IL NUOVO CIMENTO Vol. 30 C, N. 1 Gennaio-Febbraio 2007
DOI 10.1393/ncc/i2006-10037-7

Comparative analysis of Iron Age bronze archaeological objects from a Picenum necropolis of Centre Italy with Prompt Gamma Activation Analysis(*)

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(ricevuto il 31 Ottobre 2006; pubblicato online il 9 Febbraio 2007)

Summary. — An archaeological area from the 8th and 7th centuries B.C. has been recently discovered during a rescue excavation near Matelica site (Marche Region, Italy) in the period 1994-2005. Out of the treasures found in the graves, 18 bronze objects have been chosen for Prompt Gamma Activation Analysis (PGAA) at the Budapest Research Reactor (BRR), selected from the 7th century B.C. archaeological founds of Matelica and Fabriano sites. Various investigations, already performed in the same field, have confirmed the applicability of the considered technique and the feasibility of the proposed experiment. Besides determining the major components of the analyzed fragments, some trace elements, such as Sb, As and Ag, have also been identified. The compositions of the different samples have been also compared, in order to gain information regarding possible workshops and provenance. The comparative analysis will be useful, moreover, to establish an eventual classification according to the chemical composition. The obtained results are complementary to those already achieved for the considered objects, including atomic absorption, atomic emission and neutron diffraction.

PACS 29.25.Dz – Neutron sources.
PACS 34.50.Dy – Interactions of atoms and molecules with surfaces; photon and electron emission; neutralization of ions.

(*) Paper presented at the Workshop "RICH—Research Infrastructures for Cultural Heritage", Trieste, December 12-13, 2005.

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1. – Introduction

Matelica (*Matilica*) was a Roman *municipium* already in the 1st century B.C., and the greatest development in the city happened among the 1st and the 2nd century B.C. The origins of *Matilica* are indissolubly connected to the Picenan civilization, that in this area has left numerous and important attestations, put again in light by the mentioned excavations. The same Picenan origin characterizes Fabriano (*Tuficum*), which was an important Roman town hall in the 1st century B.C. In 409 A.D. it suffered the first destruction from the Goths driven by Alarico, who passed through these regions direct to Rome. The final destruction of *Tuficum* happened in 896 under Berengario's hand.

A conspicuous series of very recent archaeological discoveries has revealed a rich and strong phenomenon of oriental features in the new important areas of Matelica and Fabriano, Marche Region, Italy.

The recent excavation conducted by the Superintendence for the Archaeological Heritage of Marche region have contributed to show the reality, till now almost unknown, of the contexts related to the Picenan civilization. From 1994 to 2005, by the excavation of great extra-urbane areas and the discovery of necropolis and Picenan inhabited areas, it has been possible to trace a more complete picture of the territory, documented since the prehistory by Palaeolithic and Neolithic recoveries.

A considerable quantity of built-up areas and necropolis has been brought to light, the study of which is modifying and integrating the historical-archaeological overview of Picenan civilization in Centre Italy [1-4].

Bronzes, among the discovered objects, are considered particularly important for the eventual confirmation of the hypothesis concerning a local manufacturing place of the same products: in fact, till now, such objects are believed to be produced in the far Etruria, Tuscany region. An investigation programme has been started, consequently, aiming to compare archaeological founds of the mentioned areas with other bronze objects from the same period (oriental features—7th century B.C.) belonging to other surrounding areas (*e.g.*, Fabriano and San Severino, Marche Region, Italy). In this first step of the research, 18 bronze samples have been selected, 17 coming from Matelica area, and one, as a comparison, from Fabriano area. The Fabriano sample—a biconical wall fragment found in the tomb 3 of Santa Maria in Campo site, discovered by I. Dall'Osso in 1915 [5]—represents the most relevant object either as a discovery of that area, or for the purpose of the present study.

