New Approach for Chemical Homogeneity Analysis of an AISI 316L Stainless Steel Bar Batch

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A batch of AISI 316L stainless steel bar was produced for orthopedic implant manufacture. The paper purposes a documented chemical homogeneity analysis (CHA) as a mandatory step of the chemical composition compliance practice for metallic bulk biomaterials. The CHA significantly diminishes the type II error risk. In this regard a new procedure was developed for CHA based on ASTM E826 one. The paper support the adequacy of the information mass assigned to spark discharged in argon-atomic emission spectrometry (SDAR-AES) technique. The case study demonstrates the power of this practice to discriminate among the homogenous elemental distribution (Cr, Ni, Si, etc) and heterogeneous (C, P, S).

Key words: chemical homogeneity analysis, 316L stainless bar batch, SDAR-AES technique

The metallic biomaterials are used on large scale for medical device fabrication and for implants manufacturing [1-4]. Among metallic biomaterials the AISI 316L stainless steel is one of the most used for implants manufacture as it has a superior corrosion resistance and other adequate characteristics. Thus, the 316L stainless steel grade is used for manufacturing of the cardiovascular (stents, artificial valves), orthopedic (plates, screws, pins, joints), dentistry (orthodontic wires, fillings implants), craniofacial devices (plates and screws) [5-8]. Taking into account the performances of the 316L stainless steel grade a Romanian small metallurgical enterprises has made efforts to produce this half-finished steel bars for medical applications. The main requirement for a biomaterial is to be nontoxic i.e. anything from its mass should not leach out into the tissue unless it is specifically designed for this purpose [9]. Therefore, when a new biomaterial is under development then the chemical composition with the specified compliance is a mandatory test, but the chemical homogeneity have to be validated since an inadequate sampling could lead to a false compliance. The way in which the chemical homogeneity analysis (CHA) is assessed is a matter under discussion as some authors have purposed simple procedures based on weak statistics and others emphasize the size effects [10-14].

On the other hand, there is no recognized practice for CHA of the metals, even though it is of great importance for metallic biomaterials. In this paper a new way of CHA is developed based on the practice used for the certification of spectrometric reference materials that have to comply to a high level of chemical homogeneity. In this regard, the paper adopted the Standard Practice for Testing Homogeneity of a Metal Lot or Batch in Solid Form by Spark Atomic Emission Spectrometry as is described in ASTM E 826-14 to the Homogeneity Testing of a metallic biomaterial as is the case of the 316L austenitic stainless steel which is intended to be qualified as biocompatible [15]. This standard was considered adequate as it is compliant with ISO/Guide 35:2017 (en): Reference materials / Guidance for characterization and assessment of homogeneity and stability [16].

The ASTM E 826-14 practice provides statistical criteria for CHA applicable to the results provided by SDAR -AES. Another advantage of the ASTM E 826-14 practice consists in its versatility i.e. it could be adapted for use with other instrumental techniques such as X-ray fluorescence spectrometry, atomic absorption spectrometry, etc.

The novelties addressed in the paper are: a) adaptation of the ASTM E 826-14 practice for CHA of the metallic biomaterial candidates; b) argue for CHA as a mandatory step of the certification procedure of an alloy as been biocompatible; c) overcoming of the homogeneity scale issue by demonstrating the adequacy of the information mass (IM) assigned to SDAR-AES technique i.e. argues for SDAR-AES spectrometry usage as an adequate technique for CHA of metallic biomaterials; d) procedure of CHA which fulfils the requirements of the ASTM 826-14, ISO 10993-18 [17], ISO 5832-1 [18]; e) CHA case study for a 316L stainless steel bar batch.

