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FEASIBILITY STUDY OF NATURAL HONEY USE AS CORROSION INHIBITOR IN PROTECTING THE BRONZE ARTIFACTS

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ABSTRACT

Bronze disease is the most important phenomenon giving rise to the destruction of the bronze objects. There are various methods for preventing and slackening the disease. In this regard The use of corrosion inhibitors in the field of historical metal protection has been widely considered. But, the most important method which is also the best method offered for such a purpose is the use of benzotriazol (BTA) and 2-amino-5-mercapto-1,3,4-thiadiazol (AMT) inhibitors. Under ideal circumstances, these inhibitors deliver good inhibition and can control the disease. The most important problem posed by such inhibitors is their being toxic and carcinogenic. In the current research paper, the natural inhibitors residing Honey in concentrations ranging from 1600ppm to 2000 ppm in sodium chloride corrosive solution, 0.5M, were applied on a bronze alloy in a percentage similar to the archeological alloys, 10% Wt Sn, Cu-10Sn composition. The effects were evaluated by the use of Potentiostat device based on weight loss ,humidifier space and SEM-EDX. The best inhibitory power of honey was shown in a corrosive environment of 0.5M sodium chloride, 1800ppm, According to the data from Potentialostato device and classical massometric method. SEM-EDX results of corroded surfaces of coupons after one month in inhibitive and corrosive environment showed inhibitive effect for honey.

KEYWORDS: corrosion, bronze disease, natural inhibitors, honey, Potentiostat

1. INTRODUCTION

Generally, inhibitors are substances that decrease the chemical reactions intensity if used in proper concentrations. These materials prevent the biological factors' growth and cause cessation of physiological processes. The term "inhibitor" is derived of the Latin word "Inhibere" meaning prevention, acting as a barrier or preservation. Inhibitors, if used in low concentrations in corrosive environment, can delay the corrosion of metals. These substances can be solid, liquid and/or gas; they can be applied in closed gaseous or aqueous environments (Groysman, 2010). During the late 1950s, organic inhibitors were developed in the industry. These inhibitors were utilized to preserve and repair historical metal works. One such an inhibitor is the common benzotriazole that is applied for the treatment of bronze disease and copper alloys' corrosions as well as generally for the preservation of the bronze works (Brnich and Madsen, 1967). This inhibitor was first developed in the industry for the purpose of preventing copper alloys' corrosion. Another inhibitor that has been introduced for the copper alloys' corrosion prevention is 2-amino-5-mercapto-1, 3, 4-thiadiazole. This inhibitor was first evaluated in the industry and after than its use for the preservation and repair of the metal works and as a healing method for the curing of bronze disease was proposed (Ganorkar, 1988). There have been applied other organic inhibitors for the protection of copper alloys that are inter alia the derivatives of these inhibitors. The most important problem of these inhibitors is their being toxic and carcinogenic. Natural inhibitors have also been investigated and examined in the industry. One such a natural inhibitor is honey that was tested in 1998 by E.Y.L. El-Etri in an Egyptian University (El-Etri, 1998). In 2000, another experiment was conducted on carbon steel corrosion in high-salt environments by El-Etri and M. Abdullah who introduced honey as a proper inhibitor in salty environments (El-Etri, et al, 2000). In May, 2004, in Manchester University, an organic combination of honey and rosemary was tested as an inhibitor on four metals, namely aluminium, copper, iron and zinc (Yee, 2004). In 2008, experiments were undertaken on natural honey and the black radish sap as inhibitors for preventing the tin corrosion. In the foresaid study that was conducted on the tin cans in the food industry and biology faculty of Zagreb University as well as in food industry of J.J Straus Mayer University, results were shown promising (Radojčić, 2008).

The present study examined and evaluated honey as an inhibitor on metallurgical alloys very much similar to the historical alloys (Cu-10Sn). In order to apply and use these materials as natural inhibitors on the historical metal works, it is necessary to evaluate the inhibition output and the various effects of these materials.

