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RESEARCH AND EDUCATION

Evaluation of reproducibility of the chemical solubility of dental ceramics using ISO 6872:2015

ABSTRACT

Statement of problem. The current chemical solubility method in the International Standards Organization (ISO) 6872 (2015) specifies only the total surface area of specimens for testing ($\geq$30 cm^2) but does not describe the morphology or geometry. This could impact the reproducibility of the test outcomes.

Purpose. The purpose of this in vitro study was to investigate the factors influencing the reliability of the ISO 6872:2015 'Dentistry - Ceramic materials' test for chemical solubility.

Material and methods. Chemical solubility analysis of a range of materials and specimen geometries was performed in accordance with ISO 6872:2015. Yttria-stabilized tetragonal zirconia polycrystal (Y-TZP), Vitablocs Mark II, IPS e.max Press, and IPS e.max ZirPress materials were formed into a range of cubic and spherical geometries to comply with the 30 cm^2 minimum surface area requirement. The surface microstructure of the specimens was analyzed by scanning electron microscope, inductively coupled plasma optical emission spectrometry (ICP-OES) was used to analyze the solutes, and surface hardness of the specimens was measured using a Vickers hardness tester before and after testing. An optimized solubility test was devised which eliminated specimen handling once the specimens had been ground and polished. This modified test was performed on Vitablocs Mark II and Y-TZP.

Results. The results of the original chemical solubility method of ISO 6872:2015 showed significantly variable findings for each tested material, with a predictable relationship between

geometry and chemical solubility. The hardness values decreased significantly after the solubility testing. The optimized method showed significantly improved reproducibility of the chemical solubility measurement compared with that of the original ISO 6872:2015 test.

Conclusions. The results of the current chemical solubility standard method can be manipulated while still complying with the ISO 6872:2015 standard.

CLINICAL IMPLICATIONS

A standard reproducible chemical solubility test is essential to evaluate the chemical durability of dental ceramic restorations to be placed in the oral cavity.

INTRODUCTION

As dental ceramics in the oral environment are prone to dissolution from chemical attack,[1] solubility must be assessed accurately and reproducibly. The broad pH and temperature ranges in the oral cavity might have secondary effects on the durability of ceramic restorations, requiring a reliable test to confirm that the material is not susceptible to significant damage.[2-4] In general, the microstructure patterns for glass-ceramics have indicated that the chemical solubility process is mostly linked to the glass-phase structure, while, for zirconia, it is probably related to low temperature degradation (LTD).[5-7] Since 1978, the solubility of dental ceramics has been measured with a method based on the British Standards Institute (BSI) Standard "Dental porcelains for jacket crowns."[8] Currently, the chemical solubility of dental ceramics is measured by the standardized testing method International Standards Organization (ISO) 6872 "Ceramic materials," which is an accelerated test that immerses specimens of known surface area in 4% acetic acid at 80 °C for 16 hours.[9-11] The standard determines the level of the accepted solubility

of both directly and indirectly exposed dental ceramics ("enamel" and "core") to this simulated oral environment by a measurement based on mass loss per unit of surface area. 'Enamel' class dental ceramics should display a maximum of 100 $\mu g/cm^2$ mass loss, whereas 'core' class ceramics must show less than 2000 $\mu g/cm^2$. Considering the changes happening at the surface of dental ceramics after long exposure to a wet environment, a variance in mechanical properties such as hardness after solubility testing could indicate a change in the surface microstructure.[12-16]

The most recent specification of the ISO test (2015) requires only a known total surface area ($\geq$30 cm^2) but does not describe the test specimen morphology or geometry. While allowing for the testing of an increasingly diverse range of dental ceramics, with different production methods, this modification could have a considerable impact on the reproducibility of the test outcomes.[17] The purpose of this in vitro study was to investigate the relationship between permitted specimen geometries in the ISO specification and the resulting chemical solubility of a range of dental ceramics, with a view to optimizing the current chemical solubility method of ISO 6872:2015. In addition, the hardness values of the specimens before and after solubility testing were used to assess changes to the surface microstructure. The null hypothesis was that the chemical solubility of dental ceramics is independent of specimen morphology and geometry.

