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Analysis of BOP-F polymer by Neutron Activation

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Abstract. Neutron activation analysis has been utilized to determine the presence of undesirable elements in biocompatible osseous polymer fibers (BOP-F). This material is used as osseous tissue substitute in bone damage. The analysis was carried out using thermal neutrons. A short and long irradiation schemes were applied during analysis. Na and Br were found in the samples whose ratio is close to ratio found in human corporal fluids.
Keywords: Trace elements, Neutron activation analysis, BOP-F.

Resumen. Se utilizó la técnica de Análisis por Activación con Neutrones para determinar la concentración de elementos nocivos en fibras de polímero biocompatible con tejido óseo (BOP-F). Este material se emplea como sustituto cuando se produce daño a nivel del hueso. El análisis se realizó utilizando neutrones térmicos. Durante el análisis, las muestras se irradiaron bajo dos esquemas de tiempo, corto y largo. Se encontró que las fibras de BOP contienen Na y Br cuya razón es similar a la que existe en los fluidos del cuerpo humano.
Palabras clave: Elementos traza, Análisis por Activación de Neutrones, BOP-F.

Introduction

Despite bone-grafting techniques, large bone defects still is a challenge for orthopedic and reconstructive surgeons. Interdisciplinary efforts have been carried out to develop osteoconductive, osteoinductive and osteogenic bone-replacement systems [1]. Important advances have been made in the development of biomimetic materials having the feature of interact with their biological environment [2].

The use of polymeric-materials in medicine is an expanding area. Between these, biocompatible osseous polymer fibers, BOP-F, has been pointed out as promising material. However, in some applications this material shows some drawbacks [3, 4].

The BOP-F is a copolymer made of two homopolymers-*N*-vinyl pyrrolidone and methyl metacrylate – combined with calcium gluconate and 6-polyamide fibbers to form BOP-F (fibres). These are degradable by hydrolysis permitting osteoconduction, also are radiotransparent which permits good radiological monitoring of postoperative osteogenesis at the implant [5].

The recent development in the use of resorptive biomaterials as osseous substitutes shows a growing interest. Important advances have recently been made in the development of biomimetic materials that interact with their biological environment [2].

The practical use of these substitutes (bony defect filling, prosthesis coating, etc.) introduce many scientific questions and scientific problems like biocompatibility test, need for comparisons, study of resorption and ossification kinetics. The answers to those questions and the solutions to these problems can be obtained by doing interdisciplinary research.

Histology allows identification of the morphological and structural features of the tissues, with the help of microscopic observation. Some recent improvements in this biological method have yielded quantitative measurements. Specially, histophotometry (quantitative morphological microscopy) permits the determination of the average trabecula thickness and the quantitative determination of the ratio between osseous and implant volumes. The result obtained provides information on the average behavior between the bony crystal and its mineral composition to be made. This method is still ineffective to detect and quantify the organic and mineral elements [1].

The ossification mechanism of implants used in orthopedic facial and plastic surgery is one of the application fields which have been of great interest for some time. Because of its porousness and biocompatibility, they are osteoconductor materials. Major elements contained in bone like Ca, P, Mg and Fe have been evaluated in coral before and after implantation by radioactivation with fast neutrons [5]. Fast neutron activation analysis has been used to perform quantitative studies on the transformation in biomaterials [6].

The elemental concentrations in the biomaterials must be known because its chemical and mechanical properties depend on them. Besides the major element concentration, trace element concentration data gives information about the neoformed tissue [6 - 8].

The need of the element concentration determination has been also pointed out in the case of metallic prosthesis, whose analysis has been performed by Neutron Activation Analysis (NAA) [9].

