

## FTIR and SEM of a novel chemical conditioning on the zirconia intaglio surface.

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**Abstract:** Objectives: The aim of this study was to evaluate chemical and topographical changes in the intaglio zirconia surface induced by chemical conditioning solutions using FTIR and SEM analysis. Material and method: twelve plates for each FTIR and SEM tests from each zirconia materials (UPCERA HT White, BruxZir® Solid Zirconia, and Copran® Multilayer), milled by a Yenadent CAD/CAM system, sintered and divided randomly into a three groups. A different surface conditioning was applied to the intaglio surface of each group: 30% hydrogen peroxide, 30% citric acid and control group. Result and discussion: by using of the FTIR spectroscopy, an evidence of new bands formation appeared at 1637cm<sup>-1</sup> and 3352cm<sup>-1</sup> due to the high oxidizing effect of hydrogen peroxide, and at 630cm<sup>-1</sup> and 1663cm<sup>-1</sup> due to the chelating action of citric acid, and simultaneously, SEM assessment of the surface topography took place, to identify lines, scratches, or surface dissociation that appeared on the intaglio zirconia surface after conditioning. Conclusion: such analysis provides an enhancement of new convenient, less expensive, reliable trials to improve micro-bond strength of luting cement to Y-TZP ceramics.

**Keywords:** Zirconia; citric acid; hydrogen peroxide; Fourier transform infrared spectroscopy; Scanning Electron Microscopy.

## INTRODUCTION.

Yttria-stabilized tetragonal zirconia polycrystal (Y-TZP) is an inert metal-free ceramic with superior esthetical properties.<sup>1</sup>

Three mol% yttrium oxide is the most widely used stabilizer for dental zirconia. Alternative surface modification and treatment techniques are indicated to obtain good luting cement/zirconia adhesion by formation of micromechanical retention and/or chemical bonds between the ceramic surface and the cement.<sup>2</sup>

In spite of several methods and studies regarding zirconia surface modifications having been evaluated for the enhancement of the luting of cement to zirconia, there is still no consensus regarding the best surface modifications to achieve optimal cement/zirconia adhesion.<sup>3</sup>

The objective of the present study was to evaluate the chemical and topographical changes in intaglio dental zirconia surfaces induced by a specific chemical conditioning solutions using Fourier-transform infrared

spectroscopy (FTIR) and scanning electron microscopy (SEM) techniques.

FTIR spectroscopy allows for a quick differential identification of typical dental materials produced from organic compounds for inorganic restorations. The SEM analyses allow the observation of the topography details of the surfaces.<sup>4</sup>

## MATERIALS AND METHODS.

For FTIR spectroscopy analysis, 12 zirconia plates (15.0mmx 5.0mmx 1.0mm) were prepared and milled from zirconia blocks. Three specimens were prepared from each material source: Framework Blank UPCERA HT White, China (UH); Full Dental Zirconia Blank colored with Zircoloy™ Coloring system (BC); non-colored (BN) BruxZir® Solid Zirconia, USA; and Full Dental Zirconia Blank Copran® Zr-i Monolith Symphony, White-peaks Multilayer, Germany (MM).

A Yenadent dental CAD/CAM system was used for specimens preparation.

Once milling process was completed, the specimens were carefully separated from the zirconia blanks and their margins adjusted with football shaped fine fissure diamond burs (379-023M-HP, NTI-Kahla GmbH rotary instruments, Germany). According to the manufactural instructions zirconia specimens sintered in a furnace (Kavo Everest® Therm, Kavo, Germany). For each specimen there were two base surfaces, the outer contour and the intaglio surface.

The outer contour surface of the specimens prepared from BC, BN, and MM were finely ground, polished, cleaned, dried, and finally a glaze-fired to simulate the external finished surface of the extra coronal restoration and to eliminate any evidence of flaws and defects on that surface.

The outer contour surface of the specimens prepared from UH remained as they were to simulate the external surface of the core of the extra coronal restoration. Then all specimens were ultrasonically cleaned for 15 minutes using Bio Sonic® UC50DB before any testing.

According to conditioning surface that preformed on their intaglio surfaces the specimens for each type of zirconia materials were assigned randomly into three groups:<sup>1</sup> control group; 30% hydrogen peroxide (HP)

(TEDIA company INC, China) applied for 5min; and 30% citric acid (CA) (Loba Chemie Pvt. Ltd., India) applied for 10 min.

