Archives decontamination by gamma irradiation*

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Abstract. The treatment of archives with gamma irradiation is an efficient and environmental friendly alternative for biological decontamination of large volume of archives. It substitutes the use of chemicals for conservation and contributes to safer workplaces. This work is targeting documents from recent archives where the value of information is not obsolete and may become an important historical and cultural testimony. For a successful treatment, an optimal absorbed dose has to be established. An excessive dose may damage papers and an insufficient one will not reduce bioburden to the desired level. An interdisciplinary team was performing various physical and chemical tests in order to evaluate deterioration of paper at high doses. In the case of natural disaster, it is not excluded the "emergency" treatment for documents in immediate danger of total destruction.

Key words: decontamination • archives • gamma irradiation • treatment • tests

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Received: 3 November 2008
Accepted: 31 March 2009

Archives decontamination

In any stage of social development the preservation and spreading of knowledge is an important desideratum. The present society still relies on the information written on paper and stored in archives, libraries and collections. The lack of funding, adequate spaces and personnel, various calamities, biological aggression and acid paper technology were the main damaging factors for a large number of archives. Humidity, temperature and pollutants also had a significant role to the degradation of the paper.

Paper is a good food supply for some microorganisms and insects. Hygroscopic environment makes paper susceptible to biodegradation. The most important species involved in the degradation of paper are insects, fungi and bacteria. They are changing the chemical and physical structure of the paper by the alteration of cellulose links with products of metabolism. Some fungi as *Aspergillus* and *Penicillium* have a high tolerance to environmental conditions and they can proliferate with a low content of water (62–65% RH), conditions encountered in libraries and archives. From the fungal damage can result acidification of the paper and a variety of spots with different shapes and colours [3]. Bacteria attack on paper occurs in conditions of humid environment (> 85% RH).

Insects are also involved in the damage of paper. Some are capable to alter the cellulose; others are feeding from glue, textile fibber, leather or other materials from the books. The damages may vary from the

* Presented on the International Conference on Recent Developments and Applications of Nuclear Technologies, 15-17 September 2008, Białowieża, Poland.

erosion of surfaces, micro and macrocavities, until the total degradation.

By metabolic processes, biological agents are producing different kind of acids, responsible for paper brittleness.

The last century shows a permanent seeking for an efficient method for paper biological decontamination. Very few methods are efficient for the mass treatment. Chemical methods borrowed from other fields (ethylene oxide, methyl bromide) have a good efficiency, but present more or less known risks concerning the long-term stability of the documents. Toxic chemicals involve risks for contamination of the environment and for the health of the personnel. Other chemical or physical methods are not so efficient against resistant or inactive forms: spores from fungi and bacteria or eggs and pupae of insects.

Gamma irradiation has multiple advantages: guaranteed biocide effect; short time process (hours); the highest degree of penetration (mass treatment); easy handling (the material is irradiated in transport package); can be applied to composite materials (paper, cardboard, wood, leather, textiles); treated object does not contain any toxic or radioactive residues.

Research concerning the application of the ionizing radiation for the decontamination of paper has been developed in the 1970-ies when the radiation resistance of the most common microorganisms was tested. The research aimed to establish a dose that kills all the biodegrading agents [3]. The studies were interrupted because of the spreading of decontamination with fumigants, especially ethylene oxide. After revealing the bad effects of ETO for human health, the ionizing radiations come back into attention of the conservators and restaurateurs [1].

In Romania, studies in the field were rare and non-systematic. First experiments were done in the National Archives [6]. There were identified 16 fungal strains contaminating the archive material and their radioresistance was established. In parallel, it was investigated the modification of the physical and mechanical properties of irradiated paper and the conclusion was that the only characteristic affected, slightly decreased, is the folding endurance. At the National Institute of Physics and Nuclear Engineering (IFIN HH), some manuscripts and old books from the Romanian Literature Museum were treated. Studies on trapped free radicals and attempts to eliminate them were performed.

A good example of "emergency treatments" is the decontamination of Gantt Collection from the medical archives of Johns Hopkins University (1980). All the collection was packed in approximately 300 storage boxes, treated at 4.5 kGy, unpacked and stored in safe conditions. After 25 years, no visible damages were observed to the irradiated paper materials [7].

Treatment dose should be as high as necessary to reduce bioburden to acceptable limits, but still under the threshold where the damaging to the paper is unacceptable. The modern approach introduces the D_{10} – the absorbed dose for the reduction of a certain number of microorganisms by a factor of 10 [8]. On a log (10) scale, the number of survivors is almost linear decreasing with absorbed dose. This approach reveals an important consideration: for archives decontamination, there is no need for sterility (this term belongs exclusively to medical and pharmaceutical field), but is needed for reduction of initial bioburden to an accepted level which ensures archive safe storage and safe working conditions.

An interdisciplinary group issued important studies of paper conservation by gamma irradiation in Italy. Doses up to 5 kGy were providing levels of bioburden less than ones encountered under natural conditions and doses up to 10 kGy still did not produce any significant damage to paper [5].

