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*Original Article*

# Surface Chemical Analysis of Hydroxyapatite Compared to Glass Ionomer and Amalgam Materials Used as Retrograde Filling Material in Dentistry

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## ABSTRACT

*The aim of this study was to analyses the surface chemistry of different materials used as retrograde filling and compare it with bulk chemical analyses reported. Surface analysis carried out using an X—ray Photoelectron Spectrometer (XPS) built by VG Scientific. Samples of HAP, GIC and Amalgam materials used were prepared as Discs of 10 mm diameter. These transferred on to XPS aluminum stubs. XPS spectra were obtained from the wide scan spectrum of amalgam, the following elements are present: tin (23.2%); mercury (6.6%); carbon (19%) and oxygen (51.2%). The wide scan spectrum of GIC the elements present in the surface of the material are: oxygen (41.1%); aluminum (5%); silicon (4.6%); carbon (36.1%); calcium (11.3%); fluorine (2.1%) and sodium (0.T). The XPS spectra were obtained from the wide scan spectrum of Hydroxyapatite the elements present in the surface are: Oxygen (49-4%), Carbon (33-9%), calcium (8-6%), and Phosphorus (8-4%). In conclusion, the chemical XPS analyses of the materials used as retrograde filling, have shown them to vary considerably with respect to bulk chemical composition. Further surface analysis could include narrow scans, manipulation of surface chemistry, coupled with in vitro and in vivo tests and experiments to determine the importance of different surface components on biocompatibility.*

**Keywords**: Surface, Chemical, Analysis, Hydroxyapatite

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## INTRODUCTION

Peri-apical surgery with retrograde root filling is an accepted alternative following failure of conventional endodontic treatment. It is a particularly useful procedure in that the retrograde filling seals the apical portion of the root canal, thus eliminating the spread of bacteria or toxins from it. The most widely used material for this purpose has been amalgam which, although considered as the material of choice, is still far from ideal. Questions still exist as to its biocompatibility and its toxic effects. The debate regarding the micro—leakage which occurs with amalgam restorations is a long—standing one. An ideal retrograde root filling material, therefore, would be one which had the following properties;

a) Biocompatibility (i.e. exhibiting a favorable response to surrounding tissues);
b) No toxic or adverse effects, locally or systemically;

c) The ability to form a chemical bond with dentine, thus producing an effective seal and eliminating the possibility of micro-leakage;
d) Satisfactory clinical properties to ease manipulation and handling.

Hydroxyapatite (HAP) has been studied extensively and its biocompatibility is well recognized whether implanted in bone or soft tissue [1-3], or hard tissue synthetic hydroxyapatite with a stoichiometric composition as $Ca10 (PO4)6(OH)2$ has an excellent biocompatibility with human teeth and bone. Mangin et al. (2003) tested its sealing ability in its use as a root-end filling material. Lucas et al. (2003) tested the improvement of the mechanical strength of glass ionomer cement by adding HA. Their results indicated that hydroxyapatite-added glass ionomer cement has a greater potential as a reliable restorative material with improved fracture toughness, long-term bonding strength to dentin and unimpeded ability of sustained fluoride release 23. Kouassi. etal. (2003) 20

Recently, the use of glass—ionomer cements as root fillers has received widespread interest, these cements were invented in 1969 by Wilson and Kent, and are extensively used in Restorative Dentistry.

A review of the literature Shows that retrograde root filling materials have been tested in a variety of ways. Callis et al, in 1987, compared a glass—ionomer cement and gutta perchea in the adult for canine. In another Study Carried out in the same year by Zetterqvjst at al 1987, a private model was used. In vivo evaluation of materials has several disadvantages. The material is placed in a complex environment and interpretation of results, which depends on local and systemic factors, is complex too. Variations in surgical technique and the use of different in vivo models also increases experimental variability.

