Investigating the Validity of the ISO 6872:2015 ‘Dentistry - Ceramic Materials’ for Chemical Solubility

By:

Rayan Hawsawi

A thesis submitted in partial fulfilment of the requirements for the degree of

Doctor of Philosophy

Academic Unit of Restorative Dentistry

School of Clinical Dentistry

The University of Sheffield

December 2018

Summary

Most research regarding dental ceramics focuses on the mechanical, physical and optical properties. These properties are important; however, the chemical durability of dental ceramics is also significant. The oral cavity is a complex environment, '*in vitro*' studies have not succeeded in replicating the solubility measurements of dental ceramics perfectly. The International Organization for Standardisation has published revised chemical solubility testing methods for dental ceramics ISO 6872. These methods failed to improve the reproducibility of the chemical solubility findings (Stokes et al., 2002), which led many researchers to develop alternative methods.

Nevertheless, these ISO methods have received limited criticism in the literature. Therefore, the aim of this research was to investigate the validity of the ISO 6872 (BS ISO, 2015) 'Dentistry: Ceramic materials' for chemical solubility, and if required design a superior method. The current standard ISO 6872 (BS ISO, 2015) specifies the total surface area of the test specimens only. Therefore, the research hypothesis is that any alteration of the specimens' geometry will affect the chemical solubility value of the same material.

The initial findings showed that chemical solubility can be manipulated by altering the geometry of individual test specimens whilst still complying with the current standard. Characterisation tests such as SEM, EDS, XRD, ICP and Vickers hardness were performed to investigate the effects of the test environment on the specimens. As a result, the physical handling of the specimens was assumed to affect the outcomes of the chemical solubility test. An optimised test was designed to minimise the contact of the specimens and the findings showed that there is no significant difference between different specimens' geometries.

The study concluded that the current prescribed chemical solubility method of ISO 6872 (BS ISO, 2015) lacks some specifications in order to be reliable in measuring the chemical solubility values of dental ceramics.

بسم الله الرحمن الرحيم

In the Name of God, Most Gracious, Most Merciful

I would like to dedicate this thesis to:

My beloved parents 'Badrya' and 'Abdullah'

Your endless love, support, guidance & prayers were the reasons for every success in my life

My wife 'Shuruq'

For your endless love, support, encouragement & being in my life

My children 'Yasmin' and 'Abdullah'

For filling my life with happiness and joy

And my entire family

For your support and prayers

Acknowledgement

Firstly, I would like to thank my supervisory team. Professor Christopher Stokes, Dr. Cheryl Miller and Dr. Robert Moorehead for all their immense support and guidance throughout the whole PhD duration. Without them, this research would not have been completed.

Secondly, a special thanks to Dr. Anthony Johnson, who supervised me during the first year of my PhD, for his valuable support and guidance.

Also, I would like to thank Dr. Duncan Wood, Dr. Caroline Harrison and Mrs. Brenka McCabe for their help and valuable consultations.

I am grateful to my employer, Umm Alqura University, Saudi Arabia, for sponsoring my entire postgraduate studies in the United Kingdom.

Gratitude to fellow students: Omar, Ahmed, Abdulraouf, Saja, Altair, Amnael and Hathal for their technical support and advice.

Finally, thanks to all my friends and staff of the University of Sheffield for being supportive, helpful and kind during my studies in Sheffield.

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Glossary

ASTM	American Society for Testing and Materials
BS	British Standards
CAD/CAM	Computer-Aided Design/Computer-Aided Manufacturing
EDS	Energy Dispersive X-ray Spectroscopy
Hybrid ceramic	Ceramic + resin-based composite
ICP-MS	Inductively coupled plasma mass spectrometry
ICP-OES	Inductively coupled plasma - optical emission spectrometry
ISO	International Organization for Standardization
LTD	Low temperature degradation
JCPDS	Joint Committee on Powder Diffraction Standards
SEM	Scanning Electron Microscopy
VMII	VITABLOCS® MARK II
XRD	X-ray Diffractometry
Y-TZP	Yttria-Tetragonal Zirconia Polycrystalline

Chapter 1

Introduction

Chapter 1: Introduction

Dental ceramics are among the most significant restorative materials due to their biocompatible, aesthetic and physical properties that are comparable to the natural tooth structures (Conrad et al., 2007). In modern dentistry, the interest in developing improved dental ceramic materials has become obvious over the last few years. This development is also associated with inventing novel processing techniques, such as computer aided design/computer assisted manufacture (CAD/CAM) and hot pressing (Usha et al., 2014), which in turn have motivated an exploration of new materials due to new routes of fabrication.

Dental ceramics are generally more durable than other dental restorative materials in the oral environment. However, the degradation of those materials may occur due to chemical attack, mechanical forces or a combination of both (Anusavice, 1992). Previous research has shown that degradation may increase the surface roughness of dental ceramics, which may increase the abrasion of opposing teeth, increase plaque adhesion or affect the optical properties (Al-Shammery et al., 2007). In addition, this degradation could lead to releasing of toxic elements because of mechanical and chemical attack.

The International Organization for Standardisation (ISO) has established requirements, specifications, guidelines or characteristics covering almost all aspects of industry. The value of the ISO standards lies in providing the confidence to consumers and the developers about the safety, reliability and the quality of the products. In general, it is a legal requirement that dental manufacturers should follow certain regulations before placing their products on the market, which could be different between countries. It is therefore essential to have a recognised international reference that can provide globally established guidelines such as the ISO standards.

ISO 6872 specifies guidelines and appropriate test methods for assessing dental ceramic materials in order to confirm their suitability to achieve the required purposes. This ISO standard allocates different standardised methods including a specific method to evaluate the chemical solubility of dental ceramics. The ISO 6872 (BS ISO, 1995b) method measured the solubility values using a refluxing solute system. In 2008, this method was modified from refluxing to a static method (sealed jar), it also removed the specimens' geometry specifications, instead only specifying a total surface area.

Unfortunately, there is very little data in the literature relating to this method within the field of dental materials. Many researchers have either developed their own solubility-testing methods or amended the current standard making comparison difficult (McLean, 1979, Anusavice and Zhang, 1998, Milleding et al., 1999, Kukiattrakoon et al., 2010); hence, the purpose for undertaking this research was to investigate the validity of the latest chemical solubility method of the ISO 6872 (BS ISO, 2015) 'Dentistry - Ceramic materials'.

Chapter 2

Literature Review

Chapter 2: Literature Review

2.1. Restorative dentistry

A dental restoration generally can be defined as a treatment to replace missing parts of dental structure due to decay, fracture or any other reason in order to restore morphology, integrity and function (Schulein, 2005). Restorative dentistry can be divided generally into two main sections, which are direct and indirect restorative techniques. Direct restorative dentistry can be defined as an immediate placing of a restorative material directly in a prepared tooth cavity. Whilst, indirect restorative dentistry can be defined as fabricating a restorative material outside the oral cavity in the dental laboratory before placing it in a prepared tooth cavity, which requires more than one appointment for completion (ADA, 2003).

Historically, dentistry has not always existed as a profession. Therefore, they were usually implementing simple procedures, which their main option of treatment was straightforward extraction to eliminate pain and related infections rather than dealing with complicated cases. This was due to a lack of knowledge during that period (Fauchard and Lindsay, 1946). There is not much documentation about early restorative dentistry, however it is claimed that some ancient civilizations used materials to replace and restore teeth such as bone, ivory, ground mastic, waxes and gold (Craig, 1997).

Around 1728, Fauchard brought the science of dentistry as well as dental instrumentation to a new level. He modified various tools that were used by barbers as well as watchmakers to fit dental practice. Fauchard spotlighted different methods to adapt different restorative and operative conditions. Thus, he became known as the father of modern dentistry (Fauchard and Lindsay, 1946, Lynch et al., 2006, Maloney and Maloney, 2009). Fauchard mentioned in his book using some other materials to restore damaged teeth including gold, lead and tin.

In the late 18th century, a huge growth in prosthetic dentistry paved the way for contemporary cosmetic dentistry. In 1770, the dental field witnessed the fabrication of the first porcelain dentures, but it took nearly ten years to be used in patients' mouths. In the early 19th century, clinicians started to use a form of plaster in order to make moulds of their patients' mouths that would give better-fitting dentures.

In 1826, the restorative dentistry field witnessed the early development of dental amalgam as a new restorative material by combining silver and mercury (Schulein, 2005). However, this material did not received a significant attention in dental profession until a suggestion of a balanced formula by G. V. Black in 1895 (Cannon et al., 1985). In the early 20th century, silicate cement was introduced as the first tooth-coloured restorative material in dental cosmetic field (Glenner, 1993). In 1907, the introduction of the precise casting technology and the use of electric furnaces facilitated the production of metal crowns and bridges (Slokar et al., 2017).

Land introduced porcelain jacket crown (PJC) as new technique in restorative dental field in 1889 (Taylor, 1922). Dental porcelains had been developed from feldspathic glasses, which offered better aesthetic properties. However, they have since been shown to have poor fracture toughness, improper fitting and inadequate marginal adaptation (McLean and Hughes, 1965, Anusavice, 2003). An improvement in fracture resistance has been made by McLean and Hughes (1965) by the addition of alumina particles. Since then, dental porcelain has become a primary restorative material in the oral cavity. Moreover, the recent introduction of CAD/CAM technology has aided to improve fitting and marginal adaptation of restorations (Li et al., 2014). In general, the continuous improvements of the different restorative materials provided more benefits in the restorative dentistry field.

In 1947, methyl methacrylate resins were developed as a direct restorative material (Ferracane, 2011). This material did not last long due to its polymerisation shrinkage, inconvenient coefficient of thermal expansion, postoperative sensitivity, staining and secondary decay (Noort et al., 1993). However, these drawbacks were improved later by modifying the structure of this material such as adding filler particles. In 1955, an important discovery of phosphoric acid led to improve mechanical bonding of resin to dental structure (Ring, 1992). Later on, the introduction of composite resin and ultraviolet light-curing system has changed the restorative dentistry considerably in the 1970s (Minguez et al., 2003). In 1968, glass ionomer cement (GIC) was introduced and developed from combining silicate and polycarboxylate cement (Wilson, 1991).

This material became popular due to its properties of releasing fluoride and chemically bonding to the dental structure.

In the 1950s, Corning Glass Works (Dicor®) developed the first castable glass-ceramic. This product laid the first stone to dental ceramic system that rely on glass strengthening with different forms of mica ($SiO_2.K_2O.MgO.Al_2O_3.ZrO_2$, with some added fluorides) (Raghavan, 2012). The presence of fluoride molecules within these materials provides them with nature-like fluorescence. By 1957, conversion of glass particles into fine-grained crystalline materials had been successfully developed by Corning Glass Works (Stookey, 1959). During the 1970s, these products 'glass-ceramics' are actually polycrystalline structures formed by controlled glass crystallisation (Atkinson and McMillan, 1976). Glass-ceramics were developed into a broad range of applications as a result of their abundant beneficial properties and convenient methods of production (Doremus, 1994). In 1980s, most of dental ceramics were prepared as powders or powders and clay (Kelly et al., 1996). By the late 1990s, many different ways were developed to minimise or avoid shrinkage such as pressing, casting, sintering and CAD/CAM technology (Kelly and Benetti, 2011). Recently, VITA Zahnfabrik has introduced the first hybrid dental ceramic into the restorative field in 2013, which combine the best properties of ceramic and composite resin materials.

2.1.1. Indirect restorative dentistry

Indirect restorative dentistry generally requires more than one visit to obtain a complete restoration. Historically, it was reported that beeswax, gutta-percha and plaster of Paris were the earliest known materials used for dental impressions (Schulein, 2005). Later on, dental impression materials have been developed considerably to increase the accuracy of obtained restorations.

A dental restorative material is a subgroup of biomaterials that can be defined as "non-living materials designed to interact with biological systems" (Noort, 2013). Therefore, the most important feature is that a material should be harmless to the biological environment and may also provide benefits to human beings by its interaction. Moreover, the maximum intraoral forces of mastication were reported to be over 60 kgf according to some studies (Rohrle et al., 2018, Ferrario et al., 2004). Thus, a restorative material should display appropriate mechanical properties in order to withstand the forces of mastication placed on it.

The oral cavity demonstrates a complex environment, which has a different range of temperature and pH due to the different consumption of food and drinks. It was reported that the range of temperature of consumed food and drinks is between 0°C and 70°C (Barclay et al., 2005). Therefore, restorative materials should display proper thermal properties to avoid failure due to variable contraction and expansion of a dental material and dental structures. Moreover, the oral cavity is a wet environment with different acidity levels due to food and drink consumption. In general, dental restorative materials tend to suffer from water absorption, corrosion or chemical dissolution because of this complex environment. Although all materials are prone to be affected in the oral environment, a restorative material should demonstrate adequate chemical properties in order to be considered as a restorative material.

Furthermore, the oral cavity contains many types of bacteria that have been related with some oral conditions such as dental and periodontal diseases (Aas et al., 2005). Bollen et al. (1997) stated that a surface roughness of $R_a = 0.2$ µm is the threshold level for bacterial retention. In addition, it has been reported that increasing in the average surface roughness of dental restorations increases the level of friction (Thomas, 1998). Therefore, dental restorations should demonstrate minimum and acceptable surface roughness in order to be applied in the oral cavity.

The development of restorative dentistry is an ongoing process and therefore there are different types of indirect restorative treatments including inlays, onlays, crowns, bridges and veneers. These different techniques require certain properties of dental restorative materials. For example, a specific material can be used for single crowns but could not be appropriate for long span bridges. In addition, some techniques as crowns and bridges may involve using two different materials as core (substructure) and enamel parts. A core material should display adequate strength, proper coefficient of thermal expansion and bonding to dental structures but does not have to be aesthetics as the core material will be covered by an enamel material (Kao, 1991). On the other hand, an enamel material should display proper aesthetic properties that match the appearance of natural teeth.

Therefore, minimal acceptable levels of biocompatibility, mechanical, physical, and chemical properties should be shown by restorative dental materials based on the required function (Noort, 2013).

2.1.2. Indirect restorative materials

Indirect restorative dentistry includes different types of materials such as metal, glass-ceramics, ceramics, and composite resins materials.

2.1.2.1. Metals

In dentistry, metals have been widely used in the restorative field due to their good mechanical properties such as hardness, elastic modulus and tensile strength (Slokar et al., 2017). However, the applied metals are generally alloys, and not in their pure forms as in the past in order to meet the requirements of restorative materials. For example, the hardness of gold is too low to be used in the oral cavity. Therefore, alloying metals with other metals or non-metals result in a superior metallic alloy by exploiting the positive properties and reducing the negative properties of each component (Slokar et al., 2017). Today, the recent advancements of new technologies allow for producing improved materials in restorative dentistry. However, this literature review will concentrate on non-metallic indirect restorative materials (dental ceramics).

2.1.2.2. Glasses and glass-ceramics

Glasses are amorphous solids and mainly transparent structure as liquids but in a solid form. An amorphous structure displays an irregular arrangement of its molecules. ASTM (C-162-92) standards for glass defined glass as “an inorganic product of fusion which has been cooled to a rigid condition without crystallisation” (Doremus, 1994). Although, this definition is accurate for most commercial glassy materials, however, other routs of making glass were ignored. Therefore, the term “glass” should cover all non-crystalline solid materials, which exhibit a glass transition regardless of their production routes (Doremus, 1994).

There are many routes of production to prepare glass such as melt-quenching, sol-gel, etc. Even though there are different ways of preparing glass, melting at high temperature is still the most common used method due to its compositional flexibility compared with other techniques. In addition, the sol-gel method is mainly by converting components into colloidal solution or gel and subsequent polycondensation for producing of both glassy and ceramic materials (Hench and West, 1990, Kundu et al., 1992, Gheonea et al., 2017).

Most of glasses transmit light due to their transparency. The wide range of optical properties of glasses is very important for variable applications. Glass materials can be applied in different ways ranging from applications such as windows, lamp envelops and containers to more advanced applications such as lenses and glass fibre, etc. Moreover, the thermal expansion properties are very important in designing a glassy product. This is because glass expands under higher temperatures. Unequal heating of a glass body could cause a different expansion of the glass layers that could develop internal stresses (Jones et al., 1983). In general, glassy materials are brittle and prone to fracture due to their non-crystalline structure. This failure could occur due to a higher physical stress than the strength of the glass, surface flaws or stresses developed by a thermal shock.

Glassy materials can show higher corrosion resistance compared to other materials. Glasses can serve for many years under sunlight exposure and different atmospheric conditions. In addition, most laboratory chemical reactions are performed in laboratory glassware without any obvious damage or contamination. Although glass could be unaffected for these indications, it can be affected significantly in other certain conditions such as with hydrofluoric acid. Commonly, these materials are amorphous silicate glasses that contain other elements such as Al_2O_3, CaO, K_2O and/or Na_2O. The addition of other oxides to the composition of glass can be used to enhance thermal expansion properties, transparency, or for improving the fabrication process.

In dentistry, glass is utilised in the fabricating of a number of restorative materials such glass ionomer cements, dental composites (fillers), to glaze some ceramics and metals. The glassy state is metastable; therefore, glasses tend to be devitrified. However, the process of controlled devitrification (nucleation) has significantly developed the use of glasses in the dental restorative field by producing glass-ceramics.

It is important to understand the actual structure of glasses, in order to comprehend the nucleation process of glass. It has been stated that the production of a three-dimensional network is the result of the random structure of silicate glasses that are based on the irregular arrangement of SiO_4 tetrahedra linked by means of corner sharing (Douglas, 1968).

Crystallisation of a glass can be defined as the process of production of a regular form of crystal lattice from the irregularly ordered glass structure. This process includes two major stages, which are nucleation and crystal growth. In general, a glass-ceramic can be formed by melting glass and then converting it into a ceramic type material by a controlled heat treatment. Heating glass to a certain temperature enhance crystals to nucleate. Further increasing of the temperature leads to crystal growth and then crystallise some or all of the remaining glass. Nucleation processes can either be homogenous or heterogeneous. Homogenous nucleation can be described as the major nuclei and the growing crystals both formed from the same molecules. In contrast, nucleation could happen at the glass surface in contact with other different substances, which means that the major nuclei of the heterogeneous nucleation and the growing crystals are different (Vogel, 1966). However, most of glass-ceramics are formed by heterogeneous nucleation, which is usually involved with adding nucleating agents.

Glass-ceramic processing has been expanded to include other substances added to silicate and oxides. This expansion involves the precursor glasses being processed by sol-gel techniques. In addition, improvements have included considerably the processing route of powder. The addition of nucleating agents can possibly promote the volume nucleation of melt-derived silicate glasses. These nucleating agents can be defined as substances used in small quantities to enhance volume nucleation and production of glass-ceramics. Generally, the most added agents in silicate glasses are metallic oxides such as TiO_2, P_2O_5 and ZrO_2 (James et al., 1997). It has been stated that the proper addition of those elements can enhance the chemical and mechanical properties of glass-ceramics (Fathi et al., 2014). For example, it was reported that the chemical solubility of glass-ceramic materials containing TiO_2 was high (Barry et al., 1970), however the combination of ZrO_2 and TiO_2 was found to be better than the addition of only one agent of both (McNally and Beall, 1979).

The microstructures of glass-ceramics are ideally fine-grained with random crystal orientation that gives non-porous structure with no micro-cracks or voids (Vogel, 1966). Thus, these features enhance properties such as chemical durability, strength, toughness, thermal expansion, as well as translucency. Accordingly, these enhanced features and the growth of ceramics manufacturing were the primary factors to introduce glass-ceramics into the field of dental restorative materials. Although glass-ceramics display an acceptable level of biocompatibility and excellent aesthetics, they are commonly characterised by their refractory nature, hardness and brittleness (Yoshimura et al., 2012).

There are different categories of dental ceramic materials with different characteristics. Based on the chemical microstructural, glass-ceramics can be composed of different amounts of glass and crystalline structures. Firstly, there are materials are mainly based on a silica network. This structure, which is also known as quartz or silica, incorporates with either potash feldspar ($K_2O.Al_2O_3.6SiO_2$) or soda feldspar ($Na_2O.Al_2O_3.6SiO_2$) or both. The significance of involving feldspar compounds is its capability to forming crystalline mineral leucite. These materials show high proportion of glassy phase and therefore the mechanical properties range of flexural strength of them extends between 60 – 70 MPa (McLaren and Giordano, 2014). Under mechanical stresses, therefore, these glassy restorative materials are much more liable to fracture. Therefore, they are mainly applied as veneers that obtain their strength by bonding to a stiffer substructure.

In order to control other elements such as thermal properties and chemical solubility, the addition of other components such as glass modifiers, pigments and opacifiers are considered. The addition of glass modifiers such as boric oxide can decrease softening temperature as well as viscosity. While the addition of metallic oxides such as nickel oxides, which are basically used as pigments and opacifiers, is important for determination and specification of the colour intensity.

There are two possible ways to strengthen ceramics from this category (McLaren and Giordano, 2014). First, strengthening could be developed by the residual compressive stresses, which can be introduced inside the material by thermal tempering and ion exchange. Secondly, it could be enhanced by the interruption of crack propagation, which can be obtained by the dispersion of the crystalline phase. The microstructure of glass-based ceramics consists of at least one crystal phase, which is developed by controlled crystallization of the glass, in addition to the glass matrix phase. Different processing techniques are possible to produce glass-ceramics for all-ceramic restorations such as casting, machining, pressing, and infiltration process.

This category includes machinable glass-ceramics as well, which are considered as high-quality products. These materials are crystallised during manufacturing and produced as CAD/CAM blocks or ingots. The mechanical properties of machinable glass-ceramics are quite similar to castable glass-ceramics, they are, however, less translucent. In regards to the precision of restorations, they are clinically applicable and comparable to the castable glass-ceramics (Park et al., 2016).

Secondly, there are other glass-ceramics that have different ratios of added or grown crystals. The major current types of these crystals include leucite, lithium disilicate, or fluorapatite. Leucite crystals have been widely included within the structure of dental ceramics as constituent elements in order to modify the coefficient of thermal expansion. This feature is significant for ceramic fusing or even when it is to be veneered to metals. In addition, increasing the ratio of leucite fine particles in materials enhances flexural strength such as in the case of IPS Empress, which is a leucite-reinforced hot-pressed glass-ceramic. That means that leucite is considered as a potassium aluminium silicate structure but with much considerable coefficient of thermal expansion. Leucite crystals demonstrate obvious randomness of size and distribution, which is associated to the low fracture toughness and abrasive characteristics of these materials compared to enamel (McLaren et al., 2003).

Recent generations of glass-ceramic materials have much finer crystals that range between 10 µm – 20 µm with uniform distribution of particles within the glass structure (McLaren and Giordano, 2014). This gives the materials greater flexural strength with minimum abrasiveness. Therefore, these ceramics are commonly applied as veneers to core systems. Because of their high flexural strength, these ceramics can be used as all-ceramic restoration.

In addition, there are some glass-ceramic materials contain approximately 50 % glass (high leucite). They display a unique microstructure that includes a glass matrix surrounding crystals that are nucleated by a second phase of heat treatment. The physical presence of glass matrix generates compressive stresses around crystals. Thus, it improves the mechanical and physical properties of these ceramics. The degree of improvement relies on the size and amount of crystals, and how they interact with the glass matrix. There are many ceramic materials belonging to this group such as pressable ceramic Empress® and machinable Empress® (Ivoclar Vivadent, UK).

Lithium disilicate ($Li_2Si_2O_5$) are also utilised as the microstructure crystals phase for dental glass-ceramics such as Empress 2® (Ivoclar Vivadent, UK). This type of ceramics shows considerable strength due the nature of the microstructure crystals as well as the increased amount of crystal content to around 70 %. Fluorapatite crystals have been also included to the structure of some dental ceramics to enhance the optical properties and coefficient of thermal expansion of veneering ceramics (Raghavan, 2012).

Additionally, there is a group of dental ceramics that is mainly related to aluminous porcelain. These ceramics are characterised by the nature of the glass matrix phase, which contains at least 35 vol% of alumina (McLaren and Giordano, 2014). Thus, they exhibit greater strength than feldspathic porcelain, and they are commonly used as core ceramics. This category involves ceramics with wide variability in processing techniques, translucencies, and strengths in order to cover the different applications of all-ceramic restorations such as In-Ceram® Alumina, In-Ceram® Zirconia and In-Ceram® Spinell.

In-Ceram® Alumina have been successfully applied clinically since 1989 (Proebster et al., 1990). They have sufficient flexural strength (450 MPa) with moderate translucency. They are used as anterior and posterior crowns. Many studies reported that In-Ceram® Alumina can be used to restore any tooth in the mouth as single units (Wassermann et al., 2006). However, those studies showed that In-Ceram Alumina had a comparable survival rate to porcelain fused to metal generally up to the first molar, and a slightly lower survival rate for the second molar (Seghi et al., 1990, Giordano et al., 1992, McLaren and White, 2000).

In-Ceram® Zirconia is a modified version of In-Ceram Alumina. This material has a very high strength, but lower translucency. Therefore, it is used mainly as posterior units and should not be considered to restore any tooth in the aesthetic zone. The flexural strength is about (650 MPa), thus can be used for three-unit bridges (Giordano, 2000).

In-Ceram® Spinell has a moderately high strength and very high levels of translucency; therefore, ideal for restoring anterior teeth. The flexural strength is around 350 MPa (Giordano, 2000).

Another type of dental ceramics is polycrystalline materials, which refers to the solid-sintered monophase materials that are composed of directly sintered crystals with the absence of any types of matrix in order to produce a polycrystalline structure that is glass-free, air-free, and dense. Procera® AllCeram alumina, Al_2O_3 (Nobel Biocare) was the first product of this category. The flexural strength is about 600 MPa (Hegenbarth, 1996). This material is sintered at approximately 1600°C, which leads to a dense coping but with shrinkage of around 20 %. Another example is zirconium dioxide, ZrO_2 (zirconia) that has been substantially introduced into the field of restorative dentistry recently. This compound is not perfectly pure zirconia, some metal oxides are added in small quantities for the partial stabilisation of the zirconia. There are many types of zirconia crystals, which are characterised by the type of minor components added to the pure zirconia.

In the dental field, it is common to add yttria (3 wt%) to zirconia (Y-TZP) (Shah et al., 2008). The mechanical properties of Y-TZP in terms of strength and toughness are approximately double the values of alumina-based ceramics. Some studies reported that the flexural strength of Y-TZP varies between 900 to 1100 MPa (Piwowarczyk et al., 2005, Papanagiotou et al., 2006a). However, it is crucial to understand that the flexural strength values are not directly correlated to the clinical performance of ceramic restorations. Studies reported that fracture toughness of Y-TZP ranged from 8 to 10 MPa.m$^{1/2}$, which is considered superior to other types of dental ceramics so far (Piwowarczyk et al., 2005). Therefore, Y-TZP can be used for both anterior and posterior multi-unit fixed partial dentures. Clinical studies reported that there was not any obvious problem for applying Y-TZP as a framework (Raigrodski et al., 2006, Sailer et al., 2007, Christensen et al., 2010).

2.1.2.3. Resin-based materials (composites/hybrid ceramics)

The term dental composite is mainly used to refer to resin-based dental restorative materials. Until recently, dental composites have rapidly improved in order to produce a restorative material with high properties. The formulation of composite materials differs from one material to another based on their specific applications as restorative, cement, sealant materials, etc. However, all dental composites are composed of a polymeric matrix, fillers, a silane coupling agent and modulating chemicals (Ferracane, 2011).

In general, dental composites show great aesthetic and adequate mechanical properties to be used as restorative materials in the oral cavity. However, there are two major clinical reasons to replace composite restorations, which are fracture and secondary caries (Zimmerli et al., 2010). Therefore, there are some concerns that these materials could not be a convenient choice in high stress areas as with in patients who have parafunctional habits such as bruxism. This would lead as a result to fracture or wear of the restoration. Although the strength and toughness of dental composites are similar to amalgams, they are lower than ceramic materials. This is specifically significant if composites are used as a core material then they might fail by bulk fracture (Ferracane, 2011).

Moreover, the current dental composite resins are not totally hydrophobic and their shrinkage levels ranges between 0.5 vol% and 1.0 vol% (Ferracane, 2011). This level would seem to be an acceptable value to provide space for expansion due to water sorption. However, this may allow for developing of secondary caries.

The wide use of composite materials requires great demands in order to improve their properties. The expected development should be directed mainly to enhance their strength and fracture resistance, and to reduce the polymerization shrinkage and its stresses. Therefore, hybrid ceramics were developed by combining both composite and ceramic materials. These materials are composed of mostly a ceramic network structure that merged with a polymeric network structure. Even though there are only few studies investigating the properties of hybrid ceramic materials, it has been shown that the fracture strength of hybrid ceramics was comparable with feldspathic and leucite-reinforced glass-ceramics and lower than lithium disilicate glass-ceramics (Homaei et al., 2016, Sagsoz et al., 2018). In regard to the chemical properties, it is claimed that hybrid ceramics are insoluble in wet environments when tested by ISO 6872 (BS ISO, 2015). However, these hybrid ceramic materials require more investigations.

2.1.3. Manufacturing routes

Classification of dental ceramics by way of processing technique appears to be much more straightforward compared to any other classification. In general, there are three different processing techniques for dental ceramics, which are classified as: 1) powder/liquid; 2) hot pressing or casting systems; and 3) CAD/CAM or slurry die-processed system for crystalline-based materials. There is a direct engagement between processing techniques and clinical performance of ceramics. This appears when processing a material with different techniques, each technique would have different impacts that might improve or decline the final properties and the clinical performance of dental ceramics. For instance, machined or pressed ceramics have better performance compared to the sintered versions of the same material (McLaren and Giordano, 2014).

