fissaggio e consolidamento di pigmenti e oro, per effettuare il trattamento meno invasivo possibile, garantendo la massima stabilità.

In collaborazione con l'Istituto Nazionale Fisica della Materia e i dipartimenti di Fisica delle Università dell'Aquila e di RomaTre, sono state eseguite misure in spettroscopia Raman, che fornisce indicazioni sulla composizione molecolare dei composti analizzati.

In collaborazione con l'Istituto Nazionale Fisica Nucleare, i Laboratori Nazionali del Sud di Catania e il CNR-Istituto per i Beni Archeologici e monumentali di Catania, sono state eseguite misure in XRF e PIXE- α , che permettono di determinare gli elementi chimici nel campione in studio.

L'analisi combinata dei risultati ha permesso di identificare i pigmenti e la composizione delle

preparazioni pittoriche per l'oro.

G. Piantanida, M. Bicchieri, F. Pinzari, C. Coluzza, *Atomic force microscopy imaging “directly on paper”: a study of library materials degradation*, Proceedings of SPIE V.5857. Optical Methods for Arts and Archaeology. V. 5857 (2005) 217-227.

Abstract

Atomic Force Microscopy (AFM) has been used to study fiber degradations, as they appear on paper surface, aiming -in the midterm- at assessment of a micro-destructive technique capable of providing qualitative and semi-quantitative information on deterioration and ageing.

AFM topographies of pure cellulose paper samples artificially aged were considered as well as topographies of original paper samples naturally aged showing different kind of deterioration.

Whatman N.1 chromatography paper was used as a model system to study ageing effect on sub-micron structures on cellulose fibers. Chemical and biological deterioration processes were modeled, as well, by mean of artificial degradation treatments, following the criteria of reproducing effects frequently isolated from library materials.

The effects of chemical reaction induced by accelerated ageing in climatic chamber (80°C, R.H. 65%) on paper surface, and the effects of a fungal attack reproduced in vitro inoculating paper samples with *Aspergillus terreus* Thom (6000spores/100ml, 27°C, R.H. 100%) were evaluated by means of Atomic Force Microscopy imaging, and spectrophotometric measurement in the UV-Vis-NIR.

In order to map structure local properties, morphological variations repeated with statistical relevance were correlated to chemical, biological and spectroscopic characterization.

Information achieved from such analysis is then used for a comparison with measurements of naturally aged paper, providing insight in analysis and classification of typical phenomena, like yellowing and foxing stains, usually affecting valuables in libraries.

D. Palazzi, M. Bicchieri, E. Franceschi, G. Luciano and G. Piantanida, *A comparative study on three softening agents for parchment restoration. preliminary results*, Proceedings of the SREN 2005, Bratislava (2005), Comenius University, 179-188

Abstract

This work compares the behaviour of three softening agents (trehalose, polyethylene glycol (PEG 200), urea + NaCl) on modern parchment samples. Samples have been artificially aged, then treated and aged again. The samples have been investigated by means of Scanning Electron Microscopy, colour measurements, rigidometry. Also the first attempts for a Differential Scanning Calorimetry analysis are illustrated. The preliminary results encourage a further study for a better understanding of the behaviour of the softening agents.

G. Piantanida, M. Bicchieri, C. Coluzza, *Atomic Force Microscopy characterization of the ageing of pure cellulose*, Polymer. V 46, N 26 (2005) 12313-12321.

Abstract:

Atomic Force Microscopy was used to characterize the effects of chemical reactions induced by accelerated ageing in a climatic chamber (80°C, R.H. 65%) on Whatman N.1 chromatography paper surface, in order to study ageing consequences on sub-micron structures in cellulose. Evaluation was carried out by means of a comparison of topographic data with chemical characterization, in addition to spectrophotometric measurement in the UV-Vis-NIR range. Imaging of samples at several treatment stages showed a non-homogeneous decomposition of the fibre surface into fibril bunches. Over paper sheet surfaces, occurrence of this phenomenon increases with ageing. Spectrophotometry measurements showed a strong variation of contributions in the UV-Vis bands, both in the yellow chromophores region and in the carbonyl formation region, which was consistent

with the hypothesis that a predominant oxidation mechanism is involved.

M. Bicchieri, M.S. Storace, *Manifesti e disegni contemporanei: diagnosi e consolidamento. In Atti del II Congresso Nazionale IGHC "Lo stato dell'arte 2", Il prato, Saonara (PD), 114-123 (2004)*

Riassunto

Il principale problema delle carte moderne consiste nella degradazione ossidativa, talvolta accompagnata da degradazione acida. L'ossidazione provoca un netto imbrunimento e un indebolimento del supporto cartaceo, ma le carte imbrunite non necessariamente sono acide. Si riportano due esempi di intervento di consolidamento su due opere conservate presso la biblioteca di Storia Moderna e Contemporanea di Roma: un manifesto di sottoscrizione al prestito di guerra di Duilio Cambellotti acido e ossidato e un disegno raffigurante Giuseppe Mazzini, con frasi e firma autografa di Mazzini stesso, il cui avanzato deterioramento era dovuto esclusivamente ad ossidazione.

L'intervento è consistito in un trattamento simultaneo di deacidificazione e riduzione alcoliche, per il manifesto e in un intervento di riduzione acquosa per il disegno.

Entrambe le opere sono state poi restaurate (suture, risarcimenti, ricollocazione dei frammenti e consolidamento).

A. Sodo, M. Nardone, D. Ajò, G. Pozza, M. Bicchieri, *Optical and structural properties of gemmological materials used in works of art and handicraft, in Journal of Cultural Heritage, 4 (2003), 317s-320s*

Abstract

Disorder phenomena related to formation conditions of natural and synthetic spinels, both stoichiometric ($MgO \cdot Al_2O_3$) and exhibiting different Al/Mg ratios are investigated by photoluminescence spectroscopy. The same approach appears to be less adequate when dealing with more complex materials, such as beryls ($3BeO \cdot Al_2O_3 \cdot 6SiO_2$).