Analysis of amalgam shows an absence of surface atoms which may be capable of bonding. This may help to explain the marginal shrinkage of amalgam and thus microleakage 31,32. The presence of free mercury would possibly explain its toxicity.

The concept of biocompatibility has, in recent years, changed from one to another that's of lack of toxicity, in which materials are chosen for their inertness in the biological environment, to a more Positive concept in which a favorable interaction between the material and tissues is aimed for. When a retrograde root filling material is Considered, it is the response of the tissues that is they have concern; especially the response of the osteoblast Which is the key cell in bone healing and function

Further, an understanding of the physical, chemical, and mechanical properties of the bulk and the surface of materials is also important to ultimate clinical success. Whilst bulk properties have received considerable attention, the evaluation of surface properties still remains somewhat unexplored. Accurate surface analysis may provide some important clues to the surface structure requisites of biocompatible root fillers and, therefore, in conjunction with the qualitative in vivo evaluation, a limited study of the surface properties will undertake.1,2,3

The aim of this study was to analyses the surface chemistry of HAP compared to GIC and amalgam materials used as retrograde filling and compare it with bulk chemical analyses reported.

## METHODS

### *Surface Chemical Analysis*

Three experimental groups were included: Group1 Hydroxyapatite (HAP) (Plasma biotal UK). Group 2 Glass ionomer cement (GIC) (AHL Generic UK). Group 3 Amalgam (SDI Ltd Australia

All retrograde filling material were prepared according to the manufacturer's instructions Standardized discs of 10 mm diameter for each material

HAP, GIC and Amalgam Materials for analysis were cleaned by the following procedure:2

1- Specimens were washed thoroughly in a liquid laboratory cleaner and rinsed several times in distilled water.
2- 10 min in methanol in an ultrasonic bath

3- 10 min in ethanol in an ultrasonic bath
4- 10 min in deionized water in an ultrasonic bath
5- Washed in deionized water
6- Air dried before sterilizing kept in clean small label glass bottle
7- Sterilized in a hot air at 160 oC /1 h (dry sterilization)

Surface analysis carried out using an X—ray Photoelectron Spectrometer (XPS) built by VG Scientific. Figure 1 Samples of each of the materials used will prepared as for the root fillings used in dental surgery. These transferred on to XPS aluminum stubs and allowed to set, before being passed through the XPS.1,2.

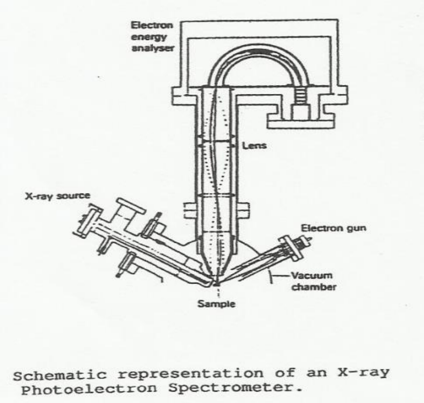

*Figure1: Schematic representation of an x-ray photoelectron spectrometer*

The XPS technique depends on the presence of an ultra-high vacuum (UHV), (Diagram 1) [203. The sample bombarded with X—rays. The photoelectrons emitted will analyzed in terms of their kinetic energies. XPS is surface sensitive because, although the X—rays penetrate to a depth of about 50 microns into the sample, the ejected electrons can only be distinguished if they escape without losing energy; this depth is typically of the order of 5nm. Non-destructive determination of chemical composition at the surface can be carried out using surface analysis techniques such as X-ray photoelectron spectroscopy (XPS), alternatively known as electron spectroscopy for chemical analysis (ESCA). In XPS a specimen is bombarded with x-rays leading to the ejection of photoelectrons from the surface of the sample; the energy of a given electron being characteristic of the emitting atom. Only electrons generated within a few nm of the surface actually escape to an energy analyzer/detector, and hence XPS is a surface sensitive analytical technique. Spectra can be quantified to give elemental compositions, and all elements can be detected. XPS studies allow the determination of the relative concentration in the elements of the uppermost layers of the surface of HAP, GIC And amalgam to a depth of 3-4 nm.

