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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

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

where Q^*_i is the cross section per atom for ionization of the selected subshell of the ith 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 ith element and the number of primary electrons, respectively. The mass fraction, atomic weight, fluorescence yield and weight of line for the ith element is designated by c^w_i, 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 ith 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 ith element in the sample. The correction factor needed to obtain a better approxiation 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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$$c_i^w \cdot \mathrm{Correction}_i^{ZAF}(E_0, \psi, c_1, .., c_n) = \frac{I_i^{unk}}{I_i^{std}} \qquad (2)$$

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*10^{23}) gives the number of molecules in that many gramms 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_nY_m than its molecular weight is nA_X+mA_Y and there are N^0n atoms of the X element and N^0m atoms of the Y element in the nA_X+mA_Y gramms of that compound. The importan 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 analyisis. 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). Than, 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" Σc_iA_i. If we take Σc_iA_i gramms of that material, it will contain N^0 "compositional blocks " [and (within that) c_iN^0 atoms of the i^th^ element]. There will be $N^0/\Sigma c_iA_i$ "compositional blocks" in 1 gramms of this material and $\rho N^0/\Sigma c_iA_i$ "compositional blocks" in 1 cm^3. If we take a layer of thickness *t*, the number of "compositional blocks" is $t\rho N^0/\Sigma c_iA_i$ and within it, the number of the ith atoms is

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

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 $c^w_i=c_iA_i/\Sigma\, c_iA_i$, the number of the ith atoms in unit surface area of this layer can be rewritten as $t\rho N^0c^w_{i/}A_i$.

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:

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

The probability of ionization is given by the geomertical 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).

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

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.

Approximations used in matrix correction procedures

Monte Carlo calculations vs. analytical approximations

X-ray generation and absorption can be calculated in two distinct ways. *As the first approach*, every elementary particle (electron or photon) can be followed in a classical manner (disregarding that many of them are indistinguishable). In that approach the sequence of interactions to be calculated is selected on a probability basis. Due to the inherent randomness (chance), this group of approaches is termed as Monte Carlo (MC) methods. Due to the large number of possible parameter-values that influence the result, the MC methods are generally used to calculate k-ratios from concentrations and known experimental condition, i.e. to generate calibration curves or reference data. Some people tend to look at Monte Carlo calculations as a reliable reference. However, one must keep in mind that the key-word Monte Carlo embraces very different physical approximations (for scattering, ionization, absorption, etc.) and the correctness of the result depends on these details [3], [4]. So, by saying simply that the results of some other calculations are compared to the results of Monte Carlo calculations one states no more than one calculation is compared to the other and reliability is not inferred (unless the particular MC method was validated separately in a previous step). With this statement we do not intend to question the reliability of the MC methods We only want to draw the attention to the fact that further specification is needed if we want to know something about the reliability of the particular method (within the group of MC methods). *As the second approach*, the same physical processes can be approximated by continuous mathematical functions treating the material as a continuum. The rest of the talk concentrates on these analytical approximations.

ZAF correction vs. $\varphi(\rho z)$ methods

The correction procedures presently in use belong to the analytical approximation category. The difference between the individual approaches (methods) lies in the way the complex process is artificially subdivided into smaller sub-processes (that are approximated independently) and which mathematical functions are used to approximate these smaller "independent" sub-processes. Such sub-processes can be the generation and the absorption of x-rays. Obviously, they are not truly independent, since absorption depends on where in the sample the photon is generated. The artificial separation is done to simplify the calculations. Following Castaing's original suggestion [1], the first methods calculated 3 factors separately: the generation factor (F_Z), the absorption factor (F_A) and the secondary fluorescence factor (F_F).

$$Correction(c_1,\ldots c_N,\ldots ,E_0,\psi) = F_Z \cdot F_A \cdot F_F \qquad (5)$$

The subscript of the first factor indicates that X-ray generation is different for elements with different atomic number (Z). Hinting to the subscripts of the 3 factors, the methods using this approximation are termed as ZAF-methods.

