Analysis of Powder and Coatings for the Qualification of Coatings from XPT-D-703

A change in hydroxyapatite powder by the supplier was made in March, 2002 without any guidance on the spray conditions that should be used for the new powder. A period of 1.5 months were spent on spraying and testing coatings under new spraying conditions to provide a coating that suits the specification according to SPEC-009-01 and Spec. HAp-coat-Vimek. The change involved an investigation of the powder and coatings as documented below.

The particle size distribution was determined with a Saturn particle sizer for different powders used for spraying coatings from hydroxyapatite powder. The first powder used was an Amdry 6021 supplied by Sulzer Metco that was superseded by XPT-D-701 in 2001 and then finally updated to XPT-D-703 in 2002. Two other powders are provided for comparison, a powder supplied by Plasma Biotal known as Captal 20 and another by CAM Implants. The particle size distribution indicates that there is a shift to slightly larger particle size values from XPT-D-701 to XPT-D-703 as observed by an increase in the average particle size from 30 to 50 microns.

The particle size provided is more accurate than that supplied by thermal spray companies that conventionally use a sieve analysis. The small changes as recorded by the Saturn microsizer would not be detected in a sieve analysis, however the results clearly show that each powder is different. The powder by CamCeram appears identical to the XPT-D-701.

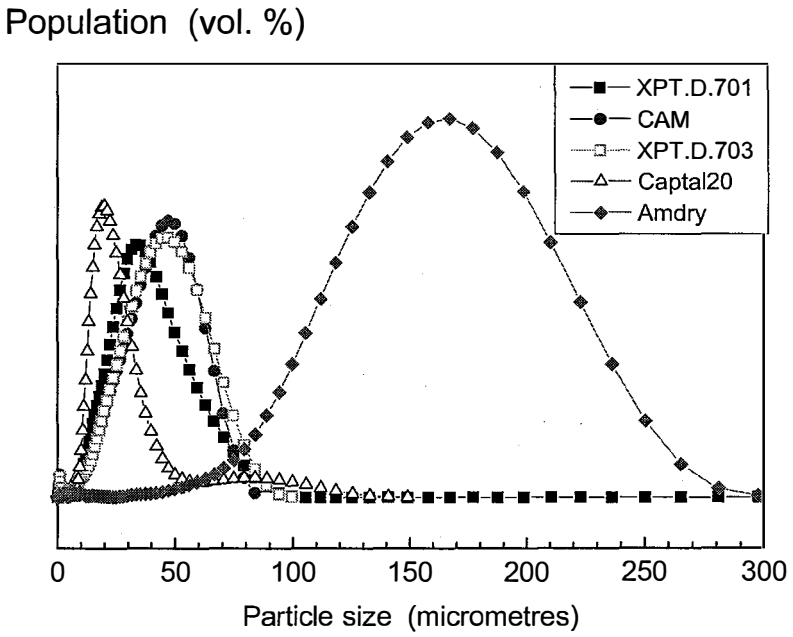
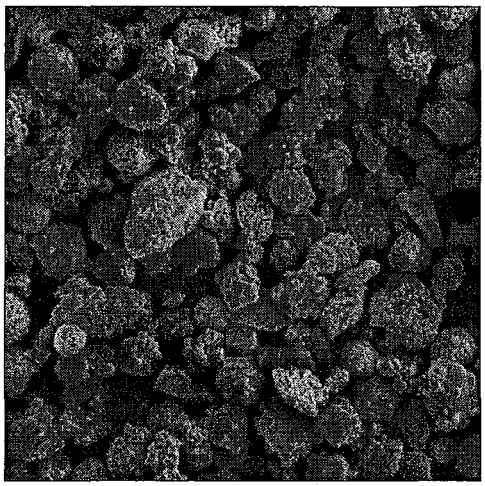
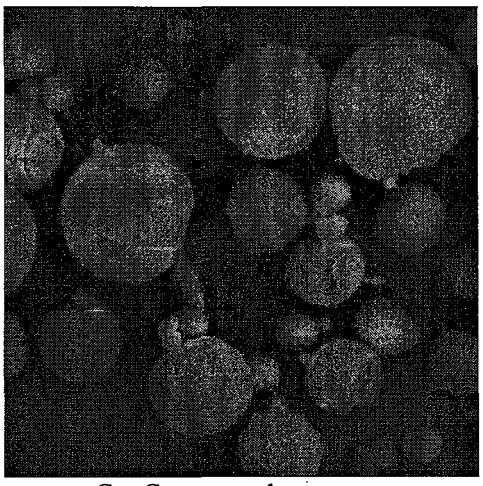


Figure 1. Particle size distribution of hydroxyapatite powders for thermal spraying.

