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2-MERCAPTO-5-ACETYLAMINO-1,3,4-THIADIAZOLE AS CORROSION INHIBITOR FOR A NATURALLY PATINATED MONUMENTAL BRONZE ARTIFACT

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ABSTRACT. The present work aims to investigate the corrosion behavior of bronze screws covered with natural patina used in assembling the statuary group of Mathias Rex, placed in the center of Cluj-Napoca, Romania, dating back to 1902. Corrosion tests were carried out in the absence and presence of inhibitors in a 0.2 g / L Na_2SO_4 + 0.2 g / L $NaHCO_3$ (pH = 5) solution simulating an acid rain. The research put on evidence the inhibiting effect of 2 - mercapto - 5 acetylamino - 1, 3, 4 - thiadiazole on the naturally patinated artefacts in order to avoid their further degradation. The obtained results were compared with those recorded in the presence of benzotriazole, the most common corrosion inhibitor for Cu and bronze.

Key words: *bronze, atmospheric corrosion, natural patina, acid rain, corrosion inhibitors*

INTRODUCTION

Bronze (Cu - Sn based alloy) is one of the most widely used alloy in the monumental art. Exposed outdoors, the bronze develops in time a layer of corrosion products, called natural patina. There are many studies on the atmospheric corrosion of bronze and on the formation mechanisms of bronze corrosion products [1-7]. Some of these studies show that, in the case of bronze, there are two types of patina, respectively: Type I, or “even” surfaces and Type II, or “coarse” or “burgeoning” surface [1]. Type I patina is very protective and develops on the bronze surface an aesthetic pleasant aspect, for this reasons being called “noble patina” [1]. It has different colours depending on the nature of the atmosphere: blue, green, dark green or dark grey. On the other hand, the Type II patina is inferior to Type I and is characterized by changes of the original surface, being rough and

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porous and coloured in red, brown or green [1]. Due to the increasing pollution in recent years is necessary to protect the “noble patina”. One common method is the use of corrosion inhibitors.

Recent studies have shown that benzotriazole (BTA), a consecrated inhibitor for cooper alloys, is highly toxic and carcinogenic [8]. Moreover, in time it leads to a depreciation of patina color (blackening). For this reason efforts are made towards finding protection methods based on the use of less toxic inhibitors for copper and bronze protection. In recent papers, different innoxious thiadiazole derivatives, namely 2 - amino - 5 - mercapto - 1, 3, 4 - thiadiazole [8-11], 2 - amino - 5 - ethylthio - 1, 3, 4 - thiadiazole [12], 2 - amino - 5 - ethyl - 1, 3, 4 - thiadiazole [13], 2 - methyl - 5-mercapto - 1, 3, 4 - thiadiazole [11], and 2 - acethylamino - 5 - mercapto - 1, 3, 4 - thiadiazole [14, 15], have been reported as efficient inhibitors for copper or bronze corrosion in different corrosive media. However, their effect on the natural patina of bronze artifacts is still to be investigated.

In this context, the present research focuses on the effect of an innoxious thiadiazole derivative on the corrosion behavior of some deteriorated bronze screws covered with natural patina, originating from the statuary group of Mathias Rex from Cluj-Napoca, Romania, in an aerated electrolyte simulating an acid rain (pH 5). The recent restoration of the bronze statuary group provided a unique occasion to better understand the impact of environmental conditions on the degradation of bronze components and to investigate the conservation possibilities directly on the bronze artifacts covered with natural patina, which had to be replaced. For this purpose, investigations have been made by means of electrochemical, microscopic and spectroscopic methods. The obtained results were compared with those recorded in the presence of BTA and could serve for the statuary group conservation well as for future protection of other monumental bronzes.

