

## Corrosion behaviour of a dental alloy in some beverages and drinks

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### ABSTRACT

The aim of the present work was to perform a systematic study of the effect of several beverages (alcoholic drinks, natural and artificial fruit juices, vinegar, soft drinks, milk) on the corrosion behaviour of an aluminum–bronze dental alloy. Results were compared to those obtained in artificial saliva and in a solution of sodium chloride. The material used was an aluminum–bronze alloy frequently used in Latin-American countries because of its similarity in appearance to the yellow gold alloys and of economic reasons. The investigation was carried out by means of traditional electrochemical techniques: polarization tests, polarization resistance measurements and weight loss tests. The ranking of aggressiveness of the beverages and solutions studied is given by the corrosion rate computed from the weight loss measurements, and it is as follows: artificial saliva, lemon juice, vinegar, 1 M NaCl, white wine, red wine and artificial orange juice. The aggressiveness of the different liquids is independent of both the pH and electrical conductivity of the solution. The most aggressive beverage (artificial orange juice) generates a corrosion rate only 1 order of magnitude higher than that of saliva, a difference that is not relevant for the odontological use considering the short time that beverages are in contact with dental alloys in the oral environment.

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### 1. Introduction

One of the primary requisites of any metal or alloy that is to be used in the mouth is that it must not produce corrosion products that could be harmful to the body. Some metallic elements that are completely safe in the elemental state can form hazardous or even toxic ions or compounds [1]. Besides, the degradation of the alloy should be limited in order to guarantee its service life.

It is important to note that the oral environment is very conducive to the formation of corrosion products. The mouth is moist and continually subjected to fluctuations in temperature. Foods and drinks cause transitory, but important and wide, variations in the chemistry of the environment. The food and liquids ingested have wide ranges of pH. Acids are liberated during breakdown of food-stuffs. This food debris often adheres tenaciously to the metallic restoration providing a localized condition that is extremely conducive to an accelerated reaction between the oral media and the metal or alloy.

The most important fluid in the oral environment is natural saliva. It is obvious that tests involving dental materials should be done in that media. However, the unstable nature of natural saliva makes it inadequate for standardized *in vitro* studies and artificial saliva is frequently used. The artificial saliva generally used in corrosion studies of dental alloys is organic compound-free: it does not contain neither proteins nor other organic compound (except urea and/or organic acids to adjust the pH) [2].

Several works dealing with the effect of different formulations of artificial saliva solutions on the corrosion susceptibility of dental alloys are found in the literature and listed in [2]. However, the effect of different beverages and drinks on the corrosion behaviour of dental alloys has not been extensively addressed in the literature [3,4]. In the present work, a systematic study of the effect of several beverages (including alcoholic drinks, natural and artificial fruit juices, vinegar, soft drinks, milk) on the corrosion behaviour of a characteristic dental alloy of aluminum–bronze was investigated by means of traditional electrochemical techniques (polarization tests, polarization resistance measurements and weight loss tests). Results were compared to the behaviour obtained in an artificial saliva previously developed [2] and in a solution of sodium chloride.

### 2. Materials and methods

The material used for testing the various liquids was an experimental aluminum–bronze (copper–aluminum alloy) alloy for dental use. These

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**Table 1**  
Different beverages and solutions used in the present study.

Substance	pH	Conductivity at 25 °C (mS cm <sup>-1</sup> )
1. NaCl 1 M	5.6	18.57
2. Artificial saliva [2]	6.9	5.67
3. Vinegar	3.3	3.31
4. White wine	3.5	1.43
5. Red wine	3.9	1.96
6. Lemon juice	2.8	4.13
7. Artificial orange juice (AOJ)	3.1	1.17
8. Natural orange juice	3.7	3.21
9. Milk	6.6	4.17
10. Beer	4.3	1.02
11. Soft drink	2.9	0.88

