**Calculation of the characteristic fluorescence for a bulk specimen**

Let consider a characteristic X-ray of energy E2 produced by an element A and being fluoresced by the characteristic X-rays of energy E1 emitted by an element B (see Figure 1). We can distinguish two cases: characteristic X-rays emitted by element B in the downward direction and in the upward direction.



Figure 1: Characteristic fluorescence in a bulk sample. Characteristic X-rays are emitted by elements B, at mass depth , in the upward direction and fluoresce element A at mass depth ρz.

The fluorescence of characteristic X-rays from element A produced by characteristic X-rays coming from element B and emitted in the upward direction is given by:

where is the ionization depth distribution of electron shell m of element B present at mass depth . The probability of producing an electron vacancy in the shell m by electron impact ionization is given by where is Avogadro’s number, is the atomic weight of element B, is the concentration (weight fraction) of element B. is the ionization cross section of the shell m of element B by electron impact of energy . The term is the enhancement factor which takes into account the fact that vacancies in the considered shell m of element B can be created, not only by direct electron impact, but also by migration of vacancies between subshells of the same shell through non-radiative transitions (Coster-Kronig and super-Coster-Kronig transitions) as well as by radiative and non-radiative transitions to most inner shells. Note that the term , the mass thickness of the material, was incorporated in the term . A given characteristic X-ray of energy is emitted during the relaxation of the ionized atom B by transition of an electron from the shell or subshell n to the shell or subshell m. These are represented by the fluorescence yield and radiation yield . The characteristic X-rays of energy , emitted with a direction , undergo absorption along their path . The probability for a photon to travel a distance s without being absorbed is given by . The absorption of the photons is represented by the MAC . The product of the ionization depth distribution by the absorption exponential is integrated over the entire mass depth of the sample, from to . The photons of energy travel a distance s before interacting with element A in the infinitely small distance . The probability for the X-ray to be absorbed by atoms of element A and to ionize the electron shell i trough photoelectric interaction, represented by the photoelectric cross section and radiative, non-radiative, Coster Kronig and super-Coster Kronig contributions represented by the term , is given by . The term can be expressed by . The term can be incorporated in the term to convert the integration on the distance into integration on the mass depth. The emission of the studied characteristic X-ray of energy produced by element A during the relaxation process from which an electron from the shell j falls into the shell i is taken into account by the fluorescence yield and radiation yield . The attenuation of these X-rays emitted towards the detector with an angle is taken into account by the exponential term with MACs . The probability of detection of the emitted X-rays by the spectrometer is represented by the terms , were is the intrinsic detection efficiency and is the solid angle subtended by the detector. The emission of X-rays of energy is integrated, using spherical coordinates, over steradians (all the upward directions) using the infinitesimal element of solid angle . The variable is integrated from to to only consider the upward direction and the variable is integrated from 0 to . Because all the terms in the equation are independent of the variable and because of the symmetry of the distribution around the axis, the integral over the angle is equal to .

Starting from the previous equation

Constant quantities can be regrouped:

with

Terms depending on z can be grouped together:

The first integration is performed on :

This leads to the following equation:

Then, by separating the two terms of the subtraction:

Then, by regrouping the exponential terms:

The equation can be written

and then

where:

Equations of the form can be solved using the following method:

By using the following change of variable:

Then, for the first integral, by doing the change of variable , we obtain:

The with the following change of variable :

And finally, with the simple change of variable the equation takes the form:

We can recognize in the integrals the exponential form defining the exponential integral:

Hence, the equation becomes:

By replacing it in , we obtain:

Equations of the form can be solved by the following method:

With the change of variable , we obtain:

It is worth noting that and are strictly positive values. Hence the function 1/x is continuous and integrable from to .

So

By replacing it in , we obtain:

The last integrals are performed on . By noting that only depends on and by rewriting , the fluorescence equation can then be written:

Using the PAP model, the distribution can be written into a polynomial form . The second integral over can be performed from 0 to Rx, where Rx is the maximum depth ionization, instead of from 0 to , because the value is negligible or null for mass depth greater than Rx.

We can show that:

We can also show, by integrating by parts, that:

These 9 equations can be used to entirely solve . Similar solutions can be found in the case where the characteristic X-rays of element B are emitted in the downward direction.