The Effects of Steam Sterilization on Stainless Steel Instruments

By Professor L’Hocine Yahia

For the unfolding of the 11th World Sterilization Congress and the 7th International Symposium of Sterilization and Hospital Infection Control in São Paulo, Brazil

Presentation on July 30th, 2010
State of the Art & Perspectives
Presentation outline

1. Introduction
2. Steam sterilization for metallic instruments and medical devices
   - 3.1 Composition
   - 3.2 Corrosion resistance
3. The effects of steam sterilization on stainless steel instruments
   - 4.1 Surface properties
   - 4.2 Corrosion resistance
   - 4.3 Mechanical Properties
4. Corrosion improvement
5. Concluding remark
6. References
1. Introduction
Re-use of Catheters


Patricia Bentolila, chief representative, Export Development Canada, Africa and Middle East pbentolila@edc.ca, tel: 613 598 3219
PROTOCOLE DE MONTREAL RELATIF A DES SUBSTANCES QUI APPAUVRISSENT LA COUCHE D’OZONE

Programme des Nations Unies pour l'environnement

La stérilisation à l’oxyde d’éthylène mélangé à des chlorofluorocarbone (CFC) ou les hydrochlorofluorocarbone (HCFC), des substances qui appauvrissent la couche d’ozone.

Le mélange de CFC-12 et d’oxyde d’éthylène (12/88) contient 12 % d’oxyde d’éthylène et 88 % de CFC-12. L’oxyde d’éthylène étant hautement inflammable, le but de l’utilisation de CFC dans le mélange est de supprimer l’inflammabilité de l’oxyde d’éthylène.

L’oxyde d’éthylène est toxique, mutagène, inflammable, explosif et suspect d’être carcinogène.
New sterilization technologies
alternative to ethylene oxide

Tabrizian, Maryam; Lerouge, Sophie; Debrée, Anne; Yahia, L'hocine

Pure ethylene oxide (EO) at low temperature and new alternative techniques such as cold gas plasma sterilization have been developed for heat-sensitive polymers.
LOW TEMPERATURE PLASMA STERILISING SYSTEM AND METHOD

Patent 2000

Inventors:

Moisan, Michel (101, Avenue Beloeil, Outremont, Québec, H2V 2Z1, CA)
Moreau, Stéphane (1611, François H. Prévost, Montréal, Québec, H2M 2M4, CA)
Tabrizian, Maryam (1406 des Sittelles, Longueuil, Québec, J4J 5K3, CA)
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Barbeau, Jean (219 Laurier Ouest, App. 04, Montréal, Québec, H2T 2N9, CA)
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Ozone Sterilization System

It can be artificially produced by the action of high voltage discharge in air or oxygen.

\[ \text{O}_2 + \text{O} \quad \text{energy} \quad \rightarrow \quad \text{O}_3 \]

Its oxidation potential (-2.07V) is greater than that of hypochlorite acid (-1.49V) or chlorine (-1.36V).

<table>
<thead>
<tr>
<th>MOYEN DE STERILISATION</th>
<th>POTENTIEL D'OXYDATION (E°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ozone</td>
<td>+ 2.07 V</td>
</tr>
<tr>
<td>Bioxyde de chlore</td>
<td>+ 1.50 V</td>
</tr>
<tr>
<td>Hypochlorite</td>
<td>+ 1.49 V</td>
</tr>
<tr>
<td>Chlore</td>
<td>+ 1.36 V</td>
</tr>
</tbody>
</table>
In his career of over 60 years, Eskil Karlson has produced about 100 inventions. His most impressive efforts have converted a poison into a purifier: ozone-based sterilization systems.

Eskil L. Karlson was born in Johnkoping, Sweden in 1920, and emigrated to the US with his family when he was young. He felt somewhat alienated from his fellow students, but was thoroughly at home in the sciences: by sixth grade, he was studying college textbooks. Meanwhile, Karlson built small-scale civil engineering projects in his backyard. He won the first of his nearly 100 patents, for an acid-resistant glass bottle capping system, in his first year of high school. In 1967, Karlson worked with ozone (O3) for the first time. This infamous, poisonous gas would become Karlson's preferred medium: in fact, in 1972 Karlson wrote an article entitled, "Ozone: Friend or Foe?" --- arguing, of course, for the former.
Ozone Sterilization System Approved

Originally Published MDDI January 2004

Ozone Sterilization System Approved; Could Compete with EtO, Gas Plasma

A Canadian company, based in Quebec, received Health Canada and FDA clearance in the autumn of 2003 to market a breakthrough technology using ozone as the sterilant. It was the first new medical device sterilization technology approved by the FDA in about 10 years.