The generation factor

The generation factor is traditionally further divided into *stopping-power* and *back-scatter* factors.

$$F_Z = \frac{\left[R \cdot \int\limits_{E_{nl}}^{E_0} \frac{Q_{nl}(E)}{\overline{S}} dE \right]_{unk}}{\left[R \cdot \int\limits_{E_{nl}}^{E_0} \frac{Q(E_{nl})}{\overline{S}} dE \right]_{std}} \tag{6}$$

where Q_{nl} is the ionization cross section and E_{nl} is the excitation energy of the atomic sub-shell with quantum numbers n and l and

$$R = 1 - \frac{\int\limits_{E_{nl}}^{E_0} \frac{d\eta}{dE_B} \cdot \left\{ \int\limits_{E_{nl}}^{E_0} \frac{Q_{nl}(E)}{\overline{S}} dE \right\} dE_B}{\int\limits_{E_{nl}}^{E_0} \frac{Q_{nl}(E)}{\overline{S}} dE} \tag{7}$$

where η is the fraction of electron leaving the sample due to back-scattering. The stopping power factor calculates the number of ionizations on the assumption that every electron deposits its entire energy within the sample and the back-scatter factor (R) corrects this assumption with the fact that a fraction of electrons leaves the sample and the energy they carry does not contribute to the ionization. Separation into these factors is again arbitrary.

The experimental data of Bishop [5] was used by Duncumb and Reed [6] for the calculation of R. The amount of experimental data is still restricted since then [7], [8], [9], [10]. Although loss of energy happens is discrete scattering events, it is approximated as a continuous function S. Bethe's continuous slowing down approximations was used for decades for this purpose [11] using the empirical mean ionization potential of Berger and Seltzer [12]. Bethe's approximation predict non-physical values (acceleration instead of deceleration) for low electron energies. Better formulas were introduced by Love et al. [13], Pouchou and Pichoir [14], Bastin and Heijligers [15] and Merlet [16] to overcome this problem. All of them represent a continuous slowing down approach. Czyzewski proposed an analytical expression for the energy distribution of back-scattered electrons [17] and for the R-factor [18]. Several polynomials were suggested to calculate the R-factor [19], [20]. Some of the analytical functions used were discontinuous as remarked by Lábár [21]. Most of the expression were only developed for perpendicular electron incidence. Newer expressions extended the formulas to the analysis of tilted samples that is important when using an EDS in an SEM [22], [23].

The absorption factor

The absorption factor can be derived from the distribution of ionization with depth, the so-called $\varphi(\rho z)$ function.

$$F_A = \frac{f(\chi_{unk})}{f(\chi_{std})}$$ where

$$f(\chi)=\frac{\int_0^\infty \varphi(\rho z)\cdot \exp\left\{-\left(\frac{\overline{\mu}}{\rho}\right)_{unk}\cdot\frac{\rho z}{\sin(\psi)}\right\}d(\rho z)}{\int_0^\infty \varphi(\rho z)d(\rho z)} \tag{8}$$

and $$\chi=\left(\frac{\overline{\mu}}{\rho}\right)\cdot\frac{1}{\sin(\psi)} \tag{8a}$$

You can notice that if the integral of the φ(ρz) function gave the total number of generated X-rays, the generation and absorption factors could be handled in one step and the arbitrary separation were not be necessary. That exactly what the group of matrix correction procedures (called φ(ρz) methods) aim at. Many authors claim that the essential difference between ZAF and φ(ρz) methods is whether X-ray generation and absorption processes are calculated separately on the one hand, or simultaneously on the other hand. However this classification is not entirely correct, since the most successful φ(ρz) methods were developed after recognizing that the integral under the φ(ρz) must be calculated separately in order to achieve the desired accuracy [37], [24]. So, the essence of difference is in the following, instead. Every *f(χ)* corresponds to a φ(ρz) and vica versa; and the φ(ρz) curves are calculated to obtain a good absorption correction. However, it makes a significant difference if we follow one of two alternative ways. On the one hand, we try to optimize the φ(ρz) curve and *f(χ)* is given automatically by the computation and we shall see if the result is as good as we anticipated. This approach is called the φ(ρz) method. On the other hand, we can disregard how well our φ(ρz) functions correspond to the experimental depth distributions, but instead we try to optimize its transformed, the *f(χ)* function to get the best absorption correction. This approach is the A-part of the ZAF method. In its extremes it is even difficult to realize what functional form of φ(ρz) would be needed to obtain the used *f(χ)*, as in Heinrich's correction [25].