2.1.3.1. Sintering (powder/liquid)

a) <u>Conventional</u>

This category is based on the construction of a ceramic restoration by compaction, firing, and glazing. Compaction includes mixing of the powder and liquid and binder in order to produce a paste like material. The firing step is performed under vacuum, which is significant for removing remaining air and improving the density and aesthetic aspect of the veneer layer. Glazing of dental ceramics is important to remove any residual porosity on the surface, which could retain and induce the colonizability of bacteria and aid crack propagation. As a result, glazing gives smooth, shiny, and impervious surface. This can be achieved by either controlled final firing that results in fusing of the superficial layer, or by applying low fusing glasses to the ceramic restoration surface after initial construction of the veneer layer.

b) Slip Casting

Slip casting is a method to produce ceramic materials by homogenous dispersion of ceramic powder in water. In general, the adjustment of water pH is considerable to produce a charge on the ceramic particles and then ceramic powder is coated by a polymer in order to create an even suspension in the water. Many ceramic materials such as In-Ceram® and some partially stabilised zirconia are produced by slip casting of alumina or zirconia. Although the rate of production of slip casting systems appears quite low compared to other systems, it produces however, a wide diversity of complex shape as well as highly homogenous ceramics.

2.1.3.2. Pressable

This method utilises the lost wax casting technique. The process requires ingots of glass-ceramic or monochromatic porcelain, which are heated to a specified temperature in order to flow and are forced under pressure into a refractory mould. The mould is made by the conventional lost-wax casting technique. Mainly, pressable ceramics are used as veneers, inlays, onlays, single crowns, and as substructures. Hot pressing technique is advantageous over other traditional methods of sintering in achieving excellent marginal fit, decreased porosity, and increase flexural strength and Weibull modulus (Gorman et al., 2000).

2.1.3.3. CAD/CAM

CAD/CAM (computer-aided design and computer-aided manufacturing) includes software that is able to design and manufacture materials such as dental ceramics. This technology has been involved with many ceramics, due to its accuracy and short processing time. Blocks of different ceramic materials are milled to fabricate inlays, onlays, veneers, and crowns using CAD/CAM systems. The standardised manufacturing process is an advantageous feature of CAD/CAM technique, which produces restorations with improved density with better mechanical properties in comparison with powder/liquid or pressable restorations.

The introduction of CAD/CAM in the dental field in the 1970s returns to the efforts of Duret and Preston (1991) who begun to explore this technology in dentistry. However, these early efforts were not enough to use CAD/CAM technology within dental clinics and it was only limited to dental laboratories.

This technology has been subjected to many stages of development. In the 1980s, further work of Moermann led to the release of the CEREC® system as chairside CAD/CAM. Moreover, the access transition from closed to open systems created much considerable flexibility in regard to acquisition of data by different sources. This also leads to increase the possibility of processing techniques with wider manufacturing range and related materials. Presently, CAD/CAM is considered one of the most popular technologies in dental laboratories and clinics.

In dentistry, CAD/CAM works by subtractive manufacturing process. The idea is based on using power-driven sharp cutting tools that are controlled by a computer programme in order to obtain the desired geometry. The unfavourable point of the subtractive machining systems is the waste of removed material as compared to the final produced object. However, the current methods have been improved to not only machine one product at a time, but they are able to lend themselves to mass production as milling multiple crowns and bridges. Thus, the transition from subtractive to additive methods, which are more advantageous manufacturing methods, can contribute effectively to overcome many issues related to milling process. This mainly appears in creating fine details such as sophisticated internal geometry, undercuts, and voids.

The American Society for Testing and Materials (ASTM) defines the additive manufacturing as ‘the process of joining materials to make objects from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing methodologies’ (ASTM Standard F42, 2009). One of the major advantages of the additives manufacturing process is the conservative use of material. The additive process has been used since 1980s for production of prototypes, casting patterns and models. Today, it has been directed from rapid prototyping models to produce objects as final real products. The overall cost, reliability, and manufacturing speed make this promising equipment as a strong competent to traditional techniques. Thus, it should be admitted that the additive manufacturing process is perfectly suitable for dental applications.

2.1.4. Current commercial dental ceramics

Regardless of the convenient use for dental ceramics, metal restorations still demonstrate superior mechanical properties compared to ceramics. However, metallic restorations tend to deform, whereas ceramic restorations commonly fail disastrously. Moreover, the production of dental ceramics is considered costly, and requires more sophisticated technical approaches as well as appliances to achieve long-term and optimal aesthetic outcomes. Therefore, it is crucial to produce inexpensive, aesthetic, tough and long-lasting ceramics materials in order to appeal the market.

The competition within the global dental ceramics market cannot be ignored. There are many market leading companies, which compete with respect to quality and price in order to meet the market needs. Therefore, there are different dental ceramic products, which cover various applications of restorative indications. The following are examples of the current commercial dental ceramics:

2.1.4.1. VITABLOCS® Mark II (VITA Zahnfabrik)

This material is composed of fine particles of feldspar ceramics (4 µm), which has sanidine ($KAlSi_3O_8$) as the crystal phase. It is pore free ceramic with fine crystalline structure as it is manufactured using fine-grained powders, which are responsible for their good strength, polishability and less abrasive behaviour to the opposed dental structures (Giordano, 2006). The clinical indications of VITABLOCS Mark II include anterior and posterior single crowns, inlays, onlays and veneers.

2.1.4.2. IPS Empress® (Ivoclar Vivadent)

This material is composed of leucite-based ceramic (1-5 µm), which is processed by hot pressing technique. It obtains its strength from the reinforcement of the dispersed fine leucite crystals as a result of hot pressing. The indications of IPS Empress include single crowns, inlays, onlays and veneers (Albakry et al., 2003). However, this product has been declined as some evidence stated that the strength of Empress is not suitable for posterior region as the manufacturer claimed (Holand et al., 2000).

2.1.4.3. IPS Empress® Esthetic and IPS Empress® CAD (Ivoclar Vivadent)

These materials are both leucite reinforced glass-ceramics (< 1-5 µm). Both materials can be processed by hot pressing and CAD/CAM techniques respectively. They are highly translucent ceramics, which make them excellent choices for aesthetic purposes. Therefore, they are indicated for veneers, inlays, onlays and crowns.

2.1.4.4. IPS Empress® 2 (Ivoclar Vivadent)

This material is lithium-disilicate-based ceramic (0.5-4 μm), which is processed by the lost wax and hot-pressing technology. It was manufactured to serve as crowns and three-unit fixed prostheses for anterior and premolar regions.

2.1.4.5. IPS e.max® system (Ivoclar Vivadent)

This system offers five different types, which can be processed by either pressing or CAD/CAM technique as demonstrated in Table 1. Based on the processing system, the mechanical properties of glass-ceramics can be affected with multiple firing treatments as with pressing technique (Mackert and Williams, 1996). Table 2 shows an example of multiple heat-treatment for preparing IPS e.max Press.

Table 1: IPS e.max systems.

Material	Processing system	Indications
IPS e.max® Press	Lithium disilicate (3-6 µm) ingot (hot pressing)	Single-tooth restorations Three-unit bridges
IPS e.max® ZirPress	Fluorapatite (0.1-0.3 µm) ingot (press-on veneer)	Press over crowns and bridges, and veneers
IPS e.max® CAD	Lithium disilicate (0.2-1.0 µm) block (CAD/CAM)	Single-tooth restorations Three-unit bridges
IPS e.max® ZirCAD	Zirconium oxide (0.5-0.85 µm) block (CAD/CAM)	Monolithic and veneered crowns and bridges
IPS e.max® Ceram	Fluorapatite (0.1-0.3 µm/1-2 µm) veneering ceramic	Layering ceramic for lithium disilicate and ZrO_2

Table 2: An example heat-treatment schedule of IPS. e.max systems (IPS e.max Press).

Ivoclar Vivadent		Stand-by temp.	Temp. increase	Holding temp.	Holding time
		°C	°C/Min	°C	mm:ss
IPS e.max Press	100g	700	60	915	15:00
	200g	700	60	920	25:00

In general, glass-ceramics exhibit excellent thermal shock resistance, good mechanical, physical and outstanding aesthetic properties compared to other all-ceramic dental materials. However, they are not suitable to be used in posterior regions due to their inadequate strength and toughness.

2.1.4.6. Zirconia, ZrO_2 (Y-TZP)

Generally, zirconia was introduced as a biomedical grade material to overcome the brittleness of alumina and the consequential failure of orthopaedic implants (Christel et al., 1988). Presently, zirconia-based ceramics are considered one of the most thoroughly investigated materials for many reasons (Denry and Kelly, 2008). The optimal mechanical properties of zirconia as well as its biocompatibility are the main factors for its wide use in biomedical applications. The chemical composition of zirconia is a crystalline dioxide of zirconium. In regard to temperature-dependent, there are three different crystallographic structures of zirconia: monoclinic, tetragonal and cubic. In 1969, zirconium oxide was applied for the first time in the medical field for orthopaedic applications. Specifically, it was introduced to replace titanium or aluminium materials for hip head replacement (Helmer and Driskell, 1969).

In the late 20th century, the interest in aesthetics and the concern of reducing the allergic and toxic effects of particular alloys, researchers have been exploring new materials that are tooth-coloured as well as metal-free restorations. Therefore, the optimum properties have nominated the worthiness of applying zirconia as dental prostheses, where aesthetic and strength are essential (McLean, 2001).

Many steps are necessary in order to prepare a dental restoration from dental zirconia, which include designing, soft machining, sintering and hard machining with an additional staining or veneering step as required (Denkena et al., 2017). This approach uses a porous blank, which is easy to be machined to achieve the required morphology and geometry of the restoration. Afterwards, the material is fired in a furnace in order to be densified. The densification of zirconia powder requires a temperature of approximately 1600°C in order to be used as dental restorative applications (Noort, 2013). The shrinkage that occurs during firing is about 20 vol%, thus this should be taken into account during designing.

Despite the fact that there are many available types of zirconia-based ceramics, yttria-stabilized zirconia (Y-TZP) is the actual material used for restorative dentistry. Although the amount of yttria is quite small (3 wt%) (Shah et al., 2008), its presence is extremely vital. Commonly, zirconia is formed of a stable monoclinic phase at room temperature; the addition of yttria leads the transformation of the monoclinic phase to a metastable tetragonal crystal phase at room temperature, even though monoclinic phase is favourable thermodynamically (Deville et al., 2005). In the case of the presence of a small defect such as a crack, which could progress from the tip and grow through the material as a result of relieving the localized stress. However, the stress at the crack tip causes the metastable tetragonal crystal structure of the yttria-stabilized zirconia to transform to the more stable monoclinic form (Noort, 2013). In other words, this transformation is an increase in volume that in effect closes the crack and inhibits its propagation. Thus, yttria-stabilized zirconia ceramic does not only display a very high strength but also a very high toughness, which makes it more resistant to crack growth compared to other ceramics. This particular characteristic makes Y-TZP an excellent possible choice as a core for both crowns and bridge frameworks.

As mentioned previously, zirconia ceramics have been considered as valid orthopaedic implant materials. However, this material is considered one of the most controversial biomedical materials among researchers. Although, biomedical grade zirconia displays superior mechanical properties, it is prone to an aging process in aqueous environments. This probably happens due to its metastability (Lawson, 1995), although it is an important feature to stop crack propagation as already stated. Specifically, a metastable tetragonal structure could transform into a stable monoclinic structure without stress, which is referred as low temperature degradation (LTD).

It has been stated that the highest degradation value of zirconia is in the range of temperature of 200-300°C, which is also time dependent. This degradation causes the transformation of tetragonal phase to monoclinic phase, and is accompanied by micro- and macro-cracking as well, where the transformation origin begins commonly at the surface and proceeds interiorly (Lawson, 1995). Further, the volume of Y-TZP structure is increased by nearly 4 % due to this transformation that would result in strain on the system causing micro-cracks and this would lead to increase the surface roughness of Y-TZP, which are critical concerns in dental applications (Chevalier, 2006, Denry and Kelly, 2008, Kelly and Denry, 2008). If these micro-cracks progress and move inward, they may cause a catastrophic failure of the material.

Conflicting findings have been reported regarding mechanical properties of Y-TZP as a result of LTD effect. Some studies stated that there was no change in the mechanical properties such flexural strength after LTD, whereas other studies reported that there was a reduction in regard to Young's modulus and hardness up to 30 % after LTD (Swab, 1991, Piconi and Maccauro, 1999, Papanagiotou et al., 2006b, Cattani-Lorente et al., 2011).

2.2. International standards

International standards can be defined as standards are introduced by international organisations and to be used worldwide. Thus, the most prominent standards organisation is the International Organisation for Standardisation (ISO) that develops, publishes and provides guidelines, specifications, characteristics and requirements to ensure the appropriateness and suitability of the applied products, services, materials and processes. All indirect restorative dental materials are covered by ISO standards, this research however focuses on dental ceramics.

In 1978, BS 5612 (BS, 1978) was introduced as the first international standard for dental porcelain for jacket crowns. Later on, a new ISO standard was introduced for dental ceramics in 1984, which is the ISO 6872 (BS ISO, 1984) "Dental ceramic". This standard has been revised three times in 1995, 2008 and 2015 (BS ISO, 1995b, BS ISO, 2008, BS ISO, 2015). In general, ISO 6872 is used to evaluate dental ceramics, which specifies the requirements and guidelines of the testing methods for all dental ceramic restorations and prostheses.

2.2.1. ISO 6872 (Dentistry - Ceramic materials)

ISO 6872 includes a number of the corresponding test methods to evaluate dental ceramics. The standard specifies processing, properties, requirements, sampling, test methods, packaging, marking and labelling of dental ceramics. One of the most important sections of this standard is its described test methods, which include radioactivity, flexural strength, linear thermal expansion coefficient, glass transition temperature and chemical solubility testing methods. Each testing method has its own specifications for specimens' preparation. Although dental ceramic restorations are subjected to the complex environment of the oral cavity, most ISO standard testing methods are performed individually to avoid adding factors that could falsify the obtained result.

It has been reported that radioactive isotopes could increase the probability of developing oral cancers (Anusavice, 1992, Porstendorfer et al., 1996), therefore it is very important to assess the level of activity of uranium-238 of any dental ceramic. The current standard specifies Gamma spectroscopy or neutron activation to determine the activity level, which should be lower than 1.0 $Bq \cdot g^{-1}$ of ^{238}U. As stated before, it is important to determine the flexural strength of dental ceramics in order to be applied for different indications appropriately. There are three acceptable flexural test methods by the current standard, which are three-point bending, four-point bending and biaxial flexural methods. The acceptable flexural strength for dental ceramics ranges between 50 MPa to 800 MPa based on the different clinical indications (Table 3).

Table 3: The table shows the classification of dental ceramics for fixed prostheses based on clinical indications (BS ISO, 2008, BS ISO, 2015).

Class	**Recommended Clinical Indications**	**Mechanical and chemical properties**	
		Flexural strength minimum (mean) MPa	**Chemical solubility maximum µg/cm²**
1	a) Monolithic ceramic for single-unit anterior prostheses, veneers, inlays, or onlays adhesively cemented. b) Ceramic for coverage of a metal framework or a ceramic substructure.	50	<100
2	a) Monolithic ceramic for single-unit anterior or posterior prostheses adhesively cemented.	100	<100
	b) Partially or fully covered substructure ceramic for single-unit anterior or posterior prostheses adhesively cemented.	100	<2000
3	a) Monolithic ceramic for single-unit anterior or posterior prostheses and for three-unit prostheses not involving molar restoration adhesively or non-adhesively cemented.	300	<100
	b) Partially or fully covered substructure for single-unit anterior or posterior not involving molar restoration adhesively or non-adhesively cemented.	300	<2000
4	a) Monolithic ceramic for three-unit prostheses involving molar restoration.	500	<100
	b) Partially or fully covered substructure for three-unit prostheses involving molar restoration.	500	<2000
5	Monolithic ceramic for prostheses involving partially or fully covered substructure for four or more units or fully covered substructure for prostheses involving four or more units.	800	<100

Moreover, it is important to determine the coefficient of thermal expansion and glass transition temperature of dental ceramics to avoid thermal mismatch and stresses if applied with other materials as in metal-ceramic restorations. The standard states that the expansion test is performed between either 25°C or 50°C and 500°C. The values of glass transition temperature of dental ceramics can be determined as performed in the latter method using the expansion curves. Lastly, it is important to measure the chemical solubility of dental ceramics to ensure their suitability within the oral cavity, which is the focus of this research. The standard specifies the acceptable solubility levels for both core and enamel classes of dental ceramic restorations as shown in Table 3, which is based on measuring the mass loss before and after the test.

2.2.1.1. Chemical solubility testing method

The development of dental restorative ceramics is directed toward exploration for enamel-like materials in their strength, toughness and chemical resistance, to produce materials with extend the average lifespan of ceramic restorations. One of the most significant parameters linked with the determination and use of any dental ceramic is its solubility in the oral cavity. Chemical solubility of dental ceramics can be defined as chemical dissolution of materials in water by releasing soluble components under some circumstances (Clark and Zoitos, 1992).

In general, dental ceramics might be subjected to chemical dissolution in the oral environment. This dissolution could alter the structural integrity of dental ceramics in different forms. It has been found that dental ceramic restorations had signs of loss of lustre, surface degradation and roughness due to the effects of the complex oral environment (Esquivel-Upshaw et al., 2013). This could increase in plaque retention, wear of the ceramic restorations and opposing dental structures (Anusavice, 1992).

In general, the chemical durability of dental ceramics is good (Kukiattrakoon et al., 2010). However, there are many types of dental ceramics, which differ in the chemical composition and microstructure. These variabilities therefore give different chemical properties of dental ceramics. These materials can only be applied as dental restorations if they are durable within the oral environment. Moreover, the variability of the chemical solubility levels of dental ceramics determines the suitability of their applications as restorative materials within the oral cavity according to the ISO 6872 (BS ISO, 2015) as shown in Table 3. Nevertheless, the future of restorative dentistry seems to be directed towards those materials due to their superior aesthetic, mechanical and chemical durability characteristics.

These unique properties of glass-ceramics are linked commonly to the development of the multiphase crystalline microstructure (Clark and Zoitos, 1992). It is crucial to identify the role of each phase, which helps to anticipate the behaviour of glass-ceramics. The multiphase system has two subdivisions: 1) the amorphous phase, and 2) the crystalline phase.

A number of studies in regards to glass corrosion have presented the mechanisms of corrosion that fall into five types (Clark and Zoitos, 1992): 1) ion exchange: between alkali ions from the glass and hydrogen from the solution, 2) total dissolution: breakdown of the silicate microstructure at the glass surface, 3) saturation and precipitation: the concentration of elements in the solution reaches the saturation limit and precipitate on the glass surface, 4) pitting: uneven attack of the surface of the glass due to stress concentration or heterogeneities, and 5) weathering: water vapour exposure to the glass surface with or without condensation. For glass-ceramics, it is often the glass remnants that exist within the microstructure after crystallisation that are the most chemical soluble (Stokes et al., 2002). It has been reported that ion exchange and uniform dissolution reactions could occur by immersing glass in an aqueous medium (Koenderink et al., 2000).

Many factors could affect the rate of these reactions, including temperature, solution pH and glass composition (El-Shamy et al., 1972). It appears that immersing glass at higher pH (>9) favours uniform dissolution, whilst ion exchange is suppressed. However, ion exchange becomes more dominant over uniform dissolution at lower pHs (<9). El-Shamy (1972) stated that ion exchange reaction rate was relative to the square root of time, as exchanging cations' diffusion appears to control the reaction. Hence, it seems that as pH decreases, the glass dissolution rate increases respectively.

Generally, dental ceramics display high chemical durability, which can be affected by a number of factors, such as the chemical composition of the dental ceramics, the nature of the acidic media, the temperature and the exposure time (Milleding et al., 2002). The chemical composition of dental ceramics can vary depending on the percentage of the glassy phase and crystalline phase (Babu et al., 2015). Thus, the chemical solubility mechanism could differ between different dental ceramics.

A number of studies investigated the effects of acidic media on the different phases of glass-ceramics microstructure (Berezhnoi, 1970). Their findings showed that some elements have high resistance to acidic media such as quartz, whereas some elements such as lithium disilicate and metasilicate are less resistant to acid solutions. In general, the amorphous phase of glass-ceramics dissolves more readily, whilst, the crystalline phase is commonly denser and has minimum ion movement (McMillian, 1964). Moreover, it has been stated that the composition, structure, volume fraction and grain size of the crystalline phase play a major rule of the overall durability of glass-ceramics (Clark and Zoitos, 1992). However, these elements are influenced by the composition of the parent glasses and the process of heat treatments (Kang et al., 2018).

In the past few decades, there is an increased emphasis in ceramics toward restorative dentistry. Della Bona and Kelly (2008) reviewed the clinical evidence of all-ceramic restorations between 1993 and 2008. They found that more than 90 % of all-ceramic restorations demonstrated a success rate of six years and the major cause of failure was due to catastrophic fractures. These fractures may occur due to internal stresses that could be induced by surface degradation. This degradation may occur due to mechanical forces, chemical attack or a combination of both (Anusavice, 1992).

As is well known, the chemical durability of dental ceramics is an important feature that affects their service performance within the oral environment. *In vitro* studies have demonstrated that ceramic materials are liable to corrosion within the pH range of human saliva (Anusavice, 1992, Kukiattrakoon et al., 2010). For this reason, the buffering capacity of saliva and the personal dietary habits have a direct influence on the pH levels inside the oral cavity (Bartlett et al., 2011), and thus the chemical durability of dental ceramic restorations might be affected as a result. Some clinical investigations reported that ceramic restorations had signs of surface degradation and roughness between 12 and 24 months (Esquivel-Upshaw et al., 2013).

It has been shown that the microstructure and the processing technique have an impact on the final properties of dental ceramics including chemical durability. For example, dental ceramics containing quartz and pyroxene are less soluble than materials containing lithium metasilicate and disilicate (Kang et al., 2018), and polycrystalline materials such as Y-TZP are more resistant to dissolution than glass-ceramics (McLaren and Giordano, 2014). Different processing techniques appear to have a great correlation to the success or the failure of dental ceramics. It has been reported that machined and pressed dental ceramics have shown better performance in the oral environment than powder and liquid versions of the same material (McLaren and Giordano, 2014).

Although dental ceramics are generally very durable and resistant materials to electrochemical corrosion, they still require a reliable test to measure solubility levels. In 1978, the first standard was introduced for measuring the solubility of dental ceramics that has been driven by the BSI standard “BS 5612: Dental porcelains for jacket crowns” (BS, 1978).

Historically, the classical feldspathic dental porcelains have evolved from European tri-axial white-ware formulations (clay, quartz and feldspar). The logical assumption would be that the methodological origin of solubility tests is most likely related to this industrial development. A good example of such an instance, during the late 1960s, numerous industrialised countries have determined regulations in order to specify the limits of metal ion release from the glazed ceramic surfaces of cooking ware and tableware by using a 4 % acetic acid solution (Gould and Moss, 1982, Abou-Arab, 2001).

Both BS 4860 (BS ISO, 1972) ‘withdrawn’ (for glazed ceramic ware and cooking ware) and BS 6748 (BS ISO, 1986+A1:2011) ‘current’ (for glassware, glass-ceramic ware and vitreous enamel ware) require 24 ± 0.5 h exposure to a 4 % (v/v) acetic acid solution at 19-21°C and 22 ± 2°C respectively. Moreover, the solubility tests for sanitary-ware require 16 h exposure to 10 % acetic acid solution at 100°C (Taylor and Bull, 1986). There are many different standards incorporating different solubility testing parameters including reagent, assessment, duration, temperature and test object as shown in Table 4.

Table 4: The table shows different chemical solubility testing standards with different parameters.

Standard	Test object	Geometry	Reagent (volume/ mass)	Measurement Outcome	Time/ Temp
Name (Date)					
ASTM C724-91: 2010	Ceramic decorations on architectural type glass	Not determined	10 % citric acid 3.7 % hydrochloric acid (by mass)	Visual evaluation	15 minutes at 20 ± 2°C
ASTM C650-04: 2014	Ceramic tile	Ceramic tile should be 50 by 50 mm^2 (Glazed or unglazed)	10 % hydrochloric acid 10 % potassium hydroxide (by volume)	Visual evaluation or Pencil test	24 h at 110 ± 5°C
ASTM C735-04: 2014	Ceramic decoration on returnable beer and beverage glass containers	The decorated ware should be representative of the lot in accordance with C224	10% hydrochloric acid (by volume)	Visual comparing	20 minutes at 25 ± 5°C
ISO 4049: 2009	Polymer based restorative materials	Specimen discs of 15.0 ± 0.1 mm in diameter and 1.0 ± 0.1 mm thick.	Water (pH 7.1)	Mass loss ($\mu g/mm^3$)	7 days at 37 ± 1°C
BS 5612: 1978	Dental porcelain for jacket crowns	10 g sample from the "pool" of powder	4 % acetic acid (by mass)	Mass loss ($\mu g/cm^2$)	16 h
BS 6748: 1986 +A1:2011	Ceramic ware, glassware, glass-ceramic ware and vitreous enamel ware	Volumetric glassware of class B, or better, accuracy as specified in BS 700, BS 846 or BS 1792	4 % acetic acid (by volume)	The nature of the article under test, the surface area or volume of the article, and the amount of lead and/or cadmium	24 ± 0.5 h at 22 ± 2°C
ISO 6872: (1984 - 1995 - 2008 - 2015)	Dental ceramics	Total surface area 30 cm^2	4 % acetic acid (by volume)	Mass loss ($\mu g/cm^2$)	16 h at 80 ± 3°C

Currently, the chemical durability of dental ceramics is measured by a standardised testing method ISO 6872 (BS ISO, 2008, BS ISO, 2015) ‘Dentistry - Ceramic materials’ that displaced the old standard ISO 6872 (BS ISO, 1995b) ‘Dental ceramic’. The standard determined the level of accepted solubility of both directly and indirectly exposed dental ceramics “enamel and core classes” to the oral environment. Enamel class dental ceramics should display up to 100 μg/cm^2 for maximum solubility level, whereas core class ceramics must show less than 2000 μg/cm^2. These values have been specified in ISO 6872:1995, however the rationale behind them have not been reported.

The ISO standard chemical solubility testing method has standard parameters, which are the test solution, temperature and duration. Even though these parameters do not simulate the exact condition found in the oral environment, they mostly simulate the aggressive chemical condition that can be found in mouth. The methodology of ISO 6872 uses 4 % (v/v) acetic acid solution as a test medium. It used to be 4 % (m/m) in regards to the BSI 5612 (BS, 1978) then it was changed to a volume ratio in the new ISO standard. The rationale behind ISO selection of this particular solution with specific concentration was dependent on the range of pH in the oral environment. The Food and Drug Administration (FDA, 2003) has analysed the acidity range of foods that are habitually consumed varies between pH 1.8 – 2.0, regarding citrus fruits and vegetables, whereas food such as prawns demonstrate a pH extend between 7.0 – 7.3. Comparatively, the pH of 4 % (v/v) acetic acid solution is about 2.4, which place it as a suitable representative of low pH levels that would be present inside the oral cavity.

The ease of reproduction is an additional factor in its accreditation as the test medium. In spite of that, many researchers have tried using other more specialised media for solubility testing. For instance, hydrochloric acid has been used to test the chemical solubility of dental ceramics (Curkovic and Jelaca, 2009), as well as de-ionized still water, artificial saliva and pH 1.0 buffer solution (Anusavice and Zhang, 1998). McLean (1979) analysed solubility levels by soaking porcelain samples for four days in 0.25 % (v/v) HCl at room temperature rather than involving acetic acid. Although artificial saliva has been used as a test medium by some investigators, the standardisation of its preparation appears to be challenging among researchers. Additionally, the low effect of artificial saliva that does not truly display any erosive actions compared to actual conditions inside the oral cavity. Likewise, Kukiattrakoon et al. (2010) experimented using several dental ceramic types with different acidic media (citrate buffered, mango and pineapple juices), and used de-ionized water as a control group.

Even though these previous articles were not criticising the standard chemical solubility method directly, the fact that some researchers are performing different tests for chemical solubility shows the lack of confidence in the current standard test. Although, the use of dental ceramics goes back to many years, the ISO 6872 solubility method have not received much criticism in the literature. Commonly, mimicking the oral cavity environment is a sophisticated task for most *in vitro* studies, including chemical solubility testing.

Another test factor is controlled temperature. Both latest versions of ISO 6872 (BS ISO, 1995b, BS ISO, 2008, BS ISO, 2015) specify 80°C as the test temperature. It is claimed that 80°C is a representative of an accelerated medium to test solubility compared to the oral environment, which commonly varies between 5 – 55°C. De Rijk et al. (1985) reported that the accelerated solubility test showed effects on ceramic samples after 1 week immersion at 80°C in 4 % acetic acid as well as the immersion in artificial saliva at 22°C for almost 22 years.

The BSI and ISO standards for dental ceramics use a 16-hour duration for the test (in 4% v/v acetic acid at 80°C). The reasons for this duration are not published, but it is believed that the timings were chosen to offer a balance between a reasonable timeframe for collecting data and a measurable mass loss for typical dental ceramics (16 hours is 'overnight', 5pm to 9am, and so allows for daily test cycles).

Before 2008, investigators used to measure the levels of chemical solubility of dental restorative ceramics by applying the former ISO 6872 (BS ISO, 1995b). The standard specified 10 discs with 12 ± 0.2 mm (diameter) and 1.6 ± 0.1 mm (thickness) for the chemical solubility test using refluxing method. The rationale of modifying this method was due to the issues that appear with inadequate exposing of the samples' surfaces to acetic acid solution, which would result in irreproducible outcomes. This methodology was subjected to clumping of the specimens inside test apparatus that lead to unequal exposure of the tested specimens' surfaces due to the effect of the refluxing process that would be an additional factor for outcomes' variability (Stokes et al., 2002).

After 2008, measuring the chemical solubility of dental ceramics is derived through the specified method of the ISO 6872 (BS ISO, 2008, BS ISO, 2015). The obvious difference between the two versions is that the current method specifies only the total surface area (≥ 30 cm^2) but determines neither the test specimens' morphology nor geometry. This modification may have a considerable impact on the reproducibility of the test outcomes. In addition, the static solution method replaces the refluxing system of the old version in order to enhance the reproducibility. The uncertainty of the solubility-testing method is not a recent matter. Fathi et al. (2014) reported that the chemical solubility value for apatite-mullite glass-ceramic was higher under the previous ISO standard method than the new standard, which could be due to the changing of the specimens' specification.