Chemical analysis of archaeological artefacts (metal objects, ceramics, polished stone tools, sculptures, etc.) has become, recently, an important tool for source identification, provenance analysis based on the determination of major- and trace elements.

The most usual analytical methods—*e.g.*, X-Ray Fluorescence Spectroscopy (XRF), Instrumental Neutron Activation Analysis (INAA) and Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS)—require partial or total destruction of the samples, which often is not allowed in case of valuable whole or fragmental artefacts.

Prompt Gamma Activation Analysis (PGAA) represents a powerful, multi-element method to cope with the need of non-destructive analysis. The investigated objects, in fact, after some days of cooling (*i.e.* decay of short-lived radioactive products) can be returned to the owner in their original form. An important advantage of PGAA is that it is a multi-element method: all the chemical elements, in theory, can be detected, although with different sensitivities. The same technique allows identifying both the major components and a variety of trace elements in different types of objects [6]. The detailed description of standardization procedure is written by Révay and Molnár [7]. The most

TABLE I. – *Archaeological description of the investigated objects.*

Sample No.	Sample name	Locality archaeological information	Specimen and typological information
1	MAT PG 1 AC	Tomb in Passo Gabella site, Matelica	*situla* (wall inferior edge fragments)
2	MAT PG 2 AC	" " "	*situla* (upper wall fragment)
3	MAT PG 10 AC	" " "	*patera* (wall fragments) rep. 25
4	MAT PG 15 AC	" " "	little *situla* (wall fragments) rep. 18
5	MAT PG 18 AC	" " "	*cista* handle, rep. 14 (powder, m = 0.1198 g)
6	MAT CR 28 AC	Tomb 172 in Crocifisso site, Matelica	*cista* (wall fragments)
7	MAT VC 30 AC	Tomb in Villa Clara site, Matelica	helmet (central element fragment) inv. 63899
8	MAT VC 31 AC	" " "	washbowl (wall fragment) inv. 63900
9	MAT VC 32 AC	" " "	lance prong coil (fragment)
10	MAT VC 34 AC	" " "	ring (fragment)
11	MAT CR 44 AC	Tomb in Crocifisso new site, Matelica	*situla* (wall fragment)
12	MAT CI 48 AC	Tomb 39 in Cimitero site, Matelica	helmet (fragment)
13	MAT CI 52 AC	" " "	*tripode* (wall fragments)
14	FAB SMC 64 AC	Tomb 3 in Santa Maria in Campo site, Fabriano	biconical (wall fragment)
15	MAT CR 80 AC	Tomb182 in Crocifisso site, Matelica	helmet (cap fragment) rep. 88
16	MAT CR 81 AC	" " "	washbowl (wall fragment) rep. 39
17	MAT CR 82 AC	" " "	*situla* (wall fragment) rep. 40
18	MAT CR 83 AC	" " "	*cista* (wall fragments) rep. 41

easily detectable elements are B, Cd, Sm and Gd (with detection limit around $0.1\,\mu$g/g). On the other hand, C, N, O, F, Sn, Pb and Bi (with detection limits above $1000\,\mu$g/g) are the elements most difficult to identify. Sensitivities for every chemical element have been determined, using internal standardization or comparator measurements at the Budapest Research Reactor. The detection limits, however, depend on the composition of the individual samples, and can be improved by increasing the acquisition time.

2. – Experimental

The PGAA facility of the 10 MW BRR has been developed since 1996. A guided thermal neutron beam of $2.5 \cdot 10^6\,\mathrm{cm^{-2}s^{-1}}$ flux, supplied by the BRR, was used until 2000

