[1-2]**Liliana Gianni,**
liliana.gianni@uniroma1.it
[1]**Annemie Adriaens,**
annemie.adriaens@ugent.be
[2]**Mauro Cavallini,**
mauro.cavallini@uniroma1.it
[2]**Stefano Natali,**
stefano.natali@uniroma1.it
[2]**Valerio Volpe,**
valerio.volpe@uniroma1.it
[2]**Laura Zortea**
laura.zortea@uniroma1.it

[1]Dept. of Analytical Chemistry
Ghent University
[2]DICMA, Sapienza
Università di Roma

Reflectance curves and CIE L* a* b* parameters to describe patina characteristics and corrosion mechanism on bronze alloys

1. INTRODUCTION AND RESEARCH AIM

Metals have had in the past and still have nowadays many applications. One of the oldest and most frequently used metals has been copper and one of its alloys: bronze, which is copper and tin alloy. Bronze is often used because of its good mechanical properties and for its colour range when corroded, which can give different aesthetic results to the artifacts. The colour of bronze depends on the concentration of the main components and any additional alloying elements. Not only gives the composition a specific colour to the alloy, it also influences the corrosion behaviour. This research focuses on the correlation between urban and marine environments and the corrosion behaviour of three bi-component copper-tin alloys used in different historical and artistic artifacts using colorimetry. Colorimetric measurements are useful because they are non-destructive and can be done using compact instruments, which are portable, implying that in-situ measurements can be done in a relatively rapid manner [1]. In addition spectrocolorimetry can detect the copper content in quasi-binary bronzes [2] and can assess the condition of metallic findings and their mineralization degree [3-4]. The characterization of bronze patina, with a possible link to a variable thickness of the layer or to a different corrosion mechanism, has also been studied [5-8]. In this work colorimetric measurements are used as a means to study the influence of the tin content on the corrosion behaviour of the bronze samples and to understand the corrosion kinetics.

2. MATERIALS, SAMPLES PREPARATION AND EXPOSURE

Three bronze alloys were selected to represent historical and artistic artifacts, with a tin concentration of 3%, 7% and 20% respectively [9]. The surfaces of the bronze coupons (diameter 12.5 mm) was ground/polished with abrasive papers of 400–1200 grades. They were then cleaned with sulphuric acid at 10%V/V, rinsed with distilled water and degreased with acetone. Two samples of each alloy were exposed to an urban pollution in the Faculty of Engineering of Sapienza University of Rome and two for each alloy to a marine environment in a coastal town (Fiumicino) from January to April 2011. The samples were oriented towards the south and had an inclination of 45° following ISO 9223 [10]. Under these conditions colorimetric variations were measured every two weeks for the urban samples and every month for the marine samples. In addition in the laboratory a third set of samples was exposed to wet and dry cycles of acid rain and marine spray (the composition of both solutions is listed in Table 1 [11-12]) for a total of 0.66 mL of vapour per cycle in a volume of 45 cm^3. The temperature was kept at 20°C. Colorimetric measurements were done on six samples of each alloy after 2 hours, 4 hours, 24 hours, 48 hours, 96 hours and 240 hours.

Acid rain (mg dm^3)		Marine spray (g/dm^3)	
H_2SO_4 (96%)	31.85	NaCl	23,5
$(NH_4)_2SO_4$	46.20	KBr	0.1
Na_2SO_4	31.95	KCl	0.7
HNO_3 (70%)	15.75	$CaCl_2$	1.3
$NaNO_3$	21.25	Na_2SO_4	4
NaCl	84.85	$MgCl_2 * 6H_2O$	10.7

3. METHODS

The colorimetric measurements were carried out with a portable sphere spectrophotometer. The spectrophotometric measurements were performed in SPIN (specular component included) mode, with D65 illuminant and 10° standard observer. The reflected light percentage (%) was measured as a function of the wavelength (nm) in the visual spectrum. In correspondence to wavelengths between 400 and 700 nanometers, the spectrophotometer reports spectral data (percentage of reflected light) every 10 nm. The colour difference (ΔE) between two measurements is based on the L*, a* and b* values as follows:

$$\Delta E = \sqrt{(\Delta L^*)2 + (\Delta a^*)2 + (\Delta b^*)2}\ [5]$$

One must note that the ΔE equation was originally designed for calculating small differences (ΔE<10). Higher values obtained here will be considered only for comparative purpose. All together with this numerical colour identification the aim is to asses the degradation levels of the three alloys exposed to natural and artificial environments and the corrosion kinetics. This is done by correlating the above-mentioned colour parameters with the patina quality and growth.