Classification of the archives by paper type and biocontamination degree is a complex task because of the large diversity of paper specifications and diversity of biocontaminants. The social and technological breakthrough from the XX century produced a huge amount of documents. Alkaline technology of paper manufacturing was a decisive factor for improving paper properties and permanence. This technology is about one hundred years old and reveals good life expectancy for the existent archives. Radiation treatment of this type of archives is a better choice than the classic treatment.

Look at the Romanian irradiator (IRASM)

In the year 2000, the first industrial irradiator was commissioned at the Romanian Institute of Physics and Nuclear Engineering (IFIN HH). The Radiation Processing Department (IRASM) operates a Co-60 irradiator with a maximum activity of 2 MCi and working with 300 kCi in 2008. The tote box-type multipurpose irradiator processes 10 m^3 of goods in batch irradiation with a maximum of 40,000 m^3/year. Since 2002, IRASM is certified according to ISO 9001 and ISO 13485 for sterilization of medical devices. Also IRASM established a microbiological laboratory, licensed for Quality Control of medicinal products (GMP) in 2003 and obtained in 2008 the Accreditation Certificate according to ISO 17025, for testing of medicinal products and medical devices. An irradiated food detection laboratory, notified by the Romanian Nuclear Regulatory Commission, was established in 2006. A new laboratory for physical and chemical testing was developed in 2007.

The tote box-type conveyor and three source racks of IRASM irradiator are shown in Fig. 1.

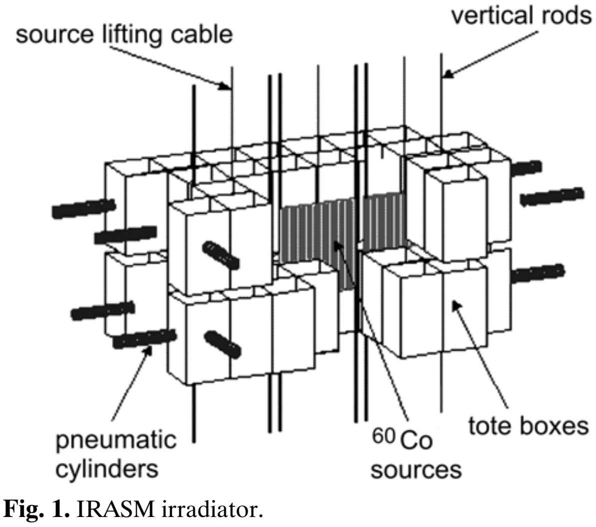


Fig. 1. IRASM irradiator.

Date:	29 July 2002
Owner:	“Moldova” National Museum
Treated objects:	4 packs containing icons and books from Iasi History Museum (Fig. 2)
Dose (KGy):	1.6–5.3

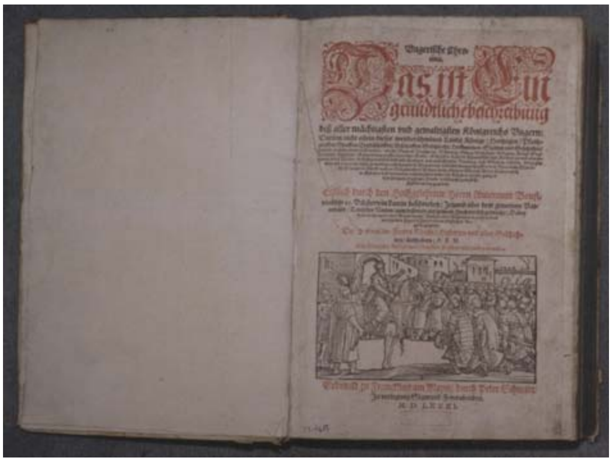


Fig. 2. Treated book.

Date:	08 June 2005
Owner:	Bucharest National Library
Treated objects:	3 books with dimensions 24 × 17.5 × 1.5 cm (Fig. 3)
Dose (KGy):	3/7/11

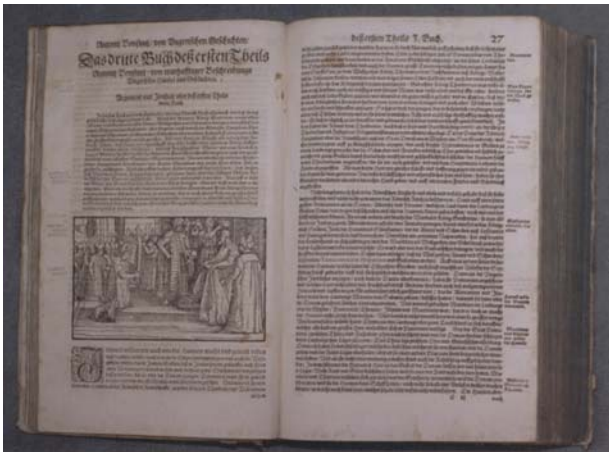


Fig. 3. Treated book.

