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Original article

Comparative corrosion behavior of different types of electrodes in orange juice, tea and honey solutions for usage in dental applications

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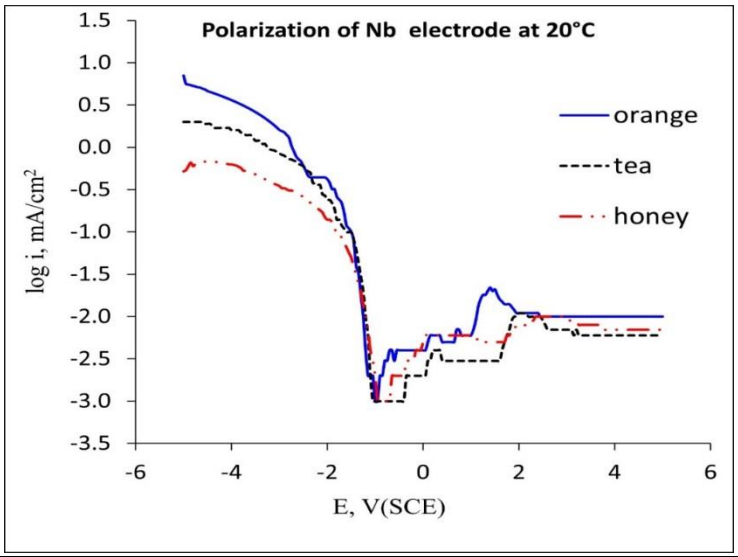
ABSTRACT

The corrosion effect of natural orange fruit juice, tea, and honey solutions on the corrosion of Au, Nb, Mo, and CoCr-alloy electrodes has been investigated to determine which material is best suited for use in each environment. The samples of the three solutions were subjugated to different Egyptian standard specifications and did not exceed the permissible limits. Open circuit potential (OCP) and potentiodynamic polarization (PDP) techniques were used. In the OCP technique, the potential was measured at different intervals of time for a total exposure of 90 minutes, and the rest potentials (E_{res}) were determined. The obtained results revealed that the values of E_{res} had a characteristic order at each temperature, and its values in all solutions decreased with increasing temperature for Au, Mo, and CoCr-alloy electrodes. Under the PDP technique, the corrosion rates (C_R) for all electrodes rose as the temperature increased. In orange juice, the electrodes follow this descending order at all temperatures: Nb > CoCr-alloy > Mo > Au. In tea and honey solutions the descending order was: CoCr-alloy > Nb > Mo > Au, at all temperatures. The apparent activation energies and the enthalpies of the corrosion process were positive in all conditions, reflecting the endothermic nature of the dissolution process for all electrodes, except for Mo in honey solutions. Values of entropy for all electrodes equaled -197 J/mol K.

Graphical abstract



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1. Introduction

The choice of dental materials, including metals and alloys, is influenced by their mechanical properties, biocompatibility, and resistance to corrosion. Fruits contain substances that can be corrosive, and can significantly affect the degradation of dental materials. Oranges (Citrus sinensis) are well-known for their vitamin C content and other components. There is no definite formula for orange juice because it is a mixture of numerous ingredients. It is mostly composed of water, glucose, and trace amounts of many minerals. A study by Afolabi *et al.* [1] analyzed the organic acids in orange juice, finding concentrations of Ascorbic, Citric, Malic, Lactic, Tartaric, and Oxalic acids at 0.652, 14.012, 1.525, 1.913, 0.382, and 0.105 g/L, respectively. It is clear from the analysis that citric acid is the predominant acid, making orange a citrus fruit [2]. Honey derives its sweetness from the monosaccharides fructose and glucose [3]. The honey analysis by Subramanian *et al* shows: Fructose: 38.2%, Glucose: 31.3%, Maltose: 7.1%, Sucrose: 1.3%, Water: 17.2%, Higher sugars: 1.5%, Ash: 0.2%, Other/undetermined: 3.2% and contains only minimal quantities of vitamins, minerals and antioxidants [4]. The water content, pH, acidity, protein content, and total metal content were determined by Dobrinas *et al.* [5]. In terms of flavor and color, polyphenols are some of the most significant chemical components of tea (*Camellia sinensis*). In unoxidized green tea, catechin chemicals account for 27% of the content; in black tea, they are reduced to approximately 4% as a result of oxidation. Black tea's color and flavor are influenced by polyphenols, which are the oxidation products of catechins. [6, 7]. The pH measurements of orange juice, honey, and tea solutions recorded the values 3.5, 4, and 5 respectively. When consumed, these acidic solutions can potentially cause degradation of dental bridges, crowns, or implants if present in the mouth.

Gold is chemically stable and does not oxidize or ionize, meaning it rarely develops chemical or biological products on its surface. As a result, gold typically maintains its luster for extended periods, whether exposed to air or submerged in solutions [8]. Banerjee [9] assessed the distinctive properties of gold alloys as traditional materials for dental restorations. Molybdenum and niobium, known for their potential to resist creep and fatigue, have been extensively tested as biocompatible materials [10]. They form highly stable oxide layers in aqueous environments, contributing to their biocompatibility [11-13]. Since 1929, cobalt-chromium-molybdenum alloys have been employed in dentistry for frameworks of removable dentures and, more recently, for cast restorations [14].

These alloys consist of the specified elements along with small amounts of nickel, manganese, and carbon. The combination of these elements strengthens the alloy four times greater than that of compact bone [15]. Cobalt enhances the alloy's elasticity and strength, while chromium offers resistance to tarnish and corrosion; however, chromium levels exceeding 29% can cause brittleness and complicate the casting process [16]. Uriciuc *et al.* [17] examined five different commercial CoCr dental alloys using electrochemical methods. Their analysis revealed that all five alloys formed a stable oxide layer on their surfaces. However, the alloy with higher levels of tungsten and iron exhibited a greater tendency to undergo anodic oxidation.

Thus, when metallic components are used at high temperatures in harsh environments, their durability is determined by the presence of a protective surface layer that acts as a defense against reactive substances. This study investigates the corrosion behavior of Nb, Mo, and CoCr-alloys compared to the Au electrode when exposed to orange juice, honey, and tea solutions at various temperatures. The goal is to determine which electrode is best suited for use in these environments.

2. Materials and methods

2.1. Preparation of electrodes

The cylindrical working electrodes were made of pure molybdenum and niobium metals with surface areas of 0.196 and 0.33 cm², respectively. A CoCr-alloy electrode, also in the shape of a cylinder, has a surface area of 1.038 cm² made up of 64% Cobalt, 28% Chromium, 6% Molybdenum, and 2% (Carbon + Silicon + Manganese). A golden cylinder with a surface area of 0.0184 cm² and composed of 98.2% Gold, 1.7% Titanium, and 0.1% Iridium was used as a blank electrode.

