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Original article

Efficiency of a corrosion inhibitor on bare, oxidized and real archeological bronze in indoor polluted atmosphere- digital image correlation approach

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ABSTRACT

A corrosion inhibitor, tolyl methyl imidazole (TMI), was tested in practice and verified in a polluted indoor atmosphere. Special attention was given to its behavior in indoor storage conditions, where volatile organic pollutants may cause damage to metal artefacts. Prepared samples of bronze and oxidized bronze were exposed to acetic acid vapors. Raman analysis showed copper acetate and copper nitrate formation. Suppression of corrosion development following the application of tolyl methyl imidazole (TMI) was observed. A simple method based on image analysis for corrosion evaluation was specifically developed. The TMI inhibition action was tested on a Roman archeological object and evaluated after exposure to indoor pollutants.

Introduction

Copper and its alloys such as bronze and brass have been used for the fabrication of different types of objects and monuments since the Bronze Age. Depending on the environmental exposure, different types of degradation can be expected. When exposed to oxygen and humidity in air, the first stage of natural patination (oxidation) of copper and bronze is formation of red cuprous oxide (cuprite). Cuprite slowly oxidizes to black colored cupric oxide, tenorite. When bronze surfaces are exposed to an outdoor environment, the aggressive pollutants in the atmosphere react with the humidity in the air to form acid rain, and secondary corrosion products such as sulfates, nitrates and chlorides may form. This results in the change in appearance of a bronze surface and/or a change in the structure of patinas and alloys due to the leaching action of acid rain [1–3]. On the contrary, deliberate artificial patination is often used by artists in order to achieve visual effects of different colors on the surface. Upon long term exposure of brown patinated bronze to atmospheric environment, patina consists of a mixture of Cu_2S, cuprite, atacamite, gerhardite and rouaite [4]. It has been shown that an artist-applied patina can be successfully distinguished from an atmospherically induced patina [5]. The composition of a patina, and the corrosive process leading to changes in copper and bronze, are different when objects are buried in soil. Corrosion of archeological metallic objects is very much dependent on the acidity of the soil and the type and amount of minerals and organic material lying in the vicinity of the objects. For example, metal oxides, carbonates, sulfates, chlorides and phosphates have been identified on bronze archeological artefacts [6].

For many years benzotriazole (BTA) was used as a corrosion inhibitor and UV stabilizer for protection of copper alloys in restorer's laquers (Paraloid B44, for example), designed for both indoor and outdoor application. It is, however, highly toxic and therefore a suitable alternative for this purpose is being sought [7]. Alternative environmentally friendly azole type inhibitors, such as 2-mercaptobenzimidazole (MBI) [8] and tolyl methyl imidazole (TMI), have been investigated for this purpose, and their action on different patinas has been studied [8–11]. Raman analysis showed chemical bonding of BTA to Cu through the triazole ring [12,13] while in the case of MBI, inhibitor interaction has been identified in both pure copper and bronze through S, the substituted element in the imidazole ring [8].

Tolyl methyl imidazole (TMI) has previously been identified to efficiently protect historical patinas and has already been electrochemically evaluated [8–10]. Moreover, it has been shown that the

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bonding of TMI to bronze and oxidized bronze is of a physical nature, as no chemical interaction of TMI was proven by Raman spectroscopy [14]. However, no studies have investigated the behavior of TMI in indoor storage conditions, where indoor pollutants may significantly impact the various types of corrosion. Such data is of extreme importance to properly plan conservation treatments or storage and display conditions of copper and bronze objects.

In museums a variety of different materials is being used. Although safe for building purposes, they may emit trace amounts of chemicals such as acids, formaldehyde, and other fumes that can harm art objects over time. A simple, yet effective and well known Oddy test has been used to identify harmful volatile organic compounds in indoor environments [15] that are being constantly upgraded [16,17]. There are variety of different approaches in literature that report on the study of the effect of volatile organic acids on copper corrosion [18] an innovative estimation of corrosion damage on copper [19] and continuous measurement of corrosion using potenciometric technique [20]. Recently, indoor pollution has raised great concerns for the safe maintenance of pieces of art and many funded European projects have addressed this (e.g. FP5 IDAP, FP5 MASTER, FP6 PROPAINT, FP7 MEMORI). Amongst these projects, the PROPAINT project focused on the understanding of environmental conditions inside enclosures which protect objects of cultural heritage. It was found that such enclosures reduce the effect of fluctuations in external humidity and reduce the negative impact of external pollutants. The MEMORI project studied the impact of volatile organic compounds (VOC), especially the more aggressive organic acids, on movable objects of cultural heritage (cellulose, leather/ parchment, textiles, pigments and varnishes). Enclosures from wood and similar materials have a low air exchange rate and are therefore likely to have a high concentration of organic acids. VOC analysis has previously been explored in the context of historic paper [21]. In particular, the synergetic effect of environmental factors (temperature, relative humidity, outdoor and indoor pollutants, particulate matter) has received a great deal of attention [22–25]. As such, polluted indoor environment has an impact on material degradation, including metals.

