



Combined PIXE and XPS analysis on republican and imperial Roman coins

A. Daccà^a, P. Prati^{a,*}, A. Zucchiatti^a, F. Lucarelli^b, P.A. Mandò^b, G. Gemme^a,
R. Parodi^a, R. Pera^c

^a *Dipartimento di Fisica and INFN, Università di Genova, Via Dodecaneso 33, 16146 Genova, Italy*

^b *Dipartimento di Fisica and INFN, L.go E. Fermi 2, 50125 Firenze, Italy*

^c *DISAMANT, University of Genova, Via Balbi 4, 16126 Genova, Italy*

Abstract

A combined PIXE and XPS analysis has been performed on a few Roman coins of the republican and imperial age. The purpose was to investigate via XPS the nature and extent of patina in order to be capable of extracting PIXE data relative to the coins bulk. The inclusion of elements from the surface layer, altered by oxidation and inclusion, is a known source of uncertainty in PIXE analyses of coins, performed to assess the composition and the provenance. © 2000 Elsevier Science B.V. All rights reserved.

PACS: 82.80.Ej

Keywords: Archaeometry; PIXE; XPS; Roman coins

1. Introduction

The importance of ancient coins as a tracer in archaeological excavations and their key role in historical studies is unanimously acknowledged. Their classification plays a fundamental role in dating historical events, in reconstructing trade routes, in establishing the populations welfare and following its evolution. For this reason it is important to resort to classification criteria that go well beyond the identification of the mint and the

emission date and concern the analysis of coins to establish, for example, the purity of the metal, the supply source of the raw materials, the possibility of forgery. Particle induced X-ray emission (PIXE) has been used successfully in this kind of analyses [1], being capable of identifying major, minor and trace elements in a non-destructive way. However, some typical problems are known to be generated in the analysis of bulk metal samples: layered structure of metals, surface roughness and corrosion. The aim of our work was to explore the perspectives offered by the combination of two techniques: X-ray photoelectron spectroscopy (XPS) and PIXE, in order to understand and disentangle corrosion effects and metal layers in the elemental analysis of coins.

* Corresponding author. Tel.: +39-10-353-6439; fax: +39-10-314-218.

E-mail address: prati@ge.infn.it (P. Prati).

2. Materials and methods

Four coins, described in Table 1, have been analysed by XPS at the INFN apparatus in Genova and by PIXE at the INFN Van de Graaff in Florence. They have been chosen essentially to cover a wide range of alloys.

The XPS analysis consists of the ejection of bound core electrons by an X-ray beam and of the measurement of their kinetic energy by an electrostatic analyser. From the knowledge of the X-ray energy and the electron kinetic energy we deduce the binding energy, characteristic of the atomic level from which the electron is ejected. This allows the determination of the elemental composition of the sample surface and, within the system resolution (about 0.5 eV), of the molecular species encountered. The INFN XPS facility [2] is a PHI ESCA 5600 Multi Technique electron spectrometer (Physical Electronics) with an X-ray Al monochromatised source ($h\nu = 1486.6$ eV) and a spherical capacitor electron energy analyser (SCA), used in the fixed analyser transmission (FAT) mode. In the standard configuration, the analyser axis forms a take-off angle of 45° with the sample surface. This technique allows a penetration depth of about 10–20 nm and a sensitivity of 0.5% in atomic concentration [2].

The PIXE facility at the University of Florence [3] is specifically designed for the irradiation of samples in air, with minimal geometrical limitations and is very good for coins although the depth of the analysis is limited to a few tens of microns. The facility includes two different Si(Li) detectors for the simultaneous acquisition of the X-ray spectra. One of them (active area 13 mm^2 , target to detector distance 40 mm, angle to the beam 146°)

looks at the sample through a cone flushed with helium and is optimised for the detection of low Z elements (Na to Fe). The other one (active area 80 mm^2 , target to detector distance 20 mm, angle to the beam 138°) is seen through a $500 \mu\text{m}$ mylar filter and is therefore optimised for the detection of medium to high Z elements (Ca to Pb). In such a way it is possible to obtain significant yields for any element between $Z = 11$ and $Z = 82$ without introducing undesirable pile-up effects.

