

## CHARACTERIZATION OF ARTIFICIAL PATINAS ON COPPER AND BRONZE BY EXTERNAL PIXE AND EDXRF

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### ABSTRACT

Artificial patina layers were obtained on the surface of copper and bronze coupons by room-temperature dabbing or immersion techniques. The samples were analysed by external PIXE and semi-portable EDXRF spectrometers, with the aim of evaluating these X-ray spectroscopic methods as analytical tools for natural corrosion layers on copper alloys and also for the analysis of the alloys when covered by those layers. As expected, external PIXE was more sensitive than EDXRF for light elements of the patina layer, as sulfur and chlorine. Furthermore, it allows absolute comparison of intensities, through the measurement of the total current value. The EDXRF spectrometer, on the other side, was able to detect K-peaks of all the main bronze constituents — except Pb —, thus allowing a precise quantitative analysis of the substrate, with the help of a home-developed Fundamental Parameters iterative software, calibrated with BAS bronze standard samples.

### INTRODUCTION

External (in-air) PIXE is an adequate method for the elemental analysis of historical and archaeological pieces which cannot be inserted into the vacuum chamber of the equipment. EDXRF, on the other side, is a powerful technique to be used for in-situ analysis. Frequently, however, historical metallic artifacts are covered with corrosion layers which place difficulties for the X-ray non-destructive elemental analysis of the substrate. With the aim of evaluating this effect for these two important X-ray analytical techniques — portable EDXRF and in-air PIXE —, copper and bronze coupons covered with artificial patina layers were analysed by them.

Artificial patina is composed by stable corrosion layers obtained by chemical attack of the substrate metal, and their use to ornament artefacts is a very old practice. For instance, a patinated nineteenth BC-century Egyptian crocodile-god is found in the Ägyptische Sammlung, in Munich, Germany [1]. Descriptions of the techniques, although have survived in Asia, were kept in secret and finally disappeared in the West [1]. In the last centuries, however, Western artists developed many patination techniques. For instances, Balta and Robbiola [2] describe many techniques utilized by artist patinateurs in the nineteenth century, especially in France, some of which are still in use until the present days. This kind of treatment is also employed by restaurateurs to mimic old artificial or natural layers on replacement pieces or cleaned surfaces in the restoration and conservation of the architectural, historical and ethnological metallic heritage. The structures of both natural and artificial patinas are usually analysed by microscopy, X-ray diffraction and spectrometry. Most of them reveal to be heterogeneous, present layered structure and are extremely dependent on the formation process [2-4]. Large list of recipes for preparing them are presented by Hughes and Rowe [5].

## MATERIALS AND METHODS

Three kinds of patina layers, denominated S1, S2 and S4, were produced on copper coupons according to the procedures described in Table 1. For comparison, S1 was also applied to a bronze coupon. Prior to the patination, the coupons were grounded with 400 and 600 emery papers, and thoroughly washed with D.I. water, alcohol and acetone. The coupons were made from a commercial bronze rod and from commercial copper rods or sheets. For S1 and S2 on copper, the areas of the coupons were around 0.3 cm<sup>2</sup>. For S1 on bronze and S4 on copper, the area was 1 cm<sup>2</sup>.

Table 1 – Preparation of the patina layers

	S1	S2	S4
solution	Cu(NO <sub>3</sub> ) <sub>2</sub>	85g/L	
	ZnNO <sub>3</sub>	85g/L	Cu(NO <sub>3</sub> ) <sub>2</sub> 200g/L
	FeCl <sub>3</sub>	3g/L	ZnCl <sub>2</sub> 200g/L
	H <sub>2</sub> O <sub>2</sub>	3%	
application	dabbing, twice a day, five days	dabbing, twice a day, five days	immersion, two weeks

A non-destructive external-PIXE arrangement was used to perform the PIXE measurements at the LAMFI (*Laboratório de Análise de Materiais por Feixes Iônicos*) at the University of São Paulo. The analyses of the elements present in different samples were performed through the characteristic X-rays produced by the interaction of the proton beam (~ 2.0 MeV) with the samples. The beam charge was monitored with a gold foil of ~100 µg/cm<sup>2</sup> and the characteristic gold X-rays were detected with a XR-100CR (Si-PIN, FWHM 220eV@MnKα). Another Si-PIN detector (FWHM 160eV@MnKα) was used to detect the characteristic X-ray from the target. Both detectors were mounted on water-cooled Al bases. Figure 1 shows the experimental view of this external beam setup. For comparison, the same samples were also analysed in the internal PIXE arrangement of LAMFI. For this configuration, a Si(LI) detector (FWHM 158eV@MnKα) was used, with an 57µm-thick Be absorber at 120° with respect to the beam. Another comparison was made, regarding the corrosion of the samples after 12-month exposition to open atmosphere. All of them were analysed again by external PIXE after this period.

