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DETERMINATION OF CORROSION CHARACTERISTICS OF DENTAL ALLOY BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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Abstract: *Corrosion resistance is one of the characteristics that dental alloy should possess as it should be placed in the oral cavity. Adverse tissue reactions of the gingiva and the periodontium close to dental cast alloys may be caused by the effects of released metal elements. Corrosion effect of dental Co-Cr-Mo alloy was investigated by ICP MS according to the EN ISO 10271 and EN ISO 22674. Co- Cr dental alloy Remanium GM 800+ (Dentaurum Ispringen, Germany was tested in artificial saliva for 7 days at 37ºC. The released metals were detected by Nexion 300X ICP MS (Perkin Elmer, USA). The results showed that the metal release was very low for Co, Cr and Mo, far below the permitted levels. ICP-MS can be considered as very reliable method for such a research.*

Key words: *dental alloy, corrosion resistance, ICP MS*

Utvrđivanje korozionih karakteristika stomatološke legure sa induktivno spregnutim plazma masenim spektrometrom. *Otpornost na koroziju je jedna od karakteristika koju poseduju stomatološke legure koje trebaju biti postavljene u usnoj duplji. Neželjene reakcije tkiva gingive i parodoncijuma sa stomatološkim legurama može biti uzrokovano efektima oslobođenih metalnih elemenata. Efekat korozije stomatološke Co- Cr -Mo legure ispitana je ICP MS prema EN ISO 10271 i EN ISO 22674 . Co- Cr stomatološke legure Remanium GM 800 + (Dentaurum Ispringen , testirano u Nemačkoj u veštačkoj pljuvački tokom 7 dana na 37 C. Otkriveni su oslobođeni metali Nekion 300Ks ICP MS (Perkin Elmer , SAD). Rezultati su pokazali veoma slabo oslobađanje metala, Cr i Mo , daleko ispod dozvoljenih nivoa. ICP -MS može smatrati veoma pouzdan metod za ovakvo istraživanje .*

Ključne reči: *stomatološke legure, otpornost na koroziju, ICP MS*

1. INTRODUCTION

Alloys are in use for many years in dentistry as a material for fabrication of dental devices. Demands for mechanical properties as well as for the stability of dental alloys in oral environment are very high. Dental alloys should withstand high cyclic loads up to 800N per occlusal unit, high humidity, temperature changes from 0ºC to 70ºC, and acidity variations from pH 2 to pH 11 [1,2,3]. Corrosion resistance is one of the characteristics that dental alloy should possess as it should be placed in the oral cavity. The release of metallic ions from the alloy into saliva should be as low as possible, because they could diffuse in mucosae tissue or they could be ingested, transported and accumulated in distant parts of the organism [4,5]. Many studies have reported toxic and carcinogenic effects induced when humans and animals are exposed to certain metals [4,5,6,7]. Adverse tissue reactions of the gingiva and the periodontium close to dental cast alloys may be caused by the effects of released metal elements. Tissue reactions depend upon the amounts of elements available which are a function of corrosion rates [8]. All previously mentioned indicate that the investigation of potential release of metals from dental alloys in oral environment is necessary step in testing new products before they are allowed to be introduced in clinical practice and in controlling products that are in use for many years.

The insight that we have on stability of the alloy and the safety for use are strongly dependent on the tools available which allow us to perform our investigation. The detection and analysis of the released metals at the trace level poses a number of challenges to the analyst [9]. In previous investigations besides atomic absorption spectrophotometry (AAS) nuclear corrosion monitoring (NCM), electron microscopy (ESCA), microphotography and SEM were used [5,10,11,12,13] . All of the mentioned methods have their limitations, for example AAS has limited linearity and therefore is recommended for low-level analytes.

ICP MS offers the capability of specification with multi-element detection, of isotope measurements to improve precision and accuracy excellent sensitivity and detection limits and wide dynamic range [14]. ICP-MS is suitable for analyzes that are requiring the lowest detection limits and the greatest level of productivity.

Favourable characteristics of ICP-MS can be summarized in a few points:

- Instrument detection limits are at or below the single part per trillion (ppt) level for much of the periodic table;
- Analytical working range is nine orders of magnitude;
- Productivity is unsurpassed by any other technique and
- Isotopic analysis can be achieved readily [15].

The principal of ICP MS function is that samples are introduced into argon plasma as aerosol droplets. The plasma dries the aerosol, dissociates the molecules and then removes an electron from the components, thereby forming singly-charged ions, which are directed into a mass filtering device known as the mass spectrometer [16]. Most commercial ICP-MS systems employ a quadruple mass spectrometer which rapidly scans the mass range. Upon exiting the mass spectrometer, ions strike the first dynode of an electron multiplier, which serves as a detector [16]. The impact of the ions releases a cascade of electrons, which are amplified until they become a measureable pulse. The software compares the intensities of the measured pulses to those from standards, which make up the calibration curve, to determine the concentration of the element [16]. For each element measured, it is typically necessary to measure just one isotope, since the ratio of the isotopes, or natural abundance, is fixed in nature [16]. ICP-MS can be used to measure the individual isotopes of each element; this capability brings value to investigations interested in one specific isotope of an element or in the ratio between two isotopes of an element.

