

## DEVELOPMENT OF EDXRF QUANTITATIVE ANALYSIS METHODOLOGY FOR THE STUDY OF FERROUS ALLOYS OF HISTORICAL IMPORTANCE

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A semiportable x ray fluorescence spectrometer was assembled with the aim of studying the Brazilian cultural heritage and is being prepared for the analysis of 18<sup>th</sup>-Century and 19<sup>th</sup> Century iron and steel Brazilian products, as a contribution for the study of the metallurgy history. The equipment consists of a 60kV/1.5 mA W-tube and a Si-drift detector with a Zr collimator, and is assembled in a flexible way in order to allow different angles and distances to be used, as well as different filters and collimators. A quantitative analysis software was developed following the fundamental parameters method, and it was successful in the analysis of a family of alloy-steel homogeneous standard samples. For the study of heterogeneous pieces, it can be used as qualitative tool. An arrangement for using Cr secondary-fluorescence emission was successful in increasing the precision of the area measurement for Ti K- $\alpha$  peaks, which partially overlap with Fe K- $\alpha$  escape peaks. Measurements done with this arrangement lead to an almost linear intensity-concentration ratio for Ti in low-alloy standard NBS steels, thus allowing Ti estimates to be made for the Ipanema samples.

**Keywords:** historical metallurgy, Ipanema steelplant, EDXRF

### INTRODUCTION

Brazil has one of the world largest iron ore reserves. The first iron and steel production unit, based on direct reduction, was started in 1591<sup>1</sup>. Other enterprises were developed in the following centuries, but in 1782 every metallurgical production in Brazil was forbidden by the Portuguese Crown. Some illegal iron production, however, was still developed, sometimes based on African technology, brought by African slaves. The Portuguese law was soon changed, and new studies were developed by the Crown to establish a more consistent iron and steel production in Brazil. One of the results was the creation, in 1810, of the Ipanema steel plant, in Sorocaba, São Paulo state, under the direction of C. G. Hedberg, a Swedish metallurgist, who built four small reduction furnaces but was not very successful in both quality or quantity of the production<sup>2</sup>. He was followed by F. L.G. de Vanhagen, a German metallurgist, who built two blast furnaces and increased the production. Even so, the productivity was still very below those of similar European plants. Vanhagen left the country in 1822. In the following decades, several modifications and improvements were made. Finally, its production was stopped in 1895. Since the end of 19<sup>th</sup>-Century, the low productivity along its existence is usually attributed to the high Ti and P content of its iron ores. Although steel making was an important part of Brazilian history, few metallurgy history studies can be found in the country. X ray fluorescence spectroscopy may be an

important tool for these studies, because it is a non-destructive technique and can be used *in situ* at museums, historical sites, mines, and so on. In the case of Ipanema samples, this technique can be used for analyzing a large number of samples *in situ*, so that those with high Ti contents could be identified, and some of them could be selected for metallography and XRD analysis.

To check if the technique was adequate for this purpose, a semiportable energy-dispersive x ray fluorescence (EDXRF) spectrometer was used to analyze three steel pieces found in the ruins of Ipanema Steelplant. It was used, as well, for initial analysis of ironware from a 19<sup>th</sup>-Century house at the region of Cananéia, São Paulo.

## EXPERIMENTAL

The spectrometer consists of an X-ray generator and an X-ray detector. The generator is an Ital Structures W-tube, with voltage range from 22 to 60kV 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. A Pb collimator with a 1,3 mm-diameter hole turns the 8° original incident beam into a 40' beam. Most measurements were made with an angle of 90° between incident beam and detector, both at 45° of the sample surface. At this arrangement, the minimum distance between sample and detector is 8 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. For special experiments, Cr filters and Cr secondary emitters were used. The filters were obtained by electrodeposition of 30 to 50µm-thick Cr layers over 2mm-thick carbon disks. The Cr layers were obtained by electrodeposition of 50µm-thick Cr layers on steel. When using the secondary emitters, the sample-detector distance was increased to 20 mm and the angle between the incident ray and the detector was reduced to 60°. Most measurements were made at 45kV and 0.3mA, for 500s. Calibration measurements with alloy-steels were done at 35, 40, 45 and 50kV, for 300s, 250s, 200s and 150s, respectively, and 0.3mA. Measurements of the historical pieces and of NBS low-alloy steel standards were made at 45kV, 0.3mA and 500s, when the conventional arrangement was used. When the special secondary-emission arrangement was used, the measurements were made at 45kV, 1.0mA and 1000s. Characteristic, escape and sum peaks were identified with special routines in Microsoft Excel. Peak area determination was done with AXIL-QXAS software.<sup>3</sup>

Three pieces obtained at Ipanema were studied (Figure 1-a). All of them are covered with corrosion products and mineral sediments. One of them, the pin, had been cut in the recent past for analysis. The surface of the cut is clean. Another piece, a door bolt found in a 19<sup>th</sup>-Century house in Cananéia, São Paulo, is composed of three parts, assembled together (Figure 1-b). It is partially covered by a blue paint. The regions without the paint are covered by a stable and thin corrosion layer. Measurements were made in the polished region or the regions without paint.