A FTIR Spectrophotometer (ALPHA, Bruker, Germany) was used to measure the vibrations of bonds and determine if there were changes in structural, chemical and band condition of the zirconia material after being chemically conditioned.

For the SEM analysis, another similar 12 specimens of prepared zirconia materials were assigned to groups as described, and the intaglio surface was conditioned in the same manner mentioned above, were then coated with gold palladium and examined with a scanning electron microscope (SEM, TESCAN, USA), to observe their ultra-structure surface changes.

## RESULTS.

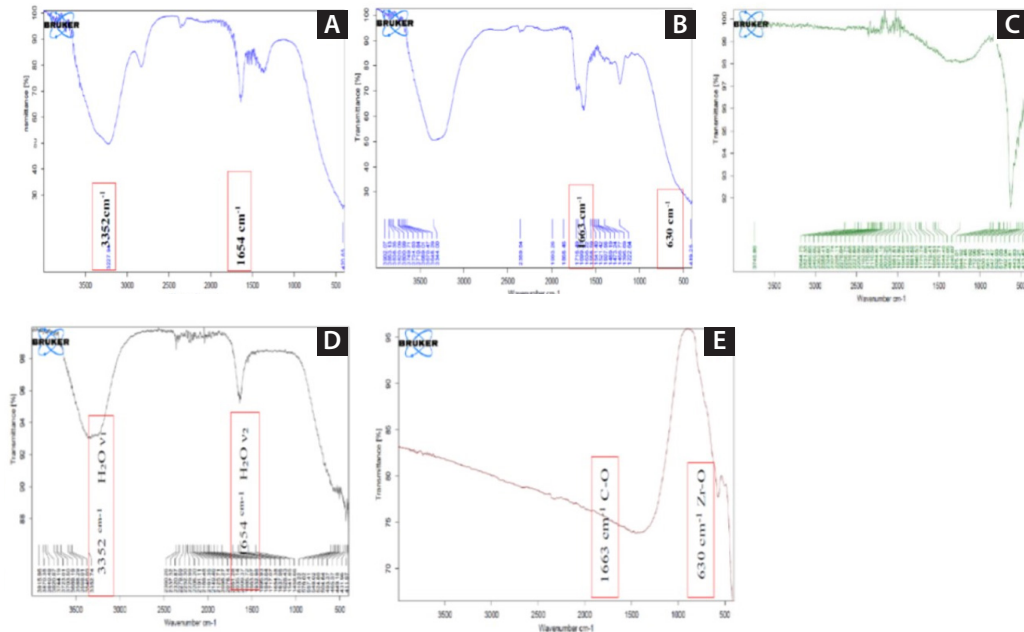
FTIR spectra charts of the base line state for HP, CA and UH zirconia are shown in Figure 1A, 1B, and 1C. Four important absorbance bands appeared at 3352 cm<sup>-1</sup>, 1654cm<sup>-1</sup>, 1663cm<sup>-1</sup> and 630cm<sup>-1</sup> regions, as illustrated in Figure 1A and Figure 1B. After condition UH zirconia with HP a new band formation appeared at 3352cm<sup>-1</sup> (that assigned to the broad H<sub>2</sub>O  $\nu_1$  stretching band) and at 1654cm<sup>-1</sup> (which was corresponding to medium H<sub>2</sub>O  $\nu_2$  stretching band). (Figure 1D)

In UH zirconia condition with CA a new bond formation appeared at the 1663cm<sup>-1</sup> region (that was assigned to a strong C-O stretching bond formation) and at 630cm<sup>-1</sup> (which was corresponding to strong Zr-O coordinated stretching complex bond formation) which consisted of an intermediate/complex of citric acid and metal ions and named zirconia-citrate complex. (Figure 1E)

For the three other zirconia types (BC, BN, and MM) the same new bands appeared as described for UH zirconia after conditioning with HP and CA solutions.

