ACTA IMEKO
ISSN: 2221-870X
September 2026, Volume 15, Number 3, 1 - 8

Evaluating the effects of gamma irradiation on early 20th-century paper for paper-based cultural heritage preservation using non-destructive and minimally destructive techniques

Rocco Carcione[1], Beatrice D'Orsi[1], Elena Palmieri[2], Jessica Scifo[1], Ilaria Di Sarcina[1], Luca Maiolo[2], Francesco Maita[2], Alessia Cemmi[1]

[1] *ENEA, Nuclear Department (NUC), C. R. Casaccia, Via Anguillarese 301, 00123 Rome, Italy*
[2] *National Research Council, Institute for microelectronics and microsystems (IMM), Via del Fosso del Cavaliere 100, 00133 Rome, Italy*

ABSTRACT
This study investigates the secondary effects of gamma irradiation on early 20th-century paper samples from historical books, aiming to evaluate the suitability of this method for preserving cultural heritage (CH) materials. In recent years, gamma irradiation has gained recognition as an effective decontamination approach, capable of eradicating biodeteriogens without the use of harmful chemicals or heat. However, concerns persist about potential alterations in the structural and chemical integrity of aged paper artifacts. To address these issues, a set of non-destructive and minimally destructive analytical techniques, such as micro-Raman, FTIR-ATR, and EPR spectroscopies, along with thermogravimetric analysis, was employed to monitor possible changes in the morphology, molecular structure, chemical composition, radical content, and thermal stability of the samples. Results indicate that gamma irradiation at doses below 10 kGy does not cause significant degradation in the physico-chemical properties of this kind of historical paper. These findings offer new insights into the effects of ionizing radiation on aged paper, and contribute to the development of safe, standardized irradiation protocols for CH conservation. Moreover, the study highlights the importance of combining multiple analytical techniques to ensure accurate diagnostics, reinforcing gamma irradiation as a reliable and practical tool for the long-term preservation of vulnerable paper-based heritage artifacts.

Section: RESEARCH PAPER

Keywords: gamma irradiation; cellulose; lignin; cultural heritage; paper materials; measurements

Citation: R. Carcione, B. D'Orsi, E. Palmieri, J. Scifo, I. Di Sarcina, L. Maiolo, F. Maita, A. Cemmi, Evaluating the effects of gamma irradiation on early 20th-century paper for paper-based cultural heritage preservation using non-destructive and minimally destructive techniques, Acta IMEKO, vol. 15 (2026) no. 3, pp. 1-8. DOI: 10.21014/actaimeko.v15i3.2125

Section Editor: Luca Tortora, University Roma Tre, Italy

Received May 29, 2025; **In final form** February 4, 2026; **Published** September 2026

Corresponding author: Beatrice D'Orsi, e-mail: beatrice.dorsi@enea.it

1. INTRODUCTION

The preservation of cultural heritage (CH) is essential for safeguarding the historical and cultural identity of nations [1]–[4]. In the scenario of CH artifacts, books and paper-based materials are particularly vulnerable to biodeterioration produced by fungi, moulds, bacteria, insect pests, and lichens. These biological agents can lead to significant physical and chemical damage, accelerating the degradation of historical documents while also posing health risks to conservators and archivists. Due to their organic nature, paper-based materials require conservation techniques that can effectively eliminate biodeteriogens while preserving the integrity of the artifacts [5], [6].

In this context, gamma irradiation has emerged as a valuable tool for CH preservation due to its ability to inactivate nucleic acids, making it effective for the eradication of insects and microorganisms [7]–[10]. Unlike chemical fumigation methods, which may leave harmful residues, or alternative non-invasive treatments, such as freezing or anoxic conditions, which have limitations in microbial eradication, gamma irradiation provides a more comprehensive decontamination approach [8], [11]–[14]. Among ionizing radiation techniques, gamma irradiation offers significant advantages, including deep penetration capability, uniform treatment of complex and multi-component objects, and the ability to process large volumes of materials at ambient temperature. For these overall advantages, this method has been widely adopted since the 1960s and has received international

validation from institutions such as the International Atomic Energy Agency (IAEA). As evaluated by these specialized organizations, the suggested dose range is (8 ± 2) kGy for the conservation of CH artifacts [12], [14], [15].

Despite its effectiveness, gamma irradiation can induce secondary effects on treated materials, potentially altering their chemical composition, structural integrity, or visual appearance [16]–[19]. These secondary effects can be categorized as direct (occurring during irradiation and dependent on the absorbed dose) and indirect (developing post-irradiation due to free radical reactions). Notable material changes may include modifications in molecular structure (such as crosslinking or bond degradation), shifts in moisture interaction, and macroscopic alterations in mechanical and optical properties, such as discoloration [1], [20]–[21]. These effects are especially pronounced in new paper samples, such as reference new Whatman paper produced from highly purified cotton linters (chemical pulp) and containing no additives, fillers, or sizing agents. This type of new paper exhibits increased oxidation and depolymerization in response to higher absorbed doses. In contrast, already-oxidized aged books show minimal changes in both oxidation level and degree of depolymerization. This behaviour can be explained by considering that the number of sites available for oxidation induced by gamma rays is higher for Whatman paper than for naturally oxidized old papers. In particular, in our recent study [22], we investigated the specific secondary effects induced on different types of paper, such as a new reference model paper (already studied in our previous works [1], [23], [24]) and two old books provided by the National and University Library of Zagreb (Croatia). This goal was achieved through the integration of non-destructive and minimally invasive techniques, including micro-Raman and infrared spectroscopy, viscosimetric measurements, and colorimetric analysis (CIE).

The results obtained in that study highlighted key differences in how new and old paper samples respond to gamma irradiation, prompting further investigation into the secondary effects of gamma rays on historical paper materials. Given these considerations, the analytical techniques used in the present work are designed to complement those employed previously, with a dual objective: to assess the efficacy of gamma irradiation for cultural heritage preservation, and to establish practical, standardized protocols for broader application by professionals in the field.

In the context of cultural heritage conservation, there is an urgent need to develop analytical approaches that are not only accurate and reliable but also non-destructive—or, at most, minimally invasive. The fragile nature and irreplaceable value of historical artifacts demand methodologies that safeguard their physical and chemical integrity while providing insightful diagnostic information [25]. Therefore, the development of simple, user-friendly, and replicable protocols is essential to support conservators, restorers, and heritage scientists in their routine work.

