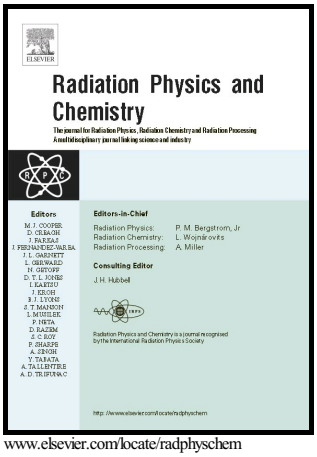

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ABOUT THE ELEMENTAL ANALYSIS OF DENTAL IMPLANTS

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ABSTRACT

In this paper we present the first results of a broad research line aiming a better understanding about dental implants as the number of procedures, successes and failures in Brazil and possible reasons of losses (from problems on diagnose to fabrication defects from different brands offered in the Brazilian market).

One thing that is already evident is the lack of details of the performed elemental analysis of implants, not only in Brazil but also on the majority of reported analyses published on international journals dedicated to the field. There are already a significant number of reports about the composition of dental implants and its surfaces, but in general they have not performed tests enough to validate the results nor reported the procedure with sufficient details establishing their comprehensiveness, which is critical to enable a comparison between those results. One detected problem is the using of a non standard geometry in some equipment that require special shapes or dimension for the analysis. The other is the determination of the uncertainties to be associated to the results.

Here we will perform a brief review of the dental implant history, of some problems found in the elemental analysis and will present two sets of measurements, one to investigate the consequences of using nonstandard geometries and another comparing elemental analyses made with different instruments.

1- INTRODUCTION

The first record of dental implants was 2000 BC, with the use of gold, platinum and porcelain. The Mayan civilization, among the many scientific advances it generated, was the first to use endosseous dental implants [1].

Over the years, various materials have been tested for dental implants, such as chromium-cobalt-molybdenum and iron-chromium-nickel alloys, stainless steel, and metals such as gold, platinum and silver. However, the clinical success obtained in the medium and long term for these materials was very low due to high peri-implant bone reabsorption [2].

The finding of the concept of osseointegration only occurred in 1965 by Brånemark in Sweden, leading a research group at the University of Gothenburg [3]. The original research of Brånemark was on the microcirculation of blood in rabbit tibias, with the assistance of a small titanium optical chamber, which was surgically inserted in the bone, to investigate the blood supply. After some time, when he tried to remove the chamber, Brånemark found it impossible because the chamber was integrated to the bone. It was thus evident that the integration between this metal and bone occurred perfectly, and there was no rejection [3].

The concept of osseointegration was then defined as the direct structural and functional connection between ordered, living bone and the surface of a load-carrying implant. [4]

Brånemark's next step was to apply his discovery to oral rehabilitation, using titanium to built dental implants. Since then it was noticed that the clinical success of the implantology is directly related to the occurrence of the phenomenon of osseointegration and the type of material used [3].

Titanium, besides being a biocompatible material and possessing biological acceptance by the bone, has several other intrinsic properties that are advantageous,

such as low specific weight, high resistance/weight ratio, corrosion and fracture resistance and low elasticity. Another advantage of the titanium comes from the great chemical stability provided by the surface's oxide layer that protects the metal from oxidation and allows osseointegration [5].

Since the concept of bone integration and the advantages of using titanium for oral rehabilitation were discovered, the number of dental implants produced and placed in edentulous patients has been increasing every year. Presently Brazil is the second largest market in the world for implants, with 2.5 million implants being applied per year, according to the Brazilian Association of the Medical and Dental Equipment and Supplies Industry (ABIMO) and this figure is expected to increase to 5 million by 2020 [6].

Even with the great advance in implantology, the number of failures, even being small, is assumed significant, with the precise figures still unknown, not just in Brazil, but also around the world [7]. The percentage of failure was reported as varying from 1.5% to 3.5%, reaching up to 10% depending on the source [8]. A study done with the Swedish population has demonstrated that early implant loss occurred in 4.4% of patients, while late implant loss occurred in 4.2% (up to 9 years after the procedure). Taken together, 7.6% of the patients had lost at least 1 implant [9].

Implant failures can be linked to several factors, such as: patient-related systemic factors (oral hygiene, smoking, excessive alcohol, osteoporosis, diabetes); biological factors (bone quality and quantity, adjacent infection, gingivitis, vascular integrity); implant-related factors (biocompatibility, surface topography, chemical composition, surface contamination, implant geometry, wettability), surgical factors (surgical trauma, contamination during surgery, condition for implant loading, improper positioning), or even misdiagnosis [10, 11].