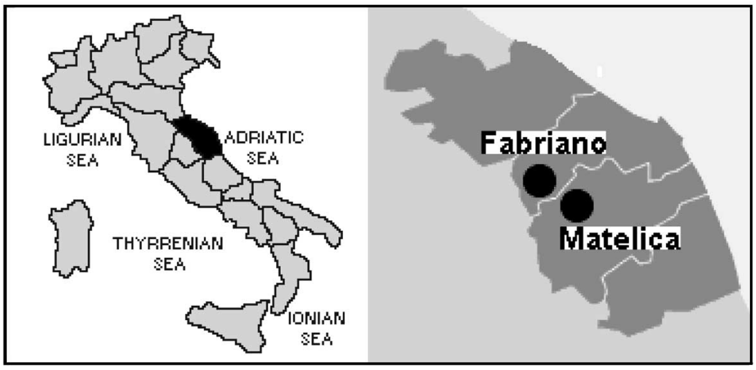

Fig. 1. – Matelica and Fabriano areas, Marche Region, Italy.

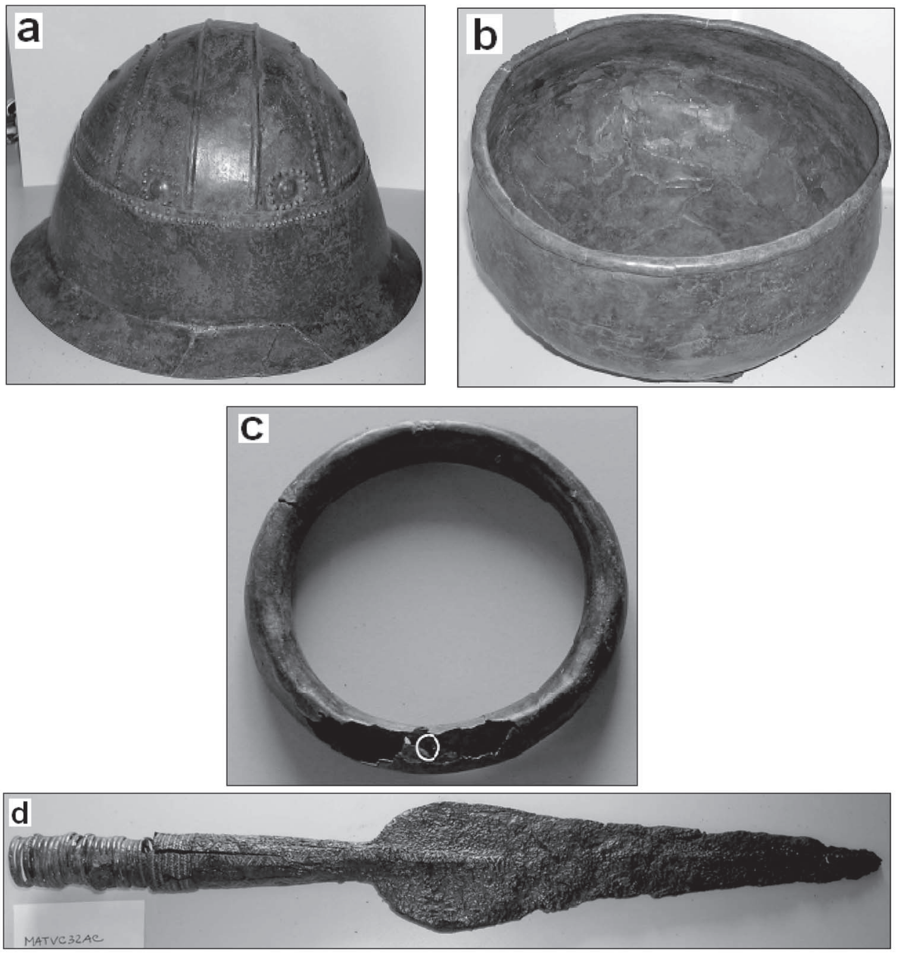

Fig. 2. – Some original objects investigated by PGAA: a) helmet (sample No. 7); b) washbowl (sample No. 8); c) ring (sample No. 10); d) lance prong (sample No. 9). The same objects belong to a tomb found in "Villa Clara" site, Matelica.

