**IN VITRO ANALYSIS OF DENTAL CERAMICS: EVALUATION OF THE RADIOPACITY AND CHEMICAL COMPOSITION BY RAMAN SPECTROSCOPY**

Abstract

Objective:This study compare the radiopacity of different ceramic systems by means of digital radiographs and evaluate the chemical composition of the samples by Raman spectroscopy. Materials and methods: The hypothesis tested was that there was a difference in radiopacity among the tested materials. Specimens were prepared for each ceramic tested: G1 - VM7 (VITA Zahnfabrik), G2 - IPS Empress e.max Press (IPS Empress), G3 - In Ceram Alumina (VITA Zahnfabrik), G4 - In Ceram Zirconia (VITA Zahnfabrik), G5 - Lava All Ceram (3M/ESPE), and G6 - Zirconzahn (Talladium Brazil). The specimens were radiographed and submitted to radiographic density readings using a histogram tool. The spectrometer coupled to a petrographic microscope was used for Raman spectroscopy measurements. Analysis of variance (ANOVA) and a Tukey post-hoc test was used to compare the groups. Results: In all tested materials, the radiopacity showed statistically significant differences, except between G5 and G6. Lava All Ceram and Zirconzahn had high radiopacity values and VM7 and IPS Empress e.max Press showed lower radiopacity than human dental structures. Conclusion: It was possible to conclude that radiopacity is closely linked to ceramic system chemical composition. Significant differences in radiopacity were found among ceramic materials.

**Keywords**: Dental ceramics, Radiopacity, Raman spectroscopy test, Restorative dentistry

**INTRODUCTION**

 Dental ceramics are the materials of choice for various esthetic restorations due to their characteristics, such as high compressive strength and abrasion resistance, chemical stability, favorable esthetic features, translucency, biocompatibility, fluorescence and thermal expansion coefficient similar to that of the dental structure1,2.

 One of the most desirable characteristics of any restorative material is a radiopacity that allows it to be distinguished from dental structures, helps with detection of secondary carious lesions, marginal defects, restoration contours, adaptation of restorations to cavity walls, contact points between adjacent teeth, cement projections, and interfacial gaps3,4 .

 Clinically, marginal adaptations to cervical and proximal margins are difficult to evaluate, especially when intragingival preparation is performed. In this case, radiopacity may help in the radiographic follow-up evaluation5,6 .

 In order to improve radiographic images, digital imaging has been proven to be an easy and fast resource. Features such as immediate image capture, patients being exposed to low levels of radiation, easy manipulation, low cost, acquisition of accurate radiodensity evaluation, and no need for developing, as in the case of traditional images, are highlighted. Another advantage is that in the evaluation of digital images, the radiographic density is easily observable, since the software can determine image pixels and have grayscale values7,8.

 The radiopacity of a material is primarily defined by the chemical elements present in its composition, with zinc, strontium, zirconium, barium, ytterbium, and lanthanum being radiopacifying elements with a high atomic number, present in the constitution of various dental materials, such as contemporary ceramic systems3.

 Raman spectroscopy allows the analysis and characterization of the vibration spectra, not only of the minerals of which the sample is composed. In this technique, more complex systems, such as dental materials, may also be evaluated by analysis of light diffusion caused by monochromatic laser excitation. This spectroscopy presents several advantages, such as simplicity of sample preparation, facility of analyzing bands, and linear response about mineral and chemical element concentrations9.

 Information on the radiopacity of different ceramics used in restorative dentistry is limited. Consequently, the aim of this study was to compare the radiopacity of different ceramic systems by digital radiography and to evaluate the chemical composition of samples using Raman spectroscopy. The study tested the hypothesis that there was a difference in radiopacity between the different tested materials.

**MATERIALS AND METHODS**

 This study was approved by Human Research Ethics Committee of the Federal University of Juiz de Fora (protocol number: 177/2010).

*Sample selection and preparation*

 Eight ceramic specimens were made for each material: G1 - VM7 (VITA Zahnfabrik, Bad Säckingen, Germany), G2 - IPS Empress e.max Press (IPS Empress, Ivoclar Vivadent, Germany), G3 - In Ceram Alumina (VITA Zahnfabrik), G4 - In Ceram Zirconia (VITA Zahnfabrik), G5 - Lava All Ceram (3M/ESPE, St. Paul, USA), and G6 - Zirkonzahn (Talladium do Brazil, Curitiba, Brazil) (Table 1).