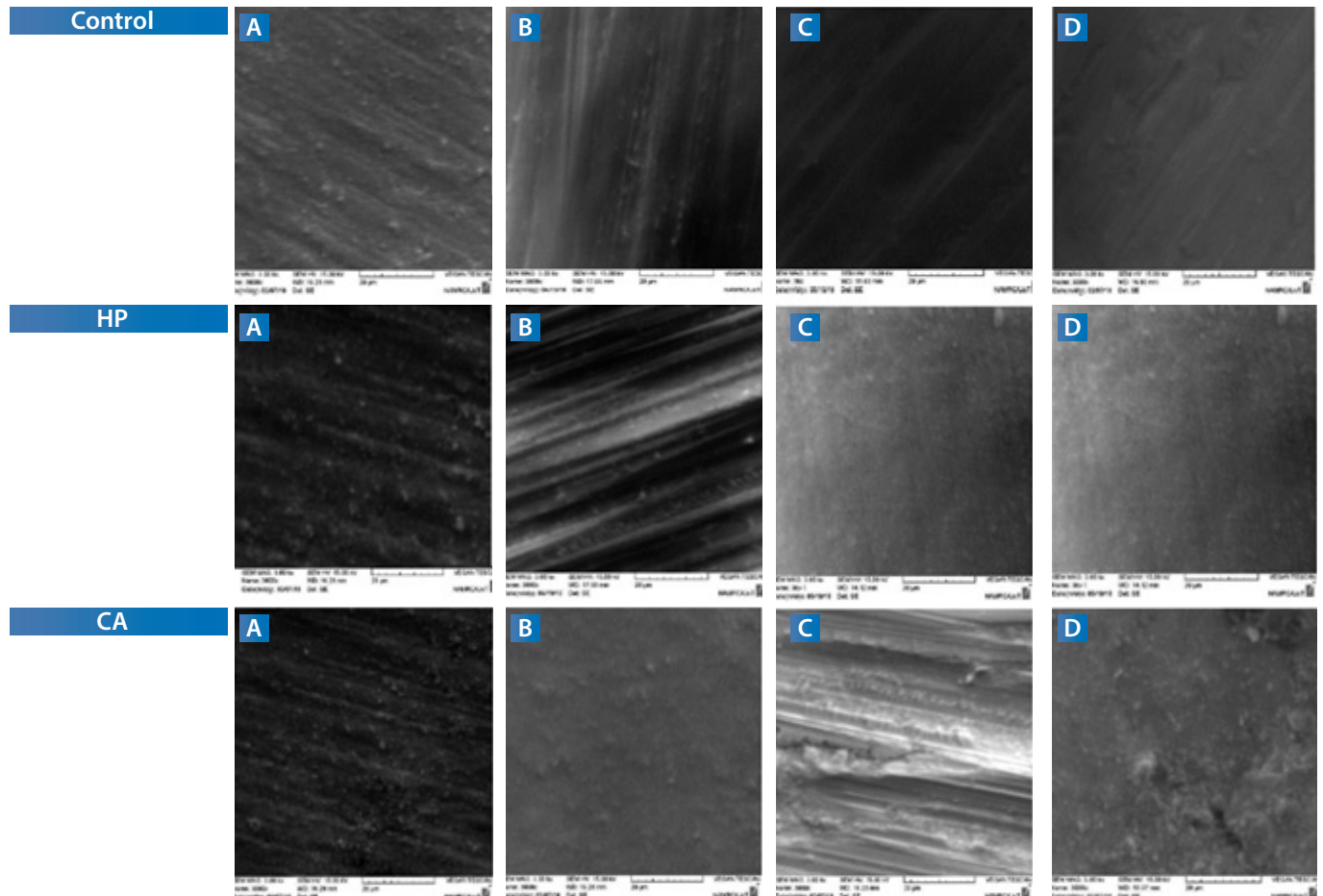
Additionally, SEM analysis showed evidence of dissociation, lines, scratches, and deformations on the intaglio surface of the zirconia materials after chemically conditioning with HP or CA solutions compared to the control groups. (Figure 2)

Figure 1. FTIR spectra.



HP (1A) and CA (1B) solutions in base line state showed the important absorbance bands responsible for their reaction with the zirconia materials in the range of 500-4000cm<sup>-1</sup>. UH zirconia in base line state (1C). UH zirconia after chemically conditioning showing evidence of the absorbance bands related to the use of HP (1D) and CA (1E).

Figure 2. Scanning electron microscopy of zirconia materials.



A and D show dissociation and deformation of the UH and MM zirconia surfaces while A, B and D showed a lines, and scratches on the BC, BN and MM zirconia intaglio surfaces as a result of a chemical conditioning either by HP or CA compared to their control groups (Control, HP, and CA). CA (C) showed darkness appearance of BN after conditioned with CA. (At 3000 X magnification).