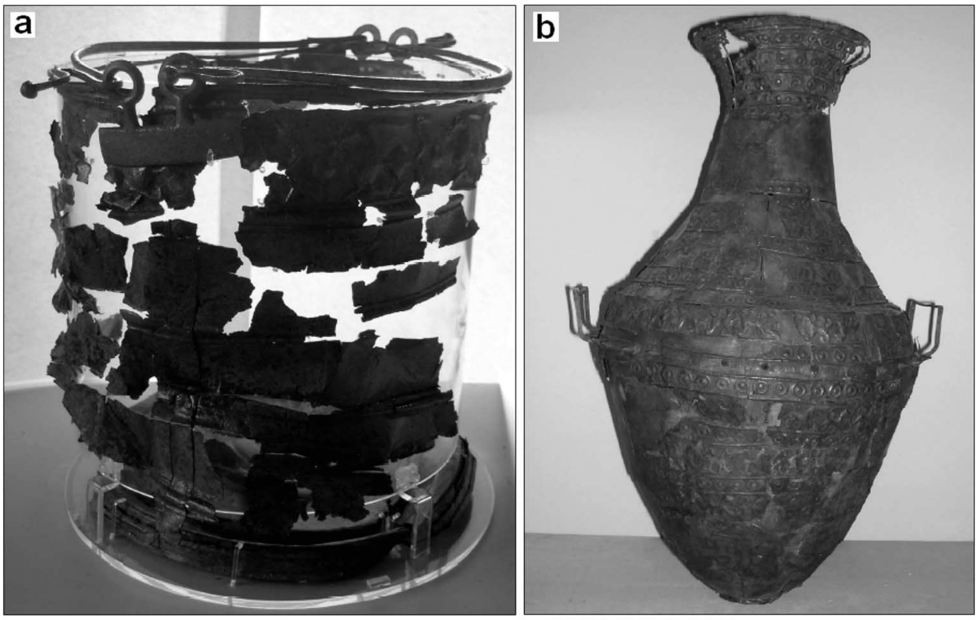

Fig. 3. – Other original objects investigated by PGAA: a) *cista* (sample No. 6), belonging to a tomb found in "Crocifisso" site, Matelica; b) biconical (sample No. 14) belonging to a tomb found in Fabriano site.

for analysis. A liquid hydrogen moderator cell was applied, in the same year, to cool the applied neutrons down to 16 K, increasing the thermal equivalent flux of the beam up to $5\cdot 10^7\,\mathrm{cm}^{-2}\mathrm{s}^{-1}$, and respectively, the analytical sensitivity by a factor of 20. The neutrons are guided by Ni-coated guide tubes towards the sample position, which is approximately 35 m away from the reactor core. The beam's usual cross-section is $2 \times 2\,\mathrm{cm}^2$, or it can be reduced to a $1 \times 1\,\mathrm{cm}^2$ or even to a smaller area. The prompt-gamma photons are detected using a complex detector system, which contains an n-type high-purity germanium (HPGe) main detector with a Bismuth Germanate (BGO) scintillator detector annulus to perform Compton-suppression measurements. All the detector system is surrounded by a 10 cm thick lead shielding. The data are collected by a 16 k PC-based MCA.

The collected spectra are evaluated by a self-developed software, named HYPERMET-PC. The detailed description of the Budapest PGAA system is given by Révay *et al.* [8] and in the Handbook of Prompt Gamma Activation Analysis [9]. The calculation of elemental composition is performed automatically, using relative standardization method, or k_0-method [10].

