Quantitative Electron Probe Microanalysis of Fe at Low Accelerating Voltage Using the Lα and Lβ X-ray Lines

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For more than six decades, electron probe microanalysis has been employed to determine the composition of unknown samples at ~micron-size domains. The introduction of the field emission gun (FEG) has allowed the reduction of the electron beam size. Electron imaging by microprobe can now reach a sub-micron resolution allowing the clearer imaging of sub-micron features such as inclusions in larger phases. To improve the X-ray lateral spatial analytical resolution, however, the interaction volume of the electrons inside the sample also needs to be reduced. This can only be done by decreasing the accelerating voltage from typically 15 kV to 5–7 kV, reducing the typical size of the electron interaction volume from ~1–2 µm to ~0.2–0.7 µm (depending upon material composition). However, by reducing the accelerating voltage, the commonly utilized X-ray lines (the Kα lines) of many of the elements of the periodic table up to Z=34, cannot be excited and thus cannot be used for analysis. Instead of using the K lines, the L lines of these elements must be used. However, for some elements, these L X-ray lines are not well known and complex chemical and physical effects can occur, making their use difficult in quantitative analysis. This is especially the case for the transition metals with the main L lines (and for many of the rare-earth elements with the main M lines). Several effects can influence the emission of X-rays produced by an electronic transition involving outer electronic shells. In the case of the transition metals, the Lα and Lβ X-ray lines involve a partially filled $3d$ electron shell which is subject to strong bonding and hybridization with electrons from the neighboring atoms. This results in a change of the state of the outer electronic orbitals and then changes the energy of the electrons and the electronic transition probabilities associated with these shells. Consequently, the value of the different atomic parameters (mass absorption coefficient, fluorescence yield, Coster-Kronig factor, …) not only depend of the studied element but also of the composition and nature of the specific material, both of the unknown and of the standard used to generate the k-ratio.

Our work was focused on the transition metal iron as it is a commonly encountered element in many materials of interest. Gopon et al [1] showed that the Fe Ll line had some utility, but its weak intensity was a drawback. Here we investigate the possible utility of Fe Lα and Lβ. The atomic parameters associated with the emission and absorption of the Fe Lα and Lβ X-ray lines were reevaluated on 15 iron-bearing standards of well-known composition (silicates and oxides). Trends are deduced from these measurements in order to predict the value of the atomic parameters in relation to the composition of the material and thus allowing their use for correct quantitative analysis. The mass absorption coefficients (MAC) of the Fe Lα and Lβ X-ray lines were first evaluated. For each standard, the L X-ray spectra of these lines were recorded with three wavelength-dispersive spectrometers on a CAMECA SXFive FE probe (on LTAP, TAP and PC0 crystals.) The spectra were recorded at 2.5, 3, 5, 7, 10, 15, 20, 25 and 30 kV with a 10 µm diameter beam at 90 nA Faraday cup current. For each accelerating voltage, at least 4 sixteen-minute-long spectra were acquired and averaged in order to reduce the statistical counting fluctuations. The intensities of the lines were obtained by non-linear fitting of the recorded spectra using a set of pseudo-Voigt functions. Due to the strong absorption of these lines in the high-energy side by the L_2 and L_3 absorption edges, the peak shapes are not symmetrical and a sum of pseudo-Voigt function is needed to ensure a good fitting. The MACs were obtained by non-linear fitting of the previously