Each electrode was affixed with Araldite epoxy glue into a hollow glass cylinder of the correct size, ensuring only the surface area touched the test solution. The electrode surfaces were smoothed using emery papers with progressively higher grit levels. Bi-distilled water was utilized for rinsing the electrodes to eliminate any slick particles. After that, the electrodes' surfaces were polished again using a soft cloth before they were fully immersed in the test solutions.

2.2. Solutions

Extraction of the juice from the orange was achieved by cutting and squeezing. To remove pulp and seeds, the juice was strained into a vacant container until reaching the required volume and was utilized undiluted. A 5g honey (Nawarat El-Barseem) completed to 100 ml tap water was used as a honey solution. A tea solution (El-Arosa) was prepared by adding 1g of black tea to 100 ml of boiling tap water and letting the solution settle. When the tea solution reached the desired temperature, it was filtered from tea leaves through a tea strainer. The power of hydrogen in the tested solutions was determined using the pH-meter Model (WTW pH 530). The recorded pH values were 3.5, 4, and 5 for orange juice, honey, and tea solutions respectively.

2.3. Analysis of solutions

The Chemical-preservative analyses for sorbic and benzoic acids and their salts were performed using HPLC-thermo. Heavy metal chemical analysis was performed using atomic absorption. Sweeteners, colors, bactericides, and toxicological herbicides analyses were detected by

LC/MS/MS instrument. Total solids were detected by refractometer, Abbemat, 550, Anton Paar, 2016.

2.4. Experimental techniques

2.4.1. Measurements of the open circuit potential (OCP)

OCP measurements were conducted in a glass cell with a capacity of 25ml solution. The saturated calomel electrode (SCE) and a digital multimeter (KEITHLEY, Model 175, USA) were used to obtain the potential readings. The electrode potentials were measured for 90 minutes at temperatures of 20, 30, 40, and 50°C.

2.4.2. Measurements of the potentiodynamic polarization

A model POS 73 Electronic Potentioscan Wenking was employed for measuring potentiodynamic polarization. Measurements were conducted with a platinum sheet used as a supporting electrode and with a saturated calomel electrode (SCE). The four tested electrodes underwent polarization by being scanned at a rate of 3.33 mV/s from -5 to +5 V/SCE, and the resulting currents were recorded. To obtain the stabilized OCP value, the electrodes were immersed in the test solution for 90 minutes before taking measurements.

3. Results and Discussion

3.1. Solutions analyses get down to human health.

3.1.1. Orange juice analysis

Three different samples of orange juice were subjected to different analyses which got down to human health. The orange extracts were subjected to microbiological (not included in this research) and chemical analysis. Concerning the chemical analyses, the three samples were positive towards citric acid detection, and the percentages of total solids were equal to 9, 10 and 16%. Thus, the three samples illustrate bacteriological and chemical identity with the standard specification 7650 for the year 2013.

Preservative analyses, which deal with the detection of sulfur dioxide, benzoic acid, sorbic acid, and their salts, all illustrate negative results. LC/MS/MS instrument which was used to detect Aspartame, Acesulfame k, Saccharin, Sucralose, and Sodium Cyclamates illustrated negative results. Thus, the analyses prove the identity of the orange samples with the decision 4- 2020 for the mentioned additives. The results of heavy metal chemical analysis (detection of lead) were negative, and the samples agreed with the standard specification 7136-2010 and its modification for lead element. The results of herbicide analyses were lower than 0.01mg/kg where the samples complied with the Egyptian specification 7136-2020. Thus, the three samples obeyed the Egyptian standard specifications and did not exceed the permissible limits.

3.1.2. Tea analysis

A tea sample was subjected to chemical (from 1 to 3 in Table 1), and heavy metals analyses (from 4 to 6 in Table 1) in which the sample agreed with the standard specification 559 for the year 2020. Preservative analyses (numbers 7 and 8 in Table 1) illustrated that the sample agreed with the decision 4-2020. There was no evidence of the presence of coloring agents in the sample (number 9 in Table 1).

Table 1: Results of chemical, heavy metals, preservatives and coloring analyses of tea sample

	Type of analysis	Data	Available range
1	Determination of iron fillings	< 150	150 mg/kg
2	Determination of Ash	5.9	4-8 %
3	Determination of ash soluble in water	40.0	UP to 45% from total ash
4	Pb	-ve	4 mg/kg
5	As	-ve	1 mg/kg
6	Cu	13.9	50 mg/kg
7	Detection of benzoic acid and its salts	-ve	1000 mg/kg
8	Detection of sorbic acid and its salts	-ve	500 mg/kg
9	Detection of color	-ve	-ve

3.1.3. Honey Analysis

The honey sample was subjected to different types of analyses which get down to human health. The plant source of honey was Trefoil (Clovers). Concerning the chemical analyses, the percentages of sucrose and humidity were 5.0% and 19.5% respectively. The sample had pH 1.1, and the detection of hydroxy methyl furfural illustrated 30.0 ppm. On the other hand, the starch, dextrin, added sucrose and commercial glucose were not detected. After subjection to the microbiological analysis, the sample agreed bacteriologically and chemically with the standard specification 355 for the year 2005.

Preservative analyses concerned with the detection of sulfur dioxide, benzoic acid, sorbic acid, and their salts all illustrate negative results. Commercial sweeteners of Aspartame, Acesulfame k, Saccharin, Sucralose, and Sodium Cyclamates which were detected by LC/HRMs instrument all illustrate negative results. The results of heavy metal chemical analysis (detection of lead) were negative, and the sample agreed with the standard specifications 7136-2010 and its modification for lead element. The results of bactericides and toxicological herbicides analyses were lower than the reference range (LOQ = 0.01mg/kg). Thus, the sample obeyed the Egyptian standard specifications and did not exceed the permissible limits.

3.2. Open circuit potential measurements

3.2.1. Effect of time on the electrode's potentials

The variations of open circuit potential (OCP) with time at 30 °C for CoCr-alloy, gold, niobium, and molybdenum electrodes carried out in orange juice, tea, and honey solutions are presented in Figures (1 – 3). The positive potential shifts in CoCr-alloy, Mo, and Nb electrodes indicated spontaneous passivation of electrode surfaces over time, attributed to oxide film formation [18]. However, the Au electrode experiences a negative potential shift over time in the orange juice and tea solution which suggests the electrode is dissolving, while in the honey solution, it

acquires a positive potential shift. Figures 1 and 2 also showed that, despite gold dissolving within the initial 30 minutes, it exhibited the highest potential values across all electrodes, indicating superior protective properties.