PGAA analysis of 18 bronze samples—fragments and a powder sample—has been carried out at the BRR. The same samples belong to the following objects found in seven different tombs of Matelica and Fabriano archaeological sites: *situlae*, *patera*, *cista*, helmets, washbowls, lance prong coil, ring, *tripode* and biconical. Some of the mentioned samples have been also submitted to the following investigations techniques: neutron diffraction (ND) [11] at ISIS, UK, in order to determine the predominant phases, the preferred orientation distribution of crystallites and the residual stresses due to cold working; atomic adsorption (AAS) at the "V. Volterra" Institute of Torrette, Ancona, Italy, concerning the

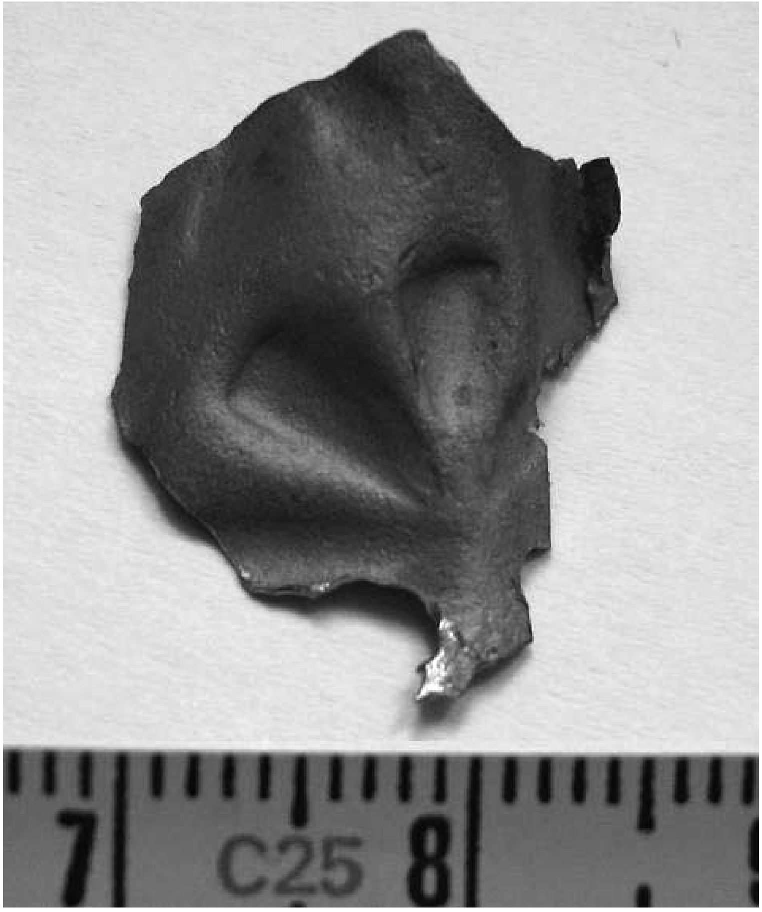

Fig. 4. – Wall fragment of a *situla* belonging to a tomb found in Crocifisso new site, Matelica (sample No. 11).

powder reducible samples, in order to obtain in a destructive way their chemical analysis. The overall investigation strategy is to achieve a set of information on the considered objects, including a technological description, to better identify their provenance and eventual relationships with known features of other production. Table I shows the main typological information and locations where the samples have been collected (see also fig. 1).

Figures 2 and 3 represent some of the original bronze objects whose fragments have been analyzed by PGAA, while fig. 4 shows sample No. 11.

The fragment samples have been simply placed into the normal sample position and irradiated in a cold neutron beam of $5 \cdot 10^7\,\mathrm{cm}^{-2}\mathrm{s}^{-1}$ thermal equivalent flux. The cross-section of the neutron beam was $2 \times 2\,\mathrm{cm}^2$ (or $1 \times 1\,\mathrm{cm}^2$, depending on the sample dimensional characteristics). Figure 5 shows sample No. 16 fastened with Teflon strings onto the aluminium frame and being introduced in the measurement chamber. Some samples, due to their reduced size, have been irradiated in vacuum, in order to decrease the background of the measured spectra.