In this framework, the studies presented here aim to contribute significantly to this goal by integrating a suite of non-destructive techniques, such as micro-Raman spectroscopy, Fourier Transform Infrared spectroscopy in Attenuated Total Reflectance (FTIR-ATR) mode, and Electron Paramagnetic Resonance (EPR) spectroscopy, along with thermogravimetric methods such as Thermogravimetric Analysis (TGA) and Derivative Thermogravimetry (DTG), to monitor changes in the structural, morphological, chemical, and radical profiles of aged paper following gamma irradiation. By comparing samples from historical books preserved at the National and University Library of Zagreb, the research sheds light on how compositional differences influence the response of paper to gamma treatment.

Irradiation tests were conducted at a dose rate of 1500 Gy/h, a value previously shown to be effective for microbial decontamination without causing detrimental effects to the paper matrix. The overall approach adopted in this work is designed to support the establishment of safe, effective, and reproducible irradiation protocols that can be confidently applied by CH operators worldwide.

In this context, the distinctive value of this work lies not only in validating the safety of irradiation on these materials, but also in contributing to the development of practical, replicable protocols that could serve as guidelines for the broader application to paper-based cultural heritage artifacts of different ages and compositions.

The findings of this study contribute to the development of best-practice protocols for gamma irradiation in CH conservation. In particular, a crucial task is the settling of reproducible analytical workflows to monitor its impact on delicate substrates. By providing reliable scientific data on irradiation-induced changes, this research supports the broader adoption of gamma technology in the field, ensuring both the effectiveness and safety of decontamination treatments while preserving the integrity of historical paper artifacts. Moreover, the proposed methodology highlights the potential for adapting irradiation and analytical techniques for the conservation of entire CH objects, paving the way for more advanced and systematic preservation strategies.

2. MATERIALS AND METHODS

2.1. Samples preparation

For the analysis and irradiation tests described in this paper, two books from the Croatian National and University Library (NUL) in Zagreb were used: Monistische Sonntagspredigten by Wilhelm Ostwald (1911) and Die Elemente der Metaphysik by Dr. Paul Deussen (1890). The samples are labelled as "O" for Ostwald's book, and "D" for Deussen's book. A photograph showing the appearance of these books is reported in Figure 1.

To obtain samples as homogeneous as possible, square pieces of 2 cm × 2 cm were cut from unprinted areas of the central pages of the books. To avoid any misleading interpretation of the results, the same samples were systematically analysed before and after irradiation by all applied techniques. For each book, three replicate samples were prepared and analysed.

Figure 1. Photo showing the appearance of (a) O and (b) D books.

2.2. Gamma irradiation tests

The irradiation tests were performed at the Calliope gamma irradiation facility (ENEA Casaccia R.C., Rome, Italy) equipped with a ^{60}Co (mean energy of 1.25 MeV) radioisotopic source array [26]. The samples were irradiated in air, at room temperature and humidity conditions, at an absorbed dose of 8 kGy at a dose rate of around 1.5 kGy/h. The absorbed dose and dose rate values are referred to water. The dose rate was experimentally determined at the dosimetric laboratory of the Calliope facility, using Fricke and alanine-EPR dosimetric systems.

2.3. Characterization techniques

To evaluate the possible radiation-induced effects on the morphological and molecular structural features of paper, optical microscope images and Raman spectra of the samples were collected using a micro-Raman spectrometer (Horiba XploRA Plus). The images were captured through a microscope with a 10X objective. Raman spectra were recorded under 785 nm laser excitation, with a laser power of 50 mW and a diffraction grating of 1200 gr/mm, with one accumulation at an objective magnification of 100X. Prior to analysis, Raman spectra were background-subtracted and smoothed. To ensure both the reproducibility and repeatability of the deconvolution procedure used for the calculation of the *RI*, the following protocol was applied: baseline subtraction at specific points (250, 550, 850, 1200, 1500, and 1750 cm^{-1}), normalization of the spectrum between 0 and 1 with respect to the most intense signal, smoothing with a 5-point algorithm to reduce spectral noise, and finally deconvolution using Lorentzian line functions for the peaks highlighted in the Raman spectra.

FTIR spectra in transmittance mode were recorded in the range of 4000–500 cm^{-1} using a Spectrum 100 Perkin-Elmer FTIR spectrometer. Each measurement consisted of 8 scans with a scan resolution of 1 cm^{-1}. The spectra were analysed in the range of 1800–1485 cm^{-1}, where the most significant peaks from oxidized carbon functional groups are located. To investigate possible oxidation processes induced by gamma rays on the paper samples, the spectra were deconvolved using multiple Gaussian functions. The maximum full width at half height (FWHH) of the Gaussian bands was approximately 150 cm^{-1}, particularly for the band associated with adsorbed water. The quality of the deconvolutions was confirmed by the high correlation values obtained, with R^2 consistently greater than 0.993. For each sample, three independent spectra were recorded, and the mean values of the investigated parameters (peak areas) were used. Background (air) subtraction and baseline correction were performed prior to analysis.

Thermogravimetric Analysis (TGA-DTG) was carried out using a TA Instruments Discovery TGA 55. Round-shaped cellulose samples (of 5 mm diameter) were placed in platinum crucibles and heated from 50 °C to 600 °C under a nitrogen atmosphere (flow rate: 40 mL/min). The heating rate was fixed at 10 °C/min. Three runs were conducted for each sample, under the same experimental conditions. The obtained thermogravimetric parameters ($T_{\text{decomposition}}$ and residual weight) were averaged, and standard errors were calculated.

EPR spectra were obtained by using an EPR Bruker e-scan spectrometer operating in the X-band, with a frequency of 9.4 GHz, microwave power of 0.14 mW, and magnetic field in the range 3390–3580 G. For this analysis, the samples were positioned within a conventional quartz tube. To this purpose, the books' samples were further cut to obtain 1.5 cm × 0.5 cm to guarantee homogeneous exposition to the magnetic field. All the spectra and the EPR data were normalized to the sample mass.