On the other hand, Raman spectroscopy allows easy identification of different varieties of beryls and of their inclusions, together with that of widely used imitation.

The above techniques are totally non-destructive and they do not require any treatment of the samples. The apparatus developed at our laboratories allows investigation of irregularly shaped samples within a large range of sizes.

M. Bicchieri, A. Di Majo, G. Martinelli, L. Mita, D. Palazzi, L. Pappalardo, F.P. Romano, S. Ronconi, *Analisi non distruttive della Chartula di Assisi, Medioevo 6, 97-115 (2003).*

Riassunto

L'approccio scientifico allo studio dei beni culturali si è recentemente sviluppato, grazie a positive interazioni fra diverse scienze: sempre più frequentemente storici dell'arte, umanisti e scienziati collaborano per risolvere problemi che altrimenti resterebbero senza risposta.

Si possono, a tal fine, utilizzare molte tecniche non distruttive, quali ad esempio le spettroscopie infrarossa in riflettanza e di fluorescenza, le spettrometrie di fluorescenza X e di emissione di raggi X indotta da particelle: ciascuna fornisce informazioni differenti e complementari.

Per la prima volta nella sua storia la *Chartula* a frate Leone è stata sottoposta ad un insieme di indagini non distruttive, finalizzate alla conoscenza del suo stato di conservazione e alla caratterizzazione degli inchiostri in essa presenti.

Le prime osservazioni si sono svolte presso il Sacro Convento di Assisi, dove la *Chartula* era collocata all'interno di un reliquiario, chiuso da un sigillo.

La pergamena si presentava in preoccupante stato di conservazione, fortemente contratta ed ondulata. Il reliquiario, infatti, non permetteva di mantenere, al suo interno, condizioni di umidità

controllata e non è stato in grado di impedire che, nel corso degli anni, si verificassero modifiche dimensionali nella pergamena, al variare delle condizioni termoigrometriche dell'ambiente di conservazione. Ciò ha causato un allargamento degli strappi nel supporto, in corrispondenza di alcune zone inchiostrate, come si evidenzia dal confronto fra l'originale e precedenti documentazioni fotografiche.

La collocazione in un contenitore sigillato, dal quale non sia stato eliminato l'ossigeno, sostituendolo con un gas inerte, inoltre, ha creato un microambiente che ha favorito le reazioni di degradazione acida, con conseguente perforazione della pergamena.

Le tecniche non distruttive di indagine sono state scelte per connotare non solo i materiali presenti, ma per permettere di valutare quali potessero essere gli interventi conservativi da porre in atto per garantire l'ulteriore conservazione della *Chartula*.

M. Bicchieri, A. Di Majo, G. Martinelli, L. Mita, D. Palazzi, L. Pappalardo, F.P. Romano, S. Ronconi, *The Assisi Chartula by the hand of Saint Francis: non-destructive characterization by spectroscopic, spectrometric and optical methods*, *Annali di Chimica* 93 (2003), 863-871.

Abstract

Just two examples of writings by the hand of S. Francesco are known to exist: a letter to Brother Leone, kept in the archives of Spoleto cathedral and the *Chartula*, displayed in the Hall of Reliquaries at Assisi's Sacro Convento.

For the first time in its history the *Chartula* has undergone a series of non-destructive analyses, with the object of establishing its current state of conservation and the types of inks used in its making. A new display case has been designed and built for the improved conservation of this precious document. The new housing substitutes an ancient case, which was located inside the original reliquary

Riassunto

Sono noti solo due scritti autografi di S. Francesco: una lettera a frate Leone, conservata nell'archivio della Cattedrale di Spoleto e la *Chartula*, esposta nella Sala delle reliquie del Sacro Convento di Assisi.

Per la prima volta nella sua storia la *Chartula* è stata sottoposta ad un insieme di indagini non distruttive, finalizzate alla conoscenza del suo stato di conservazione e alla caratterizzazione degli inchiostri in essa presenti. Per una migliore conservazione del prezioso documento è stata ideata e costruita una nuova teca da esposizione, che sostituisce l'antico contenitore, posto all'interno del reliquiario originale.

M. Bicchieri, *Raman Spettroscopy and library materials*. In "Memory and future of paper documents". A. Zappalà ed., (2002), 216-254

Abstract

The scientific investigation of Cultural Heritage has recently gained a great impulse from the positive development in the interaction between sciences. More and more frequently, art historians, humanists and scientists collaborate to solve many problems, which would otherwise be left without an answer.

Many non-destructive techniques can be used in the study of cultural heritage objects, for example Infrared in reflectance and Raman spectroscopy, X-ray fluorescence and Particle Induced X-ray Emission spectrometry, each method giving different and complementary data and results.

In this paper some results will be presented concerning the application of Raman spectroscopy to the study of the cellulose degradation and to the characterisation of graphic media. The experimental work has been carried during a well-established collaboration between the Istituto centrale per la patologia del libro and the Department of physics, Università Roma Tre, Unità di ricerca dell'Istituto Nazionale Fisica della Materia.

M. Bicchieri, M. Nardone, A. Sodo: *Raman spectroscopy: an important tool for Cultural Heritage applications*. I, Proceedings of the International Conference “Archaeometry in Europe in the third millennium” Roma (2002), Accademia Nazionale dei Lincei, 181-187.