Ceramic specimens with the same measurements were obtained for all groups (1 x 3 x 3 mm). An acrylic resin pattern was used to produce VM7, In Ceram Alumina and In Ceram Zirconia specimens. These materials were manipulated according to the manufacturers’ instructions. The ceramic specimens were placed on a refractory base in a Vacumat oven (VITA Zahnfabrik) following burning cycles as recommended by the respective manufacturers. Later, the excess was removed from the ceramic samples with diamond discs (KG Sorensen, São Paulo, Brazil)10.

 IPS Empress e.max Press specimens were fabricated using a metal matrix measuring 1 x 3 x 3 mm. The metal matrix (previously lubricated with vaseline petroleum jelly) was placed on a 10 mm-thick glass plate, also lubricated, in order to facilitate removal of the wax models afterwards. The GEO-Classic wax (RenfertGmbH, Hilzingen, Germany) was liquefied and poured onto the glass plate until the entire steel matrix cavity surface was covered. After the wax hardened, a straight sharp instrument was used to flatten it and remove excess wax. In the next step, a refractory impression was made by inverting the wax pattern in refractory material. To do this, a wax pattern was connected parallel to a cylindrical wax feeder canal (sprue). This connection was made at the edge of the pattern to enable the glass-ceramic material to penetrate into the pattern. The refractory cylinder was put into an electric ring oven EDG 3000 (EDG, São Paulo, Brazil) pre-heated to 700 °C in accordance with the manufacturer’s instructions. The next step was the injection process. A glass ceramic tablet of IPS Empress e.max Press was introduced into the central canal of the refractory mold, and then an aluminum cursor (also pre-heated) was inserted into the refractory mold. After this, the refractory mold was transferred to the hot injection chamber. At the end of this process, the refractory cylinder was removed from the oven and left on the laboratory bench to cool. When it was cold, the body-sprue was divested. The specimens were machined with a double face diamond disc (KG Sorensen) and a rubber disc with Supermax diamond paste (Edenta AG Dental, Haupstrasse, Switzerland)11.

 To construct the specimens of Lava All Ceram and Zirkonzahn, pre-sintered blocks of zirconia were used, which were sliced with a sintered diamond disc (KG Sorensen). The blocks underwent an additional sintering process in the respective ovens at 1500 oC for 4h. Shrinkage occurred in these blocks, after which they measured 1 x 3 x 3 mm12.

The final specimen thickness was measured with a digital caliper (Digimatic Caliper, Mitutoyo, Aurora, USA) confirming the final thickness of 1 mm.

The radiopacity of the ceramics was compared with that of dental structures (dentin and enamel). For this, an inferior first molar was sliced using Labcut 1010 (Excet Corp, Enfield, USA) with a diamond disc. Longitudinal slices 1 mm thick in the more central area of tooth were used.

*Radiopacity analysis*

To take the radiographs, a periapical X-ray appliance Gendex Expert DC® (Gendex, Des Plaines, USA) was used, operating at 7 mA, 65 kVp, and exposure time of 0.1 s. The object-sensor distance was kept the same, with the use of a standardized device that provided incidence of the radiation beam perpendicular to the plane in which the sensor and radiographed objects were placed. Radiographic images were obtained using a direct digital radiography apparatus Visualix eHD (Gendex). The following items were put on the sensor: a molar slice, an aluminum step wedge ranging from 1 mm to 11 mm in thickness in steps of 1 mm each, and one specimen of each tested ceramic. Three images were obtained of each radiographed set (Figure 1). They were obtained at a resolution of 1200 dpi, in TIFF format. No changes in brightness and/or contrast were made.

The radiographic density of the digital images was evaluated using the histogram tool of the Adobe Photoshop® 8.0 software (Adobe, New York, USA). With this software, mean gray values of all steps of the aluminum scale, of the studied specimens, and of the enamel-dentin of the sliced tooth were obtained. The radiopacity of the tested ceramic as well as dental structures were expressed in aluminum-equivalent millimeters (mm Al), allowing comparison among them. The comparison of the radiopacity of the different materials was done by analysis of variance (ANOVA) and a Tukey post-hoc test, with a level of significance of 5%, using BioStat software (Version 5.0, AnalystSoft, Vancouver, Canada).