For each sample type and irradiation condition, three independent replicates were produced and tested. On each replicate, measurements were performed both in the central area and on the outer regions along the longer edge of the paper strip, in order to account for potential heterogeneity. In particular, micro-Raman spectroscopy allowed us to acquire spectra exactly at the same spot where microscope images were recorded, ensuring precise spatial correspondence. FTIR analysis, while probing slightly larger areas than Raman, was carried out in the same regions of the samples where optical images and Raman spectra were acquired, thus ensuring comparability across techniques. The error bars shown in the figures, expressed as standard deviations, are calculated based on measurements performed on these three distinct samples for each condition. All the characterization measurements were conducted in air immediately after irradiation for all samples.

3. RESULTS AND DISCUSSION

To verify whether within each volume the conservation state is consistent across different pages, preliminary analyses were carried out on unirradiated samples taken from the beginning, middle, and end of each book. The preliminary results indicated that the level of degradation and oxidation was substantially the same throughout the examined sections, with only minimal variations. This demonstrates that, despite the overall poor conservation conditions, the deterioration processes affected the books in a fairly homogeneous manner, making the selected sampling points representative of the whole volume. Comprehensive information on the pre-irradiation characterization of the writing supports in the D and O books is provided in previous publications [22], [25]. Figure 2 shows representative optical microscope images of unprinted areas of Ostwald and Deussen book pages (O and D samples) before and after irradiation at an absorbed dose of 8 kGy.

The comparison between Figure 2a–b denotes that the samples before irradiation exhibit dissimilar coloration and morphology, due to the different chemical composition of the

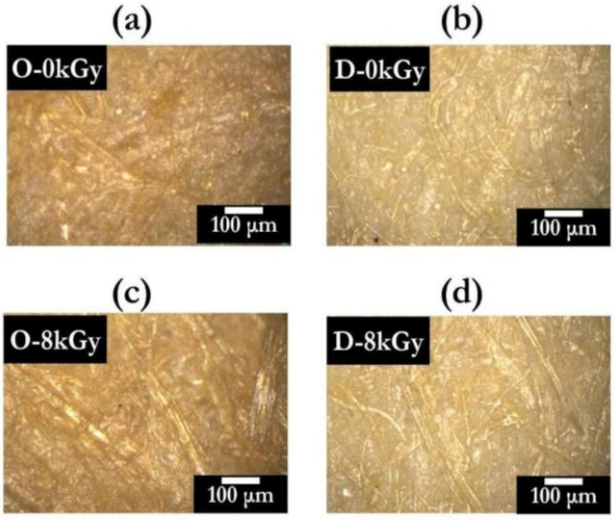

Figure 2. Optical microscope images of the books' unprinted areas at magnitude 10X for (a) O and (b) D samples before irradiation (O - 0 kGy and D - 0 kGy), and for (c) O and (d) D samples after (O - 8 kGy and D - 8 kGy) irradiation.

papery samples [27]. As demonstrated in our previous study [23], the paper used to produce D book is predominantly constituted by cellulose, while the paper employed for the fabrication of O book is composed by a consistent amount of lignin phases. On these bases, the compact morphology for O samples (Figure 2a) is ascribed to well-organized structures typical of paper with high lignin content [28], while D samples texture (Figure 2b) is constituted by fibrillar entities, typical of cellulose chains. Regardless of the different chemical compositions, Figure 2c–d shows no significant changes in either samples' morphology after irradiation. This finding confirms that irradiation under the adopted conditions not only preserves the macroscopic integrity of the materials but also produces no noteworthy effects on the texture of the analysed paper at microscopic level. This stability ensures that the topographical characteristics of the paper remain unaltered, reinforcing the suitability of irradiation as a safe preservation method for historical documents and archival materials.

Information on the effects produced by gamma irradiation on the structural features of the paper samples are obtained by Raman spectroscopy analysis. Representative deconvolved Raman spectra of the early 20th-century books' paper before and after irradiation are shown in Figure 3.

In accordance with the morphological analysis, Figure 3 shows that the Raman spectra acquired on D samples exhibit signals ascribable only to cellulose and hemicellulose chains, while the representative Raman spectrum of O samples clearly exhibits further peaks related to lignin phases [29]–[38]. The spectra show no signals attributable to fillers, foreign fibres, or metallic impurities, suggesting the lack of a significant number of crystalline phases of additional substances within the paper matrices.

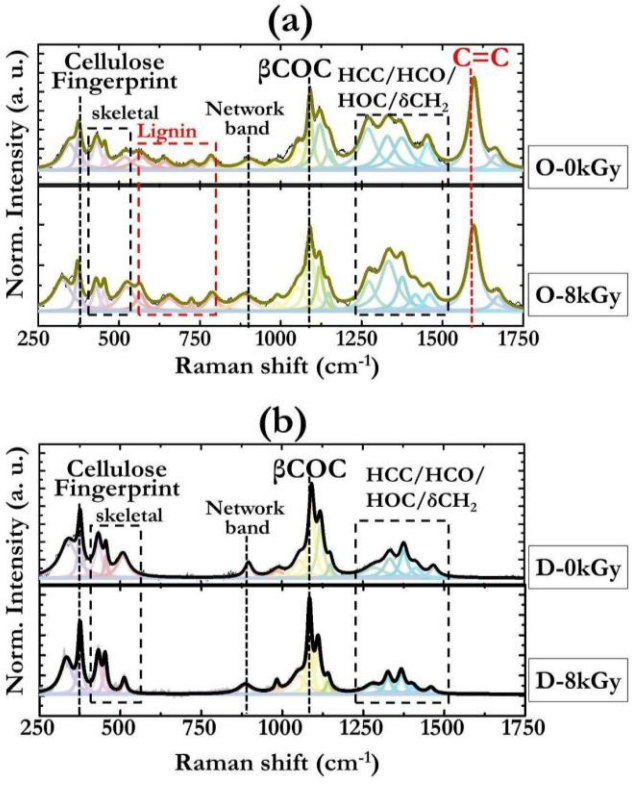

Figure 3. Representative deconvolved Raman spectra of (a) O and (b) D books' paper before (O-0kGy and D-0kGy samples) and after irradiation (O-8kGy and D-8kGy samples).