2. STUDY METHOD

In In the current article, there was made use of a Potentiostat Device, model SAMA 500 electro analyzer system, comprised of three electrodes, an auxiliary electrode made of platinium, a reference electrode made of mercury chloride (saturated calomel) and a working electrode, each 7.5cm in length and 0.73cm in diameter with Cu-10Sn composition. In order to perform the tests, a combination of 90 gr electrolytoic copper and 10%Wt tin were combined to build bronze electrolytes. After preparing bronze rods (Fig. 5), they were used as working electrode in Potentiostat device. Another electrode a diameter of 0.73 and a thickness of 2 mm were cut in order to prepare coupons. Preparation for tests was followed by grinding them with silicon carbide papers (400–2200 grit size),The coupons were placed in a control solution (corrosive solution) and a solution containing natural honey inhibitor for one month (Fig. 6). Then, in order to examine the effect and inhibitory power of honey, SEM-EDX analysis was performed on the coupons.

To calibrate the device, Linear Sweep Voltammetry (LSV) Tofel plot was applied. Also, there was made use of a classic method of weight loss in a humidifying environment. In order to examine the corroded surfaces of coupons in the presence of inhibitor and corrosive solution, a scanning electron microscopy microscope was used. EDS was used to analyze the corroded surfaces of coupons in the presence of corrosive solution and inhibitor.

SEM-EDS analyses were carried out using the VEGA II TESCAN, Czech Republic. EDS: Rontec, Quantax/QX2 Germany in Razi Metallurgical Research Center, Tehran, Iran. SEM-EDX made by the Dutch Philips Company as well as Model XL30, was applied.

The results obtained from the Potentiostat device, humidifier environment and classic weight loss are illustrated on statistical diagrams (Pourzarghan et al, 2010: 41-71).

3. DISCUSSION AND CONCLUSION

Honey is a natural product that is organically condensed by means of a complicated sugar complex. It has been found being constituted of the other ingredients like organic materials, proteins, vitamins, organic acids, flavonoids, phenolic acids and enzymes (Bertonclj, Jamnik, 2007).

The amounts of the honey ingredients corresponding to the findings obtained for the general constituents of 500 honey samples in the US (table 1) as well as the studies carried out in the other countries are presented in the table 1.

The ingredients and attributes of the various honeys depend on the vegetative sources, climate, geography as well as the other factors (Bertoncelj, Doberesk, Jamnik, Golob, 2007).

3.1 Blank Solution Preparation:

Sodium chloride, 0.5M, was used to make a blank solution. The solution was poured in a special container for a volume of 100 ml. The device starts drawing polarization diagrams after being calibrated. The notable point here in delineating the curves by the device is that it registers an error for each running time. The operation has to be repeated several times so as to be able to accurately record the corrosion potential value. In polarization curve drawn, (Fig. 1) was delineated for the 0.5M sodium chloride blank solution which illustrates a value equal to -243 as the corrosion potential.

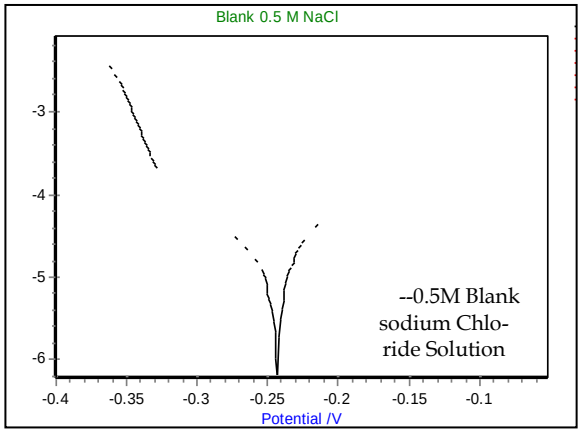

Figure 1. Tofel polarization curve for 0.5M sodium chloride

3.2 Preparing a Preliminary Honey Solution:

The required honey was procured from an agricultural and natural resources research center in Shiraz Province. To prepare the solution, honey was weighted by a digital scale and it was reached to the volume of interest by the use of distilled water.

The honey solution required for the tests was prepared in a range from 1600 ppm to 2000 ppm, then each of the solutions was separately mixed with the 0.5M sodium chloride corrosive solution with pH=5 so as to be evaluated in terms of its inhibition power by the use of Potentiostat device (Pourzarghan et al., 2010).

In order to accurately investigate and test the corrosion rate, the corrosion potential and the inhibition power of the solution of interest in each of the aforementioned ranges, it is necessary to repeat the experiments several times. The data acquired from Potentiostat device are summarized in table (2). In the following section, the diagram evaluations within a range from 1600 ppm to 2000ppm in respect to the blank solution are given.