Research aim

The focus of this work is twofold. The first focus was to propose and evaluate a simple method of visual inspection of corrosion development of copper or bronze objects when exposed to volatile organic compounds. In this method, a correlation between digital images of the corroded surfaces is made. The second goal of the research study was to evaluate the inhibiting action of TMI inhibitor in different simulated indoor environments (acetic acid and formaldehyde) on prepared model samples of bare non oxidized bronze and on patinated bronze (cuprite, ie. oxidized bronze). As a case study, Roman bronze objects, excavated in 2011 at the old military barracks archeological site in Ptuj, Slovenia, were selected and analyzed, and the effectiveness of TMI as a corrosion inhibitor was tested with respect to its exposure to indoor pollution. Raman and electron spectroscopy as well as visual and digital image studies were utilized in the study.

2. Materials and methods

2.1. Samples

Bronze samples

Bronze (Cu-4.17Zn-5Sn-0.07 Pb) discs 15 mm in diameter and approximately 2 mm thick were grinded with 1000 grit emery paper, degreased, and ultrasonically cleaned in an acetone bath for 3 min.

Fig. 1. Roman bronze objects, excavated at the old military barracks archeological site in Ptuj, Slovenia.

Bronze samples were prepared in order to test the evolution of corrosion in both freshly ground and oxidized bronze. Oxidized bronze was made by placing a bronze sample on an electrically heated surface at 100 °C for 2 min until a reddish color appeared, indicating artificially formed cuprite (Cu_2O). One half of each bronze sample was treated with a 3% ethanol solution of 4-methyl-1-p-tolyl imidazole (TMI inhibitor), which is known for its ability to inhibit an electrochemical patina, which mimics an archeological patina [9,10].

Archeological samples

Roman bronze objects (Fig. 1), excavated in 2011 at the old military barracks archeological site in Ptuj, Slovenia, were used for the study. Bronze object was analyzed by X-Ray fluorescence- XRF using a portable analyzer (Niton, USA, 2012). archeological bronze sample contained 1.1% Sn, 2.4% Pb, 10.3% Zn, 1.5% Fe, 1.6% Al, 3.4% Si beside Cu (balance). A wide variety of corrosion products, such as cuprite, chalcocite, malachite and other carbonate based minerals, were found by Raman microscopy analysis (Fig. 2). Some compounds originating from the surrounding burial environment, including hematite, amorphous carbon and quartz, were further identified (Fig. 2).

2.2. Exposure to indoor pollutants

The three metal samples (namely, 1 sample of bronze, 1 sample of oxidized bronze produced by hot oxidizing for 3 min at 100 °C, and 1 archeological sample, with half the surface brushed 3 times by the 3% ethanol solution of TMI inhibitor) were placed in the desiccator for a total exposure time of 42 days. Two different pollutant atmospheres were created: a solely acetic vapor atmosphere and a combined atmosphere consisting of acetic vapor and formaldehyde. Bronze samples were tested in the acetic vapor atmosphere, while the Roman objects were tested in combined acetic vapor and formaldehyde atmosphere. The influence of the combined acetic vapor and formaldehyde atmosphere on the prepared bronze samples is a subject of our ongoing research and is not fully discussed in this study.

The acetic vapor indoor pollutant environment was created by adding 2000 µL of conc. CH_3COOH in a saturated $MgNO_3$ solution and was maintained weekly [28]. In this way an atmosphere with an acetic vapor concentration of approx 0.23 mg/m^3 was created.

The acetic and formaldehyde indoor pollutant environment was made by combining 2000 µL of conc. CH_3COOH and 50 µL of formaldehyde in a saturated $MgNO_3$ solution [28].

