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AN IMPROVED SDAR–OES APPROACH FOR ESTIMATION OF THE DETRIMENTAL ELEMENTAL CONTENTS INTO AN AISI 316L GRADE

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Abstract: The paper addresses the issue of the detrimental elements that may occur in the metallic materials at trace level. The reliability of a metallic implant critical depends on its detrimental elements content. The ISO 10993–18:2020 addresses prerequisite for biological risk evaluation, but ISO 5832–1/2016 refers only to the main chemical composition that ensures the inertness of the implant in a tissue environment whilst the problem of detrimental element is missed. The leakage of detrimental elements as Al, Cd, Co, Hg and Pb into surrounding tissues is a potential risk for the patient. Therefore, this issue is highlighted in the paper and an adequate solution is proposed to estimate the content of detrimental elements into an AISI 316L biomaterial. Thus, the spark discharge in argon optical emission spectrometry (SDAR–OES) is proved to be an effective solution for the bulk concentration measurement of elemental constituents and the detrimental elements occurring into AISI 316L sample using. The main objects of this paper are: to enhance the measurement capability of the SDAR–OES method as to be use at least as the primary step for checking the contents of the detrimental elements into the candidate 316L biomaterial and also to argue for including the SDAR–OES method among the methods recommended by the ISO 10993–18 for measuring the chemical composition of the metallic biomaterials as AAS, ICP, MS. The novelties addressed are the method and technique used for estimating the detrimental elemental contents and providing facts for improving the chemical conformity requirements of the 316L.
Keywords: biocompatibility, product quality, chemical conformity assessment, detrimental elements, SDAR–OES, AISI 316L

1. INTRODUCTION

Metallic biomaterials are the most used in orthopaedic implantology [1–3]. As it is well known, a metallic biomaterial has to fulfil a set of requirement as adequate mechanical strength, corrosion resistance i.e. chemical inertness, reliability etc. [4 –6]. Reliability is defined as the ability of a technical system (implant) to function flawlessly for all foreseen life [7].

One of the important metallic material for orthopaedic prosthetics is the AISI 316L stainless steel. All the semi–finished steel products are subjected to contamination with unwanted chemicals during manufacture [8,9]. Even during implant manufacture the specimen can be contaminated during welding, coating etc. [7,10]. In this regard, a metallic biomaterial can fulfil the requirements of the standards, especially chemical composition, but it may produce injuries to the surrounding tissues due to the chemical impurities that occur in the implant at trace level [11–14].

A substance may be considered a "contaminant" if it occurs where it is unwanted, or in a combination with other species or in a concentration that causes a detrimental effect on human health. Metal toxicity or metal poisoning is the toxic effect of certain metals in certain forms and doses on life. Some metals are toxic when they form poisonous soluble compounds. Certain metals have no biological role, i.e. are not essential minerals, or are toxic when in a certain form [15].

The toxic effects for a particular metal are in many ways a measure of the dose–response relationships. The dose or level of exposure is the amount of metal within cells of organs manifesting a toxicological effect.

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The exposure dose to a metal is a multidimensional concept and it is a function of time as well as the concentration of metal, sources of exposure, transport, and distribution to various organs and excretory pathways [15]. When the source of toxic substance is located inside the human body then the toxic effect upon surrounding tissues increases and it can be the unwanted cases of the implants made of different metallic alloys. Thus, the metallic products released from the prosthesis may impair organs and local tissues. The leachability of the detrimental elements plays a critical role in tissue poisoning. Hence, the mathematical modelling of the leaching process is a smart approach for its mitigation [16,17]. Also, the control of the processes that lead to specific microstructures can leads to the reduction of the leaching rate. [18, 19].
Practice has shown that many semifinished metallic products contains residual elements that are classified as detrimental for the human health as As, Ba, Cd, Hg, Pb, Se.
Metal ions (Ni, Cr, and Co) and debris released from orthopaedic implants can lead to an adverse biological reaction i.e Ni ions leads to dermatitis, Co ions leads to carcinogenic effects. The long–term existence of Al and V ions has been found to cause Alzheimer's disease, osteomalacia, and neuropathy in the long term [15,20—22].
The AISI 316L is still the most used metallic biomaterial in all implants division [23]. The toxicity of the stainless steels cannot be predicted solely based on the bulk concentration, but the releasing of ions into surrounding tissues plays an essential role in their toxicity [24].
According to ISO 10993–18:2020 chemical characterization becomes a key factor in the assessment of the biological evaluation since obtained data are fundamental to correctly set the biological risk assessment of medical devices and also to plan how to evaluate biological effects relevant to the device [25]. Although, in ISO 10993–18:2020 are major changes how point out the importance of chemical characterization it still a deficit in SR ISO 5832–1 i.e. does not specified the specified content limits for possible detrimental elements other than P and S. The Al, Cd, Co, Hg and Pb are known as detrimental for the human health [26].
In this regard, the paper addresses to the chemical estimation of detrimental elements content of a batch of 316L grade and to the deficiency of the ISO 5832–1 which does not specified content limits for possible detrimental elements as Al, Cd, Co, Hg, and Pb.
The chemical conformity assessment of a metallic product to be qualified as a biomaterial based on SDAR–OES measurements is one of the important issues addressed in the paper. In this regard, according to ILAC–G8:09/2019 and ISO 98–3 no conformity can be assessed without knowing the measurement uncertainties of the measurands subjected to comparison to the specified values [27,28]. Therefore, an adequate uncertainty estimation method is proposed in the paper based on a previous work [29].
The main novelty addressed in the paper consists in proving the adequacy of the SDAR–OES technique for the measurement of the detrimental elements as Al, Cd, Co, Hg, and Pb in AISI 316L biomaterial type. Also, the introducing of the measurement uncertainty evaluation based on a proper top–down method according to ISO Guide 98–3 [28] and EUROLAB Technical Report no.1 [30] is another novelty addressed in the paper.
But, above all, the critical dependence of the reliability of a metallic implant on its detrimental elements content is the most important issue highlighted by the paper.