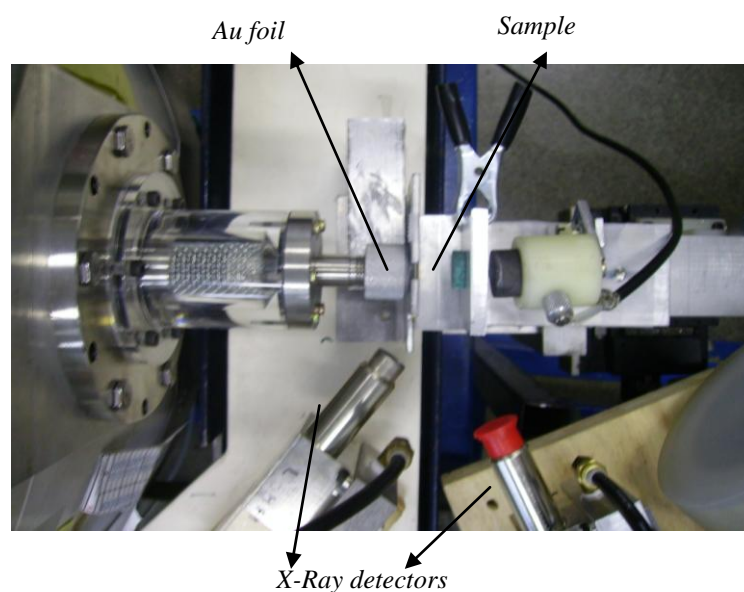


Figure 1 – View of the external beam setup

The EDXRF spectrometer, shown at Figure 2, consists of an X-ray generator and an X-ray detector, and was developed at EPUSP. The generator is an Ital Structures W-tube, with voltage range from 22 to 60 kV and current from 0.12 to 1.5 mA. The detector is a Ketek AXAS Si-drift one, with Peltier cooling, linked to a Ketek 4k-channel analog-digital converter. For the present measurements, a 1.3 mm-diameter Pb collimator was used in the incident beam, and the angle between the axis of the incident beam and the detector was 90°. Some measurements were made with both axis at 45° of the surface (denominated in this paper as “45-edxrf”). Other measurements, denominated as “0-edxrf”, were made with a glazing incident angle. For both, the minimal distance between sample and detector is 7 mm. Refrigerated water cooling was used in order to keep the detector case below 20°C, thus assuring a peak FWHM of around 150 eV. Most measurements were made at 55 kV and 0.3 mA, for 600 s.

Quantitative analysis software was used for both techniques. For EDXRF, the software, developed at EPUSP, is based in the Fundamental Parameters model proposed by Criss and Birks [6], and relies on standard samples for calibration constants. For the present study, three copper alloys from BAS (Bureau of Analysed Samples, UK) were used as standards. For PIXE, the thick target software, developed at LAMFI, was described elsewhere [7], and is supposed to be used without standards. As the patina layers are heterogeneous and the analysing volume for both techniques usually include the base-alloy, these results were used only as comparative values for most analysis, and only were considered as representative values for uncoated samples. Another reason for that is that light elements as H, C, O and N are frequently present in the patina layers and are not detected by any of the techniques.