The increase in the potential of Mo electrode in acidic solutions agrees with the creation of stable MoO_2 together with $Mo(OH)_3$ and MoO_3. Molybdenum trioxide may be reduced to Mo_2O_5 according to Eq.(1) [12, 19].

$$2MoO_3 + 2H^+ + 2e^- \rightarrow Mo_2O_5 + H_2O \quad (1)$$

In the case of CoCr-alloy electrode, the passivity, indicated by positive potential shift, was brought on by the development of a thermodynamically stable passive oxide film (Cr_2O_3) rich in chromium at the electrode surface, as shown by reaction (2) [20].

$$2Cr + 3H_2O \rightarrow Cr_2O_3 + 6H^+ + 6e^- \; E^\circ = 0.9927V \quad (2)$$

The biocompatibility of CoCr- alloy is closely related to its excellent corrosion resistance, which results from the spontaneous development of a passive oxide film.

A shift in Nb potential towards a positive direction was explained by its extremely high reactivity with water, which in accordance with reaction (3), produces the protective pentoxide film in which Nb atoms have the lowest energy state [21].

$$2Nb + 5H_2O \rightarrow Nb_2O_5 + 10H^+ + 10\,e^- \; E^o = -0.644V \quad (3)$$

The negative potential shift over time observed for Au electrode in orange juice and tea solution suggests the dissolution of the electrode. This dissolution may be due to the large difference in electrochemical potentials between the elements constituting the electrode; gold (98.2%), titanium (1.7%) and iridium (0.1%) as illustrated in the following equations [22]:

$$Au^+ + e^- \rightleftharpoons Au \qquad E^o = +1.69\,V \quad (4)$$
$$Au^{3+} + 3e^- \rightleftharpoons Au \qquad E^o = +1.40\,V \quad (5)$$
$$Ti^{3+} + e^- \rightleftharpoons Ti^{2+} \qquad E^o = -0.37\,V \quad (6)$$
$$Ti^{4+} + e^- \rightleftharpoons Ti^{3+} \qquad E^o = 0.00\,V \quad (7)$$
$$Ir^{3+} + 3e^- \rightleftharpoons Ir \qquad E^o = 1.156\,V \quad (8)$$

According to equations (4–8), corrosion in gold electrode occurs primarily in titanium-rich regions and secondarily in iridium-rich regions. Galvanic microcells can form in the multi-phase electrode, where the more active phase corrodes with respect to the noble matrix [23]. As a result, the chemical composition of the Au electrode, along with the low pH of the tested solutions, significantly affects its corrosion resistance and may be the primary cause of the dissolution seen in the orange juice and tea solution.

In orange juice, the Mo electrode reached the same potential as the gold electrode after being immersed for a certain time. At this point, the time and potential are called critical immersion time (CIT) and critical potential (CP). The CIT were 20, 70, and 80 minutes at 20, 30, and 40°C, with CP of 153, 140 and 124 mV/SCE, respectively. The consistency between Mo and Au potentials was not observed at 50°C. It was noticed that as the temperature of the juice rose, the CIT grew longer and the CP got lower. At 20 and 30°C, after passing CIT, the Mo electrode's potential slightly exceeded that of Au electrode.

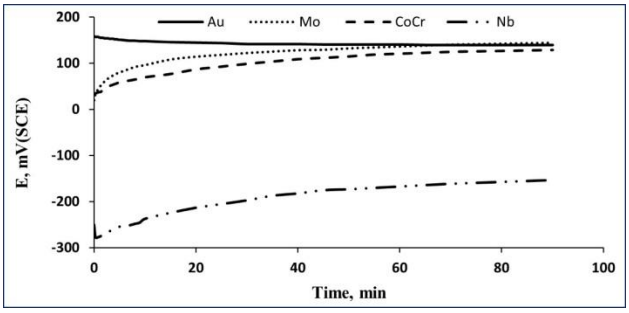

Figure 1: Potential–time curves of the four studied electrodes in orange solution at 30 °C.

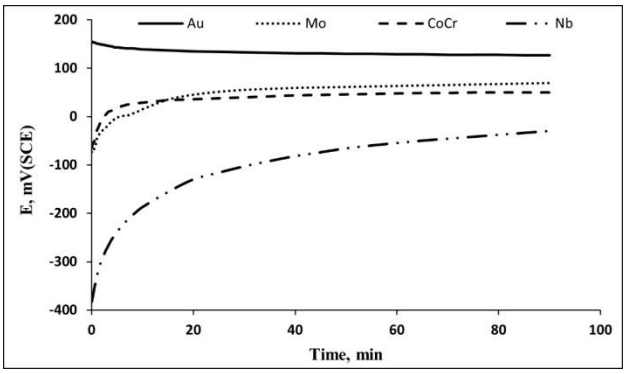

Figure 2: Potential–time curves of the four studied electrodes in tea solution at 30 °C.

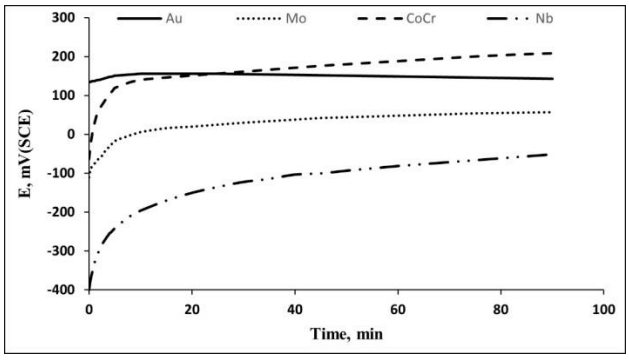

Figure 3: Potential–time curves of the four studied electrodes in honey solution at 30 °C.

In addition to citric, malic, tartaric, and oxalic acids, Olusegun *et al.*'s analysis of orange juices demonstrated the existence of other organic acids, including benzoic, succinic, formic acids, and others. Aspartic acid, glutathione, histidine, betaine, cysteine, praline, serine, and others are examples of nitrogenous molecules that were also demonstrated to be present as free amino acids [2]. Organic compounds containing nitrogen can adsorb on the surfaces of active electrodes, such as Mo, blocking their active sites and raising their potential to a level that is comparable to that of the Au electrode. As the temperature rises, the concentration of ascorbic acid (vitamin C) decreases and is easily destroyed [24]. Also, the kinetic energy of the juice's component rose as well, which re-

sulted in a decrease in the adsorption process rate and an increase in the desorption process. As a result, it took the electrodes longer to overcome the desorption process and reach the critical potential. On the other hand, the effort consumed by the electrodes to overcome the desorption process affects negatively the value of the critical potential.

The curves of CoCr-alloy electrode immersed in honey solution (Figure 3) also showed a critical immersion time. After passing CIT, and at 30 °C, the potential of CoCr-alloy exceeded that of Au electrode by a significant amount. The CIT was 75, 25, 70, and 80 minutes with CP of 201, 156, 134 and 121 mV/SCE at 20, 30, 40 and 50°C respectively. The behavior of consistency of the potential of any electrode with that of Au potentials at a certain time was not recorded in the tea solution.