All powders were examined in a scanning electron microscope for shape and particle roughness. It appears that Captal 20 supplied by Plasma Biotal is the a combination of irregular and rounded particles with a rough particle surface. Powder by CamCeram is smooth and rounded, depicting a spray dried powder. Amdry is an angular powder with a large particle size as supported by the particle size analysis. The XPT powders are both rounded and have been prepared by spray drying.

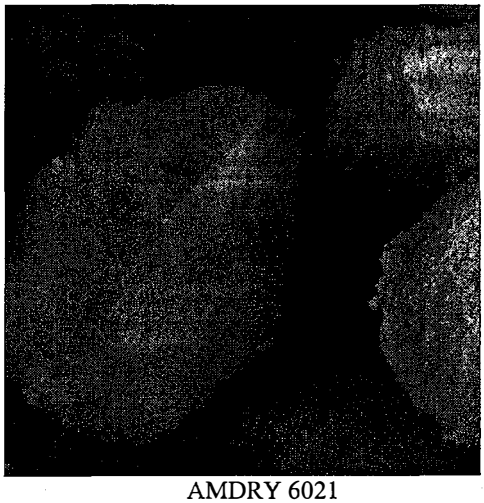


Captal 20

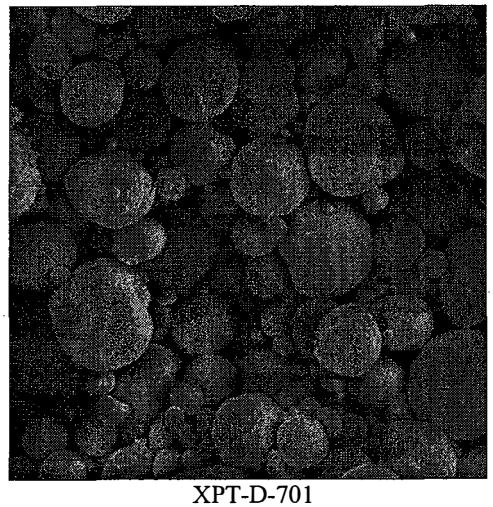


CamCeram powder

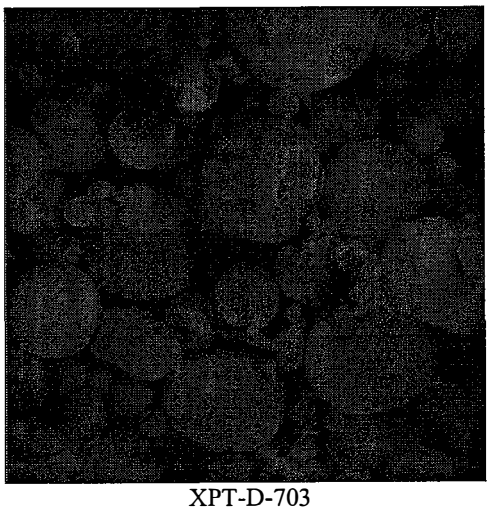
180 μm



AMDRY 6021



XPT-D-701

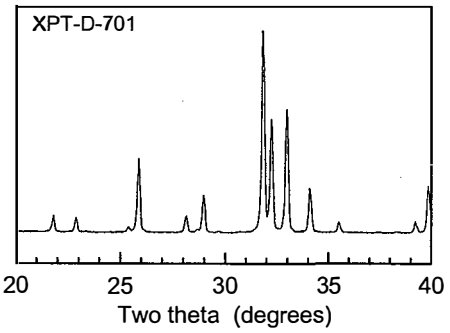


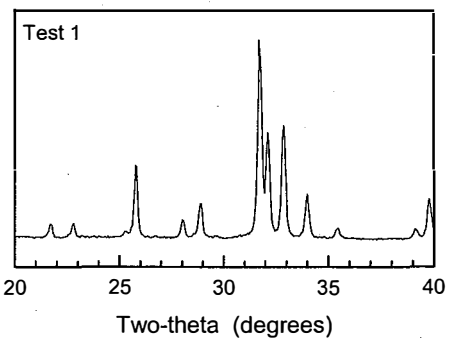
XPT-D-703

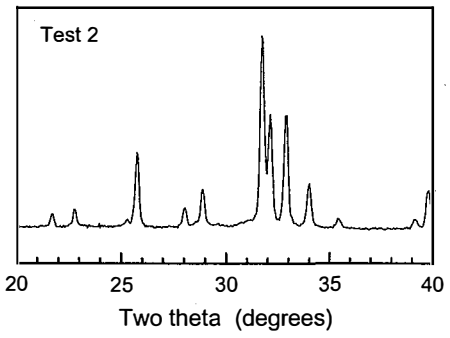
Figure 2. SEM of hydroxyapatite powders for thermal spraying

The coating was developed by a change in spray conditions and tested for crystallinity and bond strength. A series of 9 tests were conducted to determine the crystallinity and bond strength to ensure that these parameters would be in accordance with the values requested by Vimek. Coatings did not show preferential orientation, but consistently provided an amorphous content as revealed by the increase in the background intensity that peaked at 31 