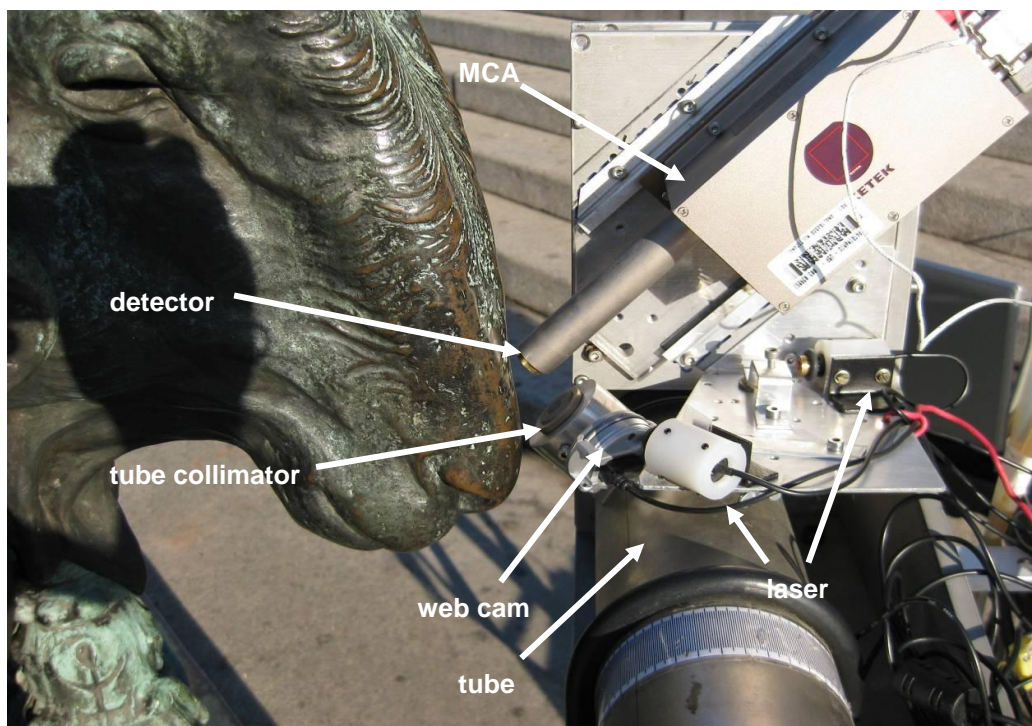


Figure 2 – View of the EDXRF spectrometer being used for outdoor *in-situ* measurements

## RESULTS

PIXE results for the uncoated coupons of copper and bronze are shown in Figure 3. Figure 4 shows these results for EDXRF. Both internal PIXE and EDXRF show the presence of a small amount of Fe in the commercial copper. Internal and external PIXE detected also S, whereas only internal PIXE detected Al. For commercial bronze, all arrangements detected the main alloying elements, Sn and Zn. Additionally, internal PIXE detected small amounts of Al and Cr, and EDXRF detected small amounts of Fe, Ni and Pb (and possibly P and S). These results confirm, as expected, that PIXE, even external,

is more sensitive than EDXRF for light elements, as Al and S, and EDXRF is more sensitive than PIXE for heavier elements, as Fe, Ni and Pb.

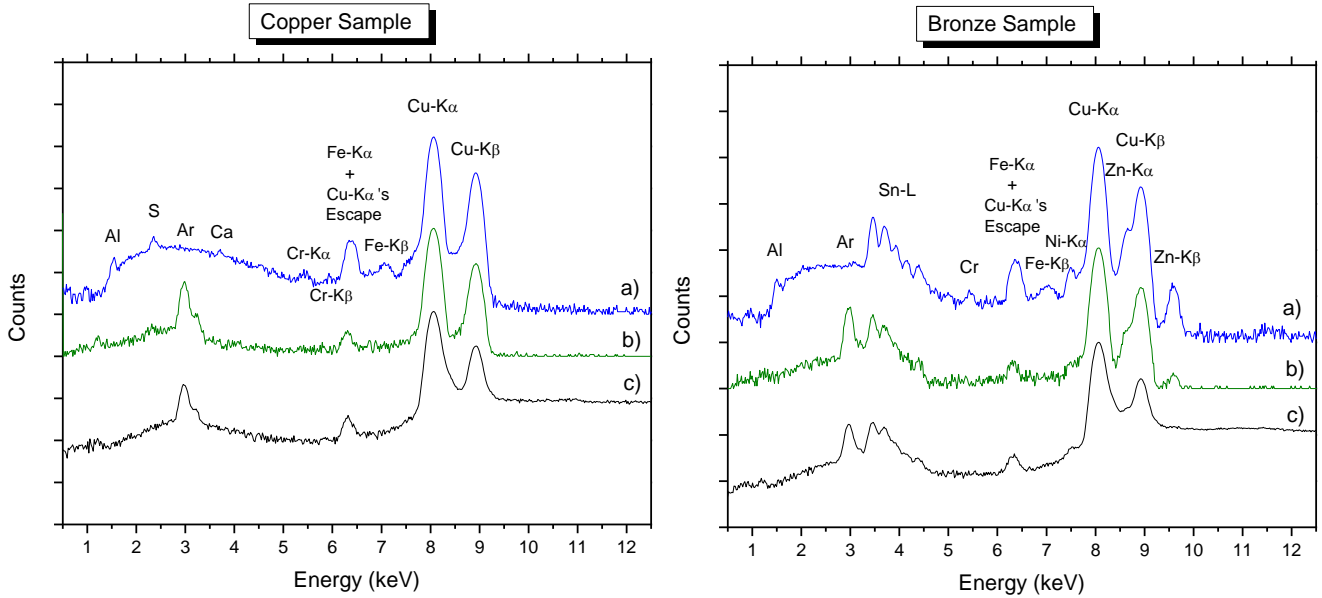


Figure 3 – PIXE spectra of uncoated copper (left) and uncoated bronze (right).

a) Internal, b) external, c) external, after 12 months.