Homogeneity, as it is defined in ASTM: E 826-14 equals *the condition of being of uniform structure or composition with respect to one or more specified properties* [8]. Accordingly, a solid-state material is considered to be in bottle homogenous with respect to a chemical composition if the elemental concentration values measured across a plane sampling areas are found to lie within the specified limits. A batch is between bottle, *the homogeneity is statistically acceptable differences among means of specimens in the test*. Therefore, the homogeneity assessment is done through statistical tests. The CHA of a metal is matter of compromise because any industrial metallic product is inhomogeneous at atomic structure level. The microstructure homogeneity of a polycrystalline alloy is a scale dependent issue, i.e. the microstructure looks like heterogeneous if the magnification overcomes a certain level. (fig. 1). As could be seen, the test results depend on the intrinsic distribution of the grains that provides the measured signal and the scale at which the signal is collected.

The analysis scale is determined by the IM that is defined as the substance mass providing the measurand value (fig. 2.a). In the SDAR-AES the IM is the mass undertaken streamer discharges, so called spark-in mass (fig. 2.b-d) [19,20].

In the case of SDAR-AES addressed in this paper the IM was estimated as being of the order of 10μg and the IM is sampled on an average area of about 10 mm^2 which is adequate to reveal the chemical heterogeneity.

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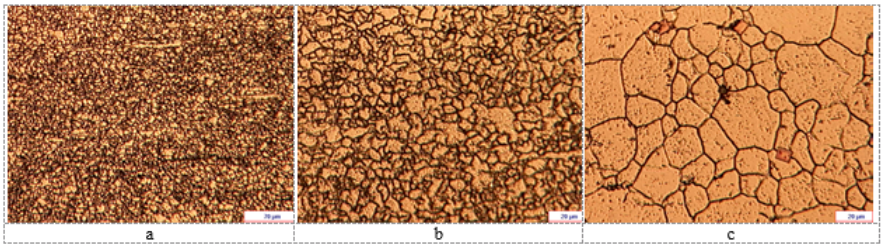

Fig.1 Homogeneity scales: a) homogeneity at low level magnification; b) homogeneity at middle level magnification; c) heterogeneity at high level magnification

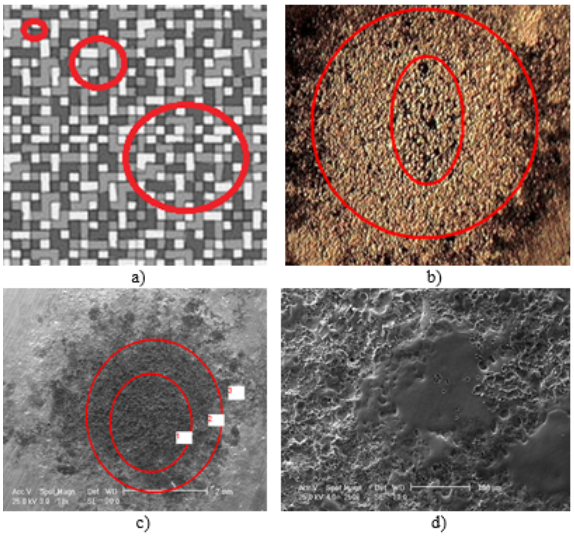

Fig. 2. Homogeneity scales for SDAR-AES measurements: a) schematic correlation of the spark-in area and microstructural features, b) SEM image of entire spark-in zone; c) detail of the central area of the Spark-in zone in b, d) details of the streamer impacts

According to ASTM E 826, two concentrations, denoted $\mathbf{c_1}$ and $\mathbf{c_2}$, are stated as being equal, with a statistical confidence α, if abs(c_1-c_2) < w(α,í)
where:

$$w = q \times s / \sqrt{b} \quad (1)$$

where **b** is the number of the repeated measurements

$$s = \sqrt{(S - S_b - S_t)/v} \quad (2)$$

s is standard deviation; **S** is sum of the squares of all the measurements in the tables; $\mathbf{S_b}$ is sum of squares due to runs, $\mathbf{S_t}$ is sum of squares due to specimens

$$S = \left(\sum_{j=1}^{t}\right)\left(\sum_{j=1}^{b}\right) Y_{ij}^2 - \left(G^2/tb\right) \quad (3)$$

where: $\mathbf{Y_{ij}}$ is individual values in the table of Random Numbers; **t** is the number of the tested specimens, and **G** is sum of $B_1 \cdots B_n$;

$$S_b = \left[\left(B_1^2 + B_2^2 + \cdots B_b^2\right)/t\right] - \left(G^2/tb\right) \quad (4)$$

where **B** is sum of each row; **T** is sum of each column

$$S_t = \left[\left(T_1^2 + T_2^2 + \cdots T_t^2\right)/b\right] - \left(G^2/tb\right) \quad (5)$$

$$v = (b-1) \times (t-1) \quad (6)$$

where ν is the number of degrees of freedom.