degrees. The experiments indicate a highly crystalline coating initially (92% crystallinity for the first sample). This high crystallinity is a result of larger particles used in the spraying process. Increasing the heat input in tests 5, 6, 7 and 8 provided a lower crystallinity and an undesirable level of decomposition phases. The coating approved for spraying was free of these decomposition phases and possessed 80% crystallinity. This was repeatable as revealed by the 78% crystallinity in the validation run.

The source powder shows well formed peaks in the correct relative intensity, indicative of a crystalline powder having no preferential orientation. The XRD pattern shows only an apatite phase that suggests that stoichiometry is retained after thermal spraying. Assuming that other bivalent ions do not replace the calcium ion, a Ca/P molar ratio of 1.6 is expected.


XPT-D-701
20
25
30
35
40
Two theta (degrees)


Test 1
20
25
30
35
40
Two-theta (degrees)


Test 2
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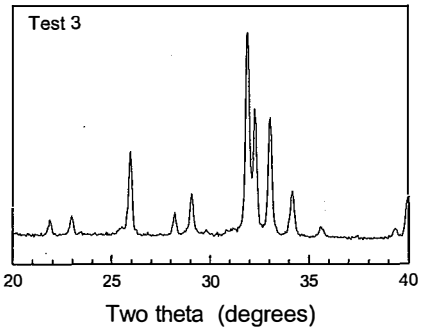
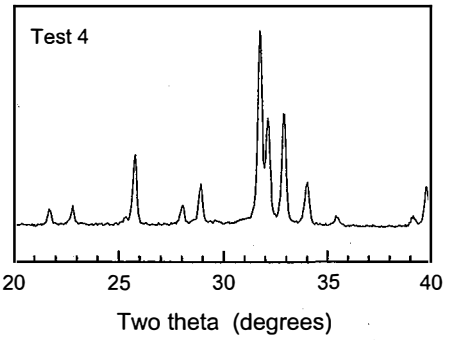
30
35
40
Two theta (degrees)


Test 3
20
25
30
35
40
Two theta (degrees)


Test 4
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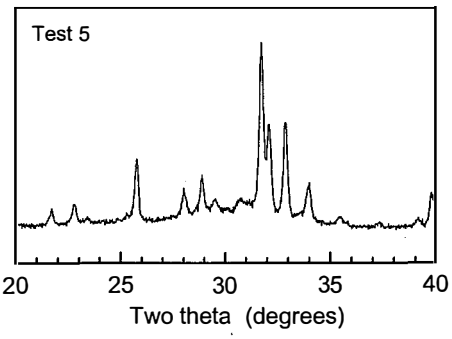
40
Two theta (degrees)