## RESULTS

### *Results of Chemical Analysis of HAP, GIC and Amalgam*

XPS spectra were obtained. From the wide scan spectrum of amalgam Figure 2, it can be seen that the following elements are present: tin (23.2%); mercury (6.6%); carbon (19%) and oxygen (51.2%). From the narrow scan of amalgam (ib), it is possible to measure the binding energy of tin and show that it Corresponds to that of tin oxide. This would account for most of the oxygen detected. Using a similar procedure to determine the chemical state of the mercury (Ic), it appears most likely that it is in its free state. This is obviously a cause for worry and demands further confirmation because its toxic effect. The remaining oxygen not associated with tin is probably bonded with carbon.

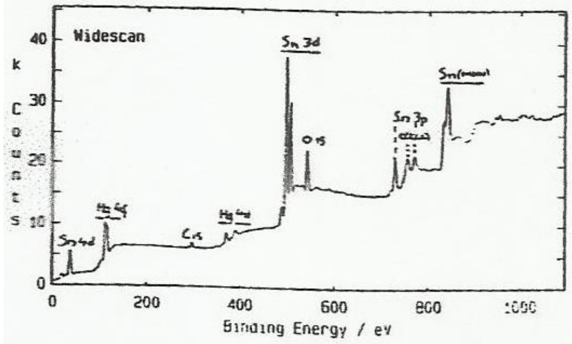

*Figure 2: XPS Spectrum of amalgam*

On the wide scan spectrum of GIC Figure 3, the elements present in the surface of the material are: oxygen (41.1%); aluminum (5%); silicon (4.6%); carbon (36.1%); calcium (11.3%); fluorine (2.1%) and sodium (0.2%). From visual examination of this spectrum, it is evident that the strongest peak is from the oxygen, The intensity of this peak corresponds to a predominance of oxygen at the material surface. This oxygen must be associated with all the other elements (except fluorine). Oxygen—rich substances are hydrophilic but do not necessarily have the facility to form strong bonds with adjacent materials. However, from the narrow scan, it is clear that there are several different carbon environments, denotes carbon bonded to carbon and denote carbon bonded to oxygen. Oxidized carbons have the capacity to form strong bonds with adjacent materials. This would perhaps explain its ability to bond to dentine.

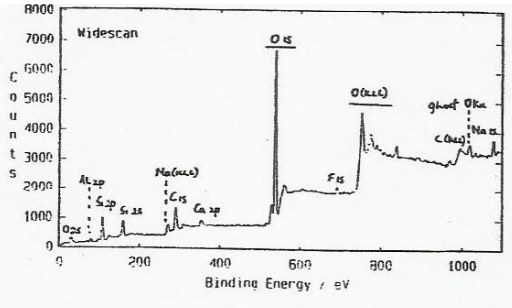

*Figure 3: XPS Spectrum of GIC*

Typical XPS spectra of HAP, are shown in Figures 4 calcium, phosphorous and oxygen were all detected. The position of the peaks was the same as those reported by other authors for HAP, 295 (Table 1). However, the Ca/P atomic ratio of the HAP surface was lower than that of stoichiometric apatite (1.67) and did not agree with those values obtained from wet chemical analysis (ICP). XPS spectra (Hilal PhD Thesis 1996 Sheffield University UK)