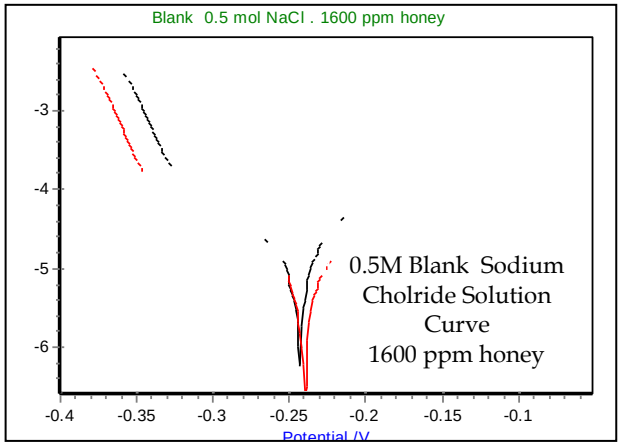

Figure 2. Polarization curve pertaining to honey in 1600 ppm concentration

No change is visible in the corrosion potential of -239 mV in the Tofel polarization curve shown on (Fig. 2)- pertaining to the 1600 ppm concentration. The drop in the corrosion trend is also tangible in two cathodic and anodic branches.

In 1800 ppm concentration as compared to the other concentrations, there are observable evident variations in corrosion potential. The corrosion potential has been displaced towards -224 mV in positive direction (anode) and as it can be seen -19 mV has become more positive in contrast to the blank solution (Fig. 3). A small descending trend is also visible in the curves.

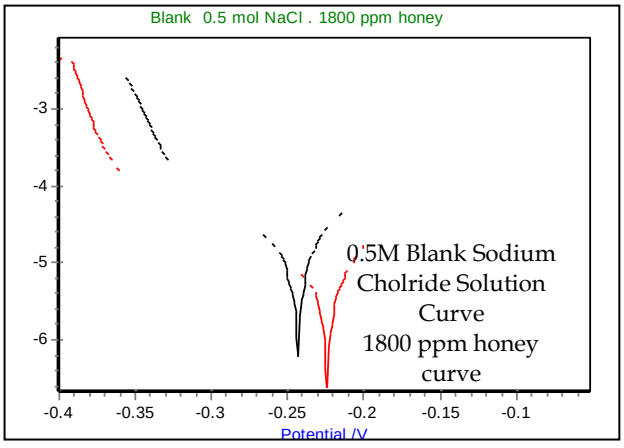

Figure 3. Polarization curve pertaining to honey in 1800 ppm concentration

In 2000 ppm concentration, as well, the corrosion potential reached to -234 mV (Fig. 4) that is more positive in contrast to 9mV potential of the blank

solution and a small descending trend is observable in anodic and cathodic branches.

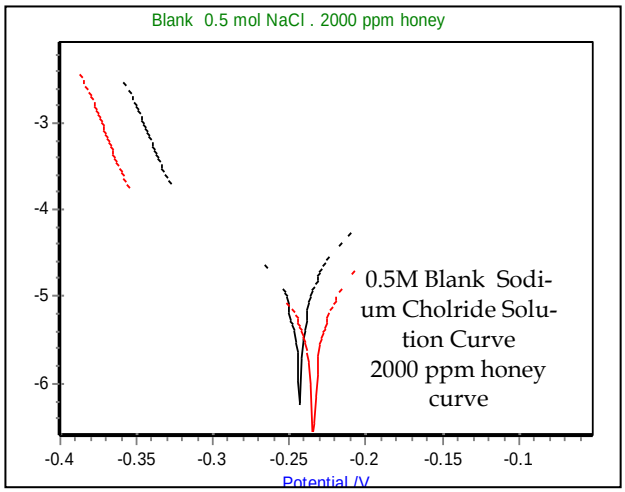

Figure 4. Polarization curve pertaining to honey in 2000 ppm concentration

3.3 Calculating the Inhibition Outcome by the Use of Potentiostat Device Computations:

To obtain the percentage of inhibition efficiency (IE%), the equation.1 given below is used in which Icorr is the corrosion current density in the presence of inhibitor and I0 is the corrosion current density in the absence of inhibitor.

$$IE = \frac{I^{0}_{corr} - I_{corr}}{I^{0}_{corr}} \times 100 \qquad \textit{Equation 1}$$

Another method, for the calculation of the inhibition efficiency percentage is according to the relation.2 , where Rp is the polarization resistivity (Dillman, 2007).

$$\theta = 1 - \frac{R_p \text{without inhibitor}}{R_p \text{with inhibitor}} \times 100 \qquad \textit{Equation 2}$$

In these experiments, the corrosion current density, corrosion rate and the equivalent weights are calculated in the presence and absence of inhibitor by means of standard ASTM, G 102-98 (Dean, 1987).