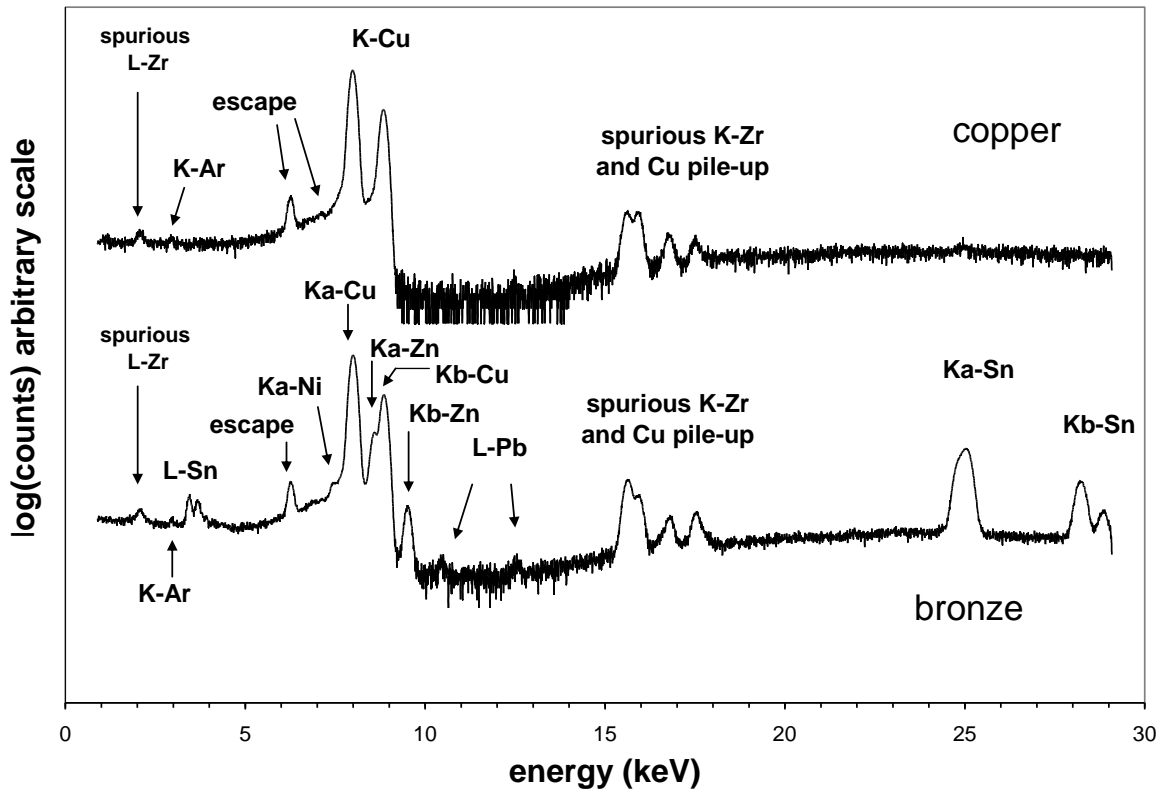


Figure 4 – EDXRF spectra of uncoated copper and uncoated bronze.

The estimated contents of the main constituents of the commercial bronze, according to the quantitative software applied in each case, are compared in Table 2 for external PIXE and EDXRF. Both indicate a larger amount of Sn than of Zn in the alloy, but no standard composition for wrought copper alloys [8] fits adequately to these values. The estimated Zn content, for instance, is too low for the C41000 tin-brass alloy (91.0-93.0 Cu, <.50 Pb, <.50 Fe, 2.0-2.8 Sn, remaining Zn). On the other side, it is too high for the C50900 phosphor-bronze alloy (<.50 Pb, <.10 Fe, 2.5-3.8 Sn, <.30 Zn, .03-3.0 P, remaining Cu). (Additionally, P has not been detected by PIXE or EDXRF.) Other standard alloys have either higher or lower Sn contents than those shown in Table 2. One observes a relative deviation of around 15% between PIXE and EDXRF, for both Sn and Zn, in opposite directions. As both analysis are normalized to 100% (for EDXRF, other elements were also considered), a deviation in one of these elements would affect the other, and vice-versa. This means that maybe both differences can be attributed to just one of them. Sn is a good candidate for that, because its content was estimated from the K-peaks areas in the case of EDXRF, and from the L-peaks areas in the case of PIXE. This hypothesis is presently under study.