The use of NAA is a non destructive analytical technique able to analyze complex matrices and determine up 30 elements in a single analytical process. In this technique thermal neutrons are used to irradiate the sample to induce radioactive isotopes. The elemental concentration is determined measuring the gamma-rays emitted by the induced radioisotopes, the photon's energy is characteristic of the radionuclide and the pho-

ton intensity is directly proportional to the elemental concentration. To perform the NAA a relative procedure is utilized were one o more standards are required, samples and standards are irradiated and measured under the same conditions. The gamma-ray spectrum has several peaks whose position indicates the photon energy that allows to identify the element, the area under the photopeak is calculated, thus the elemental concentration is determined using the equation 1.

$$m_S = C_S \left(\frac{m_{STD}}{C_{STD}} \right) \quad (1)$$

Here, m_S is the mass concentration in the sample, C_S is the count rate under the photopeak of interest, m_{STD} is the mass concentration in the standard and C_{STD} is the count rate in the photopeak in the standard. If the counting time is the same for sample and standard corrections due to cooling time must be carried out, thus the count rates are calculated to the time when the sample and standard was removed from the neutron field.

The uncertainty in the concentration mass of the element of interest in the sample is calculated using equation 2.

$$\sigma_{m_S} = \sqrt{\left(\frac{\partial}{\partial C_S} m_S \right)^2 \sigma^2_{C_S} + \left(\frac{\partial}{\partial m_{STD}} m_S \right)^2 \sigma^2_{m_{STD}} + \left(\frac{\partial}{\partial C_{STD}} m_S \right)^2 \sigma^2_{C_{STD}}} \quad (2)$$

Here, σ_{C_S} is the sample's standard deviation in the net counts under the photopeak of interest, $\sigma_{m_{STD}}$ is the standard deviation in the standard's mass concentration and $\sigma_{C_{STD}}$ is the standard deviation in the standard's net counts under the photopeak of interest.

Neutron Activation Analysis was utilized to determine the elemental concentration in fibers of BOP, the aim was to search for Ti, Cr, Mn, Co, Ni, Zn, Mo, Hg, Cd, In, Fe, that potentially may cause corrosion with the consequent damage in the stability of the material and in the health of the receptor.

Experimental

The BOP-F utilized is 10 mm long fibers, made of poliamide-6, calcium gluconate and copolymer SOP (NVP-MMA). Tridistilled water was used to wash the sample, after drying the sample's weight was 0.2103 g, Two standards reference materials were used for comparison, these included coal (NBS-1632a) and coal fly ash (NBS-1633a) from the National Institute of Standard and Technology (NIST).

In both standards the elemental concentration of these undesirable elements are: NBS-1632a has 1630 ± 130 mg/g of Ti, 34.3 ± 1.5 mg/g of Cr, 28 ± 2 mg/g of Mn, 6.7 ± 0.4 mg/g of Co, 19.4 ± 1.0 mg/g of Ni, 28 ± 2 mg/g of Zn, 130 ± 30 ng/g of Hg, 170 ± 20 ng/g of Cd, 38 ± 2 ng/g of In, and 1.11 ± 0.02 % of Fe, while NBS-1633a has 8230 ± 390 mg/g of Ti, 179 ± 8 mg/g of Mn, 43 ± 3 mg/g of Co, 127 ± 4 mg/g of Ni, 220 ± 10 mg/g of Zn, 30 ± 3 mg/g of Mo, 1.00 ± 0.15 mg/g of Cd, 160 ± 10 ng/g of Hg, 158 ± 5 ng/g of In, and 9.4 ± 0.2 % of Fe.

Sample and standards were doubly encapsulated in polyethylene vials and irradiated for 10 min (short irradiation) at a thermal neutron flux of 2×10^{12} cm^{-2}-s^{-1} in a TRIGA Mark II nuclear reactor at the Nuclear Engineering Teaching Laboratory from The University of Texas at Austin at USA. To evaluate the possible existence of impurities in the polyethylene vials, two empty vials were used as blanks. After a decay period of 15 min, blanks were counted during 10 min. A counting time of 8 min was used to measure standards and samples.

Four months later, the sample with a new set of standards and blanks were irradiated for 4 h (long irradiation) in the same thermal neutron flux. After a cooling time of 48 h blanks were counted for 15 min, while samples and standards were counted during 45 min.