As regards the signals attribution, the bands below 900 cm^{-1} are generally attributed to deformation and torsional vibrations of CCC, CCO, COC, OCO, and COH skeletal modes [37], [39], [40]. In particular, the peak at around 380 cm^{-1} is related to the cellulose rings' bending modes and is generally recognized as the cellulose fingerprint signal. The peaks at around 900, 1050, 1100, and 1160 cm^{-1} are related to the cellulose network band, CO stretching (νCO), βCOC glycosidic bonds, and CC stretching modes of cellulose and hemicellulose units, respectively [37], [39], [40]. Signals at around 990, 1280, and 1400 cm^{-1} are assigned to CH_2 vibrations, while the peaks at 1330, 1380, and 1440 cm^{-1} are attributed to the synergistic contribution of $HCC/HCO/HOC/CH_2$ modes. The signals at around 1600 cm^{-1} in the spectra of O samples are assigned to the vibrations of C=C bonds in lignin chains.

In agreement with other studies [37], [39], [40], the relative integrated intensities values (RI) between the cellulose fingerprint line and the βCOC band are a helpful tool to evaluate and compare the molecular structural order of the cellulose units contained within the investigated paper matrices. Therefore, the RI parameter for the paper samples before and after irradiation was calculated according to equation (1):

$$RI = \frac{I_{\text{cellulose fingerprint}}}{I_{\beta\text{COC}}}, \tag{1}$$

where $I_{\text{cellulose fingerprint}}$ and $I_{\beta\text{COC}}$ are the integrated intensity values of the cellulose fingerprint line at 380 cm^{-1} and βCOC glycosidic bonds band at 1100 cm^{-1}, respectively. Table 1 shows RI values for each type of paper sample before and after irradiation.

As reported in Table 1, the *RI* values derived for O and D samples before irradiation suggest a difference in the structural organization of the cellulose units within the two paper matrices. In particular, the lower *RI* value observed for O samples suggests a reduced molecular order, which can be attributed to poor paper quality and high lignin content. Specifically, the lignin phase reasonably disrupts the cellulose crystalline network, leading to a less ordered structure for O with respect to D samples, which plausibly contain a higher proportion of purified cellulose and exhibit greater molecular entanglement.

Independently of the paper matrices' composition, the RI values remain rather unchanged for both samples after gamma irradiation. These results suggest that, regardless of the differences in chemical composition between the two paper types, the tested irradiation conditions induce no significant structural modifications within the detection limits of the method. This behaviour can be explained by considering that the cellulose phase of both ancient books has undergone natural degradation over time. Consequently, the impact of irradiation on their structural integrity is minimal, and any variations observed fall within the experimental error. These outcomes reinforce the idea that gamma treatment does not substantially

Table 1. *RI* values derived for each type of paper sample before and after irradiation.

Sample	Absorbed dose (kGy)	*RI*
O	0	0.41 ± 0.08
	8	0.46 ± 0.07
D	0	0.65 ± 0.05
	8	0.62 ± 0.05

alter the molecular arrangement of old paper materials, making it a suitable decontamination method for historical documents.

Additional insights into the chemical composition of the studied materials were obtained through FTIR-ATR analysis (see reference for details). The spectra of the O book revealed signals associated with both cellulose and lignin phases [41], [42], whereas the D book displayed only peaks corresponding to cellulose units, indicating the absence of lignin in its composition. To detail whether gamma radiation treatment modifies the oxidation level of the investigated paper samples, the FTIR spectra were analyzed in the range of 1800–1500 cm^{-1}, in which cellulose oxidation bands are present [16], [41], [42]. In this spectral region, the signals assigned to adsorbed water, carbonylic (C=O) and carboxylic (COO^-) moieties are detected [16]. The further peak at around 1510 cm^{-1} observed only in the spectra of O book is related to the C=C-C bonds in lignin phase [41], [42]. The representative deconvolved spectra of the samples before and after irradiation are reported in Figure 4.

At a first glance, the deconvolved FTIR spectra in Figure 4a–b appear unchanged after irradiation for both O and D books' pages, suggesting that the adopted irradiation conditions produce no remarkable modifications in the chemical composition of either paper matrices. More in detail, the deconvolution analysis allowed for the quantification of C=O and COO group variations post-irradiation by examining peak areas. In particular, the parameters $\Delta(C=O)\%$ and $\Delta(COO)\%$ were calculated based on the difference in the peak areas of the respective groups (C=O and COO) before and after irradiation. For the O samples, both $\Delta(C=O)\%$ and $\Delta(COO)\%$ values are lower than 4 %. In contrast, the $\Delta(C=O)\%$ values derived for the D samples exhibited an increment of 10 %, while the $\Delta(COO)\%$ values remained constant after irradiation.

These findings suggest that oxidation effects are neglectable for the O book irradiated at 8 kGy, whereas a slight increase in carboxyl groups is observed for the D artifact. This different behaviour can be plausibly attributed to the distinct chemical compositions of the paper matrices, a key factor influencing their response to oxidative degradation induced by irradiation in air. Specifically, the lignin phase in the O book behaves as a shield for cellulose, reducing the number of sites accessible for the carbonyl bonds formation during gamma irradiation [41], [43]. However, it is important to note that the unchanged $\Delta(COO)\%$ values in both samples confirm that irradiation does not contribute to the formation of these functional groups, which are instead a result of pre-existing oxidation likely caused by the natural aging of the paper.

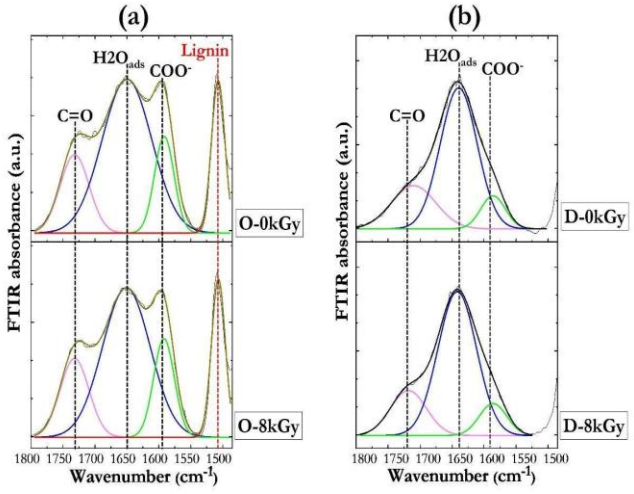

Figure 4. Representative deconvolved FTIR spectra in the range of 1800–1500 cm^{-1} for (a) O and (b) D books' paper before (O-0kGy and D-0kGy samples) and after irradiation (O-8kGy and D-8kGy samples).

