

## Analytical Surface Chemistry Comparison of Metallic Implant Passivation

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**Statement of Purpose:** Metal ion release resulting from corrosion or wear processes in orthopedic implants is an increasing concern in the orthopedic industry today. Metal ion release can result from corrosion, micro-motion, break in wear and/or mechanical dysfunction. Wear debris generated by implanted metallic-based medical devices has been implicated to cause inflammatory reactions of histiocytes to wear debris in tissues around implants. Inflammation could cause periprosthetic bone resorption leading to aseptic loosening. (1) This cycle could lead to more wear and subsequently more ion release. Presently there is much debate in literature regarding the clinical significance of metal wear debris and/or metal ions resulting from metal implants, but it is generally agreed that the best course of action would be to take appropriate steps to limit in vivo release.

The surface composition and chemistry of a metallic implant is one of the most important factors in providing corrosion protection which would subsequently reduce ion release. It is generally accepted that the corrosion resistance of Cr-based alloys is due to the formation of a relatively impervious surface Cr-oxide layer. The present study was undertaken to investigate the surface chemistry of CoCrMo alloys as a function of several different passivation methodologies. X-ray photoelectron spectroscopy (XPS) was used to characterize the surface composition and chemistry of CoCrMo coupons that had been subjected to various passivation treatments. In addition, corrosion studies were conducted by immersing the same coupons in serum and measuring the characteristic ion release using ICP-MS. The study will present the relationship between the passivation process, resulting surface chemistry and ion release properties for several treatments.

**Methods:** The samples evaluated in this study were in the form of 2.5cm polished CoCrMo disks that were passivated using either a nitric acid (5.5M) or citric acid (0.21M) solution in accordance with accepted protocols. The study also included an experimental passivation process, which is referred to as Enhanced Passivation (EP). This process utilizes a combination of plasma surface modification and acid passivation. XPS surface analysis was conducted utilizing a Quantera instrument (Physical Electronics PHI, Eden Prairie, MN). Ion release measurements were conducted by immersing the test coupons in 60mL of a 90% bovine serum solution. The experiments were conducted in a sealed container placed on a rocking plate set at 1.5 rpm in a 37°C incubator. The disks were soaked in bovine serum for a total of two weeks, with serum change at the end of week one. The two serum solutions were submitted for ICP-MS analysis, which was conducted by WCAS Bodycote, CA.

**Results:** The data obtained in this study clearly demonstrates a correlation between surface chemistry and ion release. The investigation further demonstrated that

the surface chemistry of a CoCrMo alloy can be directly correlated with the passivation process. The combined data shows that nitric acid passivation produces a more corrosion resistant surface compared to citric acid passivation. In addition, the results clearly illustrate that combining plasma treatment with acid passivation produces a surface that has an enhanced Cr-oxide passive layer, which results in significantly lower ion release characteristics. Comparing the ion values for any of the passivated materials relative to the untreated control clearly demonstrates the benefit of passivation. This data further illustrates that passivation in citric acid provides far less corrosion protection than any of the other methodologies evaluated. The data also shows that the enhanced passivation process produces the least amount of metal ion release and that using this methodology in conjunction with Citric acid greatly reduces the ion release relative to citric acid alone. The ion release values shown in Table 1 are supported by the XPS atomic concentration values shown in Table 2. This data clearly shows a correlation between the surface Cr concentration and the level of corrosion protection.

**Table 1.** Ion release values for Non Passivated (control), Citric acid, Nitric acid passivated and Enhanced Nitric and Citric passivated (EP) CoCr test Coupons. (Cumulative data for 2 weeks soaking)

Passivating Solution	Co (ug)	Cr (ug)	Mo (ug)	Total Ions (ug)
Nitric Acid	7.6	0.8	1.3	9.7
Nitric EP	3.3	0.5	2.8	6.6
Citric Acid	16.5	1.1	1.6	19.2
Citric EP	6.1	0.6	1.6	8.3
Control	27.2	0.6	2.1	29.9

**Table 2.** XPS Surface chemistry data for Non Passivated (control), Citric acid, Nitric acid passivated and Enhanced Nitric and Citric passivated (EP) CoCr test Coupons.

Average Atomic Concentration (%) N=7			
Passivating Solution	Co	Cr	Mo
Nitric Pass	27.9	66.1	6
Nitric EP	9.5	83.6	6.9
Citric Pass	44.7	49.6	5.7
Citric EP	15.6	76.0	8.4
Untreated CoCr (control)	73.4	22.9	3.8

**Conclusions:** The data obtained in this investigation clearly shows that nitric acid passivation produces an improved Cr-oxide passive layer when compared to Citric Acid passivation. The data further shows that the enhanced passivation process provides an even more robust (thicker) Cr-oxide surface layer that translates to a significant reduction in ion release compared to passivation alone. It could be argued that the magnitude of the observed differences may or may not be significant clinically, but it cannot be argued that no matter how small the increase in ion release for individuals with metal allergies, higher cannot be better.

### References:

(1) Nadim Hallab, PhD, Et. Al., *Metal Sensitivity in Patients with Orthopaedic Implants*, JBJS 83:428 (2001)