aluminum–bronzes, essentially a substitute for conventional gold-rich alloys, are employed for the fabrication of economical crowns and bridges. The composition of the alloy used in the present work was (by weight): Al, 5.73%; Fe, 1.98%; Ni, 4.29%; Mn, 0.70%; and Cu, balance. The chemical composition is selected taking into account that, for aluminum–bronzes it was found that, in general, corrosion resistance of this alloys increases with increase in aluminum content up to about 10% [5]. Besides, the addition of Fe and Ni enhances the mechanical properties of the alloy. The Mn component has a deoxidizing action and is effective in improving both the strength and corrosion resistance. This alloy is similar in composition to other commercial copper–aluminum dental alloys frequently used for cast restoratives in Latin-American countries. Aluminum–bronze has had an early introduction into dentistry and has renewed interest because of its similarity in appearance to the yellow gold alloys, because of the volatility of the gold price and for economic considerations [6]. The material was taken from a plate. It was annealed for 1 h at 800 °C in an argon atmosphere. This thermal treatment, the same used in a previous work [2], was made in order to obtain a microstructure as similar as possible to that obtained when used in dentistry by melting and casting the commercial alloy to fabricate the metallic restoration. The specimens (2.5 cm × 1.5 cm × 0.1 cm size) were successively polished with SiC papers (up to # 600) and then with diamond paste (up to 1 μm). Then, they were spot soldered to a copper wire and mounted into a glass tube by an epoxy resin. Specimens were painted with a lacquer to leave a measured surface area for exposure. Prior to the tests, the samples were degreased with acetone and dried with hot air.

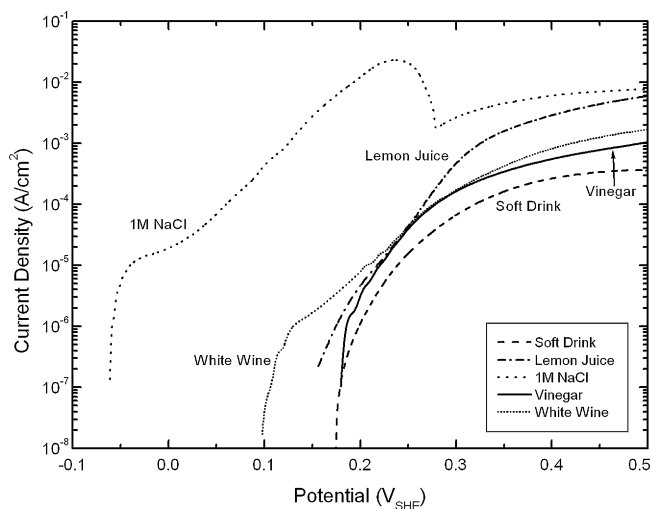
The beverages and solutions used in the present work are listed in Table 1. The pH value and electrical conductivity of each substance were measured and are also included in Table 1.

The test methods performed were potentiodynamic polarization curves, polarization resistance measurements and weight loss tests, using different specimens in each type of test. A conventional three-electrode glass cell (80 cm<sup>3</sup> capacity) was used for the polarization curves. The anodic polarization curves were potentiodynamically measured starting from the open circuit potential at a scanning rate of 0.5 mV s<sup>-1</sup>. The open circuit potential was monitored in each solution until it reached an almost constant value (approximately 1 h). Then, to standardize the procedure, the anodic polarization curves were drawn after 1 h exposure to the solutions. These measurements were carried out with an Autolab PGSTAT 30 Potentiostat. A saturated calomel electrode was used as a reference electrode and the counter-electrode was a platinum wire. Results are referred to the standard hydrogen scale (SHE). The polarization curves were drawn at least in triplicate using three independent samples and fresh solution in each test.

Linear polarization resistance measurements were performed with a GAMRY PCI4-750 mA Potentiostat. In these tests, the potential of the samples was varied ±10 mV from the corrosion potential at 0.1 mV s<sup>-1</sup> scan rate. Measurements of the polarization resistance ( $R_p$ ) were performed every half an hour, during 24 h. Triplicate tests were performed in each of the solutions listed in Table 1. The electrical conductivity of each solution was used to compute the ohmic drop correction in the electrochemical tests. However, this correction was negligible.