4. EXPERIMENTAL

4.1. URBAN ENVIRONMENT EXPOSURE

The samples exposed to the urban environment produce a brown/black patina in a few days. The reflectance curves as a function of time are shown in Figure 1 for the three samples. The difference in reflectance curves for the 3% and 7% samples is relatively large between no exposure and two weeks of exposure, indicating that the surface immediately becomes matt or textured upon exposure. The variation becomes less significant with increasing exposure time. The samples containing 20% tin, on the other hand, seem to have undergone the least damage, in that regard that the reflectance curves show a decrease but not as large as the other two samples.

These data are confirmed by the lightness and ΔE values which show a large decrease during the first weeks for the 3% and 7% samples and much less for the 20% sample (Figure 3b;

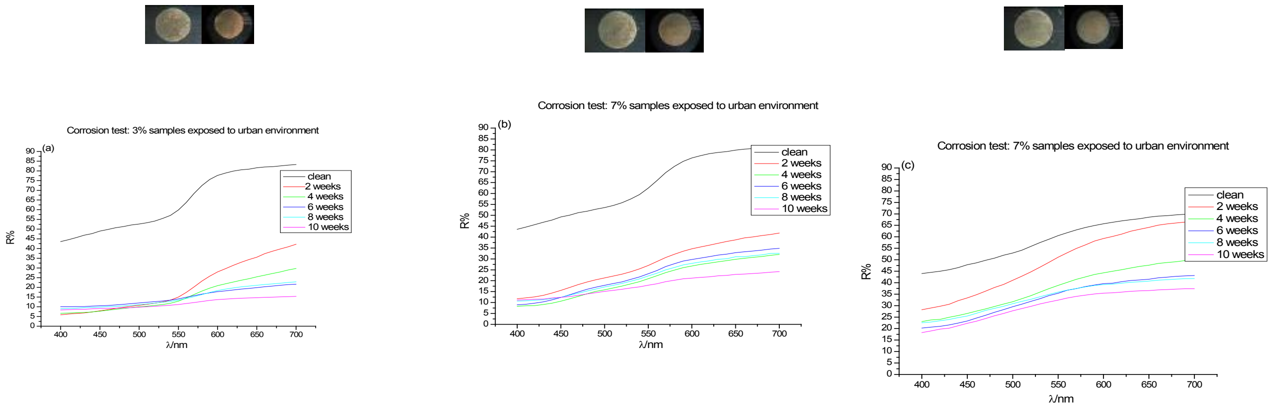
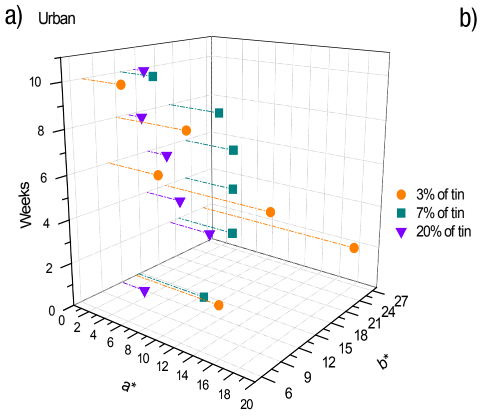


Figure 1 - Reflectance curves for samples with (a) 3%, (b) 7% and (c) 20% of tin exposed to an urban environment from January to April 2011.



b)

Table 1: 3% of tin sample exposed to urban environment				
	L*	a*	b*	ΔE
clean	83.63	10.35	14.17	37.06
2 weeks	49.48	18.21	26.24	9.82
4 weeks	45.12	12.78	19.31	10.94
6 weeks	45.15	6.11	10.63	2.67
8 weeks	44.68	8.37	11.97	7.11
10 weeks	40.51	4.77	7.46	