A software for quantitative and qualitative analysis was developed based on fundamental parameters of the elements of the sample, as the wavelengths of the emitted lines, the mass attenuation coefficients in function of the wavelength, the absorption edge for each series, the fluorescence yield for each series, the absorption jump ratios for each series, and the relative intensity factor for the lines of each series. The method takes into account the incidence and take-off angles and the intensity of the incident wavelength in function of wavelength. As the influence of tertiary fluorescence is usually very low,<sup>4</sup> only primary and secondary fluorescence were considered. The expression for primary and secondary fluorescence for thick samples was taken from Criss and Birks.<sup>5</sup> Values for the fundamental

parameters were taken from Markowicz<sup>6</sup> and NIST databases.<sup>7</sup> Intensity versus wavelength profiles for side-window W-tubes operated at 40, 45, 50 and 60kV were taken from Arai et al.<sup>8</sup> From the above calculation, one obtains the theoretical intensities of the desired lines for a given composition of the sample. These results can be compared to the experimental intensities obtained for standard samples, so that correction factors can be calculated. These factors account for both equipment and sample variables, and therefore should be calculated for each set of experimental conditions and for each family of samples. Even for a family of samples with close compositions, these factors can be assumed as composition or intensity functions. In our software, the factors were calculated as linear functions of intensity, with no constraint for zero.

For an unknown sample, the composition should be obtained by an iterative method. A first guess gives rise to theoretical intensities which, after corrected by the calibration factors, are compared to the experimental values. The difference between the calculated and the experimental values is then used to modify the guess. This process is repeated until convergence is attained. It should be emphasized that reaching all the experimental intensities with the model up to some small limit sometimes is mathematically impossible, because there is a unary correlation between compositions and intensities. Therefore, two convergence criteria were adopted: a) reach the experimental compositions within a given precision, or b) repeat previous calculated intensities within a given precision. It was observed the only the second one is really necessary, because if the first one is attained, the second one will be attained soon later. Figure 2 compares the calculated intensities of Fe K- $\alpha$  peaks to the experimental ones at 45kV for seven steel samples which had been analyzed by certified chemical methods (Table 1). One observes that a good qualitative agreement was obtained, as the relative position of every calculated value is closely the same of the experimental value. This is very clear, for instance, for samples 2 and 5, which have almost the same Fe content, and very different peak intensities, due to the absorption-enhancement effects of the other components. For these samples, at 45kV, the correction factor for Fe K- $\alpha$ ,  $K = I_{\text{experimental}} / I_{\text{calculated}}$ , was determined as  $K = 0.5005 + 0.0052 \cdot I_{\text{experimental}}$ , with  $R^2 = 0,9783$ . Figure 3 shows the correlation between the calculated intensity, so corrected, and the experimental intensity. For comparison, the same kind of graph is shown in the inset of Figure 3, using linear correlation instead of the fundamental parameters method, for the same samples. One observes that a very poor  $R^2$  value is obtained. Table 1 also compares the certified and the calculated compositions for sample 3CD, which was not used to obtain the above correction factors. One observes that a very good agreement was obtained for Fe, Cr and Mo. In this work, due to the heterogeneous nature of the samples and the presence of surface layers, this software was used as a qualitative tool.

## RESULTS

### a) Ipanema pieces and NBS standards

Figure 4 shows the spectrum obtained at the surface of the disc shown in Figure 1-a. One observes peaks of Ca, P, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Pb and Zr. Pb peaks were verified to come only from the tube collimator. Zr peaks, by comparison to the spectra of Zr-free steels, are very probably originated only from the detector collimator. As Ti is an important element for the analysis of Ipanema steels, the inset shows a detail of its K- $\alpha$  peak. It is close to the Fe K- $\alpha$  escape peak and to the Ba L- $\alpha$  peak, which increases the uncertainty of its area measurement. To improve the measurement of the Ti K- $\alpha$  peaks, we tried to obtain spectra

with lower Fe K- $\alpha$  escape peaks. Lower tube current or Cr filters were not effective, but a substantial reduction of the relative intensity of Fe K- $\alpha$  was obtained using secondary Cr emission. Figure 5-a shows the Ti K- $\alpha$  and the Fe K- $\alpha$  escape peaks obtained with the conventional configuration in a section of the Ipanema steel pin, while Figure 5-b shows the same spectrum obtained with secondary Cr emission. The relative area of the Fe K- $\alpha$  escape peak decreased 2.3 times, compared to the Ti K- $\alpha$  peak. The relative uncertainty of the Ti K- $\alpha$  area decreased correspondently: in the conventional arrangement, the area was  $286 \pm 48$  counts, while in the special arrangement it was  $748 \pm 44$  counts.