RESULTS AND DISCUSSION

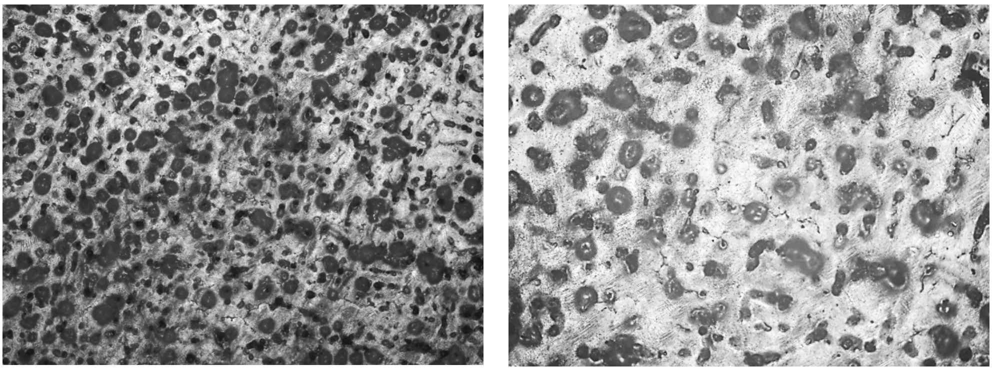
The chemical composition of bronze screws used for experiments was determined by X-ray fluorescence spectrometry (XRF). The results show that the alloy of screws is a binary Cu6Sn bronze of the following composition: 91.89 % copper, 5.15 % tin, 1.25 % zinc, 1.04 % lead and 0.57 % iron.

By microscopic observation (Fig. 1) it is shown that the corrosion products layer is porous, rough with cracks and pits. This indicated that the bronze screws analyzed were severely corroded [16]. It can be also observed that the patina layer is not uniform, so some alloy areas are not covered (Fig. 1b).

For the microscopic investigation, the bronze screws were polished on the sample polishing machine with alumina paste, after which the surface was washed with ammonia cupric chloride to bring out the grain contrast. Figure 2 presents the microscopic structures of the bronze screws, subjected to this study magnified at 100X and 200X.

(a) (b)

Fig. 1. Microscopic observation of patina on bronze screw from Matthias Rex statuary group: (a), (b) X100.



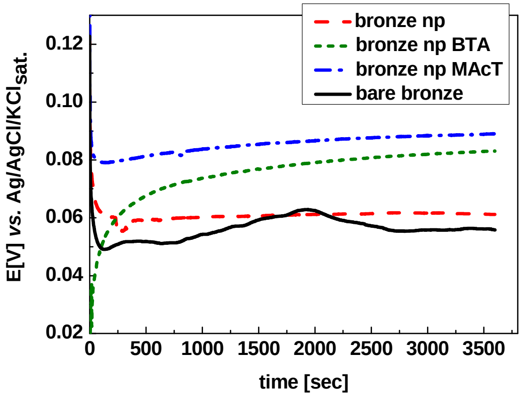
(a) (b)

Fig. 2. Microscopic structure of bronze screws used for electrochemical studies: (a) X100, (b) X200.

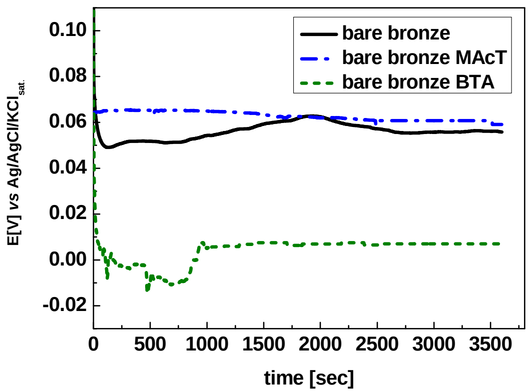
The microscopic structure of the bronze is a typical one. According to Scott [17] some of the inclusions observed in the metal are of cuprite (Cu_2O), other are of segregated lead. In our case, the surface is rich in cooper α-phase with punctiform eutectoid (α + δ) and lead segregations. This can be ascribed to the casting process that has resulted in the segregation of lead and to the fact that annealing was not extensive enough to eliminate all of the (α + δ) eutectoid [17].

Polarization measurements

In a first step, the corrosion behavior of bronze screw covered with natural patina was studied in the absence and in the presence of corrosion inhibitors in an electrolyte containing 0.2 g / L Na_2SO_4 + 0.2 g / L $NaHCO_3$, pH = 5.



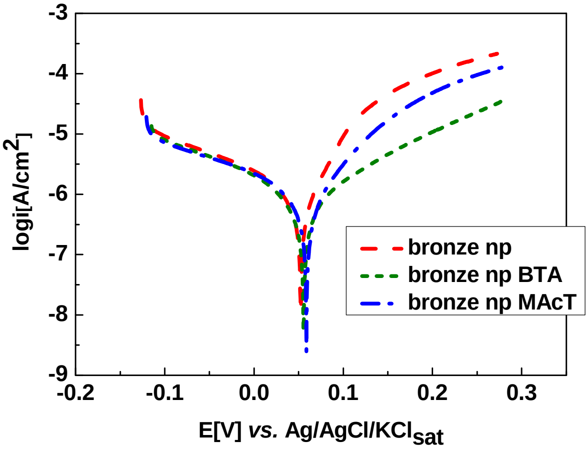
(a)



