

## Compositional inhomogeneity of an unusual Selinunte coin

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**Summary.** — EDXRF and XPS characterizations of a recently found Selinunte ancient coin are presented. Such a coin was found as essentially made up by a Sn-Pb alloy and its types have a very strong similarity with those shown by a silver set issued in the same historical period. It has been also studied by means of a SEM-EDXRF coupled apparatus in order to have information about the compositional inhomogeneity of the alloy. XPS measurements have been used to provide a more surface sensitive analysis. The different probing depths of the adopted techniques have been found useful in evidencing volume inhomogeneities of the sample, at least in the first few microns above its surface. From an archaeological point of view, the coin may be ascribed to a coinage for funerary use or, more probably, to a coin production carried out during the difficult economic period of the history of Selinunte, immediately preceding the year 409 b.C., when the city was destroyed by Carthaginian armies.

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### 1. – Introduction

In this paper, the results obtained by means of a physico-chemical analysis of a Sicilian ancient coin are presented. Such a coin presents the same types characteristic of a silver set [1] issued by the city of Selinunte and attributed to a period immediately preceding the year 409 b.C., when the city was destroyed by Carthaginian armies. Examined by experienced personnel of the Interdisciplinary Regional Museum of Messina after its finding during archaeological excavations, it was recognized as a hemidrachm in a good state of conservation attributable to the same period of the above silver set. It shows the



Fig. 1. – Comparison between the types of Selinunte coin under examination in this work (left) and the corresponding silver coin (right) quoted as no. 713 in the *Sylloge Nummorum Graecorum* of the American Numismatic Society. The upper parts of the images refer to the coin obverse, lower parts to the reverse.

following types: *Obv.* Head of Heracles, three-quarters facing; *Rev.* ΣΕΛΙΝΟΝΤΙΟΝ, quadriga galloping left, guided by charioteer in long chiton; above, a selinon leaf (fig. 1).

Firstly considered as belonging to the silver set issued by Selinunte, the coin was inserted in the collection of the Museum. However, once cleaned in order to obtain a better readability, it has revealed a surface opacity unusual for silver coins. In spite of the strong similarity of its types with those showed by the Selinunte set, our piece was found in this work as essentially made up by a Sn-Pb alloy, this certainly representing a singular case in the minting of that historical period. In antiquity, the metals used for the coinage were essentially gold, silver and copper in combination with minor quantities of other elements (As, Sb, Pb, Fe and Zn) used to make harder the alloys made up by metals too soft to be used for a good coinage. After the discovery of tin, this metal was also used as an addition to the main metal components, sometime as a partial substitution of silver. In this frame, the nearly exclusive use of tin and lead is very strange, this producing soft blanks.

After the experimental confirmation of its composition, the problem of the numismatic examination was to state if the piece was an official product of the Selinunte mint or a production of counterfeiters operating during the same period. On the other hand, on the basis of the similarity of dimensions, shape and style of the types, the second of the two above hypotheses has been considered not probable.

In order to carry out a complete physico-chemical characterization of this unusual Selinunte coin, we have used two spectroscopical techniques, EDXRF (Energy dispersed X-ray Fluorescence) and XPS (X-ray Photoemission Spectroscopy). Nowadays, such techniques are extensively used in Archaeometry for qualitative and quantitative (non-destructive) determinations of major, minor and trace elements and are also particularly useful in determining the chemical state (oxidation, corrosion, etc. . . .) of the samples analysed [2-7].

As is well known, EDXRF provides a spectrum of the characteristic X-rays emitted from each atomic species (in some instruments only heavier than Na) as a consequence of the electronic relaxation following an X-ray or an electron-beam-induced core level ionization. In the case of XPS, photoelectrons, coming from different electron core levels of any atomic species in the sample, give information about the abundance of those atoms and their chemical environment via the so-called chemical shift.

In this work the two above spectroscopies have been exploited as complementary techniques in determining the composition of our coin. Moreover, a scanning electron microscope (SEM) equipped by an EDXRF facility, was also used to provide X-ray fluorescence maps giving the surface atomic distributions.