So, in order to semiquantitatively evaluate the Ti content of the Ipanema samples, five steel standards (NBS Reference Material 1261a, 1262a, 1263a, 1264a and 1265a) were analyzed using the same secondary Cr configuration. As those standards are low-alloy steels, the absorption and enhancement effects on them are mainly due to Fe and, thus, very similar, so that an almost linear relationship was obtained between the Ti intensities and its contents (Figure 6). This kind of behavior was confirmed by simulation with our fundamentals parameters software. On the other side, both experiment and software showed that such a linear agreement is not obtained with a high-Cr steel (Euronorm – CRM 298-1 duplex stainless steel, with 24.72%Cr and 0.0014%Ti), as Cr strongly enhances Ti K lines.

Applying the linear correlation factor shown in Figure 6, one can obtain an estimate of the Ti content in the Ipanema samples. For the section of the pin, the Ti area was 650 counts, when analyzed with the special arrangement. So, one can estimate a Ti content around 0.2%. For the same pin, but analyzed at the surface, the area was 5.6 times smaller, 116 counts, what can be attributed to the presence of corrosion products and deposits on the steel. For the bar and the disc, also analyzed without sectioning, the areas are 13 and 932 counts, respectively. If we suppose that the Ti content was similarly underestimated (5.6 times), its value in the disc would be around 1%, and almost zero in the bar.

Ca, Mn, Ni, Cu and Zn peak areas in Ipanema pieces are summarized in Figure 7. Mn and Cu are present in all the pieces. Ca is probably only present in the external deposits, so it was not observed in the section of the pin. Zn is not present in the pin, and Ni is not present in the bar. Light elements as P, Si and Al show very weak peaks when their contents are below 5-10% (P K- $\alpha$  peak, additionally, is very close to the Zr L- $\alpha$  peak, which comes from the detector collimator).

### c) The door bolt

In the main body of the door bolt a small region was cleaned and polished in order to be observed in an optical microscope. Figure 8 shows the observed microstructure, which is basically composed of pearlite and equiaxed ferrite. Image analysis indicates that the steel has approximately 36% pearlite, which corresponds to 0.25 – 0.30 weight % C. The grain size is heterogeneous and there are some acicular phases. This recrystallized structure suggests that the material was hot-hammered and then air-cooled, so that the high-temperature austenite phase transformed into pearlite and ferrite. No inclusions were found, what suggests the piece may have been made from refined bars. The EDXRF analysis of this polished region showed only Fe (Figure 9-a), what is coherent with the microstructure. Analyses of the adjacent regions, which were not polished, revealed also the presence of P, Cl, Ca, Cu and high Zn (Figure 9-b). In the other two pieces, the Zn peak was even higher, and S was observed. The presence of Cu and Zn in the surface of the pieces probably is due to old paint layers which are mixed to the corrosion products. One may conclude that the surface analysis of pieces which had been painted in the past only is useful, from the metallurgical point of view, if some preparation of the surface is done.

## CONCLUSIONS

The software developed for quantitative analysis was able to obtain good values for Fe, Cr and V contents in homogeneous alloy-steels. For the analysis of heterogeneous pieces, it can be used as a qualitative tool. The use of secondary fluorescence emission was successful for increasing the Ti K- $\alpha$  intensity in relation to the Fe K- $\alpha$  escape peaks intensity, thus allowing an increase of more than three times in the precision of the area measurement. Estimates of Ti content, assuming that the effect of the corrosion layer was similar in the different Ipanema pieces, suggests values around 1%Ti for one of the pieces. In the analysis of a 19<sup>th</sup>-Century door bolt, no detectable amount of other metals than Fe were found. Analysis of unpolished surfaces of the pieces was not very useful, because the elements pertaining to old paint layers, as Cu and Zn, are presently incrustated on the corrosion products and cannot be distinguished from alloy constituents.