Weight loss measurements were carried out by triplicate in solutions 1 to 7 following the specifications given in ASTM G1-03 [7]. The initial and final weight of the specimens were measured with an electronic balance with a precision of 0.1 mg. PVC see-through cells containing 500 ml of the various solutions were used. The specimens hung down from the lid of the cells, being completely immersed in the solutions. In order to avoid the decomposition of the solutions, they were renewed by fresh ones once a week. Natural orange juice and milk were excluded from these tests because decomposition is very fast in these solutions. Fizzy drinks were also excluded because degasification of the solution was impossible to avoid, changing the pH of the solution. The total surface of each specimen was measured before the tests (approximately 8 cm<sup>2</sup>). Weight losses were measured at 7, 15 and 30 days of exposure. Corrosion rates, expressed as g (cm<sup>2</sup> day)<sup>-1</sup> were calculated.

All tests were performed at 25 °C (some potentiodynamic tests performed at 37 °C proved that the behaviour of the system was similar to that observed at 25 °C). After the tests, the specimens were rinsed with water and observed with a Philips SEM 500 scanning electron microscope (SEM).



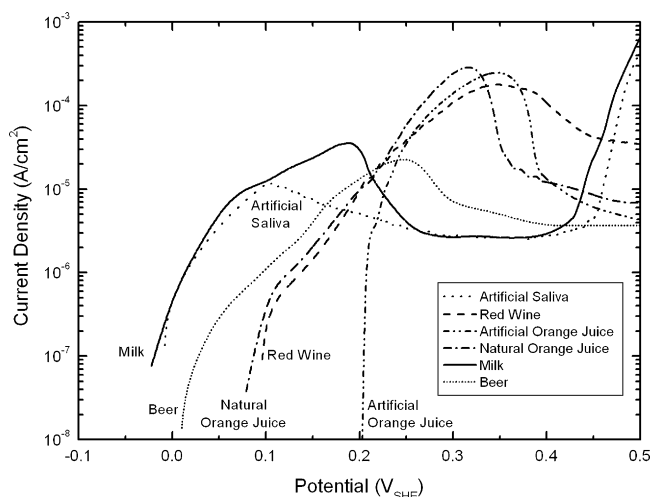
**Fig. 1.** Polarization curves of an aluminum–bronze dental alloy in NaCl 1 M, white wine, lemon juice, vinegar and soft drink.

### 3. Results

The corrosion potentials ranged from –0.050 to 0.200 V<sub>SHE</sub> in the different solutions. The polarization curves are shown in Figs. 1 and 2. Polarization curves showed good reproducibility in each solution. For the sake of simplicity, only one representative polarization curve for each system is shown in the figures.

Fig. 1 includes the curves in which the current densities reached high values when increasing the potential from the corrosion potential, and no passive region was observed. NaCl, white wine, lemon juice, vinegar and soft drink solutions are included in this group. Among them, NaCl 1 M is the one with the highest current densities. The other solutions showed a similar behaviour: a relatively abrupt increase in current was observed when increasing the potential.

Fig. 2 shows the curves in which a passive zone was observed or those curves in which current densities increased up to a maximum value and then decreased again. Milk, artificial saliva, beer, natural orange juice, red wine and artificial orange juice solutions are included in this group. The curves in milk and artificial saliva are similar: there is a passive zone followed by an abrupt increase in current at approximately 0.45 V<sub>SHE</sub>. In beer the current remained low in the whole range of potentials studied. Natural orange juice,



**Fig. 2.** Polarization curves of an aluminum–bronze dental alloy in milk, artificial saliva, beer, natural orange juice, red wine and artificial orange juice.