## 2. – Experimental set-up

As already declared in the introduction, the two main analytical techniques used for the coin characterization were EDXRF and XPS. In the first case, a Spectrace mod. QuanX spectrometer was utilized, equipped by an X-ray source (Rh anode) and a Si(Li) detector cooled at liquid-nitrogen temperature (LNT) and with a resolution of about 166 eV. The coin, previously cleaned in an ultrasound bath, was positioned on a rotating sample holder in order to minimize, during the measurements, the effects of its non-planarity. Due to its unicity no other chemical or mechanical treatment of the piece was allowed. Measurements have been carried out with a primary energy of 25 keV and with a lifetime of at least 500 s. A SLFP (Standardless Fundamental Parameters) method [8] was adopted to handle the measured characteristic X-ray spectra in order to provide a quantitative analysis. The results must be considered as the average response of a large portion of the sample surface due to the large diameter of the X primary beam.

XPS measurements were carried out by a VG Microtech ESCA system equipped with a monochromatic X-ray source with two thin anodes (Mg and Al) that give the facility of two independent primary X-ray lines. The spectra were recorded in CAE mode (10 eV pass energy) using the Mg line (1253.6 eV) and a VG CLAM 100 105° concentric hemispherical analyser with an acceptance angle of about 6°. The coin was positioned on a metal sample holder and here fixed by means of silver varnish to assure good electrical contacts with the spectrometer.

Finally, in order to put in evidence variations in local concentrations, X-ray fluorescence maps of different small areas of the coin surface (both in reverse and obverse side) were taken using a SEM Philips mod. Quanta 400 equipped by a LNT cooled Si(Li) X-detector with an UTW window and an energy resolution of about 140 eV.

Particular attention must be devoted to the different accuracy of the above techniques when used for quantitative analyses. In the case of EDXRF the precision for major components, exceeding 50%, may be better than  $\pm 0.5\%$  relative, whereas, near the detection limit, it will approach  $\pm 25\%$  relative. These values are also increased by further errors deriving from the uncertainty induced by the method of spectrum processing (in our case StandardLess Fundamental Parameters) and the approximations used (for example, neglecting the tertiary fluorescence). Moreover, it must be assumed that the XRF analysis of a coin is generally not too much accurate because it involves a surface layer, usually not homogeneous, whose depth is of the order of few microns depending on the nature of the sample and the energy of involved X-rays. In practice, the interpretation of such an analysis, as representative of the sample bulk, is a fault of the analyst rather than a failure of the technique [9].

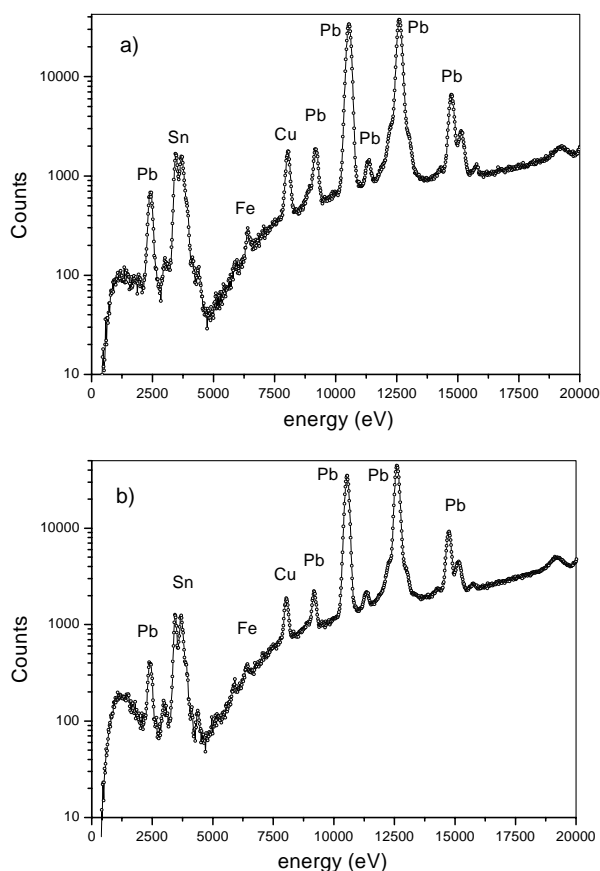


Fig. 2. – EDXRF spectra of the reverse (a) and obverse (b) coin surfaces showing the characteristic X-rays coming from the atomic constituents of the alloy. The  $M$  and  $L$  series of Pb, the  $L$  series of Sn and the  $K$  lines of Fe and Cu are present.

In the case of XPS that deals with photoelectron energies ranging from 0 to about 1 keV and electron mean free paths not greater than few tens of Ångstroms the sensitivity is limited to a surface depth of the same order of magnitude [10]. Moreover, our XPS system is characterized by a sampling area of 3–5 mm<sup>2</sup> enough smaller than that involved in our QuanX EDXRF instrument but larger than the area-sampling capability of the SEM-EDXRF system. These considerations suggest that the results obtained in the above three cases must be carefully utilized in the quantitative determination of the chemical composition of the analysed samples.

