Contamination and oxydation degree of metallic elements in periprosthetic tissues

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CONTAMINATION AND OXYDATION DEGREE OF METALLIC ELEMENTS IN PERIPROSTHETIC TISSUES

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Abstract: **The metallic prosthesis used in orthopaedic surgery undergo degradations some years after their implantation. This phenomenon induces metallic element transfer in surrounding tissues. On post-mortem and per-operatory samples, we have taken tissues around hip or knee prosthesis. We have determined the composition of the implanted prosthesis by spark spectrometer. In the first step, we manufacture slides of 10 µm of thickness and we determine the concentration of the displaced metallic elements versus depth. We use PIXE method (Particle Induced X-rays Emission), based on the X-rays spectroscopy, to analyse our samples. Then the determination of the valence suggests a model about the degradation and induced toxicity of these elements. This can be obtained by use of micro-XANES. The combination of theses two types of experiments can give informations about the condition and the mechanism of the degradation.**
Keywords: **Prostheses, Metal contamination, PIXE, Micro-XANES, Chromium speciation**

Introduction

Metallic prosthesis, whatever their type (cemented, screwed…) and their composition (stainless steel, titanium alloy, cobalt alloy…), are widely used in orthopaedic surgery. The degradation of these implants can induce transfer of metallic elements to surrounding tissues. Hence this degradation can cause not only a weakening of the prosthesis itself, but also different kinds of pathologies directly related to the metal released during the degradation process. A great accumulation of metals can cause metallosis of the tissues. It is also known that this release can induce some tumours, especially in the case of chromium and cobalt. Consequently, it is important to know the conditions and the mechanismes of the degradation. This can be obtained by the analysis of the repartition of metallic elements surrounding the implant. The determination of the valence can suggest a model about induced degradation and induced toxicity of these released elements. Recent studies confirmed the presence of contamination around the prosthesis but also in various organs [1, 2, 3]. The next step would be now to perform chemical specific experiments to establish the relation between oxidation state of the contaminant and its toxicity.

Materials and Methods

Particle Induced X-ray Emission (PIXE) has been widely used in the analyses of the major, minor and trace elements contained in human tissue samples to evaluate the contamination introduced by the prostheses. This technique is based on the X-ray spectrometry produced by a charge particle beam that irradiates a target. The quantitative analysis by PIXE microprobe consists in measuring the intensity of the characteristic X-ray of the elements in the target and its conversion in concentration. PIXE analyses were carried out in the *CENBG (Centre d'Etude Nucléaire de Bordeaux Gradignan, France*) by using a Van de Graaff accelerator [4]. The first results obtained with this method on post-mortem and per-operatory samples show a contamination of adjacent tissues [5, 6]. The concentration in metallic elements varied (some µg/g to hundred of µg/g). It depends on the state of the tissue (metallosis or not), the location along the implant, but also from the nature of the released elements. This analysis does not give the degree of oxidation, but this information is crucial to understand the type of degradation of metallic implants in the adjacent tissues and to anticipate the toxicity of the released compounds. The micro-XANES (X-ray Absorption Near Edge Structure) method allows to have this information. First experiment of cartography and micro-XANES was performed at the ESRF on the ID 21 beamline at the chromium K-edge.

Results

The results obtained by absorption spectrometry are shown on the figures below. On the figure 1 we see the cut of the analysed sample observed with an electronic microscope. We can see the presence of particles of metal released by the prosthesis (black points). The cartography obtained (figure 2) represents a surface of 36 × 44 µm² with a pixel size of 2µm. The micro-XANES spectra corresponding to the points 1 and 2 are shown in the figure 3 (dashed points). To determine the chemical state of the chromium, we compared these spectra with references such as stainless steel alloy and mineral reference as $CrK(SO_4)_2$, $Cr(NO_3)_3$ and Cr_2O_3. The linear combination of the different reference spectra (solid line) gives results about the oxidation degree of chromium.

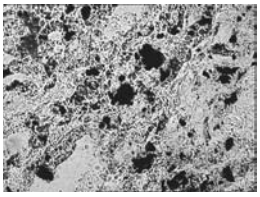

Figure 1: Cut of 10µm of the tissue taken around implanted hip. The black points correspond to the presence of metal particles.

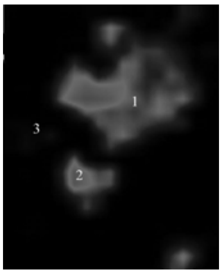

Figure 2: Cartography of a surface 36 × 44 µm² obtained by fluorescence mode on the lign ID 21 at the ESRF.

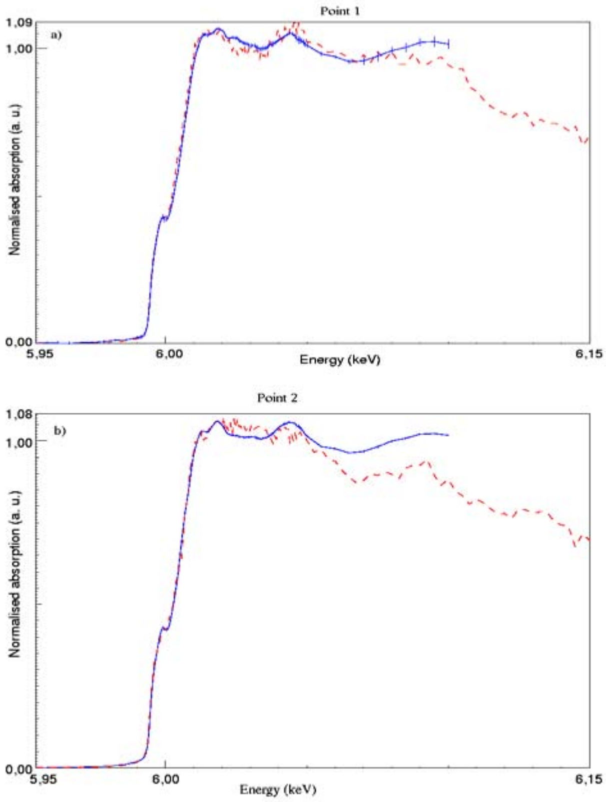

Figure 3: Micro-XANES spectra of the point 1 (a) and point 2 (b) of the cartography.

Discussion

The modelisation shows that the grain is composed of stainless steel particle and chromium +III. In all cases, there is no presence of chromium +VI which is more toxic. The spectrum obtained at the point 1 is well reproduced by a combination of 82% of $Cr(NO_3)_3$, 11% of $CrK(SO_4)_2$ and 7% of stainless steel. But in the point 2, the best modeling is obtained with 80% of stainless steel and 20% of Cr_2O_3. It suggests the coexistence, in these proportions, of these compounds in which the environment is similar to these references. Furthermore, we observe that the edge of chromium is characteristic of the environment and seems to evolve in function of the location and the concentration.

Conclusions

This study shows the existence of the contamination by metallic elements released by prostheses. Implants release metallic elements in surrounding tissues by various mechanisms. One of them may be corrosion [7] that can influence biological function. Tissular reactions depend on the quantity of fragments. The contamination is heterogeneous and depends on the degradation of the prosthesis. The cartographies and micro-XANES analysis give information about the oxidation degree of metallic elements released in tissues surrounding an implant and on their toxicity. The combination of PIXE and micro-XANES method allows to have results about the importance, the evolution and the toxicity of the released elements. Absence of chromium +VI is noticed.

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