3.2.2. Effect of temperature on the rest potential

In the three tested solutions, the rest potential values (E_{res}) of Au, Mo, and CoCr-alloy electrodes decrease with increasing temperature as illustrated in Figures 4-6. Niobium electrode behaved similarly from 20 to 30 ºC, and reversibly from 30 to 50 ºC in orange juice. In tea and honey solutions, niobium's rest potential increased with increasing temperature. Figure 4 also illustrates that, E_{res} values of Mo and Au electrodes in orange juice were very close to each other. The rest potential values for molybdenum are: 160, 144, 126, and 106 mV(SCE). While, for gold are: 145, 140, 124, and 110 mV(SCE) at 20, 30, 40, and 50 ºC, respectively. Thus, at temperatures of 20, 30, and 40 ºC, the rest potential of the Mo electrode exceeded that of the Au electrode by 15, 4, and 2 mV(SCE), while at 50 ºC, the potential of the Mo electrode is lower than that of the Au electrode by 4 mV(SCE) only. This meant that Au may be replaced by Mo electrode in dental application in orange juice at these temperatures.

The difference in potentials between Mo and CoCr-alloy electrodes were 11, 15, 36, and 52 mV(SCE), while the difference in potentials between Mo and Nb electrodes were 305, 297, 233, and 203 at 20, 30, 40, and 50 ºC respectively. These potential shifts were ineffective between Mo and CoCr-alloy although it is increased with increasing temperature. Conversely, the potential shifts between Mo and Nb electrodes are very large and decrease with increasing temperature. This makes Nb electrode inappropriate to be used in orange juice. The CoCr-alloy and Mo electrodes in orange juice illustrated a linear relation between the rest potential and temperature. The regression coefficients of the linear relations were: 0.9835 and 0.9975 while the slopes of the straight lines were: -3.24 and -1.80 respectively. The more negative slope value of CoCr-alloy meant that increasing temperature has a wicked pronounced effect on the alloy in orange juice.

In tea solutions, Figure (5), the Au electrode had the most positive rest potential for all electrodes at all temperatures, which was followed by Mo electrode. CoCr-alloy followed Mo electrode in the passivity order at 20 and 30 ºC. While at 40 and 50 ºC, Nb electrode came after Mo electrode in the passivity order. This order indicated that the tendency for the formation of a protective oxide film is great for the Au electrode at all temperatures followed by Mo electrode and that these oxides have the best corrosion protection properties than the other oxides formed on Nb and CoCr-alloy in tea solutions.

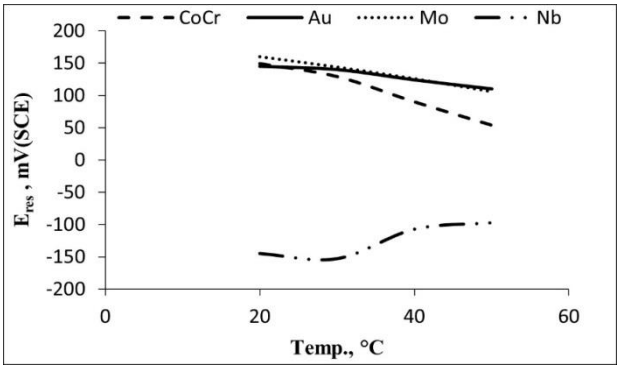

Figure 4: Dependence of the rest potential on the temperatures for the four electrodes in orange juice.

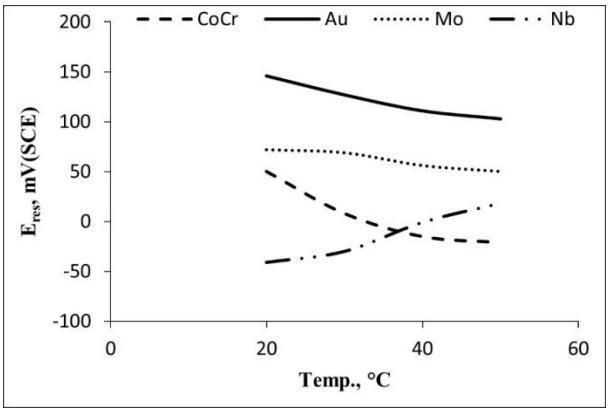

Figure 5: Dependence of the rest potential on the temperatures for the four electrodes in tea solution.

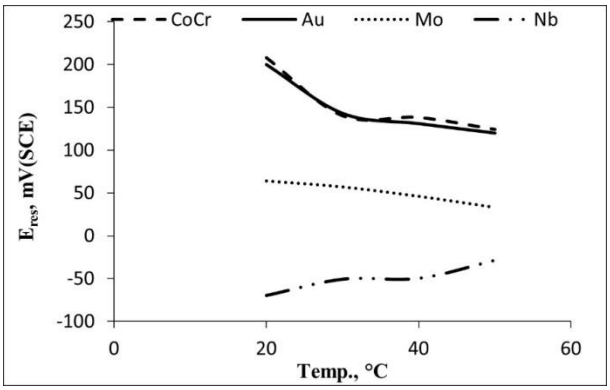

Figure 6: Dependence of the rest potential on the temperatures for the four electrodes in honey solution.

In honey solutions, Figure (6), the rest potentials of Au and CoCr-alloy electrodes are very close to each other at all temperatures and had higher rest potentials than the other electrodes. The rest potential values for CoCr-alloy are: 208, 140, 138, and 124, while for gold are: 200, 143, 131, and 120 mV (SCE) at 20, 30, 40, and 50 ºC respectively. Thus at temperatures of 20, 40, and 50 ºC, the potential of the CoCr-alloy electrode exceeded that of the Au electrode by 8, 7, and 4 mV(SCE), while at 30 ºC, the

potential of the CoCr-alloy electrode is lower than that of the Au electrode by 3 mV(SCE) only. This meant that Au may be replaced by CoCr-alloy for dental application in honey solution at the temperature range 20 – 50 ºC. The observed difference in rest potential values is moderate between Mo and each of Au and CoCr-alloy electrodes but was very large between Nb and Au or the alloy electrodes. This makes Nb electrode unsuitable to be used in honey solutions.

3.3. Potentiodynamic Polarization measurements

3.3.1. Potential – current curves

Potentiodynamic polarization plots (PDP) of the four electrodes in the orange juice, tea and honey solutions were studied at 20, 30, 40, and 50 ºC. Figures 7 – 9 display the PDP at 30 ºC. In the three solutions, the Au and Mo electrodes displayed normal Tafel behavior at all studied temperatures.

For the CoCr-alloy electrode, at specific temperatures, the anodic branches displayed passive regions located between the zero current potential (ZCP) and the breakdown potential (Eb). The existence of these inactive areas suggested the creation of protective films within these potential ranges. Zero current potential is defined as the voltage level at which the current achieves its lowest point during the forward potentiodynamic polarization scan [25].