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## REFERENCES

1. Gomes F M. *História da Siderurgia no Brasil*. Editora da Universidade de São Paulo: São Paulo, 1983.
2. Felicíssimo Jr J. *História da Siderurgia de São Paulo, seus personagens, seus feitos*. Associação Brasileira de Metais: 1969.
3. International Atomic Energy Agency. 2005. <http://www.iaea.org> [April 2005].
4. Shiraiwa T, Fujino N. *Bull. Chem. Soc. Jpn.* 1967; **40**: 2289-2296.
5. Criss JW, Birks LS. *Anal. Chem.* 1968; **40**: 1080-1086.
6. Markowicz A A. X-ray Physics, In *Handbook of X-Ray Spectrometry. Methods and Techniques*. Markowicz A A and Van Grieken R E (eds.). M. Decker: N.York, 1993; 1-73.
7. National Institute of Standards and Technology. <http://www.physics.nist.gov> [Jan 2007]
8. Arai T, Shoji T, Omote K. *Adv. X-Ray Anal.* 1986; **29**: 413-426.

**Table 1.** Composition of alloy steel standard samples (weight %)

		V	Cr	Fe	Mo	W
used as standards	1CD	0.54	3.22	91.56	2.29	2.39
	2CD	2.58	3.88	88.14	2.54	2.87
	4CD	2.08	4.04	83.07	4.58	6.24
	5CD	0.86	2.23	88.31	7.34	1.26
	6CD	2.23	3.31	84.60	8.06	1.79
	7CD	1.22	3.27	85.78	4.59	5.14
	8CD	0.74	3.26	85.38	4.95	5.68
used as unknown	3CD - certified (%)	0.74	3.26	85.35	4.87	5.79
	3CD - obtained (%)	0.67	3.22	85.21	4.86	6.05



Figure 1. a) Three pieces from Ipanema steelplant. b) Door bolt.

