Disinfestation by ionizing radiation: A chance for future of archives

Physical, chemical and microbiological tests for irradiation of paper

Ioan Valentin Moise¹, Marian Virgolici¹, Mihaela Manea¹, Mihalis Cutrubinis¹, Daniel Negut¹, Rodica Maria Georgescu¹, Mioara Alexandru¹, Laura Trandafir¹, Florina Lucica Zorila¹, Mihai Constantin¹, Ioana Stancurescu, ¹–⁵ Catalina Mihaela Talasman², Maria Haiducu³, Elena Ilie⁴

¹ IFIN-HH – “Horia Hulubei” National Institute for Physics an Nuclear Engineering
² CEPROHART SA – Pulp and Paper Research Institute
³ – “Alexandru Darabonţ” National Institute for Work Safety
⁴ – Braila Museum
⁵ – University of Bucharest, Physical Chemistry Department
Mechanical properties vs. TGA/DSC

Materials:

- Xerox Business, 80g/m², 0.1mm;
- Ceprohart, 80g/m², 0.1mm;
- Whatman (nr. 42, ICHR)
- Hardwood and softwood pulp (chemically bleached)
  - Coated paper SC GHIMBAV SA (1996)
  - Neutral sized copy paper Austria (2006)
  - Pronosport paper 70 g/m² (1996)
  - 1A type paper 60 g/m² (1996)

- Book printed in 1923 in France (private collection)
- Official Journal of RSR (newspaper) – 1968 (IFIN-HH archive)
- Book printed in 1894 (Perspessicius Collection – Braila Musem)
Mechanical properties vs. TGA/DSC

- Methods:

  IFIN-HH: Universal testing machine Zwick/Roell Z005, 5kN cell; testing speed: 10 mm/min
  TENSILE TEST: Samples according to ISO 3167 type 1A and ISO 37 type 1; TEAR TEST: Samples according to ISO 8067;
  PUNCTURE: ISO 3036:1975 Conditioning: 24 hours at 23°C and 50% rH;

  CEPROHART SA: Universal testing machine INSTRON 4411, 5 kN force cell, test speed: 20 mm/min
  — accredited pulp and paper testing laboratory (ISO 536, ISO 534, ISO 1924/2, EN 21974, ISO 2471, STAS 4748, ISO 2470, ISO 5627, ISO 2758, EN 20535, ISO 5626)

  Netzsch STA 409 PC
  Luxx Simultaneous Thermal Analyzer - TG/DSC-S sample carrier, inert (nitrogen, 40-80 ml/min) and oxidative (sintetic air, 40 ml/min) dynamic atmosphere at 2,5,10,20 K/min.
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RER/8/015

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Mechanical properties vs. TGA/DSC

F_{\text{break, MD}} / N

DSC Area / J/g

F_{\text{break, CD}} / N

Dose / kGy

Rank Xerox
Mechanical properties vs. TGA/DSC

F_{break, MD} / N

\[ y = -0.2005x + 83.974 \]
\[ R^2 = 0.9954 \]

DSC Area, J/g

\[ y = -0.0282x + 42 \]
\[ R^2 = 0.9413 \]

F_{break, CD} / N

\[ y = -0.0285x + 27.117 \]
\[ R^2 = 0.9875 \]

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Mechanical properties vs. TGA/DSC

- **$F_{\text{break, MD}}$ / N**
  - $y = -0.8144x + 88.062$
  - $R^2 = 0.9653$

- **$F_{\text{break, CD}}$ / N**
  - $y = -0.1876x + 25.683$
  - $R^2 = 0.6254$

- **DSC Area, J/g**
  - $y = -0.1429x + 45.125$
  - $R^2 = 0.8308$

Rank Xerox

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Mechanical properties vs. TGA/DSC

(Adamo, 2001: no significant changes below 5 kGy)

Rank Xerox

Whatman

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# Mechanical properties - Summary

