Disinfestation by ionizing radiation: A chance for future of archives

Physical, chemical and microbiological tests for irradiation of paper

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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 Museum)
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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Mechanical properties vs. TGA/DSC

F_{break, MD} / N

DSC Area / J/g

F_{break, CD} / N

Dose / kGy

Rank Xerox
Mechanical properties vs. TGA/DSC

- For $F_{\text{break, MD}}$, the linear relationship is:
  \[ y = -0.2005x + 83.974 \]
  \[ R^2 = 0.9954 \]

- For $DSC$ Area, the linear relationship is:
  \[ y = -0.0282x + 42 \]
  \[ R^2 = 0.9413 \]

- For $F_{\text{break, CD}}$, the linear relationship is:
  \[ y = -0.0285x + 27.117 \]
  \[ R^2 = 0.9875 \]

Rank Xerox

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Mechanical properties vs. TGA/DSC

\[ y = -0.1429x + 45.125 \]
\[ R^2 = 0.8308 \]

\[ y = -0.8144x + 88.062 \]
\[ R^2 = 0.9653 \]

\[ y = -0.1876x + 25.683 \]
\[ R^2 = 0.6254 \]

Rank Xerox

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Mechanical properties vs. TGA/DSC

Rank Xerox

Whatman

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

**Measurement after irradiation (days)**

- 0
- 5
- 10
- 15
- 20
- 25
- 30

**Dose (kGy)**

- 0
- 25
- 50
- 75
- 100

**Intensity (a.u.)**

- 0
- 500
- 1000
- 1500
- 2000
- 2500
- 3000
- 3500
- 4000
Trapped free radicals

![Graph showing the decrease in trapped free radicals over time after irradiation. The x-axis represents time in months after irradiation, ranging from 0 to 25. The y-axis represents the number of trapped free radicals, ranging from 0 to 10,000. Two lines are shown: one for 4 months after irradiation and another for 1 month after irradiation. The 4-month line shows a more significant decrease compared to the 1-month line.]

Rank Xerox
Dose rate effects

4 months after irradiation, 21 kGy/h
1 month after irradiation, 6 kGy/h
1 month after irradiation, 0.5 kGy/h

Rank Xerox
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

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

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

\[ \text{CaCO}_3: 1445.51 \text{ cm}^{-1}, \ 874.33 \text{ cm}^{-1} \text{ and } 712.82 \text{ cm}^{-1} \]

\[ \text{CaSO}_4: 1100-1020 \text{ cm}^{-1} \]

\[ \text{H}_2\text{O (adsorbed): } 3446-3467\text{ cm}^{-1} \]

FT-IR spectra for pyrolised (600°C) paper

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FT-IR and FT-Raman
ORIGENES ADAMATI VOL I (XVI century)
FT-IR

CEPROHART copy paper
0 kGy
100 kGy

Wavenumber cm⁻¹

Absorbance Units
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)
TD-GC-MS

GC/MS chromatogram, dynamic headspace - thermal desorption of air samples from irradiated canisters (A). 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:

Abundance

Time (min)

Whatman

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## 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(5H)-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-furandionä</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-ciclopentandionä</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>Levoglucosenonà</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-(hidroximetil)-2-furancarboxaldehidă</td>
<td>2</td>
</tr>
<tr>
<td>42.40</td>
<td>1,6-Anhidro-à-D-glucopiranoz (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

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

\[ D_{10} = 0.60 \]
# 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) $\rightarrow$ irradiation of 100 samples
- Number of positives from 100 sterility tests (according to standard) $\rightarrow$
  Sterilization dose (from table) $\equiv$ SAL $10^{-6}$

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

**Method 2:**
- Average bioburden (3x10 items) $< 1000$
- SAL $10^{-1}$ verification dose (from table) $\rightarrow$ irradiation of 10 samples
  Number of positives from 10 sterility tests (according to standard) $\rightarrow$
  25 kGy $\equiv$ SAL $10^{-6}$
Thank you for your attention!