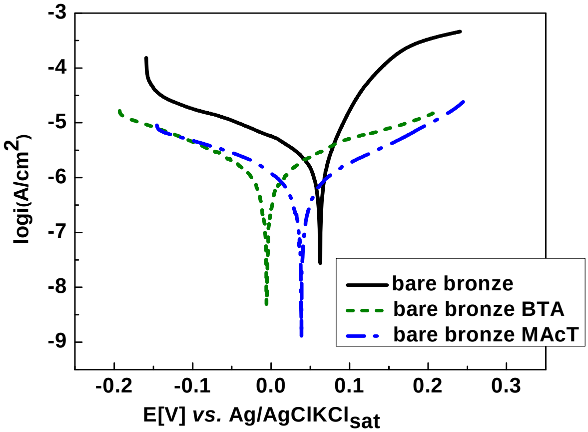
(b)

Fig. 3. Time variations of the open circuit potential (OCP) of the bronze screws exposed in the urban atmosphere of Cluj-Napoca, Romania, tested in 0.2 g / L Na_2SO_4 + 0.2 g / L $NaHCO_3$ (pH = 5) in the presence and absence of inhibitors, (a) – natural patina, (b) – bare bronze. In this figure “np” means natural patina.

The experiments started with measuring the open circuit potential of the bronze screws covered with natural patina, for a period of 3600 s, in the absence and in the presence of inhibitors, the results being presented in Fig. 3.



(a)



(b)

Fig. 4. The polarization curves (± 200 mV *vs*. OCP) for the bronze screws exposed in the urban atmosphere of Cluj-Napoca, Romania, immersed in 0.2 g / L Na_2SO_4 + 0.2 g / L $NaHCO_3$ (pH = 5) in the presence and absence of inhibitors, a) - with natural patina, b) - bare bronze, scan rate, 10 mV / min. In this figure “np” means natural patina.

It can be observed that, in all cases, the OCP has positive values and the values recorded for the bronze screw covered with natural patina are more positive than that of bare bronze screw (Fig. 3a), suggesting an ennoblement of the surface and, consequently, a braking of the anodic process (the metal dissolution). OCP values for bare bronze are more positive in the presence of MAcT than in its absence and more negative in the presence of BTA (Fig. 3b). In the last case, this could be due to interactions of the inhibitor with the cathodic depolarization reaction, in particular the reduction of O_2, which is diffusion-controlled.

To determine the polarization resistance of the electrodes, linear polarization curves were recorded, in the potential domain of ± 20 mV around the value of OCP. The polarization resistance values for each electrode, calculated as the inverse of the slope of each curve, are shown in Table 1.

As it can be observed, the natural patina increases only slightly the corrosion resistance of the bronze, due to the fact that the corrosion products layer is not nor continuous, neither compact. As expected, the highest value for R_p is noticed in the case of the bronze screw covered with natural patina, immersed in solution containing 0.2 g / L Na_2SO_4 + 0.2 g / L $NaHCO_3$ (pH = 5) in the presence BTA inhibitor, followed by the case when MAcT was present.

To determine the kinetic parameters of the corrosion process, polarization curves were recorded in the potential range of ± 200 mV *vs.* OCP (Fig. 4). The Tafel interpretation of the polarization curves led to the results presented in Table 1.

Table 1. Corrosion process parameters for the bronze screws exposed in the urban atmosphere of Cluj-Napoca, Romania, immersed in 0.2 g / L Na_2SO_4 + 0.2 g / L $NaHCO_3$ (pH = 5) in the presence and absence of inhibitors

Electrode	E_{corr} [mV *vs* Ag/AgCl]	i_{corr} [μA/cm^2]	β_a [mV/ decade]	- β_c [mV/ decade]	R_p [kΩcm^2]
Bare bronze	62	0.71	44	162	2.98
Bronze with natural patina	52	0.81	49	117	2.77
Bronze with natural patina BTA	56	0.32	72	68	17.74
Bronze with natural patina MAcT	59	0.38	42	63	5.41
Bare bronze BTA	5	0.25	131	135	41.10
Bare bronze MAcT	39	0.14	112	108	139.22

β_a and β_c are the Tafel coefficients

Analyzing the data in Table 1 it can be observed that, in the absence of inhibitors, the screw covered with natural patina has the lowest corrosion resistance (R_p=2.77 [kΩcm^2], and the highest i_{corr} (0.81 [μA/cm^2]), followed by the bare bronze sample.