2.3. Raman spectroscopy and electron microscopy

Raman analysis

Raman analysis of exposed bronze, oxidised bronze and archeological samples was performed using 514 nm laser excitation lines with a Horiba Jobin Yvone LabRAM HR800 Raman spectrometer coupled to an Olympus BXFM optical microscope. The spectra were recorded using *a* × 100 objective lens and a 600 grooves/ mm grating, which gave the spectral resolution of ca. 2 cm^{-1} pixel^{-1}. The

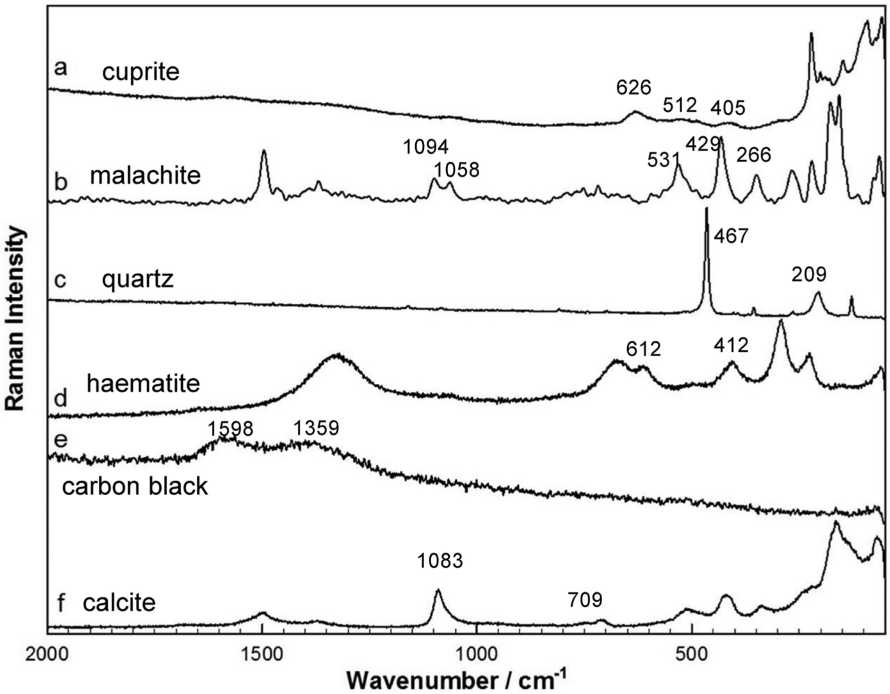

Fig. 2. Raman spectra of identified compounds present at the surface of the Roman bronze objects: a) cuprite, b) malachite, c) quartz, d) hematite, e) carbon black, f) calcite. For characterization of present compounds, the reference Raman databases were used [26,27].

power at the samples was set to 0.14 mW using neutral density filters. A multi-channel, air cooled CCD detector was used, with integration times between 5 and 20 s, and the spectral range was set between 50 and 4000 cm^{-1}. Wave number calibration was performed using a silicon wafer.

Electron microscopy

An electron microscope JEOL JSM-IT500LV with an Aztec Live Advanced ULTIM 65 detector (Oxford Instruments, 2019) equipped with energy-dispersive spectroscopy (EDX) was used to observe archeological bronze object at an accelerating voltage of 20 kV.

2.4. Visual examination (visual and digital image studies)

The program Matlab was used to define areas, covered by green corrosion product, using the color weight program. The bronze samples exposed to the different atmospheres were photographed once a week using macro lens at a resolution of 1772 × 1181 pixels. At the end of the exposure the macro photos of the exposed bronze samples were first cut off the background and the edge of the sample was refined. Then, the prepared images were imported into the Matlab program, where the colors of individual pixels of macro photos were detected. Colors which represented the corrosion products were then selected and the number of pixels counted. The proportion of corrosion on the bronze samples was calculated by dividing the number of pixels that represented corrosion products by the number of pixels that represented the exposed area.

3. Results and discussion

3.1. Bronze samples

Table 1
Reference Raman shifts of copper(II) acetate monohydrate and band assignments (Frost 2007) compared to the experimental Raman data. Letters next to a number denote strength of the band: vw (very weak), w(weak), s (strong) and vs (very strong).