The manufacturer, TSO3 Inc. (Quebec City, QC, Canada), claims the technology is safer, faster, and more cost-effective than those that currently serve medical products that can withstand high temperatures or radiation when sterilized.

EtO is still the most commonly used "cold" sterilization, even though it is very toxic and requires such a long aeration time that you need a big inventory to justify it.

The ozone sterilization process requires only medical-grade oxygen, and only oxygen and water are released into the air when it is completed.
2. Steam sterilization for metallic instruments and medical devices
World Biomedical Metal Market

The global demand on biomedical metals reached US$11.5 billion in 2009, approximately 6% up from the previous year. **Stainless steels** are the largest product group of the biomedical metals, accounting for more than half of the total biomedical metal market, followed by titanium/Ti-alloys and cobalt-based alloys.

**Surgical instrument** is the largest and dominant application area of biomedical grade stainless steels, accounting for 55% of total consumption. Estimated at approximately US$3.98 billion in 2009.
Medical instruments

Various Steels

Nitinol

Table 1.11 Price of semiproducts (bar with a diameter of 20 mm) and volume price of various metallic biomaterials

<table>
<thead>
<tr>
<th>Material</th>
<th>Price ($ kg⁻¹)</th>
<th>Weight (kg dm⁻³)</th>
<th>Volume price ($ dm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless steel</td>
<td>10</td>
<td>8</td>
<td>80</td>
</tr>
<tr>
<td>CoCrNi</td>
<td>200</td>
<td>9.1</td>
<td>1820</td>
</tr>
<tr>
<td>cp-Ti</td>
<td>35</td>
<td>4.5</td>
<td>159</td>
</tr>
<tr>
<td>Ti6Al4V</td>
<td>53</td>
<td>4.43</td>
<td>235</td>
</tr>
<tr>
<td>cp-Nb</td>
<td>206</td>
<td>8.56</td>
<td>1762</td>
</tr>
<tr>
<td>cp-Ta</td>
<td>368</td>
<td>16.6</td>
<td>6103</td>
</tr>
</tbody>
</table>
Nitinol

Vena Cava Filters

CR Bard/NMT

J&J Cordis
Metals used in medical devices and surgical instruments

Global demand from endoscope market on stainless steel was valued at approximately US$532 million in 2009. It also presents above average growth, driven by increasing popularity of minimal invasive surgery. The stainless steel in endoscope is expected to reach US$786 million in 2015 and to approach US$1 billion by 2018.
A sampling of time-temperature relationships for steam sterilization

<table>
<thead>
<tr>
<th>TEMPERATURE</th>
<th>TIME (MIN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>132°–134°C</td>
<td>3–4 minutes&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>121°C</td>
<td>8–30 minutes&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>115°C</td>
<td>35–45 minutes</td>
</tr>
<tr>
<td>111°C</td>
<td>80–180 minutes</td>
</tr>
</tbody>
</table>

<sup>a</sup> Unwrapped items have been shown to be sterile at short times. Wrapped items and load sizes may require longer times for adequate heating and a sterility assurance level of $10^{-6}$, or shorter times depending upon bioburden, product mix, processing, and characteristics of the product. Significantly higher time and temperature is required for inactivation of prions (e.g., 134°C for longer than 1 hour).
The Sterile Supply Cycle: Cleaning
Author: Jan Huys

Instruments used during an operation will be covered with blood and remains of tissues; they may have been in touch with chemicals and fluids, dirt and dust.

….first have to be thoroughly cleaned before sterilization

In one way or the other, the items have to be reprocessed so that they can be safely used on another patient again. Cleaning plays an immensely important role in this process...

A major requirement for equipment intended to be in touch with inner fluids of the body (the high risk areas) is that they should be sterile.

However sterility (the absence of any viable organism) alone is not sufficient for safe use. An instrument, which is covered with sterile dirt or with remains of chemicals or corrosion, still is a serious health hazard.
Corrosion of surgical instruments

Medical instruments are usually expensive precision instruments (NiTi...).