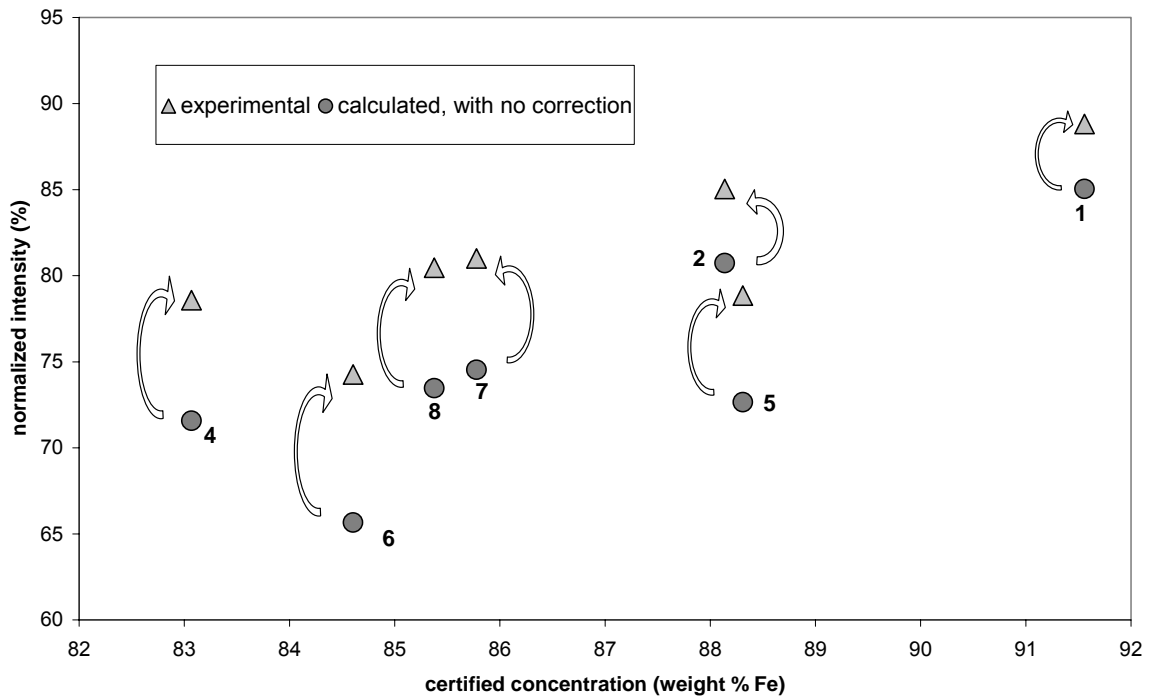
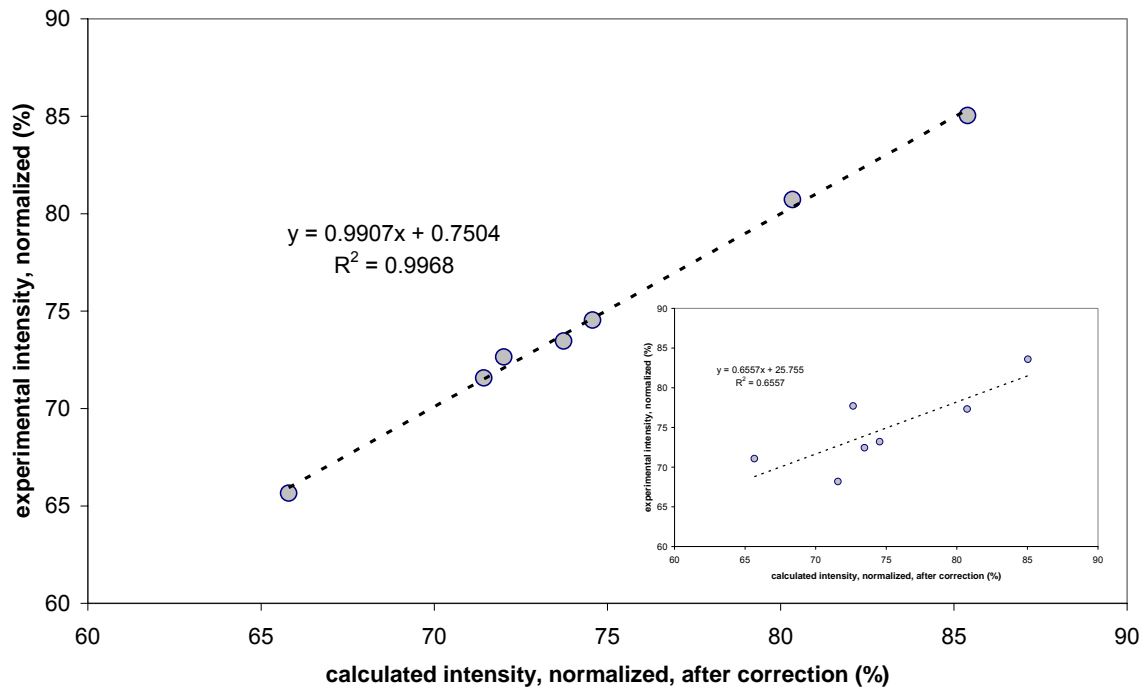
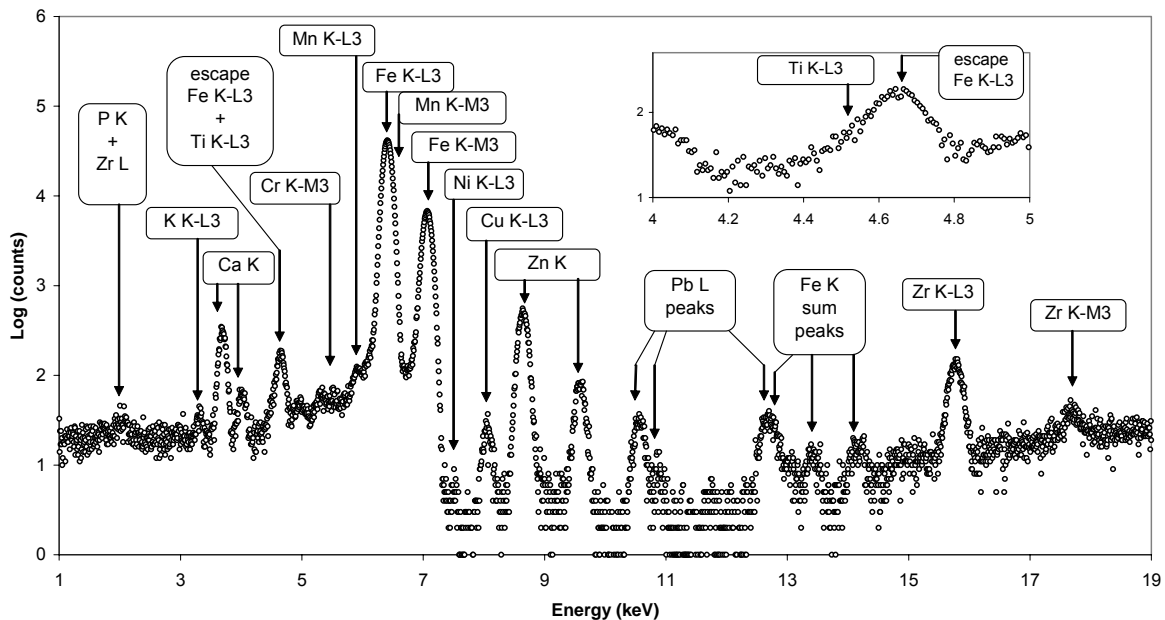