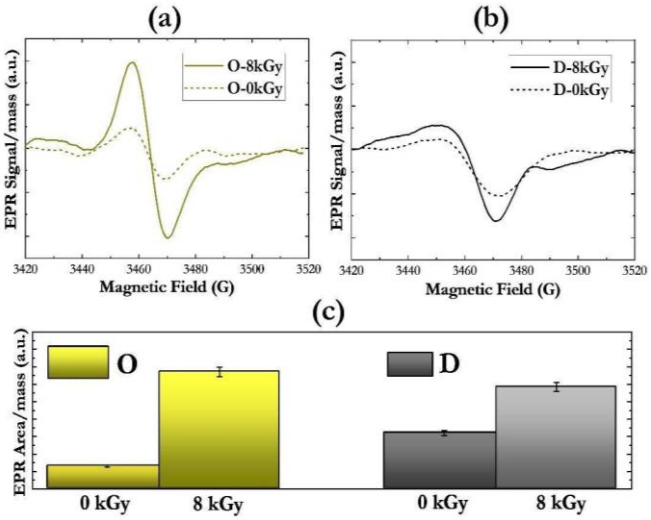

Figure 5. EPR spectra (represented by the first derivative of the physical signal) for (a) O and (b) D samples before (dashed lines) and after (straight lines) irradiation; (c) EPR peaks' area derived for O and D samples before and after irradiation.

To investigate the behaviour of the radical species induced by gamma exposure that are responsible of the post-irradiation processes, the EPR spectra (represented by the first derivative of the physical signal) were recorded for the samples before and after irradiation. The measurements performed right after the end of the irradiation tests for the two analysed samples before and after irradiation at 8 kGy absorbed are shown in Figure 5.

As shown in Figure 5a and Figure 5b, a general increase in EPR signal intensity is observed for both types of paper samples following gamma irradiation. This trend is clearly attributable to the formation of free radicals within the paper matrices as a direct consequence of their interaction with gamma rays.

A more detailed comparison of the two spectra highlights distinct differences between the O and D samples' spectra, which reflect their divergent chemical compositions. In both cases, the positions of the EPR peaks are indicative of organic radicals, likely originating from the biomolecular components of the paper. However, assigning a specific radical species to each signal remains challenging. This occurs because EPR spectra of cellulose-based materials typically result from the superposition of multiple radical species, producing singlet, doublet, or triplet patterns that are difficult to deconvolute [20], [44]. In this context, it is worth noting that the O sample exhibits a more intense and complex EPR profile compared to the D sample. This behaviour can be attributed to the presence of lignin and other aromatic compounds in the O paper, which contribute additional radical signals. These lignin-associated radicals overlap with those derived from cellulose, enhancing the overall spectral intensity and complexity. In contrast, the D sample, being lignin-free, shows a simpler EPR spectrum dominated by cellulose-related radicals.

A quantitative analysis of the EPR spectra was carried out by performing a double integration of the signal to determine the peak area. As shown in the histogram in Figure 5c, the EPR area derived before irradiation for sample D is around three times higher than that of sample O. This lower radical content in the

O sample is likely due to the presence of lignin and aromatic structures that reduce the steady-state radical population.

In addition, the histogram in Figure 5c highlights different trends in radical formation after irradiation. As shown in Figure 5c, the EPR signal for the O sample increases by a factor of six post-irradiation, whereas the signal for sample D increases only by a factor of three. This behaviour can be reasonably explained by a different interplay between the components of the paper and gamma radiation. In the O sample, the presence of lignin and other organic structures not only provides a degree of shielding to cellulose units against oxidative degradation but also contributes to radical formation within the paper matrix. Conversely, sample D, composed primarily of cellulose, experiences an increase in carbonyl (C=O) groups after irradiation, but the relative number of generated radicals is lower compared to the lignin-rich O sample.

Further information on the thermal stability of the samples before and after irradiation was achieved by TG-DTG analysis. The TGA data of the paper samples from the two examined books are presented in Figure 6. Along with the TG curves (dotted), the derivatives of the weight loss curves (DTG, continuous lines) were also analysed to better identify the degradation temperatures.

For all the samples, the initial part of the curve (up to around 100 °C) is characterized by a small weight loss (~ 4 %) due to moisture bonded on the paper samples surfaces. The degradation of the sample occurs in the temperature range from 220–360 °C. More specifically, in the case of the O book paper, both the unirradiated (black curve) and irradiated (grey curve) samples show a gradual onset of degradation, progressing slowly and with a less steep slope. This behaviour is likely attributed to the heterogeneous composition of this paper matrix, which includes components such as lignin that degrade at temperatures different than those of cellulose, leading to a broader and less pronounced degradation curve. This characteristic is also reflected in the derivative curve, where the main degradation peak is less sharply defined. In particular, a noticeable shoulder appears at around 260 °C, likely due to impurities and residual moieties, while another shoulder emerges at approximately 309 °C, at a temperature lower than the main degradation process (occurring at around 334 °C). Other degradation phenomena start at around 450–500 °C. For the D book, both not irradiated (purple curve) and irradiated (violet curve) samples show a degradation onset at a higher temperature than the O book, however, with a much steeper degradation curve. In line with FTIR-ATR and Raman spectroscopy analyses, this finding is plausibly due to the homogeneous composition of D paper.