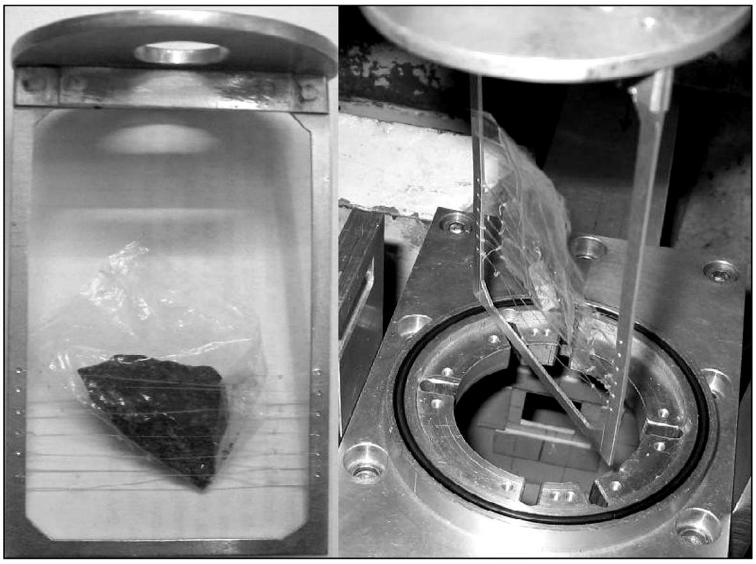

Fig. 5. – Wall fragment of a washbowl (sample No. 16) fastened with Teflon strings onto the aluminium frame and being introduced in the PGAA measurement chamber.

The data acquisition time has varied between 5000 and 50000 seconds, depending on the sample size, in order to gain sufficiently good statistics for spectrum evaluation. After irradiation, the samples have been stored for a few days, in order to let the residual radioactivity decay. All the objects have been checked prior to returning back to the involved National Archaeological Museum of Marche Region, Italy.

3. – Results

With PGAA we were able to quantify the major elements of Cu and Sn in bronzes, while the amount of Pb was under our detection limit in all samples. Additional minor components of Fe, Co, Zn, As, Ag and Sb were possible to detect in some of the objects. Moreover, the presence of H, Si, and Cl can be attributed to contamination from the environment. Table II reports the detailed PGAA results, including the concentrations under the given detection limits. Concerning our bronze objects, the approximate detection limits found to be the following (in wt%): Zn: 0.5, Sn: 2, Pb: 2, H: 0.005, B: 0.00003, Al: 1.5, Si: 1.6, P: 3.1, S: 0.3, Cl: 0.05, K: 0.74, Ca: 1.8, Ti: 0.09, Cr: 0.1, Mn: 0.22, Fe: 0.48, Co: 0.014, Ni: 0.078, As: 0.28, Ag: 0.049, Cd: 0.0009, Sb: 0.55, Au: 0.037, Hg: 0.006, supposing a 10000 s irradiation of a 0.1 cm thick sample with a $2 \times 2\,\mathrm{cm}^2$ beam.

In order to compare the alloying composition of the investigated objects, the Sn/Cu mass ratios have been determined (see fig. 6).

The significant difference in Sn/Cu ratios reveals that sample No. 6 (MATCR28AC: *cista* found in the Tomb 172 of "Crocifisso" site, Matelica) is presumably distinct from the others.

Concerning the comparison of Matelica samples with the biconical from Santa Maria in Campo site (sample No. 14), no significant differences can be seen on fig. 6. This implies a further confirmation of a compositional uniformity of the bronze objects between the two considered areas.

