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Characterization of ear piercing studs and their corrosion products by neutron activation analysis

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Neutron activation analysis has been applied to analyse ear piercing studs manufactured with three different types of metallic materials and also in the analyses of cell culture media in which these studs were immersed. Results obtained in these analyses indicated the release of metal from the studs to the culture media. Zn and Fe were found, respectively, in the extracts of gold coated copper-zinc alloy and stainless steel. These findings were correlated with the results already obtained for studs surface analysis by scanning electron microscopy and for the cytotoxicity tests of culture extracts.

Introduction

In the last few years, piercing of one or both ear lobes has become a very popular fashion mainly among teenagers in many countries. Nevertheless, for some people, gold coated ear piercing studs have caused serious problems of allergic and inflammatory reactions on skin.

Since gold is known as a metal having little or no toxicity, it is of great interest to evaluate the composition of the metallic substrates underneath the gold coatings as well as their corrosion products in order to investigate if there is a correlation between the elements released from them and the skin reactions.

In this paper this investigation was carried out using in vitro tests and neutron activation analysis (NAA) which was applied in the analyses of ear piercing studs, manufactured by using different types of metallic materials, and also in the analyses of cell culture media in which these studs were immersed.

The release of metal from a variety of alloys, including stainless steels and dental amalgam has been evaluated using in vitro tests in order to help in the understanding and prediction of the complex in vivo release phenomena.[1] On the other hand, the analyses of metals released in the extract solution are not easy due to their low concentrations and also due to the interference of high concentration of Na. The methods commonly used in this type of matrix are atomic absorption spectrometry,[2] stripping voltametry[3] and neutron activation analysis.[4]

Experimental

Materials

The materials tested consisted of two types of commercial gold-coated studs and one type of titanium studs, manufactured using high-purity Ti especially for this work. Metal Ti was chosen because it exhibits properties of high resistance to corrosion, low specific weight, very low toxicity and high biocompatibility. In our laboratory, studs made of gold coated austenitic stainless steel was coded as ST and the ones of gold coated copper–zinc alloy were coded as PF. All types of studs had the same shapes and sizes.

Analyses of the gold coated ear piercing studs substrates and of titanium ear piercing studs

Preparation of the samples for irradiation at the nuclear reactor: The stems and the butterfly backs of ear piercing studs were analysed individually. Firstly, gold free substrates were obtained by removing the gold coatings with a mixture of nitric and hydrochloric acids, and then they were washed using distilled water. These samples were dried and cut into small chips, and a mass varying from 15 to 35 mg of each sample was weighed in a clean polyethylene envelope for irradiation in the nuclear reactor. The titanium ear piercing sample was analysed without acidic treatment.

Preparation of the elemental standards: 50 µl of single or multielemental solutions were pipetted onto small sheets of Whatman filter paper No. 41, and after drying they were placed in polyethylene envelopes.

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These elemental solutions were previously prepared using the certified standard solutions provided from Spex Certiprep Inc, (USA) or they were prepared by dissolving high-purity metals with appropriate reagents. For Fe and Ti standards, the metals of these elements were used. The masses of the elements in the standards were: 50 µg for each one of the elements Co, Cr, Cu, Mo and V; 500 µg for Zn and Ni; 270 µg for Mn and 20 mg for Fe and Ti.

Instrumental neutron activation analysis of studs: Samples and standards were irradiated under thermal neutron flux of the IEA-R1m nuclear reactor in two different conditions. Irradiations of 1 minute with thermal neutron flux of $5\cdot10^{11}$ $n\cdot cm^{-2}\cdot s^{-1}$ were carried out for Mn and V determination and irradiations of 1 hour under thermal neutron flux of 10^{12} $n\cdot cm^{-2}\cdot s^{-1}$ were used to determine As, Co, Cr, Cu, Fe, Mo, Ni, Ti and Zn. After adequate decay times, the irradiated samples and standards were measured using a Model GX2020 hyperpure Ge detector coupled to Model 1510 Integrated Signal Processor and MCA System 100 both from Canberra (USA). Counting times of 200 seconds and 5 to 8 hours were used, depending on the half lives or activities of the radioisotopes considered. The S100 software from Canberra was used to obtain gamma-spectrum data that were processed using the VISPECT2 computer program.[5] In this work the following radioisotopes were used: ^{76}As, ^{60}Co, ^{52}Cr, ^{64}Cu, ^{59}Fe, ^{56}Mn, ^{99}Mo, ^{58}Co (for Ni analysis), ^{47}Sc (for Ti analysis), ^{52}V and ^{65}Zn. The concentrations of elements were calculated by comparative method used in INAA. Detection limit values were also evaluated according to CURRIE[6] for elements not detected in the ear piercing samples.