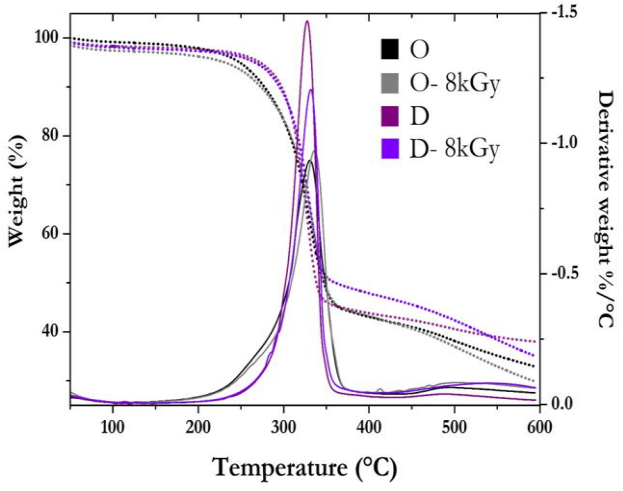

Figure 6. TG (dotted) and DTG (continuous) curves of paper samples from the O book and from the D book before and after irradiation (8 kGy).

Table 2. Degradation temperature and residual weight of samples of the O book and the D book, before and after irradiation at 8kGy.

Sample	Absorbed dose (kGy)	T_{deg} (°C)	Residual weight (%)
O	0	334 ± 4	33.3 ± 0.3
	8	339 ± 3	32.2 ± 2.4
D	0	327.2 ± 0.3	38.0 ± 0.1
	8	335 ± 1	36 ± 4

More details on degradation temperature and residual weight for O and D book samples, before and after irradiation at 8 kGy, are reported in Table 2.

The mean values from multiple analyses suggest that the O samples irradiated at 8 kGy (O-8kGy samples) tend to show a slightly higher degradation temperature, implying that this rather low irradiation dose may have reinforced the paper's structure. However, it is worth to point out that a clear conclusion cannot be drawn due to variability among the tested paper samples (data summarized in Table 2). The residual weight at 600 °C is approximately 33 % for the not irradiated and 32 % for the irradiated sample, corroborating that gamma irradiation up to 8 kGy does not significantly affect the thermal stability of O paper.

Conversely to O samples, the homogenous composition of D samples, predominantly composed by cellulose molecules, is reflected in the smaller error margins in temperature values and the nearly superimposable curves from different analysed samples (not shown). Regarding the effect of irradiation, as observed for O book, the irradiated D book samples show a slightly higher degradation temperature than the unirradiated counterparts, suggesting that irradiation may contribute to structural reinforcement. Given the lower error margins in this case, the increase in degradation temperature is considered significant. Additionally, the residual weight at 600 °C is higher than that of the O, approximately 37 %.

These data are consistent with findings reported in reference [1], which showed that degradation of the polymeric structures occurs at irradiation doses higher than 10 kGy.

4. CONCLUSIONS

This study demonstrates the effectiveness of combining non-destructive and minimally destructive techniques, such as micro-Raman, FTIR-ATR, EPR spectroscopies, and TGA to evaluate the secondary effects of gamma irradiation on early 20th-century paper samples from historical books. The integrated, non-destructive and minimally invasive analytical approach enables a comprehensive evaluation of morphological, structural, chemical, and thermal parameters, offering a reliable methodology for monitoring changes induced by irradiation.

The results confirm that gamma irradiation at doses below 10 kGy does not cause significant degradation in the physico-chemical properties of naturally aged paper materials. This finding is crucial for validating gamma technology as a safe and effective option for the microbial decontamination of cultural heritage library artifacts, addressing longstanding concerns about the preservation of structural integrity during such treatments.

Importantly, this work offers new insights and opens frontier perspectives in the field of CH conservation. By analysing real historical artifacts, the study provides valuable, application-oriented data that more closely reflects the actual conditions encountered in heritage preservation contexts.

In this way, the study goes beyond confirming the efficacy of gamma irradiation, providing instead a reproducible framework of analytical protocols that can support the development of standardized guidelines for the safe and practical preservation of delicate paper-based cultural heritage materials. This case-study-based approach strengthens the scientific foundation for establishing standardized irradiation protocols and promotes the broader adoption of non-invasive diagnostics in the development of best practices for safeguarding library collections. Based on the results of this study, the next step will involve future studies to investigate the effects of the treatments on more fragile and biodeteriorated paper.

AUTHORS' CONTRIBUTION

Conceptualization: Rocco Carcione (R.C.), Beatrice D'Orsi (B.D.), and Alessia Cemmi (A.C.); methodology: R.C., B.D., Ilaria Di Sarcina (I.D.S.), Jessica Scifo (J.S.), and A.C.; software: R.C., B.D., and Elena Palmieri (E.P.).; validation: A.C., I.D.S., Luca Maiolo (L.M.), Francesco Maita (F.M.), and J.S.; formal analysis: R.C., B.D., and E.P.; investigation: R.C. and B.D.; resources, A.C.; data curation, R.C., B.D., and E.P.; writing—original draft preparation, R.C. and B.D.; writing—review and editing: R.C., B.D., E.P., and A.C.; visualization, R.C., B.D., A.C., I.D.S., L.M., F.M., E.P., and J.S.; supervision, A.C. All authors have read and agreed to the published version of this manuscript.

ACKNOWLEDGEMENTS

The authors are grateful to K. Kavler and B. Mihaljevic from the Ruđer Bošković Institut (Zagreb, Croatia), who have provided the old books employed in this study. The authors acknowledge the DTC Lazio for funding the PERGAMO project 305-2020-35549.

REFERENCES

[1] S. Baccaro, M. Carewska, C. Casieri, A. Cemmi, A. Lepore, Structure modifications and interaction with moisture in γ-irradiated pure cellulose by thermal analysis and infrared spectroscopy, Polym Degrad Stab 98 (2013), pp. 2005–2010. DOI: 10.1016/j.polymdegradstab.2013.07.011

[2] E. Palmieri, C. Cicero, N. Orazi, F. Mercuri, U. Zammit, C. Mazzuca, S. Orlanducci, Nanodiamond composites: A new material for the preservation of parchment. Journal of Applied Polymer Science 139 (2022), Art. No. e52742. DOI: 10.1002/app.52742

[3] A. Moropoulou, K. C. Labropoulos, E. T. Delegou, M. Karoglou, A. Bakolas, Non-destructive techniques as a tool for the protection of built cultural heritage, Constr Build Mater 48 (2013), pp. 1222–1239. DOI: 10.1016/j.conbuildmat.2013.03.044

[4] G. Bitossi, R. Giorgi, M. Mauro, B. Salvadori, L. Dei, Spectroscopic Techniques in Cultural Heritage Conservation: A Survey, Appl Spectrosc Rev 40 (2005), pp. 187–228. DOI: 10.1081/ASR-200054370