The value of the **q** parameter depends on the CH test significance level and on the number of degree of freedom (ν). The **q** values, for the specific **t** and ν, could be found in the statistical books [21].

Experimental part

An AISI 316L bar batch was subjected to CHA. The bars are of 1 m in length and of 30 mm in diameter. Five bars were sampling using the random number procedure. Each sampled bar was cut into 4 parts and three disks of about 30 mm in length were cut as is shown in figure 3.

Buhler and MLG 11 equipment were used for specific sample surface finishing needed for microscopically investigations and for SDAR-AES analysis. The cross sections were grinded with corundum abrasive paper (mesh 1200) before starting each spark-in session. The elemental concentrations were measured with a SpectromaxX (Ametec, Thermo Instruments) SDAR –AES spectrometer having the following characteristics: Paschen-Runge optic with 140-500 nm wavelength range; spark discharge source of 500V at 450 Hz rate; Ar purged stand; tungsten counter-electrode washed with argon in Ar thermo stabilized optic. The microstructure and SEM images were obtained by using a optical microscope type REICHERT UnivaR and XL-30-ESEM TMP electronic microscope.

Results and discussions

Each disk was carefully 10 times sparked in repetitive conditions aiming a uniform distribution of the bur-off spots across the sparking area and a full burning of the spark-in area (fig. 4).

The spectrometric results were recorded in the SpectromaxX data-log as is shown for Cr in table 1.

For the *in bottle* CHA a t-Student test was applied (table 1).

As could be seen in table 1, all sampled cross sections passed the in bottle CHT for Cr element.

The **w** criterion for the Cr homogeneity assessment was calculated based on the data given in table 1 using the statistics given in (2) - (8) and the outcome is w = 0.172. According to ASTM 826-14, if the absolute difference between any two mean values of Cr concentration given in table 2 is smaller than 0.172 then there is strong evidence, at the 95% confidence level, that the bar batch shall be considered homogeneous.

A matrix was designed for comparing **w** with absolute values of the differences between means (table 3). The