Table 2: 7% of tin sample exposed to urban environment				
	L*	a*	b*	ΔE
clean	84.07	8.26	14.63	25.50
2 weeks	59.58	6.98	21.64	6.61
4 weeks	53.16	6.14	22.96	2.55
6 weeks	55.7	6.32	22.77	2.79
8 weeks	54.48	6.25	20.26	9.21
10 weeks	49.61	4.01	12.76	

Table 3: 20% of tin sample exposed to urban environment				
	L*	a*	b*	ΔE
clean	81.76	2.99	11.94	9.85
2 weeks	76.44	5.29	19.91	8.95
4 weeks	68.35	4.34	16.18	3.31
6 weeks	65.65	2.46	16.59	3.09
8 weeks	65.99	1.84	13.58	3.05
10 weeks	63.23	1.27	14.76	

Figure 3 - The CIEL* a* b* parameters detected for the samples exposed to urban environment. a) a* and b* parameters plotted vs exposure time; b) tables of L*, a*, b* and ΔE for the three alloys.

Table 1-3). In addition the ΔE values show for the 3% and 7% samples an increase during the ninth week, which indicates that the first patina formed slows down the corrosion process that restarts during the ninth week. From the ΔE values decreases we can deduce that the patinas formed on the 20% tin samples progressively slow down the corrosion process (Figure 3b; Table 3). Nevertheless, also here the largest difference in colour values of the corrosion products can be deduced from L* and ΔE values between the clean alloy and after the first weeks. This difference indicates a fast oxide passivating layer formation.

The colour parameters can be correlated with patina quality and growth: the advanced corrosion of the 3% alloy is shown by the L*, a* and b* compared with the 7% and 20% of tin parameters. The kinetic aspects are correlated to the fact that the ΔE values of 3% tin samples are larger than for the other alloys (Figure 3b; Tables 1-3).

4.2. ACID RAIN VAPOUR IN THE CORROSION CHAMBER

In the laboratory environment, the colour evolution of the three alloys was examined while being exposed to acid rain vapour for 10 days. The reflectance curves as a function of time are shown in Figure 2, while the values of the lightness and colour are reported in the Tables 1 through 3 of Figure 4b.

The reflectance curves show a similar trend, though with a smaller dynamic range, as for the urban environment: a relatively large difference between no exposure and two hours of exposure for the 3% and 7% samples (after which the curves seem to stabilize) and only a small variation for the 20% sample. The latter demonstrates again that the 20% samples seem to be the less attacked: the reflectance values are higher and the ΔE values are lower than for the other samples, as is shown in Figure 2 and in the tables of Figure 4b. The differences detected by the reflectance, lightness, a* and

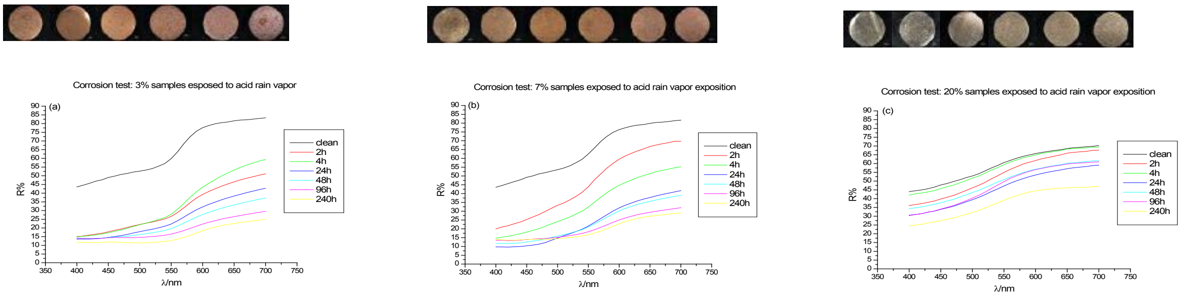
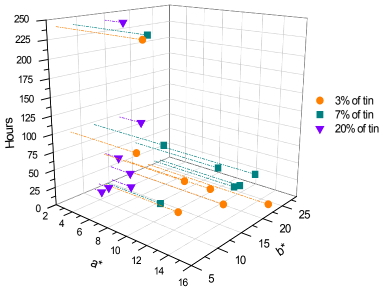