[5] K. Karakasidou, K. Nikolouli, G.D. Amoutzias, A. Pournou, C. Manassis, G. Tsiamis, D. Mossialos, Microbial diversity in biodeteriorated Greek historical documents dating back to the 19th and 20th century: A case study. Microbiologyopen 7 (2018), Art. No. e00596. DOI: 10.1002/mbo3.596

[6] P. Tiano, Biodegradation of cultural heritage: Decay mechanisms and control methods, Proc. of the Seminar, New University of Lisbon, Department of Conservation and Restoration, Portugal, April 2002, pp. 7–12. Online [Accessed 24 July 2026] https://www.arcchip.cz/w09/w09_tiano.pdf

[7] M. Adamo, S. Baccaro, A. Cemmi, Radiation processing for bio-deteriorated archived materials and consolidation of porous artefacts, RT/2015/5/ENEA (2015). Online [Accessed 24 July 2026] https://hdl.handle.net/20.500.12079/6699

[8] I. V. Moise, M. Ene, C. D. Negut, M. Cutrubinis, M. M. Manea, Radiation processing for cultural heritage preservation - Romanian experience, Nukleonika 62 (2017), pp. 253–260. DOI:10.1515/nuka-2017-0037

[9] I. V. Moise, M. Virgolici, C. D. Negut, M. Manea, M. Alexandru, L. Trandafir, F. L. Zorila, C. M. Talasman, (+ 4 more authors), Establishing the irradiation dose for paper decontamination, Radiation Physics and Chemistry 81 (2012), pp. 1045–1050. DOI: 10.1016/j.radphyschem.2011.11.063

[10] M. Vadrucci, G. De Bellis, C. Mazzuca, F. Mercuri, F. Borgognoni, E. Schifano, D. Uccelletti, C. Cicero, Effects of the Ionizing Radiation Disinfection Treatment on Historical Leather, Front Mater 7 (2020) 21. DOI: 10.3389/fmats.2020.00021

[11] A. Cemmi, I. Di Sarcina, G. Ferrara, Cultural Heritage preservation and conservation of archived materials: gamma radiation processing and characterization at the Calliope facility (Casaccia R.C., Rome - Italy), RT/2020/1/ENEA (2020). Online [Accessed 24 July 2026] https://hdl.handle.net/20.500.12079/52861

[12] L. Cortella, W. Głuszewski, I. V. Moise, C. C. Ponta, Q. K. Tran, Nuclear techniques for preservation of cultural heritage artefacts. IAEA Technical Cooperation Project–RER 8015 (2011). Online [Accessed 26 July 2026] https://www.researchgate.net/profile/Wojciech-Gluszewski/publication/282274864_Nuclear_Techniques_for_Preservation_of_Cultural_Heritage_Artifacts/links/560a3e5508ae576ce63fb7c8/Nuclear-Techniques-for-Preservation-of-Cultural-Heritage-Artifacts.pdf

[13] B. Katušin-Ražem, D. Ražem, M. Braun, Irradiation treatment for the protection and conservation of cultural heritage artefacts in Croatia, Radiation Physics and Chemistry 78 (2009), pp. 729–731. DOI: 10.1016/j.radphyschem.2009.03.048

[14] IAEA. Uses of Ionizing Radiation for Tangible Cultural Heritage Conservation, IAEA Radiation Technology Series No. 6 (2017), pp. 241. Online [Accessed 24 July 2026] https://www-pub.iaea.org/MTCD/Publications/PDF/16-17821_PUB1747_web.pdf

[15] IAEA. Nuclear Techniques for Cultural Heritage Research. IAEA Radiation Technology Series No. 2 (2011) pp. 1–205. Online [Accessed 24 July 2026] https://www-pub.iaea.org/MTCD/Publications/PDF/p1501_web.pdf

[16] M. C. Area, A. M. Calvo, F. E. Felissia, A. Docters, M. V. Miranda, Influence of dose and dose rate on the physical properties of commercial papers commonly used in libraries and archives, Radiation Physics and Chemistry 96 (2014), pp. 217–222 DOI: 10.1016/j.radphyschem.2013.10.004

[17] M. C. Area, H. Cheradame, Paper aging and degradation: Recent findings and research methods, Bioresources 6 (2011), pp. 5307–5337. DOI: 10.15376/biores.6.4.5307-5337

[18] M. Bicchieri, M. Monti, G. Piantanida, A. Sodo, Effects of gamma irradiation on deteriorated paper, Radiation Physics and Chemistry 125 (2016), pp. 21–26. DOI: 10.1016/j.radphyschem.2016.03.005

[19] K. Drábková, M. Ďurovič, I. Kučerová, Influence of gamma radiation on properties of paper and textile fibres during

disinfection, Radiation Physics and Chemistry 152 (2018), pp. 75–80.
DOI: 10.1016/j.radphyschem.2018.07.023

[20] A. Cemmi, I. Di Sarcina, B. D'Orsi, Gamma radiation-induced effects on paper irradiated at absorbed doses common for cultural heritage preservation, Radiation Physics and Chemistry 202 (2023), pp. 110452.
DOI: 10.1016/j.radphyschem.2022.110452

[21] K. T. Gillen, R. L. Clough, N. J. Dhooge, Density profiling of polymers, Polymer (Guildf) 27 (1986), pp. 225–232.
DOI: 10.1016/0032-3861(86)90330-7

[22] B. D'Orsi, R. Carcione, I. Di Sarcina, G. Ferrara, M. Oliviero, T. Rinaldi, (+ 3 more authors), Gamma irradiation for Cultural Heritage conservation: comparison of the side effects on new and old paper soon, Journal of Cultural Heritage 70 (2024), pp. 335–344.
DOI: 10.1016/j.culher.2024.10.009

[23] International Atomic Energy Agency, Best Practices in Disinfection of Cultural Heritage Artefacts and Archives Using Ionizing Radiation, IAEA Radiation Technology Series No. 8 (2025). Online [Accessed 26 July 2026] https://preprint.iaea.org/search.aspx?orig_q=reportnumber:IAEA-PC--9083