The protective film breakdown took place in orange juices at 40 and 50 °C only. In tea solutions, this happened at 20, 30, and 40°C, while in honey solutions, this happened at all temperatures. The passive current density (Ip) was determined to correspond to the middle of the passive regions. Values of ZCP, Ip, and Eb for CoCr-alloy at different temperatures are presented in Table (2). The passive current density of the CoCr-alloy in all examined solutions rose as the temperature increased. It is widely recognized that if the metal exhibits a lower Ip over an extended potential range, it is deemed to have enhanced and more stable passivity [25]. Values of Ip indicate that CoCr-alloy has its best protective properties in honey followed by tea solutions each at 20°C.

The niobium electrode exhibited standard Tafel characteristics in the cathodic branch; however, when switched to the anodic direction, the Nb electrode stayed passive throughout the entire studied potential range, which is not consistent with Tafel's behavior. Niobium therefore creates a passive film that, when exposed to oxygen or water, self-heals and repairs. This passive film is of low electrical conductivity and grows gradually when the anodic potential increases with the installation of new films on top of the pre-existing ones [26].

The passive films that were created inhibited any redox reactions by avoiding direct contact between the crack surface and the solution [27]. This behavior was comparable to that observed for the Nb electrode in solutions of artificial saliva, meat soup, milk, and tap water [28-30]. In these situations, the cathodic polarization curves alone were used to determine the corrosion rates and corrosion current densities.

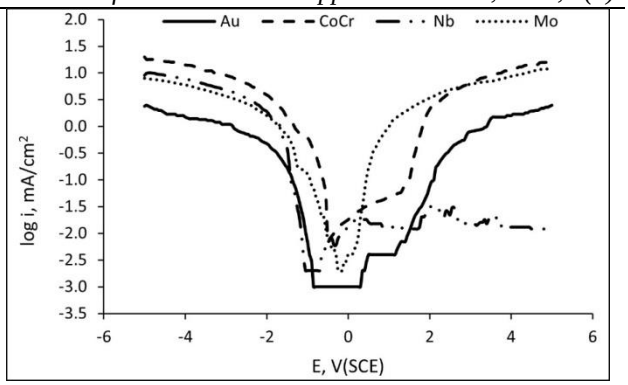

Figure 7: Potentiodynamic plot of CoCr-alloy, Nb, Mo, and Au electrodes in orange juice at 30°C.

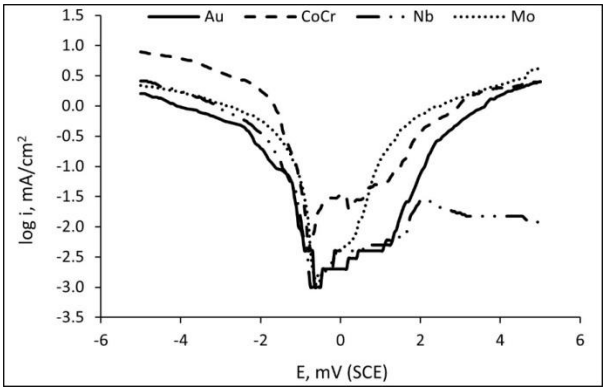

Figure 8: Potentiodynamic plot of CoCr-alloy, Nb, Mo, and Au electrodes in tea solution at 30°C.

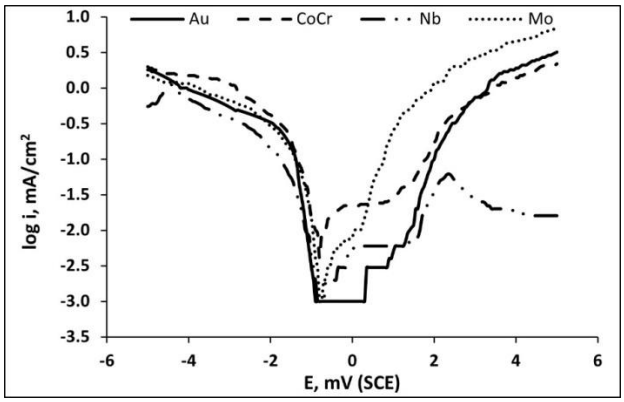

Figure 9: Potentiodynamic plot of CoCr-alloy, Nb, Mo, and Au electrodes in honey solution at 30°C.

The behavior of Nb electrode in orange juice, tea, and honey solutions at the studied temperatures was illustrated in Figure 10. The figure illustrated the presence of passive regions in the anodic branches of the curves. The potential range of the passive regions of niobium electrode in the three solutions is illustrated in Table (3).