### 3. – EDXRF and XPS results

In fig. 2 the QuanX EDXRF spectra of the reverse and obverse surfaces of the coin are reported, showing the characteristic lines of Pb( $L_{\alpha}$ ) and Sn( $L_{\alpha}$ ) together with those of the two minor alloy constituents, Fe( $K_{\alpha}$ ) and Cu( $K_{\alpha}$ ). The results of the quantitative analyses carried out on the two whole coin surfaces (about 130 mm<sup>2</sup>) are reported in table I, representing their average atomic compositions. In order to have information

TABLE I. – *Results of the quantitative determinations for the main constituents of the coin obtained by EDXRF on the whole sample and SEM-EDXRF for four selected areas (1 to 4). In the last column, the results from Area 4 are also reported as deduced by XPS measurements.*

Coin reverse		EDXRF				XPS
Element	Whole surface	Area 1	Area 2	Area 3	Area 4	Area 4
Sn	76.55	70.53	82.36	93.67	38.87	47.50
Pb	19.46	13.26	14.24	4.58	54.30	39.40
Cu	2.99	15.22	2.53	0.72	4.67	10.20
Fe	1.00	0.99	0.87	1.03	2.16	2.90
Coin obverse		EDXRF				
Element	Whole surface	Area 5	Area 6	Area 7	Area 8	
Sn	79.04	76.33	45.98	75.96	82.45	–
Pb	16.86	19.95	50.85	21.30	13.02	–
Cu	3.08	2.66	1.63	1.79	3.40	–
Fe	1.02	1.06	1.55	0.96	1.13	–

about the inhomogeneity of the elemental distribution on the surfaces of the coin, we have also performed local analyses in eight different areas (four on the reverse and four on the obverse) of about  $1.24 \mu\text{m}^2$  using the SEM-EDXRF coupled apparatus. The results are also reported in table I. The averages of the concentration values obtained for each element in these areas are in a satisfactory agreement (at least for the major constituents) with the results obtained for the whole coin surfaces. The inhomogeneity of the alloy was characterized, for the reverse surface, by compositional variations of 58.5% for tin, 91.5% for lead, 59.7% for iron and 95.3% for copper. On the obverse surface such variations are 44.2% tin, 74.4% for lead, 38.1% for iron and 52.1% for copper. This is not surprising, such differences being essentially a consequence of all the structural anomalies induced by the various melting and solidification temperatures of the single elemental constituents, according to the phase diagram of the alloy.

In fig. 3, maps taken with a magnification of  $150\times$  by a SEM-EDXRF coupled system, showing the same area of about  $9 \times 9 \mu\text{m}^2$  on the coin reverse are reported. In the figure, the surface atomic distributions of major (Pb and Sn) and minor components (only Cu) can be observed.

Finally, in order to have information about the volume inhomogeneity of the coin, XPS measurements (see fig. 4) have been carried out in correspondence of a sample area already probed by the SEM-EDXRF coupled system (Area 4 in table I). After the elimination of the secondary electrons background according to the Tougaard procedure [11] and taking into account the proper sensitivity factors for the considered XPS lines ( $3d_{5/2}$  for Sn,  $4f_{7/2}$  for Pb,  $2p_{3/2}$  for Cu and  $2p_{3/2}$  for Fe), a quantitative analysis has been performed. The results are shown in table I together with the EDXRF ones.

A simple comparison between the two sets of data, concerning two different probing depths (greater for EDXRF and smaller for XPS), suggests an inhomogeneous volume distribution of the elemental constituents of the alloy. In particular, for Area 4, the coin shows tin and copper concentrations decreasing from surface to bulk, while the opposite behaviour is shown by lead which tends to have a more evident surface localization. Iron seems to be nearly unaltered as a function of the depth. The same procedure