2. MATERIALS AND METHOD

Corrosion effect of dental Co-Cr-Mo alloy was investigated by ICP MS according to the EN ISO 10271 and EN ISO 22674 [16,17]. A rectangular plate sample of 34mm x 13mm x 1.5mm of dental Co-Cr-Mo alloy was made according to the standard technological procedure that was common in today dental laboratory using lost wax technique. Non precious Co-Cr alloy Remanium GM 800 + (Dentaurum Ispringen, Germany) was used. The composition of the alloy is given in Table 1. First, wax model was made. It was invested in Rema dynamic investment and vacuum casted in Nautilus CC system (Bego, Germany). After casting the sample was divested, blasted and polished. The sample was fixed with nylon thread and immersed in glass container with artificial saliva with pH=6.8 [18]. It was held for 7 days (+/- 0.1) at 37°C. After that the sample of artificial saliva was taken and was analyzed in Nexion 300X ICP-MS (Perkin Elmer, USA) (Fig. 1).

Chemical composition (in mass %)	Co	Cr	Mo	Si
	63.3	30	5	1
Others less than 1%: Mn, N, C				

Table 1. Chemical Composition of Remanium GM800+ (Dentaurum Ispringen, Germany) dental alloy according to the manufacturer

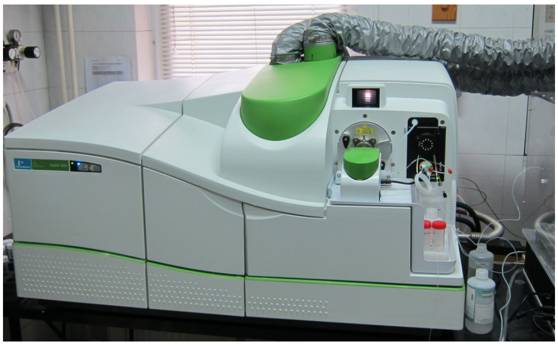

Fig. 1. Nexion 300X ICP-MS

An ICP-MS consists of the following components (Fig. 2):

- Sample introduction system – composed of a nebulizer and spray chamber and provides the means of getting samples into the instrument;
- ICP torch and RF coil – generates the argon plasma, which serves as the ion source of the ICP-MS;
- Interface – links the atmospheric pressure ICP ion source to the high vacuum mass spectrometer;
- Vacuum system – provides high vacuum for ion optics, quadrupole, and detector;
- Collision/reaction cell – precedes the mass spectrometer and is used to remove interferences that can degrade the detection limits achieved;
- Ion optics – guides the desired ions into the quadrupole while assuring that neutral species and photons are discarded from the ion beam;
- Mass spectrometer – acts as a mass filter to sort ions by their mass-to-charge ratio (m/z);
- Detector – counts individual ions exiting the quadrupole and
- Data handling and system controller – controls all aspects of instrument control and data handling to obtain final concentration results.

3. RESULTS

The corrosion characteristics of Co-Cr alloy was investigated by analysis of element release in artificial saliva. After the investigating period of 7 days the results of the released metals from the Co-Cr dental alloy were far under the permitted level.

According to ISO 22674 the quantity of released metal from the alloy should not exceed 200μg/cm^2 in 7 days period [17]. The results of the investigation are shown in Table 2.

4. DISCUSSION

The investigation of corrosion characteristics of dental alloy can be done by analysing the release of metal ions in electrolytic solution. Today, there are three widely accepted analytical methods for analyze of metal release: atomic absorption, atomic emission and mass spectrometry. The most common techniques in use today are:

- Flame Atomic Absorption Spectroscopy;
- Graphite Furnace Atomic Absorption Spectroscopy (GFAA);
- Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and
- Inductively Coupled Plasma Mass Spectrometry (ICP-MS) [16].

Performing atomic absorption spectroscopy requires a primary light source, an atom source, a monochromator to isolate the specific wavelength of light to be measured, a detector to measure the light accurately, electronics to process the data signal and a data display or reporting system to show the results. Whatever the system, the atom source used must produce free analyte atoms from the sample [16]. The source of energy for free atom production is heat, most commonly in the form of an air/acetylene or nitrous-oxide/acetylene flame. The sample is introduced as an aerosol into the flame by the sample-introduction system consisting of a nebulizer and spray chamber. The burner head is aligned so that the light beam passes through the flame, where the light is absorbed. The major limitation of Flame AA is that the burner-nebulizer system is a relatively inefficient sampling device. Only a small fraction of the sample reaches the flame, and the atomized sample passes quickly through the light path. An improved sampling device would atomize the entire sample and retain the atomized sample in the light path for an extended period of time, enhancing the sensitivity of the technique [15,16]. This leads us to the next technique – electrothermal vaporization using a graphite furnace. With Graphite Furnace Atomic Absorption (GFAA), the sample is introduced directly into a graphite tube, which is then heated in a programmed series of steps to remove the solvent and major matrix components and to atomize the remaining sample [20]. Graphite Furnace analysis times are longer than those for flame sampling, and fewer elements can be determined using GFAA. However, the enhanced sensitivity of GFAA, and its ability to analyze very small samples, significantly expands the capabilities of atomic absorption.