MATERIALS AND METHODS

A selection of materials and specimen geometries were prepared in accordance with ISO 6872:2015. Yttria-stabilized tetragonal zirconia polycrystal (Y-TZP) (StarCeram Z-Al-Med-HD; H.C. Starck GmbH), feldspar glass-ceramic (Vitablocs Mark II; VITA Zahnfabrik GmbH), lithium disilicate glass-ceramic (IPS e.max Press; Ivoclar Vivadent AG), and fluorapatite glass-ceramic (IPS e.max ZirPress; Ivoclar Vivadent AG) were used in this study.

Cubic (C) and spherical (S) specimens were prepared with a minimum total surface area of 30 cm^2. Table 1 shows the individual specimen surface area and the number of specimens needed to produce a total surface area above 30 cm^2. The size of the material available from the manufacturer limited the maximum individual specimen surface area for Vitablocs Mark II (7.5 cm^2), IPS e.max press (6.0 cm^2), IPS e.max ZirPress (6.0 cm^2), and Y-TZP (10 cm^2).

For the Y-TZP specimens, 3-dimensional designs were created using computer-aided design (CAD) software (Tinkercad; Autodesk Inc) and then machined using a 5-axis dental milling machine (DWX-50; Roland DG Ltd). For the cubic specimens (C), each surface of the specimens was polished using a grinder polisher (Buehler Metaserv; ITW Test & Measurement GmbH) using silicon carbide (SiC) grinding papers of P600, P800, and finally P1000. The spherical specimens (S) were finished and polished using a tumbling polisher. Identical grade SiC grinding papers were pasted on the internal walls of the tumbler. The Y-TZP specimens were sintered after finishing (Ceramill Therm;Amann Girrbach AG) to achieve the planned size and density.

Vitablocs Mark II specimens were cut to the required dimensions using a diamond blade sectioning saw (ISOMet 1000; ITW Test & Measurement GmbH) equipped with a 0.5mm thick diamond wafering blade. IPS e.max Press and IPS e.max ZirPress were fabricated using hot pressing. The selected specimen morphology was designed using CAD (Tinkercad; Autodesk Inc) and milled in a clean-burning wax (DWX-50; Roland DG Ltd). The wax patterns were then invested (IPS PressVEST Speed Powder; Ivoclar Vivadent AG) and hot pressed (Programat EP 3000; Ivoclar Vivadent AG). All specimens were polished using the same method and to the same standard as the Y-TZP specimens.

Chemical solubility testing was performed in accordance with ISO 6872:2015. Distilled water (grade 3 as per ISO 3696) was used to wash the specimens, which were placed in a clean and dry glass jar. The glass jar was placed at 150 ±5 °C in a thermostatically controlled oven for 4 hours, removed using plastic tweezers, and left for 15 minutes to cool. The specimens were weighed to the nearest 0.1 mg (AJ100; Mettler Toledo Ltd) and then immersed in 100 mL acetic acid 4% (by volume) in a 250-mL Pyrex glass bottle. The glass bottle was sealed with a glass slab to prevent evaporation and placed in a preheated oven to 80 ±3 °C for 16 hours. The specimens were removed, washed with distilled water, dried to constant mass at 150 ±5 °C, and then reweighed to the nearest 0.1 mg. Chemical solubility was determined by calculating the mass loss of the specimens in $\mu g/cm^2$: (chemical solubility ($\mu g/cm^2$) = weight loss (μg) / surface area (cm^2). For each geometry, Vitablocs mark II, IPS e.max Press, and IPS e.max ZirPress were tested once, as per the ISO 6872:2015, while testing on Y-TZP was performed in triplicate to determine any variability in the measurements.

