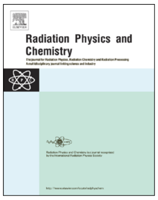
Radiation Physics and Chemistry 95 (2014) 368–372

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem



Evaluating the presence of titanium in XIX-century Brazilian steels by energy-dispersive X-ray fluorescence

Augusto Camara Neiva [a,]*, Herbert Prince Favero Pinto [a], Fernando José Gomes Landgraf [b]

[a] *Escola Politécnica da Universidade de São Paulo, Departamento de Engenharia Química, Avenida Professor Luciano Gualberto, Travessa 3, 380 São Paulo, SP, Brazil*
[b] *Escola Politécnica da Universidade de São Paulo, Departamento de Engenharia Metalúrgica e de Materiais, Avenida Professor Luciano Gualberto, Travessa 3, 380 São Paulo, SP, Brazil*

HIGHLIGHTS

- Ores and products from the XIX Century Ipanema Ironworks were analyzed by EDXRF.
- Ti and P detection improved by the use of Cr-tube instead of W-tube.
- Detection improved by using detector with multilayer, instead of Zr, collimator.
- High Ti and P contents were found in ores and products from Ipanema.
- Ipanema ores were found to be very heterogeneous.

ARTICLE INFO

Article history:
Received 31 October 2012
Accepted 3 March 2013
Available online 15 March 2013

Keywords:
EDXRF
Ipanema ironworks
Industrial archeology

ABSTRACT

Ores, pig iron and steel pieces from the XIX Century ironworks Royal St. John of Ipanema Iron Foundry (*Real Fábrica de Ferro São João do Ipanema*), in Iperó, Brazil, were analyzed by Energy-Dispersive X-Ray Fluorescence (EDXRF) spectroscopy, with the aim of investigating the presence of deleterious elements as Ti and P in the minerals and in the resulting products. Analytical modifications made in order to improve the detection limits for Ti and P are discussed. Both elements were found in the raw material and in the products, but large differences in chemical composition were found in different samples or regions of samples.

1. Introduction

Although a small direct reduction ironworks was already installed near São Paulo in the XVI Century, the first larger-scale ironworks in Brazil were created only in the end of the XVIII Century and beginning of the XIX Century. One of the most important of them was the Royal St. John of Ipanema Iron Foundry (*Real Fábrica de Ferro São João do Ipanema*), installed in the region of the Araçoiaba Hill—an iron-ore, limestone and phosphate deposit, in Iperó, São Paulo state. However, although designed according to the best European models at the time, it has never achieved comparable levels of quality and efficiency. This fact is usually attributed to a high content of deleterious elements in the raw material, especially phosphor and titanium. Calógeras (1904, 1905), for instance, reported the presence of titanium in Ipanema ores, according to analyses made by the laboratories of the Ouro Preto School of Mines (EMOP, Minas Gerais, Brazil), and mentioned the comments of Professor F. Gautier in 1891, who observed cracks in Ipanema cemented bars—bars which had been submitted to surface carburization — and considered them as typically originated by phosphor. The presence of phosphor in Ipanema iron-ores, however, remained a controversial question. Dupré (1885) reported that, according to analyses at EMOP reported by Claude Henri Gorceix, only traces of phosphor were found in the ores, while the soil which surrounded these mineral blocks contained "remarkable amounts of phosphoric acid". Dupré commented: "where should this phosphoric acid come from, if only traces of phosphor have been found in the mineral, and not even traces were found in the diorite analyzed in the Polytechnic School of Dresden" (translated from Portuguese).

This paper presents the analysis of Ipanema ores and products by portable Energy-Dispersive X-Ray Fluorescence (EDXRF) spectroscopy. As the detection and peak-area determination of some low-content elements, as P and Ti, are very much affected by the experimental setup, the comparison of three different incident beam setups and two different detectors is also presented.

2. Experimental

Two spectrometers were used in this work. Spectrometer I uses a water-cooled ItalStructures W-tube (60 kV/1.5 mA maximum)

---

* Corresponding author. Tel.: +55 11 30912228; fax: +55 11 30912238.
E-mail addresses: acneiva@usp.br, acneiva@gmail.com (A.C. Neiva), herbertpfp@hotmail.com (H.P.F. Pinto), f.landgraf@usp.br (F.J.G. Landgraf).

0969-806X/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.radphyschem.2013.03.015

and a Ketek Si-drift X-ray detector with a Zr collimator, and was used for the first measurements. To improve the determination of Ti and P, a second spectrometer was assembled with two Oxford XTF5011 X rays tubes (50 kV/1 mA maximum), one of them with a W-anode, as in spectrometer I, and the other with a Cr-anode, whose energy profile is more adequate to excite light elements. To avoid the Zr–L peaks generated by the old detector of spectrometer I, which overlap with P–K peaks, an Amptek Si-drift detector, with multilayer collimator, was used in spectrometer II.

With spectrometer I, most measurements were done with 55 keV and 1.1 mA, for 1000 s live time. With spectrometer II, most of them were done with 50 keV,.2 mA and 500 s live time. With this spectrometer, each sample was usually analyzed both with the Cr- and the W-tubes, for two reasons. First, it was important to cover both low and high energies adequately. Second, it was necessary to verify if the Cr peaks observed with the Cr-tube and the W-peaks observed with the W-tube were due only to scattering of the incident beam, or were also due to the presence of these elements in the samples. For some measurements with spectrometer I, a Cr-coated steel plate was used as a target for secondary-Cr excitation. In this case, no collimator was used in the X-ray tube. Even so, rather large areas of the samples had to be analyzed in each measurement in order to get a reasonable flux of photons in the detector.