Abstract

Raman spectroscopy, a highly sensitive non-destructive spectroscopic technique has been used for several applications in the field of Cultural Heritage. We report a study, based on micron-scale space-resolved Raman microscopy, of the cellulose degradation and some results obtained in the identification of medieval pigments. Since, owing to their dimensions or their value art objects can not always be moved to our laboratory, we have set up a portable instrumentation to be carried out for in situ measurements, specifically designed for Cultural Heritage field applications

M. Bicchieri, M. Nardone, A. Sodo, *Application of micro-Raman spectroscopy to the study of differently degraded papers*. In 2nd International Congress on “Science and Technology for the Safeguard of Cultural Heritage in The Mediterranean Basin”, Proceedings Vol II: 969-972, Elsevier, Paris (2002)

Abstract

Scientific approach to Cultural Heritage conservation is very important for cultural reasons and also in order to escape from restoration mistakes. Acidity and oxidation play a very important role in paper conservation. Deacidification is a widely used method to remove acidity on aged papers, but if a large amount of carbonyl groups is present in the papers the deacidification can promote an alkali catalysed β -alkoxy-elimination mechanism, leading to the breaking of the anhydroglucose ring in the cellulose chain. Because of the high costs of restoring procedures, it is essential to determine if the reduction treatment is a primary need.

We report a study, based on micron scale space resolved Raman microscopy, of different forms of degradation on differently treated samples of Whatman paper. Polarised spectra are collected both from the whole paper samples and from oriented single fibre bundles and fibrils obtained by dispersing paper in water. In both cases we have compared the spectra of untreated samples with those subjected to selective oxidation or hydrolysed in vapour phase. The aim of the work is to recognise the kind of degradation for a better understanding of the degradation pattern of a real sample, using a non-destructive spectroscopic technique to choose the most appropriate restoration treatment. Analysis of the fragmented samples show that degradation processes occur mainly on fibrils and on the fibres wall. Indeed the spectra collected from the central part of oriented whole fibres and fibre bundles appear to be identical before and after the various chemical treatments. Significant differences, namely the appearance of new bands and /or intensity variations, are detected analysing the fibrils and sometimes fibre walls coming from oxidised, hydrolysed or untreated papers.

M. Bicchieri, S. Ronconi, F.P. Romano, L. Pappalardo, M. Corsi, G. Cristoforetti, S. Legnaioli, V. Palleschi, A. Salvetti, E. Tognoni, *Study of foxing stains on paper by chemical methods, infrared spectroscopy, micro-X-Ray Fluorescence spectrometry and Laser Induced Breakdown Spectroscopy*, Spectrochimica Acta part B: Atomic Spectroscopy, 57/7 (2002), 1233-1246.

Abstract

Foxing spots appear on the paper as stains of reddish-brown, brown or yellowish color, generally of small dimensions, with sharp or irregular edges, most of which, if excited with UV light, show fluorescence. The formation mechanisms of foxed areas have been studied since 1935 however, despite more recent intensive research there are still no conclusive results. Some authors found evidence of bacterial or fungal growth in some foxed areas sometimes associated with the presence of iron.

We decided to focus our attention on the influence of the different iron valence in the formation of stains in the paper. For this reason, we artificially induced the formation of foxing by adding to the

paper small, known quantities of iron(III) and iron (II) ions.

We prepared aqueous solutions of ferric chloride and ferrous sulfate at three different concentrations and we always used the same quantity of each solution (5 ml) to obtain a foxing stain. Part of the paper samples were artificially aged in a climatic chamber at 80°C 65% relative humidity for 15 days and part were submitted to aging for the same period at ambient temperature under UV light at 240 nm.

All papers were then analyzed for stain diameter, chromaticity coordinates, fluorescence under UV illumination, water content in the paper and in the spots, carbonyl content and then submitted to infrared spectroscopy, X-ray fluorescence spectrometry and laser induced breakdown spectroscopy. Infrared spectra were collected in transmittance from potassium bromide pellets; X-ray fluorescence analyses were carried out using an X-ray microbeam (400 mm beam spot; W X-ray tube) and LIBS analyses with Nd:YAG laser coupled with a Czerny-Turner spectrometer.

As a result it is stated that the foxing phenomenon is related to a strong oxidation of the cellulose chain. Concerning the color coordinates there are no great differences between samples treated with iron (III) and iron (II). Carbonyl content, on the contrary, varies for the two set of samples, especially in relation with the kind of aging. μ -XRF and LIBS measurements show a relationship between iron valence and calcium ion displacement in the foxed areas.

M. Bicchieri, *Il laboratorio di chimica dell'Istituto centrale per la patologia del libro, Analysis 1+2, 28-37 (2002).* La tutela del patrimonio culturale scritto implica la necessità di conoscere la storia e la chimica dei materiali che compongono libri e documenti, nonché le loro interazioni con l'ambiente di conservazione. L'articolo tratta i fattori di degradazione e i metodi di intervento conservativo, presentando l'attività di ricerca del laboratorio di chimica dell'Istituto centrale per la patologia del libro.

M. Bicchieri, G. Pappalardo, F.P. Romano, F.M. Sementilli, R. De Acutis, *Characterisation of foxing stains by chemical and spectrometric methods, Restaurator 22, 1 (2001): 1-19*

Abstract

Foxing stains on six different papers from the 16th-18th centuries and additionally fox-like stains produced by dripping different amounts (1, 3 and 5 ml) of solutions of FeCl₃, KCl and FeCl₃+KCl ($5 \cdot 10^{-3}$ M) on modern paper artificially aged were analyzed for chromaticity, fluorescence under UV illumination, carbonyl content, thickness and submitted to IR spectroscopy and XRF spectrometry. As a result it is stated that the foxing phenomenon is related to a strong oxidation of the cellulose chain. Not regarding certain and possibly specific differences between different kinds of foxing stains, this strong oxidation is the only common characteristics for foxed areas.