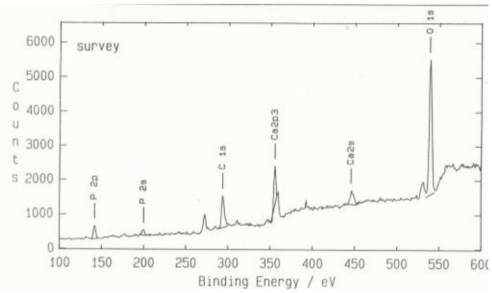

*Figure 4: XPS Spectrum of HAP*

*Table 1: Percentage of elements found at the surface of the HAP material when analyzed by ICP, EDX and XPS.*

| El* | HAP | | |
|---|---|---|---|
| | ICP | EDX | XPS |
| O | - | 42.9 | 49.4 |
| C | - | - | 33.9 |
| Ca | 32.5 | 38.1 | 8.6 |
| P | 15.0 | 20.9 | 8.4 |

The Ca/P molar ratios were calculated from the data presented in Table 1 and presented in Table 2.

*Table 2. Ca/P molar ratio results from wet chemistry (ICP), XPS and EDX analysis*

| Materials | Wet chemistry (ICP) | XPS | EDX |
|---|---|---|---|
| HAP | 1.67 | 1.1 | 1.50 |

## DISCUSSION

The purpose of surface analysis has been to identify the surface chemistry of the materials which would influence the initial stage of the healing process following apicectomies. Not only would this affect adsorption of some of the components of tissue fluids but it would also influence chemical bonding to dentine and bone

The XPS is an extremely sensitive piece of apparatus, especially to moisture. Since some of the dental materials in question contained considerable quantities of water, the technique had to be somewhat modified. These samples had to be dried overnight in a vacuum oven at 5O oC prior to placement in the XPS chamber. Once this had been carried out, the experiment proved to be satisfactory. Surface analysis study may help to eliminate unsuitable materials for in vivo or in vitro or clinical trial or study, if by its application, one could establish 'ideal surface properties' for biocompatibility.1,2

An amalgam is a substance formed by the reaction of mercury with another metal. Almost all metals can form amalgams with mercury, the notable exception being iron. Silver-mercury amalgams are important in dentistry, and gold-mercury amalgam is used in the extraction of gold from ore.3

Chemical Composition of the Conventional amalgam (Traditional).3

a) Silver (Ag) 65%: b- Tin (Sn) 25-29%: c- Copper (Cu) 6%:
b) d- Zinc (Zn) 0-2 %: e-Palladium: 0-l %: f-Indium: 0-4 %:

Study done by Kaga et al 1991 suggest that the major contributor to the cytotoxicity of alloy for amalgam is probably copper, while that for amalgam is zinc35.

In this study the XPS spectra were obtained. from the wide scan spectrum of amalgam, the following elements are present: tin (23.2%); mercury (6.6%); carbon (19%) and oxygen (51.2%). Analysis of amalgam shows an absence of surface atoms which may be capable of bonding. This may help to explain the marginal shrinkage of amalgam and thus microleakage 31,32. The presence of free mercury would possibly explain its toxicity.

The Glass ionomer cement GIC powder is an acid-soluble calcium fluor aluminosilicate glass similar to that of silicate but with a higher alumina-silicate ratio that increases its reactivity with liquid. The fluoride portion acts as a “ceramic flux”. Lanthanum, Strontium, Barium or Zinc Oxide additives provide radiopacity. The raw materials are fused to form a uniform glass by heating them to temperatures of 1100°C to 1500°C. The glass is ground into a powder having particles into a powder in the range of 15 to 50  µm.

Typical percentages of the raw materials are: 1 Silica 41.9% Alumina 28.6%, Aluminum Fluoride 1.6% Calcium Fluoride 15.7% Sodium Fluoride 9.3% Aluminum Phosphate 3.8%

In this study the wide scan spectrum of GIC, the elements present in the surface of the material are: oxygen (41.1%); aluminum (5%); silicon (4.6%); carbon (36.1%); calcium (11.3%); fluorine (2.1%) and sodium (0.1%). Analysis of the Glass ionomer cement reveals highly activated surface and possible capability for chemical bonding