Pivots and hinges are very sensitive to any left-over deposits of dirt. Small deposits of blood may easily develop into serious corrosion (rust).
This corrosion is aggravated by the moisture and high temperatures during the processes used for sterilization, especially when steam is used. Corrosion may result in serious damage to the instruments and even render them useless or dangerous for the patient.
2. Stainless steels for surgical instruments /implants
2.1 Composition

Stainless Steels (3 main types):
- **Ferritic** alloys for use in automobiles
- **Martensitic** alloys used for knives and surgical tools due to its great hardness
- **Austenitic** steels types 316, 316L and 317

Organizations such as the International Organization for Standardization (ISO) classifies and advises on which grade of stainless steel is appropriate for distinct types of surgical instruments. ISO also advises on tempering steel and the rust and corrosion processes on the different grades available.

<table>
<thead>
<tr>
<th>Steels</th>
<th>C</th>
<th>Cr</th>
<th>Ni</th>
<th>Mn</th>
<th>Mo</th>
<th>Cu</th>
<th>Si</th>
<th>N</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>F138,139</td>
<td>≲ 0.03</td>
<td>17–19</td>
<td>13.0–15.0</td>
<td>≲ 2.0</td>
<td>2.25–3.0</td>
<td>≲ 0.5</td>
<td>≲ 0.75</td>
<td>≲ 0.1</td>
<td>–</td>
</tr>
<tr>
<td>F745</td>
<td>≲ 0.06</td>
<td>16.5–19.0</td>
<td>11.0–14.5</td>
<td>≲ 2.0</td>
<td>2.0–3.0</td>
<td>≲ 0.5</td>
<td>≲ 1.0</td>
<td>≲ 0.2</td>
<td>–</td>
</tr>
<tr>
<td>F1314</td>
<td>≲ 0.03</td>
<td>20.5–23.5</td>
<td>11.5–13.5</td>
<td>4.0–6.0</td>
<td>2.0–3.0</td>
<td>≲ 0.5</td>
<td>≲ 0.75</td>
<td>0.2–0.4</td>
<td>V,Nb: 0.1–0.3</td>
</tr>
<tr>
<td>F1586</td>
<td>≲ 0.08</td>
<td>19.5–22.0</td>
<td>9.0–11.0</td>
<td>2.0–4.25</td>
<td>2.0–3.0</td>
<td>≲ 0.25</td>
<td>≲ 0.75</td>
<td>0.25–0.5</td>
<td>Nb: 0.25–0.8</td>
</tr>
<tr>
<td>F2229</td>
<td>≲ 0.08</td>
<td>19.0–23.0</td>
<td>≲ 0.05</td>
<td>21.0–24.0</td>
<td>0.5–1.5</td>
<td>≲ 0.25</td>
<td>≲ 0.75</td>
<td>0.85–1.1</td>
<td>–</td>
</tr>
<tr>
<td>F2581</td>
<td>0.15–0.25</td>
<td>16.5–18.0</td>
<td>≲ 0.05</td>
<td>9.5–12.5</td>
<td>2.7–3.7</td>
<td>≲ 0.25</td>
<td>0.2–0.6</td>
<td>0.45–0.55</td>
<td>–</td>
</tr>
</tbody>
</table>
Nickel toxicity

Ke Yang and Yibin Ren


Figure 1. Percentage of young people sensitized to nickel allergy has risen dramatically over the years (reproduced with permission from [28] ©1998 vdf Hochschulverlag AG an der ETH Zürich).
2.2 Corrosion Resistance (Standard tests !)