Figure 2 - Reflectance curves for samples with (a) 3%, (b) 7% and (c) 20% of tin exposed to acid rain vapour respectively for 2, 4, 24, 48, 96 and 240 hours.

a)



b)

Table 1: 3% tin sample exposed to acid rain vapour

	L*	a*	b*	ΔE
0h	83.63	10.35	14.17	22.78
2h	61.06	12.38	19.73	4.95
4h	62.66	15.25	23.44	8.83
24h	56.26	11.54	18.61	5.53
48h	53.26	11.07	13.98	7.32
96h	49.31	9.39	8.05	5.22
240h	44.57	10.98	6.53	

Table 2: 7% tin sample exposed to acid rain vapour

	L*	a*	b*	ΔE
0h	84.07	8.26	14.63	16.32
2h	73.31	11.3	26.52	8.56
4h	64.85	11.21	25.18	10.19
24h	54.92	12.6	27.04	2.83
48h	54.48	11.43	20.56	4.53
96h	51.38	9.79	12.4	3.57
240h	49.55	9.88	9.33	

Tab 3: 20% tin sample exposed to acid rain vapour

	L*	a*	b*	ΔE
0h	81.76	2.99	11.94	4.99
2h	78.71	4.35	15.65	3.78
4h	81.17	3.21	13	7.56
24h	74.09	4.42	15.38	2.63
48h	76.36	3.74	14.23	3.05
96h	75.45	4.64	17.4	7.36
240h	68.48	4.1	15.09	

Figure 4 - The CIEL* a* b* parameters detected for the samples exposed to acid rain vapour. a) a* and b* parameters plotted vs exposure time; b) tables of L*, a*, b* and ΔE for the three alloys

b* measured on the alloys (Figure 4b; Tables 1-3) are due to the composition and physical-chemical property of the patinas.

A comparison between the natural environment and the artificial one is possible with the samples of the second week and of the 240th hour (corresponding to ten days) if some caution is taken. For the 3% samples the lightness values reduction is bigger in the laboratory test (49.48 vs 44.57) while the a* values increases for both samples but more significant for the natural corrosion (18.21 vs 10.98). Also the b* (26.24 vs 6.53) is bigger for the sample exposed to acid rain vapour. That means there is a patina more formed on the sample exposed to acid rain vapour because of higher red and yellow values and lower lightness.

The 7% sample shows a big difference for the L* (59.58 vs 49.55) and the b* (21.64 vs 9.33). Also in this case the sample exposed to laboratory test shows a patina more developed. However the differences between the two patina are less accentuated for the colour parameters than in the 3% samples. The 20% samples maintain a rather similar colour patina