3. Results and discussion

The XPS analysis, without any kind of polishing, gives quite similar results about the raw surface state in all the coins (Table 2). The elements identified can be divided in two categories: those that compose the coins bulk (such as Cu, Ag, Sn, Pb) and those (C, O, Na, Mg, Si, S, Cl, Ca and Fe) that could come from manipulation but could as well be the result of the surface corrosion. Carbon and oxygen are found to be the most abundant elements on the surface and add up to about 80% of the atomic concentration in all four coins. The analysis of the O1s and C1s lines shows that oxygen is present as metal oxide and hydroxide, while carbon is mainly in the form of graphite. Sodium, Si, S, Ca and Fe are basically present as oxides (SiO_2 , CaSO_4 , Na_2SO_4 , CaCO_3 , Fe_2O_3) while Cl forms molecules with Cu (CuCl). The thickness of the carbon and metal oxide layer, present above the metallic surface of the coin, could be estimated by means of an in-depth profile. We alternated the XPS analysis with an erosion procedure that removes progressively the atomic layers by ionic sputtering (Ar^+) of the surface. The parameters

Table 1
The list of the selected coins

#	Type	Date	Material	Mint
1	Gallifono Antoniano	260–268 AC	Bronze–silver	Roma
2	Follis, emperor Massentius Pius Felix	307–310 AC	Bronze	Ticinum (Pavia)
3	Assis, Effigy of emperor Augustus, Minted under Tiberius	9–14 AC	Copper	Lugdunum (Lyon)
4	Quinarium	90 BC	Silver	Roma

Table 2

Atomic concentration (%) on the raw surface of the four coins as measured by XPS

Coin	C	N	O	Na	Mg	Si	S	Cl	Ca	Cu	Mo	Ag	Sn	Pb
1	24		51	1.4	1.6	11	1.8	1		2	2.5	2.8	0.1	0.6
2	15		57		2.5	14			2.2	5.6	0.3	0.8	1	0.4
3	39	1	38					2.1		19				
4	42	3.6	35			4.3	2.8	2.4		5.2		4.1		

used during the sputtering profile were established so to minimise the damage to the coins: the sputtered area was the minimum allowed for a focused ion beam ($2 \times 2 \text{ mm}^2$); the energy of the Ar^+ ions was 4 keV; the sputtering current on the sample was about $1 \mu\text{A}$. These settings produced a nominal sputter rate of 1 nm/min [4]; to determine the real sputter rate we should have had a calibrated sample. The in-depth profiles were measured only for coins 3 and 4 and are reported in Tables 3 and 4, respectively. The depth profiling shows some common behaviour. The graphite layer is quite thin (5–30 nm) and the intensity of the C1s line decreases very quickly after the first minutes of sputtering. The O1s signal, instead, is associated to

an atomic concentration almost constant along the profile even after 90 min of sputtering. The relation of sputtering time to sputtering depth is not straightforward since it could be altered by surface roughness. Indeed a measurement in the same region where we performed XPS analysis gave a value of $5 \mu\text{m}$ as the root mean square of the surface roughness with peak to valley value up to $31 \mu\text{m}$. We can only conclude that the oxide layer still persists at least up to a depth of $0.1 \mu\text{m}$ (which could in reality be lower due to roughness) but could extend well beyond. Longer sputtering cycles could not be executed to avoid the appearance of tags on the coins.

Table 3

Atomic concentration (%) obtained by XPS for coin 3 after sputtering down to an estimated depth (nm)

Depth	C	N	O	Cl	Cu
0	39	1	38	2	19
10	2.3		34	1.1	62
30			35		64
60			36		63
90			33		66

PIXE analysis has been performed with a circular beam of 0.5 mm diameter in five different spots for each coin, taking care of not to touch the few visibly corroded areas. Spectra de-convolution, by the GUPIX package [5], identified essentially the same elements as XPS. Actually, PIXE detected also some minor elements (estimated concentration $<0.1\%$) not identified by the less sensitive XPS analysis while light elements (C and O) were not detectable in PIXE.