The wet chemical analysis for HAP were equal to the stoichiometric ratio of 1.67 and in agreement with previous studies.8-11 However, XPS analysis of the surface showed a much lower in Ca/P molar ratio (*1.0), suggesting that the surface may contain different calcium phosphates.8-11 Thus there was a large discrepancy between the Ca/P ratios from the surface analysis technique when compared with the bulk analysis technique. All percent for XPS errors were within the 10 % expected error of the instrumentation.12,13 The ability to relate the Ca/P ratio obtained from a surface analysis technique to one obtained by wet chemistry analysis of the bulk by a calibration curve can be useful in examine Ca/P implant surface as shown by Kiewetter, et al (1994).16 It appears that very low Ca/P ratios obtained from XPS analysis are close to dicalcium phosphate (1.0),8 whereas that obtained from EDX analysis, close to TCP (1.50). The Ca/P molar ratio for the HAp.17 In another study (EDX), plasma sprayed non-implanted HAp-coated pins were shown to have a Ca/P ratio of 1.48 on the outermost surface examined.18

Carbon contamination was detected on the surface of all materials analysed. This may have arisen from graphite mould during processing. Various reports, however, have shown that the feed powder's composition may be altered by processing, resulting in a material whose composition differs from the stock powder.2,4-7 Carbon, contaminants have been reported by other investigators for HAp.8,16 A second possible source of contamination may have been the cleaning, sterilization or handling of the Materials.17,18 The presence of organic contaminations may be of some importance. Cellular response to implant materials may be affected by adsorbed surface species. Surface contamination has received only little attention until quite recently in Implantology research in spite of its importance to cell attachment.18

Surface analysis was carried out on dry surfaces after cleaning in ethanol, methanol, laboratory cleaning solution and rinsing in distilled water. The mineral surface may be affected by these procedures.8,19,31 Therefore the changes reported in this study may be related to the effect of cleaning procedure.

Many studies of materials may be criticized for inadequate or incomplete characterization of bulks and surface chemistry. Furthermore, the effects of cleaning and sterilization have until recently received little detailed investigation, particularly for their effects on biocompatibility.1,18,20,31 Plasma cleaning of dental implants for a low-energy surface has been recommended.1,21 Rapid bone apposition following an argon plasma treatment was reported by Hartman et al.22 Conversely, Carlsson et al.23 found poor results using air plasma. Brunette24 has illustrated the pronounced effect of dental-implant surface topography on orientation and migration. Thus, in future studies it is essential to fully characterize the surface materials physically and chemically before in vitro and in vivo evaluation.1,2,30-33

The data for the bulk and surface analysis suggested that whereas the bulk of the material is hydroxyapatite (as confirmed by XRD) Hilal 19961 the surface has different composition. The EDX analysis has value between the bulk and the surface analysis probably because it reflects partly the bulk and surface compositions. It also is clear that the surface composition should not be assumed from measurements of bulk composition or XRD1,30,31,32. This is of importance to the biological response to the retrograde materials. It would appear that HAp may have a surface layer of GIC for which a different biological response might be expected when compared with a hydroxyapatite surface.

Analysis of the feed stock and the final or produced material could allow inferences to be drawn regarding the effect of processing parameters on surface composion.1

Ideally, the physical and chemical properties of an biomaterials should match the tissue being replaced. The long-term challenge is to provide high suitable retrograde materials that will stimulate repair and regeneration of tissue.

For most implants, failure originates at the interface between the biomaterial and its host tissue. Two factors contribute to this interfacial failure. They are biomechanical and biochemical in nature and depend on the type of tissue being replaced.

## CONCLUSION

the XPS chemical surface analyses of the materials used as retrograde filling, have shown them to vary considerably with respect to bulk chemical composition. Further surface analysis could include narrow scans, manipulation of surface chemistry, coupled with in vitro tests and experiments to determine the importance of different surface components.

### *Disclaimer*

The article has not been previously presented or published and is not part of a thesis project.

### *Conflict of Interest*

There are no financial, personal, or professional conflicts of interest to declare.

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