obtained L line intensities in relation to the accelerating voltage using the PAP model [1] with the MAC of the Fe L lines in the specific sample as set a free fitting parameter. The obtained values of the MAC vary greatly in relation to the sample. For example, the determined MAC for the Fe Lα line in pure Fe is 3359 cm².g^{-1}, which is similar to the values obtained by Pouchou and Pichoir (3350 cm².g^{-1}) [2], Pinard (3598.5 cm².g^{-1}) [3] and Gopon et al (3639 cm².g^{-1}) [1], while the obtained value with a fayalite standard is 10120 cm².g^{-1}. The variations of the MAC in relation to the photon energy can be evaluated with the self-absorption spectrum which is constructed by comparing the spectrum acquired at 2.5 kV with the spectrum acquired at 30 kV. As seen in Figure 1, the self-absorption spectra measured on pure Fe and on fayalite differ greatly. Notice that the self-absorption spectra were obtained by removing the continuum from the experimental spectra. The self-absorption spectrum measured on the fayalite standard, consistent with the measurements of Höfer et al [4], exhibits a strong absorption close to the L_3 edge, indicating a strong correlation between the $2p$ electrons and the empty $3d$ states. This result is also consistent with the high MAC obtained. As pointed out in a recent publication by Llovet et al [5], the value of the fluorescence yield is also largely modified by the composition of the sample for the transition metals. This has a consequence that the PAP theoretically calculated and measured k-ratios formed with the intensity of the unknown, for example the fayalite sample, and of the pure Fe standard, differ by a scaling factor (Figure 2). By enhancing the fluorescence yield for the fayalite by a factor of ~1.2, the k-ratios are in good agreement, except at very low accelerating voltage (2.5 and 3 kV).

These procedures will be repeated on the 13 others Fe-bearing standards and will permit the determination of the MACs and fluorescence yields as a function of the composition and state of the element Fe in the sample. These results will then be used to develop calibration curves which will permit to quantify the amount of Fe in unknown samples at low accelerating voltage using the Fe Lα X-ray line.

References:
[1] P Gopon *et al*, Microsc. Microanal. **19** (2013), p. 1698.
[2] J L Pouchou and F Pichoir, "Quantitative analysis of homogeneous or stratified microvolumes applying the model PAP", ed. K F J Heinrich and D E Newbury, (Plenum Press) p. 31.
[3] P Pinard, "Electron probe microanalysis of carbon containing steels at a high spatial resolution", Doctoral thesis, RWTH Aachen University, Aachen, Germany, 2016.
[4] H E Höfer *et al*, Eur. J. Mineral. **6** (1994), p. 407.
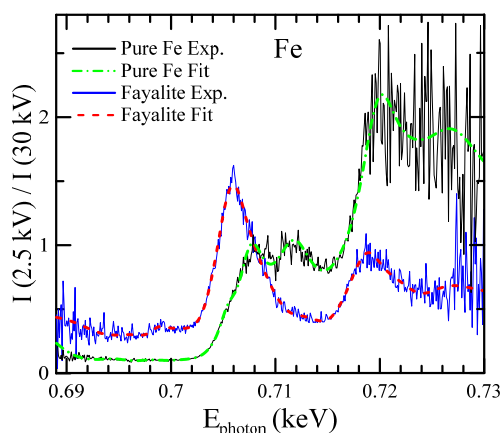[5] X Llovet *et al*, Microsc. Microanal. **22** (2016), p. 1233.

Figure 1. Self-absorption spectra of Fe Lα and Lβ X-ray lines measured on pure Fe and fayalite.
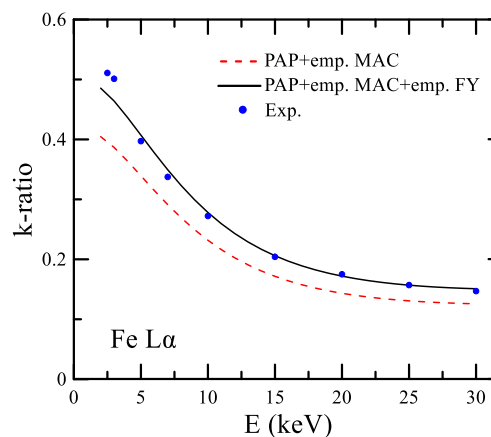

Figure 2. Experimental and calculated Fe Lα k-ratios for fayalite with empirical MACs and fluorescence yield.