Inductively coupled plasma optical emission spectrometry (ICP-OES) was used to determine the chemical composition of the solutions used to dissolve Y-TZP. Y-TZP powders were collected after milling and dissolved in either a mixture of sulfuric (H_2SO_4) and hydrofluoric (HF) acids or in 4% (v/v) acetic acid using a digestion bomb at 200 °C. The dissolved solutions were analyzed using ICP-OES (Ciros Vision; SPECTRO Analytical Instruments Inc) to determine the composition of the Y-TZP powder and whether acetic acid could dissolve Y-TZP. The acetic acid solution was then passed through an 8 µm pore-size filter and re-analyzed to determine whether particulate zirconia was present in the solution. Filtered samples of acetic acid were collected at the end of the C1.5 and C10 solubility experiments to determine the composition of the solution after the test. To determine whether the duration of

exposure was a factor in the concentration and composition of the solution, experiments were performed where C1.5 and C10 specimens were exposed to 4% (v/v) acetic acid for 7 days at 80 °C and the solutions were once again analyzed using ICP-OES.

Qualitative surface microstructure (before and after testing) for Y-TZP, Vitablocs Mark II, IPS e.max Press and IPS e.max ZirPress was determined using scanning electron microscopy (Inspect F50; FEI Co).

Vickers hardness (Foundrax hardness indenter; Foundrax Engineering Products Ltd) was determined with a load of 9.8 N and a dwell time of 15 seconds for 10 specimens from each test group. Five indentations were measured per specimen, and an average hardness was calculated.[12,13] This test was performed on Y-TZP and Vitablocs Mark II materials before and after solubility testing.

To determine whether specimen handling impacted the solubility, further tests were performed with changes made to the washing and weighing procedures detailed in ISO 6872:2015. Rather than removing and replacing the specimens to wash and weigh them, they were left inside the 250-mL Pyrex flask during the whole experiment to minimize physical contact. The specimens were washed in distilled water using an ultrasonic bath for 5 minutes, and the water was removed using an automatic pipette (Gilson Pipetman G; Scientific Laboratory Supplies) before the drying step. The Pyrex flask was washed, dried, and weighed before and after the specimens were immersed in the acidic solution as prescribed by the ISO to determine mass loss.

All chemical solubility values were statistically evaluated using a full factorial ANOVA with a Bonferroni post hoc test (α=.05). An independent *t* test was performed to compare the average hardness values of the specimens before and after the chemical solubility testing.

RESULTS

Figure 1 shows the relationship between the solubility rate and the individual surface area of Vitablocs Mark II, IPS e.max Press, and IPS e.max ZirPress. A downward trend in chemical solubility rate with increasing individual specimen size was observed for all materials. The statistical analysis showed a significant difference among groups for each of the materials tested ($P<.05$).

Figure 2 shows the relationship between the solubility rate and the individual surface area of cubic and spherical groups of Y-TZP. Again, a downward trend in chemical solubility rate with increasing individual specimen size was observed. The overall chemical solubility rates of spherical morphologies were lower than those of the corresponding cubic morphologies. The statistical analysis showed a significant difference among these groups($P<.05$).

The results of ICP-OES (Table 2) show high amounts of zirconium (64000 µg/L) and yttrium (42100 µg/L) in the Y-TZP powder digested in H_2SO_4/HF at 200 °C. The specimen digested in 4% acetic acid at 200 °C showed lower amounts of zirconium (5000 µg/L) and yttrium (700 µg/L). Upon filtering, the amount of zirconium decreased by more than 600%, and the amount of yttrium decreased by around 50%. Specimens of both tested groups C1.5 and C10.0 (16 hours in 4% acetic acid at 80 °C) revealed only small amounts of zirconium and yttrium. The amount of yttrium present was 10 times larger than the amount of zirconium for group C1.5, and 5 times larger for group C10.0. For extended-time specimens (7 days), ICP-OES showed only small amounts of both elements for each group. The results showed that the amount of yttrium was twice the amount of zirconium for both C1.5 and C10.0 groups. Particulates were detected in the solutions of all specimens after solubility testing.