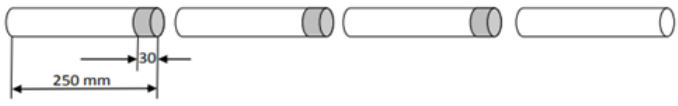

Fig. 3 Sampling scheme

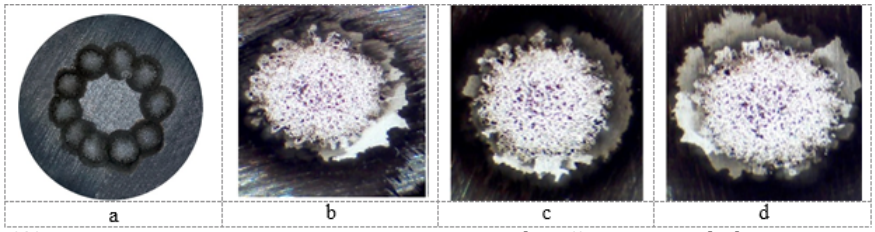

Fig. 4. The images of: a) a sparked-in cross section; b, c, d) 3 burn-off areas

Table 1

THE RAW DATA AND THE STATISTICAL PARAMETER USED FOR Cr *IN BOTTLE* CHA

No.crt.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Sample No.	**2**	**4**	**5**	**9**	**10**	**13**	**15**	**17**	**19**	**21**	**22**	**23**	**24**	**25**	**26**
1	17.5	17.4	17.3	17.3	17.4	17.4	16.8	17.8	17.8	17.3	17.3	17.3	17.5	17.3	17.5
2	17.7	17.4	17.5	17.4	17.5	17.6	17.4	17.4	17.3	17.3	17.3	17.4	17.7	17.6	17.5
3	17.7	17.5	17.5	17.3	17.6	17.8	17.6	17.6	17.4	17.4	17.4	17.7	17.6	17.7	17.4
4	17.6	17.6	17.7	17.5	17.7	17.7	17.7	17.7	17.6	17.7	17.6	17.6	17.6	17.7	17.6
5	17.7	17.7	17.8	17.6	17.8	17.7	17.7	17.7	17.7	17.7	17.6	17.5	17.7	17.5	17.7
Mean 1	**17.6**	**17.5**	**17.5**	**17.4**	**17.6**	**17.6**	**17.4**	**17.6**	**17.6**	**17.5**	**17.4**	**17.5**	**17.6**	**17.5**	**17.5**
STD 1	**0.07**	**0.12**	**0.19**	**0.13**	**0.18**	**0.17**	**0.38**	**0.15**	**0.19**	**0.19**	**0.16**	**0.15**	**0.08**	**0.18**	**0.10**
6	17.7	17.7	17.7	17.7	17.9	17.7	17.8	17.6	17.7	17.8	17.7	17.6	17.6	17.5	17.6
7	17.8	17.7	17.8	17.6	17.9	17.8	17.8	17.6	17.8	17.6	17.7	17.6	17.6	17.5	17.5
8	17.8	17.8	17.8	17.7	17.7	17.8	17.8	17.7	17.8	17.7	17.8	17.6	17.6	17.5	17.6
9	17.8	17.8	17.8	17.7	17.8	17.8	17.8	17.8	17.7	17.7	17.8	17.6	17.7	17.6	17.6
10	17.6	17.8	17.8	17.7	17.8	17.8	17.9	17.7	17.7	17.7	17.7	17.8	17.7	17.6	17.7
Mean 2	**17.7**	**17.8**	**17.8**	**17.7**	**17.8**	**17.8**	**17.8**	**17.7**	**17.7**	**17.7**	**17.7**	**17.6**	**17.7**	**17.6**	**17.6**
STD 2	**0.07**	**0.03**	**0.04**	**0.04**	**0.06**	**0.03**	**0.04**	**0.09**	**0.04**	**0.06**	**0.07**	**0.08**	**0.05**	**0.06**	**0.06**
Te*	2.20	5.00	2.70	4.60	2.60	1.70	2.30	0.10	1.90	2.70	4.00	1.40	1.60	0.10	1.00
CHA result (1/0) tc*** = 5.041**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**

*Student t experimental value; ***1 stands for passing the test while 0 for fail; *** Student t(0.05;8) tabulated value