The gamma irradiation can be achieved in several ways:

– “Batch” mode, when product containers are loaded inside an irradiation room, a source is placed in the irradiation position and the containers are moved in steps round the source until finish.
– “Continuous” mode, when the source is raised and the containers are entering, moving around the source and exiting after the irradiation time is finished.
– “Static” mode, when the products are not moving at all during the irradiation time.

Decontamination experiments at IRASM

First experiments concerning irradiation treatment for collection books were intended to reduce bioburden using doses from the international scientific literature.

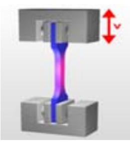
Among the irradiation treatments performed at IRASM facility for cultural heritage preservation, important works were done over several historical books belonging to museums and libraries in Romania. After treatment, no mechanical or physical tests were performed (Figs. 2 and 3).

Tests on irradiated paper

In order to evaluate the degradation of paper irradiation doses of 25 kGy and 50 kGy were used, much higher than those necessary to reduce bioburden. The reasons were to evaluate the cumulative effect of successive treatments, to show that three is no need to achieve sterilization level in any archive treatment and to validate the testing methods to a range where the results are less affected by the sample uncertainty. After irradiation, several types of tests were performed: mechanical, EPR, colorimetric, thermogravimetric TGA-DTG and DSC.

Two different types of paper, one of high quality printing paper and the other of low quality recycled paper, were irradiated at the two different doses mentioned above. The specific weight of the high quality

Table 1. Mechanical tests on paper

Tensile test 	Determination of: – breaking force – tensile strain (elongation) – tensile stress – flow limit	ISO 3781 (wet paper) ISO 1924 (dry paper) ISO 12625-4 (sanitary paper)
Tear test 	Determination of: – tear threshold – average tear force – tear stress	ISO 1974 (paper) ISO 11897 (tear growth test)
Penetration test 	Determination of puncture resistance by measuring: – minimal penetration force – penetration stress – strain before puncture	ISO 3036 (paper, card boxes)

Tensile test results for high quality paper			
$F_{break}(N)$	42.87	36.63	35.49
Prop. loss	100%	85.44%	82.79%
Dose (kGy)	0	25	50

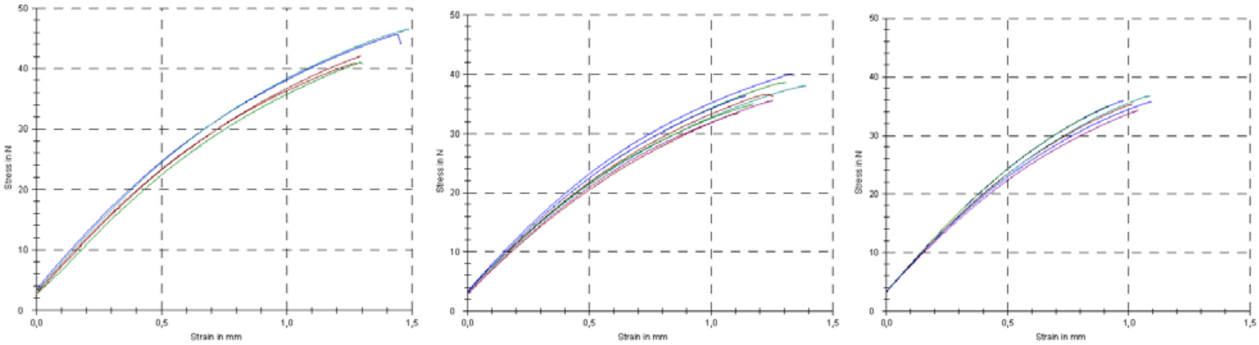


Fig. 4. Tensile test for high quality paper at 0, 25 and 50 kGy.

Tensile test results for low quality paper			
$F_{break}(N)$	8.63	8.32	7.83
Prop. loss	100%	96.41%	90.73%
Dose (kGy)	0	25	50

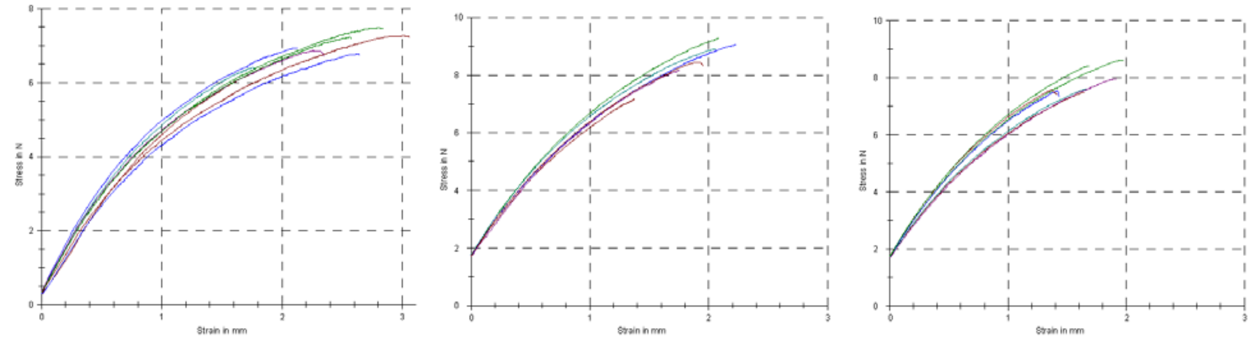


Fig. 5. Tensile test for low quality paper at 0, 25 and 50 kGy.

printing paper was 80 g/m^2 and of the low quality paper (newspaper) 60 g/m^2.