(Frost 2007) Raman shifts /cm^{-1}	Experimental Raman shifts /cm^{-1}	Assignment [29]
3478	3480 (w)	ν (O–H)
3024	3028 (w)	ν (C–H) of methyl
2989	2987 (w)	
2941	2945(vs)	
2862	2862	
1449	1448 (w)	δ(CH_3) deformation
1440	1443 (w)	ν (COO)
1418	1418	δ (CH_3) deformation
1360	1360 (w)	methyl (HCH) deformation
948	949(s)	ν (CC) of acetate anion
938	939	
703	704	δ (OCO) deformation of acetate anion
684	685(s)	
322	321	
297	299(vs)	
252	251	
212	215	

Bronze model samples exposed to the acetic acid atmosphere became covered with green corrosion products. The intensity of the growth of green to blue corrosion product was different whether the bronze surface was exposed bare or brushed with 3% ethanol solution of TMI corrosion inhibitor. Blue corrosion product was analyzed and the presence of copper(II) acetate monohydrate ($Cu(CH_3COO)_2{\bullet}H_2O$) was confirmed by Raman analysis (Fig. 3). Table 1 shows a good agreement between the Raman modes of the exposed sample and the published reference data [29].

In addition to the presence of copper(II) acetate monohydrate at the surface, copper nitrate was also found, with the strongest Raman band at 1050 cm^{-1}.

The presence of copper nitrate is connected to the promoter of a stable acetic vapor atmosphere, since magnesium nitrate was used. The Raman spectra were analysed on oxidized bronze as well, similar products were analysed, namely copper nitrate and copper acetate. However, results are not shown in Fig. 3.

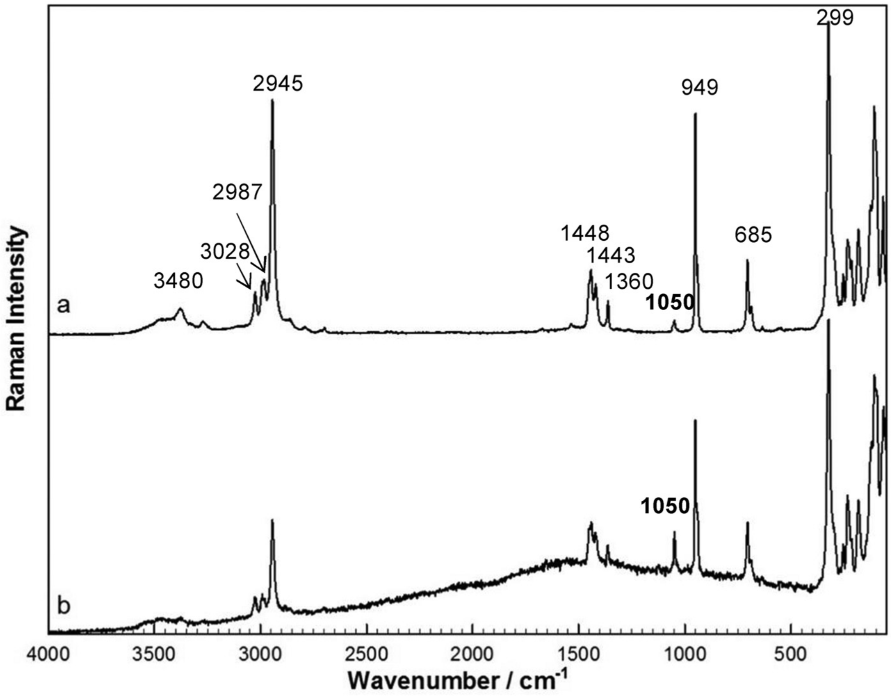

Fig. 3. Raman spectrum of copper (II) acetate monohydrate formed at the surface of the non-oxidized bronze sample investigated: a) non-protected surface; b) surface protected by application of TMI.

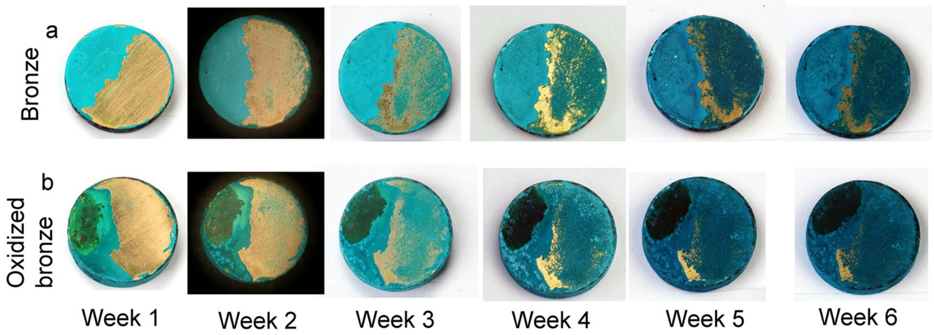

Fig. 4. Images of bronze samples: non oxidized a) and oxidized b), the right half brushed with 3% ethanol solution of TMI.