2- REQUIREMENTS FOR AN EFFECTIVE OSSEOINTEGRATION

Because it is highly reactive, possessing affinity for oxygen, a thin layer of native titanium oxide quickly covers the titanium surface as soon as it is exposed to air, (in about 30 milliseconds). This layer is commonly composed of TiO2 with a thickness varying from 1 to 20 nm and it's called a passive film because it has a stable and

compact structure, which indicates its high resistance to corrosion in physiological solution. The biocompatible characteristics of titanium are attributed to this passive film [12,13].

In order to improve osseointegration, different coatings and treatments of the implant surface have been investigated. The clinical success of implantology has come to depend not just on the implant material but also on its design, the type of surface treatment and surface quality [5].

Presently there are many different types of surface treatments, like acid etching, plasma spraying, sandblasting and hydroxyapatite-blasting [5, 13, 16, 17, 18]; they are used to modify the chemical composition and the topography of the implant's surface.

Factors such as cleaning, manufacturing, sterilization, packaging and surface treatments can lead to contamination [14]. Even when present in small quantities, they may alter the biocompatibility of the implant for better or worse. When present in large quantities they may interfere with the formation of the titanium oxide layer and consequently osseointegration [15].

Another way to increase clinical success is through topography, enlarging the contact surface between the bone and the implant. The purpose of the larger rough surfaces of the implants is also to improve the bone healing process [16].

These two previously discussed factors, chemistry and topography of the surface, are interconnected, being impossible to modify one without changing the other, turning useful and necessary to characterize the implant surface.

A multidisciplinary project aiming a better understanding about dental implants, including the annual number of procedures in Brazil, proportion between successes and failures and possible reasons of losses (from problems on diagnose to fabrication of the different brands offered in the Brazilian market) was initiated at the Federal University of Rio de Janeiro with participants from different expertise and professions such as implantodontists, academic professors and students from the Dentistry, Physics and Chemistry Institutes.

The idea is to cover many aspects of the problem through different procedures:

a) Inquests to discover the number of successes, failures and implant loss.

b) Material analysis of the implants in order to identify possible contaminations or structural flaws that could be responsible for failures or implant losses.

c) Inquests trying to correlate the diagnosis praxis with failures.

d) At the end we intend to propose some rules to the health authorities in order to establish a normalization of the implantology in Brazil.

In this paper we will present a review of the determination of the implant components. The material analysis of the implants have been performed with different methods providing a considerable amount of data [5, 16, 17, 18] but in general the method of analysis itself is not discussed in detail. This is important, because since each process (machine) uses different probing radiation (photons, electrons) and/or energy, the layer of material inspected could be different due to attenuation and absorption processes. We will also present results of some analysis made by ourselves in order to test some critical aspects of elemental analysis.

3- DETERMINATION OF THE IMPLANT COMPOSITION

As mentioned in the former item, the titanium implant surface layer is fundamental for the osseointegration. Consequently, when analyzing the composition, the choosing of the technology and method should be focused in getting information on the deepness ranging from zero to a few microns.

The way to reach this goal is to choose carefully the energy and the nature of the projectile, or in other words, to make a choice based on the attenuation coefficients of photons and the stopping power of electrons.

The mostly used technologies to determine the composition of the implants are the ones based on Energy Dispersive X-ray Fluorescence (EDXRF or EDS; the later can also be coupled with Scanning Electron Microscopy, SEM), X-ray Photoelectron Spectroscopy (XPS), X-ray Diffraction (XRD) or Auger Electron Spectroscopy (AES) [5, 16, 17, 18].

The Wavelength Dispersive X-ray Fluorescence (WDS or WDXRF) is a technique that can also be used to determine the chemical composition, although yet not mentioned in previous implant studies.

a) Energy Dispersive Spectroscopy (EDS): the method is based on X-ray fluorescence generated by photons or electrons (when coupled with SEM). The system is able to discriminate the photon energy, characteristic of a specific element. The

analysis depth is in the μm range. There are commercial equipments available such as Hitachi, model TM-3000 (USA) and JEOL, model JXA-8900RJ (Japan) [19].

b) X-ray Photoelectron Spectroscopy (XPS): is based on the photoelectron effect and uses an x-ray beam to irradiate a sample measuring the kinetic energy of the electrons generated. The maximum analysis depth is approximately 10 nm. There are commercial equipment available such as Sigma Probe, model Thermo-VG (UK) and CLAM2 Electron Analyzer, model VG Microtech (UK)[20].