The origin of the ISO solubility method refers to the BSI standard (BS 5612) "Dental porcelains for jacket crowns". As already stated, the chemical solubility test of this standard was based on refluxing porcelain specimens for 16 h in 4 % (m/m) acetic acid in water. The chemical solubility test of the previous standard ISO 6872 (BS ISO, 1995b) was similar to the BS method, the ISO standard however stipulates 4 % (v/v) acetic acid in water of grade 3, as defined in ISO 3696 (BS ISO, 1995a). The solubility test of the ISO standard (BS ISO, 2008, BS ISO, 2015) is similar to the previous standard, except replacing refluxing solution by static solution method, where specimens with specific surface area are immersed for 16 h in 4 % acetic acid solution at 80°C. None of these methods provide sources about the methodological origins of chemical solubility testing.

The lack of confidence of the ISO solubility-testing standard can be recognised within the scope of dental materials. Many researchers have developed alternative methods for chemical solubility assessment of dental ceramics as stated previously (McLean, 1979, Anusavice and Zhang, 1998, Kukiattrakoon et al., 2010). However, some researchers have applied the ISO method of testing solubility of some ceramic materials. For instance, a comparison study demonstrated the chemical solubility of three different "core class" porcelains (Procera®, IPS Empress® and In-Ceram®), and concluded that the last type displayed the highest solubility level (Esquivel-Upshaw et al., 2001). GeisGerstorfer and Schille (1997) investigated different dental ceramics and reported that most showed acceptable chemical solubility values as stated in the standard.

There are however few studies that criticised the methodology of the ISO 6872 (BS ISO, 1995b) standard and attempted to improve the findings reproducibility. For instance, a study by Stokes et al. (2002) modified specimens' morphology from discs to beads of glass that were immersed in acetic acid solution in accordance with ISO 6872 testing method. This novel modification of sample geometry seemed to be more reliable than the actual standard test. Consequently, this method, which utilised beads specimens aimed to provide much more exposure effects than discs with sharp edges, could alter the solubility value.

2.3. Research significance

The interest of the chemical durability of dental ceramic materials is strongly significant as much as the importance of gaining superior mechanical strength, fracture toughness or aesthetic appearance. Measuring the level of solubility plays a considerable role in determining the success or failure status of dental ceramic restorations. Likewise, it can assist in anticipating the durability and the lifespan of a dental restoration. Thus, dental ceramics' solubility in the oral cavity is considered a primary interest. It is important that dental ceramics demonstrate solubility levels parallel with the International Organization for Standardization (ISO). It is therefore important that a reliable and clinically relevant test can be applied to dental ceramics.

The lack of data in the literature indicates the significance of this research in order to assess thoroughly the current ISO solubility testing method. As stated before, the current ISO 6872 (BS ISO, 2015) method does not specify the specimen's geometry. Therefore, the specimens could be designed in any shape if it was possible to calculate the surface area. This research will investigate the reliability and relevance of the existing standard method of solubility testing for a range of dental ceramics and seek to improve the method if found necessary.

Chapter 3

Aim and Objectives

Chapter 3: Aim and Objectives

3.1. Aim

The aim of this research is to investigate the validity of the ISO 6872 (BS ISO, 2015) ‘Dentistry - Ceramic materials’ for chemical solubility and to develop a methodology for testing the chemical solubility of dental ceramics in order to improve the reproducibility of solubility findings.

3.2. Objectives

- Review the existing literature on (a) the different chemical solubility methods for dental ceramics, and (b) relate them with other chemical solubility methods of similar materials.
- Design and conduct a verification study of a dental ceramic material with a specific standard morphology and geometry to obtain evidence of the reliability of the current ISO standard method.
- Conduct a comparative benchmarking study of different types of dental ceramics and different geometry with the exact methodology design of the verification study.
- Design and conduct experimental studies with different shapes and different geometries.
- Observe and investigate the mechanical and physical properties of the specimens’ surfaces pre and post-solubility testing.
- Design an improved (for inter-operator reliability) chemical solubility method for dental ceramics.

Chapter 4

Verification Study

Chapter 4: Verification Study

4.1. Introduction

The ISO standard 6872 (BS ISO, 2015) for dental ceramics specifies minimum values for chemical solubility. The losses for a substructure ceramic should be less than 2000 µg/cm^2 and less than 100 µg/cm^2 for a body ceramic. The standard specifies only the total surface area and does not define the geometry nor the number of the test specimens. Therefore, it is possible to choose any number of specimens or geometries to perform the test.

A market leading and established dental ceramic, VITABLOCS® Mark II (coded "VMII") dental ceramic (VITA Zahnfabrik, Bad Säckingen, Germany), was chosen to conduct the chemical solubility testing for this verification study in accordance to the ISO 6872 (BS ISO, 2015). This material is composed of fine-particle feldspar ceramic pre-formed blocks. This experiment included three separate repeated tests that were performed with identical methodology parameters. A cubic shape was chosen as a standard test morphology with an individual surface area of 5 cm^2 (a naming scheme was devised where C means cubic, with following number being the individual specimen surface area, e.g., C1.5 means a cubic specimen with 1.5 cm^2 surface area and C5.0 means a cubic specimen with 5.0 cm^2 surface area). Each test comprised of six specimens in order to reach the minimal required total surface area (30 cm^2) in accordance to the standard method.

4.2. Aim

- To obtain a standardised method for solubility testing compliant with the ISO 6872 (BS ISO, 2015) in order to establish a foundation for subsequent studies.

4.3. Objectives

- To conduct a chemical solubility test on a dental ceramic with a specific and identical geometry (cube).
- To assess the repeatability of the test under one operator and controlled conditions.

4.4. *Materials and Methodology*

4.4.1. Sample Preparation

The test specimens were prepared to the required dimensions using an ISOMet 1000 (Buehler, Warwick, UK) sectioning saw and were cut precisely using the Precision Diamond Wafering Blade (Buehler, Warwick, UK) (15.2 cm diameter x 0.5 mm thickness). The specimens were cut slightly larger than the required size to allow for further finishing.

The surface areas of the cubic specimens were determined by measuring the dimensions at three different points along each axis using a Vernier caliper (± 0.0005 m) to ensure equal planes of the specimens' surfaces, taking the average, squaring it and multiplying by six.

According to the manufacturer recommendations (VITA Zahnfabrik, 2009), this material should be finished by Al_2O_3 coated flexible discs and polished by Occlubrush and diamond polishing paste. However, this method was found to be time consuming and impractical to prepare large number of specimens for this research. Therefore, a more feasible method was required.

Each surface of the specimens was finished and polished by Buehler Metaserv Grinder Polisher (Buehler, Warwick, UK). Each surface of the specimens was initially finished with SiC grinding papers (P120), (P600), and then (P1000) for 1 minute each. The specimen surfaces were then polished using 8-inch micro-cloth with 6 μm and then 1 μm polycrystalline diamond suspension (Buehler, Warwick, UK), for 2 minutes each. The surface roughness analysis was performed on all specimens using a surface roughness tester (TR-200 (Beijing TIME High Technology Ltd, China)) in order to obtain a standardised roughness for all specimen surfaces. The surface roughness values by this applied method was similar to the values of the recommended polishing method by the manufacturer.

Three groups of specimens were prepared to perform the test three times for reliability.

4.4.2. Methodology

According to the ISO recommendations as shown in Table 5, distilled water of grade 3 as per ISO 3696 (BS ISO, 1995a) was used to wash the specimens, which were placed in a clean and dry glass jar. The glass jar was placed and dried at 150 ± 5°C in a thermostatically controlled oven for 4 h, then removed and left for 15 minutes to cool. The specimens were weighed to the nearest 0.1 mg using a Mettler AJ100 Analytical Balance (Scientific Support, USA). Plastic tweezers were used to limit the possibility of damage to the specimens.

The specimens were immersed in 100 ml acetic acid 4 % (v/v) solution in water of grade 3 in accordance to ISO 3696 (BS ISO, 1995a) using a 250 ml Pyrex glass bottle. The glass bottle was sealed with a glass slab to prevent evaporation, and was then placed in a calibrated, preheated oven to 80 ± 3°C for 16 h. Afterwards, the specimens were washed using distilled water and dried at 150 ± 5°C to constant mass as performed previously. The specimens were reweighed to the nearest 0.1 mg. The solubility values were determined by calculating the mass loss of the specimens in micrograms per square centimetre: (chemical solubility (μg/cm^2) = weight loss (μg) / surface area (cm^2)). Each test was performed and analysed individually.

Table 5: The table demonstrates the current methodology for measuring the chemical solubility values of dental ceramics according to ISO 6872 (BS ISO, 2015).

Reagent	4 % (V/V) solution in water of grade 3 as specified in ISO 3696 (analytical grade)	
Apparatus	Balance	Accurate to 0.1 mg
	Drying oven	Capable of being controlled at (150 ± 5)°C
Preparation	At least 30 cm^2 of exposed surface area freely accessible to the test solution	
Procedure	Wash	With water grade 3 as per ISO 3696
	Dry	At (150 ± 5)°C for 4 h
	Weigh	To the nearest 0.1 mg
	Immerse	In 100 ml acetic acid (analytical grade) and 4 % (V/V) solution in water of grade 3 as specified in ISO 3696.
	Test	Place specimen bottle in a preheated oven at 80 (±3)°C for 16 h
	Wash	With water grade 3 as per ISO 3696
	Dry	150 (±5)°C for 4 h
	Reweigh	To the nearest 0.1 mg
	Calculate the mass loss	In micrograms per square centimetre of the specimens
Check for compliance	As stated in Table 3.	

4.5. Results

The chemical solubility values measured for VMII were comparable among the three tests as shown in Table 6. Figure 1 shows comparable chemical solubility values of this material. One-way ANOVA indicated that there was no significant difference between the three tests.

Table 6: The table shows the chemical solubility of VITABLOCS Mark II for the three test groups. The individual surface area of each specimen= 5 cm^2. Chemical solubility is in $\mu g/cm^2$.

Material	**Test**	**Chemical solubility ($\mu g/cm^2$)**
VMII	1 (n=6)	289
	2 (n=6)	295
	3 (n=6)	292

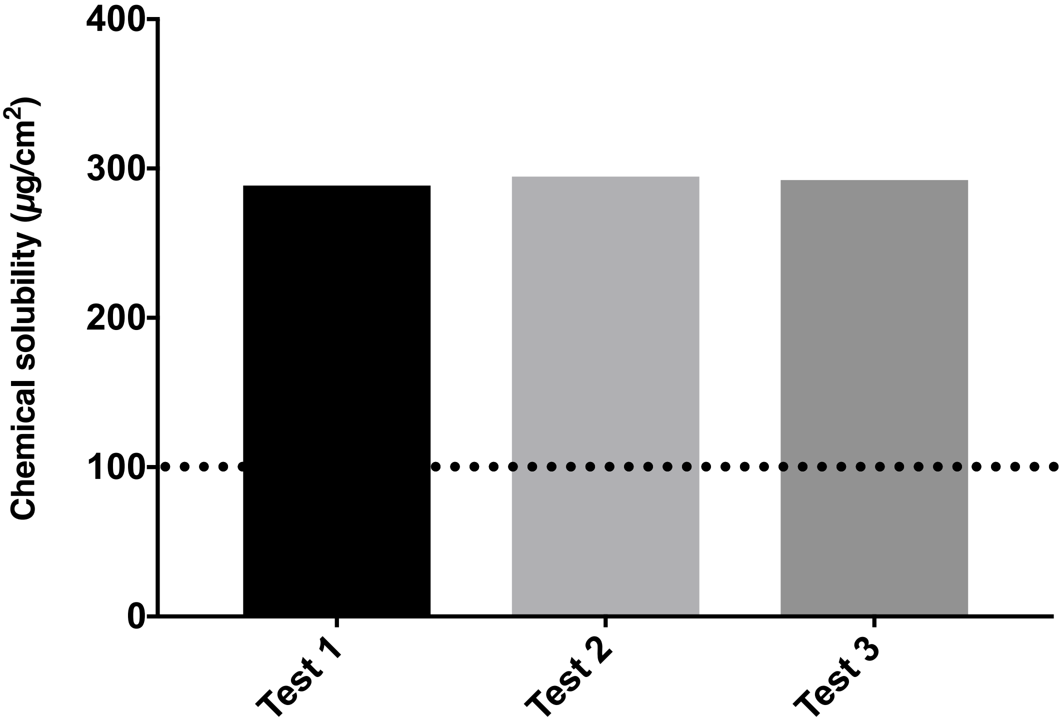

Figure 1: The bar chart shows comparable solubility values of the three tests of VMII dental ceramics (Individual specimen surface area = 5 cm^2). The dotted line demonstrates the maximum acceptable chemical solubility (100 µg/cm^2) for enamel ceramics according to the ISO 6872 (BS ISO, 2015).

4.6. Discussion

The method for testing solubility as described in ISO 6872 (BS ISO, 2015) has shown that it is possible to obtain relatively consistent results, although these figures do mask a number of concerns about the potential reliability of the test. As stated previously, the current standard does not specify the specimen's number or shape. Therefore, it was necessary to define the specimen's shape and number, which should be in accordance with the standard specification of the minimum total surface area (30 cm^2). The specimens of this verification study were set to cubes with individual surface area equals to 5 cm^2. Although the current ISO 6872 requires performing the chemical solubility test for one time only, three repeated tests were performed to determine the variability in the measurements.

VITABLOCS Mark II dental ceramic (feldspar) is classified as an enamel material. The manufacturer recommends using this material as inlays, onlays or partial crowns (Datzmann, 1996). It was predicted from the former indications that this material should exhibit a chemical solubility value that is acceptable for enamel type dental ceramics (less than 100 μg/cm^2). Positively, the results of this study revealed comparable chemical solubility values when the test was repeated three times. However, these results were *above* the specified maximum limit of chemical solubility, which ranged from 289 to 295 μg/cm^2, for enamel type materials according to the current standard, which is a 100 μg/cm^2.

Even though, no studies have been found in regard to investigating the chemical solubility values of VMII using the ISO standard, a number of clinical studies have claimed that this material has a good survival rate up to 10 years (Reiss and Walther, 2000, Posselt and Kerschbaum, 2003, Bindl and Mormann, 2004). The findings of these studies indicate that the performance of VMII is clinically acceptable, which could indicate the current solubility findings are not decisive enough.

In regard to specimens' preparation, the preferred way to mill VMII is using CAD/CAM wet milling. Because of the required specimen geometry made using this technique impossible, the ISOMet 1000 Buehler (Buehler, Warwick, UK) sectioning saw machine was considered. Limitations were encountered while using this device to prepare the test specimens of VMII in this study. The cutting speed itself was not a problem, but the preparation process was time consuming.

As mentioned before, the VMII specimens were not finished following the advised way by the manufacturer, however the performed method in this research was very similar and produced nearly identical results. It was important to prepare the specimens to slightly larger dimensions to allow further finishing and avoid the risk of preparing smaller specimens, which cannot be used in the test. Therefore, finishing the specimens to obtain the required dimensions took many days to complete. Although, it takes significantly a longer time than using CAD/CAM, it also provides accurate measurements if used carefully.

The parameters of the current study are already specified by the ISO 6872 (BS ISO, 2015) except the specimen geometry and number that were defined randomly as 6 specimens with 5 cm^2 individual specimen surface area to perform the chemical solubility test. As stated before, Fathi et al. (2014) has claimed that the chemical solubility values of apatite-mullite glass-ceramics were different by the previous and the current versions of ISO 6872 (BS ISO, 1995b, BS ISO, 2008) due to the lack of specimen specification. An important question would be raised 'will other numbers or shapes of the test specimens affect the solubility outcomes or not?'. Therefore, further investigations are required to answer this question.

4.7. Conclusion

The study shows that is the specimen geometries are maintained, and the specimens are treated equally during the test, there is very little variability in the chemical solubility. Although VMII is a well-established dental ceramic material, the solubility values of VMII were considerably greater than the standard maximum limit of the ISO 6872.

Chapter 5

Investigating the Effect of Individual Specimen Size

Chapter 5: Investigating the Effect of Individual Specimen Size

5.1. Introduction

As described in Chapter 4, the verification study demonstrated that the current chemical solubility method of ISO 6872 (BS ISO, 2015) can be reproducible if the specimens have the same shape and the same individual specimen surface area. However, this might or might not be the case with different individual surface areas. Therefore, this chapter investigates the impact of specimen sizes on the chemical solubility.

This chapter explores the chemical solubility values of ceramic materials that were selected as being representative of different categories of dental ceramics in the current use. It also investigates the effect of altering the individual specimen surface area.

The null hypothesis was that the chemical solubility measurements of different individual specimens' sizes are the same.

5.2. Aim

- This experiment aims to study the effect of altering the individual specimen surface area on the chemical solubility, whilst still conforming to ISO 6872 (BS ISO, 2015).

5.3. Objectives

- To perform the chemical solubility test on a selection of dental ceramic materials currently available in the market.
- To investigate the chemical solubility values of a range of individual specimen surface areas.

5.4. Materials and Methods

A selection of materials and sample geometries were prepared in accordance with ISO 6872 (BS ISO, 2015). Zirconium oxide (Y-TZP, StarCeram® Z-Al-Med-HD, H.C. Starck, Germany), a feldspathic dental ceramic (VITABLOCS® Mark II, VITA Zahnfabrik, Bad Säckingen, Germany), a lithium disilicate glass-ceramic (IPS e.max® Press, Ivoclar Vivadent, UK), a fluorapatite glass-ceramic (IPS e.max® ZirPress, Ivoclar Vivadent, UK), and a hybrid ceramic (ceramic + resin-based composite) (Cerasmart™, GC Europe, Belgium) were used in this study as shown in Table 7.

Cubic specimens were prepared with a total surface area of 30.5 ± 0.5 cm^2. Table 8 & Figure 2 show the individual specimen surface area and the number of specimens needed to get the total surface area above the required $30cm^2$. The size of the material available from the manufacturers limited the individual specimen surface area possible for VMII ($7.5cm^2$), Cerasmart ($7.5cm^2$), IPS e.max press ($6.0cm^2$), IPS e.max ZirPress ($6.0cm^2$), and Y-TZP ($10cm^2$).

Table 7: Table shows materials were selected as being representative of different categories of dental ceramics and their characteristics (H. C. Starck, 2017, VITA Zahnfabrik, 2009, GC Europe, 2019, Ivoclar Vivadent 2018, Ivoclar Vivadent 2005).

Category	Material	Manufacturer	Composition	Characteristics
Sintered ceramics	StarCeram Z	H.C. Starck	Y-TZP	High strength to be applied as frameworks for crowns and bridges.
Milled ceramics	VMII	VITA Zahnfabric	Feldspatheic	Aesthetic to be applied as inlays, onlays and partial crowns.
	Cerasmart	GC Europe	Hybrid ceramic (70% silica, 30% composite)	Aesthetic, proper marginal fit and strength to be applied as veneers, inlays, onlays and crowns.
Pressed ceramics	IPS e.max Press	Ivoclar Vivadent	Lithium disilicate	High strength and aesthetic to be applied as thin veneers, inlays, onlays and crowns.
	IPS, e.max ZirPress		Fluorapatite	Aesthetic and proper marginal fit to be applied as veneers.

Table 8: Table shows the details of the possible geometries of cubes with selected materials.

Materials			**Y-TZP**	**VMII**	**IPS e.max Press**	**IPS e.max ZirPress**	**Cerasmart**
Group	**Individual surface area (cm^2)**	**No. of specimens required for 30 cm^2**					
C1.5	1.5	20	√	√	√	√	√
C3.0	3	10	√	√	√	√	√
C4.3	4.3	7	√	√	√	√	√
C6.0	6	5	√	√	√	√	√
C7.5	7.5	4	√	√			√
C10.0	10	3	√				

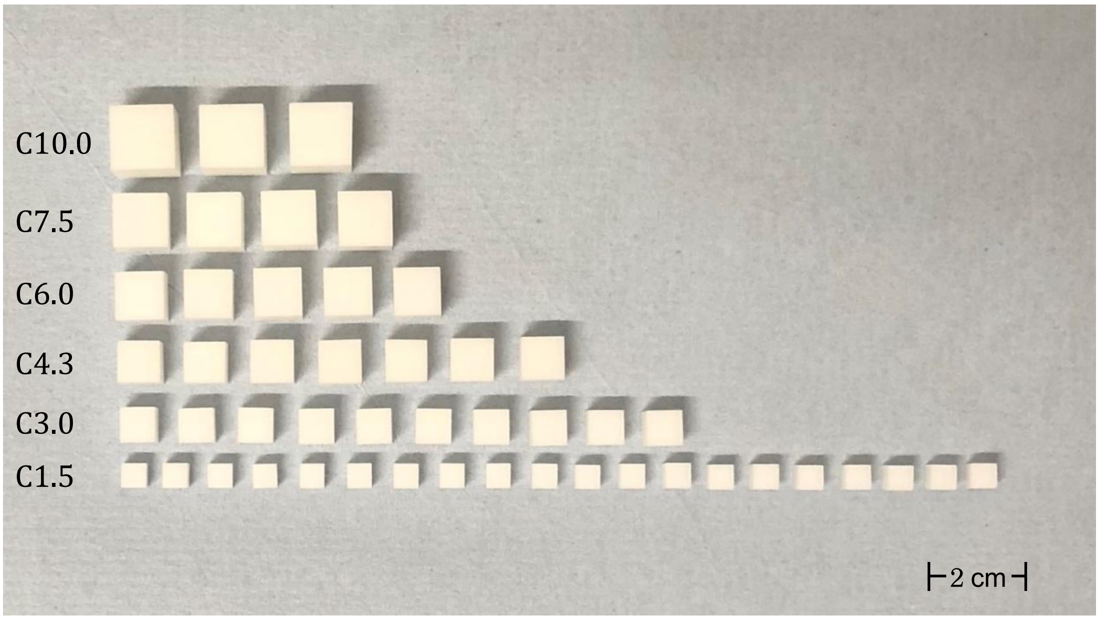

Figure 2: The figure shows the six different size groups of possible cubes as explained in Table 7, with the number required for a total surface area of at least 30cm^2.

The surface areas and surface roughness of the cubic specimens of all the study materials were determined as mentioned in Chapter 4. As each group had a different individual surface area, each group required a different number of specimens to fulfil approximately the required total surface area. This was applied to all of the chemical solubility tests in this project.

5.4.1. Sample preparation

5.4.1.1. Y-TZP

StarCeram® Z-Med (H.C. Starck, Germany) was selected to be the zirconia material for this experiment. The plan included testing six groups individually where each group had a different size from the other (C1.5, C3.0, C4.3, C6.0, C7.5 and C10.0) and repeating the test three times to determine the variability in the measurements. Each group must fulfil the minimum requirement of the total surface area of samples as stated in the ISO standard. Table 8 (see page 72) illustrates the samples' numbers and geometries.

The preparation of the Y-TZP cubes started with creating three-dimensional designs using Computer Aided Design (CAD) software (Tinkercad, Autodesk, USA). The different sizes of cubes were designed slightly larger than the required size to allow for polishing. They were machined using a 5-axis dental milling machine (DWX-50, Roland DG Corporation, UK) as shown in Figures 3 & 4. Each surface of the samples was polished using a Buehler Metaserv Grinder Polisher (Buehler, Warwick, UK) using silicon carbide (SiC) grinding papers through graduated steps of P600 to P1000 (P600 for 30 seconds, P800 for 30 seconds, and finally P1000 for 30 seconds). The sintering process was performed using a dental sintering furnace (Ceramill® Therm, Amann Girbach, Germany). The furnace was set according to the manufacturer recommendations as shown in Table 9.

Table 9: The table shows the sintering parameters of StarCeram® Z-Med. Source: User guide for StarCeram® Z-Med dental zirconia (H.C. Starck, Germany).

	Temp rise/min	**Hold**	**Temp rise/ min**	**Hold temp time**	**Temp rise/min**	**Cooling/min**
Monolithic up to 5	5°C	30 minutes @900°C	2.5°C	2 h @1500°C	5°C/ minutes to 800°C	Natural

Figure 3: Milling of Y-TZP cubes using DWX-50 CAD/CAM milling machine (Roland DG Corporation, UK).

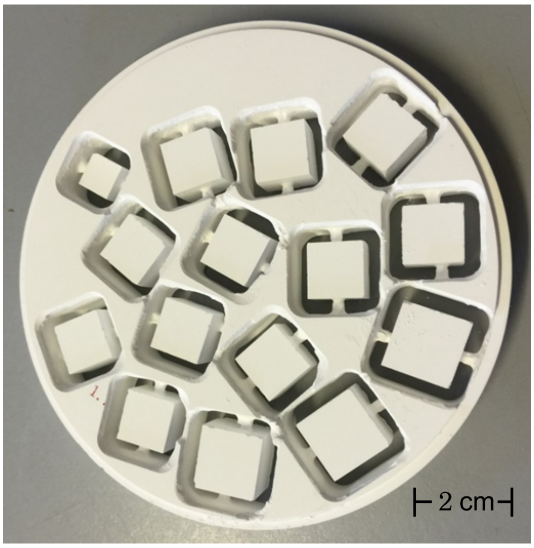

Figure 4: Milled Y-TZP cubes.

5.4.1.2. Feldspar ceramic (VITABLOCS® Mark II, VMII)

VITABLOCS Mark II dental ceramic (VITA Zahnfabrik, Bad Säckingen, Germany), a popular feldspathic dental ceramic was chosen due to its prevalence on the market and suitability for CAD/CAM milling. The specimens were prepared and finished to the required geometries as detailed in Chapter 4. Five specimen groups (C1.5, C3.0, C4.3, C6.0 and C7.5) of VMII were prepared in accordance with the individual surface area as illustrated in Table 8 (see page 72).

5.4.1.3. Lithium disilicate glass-ceramic (IPS e.max® Press, Ivoclar Vivadent)

IPS e.max Press was chosen as a representative lithium disilicate and pressable dental ceramic. The fabrication process for this material was performed using a hot pressing technique to obtain an authentic material structure. The selected specimen morphology was designed for various required geometries using CAD (Tinkercad, USA), and milled in a clean-burning wax using a DWX-50 milling machine (Roland DG Corporation, UK).

The wax patterns were encased in IPS PressVEST Speed Powder investment material (Ivoclar Vivadent, UK) and were left for 30 minutes as per manufacturer recommendations. The investment moulds were then placed in a burn-off furnace (Vecstar Limited, UK) for nearly 1 hour to burn off all the wax patterns. The ingots were pressed at (915°C) in the ceramic furnace Programat EP 3000 (Ivoclar Vivadent, UK), which has been incorporated with the combination furnace software for different materials (Ivoclar Vivadent, 2016). The moulds were removed and cooled for 60 minutes. The ceramic specimens were retrieved using sand blasting[1] (BEGO Korox 50, Germany). Each specimen surface was finished and polished using the same as performed in the verification study in Chapter 4.

Four specimen groups (C1.5, C3.0, C4.3 and C6.0) of IPS e.max Press (Ivoclar Vivadent, UK) were prepared in accordance with the individual surface areas as illustrated in Table 8 (see page 72).

1) Material: 99.6 % aluminium oxide, grain size: 50 μm

5.4.1.4. Fluorapatite glass-ceramic (IPS e.max® ZirPress, Ivoclar Vivadent)

IPS e.max ZirPress was chosen as a representative fluorapatite and pressable dental ceramic. The specimens were prepared and finished as performed with IPS e.max Press (Ivoclar Vivadent, UK). Four specimen groups (C1.5, C3.0, C4.3 and C6.0) of IPS e.max Zirpress were prepared in accordance with the individual surface areas as illustrated in Table 8 (see page 72) using the manufacturer's recommended methods as performed with IPS e.max Press (Ivoclar Vivadent, UK).

5.4.1.5. Cerasmart® – Hybrid ceramic (silica ~70 wt% + composite resin ~30 wt%)

Cerasmart is a CAD/CAM hybrid ceramic block containing a mixture of silica and composite resin. It is formed using CAD/CAM, and, it was necessary to create three-dimensional designs using CAD (Tinkercad, USA). The specimens were designed slightly larger than the required geometries to allow for further finishing. These designs were exported to the DWX-50 CAD/CAM milling machine (Roland DG Corporation, UK) as STL files. The specimens were finished and polished, and the surface roughness analysis was performed as conducted on VMII and this was illustrated in Chapter 4.

Five specimen groups were prepared (C1.5, C3.0, C4.3, C6.0 and C7.5) in accordance with the individual surface area as illustrated in Table 8 (see page 72).

5.4.2. Methodology

5.4.2.1. Chemical solubility testing

The chemical solubility tests were performed according to the ISO 6872 (BS ISO, 2015) requirements as mentioned in Table 5 (Chapter 4). Each test (group) was performed and analysed individually. Each geometry (size) of tested materials was tested once, as per the ISO standard, whilst the zirconia cubes the test was performed an additional twice to determine if there was any variability in the measurements.

5.4.2.2. Statistical analysis

All data were compared using Welch's ANOVA and a Games-Howell post-hoc test. The alpha value (p) was set at 0.05. Welch's ANOVA was performed to compare unequal variances as found in this study.

5.5. Results

5.5.1. Y-TZP

The solubility findings were varied among the six groups of Y-TZP for the three repeated tests, although the results were comparable for each group when was repeated for three times as shown in Table 10. The standard deviation of the average chemical solubility results among the cubic groups was ± 13. Although, all groups of Y-TZP showed a solubility value lower than 100 μg/cm^2, a downward trend in chemical solubility value with increasing individual specimen surface area was observed for this material.

Figure 5 shows the relationship between the solubility value and the individual specimen surface area. Welch's ANOVA showed a significant difference between groups of Y-TZP material. A Games-Howell post-hoc test indicated that there was a significant difference between all groups except between groups C4.3 and C6.0, and between group C7.5 with groups C6.0 and C10.0.

Table 10: The table shows the chemical solubility of the Y-TZP cubic groups. Chemical solubility is in μg/cm^2.