Fig. 4 presents images of bronze and oxidized bronze after different times of exposure. Each sample was exposed on the following manner. Half of the sample was bare and the right half of the sample was brushed with 3% ethanol solution of TMI. At the end of weakly exposure, the sample was taken out, image was taken and the new acetic vapor atmosphere was prepared. Sample was freshly exposed for another week and so forth until 6 weeks of exposure. It can be observed that the acetic atmosphere is very corrosive since corrosion products formed already in the first week of exposure. The formation of corrosion product on surfaces, with TMI progressed in a slower manner, but still intensively. No big difference is observed between non oxidized and oxidized bronze. Then, the images were background subtracted and the edges where corrosion is intensive was eliminated. These images were then imported in a lab made program for recognition of colors and the intensity of areas with blue corrosion product were defined. Three different observers made evaluation, which is shown with error bars in Fig. 5.

Fig. 5 shows the percentage of coverage of corrosion products in the bronze and oxidized bronze samples relative to the length of exposure to acetic acid vapors. In the first week of exposure both the bronze and oxidized bronze samples without protection already showed 95% of corrosion development. By the fourth week of exposure 100% of the surface was corroded in both samples. It appeared that the oxidized bronze surface did not slow down the process of secondary corrosion development. In the first week of exposure, the TMI inhibitor significantly reduced the development of corrosion, allowing only 8% of the surface area to be corroded on the bronze and 6% on the oxidized bronze surface. It is evident that the formation of corrosion on a non-protected surface is much faster than on a surface protected by the TMI inhibitor.

Previously, the protective effectiveness of nontoxic and innoxious compounds of 1-(p-tolyl)–4-methyl imidazole (TMI) were found to be efficient. The inhibiting efficiency TMI was close to 70% after 72 h of immersion in artificial rain at pH 5 [9]. In our previous studies, the inhibiting effect of BTAH and TMI on electrochemically patinated bronze was observed in cases when the inhibitor was applied as a topcoat in ethanol solution, and also when it was dissolved in the test solution. In the latter case, the anticorrosive properties were more pronounced and the corrosion current density decreased more of BTA was applied when compared to TMI, which was efficient even though [10]. In the case of bronze samples in our experiment the surface protected by the TMI inhibitor also became 100% covered by copper(II) acetate monohydrate af-