c) X-ray Diffraction (XRD): is a technique that relies on dual/wave x-rays to obtain information about the structure of crystalline materials. The maximum analysis depth is in sub-micron range. There are commercial equipment available such as D/Max Ultima X-ray diffractometer (Japan) and Shimadzu, model Lab X XRD-6000 (Japan); obviously the method requires crystalline samples [21].

d) Auger Electron Spectroscop (AES): is based on the production of Auger electrons. Consists in exciting the sample's surface with a finely focused electron beam which causes Auger electrons to be emitted from the surface. The average depth of analysis is approximately 5 nm. There are commercial equipment available such as Physical Electronics, model PHI650 (USA) [22].

e) Wavelength Dispersive Spectroscopy (WDS or WDXRF): here the sample is irradiated and with X-rays and fluorescence photons are produced. A crystal is used to the analysis of the photon energy and so identifying the element. The analysis depth is micrometer range. There are commercial equipment available such as Bruker, model S8 Tiger (USA) [23].

All the previously mentioned methods require standard sample geometry in the form of disks (according to the manuals), except from XPS and AES, where these characteristics are not specified.

In trying to establish a standard process to investigate different brands of dental implants we began with two processes: EDS (couple with SEM) and WDS that were available at the University. Both methods are based on detecting fluorescence x-rays produced in the sample and identifying their energies. The differences between both methods are: radiation source; analyzing depth (about nm for the SEM/EDS and μm for the WDS); resolution (higher for WDS) and radiation background (lower for the SEM/EDS due to a higher excitation efficiency).

3.1 Materials And Methods

As a first investigation we have performed EDS/SEM and WDS measurements. On both machines we have measured five brass samples (three small cylinders, comparable to the implant dimensions, one disk and scobs (packed in a disk shape) in order to investigate the influence of different, nonstandard geometries. We have also measured an old discarded dental implant to check the differences between the results from both equipment in a real implant.

Since dental implants are essentially a screw, its geometry is quite apart from the usual required disks (radius varying from 5mm to 50mm and thickness of maximum 47mm), then it is important to verify if the equipment would work satisfactorily with the implant geometry. If cutting or grinding is necessary, the procedure could modify the composition and/or structure of the analyzed sample,

The characteristics of the five brass samples are: (1) a disk with 40mm diameter and 7mm thickness; (2) three small cylinders, similar in dimensions to the implant (4.01 mm diameter and 11mm length) and (3) scobs (each chip having in average 2.3mm length) packed in a disk shape. The samples are depicted in Figures 1 a, b and c, respectively. The last sample is an old discarded implant, with a chemically saturated surface.

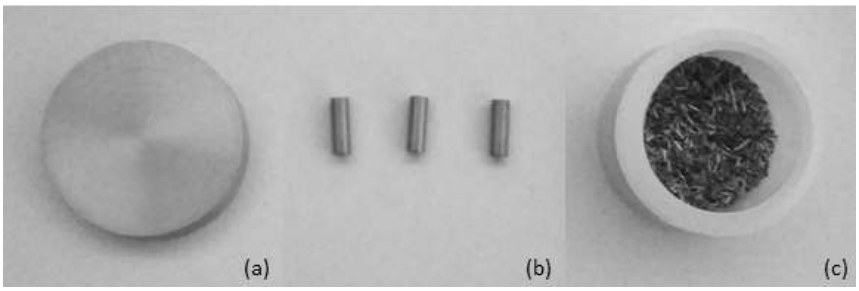

Figure 1: Brass samples with different geometries

The equipment used for WDXRF was a Bruker S8 Tiger model 1 kW (Massachusetts, USA) of the Laboratory of Photon and Electron Impact (LIFE), from the Department of Physical Chemistry of the Federal University of Rio de Janeiro

(UFRJ). The instrument allows the maximum voltage of 50 kV and 50 mA, with the power limited to 1kW. The analyzed layer can reach the depth of microns in the studied sample. To measure the cylinders and implant it was used a carbon disk as base, with the samples fixed and covered with a 3525 Ultralene film with thickness 4μm from SPEX SamplePrep (Figure2). For the analysis it was used the QUANT-EXPRESS software.

Figure 2: Sample preparation for the cylinder and implants in WDS.

All the samples were also analyzed in a SEM/EDS equipment from Hitachi, model TM3000 (Tokyo, Japan) coupled with Bruker Scan Generator and X-Flash Detector (Massachusetts, USA) of the Laboratory of Scanning Electron Microscopy from the Materials and Chemistry Technology Sector (STMQ) of the Institute of Nuclear Engineering (IEN). During the acquisition data the samples were maintained in place on the standard equipment support. All measurements were performed with the same magnification (300X). To analyze the data, the software QUANTAX 70 was used.

