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Classification Studies on Etruscan Archaeological Copper-Based Alloy Findings from the Necropolis of 'Pratino' in Tuscania

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ABSTRACT

In this communication, an extensive study and its results are presented about the composition of some Etruscan copper alloy findings. The objects came from Tomb 20 of the "Pratino" necropolis in Tuscania, near Viterbo (Italy), dating back to the late Hellenistic period. The excavation and study of the site was granted to the Lorenzo de' Medici Italian International Institute (Ld'M) in 2005. Since 2011, the activity is directed by the Center for Ancient Mediterranean and Near Eastern Studies (CAMNES). The archaeological materials were classified according to their composition, determined by a portable Energy Dispersive X-Ray Fluorescence (ED-XRF) instrument.

1. INTRODUCTION

Tuscania is a small village in northern Lazio, in the innermost part of southern Etruria. As for many other cities of antiquity, we known the Etruscan site of Tuscania only thanks to its necropolises, which are distributed around the San Pietro hill, where the Acropolis of the city was probably located.

In North-West of the Tuscania territory lies an area currently known as "Macchia della Riserva", characterized by a thick scrub. The area has always been affected by unauthorized excavation, but only in 2005 the *Soprintendenza per i Beni Archeologici dell'Etruria Meridionale,* the government body in charge of protecting Italian archaeological patrimony, entrusted to the *Istituto d'Arte e Cultura "Lorenzo de'Medici" (Ld'M)* in collaboration with the *Center for Ancient Mediterranean and Near Eastern Studies (CAMNES)* from 2011, to start a campaign of research and excavation in this area. As a result, two distinct cores of Etruscan necropolises were uncovered: one was found in a locality called 'Pian delle Rusciare' and the other in 'Pratino'. In this second necropolis the excavation was started in 2008 and is currently in progress [1].

Tomb 20 of the Pratino necropolis was discovered in July, 2009. The tomb dates back to the late Hellenistic period, is dug into a tuff rock and is characterized by a short *dromos* going downhill to the burial chamber that has a roughly elliptical elongated plan. In the lateral walls of the *dromos* there are two niches and in the west wall there is another vertical niche. In the burial chamber thirty seven niches (nineteen in the west side and eighteen in the east) dug into the rock were found, divided in two rows by a central narrow passageway. Three stone slabs close the entrance located on the south side of the chamber. One incinerate body, a few bone fragments and more than five hundred objects including ceramics, bronze, iron and silver artifacts were found inside this tomb.

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Id	Inventory number	burial
	VARIOUS	
1	11	XXI-XXIV
2	241	XXIX
	COINS	
3	300	XXXI
62	141b	XXXI
	NAILS	
4	381/1	XXXIV
5	381/2	XXXIV
6	381/3	XXXIV
	ARMILLAE	
7	88	XXI
8	15	VI
9	298	XXXI
10	52	XIII
	MIRRORS	
11	77	XX
12	254	XXX
13	379	XXXIV
14	31	VII
15	54	XIV
16	195	XXVI
17	299	XXXI
18	114	XXIII
19	3	XXI-XXIV
	HANDLES	
20	295	XXXI
21	378	XXXIV
22	240	XXIX
23	137	XXIV
24 a	247 (attributed)	XXX
25 a	247 (attributed)	XXX
26	251	XXX
27	252	XXX
28	253	XXX
29	403	XXXVI