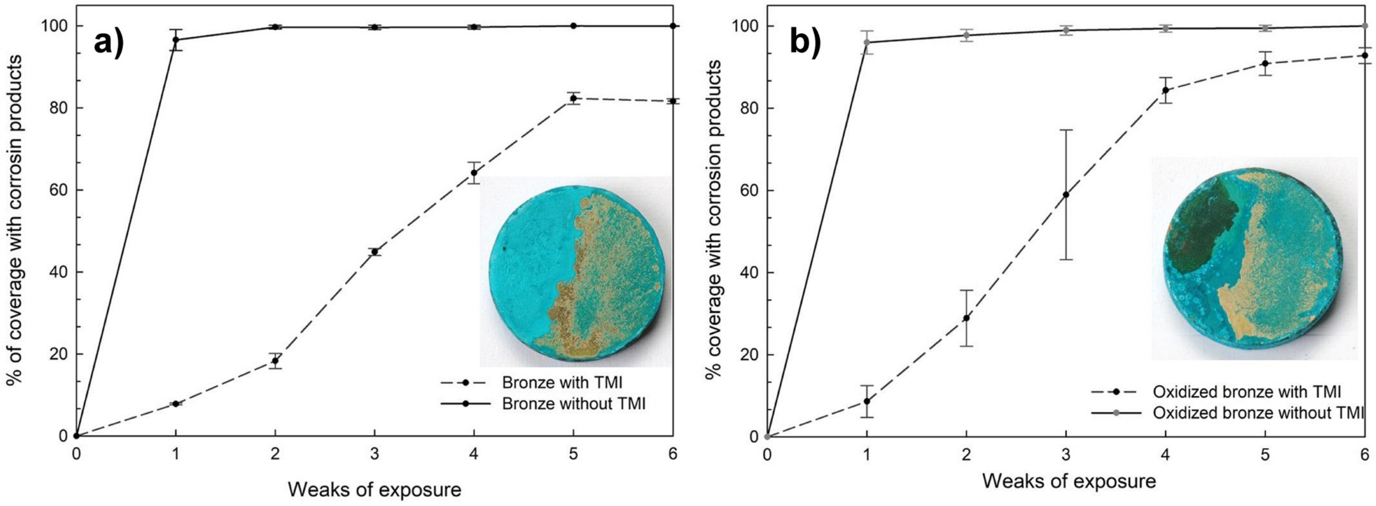

Fig. 5. % of coverage of samples relative to the number of weeks of exposure, and a photo of bronze and oxidised bronze samples after 6 weeks of exposure. Dotted line: pure bronze surface of the sample. Solid line: surface of bronze with TMI application: a) bronze sample, b) oxidized bronze sample.
Coverage with corrosion products in% for bronze samples relative to the number of weeks of exposure, and a photo of bronze and oxidized bronze samples after 3 weeks of exposure. Solid line: pure bronze a) and oxidized bronze surface of the sample b); Dashed line: surface of bronze a) and oxidized bronze with TMI application b).

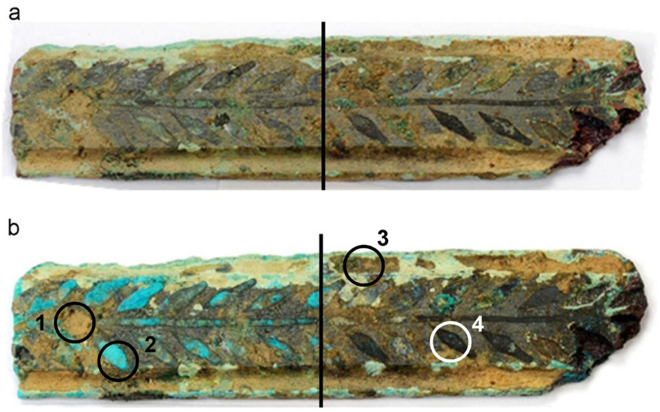

Fig. 6. The selected archeological sample which is supposed to compose part of a bronze earring. The right half of the sample was covered by TMI. a) before exposure; b) after exposure to the acetic acid and formaldehyde atmosphere. EDS analysis was performed on areas denoted.

ter 6 weeks of exposure. It is known that BTA acts as an excellent inhibitor which is still used in practice nowadays. In searching for non-hazardous, innoxious inhibitors for archeological samples, TMI might play a good role, being aware that weaker inhibiting efficiency is achieved. In any case, whenever possible, the alternative method is to control the indoor atmosphere and keeping it as little corrosive as possible with minimal presence of carboxylic acids which affect copper and bronze corrosion to a great extent [18].

The bronze samples that were exposed in the combined atmosphere of acetic vapor and formaldehyde did not show any differences when compared to the samples exposed to an only acetic vapor atmosphere. Moreover, no additional corrosion products were found by Raman microscopy. This suggests the need for a more in-depth study on the influence of combined or synergetic effects of harmful volatile organic compounds, and is a subject of our future research.

3.2. Archaeological sample

One archeological sample was selected to be tested in the atmosphere of acetic acid and formaldehyde. Fig. 6 shows the sample before and after 12 weeks of exposure. The application of TMI on the archeological samples was made directly on the as excavated sample.

Visual examination of the sample shows intense green areas representing corrosion development in the area that was not protected by the TMI inhibitor, while the protected area shows very little corrosion development after 12 weeks of exposure. Since TMI was applied on as excavated samples the possible presence of chlorides could interfere with TMI solution and originate further localized corrosion, thereby EDS analysis was performed on areas denoted on Fig. 6.

It seems that some localized infections of corrosion started on the protected part of the sample (Fig. 6b, right). Localized corrosion could be more dangerous than the more evident general corrosion observed in the Fig 6a, but the estimation is that around 5–10% of the surface became greener after exposure to acetic vapor and formaldehyde atmosphere for 12 weeks and that TMI protected the surface of excavated archeological sample sufficiently well. The results correspond to the results of the exposure of bronze samples as explained and presented in Fig. 5.

It appears that the already corroded surface (composed of cuprite, chalcocite and malachite) protects the object in addition to the applied TMI. The intense green areas are barely visible compared to the bronze models where 100% of the surface was corroded, regardless of protection, after 12 weeks of exposure.

The morphology of the surface on four different area on archeological sample after 12 week exposure is presented on Fig. 7 and the EDS analysis report is given in Table 2.

In area 1 the composition of the analyzed surface points at the presence of the remains of soil deposit, since high amount of Si, Al, P, K and Ca is present (Table 2, spot 1).