Three-electrode cell used

Figure 1. Corrosion parameters defined by a cyclic potentiodynamic polarization curve.
Figure 7 ♦ Typical cyclic polarization curves in de-aerated Hank’s balanced salt solution of electropolished NiTi and stainless steel (316L). NiTi alloy shows higher breakdown potential ($E_{bd}$), lower corrosion current ($I_{corr}$), and smaller hysteresis than stainless steel. Reproduced with permission from *J Biomed Mater Res.* Copyright 2000, John Wiley & Sons Inc.
<table>
<thead>
<tr>
<th></th>
<th>5</th>
<th>0</th>
<th>1168 ± 137</th>
<th>-210 ± 222</th>
<th>1374 ± 196</th>
<th>1473 ± 139</th>
<th>1.950 ± 0.777</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50</td>
<td>1166 ± 120</td>
<td>-108 ± 102</td>
<td>1274 ± 220</td>
<td>1486 ± 121</td>
<td>2.579 ± 1.215</td>
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<tr>
<td></td>
<td>100</td>
<td>1136 ± 55</td>
<td>-181 ± 140</td>
<td>1317 ± 195</td>
<td>1460 ± 58</td>
<td>4.259 ± 0.603</td>
<td></td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>1193 ± 148</td>
<td>-186 ± 91</td>
<td>1379 ± 239</td>
<td>1520 ± 153</td>
<td>2.146 ± 1.886</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0</td>
<td>484 ± 126</td>
<td>-206 ± 59</td>
<td>694 ± 349</td>
<td>635 ± 128</td>
<td>18.333 ± 3.168</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>497 ± 101</td>
<td>-60 ± 156</td>
<td>557 ± 54</td>
<td>647 ± 104</td>
<td>18.013 ± 5.429</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>504 ± 86</td>
<td>-57 ± 135</td>
<td>561 ± 48</td>
<td>630 ± 85</td>
<td>13.405 ± 6.584</td>
<td></td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>510 ± 100</td>
<td>-30 ± 182</td>
<td>540 ± 81</td>
<td>660 ± 102</td>
<td>18.259 ± 5.725</td>
<td></td>
</tr>
</tbody>
</table>

*aValues are means ± SD.*
Figure 9. Localized corrosion potentials obtained in ASTM F746 tests on mechanically polished samples of various medical alloys and on NiTi* wires chemically etched and aged in boiling water.
Figure 6 ◆ Effect of passivation: nickel release in Hank's physiological solution for mechanically polished (MP) stainless steel (MP ST), NiTi (MP NiTi) and MP35N (MP MP35N); electropolished stainless steel (EP ST) and NiTi (EP NiTi); and acid passivated MP35N (PA MP35N). Reproduced with permission of C. Trépanier.
Metal release from 316L and CoCrMo (Okazaki Y)

Biomaterials 26 (2005) 11–21

Fig. 1. Quantity of each metal element released from SUS 316L stainless steel into various solutions at 37°C after 1 week: (a) released Fe; and (b) released Cr, Ni and Mo.

Fig. 2. Quantity of each metal element released from Co–Cr–Mo casting alloy into various solutions at 37°C after 1 week: (a) released Co; and (b) released Cr and Mo.
3. The effects of steam sterilization on stainless steel instruments
All moist heat sterilization cycles consist of a heating, sterilizing and cooling phase. During each of these phases unacceptable stresses or excessive oxidation resulting from temperature or pressure changes could result in damage to the medical devices.

**Cumulative damage**

However, there has been only one publication thus far addressing the effects of multiple cycles of steam sterilization on the properties of oxide films on stainless steel implants.
Effects of steam sterilization

3.1 Surface properties
3.2 Corrosion resistance
3.3 Mechanical properties
3.1 Surfaces Properties

Effect of steam versus dry-sterilization on the orthodontic ligature-cutting pliers.

Steam sterilization conditions
- A total of 50 ligature-cutting pliers with stainless steel inserts,
- Each plier was subjected to a series of ligature wire cuts and then sterilized with either steam autoclave or dry heat. For steam autoclave sterilization, a Castle M/C3533 Vacuum Steam Sterilizer (Castle, Rochester, NY) was used (45-minute cycle at 135° C). For dryheat sterilization, the Dentronix DDS 5000 sterilizer was used (24-minute cycle at 205° C).
Each plier was subjected to 12 cycles.
Vendrell et al. (2002)

Note variability of plier tips before use or sterilization. Some pliers appeared worn, as shown in lower left enlargement (illustration by Wilford Hall Medical Center, Lackland Air Force Base).
no significant difference in the wear at the tip of the ligature-cutting pliers whether the instruments were sterilized with steam or dry heat. no difference in coloration could be seen among the pliers in both.

Initial photomicrograph of plier tip at 32 magnification.

Wear at plier tip after 6 cycles of wire cuts and steam sterilization (32 magnification).
Shih et al (2010)

Effects of multiple cycles of steam sterilization on the properties of oxide films on 316L stainless steel devices (strenal wires).