<table>
<thead>
<tr>
<th>Property</th>
<th>Paper</th>
<th>~ % change*</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_{\text{break}}$ &amp; $L_{\text{break}}$, MD/CD</td>
<td>Copier paper</td>
<td>- 10% / -15%</td>
</tr>
<tr>
<td></td>
<td>Whatman paper</td>
<td>+5% / +10%</td>
</tr>
<tr>
<td>Folding endurance, MD/CD</td>
<td>Rank XEROX Copier paper</td>
<td>- 40% / -15%</td>
</tr>
<tr>
<td></td>
<td>CEPROHART Copier paper</td>
<td>- 20%</td>
</tr>
<tr>
<td></td>
<td>Whatman</td>
<td>- 6%</td>
</tr>
<tr>
<td>Tearing resistance</td>
<td>Rank XEROX Copier paper</td>
<td>- 10%</td>
</tr>
<tr>
<td></td>
<td>CEPROHART Copier paper</td>
<td>- 20%</td>
</tr>
<tr>
<td></td>
<td>Whatman</td>
<td>- 6%</td>
</tr>
<tr>
<td>Burst strength</td>
<td>Rank XEROX Copier paper</td>
<td>- 5%</td>
</tr>
<tr>
<td></td>
<td>CEPROHART Copier paper</td>
<td>- 3%</td>
</tr>
<tr>
<td></td>
<td>Whatman</td>
<td>- 5%</td>
</tr>
<tr>
<td>Puncture resistance</td>
<td>Rank XEROX Copier paper</td>
<td>- 5%</td>
</tr>
<tr>
<td></td>
<td>CEPROHART Copier paper</td>
<td>- 3%</td>
</tr>
<tr>
<td></td>
<td>Whatman</td>
<td>-10%</td>
</tr>
<tr>
<td>Cobb$_{60}$ size test</td>
<td>Hartie copiator XEROX</td>
<td>+ 15% / +5%</td>
</tr>
<tr>
<td></td>
<td>Hartie Whatman - ICHR</td>
<td>- 7%</td>
</tr>
</tbody>
</table>

* Change from nonirradiated for irradiation in the range of 6-13kGy
Folding endurance

XEROX copier paper

Whatman paper

BORSR'68

XEROX copier paper

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Colour

**Instrument:** Miniscan XE Plus, Hunter Lab.

**Geometry:** diffuse / 8° (sphere); specular component included

**View diameter:** 4 mm

**Illuminant / standard observer:** $D_65 / 10°$
10
98
96
94
92
90
88
86
84
0 2 4 6 8 10 20 40 60 80 100
L* [CIELAB units]
Dose [kGy]

10
5
0
-5
-10
0 20 40 60 80 100
b* [CIELAB units]
Dose [kGy]

10
2
1
0
0 20 40 60 80 100
a* [CIELAB units]
Dose [kGy]

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copier paper (l.q.)
copier paper (l.q.), aged
copier paper (h.q.)
Whatman paper
• No significant changes of lightness, $L^*$, except for aged low quality copier paper
• Red/green value, $a^*$, decreases (less red) with absorbed dose for low and high quality copier paper
• All the samples are less blue / more yellow after irradiation ($b^*$ value increases with absorbed dose)
• Total colour difference induced by ageing is higher than that induced by irradiation at 100 kGy
• Both 457-nm Brightness and WI E313 indexes decreased with the absorbed dose; aged samples show the most important reduction in indexes values
Trapped free radicals

Instrument: X band ESR spectrometer Magnettech MiniScope MS 200
Measurement settings: B0 field 3350 Gauss, Sweep 200 Gauss, Modulation 5 Gauss, MW attenuation 21 Db
Reference: EN 1787 / Foodstuffs – Detection of irradiated food containing cellulose by ESR spectroscopy
Trapped free radicals

Intensities after irradiation

- Leafy
- Resinous
- Printing paper
- Cotton wool
- Whatman 42

Paper Whatman 42

- 5 kGy
- 10 kGy
- 25 kGy
- 50 kGy
- 100 kGy

Dose (kGy)

Measurement after irradiation (days)
Trapped free radicals

![Graph showing the decay of trapped free radicals over time after irradiation. The graph plots the number of trapped free radicals (L_{\text{break,MD m}}) against time (0 to 25 months) with different markers for 4 months and 1 month after irradiation. The x-axis represents time in months, and the y-axis represents the number of trapped free radicals. The graph shows a decreasing trend in trapped free radicals over time.]
Dose rate effects

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FT-IR and FT-Raman

FT-IR spectrometer Vertex 70 class, Bruker Optics:
- Raman module (RAM II) and probe (RAMPROBE)
- Probe for non-contact and non-destructive FT-IR
FT-IR and FT-Raman

