

Quantitative electron microprobe analysis of homogeneous bulk samples

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Introduction

As we mentioned in the introductory paper, the measured input for quantitative analysis consists the intensities of the analytical X-ray lines (one line per element). Based on physical reasoning, we can give a formula that relates the X-ray intensity emitted by the selected analytical line as a function of both materials constants and experimental parameters. That formula is given by

$$I_i = Q_i^*(E) \cdot \left\{ N^0 \cdot \rho \cdot t \frac{c_i^w}{A_i} \right\} \cdot N \cdot \left\{ \int \varphi(\rho z) \cdot \exp(-\chi \cdot \rho z) \cdot d(\rho z) \right\} \cdot \omega \cdot a \cdot \left\{ \frac{\Omega}{4\pi} \varepsilon \right\} \quad (1)$$

where Q_i^* is the cross section per atom for ionization of the selected subshell of the i^{th} element, taking into account both direct ionization by the electrons of energy E and the effect of indirect ionizations at that subshell caused by the Coster-Kronig transitions. N^0 , ρ , t and N are Avogadro's number, the density and thickness of a very thin tracer layer made of the i^{th} element and the number of primary electrons, respectively. The mass fraction, atomic weight, fluorescence yield and weight of line for the i^{th} element is designated by c_i^w , A_i , ω and a , respectively, while Ω and ε are the solid angle and the detection efficiency of the detector. The integral in curly bracket in the center describes the depth distribution of ionization in the bulk sample with respect to the tracer layer and the self-absorption of the X-rays. We shall deal with these quantities in more details later.

If this formula is accurate enough, all the data like atomic constants and geometric parameters are known and the measurement is done on the absolute basis (giving the number of photons per primary electron) the composition of the sample can be given directly and no additional measurements are needed. The above idealised situation means a true standardless analysis. The traditional approach is different, however. The ingenious in Castaing's approach was that he realized that by comparing the measured intensity to another measurement on a known material (the so-called standard), we can get rid of many of the unknown constants and parameters. For a standard, he originally selected a (known) sample made of a single chemical element only. He showed (for a selected X-ray line of the i^{th} element in the unknown sample) that the ratio of the intensity, measured in the unknown (I_i^{unk}) to that, measured in the elementary standard (I_i^{std}) represents a good approximation of the mass fraction of the i^{th} element in the sample. The correction factor needed to obtain a better approximation of the mass fraction is of the order of unity and depends on all the n elements present in the sample (in contrast to depending only on the selected element for which the ratio is formed).

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$$c_i^w \cdot \text{Correction}_i^{\text{ZAF}}(E_0, \psi, c_1, \dots, c_n) = \frac{I_i^{\text{unk}}}{I_i^{\text{std}}} \quad (2)$$

The additional dependence on the primary beam energy (E_0) and on the geometry of the measurement (ψ) is also indicated in (2). Variants of quantitative analysis are nothing else than different approaches to the calculation of the mentioned correction factor. Present paper explains the relation between equations (1) and (2) and gives a short overview of the most frequently used approximations in the calculation of the correction factors. The possibility of and the limitations in calculating the standard intensities (in contrast to measuring them) is also outlined. Although, before we start, let's take a diversion.

There is a regularly returning confusion, why the generated X-ray intensity is proportional to the mass fraction of the elements present, in contrast to the atomic fraction. This fact is contradictory to our first physical anticipation, since the ionization cross section is defined for one atom, so it is the number of atoms that should be important (irrespective of their masses). It is a correct assumption and we recall it below, how the mass fraction results from the starting number of atoms.

Avogadro's number, $N^0 (=6.02 \cdot 10^{23})$ gives the number of molecules in that many grams of a chemical compound as the value of its molecular weight. If, for the sake of simplicity, we assume that the chemical formula of the molecule is $X_n Y_m$ than its molecular weight is $nA_X + mA_Y$ and there are $N^0 n$ atoms of the X element and $N^0 m$ atoms of the Y element in the $nA_X + mA_Y$ grams of that compound. The important feature of the molecule here is the constant proportion of its constituents (and not the type of bond between them).