To calculate the current density, the following eq.3 is utilized:

$$icorr = \frac{Icorr}{A} \qquad \textit{Equation 3}$$

Where,
A= contact surface (cm^2)
icorr= the corrosion current density ($\mu A/cm^2$)
Icorr= corrosion current (μA)
The corrosion rate or speed is computed corresponding to the eq.4 below:

$$CR = K1 \frac{i\,corr}{\rho} EW \qquad \textit{Equation 4}$$

CR= corrosion rate (mpy)
K1= 3.27×10^{-3} (mm g/μA cm yr)
ρ=density (g/cm^3)

The Potentiostat device data have been calculated by the use of the abovementioned relations and presented in Table 2.

By making use of the data, obtained from Potentiostat device, the inhibition power of the acacia solution has been calculated as tabulated in Table 3.

3.3 Classic Weight Loss Method:

The weight loss method is the simplest method of investigating the corrosion inhibition due to its being needless of any device (except a digital scale). In this method, the metal specimen's weight is calculated before and after being exposed to corrosion by a corrosive agent (in the presence and absence of inhibitor). The experiment takes a long time to complete, but it is still utilized because the results obtained by this method are more realistic than the electrochemical methods (Tang et al., 2005). In such experiments the sample loss of weight is designated by Wcorr in the presence of the inhibitor and W0 is the sample weight in the absence of the inhibitor and they are computed according to the eq.5.

$$IE = 1 - \frac{\Delta W\ inhibitor}{\Delta W\ blank} \times 100 \qquad \textit{Equation 5}$$

Figure 5 Electrodes prepared for the coupons' incision.

To carry out the experiments based on the classic method, the electrodes (Fig. 5) with the percentage of Cu-10Sn, 0.73 cm in diameter and 2 mm in thickness, were cut into round coupons which were subsequently polished and varnished by the use of sandpapers with different degrees ranging from 400 to 800 and to 2200. Then, the coupons were washed in de-fatting alcohol and distilled water. The washed samples were heated for an hour in an 80-degree-

centigrade oven after which they were placed on a desiccator for an hour and they were eventually weighted before being placed in honey solution.

After the elapse of one month since the onset of soaking in an inhibitory solution in a 0.5M sodium chloride corrosive environment, a coupon from the blank solution and another from the honey solution were picked up once a week and the inhibitor efficiency was computed weekly based on the eq.(5). The coupons underwent the foresaid operation for four weeks. The results of the corresponding sample inhibition power are summarized in the following tables (Table 4 and Fig. 7).

Figure 6. coupons prepared for soaking

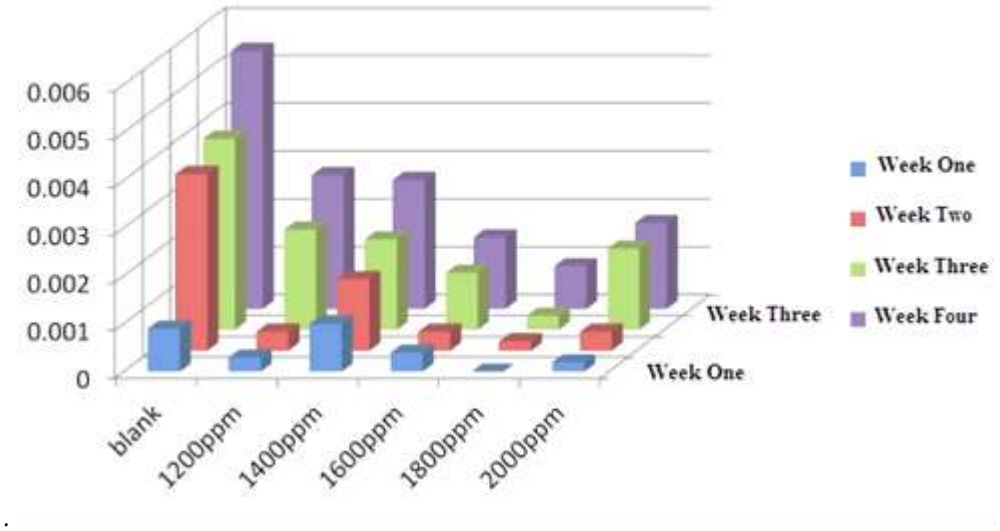

Figure 7. Weight reduction rates based on 1800ppm concentration after one to four week floatation