Group	**Number of specimens**	**Individual surface area (cm^2)**	**Chemical solubility (μg/cm^2)**			**Mean**	**SD**
			Test 1	**Test 2**	**Test 3**		
C1.5	**20**	**1.5**	63	63	66	64	± 2
C3.0	**10**	**3.0**	53	56	56	55	± 2
C4.3	**7**	**4.3**	46	46	49	47	± 2
C6.0	**5**	**6.0**	40	43	40	41	± 2
C7.5	**4**	**7.5**	33	36	33	34	± 2
C10.0	**3**	**10.0**	30	33	30	31	± 2

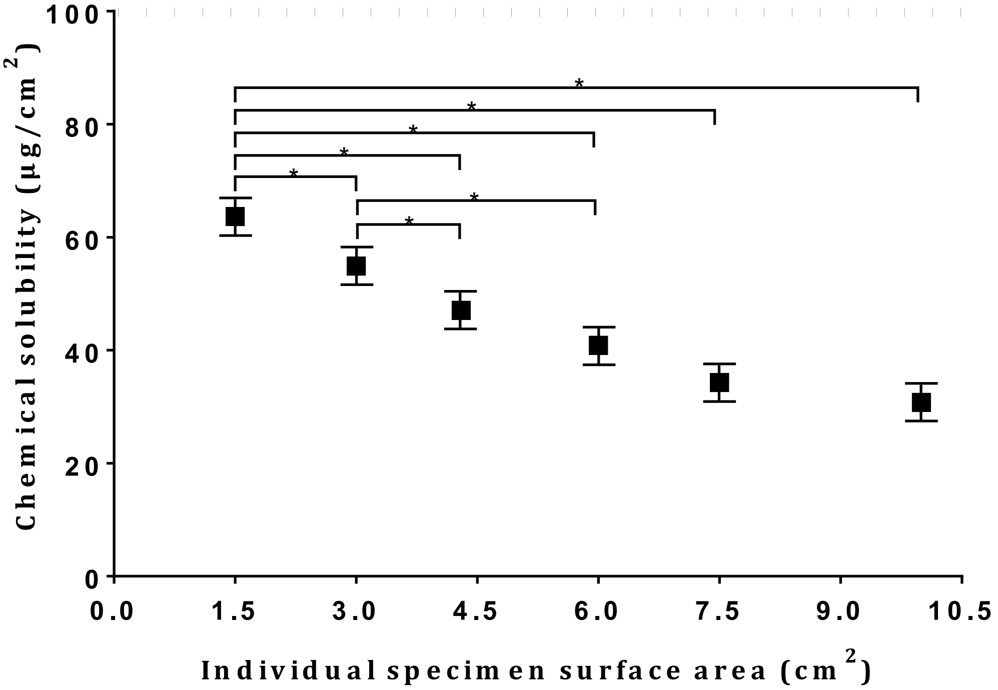

Figure 5: The dotted line demonstrates the maximum acceptable chemical solubility (100 µg/cm^2) for enamel ceramics according to the ISO 6872 (BS ISO, 2015). The graph shows the average chemical solubility of the cubic groups of Y-TZP (bars represent standard deviation), (n=3). Asterisks indicate significant difference between groups, *$p < 0.05$.

5.5.2. VMII

The chemical solubility values of VMII were varied among the four tested groups as shown in Table 11. A downward trend in chemical solubility value with increasing individual sample size was observed. As VMII material is indicated for use as an ‘enamel ceramic’, it should show a solubility value lower than 100 μg/cm^2. All groups of this material exceeded this limit.

Figure 6 shows the relationship between the solubility value and the individual surface area. Welch’s ANOVA showed a significant difference between groups. Games-Howell post-hoc test indicated that there was a significant difference between all groups except between groups C3.0 and C4.3, and between group C4.3 with groups C6.0 and C7.5, and finally between groups C6.0 and C7.5.

Table 11: The table shows the chemical solubility of VMII for the five different size groups. Chemical solubility is in µg/cm^2.

Group	**Number of specimens**	**Individual surface area (cm^2)**	**Chemical solubility (µg/cm^2)**
C1.5	**20**	**1.5**	404
C3.0	**10**	**3.0**	336
C4.3	**7**	**4.3**	300
C6.0	**5**	**6.0**	242
C7.5	**4**	**7.5**	215

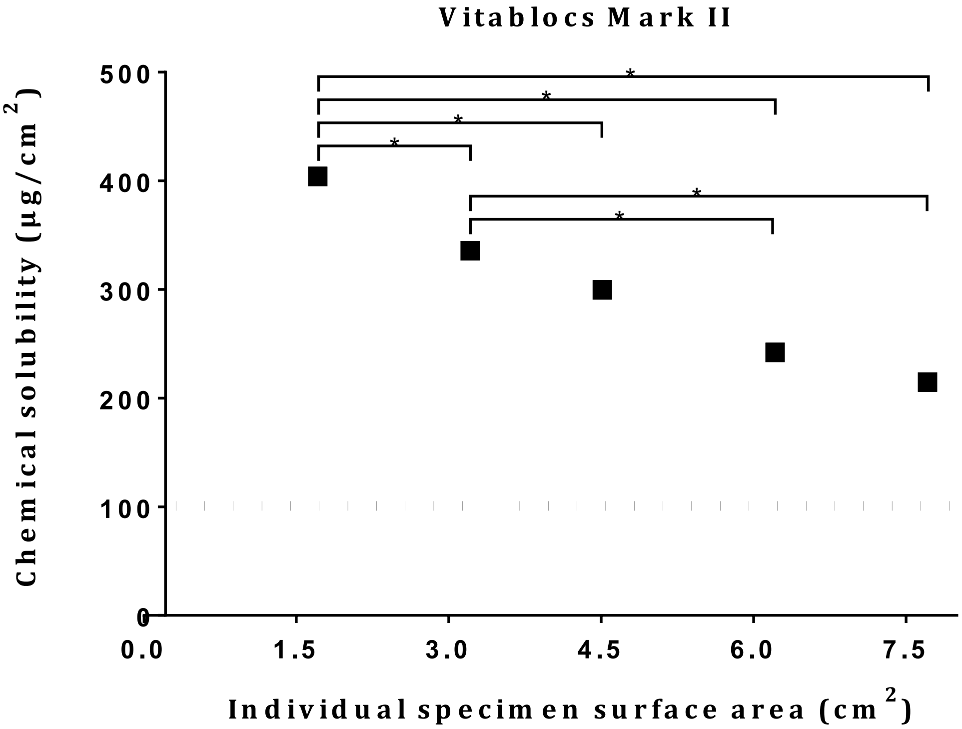

Figure 6: The dotted line demonstrates the maximum acceptable chemical solubility (100 µg/cm^2) for enamel ceramics according to the ISO 6872 (BS ISO, 2015). The graph shows a relationship between the chemical solubility value and the individual surface area of VMII groups (n=1). Asterisks indicate significant difference between groups, *p < 0.05.

5.5.3. IPS e.max Press

The solubility findings were varied among the four groups as shown in Table 12. A downward trend in chemical solubility value with increasing individual sample size was observed. As this ceramic material is indicated for use as an ‘enamel ceramic’, it should show a solubility value lower than 100 µg/cm^2. All groups of this material exceeded this limit except group C6.0.

Figure 7 shows the relationship between the solubility value and the individual surface area of IPS e.max Press groups. Welch’s ANOVA showed a significant difference between groups. A Games-Howell post-hoc test indicated that there was a significant difference between all groups except between group C3.0 with groups C1.5, C4.3 and C6.0, and between group C4.3 and C6.0.

Table 12: The table shows the chemical solubility of IPS e.max Press. Chemical solubility is in µg/cm^2.

Group	Number of specimens	Individual surface area (cm^2)	Chemical solubility (µg/cm^2)
C1.5	**20**	**1.5**	158
C3.0	**10**	**3.0**	152
C4.3	**7**	**4.3**	113
C6.0	**5**	**6.0**	88

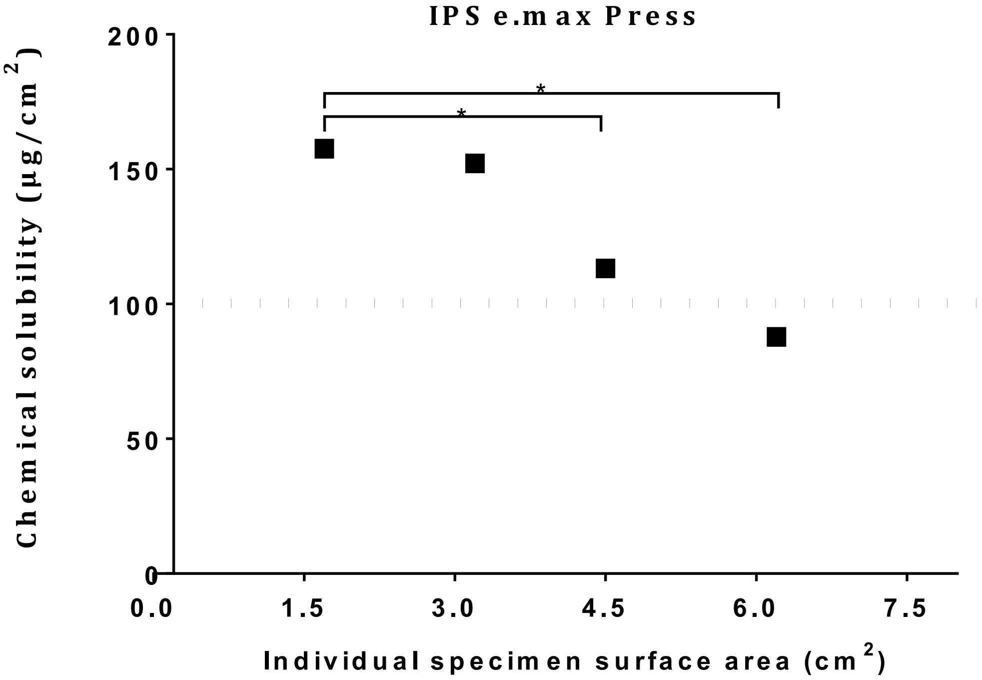

Figure 7: The dotted line demonstrates the maximum acceptable chemical solubility (100 µg/cm^2) for enamel ceramics according to the ISO 6872 (BS ISO, 2015). The graph shows a relationship between the chemical solubility value and the individual surface area of IPS e.max Press groups, (n=1). Asterisks indicate significant difference between groups, *$p < 0.05$.

5.5.4. IPS e.max ZirPress

The four groups of IPS e.max ZirPress specimens showed variable solubility outcomes as shown in Table 13. Likewise, a downward trend in chemical solubility value with increasing individual sample size was observed. As this ceramic material is indicated for use as an ‘enamel ceramic’, it should show a solubility value lower than 100 μg/cm^2. Groups C1.5 and C3.0 of IPS e.max ZirPress material exceeded this limit.

Figure 8 shows the relationship between the solubility value and the individual surface area. Welch’s ANOVA showed a significant difference between groups. A Games-Howell post-hoc test indicated that there was a significant difference between all groups except between groups C1.5 and C3.0, and between group C4.3 with groups C1.5, C3.0 and C6.0.

Table 13: The table shows the chemical solubility of IPS e.max ZirPress. Chemical solubility is in µg/cm^2.

Group	**Number of specimens**	**Individual surface area (cm^2)**	**Chemical solubility (µg/cm^2)**
C1.5	**20**	**1.5**	117
C3.0	**10**	**3.0**	116
C4.3	**7**	**4.3**	81
C6.0	**5**	**6.0**	49

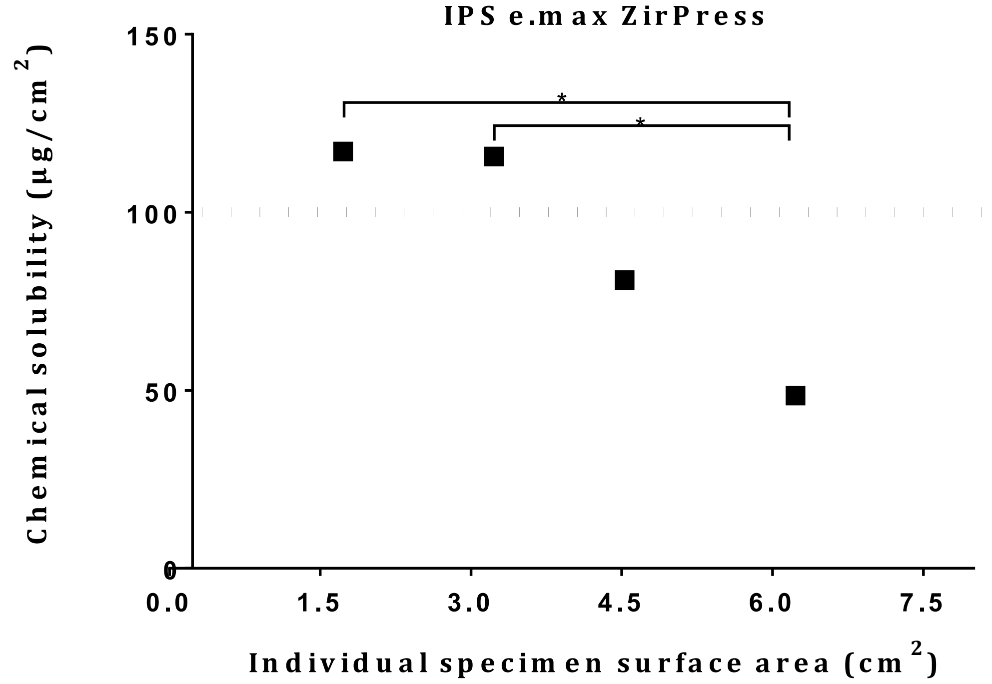

Figure 8: The dotted line demonstrates the maximum acceptable chemical solubility (100 µg/cm^2) for enamel ceramics according to the ISO 6872 (BS ISO, 2015). The graph shows a relationship between the chemical solubility value and the individual surface area of IPS e.max ZirPress groups, (n=1). Asterisks indicate significant difference between groups, *$p < 0.05$.

5.5.5. Cerasmart

The four groups of Cerasmart specimens showed variable solubility (and sorption) outcomes. As this hybrid material is indicated for use as an 'enamel ceramic', it should show a solubility value lower than 100 μg/cm^2. All groups of this material showed that there was not a mass loss as shown in Table 14.

Figure 9 shows a relationship between the solubility value and the individual surface area. Welch's ANOVA showed a significant difference between groups. Games-Howell post-hoc test indicated that there was a significant difference between all groups except between group C3.0 with groups C4.3 and C6.0.

Table 14: The table shows the chemical solubility of Cerasmart groups. Chemical solubility is in µg/cm^2.

Group	Number of specimens	Individual surface area (cm^2)	Chemical solubility (µg/cm^2)
C1.5	**20**	**1.5**	-78
C3.0	**10**	**3.0**	-85
C4.3	**7**	**4.3**	-90
C6.0	**5**	**6.0**	-85

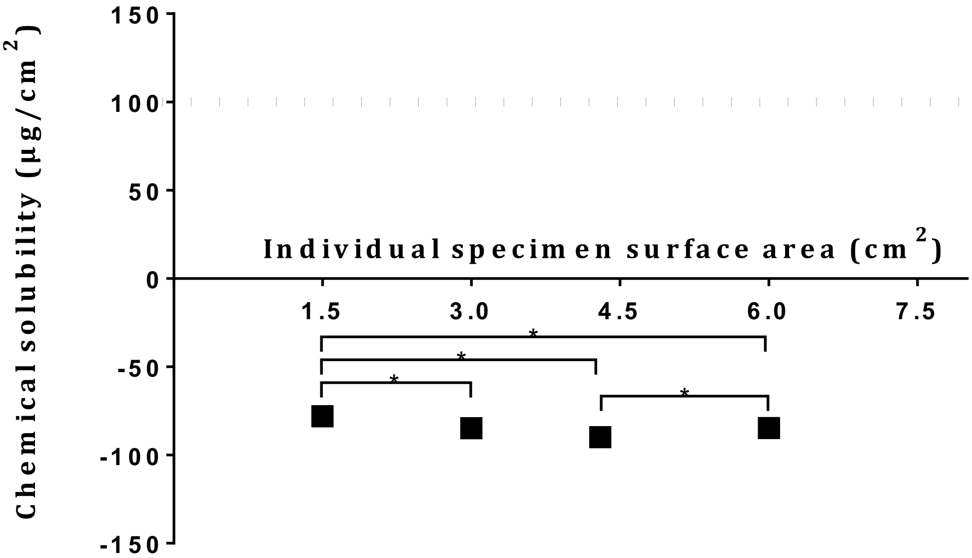

Figure 9: The dotted line demonstrates the maximum acceptable chemical solubility (100 µg/cm^2) for enamel ceramics according to the ISO 6872 (BS ISO, 2015). The graph shows variable chemical solubility values (sorption) of different individual surface areas of Cerasmart. (n=1). Asterisks indicate significant difference between groups, *p < 0.05.

5.6. Discussion

The results showed that the highest chemical solubility was observed in specimens with the smallest individual surface area for all tested materials except Cerasmart (hybrid ceramic). This high variability is not an unusual finding when compared to previous solubility experiments (Stokes et al., 2006). As the total edge length and number of corners increases as the individual specimen size decreases, this indicated that there is a positive relationship between the total edge length and number of corners with the chemical solubility value. The Gibbs-Thomson relation (Cao, 2004) states that particles with a smaller radius of curvature dissolve more readily. This would therefore lead to faster dissolution in specimens with an increased total edge length as there would be more areas with a decreased radius of curvature.

Welch's ANOVA was performed for all tested materials, which indicated a significant difference between the groups for each material. Although a Games-Howell post-hoc test indicated only a significant difference between some groups of each material, the trend of solubility values indicated a constant negative slope that begins at the smallest size group towards the largest size group. Therefore, the null hypothesis for this study was rejected. A complication with the test was that as the study investigated specimens with different individual surface areas, the comparison groups contained an unequal number of specimens. This meant the data violated the assumption of homogeneity of variance, which indicated the use of Welch's ANOVA.

The reason that the outcomes of the previous verification study showed low variability is that the study was standardised in all parameters. Although this would indicate the test can be reproducible if performed on an exact specimens' geometry and number, the current ISO standard does not provide any specifications other than the total surface area of specimens. In this chapter, the aim was to investigate the effect of altering the individual surface area of specimens on the chemical solubility values of different types of dental ceramics.

This study tested four different representative dental ceramic materials of different categories and a new hybrid dental material that combines a ceramic and a composite. There is not a standard methodology to measure the chemical solubility levels of these new hybrid materials. Therefore, it was interesting to investigate the chemical solubility using the ISO 6872 (BS ISO, 2015) method that is designed only for conventional dental ceramics.

The development of the industry of dental ceramics has supported the introduction of partially stabilized zirconia in the dental field. This material has earned great popularity in the modern dental field due to its great inertness, biocompatibility, toughness, strength, aesthetic, and low bacterial adhesion (Egilmez et al., 2014). Therefore, Y-TZP was chosen for this experiment for the former reasons, and additionally its ease of milling using CAD/CAM technology and the possibility to produce standardised specimens in a reasonable time. However, benchmarking other different dental ceramic materials was necessary for further comparison.

The sizes of specimens for cubes were slightly larger than they should be to allow for further finishing. It was found that the fragility of the un-sintered zirconia required careful handling of the specimens to maintain the required cubic shape. Although CAD/CAM provides an accurate shape of specimens, they still required finishing to have consistently smooth surfaces. During the testing procedure, careful handling of the ceramic specimens by plastic tweezers was carried out to minimise any possible damage.

The current findings would indicate that the chemical solubility outcomes of a dental ceramic are not repeatable due to the lack of specification of specimens' geometry and number of the ISO 6872 (BS ISO, 2015). However, further investigations are needed in order to obtain a broader understanding on the reliability of this method.

5.7. Conclusion

This experiment indicated that chemical solubility standard method can be manipulated by altering the geometry (size) of individual specimen surface area whilst still complying with the ISO 6872 (BS ISO, 2015) standard. The trend of solubility values indicated a constant negative slope that begins at the smallest size group towards the largest size group of all tested materials.

Chapter 6

Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS) and X-ray Diffractometry (XRD) Analysis

Chapter 6: Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS) and X-ray Diffractometry (XRD) Analysis

6.1. Introduction

The outcomes of the chemical solubility tests of a selection of dental ceramics reported a range of solubility values that were dependent on the individual surface area of the specimen. The best performing material was Y-TZP, with a solubility well within the acceptable limit as specified in ISO 6872 (BS ISO, 2015), but these results still demonstrated a variance with specimen size. To understand what may be happening at a surface microstructure level, it was necessary to analyse the specimens using a scanning electron microscopy (SEM) pre and post-solubility for further comparison.

Furthermore, it was also crucial to confirm if the surfaces of the specimens were significantly different pre- and post-solubility testing, achieved through analysing the elemental distribution on these surfaces using Energy-Dispersive X-ray Spectroscopy (EDS) and investigating the possibility of phase transformation using X-ray Diffractometry (XRD).

EDS analysis could be used to analyse the surface of the Y-TZP specimens to detect any elemental variations across the sample surface pre and post solubility testing. As the surface of Y-TZP specimens could be expected to form cracks and elevations post-solubility testing this would reveal if there is preferential loss of material at the surface during the test. In addition, XRD analysis can be used to investigate any possible phase transformation of Y-TZP surfaces post-solubility testing.

6.2. Aim

- To compare the specimen surfaces pre and post-solubility testing of dental ceramics using the ISO 6872 (BS ISO, 2015) solubility test.

6.3. Objectives

- To investigate the surface microstructure of the specimens pre and post-solubility testing using the SEM.
- To analyse the element distribution on the surface of specimens using the EDS.
- To investigate the structural transformation of the specimen surface post-solubility testing using the XRD.

6.4. Materials and methods

6.4.1. Scanning Electron Microscopy (SEM)

Qualitative surface microstructure analysis was performed pre and post-solubility testing by selecting random specimens of Y-TZP (C6.0), VMII, IPS e.max Press, IPS e.max ZirPress, and Cerasmart using a scanning electron microscopy (SEM) (Philips LX-20, Eindhoven, Netherlands). First, the specimens were mounted in a SEM pin mount specimen holder (TED PELLA, INC). An ion sputtering device (Evaporation unit, Edwards, UK) was used to coat the specimens with a thin layer of gold before the scanning process as shown in Figure 10. Each presented SEM image in the result section was a representative of many obtained images that showed similar findings.

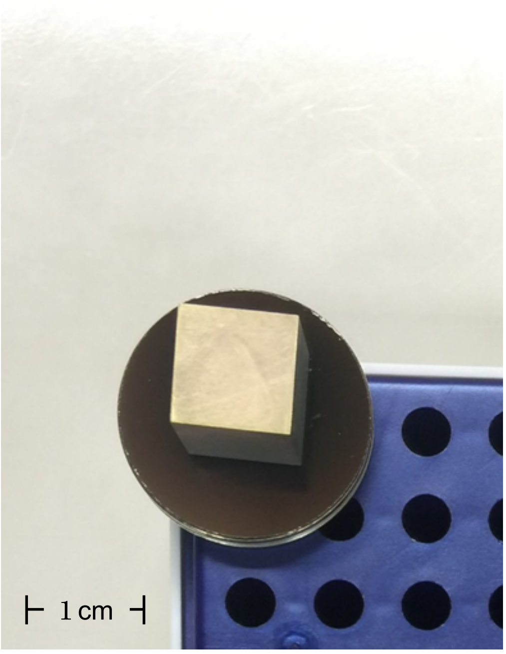

Figure 10: Coated specimen with gold sputter coat.

6.4.2. Energy Dispersive X-ray Spectroscopy (EDS)

For EDS, the tested specimens were Y-TZP cubes. One specimen pre and one specimen post-solubility testing were prepared. A thin layer of conductive carbon was applied on the surface of all the specimens using a sputter-coating unit (Edwards, UK). The specimens were subjected to SEM imaging at 5000x magnification. Three regions of interest for each specimen were obtained for further comparison. The elemental compositions of each specimen were determined by EDS analysis (FEI, Netherlands).

6.4.3. X-ray Diffractometry (XRD)

For XRD, the tested specimens were Y-TZP cubes. Pre and post-solubility testing samples were analysed. The data were collected on a D2 Phaser XRD diffractometer (Bruker, Germany) using Cu K_α radiation and a LynxEye detector. The XRD diffraction patterns were obtained in the 2θ range of 20° to 70° to cover the areas of the highest peaks of the tetragonal and the monoclinic phases of Y-TZP as performed in previous studies (Tong et al., 2016, Ardlin, 2002).

6.5. Results

6.5.1. Scanning Electron Microscopy (SEM)

6.5.1.1. Y-TZP

The SEM image of Y-TZP shows a dense surface with scratches due to grinding pre-solubility testing (Figure 11). Interestingly, an apparent visual difference could be determined at magnification 250x and 500x between pre-solubility and post-solubility images in regard to edges and corners. The post-solubility image shows that edges and corners had visible damage and were more abraded and rougher compared with the pre-solubility SEM image (Figure 12). Moreover, it was only possible to compare the Y-TZP flat surfaces pre and post-solubility testing at higher magnification. At 5000x, the microstructure of the surface before the test is relatively homogenous (Figure 13), and Figure 14 shows missing of some particulates from the surface after the solubility test.

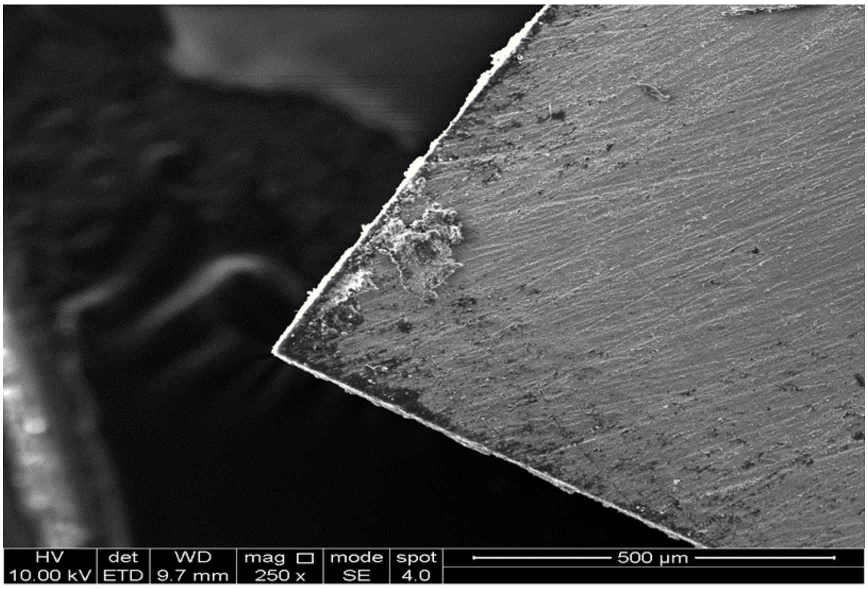

Figure 11: SEM image of Y-TZP specimen (C6.0) pre-solubility testing shows a dense surface with scratches due to grinding pre-solubility testing, precise edge and corner.

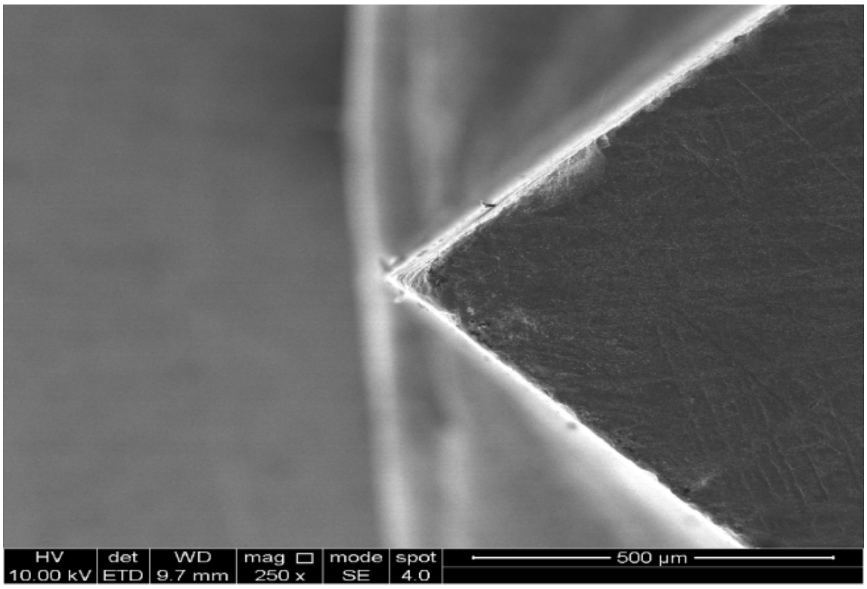

Figure 12: SEM image of Y-TZP specimen (C6.0) post-solubility testing shows the specimen's edges and corner had visible damage.

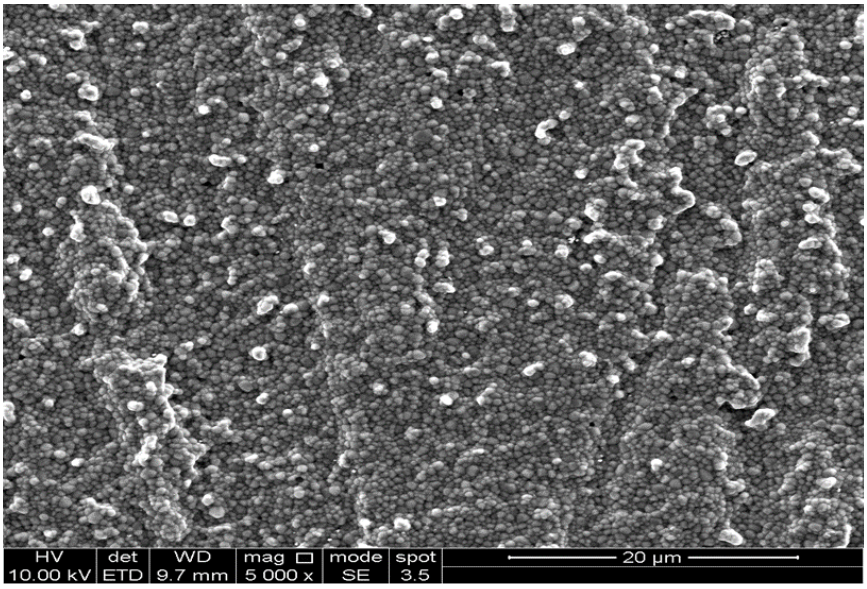

Figure 13: SEM image of Y-TZP (C6.0) at a higher magnification (5000x) pre-solubility testing shows homogenous surface.