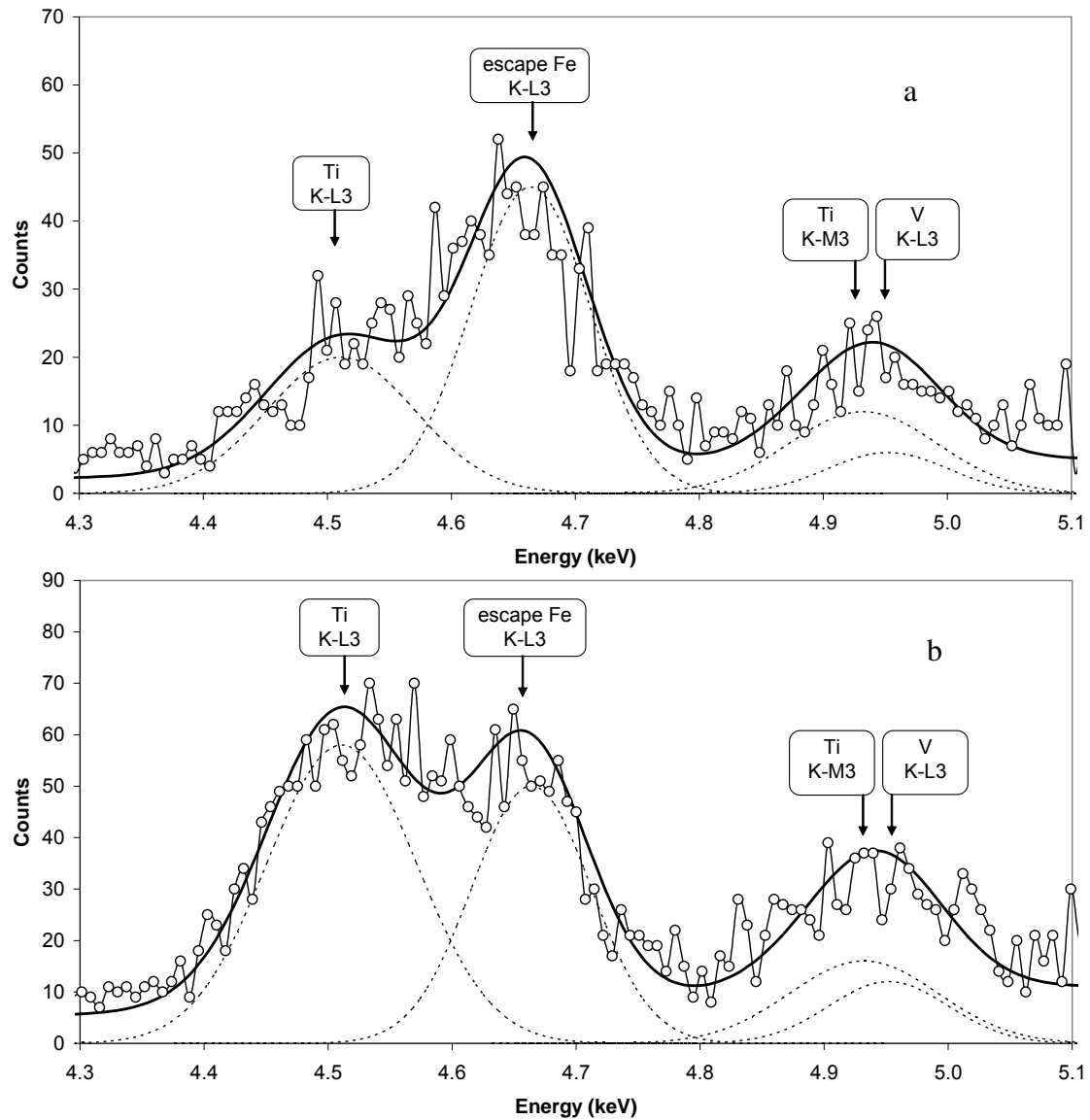
Figure 2. Fe K- $\alpha$  intensities calculated by the software and experimental intensities versus the certified concentrations. Measurements made at 45kV.



**Figure 3.** Fe K- $\alpha$  experimental intensity versus calculated intensity after calibration correction, using the fundamental parameters method. In the inset, a similar graph, using a single regression method.