Steam sterilization conditions:
- Temperature of 121° C;
- Processing time of 30 min, according to the recommended standard [14].
- Dry time between cycles $t = 24$ hrs (the 10 cycles of sterilization were not done consecutively. The dry time between cycles was one full day to simulate the actual conditions in hospitals).
- De-ionized water was used during steam sterilization (to prevent any contamination).
Shih et al (2010)

The wide range of oxide particles observed by transmission electron microscopy on the as-received stainless steel sternal wire

(a) Non-uniform oxide particles examined by AFM at low magnification on as-received stainless steel sternal wire.

(b) Details at the nano-scale of oxides and corrosion pits on the as-received stainless steel sternal wire.
Pernier et al (2005)
Influence of autoclave sterilization on the stainless steel orthodontic wires

Steam sterilization conditions:

- A treatment at 134°C for at least 18 minutes;
- In order to comply with current norms, the wires had previously been placed in 5% Micro 10+ solution (detergent, bactericide, fungicide, virucide solution), in an ultrasonic bath for 10 min, followed by rinsing in distilled water, drying on absorbent paper, and placement in a sealed bag.
- One cycle
3D reconstruction obtained by AFM, before and after sterilization of SS alloy (Tru-Chrome). Heterogenous surface parameters, smooth streches and rough surface, hollows and random striation (production process?). A slight increase in roughness.
The profilometry study did not identify statistically significant roughness differences before and after autoclave sterilization.

Figure 3  Average roughness $Ra$ (μm), obtained by profilometry, before and after sterilization.

Figure 5  Average elastic modulus (GPa), before and after sterilization.
Valois et (2008)
Evaluation of the surface of rotary nickel-titanium (Ni-Ti) files after multiple autoclave cycles.

Steam sterilization conditions:
2 commercial rotary NiTi files were studied (Greater Taper & Profile).
Each cycle was performed at 121°C, with a pressure of 15 psi, for 15 minutes.
After 1, 5, and 10 autoclave cycles the files were observed by AFM.

The results indicated that multiple autoclave cycles increase the depth of surface irregularities located on rotary Ni-Ti files.
Figure 1. Contact mode AFM 3-dimensional images of typical surface topography of rotary Ni-Ti files from control (0 cycles) and after multiple autoclave cycles (1, 5, and 10). Visual irregularities in the surface topography were observed for both Greater Taper and Profile in all conditions analyzed.

Effects of Multiple Sterilization on Surface Characteristics and In Vitro Biologic Responses to Titanium

The goal of this study was to observe the surface changes to commercially pure titanium (cpTi) brought about by multiple exposure to common sterilization techniques:

- ultraviolet light
- ethylene oxide sterilization (1, 5, or 10 cycles)
- steam autoclaving (1, 5, or 10 cycles)

Surfaces were examined using SEM, x-ray photoelectron spectroscopy, Auger electron spectroscopy, and equilibrium wetting angles to determine alterations in surface morphology, oxide composition, and thickness and surface energetics after sterilization.
The increased level of contamination, as determined by XPS, and the increased wetting angles, were probably attributable, in part, to the presence of these contaminants. This is especially true for the SA surfaces, because some inorganic-containing contaminants (Fe, Na, P, Si, etc) most likely were related to the purity of the water used to prepare the steam.

On all SA surfaces, particulate contaminants of variable size were observed (Fig 4). The nature of the surface particulate contaminant did not change between SA 1, 5, or 10 cycle groups.
FIGURE 4. Scanning electron micrograph of treated cpTi disc, sterilized by SA-10 cycles. Note particulates present on surface.
<table>
<thead>
<tr>
<th>Oxide Composition (atomic ratios compared to Ti)</th>
<th>Oxide Thickness (Å)</th>
<th>Contact Angles (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>UV-treated</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C: 0.73 ± 0.01</td>
<td>26.2 ± 5.7</td>
<td>52.0 ± 3.2</td>
</tr>
<tr>
<td>O: 2.07 ± 0.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N: 0.03 ± 0.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>SA 1</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C: 2.80 ± 1.38</td>
<td>35.0 ± 6.2</td>
<td>75.4 ± 3.3</td>
</tr>
<tr>
<td>O: 3.26 ± 0.97</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N: 0.1 ± 0.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe: 0.1*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na: 0.04*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl: 0.10*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si: 0.54*</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>SA 10</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C: 2.66 ± 0.63</td>
<td>70.0 ± 7.2</td>
<td>71.2 ± 1.7</td>
</tr>
<tr>
<td>O: 2.96 ± 0.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N: 0.10 ± 0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na: 0.003 ± 0.002</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P: 0.03*</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>EO-1</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C: 2.29 ± 0.68</td>
<td>27.9 ± 0.8</td>
<td>54.3 ± 3.1</td>
</tr>
<tr>
<td>O: 2.80 ± 0.45</td>
<td></td>
<td></td>
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<tr>
<td>N: 0.08 ± 0.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si: 0.30*</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>EO-10</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C: 1.51 ± 0.55</td>
<td>33.7 ± 4.5</td>
<td>58.7 ± 4.0</td>
</tr>
<tr>
<td>O: 2.61 ± 0.47</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N: 0.03 ± 0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe: 0.31*</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**NOTE.** n = 3, mean ± SD.