Mechanical tests

10 samples were taken for each type of test/material/dose, obtaining 18 sets of samples. These sets of samples, after destructive mechanical tests, were used for the other types of tests. Three main types of mechanical tests were used, as shown in Table 1.

Before performing tensile test, six sets of samples (each containing 10 pieces) were obtained from both types of high and low quality paper. Samples were cut according to ISO 3167 type 1A with a press cutting device. After conditioning at 23°C and 50% RH, the samples were tested with a universal testing machine Zwick/Roell Z005. For best results testing speed was established at 10 mm/min. Data acquisition was made with testXpert V12.0 firm software (Figs. 4 and 5).

For tear test also a 6 × 10 set of samples was cut at dimensions required by ISO 8067. Conditioning, testing and data acquisition were identically with tensile tests (Figs. 6 and 7).

In the literature concerning paper testing there is a relationship between penetration (puncture) test and folding endurance [4]. Penetration test require less sample material and is performed several times quicker than folding endurance test.

Square samples 110 × 110 mm were cut and tested according to ISO 3036. Conditioning, testing and data acquisition were identically with previous tests (Figs. 8 and 9).

All mechanical tests demonstrate acceptable loss of properties in the case of 25 kGy irradiation dose and significant changes in paper resistance at a 50 kGy dose. Even if high quality paper is more resistant than low quality paper in absolute values, it is important to notice that low quality paper has a percent loss of properties smaller than high quality paper due to recycling process. This fact is more obvious after EPR test, which showed an important quantity of free radicals in non-irradiated samples of low quality paper compared with almost no presence of free radicals in non-irradiated high quality paper (Fig. 10).

Further studies concerning archive irradiation will cover the 2–12 kGy domain and we expect to obtain results that will satisfy restaurateur's requests for irradiation treatment of historical papers.

EPR tests

Samples of high quality paper (printing paper) and low quality paper (newspaper) were analysed by EPR spectra in order to establish the level of free radicals in irra-

Tear test results for high quality paper			
$F_{av}(N)$	0.74	0.64	0.52
Prop. loss	100%	86.49%	70.27%
Dose (kGy)	0	25	50

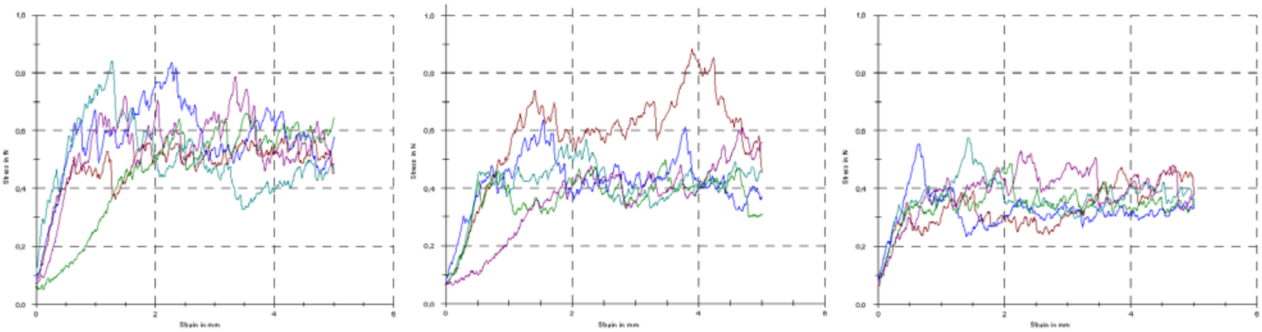


Fig. 6. Tear test for high quality paper at 0, 25 and 50 kGy.

Tear test results for low quality paper			
$F_{av}(N)$	0.33	0.25	0.22
Prop. loss	100%	75.75%	66.67%
Dose (kGy)	0	25	50