*Raman spectroscopy analysis*

The Raman spectra were obtained in a Horiba Jobin-Yvon LabRam HR spectrometer, coupled with a full petrographic microscope using 10x, 50x, or 100x magnification objectives, and a Peltier-cooled (-70°C) CCD detector. A 10 mW HeNe laser with 632.8 nm wave-length was used, and neutral density filters were selected to adjust the laser power in order to avoid damage and/or transformation of the samples. Laser power over the samples was used at less than 1 mW, to avoid any thermal damage, and each spectrum was obtained at least twice to guarantee wavenumber precision and intensity reproducibility.

**RESULTS AND DISCUSSION**

 In order to compare the radiopacity of ceramic systems with that of human dental structure, the radiopacity of the tested materials, enamel, and dentin were presented in aluminum-equivalent thickness (mm Al).

 The radiopacity found for 1 mm of aluminum corresponded to radiopacity of the dentin in the same thickness, and for 2 mm corresponded to radiopacity of the enamel.

The radiopacity of all the tested materials presented statistically significant differences (p < 0.01) except between G5 (Lava) and G6 (Zirkonzahn) (Table 2).



The Raman spectra are represented in Figures 2A to 2F. They show the different chemical and behavioral patterns of each analyzed ceramic system.

 Ceramic systems should have a radiopacity similar to or higher than the aluminum-equivalent thickness in order to enable materials, marginal infiltrations, and cementation failures to be distinguished3,9. Aluminum is a comparison reference material because it has a radiopacity similar to that of dentin4, corroborating the results found in this study. The International Standards Organization (ISO 4049) established that the radiopacity of restorative materials should be equal to or greater than that of 1,100 aluminum alloy with the same thickness13.

 It is undesirable for the radiopacity of restorative materials to be lower than that of the replaced hard dental tissues. Therefore, it is important that dental ceramics, which are used to replace enamel tissue, are more radiopaque than human dental enamel1,7. Based on the aluminum scale, an aluminum equivalent of 2 mm corresponds to enamel radiographic density, and 1 mm to dentin radiographic density. The feldspathic ceramic VM7 and IPS e-max Press presented a lower density than dentin. The In Ceram Allumina showed the same radiopacity than enamel and all other tested ceramics presented higher density than enamel.

The results support the hypothesis that the radiopacity measurements of ceramic materials differ from one another. Ceramic material radiopacity is directly linked to its chemical composition. This finding was noted in this study, as there was statistical difference in radiopacity between ceramics with different chemical compositions. Only for G5 (Lava All Ceram) and G6 (Zirkonzhan) presented no statistical difference between them, confirmed by Raman spectra vibration bands that did show similar intensity and wave number values. This fact confirms that the chemical composition of the two ceramics is very similar. The superior radiopacity of Y-TZP ceramics is probably a result of the high atomic number and molecular weight of yttrium (Y, atomic number 39), zirconium (Zr, atomic number 40), and hafnium (Hf, atomic number 72)14.

Also in relation to Raman spectra, some vibrational modes characteristic of each system were found. For example, it was possible to observe a band at 1100 cm-1 in G1 and G2, which refers to the symmetrical stretching mode for the Si-O bond, while a band at 580 cm-1 corresponds to the symmetrical stretching mode for of Si-O group coupled to the deformation mode of the Si-O-Si structure15. For samples G3 and G4, the appearance of vibrational bands characteristic of ceramic materials was found to be inhibited by the emission of fluorescence resulting from the high concentration of Al2O3, as has previously been described by GOUADEC, et al.16. The appearance of bands at 148 cm-1 and 266 cm-1 was found in groups G5 and G6, which are vibrations characteristic of the tetragonal phase of ZrO2 17.

The International Standards Organization (ISO 6872)17 recommends that a spectroscopy test should be used to study the screening of specimen adulteration. This procedure was performed by Raman spectroscopy, which did not detect the presence of any impurity in the chemical composition of each tested ceramic. Furthermore, this test is an excellent tool for the characterization of the various chemical systems present in the composition of each sample, in addition to being a nondestructive analytical technique.