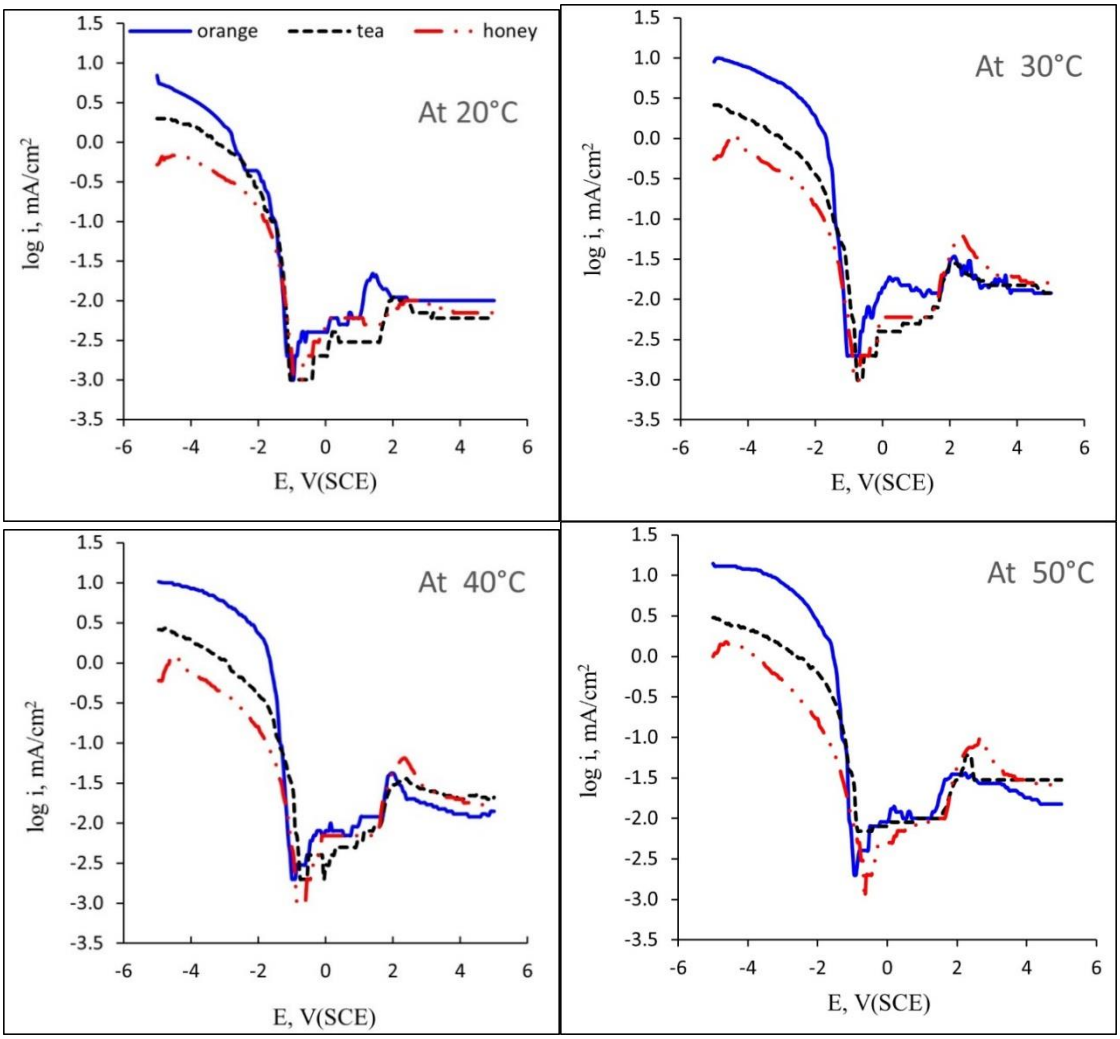

Figure 10: Potentiodynamic plots of Nb electrode in the different tested solutions at different temperatures.

The extension of niobium passive regions in different potential ranges at different temperatures can be attributed to the formation of surface layers of dense, adhesive niobium-stable oxides which act as a corrosion barrier on the surface of the electrode [31]. It can be detected from Table 3 that the potential range of the passive regions in honey solutions is more extended than that recorded in orange juices at all temperatures, and more extended than that recorded in tea solutions at 20, 40, and 50 °C and the least extending potential range was detected in tea solutions at 20, 40 and 50 °C.

The more extends in the potential ranges of the passive regions meaning increasing in the stability of the protective layers formed on the electrode surface.

Thus, the most protective layers formed on the surface of the Nb electrode in the tested solutions were constructed according to the following order:

honey > orange > tea at 20, 40, 50°C

tea > honey > orange at 30°C

Table (2): Analysis of the polarization curves for CoCr- alloy in orange juice, tea, and honey solutions.

Solution	Temp. °C	ZCP mV(SCE)	Ip µA/cm²	Eb mV(SCE)
Orange	20	-500	-	-
	30	-500	-	-
	40	-400	35.0	900
	50	-350	49.0	1300
Tea	20	-700	17.8	400
	30	-800	31.6	1050
	40	-850	50.0	1100
	50	-750	-	-
Honey	20	-750	15.8	1400
	30	-800	22.4	1000
	40	-850	39.8	1050
	50	-850	39.8	950

Anodic current peaks, following all the passive regions, were also observed in the Nb polarization curves. All peaks reached their maximum falling-out at a definite potential at a specific temperature. The growth of the

anodic peak indicated the rupture of the previously formed oxide layers in the passive region. For Nb in orange juices, the anodic peaks largely flattened at 30 and 50 °C. The same behavior was observed in honey solution at 20°C. The little increase in current density may considered as a decrease in protective properties of the passivating layers. The potentials ($E_{P_{max}}$) and current density ($I_{P_{max}}$) at which the anodic peaks reached their maximum values are illustrated in Table 3.

Table (3): Values of Passive potential ranges, the maximum potentials ($E_{P_{max}}$) and current density ($I_{P_{max}}$) peaks and film thickness on the Nb electrode at different temperatures.

Type of Solution	Temp. °C	Passive potential ranges, mV(SCE).	$E_{P_{max}}$, V(SCE)	$I_{P_{max}}$, μA/cm^2	d, nm
orange	20	-500 – 1000	1.400	22	10.17
	30	330 – 1700	2.125	34	11.10
	40	250 – 1700	1.975	42	18.49
	50	350 – 1250	1.950	35	24.96
Tea	20	350 – 1600	2.075	11	6.47
	30	-150 –1700	2.100	28	14.79
	40	300 –1500	2.400	36	19.41
	50	700 –1550	2.325	60	27.73
Honey	20	100 –1700	2.625	10	7.39
	30	100 – 1600	2.350	62	22.18
	40	-100 –1600	2.350	65	16.64
	50	-200 –1650	2.675	98	27.73

Table (4): Potentiodynamic characteristics of the different electrodes in orange juice, tea and honey solution instead of different electrodes in orange juice

		Orange		Tea		Honey	
Electrode type	Temp. °C	E_{corr} mV(SCE)	C_R mpy	E_{corr} mV(SCE)	C_R mpy	E_{corr} mV(SCE)	C_R mpy
Au	20	400	1.29E-06	600	1.02E-06	-100	1.63E-06
	30	300	3.24E-06	400	2.05E-06	-200	3.24E-06
	40	100	5.13E-06	300	4.08E-06	-300	4.08E-06
	50	-100	6.46E-06	200	5.14E-06	-300	6.47E-06
CoCr-	20	200	1.23E-02	200	1.94E-02	-100	1.94E-02
	30	100	3.08E-02	100	4.88E-02	-300	2.45E-02
	40	100	4.87E-02	-200	7.74E-02	-350	3.08E-02
	50	100	1.23E-01	-300	9.74E-02	-400	4.88E-02
Mo	20	-100	2.02E-03	-400	5.08E-03	-300	5.06E-03
	30	-200	3.22E-03	-400	8.05E-03	-500	1.01E-02
	40	-300	6.39E-03	-600	1.01E-02	-600	1.27E-02
	50	-300	1.01E-02	-700	2.55E-02	-650	1.60E-02
Nb	20	-900	5.62E-02	-700	2.82E-02	-800	1.41E-02
	30	-900	8.90E-02	-700	3.54E-02	-800	1.78E-02
	40	-900	2.24E-01	-700	4.46E-02	-800	2.24E-02
	50	-900	3.54E-01	-700	7.07E-02	-650	2.82E-02

All the anodic peaks are followed by passive regions indicating the reformation of new passive films. The thickness *d* of the passive films was determined by using Faraday's law (Eq. 9):

$$d = \frac{q \cdot M}{n \cdot F \cdot \rho} \quad (9)$$

where *d is* the film thickness (cm/V), q is the amount of charge crossed the film, M is the molecular weight of the passive film, n is the number of electrons exchanged, ρ is the density of a presumed homogeneous oxide film and *F* is the Faraday constant. In our case, and according to reaction (3), the passive film is supposed to be Nb_2O_5. Consequently M = 265.8 g/mol, n = 10, and ρ = 4.47 g/cm^3. The values of film thickness were calculated at potentials corresponding to the first stability in current density subsequent to the anodic peak and tabulated in Table 3.