In area 2 (Table 2, spot 2) the soil remaining are in minor presence, while a higher amount of copper corrosion product is present as observed from higher weight percentage of carbon, oxygen and copper. In area 3 (Table 2, spot 3) the remains of soil deposit is visible since Si, Al, Ca, Mg were analysed. Copper corrosion product is also present. The difference in analysed spot 4 and 5 in area 4 (Table 2) is in the thickness of corrosion product, zinc is analyzed at area 4, where also higher amount of Fe and S is present. The source of sulfur cannot be explained, but it is present most of the time when Fe was analyzed and with Raman, hematite was confirmed.

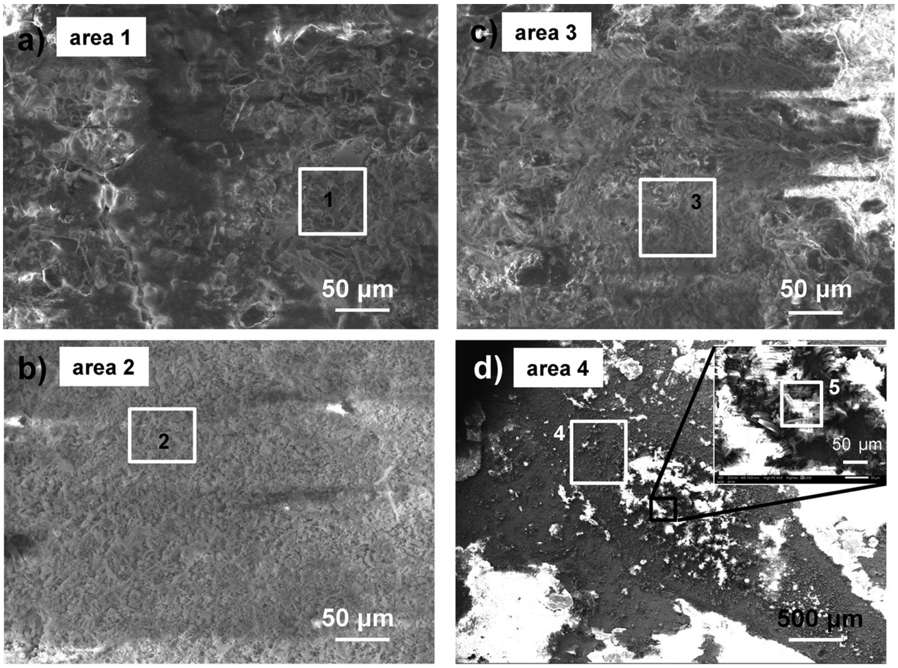

Fig. 7. Morphology of corrosion products found on archeological sample with and without TMI after 12 week exposure to acetic vapor and formaldehyde atmosphere.