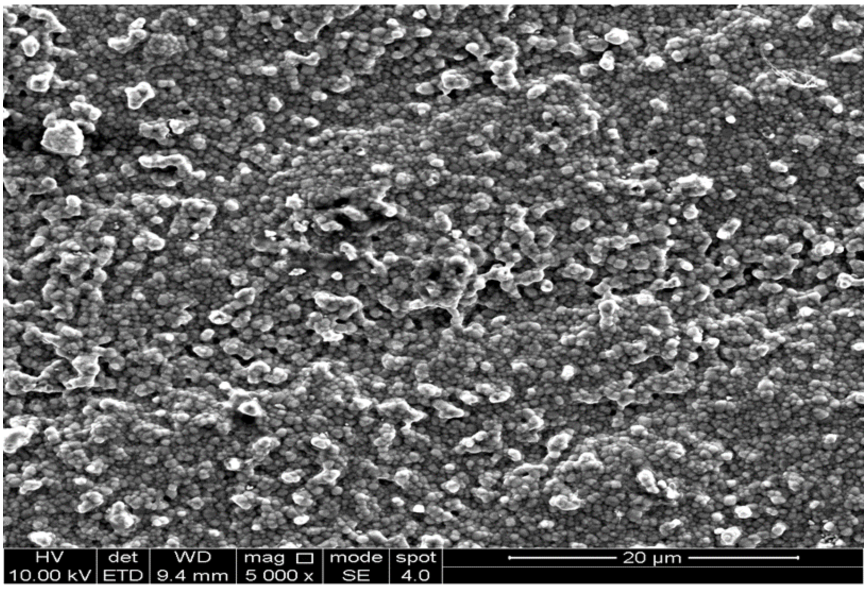

Figure 14: SEM image of Y-TZP (C6.0) at a higher magnification (5000x) post-solubility testing shows missing some particulates.

6.5.1.2. VMII

The SEM image of VMII specimen shows a smooth homogenous surface prior to the solubility test as shown in Figure 15. A precise edge of VMII specimen was shown prior to perform the solubility test, while the image shows that some corners had some defects. In the post-solubility, the SEM image shows a pitted and cracked surface with rounded and eroded structure as shown in Figure 16. The image also shows more damage and exposed fine crystals in the edge and corner areas and missing of some particulates from the surface after the solubility test.

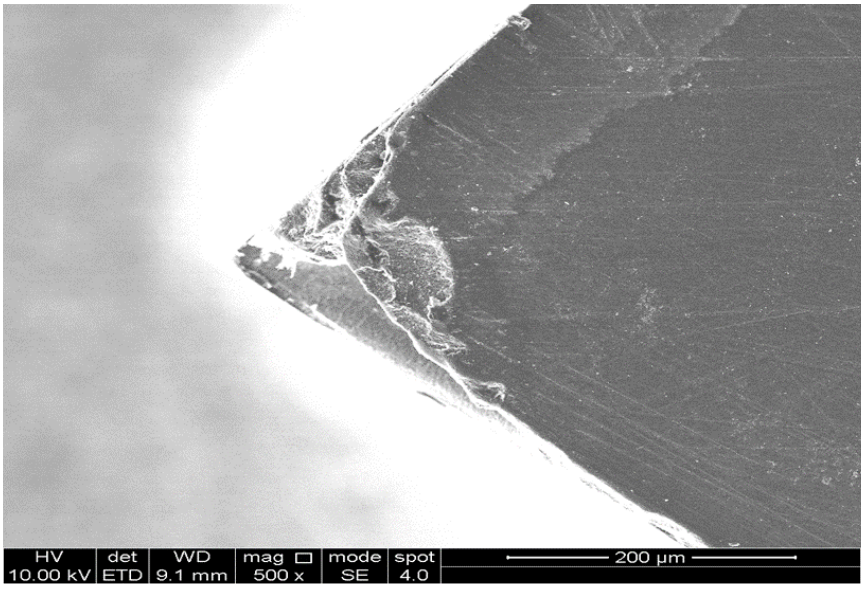

Figure 15: SEM image of VMII specimen (C6.0) pre-solubility testing shows a smooth homogenous surface and precise edge. Corner had some defects due to possible physical handling.

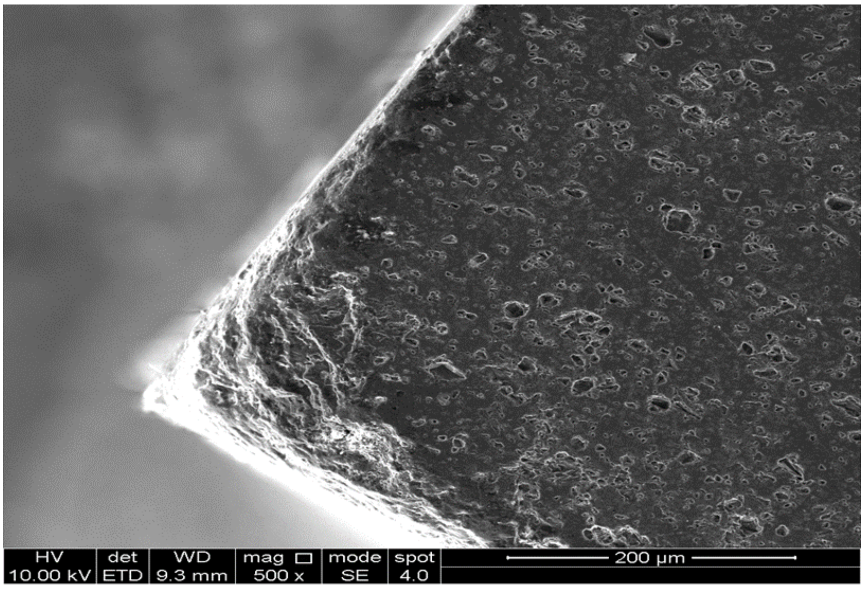

Figure 16: SEM image of VMII specimen (C6.0) post-solubility testing shows erosions at surface and more damage at edges and corner.

6.5.1.3. IPS e.max Press

The SEM image of pre-solubility test of IPS e.max Press shows a precise edge and corner and a smooth homogenous surface, although there were some scratches and very little porosities due to grinding as shown in Figure 17. While, the post-solubility image shows an orange peel appearance of the specimen surface with evenly distributed porosities as shown in Figure 18. In addition, the image shows that the edges and corners were more damaged than the flat surface and missing of some particulates from the surface after the solubility test.

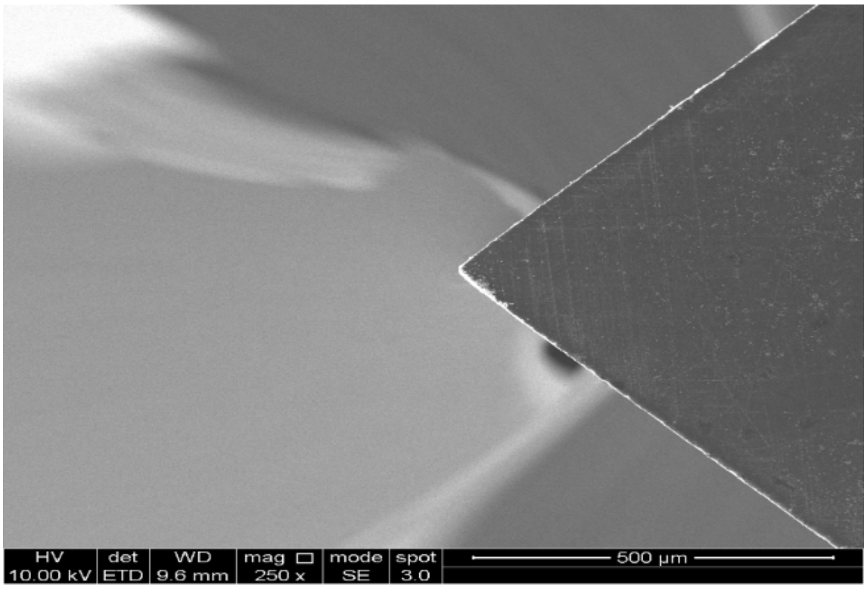

Figure 17: SEM image of IPS e.max Press specimen (C6.0) pre-solubility testing shows smooth and homogenous surface, precise edges and corner.

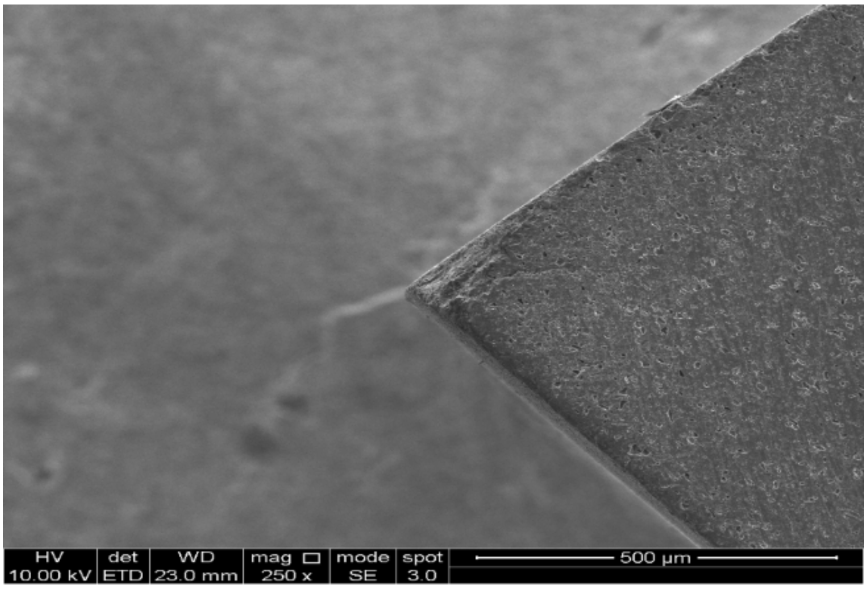

Figure 18: SEM image of IPS e.max Press specimen (C6.0) post-solubility testing shows erosion at surface and more damage at edges and corner.

6.5.1.4. IPS e.max ZirPress

The SEM image (Figure 19) of pre-solubility test of IPS e.max ZirPress shows a smooth, homogenous dense surface with precise edges and corners. After contact with the test solution, the specimen had a visible damage at the surface, edge and corner as shown in Figure 20. However, the image showed that the edges and corners were more damaged and lost more particulates than the flat surface after the solubility test.

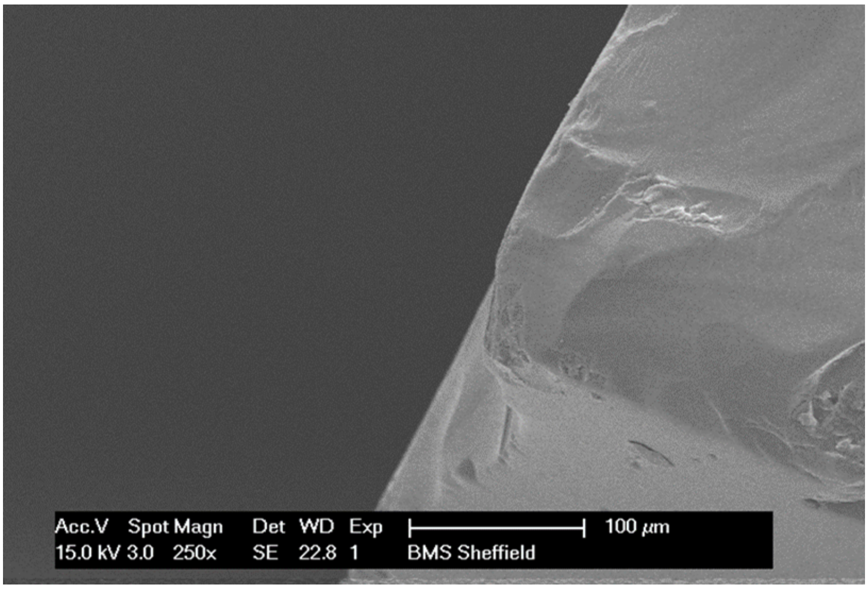

Figure 19: SEM image of IPS e.max ZirPress specimen (C6.0) pre-solubility testing shows smooth and homogenous surface, edges and corner.

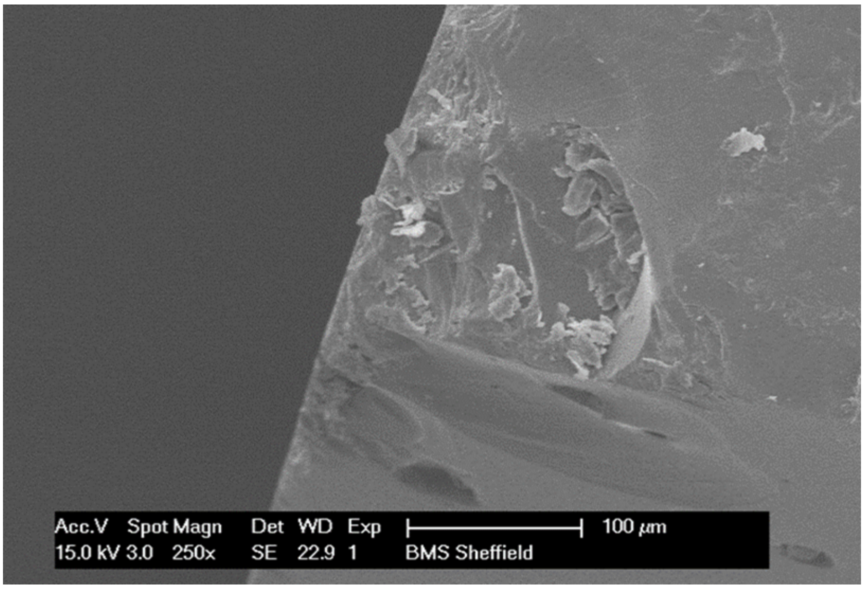

Figure 20: SEM image of IPS e.max ZirPress specimen (C6.0) post-solubility testing shows erosion at surface and more damage at edge and corner.

6.5.1.5. Cerasmart

Figure 21 shows an SEM images of Cerasmart with a smooth homogenous surface and a precise edge before performing the test, although the corner was damaged and there were some scratches due to grinding. An apparent visual difference could be determined at magnification 500x between pre-solubility and post-solubility images in regard to edges and corners. The post-solubility image shows that edges and corners had visible damage and missing of some particulates from the surface following the solubility testing as shown in Figure 22. Also, it shows that the edges and corners were more abraded (post-solubility) compared to the pre-solubility image. Moreover, it was only possible to compare Cerasmart flat surfaces pre and post-solubility testing at higher magnification. At 2500x, the microstructure of the surface before the test was very smooth and homogenous as shown in Figure 23. In the post-solubility image, the surface was rougher and contained well distributed micropits as shown in Figure 24.

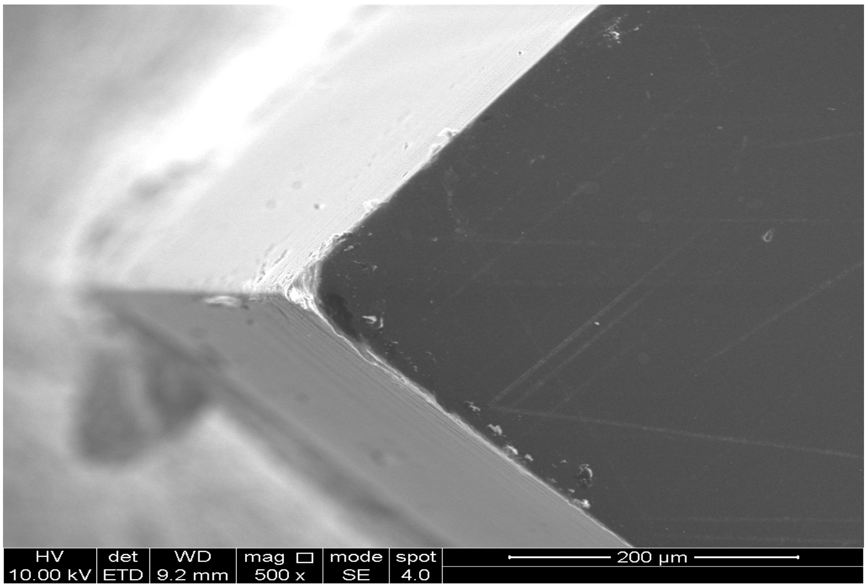

Figure 21: SEM image of Cerasmart specimen (C6.0) pre-solubility testing shows smooth and homogenous surface, precise edges and corner.

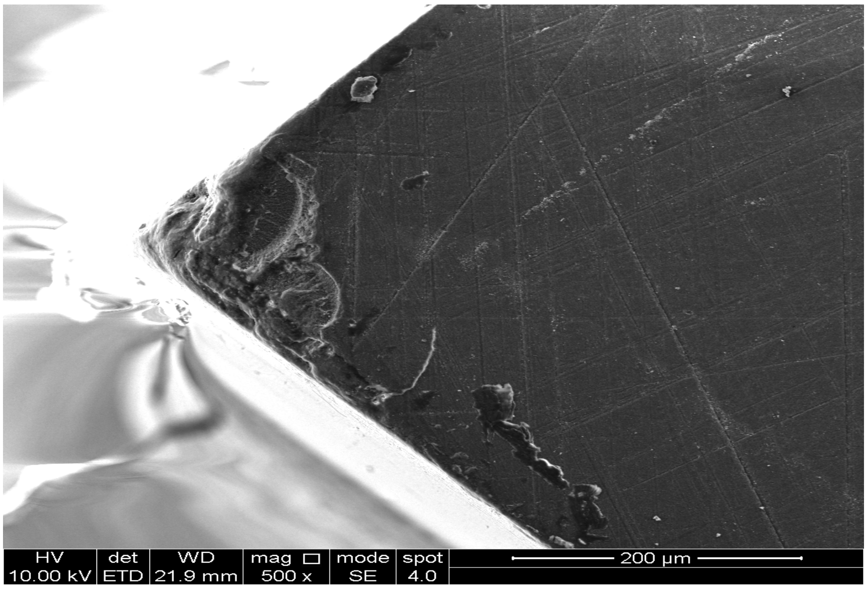

Figure 22: SEM image of Cerasmart specimen (C6.0) post-solubility testing shows some damages at edges and corner.

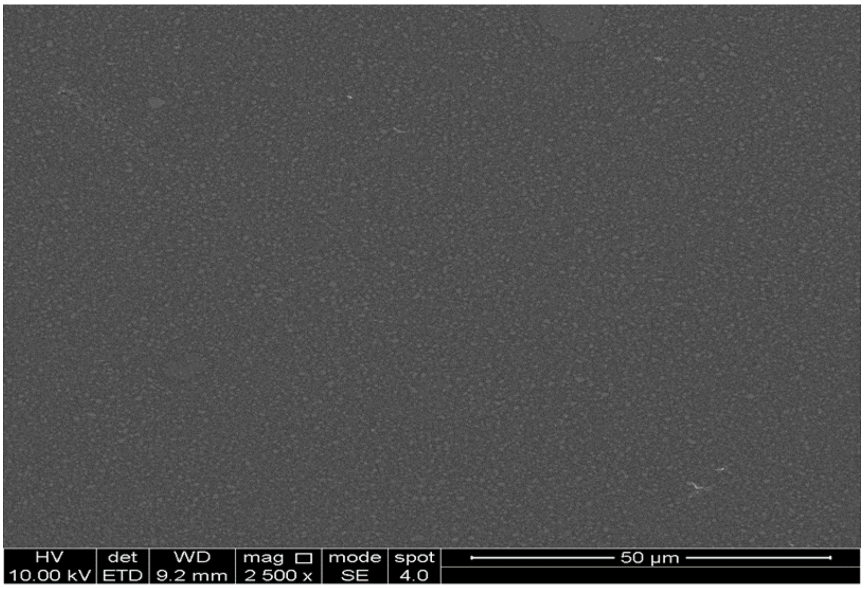

Figure 23: SEM image of Cerasmart (C6.0) at a higher magnification (2500x) pre-solubility testing shows smooth and homogenous surface.

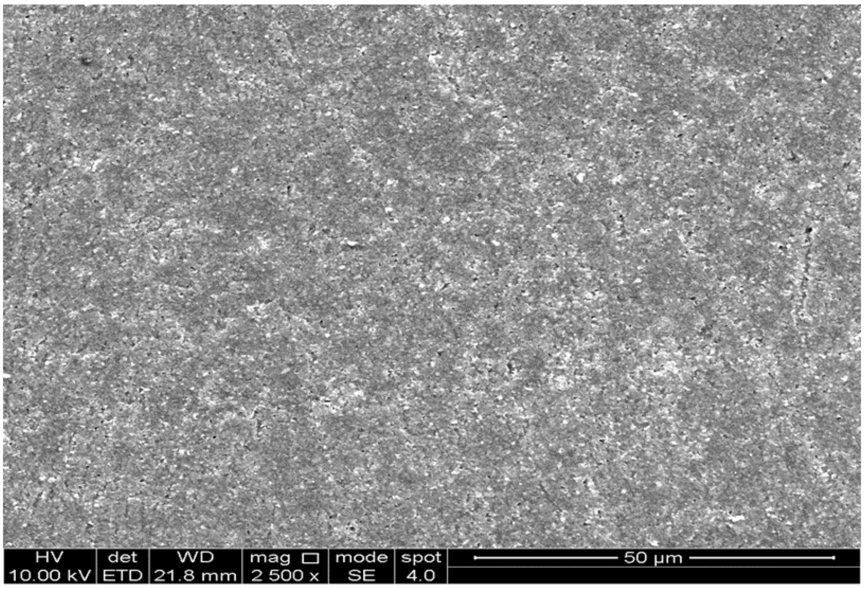

Figure 24: SEM image of Cerasmart (C6.0) at a higher magnification (2500x) post-solubility testing shows pitted surface.

6.5.2. Energy Dispersive X-ray Spectroscopy (EDS)

EDS scans of Y-TZP specimens were obtained of pre and post-solubility testing as shown in Figures 25 & 26. Three randomly selected spectra were representative of each specimen. The EDS analysis showed that the surface of Y-TZP was mainly composed of Zr, O, Y and Hf, and there was no significant difference in the composition pre and post-solubility testing as shown in Figure 27. The quantitative findings are summarised in Table 15.

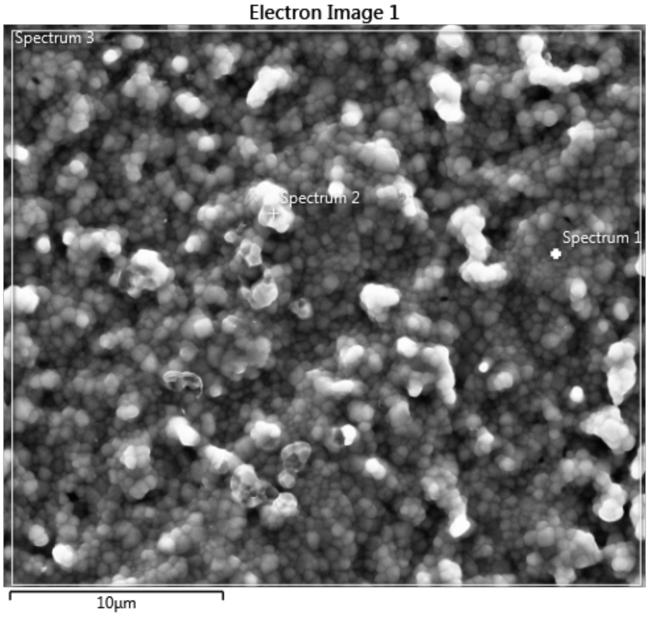

Figure 25: SEM image shows the surface microstructure of Y-TZP (C6.0) pre-solubility testing. Three randomly selected spectra (spectra 1, 2 and 3) were taken from the points shown in the image.

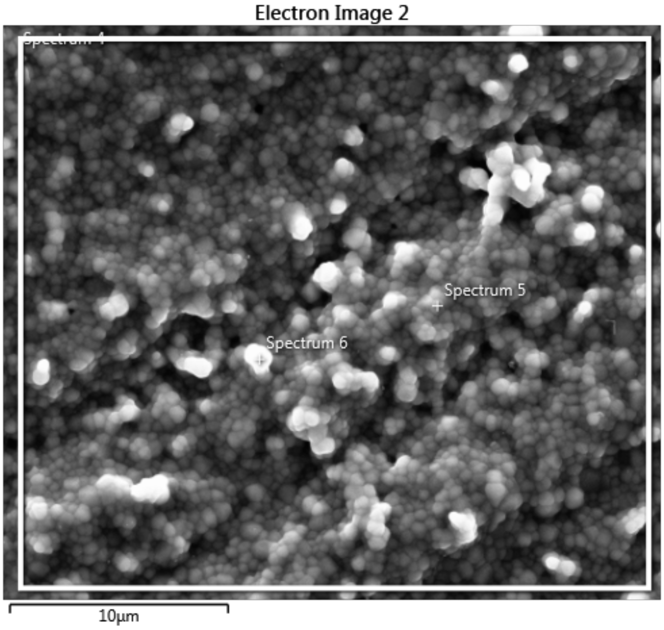

Figure 26: SEM image shows the surface microstructure of Y-TZP (C6.0) post-solubility testing. Three randomly selected spectra (spectra 4, 5 and 6) were taken from the points shown in the image.

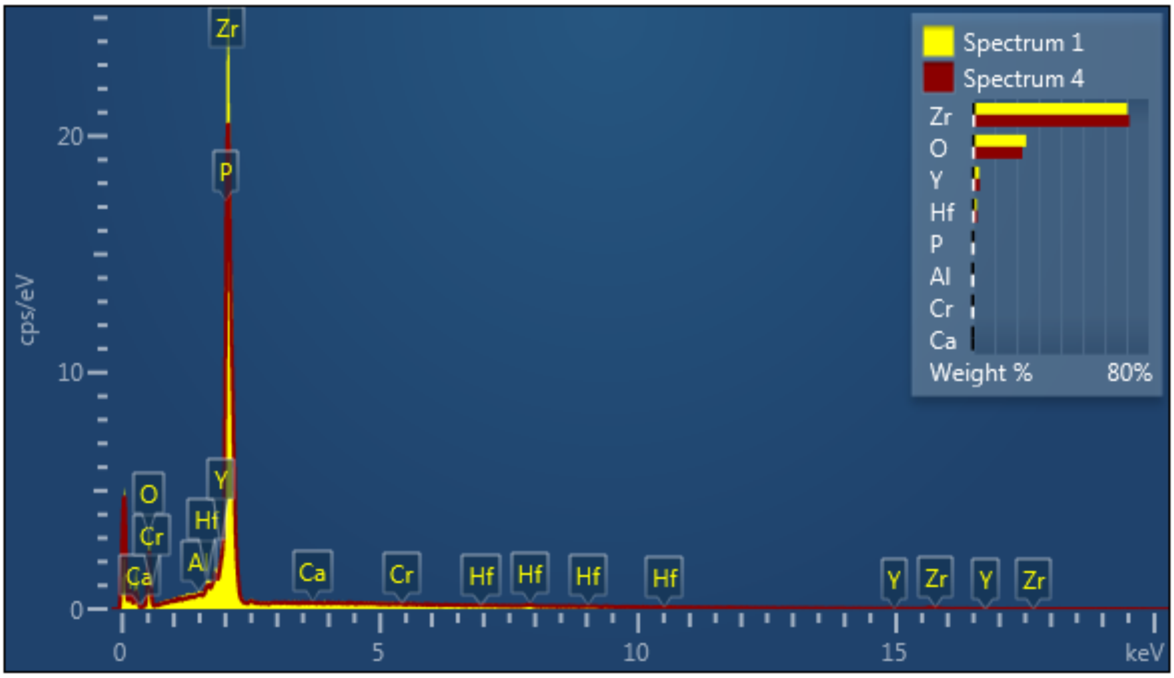

Figure 27: EDS analysis showing the comparison between pre and post-solubility testing. Red indicates a pre-solubility spectrum and yellow indicates a post-solubility spectrum.

Table 15: The table shows the detected elements in the Y-TZP (StarCeram® Z-Med) specimens as determined with EDS. S1, S2 & S3 indicate the spectra.

Element	**wt% Pre-solubility**				**SD**	**wt% Post-solubility**				**SD**
	S1	**S2**	**S3**	**Mean**		**S1**	**S2**	**S3**	**Mean**	
Zr	70	59	72	67	± 7	72	66	66	68	± 3
O	24	37	22	28	± 8	23	29	30	28	± 4
Y	3	3	3	3	± 0.4	3	3	3	3	± 0.4
Hf	2	2	2	2	± 0.4	2	2	2	2	± 0.4

6.5.3. X-ray Diffractometry (XRD)

Figures 28 & 29 show the highest peaks of the tetragonal and the monoclinic phases of Y-TZP that were observed within the 2θ range of 20° to 65°, which were matched with specific JCPDS (Joint Committee on Powder Diffraction Standards) cards; JCPDS-70-4426 and JCPDS-37-1484 respectively. The highest peak was observed at 30.2°, which indicated a predominant tetragonal phase of both specimens. An evidence of a monoclinic phase was observed by analysing the post-solubility specimen, which indicated that the structural arrangement was tetragonal, however some evidence of a monoclinic crystalline structure was found as shown in Figure 29.

