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Effects of gamma irradiation on deteriorated paper

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HIGHLIGHTS

- γ-rays irradiation has been proposed to treat cultural heritage objects on paper.
- The effect of low dose γ-rays on paper was investigated.
- Chemical and spectroscopic techniques were used to evaluate the induced modifications.
- Results showed a noticeable degradation of the paper support after irradiation.
- The application to cultural heritage artefacts on paper seems inadvisable.

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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 vapors, avoiding any contact of the samples with water. This method induces a degradation similar to that observed on original documents.

The samples were then irradiated with 3 kGy γ-rays at a 5258 Gy/h rate. The aforementioned analyses were performed on the samples just irradiated and after artificial ageing. All tests showed negative effects of gamma irradiation on paper. Non-irradiated paper preserves better its appearance and chemical properties both in the short term and after ageing, while the irradiated samples show appreciable color change and higher oxidation extent. Since the Istituto centrale restauro e conservazione patrimonio archivistico e librario is responsible for the choice of all restoration treatments that could be applied on library and archival materials under the protection of the Italian State (http://www.icpal.beniculturali.it/allegati/DM-7-10-2008-Istituto.pdf), it has been evaluated that the modifications induced by γ-rays irradiation are not acceptable as safe conservation treatment (http://www.icpal.beniculturali.it/allegati/Nota_uso_raggi_gamma.pdf).

1. Introduction

Biodeterioration of paper materials is caused by bacteria, fungi and protozoa and, to a smaller extent, by insects and rodents. Library and archival materials may suffer particularly from fungi and insect attack. Preventing and inhibiting their action on paper is a major task in library and archives preservation. Developing new and optimizing existing treatment methods is an ongoing task in conservation science.

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Gamma radiation application for paper disinfection purposes has long since been studied (Horio et al., 1963) and long since it has been observed that, for doses strictly above 1 kGy, the treatment induces an immediate strong depolymerization, much more pronounced than the one induced by an accelerated ageing that alternates cycles of controlled temperature and humidity (80 °C, 65%RH) to cycles of ageing under vacuum at ambient temperature (Calvini and Santucci, 1978–1979). Considering that a satisfactory disinfection only happens at irradiation about 5 kGy, the treatment was found unadvisable for paper. However, due to wide range of radiation application in medical sterilization and food disinfestations, the question was reopened in the last decades (Sinco, 2000) and a number of other experiments have been carried out. As far as high dosages effects are concerned, it has been demonstrated by a thorough chemical analysis that serious depolymerization and oxidation is originated on pure cellulose paper and that scission route can be expressed directly as a function of each radiation beam energy (Bouchard et al., 2006). An experiment on gamma irradiation of paper at 1–5 kGy (Adamo et al., 2001) demonstrated depolymerization of cellulose above 2 kGy. However, the same authors reported a possible usage of radiation at 2 kGy, for already damaged paper, since other parameters (pH, tearing resistance, folding endurance) were found not to vary significantly for that dose.

Recent literature (Otero D'Almeida et al., 2009; Choi et al., 2012; Moise et al., 2012; Nunes et al., 2012; Area et al., March 2014; Michaelsen et al., 2013; Negut et al., 2012) reports positive results in the use of γ rays for library materials conservation. The problem we always remarked in many papers is related to the use of few chemical data but mechanical, optical or biological tests to substantiate the validity of γ rays treatment.

It is to underline that during the first ageing stages -natural or accelerated- there are no significant variations in mechanical properties: degradation evidence is only provided by measuring chemical processes (Porck, 2000; Bicchieri et al., 1993). Oxidation and depolymerization induced by the treatment, in fact, cause carbonyl and carboxyl groups formation, with great impact on paper permanence and durability, even if mechanical characteristics are not affected in the short term.