Parametrization of the shape of the φ(ρz) and its integral

It is only practical to apply the φ(ρz) in an analytical procedure, if it is given in a parametric form as a function of both sample parameters and experimental conditions. The most justified form, from a physical point of view, for the φ(ρz) is a modified, surface centered Gaussian function (MSG) which has been introduced by Packwood and Brown [26]. The random walk of electrons justifies the Gaussian shape after a transient region where the original persistent walk prevails. The approach runs into difficulty when the randomization is not completed in a reasonable distance as it is the situation for Z≤13, especially for higher E_0 [27]. It might be one reason why a further optimization of the method became necessary [32], [28]. In spite of the early efforts, it became obvious that it is necessary to calculate the integral of the φ(ρz) separately and use this integral in the subsequent description of the shape of the curve [37], [24]. Without this separation the atomic number correction did not work accurately. Although physically not supported, other mathematical functions can at least as well approximate the shape of the φ(ρz) distribution. Both double parabolic (PAP) and exponential approximations (XPP) perform excellently [37]. The latter one has a further advantage that easily can be adopted for tilted samples, as well. The double Gaussian approach seems to be a variant of the Gaussian shapes, different form the others in that how the transient region in the MSG approach can be handled [29], [16]. A common feature of the approximations that they use 4 shape-parameters. They may be different, but the physically controlled quantities like the surface ionization (φ_0), X-ray range and the position and height of the maximum must be determined accurately. All three approximations (MSG, PAP and XPP) can also be considered for the analysis of inhomogeneous structures.

As for the analytical functions used to represent the shape of depth distributions, different forms of exponential (including Gaussian functions) are the most popular, since integration is easy and can be done in closed form [30], [31] [26], [32], [33], [34], [29]. Parabolic expression of Pouchou (although good for perpendicular electron incidence) proved difficult for inclined geometry, so he also selected an exponential form in his last version [35], [22].

Fluorescence

The secondary fluorescence term should really be additive, since if the intensity I_i of line l of element i is concerned, the enhancement to this intensity is proportional to the number of X-ray photons (both characteristic and Bremmstrahlung) with higher energy than the energy of line l of element i; and this number is not proportional to the concentration of element i. However, proportionality exists between the intensities I_i and I_j of elements i and j, so the effect can be approximated as a multiplicative factor. Except for the program CORR2 [36], continuum fluorescence was disregarded in most of the correction procedures for decades until Pouchou reintroduced it with an improved formula [37]. For characteristic fluorescence, Reed's formula retained its popularity for decades [38].

In between: the multiple reflection method

This method virtually cuts the sample into thin layers parallel to the surface and calculates transmission through and reflection from these layers individually. Ionization events in the layers are then summed up. The discrete treatment of layers reminds the MC methods, while analytical calculation of the averaged quantities for the layers resemble the analytical approximations. The number of steps is lower than in the MC methods by orders of magnitude, so the method is fast as compared to MC. The original idea of Cosslett and Thomas [39] was refined by August and Wernisch [40] and was applied successfully to several problems [41], [42], [43].

The role of standards and standardless methods

Measurement on standards was introduced to improve accuracy by neutralizing the effect of parameters not known with the desired accuracy. Such parameters include atomic data as fluorescence yield and Coster-Kronig transition rates and experimental parameters as detection efficiency as a function of photon energy. The atomic data are important for complex electronic shells as the L and M shells. The experimental parameters are problematic for WD spectrometers [and/or for soft radiation (e.g. light elements) even if an EDS is used]. Although special methods were developed to overcome the need for standards (these are the so-called standardless methods), the situation did not change that accuracy can be increased by making measurements on standards and this is the way to do the analysis if utmost accuracy is preferred (to reduced time and costs).