Although manufacturers do not show the quantity of each radiopacifying agent, it was possible to observe statistically significant differences in radiopacity values between materials and their relationships with the atomic number of components. If the atomic number is high, the material is more radiopaque3,18. Corroborating the findings of OZKURT, et al.18 and PEKKAN, et al.19, this study showed that zirconia has the highest radiopacity level. These higher levels are useful to monitor marginal adaptation by radiographic examination 6,20. But these materials, when used in the clinical practice, may mask cement dissolutions and caries, which could occur under the crown20.

The difference found in the radiopacity values is of clinical significance in radiographic evaluation. Zirconia-based materials are more radiopaque and are easier to detect in a radiographic examination. On the other hand, less radiopaque materials, such as silica-based vitreous ceramics, may be mistaken for dental structures, carious lesions, restoration failures and marginal defects. The maximum radiopacity value has not yet been established. However, extremely radiopaque materials may be difficult to identify at the tooth/restoration interface. Moderate radiopacity may be more favorable and could facilitate the detection of tooth/restoration interface3,4,21.

The adequate radiopacity must be accepted as a factor when evaluating the clinical success of ceramic restorations. Furthermore, studies are needed to compare the radiopacity of the adhesive cements used with the different ceramics systems.

**CONCLUSION**

 Radiopacity is closely linked to the chemical composition of each ceramic system. The groups containing zirconia demonstrated more radiopacity. The feldspathic ceramic VM7 and the vitroceramic of dissilicate of litium IPS Empress e.max Press presented lower radiopacity than that of human dental structures.

