Parameters influencing oxygen ingress, test procedures, shelf life extrapolation for beer, fruit juice and wine packed in PET bottles

Performance BiB General Meeting,
La Rochelle,
France 27 Nov. 2006
Sidel Group is part of the Tetra Laval Group

A private, industrial and financially very stable ownership

- **Tetra Pak**: Develops, manufactures and markets food processing and packaging systems
  - Processing
  - Carton Packaging
  - Dairy, cheese, beverages

- **DeLaval**: Drives progress in milk production
  - Systems for farmers
  - Aftermarket
  - Cows, sheep, goats and buffaloes

- **Sidel**: Designs, produces and markets plastic, glass and can packaging solutions for the liquid food industry
  - Equipment
  - Engineering
  - Soft drinks, water, dairy, beer, liquid food, juices

2004 figures:
- 29,500 employees
- 9 billion euros sales
Sidel Group

We offer complete integrated SOLUTIONS for your bottling line for:

- Metal cans,
- Plastic bottles, (HDPE, PP, PET)
- Glass bottles

Sidel Group means:

- 1,100 million euros sales,
- 5,000 people (1,350 outside Europe in 26 countries,
- More than 50 nationalities,
- Worldwide sales & services presence in 184 countries

Sales activities distribution
Africa & Middle East

33%
33%
15%
8%
44%
Asia
Americas
Europe
R&D areas of activity

- **ACTIS™:**
  - Contribution to ACTIS™ 48
  - Plasma process modeling
  - Fundamentals, adhesion, Process…
  - Competition watch on barrier technologies
  - Regulation / Food Contact / Functional barrier

- **Packaging materials:**
  - PET, additives, Polyesters (LACPET, PTN, PEN…)
  - PLA, Bio Materials
  - BO PP
  - Recycling
  - Data base
R&D areas of activity

- **Laboratory:**
  
  ➤ Package barrier laboratory:
  1. OTR (Mocon, Systech),
  2. CO2 retention (FTIR, Zahn...),
  3. Light: Perkin Elmer spectrometer

  ➤ Package testing
  1. Pasteurization
  2. Thermal stability
  3. Carbonation....

  ➤ Material testing
  1. Moisture pick-up
  2. AA
  3. Light aging....

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Spectra UV/VIS in clear, amber & green bottles

- green - ep = 0.51mm
- clear - ep = 0.54mm
- amber - ep = 0.40mm
R&D Laboratory equipments for $O_2TR$ evaluation

- 23 Ox-tran® 2/20 Mocon® H & S types
  - 46 measurement cells

- 1 Systech 8700 (prototype)
  - 11 measurement cells

- 1 Presens
  - Non destructive dissolved O2

- 1 package analyzer Orbisphere
  - Dissolved and head space $O_2$ measurement

- Vitamin C analysis
  - Indicator : Indophenol

- Techno watch for new devices
TWO MAIN DANGERS FOR A SENSITIVE BEVERAGE

The degradation of sensitive beverages could be microbiological and organoleptic. 2 dangers implicated in the degradation of a sensitive beverage:

- Oxidation is responsible for the breakdown and loss of vitamin C and browning of the product
- Necessity of extreme care to eliminate oxygen from the product and packaging

**Solutions:**
- Packaging
  - PET with additional oxygen barrier or oxygen scavenger
  - Closures with oxygen scavenger
- Filling system
  - Long filling tubes (to avoid foaming)
  - By injecting of inert gas (nitrogen)

- Bacteria, yeasts, fungal spores
- Can proliferate and spoil the taste, appearances and smell of the beverage

**Solutions:**
- Thermal treatment
- Storage conditions
  - Before filling
  - Of finished product (heat and/or long term storage)
MICROBIOLOGICAL SENSITIVITY OF BEVERAGES

Germs able to grow in the beverage:

- Pathogenic germs
- Heat-resistant bacteria
- Heat-labile bacteria
- Mould fungi
- Yeasts

<table>
<thead>
<tr>
<th>CSD</th>
<th>High acid juices, ice-tea</th>
<th>Low acid juices (vegetables)</th>
<th>Tea, tea beverages</th>
<th>Milkmix drinks</th>
<th>UHT milk, soya beverages</th>
</tr>
</thead>
</table>
Parameters influencing $O_2$ Transmission Rate (OTR)

- **Main bottles parameters**
  - surface area/volume Ratio
  - Material type
  - Crystallinity
  - BO rate (Stretching ratio)
  - process temperature
  - material distribution
  - Thickness

- **Environmental conditions**
  - Temperature
  - Relative humidity
# Parameters influencing O$_2$ Transmission Rate (OTR)