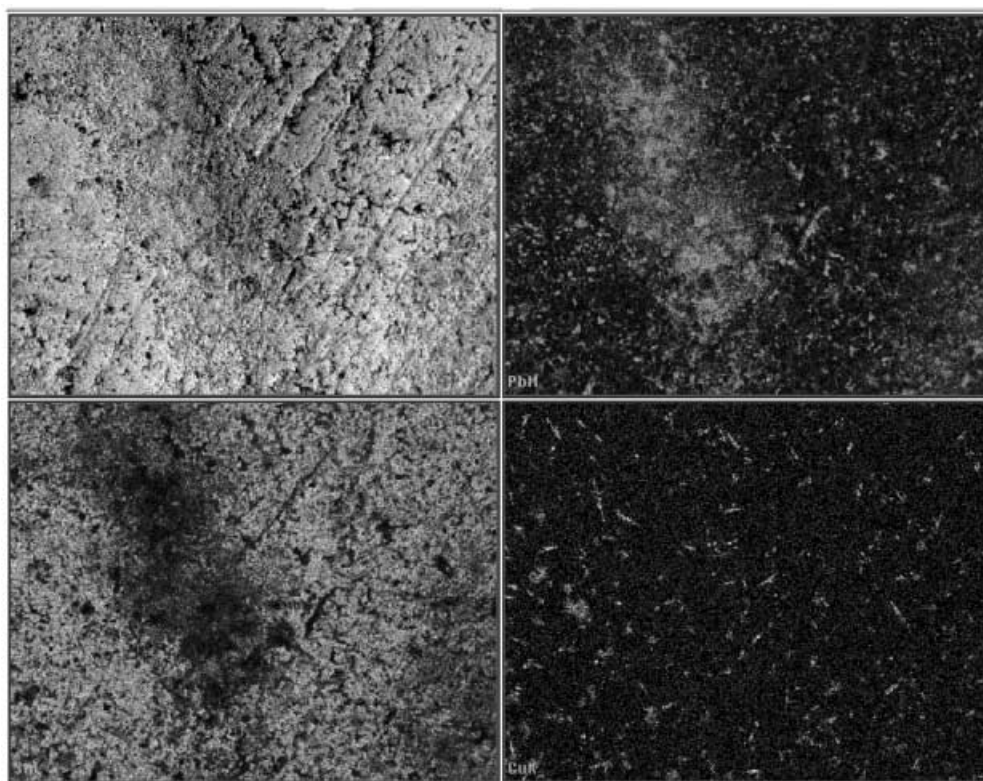


Fig. 3. – Maps of the coin reverse taken at a magnification of  $150\times$  by a SEM-EDXRF coupled system showing an area of about  $9 \times 9 \mu\text{m}^2$  with the surface distributions of lead (upper right), tin (lower left) and copper (lower right) atoms. In the upper left frame the image is reported as seen by backscattered electrons.

can be repeated for any other area obtaining specific, and possibly different, in-depth concentration behaviours.

#### 4. – Conclusions

The elemental composition and its volume and surface inhomogeneities in the coin studied have been put in evidence exploiting the different probing depths of the techniques used. As already pointed out, the compositional disorder of the alloy is not surprising. During its formation by casting, components segregation phenomena take place and, if the cooling is slow enough, the growth of metallic microcrystals assumes generally a dendritic structure built up by the component that first solidifies and has the higher melting point (m.p.). In our case, copper (m.p.  $1083^\circ\text{C}$ ) concentrations were not so high to have allowed the formation of large observable microstructures, this effect being much more evident for lead as shown in fig. 5 where the superposition of the two Pb (m.p.  $327.4^\circ\text{C}$ ) and Sn (m.p.  $231.8^\circ\text{C}$ ) maps of fig. 3 puts in evidence large lead, possibly dendritic, segregations. In fact, during the cooling of the fused liquidus, with a composition not too much different from the eutectic one, a nucleation of crystals of a Pb-rich phase starts

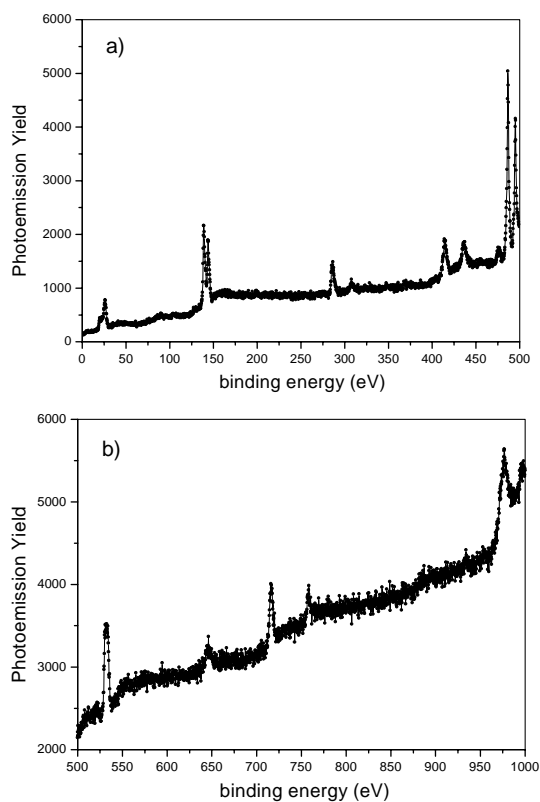


Fig. 4. – XPS spectra from 0–500 eV (a) and 500–1000 eV (b) carried out on the obverse coin surface.