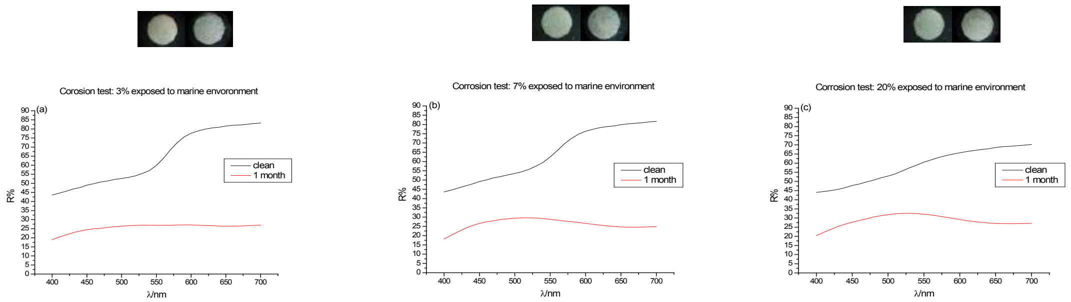
4.3 MARINE ENVIRONMENT EXPOSURE

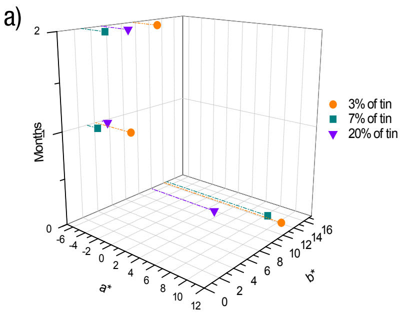
The colour measurements for the marine environment were performed once per month. Figure 5 shows the reflectance values for the first two months of exposure. The patinas formed in this environment have a characteristically green colour due to the chloride presence in the marine environment.

In the 3% of tin samples the green grows continuously whilst for the 7% and 20% it decreases in the second month as a* values underline (Figure 7; Tables1-3). Nevertheless the green colour remains always more accentuated than in the 3%.

Different in comparison to the samples exposed to the urban environment, the CIE L*a*b* parameters for the marine environment are very similar in the three alloys. This happens because of the strong aggressiveness of the marine environment that has the same effects on the surfaces, also in the presence of tin that generally has a good corrosion resistance. The ΔE differences between the three alloys are less than in the tests before but also in this environment the smaller difference colour is on the 20%.

Figure 5 - Reflectance curves for samples with (a) 3%, (b)7% and (c) 20% tin exposed to marine environment from January to April 2011.





b)

3% tin sample exposed to marine environment				
	L*	a*	b*	ΔE
Clean	83.63	10.35	14.17	29.37
1 month	58.69	-1.49	4.16	4.31
2 months	56.3	-3.1	0.95	

7% tin sample exposed to marine environment				
	L*	a*	b*	ΔE
Clean	84.07	8.26	14.63	29.95
1 month	59.99	-5.24	3.01	7.01
2 months	53.23	-3.4	2.86	

20% tin sample exposed to marine environment				
	L*	a*	b*	ΔE
Clean	81.76	2.99	11.94	22.42
1 month	62.45	-6.01	4.94	3.74
2 months	60.47	-2.86	5.3	

Figure 7 - The CIEL* a* b* parameters detected for the samples exposed to marine environment. a) a* and b* parameters plotted vs exposure time; b) tables of L*, a*, b* and ΔE for the three alloys.

4.4 MARINE SPRAY VAPOUR IN THE CORROSION CHAMBER

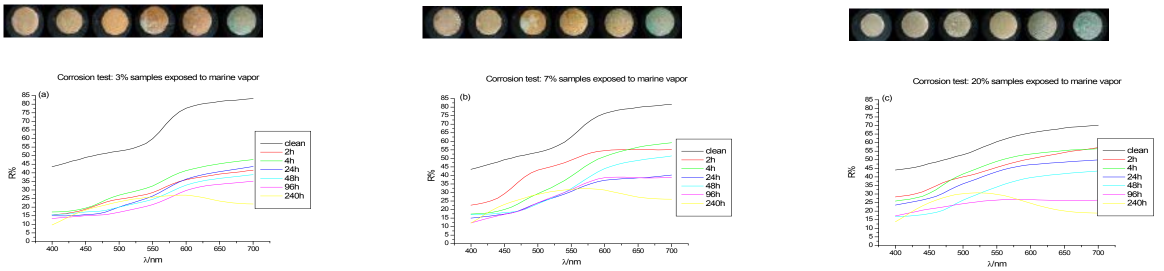
In the vapour chamber the three sets of samples were sprayed with synthetic marine water for ten days. The colour measurements were taken at the same time intervals as was done for the synthetic acid rain vapour tests. The optical microscopy images and the reflectance curves are shown in Figure 6. The surface patinas are not homogeneous and exhibit patches of different dimensions on inner corrosion layer. Spectrocolorimetric measurements are performed on small areas and in this case different spots are present. Results of the instrument are therefore the integration of values of each colour contribution. In the first hours of exposure the reflectance shows dominant values in the green region because the chloride patinas are immediately formed. The 3% samples in the area analysed have less patches despite inversion of the reflectance values. Samples containing 7% of tin undergo a larger attack in the first 4 hours. 20% samples have higher reflectance values than the other alloys, which may indicate they are less prone to corrosion, nevertheless the samples always present green spots from the first exposition.