Figures 3 to 6 show SEM images of Vitablocs Mark II, IPS e.max Press, IPS e.max ZirPress, and Y-TZP. For all tested materials, the images showed a higher surface roughness after solubility testing, with increased damage at edges and corners. The images showed that the Vitablocs Mark II and IPS e.max Press specimens were more damaged by the solubility testing than the IPS e.max ZirPress and Y-TZP specimens. For both Vitablocs Mark II and Y-TZP, an independent *t* test showed that the average hardness of the specimens significantly decreased after chemical solubility testing ($P<.05$). The results showed that the hardness of Y-TZP reduced by approximately 21% after chemical solubility testing and by 28% for Vitablocs Mark II (Fig. 7). Figure 8 shows the relationship between the solubility rate and the individual surface area for Vitablocs Mark II, Y-TZP cubes, and spheres tested using the optimized methodology.

DISCUSSION

The null hypothesis, which stated that the chemical solubility was independent of specimen morphology and geometry, was rejected. The results showed that the highest chemical solubility was observed in specimens with the smallest individual surface area for both the cubic and spherical specimens, with the cubic specimens dissolving more readily than the spherical specimens, for all materials. For the cubic specimens, the total edge length and number of corners increased as the individual specimen size decreased, indicating a positive relationship between the total edge length, the number of corners and the chemical solubility rate. This suggests that specimens with a larger radius of curvature dissolve more readily, leading to faster dissolution in specimens with an increased total edge length (as observed in the smaller cubic specimens) and in smaller spherical specimens, but to a lesser extent. These results indicate that the ISO6872:2015 test for chemical solubility can be manipulated by altering the geometry and

morphology of individual test specimens while still complying with its stipulations, making comparison of the chemical solubility values found in the literature difficult.

As expected, ICP-OES showed that zirconium (Zr) and yttrium (Y) are the main constituents of the Y-TZP specimens, as shown by the results of the powders dissolved in H_2SO_4/HF. The specimens digested in acetic acid dissolved into the same constituents, and filtering the specimen decreased the mass of the Zr and Y by more than 600% and 50% respectively. The ICP-OES results from the specimens tested for chemical solubility show that, while the amounts are small, Y-TZP does dissolve in acetic acid, confirming findings from Kvam and Karlsson.[18] While the chemical solubility of the specimens increased with decreasing individual specimen size, there was no concordant increase in Zr and Y in the solutions analyzed with ICP-OES. This suggests that most of the mass lost during the solubility experiment was from particulates which had detached from the surface of Y-TZP specimens during the tests.

The SEM images showed that the specimen edges and corners were more susceptible to damage than the flat surfaces of a specimen for all materials. This could explain the large difference of the solubility rates between cubic and spherical groups, as the sphere did not have edges and corners. The increased damage on the edges and corners could be from an increase in dissolution in these areas compared with the flat surface, a percussive effect on these weak areas, or a combination of both.

The hardness of both Y-TZP and Vitablocs Mark II showed a significant reduction after immersion in 4% acetic acid at 80 °C, a finding confirmed generally for dental ceramics.[13] Conflicting findings have been reported regarding mechanical properties of Y-TZP as a result of low temperature degradation (LTD), a phenomenon resulting from the exposure of zirconia-based materials to the humid environment, either intraoral or implanted. Some studies have

concluded that there is no change in mechanical properties such flexural strength after LTD, whereas other studies have reported a reduction in the Young modulus and hardness up to 30% after LTD.[12-15]

The chemical solubility, ICP-OES, SEM, and hardness results indicate that percussive effects during the washing and drying stages of the test are a significant factor in the mass loss. The optimized method that removed the operator handling factor showed no significant difference in chemical solubility between cubes and spheres of Y-TZP or between cubes of different size in both Y-TZP and Vitablocs Mark II. This finding confirms that chemical solubility, as determined by ISO-6872:2015, is dramatically influenced by the percussive nature of transferring the specimens to and from the flask used for solubility testing.

With the optimized method, it can take a significantly longer to remove fluids from the glass jar with a conventional automated pipette designed for smaller volumes of liquid. A possible criticism of this method is that some of the dissolved particulates were dislodged from the specimen but were not removed from the conical flask during pipetting. This would result in their mass being included in the remaining weight of the material. Residues of this type were not noted in the flask but may not necessarily be visible to the operator.