Table 2

THE RAW DATA AND THE STATISTICAL PARAMETER USED *BETWEEN BOTTLE* CHA of Cr

No. crt. / Sam. No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	B_j**
	2	**4**	**5**	**9**	**10**	**13**	**15**	**17**	19	**21**	**22**	**23**	**24**	**25**	**26**	
1	17.5	17.4	17.3	17.3	17.4	17.4	16.8	17.8	17.8	17.3	17.3	17.3	17.5	17.3	17.5	260.5
2	17.7	17.4	17.5	17.4	17.5	17.6	17.4	17.4	17.3	17.3	17.3	17.4	17.7	17.6	17.5	261.9
3	17.7	17.5	17.5	17.3	17.6	17.8	17.6	17.6	17.4	17.4	17.4	17.7	17.6	17.7	17.4	263.1
4	17.6	17.6	17.7	17.5	17.7	17.7	17.7	17.7	17.6	17.7	17.6	17.6	17.6	17.7	17.6	264.6
5	17.7	17.7	17.8	17.6	17.8	17.7	17.7	17.7	17.7	17.7	17.6	17.5	17.7	17.5	17.7	264.9
8	17.7	17.7	17.7	17.7	17.9	17.7	17.8	17.6	17.7	17.8	17.7	17.6	17.6	17.5	17.6	265.2
9	17.8	17.7	17.8	17.6	17.9	17.8	17.8	17.6	17.8	17.6	17.7	17.6	17.6	17.5	17.5	265.3
8	17.8	17.8	17.8	17.7	17.7	17.8	17.8	17.7	17.8	17.7	17.8	17.6	17.6	17.5	17.6	265.6
9	17.8	17.8	17.8	17.7	17.8	17.8	17.8	17.8	17.7	17.7	17.8	17.6	17.7	17.6	17.6	266.0
10	17.6	17.8	17.8	17.7	17.8	17.8	17.9	17.7	17.7	17.7	17.7	17.8	17.7	17.6	17.7	266.0
Ti*	**176.8**	**176.3**	**176.4**	**175.6**	**176.9**	**177.0**	**176.1**	**176.5**	**176.4**	**175.9**	**175.9**	**175.6**	**176.2**	**175.5**	**175.6**	**G= 2643.0**
Mean	**17.68**	**17.63**	**17.64**	**17.56**	**17.70**	**17.70**	**17.61**	**17.65**	**17.64**	**17.59**	**17.59**	**17.56**	**17.63**	**17.55**	**17.57**	
SD	**0.08**	**0.16**	**0.18**	**0.17**	**0.17**	**0.13**	**0.33**	**0.12**	**0.15**	**0.18**	**0.20**	**0.13**	**0.07**	**0.13**	**0.09**	

** i=1÷15; ** j=1÷10; S.N.- is specimen number; R.N- run number*

Table 3

THE DATA MATRIX FOR THE CHT OF THE Cr CONCENTRATION (LOWER LEFT TRIANGLE) AND THE TEST RESULTS (UPPER RIGHT TRIANGLE)

No. crt.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
Mean	**17.68**	**17.63**	**17.64**	**17.56**	**17.70**	**17.70**	**17.61**	**17.65**	**17.64**	**17.59**	**17.59**	**17.56**	**17.63**	**17.55**	**17.57**
1	0	1	1	1	1	1	1	1	1	1	1	1	1	1	1
2	0.0052	0	1	1	1	1	1	1	1	1	1	1	1	1	1
3	0.046	0.006	0	1	1	1	1	1	1	1	1	1	1	1	1
4	0.125	0.073	0.079	0	1	1	1	1	1	1	1	1	1	1	1
5	0.014	0.066	0.060	0.139	0	1	1	1	1	1	1	1	1	1	1
6	0.022	0.074	0.068	0.147	0.008	0	1	1	1	1	1	1	1	1	1
7	0.074	0.022	0.028	0.051	0.088	0.096	0	1	1	1	1	1	1	1	1
8	0.035	0.017	0.011	0.090	0.049	0.057	0.039	0	1	1	1	1	1	1	1
9	0.041	0.011	0.005	0.084	0.055	0.063	0.033	0.006	0	1	1	1	1	1	1
10	0.09	0.038	0.044	0.035	0.104	0.112	0.016	0.055	0.049	0	1	1	1	1	1
11	0.088	0.036	0.042	0.037	0.102	0.110	0.014	0.053	0.047	0.002	0	1	1	1	1
12	0.120	0.068	0.074	0.005	0.134	0.142	0.046	0.085	0.079	0.030	0.032	0	1	1	1
13	0.053	0.001	0.007	0.072	0.067	0.075	0.021	0.018	0.012	0.037	0.035	0.067	0	1	1
14	0.130	0.078	0.084	0.005	0.144	0.152	0.056	0.095	0.089	0.04	0.042	0.010	0.077	0	1
15	0.116	0.064	0.070	0.009	0.130	0.138	0.042	0.081	0.075	0.026	0.028	0.004	0.063	0.014	0

Table 4

THE DATA MATRIX FOR THE *BETWEEN BARS* CHA OF THE C CONCENTRATION (LOWER LEFT TRIANGLE) AND THE TEST RESULTS (UPPER RIGHT TRIANGLE)