The ΔE value is strongly affected by the patina inhomogeneity as is the case for the other parameters. It is possible to extract only an indicative evaluation that shows a smaller difference in colour for all the 20% samples compared to the 3% and 7%. The 7% samples present always more colour differences (Figure 8b).

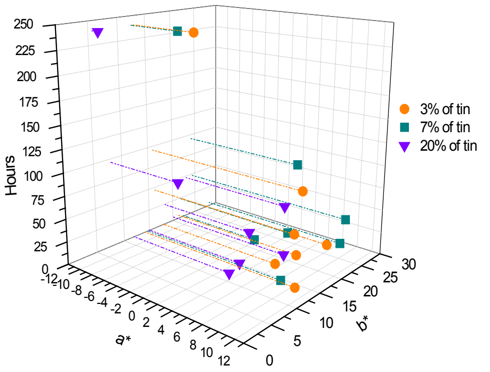
5. CONCLUSIONS

The colour measurements are able to demonstrate the patina formation with a good sensibility also for the first steps, which cannot be evaluated with visual analyses. The difference in colour between two measurements gives an idea about the kinetics of the corrosion process, whilst the reflectance and lightness values can be correlated to the layer growth. The a* and b* values are associated with the patina composition. The study shows the

Figure 6 - Reflectance curves for samples with (a) 3%, (b) 7% and (c) 20% tin exposed to marine spray respectively for 2, 4, 24, 48, 96 and 240 hours.



a)



b)

3% tin sample exposed to marine vapour				
	L*	a*	b*	ΔE
0h	83.63	10.35	14.17	23.02
2h	61.33	5.7	17.55	4.89
4h	64.52	6.41	21.19	6.17
24h	59.58	10.06	21.81	6.15
48h	57.86	9.04	15.99	3.20
96h	54.84	10.08	15.77	13.34
240h	57.16	-2.74	12.93	

7% tin sample exposed to marine vapour				
	L*	a*	b*	ΔE
0h	84.07	8.26	14.63	14.30
2h	75.11	-0.1	22	12.05
4h	69.5	8.48	28.34	10.58
24h	62.08	4.87	21.72	7.09
48h	64.41	10.99	24.44	6.50
96h	62.81	4.71	23.94	14.89
240h	62.07	-4.68	12.41	

20% tin sample exposed to marine vapour				
	L*	a*	b*	ΔE
0h	81.76	2.99	11.94	9.06
2h	73.13	2.56	14.67	6.03
4h	74.76	0.53	20.11	4.37
24h	70.86	1.48	18.37	8.19
48h	64.46	3.59	23.03	17.14
96h	57.87	-1.39	8.01	9.91
240h	59.87	-10.74	5.39	

Figure 8 - The CIEL* a* b* parameters detected for the samples exposed to marine vapour. a) a* and b* parameters plotted vs exposure time; b) tables of L*, a*, b* and ΔE for the three alloys

differences between the corrosion behaviour of three bronze alloys exposed to urban and marine environment. In the urban environment, in both exposition tests, the 3% tin samples are the most attacked especially in the fist time (this is better underlined with the laboratory tests) while the 7% sample has a slower reaction with the environment but the processes goes on as in the 20% that are however less damaged. Natural and laboratory exposition reach the same results but the second tests are most focused on the first corrosion products that are the internal layers of the corrosion product of the samples exposed to the natural urban environment. The samples exposed to the marine environment are more attacked than the samples exposed in urban environment. The patina is thick and massive until the first month. The colour depends mainly on the presence of the sodium chloride. The green products are present from the first hours in the laboratory tests. The formation proceeds with separate spots under which are hidden also other corrosion products. The 7% of tin in this environment show more colour difference than the 3% whilst the 20% have the best corrosion behaviour also in this case.

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