It is clear from the data in Table 3 that the passive film thickness increased with increasing temperature. One exception was observed in the honey solution at 40 °C. These results indicated that Nb passive film was greatly affected by the type of solution and degree of temperature.

The respective potentiodynamic parameters including corrosion potentials (E_{corr}) and corrosion rates (C_R), for

the different electrodes in orange juice, tea, and honey solutions are tabulated in Table 4. The corrosion rates in mpy were computed using equation 10.

$$C_R = 0.13 \times I_{corr} \times e/d \qquad (10)$$

where 0.13 is the metric and time conversion factor, I_{corr}, is the corrosion current density in mA/cm², e is the equivalent weight of metal in g. Eq/mol and d is its density in g/cm^3.

Examination of the data in Table 4 showed that in each examined solution, the Au electrode had the highest corrosion potentials (E_{corr}) while the Nb electrode had the lowest potentials. Alternatively, there were huge differences between the corrosion rate values of Au electrode and the survivor electrodes. The sequence of corrosion rates decreasing in orange juice for the different electrodes was: Nb > CoCr- alloy > Mo > Au, while in tea and honey solutions was: CoCr- alloy > Nb > Mo > Au. These orders functioned effectively in all temperatures. This makes Nb metal the least practical electrode in orange juice, while CoCr- alloy is the least practical electrode in tea and honey solutions. In terms of electrochemistry and according to the galvanic series, Mo is slightly more noble than Nb, and both are less noble than Au. It can be anticipated that the Mo electrode will offer superior corrosion resistance compared to Nb and CoCr-alloy electrodes.

For Nb electrode, the greatest corrosion rates were recorded in orange juice at all temperatures. pH measurements of the three solutions illustrate the following values: 3.5, 4.0, and 5.0 for orange juice, honey, and tea solutions respectively. Therefore, it is likely that orange juice has a higher concentration of acidic ions with lower pH compared to honey and tea solutions. This could certainly greatly influence the breakdown of passivating oxide layers on the Nb electrode, resulting in a quicker corrosion rate [1].

Comparing the behavior of the tested electrodes in orange and lemon solutions, Attia *et al* [32] demonstrated higher corrosion rates of the same electrodes immersed in lemon solution. The high amount of citric acid in lemon (4 to 8% of citric acid by weight) compared to that in orange (0.6 to 1% of citric acid by weight) was an important reason for rising C_R values as a general behavior in all electrodes, where citric acid is recognized as an oxidizing agent.

3.3.2. Effect of temperature on the corrosion rates of the different electrodes

The relationship between temperature and corrosion rate can be described using the well-known Arrhenius equation [30].

$$\log C_R = A - (E_a/2.303\,RT) \qquad (11)$$

In the above equation; the logarithm of the corrosion rate at a certain temperature equals the collision frequency factor (A) minus the activation energy of the dissolution reaction (E_a), divided by 2.303 times the universal gas constant (R) times the absolute temperature (T). Graphs of the corrosion rates in logarithmic form against the inverse of absolute temperatures produced linear patterns with slopes of $-(E_a/2.303\,R)$ as illustrated in Figures 11 – 13.

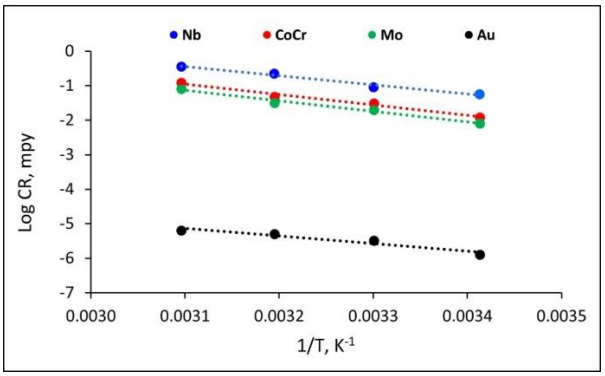

Figure 11: Arrhenius plots of the studied electrodes in orange juice.

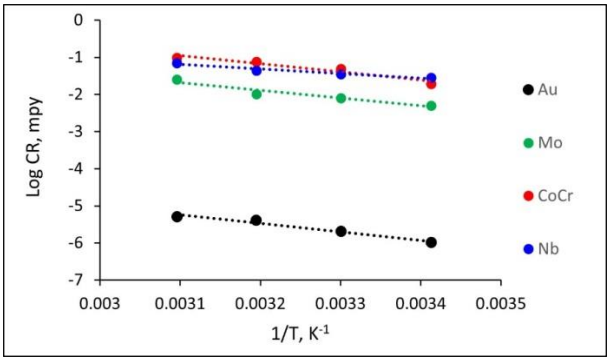

Figure 12: Arrhenius plots of the studied electrodes in tea solutions.

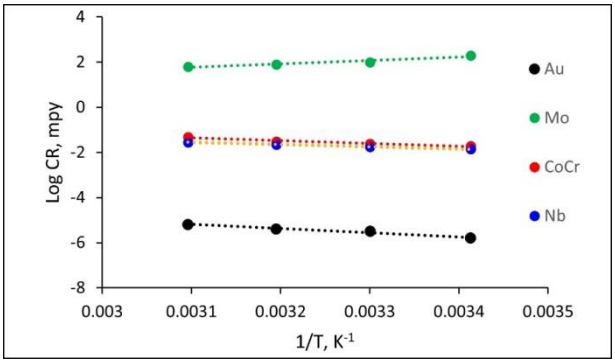

Figure 13: Arrhenius plots of the studied electrodes in honey solutions.

Arrhenius plots showed that the corrosion rates rose as temperatures increased for all electrodes at all solutions. One exception was recorded in the case of molybdenum electrode in honey solution. The rise in C_R with rising temperature happened because some of the extremely slow molecules constituting the juice, honey, or tea solutions acquire increased energy and thus, a much higher fraction of the molecules will be able to react, and extra molecules can surpass the energy barrier more quickly

leading to a high rate of corrosion. A rise in temperature can also enhance the solubility of the films adsorbed on the electrodes, leading to a higher susceptibility of the electrodes to corrosion. The kinetic parameters derived from the Arrhenius equation, and regression coefficients (R^2) are listed in Table 5.

Table 5 demonstrates that the activation energies for the dissolution processes of the passive films created on the CoCr-alloy and Mo electrodes in orange juice had an identical peak E_a values under all conditions. This indicates the relative difficulty of dissolving these passive films compared to those created on gold and niobium electrodes. The negative value of the collision frequency factor (A), and negative activation energy recorded for Mo electrode in honey solutions indicates that the process is exothermic and spontaneous. This means that the reaction occurs readily and quickly, without a significant energy barrier. This action may be attributable to the odd behavior of Mo electrode recorded with increasing temperature.