- Weight/Volume & Surface area/Volume ratios

<table>
<thead>
<tr>
<th>Volume (V)</th>
<th>l</th>
<th>0.25</th>
<th>0.33</th>
<th>0.5</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight (W)</td>
<td>g</td>
<td>18</td>
<td>20</td>
<td>24</td>
<td>36</td>
<td>52</td>
</tr>
<tr>
<td>Surface (S)</td>
<td>cm$^2$</td>
<td>260</td>
<td>300</td>
<td>400</td>
<td>630</td>
<td>1000</td>
</tr>
<tr>
<td>Ratio W/V</td>
<td>g/l</td>
<td>72</td>
<td>60</td>
<td>48</td>
<td>36</td>
<td>26</td>
</tr>
<tr>
<td>Ratio S/V</td>
<td>cm$^2$/ml</td>
<td>1.04</td>
<td>0.91</td>
<td>0.8</td>
<td>0.63</td>
<td>0.5</td>
</tr>
</tbody>
</table>

- The 0.25l bottle is 2 times more heavy than the 1liter per ml of capacity.
- The 0.25l bottle has a 1.5 times more important surface area than the 1liter per ml of capacity.
Parameters influencing O₂ Transmission Rate (OTR)

PET Packaging weight:

- 70 grs (55 grs PET + 15 grs base cup (PE))
- 46 grs
- 45 grs
- 26 grs

Container typical weight - 1978 / 2002 (Source Sidel)

2 l CSD

1.5 l Water

Source: Sidel
Ox-tran® 2/20 O₂ TR results at 23°C

\[ y = -0.0045x + 0.3278 \]
\[ y = -0.0021x + 0.1604 \]
\[ y = -0.0017x + 0.0915 \]
\[ y = -0.0006x + 0.0482 \]
\[ y = -0.0006x + 0.0458 \]

weight (g)

16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60

O₂ TR (cc/pack/day) Ox-tran 2/20 at 23°C
Parameters influencing $O_2$ Transmission Rate (OTR): Material characteristics

<table>
<thead>
<tr>
<th>Material</th>
<th>CO2</th>
<th>O2</th>
<th>Vapeur H2O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm3/m2/24h 25µ-23°C-0% HR</td>
<td>cm3/m2/24h 25µ-23°C-0% HR</td>
<td>g/m2/24h 25µ-38°C-90% HR</td>
</tr>
<tr>
<td>PAN</td>
<td>30</td>
<td>14</td>
<td>75</td>
</tr>
<tr>
<td>PA6</td>
<td>210</td>
<td>50</td>
<td>190</td>
</tr>
<tr>
<td>PEN</td>
<td>40</td>
<td>16</td>
<td>7</td>
</tr>
<tr>
<td>APET</td>
<td>340</td>
<td>110</td>
<td>50</td>
</tr>
<tr>
<td>OPET</td>
<td>210</td>
<td>62</td>
<td>25</td>
</tr>
<tr>
<td>PVC</td>
<td>420</td>
<td>185</td>
<td>42</td>
</tr>
<tr>
<td>OPVC</td>
<td>250</td>
<td>110</td>
<td>30</td>
</tr>
<tr>
<td>PEBD</td>
<td>38000</td>
<td>8000</td>
<td>15</td>
</tr>
<tr>
<td>PEHD</td>
<td>9700</td>
<td>2300</td>
<td>6</td>
</tr>
<tr>
<td>PP</td>
<td>9700</td>
<td>3000</td>
<td>8</td>
</tr>
<tr>
<td>OPP</td>
<td>6300</td>
<td>1900</td>
<td>4</td>
</tr>
<tr>
<td>PS</td>
<td>30000</td>
<td>5800</td>
<td>150</td>
</tr>
<tr>
<td>PC</td>
<td>21000</td>
<td>3700</td>
<td>170</td>
</tr>
<tr>
<td>EVOH</td>
<td>0.8-3</td>
<td>0.5</td>
<td>40</td>
</tr>
<tr>
<td>PVDC</td>
<td>5</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>NMXD6</td>
<td>12</td>
<td>10</td>
<td>80</td>
</tr>
</tbody>
</table>
Parameters influencing \( \text{O}_2 \) Transmission Rate (OTR): Material characteristics

Oriented and non Oriented PET (films)

![Graph showing permeability vs. crystallinity for oriented and non-oriented PET films. The graph indicates a decrease in permeability as crystallinity increases for both types of PET.]
Parameters influencing $O_2$ Transmission Rate (OTR):
Storage temperature

![Graph showing the relationship between CO2 Permeation Coefficient and Temperature]

- CO2 Permeation Coefficient: cc/mil/100 sq in/day/atm
- Temperature: °C

Storage temperature influences the $O_2$ Transmission Rate (OTR).
## SPECIFICATIONS: impact of filling conditions