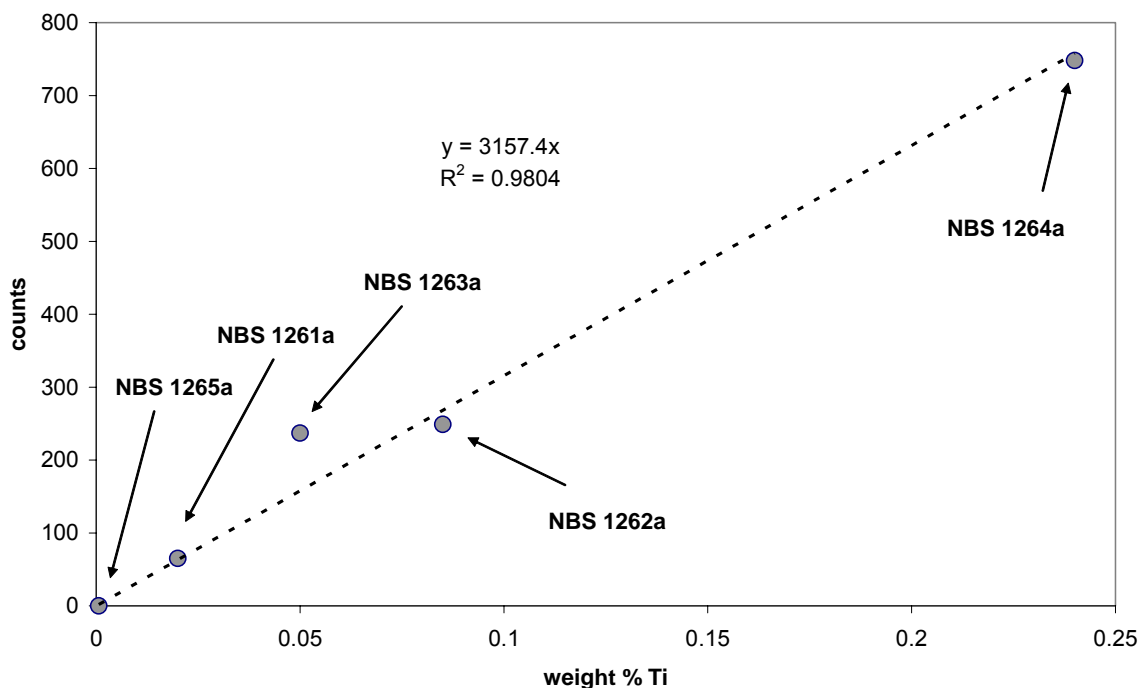


**Figure 4.** Spectrum of the Ipanema disc surface

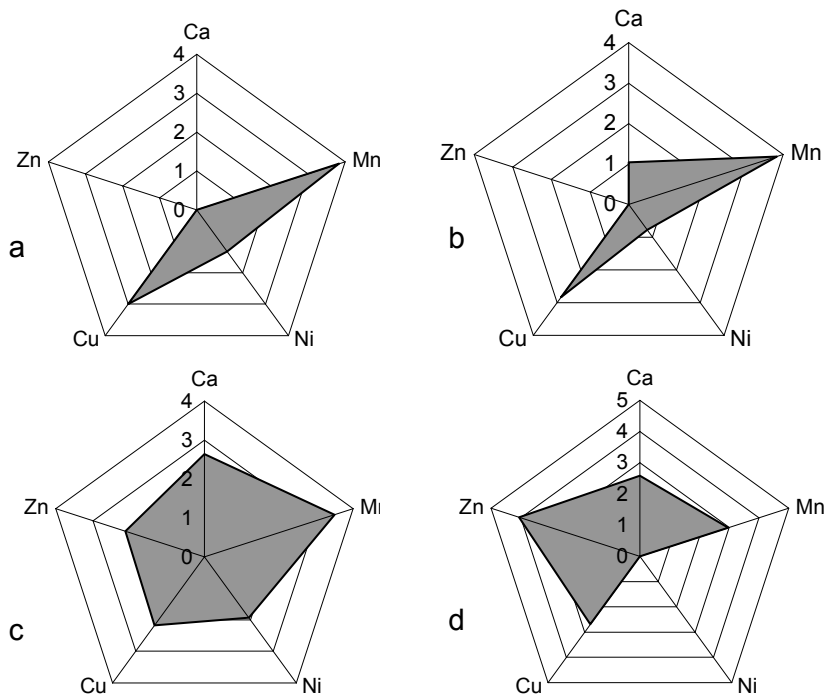


**Figure 5.** Ti and escape Fe peaks in the spectrum of the polished section of Ipanema pin. a) Obtained with the conventional arrangement. b) Obtained with the special arrangement.