A further criticism is that the polishing regimen for the spherical specimens was not identical to that used for the cubic specimens. While the interior part of the tumbler was covered with identical grade polishing papers as used to finish cubic specimens, measuring the surface roughness was impossible because of the curved surface of spheres. SEM images were instead used to visually confirm similar surface roughness between spherical specimens and the groups of each shape to standardize the test parameters.

Interestingly, the chemical solubility of Vitablocs Mark II failed to achieve an acceptable chemical solubility value for the 'enamel' class of dental ceramics[11] of 100 µg/cm^2 for either the standard or the optimized methods. As Vitablocs Mark II are considered clinically acceptable, the maximum solubility value for enamel class materials could be reconsidered and increased to around 150 µg/cm^2.

CONCLUSIONS

Based on the findings of this in vitro study, the following conclusions were drawn:

1. The chemical solubility methodology in ISO 6872:2015 is dependent on the geometry and morphology of the individual test specimens while still complying with its stipulations.
2. Physical handling required by the ISO standard damages the specimens, which leads to variability in the results.
3. Cubic specimens were more damaged on their edges and corners, as shown by SEM.
4. ICP-OES results confirmed that the reduction in mass, and therefore the increase in solubility, was due to physical loss of material (at edges/corners) rather than dissolved material, which would have been present in the solution.
5. The hardness results confirmed that the specimens were less resistant to indentation after exposure to the acidic solution.

   The optimized method used demonstrated that when specimen handling was limited, chemical solubility was independent of specimen geometry and morphology.

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TABLES

Table 1. Possible geometries of specimens (cubes or spheres)

Individual surface area (cm^2)	Edge length of a cube (cm)	Diameter of a sphere (cm)	No. of specimens required for 30-cm^2 area
1.5	0.50	0.70	20
3.0	0.71	1.00	10
4.3	0.85	1.18	7
6	1.00	1.40	5
7.5	1.12	1.56	4
10	1.30	1.80	3

Table 2. Amount of zirconium and yttrium in µg/L using inductively coupled plasma optical emission spectrometry

Sample I.D.	Zr (µg/L)	Y (µg/L)
Blank/H_2SO_4/HF	640000	42100
Blank/acetic acid	5000	700
Blank/acetic acid (filtered-8µm)	7.5	375
C1.5/16-hours	0.006	0.056
C10/16-hours	0.011	0.050
C1.5/7-days	0.049	0.077
C10/7-days	0.021	0.042

FIGURES

Figure 1. Relationship between chemical solubility rate and individual surface area of Vitablocs Mark II, IPS e.max Press, and IPS ZirPress (cubes). Dotted line shows maximum acceptable chemical solubility (100 µg/cm^2) for enamel ceramics according to ISO 6872:2015 (bars represent standard deviation). (n=1).