Id	Inventory number	burial
	VASES	
24	247	XXX
25	247	XXX
30	45	XI
31	250	XXX
32	402	XXXVI
33	135	XXIV
34	17	VI
35	240	XXIX
36	239	XXIX
37	136	XXIV
38	16	VI
39	113	XXIII
40	247	XXX
41	249	XXX
42	251	XXX
43	252	XXX
44	404	XXXVI
45	34	X
46	128	XXIII
47	248	XXX
	FRAGMENTS	
48	1/ XXI-XXIV	XXI-XXIV
49	2/ XXI-XXIV	XXI-XXIV
50	4/ XXI-XXIV	XXI-XXIV
51	5/ XXI-XXIV	XXI-XXIV
52	6/ XXI-XXIV	XXI-XXIV
53	7/ XXI-XXIV	XXI-XXIV
54	8/ XXI-XXIV	XXI-XXIV
55	9/ XXI-XXIV	XXI-XXIV
56	10/ XXI-XXIV	XXI-XXIV
57	1/XXXVI	XXXVI
58	2/XXXVI	XXXVI
59	3/XXXVI	XXXVI
60	1/Dromos	Dromos
61	2/Dromos	Dromos

Table I – List of the samples studied in this work

The findings of this tomb were already analysed by the authors with non-destructive method and portable equipment such as Energy Dispersive X-Ray Fluorescence (ED-XRF) and Laser-Induced Breakdown Spectroscopy (LIBS) [2]. A specially attention was devoted to the study of the elemental exchanges between the archaeological findings and the environment. In this communication, we focus our attention on the copper-based alloy objects, which represent the majority of the findings in Tomb 20, with the purpose of proposing a classification based on their compositional characteristics, determined by ED-XRF.

2. RESULTS AND DISCUSSION

The spectrographic analysis of the findings was carried out using an ED-XRF (Energy Dispersive X-Ray Fluorescence) instrument produced by Amptek Inc. (Bedford, MA, USA). The X-ray tube produces a beam of 40keV maximum energy, while the detector is of the Silicon-drift type with thermoelectric cooling. The ED-XRF technique is capable of analyzing the surface of the object to a depth of a few tens of microns, depending on the element under analysis; it is not able to detect the elements at low concentration (typical Limit of Detection around 100 parts per million) and with atomic weight less than 14 [3].

In archaeological findings, the surface is usually characterized by a typical oxidation layer due to chemical-physical alteration process and interchange with the environment that may cause either enrichment or depletion of the elements on the surface [4]. This is an important limit which reduces the possibility of performing accurate quantitative analysis using ED-XRF, since the composition of the surface altered material might not be representative of the composition of the original material. However, it has been demonstrated that the enrichment or depleting of some elements at the sample surface does not prevent the possibility of obtaining a correct qualitative analysis of the bulk alloy [5]. In this study, we analyzed all the copper alloy findings of the Tomb 20, sixty-four object in total, as reported in Table I. The entry on the table are color-coded for evidencing the main typologies of the findings (Coins, Nails, *Armillae*, Mirrors, etc.).

The findings were not restored and show a heavy corroded layer at their surface. Moreover, some objects were still partly covered by the soil in which they laid and it was possible to mechanically remove only a part of it for the analysis. Due to the heterogeneous nature of the artifacts, we analyzed by ED-XRF at least two points on each artifact; the compositional results obtained for each sample were then averaged. The acquisition time was 60 seconds per point. For obtaining the samples' composition starting from the XRF spectrum, the ED-XRF spectra were analyzed using the PyMCA software, implementing the Fundamental Parameters algorithm [6]. According to the procedure, the software was calibrated using a series of bronze reference samples of known composition. On the basis of the above considerations on the various sources of indetermination affecting the ED-XRF analysis of heavily corroded bronze samples, we estimate an experimental error on the concentration of the main elements of the order of +/- 5 %, produced by the previously discussed effects of enrichment and depleting of some elements, due to the presence of a thick corrosion layer at the surface of the findings. In spite of this large (and unavoidable) experimental error, the quantitative analysis is nevertheless useful for classification purposes [5]. The results of the compositional analysis of the findings are reported in Table II. The main elements of interest are Sn, Pb, Zn, Ag, Sb, As and Au. Other elements, such as Fe, Mn, Ca, Ba, etc… are measurable in the XRF spectra but not meaningful, since they are related to the environment and their concentration on the findings' surface is not representative of the original composition of the samples [2].