2. MATERIALS AND METHODS

A batch of 316L bars has been produced for medical applications. The qualification of these bars as biocompatible is a complex issue as the standard ISO 10993–18 does not provide the scale at which the chemical conformity test should be applied. Also, the ISO 10993–18 standard does not specify the appliance of Spark Discharge in Argon–Optical Emission Spectrometry (SDAR–OES) in this regard. The elemental analysis was performed with a SpectromaXx equipment (SpectromaXx, Analytical Instruments GmbH and Co) equipped with CCD and powered with spectral Ar.

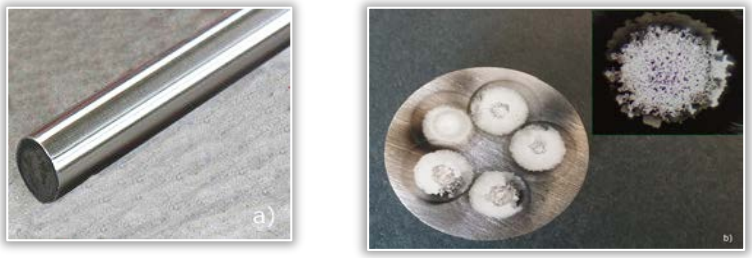

Figure 1. Representative image of the a) bar batch b) specimen sparked 5 times

The SDAR–OES measurements were carried on 5 specimens sampled from a bar batch of 1m in length and 30 mm in diameter (fig.1a, b) which was produced at laboratory scale.

The composition of the bar was designed to fulfil the requirements of the ISO 5832–1 standard for the 316 L biomaterial [26]. The disks of 1 cm in length were milled with corundum paper and sparked 5 times on both sides. The elemental concentration results reported for each specimen tested is the average of ten measurements carried out, in reproductive conditions, on 5 specimens of the same bar. The expanded measurement uncertainty (U) was estimated taking into account the top–down procedure [28,29]. The U of each measuring was estimated using an extended coefficient k = 2 for the 0.95 confidence level.

The procedure for MU estimation is described in detail in [29] and consists of five steps:

a. Verification of traceability

$$t_{cal} = \frac{|c_{CRM} - \bar{c}|}{\sqrt{u_{CRM}^2 + \frac{s_{CRM}^2}{n}}} \quad (1)$$

where: u_{CRM} is the standard uncertainty of the Certificated Reference Material (CRM); s_{CRM} is the standard deviation of test results carried on the CRM and n is the test number

b. Uncertainty of verification of traceability

$$u_{trac} = \sqrt{u_{CRM}^2 + \frac{s_{CRM}^2}{n}} \quad (2)$$

c. Uncertainty of the analytical procedure

$$u_{proc} = s_m^2 \quad (3)$$

where: s_m is the standard deviation of the mean

d. Calculating the combined standard uncertainty

$$u_c = \sqrt{u_{trac}^2 + u_{proc}^2} = \sqrt{u_{CRM}^2 + \frac{s_{CRM}^2}{n} + s_m^2} \quad (4)$$

where the u_c is the combined uncertainty

e. Calculating the extended uncertainty

$$U\ (95\%) = 2 * u_c \quad (5)$$

where U (95%) is expanded uncertainty with 95% confidence level can be calculated

The measurements results were checked for outliers based on Grubbs test and on MU estimated according to above procedure [29, 31]

3. RESULTS AND DISCUSSIONS

The qualification of an alloy as 316L must be performed in accordance with the ISO 5832–1 (Table 1). The average elemental concentrations of the specimens no. 1–5 and their U (95%) is presented in table 2.