Test 5
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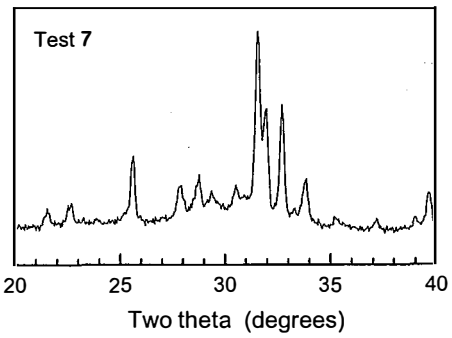
25
30
35
40
Two theta (degrees)


Test 7
20
25
30
35
40
Two theta (degrees)

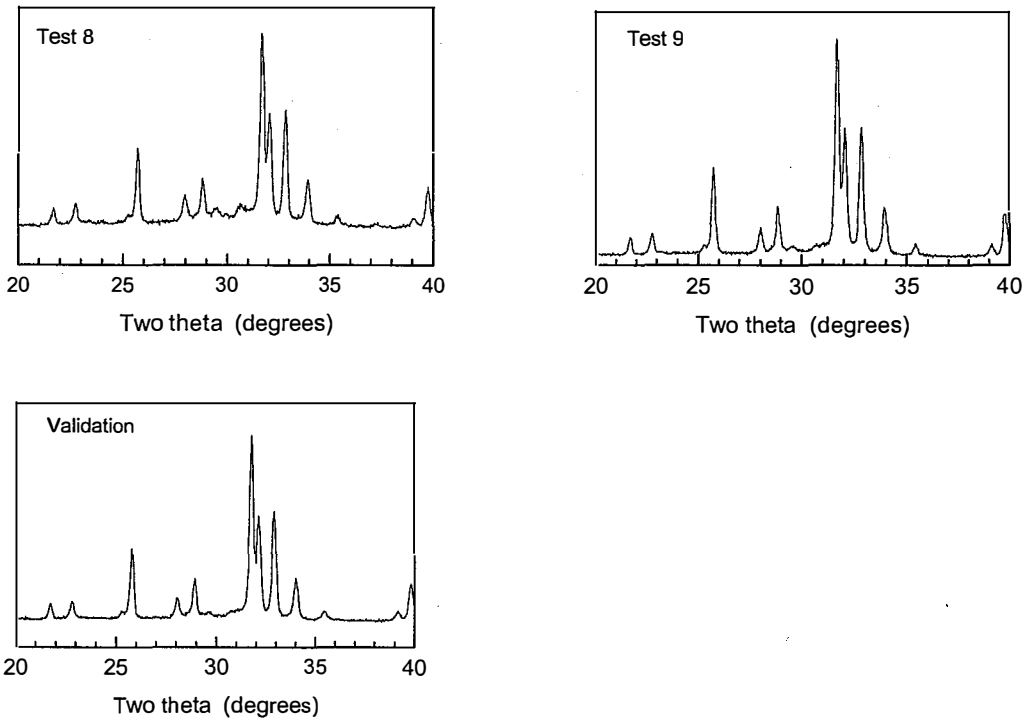


Figure 3. XRD patterns of hydroxyapatite coatings developed for powder XPT-D-703

Table 1. Mechanical properties of coatings.

Mech. Property		*Values*	*Average*
Tensile bond strength (MPa)	Test 1	13, 13, 18	14 ± 3
	Test 2	12, 15, 16	14 ± 2
	Test 3	8, 16, 8	11 ± 5
	Test 4	19, 24, 39	27 ± 10
	Test 5	19, 24, 39	27 ± 10
	Test 6	23, 10, 20	18 ± 7
	Test 7	15, 44, 40	32 ± 16
	Test 8	19, 21, 26	22 ± 4
	Test 9	40, 48, 56	48 ± 8
	Validation	45, 32, 39, 31, 55, 40 58, 54, 45, 39, 37, 51	44 ± 9
Shear strength (MPa)	Validation	42.7, 56.6, 45.5, 50.7, 53.8, 52.7, 55.3	51 ± 5

The FTIR spectra of two coatings are provided indicating both phosphate groups and the presence of a hydroxyl group shown with arrows and a rounded end, respectively. These indicators are only provided for the upper spectra, but apply equally to the bottom spectrum. No carbonate is distinctly detected in the spectra. The broad nature of the phosphate peaks indicates flexibility in the arrangement of the phosphate groups that can be occur within an amorphous calcium phosphate, a product which is present in the coatings and decreases the crystallinity of the coating.