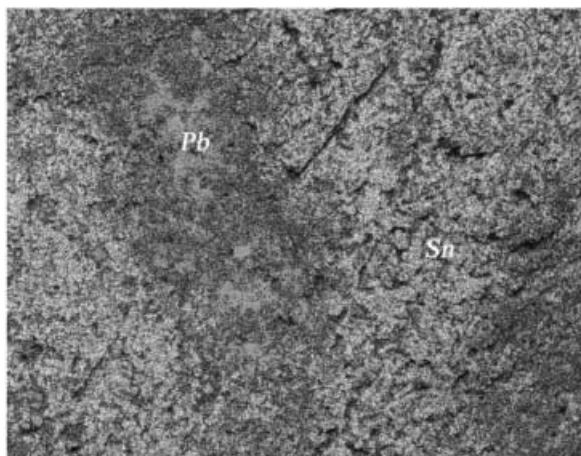


Fig. 5. – Map of the coin reverse taken at a magnification of  $150\times$  by a SEM-EDXRF coupled system showing an area of about  $9 \times 9 \mu\text{m}^2$  with the superposition of the contributions from lead and tin. Note the noticeable dimensions of the lead-rich area.

at 189 °C, while the surroundings show a tendency to a Sn enrichment. After a further cooling, when the eutectic temperature is finally reached, the still liquid phase solidifies in a microstructure similar to that one of the eutectic alloy [12]. The result is an eutectic microstructure in which crystals of a Pb-rich dendritic phase are dispersed.

In conclusion, in this paper we have presented an attempt to characterize a recently found ancient coin of Selinunte, never inserted before in the official coinage catalogues. Our experimental procedures have been subjected to the inevitable restrictions due to the impossibility to destroy the sample in order to have complete information about its composition. However, the obtained results may be considered a contribution to the study of the alloys utilized by ancient minting metallurgy.

#### REFERENCES

- [1] *Sylloge Nummorum Graecorum: American Numismatic Society - 4: Sicily 2: Galaria-Styella*, New York (1977), n. 713-715.
- [2] DACCÀ A., PRATI P., ZUCCHIATTI A., LUCARELLI F., MANDÒ P. A., GEMME G., PARODI R. and PERA R., *Nucl. Instrum. Methods B*, **161-163** (2000) 743.
- [3] MILAZZO M. and CICARDI C., *X-ray Spectrometry*, **26** (1997) 211.
- [4] SELIN LINDGREN E., *Encyclopedia of Analytical Chemistry*, edited by MEYERS R. A. (John Wiley & Sons Ltd. Chichester) ISBN 0471 97670 9.
- [5] PAPPALARDO L., ROMANO F. P., GARRAFFO S., DE SANOIT J., MARCHETTA C. and PAPPALARDO G., *Archaeometry*, **45.2** (2003) 333.
- [6] CALARESO C., GRASSO V., MONDIO G., SILIPIGNI L. and MASTELLONI M. A., *Annali dell'Istituto Italiano di Numismatica*, **45** (1998) 87.
- [7] BERTI R., BUFFAGNI M., RUSSO F., RUSSO G. and SERAFIN PETRILLO P., *Bollettino di Numismatica del Ministero per i Beni Culturali e Ambientali*, no. 8 (1987) 147.
- [8] LACHANCE G. R. and CLAISSE F., *Quantitative X-Ray Fluorescence Analysis, Theory and Application* (Wiley) 1995.
- [9] COWELL M. R., in *Metallurgy in Numismatics*, edited by ODDY W. A. and COWELL M. R., Royal Numismatic Society Special Publication, no. 30, vol. 4 (London) 1998.
- [10] BRIGGS D. and SEAH M. P., *Practical Surface Analysis*, second edition, Vol. 1 – *Auger and X-ray Photoelectron Spectroscopy* (Wiley, New York) 1996.
- [11] TOUGAARD S., *J. Electron. Spectrosc. Relat. Phenom.*, **52** (1990) 243.
- [12] ASM Handbook *Metallography and Microstructures*, **9** (1985) 452.