A. Zappalà, C. Cantoni, D. Palazzi, E. Vitrano, L. Cordone, *Effect of trehalose treatment on paper stability - Preliminary experiments, Restaurator, 22, 1 (2001): 41-50*

Abstract

Trehalose, a non-reducing disaccharide, is supposed to be responsible for the survival of anhydrobiotic organisms when under stress. This sugar prohibits the formation of damage during adverse external conditions such as extremely high temperature or dehydration. In this paper we report preliminary experiments on paper stabilisation by treatment with trehalose; the experimental results are encouraging and suggest further study on this topic would be worthwhile.

L. Santucci, M. Plossi Zappalà *Cellulose Viscometric Oxidation, Restaurator, 22,1 (2001): 51-65*

Abstract

It is suggested that the depolymerization of oxidized cellulose (e.g. paper) caused by alkalinity can

be exploited to evaluate its degree of oxidation. A rough estimate can be obtained with just one sample measured before and after heating in the alkaline solvent for viscosity itself; a more accurate evaluation requires reduction of the sample prior to the viscometric measurement. This procedure should not be identified with determinations of total carbonyl and carboxyl contents.

M. Adamo, M. Brizzi, G. Magaudda, G. Martinelli, M. Plossi Zappalà, F. Rocchetti, F. Savagnone, *Gamma radiation treatment of paper in different environmental conditions, Restaurator, 22, 2 (2001): 107-131*

Abstract

A multidisciplinary team studied the effects of a decontaminating treatment with gamma radiation applied to a paper, which had been damaged by microscopic cellulolytic fungi (mildews). Special attention was paid to the potentially negative effects of gamma rays on cellulose. The investigation was extended to the effects of some associated environmental treatments, such as the absence of oxygen and water saturation. The mechanical, chemical, physical and microbiological tests confirmed well-known observations already published. They indicated that the microbial population decreases proportionally to the gamma rays dosage together with the depolymerization of the cellulose molecule. Nevertheless, this negative effect does not significantly affect the basic properties of a good printing paper. A correct analysis of costs and benefits would suggest the use of a dose of 2-3 kGy. However, this analysis has still to be further investigated for the practical application of irradiation on deteriorated books and documents.

C. Andalò, M. Bicchieri, P. Bocchini, G.C. Galletti, G. Casu, P.A. Mandò, M. Nardone, A. Sodo, M. Plossi Zappalà, *The beautiful "Trionfo d'Amore" attributed to Botticelli: a chemical characterisation by proton-induced X-ray emission and micro-Raman spectroscopy, Analitica Chimica Acta 429, 279-286 (2001)*

Abstract

The drawing "Trionfo d'Amore" (1480-1500) is attributed to Sandro Botticelli, the great master of the Italian Renaissance. It is included in manuscript nr. 143 (Biblioteca Classense, Ravenna, Italy) containing the "Canzoniere" and the "Trionfi" of Francesco Petrarca.

The goal of the present research is to achieve a thorough chemical characterisation of the drawing using non-destructive techniques: PIXE and Micro-Raman spectroscopy. The combined use of these analytical tools may provide a wealth of information about the composition and the physical structure of the paint layer. Indeed, while PIXE yields the elemental composition of colours, inks and parchment, in particular unveiling possible variations over the entire surface of the drawing, Micro-Raman spectroscopy can yield valuable information on the chemical structure of the compounds characterising each single colour in the drawing. The peculiar aspect of this work stands in the complementary use of these already well-established non-destructive techniques, to reach a better understanding of the information provided by each of the two techniques alone.

M. Bicchieri, M. Nardone, P.A. Russo, A. Sodo, M. Corsi, G. Cristoforetti, V. Palleschi, A. Salvetti, E. Tognoni, *Characterization of azurite and lazurite based pigments. Spectrochimica Acta Part B, 56 (2001): 915-922*

Abstract

The most used blue pigments in medieval manuscripts are azurite and lapis lazuli. The first one is a copper-based pigment; the coloring compound of the latter is lazurite, a sodium silico-aluminate in a sulphur matrix. The knowledge of the chemical composition of the materials is essential for connotation of illuminated manuscripts. In this paper, micro-Raman and LIBS have been used for the study of azurite and lapis lazuli, as well as different mixtures of these pigments applied to parchment to simulate an illuminated manuscript. The results of our work show the importance of

using more than one technique for a good comprehension of a manuscript. In particular the opportunity of combining elemental information (obtained from Laser Induced Breakdown Spectroscopy) and vibrational spectroscopy information (obtained from Raman) will be fully exploited.

M. Bicchieri, M. Nardone, A. Sodo, M. Corsi, G. Cristoforetti, V. Palleschi, A. Salvetti, E. Tognoni, *The characterization of historical pigments: a crucial problem in the connotation of ancient manuscripts*. In *Proceeding of the International Conference on LASERS 2000*, ed. by V.J. Corcoran and T.A. Corcoran, 803-806, STS Press, McLean, VA (2001)

Abstract

The connotation of an illuminated manuscript relies heavily on the knowledge of the chemical composition of all the materials employed. If trace elements are found, it is also necessary to understand whether they belong to the substrate (paper or parchment), to impurities originally present in the coloring materials, or to moderate quantities of different pigments added in order to obtain a particular hue. For these purposes it is crucial to choose micro or non-destructive analytical techniques such that the risk of an erroneous attribution of the chemical composition of inks or pigments is minimized.

Starting from a real problem encountered in analyzing a medieval illumination, we have undertaken a specific research on the spectroscopic characterization of some pigments.

Micro-Raman and LIBS have been used for the study of azurite and lapis lazuli as well as different mixtures of these pigments applied to parchment to simulate an illuminated manuscript.

For the trace element composition of lapis lazuli, several samples have been examined namely: more or less purified powdered samples specifically prepared for illuminations, a lapis lazuli stone and a pure lazurite crystal both coming from the "historical" mine of Sar-El-Sang, in Badakhshan, Afghanistan.