<table>
<thead>
<tr>
<th></th>
<th>JUS DE FRUITS et BOISSONS A TENEUR DE JUS DE FRUITS GAZEIFIES</th>
<th>BIERE SANS ALCOOL PANACHE SHANDY COOLER</th>
<th>BIERE</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reprise en O2</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moyenne</td>
<td>&lt;0.5 ppm</td>
<td>&lt;0.05 ppm</td>
<td>&lt;0.05 ppm</td>
</tr>
<tr>
<td>Individuelle</td>
<td>&lt;1 ppm</td>
<td>&lt;0.07 ppm</td>
<td>&lt;0.07 ppm</td>
</tr>
<tr>
<td><strong>O2 dans le col de la bouteille</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moyenne</td>
<td>&lt;2% O2</td>
<td>0.30 ppm</td>
<td>0.12 ppm</td>
</tr>
<tr>
<td>Individuelle</td>
<td>0.60 ppm</td>
<td>0.17 ppm</td>
<td></td>
</tr>
<tr>
<td><strong>Perte en CO2 au soutirage</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moyenne</td>
<td>&lt;0.15 g/l</td>
<td>&lt;0.15 g/l</td>
<td>&lt;0.15 g/l</td>
</tr>
<tr>
<td>Individuelle</td>
<td>&lt;0.3 g/l</td>
<td>&lt;0.3 g/l</td>
<td>&lt;0.3 g/l</td>
</tr>
<tr>
<td><strong>Microbiologie</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Levures</td>
<td>0 germe /100ml</td>
<td>&lt;20 germes /100ml (*)</td>
<td>&lt;20 germes /100ml (*)</td>
</tr>
<tr>
<td>Bacilles</td>
<td>0 germe /100ml</td>
<td>0 germe /100ml</td>
<td>0 germe /100ml</td>
</tr>
<tr>
<td>moisissures</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(*) : 0 germe /100ml
SPECIFICATIONS: Beer application

- **total 02**
- **02 increase through packaging**
- **bottle headspace**
- **02 increase during filling**
- **beer before filling**

X-axis: 0, 0.2, 0.4, 0.6, 0.8, 1, 1.2

Y-axis: Various oxygen levels.
**Juice Shelf life extrapolation from Ox-tran® tests**

<table>
<thead>
<tr>
<th>Capacity (ml)</th>
<th>Weight (g)</th>
<th>ppm/day extrapolated from Ox-tran® measurement at 23°C</th>
<th>Shelf life for 15ppm (days)</th>
<th>Shelf life for 15ppm (months)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>16/17</td>
<td>0,206</td>
<td>73</td>
<td>2,4</td>
</tr>
<tr>
<td>330</td>
<td>18/19</td>
<td>0,154</td>
<td>97</td>
<td>3,2</td>
</tr>
<tr>
<td>1000</td>
<td>37/39</td>
<td>0,117</td>
<td>128</td>
<td>4,2</td>
</tr>
<tr>
<td>1500</td>
<td>47/49</td>
<td>0,106</td>
<td>142</td>
<td>4,7</td>
</tr>
</tbody>
</table>

- **Remarks:**
  - ➡️ evaluation without cap
  - ➡️ always pessimistic compared to real testing
Impact of closure on O2 ingress

Presens / tap water
O₂ ingress control (Presens method)
Storage at 23°C
Real testing

- Quality criteria:
  - Color changes
  - Taste change
  - C Vitamin drop

- Factors
  - $O_2$
    1. Permeation through bottle wall
    2. $O_2$ dissolved on bottle wall
    3. $O_2$ dissolved in the liquid (product des-aeration)
    4. $O_2$ permeation of the cap
    5. $O_2$ head space (Nitrogen flushing)
  - UV Light
  - Temperature
  - Microbiology
  - Process (thermal treatment, filling…)
  - Distribution conditions
Some examples

- Example # 1
  - Orange juice 100% pure
  - Des-aeration at 1ppm + head space N₂ flush to approx. 10%
  - PET bottles 330 ml (Ox-tran® 0.022) & 250ml (Ox-tran® 0.030)
  - 38mm neck & aluminum cap
  - storage at 20°C

- Results
  - Taste test: 4-5 months

- Color
  - L,a*,b* & ΔE criteria

Results
  - Taste test: 4-5 months
Some examples

- Example # 2
  - Orange juice 100% pure
  - Des-aeration at 0.2ppm + head space $N_2$ flush to approx. 5%
  - PET bottles 330 ml (Ox-tran® 0.022) & 250ml (Ox-tran® 0.030)
  - 38mm neck & aluminum cap
  - storage at 20°C

- Results
  - Taste test : 5-6 months

- Colour
  - $L, a^*, b^*$ & $\Delta E$ criteria

![After 6 months](image-url)
Some examples

- Example # 3
  ➔ Orange juice 100% pure
  ➔ head space $N_2$ flush to approx. 5%
  ➔ PET bottles 500 ml (Ox-tran® 0.040)
  ➔ 28mm neck & standard cap
  ➔ storage at 4 & 23°C (dark condition)

- Results
  ➔ C Vitamin evolution :
    1. at 4°C : -0.47ppm/day equivalent to 0.042ppm$O_2$/day (SL15ppm=11.7months)
    2. at 23°C : -0.95ppm/day equivalent to 0.086ppm$O_2$/day (SL15ppm=5.7months)
  ➔ Remarks : 15ppm $O_2$ are reduced by 165ppm C Vit.
    1. General initial C Vitamin concentration : 400-600ppm
CONCLUSION

Extrapolation for Vine: Points to consider

- Expected shelf life:
  - Max O2 ingress
  - Light protection
  - Storage temperature
  - Microbiology

- Filling technology:
  - O2 Ingress
  - Head space

- Closure

- Container Technology:
  - Material, weight…
  - Gas Barrier technology (Active, Passive, BIF ?)