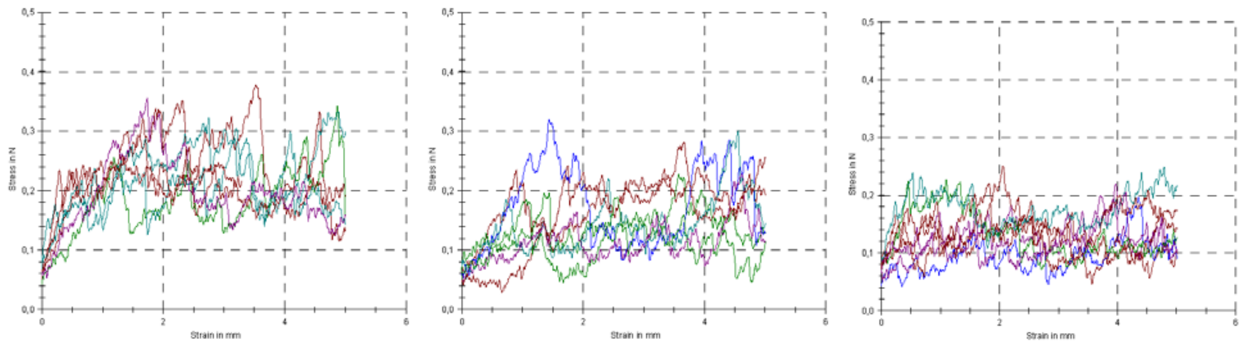


Fig. 7. Tear test for low quality paper at 0, 25 and 50 kGy.

diated and non-irradiated samples. All the EPR samples were obtained from mechanically tested samples.

One of the paper's characteristics is its content of cellulose free radicals. A single signal C ($g_{symm} = 2.004$) could be observed in the EPR spectra of non-irradiated paper. The intensity of this signal depends on the quality of the paper (Table 2 and Fig. 10).

As previous mechanical tests have shown, the initial presence of free radicals in newspaper is the main factor responsible for lower mechanical properties than in printing paper. The presence of free radicals in newspaper is related to the recycling process.

In the case of irradiated paper, the intensity of the signal C becomes usually greater and, in addition, a

Penetration test results for high quality paper			
F_{break} (N)	23.68	19.74	16.54
Prop. loss	100%	83.36%	69.85%
Dose (kGy)	0	25	50

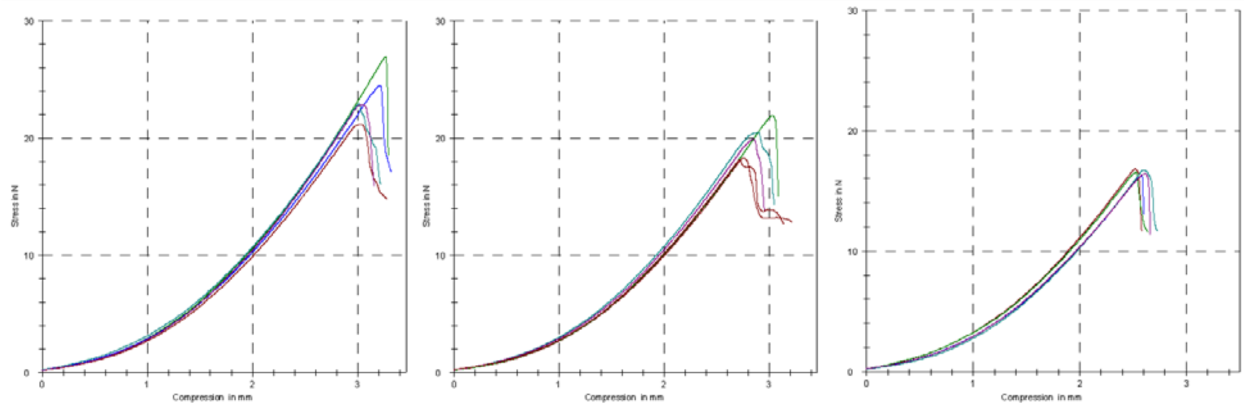


Fig. 8. Penetration test for high quality paper at 0, 25 and 50 kGy.

Penetration test results for low quality paper			
F_{break} (N)	8.23	7.92	7.04
Prop. loss	100%	96.23%	85.54%
Dose (kGy)	0	25	50

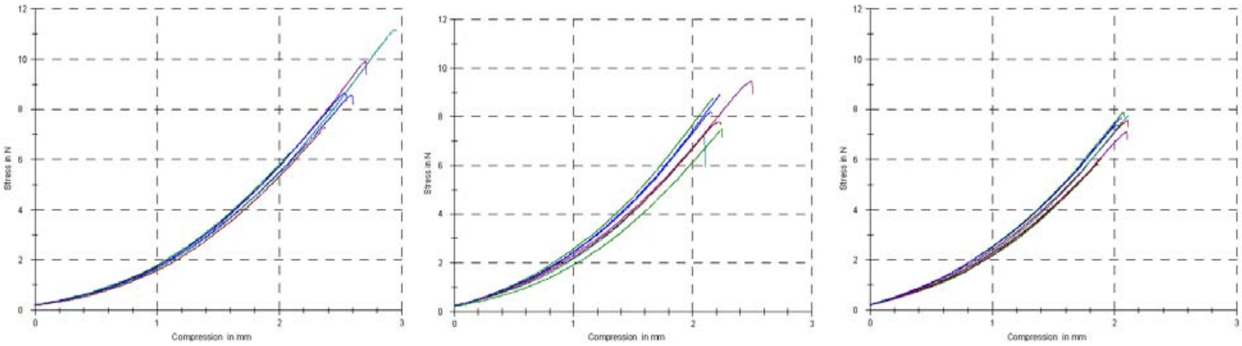


Fig. 9. Penetration test for low quality paper at 0, 25 and 50 kGy.