Since we could not reach with XPS the limits of the oxide layer, which is known to be very deep in several cases [6,7], we have analysed the PIXE

Table 4

Atomic concentration (%) obtained by XPS for coin 4 after sputtering down to an estimated depth (nm)

Depth	C	N	O	Na	Mg	Si	S	Cl	Ca	Fe	Cu	Ag
0	42	3.6	35			4.3	2.8	2.4			5.2	4.1
10	12		39	2		8.4	2	5	1.6	11	7.2	11
30	3.9		46	1.2	3.9	6.4	1.3	4.4	2.7	12	4.7	12
60	3.9		43	1.6	4.8	5.3	2	3.6	2.6	13	5.1	13
90	2.8		45	1.4	3.8	4.7	1	3.4	2.2	13	7.8	14

Table 5
Weight concentration (%) obtained by PIXE and XPS for coins 3 and 4^a

#	Technique	O	Si	S	Cl	Ca	Fe	Cu	Ag
3	PIXE	22 ± 3	10 ± 2	0.4 ± 0.2	2.6 ± 0.9	1.0 ± 0.5	0.4 ± 0.1	61 ± 6	
	XPS	11.2						88.8	
4	PIXE	20 ± 1	2.6 ± 0.4	6.3 ± 0.5	3 ± 1	2.1 ± 0.6	4 ± 1	6 ± 3	54 ± 3
	XPS	18	3.3	1	3	2.2	18	12.4	37

^a Some minor elements (Na, Mg, Al) have not been included.

spectra assuming that all elements were present in oxide form with no layered structure. The coins 3 and 4 average mass concentrations, from this PIXE analysis, are compared in Table 5 with the in-depth XPS mass concentrations, i.e. concentrations after 90 min of sputtering. The errors quoted in Table 5 for PIXE data are the standard deviations of the five measurements of each coin. We could expect a similar variability for the in-depth XPS data if collected in more than one point per coin. Indeed, the XPS analysis performed in another point on the surface of coin 3 showed a significant presence of Si and a Cu mass concentration around 60%, in agreement with the average PIXE result. Since in coin 3, the Cu mass concentration obtained by PIXE and in-depth XPS are compatible (see Table 5) and since the in-depth XPS indicated that more than 50% of copper is in oxide form, it is reasonable to conclude that, by PIXE, we could explore only a quite thick oxide layer, without reaching the pure metal bulk.

The situation is somehow different in coin 4, where the Ag PIXE concentration is significantly higher than the in-depth XPS concentration. Furthermore, the in-depth XPS spectrum showed that 70% of Ag is already in the metallic form. We therefore repeated the analysis of the PIXE spectra assuming that this coin has a layered structure. The code [5] found a minimum solution with a very thin layer (about 1.3 μm) made of light elements oxides on top of an “infinite” metallic layer, where the Ag mass concentration is around 85%.

For coin 4, a difference between PIXE and XPS analyses is the high S concentration measured by PIXE (but not by XPS) and the high Fe content detected only by XPS. Being S an external contaminant, it is well possible that very high varia-

tion is observed in different spots. The high Fe content revealed by XPS is probably due to a surface contamination since 70% of iron is present as oxide.

4. Conclusion

The XPS analysis of some Roman coins indicated that this technique can give useful information on the composition of the surface patina also if too deep measurements are problematic. The quantitative in-depth XPS data turned out to be compatible with PIXE results, provided the deconvolution of PIXE spectra was performed in an appropriate way: assuming an oxides matrix in one case and a two layer structure in a second case. While the XPS results seem to be capable of integrating and better addressing the PIXE analysis, it is however clear that, whenever possible, several PIXE runs on the same sample, at different beam energies or with different beam impact angles, should be used for a completely non-destructive investigation of the layered structure in ancient coins. In case signs of a sputtering process can be accepted on ancient coins, the two techniques integrate one another. XPS can supply both the thickness and composition of the external corroded layer and PIXE can extend the analysis of major and trace elements in the coin bulk up to several tens of microns.

References

- [1] N. Kallithrakas-Kontos, A.A. Katsanos, C. Potiriadis, M. Oeconomidou, J. Touratsoglou, Nucl. Instr. and Meth. B 109/110 (1996) 662.

- [2] A. Daccà, G. Gemme, R. Parodi, Internal Note INFN/TC-97/14, 7 May 1997.
- [3] J.D. MacArthur, P. Del Carmine, F. Lucarelli, P.A. Mandò, Nucl. Instr. and Meth. B 45 (1990) 315.
- [4] D. Briggs, M.P. Seah, Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy, Wiley, New York, 1983.
- [5] J.A. Maxwell, W.J. Teesdale, J.L. Campbell, Nucl. Instr. and Meth. B 95 (1995) 407.
- [6] C.P. Swann, S.J. Fleming, M. Jaksic, Nucl. Instr. and Meth. B 64 (1992) 499.
- [7] G. Demortier, Nucl. Instr. and Meth. B 54 (1991) 334.