Table (5): Activation parameters for the different electrodes

Type of solution	Type of electrode	A	E_a, kJ/mol	R^2
Orange juice	Au	1.6	42.0	0.9346
	CoCr-alloy	8.4	58.0	0.9836
	Mo	8.2	58.0	0.9836
	Nb	7.7	51.0	0.9790
Tea solution	Au	1.8	43.5	0.9698
	CoCr-alloy	5.8	42.0	0.9349
	Mo	4.7	39.6	0.9193
	Nb	2.5	23.3	0.9544
Honey solution	Au	0.4	34.9	0.9671
	CoCr-alloy	2.4	23.4	0.9553
	Mo	-2.9	-29.1	0.9269
	Nb	1.3	18.1	0.9992

3.3.3. Thermodynamic considerations

Applying the Eyring transition-state, equation (12), yielded the thermodynamic functions for the dissolution process.

$$\log C_R/T \log\ (R/Nh) + (\Delta S^*/2.303R) - (\Delta H^*/2.303RT) \quad (12)$$

where N is Avogadro's number, h is Planck's constant, and the entropy and enthalpy of activation are represented by the terms, ΔS^* and ΔH^*, respectively. As shown in Figures (14 – 16), plots of $\log C_R/T$ *vs.* $1/T$ produced straight lines with slopes of $[-\Delta H^*/2.303R]$ and intercepts of $[\log(R/Nh) + (\Delta S^*/2.303R)]$ [30]. Table (6) contains a tabulation of the obtained values.

The endothermic nature of the dissolution process is indicated by the positive values of ΔH^* for all electrodes in all tested solutions, suggesting a slow and challenging dissolution process. An exception was recorded for Mo electrode in honey solutions. Higher values for ΔH^* corresponded to greater protection effectiveness [28]. The reason for this could be due to an energy barrier in the reaction, where the adsorption of the solutions on the electrodes' surface caused an increase in the enthalpy of the corrosion process. The highest ΔH^* values indicating the greatest corrosion resistance were found with a gold electrode in all solutions, followed by a molybdenum electrode in orange juice and tea solutions.

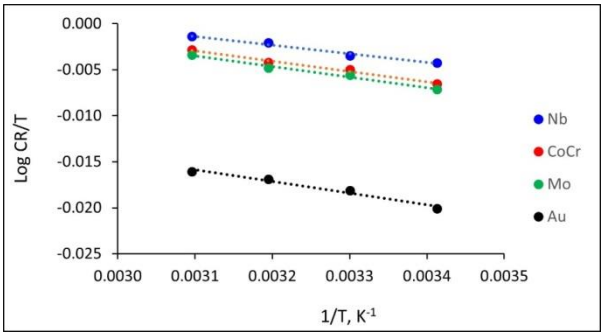

Figure 14: Transition state plot displaying the examined electrodes' corrosion behavior in orange juice.

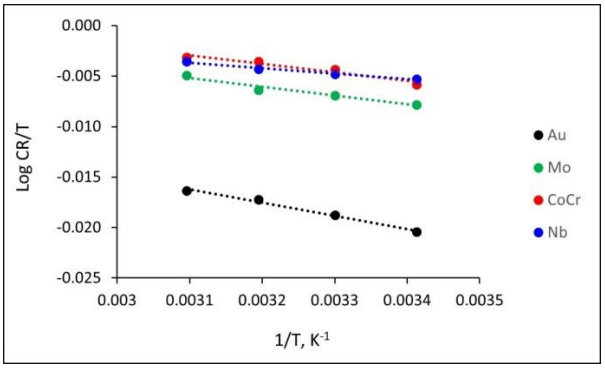

Figure 15: Transition state plot displaying the examined electrodes' corrosion behavior in tea solution.

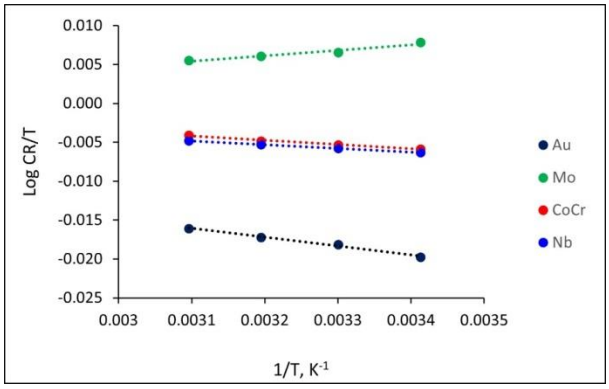

Figure 16: Transition state plot displaying the examined electrodes' corrosion behavior in honey solution.

Furthermore, all electrodes exhibited considerable, negative entropy changes (ΔS^*), which all closed to a value of -197 J/mol K. This suggested that as the corrosion process progresses, the metal ions get more systematized. This might occur if the metal ions in the solutions collect together, reducing the degree of unpredictability [29]. It was thus proven that the type of electrode had a significant impact on the corrosion process' activation parameters.

Table (6): Thermodynamic parameters for the different electrodes in orange juice, tea, and honey solutions.

Type of solution	Type of electrode	ΔH°, KJ/mol	ΔS°, J/mol K	R^2
Orange juice	Au	242	-197.1	0.9732
	CoCr-alloy	215	-196.9	0.9880
	Mo	219	-196.9	0.9884
	Nb	181	-197.0	0.9834
Tea solution	Au	249.	-197.1	0.9874
	CoCr-alloy	162	-197.1	0.9425
	Mo	166	-197.1	0.9588
	Nb	102	-197.3	0.9807
Honey solution	Au	218	-197.2	0.9888
	CoCr-alloy	105	-197.3	0.9822
	Mo	-134	-197.2	0.9535
	Nb	92	-197.4	1.0000

4. Conclusions

1. Niobium electrodes had special behavior in OCP and PDP techniques.
2. Measurements of the open circuit potential showed that the CoCr-alloy, Mo, and Nb electrodes in orange juice, tea, and honey solutions have developed passive oxide layers.
3. Au may be replaced by Mo electrode in orange juice, and by CoCr-alloy in honey solution, for dental application at the temperature range 20 – 50 ºC.
4. In tea solutions, Mo electrode follows the gold electrode in the tendency for the formation of a protective oxide film at all temperatures.
5. According to polarization measurements, niobium creates an oxide film that is capable of repairing itself in all tested solutions, but it has the least corrosion resistance compared to the other tested electrodes.
6. Mo electrode always follows the gold electrode in the passivity order in the three tested solutions at all temperatures.
7. The enthalpy change measurements indicate the best corrosion resistance was confirmed for Au electrode, followed by Mo and CoCr -alloy.

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