4- RESULTS AND DISCUSSION

The results obtained for the brass samples in both SEM/EDS and WDS are presented in the graph depicted in figure 3. The main detected elements are, as expected, copper and zinc. Lead was also detected in both methods for all brass samples, having a higher concentration for the scobs, as it can be seen in figure 4. This could be explained by the manufacturing process. The chips have more contact with the cutting tool which could be the source of lead. Carbon was detected on the SEM/EDS but not on the WDS, which is not equipped with the proper crystal to detect low Z

elements. The other elements detected, completing the normalization to 100% are Na, Sn, Fe, As, Si, Ca, S, Cl, Ni, Al and O.

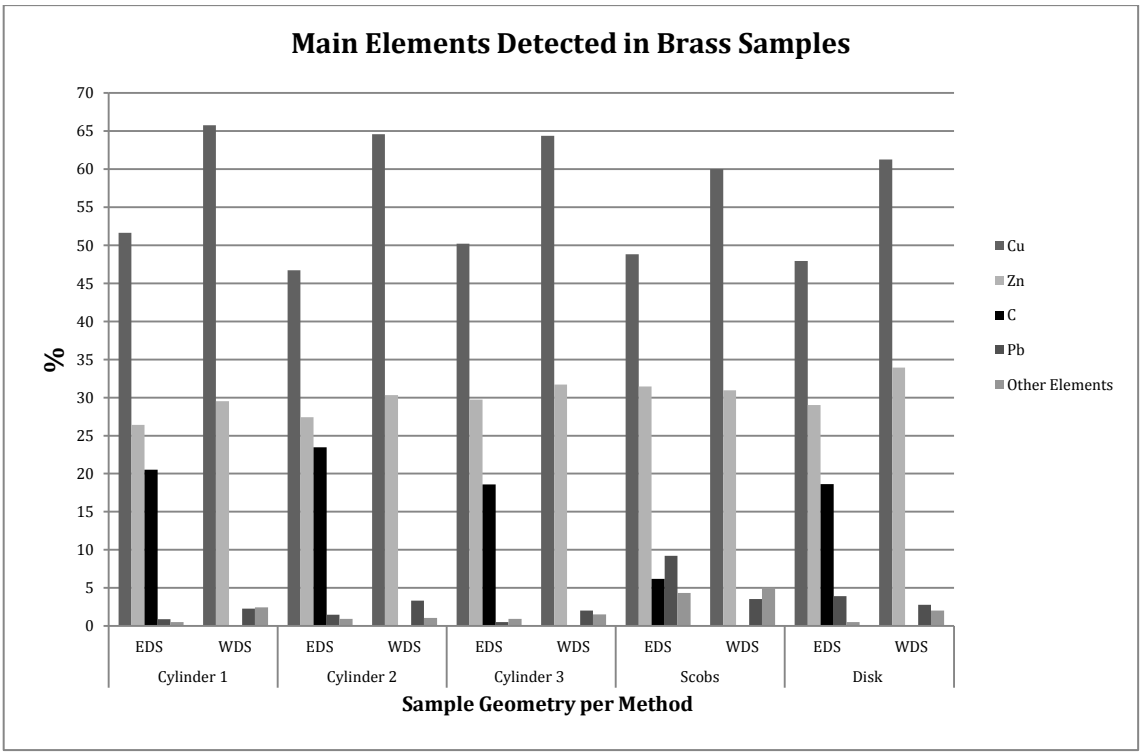

Figure 3: Main elements detected for the different brass sample geometries in both EDS and WDS.