ICP is argon plasma maintained by the interaction of an RF field and ionized argon gas [16]. The plasma can reach temperatures as high as 10 000 K, allowing the complete atomization of the elements in a sample and minimizing potential chemical interferences. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) is the measurement of the light emitted by the elements in a sample introduced into an ICP source. The measured emission intensities are then compared to the intensities of standards of known concentration to obtain the elemental concentrations in the unknown sample [16]. Sequential-type systems can select any wavelength and focus it on a single detector. However, this is done one element at a time, which can lead to longer analysis times.

With Inductively Coupled Plasma Mass Spectrometry (ICP-MS), the argon ICP generates singly charged ions from the elemental species within a sample that are directed into a mass spectrometer and separated according to their mass-to-charge ratio. Ions of the selected mass-to-charge ratio are then directed to a detector that determines the number of ions present [16]. ICP-MS combines the multi-element capabilities of ICP techniques with exceptional detection limits equivalent to or below those of GFAA. It is also one of the few analytical techniques that allows the quantification of elemental isotopic concentrations and ratios, as well as precise speciation capabilities when used in conjunction with HPLC or GC interfaces [15]. This feature enables the analytical chemist to determine the exact form of a species present – not just the total concentration. However, due to the fact that the sample components are actually introduced into the instrument, there are some limitations as to how much sample matrix can be introduced into the ICP-MS.

In addition, there are also increased maintenance requirements as compared to ICP-OES systems. Inductively coupled plasma-mass spectrometry (ICP-MS) is the method of choice for analyzing metal release from dental alloy in investigated medium because of its multi-element capability, low detection limit (ppt) and wide dynamic range (109 orders of magnitude)

Mean value of the released element (μg/l)	70.52	35.27	0.74
Volume of the artificial saliva	0.05	0.05	0.05
Dilution	1	1	1
Mean value (μg)	3.53	1.76	0.04
The surface area of the sample (mm^2)	990.09	990.09	990.09
The result of element release ($\mu g/cm^2$)	0.356	0.178	0.004

Table 2. The results of the investigation

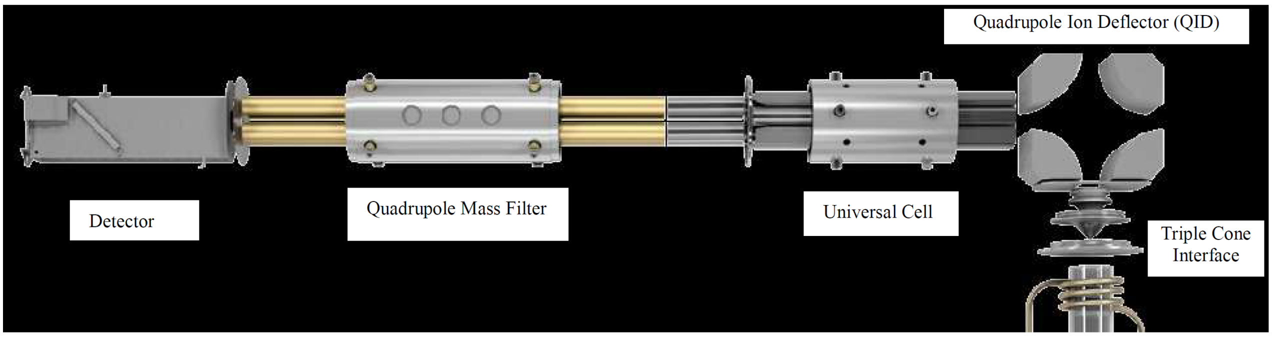

Fig. 2. The ion optic path of the PerkinElmer NexION ICP-MS

5. CONCLUSION

Although Co-Cr dental alloys are used for fabrication of dental devices for many years the research of their stability in oral environment are current. A growing amount of results provide evidence that toxic and carcinogenic metals are capable of interacting with nuclear proteins and DNA causing oxidative deterioration of biological macromolecules [4, 21]. Detailed studies in the past two decades have shown that metals like iron, copper, cadmium, chromium, mercury, nickel, vanadium possess the ability to produce reactive radicals, resulting in DNA damage, lipid peroxidation, depletetion of protein (4). Current analytical methods for analysing metals at trace levels give researchers new opportunities for detection and quantification of metals with possible new perspective on their interaction with biomolecules.

According to presented results investigated Co-Cr dental alloy Remanium GM 800 + (Dentaurum Ispringen, Germany) has good corrosion characteristics and stability in oral environment. ICP-MS can be considered as very reliable method for such a research.

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