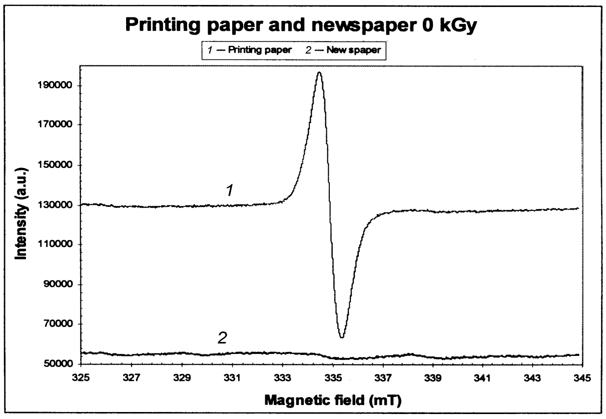


Fig. 10. Non-irradiated printing paper and newspaper.

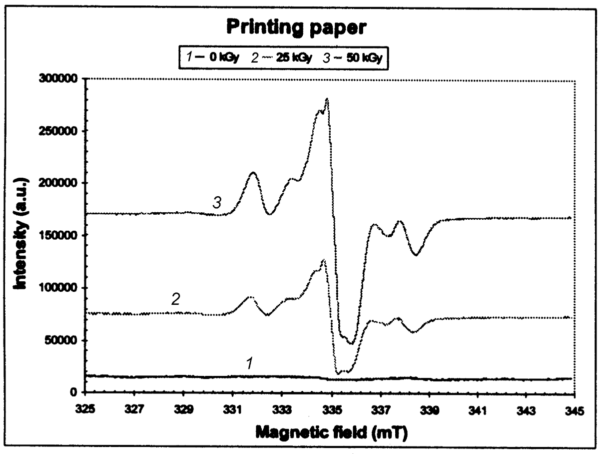


Fig. 11. Printing paper irradiated to dose 0, 25 and 50 kGy.

pair of lines occurs to the left (at lower field) and right (at higher field) of the central signal (Figs. 11 and 12). This pair of lines is due to cellulose free radicals formed by the ionizing radiation. The spacing of this radiation-induced signal pair is about 6.05 mT and is symptomatic of radiation treatment having taken place.

In some types of paper, broad lines of low intensity due to paramagnetic Mn^{2+} ions are observed in addition to the signals mentioned. However, their position in the magnetic field is different, and the spacing between two manganese lines being about 9.0 mT differs from the spacing of the irradiation specific signals of cellulose.

Colorimetric tests

The reflectance spectrophotometer used for colour measurement of copy paper samples was Miniscan XE Plus, Hunter Associates Laboratory with a $d/8°$ geometry of measurement, 400–700 nm spectral range and 10 nm spectral resolution, 0–150% reflectance range, 4 mm beam diameter. The combination illuminant/standard observer was $D_{65}/10°$.

Results are reported in CIE $L^*a^*b^*$ colour space together with total colour differences between non-irradiated and irradiated samples computed in two ways: dE^* and dE CMC with a lightness to chroma ratio of 2:1 (Table 3). Rectangular tolerances (i.e. limits within a

Table 2. Intensities of signal C for printing paper and newspaper

Sample	Intensity (a.u.)
Printing paper 0 kGy	3840
Printing paper 25 kGy	110,080
Printing paper 50 kGy	234,240
Newspaper 0 kGy	133,376
Newspaper 25 kGy	155,712
Newspaper 50 kGy	231,616

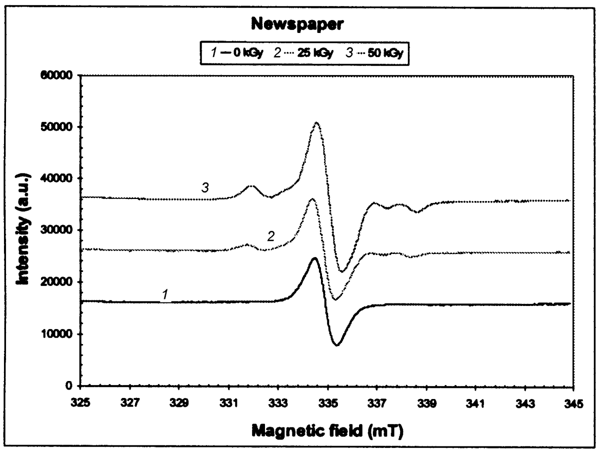


Fig. 12. Newspaper irradiated to dose 0, 25 and 50 kGy.