TABLE II. – *Results of PGAA measurements.*

No.	Inventory no.	H	Si	Cl	Fe	Co	Cu	Zn	As	Ag	Sn	Sb
1	MAT PG 1 AC	< 0.03	< 1	0.02	< 0.4	0.016	90.7	0.83	0.21	0.073	7.2	0.93
2	MAT PG 2 AC	< 0.03	< 1	0.01	< 0.4	0.011	92.3	0.89	0.24	0.119	5.6	0.81
3	MAT PG 10 AC	0.121	< 1	0.04	< 0.4	< 0.006	92.2	< 0.8	0.61	0.128	6.9	< 0.4
4	MAT PG 15 AC	0.065	< 1	0.01	< 0.4	0.021	88.3	< 0.8	< 0.2	0.085	11.5	< 0.4
5	MAT PG 18 AC	< 0.03	< 1	0.02	< 0.4	0.059	91.5	< 0.8	< 0.2	0.122	8.3	< 0.4
6	MAT CR 28 AC	1.265	< 1	0.04	0.50	0.010	74.2	< 0.8	0.54	0.275	22.3	0.88
7	MAT VC 30 AC	< 0.03	< 1	0.02	< 0.4	< 0.006	84.5	< 0.8	3.32	0.064	11.6	< 0.4
8	MAT VC 31 AC	0,076	< 1	0.02	< 0.4	< 0.006	87.2	< 0.8	< 0.2	0.092	12.7	< 0.4
9	MAT VC 32 AC	0.038	< 1	0.03	< 0.4	0.024	90.8	< 0.8	< 0.2	0.052	9.1	< 0.4
10	MAT VC 34 AC	0.172	< 1	< 0.01	< 0.4	0.006	83.6	< 0.8	< 0.2	0.059	16.2	< 0.4
11	MAT CR 44 AC	< 0.03	< 1	< 0.01	< 0.4	< 0.006	90.1	< 0.8	0.45	0.130	9.3	< 0.4
12	MAT CI 48 AC	0.018	< 1	0.03	< 0.4	0.012	89,5	< 0.8	0.23	0.100	9.7	0.40
13	MAT CI 52 AC	0.273	2,8	0,09	0.42	0.018	82.0	< 0.8	< 0.2	0.094	13.8	0.41
14	FAB SMC 64 AC	0.680	1.9	1.01	< 0.4	0.012	83.4	< 0.8	< 0.2	0.072	12.9	< 0.4
15	MAT CR 80 AC	0.246	1.5	0.02	< 0.4	< 0.006	85.6	< 0.8	< 0.2	0.052	11.9	0.67
16	MAT CR 81 AC	0.280	2.2	0,10	0.45	0.007	86.1	< 0.8	0.86	0.160	8.7	1.12
17	MAT CR 82 AC	1.326	< 1	0.05	0.67	0.009	88.6	< 0.8	< 0.2	0.171	8.4	0.79
18	MAT CR 83 AC	0.659	3,4	0.09	0.63	0.007	80.6	< 0.8	< 0.2	0.00	14.1	0.51

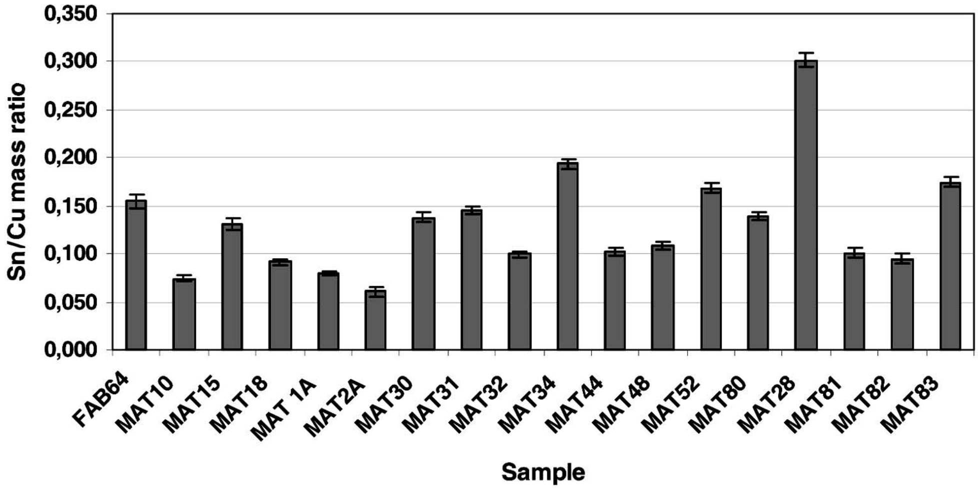

Fig. 6. – Sn/Cu mass ratio of the investigated samples.