The results of our work show the importance of using more than one technique for a good comprehension of the chemical composition of a manuscript. In particular the opportunity of combining elemental composition information (obtained from LIBS) and vibrational spectroscopy information (obtained from Raman) will be fully exploited.

M. Bicchieri, M. Monti, M.L. Antonelli: *A new low-cost and complete restoration method: a simultaneous non-aqueous treatment of deacidification and reduction*. In *Atti 3rd international congress on "Science and Technology for the safeguard of cultural heritage in the mediterranean basin"*, Alcalà (Madrid) (2001) I.S.B.N. 84-8138-453-4

Abstract

Water solutions can not always be used in paper restoration because of problems related to soluble graphic media and eventually to the need to operate on bonded books. It is then necessary to find alternative solutions for the normal aqueous treatments.

Frequently both deacidification and reduction of oxidized functions in cellulose are needed for a complete restoration but sometime it is impossible to submit a book to two separate treatments. We tried to verify the possibility to achieve effective simultaneous deacidification and reduction in non-aqueous medium. Ethyl alcohol was chosen as a solvent, due to the insolubility of historically used sizing agents in this solvent; calcium propionate for deacidification and borane ammonia complex (NH₃.BH₃) for reduction.

To test the effectiveness of the method papers were artificially oxidized or hydrolyzed, then they were treated with the

studied solution and artificially aged for a maximum time of 35 days at 80°C 65%R, drawing samples each 7 days. Carbonyl and carboxyl groups content, pH of paper, chromaticity coordinates, average degree of polymerization were measured after each ageing period.

Tests were carried out also on commercial old books sized with starch and with gelatine, to check

the effect of the treatments on bonded sized papers. No blocking of sheets arose. As a conclusion we want to add the following remarks: the method of simultaneous deacidification and reduction is able to contrast both the acidity and the oxidation of the paper, offering also a chemical bleaching; the method is very close to a mass deacidification allowing the treatment of large amount of books without huge plants; the method is simple, effective and not expensive: the restoration of a book costs about 1.5 US\$, taking into account the possibility to recover ethyl alcohol for a subsequent similar utilisation.

M. Bicchieri, M. Nardone, G. Pappalardo, L. Pappalardo, F.P. Romano, A. Sodo, *PIXE- α and micro-Raman analysis for a non destructive characterisation of the Salerno Exultet*. In Atti 3rd international congress on “Science and Technology for the safeguard of cultural heritage in the mediterranean basin”, Alcalà (Madrid) (2001)

I.S.B.N. 84-8138-453-4 Abstract

The collaboration between Istituto Centrale per la Patologia del Libro, Rome, Dipartimento di Fisica, Università Roma Tre - Sezione INFM and LNS/INFN LANDIS laboratory, Catania, allowed the complete characterization of the Salerno Exultet, a XIII century parchment scroll.

PIXE measurements were obtained using the portable PIXE- α system, entirely designed and realised by the LNS/INFN LANDIS laboratory. It consists of a sealed 210 Po source emitting a particles at energy of about 4.5 MeV, enough to investigate the sample up to a thickness of about 10-40 mm. The activity of the 210 Po source is 1 mCi while the spot diameter is about 1 cm. The PIXE system was completed with a germanium detector with energy resolution of 130 eV at 5.9 keV. Its good resolution allowed us to separate the S-K line at 2.30 keV, Hg-M line at 2.19 keV and Pb-M line at 2.34 keV.

Raman analyses were performed with a Dilor Labram spectrometer, equipped with two different laser sources at 632.8 nm (He-Ne) and at 785.5 nm (diode laser). The illumination and collecting optics of the system consists in a microscope in confocal configuration. This configuration limits the dimensions of the analysed sample. For this reason, to investigate larger samples, we realised a special hand-piece that was equipped with an external laser source at 632.8 nm and connected to the Labram system by optical fibres. We tried to perform all measurements in the same points both with the PIXE- α system and with the Raman spectrometer. Due to the different nature and spatial resolution of the two techniques it was not always possible perform measurements in the same point: sometimes Raman spectra gave no information because of the intense fluorescence of the sample; sometimes the analysed zone was too small for carrying out PIXE measurements. In any case the whole analysis allowed us to reveal the Salerno Exultet palette.

M. Bicchieri, M. Nardone, A. Sodo, *Applications of Raman spectroscopy to Library Heritage*, *Annali di Chimica*. 91 (2001): 693-700

Abstract

This work reports some different applications of Raman spectroscopy, a high-sensitive non-destructive technique, to the conservation of Library Heritage. By Raman spectroscopy we were able to detect the chemical mechanisms leading to cellulose degradation, identifying the different functional groups formed during the paper ageing. This kind of information is fundamental to choose a suited restoration treatment. We characterised a new series of reducing agents for oxidised paper, the amino-borane complexes, that present all the needed requirements to be used in restoration. Among them we choose borane ammonia (AB), NH_3BH_3 , and borane tert-butylamine (TBAB), $\text{NH}_2[\text{C}(\text{CH}_3)_3]\text{BH}_3$ that showed the best effectiveness. We were able to assign the BH, BN and NH stretching bands. A third reported application is the identification of pigments used to decorate paper and parchments. We report some results obtained from analysis of a XV and a XIII century illuminations.

E. Franceschi, D. Palazzi, E. Pedemonte, *Thermoanalytical contribution to the study on paper degradation. Characterisation of oxidised paper*, *Journal of Thermal Analysis and Calorimetry*, **66,1 (2001): 349-358**

Abstract

In this paper we studied the effect of oxidation on paper stability by means of simultaneous differential thermal analysis and thermogravimetry. In our laboratory we oxidised Whatman n. 1 chromatography grade paper and performed thermal analyses both on non-oxidised and on 6, 21 and 96 h oxidised samples. The results showed characteristic thermal effects, particularly performing the experiments under oxygen flow: it was noticed that the temperature of the main cellulose degradation DTA peak gradually decreases with the paper oxidation degree. An application of this method was extended to the study of differently oxidised parts of a 1948's book.