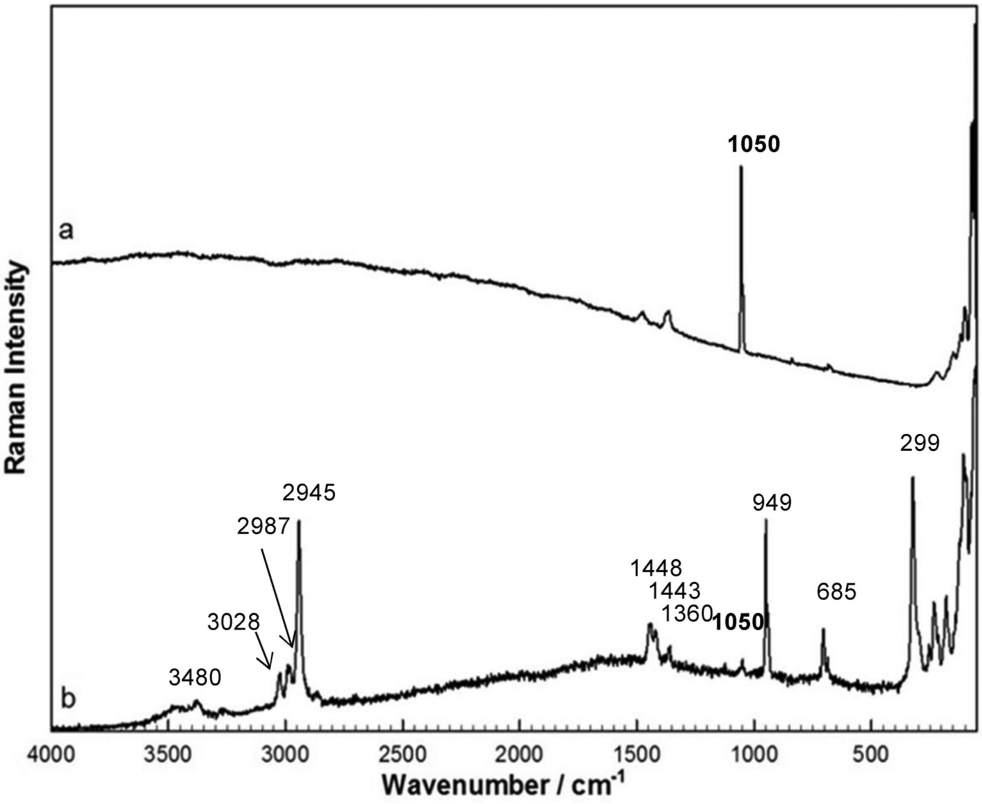

Fig. 8. Raman analysis of the intense green areas protected by the TMI inhibitor: a) Copper nitrate, b) copper acetate monohydrate and weak bands of copper nitrate (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

Further Raman analysis showed the presence of copper acetate monohydrate and copper nitrate in the intense green areas of the surface in both TMI protected and non-protected surfaces, as shown in Fig. 8. The band positions of Raman peaks for copper(II) acetate monohydrate are explained in Table 1.

Although the protection of the surface of the archeological sample is clearly improved after the application of the inhibitor TMI, it is evident that its surface is not completely protected against the attack from acetic acid vapors. The local infected areas could be due to the porous nature of the surface and that penetration

Table 2
EDS analysis of the four different areas on archeological sample after 12 weeks of exposure in acetic vapor and formaldehyde, spot 1 and 2- not protected by TMI, analyzed spot 3,4, 5 protected with TMI, the four areas denoted in Fig. 6, in weight%, analysed spot 5 in the table is smaller green spot on more voluminous corrosion product in area 4 on Fig. 6.

	C	O	Mg	Al	Si	P	Cl	K	Ca	S	Fe	Cu	Zn	Sn	Pb
spot (1)	12	47	1.2	8.3	14.4	1.6	0.1	1.8	1.7	–	5.2	3.4	1.9	0.1	0.5
spot (2)	28	32	–	–	0.2	0.3	0.1	–	0.2	–	–	39	0.3	–	0.1
spot (3)	13	22	0.3	2.6	2.9	1	0.8	–	2.6	1.6	4	44	4.8	–	0.5
spot (4)	24	25	–	0.4	–	–	0.3	–	–	4.5	4	37	1.8	0.5	0.8
spot (5)	30	32		0.2	–	0.2	0.1		0.2		0.1	36	–	–	0.1

depth and effectiveness was weaker at these spots. Furthermore, the intense green appearance of corrosion is very easily noticeable, which enables a very simple evaluation of the status of bronze objects. In the case of the appearance of green corrosion it is therefore recommended to change the environmental conditions in which bronze objects are stored, instead of, or in combination with, the application of an additional corrosion inhibitor.

Conclusions

The influence of the presence of the most harmful indoor pollutant, acetic acid, on bronze objects was studied and compared to the surface of samples that had been previously protected by a tolyl methyl imidazole (TMI) inhibitor. By Raman analysis it was found that copper(II) acetate monohydrate and copper nitrate formed on bronze and oxidized bronze samples as early as the first week of exposure to acetic acid vapors. After 4 weeks of exposure the non-protected surfaces developed 100% of corrosion, which was evaluated by visual and digital image studies. A suppression of corrosion was determined after the TMI application; however, the protected surfaces still developed high corrosion products coverage towards the end of exposure. Nevertheless, a relatively good efficiency was proved for the TMI inhibitor.

The efficiency of TMI was even more pronounced after its application to the selected archeological sample, where the presence of archeological patina probably further suppressed the development of corrosion.

Despite good effectiveness of TMI when applied to archeological bronze samples it is recommended to take special care against indoor pollutants in storage rooms or boxes where objects are held. The degradation of bronze objects was shown in a simple demonstration using visual assessment in order to define corrosion development over time due to the influence of acetic acid vapors. Our future work, however, will focus on the synergetic effect of acetic acid, either in combination with other indoor pollutants, such as formic acid and formaldehyde, or at differing levels of relative humidity. Also, TMI will be compared to BTA inhibitor to define inhibition efficiency relative to each other in different application manners.

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