X-ray mapping of the screws surface covered with corrosion products

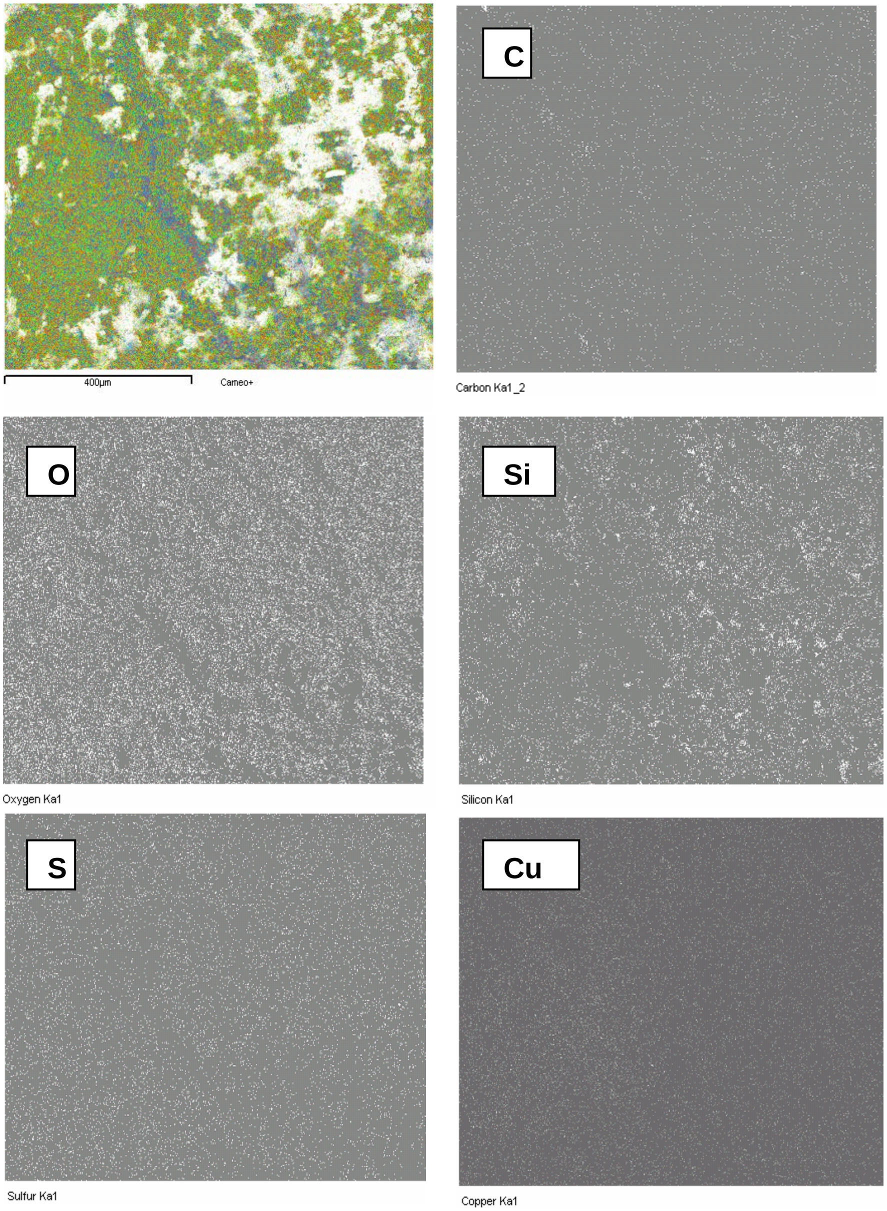


Fig. 5. Mapping results obtained on screw surface covered with natural patina. X-ray maps for C, O, Si, S, Cu

The lack of protection of the natural patina could be attributed to the advanced stage of degradation of the screw, with the appearance of intergranular corrosion. Also this behavior can be ascribed to the absence of tin compounds on the surface, which are usual in the case of Type II patinas [1] and which hinder the oxidation process of copper to Cu(I) oxide [18]. This is in accordance with the results obtained by SEM / EDX analysis reported elsewhere [19]. According to [19] the natural patina formed on screw surface is discontinuous, porous and has tendency to retain contaminant elements. It can observed from Fig. 5 that the natural patina layer is not continuous nor homogeneous, fact confirmed by the absence of O and S in some areas (see X-Ray maps for O and S). Therefore the corrosion compounds such as brochantite [$Cu_4(SO_4)(OH)_6$] which would protect the surface of the screw, are missing. On the other hand, X-ray mapping analysis indicates the presence of Si, confirming the ability of the natural patina to retain pollutants.