No.crt.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Means	**0.022**	**0.024**	**0.022**	**0.026**	**0.026**	**0.023**	**0.022**	**0.024**	**0.024**	**0.022**	**0.022**	**0.023**	**0.021**	**0.023**	**0.021**
1	0	1	1	0	0	1	1	1	1	1	1	1	1	1	1
2	0.003	0	1	1	1	1	1	1	1	1	1	1	1	1	1
3	0.001	0.003	0	0	0	1	1	1	1	1	1	1	1	1	1
4	0.006	0.003	0.005	0	1	1	0	1	1	0	0	1	0	0	0
5	0.006	0.003	0.005	0.000	0	1	0	1	1	0	0	1	0	0	0
6	0.002	0.002	0.001	0.004	0.004	0	1	1	1	1	1	1	1	1	1
7	0.001	0.002	0.001	0.005	0.005	0.000	0	1	1	1	1	1	1	1	1
8	0.003	0.000	0.003	0.002	0.002	0.002	0.002	0	1	1	1	1	1	1	1
9	0.003	0.001	0.002	0.003	0.003	0.001	0.001	0.001	0	1	1	1	1	1	1
10	0.001	0.002	0.000	0.005	0.005	0.001	0.000	0.002	0.002	0	1	1	1	1	1
11	0.001	0.002	0.001	0.004	0.004	0.000	0.000	0.002	0.001	0.000	0	1	1	1	1
12	0.002	0.001	0.002	0.003	0.003	0.001	0.001	0.001	0.000	0.001	0.001	0	1	1	1
13	0.000	0.003	0.001	0.006	0.006	0.002	0.001	0.003	0.003	0.001	0.001	0.002	0	1	1
14	0.002	0.002	0.001	0.004	0.004	0.000	0.000	0.002	0.001	0.001	0.000	0.001	0.002	0	1
15	0.000	0.003	0.001	0.006	0.006	0.002	0.001	0.003	0.003	0.001	0.001	0.002	0.000	0.001	0

values of the differences between means are shown in the lower- left triangle of the matrix while the right one shows **1** if the homogeneity criterion is fulfilled or **0** if the absolute value of the abs($\mathbf{C_i - C_j}$) is greater than **w**.

As the upper right triangle contains only 1 values it can be considered that the Cr concentration is homogeneous with a 95 % confidence level.

The same approaches have demonstrated that the Ni, Cr, Si, Mn, Mo, Cu, N are homogeneous distributed across the bar batch. The bar batch has shown heterogeneity at *between bottle* level for C, P, S element as it is shown in table 4 for C, which shows **0** values in the upper-right triangle that indicate unacceptable differences.

As the ASTM-14 standard does not specify exceptions for homogeneity compliance then the bar batch has to be declared as heterogeneous, besides only three elements do not fulfil the homogeneity criteria.

Conclusions

The study regarding the CHA carried out on a bar batch that candidates to be qualified as AISI 316L stainless steel grade has demonstrated the efficiency and the capability of the developed practice to reveal the chemical homogeneity or heterogeneity for different elements.

The major advantages of this approach can be summarized as follows:

The specimen preparation is simple and inexpensive.

The burn-off area of the SDAR-AES technique ensures a well fitted micro structural scale for the CHA.

The spark-in volume provides an IM of 10 µg level.

The developed procedure given in the paper can be easily implemented with the well-known analytical techniques such as AAS, ICP, XRFS, PIXE, etc.

The CHA demonstrated that Ni, Cr, Si, Mn, Mo, Cu, N are homogeneously distributed across the bars, but C, P and S are heterogeneously distributed.

The paper argues for introducing the CHA/CHT as a mandatory step of the chemical conformity assessment practice designed to qualify an alloy as a biomaterial. The CHA step is aimed to a significantly diminishing of the type II error/risk consisting in the acceptance of a false chemical conformance which could cause detrimental effects to patients.

Many papers and some normative documents show a lack of concern regarding the risk arising due to the insufficient care drawn to the detrimental effects caused by an improper chemical constrains specifications as the concentration limits of the detrimental elements e.g. Cd, Pb, Hg etc even the usage of different significant digits for the specified concentration limits of the same element, such as wrought stainless steel standard for use in the manufacture of surgical implants [22].

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