* Element observed on only one sample.
The thickest oxide was found in multiple SA group 10, which was statistically significantly greater than all other treatment groups and was three times as thick as the oxide on the UV-treated surfaces.

UV-treated surfaces resulted in the lowest contact angles, whereas SA resulted in the highest contact angles.
Comparative study of ozone and steam sterilization on stainless steel surgical instruments

• Experiment:
  – Scissors (Mayo and Lister) X 10
  – Control: cleaning + lubrication X 100
  – Steam (132°C X 60 min): cleaning + lubrication + sterilization X 100
  – Ozone ([85mg/L X 15 min ] X 2): cleaning + lubrication + sterilization X 100
  – (5) Observations points 0 – 10 – 25 - 50 – 100 of:
    • Cutting edge efficiency (ASTM F1079-87)
    • Overall cosmetic appearance
    • Cutting edge microscopic analysis (SEM)
    • Cutting edge oxygen analysis (SEM-EDS)
- Control unexposed
- Ozone Sterilization X 100
- Steam Sterilization X 100
• Cutting edge SEM analysis sampling chart

• Control – “Vue 4”
• Cutting edge (100X) - Ozone

• Cutting edge (100X) - Steam
- Oxygen – Ozone Sterilized

- Oxygen – Steam Sterilized
### Summary test results

<table>
<thead>
<tr>
<th>Inspected item</th>
<th>Control</th>
<th>Ozone</th>
<th>Steam</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cutting edge efficiency</td>
<td>Good</td>
<td>No change</td>
<td>No change</td>
</tr>
<tr>
<td>Overall cosmetic appearance</td>
<td>Good</td>
<td>No change</td>
<td>Gold color finish</td>
</tr>
<tr>
<td>Cutting edge surface analysis (SEM)</td>
<td>Uneven cutting edge, machined surface</td>
<td>No change</td>
<td>No change</td>
</tr>
<tr>
<td>Cutting edge oxygen analysis (SEM-EDS)</td>
<td>n/a</td>
<td>Lower than control with no significant increase</td>
<td>Higher than control with linear increase</td>
</tr>
</tbody>
</table>
Conclusions:

Definite difference between ozone and steam sterilization toward stainless steel surgical instruments

Low temperature ozone sterilization has no cosmetic impact on the surface of stainless steel surgical instruments as compared to steam sterilization

Continued chemical modification (oxygen intake) of steam sterilized surgical stainless steel surface throughout 100 cycles

Early chemical stabilization (ozone intake) of ozone sterilized surgical stainless steel surface over 100 cycles study
3.2 Corrosion resistance

• 316 L stainless Steel
• Cr-Ni-Mo Steel
• Ti-8N-Cr
(a) Analysis of oxide thickness on the as-received, one cycle, five cycle and ten cycle steam sterilized stainless steel sternal wires by cathodic reduction at 4 $\mu$A cm$^{-2}$ in deaerated 0.1 mol l$^{-1}$ sodium bicarbonate solution.
(b) Oxide thickness showing a linear relationship with the cycles of steam sterilization.
Results of anodic polarization measurements on the as-received, one cycle, five cycle and ten cycle steam sterilized stainless steel sternal wires in deaerated Ringer’s solution at 37 C. Breakdown potentials decreased as the number of cycles of steam sterilization increased
Table 1
Time constants of stainless steel sternal wires after various cycles of steam sterilization.