Hardwood and softwood pulp

CF:
- 1372–1375 cm\(^{-1}\) (C-H)
- 2900 cm\(^{-1}\) (C-H stretch)

HB:
- 1429 cm\(^{-1}\) (CH\(_2\) scissoring)
- 898 cm\(^{-1}\) (H bonded)
FT-IR and FT-Raman

Hardwood and softwood pulp

CF :
1372–1375 cm\(^{-1}\) (C-H)
2900 cm\(^{-1}\) (C-H stretch)

HB :
1429 cm\(^{-1}\) (CH\(_2\) scissoring)
898 cm\(^{-1}\) (H bonded)
FT-IR and FT-Raman

CaCO$_3$: 1445.51 cm$^{-1}$, 874.33 cm$^{-1}$ and 712.82 cm$^{-1}$
CaSO$_4$: 1100-1020 cm$^{-1}$
H$_2$O (adsorbed): 3446-3467 cm$^{-1}$

FT-IR spectra for pyrolised (600°C) paper
FT-IR and FT-Raman
ORIGENES ADAMATI VOL I (XVI century)
FT-IR

CEPROHART copy paper
0 kGy
100 kGy
FT-IR

ORIGENES ADAMATI VOL I (XVI century) – leather cover
TD-GC-MS & Py-GC-MS

DTU „UNITY” (Markes) → GC 6890N (Agilent) → 5975 inert MSD (Agilent)
A - Volatile Radiolysis Products qualitative identification
TIC: High quality copier paper irradiated at 100kGy in PET canisters filled with air [1]

Identification made by means of calibration standards and retention index calibration combined with mass spectra matching in NIST 2005 GC/MS library
The VCs concentration increases with the radiation absorbed dose in a non-linear manner. A part of the VCs formed after irradiation can be further found also after accelerated ageing tests, which may propose them as cellulose structure degradation markers. In this case their absorbed dose concentration dependence follows almost a linear trend. Although the concentration level of the monitored VCs ranges up to some **hundreds of ppm at higher doses than 50 kGy**, at usual doses used for archives conservation the order concentration level ranges up to **tens of ppm** and further quantitative measurements can be made to prove safe levels of possible toxic VCs. There is known that large quantities of irradiated paper have a certain smell. VOC analysis at the doses on interest for the irradiation treatment of paper documents may not supply reliable results (there are close to the limit of detection) but the studies at higher doses will eliminate one of the fears about the toxicity of the treatment. The following studies will focus on ageing tests on irradiated paper to make further correlations between ageing markers concentration and the end of life criteria established by color and mechanical tests.
Py-GC-MS

TIC: \data.ms

Abundance

Time (min)

Whatman
# Py-GC-MS

<table>
<thead>
<tr>
<th>$T_r$ (min)</th>
<th>Target</th>
<th>Conc. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.28</td>
<td>Formaldehidă</td>
<td>1</td>
</tr>
<tr>
<td>1.68</td>
<td>Hidroxi-acetaldehidă</td>
<td>6</td>
</tr>
<tr>
<td>1.80</td>
<td>2-metil-furan</td>
<td>1</td>
</tr>
<tr>
<td>1.89</td>
<td>Acid acetic</td>
<td>1</td>
</tr>
<tr>
<td>2.23</td>
<td>1-hidroxi-2-propanonă</td>
<td>1</td>
</tr>
<tr>
<td>2.68</td>
<td>2,5-dimetil-furan</td>
<td>0</td>
</tr>
<tr>
<td>5.80</td>
<td>Furfural</td>
<td>6</td>
</tr>
<tr>
<td>6.68</td>
<td>2-Furanmetanol</td>
<td>0</td>
</tr>
<tr>
<td>6.93</td>
<td>2-propil-furan</td>
<td>1</td>
</tr>
<tr>
<td>8.57</td>
<td>1-(2-furanil)-etanonă</td>
<td>0</td>
</tr>
<tr>
<td>8.78</td>
<td>2(SH)-Furanonă</td>
<td>1</td>
</tr>
<tr>
<td>9.30</td>
<td>1,2-Ciclopentandionă</td>
<td>1</td>
</tr>
<tr>
<td>9.84</td>
<td>3-metil-2,5-furandionă</td>
<td>0</td>
</tr>
<tr>
<td>10.49</td>
<td>5-metil-2-furancarboxaldehidă</td>
<td>1</td>
</tr>
<tr>
<td>12.93</td>
<td>3-metil-1,2-ciclopentandionă</td>
<td>1</td>
</tr>
<tr>
<td>14.41</td>
<td>Esterul metilic al acidului 3-furancarboxilic</td>
<td>0</td>
</tr>
<tr>
<td>14.75</td>
<td>Esterul metilic al acidului 3-furancarboxilic</td>
<td>2</td>
</tr>
<tr>
<td>15.81</td>
<td>Levoglucosenonă</td>
<td>13</td>
</tr>
<tr>
<td>15.86</td>
<td>Maltol</td>
<td>0</td>
</tr>
<tr>
<td>16.91</td>
<td>2,3-dihidro-3,5-dihidroxi-6-metil-4H-Piran-4-onă</td>
<td>2</td>
</tr>
<tr>
<td>19.24</td>
<td>1,4:3,6-Dianhidro-à-d-glucopiranoză</td>
<td>6</td>
</tr>
<tr>
<td>20.20</td>
<td>5-(hidroxielmetil)-2-furancarboxaldehidă</td>
<td>2</td>
</tr>
<tr>
<td>42.40</td>
<td>1,6-Anhidro-à-D-glucopiranoză (levoglucosan)</td>
<td>6</td>
</tr>
<tr>
<td>43.18</td>
<td>1,6-Anhidro-à-d-galactofuranoză</td>
<td>3</td>
</tr>
</tbody>
</table>