The findings can be preliminary divided in two groups, according to their concentration of zinc. In fact, some samples show a considerable quantity of zinc in their composition, estimated between 3 and 10% in weight (see Table II).

Id	Zn (w%)	Sn (w%)	Pb (w%)	Ag (w%)	As (w%)	Sb (w%)	Au (w%)
20	7	0.8	3	0.3	0.8	0.06	0.3
30	10	1.8	1.5	0.1	0.02	0.2	0.1
31	4	0.8	4	0.2	0.6	0.2	0.1
49	6	0.8	2	0.3	1.2	0.2	0.2
50	3	1.1	1	0.5	0.3	0.2	0.2
51	7	1.0	2	0.3	0.2	0.3	0.1
52	10	0.9	10	0.3	0.1	0.2	0.3
53	5	1.4	3	0.3	0.01	0.4	0.9
54	6	1.8	4	0.5	0.02	0.4	0.3
56	9	0.4	2	0.1	0.3	0.05	0.2

Table II – Samples with high zinc concentration (> 3%)

These samples correspond to one handle (sample 20), two vase fragments (30 and 31) and seven undetermined fragments (49, 50, 51, 52, 53, 54, 56).

It should be noted that the samples with high Zn concentration are also characterized by a low tin concentration (between 0.5 to 2%), so they can be defined as brass (copper alloy with zinc). All these samples also have relatively low Pb concentrations (<4%), except sample 52, where the lead concentration is around 10%.

The use of brass by the Etruscans is the subject of some debate [7,8]. According to Craddock [9, 10] the use of brass, although very rare in Etruscan artifacts, is testified by the finding of a statuette of a naked youth, with around 10% of zinc and less than 1% of tin, dated around III-II century B.C. [11]. The results that we have obtained on the fragments form the Tomb under study are coherent with the dating and composition of this statuette.

The other bronze samples can be further classified according to their composition (shown in Table III).

Table III represents a matrix of data that are usually analyzed with statistical methods such as the Principal Component Analysis (PCA) algorithm [11].

Id	Sn (w%)	Pb (w%)	Ag (w%)	As (w%)	Sb (w%)	Au (w%)
1	2	1	0.7	0.0	0.4	0.1
2	18	13	0.2	0.9	0.2	0.0
3	5	19	0.1	5.2	0.2	0.2
62	4	24	0.2	3.9	0.6	0.0
4	7	1	0.3	0.1	0.5	0.0
5	6	2	0.4	1.1	0.2	0.0
6	4	1	0.4	0.9	0.3	0.0
7	10	11	0.3	1.0	0.4	0.7
8	9	10	0.2	2.5	0.4	0.7
9	7	12	0.4	0.0	0.4	0.1
10	6	18	0.2	2.4	0.2	0.3
11	29	21	0.3	0.1	0.3	0.1
12	35	4	0.2	0.6	0.3	0.0
13	25	1	0.1	0.8	0.2	0.1
14	16	5	0.2	0.9	0.5	0.1
15	18	17	0.2	0.7	0.6	0.2
16	13	15	0.3	1.1	0.3	0.1
17	18	9	0.2	0.1	0.3	0.1
18	11	2	0.2	0.5	0.3	0.0
19	24	17	0.3	0.3	0.4	0.2
21	7	29	0.1	6.0	0.2	1.2
22	3	21	0.1	0.5	0.2	0.1
23	26	43	0.3	3.2	0.3	0.2
24a	25	38	0.3	2.2	0.4	0.2
25a	30	6	0.3	0.2	0.3	0.0
26	18	57	0.2	4.5	0.2	0.3
27	33	20	0.2	0.1	0.3	0.1
28	15	57	0.1	3.3	0.2	0.3
29	27	49	0.2	7.8	0.2	0.8
24	27	4	0.2	3.7	0.3	0.1
25	16	1	0.1	2.1	0.2	0.1
32	2	1	0.1	0.0	0.3	0.1
33	8	0.4	0.1	0.1	0.1	0.2
34	9	2	0.0	0.0	0.0	0.2
35	6	0.5	0.3	0.6	0.3	0.0
36	20	6	0.3	0.0	0.3	0.5
37	14	0.2	0.5	1.0	0.6	0.6
38	15	0.1	0.2	0.1	0.1	0.1
39	13	0.3	0.2	0.1	0.2	0.0
40	19	2	0.2	2.9	0.2	0.1
41	19	1	0.2	1.0	0.2	0.1
42	28	4	0.2	0.6	1.4	0.0
43	27	1	0.2	0.2	0.2	0.1
44	26	0.4	0.2	1.5	0.2	0.0
45	4	0.2	0.1	0.2	0.1	0.1
46	7	0.8	0.1	0.9	0.2	0.1
47	13	0.2	0.3	0.1	0.2	0.0
48	18	10	0.3	0.7	0.3	0.1
55	9	1	0.1	0.1	0.1	0.2
57	13	8	0.2	1.3	0.5	0.5
58	17	6	0.1	0.0	0.3	0.5
59	13	0.3	0.1	1.3	0.1	0.3
60	17	6	0.2	1.7	0.2	0.7
61	0.2	4	0.0	0.5	0.1	0.1