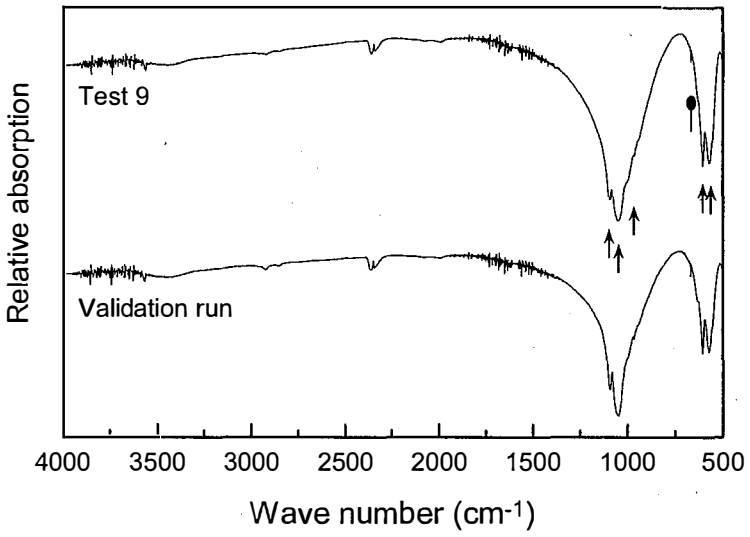


Figure 4. FTIR spectra of coatings from Test 9 and the validation run.

Cross-section of coating reveals the coating thickness, uniformity of coating thickness and the amorphous calcium phosphate distributed in the coating. The coating thickness for both polished cross-sections is about 45 ± 5 microns.