## DISCUSSION.

Infrared spectroscopy (IR) is an analytical technique that uses the spectral information characteristics of the individual substances. In terms of analytical chemistry, the wave number (wavelength) range used in IR is between  $4000\text{cm}^{-1}$  and  $400\text{cm}^{-1}$  ( $2.5\mu\text{m}$  and  $25\mu\text{m}$ ) corresponding to an energy absorbed between 11 to 1kcal/mole.

Representative IR spectroscopy, a very powerful identification method for the functional groups where most fingerprint appeared beyond this  $1650\text{cm}^{-1}$  region, which is the most important area of the IR spectrum. But the  $600\text{-}1500\text{cm}^{-1}$  fingerprint region of the spectrum cannot be easily used for unknown compounds identification. So, infrared spectroscopy can provide a positive qualitative identification of different kinds of material.

In addition, the spectrum peaks size are considered as a direct indication of the amount of material present. With modern software algorithms, infrared is an excellent tool for quantitative analysis, so FTIR provides both a qualitative and quantitative analysis.<sup>5</sup>

To identify the changes for UH zirconia after conditioning it was compared to the base line charts for both the conditioned solutions alone and the zirconia material before conditioning.

Hydrogen peroxide conditioning (Figure 1D) resulted in the presence of new bands at  $3352\text{cm}^{-1}$  and  $1654\text{cm}^{-1}$ , within the zirconia intaglio surface. The highly oxidizing effects of HP on the zirconia lattice was responsible for such new bands formation, and with evidence of the liberation of water molecules.<sup>6</sup>

While for CA conditioning, Figure 1E showed a new strong band that appeared at  $1663\text{cm}^{-1}$  as a result of the chelating effect between the CA carboxyl groups and zirconium ion. Also a new band appeared at the  $630\text{cm}^{-1}$  region corresponding to the stretching (Zr-O) zirconia-citrate complex bond formation (shifting of the carboxyl group and distortion in the bands due to the coordination).<sup>7</sup>

The FTIR analysis was used in this study to

investigate chemical structural changes in the zirconia after different surface chemical conditioning. From FTIR analysis. (Figure 1)

There were alterations in bands, new band formation, and a significant shift of bands evident in the IR charts of the tested zirconia materials as a result of chemically surface conditioning compared to the respective base line IR charts. Such alterations may result from the chemical coordination between the zirconia materials and conditioning solutions.

The specific chemical and topographical changes appeared within the zirconia intaglio surfaces were a result of such alteration. Such findings are in agreement with some investigators who observed that the benefit of using the FTIR spectroscopy as a quick differential identification analysis for typical dental materials changes concerning chemical functional groups of material chemical compositions. In other words, there was evidence of chemical changes in the nature of the zirconia materials, responsible for increasing the micromechanical topographical irregularities of their intaglio surface.<sup>8</sup>

By aid of FTIR spectroscopy such finding is in agreement with researchers who examined the dissolution effect of a fluoridated chemical conditioning solutions on the  $\text{ZrO}_2$  that gave a rough etched zirconia surface that may be suitable for good and durable resin luting cement/zirconia adhesion.<sup>2</sup>

The intaglio surface of the zirconia material (Figure 2) showed a dissociation and deformation in the of UH and MM zirconia surfaces, while lines and scratches on the BC, BN and MM zirconia intaglio surfaces were shown as a result of chemical conditioning either by HP or CA compared to the respective control groups.

This finding is in agreement with authors who have stated that surface modifications used for roughening zirconia prior to cementation, created deformations, lines, and scratches on that surface. Such surface alteration probably improve their micromechanical retention and bonding to zirconia.<sup>9</sup> The darkened appearance of SEM image of the CA conditioned BN

zirconia compared to its control and other conditioned zirconia material groups (Figure 2C and Figure 3C) may be due to two reasons: Firstly the BN zirconia fine particle size make the anti-agglomerated chelating action of CA more prominent with the formation of a ligand exchange reaction complex.<sup>10</sup> Secondly, ZrO<sub>2</sub> chelation was more evident due to a low presence of the coloring agent within its content.

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## CONCLUSION.

With limitations of such *in vitro* type studies, FTIR spectroscopy and SEM analyses allowed for an accurate quick identification of the chemical and topographical changes in intaglio zirconia surface conditioned with either HP or CA, and may be considered as new convenient, less expensive, reliable methods for a bond strength improving of a luting cement to Y-TZP ceramics.

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