3.4 Experimenting in a Humid Chamber:

After the preparation of the coupons, in a Cu-10Sn percentage, they were completely polished with sandpapers ranging in degree from 400 to 2200 so as to create a completely smooth and uniform surface. After that, the coupons were washed in distilled water and the remaining fat was removed by the use of alcohol. The samples were placed inside a 120°C oven for one hour. The coupons were then soaked in a 1000ppm honey concentration for a period between 24 and 48 hours. After, removing the coupons from the solutions, they were left to be dried for an hour in the room temperature and images were taken from them so as to detect any apparent color changes on the surface (Figs. 8 to 11). To accelerate the corrosion, the samples were taken to a humid chamber. The coupons were kept in a relative humidity of 95 and temperature ranging from 25°C to 30°C following which they were sprayed with 0.5M sodium chloride corresponding to ASTM, G85 and ISO, 9227 standards. The samples were picked up from the humid chamber after four weeks and they were evaluated in SEM-EDX device for the assessment of the inhibitory effects on the coupons' surfaces.

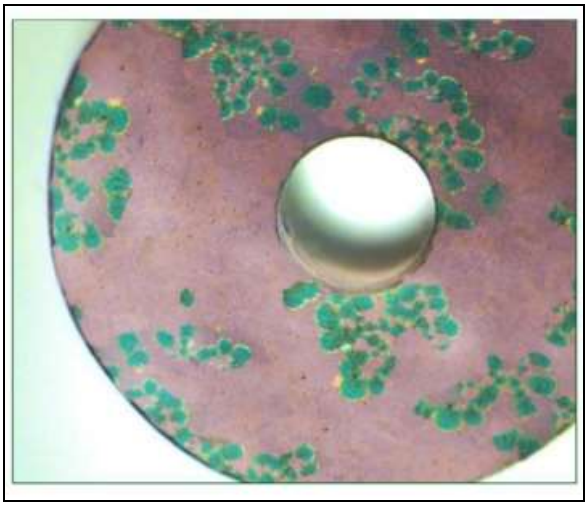

Figure 8. Coupon in corrosive solution of 0.5M sodium chloride after 30 days of floatation, magnified 40X

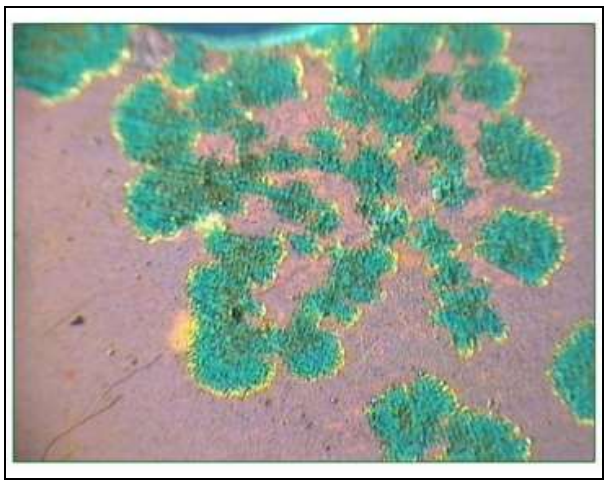

Figure 9. Coupon in 0.5M sodium chloride corrosive solution after 30 days of floatation, magnified 60X

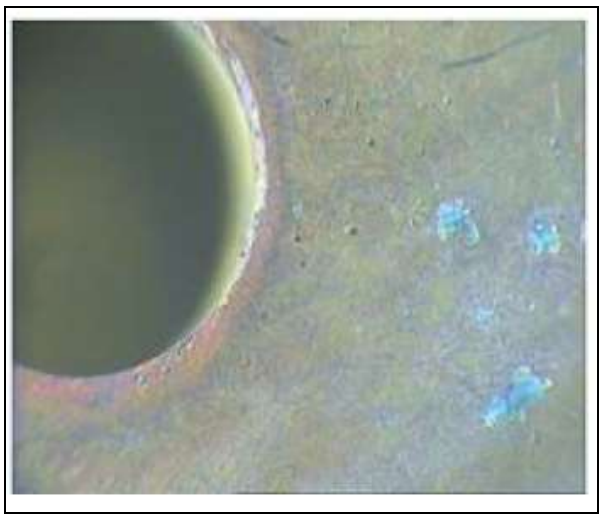

Figure 10. Corrosion of the coupon surface in 1200 ppm concentration of honey, magnified 80X