M. Plossi Zappalà, R. De Acutis, *Non-Toxic Antioxidants and Preservatives in the Treatment of Paper*, *Qvinio*, **3 (2001): 87-107**

Abstract

One of the most serious problems encountered in the conservation of books and documents made of paper stems from the readily oxidizable nature of the material. In addition to discoloration (yellowing), oxidation results in significant mechanical weakening of paper. Because certain microbiological by-products favour the catalysis of oxidation, it has seemed profitable to evaluate the effect on paper of both true antioxidants and substances whose action is principally anti-microbial. The study has focused on non-toxic antioxidants and preservatives: Methyl, Ethyl and Propyl p-hydroxybenzoates, Butylated Hydroxyanisole BHT, Butylated Hydroxytoluene BHT and Calcium Ascorbate. Solutions at concentrations of 0.1M and 0.01M in ethyl alcohol of these chemicals were tested, with the exception of the Calcium Ascorbate, which was dissolved in distilled water. Papers treated included Whatman Paper, which was oxidized using Sodium Hypochlorite, and "Mezzofino" Paper, containing mechanical woodpulp. The Average Viscometric Degree of Polymerization DP, the Carbonyl content, the Colour Coordinates, and the Cold Extraction pH were measured.

The BHT, BHA, and in particular the Calcium Ascorbate, all yellowed after accelerated ageing, whilst the Methyl, Ethyl and Propyl p-hydroxybenzoates demonstrated greater stability. The DP measurement on the Whatman paper and the "Mezzofino's" Carbonyl content showed the protective effect of Propyl p-hydroxybenzoate after ageing. Because the p-hydroxybenzoates themselves - if used in sufficiently concentrated solutions - tend to have a yellowing effect, their use in library restoration is necessarily limited to low concentrations.

M. Bicchieri, F.P. Romano, L. Pappalardo, L. Cosentino, M. Nardone, A. Sodo, *Non-destructive Analysis of the Bibbia Amiatina by XRF, PIXE-a and Raman*, *Qvinio* **3 (2001): 169-179**

Abstract

The Bibbia Amiatina has been analyzed, using non-destructive techniques. The original goal of these research was to establish the original arrangement of the sheets, numbered I to VIII, present in the first booklet. To this end, the pigments that left impressions (offsets) on adjacent sheets and the offsets themselves, were analyzed with XRF, PIXE-a and Raman. They were then observed under UV light it has been possible to hypothesize an order for the sheets, even if it is impossible to establish whether or not this sequence truly represents the original one, or simply that which the sheets have assumed for most of the document's lifetime.

For a complete characterization all pigments were analyzed, allowing to detect the color palette.

M. Bicchieri, G. Pappalardo, F.P. Romano: *Foxing spots: chemical and spectrometric characterisation*, "The Science of art", 410-415 (2001).

Abstract

Il foxing è un fenomeno complesso, la cui natura, chimica o biologica, non è ancora perfettamente compresa. Provoca la formazione di alterazioni cromatiche sul materiale celluloso ed è stato studiato sin dagli anni '30; negli anni '80 le ricerche si sono intensificate, senza, però, raggiungere risultati esaurienti.

Il foxing consiste nella formazione di macchie di colore bruno-rossiccio, bruno o giallastro, generalmente di piccole dimensioni e con bordi netti oppure frastagliati. La maggior parte di tali macchie, se eccitata con radiazioni UV, presenta fluorescenza. Questa spesso appare anche in zone nelle quali l'alterazione cromatica non è ancora visibile sotto luce naturale, ma nelle quali probabilmente il foxing è in formazione.

La nostra ricerca si proponeva di stabilire se vi fossero delle caratteristiche chimiche comuni in macchie di foxing presenti su carte antiche, allo scopo di comprendere meglio il fenomeno e di trovare idonei metodi di restauro. A tal fine sono state analizzate delle carte antiche datate dal XVI al XVIII secolo.

Sono stati poi preparati alcuni campioni di carta moderna, datata 1965, nei quali è stata indotta chimicamente, dopo invecchiamento accelerato di 15 giorni a 80°C e 65% U.R., la formazione di macchie di foxing. Per ottenere ciò, sono stati applicati, in diversi punti delle carte, 1, 3 e 5 ml di FeCl₃, KCl e FeCl₃+KCl. Le soluzioni impiegate sono state preparate a concentrazione 5.10⁻³ M.

Tutte le carte sono state analizzate con metodi non distruttivi (coordinate di colore, pH di superficie, XRF, spessore, aspetto sotto illuminazione UV). Su alcuni campioni è stato possibile eseguire analisi distruttive (contenuto in gruppi carbonilici, grado di polimerizzazione medio viscosimetrico, IR in trasmittanza). È stato saggiato anche l'effetto dei riducenti sulle macchie di foxing.

L'analisi dei risultati sperimentali ha mostrato che l'unica caratteristica comune a tutti i tipi di foxing consiste in un'ossidazione spinta della cellulosa con conseguente forte disidratazione. L'effetto dei riducenti conduce ad un alleggerimento delle macchie, qualora il fenomeno chimico predominante sia la formazione di gruppi carbonilici e di doppi legami carbonio-carbonio.

La ricerca è stata svolta nell'ambito del Progetto Finalizzato Beni Culturali del CNR.