Bare screw has the highest corrosion resistance in the presence of inhibitor MAcT. This is suggested by the high value of the polarization resistance (R_p=139.22 [kΩcm^2]) and the low value of the corrosion current density (i_{corr}= 0.14 [μA/cm^2]).

Based on the corrosion current density (i_{corr}) calculated from Tafel representation, the protection efficiency (PE) conferred by inhibitors can be determined using the following formula:

$$PE[\%] = \frac{(i_{corr})without.inhibitor - (i_{corr})inhibitor}{(i_{corr})without.inhibitor} x100 \qquad (1)$$

Another way of appreciation of inhibitor effectiveness is based on the variation of polarization resistance (R_p), according to the relation:

$$PE[\%] = \frac{R_p inhibitor - R_p without.inhibitor}{R_p inhibitor} x100 \qquad (2)$$

The protection efficiencies of corrosion inhibitors for bronze screws calculated with formula 1 and 2 are depicted in Figure 6.

It is worth mentioning that, despite the differences between the values of PE, the variation tendency of inhibition efficiencies is the same for both methods.

It was observed that the best results were obtained in the case of bare bronze in presence of MAcT (efficiency between 80 - 97 %). For bronze screw covered with natural patina the best results were in case of inhibitor BTA (efficiency between 55 - 83%). The rough surface of patinated bronze along with its different adsorption properties toward the two organic compounds could explain this behavior. However, the relatively good efficiency of MAcT especially for bare bronze surfaces and its non-toxic nature recommend it as possible substitute of BTA for bronze artifacts.

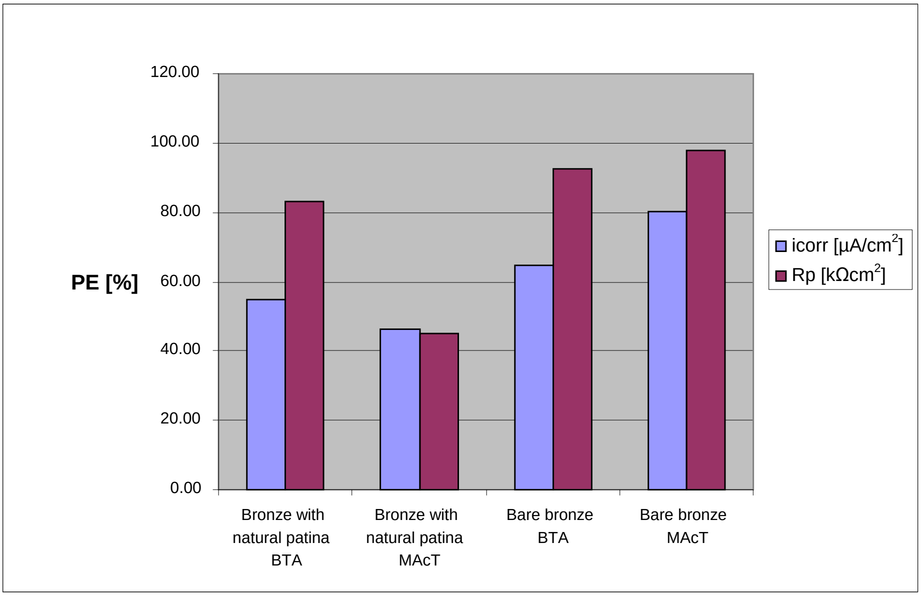


Fig. 6. Protection efficiency (PE) of inhibitors, calculated according to corrosion current density and polarization resistance.

CONCLUSIONS

The corrosion of bronze screws used to assemble Matthias Rex statuary group, Cluj-Napoca, Romania was investigated, in the presence and absence of natural patina and of corrosion inhibitors in an attempt to improve bronze monuments protection against corrosion in urban atmospheric conditions.

Accelerated corrosion tests in an environment that simulated acid rain on bronze screw covered with a patina formed over 100 years, showed that the natural patina does not confer complete protection against corrosion to the bronze, due to its discontinuity.