Figure 11. Corrosion of the coupon surface in a 1200 ppm honey concentration, magnified 40X

(According to the Figs. 12-13) of control coupon (in the presence of NaCl corrosive solution), corrosion products at the grain boundaries and pitting corrosion and/or morphology of needle- and Rhombus-shaped crystals formed on the surface of coupon, corrosion products can be of Atacamite $Cu_2(OH)_3Cl$ and paratacamite $Cu_2(OH)_3Cl$ and these products aggregate at the grain boundaries.

(Figs. 14-15) of coupon in 1800 ppm honey solution in the presence of 0.5M NaCl solution shows a completely uniform surface in the presence of an inhibitor.

Figure 12. SEM analysis of the blank sample versus the 0.5M sodium chloride corrosive solution

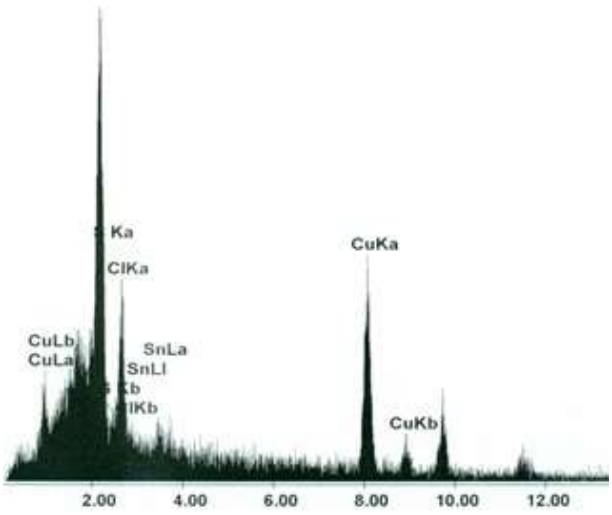

Figure 13. EDX analysis of the blank sample versus the 0.5M sodium chloride corrosive solution

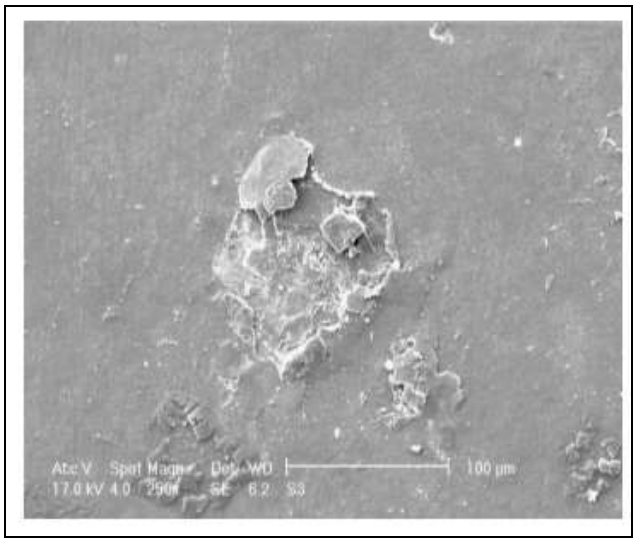

Figure 14. SEM analysis of the coupon surface containing inhibitor in the presence of 0.5M sodium chloride corrosive solution

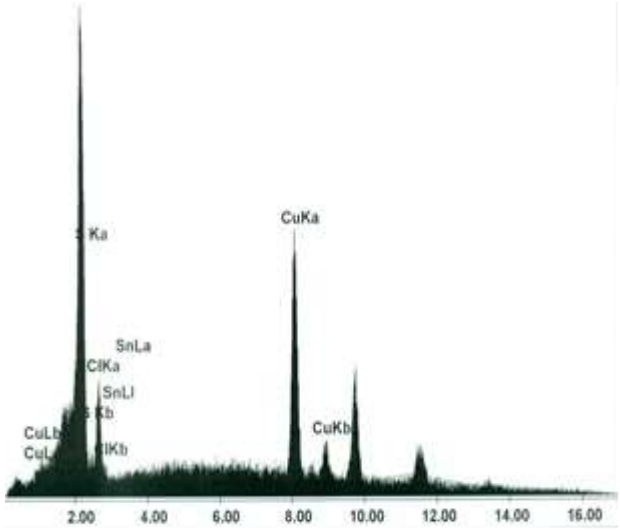

Figure 15. EDX analysis of the coupon surface containing inhibitor in the presence of sodium chloride corrosive solution