Table 1. The chemical composition of the 316L specified by SR ISO 5832–1/2016

Element	C	Si	Mn	P	S	Cr	Ni	Mo	Cu	N	Fe
Limits	Max 0.03	Max. 0.1	Max. 2.0	Max. 0.025	Max. 0.01	17.0–19.0	12.0–14.0	2.0–3.0	Max. 0.5	Max. 0.01	Bal.

Table 2. The average elemental concentrations of the specimens and their U (95%) at local level

No.	C	Si	Mn	P	S	Cr	Ni	Mo	Cu	N	Al	Co	Pb	As	Fe
1.	0.025	0.086	1.48	0.020	0.008	17.61	12.32	2.21	0.32	0.009	0.026	0.32	0.020	0.048	Bal.
U	0.005	0.010	0.07	0.005	0.002	0.51	0.21	0.31	0.10	0.003	0.014	0.08	0.007	0.022	–
2.	0.022	0.083	1.47	0.018	0.009	17.61	12.32	2.21	0.32	0.006	0.023	0.32	0.021	0.044	Bal.
U	0.006	0.011	0.07	0.004	0.001	0.51	0.21	0.32	0.09	0.002	0.012	0.09	0.006	0.021	–
3.	0.023	0.082	1.48	0.016	0.007	17.62	12.32	2.21	0.32	0.007	0.024	0.32	0.019	0.046	Bal.
U	0.006	0.012	0.06	0.004	0.002	0.52	0.21	0.31	0.11	0.002	0.013	0.08	0.005	0.023	–
4.	0.024	0.085	1.48	0.017	0.008	17.62	12.32	2.21	0.32	0.008	0.023	0.32	0.023	0.049	Bal.
U	0.006	0.011	0.07	0.005	0.002	0.52	0.21	0.32	0.09	0.003	0.013	0.09	0.008	0.025	–
5.	0.023	0.087	1.47	0.018	0.007	17.62	12.32	2.21	0.32	0.008	0.025	0.33	0.024	0.050	Bal.
U	0.006	0.012	0.07	0.005	0.002	0.52	0.21	0.31	0.1	0.003	0.014	0.10	0.009	0.028	–

Table 3. The average elemental concentrations of the specimens and their U (95%) at global level

Element	C	Si	Mn	P	S	Cr	Ni	Mo	Cu	N	Al	Co	Pb	As	Fe
Mean	0.023	0.085	1.48	0.018	0.008	17.61	12.32	2.21	0.32	0.008	0.024	0.32	0.021	0.047	Bal.
U 95%)	0.006	0.012	0.07	0.005	0.002	0.50	0.20	0.30	0.09	0.001	0.015	0.10	0.010	0.024	–

The data were checked for outliers based on Grubb's and it was found that there is no outlier among data in Table 1. The overall average outcomes for one bar are given in Table 3. Also, the specified chemical composition given in the SR ISO 5832–1 is given in Table 1 to be compared with the measured one.

4. CONCLUSIONS

Comparing the measured values with those specified in ISO 5832–1 standard it results that specimens fulfil the requirements of this standard. On the other hand, the specimens contain detrimental elements with significant potential to promote local adverse reactions if an implant is made of this material.

Even though the Pb, As and Al concentrations are smaller, the risk of their release from stainless steel 316L implant into the surrounding tissues is unknown. In this regard, the paper supports the usage of the SDAR–AES technique for preliminary assessment of the chemical conformity of the 316L candidate billets and for the preliminary measurement of the detrimental elemental concentrations whose occurrence is not foreseen by the SR ISO 5832–1.

The paper supports the usage of the SDAR–OES technique for the assessment of the chemical conformity of the 316L candidate billets and for the preliminary measurement of the detrimental elemental concentrations whose occurrence is not foreseen by the SR ISO 5832–1.

The main novelty addressed in the paper is the appliance of the SDAR–OES technique and the way in which the measurement uncertainties were used for a parsimonious appraisal of the concentration of the detrimental elements into 316 L specimens.

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