Gamma rays were counted at a fixed geometry with a high-purity germanium detector (TENNELEC, TN) coupled to a 4096 multichannel pulse-height analyzer. The detection system has a resolution of 1.90 keV full width at half maximum for ^{60}Co 1332 keV g-ray with a relative efficiency of 40% [10]. Spectrometric system was calibrated in energy with an ^{152}Eu gamma-ray source that emits several photons from 0.122 to 1.408 MeV.

During sample measurement the presence of Na and Br was noticed, therefore the calculation of concentration was carried out with the NBS 1632a standard that has both elements. In natural concentration sodium is 100% of ^{23}Na, when it is bombarded by thermal neutrons ^{24}Na is produced through n + 23Na → 24Na, this decays with a half life of 15 h, during disintegration it emits two photons 1.368 and 2.754 MeV. On the other hand, bromine is formed by two stable isotopes: 51% ^{79}Br and 49% ^{81}Br; after activation reaction the first isotope is converted in ^{80}Br that decay with a half life of 4.42 min, while ^{81}Br is converted in ^{82}Br that has a half life of 1.5 days. During disintegration emits photons 0.554 MeV with 80% of probability.

Results and discussion

From the analysis of vials no impurities were detected. In the Table 1 are shown the photopeak features of the BOP-F samples, obtained during the short irradiation, where only the presence of Na was found. Here, is also included the respective photopeak for the NBS-1632a standard.

In the Table 2, the photopeaks features obtained during the long irradiation for the sample and the respective photopeaks in the standard are shown. Here, the BOP-F shows the presence of Br and Na. The Br concentration in the BOP-F is included, the Na concentration was not calculated with long

Table 1. Photopeak features and element concentration in BOP-F found during the short irradiation.

Sample	Weight [g]	Energy [MeV]	Photopeak net area [counts]	Isotope	Concentration [µg/g]
BOP-F	0.12905	1.36855	26318 ± 162	^{24}Na	2130 ± 192
NBS1632a standard	0.06985	1.36854	5495 ± 74	^{24}Na	828 ± 77

Table 2. Photopeak features and element concentration in BOP-F found during the long irradiation.

Sample	Weight [g]	Energy [MeV]	Photopeak net area [counts]	Isotope	Concentration [[µg/g]
SBOP-F	0.12905	0.55422	23127 ± 152	^{82}Br	144 ± 7
		1.36855	11556 ± 107	^{24}Na	Not determined
NBS 1632a Standard	0.19537	0.55423	9989 ± 100	^{82}Br	41 ± 2
		1.36859	60473 ± 246	^{24}Na	828 ± 77

irradiation features because the long irradiation can produce Na burnout.

No evidence of the presence of elements such as Hg, Cd, Ti, Cr, Mn, Fe, Co, Ni, Zn or Mo was found. These elements are in the majority of the metallic prostheses that eventually are transferred to the tissues [8, 9, 11].

Sodium is an essential electrolyte in the corporal fluids and the normal concentration is 144 meq/L, and the bromine is 8 meq/L in the humans, this gives a Na to Br ratio of 18, meanwhile the BOP-F has a Na to Br ratio of 14.8. Human blood tissue has a total amount of 10 g of Na and 0.026 g of Br, meanwhile the skeleton has a total amount of 0.032 g of Na and 0.028 g of Br [11]. Therefore the elements found in BOP-F do not represent any risk in the implant performance due to the presence of these elements.

Conclusions

BOP-F is mainly made of light elements, these are hard to measure using neutron activation analysis with thermal neutrons because these elements have low activation cross section, this situation make the neutron activation analysis a good technique to detect trace levels of impurities.

The presence of sodium and bromine in the BOP-F sample could be due to the manipulation during the manufacturing process; nevertheless, these elements do not represent any risk during actual BOP-F applications. Elements like Cd, Hg or Fe that could represent a risk in the receptor's health or in the implant performance were not found.

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