Table III – Composition of the other bronze samples.

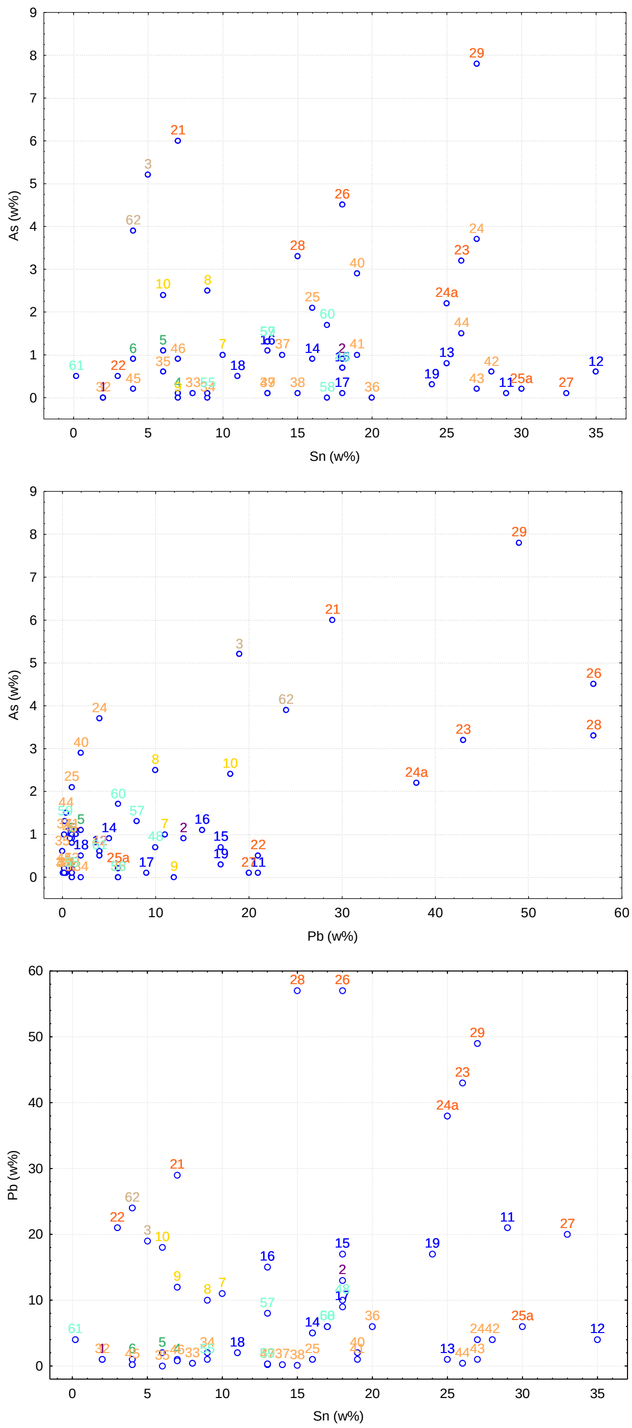

Figure 1 – Representation of the samples' composition in the Pb vs. Sn (bottom), As vs. Sn (top left) and As vs. Pb (top right) planes.