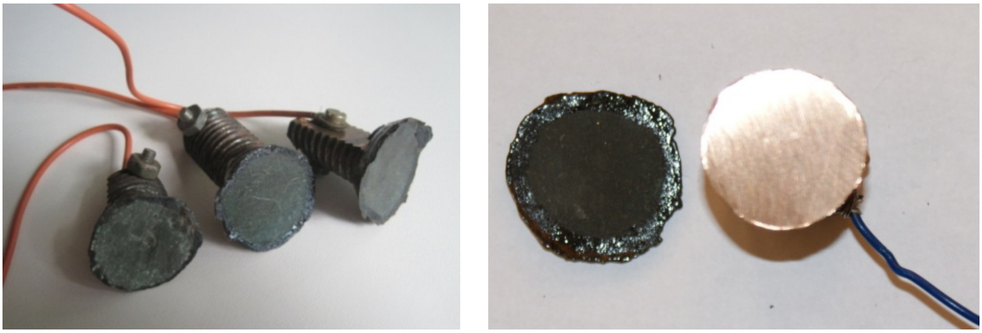
The investigation indicates that both studied inhibitors provide protection to bronze monuments in the tested conditions. BTA showed best efficiency on patinated bronze, (65 - 92 %), while the best protection efficiency on bare bronze was exerted by MAcT (80 - 97 %). The good efficiency of MAcT (even on patinated bronze) and its non-toxic nature recommend it as possible substitute of BTA for the protection of bronze monuments exposed to the atmosphere.

EXPERIMENTAL

The bronze screws covered with natural patina, and cylindrically shaped were sampled during the restoration of the bronze statue of Mathias Rex in 2011. They were used as working electrodes during the corrosion measurements. The surface of the electrode exposed to the solution was disk - shaped, with a surface S = 3.14 cm^2. The rest of the screw was isolated from the contact with the electrolyte by using a lacquer. For electrical contact, a metal wire was attached to the screw (Fig. 7).

The corrosion behavior of bronze screws covered with natural patina (Fig. 7a) in conditions that simulate acid rain was compared with that of a bronze screw without patina (Fig. 7b), obtained by cutting the original screw's head and by polishing it on emery paper and finally with alumina (Al_2O_3), so that it did not present dents, goals, porosity, cracks, inclusions or other non-metallic impurities.

The study of the screws'surface was done by optical microscopy (OLIMPUS GS 51).



(a) (b)

Fig. 7. Bronze screws used in the experiments: (a) with natural patina, (b) the original screw's head and the bare bronze screw.

The electrochemical corrosion measurements were performed on a PC - controlled electrochemical analyzer AUTOLAB - PGSTAT 10 (Eco Chemie BV, Utrecht, The Netherlands) using a three electrodes cell containing a working electrode (bronze screws), an Ag/AgCl electrode as reference electrode and a platinum counter electrode. Anodic and cathodic polarization curves were recorded in a potential range of ± 20 mV and of ± 200 mV *vs.* the value of the open circuit potential, with a scan rate of 10 mV / min, after 1 hour immersion in corrosive solution.

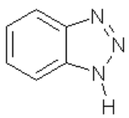
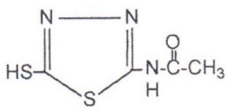
The chemical composition of bronze screws used for experiments was determined by X - ray fluorescence analysis (XRF). Analyses were performed using an installation type InnovX System Alpha Series with W anticathode, at 30 kV, 40 µA, exposure time 60 seconds. SEM analysis were performed with a Scanning Jeol JEM5510LV (Japan) coupled with Oxford Instruments EDX Analysis System Inca 300 (UK) at 15kV and spot size 39 µm.

Reagents

The inhibitor used in the experiments was a non-toxic thiadiazole derivative, respectively 2 - mercapto - 5 acetylamino - 1, 3, 4 - thiadiazole (MAcT, from Sigma Aldrich) in a concentration of 1mM and the obtained results were compared with those recorded with benzotriazole (BTA) (Sigma Aldrich). The physical - chemical properties of the two compounds are presented in Table 2.

The electrolyte solution for corrosion measurements contained 0.2 g / L Na_2SO_4 + 0.2 g / L $NaHCO_3$ (pH = 5). All the other chemicals were of analytical grade and used as received.

Table 2. The physical-chemical characteristics of tested inhibitors

Inhibitor	Molecular formula		Molar mass [g/mol]	Melting point [ºC]
BTA		$C_6H_5N_3$	119,12	100
MAcT		$C_3H_5N_3OS_2$	175,2	295

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