M. Bicchieri, M. Nardone, A. Sodo, *Application of micro-Raman spectroscopy to the study of an illuminated medieval manuscript*, J. Cult. Heritage 1 (2000): S277-279

Abstract

We analysed, using Micro-Raman spectroscopy, two decorations of a medieval manuscript containing the "Canzoniere" and the "Trionfi" of Francesco Petrarca; namely a drawing attributed to Botticelli and the illumination of the Incipit of the "Trionfi". All measurements were carried out at two excitation wavelengths ($\lambda = 632.8$; $\lambda = 514.5$ nm). The spectra of the drawing showed the presence of lazurite, Na₈[Al₆Si₆O₂₄]Sn, the coloured matter of lapis lazuli, and of lead dioxide, coming from the oxidation of lead white or biacca, 2 PbCO₃ × Pb(OH)₂. The illuminations in the nearby page is a flower decoration, surely made by a different artist, in which we recognised the presence of cinnabar, HgS, lead tin yellow (type I), PbSnO₄ and azurite, 2 CuCO₃ × Cu(OH)₂, a blue pigment cheaper than lazurite.

D. Capitani, A.L. Segre, M. Pentimalli, M. Bicchieri, P.F. Munafò, *Ancient Deteriorated Paper: Washing and Restoring Processes as studied by 13C CP-MAS NMR Spectroscopy*, Qvinio 2 (2000): 37-43.

Abstract

¹³C CP-MAS NMR Spectroscopy has been used as an analytical tool establishing the best procedure in whitening ancient deteriorated paper. While a previous paper showed the feasibility of X-Ray

Photoelectron Spectroscopy in detecting the presence of oxidized carbon species near the surface layers of the paper, NMR easily detects these carbon species in the bulk material. NMR suggests that the soaking in water, able to obtain a remarkable cleaning of the paper itself, is the best procedure for the elimination of soluble cellulose fractions, containing oxidized carboxyl groups. Note that surface methods such as the measurement of the brightness give a clear indication that chemical methods, such as reduction of aldehydes and ketones or treatment with basic substances, obtain better results than simple washing procedure. We wish to point out that NMR measurements, i.e. a bulk method, clearly confirm the inefficiency of these methods, as the organic chemistry foreseen, in the treatment of an esterified function as that observed by NMR.

M. Bicchieri, R. Curini, G. D'Ascenzo, M. A. Orrù, *Characterization of Oxidized and Reduced Papers by Thermogravimetric Analysis - Effectiveness of Reducing Treatments*, Qvinio 2 (2000): 93-102.

Abstract

The aim of our experimental work was to ascertain whether reduction treatments with borane tert-butylamine complex could improve the paper resistance to aging. For this purpose, TG and DTG analysis were applied to Whatman paper, which was oxidized, oxidized and reduced and then subjected to aging. Untreated samples were also aged and used as a reference.

Experimental results lead to the conclusion that reduction treatments with borane tert-butylamine complex protect the paper against the aging and oxidation to which it is liable. Furthermore, the samples thus treated are found to be thermally more stable.

M. Bicchieri, A. Di Majo, C. Federici, L. Mita, F. Pascalicchio, M. Plossi Zappalà, *The Nitrogen Packaging of contemporary Paper as preservation Method*, Qvinio 2 (2000): 145-156

Abstract

One of the major problems affecting libraries and archives throughout the world regards the preservation of contemporary paper items. Efforts have been made to develop confined microenvironments by encapsulating such material in large-sized envelopes made of composite material (polyethylene, aluminium and polyester) capable of providing excellent protection against light, dust and various types of mishap. Our studies focused initially on experiments with vacuum packing. The vacuum conditions were subsequently replaced with a small amount of nitrogen in order to lessen the tension induced in the walls of the containers by the vacuum itself and to minimize the chemical degradation that could in any case occur in the confined microenvironment. It should be pointed out that the containers used are inexpensive and large enough to contain a week's issues of a newspaper with a margin of safety allowing them to be opened and closed at least 5 or 6 times.

The results of our study show that, subsequent to artificial aging, the nitrogen atmosphere has a net protective effect on pH, degree of polymerization, carboxyl and carbonyl content, and the variation of chromatic coordinates.

M. Bicchieri, M. Nardone, G. Pappalardo, L. Pappalardo, F.P. Romano, P.A. Russo, A. Sodo, *Raman and PIXE Analysis of Salerno Exultet*, Qvinio 2 (2000): 233-240

Abstract

Raman spectroscopy and PIXE-alpha spectrometry were used as non-destructive techniques to study the Salerno Exultet.

The whole analysis revealed a palette formed by gold, lapis-lazuli, cinnabar, verdigris, earths (white, red, brown, green), organic lakes and chalk and to highlight the presence of many restorative interventions.

G. Martinelli, *Infrared Analysis of Salerno Exultet*, *Qvinio*, 2 (2000): 241-253

Abstract

Infrared Fourier transform spectrophotometry was employed in this study to identify pigments and binders, and to assess the state of preservation of the parchment support. It was established that the substrate is in a fairly good state of preservation and that the palette of pigments is quite varied. Infrared spectra also revealed the repetition of various strata of colour and other compounds, demonstrating considerable modification due to repeated episodes of conservation work.

M. Plossi Zappalà, *Cause chimico-fisiche di danno per i materiali archivistici e librari*, in *Il materiale scrittoria: papiri, pergamene, carta*, III Scuola Nazionale di chimica per i Beni Culturali, Gruppo Interdivisionale di Chimica per i Beni Culturali, Palazzo Mansi 24-28 gennaio 2000, pp. 71-82.

Riassunto

L'invecchiamento dei materiali librari è un processo evolutivo naturale, spontaneo, irreversibile che non può essere arrestato; è possibile solamente cercare di rallentare la velocità di degradazione, minimizzando o eliminando tutte le cause concomitanti che tenderebbero invece ad accelerarla. L'invecchiamento naturale, infatti, sarebbe abbastanza lento se determinati fattori, considerati in questa trattazione, legati all'ambiente di conservazione o all'instabilità intrinseca dei materiali, non intervenissero ad aumentarne la velocità. Sono proprio questi fattori che devono essere valutati da chi ha l'incarico della tutela in modo che, almeno quando è possibile, essi non concorrano alla distruzione del patrimonio librario e d'archivio.