Table 2 – Quantitative results for the commercial bronze coupon

	external PIXE (%)	EDXRF (%)	absolute difference (%)	relative difference (%)
Zn	2.1	1.7	0.4	16.8
Sn	2.9	3.4	-0.4	-14.1
Cu	95.0	93.4	1.5	1.6

Figures 5, 6, 7 and 8 show the spectra obtained for, respectively, bronze + S1, copper + S1, copper + S2 and copper + S4, both by PIXE and EDXA. The important anionic constituents of the patina layers that can be detected by PIXE and EDXRF are Cl and S. For S1 and S2 samples, Cl was detected by both techniques. For S4, only a very small amount was detected (by EDXRF). On the other side, S was detected in all samples, but predominantly in S4.

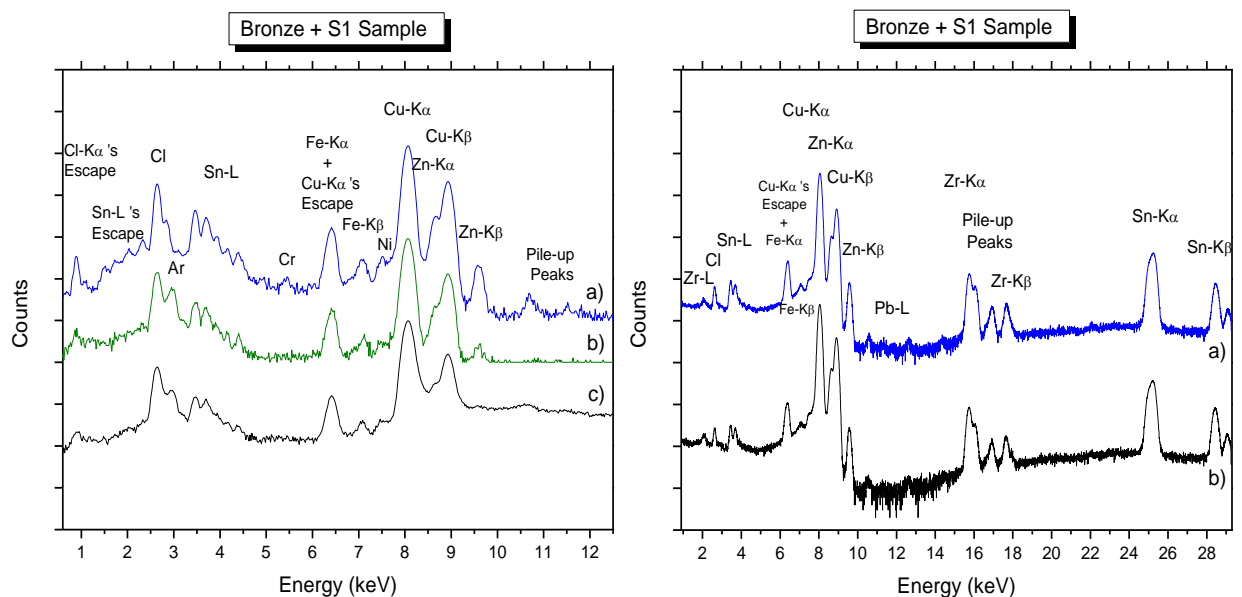


Figure 5 – Spectra of bronze coated with S1 patina. In the left, PIXE: a) internal, b) external, c) external, after 12 months. In the right, EDXRF: a) 45-edxrf, b) 0-edxrf

One should be careful, however, when comparing the spectra of different samples. As the thickness and the structure of the patina layers are different in each case, the fractions of spectral information that are originated in the substrate and in the layers are also different in each case. For a thin patina layer, for instance, the Cl/Cu and the S/Cu peak-area ratios should be smaller than those of a thick one with the same composition, because in the first case the contribution of the copper from the substrate is larger. For the same reason, comparison of results between PIXE and EDXRF should be careful, because the analysis volume in these techniques are different, thus affecting again the fraction of spectral information from patina and substrate.