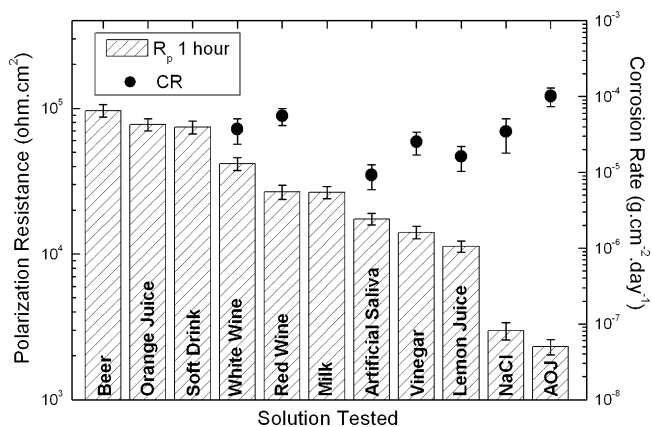


Fig. 3. Polarization resistance ( $R_p$ ) in decreasing order and corrosion rates (CR) computed from the weight loss measurements.

red wine and artificial orange juice showed an increase in current at approximately  $0.2 V_{SHE}$  and then the current decreased, particularly in the orange juice solutions. SEM observations of the specimens after the polarization tests showed that those specimens tested in milk and artificial saliva had undergone pitting, as suggested by the curves in Fig. 2. In those specimens tested in NaCl, lemon juice and vinegar the microstructure (grain boundaries) was clearly seen and the attack followed certain crystallographic planes. In the other solutions the attack was uniform and, in particular, the specimens exposed to beer showed very little signs of corrosive attack.

$R_p$  measurements were performed during 24 h to follow the evolution of this parameter with time. In general it was found that  $R_p$  increases with time (with the exception of vinegar), indicating that the alloy is undergoing some kind of passivation and the corrosion current is decreasing with time. Considering that the beverages under study are usually in contact with the dental alloy only for a short period of time, and the fact that  $R_p$  reaches the lowest values (highest corrosion currents) immediately after immersion, the values of  $R_p$  measured after an hour were considered. These values (mean and standard deviation) are plotted in a histogram (Fig. 3), ranking the solutions due to their  $R_p$  values in decreasing order as follows: beer, orange juice, soft drink, white wine, red wine, milk, artificial saliva, vinegar, lemon juice, NaCl 1 M, artificial orange juice.

Weight loss (WL) measurements were performed after 7, 15 and 30 days of immersion and corrosion rates (CR), expressed as  $g(cm^2 day)^{-1}$  were calculated. Results (mean CR and standard deviation over 3 different measurements in each solution) are shown in Table 2. It was found that the corrosion rates decreased with time, save in the case of lemon juice in which a slight increase was observed. With the purpose of correlating the measured corrosion rates with the polarization resistance values obtained after 1-h immersion, the corrosion rate values were extrapolated to 1 h. These values are plotted in Fig. 3.

Table 2

Mean corrosion rates (CR) and standard deviation expressed as  $g(cm^2 day)^{-1}$  after 7, 15 and 30 days of immersion to the solutions.

Solution	7 days	15 days	30 days
NaCl 1 M	$2.87 \times 10^{-5} \pm 0.29 \times 10^{-5}$	$1.76 \times 10^{-5} \pm 0.07 \times 10^{-5}$	$1.01 \times 10^{-5} \pm 0.09 \times 10^{-5}$
Artificial saliva	$8.02 \times 10^{-6} \pm 3.19 \times 10^{-6}$	$6.79 \times 10^{-6} \pm 0.89 \times 10^{-6}$	$5.22 \times 10^{-6} \pm 0.57 \times 10^{-6}$
Vinegar	$2.06 \times 10^{-5} \pm 0.16 \times 10^{-5}$	$1.32 \times 10^{-5} \pm 0.04 \times 10^{-5}$	$7.59 \times 10^{-6} \pm 0.88 \times 10^{-6}$
White wine	$3.42 \times 10^{-5} \pm 1.22 \times 10^{-5}$	$2.92 \times 10^{-5} \pm 1.65 \times 10^{-5}$	$2.00 \times 10^{-5} \pm 0.84 \times 10^{-5}$
Red wine	$7.10 \times 10^{-5} \pm 3.82 \times 10^{-5}$	$4.52 \times 10^{-5} \pm 1.77 \times 10^{-5}$	$3.17 \times 10^{-5} \pm 0.86 \times 10^{-5}$
Lemon juice	$2.53 \times 10^{-5} \pm 0.38 \times 10^{-5}$	$3.89 \times 10^{-5} \pm 0.07 \times 10^{-5}$	$6.06 \times 10^{-5} \pm 0.23 \times 10^{-5}$
Artificial orange juice	$8.28 \times 10^{-5} \pm 2.23 \times 10^{-5}$	$4.47 \times 10^{-5} \pm 1.09 \times 10^{-5}$	$2.81 \times 10^{-5} \pm 0.52 \times 10^{-5}$