**REFERENCES**

**REFERENCES**

1. Conrad HJ, Seong WJ, Pesun IJ. [Current ceramic materials and systems with clinical recommendations: a systematic review](http://www.sciencedirect.com/science/article/pii/S0022391307601243?_alid=1765490308&_rdoc=1&_fmt=high&_origin=search&_docanchor=&_ct=1215&_zone=rslt_list_item&md5=f8c91c102c8f2b510219a8272f05545c). J Prosthet Dent. 2007 nov 98(5): 389-404.
2. Cavalcanti AN, Foxton RM, Watson TF, Oliveira MT, Giannini M, Marchi GM. Y-TZP ceramics: key concepts for clinical application. Oper Dent. 2009 may 34(3): 344-351.
3. Fonseca RB, Branco CA, [Soares](http://www.springerlink.com/content/?Author=Paulo+Vin%c3%adcius+Soares) PA, [Correr-Sobrinho](http://www.springerlink.com/content/?Author=Louren%c3%a7o+Correr-Sobrinho) L, [Haiter-Neto](http://www.springerlink.com/content/?Author=Francisco+Haiter-Neto" \o "View content where Author is Francisco Haiter-Neto) F, [Fernandes-Neto](http://www.springerlink.com/content/?Author=Alfredo+J%c3%balio+Fernandes-Neto) AJ, Soares CJ. Radiodensity of base, liner and luting dental materials. Clin Oral Investig. 2006 jun 10(2): 114–118.
4. Rasimick BJ, Gu S, Deutsch AS, Musikant BL. Measuring the radiopacity of luting cements, dowels, and core build-up materials with a digital radiography system using a CCD sensor. J Prosthodont. 2007 sep/oct 16(5): 357-364.
5. Cruvinel DR, Garcia LFR, Casemiro LA, Pardini LC, Pires de Souza FCP. Evaluation of radiopacity and microhardness of composites submitted to artificial aging. Mat Res. 2007 jul/sep 10(3): 325-329.
6. Manicome PF, [Rossi Iommetti P](http://www.ncbi.nlm.nih.gov/pubmed?term=%22Rossi%20Iommetti%20P%22%5BAuthor%5D), [Raffaelli L](http://www.ncbi.nlm.nih.gov/pubmed?term=%22Raffaelli%20L%22%5BAuthor%5D). An overview of zirconia ceramics: basic properties and clinical applications. J Dent. 2007 nov 35(11) 819-826.
7. Gu S, Rasimick BJ, Deutsch AS, Musikant BL. Radiopacity of dental materials using a digital X-ray system. Dent Mater. 2006 aug 22(8): 765-770.
8. Dukic W, Delija B, Derossi D, Dadic I. Radiopacity of composite dental materials using a digital X-ray system. Dent Mater J. 2012 feb 31(1): 47-53.
9. Yan M, Song W, Zhao-Hui C. Raman spetroscopy studies of the high-temperature evolution of the free carbon phase in polycarbosilane derived sic ceramics. Ceramics Int. 2010 dec 36 (8): 2455-2459.
10. Spohr AM, Borges GA, Burnett Júnior LH, Mota EG, Oshima HMS. Surface modification of In-Ceram Zirconia ceramic by Nd: YAG laser, Rocatec system, or aluminum oxide sandblasting and its bond strength to a resin cement. Photomedic Laser Surg.2008 jun 26(3): 203-208.
11. Guess PC, Strub JR, Steinhart N, Wolkewitz M, Stappert CF. All-ceramic partial coverage restorations--midterm results of a 5-year prospective clinical split mouth study. Dent Mater. 2009 aug 37(8): 627-637.
12. Hjerppe J. [Vallittu PK](http://www.ncbi.nlm.nih.gov/pubmed?term=%22Vallittu%20PK%22%5BAuthor%5D), [Fröberg K](http://www.ncbi.nlm.nih.gov/pubmed?term=%22Fr%C3%B6berg%20K%22%5BAuthor%5D), [Lassila LV](http://www.ncbi.nlm.nih.gov/pubmed?term=%22Lassila%20LV%22%5BAuthor%5D). Effect of sintering time on biaxial strength of zirconium dioxide.Dent Mater. 2009 feb 25(2): 166-171.
13. The International Standards Organization – (ISO 4049), Dentistry - polymer-based filling, restorative and luting materials, third ed, 2000.
14. Pekkan G. Saridag S, Pekkan K, Helvacioglu DY. Comparative radiopacity of conventional and full-contour Y-TZP ceramics. Dent Mater J. 2016; 35(2): 257–263.
15. [Masaru](http://adsabs.harvard.edu/cgi-bin/author_form?author=Iwao,+M&fullauthor=Iwao,%20Masaru&charset=UTF-8&db_key=PHY) I, [Masayuki](http://adsabs.harvard.edu/cgi-bin/author_form?author=Okuno,+M&fullauthor=Okuno,%20Masayuki&charset=UTF-8&db_key=PHY) O, [Mikio](http://adsabs.harvard.edu/cgi-bin/author_form?author=Koyano,+M&fullauthor=Koyano,%20Mikio&charset=UTF-8&db_key=PHY) K, [Shin'ichi](http://adsabs.harvard.edu/cgi-bin/author_form?author=Katayama,+S&fullauthor=Katayama,%20Shin%27ichi&charset=UTF-8&db_key=PHY) K. Structural changes of Sio2 glass by mechanical milling. J Mineralog Petrolog Sci. 2010; 105: 135-141.
16. Gouadec G, Makaoui K, Perrière L, Ph. ColombanPH, Mazerolles L. Polarized micro-Raman study of Al2O3-based directionally solidified oxide eutectics containing GdAlO3 perovskite, Er3Al5O12 garnet and cubic ZrO2. J Raman Spectrosc. 2010; 41: 969-977.
17. The International Standards Organization – (ISO 6872), British Standard Dentistry - Ceramic materials, 2008.
18. Ozkurt Z, Iseri U, Kazazoglu E. Zirconia ceramic post systems: a literature review and a case report. Dent MaterJ. 2010 may 29(3): 1-13.
19. Pekkan G, Pekkan K, Hatipoglu MG, Tuna, SH. Comparative radiopacity of ceramics and metals with human and bovine dental tissues. J Prosthet Dent. 2011 aug 106(2): 109-117.
20. Neuhaus KW, Rodrigues JA, Seemann R, Lussi A. Detection of proximal secondary caries at cervical glass II- amalgam restoration margins in vitro. J Dent. 2012; 40(6): 493-499.
21. Soares CJ, Santana FR, Fonseca RB, Martins LRM, Neto FH. In vitro analysis of the radiodensity of indirect composites and ceramic inlay systems and its influence on the detection of cement overhangs. Clin Oral Investig. 2007 dec 11(4): 331–336.

**FIGURES**

Figure 1- Radiographic image including specimens of each tested material (G1, G2, G3, G4, G5 and G6), molar slice (enamel and dentin), and aluminum stepwedge

Figure 2- Raman Spectra of evaluated ceramic

**TABLES**

Table 1- Manufacturer name and chemical composition of ceramic system according to groups

Table 2. Mean of radiopacity and thickness equivalent in aluminum for tested ceramic