4. CONCLUSION

According to the investigations undertaken so far on the honey by means of a Potentiostat device, it was made clear that the data obtained from the foresaid device are suggestive of a value equal to 73% for honey inhibition power in 1800 ppm with a corrosion rate of 7.911 in regard of bronze alloys featuring a Cu-10Sn percentage. Utilizing the Potentiostat data, it was confirmed that the inhibitor exerts its influence in a mixed manner. Based on the classic weight reduction method, a value equal to 81% was computed as the inhibitory power of Honey. In the SEM images that were taken for the investigation of the coupons' surfaces in a 0.5M sodium chloride corrosive solution in the presence of honey inhibitors, the surface uniformity and the lack of corrosion were documented. Although such inhibitors like BTA and AMT enjoy an inhibitory power a little more than honey but the most important problem of these industrial inhibitors is their toxicity and carcinogenicity. But, these problems can be met via shortening the period of treating these archaeological works with optimized honey.

Natural honey inhibitor is superior to other synthetic inhibitors such as BTA and AMT due to its availability, low cost, being environmentally-friendly, non-toxicity.

Further studies on bronze antiquities in different laboratory conditions for evaluating the various feedbacks of this inhibitor can be useful in examining its effective role in preventing corrosion in bronze antiquities.

Table 1: The main ingredients of 500 honey samples and the range variation (white, 1962; p 297)

Characteristics measured	Average	Range
Misture, perecentage	17.2	**13.4-22.9**
Levulose, perecentage	38.19	**27.25-44.26**
Dextrose, perecentage	31.28	**22.03-40.75**
Sucrose, perecentage	1.31	**0.25-7.57**
Maltose, perecentage	7.31	**2.74-15.98**
Highersugras, perecentage	1.50	**0.13-8.49**
Undetermined, percentage	3.1	**0.0-13.2**
pH	3.91	**3.42-6.10**
Free acid, (meq/kg)	22.03	**6.75-47.19**
Lactone, (meq/kg)	7.11	**0.00-18.76**
Total acid, (meq/kg)	29.12	**8.68-59.49**
Lactone/ free acid	0.335	**0.000-0.950**
Ash, perecentage	0.169	**0.020-1.028**
Nitrogen, perecentage	0.041	**0.000-0.133**
Diastase value	20.8	**2.1-61.2**

Table 2: calculations of the corrosion current and potential, electrolyte resistance, current density, cathodic and anodic gradient coefficients and honey corrosion rate by the use of Potentiostat device.

Honey concentration (w/v)	$-E_{corr}$ (mv)	R_p (ohm)	B_a (v/dec)	B_c (v/dec)	$I_{corrosion}$ (A)	$i_{corrosion}$ (A/cm^2)	Corrosion rate (mpy)
1200 ppm	239	916.7	0.0441	0.0512	$2.371*10^{-5}$	$5.673*10^{-5}$	24.781
1400 ppm	245	1940	0.0426	0.0543	$1.121*10^{-5}$	$2.681*10^{-5}$	11.711
1600 ppm	239	1458	0.0614	0.0795	$1.491*10^{-5}$	$3.567*10^{-5}$	15.581
1800 ppm	224	2871	0.0572	0.0672	$7.572*10^{-6}$	$1.81*10^{-5}$	7.911
2000 ppm	234	1743	0.0378	0.0402	$1.247*10^{-5}$	$2.984*10^{-5}$	13.035

Table 3: Honey inhibition percentage in various concentrations in the 0.5 molar sodium chloride corrosive environment from the week one to the week four of the floatation.

Honey and 0.5M NaCl concentrations (w/v)	IE% (week one)	IE% (week two)	IE% (week three)	IE% (week four)
Blank	-	-	-	-
1200 ppm	92	56	49	47
1400 ppm	-	60	54	41
1600 ppm	56	90	71	72
1800 ppm	100	95	66	81
2000 ppm	90	91	53	61

Table 4: Honey inhibition percentage in various concentrations in the 0.5 molar sodium chloride corrosive environment from the week one to the week four of the floatation

Honey and 0.5M NaCl concentrations (w/v)	IE% (week one)	IE% (week two)	IE% (week three)	IE% (week four)
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