The effect of replacing a measurement on a standard by calculation can be understood from the inspection of equation (9), which gives the number of detected X-ray photons (with a pre-selected energy that corresponds to a main characteristic line of the element to be analyzed).

$$I_{i,l_a} = Q^*_{i,a} \cdot \omega_a \cdot F_{l_a,a} \cdot f\left(\overline{\chi}_{i,l_a}\right) \cdot \varepsilon\left(E_{i,l_a}\right) \qquad \text{and} \qquad (9a)$$

$$Q^{*}_{i,a} = \sum_{j \in n} N_j \cdot \left(R_j \cdot \int_{E_j}^{E_0} \frac{Q_j(E)}{\overline{S}} dE \right) \cdot f_{a,j} \qquad (9b)$$

where I_{i,l_a}, the intensity of line l_a (belonging to sub-shell a of shell n) in (9a) depends on $Q^*_{i,a}$, the number of total ionizations and ω_a fluorescence yield in sub-shell a, $F_{l_a,a}$, the fraction of the analytical line within the lines originating from the same sub-shell a, $f(\chi)$, the absorption factor (giving the fraction not absorbed) and ε, the detection efficiency for the energy of the given line. As you can see from (9b), there are two processes contributing to the total number of ionizations: direct ionizations of the given sub-shell by electrons ($f_{a,a}$=1) and indirect ionizations caused by redistribution of empty states within the atomic shell (through non-radiative, two-electron process, the so-called Koster-Kronig transition, with rates $f_{a,i}$).

The problems to be solved by standardless analysis are twofold. On the one hand, the atomic data as the Koster-Kronig rates $f_{a,j}$ and fluorescence yield ω_a are only known with limited accuracy (5-30%). Similarly, detection efficiency is difficult to measure and might change due to contamination built up on the detector window. Neither of these quantities influence the result if standards are used but the errors of all of them directly propagates into the error of the analysis in a standardless procedure. For example a 10% error in the knowledge of the value of the detection efficiency induces 10% error in the concentration result, unless two different sources of error luckily compensate each other’s effect. On the other hand, the factors that are identical to the generation and absorption factors in the correction procedure cause more problems if the standards are not measured. In a matrix correction procedure one always encounters a ratio of such quantities (one for the unknown and one for the standard). Consequently the errors in these factors partially compensate each other’s effect when the ratios are formed. This type of compensation of errors is missing if only a calculated value is used to replace a measurement on the standard [44], [45]. Similarly, variation of the emitted intensity with primary beam energy (and as a consequence of absorption path length) is a sensitive measure of the absorption correction and the mass absorption coefficient used in it. Pouchou used this fact to determine mass absorption coefficient optimal for use in correction procedures in microprobe analysis [46].

Altogether, a root mean square of error (RMS) of 2-3% can be anticipated for major elements with medium atomic munber on the basis of many analyses if standards are used [47] and 10% if a standardless procedure is followed [44], [45]. Obviously, individual errors might be higher than the average in a particular analysis. For complex shells (L or M) the effect of Coster-Kronig transitions plays a major role and must be taken into account either directly by including the effect into the standardless calculation or indirectly, when the k-ratios are determined by comparing the spectrum of unknown to stored standard spectra and it is only a correction for the differences between the measurement of the unknown and of the stored profile that is to be taken into account. (The stored profiles are usually measured by the manufacturer and supplied to the user who need not be aware of the details what is given within the commercial software. So, not every program is a true standardless procedure that claims that classification to itself.) The light elements represent larger problems and the accuracy is 3-5% [24]. Standardless procedures are not properly tested in the light element region.

How to get optimal results?

The most important factor affecting your result is the quality of the measurement (including the quality of standards). Details of this factor are elaborated in accompanying lectures.

If any doubt arises, check your results by performing the measurements by different primary beam energies and/or using different analytical lines (K, L and M), applying different standards for the same elements. If they coincide, you can definitely trust your results. This kind of cross-checking is especially important if you use the procedure for the first time for the given type of samples. If standards are not used, you should be even more distrustful. In that case the experimental part is emphasized again, because many people erroneously use standardless procedures to get concentrations from doubtful experimental data obtained in an SEM from samples with undefined geometry. The requirements for the sample and for the measurement are the same regardless of the fact if standards are also measured or not. On the other hand always avoid extreme experimental conditions (overvoltage <1.5 or extremely high absorption). Most of the alternative matrix correction procedures give good results nowadays if the input is reliable. So, matrix correction procedures reached their maturation and can be regarded as established variants of the method.

Acknowledgement

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Further reading

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