<table>
<thead>
<tr>
<th>Cycles</th>
<th>Resistance (MΩ cm(^{-2}))</th>
<th>Interfacial capacitance (μF cm(^{-2}))</th>
<th>Time constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.45 ± 0.08</td>
<td>822 ± 18.6</td>
<td>3657.9 ± 1.52</td>
</tr>
<tr>
<td>1</td>
<td>2.50 ± 0.14</td>
<td>470 ± 20.5</td>
<td>1175.0 ± 3.21</td>
</tr>
<tr>
<td>5</td>
<td>1.82 ± 0.19</td>
<td>332 ± 46.2</td>
<td>604.2 ± 9.8</td>
</tr>
<tr>
<td>10</td>
<td>0.58 ± 0.26</td>
<td>114 ± 71.5</td>
<td>66.1 ± 18.6</td>
</tr>
</tbody>
</table>

Fig. 8. SEM micrographs of severely corroded sternal wires after ten cycles of steam sterilization following cyclic anodic polarization measurement. A pitting-free micrograph of the as-received stainless steel wire was shown in Fig. 4a.
Results

The thickness and properties of oxide films have been proven to be a function of the number of steam sterilization cycles, and the films deteriorated with increasing number of cycles.

The corrosion resistance of stainless steel wires could be significantly reduced by multiple cycles of steam sterilization; the integrity of stainless steel wires could be severely compromised by increasing the number of cycles of steam sterilization.

Heavy metals could be released to the surrounding tissues due to deterioration of the oxide film.
Cr-Ni-Mo Steel
Marciniak et al (2007)

<table>
<thead>
<tr>
<th>Sterilization program</th>
<th>Temperature $T$, °C</th>
<th>Pressure $p$, bar</th>
<th>Time $t$, min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>134</td>
<td>2.1</td>
<td>4</td>
</tr>
<tr>
<td>P2</td>
<td>121</td>
<td>1.1</td>
<td>20</td>
</tr>
<tr>
<td>P3</td>
<td>134</td>
<td>2.1</td>
<td>12</td>
</tr>
<tr>
<td>P4</td>
<td>121</td>
<td>1.1</td>
<td>30</td>
</tr>
</tbody>
</table>
Results

Passivation and sterilization process of CrNiMo steel realized with the use of steam in pressure improved the corrosion resistance of the tested samples.

Analysis of the results which describe the changes of all parameters relating to pitting corrosion resistance has shown the favorable interaction of steam sterilization process.

The advantageous influence of high pressure steam treatment was also expressed in decrease of current corrosion density $i_{\text{corr}}$ values and in increasing of polarization resistance $R_p$ of all samples.

The analysis of particular influence of sterilization parameters has shown the most significant effect of the time of acting of steam. It should be pointed out that increasing the time of sterilization for constant parameters of temperature and pressure of steam was the factor which improved all parameters describing the corrosion resistance of specimens of Cr-Ni-Mo steel.
3.3 The effects on mechanical properties
Pernier et al (2005)

Influence of autoclave sterilization on the stainless steel orthodontic wires

The elastic modulus values were similar for SA sterilized and unsterilized stainless steel and NiTi wires.
Alavi et al (2009)

Effects of steam and dry-heat sterilization on bending properties of NiTi wires

Steam and dry-heat sterilization cause changes in the mechanical properties of superelastic NiTi arch wires
Experimental static tests have shown that all tested miniplates did not have notable differences and this suggests that SA sterilization cycles (0, 10, 50 100 cycles) do not affect mechanical characteristics.
R T Adelson et al (2007)

Integrity of Craniofacial Plating Systems After Multiple Sterilization Procedures

Repeated cycles (10 cycles) of autoclaving had no significant effect on the integrity of titanium plates and screws routinely used in craniofacial surgery.
4. Corrosion improvement

Corrosion inhibitors
Surface modification
Water and steam quality

Holmlund (1965) found that the amount of iron dissolved from surgical steel (carbon steel and stainless steel) during a period of autoclave sterilization can be controlled and reduced by 96–99% with the addition of corrosion inhibitors, such as cyclohexylamine or decylamine.
CONCLUSION
Solutions containing Biolot or disodium hydrogen phosphate that have been recommended for presterilization processing showed little corrosion of metal instruments made of carbon and stainless steels.
These studies have shown that the corrosiveness of these sterilizing solutions for carbon-steel medical instruments can be reduced considerably by the addition of sodium benzoate or calcium gluconate.
Discussion