Table 3. Colour measurements – copy paper samples

Reference (non-irradiated)			25 kGy					50 kGy				
L^* (± T)	a^* (± T)	b^* (± T)	ΔL^*	Δa^*	Δb^*	ΔE^*	ΔE_{CMC}	ΔL^*	Δa^*	Δb^*	ΔE^*	ΔE_{CMC}
94.56 (±2.18)	2.42 (±0.78)	–11.64 (±1.28)	–0.13	–0.58	**2.72**	2.8	**2.15**	–0.04	**–1.02**	**4.87**	4.98	**3.84**

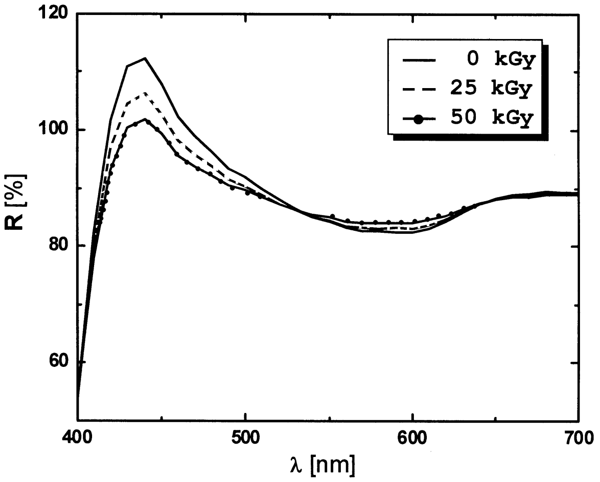


Fig. 13. Reflectance spectra of non-irradiated and irradiated copy paper samples.

normal observer shall not perceive any colour difference between two samples) are computed on dE CMC; values that are out of tolerance interval are showed in the bold font. One can see the yellow/blue value, b^* is the most sensitive to gamma irradiation, irradiated samples being less blue in comparison with the non-irradiated reference. Regarding red/green value, a^*, a small decrease in respect with increasing absorbed dose can be observed. Variations in lightness, L^*, are negligible. Total colour differences are small (i.e. $dE^* < 5$ CIELAB units) but observable, because dE CMC values are greater than one unit for both absorbed doses.

Reflectance spectra of non-irradiated and irradiated samples are given in Fig. 13. Although the absorbed doses used in recent experiments are much higher than those used in decontamination treatment, the changes in the reflectance factors are significant only in the blue region of the visible spectrum, around 450 nm. For the human eye, the colour change at 25 kGy was hard to observe but it was obvious at 50 kGy.

Termogravimetry tests

Thermal degradation of cellulose was investigated by thermogravimetry (TG) and dynamic scanning calorimetry (DSC). Thermal degradation of cellulose under inert atmosphere produces smaller molecules, mainly monomer components of macromolecular structure and is accompanied by endothermic peaks in the DSC signal. In the presence of oxygen, organic materials are oxidized and eventually burned with exothermic peaks in the DSC curve (Fig. 15).

The TG and DSC curves recorded under inert and oxidative atmosphere can be used for correlations with structural, physical and mechanical property changes in on investigated materials regarding the composition and degree of structural degradation, both at molecular and macro scales [2]. In Fig. 15 are shown the DTG (time derivative of TG signal) and DTA curves (differential thermal analysis, without temperature or specific heat calibration) for high (printing paper) and low (newspaper) quality papers. It can be observed a higher thermal stability of high quality paper compared with the low quality one. This result can also be correlated with a higher content of non-organic fillers in a high quality paper (Fig. 14).

The degradation of cellulose macromolecular structure due to ionizing radiation treatment at high--absorbed doses (25–50 kGy) can be seen in the DTG curves with a decrease in the decomposition tempera-