Let's take the excited volume in a thin layer first, for which we want to calculate the generated intensity during our EPMA analysis. Extension to a bulk sample will be examined in a next step. The excited volume is assumed to be homogeneous, so it can be characterized by a constant composition (that is what we want to determine with EPMA). Let the atomic fractions be c_i ($i=1, n$ for the the n elements present in the layer). Then, the material can be thought of being similar to a chemical compound (irrespective of the chemical bounds) made up of fixed "compositional blocks" with "block weight" $\sum c_i A_i$. If we take $\sum c_i A_i$ grams of that material, it will contain N^0 "compositional blocks" [and (within that) $c_i N^0$ atoms of the i^{th} element]. There will be $N^0 / \sum c_i A_i$ "compositional blocks" in 1 grams of this material and $\rho N^0 / \sum c_i A_i$ "compositional blocks" in 1 cm^3 . If we take a layer of thickness t , the number of "compositional blocks" is $t \rho N^0 / \sum c_i A_i$ and within it, the number of the i^{th} atoms is

$$N^0 \cdot \rho \cdot t \frac{c_i}{\sum c_i \cdot A_i} \quad (3a)$$

per unit surface area. You can see that linear dependence on the number of atoms of an element in a given piece of material does not mean linear dependence on the atomic fraction of that element. Since the mass fraction can be calculated from the atomic fractions as $c_i^w = c_i A_i / \sum c_i A_i$, the number of the i^{th} atoms in unit surface area of this layer can be rewritten as $t \rho N^0 c_i^w / A_i$.

The effective area of one atom from the point of view of ionization (as seen by one bombarding electron) is given by the ionization cross section, $Q(E)$. By multiplying one atom's area (cross section) with the number of atoms (in a unit surface area) we obtain the effective area (per unit surface area) of all the atoms seen by the bombarding electron:

$$Q(E) \cdot \left\{ N^0 \cdot \rho \cdot t \frac{c_i^w}{A_i} \right\} \quad (3b)$$

The probability of ionization is given by the geometrical probability, i.e. by the ratio of that effective area to the total area considered, which is unity. That is why (3b) gives the ionization probability per incident electron for our thin layer. Although the concentration dependence described in (3a) is identical to that given in (3b), it is expressed simpler in (3b), which describes a linear dependence on its variable (c_i^w) than how it is expressed in (3a) where both the numerator and the denominator depends on the variable (c_i).

So, we can see that linear dependence of the number of ionizations on the areal density of the atoms (corresponding to a complicated dependence on the atomic fractions) translates into a simple linear dependence on the mass fraction for a thin layer and this dependence is also inherited to the bulk samples, as seen in eq. (1). Division by the standard intensity (implying $c^w=1$) does not change this dependence.

Matrix correction: derivation of composition from X-ray intensities

Simplicity of quantitative microprobe analysis derives from the fact that the emitted X-ray intensity is roughly proportional to the mass fraction of that element within the sample, as we reiterated above. A better approximations of the sample composition can be obtained from this so-called *k-ratio* by applying a *matrix-correction* for the differences in different physical processes between the unknown and the standard [1]. For the sake of convenience, usage of compound standards was also introduced (and that amounts to a double-correction), resulting in a generalization of (2).

$$k_i \equiv \frac{I_i^{unk}}{I_i^{std}} \quad \text{and} \quad k_i = \frac{c_i^{unk}}{c_i^{std}} \cdot \text{Correction}(c_1, K, c_N, K, E_0, \psi) \quad (4)$$

The matrix correction can be based either on empirical data (for simple systems) [2] or on calculated correction factors. The correction factor depends on all of the concentrations of the components, on the selected analytical lines (and ensuing atomic data like mass absorption coefficients) and on the experimental parameters like primary beam energy (E_0) and geometry (ψ , the angle between the sample surface and the detector, the so-called *take-off-angle*). Due to this inter-dependence, equation (4) can only be solved by iteration, an ideal task for computers. The physical processes to be taken into account are the of electron-specimen interactions and the X-ray photon-specimen interactions. Namely, electrons are scattered and decelerated, they ionize the atoms, the atoms emit characteristic X-ray photons and these photons are partially absorbed in the sample. Second order effect of fluorescence (i.e. emission of X-ray photons in response to the ionization caused by the absorption of other X-ray photons) is also part of this correction, but its magnitude is smaller. The photon-detector interactions are identical for photons originating either from the unknown sample or from the standard, so detection efficiency need not be taken into account if standards are used. Modern correction procedures can calculate the concentrations of any element between B and U, handle many elements simultaneously, use K, L or M lines and primary beam energies between 2 and 50 keV. If the experiment is carried out carefully and the standard is good enough, 1-2 % relative accuracy can be achieved for major components with medium or high atomic number on a routine basis. For light elements it is more difficult to obtain reliable experimental data but the modern correction methods can still achieve about 5 % relative accuracy. In summary, microprobe analysis is a quantitative, multi-elemental method.