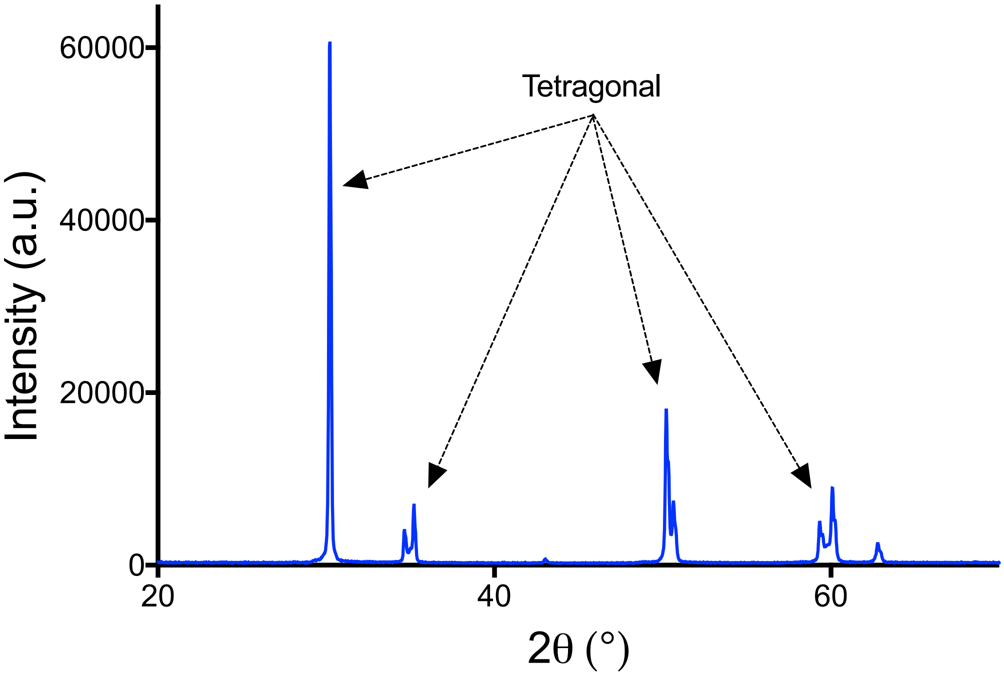

Figure 28: XRD pattern for a pre-solubility specimen of Y-TZP showing major peaks of the tetragonal phase (as matched with JCPDS-70-4426).

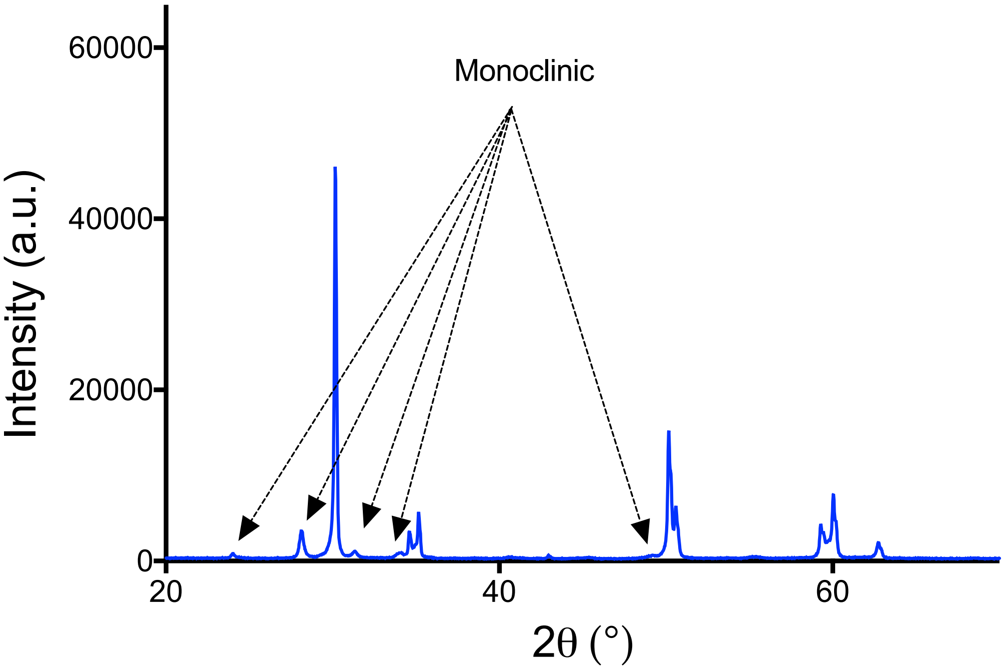

Figure 29: XRD pattern of a post-solubility specimen of Y-TZP showing a trace of monoclinic transformation (as matched with JCPDS-37-1484).

6.6. Discussion

The SEM analysis of pre and post-solubility testing for all tested materials in this research provided visible evidence that the surfaces of dental ceramics can be affected when subjected to a corrosive environment, however the degree of effect differs between different materials as shown with other studies (Milleding, 1999). In general, the SEM images showed that edges and corners were more affected than flat surfaces of all materials after performing the solubility testing.

The previous chemical solubility outcomes indicated that there was a positive relationship between the total edge length and the average of the chemical solubility of each group; as the total edge lengths increased, the average of chemical solubility increased as a result. Similarly, it was shown that as the number of corners increased, the rate of chemical solubility increased as well. This could be because that the angled surfaces (edges and corners) might be subjected to a double or triple attack by the chemical agent, which would generate hypothetically a double or triple effect of chemical solubility compared to the flat surfaces of a specimen. Interestingly, the SEM images showed that the specimen edges and corners were more vulnerable to acidic attack than the flat surfaces of a specimen for all materials.

The Gibbs-Thomson relation states that particles with a smaller radius of curvature dissolve more readily (Cao, 2004). This would therefore lead to faster dissolution in samples with an increased total edge length as there would be more areas with a decreased radius of curvature. From the current SEM findings, it appears that edges and corners are not only induced by double and triple effects, but it is also that edges and corners can have rougher surfaces due to the difficulty of polishing at those areas as shown in Figure 15. This would add more factors that can create the variability of the chemical solubility values when altering the individual surface area of a specimen. It has been stated that rougher surfaces may contain densely distributed cracks that could lead to the failure of dental ceramics (Rashid, 2014).

For Y-TZP, although the solubility values were well below the specified acceptable value, these findings could be due to the process of the structural transformation of grains from the tetragonal to the monoclinic phase as shown by the XRD findings. After the chemical solubility test, SEM images revealed slight elevations on the Y-TZP surfaces, which are a sign of grain transformation as reported in previous studies (Ardlin, 2002). If these elevations occurred in the interface between Y-TZP prostheses and luting cements in the oral cavity, this could affect the bonding strength. Although the difference between Y-TZP images (pre-solubility and post-solubility test) was small, it was confirmed that dental zirconia can be affected by an exposure to acetic acid at elevated temperature.

For all tested material, the images showed a higher surface roughness post-solubility testing. In addition, it was found that the damage was increased at edges and corners. It has been stated that corrosion attack is happening more at defected areas (Milleding et al., 1999). In addition, the images showed that VMII and IPS e.max Press samples were more damaged by the solubility testing than

IPS e.max ZirPress and Y-TZP samples. This is because VMII is composed of a feldspathic glass matrix, which could be the reason of the increase surface degradation and roughness of this material. Moreover, IPS e.max Press is a lithium disilicate glass-ceramics, which is composed of two different crystals imbedded in the glass matrix. This heterogenous microstructure causes a non-uniform dissolution of the surfaces of this material (Milleding et al., 1999). Although the chemical solubility of IPS e.max ZirPress was low generally, the SEM images showed that the surface of this material was affected and exposed the various sizes of fluorapatite crystals following the solubility testing. In addition, the SEM findings indicated that the surfaces of hybrid ceramic materials are also affected when exposed to 4 % acetic acid, although the chemical solubility outcomes of Cerasmart have not shown any mass loss, possibly due to water sorption.

In general, the microstructure patterns for glass-ceramics indicated that the chemical solubility process is mostly linked to the glass-phase structure, whilst it is probably related to LTD for zirconia (Stokes et al., 2002, Ardlin, 2002, Egilmez et al., 2014). Also, the images showed that edges and corners were eroded extensively that could be due to double and triple effects brought about by the specimen shape.

The EDS findings of this study confirmed that the surfaces of the Y-TZP specimens' pre and post-solubility testing contain mainly Zr, O, Y and Hf. Figure 27 shows an example of EDS spectra for pre and post-solubility testing of the surface structure of Y-TZP. By comparing the two spectra, the intensity of the key elements was similar. This indicated that the elemental distribution on the surfaces was not significantly changed unexpectedly, although the previous chemical solubility findings revealed mass loss. This would indicate that the mass loss of Y-TZP specimens was not mainly due to elemental dissolution, but it could be due to loosening of some particulates from the specimens' surfaces during or after performing the test.

As this study demonstrates a concern over the concentration of damage to the edges and corners of cubic samples, it was planned to re-run the tests on a different geometry, spheres, to remove any edges and corners.

6.7. *Conclusion*

- All specimens of tested materials demonstrated damage on specimens' surfaces and more around the edges and corners as shown by SEM images.
- SEM findings indicated that the highest soluble materials are the most damaged as shown in VMII results.
- It can be concluded that groups with the longest total edge length and higher number of corners have shown higher solubility values as group C1.5 of all tested materials.
- Surface XRD of the Y-TZP specimens showed evidence of 'ageing' (transformation from the tetragonal to the monoclinic form) after the ISO chemical solubility test.

Chapter 7

Investigating the Chemical Solubility Values with Spherical Specimens

Chapter 7: Investigating the Chemical Solubility Values with Spherical Specimens

7.1. Introduction

It has been shown so far that chemical solubility as reported by ISO 6872 (BS ISO, 2015) is related to the specimen geometry for cubic specimens. SEM findings have shown significant post-solubility testing damage at areas around edges and corners. EDS findings of Y-TZP have not shown any compositional changes at the specimen's surface indicating that the mass loss is mainly due to detached parts of the specimens rather than dissolution. It was important to investigate the effects of removing edges and corners from the specimens' shape to better understand the mechanisms leading to the chemical solubility values being obtained.

Stokes et al. (2002) proposed a change in the specimen's morphology of the previous ISO 6872 (BS ISO, 1995b) from discs to spheres to avoid clumping of the specimens and to increase their exposure to the test medium. Although his suggestion was not considered before because of the difficulty of preparing beads at that time, it is now feasible to prepare such complicated morphologies due to the recent technological advances in the CAD/CAM.

Following on from the previous results, it was planned to investigate the effect of spherical specimens on the chemical solubility, using the most durable material and the one allowing a large range of specimen size (Y-TZP) (a naming scheme was devised where S means sphere, with following number being the individual specimen surface area, e.g., S1.5 means a spherical specimen with 1.5 cm^2 surface area).

The null hypothesis was that the chemical solubility measurements of different individual specimens' shapes are the same.

7.2. Aim

- To investigate for possible variance in the chemical solubility levels of edgeless (spherical) and edged (cubic) specimens of a dental ceramic.

7.3. Objectives

- To perform a chemical solubility test using a spherical sample geometry.
- To compare the findings of cubic and spherical groups.

7.4. *Materials and Methods*

7.4.1. Sample preparation

Six different size groups of Y-TZP (StarCeram® Z-Med) spheres were prepared to compare with the data obtained for the equivalent cubic specimens already tested. Each group was designed to fulfil the minimum requirement of the total surface area of samples as stated in the ISO 6872 (BS ISO, 2015). Figure 30 & Table 8 (Chapter 5) illustrate the samples' numbers and geometries.

The three-dimensional designs of Y-TZP spheres were prepared using computer aided design software (Tinkercad, Autodesk, USA) as performed in Chapter 5. The specimens were finished and polished using a tumble polisher, which is used commonly to polish stones. SiC grinding papers were pasted on the internal walls of the tumbler to finish and polish the spheres. The process used was P400 for 6 h, P600 for 12 h, P800 for 12 h, and then P1000 for 12 h. The specimens were sintered as described in Table 9 (Chapter 5). The surface areas of the spherical specimens were determined by measuring the diameter in three orthogonal axes, taking an average, dividing by two and using it as r in the surface area of a sphere formula, $4\pi r^2$.

The surface roughness analysis of spherical groups was performed using SEM to confirm a standardised roughness.

7.4.2. Methodology

7.4.2.1. Chemical solubility testing

As with the cubic groups, the chemical solubility tests were performed according to the ISO 6872 (BS ISO, 2015) requirements as described in Table 5 (Chapter 4). Each group was tested and analysed individually, and the test was performed three times to determine the variability in the measurements as performed on Y-TZP cubes in Chapter 5.

7.4.2.1. Statistical analysis

All data were compared using Welch's ANOVA and a Games-Howell post-hoc test. The alpha value (p) was set at 0.05. Welch's ANOVA was performed to compare unequal variances as found in this study.

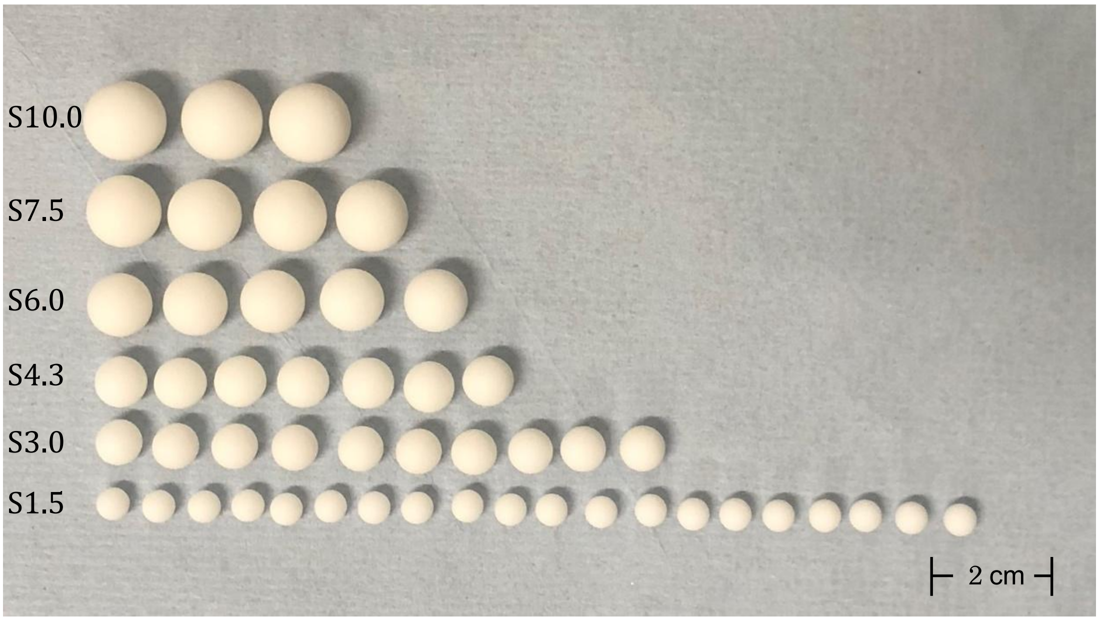

Figure 30: The figure shows the six different size groups of possible spheres as explained in Table 7 (See Page 72).

7.5. Results

7.5.1. Chemical solubility

The solubility findings were varied among the six groups of Y-TZP for the three repeated tests as shown in Table 16. However, the results were comparable for each group when repeated three times. The standard deviation of the average chemical solubility results among the spherical groups was ± 4. Although all groups of Y-TZP spheres showed a solubility value lower than parallel cubic Y-TZP groups, a less pronounced downward trend in chemical solubility value with increasing individual sample size was observed for this material.

Figure 31 shows the relationship between the solubility value and the individual surface area. Welch's ANOVA showed a significant difference between groups. A Games-Howell post-hoc test indicated that there was no a significant difference between all groups except between groups S1.5 and S10.0, and between groups S3.0 with S6.0.

Table 16: The table shows the chemical solubility of the spherical groups (Y-TZP). Chemical solubility is in μg/cm^2.

Group	**Number of specimens**	**Individual surface area (cm^2)**	**Chemical solubility (μg/cm^2)**			**Mean**	**SD**
			Test 1	**Test 2**	**Test 3**		
S1.5	**20**	**1.5**	36	35	32	35	± 2
S3.0	**10**	**3.0**	32	32	31	32	± 0.3
S4.3	**7**	**4.3**	31	30	30	30	± 1
S6.0	**5**	**6.0**	29	28	28	28	± 1
S7.5	**4**	**7.5**	29	25	25	27	± 2
S10.0	**3**	**10.0**	26	22	25	24	± 2

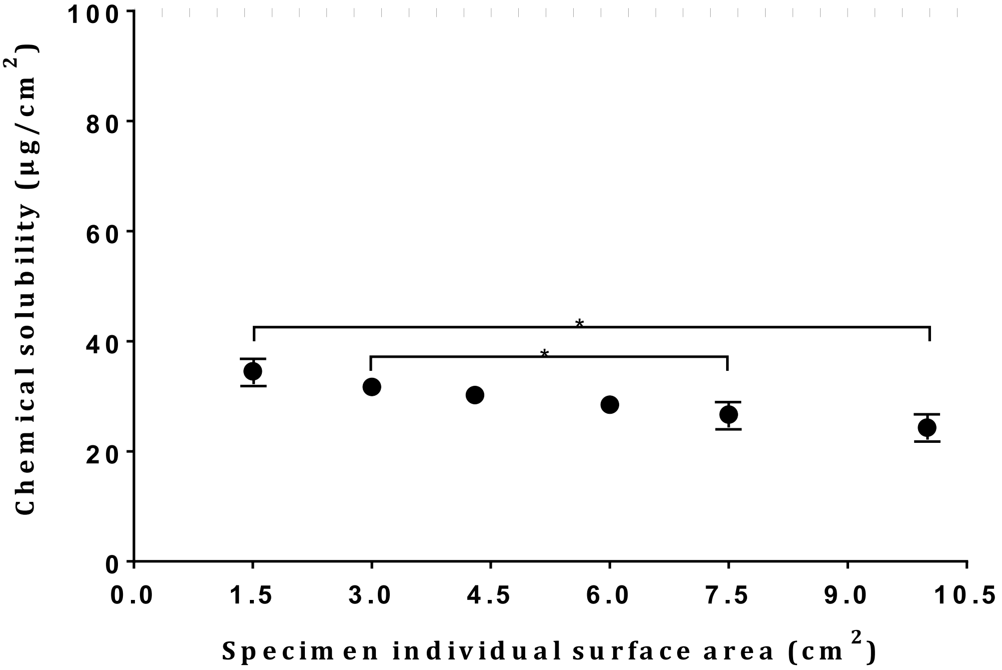

Figure 31: Chemical solubility average of the spherical groups of Y-TZP (bars represent standard deviation. SDs of S3.0, S4.3 and S6.0 are too small to be seen). The dotted line demonstrates the maximum acceptable chemical solubility (100 µg/cm^2) for enamel ceramics according to the ISO 6872 (BS ISO, 2015), (n=3). Asterisks indicate significant difference between groups, *$p < 0.05$.

7.5.2. Scanning Electron Microscope (SEM)

Figure 32 shows an SEM image of the specimen surface of Y-TZP sphere prior to solubility test, which showed a homogenous surface. For post-solubility testing, the image shows a rougher surface, slight elevations on the surface and some cracks as shown in Figure 33.

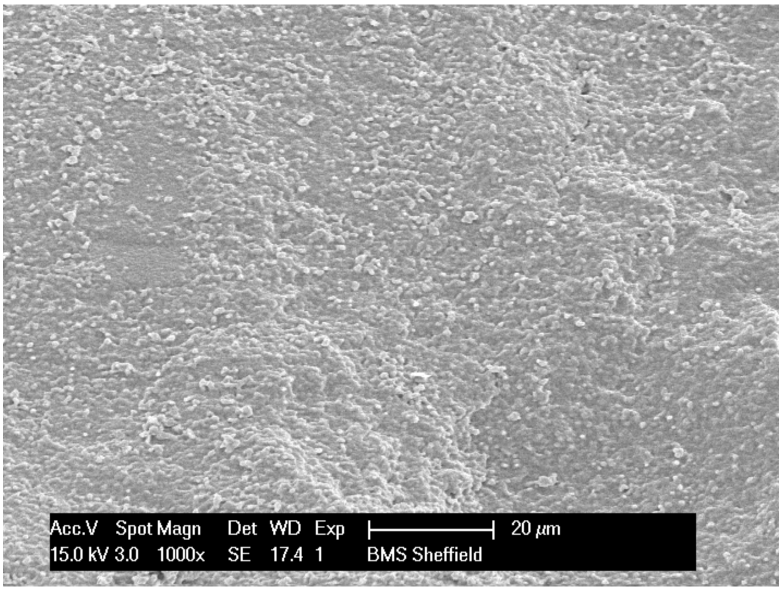

Figure 32: Y-TZP surface of a sphere (S6.0) pre-solubility testing.

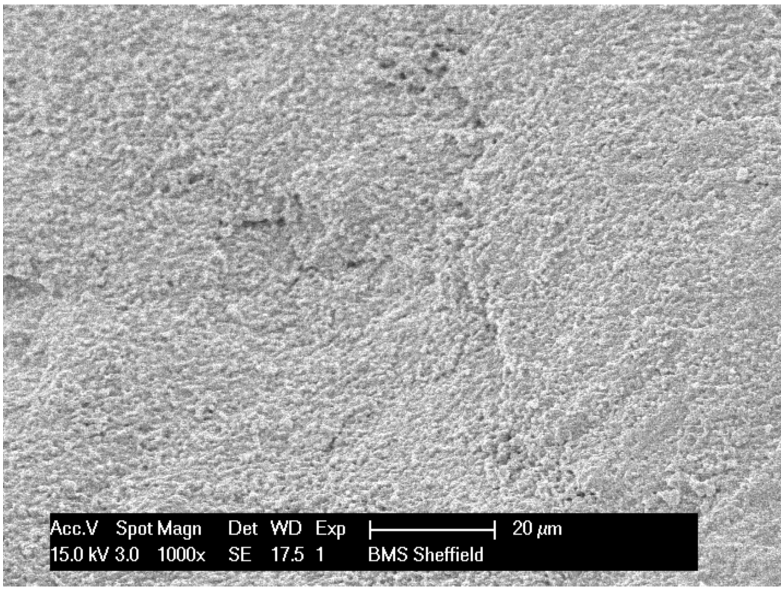

Figure 33: Y-TZP surface of a sphere (S6.0) post-solubility testing.

7.6. Discussion

The previous chemical solubility findings indicated that the smaller radius of curvature surface such as edges and corners dissolve more readily than flat surfaces. Therefore, it was necessary to investigate spherical shape specimens for further comparison with the previous results.

The findings of the chemical solubility values of spheres were generally consistent. However, Welch's ANOVA indicated a significant difference between spherical groups. Games-Howell post-hoc indicated that there was a significant difference only between groups S1.5 and S10.0, and between groups S3.0 and S6.0. Although the findings showed a similar trend of the results as for the cubic groups, it was less pronounced with spherical groups as shown in Figure 34. The standard deviation of the average chemical solubility results among the cubic groups was higher (± 13) than the spherical groups (± 4). This indicated that spherical specimens performed more consistently over the specimen size range than cubic ones. Therefore, the null hypothesis was rejected for this study and the current results showed that edges and corners affect the value of chemical solubility undoubtedly.

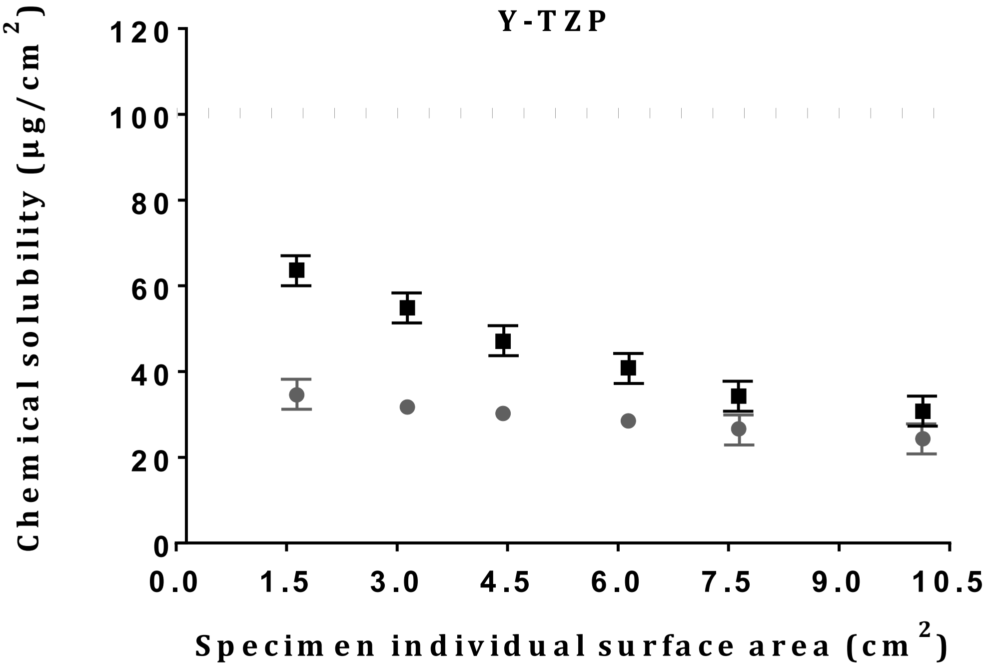

Figure 34: Chemical solubility average of both cubic and spherical groups of Y-TZP (bars represent standard deviation. SDs of S3.0, S4.3 and S6.0 are too small to be seen). The dotted line demonstrates the maximum acceptable chemical solubility (100 µg/cm^2) for enamel ceramics according to the ISO 6872 (BS ISO, 2015), (n=3).

The sizes of specimens for spheres were prepared slightly larger than they should be to allow for further finishing steps as performed on cubes. Although CAD/CAM provides an accurate shape of specimens, they still needed more finishing to have smooth finished surfaces. The finishing step of spheres was performed using a rock tumbler that is used to polish rounded stones. Even though this process requires a long duration, the tumbler succeeded to provide well-polished spherical specimens. It was important to maintain the minimal individual surface area of spherical specimens; therefore, the six different spherical groups of this study were divided into three groups for finishing by the tumbler to avoid any impact of a wide range of sizes. Also, it was crucial to check the dimensions of the specimens frequently.

Although, the interior part of the tumbler was covered with similar finishing silicon papers as used to finish cubical specimens, it was difficult to confirm an equal surface roughness using the surface roughness tester as performed with cubic specimens because of the curved surface of spheres. Therefore, SEM images were used to confirm similar roughness between spherical specimens. It was important to obtain a similar surface roughness between the groups of each shape to standardise the tests' parameters. However, the SEM images of both cubes and spheres indicate a comparable surface roughness.

7.7. Conclusion

The chemical solubility decrease with increasing individual specimen sizes was less pronounced in spherical specimens, indicating that areas with small radius of curvature dissolve more readily.

Chapter 8

Solution Analysis and Hardness Analysis

Chapter 8: Solution Analysis and Hardness Analysis

8.1. Introduction

The oral cavity demonstrates a complex environment as stated previously, which has a different range of temperature and pH that would affect dental restorative materials. Although studies have shown that the released ions from these materials are insignificant and have low toxicity levels (Anusavice, 1992), however if the degradation of a restorative material in the oral cavity led to broken 'parts' that could be swallowed accidentally and could have an influence on health.

A study has claimed that measuring the amount of released ions from dental ceramics would determine the amount of degradation more accurately than measuring the total weight loss of specimens (Jakovac et al., 2006). There are various methods to perform elemental analysis. Inductively coupled plasma optical emission (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) were chosen due to their analytical ability to detect the different chemical elements. For this project, both techniques were used to compare what can be found in the solutions after performing the solubility tests with the actual compositions of the tested dental ceramics.

ICP-OES technique is based on detecting the intensity of the emitted light and calculating the concentration of the specific elements in the tested sample. However, its precision limits are considered low to moderate sensitivity (Thermo Elemental, 2001). In contrast, ICP-MS technique is based on dissociating the sample into its component elements or ions. The detection limits of this technique are better than ICP-OES. However, the high cost of using ICP-MS technique limits its use as a first choice (Thermo Elemental, 2001).

Considering changes happening at the surface during chemical solubility testing, a change in hardness pre and post-test could indicate a change in the surface microstructure. Hardness can be defined as the measurement of the resistance of the surface to penetration of a specified indenter using a certain loading conditions (Quinn et al., 2004). It was important to investigate the hardness values of the specimens pre and post-solubility testing in order to assess the effect of 4 % acetic acid exposure on dental ceramics.

8.2. Aim

- To determine the degradation products of the chemical solubility test on Y-TZP.
- To determine the effect of the chemical solubility test has on the hardness of Y-TZP and VMII.

8.3. Objectives

- To determine the elemental composition of Y-TZP by performing a solution analysis.
- To perform ICP-OES analysis on test solutions following the chemical solubility testing.
- To perform ICP-MS analysis if needed to detect extremely low limits of elements.
- To compare the hardness of Y-TZP specimens pre and post-solubility testing.
- To perform the hardness test on a dental ceramic material (VMII) pre-solubility and post-solubility testing for comparison with Y-TZP findings.

8.4. Materials and methods

8.4.2. Inductive Coupled Plasma (ICP)

Inductively coupled plasma optical emission spectrometry (ICP-OES) was used in this study to determine the chemical composition of the solutes after testing, and after prolonged exposure. To determine the elemental composition of the zirconia specimens' and compare it to the manufacturer's data (Table 17) powders were collected after milling and dissolved into a mixture of sulphuric and hydrofluoric acids in a digestion bomb at 200°C and the dissolved solutions were analysed using ICP-OES. To determine whether acetic acid would dissolve the zirconia specimens were added to 4 % (v/v) acetic acid solution in a digestion bomb at 200°C and the solution was analysed using ICP-OES. These solutions were then passed through an 8μm pore size filter (Whatman®, Grade 540) and re-analysed to determine if particulate zirconia was present in the solution. Inductively coupled plasma Mass spectrometry (ICP-MS) was also used to detect low limits of elements in this project due to its high detection limits.

Samples of the acetic acid were collected from the C1.5 and C10 at the end of the solubility experiments to determine the composition of the solute after testing. In order to determine if the duration of exposure was a factor in the concentration and composition of the solute, chemical solubility 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 solutes once again analysed using ICP-OES.

Table 17: The table shows the existing elements in Y-TZP (StarCeram® Z-Med). (Provided by the manufacturer).