Three Ipanema iron-ore samples, identified as M1, M3 and M98, and one pig iron sample, identified as G1, were measured without any surface preparation. Three Ipanema steel pieces, identified as P25, P99 and P100, were analyzed on flat, polished surfaces. Previously, calibration measurements were made with five NBS low-alloy steel samples, in order to check for the sensibility of the method to light elements. The areas of the peaks were determined by the PyMCA software (Solé et al., 2007). As most samples were heterogeneous and did not present a flat surface for analysis, sample compositions obtained in these calculations were disregarded, and only peak areas were considered for quantitative comparisons.

3. Results and discussion

3.1. Analytical questions

3.1.1. Overlapping of Ti–K and P–K peaks with escape peaks

Overlapping of peaks may impair the area determination of them, especially of the weaker one. If the stronger peak is an escape-peak, its area determination is not important, and it would be interesting to reduce its intensity, while maintaining or increasing the intensity of the other one. As the characteristic energy corresponding to the escape peak is around 1.7 keV above the energy of the overlapping peak of interest, improving the detection efficiency at lower energies will improve the desired peak/escape peak intensity ratio. This can be done, for instance, by using helium or a smaller working distance. On the other hand, changing the incident beam profile should also affect significantly that ratio if the critical absorption energies of the two elements are far apart, which is necessarily the case when one is dealing only with K peaks. Fig. 1 shows examples which illustrate both kinds of improvement. In Fig. 1a, three exciting sources are compared regarding the overlapping of Ti-KL3 with escape-Fe-KL3 peaks for the same sample (NBS-1264A standard steel, with 0.24%Ti). Two spectra were obtained with a W-tube (spectrometer I): the first one was obtained with the direct beam, and the second one with a secondary Cr-target. The third spectrum was obtained with the Cr-tube of spectrometer II. The areas of the peaks are shown in Table 1. As expected, K–Fe peaks are very strong and Ti peaks are weak with the W-tube, so that a small KL3-Ti/escape-KL3-Fe area ratio is observed. With secondary Cr radiation, the ratio increased around three times. With Cr-tube, it increased around 25 times. One observes, too, that, even with the improvement of the intensity ratio, the sigma value of the Ti-KL3 fitting by PyMCA becomes worse (from 4.3 to 6.3%) when secondary-Cr is used, because a very small photon flux was obtained with this setup, but becomes much better (0.5%) with the Cr-tube, due to the high intensities obtained and to the absence of overlapping.

Fig. 1b, on the other hand, shows the overlapping of P-KL3 (2.014 keV) and the escape peak of Ca-KL3 (1.95 keV) for an Ipanema pig iron. Decreasing the detector-sample distance improves the determination of P peaks, because their intensities are much more affected by atmosphere-attenuation than the intensity of the characteristic Ca-KL3 peak (3.692 keV), and therefore of its corresponding escape-peak. Table 2 shows these results. For approximately the same photon flux (as indicated by the total counts), one can observe that the area of P–K increased 80% when the detector was placed closer to the sample, while the Ca peaks increased only 2%.

Table 2 also shows P and Ca mass fractions, obtained from the Fundamental Parameters option of PyMCA. The close accordance of these values for the same sample with different working distances (and peak areas) was used as a quality criterion for

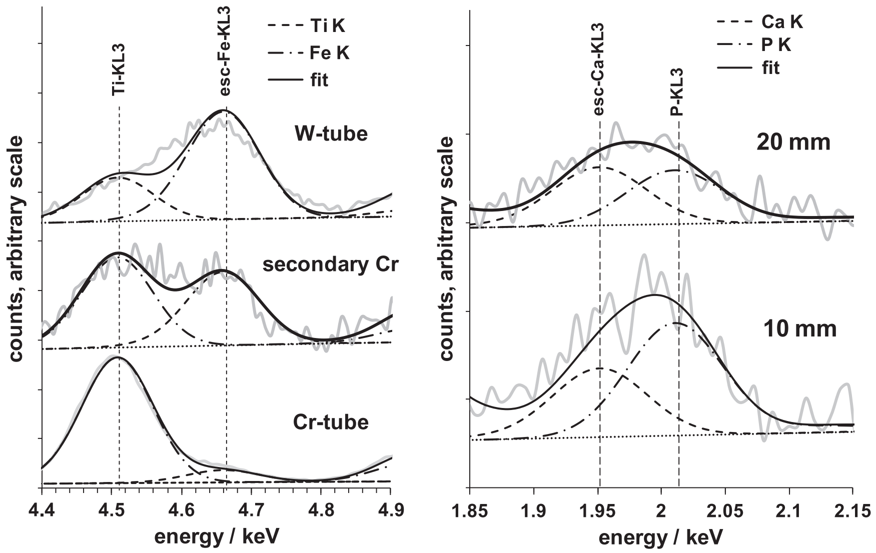


Fig. 1. Overlapping of peaks in different conditions: (a) three different exciting sources; (b) two different sample-detector distances (see Table 1 for details).