The first Principal Components can then be used for classification purposes, applying to them, for example, a K-means procedure, as proposed in ref. [12, 13]. However, the results of this classification can be extremely difficult to interpret, also considering the fact that the minor elements in the alloy would not give a sound information, at least for what concerns the classification of the samples, because of the rather limited variability of their concentration in the samples. An exception to this consideration is the case of arsenic, which is present in considerable concentration (of the order of a few percents) in a some samples. In the following figures are reported the binary diagrams (Sn, Pb), (Sn, As) and (Pb, As) for all the samples here considered.On the basis of these plots, the findings can be classified in several broad clusters, according to their composition; for example the three nails (4,5 and 6) were realized with a bronze alloy with a relatively low Pb concentrations (less than 5%). The *armillae* (7,8, 9 and 10) have very similar compositions, characterized by higher lead concentrations (between 10 and 20%).

It is interesting to note that the two coins found in the Tomb (sample 3 and sample 62) are both characterized by high concentrations of Pb (around 20%) and As (around 5%). Although their details are practically unreadable (see figure 2), the peculiar composition [15], along with the their weight and dimension, might suggest the identification as Roman asses of the Janus/Prow type [16]. The other bronze samples are distributed among five broad clusters. The classification of all the fragments, according to their composition, is summarized in Table IV.

It should be noted that the samples 21, 23, 24, 26, 28 and 29 are also characterized by a As concentration larger than 3%. All the fragments and the vases (samples from 30 to 61) are characterized by a lead concentration < 10%, while most of the handles (except the brass sample 20 and the handle 25a) have lead concentration > 20%.

It is interesting to see that the mirror fragments (samples from 11 to 19) are all characterized by a high concentration of tin (between 10 and 35%) but their Pb concentration varies substantially, so that about one half of them are classified in cluster 3 (Pb concentration < 10 %) and the other half in cluster 5 (Pb concentration > 10%). Arsenic concentration stay around 2% for all the mirror fragments. The high tin concentration, associated to a large variability of lead concentration, is typical of Etruscan mirrors of the Hellenistic period, as demonstrated by Ferro et al. in a compositional study on more than 90 Etruscan mirror fragments [17].

Cluster 1 (Zn > 3%, Sn < 10%, Pb <10 %)	Cluster 2 (Sn < 10%, Pb <10 %)	Cluster 3 (Sn > 10%, Pb <10 %)	Cluster 4 (Sn < 10%, Pb > 10 %)	Cluster 5 (Sn > 10%, Pb > 10 %)
20	1	12	3	2
30	4	13	62	11
31	5	14	7	15
49	6	17	8	16
50	32	18	9	19
51	33	25a	10	23
52	34	24	21	24a
53	35	25	22	26
54	45	36		27
56	46	37		28
	55	38		29
	61	39		
		40		
		41		
		42		
		43		
		44		
		47		
		48		
		57		
		58		
		59		
		60		

Table IV – Classification of the samples

3. CONCLUSION

The results presented are the first attempt to a classification of the large number of copper-based alloy objects found in Tomb 20 of the "Pratino" necropolis in Tuscania. Although a quantitative analysis of the samples is made very difficult by the combined requirement of using in situ and non-destructive techniques on object not restored and not even cleaned by the soil in which they were found, we demonstrated that a grouping of the findings in at least five well defined groups is possible, which are coherent with the different typologies of the fragments analyzed.

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