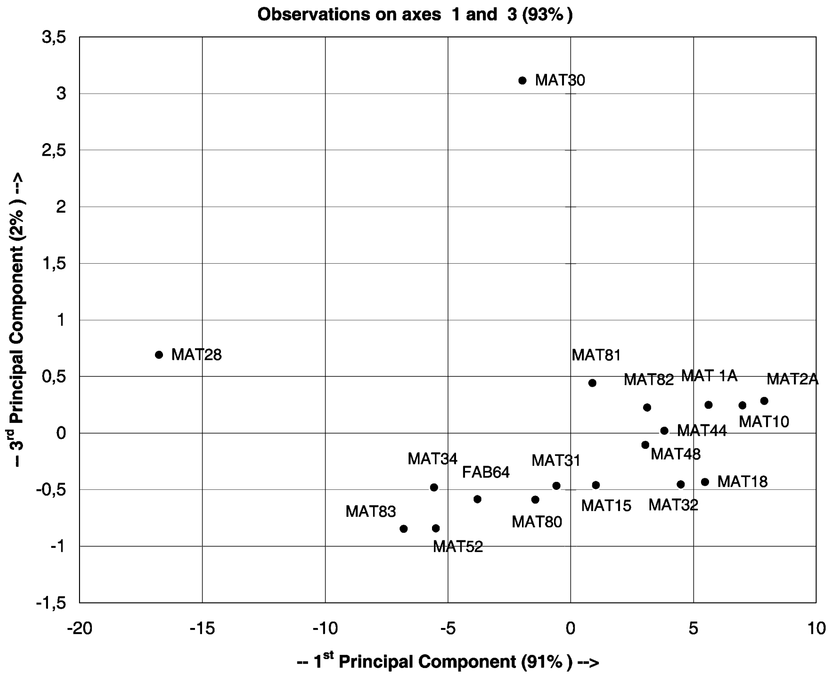

Fig. 7. – Principal Component Analysis of Picenum necropolis bronze objects.

Another comparison of the objects, based on their composition, Principal Component Analysis (PCA) has been performed, using "EXELSTAT" software. The results are plotted on fig. 7.

PCA, which operates with linear combinations of the original composition data, is a common multivariate numerical method is widely applied in comparative studies of archaeological objects. It is able to show some significant differences/similarities between the considered objects [12]. The chart represented in fig. 7 confirms the above mentioned considerations regarding the samples No. 6 and No. 14. In this chart, also the sample No. 7 (MATVC30AC: helmet found in the tomb of Villa Clara site, Matelica) appears to be distinct from the others. Such diversification indicates the necessity of further investigations concerning the manufacturing places of the objects.

4. – Conclusions

In this paper, application of PGAA is discussed in the investigation of Picenum necropolis bronze objects. With PGAA, most of the major components and some interesting trace elements of the bulk material have been determined, which may give useful information on the provenance. A significant difference between the objects has been outlined, which could represent a substantial indication for future discussions from the archaeological point of view. The absence of differences found between Matelica and Fabriano samples, on the other hand, gives a further argument to consider Matelica archaeological area as a possible manufacturing metallurgical centre independent from the Etruria one.

PGAA gives information on the sample as a whole. Since neutrons go through deeper—as well as the surface—layers of the material, the method cannot distinguish between "bulk" and "surface" composition of the sample. Thus, whenever significant effect of weathering is presumed on the surface, complementary analytical investigations, such as PIXE are suggested.

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EC is acknowledged for its support for access to the BRR facilities, under the 6th Framework Programme through the Key Action: Strengthening the European Research Area, Research Infrastructures. Contract no. R113-CT-2003-505925. It is a pleasure to thank Prof. L. Pallottini for useful discussions.

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