Chemical characteristics	**Wt%**
ZrO_2	> 99.0
Y_2O_3	5.15 ± 0.2
HfO_2	< 5.0
Al_2O_3	< 0.1
Fe_2O_3	<0.1
Na_2O	< 0.04

8.4.3. Hardness test

Hardness was measured using a Vickers hardness tester (Foundrax, UK); a load of 9.8 N with a dwell time of 15 seconds for 10 specimens for each test group. Five indentations were measured per specimen, and an average hardness was calculated (Morrell, 1990, Nam and Park, 2017). This test was performed on Y-TZP and VMII materials pre and post-solubility testing.

An independent t-test was performed to compare the differences between the specimens before and after the chemical solubility testing.

8.5. Results

8.5.1. Inductive Coupled Plasma – Optical Emission Spectrometry (ICP-OES)

The results of ICP-OES showed 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 as shown in Table 18. The sample digested in 4 % acetic acid at 200°C showed a lower amount 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 %. Samples of both tested groups C1.5 and C10.0 (16 h in 4 % acetic acid at 80°C) revealed only small amounts of zirconium and yttrium. The amounts of yttrium present were ten times the amounts of zirconia for C1.5, and five times for C10.0. For extended-time samples (7 days), the findings also showed that there were 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. Table 19 shows unexpected dissolved elements in the tested samples.

Table 18: The table shows amount of zirconium and yttrium in µg/l using the ICP-OES.

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

* Y-TZP powder digested in H_2SO_4/HF at 200°C.

** Y-TZP powder digested in 4 % acetic acid at 200°C.

Table 19: The table shows amount of all elements that found in the solutions in μg/l using the ICP-OES.

Element	**Sample ID**			
	C1.5/16-h	**C10/16-h**	**C1.5/7-days**	**C10/7-days**
Al	0.204	0.158	0.725	0.186
Na	3.38	1.97	10.8	4.05
B	1.96	1.32	9.23	2.19
Ba	0.010	0.003	0.014	0.005
Ca	0.386	0.244	0.812	1.41
Si	3.69	1.43	9.48	1.45
Fe	0.051	0.029	0.242	0.051
Sr	0.001	0.002	0.003	0.004
K	0.41	0.24	1.15	0.64
Mg	0.031	0.019	0.061	0.044
Mn	0.001	0.001	0.003	0.002
Y	0.056	0.050	0.077	0.042
Zn	0.023	0.017	0.048	0.042
Zr	0.006	0.011	0.049	0.021
Hf	<0.005	<0.005	<0.005	<0.005
Ni	<0.01	<0.01	0.148	0.044

8.5.2. Inductive Coupled Plasma Mass Spectrometry (ICP-MS)

Samples of both tested groups C1.5 and C10.0 (16 h and 7 days in 4 % acetic acid at 80°C) revealed only small amounts of zirconium and yttrium. The amounts of zirconia and yttrium were nearly similar to the findings of ICP-OES as shown in Table 20.

Table 20: The table shows amount of zirconium and yttrium in μg/l using the ICP-MS.

Sample I.D.	**Zr**	**Y**
C1.5/16-h	0.007	0.055
C10/16-h	0.013	0.051
C1.5/7-days	0.034	0.073
C10/7-days	0.023	0.042

8.5.3. Hardness test

Tables 21 & 22 show the average hardness for both Y-TZP and VMII pre and post-solubility testing. An independent t-test showed that the average hardness of the specimens significantly decreased after chemical solubility testing ($p > 0.05$) for both materials. The results showed that the hardness of Y-TZP reduced by approximately 21 % after chemical solubility testing, and by 28 % for VMII as shown in Figures 35 & 36.

Table 21: Pre-solubility and post-solubility average hardness of Y-TZP specimens (n=10).

Sample	**Pre-solubility Average Hardness (HV 1)**	**SD**	**Post-solubility Average Hardness (HV 1)**	**SD**
1	1571	± 34	1271	± 44
2	1578	± 83	1269	± 50
3	1626	± 34	1256	± 80
4	1623	± 22	1272	± 26
5	1609	± 49	1274	± 45
6	1618	± 49	1244	± 55
7	1584	± 63	1271	± 74
8	1599	± 56	1264	± 68
9	1625	± 107	1270	± 41
10	1598	± 59	1262	± 46
SD	± 20		± 9	

Table 22: Pre-solubility and post-solubility average hardness of VITABLOCS Mark II specimens (n=10).

Sample	**Pre-solubility Average Hardness (HV 1)**	**SD**	**Post-solubility Average Hardness (HV 1)**	**SD**
1	556	± 33	398	± 29
2	532	± 8	378	± 30
3	550	± 33	385	± 33
4	539	± 5	396	± 14
5	528	± 11	388	± 29
6	547	± 29	381	± 20
7	538	± 17	389	± 29
8	542	± 31	394	± 11
9	535	± 5	390	± 19
10	549	± 35	393	± 19
SD	± 23		± 23	

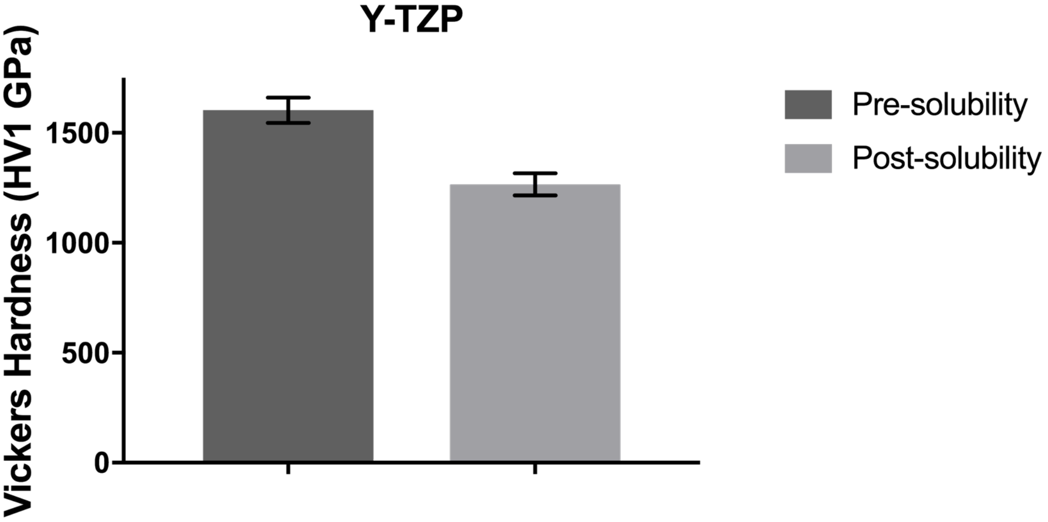

Figure 35: The difference of the average hardness values of Y-TZP specimens before and after the chemical solubility tests is significant (bars represent standard deviation). The alpha value (*p*) was set at 0.05.

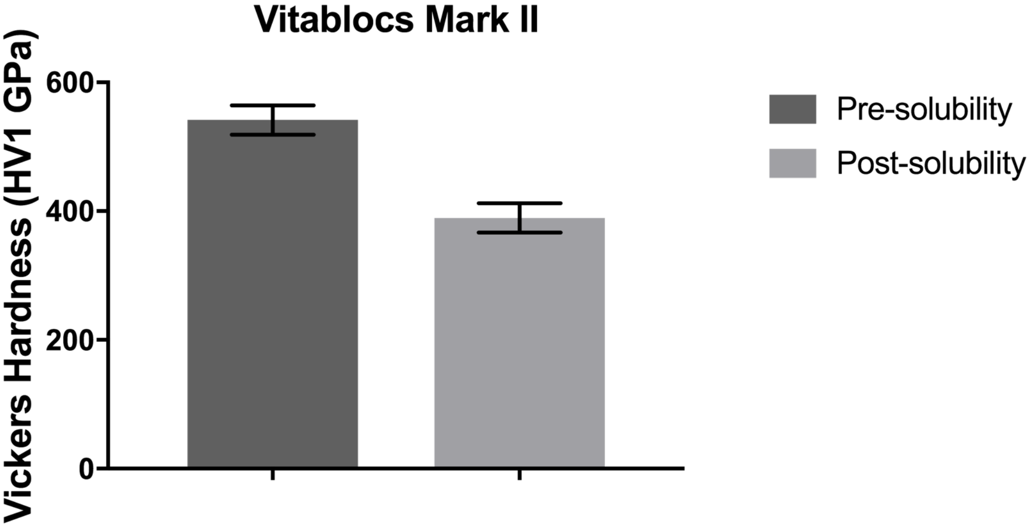

Figure 36: The difference of the average hardness values of VMII specimens before and after the chemical solubility tests is significant (bars represent standard deviation). The alpha value (*p*) was set at 0.05.

8.6. Discussion

The purpose of this study was to relate the findings of the chemical solubility values of the different specimens' groups of Y-TZP in Chapter 5 and the dissolved elements in the test solutions. Specifically, the study focused on measuring elution of zirconium and yttrium ions from solutions of only two different groups of Y-TZP cubes (C1.5 and C10.0). The null hypothesis was that the levels of detected elements in the solutions will be higher in the group with higher solubility value, and higher in longer duration samples. Moreover, the preparation of the samples was based on the duration of the chemical solubility tests as 16 h and 7 days, and on the individual surface area of specimens, which are the two extreme groups (C1.5 and C10.0).

ICP-OES was used to investigate the leachates of zirconia specimens in the test solution. Prior to performing the analysis, samples of zirconia powder were digested in a mixture of sulphuric acid and hydrofluoric acid as well as in 4 % acetic acid at 200°C until complete decomposition. As expected, zirconium and yttrium elements were detected as the main elements of zirconia. However, it was noticed that the latter sample was cloudy, which indicated a suspension of elements in the solution. Therefore, further filtration was required to ensure obtaining accurate readings. Filtering the sample decreased the mass of the zirconium and yttrium by more than 600 % and 50 % respectively. This indicates that zirconium particulates >8μm detach from the surface of zirconia specimens during the chemical solubility test. Although the findings of samples from this study (16 h) and from the extended-test (7 days) showed very little amounts of these elements, the presence of yttrium indicates a local loss of surface stability (Kvam and Karlsson, 2013). Yttrium oxide actually plays a significant role to stabilize the tetragonal phase of Y-TZP; any loss of yttrium would initiate the (t-m) phase transformation that could create internal stresses and impair the mechanical properties (Mukaeda et al., 2012, Gui and Xie, 2016). Therefore, this would indicate that the surfaces of Y-TZP specimens are affected by an immersion in the 4 % acetic acid for extended durations.

Table 19 shows that the test solutions contained dissolved elements, which were not expected to appear in the analysis, however their amounts were not considerable. The possible explanation of the presence of these elements is that they were introduced through the productions steps of milling and polishing of Y-TZP specimens as reported in a previous study (Kvam and Karlsson, 2013). The main compositional elements of this material were reported from the manufacturer in Table 18. The composition of Y-TZP material was confirmed by dissolving powder of Y-TZP in a strong acid (H_2SO_4 + HF) and matched the reported percentages by the manufacturer.

Although, ICP-OES and ICP-MS are sensitive analytical tools for detecting depleted ions, the current findings were not parallel with the chemical solubility results. However, the cloudy samples that indicated a suspension of elements in the solution led to considering that it might be a physical change damage to the specimens while performing the solubility testing. Therefore, it was important to perform further investigation to confirm that Y-TZP specimens are affected by the immersion in 4 % acetic acid for 16 h by comparing the microhardness of Y-TZP specimens pre and post solubility testing. Many researchers have stated that dental ceramics showed lower strength values when subjected to water (Addison et al., 2003, Morena et al., 1986, Kosmac et al., 2007).

Conflicting findings have been reported regarding the mechanical properties of zirconia as a result of LTD effect. Some studies stated that there was no change in the mechanical properties, such flexural strength, after LTD, whereas other studies reported that there was a reduction in regard to Young's modulus and hardness up to 30 % after LTD (Swab, 1991, Papanagiotou et al., 2006b, Piconi and Maccauro, 1999, Cattani-Lorente et al., 2011).

As for this study, hardness values of Y-TZP showed a reduction of nearly 20 % after immersion in 4 % acetic acid at 80°C. Moreover, VMII specimens showed a reduction in hardness levels up to 30 % following the chemical solubility test. The results of this study were in agreement with other studies where the mechanical properties of dental ceramics reduce after an exposure to wet environments (Kvam et al., 1995, Kukiattrakoon et al., 2010, Kvam and Karlsson, 2013).

Even though each specimen should be washed thoroughly by distilled water pre and post-testing, there is a chance of having loose particles on the surfaces that would have an impact on the final results. This may happen by losing of any of those particles at any step of the test. Therefore, the ICP & XRD findings, SEM images and hardness results would indicate that percussive effects during the test are a significant factor in the mass loss.

8.7. Conclusion

- ICP findings showed there is not an increase in zirconium in the solute of the samples, which have a higher degree of solubility findings.
- The hardness investigation confirmed that the surfaces of Y-TZP and VMII specimens were softer after performing the chemical solubility testing.
- The variability of the solubility findings is likely due to specimen handling indicated by the ISO standard.

Chapter 9

Designing an Optimised Chemical Solubility Method

Chapter 9: Designing an Optimised Chemical Solubility Method

9.1. Introduction

Developing a reproducible method for measuring the chemical solubility values is essential. Although the existing method is uncomplicated to perform, it fails to improve the reproducibility and the accuracy of solubility findings. The former findings of this research show that the current ISO 6872 (BS ISO, 2015) standard provides inconsistent results. The findings of SEM, EDS, XRD, ICP and hardness would indicate that percussive effects during the test are a significant factor in the mass loss.

The steps of the current method include physical handling of the test specimens frequently. The method requires washing the specimens before and after immersing them in the test solution beside drying and weighing steps as well. All these steps could have significant impacts on the specimens' structure. In other words, a specimen may lose some particulates during frequent physical handling that would result in inaccurate measurements of the chemical solubility values. Therefore, there is a lot of room for optimisation of this testing method to standardise some factors, and also to optimise it to limit damage to the specimens.

9.2. Analysis of specimens' physical handling during the ISO test procedure

Determining the extent of chemical solubility of dental ceramic materials is linked to mass loss. However, the current standard test requires significant specimen handling, which could result in damage or chipping, especially at fragile areas with small radius of curvature. This section identifies the steps that require physical handling of the specimens and the outcomes that indicated the effects of handling.

There are seven steps that require physical handling of the test specimens as per the current ISO standard as follows:

1. The specimens should be washed by water grade 3 as per ISO 3696. This is most likely achieved through handling the specimens for proper washing.
2. The specimens should be then moved to be dried in an oven at 150 ± 5 °C, which requires the operator to place the specimen in a clean jar after the washing step.
3. The specimens should be then weighed, which requires the operator to move the specimens from the glass jar to the balance.
4. The specimens then should be then immersed in 4% acetic acid, which requires the operator to move the specimens from the balance to the glass jar.

5. The specimens should be then moved from the glass jar for a further washing step with water.
6. The specimens should be then moved to be dried in an oven at 150 ± 5 °C, which requires the operator to place the specimen in a clean jar after the washing step.
7. The specimens should be then reweighed, which requires the operator to move the specimens from the glass jar to the balance.

Furthermore, SEM images have shown damage at edges and corners of some of the tested glass-ceramic specimens pre-solubility testing and found at edges and corners of all tested specimens post-solubility testing, as shown in Chapter 6.

In Chapter 8, the prepared solution samples for ICP analysis were cloudy, which indicated physical damage to the specimens while performing the solubility testing.

In Chapter 6, the outcomes of the XRD analysis have indicated that the surfaces of Y-TZP specimens had some structural transformation of grains from the tetragonal to the monoclinic phase. It has been stated that this transformation would result in strain on the system causing micro-cracks, which would make areas with small radius of curvature more vulnerable to damage.

In Chapter 8, the findings of the hardness analysis have shown that the hardness values of dental ceramics can be reduced by up to 30% after immersion in 4 % acetic acid at 80 C. This has indicated that all tested specimens were softer after performing the chemical solubility testing and therefore increasing the possibility of physical damage.

In addition to the shortcomings of the unstipulated geometry of the specimens of the current ISO standard method, it can be concluded that physical handling of the specimens had a significant effect on the specimens' surfaces, which therefore had impact on the chemical solubility values measured.

It can be concluded that in order to create a more reliable test the goal should be to reduce the seven incidences of physical handling ideally to zero. It is proposed that this could be achieved without significantly changing the test methodology (same solute and times) but by standardising the specimen geometry to one less likely to be physically damaged and with a refined process that reduces sample handing significantly.

9.3. Aim

- To explore a reproducible method based on the current ISO standard to measure the chemical solubility values of dental ceramics.

9.4. Objectives

- To devise an optimised chemical solubility method ‘modifying the current method of ISO 6872 (BS ISO, 2015)’, which minimise the physical handling of the test specimens.
- To perform the new optimised method using cubic and spherical specimens as performed in the previous experiments on Y-TZP. This was to investigate the effect of altering the individua surface area and the morphology on the chemical solubility values of the optimised method.
- To perform the method on one of the previously tested dental ceramics (VMII) in Chapter 5 and compare the findings.
- To repeat each test three times to determine the variability in the measurements.
- To compare the findings of the different specimen groups and with the previous results.

9.5. Materials and Methods

9.5.1. Morphology C (cubes) preparation

The Y-TZP specimens were prepared as mentioned in Chapter 5 and the VMII specimens were prepared as mentioned in Chapter 4.

9.5.2. Morphology S (spheres) preparation

The Y-TZP specimens were prepared as mentioned in Chapter 7.

9.5.3. Methodology

9.5.3.1. The new optimised chemical solubility testing method

The chemical solubility tests were performed according to the ISO 6872 (BS ISO, 2015) requirements as mentioned in Table 5 (Chapter 4) with the following changes:

- The specimens were left inside the Pyrex flask during the whole experiment to minimise physical contact.

- The specimens were washed in distilled water using an ultrasonic bath for 5 minutes. This step was performed pre and post-solubility test prior to the drying step.

- The solutions were removed using automatic pipette.

- The whole Pyrex flask containing the specimens was weighed pre and post-testing to determine mass loss.

9.5.3.2. Statistical analysis

All data were compared using Welch's ANOVA and a Games-Howell post-hoc test. The alpha value (p) was set at 0.05. Welch's ANOVA was performed to compare unequal variances as found in this study.

9.6. Results

9.6.1. Y-TZP cubes

Table 23 shows comparable findings of the chemical solubility value of the cubic groups of Y-TZP. Figure 37 shows the relationship between the solubility value and the individual surface area for Y-TZP cubes tested using the optimised methodology. Welch's ANOVA indicated that there is no significant difference between the groups of this material. The standard deviation of the average chemical solubility results of the optimised method among the cubic groups was ± 1.

Table 23: The chemical solubility of Y-TZP groups. Chemical solubility is in μg/cm^2.

Group	Number of specimens	Individual surface area (cm^2)	Chemical solubility (μg/cm^2)			Mean	SD
			Test 1	Test 2	Test 3		
C1.5	**20**	**1.5**	23	26	23	24	± 2
C3.0	**10**	**3.0**	26	23	23	24	± 2
C4.3	**7**	**4.3**	23	23	23	23	± 0.2
C6.0	**5**	**6.0**	23	23	23	23	± 0.1
C7.5	**4**	**7.5**	23	23	23	23	± 0.1
C10.0	**3**	**10.0**	23	23	23	23	± 0.1

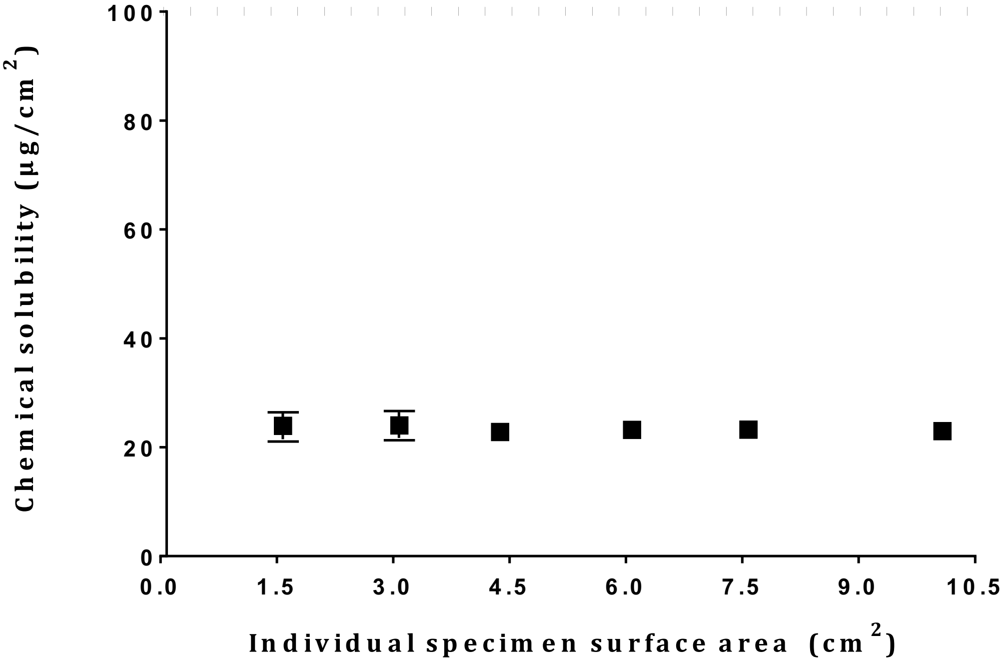

Figure 37: The dotted line demonstrates the maximum acceptable chemical solubility (100 µg/cm^2) for enamel ceramics according to the ISO 6872 (BS ISO, 2015). The graph shows the chemical solubility average of the cubic groups (Y-TZP) using the new optimised method (bars represent standard deviation. SDs of C4.3, C6.0, C7.5 and C10.0 are too small to be seen), (n=3).

9.6.2. Y-TZP spheres

Table 24 shows comparable findings of the chemical solubility value of the spherical groups of Y-TZP. Figure 38 shows the relationship between the solubility value and the individual surface area for Y-TZP spheres tested using the optimised methodology. Welch's ANOVA indicated that there is no significant difference between the groups of this material. The standard deviation of the average chemical solubility results of the optimised method among the spherical groups was ± 1. Figure 39 shows that the chemical solubility findings of Y-TZP cubes and spheres were comparable as well.

Table 24: The chemical solubility of Y-TZP groups. Chemical solubility is in μg/cm^2.

Group	**Number of specimens**	**Individual surface area (cm^2)**	**Chemical solubility (μg/cm^2)**			**Mean**	**SD**
			Test 1	**Test 2**	**Test 3**		
S1.5	**20**	**1.5**	23	23	23	23	± 0.3
S3.0	**10**	**3.0**	22	22	22	22	± 0.04
S4.3	**7**	**4.3**	22	22	22	22	± 0.1
S6.0	**5**	**6.0**	23	22	22	22	± 0.1
S7.5	**4**	**7.5**	26	23	23	24	± 2
S10.0	**3**	**10.0**	23	22	22	22	± 0.2

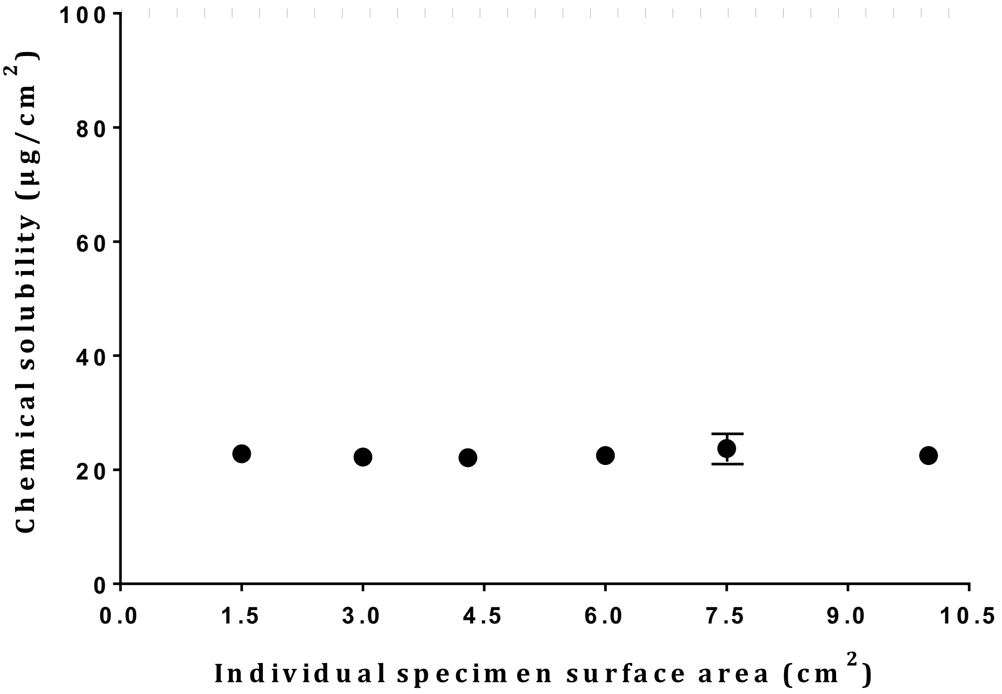

Figure 38: The dotted line demonstrates the maximum acceptable chemical solubility (100 µg/cm^2) for enamel ceramics according to the ISO 6872 (BS ISO, 2015). The graph shows the chemical solubility average of the spherical groups (Y-TZP) using the new optimised method (bars represent standard deviation. SDs of S1.5, S3.0, S4.3, S6.0 and S10.0 are too small to be seen), (n=3).

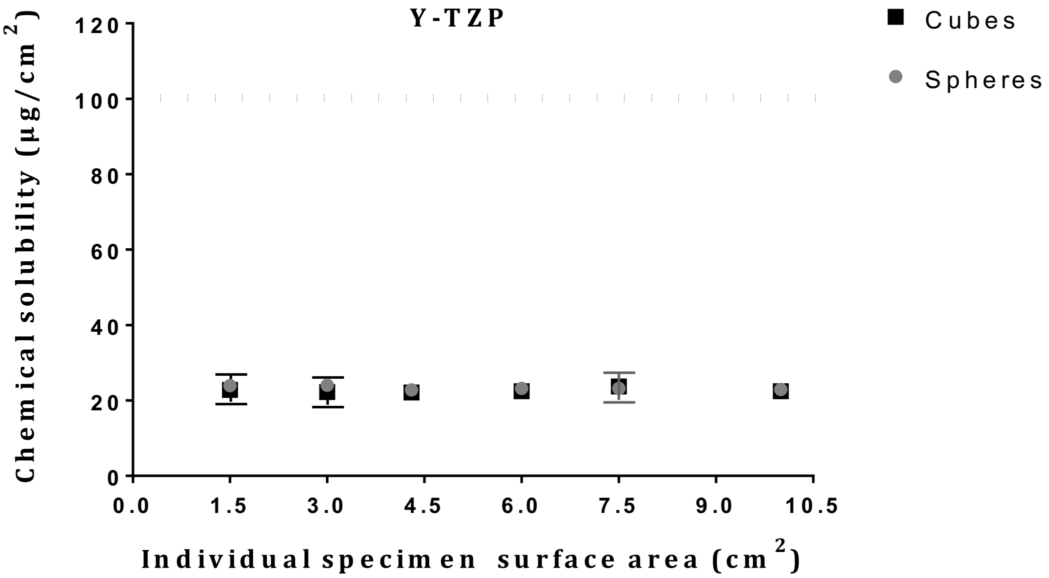

Figure 39: The dotted line demonstrates the maximum acceptable chemical solubility (100 µg/cm^2) for enamel ceramics according to the ISO 6872 (BS ISO, 2015). The graph shows the chemical solubility average of both cubic and spherical groups (Y-TZP) using the new optimised method (bars represent standard deviation. SDs of C4.3, C6.0, C7.5, C10.0, S1.5, S3.0, S4.3, S6.0 and S10.0 are too small to be seen).

9.6.3. VMII cubes

Table 25 shows the chemical solubility value of the cubic groups of VMII using the revised test scheme. Figure 40 shows the relationship between the solubility value and the individual surface area using the optimised methodology. Welch's ANOVA indicated that there is no significant difference between the groups of this material. Although the outcomes of the optimised method were repeatable for all tested groups, the chemical solubility values of VMII groups were still higher than the limit indicated for enamel ceramics. The standard deviation of the average chemical solubility results of the optimised method among the VMII groups was ± 2.

Table 25: The chemical solubility of VMII groups. Chemical solubility is in μg/cm^2.

Group	Number of specimens	Individual surface area (cm^2)	Chemical solubility (μg/cm^2)			Mean	SD
			Test 1	Test 2	Test 3		
C4.3	**7**	**4.3**	153	165	156	158	± 7
C6.0	**5**	**6.0**	165	142	158	155	± 12
C7.5	**4**	**7.5**	149	155	168	157	± 10

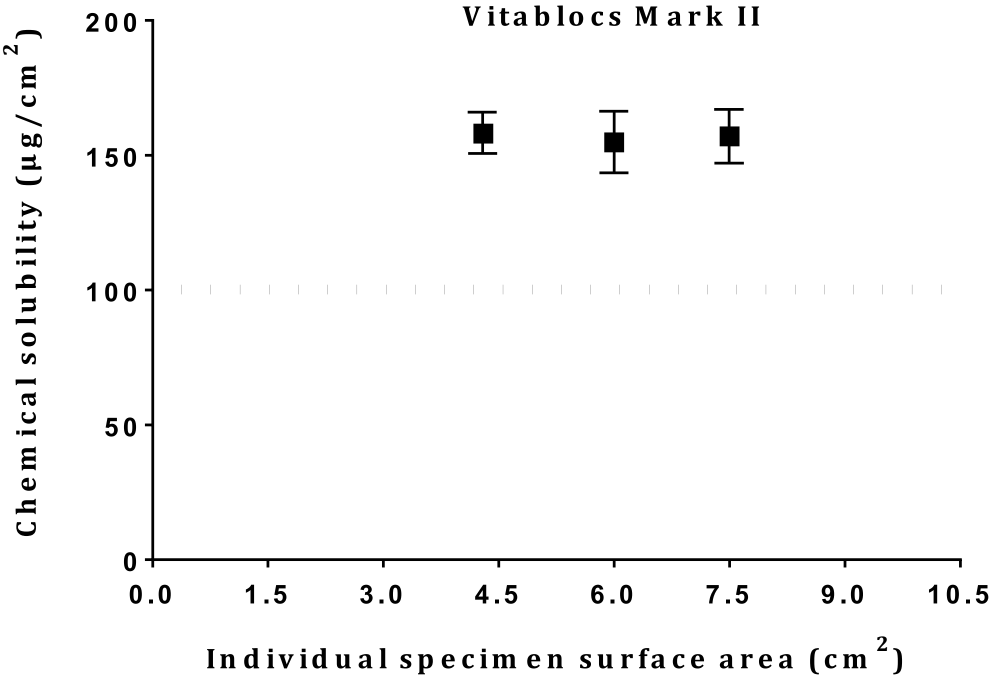

Figure 40: The graph shows the chemical solubility average of the cubic groups (VMII) using the new optimised method (bars represent standard deviation). The dotted line demonstrates the maximum acceptable chemical solubility (100 µg/cm^2) for enamel ceramics according to the ISO 6872 (BS ISO, 2015), (n=3). The chemical solubility values of VMII were above 150 µg/cm^2, therefore the scale is different.