M. Plossi Zappalà, *Problematiche connesse al trasporto e all'esposizione di libri e documenti d'archivio*, "Discipline del libro", 4 (2000), pp.1-6, *Rivista elettronica della Facoltà di Lettere e Filosofia dell'Università di Udine*, in *Il libro antico*, <http://www.uniud.it/lettere/libroantico/>

Riassunto

Nell'allestimento di una mostra, o quando si deve organizzare il trasporto di un libro o di un documento, è doveroso tenere conto di alcuni accorgimenti atti a impedire che il libro possa subire danni. Senza queste cautele può accadere che l'esposizione, invece di costituire l'occasione per una maggiore fruizione e quindi sia fonte di cultura, arrechi danno ai materiali librari, o d'archivio, e possa quindi pregiudicare proprio la fruizione futura. I fattori degradanti da considerare per una corretta impostazione di una mostra, o per organizzare un trasporto, sono logicamente quelli ambientali: l'ambiente e il microambiente, che si viene a formare nei contenitori per il trasporto o nelle bacheche, devono soddisfare a determinati requisiti che vengono elencati in questa trattazione.

M. Bicchieri, F.M. Sementilli, A. Sodo, *Application of seven borane complexes in paper conservation*, *Restaurator* 21(4) (2000): 213-228

Abstract

Seven borane complexes were tested for aqueous and non-aqueous restoring treatments of paper. All the reducers gave very good results when used in aqueous solutions with an effectiveness of 66 ÷ 88% before the ageing, of 30 ÷ 52% after 28 ageing days.

The best results were obtained for borane ammonia complex (AB), borane tert-butylamine complex (TBAB) and borane N,N-diisopropylethylamine complex (DIPEAB). The latter reducer leaves unfortunately an unpleasant residual odour on the treated papers. AB and TBAB can also be used in organic solutions, avoiding the treatment of graphic media soluble in water.

G. Pappalardo, M. Bicchieri, C. Giuliani, L. Pappalardo, F.P. Romano, *Il sistema PIXE- α in una ricognizione "in situ" su un dipinto attribuito a Botticelli*, Boll. Acc. Gioenia Sci. Nat., 33(357) (2000): 415-420

Riassunto

Presso la Biblioteca Classense di Ravenna è custodito un manoscritto del '400 contenente i Trionfi del Petrarca ed un dipinto raffigurante il Trionfo d'Amore che, per le sue caratteristiche stilistiche ed iconografiche, è stato attribuito al Botticelli (Garzelli A. 1985; Zambrelli C., 1996).

Una prima analisi volta a caratterizzare i pigmenti aveva lasciato delle incertezze sulla reale composizione dell'azzurro dello sfondo (Andalò C. et al., 1999). L'analisi effettuata in Situ mediante il sistema PIXE- α del laboratorio LANDIS (Laboratorio di Analisi Non DISTRuttive) dei LNS/INFN di Catania, ha consentito di mettere in evidenza la presenza di lapislazzuli steso su un pigmento azzurro contenente Cu. Il sistema PIXE- α è in grado infatti di effettuare indagini elementari su pigmenti superficiali. La plausibilità di tali affermazioni è confermata dal confronto fra gli attuali dati e quelli precedentemente ottenuti mediante analisi Raman e l'uso di tecniche PIXE da acceleratori.

M. Bicchieri, M. Nardone, F.M. Sementilli, A. Sodo, *Chemical and Raman characterisation of borane complexes, a new series of reducers for degraded papers*, INFMeeting 2000, ABS I-15: 99

Abstract

Cellulose degradation is one of the greatest problems for the conservation of paper supports such as archival documents, books and artistic works. Degradation occurs because of internal or external factors, such as intrinsic acidity of the paper or storage in an unsuited place. Degraded papers show an evident fragility and a yellowing, compromising in some cases the readability of the text. The main degradation mechanisms are oxidation and hydrolysis. It is really important to be able to distinguish the kind of degradation occurring in the paper, because the restoration treatments are very specific.

For hydrolysed papers, deacidification treatments are necessary, in order to obtain the neutralisation of the carboxylic groups, while reduction processes are suitable for oxidised papers.

The reducers have to react selectively with the different oxidised functional groups and the reactions should be slow enough to avoid mechanical breaking of cellulose fibres, due to the evolution of hydrogen produced during the treatment. There are several fundamental requirements for the choice of good reducers. First of all they must be soluble in water or in organic solvents compatible with cellulose, adhesive, inks and coloured pigments. The resulting water solutions must be alkaline, with pH values not above 10.

Our present work wants to characterise, through chemical analyses and Raman spectroscopy, a new series of reducing agents for paper: the amino-borane complexes. These compounds exhibit all the requirements above mentioned and can be fundamental to treat oxidised papers.

Five amino-borane complexes were studied: borane ammonia complex (AB), borane dimethylamine complex (DMAB), borane trimethylamine complex (TMAB), borane tert-butylamine complex (TBAB) and borane morpholine complex (MB). They all can be used in water solution, giving pH values always above 10. Some of them maintain almost their efficiency in several organic solvents. They act as mild, efficient and stereoselective reducing agents for aldehydes and ketones in protic and non-protic solvents.

We report the study of these compounds by Raman spectroscopy, due to the lack of literature data. From the analysis of the Raman spectra we identified the bands corresponding to the NH, BH and BN stretching vibrations. The NH stretching vibrations all fall in the 3100-3350 cm^{-1} , while the BH stretching region lies between 2250 and 2350 cm^{-1} and the BN stretching at lower frequencies, below 1000 cm^{-1} . We are planning a more detailed study, varying the experimental conditions, in order to attribute unambiguously the Fermi resonance bands.