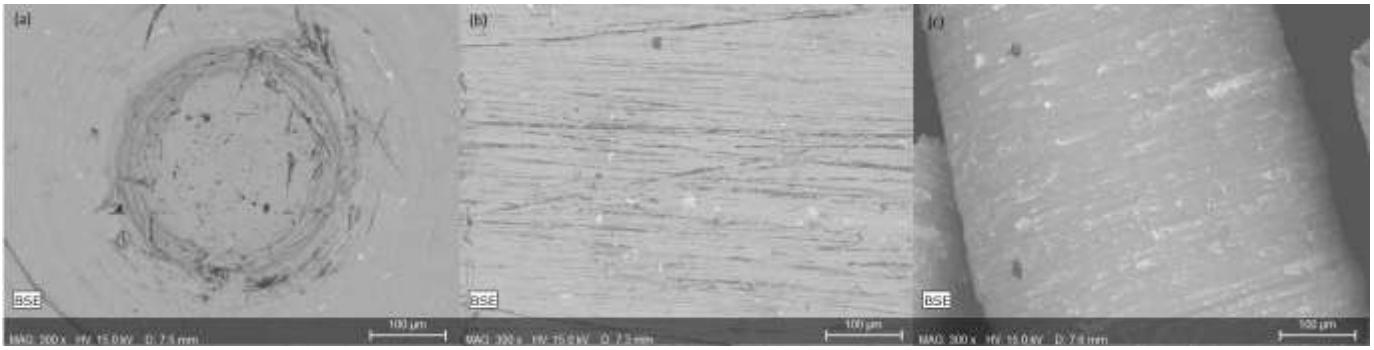

Figure 4: Comparison of the surface image of the three different sample geometries. The white spots correspond to lead: (a) disk, (b) cylinder and (c) scobs. The lead is more frequent on the scobs surface.

Copper was the element with the higher concentration found by both methods. The measures in SEM/EDS for cylinders 1, 2, and 3 were of 51.65%, 46.73% and 50.2% respectively, while the scobs presented 48.81% and the disk 47.93% with an average uncertainty of 1.5%. On the other hand, the Cu concentration obtained in the WDS were of 65.75%, 64.57%, 64.37% for the cylinders 1, 2 and 3 respectively,

60.02% for the scobs and 61.24% for the disk with an uncertainty around 0.55% (provided by the analyzing software). In both cases it would more correct to use just one decimal for the data but we decided to keep the number of digits provided by the software. The results found on the WDS for the cylinders present a closer relation to each other, but also larger than the uncertainty. The differences between these ones and the other geometries must also be due to the geometry. The results for the cylinders on the EDS show a fluctuation around 4% that could be related to the different concentration of the contaminants in each sample surface.

The different analysis show other elements (Na, Sn, Fe, As, Si, Ca, S, Cl, Ni, Al and O), in different amounts on each sample, in a very low concentration with uncertainty similar to the amount found. This should be better investigated.

Both software provide uncertainties associated with the measurement. The average uncertainty related to the measure for each element of the samples for the EDS is: 1.5% for Cu, 0.9% for Zn, 3.3% for C, 0.5% for Pb. For WDS it is: 0.55% for Cu, 0.39 for Zn, 15% for Pb.

The discrepancies between the concentrations found in both methods can be justified by the fact that the SEM/EDS data refers to a thinner layer than in the WDS, allowing superficial elements, not present in the inner core, to be detected.

Taking into consideration the characteristics mentioned above, it is possible to conclude that for both methods the validation of the cylinder geometry was satisfactory, keeping the same proportion of elemental concentration for all of the samples, but with a larger uncertainty than the statistical one provided by the used software.

After the validation of the non-conventional geometry, a discarded implant was measured with both methods. The results are presented in table 1. On the EDS results it was possible to see that the surface of the implant is composed of Ti, C and O, a well-known result already cited in many references, since TiO2 is a native layer present in all implant surfaces and C is the most found contaminant [5, 16, 17, 18]. WDS results show basically Ti, with 98.6%, together Si, S and Al in much lower concentrations. It should be noted that O and C are not detected in WDS due to limitation of the equipment.

Equipment	EDS		WDS	
Element	Weight Conc. (%)	Error (%)	Weight Conc. (%)	Error (%)
Ti	74.46	2.3	98.6	1.4
C	13.92	3.4	-	-
O	11.62	4.2	-	-
Si	-	-	0.6	22.2
S	-	-	0.4	18.4
Al	-	-	0.4	28.3

Table 1 - Comparison between EDS and WDS analysis of a discarded implant.

4. CONCLUSION

The results have demonstrated the elemental analysis, particularly of dental implants, depends on the technique, meaning the radiation and energy chosen as well as the selected region of interest on the sample. For surface layers, the most important region for dental implants, electron microscope coupled to EDS analysis is a suitable technique but requires some attention specially when evaluating the uncertainty, avoiding to just use the statistical one provided by the equipment, and verifying the reproducibility.

Using a second method as WDS, on the other hand, allows analyzing a deeper layer of the sample. But in this case special attention to the sample geometry should be paid. The combination of both methods allows a more complete evaluation of the dental implant: the surface layer, showing the oxidation and/or coating properties as well as the characteristics of the titanium core used for the implant. The next step of our study is to analyze the temporal evolution of the surface layer when exposed to the atmosphere. And then to test different brands offered in the Brazilian market.

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HIGHLIGHTS

- We investigate the influence of sample geometry on the elemental analysis of dental implant
- The history and a short review of the area is performed
- Elemental analysis of five brass samples with SEM-EDS and WDS
- The results show that the geometry has influence on the detected amount of the components
- It was found that the uncertainty was larger than the one provided by the equipment