9.7. Discussion

In this chapter, the aim was to design an optimised version of the current ISO standard for measuring the solubility values by minimising the physical contact of specimens, which was a challenge because the standard method requires handling the test specimens in many steps.

Interestingly, the findings of the optimised method that removed the operator handling factor show that there is no significant difference in chemical solubility between cubic specimens of different size in both Y-TZP and VMII and between Y-TZP cubes and spheres as shown in Figures 40-42. This finding indicates that the chemical solubility measurement is dramatically influenced by the percussive nature of transferring the specimens to and from the flask used for solubility testing. Although VMII findings showed also comparable solubility values, this material failed to demonstrate an acceptable chemical solubility value for enamel class of dental ceramic (up to 100 μg/cm^2) for both methods. These findings may indicate that either the material is not suitable for enamel-type restorations, or the current standard method still requires more investigations.

As is well known, one of the main issues of ceramics is brittleness (Babu et al., 2015), as indicated by the hardness results in Chapter 8. Therefore, it seems to be that the physical handling of the specimens has a major impact on the solubility values. Although the outcomes of the optimised method showed that there was not a difference between edged and edgeless specimens, the physical handling factor is mainly related to the edges and corners. The current standard method requires the operator to handle the specimens during washing, drying and weighing steps before and after the chemical solubility testing. Whereas the optimised method suggested the specimens should be left inside the glass jar from the beginning to the end of the test without any physical handling. Therefore, the recommendations of this optimised method could be reasonable to eliminate the factor of losing any particle while performing the test.

It was found that handling of small specimens (surface area of 1.5 – 4.3 cm^2) was not an easy process specifically with finishing and polishing steps. Because of the manufacturers' limitations of some of the dental ceramics and the ease of handling, the study recommends considering an individual surface area of 6.0 cm^2, using cubes to enable simple fabrication following the suggested method.

It is thought that any considerable thermal difference to the specimen could affect the surface structure as induced by the test (80 ± 3°C), which could lead to shaking off the crazed surface and thus increase the chemical solubility values. Therefore, it would not be accurate to compare the chemical solubility values for a material by different operators, who may handle the test specimens differently during the washing step. It is possible to solve this issue by considering a thorough and defined washing process of specimens in order to provide an effective foundation for comparison.

Even though each specimen should be washed thoroughly by distilled water before and after the solubility test, there is a chance of having loose particles on the surfaces that would have an impact on the final results. Therefore, an ultrasonic bath was considered to clean specimens in this experiment, which is widely used in some different sectors to remove loose particles from the specimens' surfaces (Oberlander et al., 2001). This cleaning method would keep any chipped off parts in the flask throughout the washing and drying steps, which would provide accurate values of the solubility.

9.8. Conclusion

The optimised method described shows that when specimen handling is limited the chemical solubility is independent of specimen geometry and morphology. The revised method reduces the incidences of specimen handing from 7 (ISO 6872) to 0 (optimised method).

Chapter 10

General Discussion

Chapter 10: General Discussion

The evidence presented in this work shows that the current standard method for measuring the chemical solubility of dental ceramics is not reproducible. The outcomes could be of interest to the ISO panel, manufacturers, researchers and the end users who desire for more accurate determination of the chemical durability of dental ceramic restorations. Therefore, some objectives were set in order to provide a broader understanding of the issues of the current standard method in this research.

The aim of the study as described in Chapter 3 was to:

> "… investigate the validity of the ISO 6872 (BS ISO, 2015) 'Dentistry - Ceramic materials' for chemical solubility and to develop a methodology for testing the chemical solubility of dental ceramics in order to improve the reproducibility of solubility findings. "

From this aim six objectives were identified, and they are reviewed below.

The first objective identified was to review the existing literature on (a) the different chemical solubility methods for dental ceramics, and (b) relate them with other chemical solubility methods of similar materials.

The search did not find much data criticising the ISO chemical solubility method in the existing literature, thus indicating the significance of this research. However, some investigators have modified the ISO method to assess the chemical solubility of dental ceramics, which indicates the lack of trust of the method (Anusavice and Zhang, 1998, Kukiattrakoon et al., 2010). Although, Stokes et al. (2002) has claimed that modifying the test specimens from discs to beads and replacing the refluxing system to a static solution has improved the reproducibility of the previous standard method ISO 6872 (BS ISO, 1995b), this work has shed light on the issues of the ISO standard methods.

In addition, Fathi et al. (2014) has investigated the chemical solubility apatite-mullite glass-ceramics using the ISO standard method and found that this material has shown lower solubility values compared to the outcomes of the previous standard method. As the current method does not specify the specimen's geometry, more investigations were required in order to validate the reliability of this method.

The second objective was to design and conduct a verification study of a dental ceramic material with a specific standard morphology and geometry to obtain evidence of the reliability of the current ISO standard method.

It was important to perform a verification study in order to confirm the reproducibility of the method if the specimen geometries are kept the same and if the test is performed by the same operator. It has been shown that the results were repeatable, however the tested material (VMII) did not pass the test, even though it is indicated for use as an enamel ceramic and has shown up to 10-year survival rate according to some clinical studies (Reiss and Walther, 2000, Posselt and Kerschbaum, 2003).

The third objective was to conduct a comparative benchmarking study of different types of dental ceramics and different geometry with the exact methodology design of the verification study.

The project attempted to detect the issues of causing the variability in the current standard method thoroughly. This phase aimed to study the effect of altering the individual surface area of the specimens, while maintaining the specified total surface area in the standard. To establish a solid assessment, benchmarking a number of representative materials of the different categories of dental ceramics in current use was performed. The overall outcomes have revealed that the existing standard method is not very reproducible. This variability was predictable, that some of the tested materials could pass or fail based on the individual surface area. For all the tested dental ceramic materials, the chemical solubility increases when the individual specimen size decreases. Moreover, the outcomes of Cerasmart material have indicated that hybrid ceramics gain weight during chemical solubility testing, therefore they should not be included in the scope of the ISO chemical solubility method of dental ceramics and may require a specified testing method. In general, it was important to explore the test method and its findings from different angles in order to reveal the ambiguity.

The forth objective was to design and conduct experimental studies with different shapes and different geometries.

It was important to investigate the difference of the chemical solubility values between edged and edgeless specimens. This was obtained by testing spherical specimens of Y-TZP with a range of different individual surface areas as performed with cubic groups. Interestingly, the findings of this study have shown lower chemical solubility values compared to cubic groups and less variability between different groups. However, it has been indicated that smaller individual specimens dissolve more readily even when spherical specimens are used, although the effect is less pronounced than in cubic specimens.

The fifth objective was to observe and investigate the mechanical and physical properties of the specimens' surfaces pre and post-solubility testing.

Consequently, the next phase was to perform a number of relative investigations to provide a better understanding of the standard method. A major tool in evaluating ceramics subjected to chemical solubility test is to perform SEM analysis pre and post-testing. All five tested materials in this project have shown that they were affected after an immersion in 4 % acetic acid at 80°C for 16 h. The previous results of Chapter 5 have revealed that as the individual surface area of the specimens decreased, the chemical solubility value increased. In other words, the chemical solubility values increased as the total edge lengths and number of corners increased as well. Thus, these SEM images have demonstrated that areas with small radius of curvature, i.e., the edges and corners were more damaged than flat surfaces during the test process, which may support the trend of the previous results. In addition, it has been shown that edges and corners were not only vulnerable areas, but it has also been shown that edges and corners can have rougher surfaces due to the difficulty of polishing at those areas. On the other hand, spherical morphology does not have weak areas that could lead to an equal finishing or losing some small particulates during the experiment as it could happen with cubic morphology. Therefore, it was assumed that angled surfaces such as edges and corners play a significant role in measuring the chemical solubility values.

Further analysis was needed to support this hypothesis. It was planned to analyse the test solutions post-solubility testing and attempting to relate the findings of the ICP analysis with the findings of the chemical solubility values of Chapter 5. The findings have not shown an increase of zirconium and yttrium element with higher dissolution groups. Thus, it was not possible to use these findings to support the former assumption. Nevertheless, ICP findings have shown other elements in the test solutions that were not expected to appear, which were considered as a sign of contamination as indicated with other studies (Kvam and Karlsson, 2013). However, it has been shown that some particulates participated in the test solution indicating the impact of edges and corners to the chemical solubility values as indicated by SEM images.

In addition, it was useful to use EDS analysis to assess the elements' distribution of the specimens' surface pre and post-solubility, which has shown no compositional change on the surface after solubility testing. Additionally, the analysis has shown that the surfaces of Y-TZP specimens did not contain unexpected elements as it happened with ICP analysis, which confirmed the existence of some contamination as reported also in other studies (Kvam and Karlsson, 2013). XRD analysis has shown some evidence of a transformation from the tetragonal to the monoclinic phase of Y-TZP specimens that is related to the chemical solubility test. Even though the transformation from the tetragonal to the monoclinic grains would prevent the propagation of an existing crack, slight structural elevations can be formed that could have clinical impact (Ardlin, 2002).

Based on the ICP findings, hardness analysis has been undertaken on Y-TZP and VMII in order to confirm that the mechanical properties of dental ceramics are affected after performing the chemical solubility testing. The reason was because the low levels of the main elements of dental zirconia of the former ICP analysis were confusing. The findings have confirmed that dental ceramics are affected by an immersion in 4 % acetic acid and indicated that the hardness values decrease after the chemical solubility testing. Therefore, specimen handling is likely the cause of increased solubility in smaller specimens. These findings were important because it is known that the oral cavity is a complex environment (Kukiattrakoon et al., 2009). This moist and warm environment exhibits different factors such as saliva, water from dentinal tubules and luting cements, chewing or mastication stresses, different coefficient of thermal expansion stresses and temperature and pH variations that would negatively influence the mechanical properties of dental ceramics (Studart et al., 2007, Pinto et al., 2008).

The final objective was to design an improved (for inter-operator reliability) chemical solubility method for dental ceramics.

The findings of the ICP, SEM images, XRD and hardness analysis indicated that percussive effects during the test are a significant factor in the mass loss. It can be assumed, therefore, that if the test specimens were protected against any possible defect, the actual chemical solubility value can be determined. Therefore, an optimisation of the current standard method was considered. The enhancements of this method did not change the main core of the standard method, the changes only involved the specimen handling by reducing the incidences of specimen handing from 7 (ISO 6872) to 0 (optimised method) as follows:

1) The test specimens stay inside the glass jar during the whole test.
2) Removing the test solution using an automated pipette.
3) Using ultrasonic bath as the main washing system of the test.

The findings have shown that by minimising the physical handling of the specimens, the reproducibility was improved by this optimised method. This means that physical damage is expected to happen at any step of the current ISO standard method, whilst the optimised method eliminates any effect of specimen geometry and morphology have on the chemical solubility results. Moreover, using an automated pipette with a narrow orifice (micropipette tips) is useful for absorbing the test solution without removing any separated specimens' particles. However, this method takes a long time to remove fluids from the glass jar as the automated pipette is designed for small amounts. A possible criticism of this method is that some of those broken parts may have been broken off due to chemical action and were not included in the outcomes of the optimised method. This may require additional investigations in the future.

Regarding reproducibility, the results of both Y-TZP and VMII have shown that this optimised method was reproducible. However, the solubility values of VMII exceeded the ISO specifications for both methods, which is not in line with the manufacturers' reports. The literature offers no evidence of a proven link between clinical performance and a chemical solubility value; it could be accepted by the lack of evidence of clinical failures due to solubility that the standard values given in ISO 6872 are appropriate. The work demonstrated here should provide a sufficiently reliable measurement that these values can be compared and further work on clinical relevance could be achieved.

As the VMII material is well known (and proven) and among the most common dental ceramics the fact it has 'failed' would not seem to offer a cause for concern at this stage. However, the current 'pass' limit of the ISO standard might be reconsidered to include such a clinically acceptable material (i.e. to raise the ‘maximum permitted limits of chemical solubility) in light of this more reliable test methodology, and this would be a recommendation to the ISO Standard technical committee.

As previously mentioned in this research, the current standard method can be manipulated by altering the geometry of individual test specimens whilst still complying with the ISO 6872 (BS ISO, 2015) specifications. Even though this optimised method proved that there was not a significant difference of the chemical solubility values between cubic and spherical geometries, it is very important to establish standard method that stipulates specimens’ geometry. Companies that work on developing and producing new dental ceramics as well as researchers need explicit instructions to perform the chemical solubility test without the need to design specimens’ geometries that may affect the reproducibility of the test method.

In conclusion, the current standard method ISO 6872 (BS ISO, 2015) for measuring the chemical solubility levels of dental ceramics is not reproducible due to the undefined test specimens’ geometry and number. Within the limitations of this research, the findings show that the surface integrity and mechanical properties are affected following the solubility testing, which is very important for clinical considerations. The optimised method gave promising findings. It is believed that the improvement of the reproducibility given by this optimised method will help researchers and manufacturers to obtain fast and accurate assessment of the chemical solubility values.

Chapter 11

General Conclusions

Chapter 11: General Conclusions

Within the limitation of this project, the following conclusions can be drawn:

1) By analysing the literature review, it was apparent that few published studies of the chemical solubility of dental ceramics had adhered to the method described in the ISO 6872 standard. Many researchers had instead developed alternative methods for chemical solubility assessment, indicating a possible lack in confidence or awareness of the ISO standard method.
2) A verification study showed that by keeping the same specimen specification, there is a very little variability in the chemical solubility using the ISO method.
3) Benchmarking current dental ceramic materials using the ISO method demonstrated that the chemical solubility standard value can be manipulated by altering the geometry of individual specimen's surface area whilst still complying with the ISO 6872:2015 standard. Therefore, it was observed that the current chemical solubility testing method of ISO 6872:2015 is not valid, as the variability in geometry can positively or adversely affect the result. The benchmarking study showed a correlation between specimen size and chemical solubility, with the smallest specimens demonstrating an elevated solubility. It was also noted that existing clinically acceptable ceramics do not pass the ISO standard test for chemical solubility. Therefore, the current standard method cannot be

a useful tool for dental professionals because it makes comparison difficult.

4) SEM analysis indicated that the most soluble material is the most damaged and all tested specimens showed enhanced damage around edges and corners. To test the impact of this, the chemical solubility values of spherical groups were measured and were lower than the results of the equivalent cubic specimens. In addition, the cubic groups with the longest edge length and higher number of corners had the highest chemical solubility.
5) The variability of the chemical solubility values of spherical groups was less pronounced than cubic groups, leading to a working hypothesis that areas with a small radius of curvature dissolve more readily.
6) ICP and the Vickers hardness investigations confirmed that the variability of the solubility findings was likely due to specimen handling indicated by the ISO standard. In addition, surface XRD of the Y-TZP specimens showed evidence of 'ageing' (transformation from the tetragonal to the monoclinic form) after the ISO chemical solubility test.
7) An optimised method was developed that adhered to the original ISO standard method, but significantly reducing the manipulation of the specimens (from 7 incidences to 0) demonstrated that when specimen handling is limited the chemical solubility is independent of the specimen geometry and morphology. Therefore, it was crucial that a valid, reproducible and clinically relevant testing method can be applied to measure the chemical solubility of dental ceramics.

8) The benchmarking of currently available dental ceramics using the revised test methodology demonstrated that some established materials (e.g. VMII) did not ‘pass’ according to the thresholds described in the current standard. This would not seem to offer a cause for concern at this stage, as there no literature describing failure due to chemical solubility *in vivo*. However, the current ‘pass’ limit of the ISO standard might be reconsidered to include existing clinically acceptable materials (i.e. to raise the ‘maximum permitted limits of chemical solubility) in light of this more reliable test methodology, and this would be a recommendation to the ISO Standard technical committee.

Chapter 12

Future Work

Chapter 12: Future Work

In regard to this work, there are some suggestions for future work as follows:

- Investigate if the broken parts are broken off due to only percussive forces or a combined effect with the chemical action of the test.
- Investigate the current acceptable maximum chemical solubility values for both enamel and core types of dental ceramics by studying the relationship between the solubility values and surface roughness of specimens.
- Investigate the surface microstructure of clinical specimens for a given time and relate them to the solubility tested specimens.
- Explore a method of measuring the chemical solubility values of hybrid ceramic materials.

Chapter 13

Reference List

Chapter 13: Reference List

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Chapter 14

Appendices

Chapter 14: Appendices

14.1. Calibrations

It was important to confirm that all experimental elements are functionally valid and accurate before performing any solubility test in order to obtain accurate results. Thus, every furnace that used for solubility testing was subjected to temperature analysis using (Pico technology, United Kingdom). This procedure was implemented in a regular base.

Furnace-1 (drying furnace):

It was found that the furnace should be set at 175°C in order to give 150 ± 5°C as required by the ISO chemical solubility testing.

Furnace-2 (solubility testing furnace):

It was found that furnace-2 should be set at nearly 78°C to produce the 80 ± 3°C as required.

Furnace-3 (wax burn off furnace):

This furnace can be used sometimes in cases such as burning off wax in ceramic pressing technique. It was found that the furnace is within tolerance; therefore, the required temperature can be set as desired.

14.2. The optimised chemical solubility method of dental ceramics

14.2.1. Reagent, acetic acid (analytical grade), 4 % (V/V) solution in water grade 3 as specified in ISO 3696.

14.2.2. Apparatus

14.2.2.1. Balance, accurate to 0.1 mg.

14.2.2.2. Drying oven, controlled at (150 ± 5) °C.

14.2.3. Preparation of test specimens, as prescribed in ISO 6872:2015. (Recommended: 5 cubes with 6 cm^2 individual specimen surface area)

- Because of limitations on the availability of some sample geometries (manufactured blanks for milling), and the ease of handling for testing.

14.2.4. Procedure

1) Place and keep all specimens in a Pyrex flask (recommend 250 ml) during the whole experiment.
    - This minimises physical contact with specimens. In addition, this keeps specimens from damages during the whole experiment and any separated particles.
2) Wash the specimens with distilled water (water of grade 3 as per ISO 3696) using an ultrasonic bath for 5 minutes.
    - Using an ultrasonic bath is more efficient and effective process to remove contaminants from solid surfaces compared to the simple washing technique of the ISO standard.

3) Remove distilled water from the flask using an automatic pipette.
    - Using an automated pipette helps to remove the test solutions effectively and minimise the risk of damage to specimens.
4) Dry the specimens at (150 ± 5) °C for 4 h in the flask.
5) Weigh the flask containing the specimens to the nearest 0.1 mg.
    - This also to minimise the risk of damaging the test specimens.
6) Pour 100 ml of 4 % acetic acid into the Pyrex flask.
7) Preheat oven to (80 ± 3) °C and place the sealed flask inside the oven for 16 h.
8) Drain and wash the specimens with distilled water (water of grade 3 as per ISO 3696) using an ultrasonic bath for 5 minutes.
9) Dry the specimens at (150 ± 5) °C for 4 h.
10) Reweigh the Pyrex flask containing the specimens to the nearest 0.1 mg.

14.2.5. Calculation and assessment of results

Calculate the mass loss in micrograms per square centimetre of the specimens. As stated by the ISO 6872:2015, enamel class dental ceramics should display up to 100 μg/cm^2 for maximum solubility level (should be reconsidered by future studies), whereas core class ceramics must show less than 2000 μg/cm^2.

14.3. Poster presentation, BSORD, September 2015, Cardiff, Wales.

Benchmarking The Chemical Solubility of Restorative Dental Ceramics

The
University
Of
Sheffield.

R. A. HAWSAWI[1], A. JOHNSON[1], C. W. STOKES[1]
[1]University of Sheffield, Sheffield, England

School of Clinical Dentistry, University of Sheffield, UK

INTRODUCTION

The current **ISO 6872:2008** specifies a standardized testing method to measure the chemical solubility of dental ceramics. Unfortunately, few published studies of chemical solubility have adhered to the ISO test. This standard replaced the older method (1995) by replacing a refluxing method with the current static solution method. However, the new current does not specify a specific geometry and morphology for test samples, only a surface area, as the previous test has done.

AIMS

The aim of this study was **to assess the current ISO solubility test** for benchmarking the chemical solubility of restorative dental ceramics and to investigate the impact of the flexibility in sample size afforded by the new standard.

MATERIALS & METHOD

The chemical solubility analysis has been performed to study samples according to the (ISO 6872:2008).

Two types of ceramic materials were used:
1)Vitablocs Mark II (3 groups)
2)Vita In-Ceram Alumina (3 groups)

G	Individual surface area	Specimens	Total surface area
1	4.6 	7	≥ 30 cm²
2	5.8 	6	≥ 30 cm²
3	7.68 	4	≥ 30 cm²

The surface microstructure of VMK II and In-Ceram specimens was analyzed by scanning electron microscope (SEM, CamScan) before and after chemical solubility test (Figure 3).

RESULTS

ANOVA indicated a significant difference between **groups 1 and 2, and 1 and 3** (Figure 1). Particularly, the present outcomes possibly indicated as the overall sample edge length increases, the chemical solubility also increases (Figure 2).

Figure 1 – The graph shows a negative relationship between the solubility rate (µg/cm²) and the individual surface area of a specimen.

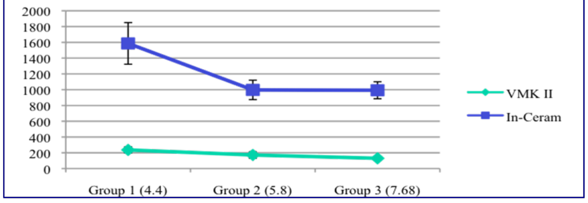


Figure 2 – The graph shows a positive relationship between the solubility rate (µg/cm²) and the edge length of each group of specimens.

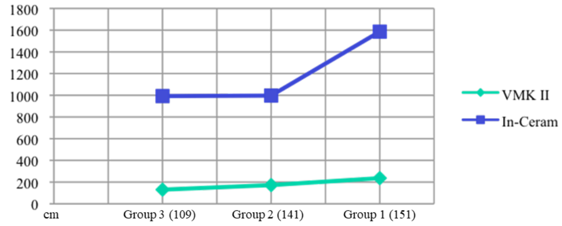
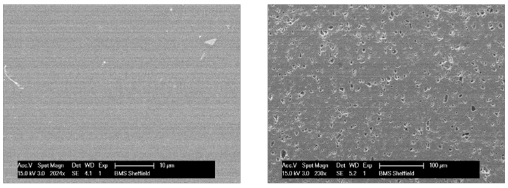


Figure 3 – SEM micrographs of specimens (VMK II) before and after immersion in acetic acid (4%)



CONCLUSIONS

- Although the results of the current ISO chemical solubility test appear with low variability, these results can be manipulated by modifying the specimens' dimensions or morphology.
- Maintaining a standard surface area, the chemical solubility decreases as the sample size increased for both 'enamel' and 'core' classes of dental ceramic.
- The test did not succeed to improve the reproducibility of solubility findings.
- It is recommended that the test be amended to stipulate sample morphology and geometry.

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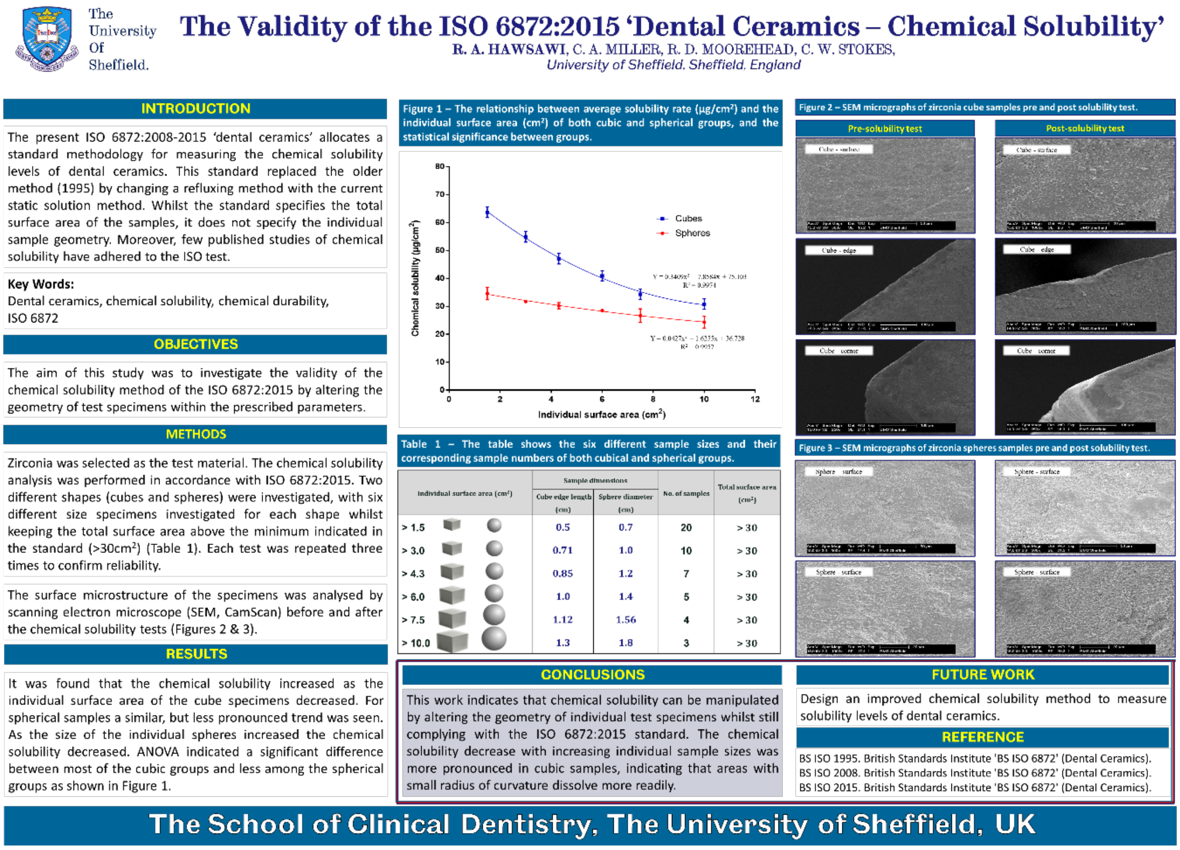

The University Of Sheffield.

The Validity of the ISO 6872:2015 'Dental Ceramics – Chemical Solubility'

R. A. HAWSAWI, C. A. MILLER, R. D. MOOREHEAD, C. W. STOKES,
University of Sheffield, Sheffield, England

INTRODUCTION

The present ISO 6872:2008-2015 'dental ceramics' allocates a standard methodology for measuring the chemical solubility levels of dental ceramics. This standard replaced the older method (1995) by changing a refluxing method with the current static solution method. Whilst the standard specifies the total surface area of the samples, it does not specify the individual sample geometry. Moreover, few published studies of chemical solubility have adhered to the ISO test.

Key Words:
Dental ceramics, chemical solubility, chemical durability, ISO 6872

OBJECTIVES

The aim of this study was to investigate the validity of the chemical solubility method of the ISO 6872:2015 by altering the geometry of test specimens within the prescribed parameters.

METHODS

Zirconia was selected as the test material. The chemical solubility analysis was performed in accordance with ISO 6872:2015. Two different shapes (cubes and spheres) were investigated, with six different size specimens investigated for each shape whilst keeping the total surface area above the minimum indicated in the standard (>30cm²) (Table 1). Each test was repeated three times to confirm reliability.

The surface microstructure of the specimens was analysed by scanning electron microscope (SEM, CamScan) before and after the chemical solubility tests (Figures 2 & 3).

RESULTS

It was found that the chemical solubility increased as the individual surface area of the cube specimens decreased. For spherical samples a similar, but less pronounced trend was seen. As the size of the individual spheres increased the chemical solubility decreased. ANOVA indicated a significant difference between most of the cubic groups and less among the spherical groups as shown in Figure 1.

Figure 1 – The relationship between average solubility rate (µg/cm²) and the individual surface area (cm²) of both cubic and spherical groups, and the statistical significance between groups.

Table 1 – The table shows the six different sample sizes and their corresponding sample numbers of both cubical and spherical groups.

Individual surface area (cm²)	Sample dimensions		No. of samples	Total surface area (cm²)
	Cube edge length (cm)	Sphere diameter (cm)		
> 1.5	0.5	0.7	20	> 30
> 3.0	0.71	1.0	10	> 30
> 4.3	0.85	1.2	7	> 30
> 6.0	1.0	1.4	5	> 30
> 7.5	1.12	1.56	4	> 30
> 10.0	1.3	1.8	3	> 30

Figure 2 – SEM micrographs of zirconia cube samples pre and post solubility test.

Figure 3 – SEM micrographs of zirconia spheres samples pre and post solubility test.

CONCLUSIONS

This work indicates that chemical solubility can be manipulated by altering the geometry of individual test specimens whilst still complying with the ISO 6872:2015 standard. The chemical solubility decrease with increasing individual sample sizes was more pronounced in cubic samples, indicating that areas with small radius of curvature dissolve more readily.

FUTURE WORK

Design an improved chemical solubility method to measure solubility levels of dental ceramics.

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The School of Clinical Dentistry, The University of Sheffield, UK