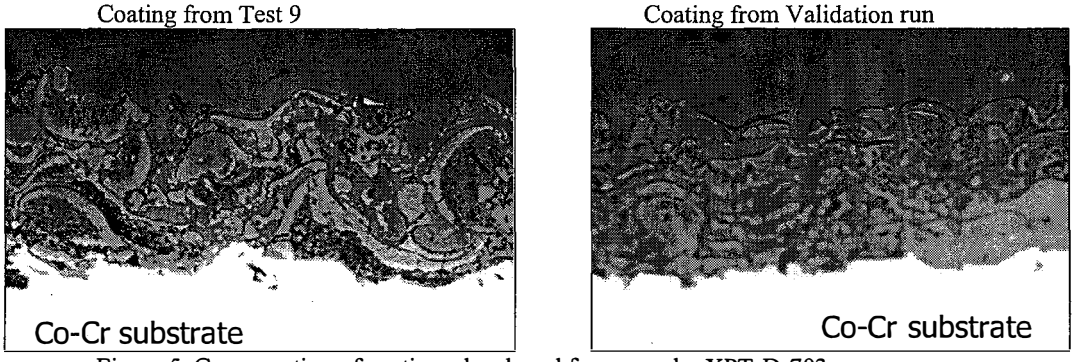


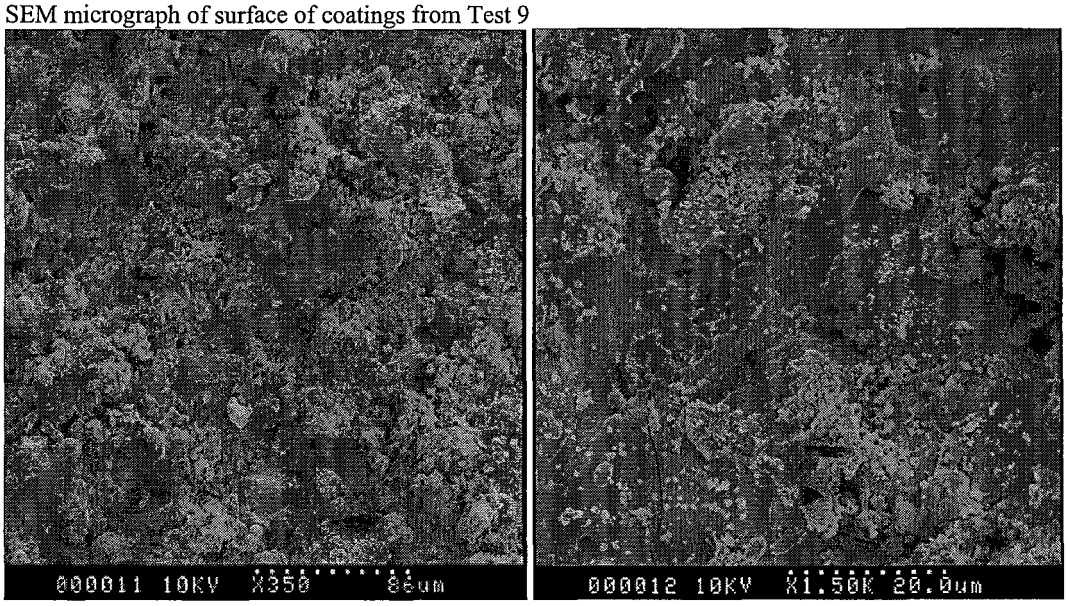
Figure 5. Cross-section of coatings developed from powder XPT-D-703.

The coating surface from Test 9 and the validation run provides a coating roughness of 5.6 ± 0.7 and 5.8 ± 0.5 μm, respectively.

A scanning electron micrograph revealed that a portion of the original powder was melted, as revealed by the smooth areas on the micrographs. The low magnification (x350) provided an overall view, and the high magnification (x1500) shows the well molten areas with the inclusion of fine crystalline debris scattered over the surface of the coating.

The porosity of the coating can be indirectly assessed from the cross-section and the surface toography. Submicron cracks are visible on the coating surface, a typical characteristic of the coatings. The cross-section does not show the presence of large pores. Since plasma sprayed coatings typically contain a density greater than 95%, the closer inspection of these coatings suggest that the porosity is less than 8%.

SEM micrograph of surface of coatings from Test 9



SEM micrograph of surface of coatings from the validation run

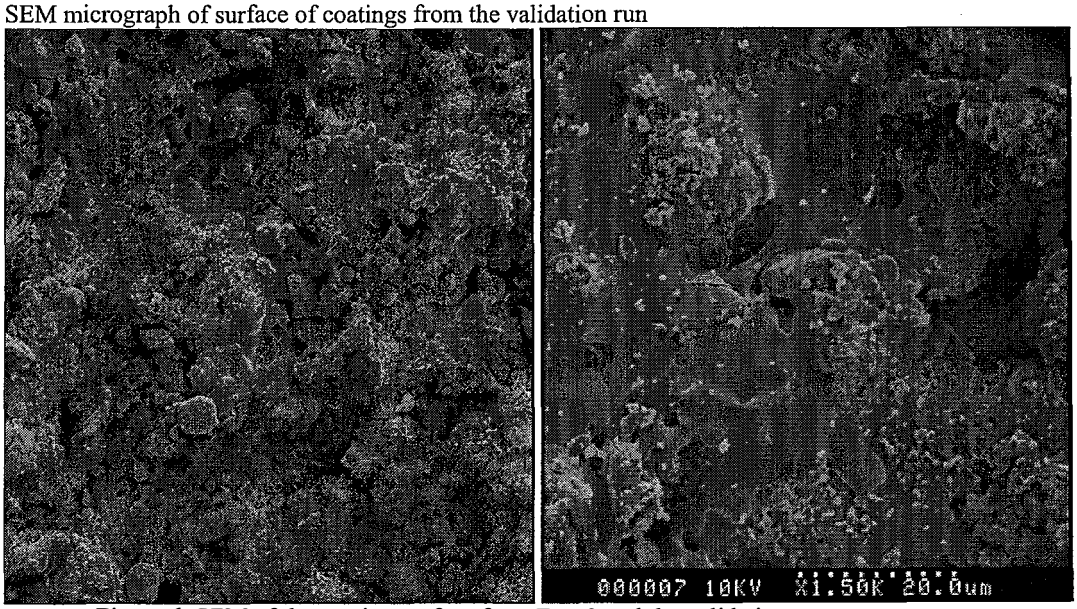


Figure 6. SEM of the coating surface from Test 9 and the validation run.