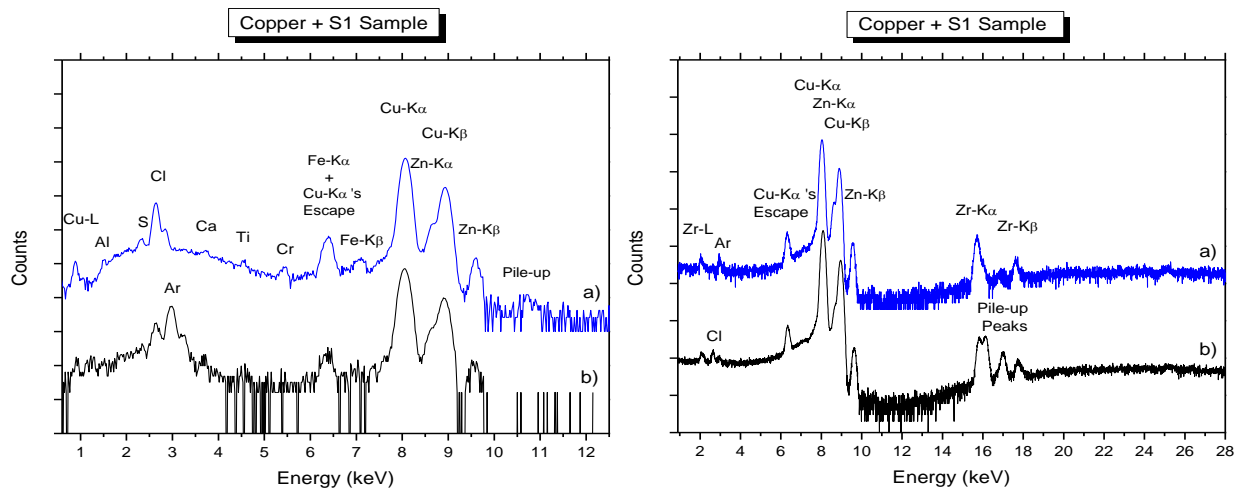


Figure 6 – Spectra of copper coated with S1 patina. In the left, PIXE: a) internal, b) external, after 12 months. In the right, EDXRF: a) 45-edxrf, b) 0-edxrf

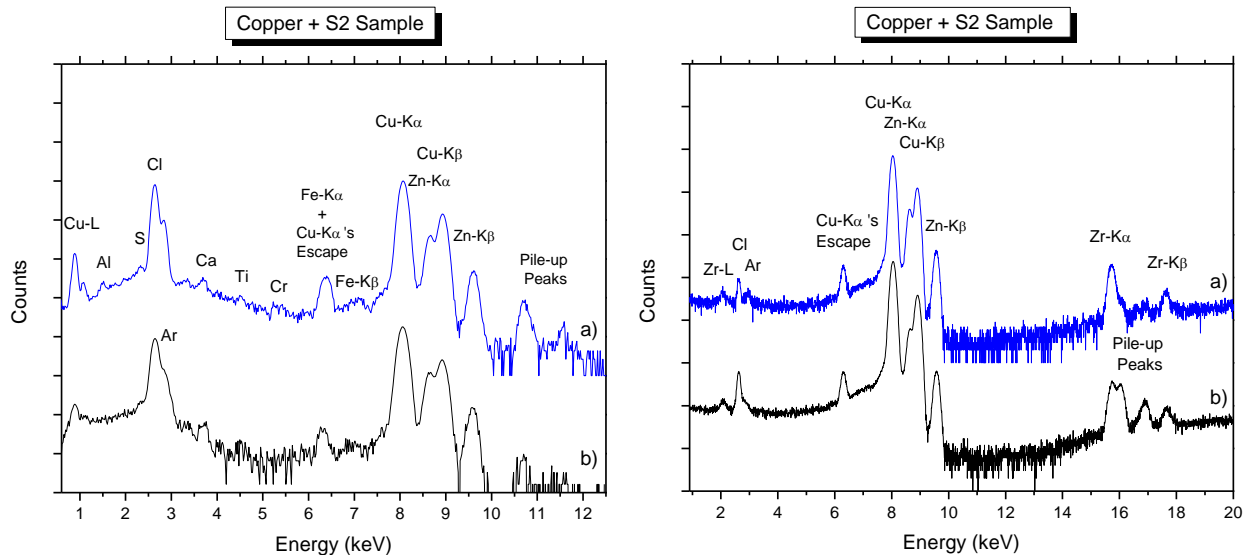


Figure 7 – Spectra of copper coated with S2 patina. In the left, PIXE: a) internal, b) external, after 12 months. In the right, EDXRF: a) 45-edxrf, b) 0-edxrf