In order to evaluate the accuracy of the results obtained in the analysis of substrates of ear piecing studs, the British chemical standard certified reference material BCS/SS-CRM No. 466/1 of austenitic stainless steel from Bureau of Analysed Samples Ltd, England, was analysed.

Analysis of culture medium extracts

Preparation of extract: Twelve pairs of studs were sterilised by autoclaving at 120 °C for 20 minutes in a screw capped glass bottle. Subsequently, 60 ml of the cell culture medium MEM-FCS (Minimum Eagle Medium supplemented with 10% fetal calf serum and 1% penicillin-streptomycin solution) were added to the bottle, shaken, and incubated stationary at 37 °C for 10 days. The medium culture extracts resulting from this corrosion test were used for neutron activation analysis and for cytotoxicity assays. The same set of studs were submitted twice to the corrosion test. After the first immersion the studs were immersed again in a new medium culture solution for 10 days to obtain a second extract solution.

Instrumental neutron activation analysis of extracts: The extracts were analysed according to the procedure already described in a previous paper.[7] 500 µl of each extract solution were pipetted and dried in polyethylene capsules from Faculty of Biology, (Vrije Universiteit, Amsterdam) for irradiation at the IEA-R1m nuclear reactor with elemental synthetic standards. These synthetic standards were prepared drying 50 µl of multielemental standard solutions in polyethylene capsules. The masses of each element in these standards were: 50.0 µg for each one of the elements Ni and Zn; 2.0 µg for Cr and Mo, 0.20 µg for Co and 500 µg for Fe. Samples and standards were irradiated for 16 h with thermal neutron flux of 10^{13} $n\cdot cm^{-2}\cdot s^{-1}$. After 10 and 20 days of decay times, gamma-ray measurements were carried out using hyperpure Ge detector. Blanks of the medium culture were also evaluated.

Results and discussion

The results obtained in the analyses of ear piercing studs substrates shown in Table 1 indicate that titanium ears piercing studs were manufactured with high purity Ti. Impurities present in these studs were very small. The studs PF of gold coated copper–zinc alloy substrates showed that metallic materials used for stems and butterfly back are different. The stems presented high concentrations of Cu, Mn and Zn while the butterfly backs showed high levels of Cr and Fe. For ST ear piercing studs substrates, the stems and butterfly backs were of the same type of metals. These analyses also showed that PF and ST studs substrates contain about 7.7% of Ni.

Table 1. Results obtained in the analyses of ear piercing studs substrates carried out by INAA

Element	PF ear piercing studs substrate Stem	PF ear piercing studs substrate Butterfly back	ST ear piercing studs substrate Stem	ST ear piercing studs substrate Butterfly back	Stem of titanium ear piercing studs
As, μg·g^{-1}	8.1 ± 0.5*	69.6 ± 0.4	57.4 ± 0.8	72.5 ± 1.0	17.7 ± 0.3
Co, μg·g^{-1}	27.4 ± 0.4	722 ± 4	2203 ± 11	737.9 ± 3.7	≤1
Cr, %	0.0070 ± 0.0005	17.6 ± 0.2	16.1 ± 0.2	16.3 ± 0.2	0.0096 ± 0.0001
Cu, %	36.5 ± 1.2	0.26 ± 0.01	0.35 ± 0.01	0.226 ± 0.008	≤0.04
Fe, %	9.0 ± 0.2	73.5 ± 0.2	67.9 ± 0.2	71.4 ± 0.2	≤0.04
Mn, %	2.34 ± 0.07	0.90 ± 0.01	1.81 ± 0.02	1.03 ± 0.02	0.0007 ± 0.0002
Mo, %	≤0.2	0.328 ± 0.002	0.394 ± 0.002	0.321 ± 0.009	≤0.0003
Ni, %	6.80 ± 0.07	8.6 ± 0.1	7.86 ± 0.07	7.11 ± 0.06	0.009 ± 0.001
Ti, %	≤23	≤23	≤23	≤18	97.4 ± 6.4
V, μg·g^{-1}	≤77	≤85	987 ± 26	≤9	33 ± 3
Zn, %	36.4 ± 3.3	≤0.06	≤0.7	≤0.7	≤0.002

* Uncertainties calculated using statistical counting errors of standards and samples.