Inductively coupled plasma – mass spectrometry was conducted on the powder sprayed into water. The suspension was dried, dissolved in ultrapure nitric acid and then diluted for analysis. The analysis of powder from Test 9 and also from the validation was repeated to ensure consistency of results. The results, provided as parts per billion, show concentrations of less than 1ppm for As, Cd, Hg and Pb, the four elements subjected to examination for materials to be implanted in the body.

Table 2. Trace element impurities of sprayed powder (in parts per billion).

Element	*Powder*	*Spray*
Ag	80	69
Al	547	312
As	**N/D**	**N/D**
Au	664	547
Ba	462	365
Cd	**N/D**	**N/D**
Ce	103	90
Co	939	847
Cr	<1000	<1000
Cs	41	36
Cu	1,499	782
Dy	60	54
Er	81	72
Eu	32	28
Ga	N/D	N/D
Gd	84	75
Ge	N/D	N/D
Hf	453	388
Hg	**61**	**48**
Ho	94	83
La	56	49
Lu	50	45
Mg	6,242	4,182
Mn	909	227
Mo	331	310
Nb	137	119
Nd	16	12
Ni	7,108	4,170
Pb	**148**	**91**
Pd	87	79
Pr	78	69
Pt	81	72
Rb	58	51
Rh	58	51
Ru	82	72
Sb	398	384
Sc	155	124
Sm	101	89
Sn	134	48
Sr	1,669	1,217
Ta	371	330
Tb	88	78
Th	182	159
Tl	87	77
Tm	56	50
U	71	62
W	1,544	1,454
Y	80	70
Yb	68	60
Zn	1,819	645
Zr	588	559

N/D = not detected (<500 ppb)

Coatings were immersed in pH 7.3 tris buffer at 37 °C for an hour and the evolved calcium was measured with a calcium ion electrode. The dissolution occurred at a fast rate initially and slowed as the solution was filled with dissolved ionic species from the coating. Both coatings display the tendency to plateau at about 60 ppm of dissolved calcium. Assuming that this will be the plateau after dissolution of coatings at long periods of time, the solubility product, K_{sp} can be calculated and will provide a value of 2.63×10^{-54}.

The wash-out from the coatings was 5% for Test 9 and 7.2% for the validation run, both values in line with previously reported behaviour of plasma sprayed hydroxyapatite.

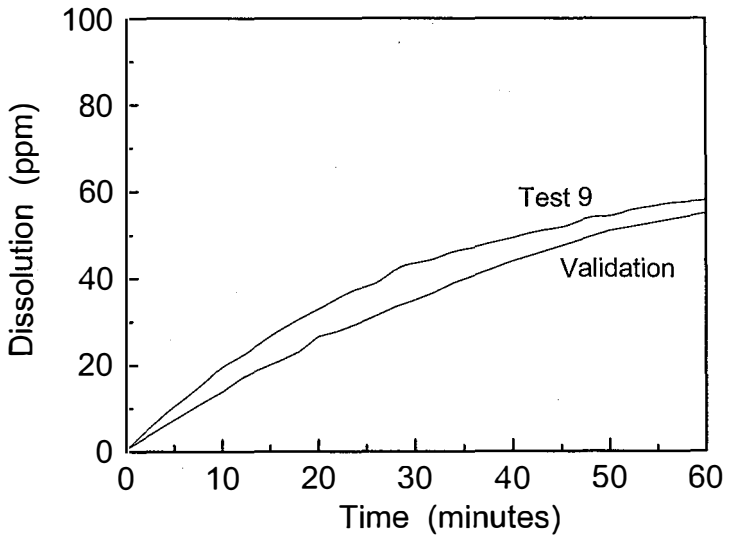


Figure 7. Dissolution of coatings after immersion in a tris buffer solution at pH 7.3 for 1 hour.

Concluding remarks

The spray parameters developed for powder XPT-D-703 exhibit characteristics that satisfy the specifications for implantation by Vimek Pty Ltd, according to SPEC-009-01.

This report has been compiled by Dr. Karlis A. Gross

December 3, 2003