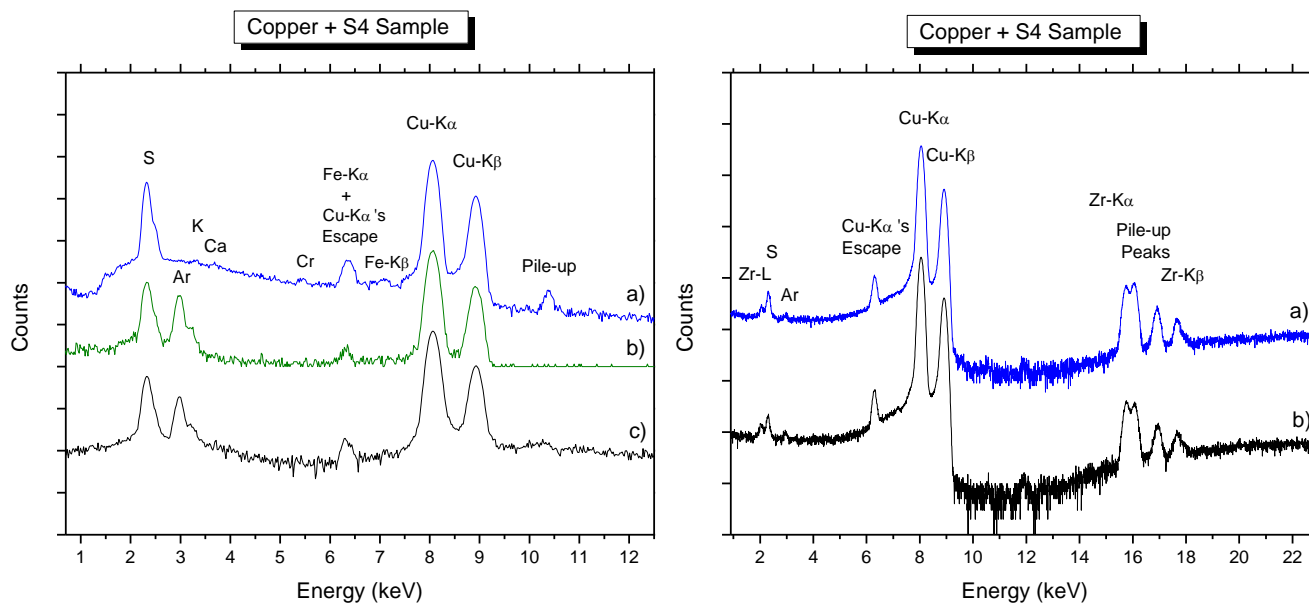


Figure 8 – Spectra of copper coated with S4 patina. In the left, PIXE: a) internal, b) external, c) external, after 12 months. In the right, EDXRF: a) 45-edxrf, b) 0-edxrf

Even so, the relative contents of chlorine and sulfur in S1, S2 and S4, as estimated from PIXE measurements, follow the same pattern as the Cl/Cu and S/Cu peak-area ratios obtained with EDXRF, as can be seen in Figure 9. For both techniques, there is a small increase in chlorine from S4 to S1 (with a slight exception for 0-edxrf results), and a large increase from S1 to S2. For sulfur, there is a large decrease from S4 to S1, and then a small increase from S1 to S2.

Figure 9 also allows the comparison of the results between internal and external PIXE, and between 45-edxrf and 0-edxrf. Regarding PIXE, no remarkable difference for Cl and S arises between the two operating modes. Regarding EDXRF, however, large differences arise, but, in some cases, their meaning is not clear. One would expect that the use of a glazing angle would improve both Cl/Cu and S/Cu ratios, because less copper from the substrate would affect the spectra. This was true for S4: the Cl/S ratio increased 4.6 times, and the S/Cu ratio increased 1.4 times. This was also true for S1 on bronze (not shown in Figure 9): the values are 1.8 and 1.1, respectively. For S1 on copper, however, the results are apparently contradictory: there was a large increase for the S/Cu ratio (12 times), but simultaneously a large decrease in Cl/Cu (24 times). For S2, both values decreased. Although some fundamental reasons, as the structure of the layers, may possibly explain the differences between S and Cl in copper S1, one might remark that, as mentioned before, two different areas were used for the experiments. For the larger area (1 cm<sup>2</sup>), the results were as expected (S4 and S1 on bronze). For the smaller areas (0.3 cm<sup>2</sup>), they were not. The use of a smaller area should not affect the 45-edxrf measurements, because the analysing spot is much smaller than it. But, for the glazing mode, the analysing volume increases and can include regions out of the smaller sample.