#### 4. Discussion

The  $R_p$  values of the aluminum–bronze alloy measured in this work were compared to other dental alloys in a similar electrolyte. It was found that a wide range of  $R_p$  values may be obtained. For example, Eschler et al. [8] reported  $R_p$  values for two different copper–aluminum bronze alloys in an artificial saliva of the Fusayama type of 4.3 and  $6.1 k\Omega cm^2$  (somewhat low compared to the value of  $15 k\Omega cm^2$  obtained in the present work in an artificial saliva of different composition). Al-Hity et al. [9] studied the corrosion behaviour of eight different dental alloys (high-noble alloys, noble alloys and base metal alloys) in Fusayama artificial saliva and they reported  $R_p$  values ranging from 29 to  $281 k\Omega cm^2$  (all these values are higher than the one obtained in the present work in artificial saliva, showing that all the alloys tested by these authors are more noble than the aluminum–bronze tested in the present work, as is evident from the composition analysis in [9]). In another study [10],  $R_p$  values for an amalgam alloy tested in a NaCl 0.9% solution varied from 1.6 to  $15 k\Omega cm^2$ . Some *in vivo*  $R_p$  measurements are also found in the literature [11], obtained by means of a specific set-up recently developed. The study was performed on six different dental alloys (Co-based alloys, Ni-based alloys, Pd–Ag alloys, and Au alloys) and  $R_p$  values ranged from 1.5 to  $100 k\Omega cm^2$ .

Following earlier studies done by other authors [9] and despite the differences in the corrosion behaviour resulting from differences in the dental alloys employed or in the test solutions used, a correlation between two quantitative characterizations of the corrosion behaviour was investigated. The two quantitative characterizations were the polarization resistance and the corrosion rates. Fig. 3 shows that there is no correlation between these magnitudes. The existence of such a correlation was proved for different dental alloys tested in a unique solution (artificial saliva) in [9]. In the present work a similar correlation was investigated for a given alloy (aluminum bronze) in different solutions with a negative result.

Then, it can be inferred that in those solutions in which no weight loss measurements for long periods of time were possible due to the characteristics of the solutions (natural orange juice, milk and fizzy drinks), the corrosion rates cannot be estimated. From the present work the ranking of increasing aggressiveness must be taken from the corrosion rate values (Fig. 3) and is as follows: artificial saliva, lemon juice, vinegar, 1 M NaCl, white wine, red wine and artificial orange juice.

The corrosion rates (CR) computed from the weight loss (WL) measurements can be converted to corrosion current densities ( $i_{corr}$ ) through the Faraday's Law:

$$CR = ki_{corr} \quad (1)$$

where the constant  $k$  contains the electrochemical equivalent weight of the alloy and the Faraday constant ( $96,500 C equiv^{-1}$ ). On the other hand, according to the Stern–Geary equation, the corrosion current density is also related to the polarization resistance:

$$i_{corr} = \frac{B}{R_p} \quad (2)$$

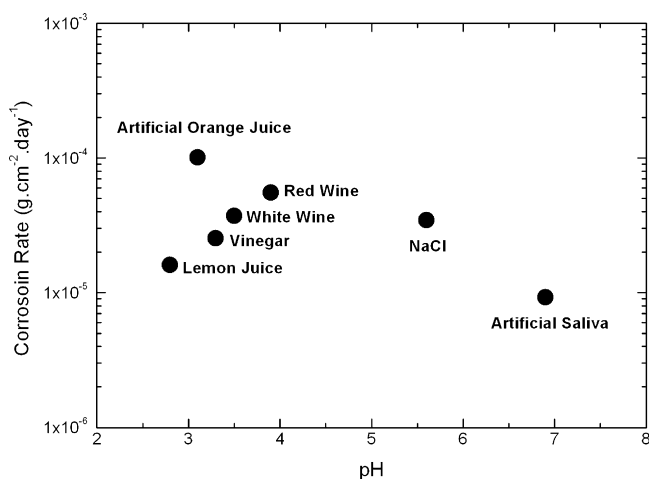


Fig. 4. Mean corrosion rate values as a function of the pH of the solution.

where  $B$  depends on the anodic and cathodic Tafel slopes of the system. From Eqs. (1) and (2) the following relation between corrosion rates and polarization resistance is obtained:

$$CR = \frac{B}{k} \frac{1}{R_p} \quad (3)$$

For a given alloy, tested in different solutions there is no reason *a priori* to expect a relation between CR and  $R_p$  because  $B$  values are highly dependant on the electrochemical behaviour of the metal/environment system. Values of  $B$  ranging from 10 to 95 mV are found in literature. In particular,  $B$  can vary as much as five times its value for a given material when changing the solution [12].

All of the ingredients found in foods and drinks contain chemicals that may become dissolved in saliva and affect the tarnish and corrosion of metallic materials. Some of these include various organic acids, such as acetic, lactic, tartaric, oleic, ascorbic, fumaric, maleic, and succinic, as well as sulfates, chlorides, nitrates, sulfides, acetates, urea, and the nutrients themselves of lipids, carbohydrates, proteins, vitamins, and minerals [6]. The interactions of the various compounds contained in drinks are complex and probably synergetic. As a consequence, it is difficult to assess the particular effect of each of the drinks studied in the present work on the material behaviour, namely what specific effect may have the components of each beverage on the corrosion susceptibility of the alloy.

The acidity of the environment (low pH values) sometimes shifts the electrochemical equilibrium towards unfavourable conditions, increasing the corrosion rate. In order to investigate whether there is a correlation between the corrosion rates and the pH of the solutions, the mean corrosion rate values were plotted as a function of the pH (Fig. 4). No such correlation was found. For instance, liquids that showed similar corrosion rates as lemon juice and artificial saliva differ in almost 4 units of pH. Similarly, solutions with almost the same pH as lemon juice and artificial orange juice yielded corrosion rates that differ in almost an order of magnitude. The same lack of correlation was obtained between the corrosion rates and the electrical conductivity of the solutions.

The beverages studied showed higher corrosion rates than artificial saliva but the increase in this magnitude was at most one order of magnitude (in the case of artificial orange juice). It is considered that this difference is not relevant for the odontological use taking into account the short time (much less than one order of magnitude of the total time that the dental alloys are in contact with saliva) that beverages are in contact with dental alloys in the oral environment. Then, for aluminum–bronze dental alloys the effect of different beverages and drinks on the corrosion behaviour is not a limiting factor for their use.

## 5. Conclusions

From the present work the following conclusions can be drawn:

- (1) No correlation between polarization resistance measurements and corrosion rates was found in the different solutions tested, a fact that can be explained on an electrochemical basis.
- (2) The ranking of aggressiveness of the different beverages and solutions studied is given by the corrosion rate and it is as follows: artificial saliva, lemon juice, vinegar, 1 M NaCl, white wine, red wine and artificial orange juice.
- (3) The aggressiveness of the different liquids is independent of both the pH and electrical conductivity of the solution.
- (4) The most aggressive beverage (artificial orange juice) generates a corrosion rate only 1 order of magnitude higher than that of saliva. This difference is not relevant for the odontological use considering the short time that beverages are in contact with dental alloys in the oral environment.

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