Poor quality of water or incorrect dosing or cleaning agent may be a cause of corrosion. In an adequate cleaning process the chemistry of the cleaning agent, the quality of the water, the materials to be cleaned and the other process variables (temperature and time) are carefully considered, leading to the correct choice of chemicals and processes (Standardisation)
Water for Autoclaves

The European standard EN 285:2006 and the United States standard ANSI/AAMI ST79:2006 both suggest maximum water impurity levels for steam generation:

<table>
<thead>
<tr>
<th>Parameters</th>
<th>AAMI ST79</th>
<th>EN 285</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evaporation residue</td>
<td>≤ 15 mg/L</td>
<td>≤ 10 mg/L</td>
</tr>
<tr>
<td>Silica</td>
<td>≤ 2 mg/L</td>
<td>≤ 1 mg/L</td>
</tr>
<tr>
<td>Iron</td>
<td>≤ 0.2 mg/L</td>
<td>≤ 0.2 mg/L</td>
</tr>
<tr>
<td>Cadmium</td>
<td>≤ 0.005 mg/L</td>
<td>≤ 0.005 mg/L</td>
</tr>
<tr>
<td>Lead</td>
<td>≤ 0.05 mg/L</td>
<td>≤ 0.05 mg/L</td>
</tr>
<tr>
<td>Other heavy metals</td>
<td>≤ 0.1 mg/L</td>
<td>≤ 0.1 mg/L</td>
</tr>
<tr>
<td>Chloride</td>
<td>≤ 3 mg/L</td>
<td>≤ 2 mg/L</td>
</tr>
<tr>
<td>Phosphate</td>
<td>≤ 0.5 mg/L</td>
<td>≤ 0.5 mg/L</td>
</tr>
<tr>
<td>Conductivity (at 25°C)</td>
<td>≤ 50 μS/cm</td>
<td>≤ 5 μS/cm</td>
</tr>
<tr>
<td>pH</td>
<td>6.5 to 8</td>
<td>5 to 7.5</td>
</tr>
<tr>
<td>Appearance</td>
<td>Clean, colorless, no sediment</td>
<td>Clean, colorless, no sediment</td>
</tr>
<tr>
<td>Hardness</td>
<td>≤ 0.1 mmol/L</td>
<td>≤ 0.02 mmol/L</td>
</tr>
</tbody>
</table>

NOTE: The values reported in this table are for information only. It is the responsibility of the user to verify the values that apply in his/her specific case.
L'objectif de ce guide est de fournir une aide aux personnels qui ont en charge l'instrumentation dans les établissements de santé, afin de prévenir et limiter autant que possible la dégradation due à la corrosion.

Les principales familles de matériaux utilisés et formes de corrosion rencontrées, le rôle des états de surface et de l'eau sont présentées de façon synthétique en une vingtaine de pages. Dix fiches de reconnaissance des faciès de corrosion illustrent et complètent cette partie didactique.

Les phases critiques du cycle de vie des instruments du strict point de vue de la corrosion, font l'objet de sept fiches de bonne pratique dont les préconisations interviennent dans la pratique hospitalière. Elles ont été longuement débattues au sein d'un groupe de travail constitué notamment de responsables d'unité de stérilisation, d'utilisateurs (IBODES, pharmaciens, chirurgiens, orthopédistes..) d'industriels fabricants d'instruments et d'ancillaires, et d'experts.
5. Concluding Remark

Further investigations and money are required to elucidate the safety of the new sterilisation protocols needed to eliminate prions, endotoxins, etc…
Thank you
7. References


The novel method that we present allows polystyrene (PS) Petri dishes to acquire biocidal features ensuring microorganism inactivation. These properties were demonstrated for both vegetative and sporulated bacteria. Our method requires no grafting reactions with chemical precursors, but simply exposure to an ozone flow.

Such treated PS surfaces are able to inactivate various species of vegetative and sporulated bacteria on a relatively short contact time. Denaturation of proteins seems likely based on a significant loss of enzymatic activity of the lysozyme protein.
Fig. 2. SEM micrographs of *B. atrophaeus* (a–c) and *B. pumilus* (d–f) spores after having been in contact with PS Petri-dish surfaces previously treated 60 min with 4000 ppmv of dry gaseous O$_3$ (b, c, e, and f) and with untreated ones (a and d).