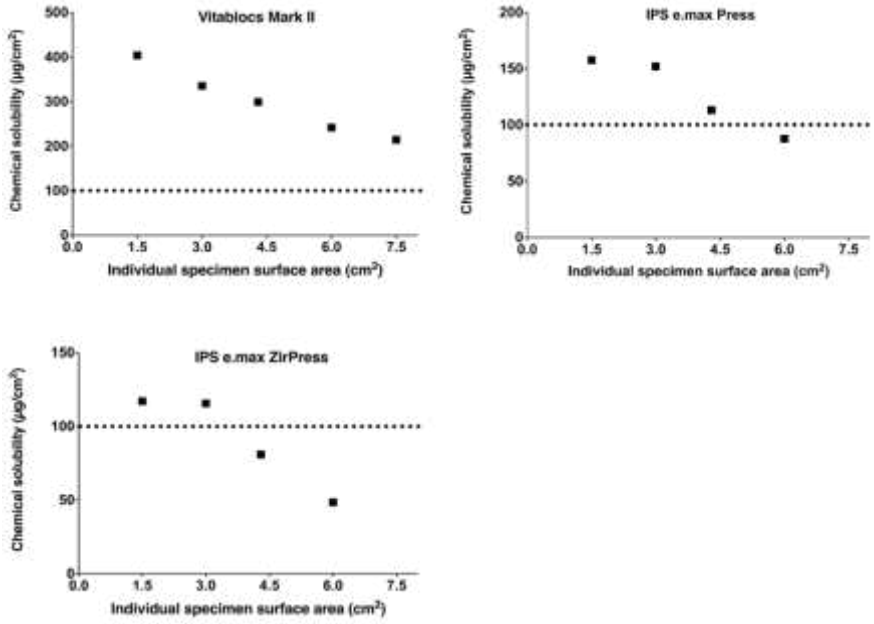


Figure 2. Comparison between average chemical solubility and individual surface area of Y-TZP cubes (*black*) and spheres (*grey*). Dotted line shows maximum acceptable chemical solubility (100 µg/cm^2) for enamel ceramics according to ISO 6872:2015 (bars represent standard error). (n=3).

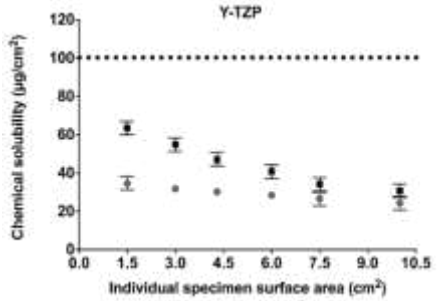


Figure 3. Scanning electron micrographs of Vitablocs Mark II before (left) and after (right) solubility testing (surface, edge, and corner). Scale bar equals 200 µm. Original magnification ×500.

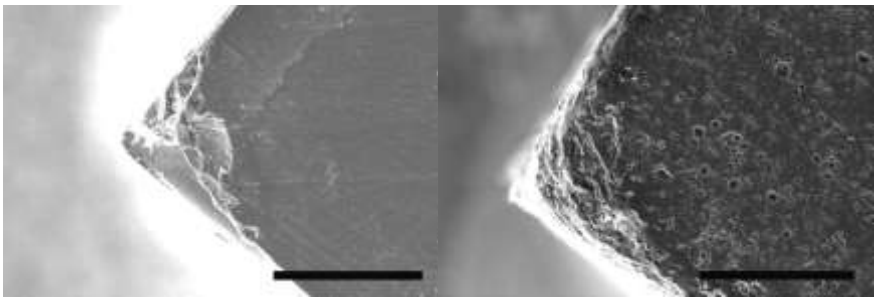


Figure 4. Scanning electron micrographs of IPS e.max Press before (left) and after (right) solubility testing (surface, edge, and corner). Scale bar equals 500 µm. Original magnification ×250.

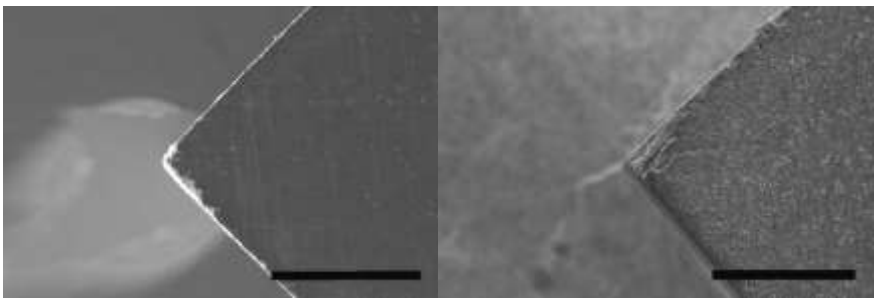


Figure 5. Scanning electron micrographs of IPS ZirPress before (left) and after (right) solubility testing (surface, edge, and corner). Scale bar equals 100 µm. Original magnification ×250.