→ Degradation markers
Microbiological tests
Radiation resistance

\[ y = 623.92e^{-3.8668x} \]

\[ D_{1\alpha} = 0.60 \]
# Bioburden

<table>
<thead>
<tr>
<th>Paper</th>
<th>CFU/g</th>
<th>CFU/A4</th>
<th>CFU/50xA4</th>
<th>CFU/cm² (surface swab test)</th>
<th>CFU/A4 (surface swab test)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Journal 1968</td>
<td>25</td>
<td>94.5</td>
<td>4725</td>
<td>0.04</td>
<td>25.2</td>
</tr>
<tr>
<td>Book 1992</td>
<td>45</td>
<td>170.1</td>
<td>8505</td>
<td>0.04</td>
<td>25.2</td>
</tr>
<tr>
<td>File cover 1977</td>
<td>235</td>
<td>2961</td>
<td>148050</td>
<td>0.14</td>
<td>88.2</td>
</tr>
<tr>
<td>Notebook 1981</td>
<td>115</td>
<td>579.6</td>
<td>28980</td>
<td>0.04</td>
<td>25.2</td>
</tr>
<tr>
<td>Form 1983 (1)</td>
<td>20</td>
<td>100.8</td>
<td>5040</td>
<td>0.12</td>
<td>75.6</td>
</tr>
<tr>
<td>Form 1983 (1)</td>
<td>60</td>
<td>302.4</td>
<td>15120</td>
<td>0.04</td>
<td>25.2</td>
</tr>
<tr>
<td>Newsletter 1983</td>
<td>140</td>
<td>705.6</td>
<td>35280</td>
<td>0.06</td>
<td>37.8</td>
</tr>
<tr>
<td>Book 1894 (MzBr)</td>
<td>5</td>
<td>31.5</td>
<td>1575</td>
<td>0.04</td>
<td>25.2</td>
</tr>
<tr>
<td>Book 1952 (INCDPM)</td>
<td>650</td>
<td>4095</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Validation techniques
(work in progress)

Medical devices sterilization (ISO 11137):

Method 1:
- Average bioburden (3x10 items)
- SAL 10^{-2} verification dose (from table) → irradiation of 100 samples
- Number of positives from 100 sterility tests (according to standard) →
  
  Sterilization dose (from table) ≡ SAL 10^{-6}

Method 2:
- Incremental dose irradiation + sterility test (3x9x20 items)
- Number of positives (according to standard) → SAL 10^{-2} verification dose →
  
  irradiation of 100 samples
- Number of positives from 100 sterility tests (according to standard) →
  
  Sterilization dose ≡ SAL 10^{-6}

Method 2:
- Average bioburden (3x10 items) < 1000
- SAL 10^{-1} verification dose (from table) → irradiation of 10 samples

  Number of positives from 10 sterility tests (according to standard) →
  
  25 kGy ≡ SAL 10^{-6}
Thank you for your attention!