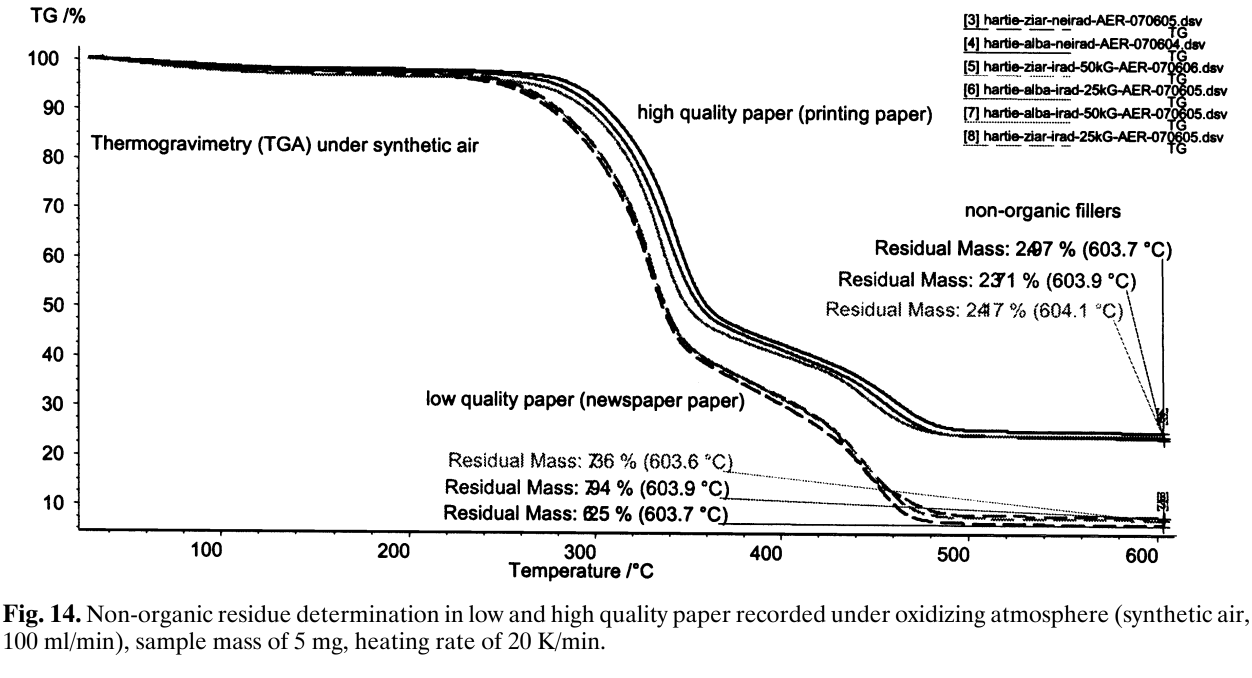


Fig. 14. Non-organic residue determination in low and high quality paper recorded under oxidizing atmosphere (synthetic air, 100 ml/min), sample mass of 5 mg, heating rate of 20 K/min.

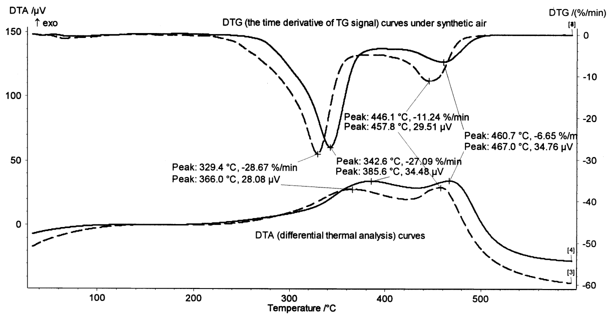


Fig. 15. DTG and DTA curves of low quality paper (interrupted line) and high quality paper (straight line) under oxidizing atmosphere (synthetic air).

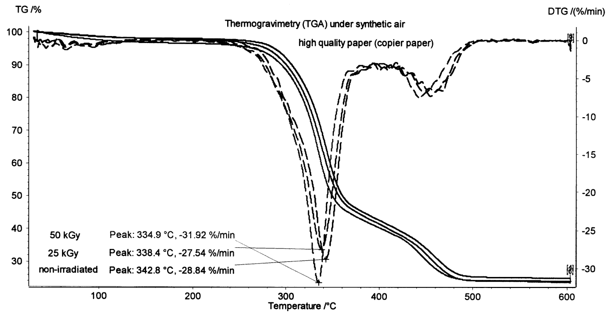


Fig. 16. TGA and DTG curves of high quality paper (copier paper) irradiated at 25 and 50 kGy.

tures under oxidizing atmosphere (Fig. 16). The investigation of thermal stability of paper will complete the physical properties assessed in the process of qualification for radiation treatment.

By coupling the TGA with structural detectors like FT-IR, the chemical classes of desorbed compounds or pyrolysis products formed by thermal decomposition. The chemical classes of volatile organic compounds evolved from the sample can be associated with mass loss steps in the TG curve and can be used as a fingerprint for the investigated material. Whenever necessary, controlled sampling from evolved gases can be made through a transfer line to a GC/MS (gas chromatograph coupled with a mass spectrometer) system for chromatographic separation of individual compounds and structural prediction by comparison of experimental mass spectra with NIST 2005 library.

Conclusions

– Irradiation treatment of archives with ^{60}Co gamma rays is intended to reduce the level of biological contamination to normal conditions required for archives and also to reduce to a minimum the irradiation effects over archive papers.
– Experiments on paper samples at high doses (25 and 50 kGy) were done in order to overestimate paper degradation in case of repeated treatments and also to validate the further tests at lower doses between 2 and 12 kGy.
– In case of fragile historic paper, much lower doses are requested in order to minimize irradiation effects.
– The correlation between different types of tests was established, showing a need for interdisciplinary approach in studies concerning paper irradiation.
– Irradiation treatment of archives requires low operation time, low level of handwork, less qualified personnel, no consumption of expensive chemical compounds and no need for toxic compounds evacuation systems.
– A special care must be taken in public acceptance activities; there are some basic facts which should be very well explained in order to avoid treatment misunderstanding. Irradiation treatment does not induce any radioactivity or toxic compounds inside treated materials. There are no toxic compounds before, during and after treatment which can lead to work accidents or professional illness.

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