Table 2. Analysis of austenitic stainless steel reference material (BCS/SS – CRM 466/1 and CRM 464). Results are given in percentages

Element	n	Found in this work mean	s_r, %	Certified values	E_r, %
As	4	0.0171 ± 0.0003	1.6	0.017 ± 0.002	0.6
Co	4	0.0167 ± 0.0004	2.6		
Co*	5	0.055 ± 0.002	3.0	0.054	1.8
Cr	4	17.3 ± 0.8	5.0	17.65 ± 0.04	1.8
Fe	5	69.3 ± 1.2	1.7		
Mn	4	0.697 ± 0.007	1.0	0.698 ± 0.008	0.07
Mo	5	2.12 ± 0.06	2.9	2.19 ± 0.01	3.2
Ni	4	8.51 ± 0.45	5.5	8.61 ± 0.04	1.2

* Result for BCS CRM No. 464 austenitic stainless steel; n – number of determinations; s – standard deviation; s_r – relative standard deviation; E_r – percentage of relative error.

Table 3. Determination of Co, Cr, Fe, Ni and Zn released in culture medium

Element	Blank of culture medium + capsule	Extract after 1st immersion			Extract after 2nd immersion		
		PF	ST	Titanium	PF	ST	Titanium
Co, ng/ml	12.1 ± 1.2*	61.6 ± 0.5	99 ± 10	53.8 ± 2.1	6.4 ± 0.2	27.6 ± 4.8	2.7 ± 0.5
Cr, μg/ml	0.72 ± 0.02	0.73 ± 0.04	0.73 ± 0.03	0.75 ± 0.03	0.74 ± 0.02	0.75 ± 0.02	0.72 ± 0.02
Fe, μg/ml	0.60 ± 0.09	0.61 ± 0.08	**4.03 ± 0.31**	0.43 ± 0.11	0.72 ± 0.02	**3.45 ± 0.23**	0.44 ± 0.08
Ni, μg/ml	ND**	**0.96 ± 0.09**	**0.66 ± 0.06**	ND	**1.63 ± 0.22**	**0.62 ± 0.08**	ND
Zn, μg/ml	0.58 ± 0.05	**3.84 ± 0.41**	0.61 ± 0.01	0.75 ± 0.10	**3.39 ± 0.15**	0.52 ± 0.04	0.60 ± 0.01

* Uncertainties calculated using statistical counting errors of standards and samples.
** ND – indicates that the element was not detected.

Analytical results obtained for certified reference material BCS/SS-CRM No. 466/1 austenitic stainless steel are shown in Table 2. It can be observed that good results were obtained with relative standard deviations lower than 5.5% and percentage of relative errors lower than 3.2%.

Table 3 shows the results of Co, Cr, Fe, Ni and Zn obtained in the analysis of the extracts of culture media where the studs were immersed for corrosion test and also of the blank. Results obtained for Co presented a fluctuation from 2.7 to 61.6 probably due to low concentration of this element in the samples. Concentrations of Cr obtained in these analyses were of the magnitude of those obtained in the blank (capsule plus 500 μl of culture medium). Very low amounts of Cr and Zn (535 and 52 ng, respectively) were also found in the T type capsule used for irradiation. The results show that Ni was found in the extracts of PF and ST studs, Fe in the extract of ST studs and Zn in the extract from PF. These findings indicate the occurrence of the corrosion process and the release of these elements from the substrates to the extracts. The corrosive action onto the studs surface begins when the culture medium comes into contact with the substrate material due to the presence of defects on their surfaces. The presence of these defects on the gold coated stud surfaces have been already confirmed by scanning electron microscopy.[9] Also results from cytotoxicity assay of these solutions were presented in a previous paper.[9] As expected, the concentrations of Co, Cr, Fe and Zn were very low or of the same magnitude of the blank of the extract solution in which Ti studs were immersed. This extract had shown not to be cytotoxic. On the other hand, elements such as Ni and Fe, or Zn were found in the extracts in which gold coated studs were immersed and this extract presented cytotoxicity. Therefore, the toxic effects presented by these extracts may be attributed to elements released from ear piecing studs substrates. For example, nickel allergy and its relationship with ear piercing has been reported in several papers.[10–12]

Results obtained in this work indicated the necessity to improve quality control of the coating process of studs and the appropriate choice of material used as substrate. Alloys containing toxic materials should not be used as substrates for ear piercing studs. The high corrosion resistance and no cytotoxicity property of Ti suggest that it could be conveniently used as a manufacturing material for ear piercing studs.

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