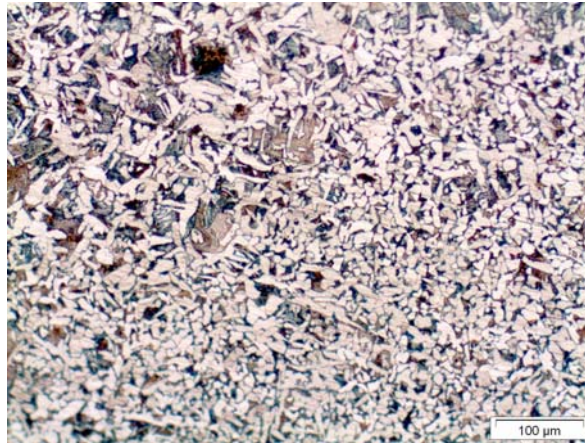




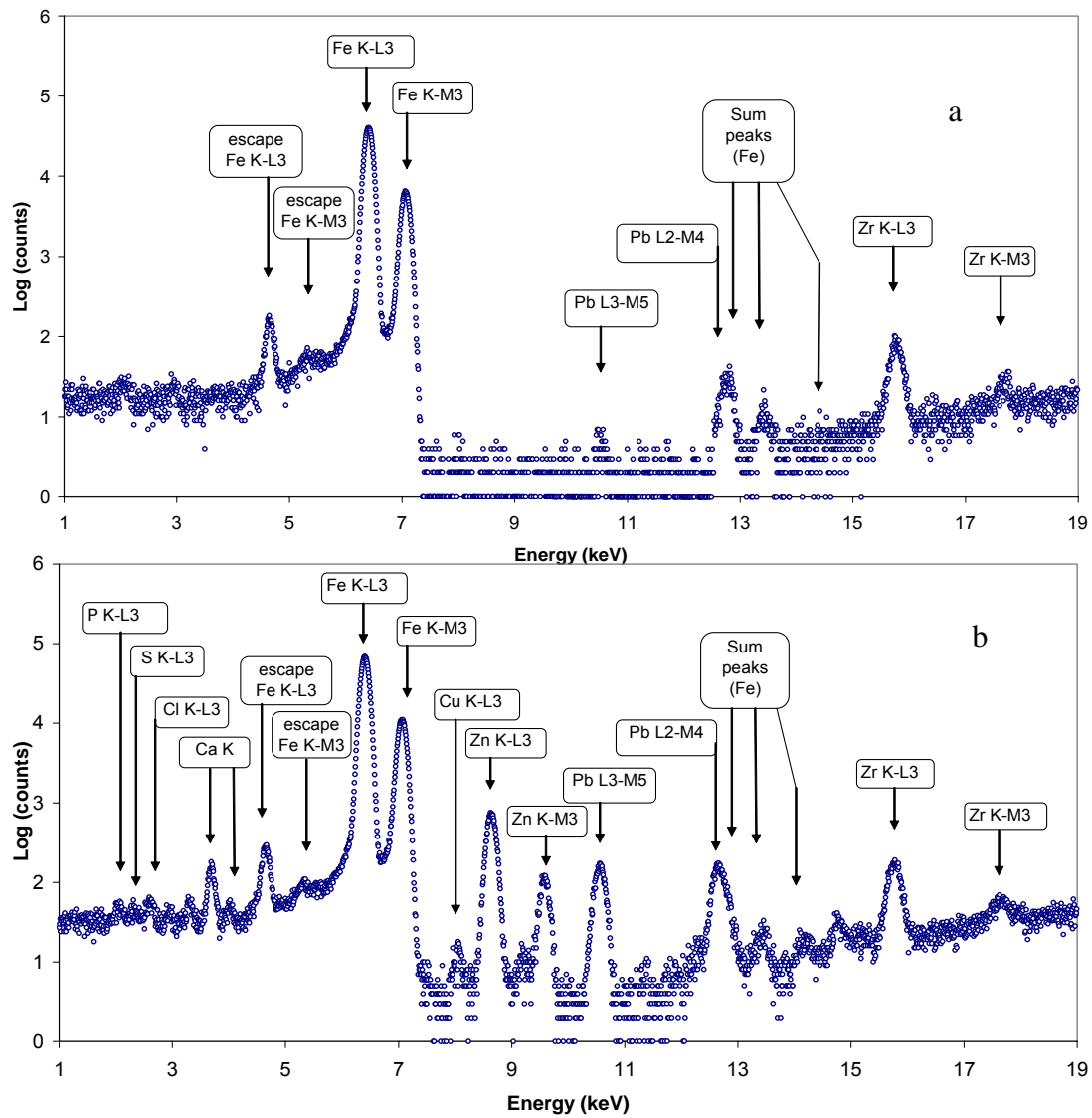
**Figure 6.** Area of the Ti K- $\alpha$  peaks obtained with the special arrangement versus the certified content, for five NBS low-alloy steel standards.



**Figure 7.** Areas of the K- $\alpha$  peaks, in log scale, for a qualitative comparison of the content of Ca, Mn, Ni, Cu and Zn in the Ipanema pieces. a) polished region of the pin; b) external surface of the pin; c) disc; d) bar.



**Figure 8.** Microstructure of the main body of the door bolt, by optical microscopy.



**Figure 9.** Spectra of the door bolt. a) Polished surface. b) Unpolished surface.