One should address also to the fact that, although some changes in the colour of the surfaces were observed after 12-month exposition to air, no remarkable difference was detected in the spectra. Two reasons may be suggested for that. First, the change of colour may be due to modifications that occurred mainly in the surface of the patina layer, thus corresponding to just a very slight change of average composition. Second, the changes, even if occurring also in the bulk of the patina layers, may have not changed significantly the S/Cu and Cl/Cu ratios, as would be the case of the increase of the number of hydration molecules in the compounds, the changes of oxidation states, and so on.

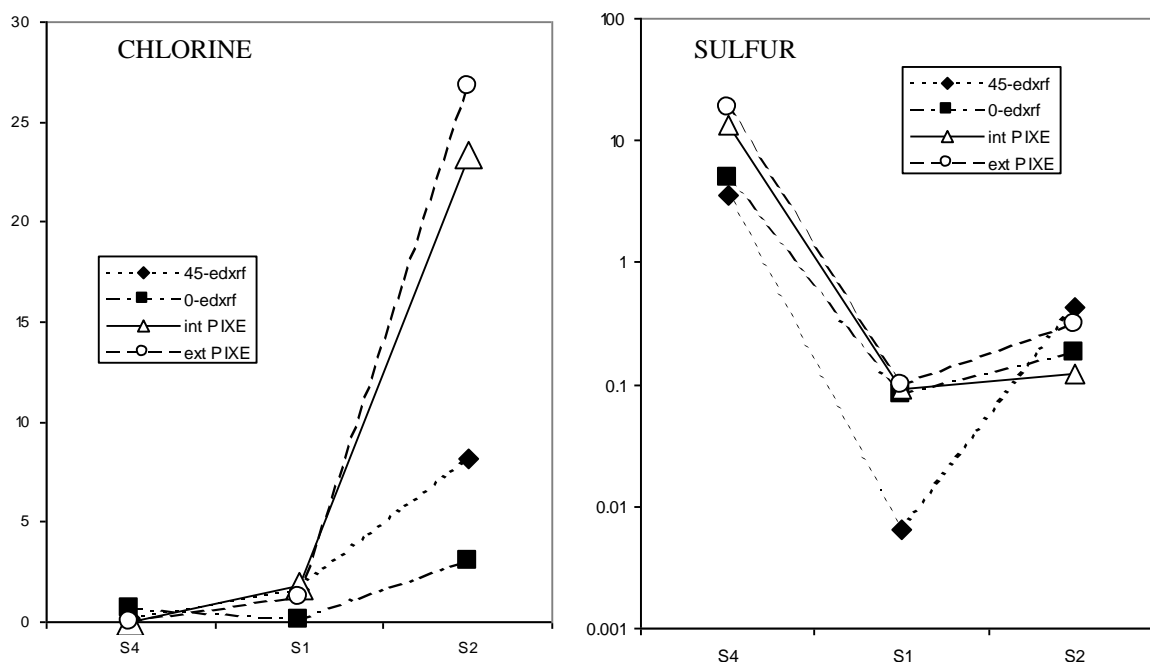


Figure 9 – Comparison of relative chlorine and sulfur contents for the patinas on copper. For PIXE, values are represented by the contents calculated by CLARA software. For EDXRF, they are represented by the Cl/Cu and S/Cu peak-area ratios, multiplied by 10000.

## CONCLUSION

In-air PIXE analysis and in-situ EDXRF can be used to estimate S and Cl contents of different kinds of patina layers on copper and bronze, as well as to determine precisely the composition of these alloys when uncoated. The comparison between in-air PIXE and internal PIXE shows that, as expected, internal measurements are much more sensitive, but that, even so, in-air PIXE was able to detect low-content elements, especially when they have relatively low atomic number. On the other side, the comparison between PIXE and EDXRF shows that, as also expected, PIXE is more sensitive than EDXRF for light elements as Al, Cl and S, whereas EDXRF can be more sensitive for heavier elements, as Fe, Ni and Pb.

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