[24] A. Lepore, S. Baccaro, C. Casieri, A. Cemmi, F. De Luca, Role of water in the ageing mechanism of paper, Chem. Phys. Lett. 531 (2012), pp. 206–209.
DOI: 10.1016/j.cplett.2012.01.083

[25] I. Di Sarcina, G. Ferrara, A. Verna, A. Cemmi, A., Optimization of paper characterization procedures for cultural heritage. RT/2024/2/ENEA (2024). Online [Accessed 26 July 2026] https://hdl.handle.net/20.500.12079/74291

[26] S. Baccaro, A. Cemmi, I. Di Sarcina, G. Ferrara, Gamma irradiation Calliope facility at ENEA Casaccia Research Centre (Rome, Italy), RT/2019/4/ENEA (2019). Online [Accessed 24 July 2026] https://hdl.handle.net/20.500.12079/6838

[27] A. Azarpira, F. Lu, J. Ralph, Reactions of dehydrodiferulates with ammonia, Org. Biomol. Chem. 9 (2011), pp. 6779–6787.
DOI: 10.1039/C1OB05677H

[28] F. Bausch, M. J. Rosado, J. Rencoret, G. Marques, A. Gutiérrez, J. Graf, J. C. del Río, T. Rosenau, (+ 1 more author), Papyrus production revisited: differences between ancient and modern production modes. Cellulose 29, 4931–4950 (2022).
DOI: 10.1007/s10570-022-04573-y

[29] C. Yan, Z. Cheng, S. Luo, C. Huang, S. Han, X. Han, Y. Du, C. Ying, Analysis of handmade paper by Raman spectroscopy combined with machine learning, Journal of Raman Spectroscopy 53 (2022), pp. 260–271.
DOI: 10.1002/jrs.6280

[30] J. Zięba-Palus, A. Weselucha-Birczyńska, B. Trzcińska, R. Kowalski, P. Moskal, Analysis of degraded papers by infrared and Raman spectroscopy for forensic purposes, J. Mol. Struct. 1140 (2017), pp. 154–162.
DOI: 10.1016/j.molstruc.2016.12.012

[31] D. Chiriu, P. C. Ricci, G. Cappellini, M. Salis, G. Loddo, C. M. Carbonaro, Ageing of ancient paper: A kinetic model of cellulose degradation from Raman spectra, Journal of Raman Spectroscopy 49 (2018), pp. 1802–1811.
DOI: 10.1002/jrs.5462

[32] S. Botti, F. Bonfigli, V. Nigro, A. Rufoloni, A. Vannozzi, Evaluating the Conservation State of Naturally Aged Paper with Raman and Luminescence Spectral Mapping: Toward a Non-Destructive Diagnostic Protocol, Molecules 27 (2022), 1712.
DOI: 10.3390/molecules27051712

[33] 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, J. Anal. Methods Chem. 2017 (2017), 2372789.
DOI: 10.1155/2017/2372789

[34] D. Chiriu, P. C. Ricci, G. Cappellini, C. M. Carbonaro, Ancient and modern paper: Study on ageing and degradation process by means of portable NIR μ-Raman spectroscopy, Microchemical Journal 138 (2018), pp. 26–34.
DOI:10.1016/j.microc.2017.12.024

[35] U. P. Agarwal, Beyond Crystallinity: Using Raman Spectroscopic Methods to Further Define Aggregated/Supramolecular Structure of Cellulose, Front. Energy Res. 10 (2022), 857621.
DOI: 10.3389/fenrg.2022.857621

[36] A. L. P. Queiroz, B. M. Kerins, J. Yadav, F. Farag, W. Faisal, M. E. Crowley, S. E. Lawrence, H. A. Moynihan, (+ 3 more authors), Investigating microcrystalline cellulose crystallinity using Raman spectroscopy, Cellulose 28 (2021), pp. 8971–8985.
DOI: 10.1007/s10570-021-04093-1

[37] U. P. Agarwal, S. A. Ralph, C. Baez, R. S. Reiner, Detection and quantitation of cellulose II by Raman spectroscopy, Cellulose, 28 (2021), pp. 9069–9079.
DOI: 10.1007/s10570-021-04124-x

[38] U. P. Agarwal, R. R. Reiner, S. A. Ralph, Estimation of cellulose crystallinity of lignocelluloses using near-IR FT-Raman spectroscopy and comparison of the Raman and Segal-WAXS methods, J. Agric. Food Chem. 61 (2013), pp. 103–113.
DOI: 10.1021/jf304465k

[39] U. P. Agarwal, S. A. Ralph, Raman Spectra of Delignified Plant Fibers: Exploring the Impact of Xylan's Presence on the Spectral Features of Cellulose, Fibers 12 (2023), 5.
DOI: 10.3390/fib12010005

[40] U. P. Agarwal, S. A. Ralph, R. S. Reiner, C. Baez, Probing crystallinity of never-dried wood cellulose with Raman spectroscopy, Cellulose 23 (2016), pp. 125–144.
DOI: 10.1007/s10570-015-0788-7

[41] E. Małachowska, M. Dubowik, P. Boruszewski, J. Łojewska, P. Przybysz, Influence of lignin content in cellulose pulp on paper durability, Scientific Reports 10 (2020), pp. 1–12.
DOI: 10.1038/s41598-020-77101-2

[42] J. Łojewska, P. Miśkowiec, T. Łojewski, L. M. Proniewicz, Cellulose oxidative and hydrolytic degradation: In situ FTIR approach, Polym. Degrad. Stab. 88 (2005), pp. 512–520.
DOI: 10.1016/j.polymdegradstab.2004.12.012

[43] E. Małachowska, M. Dubowik, P. Boruszewski, P. Przybysz, Accelerated ageing of paper: effect of lignin content and humidity on tensile properties, Herit. Sci. 9 (2021), pp. 1–8.
DOI: 10.1186/s40494-021-00611-3

[44] Y. Kodama, O. Rodrigues, R. H. L. Garcia, P. de S. Santos, P. A. S. Vasquez, Study of free radicals in gamma irradiated cellulose of cultural heritage materials using Electron Paramagnetic Resonance, Radiation Physics and Chemistry 124 (2016), pp. 169–173.
DOI: 10.1016/j.radphyschem.2016.02.018