A paper hosted on Restaurator (Adamo et al., 2007) reports the mechanical, optical and biological evaluation on γ rays effects on the same papers analysed in the present work and chemically pretreated at ICRCPAL (Istituto centrale restauro e conservazione patrimonio archivistico e librario; Istituto Centrale Patologia del Libro -ICPL- at that time) chemistry laboratory using a method developed at our laboratory (hydrolysis induced by HCl vapors as reported in Ref. 17).

In a first moment we decided not to publish our data, supposing that the treatment with γ rays would have been not taken into account by library heritage conservators. We see now the rise of many articles on this topic. Therefore, we decided to add our opinion on the debate.

In our paper, we analyse the chemical and physical effects of γ rays, not only on not-treated papers, but also on pre-hydrolyzed samples, that should simulate an original damaged document. The experiment includes both irradiated and non-irradiated papers and studies them along ageing, by means of chemical, optical and spectroscopic measurements.

2. Materials and methods

2.1. Samples and treatments

Two kinds of paper were used:

- Whatman paper CHR 1 (pure cotton paper, ash-free, not sized)
- Permanent paper manufactured by Cartiere Miliani Fabriano S.p.A. which composition is reported in Table 1 (additives percentage are referred to the weight of the fibrous materials).

Table 1
Permanent paper composition (additives percentage are referred to the weight of fibrous materials).

Bleached sulfite softwood	8.0%
Bleached soda softwood	37.0%
Bleached soda hardwood	55.0%
Calcium carbonate	18.0%
Starch	4.0%
AKD (alkyl ketene dimer)	0.2%
Optical bleacher from stilbene	0.2%
Sodium chloride	0.3%

To obtain samples that would simulate original documents damaged by acids, some papers were exposed to hydrochloric acid (37%) vapors for 20 min then let dry at room temperature. This treatment does not simulate an ageing treatment, but the "original" conditions in which we often find the documents.

Three examples of chemical data on original documents can be found in Table 5

Each group of samples (hydrolyzed Whatman; permanent paper hydrolyzed and untreated) was divided in two portions, one of which underwent to gamma irradiation while the other remained untreated. We report, for comparison, the data obtained from paper made of pure cotton untreated (Whatman) about which, moreover, there is a large amount of literature (Horio et al., 1963; Calvini and Santucci, 1978–1979; Bouchard et al., 2006; Adamo et al., 2001).

The irradiation of paper was carried out at the "Calliope" plant of ENEA (Agenzia nazionale per le nuove tecnologie, l'energia e lo sviluppo economico sostenibile) in its Research Center in Casaccia (Rome), during the same experiment and on the same samples reported in Ref. 17. The chosen dose of radiation declared by ENEA staff was 3 kGy at a 5258 Gy/h rate.

The prepared samples were artificially aged in a climatic chamber at 80 °C and 65% R.H. for 12 and 24 days, according to ISO 5630/3 (ISO 5630/3, 1996).

2.2. Analysis procedures

A Minolta CHROMA METER CR-221 was used to obtain L*a*b* coordinates(ASTM E1347-06, 2011). The color distance parameter $\Delta E=(L^{*2}+a^{*2}+b^{*2})^{1/2}$ expresses the geometric distance of two points in the CIELAB space. Color variation appreciated by human eye corresponds to $\Delta E \geq 4$.

In order to provide insight and a better interpretation of the observed color variation on permanent paper, a series of optical measurements of reflectance R and transflectance T_F (Edwards et al., 1961; ASTM E903-E996) (reflectance R plus transmittance T, measured on the sample suspended in a Spectralon™-Labsphere integrating sphere) was executed in the UV–vis-NIR range (200–1800 nm), both immediately after the irradiation and after accelerated ageing.

The tests were executed with a Varian Cary 5 with a resolution of 1 nm in the visible spectrum and 3 nm in the Near Infrared (NIR).

On the basis of the reflectance spectra we decided to carry out a series of tests using the transflectance technique that is the stimulation and measure of the visible radiation on samples suspended in the center of an integrating sphere. Working in that way allows collecting entirely the radiation, both transmitted and reflected by the sample, so that it is possible to collect spectra directly and quantitatively correlated to the optical density OpD and