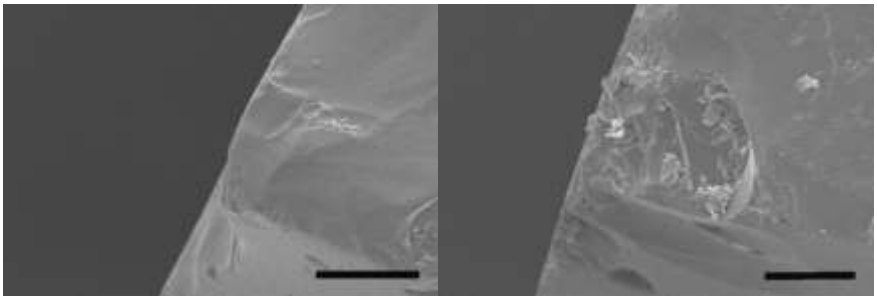


Figure 6. Scanning electron micrographs of Y-TZP before (left) and after (right) solubility testing (surface, edge, and corner). Scale bar equals 500 µm. Original magnification ×250.

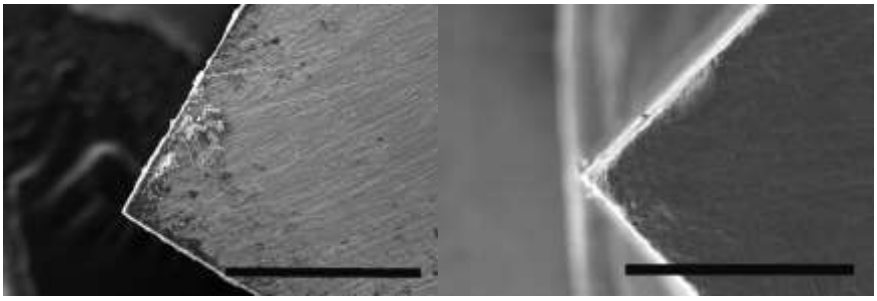


Figure 7. Difference of average hardness values of both Y-TZP and Vitablocs Mark II specimens before and after chemical solubility tests (bars represent standard deviation) (n=10).

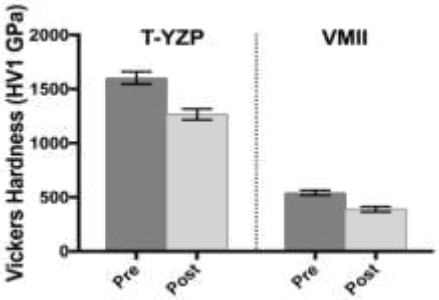
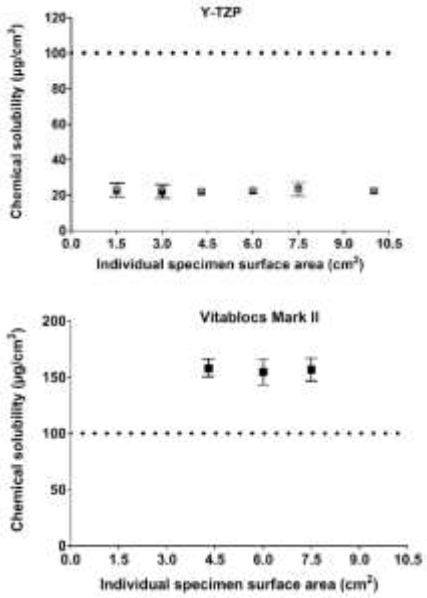


Figure 8. Comparison between average chemical solubility and individual surface area cubes (*black*) and spheres (*grey*). Dotted line demonstrates maximum acceptable chemical solubility (100 µg/cm^2) for enamel ceramics according to ISO 6872:2015 (bars represent standard deviation). (n=3) A, Y-TZP. B, Vitablocs Mark II.


Y-TZP
Chemical solubility (µg/cm²)
120
100
80
60
40
20
0
0.0
1.5
3.0
4.5
6.0
7.5
9.0
10.5
Individual specimen surface area (cm²)
Vitablocs Mark II
Chemical solubility (µg/cm²)
200
150
100
50
0
0.0
1.5
3.0
4.5
6.0
7.5
9.0
10.5
Individual specimen surface area (cm²)