

Basic Fundamental Parameters in X-Ray Fluorescence

The “fundamental parameters” approach to calibration in X-ray fluorescence is unique because it is based upon the *theoretical* relationship between measured X-ray intensities and the concentrations of elements in the sample. This theoretical relationship is based upon X-ray physics and the measured values of fundamental atomic parameters in the X-ray region of the electromagnetic spectrum. In this tutorial, an introduction to the means of calibration is provided based upon a simplified instrument-sample geometry, thus eliminating some of the mathematical details of the traditional derivations.

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In X-ray fluorescence (XRF) spectrometry, the characteristic spectral line radiation emitted by the analyte is measured to determine the concentration. The theoretical relationship between these two quantities was first developed in the mid-1950s (1) and is the basis of the “fundamental parameters” approach to calibration in XRF, based upon the X-ray properties of the elements.

Primary fluorescence is fluorescence that results from the exciting beam of X-ray photons, producing the characteristic radiation of an element or elements (Figure 1a). Some of the XRF of these elements returns to the detector, as indicated by the direction of the thin arrows.

Secondary fluorescence occurs when the characteristic radiation produced in turn induces the characteristic radiation of another element in the sample (Figure 1b). Tertiary fluorescence results when the characteristic radiation of the secondary fluorescence results in the production of the characteristic radiation of a third element (Figure 1c).

In this tutorial, we consider only primary fluorescence and present a somewhat simplified derivation of the relationship between the primary fluorescence intensity and the associated analyte concentration. Nevertheless, it basically follows the treatments available in standard texts on quantitative X-ray spectrometry (2–4). These works are also the sources for the data provided in the tables below.

Consider the geometry of Figure 2 and note the following simplifying assumptions:

- A beam of monochromatic and parallel X-rays of energy (E_0) and intensity (I_0) is incident on a sample of thickness h .
- The angle of incidence is 90° and the detector is on the same side of the sample, adjacent to the source. (Note: This eliminates the trigonometric functions that clutter the mathematics of the derivation.)

- We will focus on the $K\alpha$ X-ray emission of element i with concentration C_i .

The problem is approached in steps, first examining the attenuation of the incident beam and the absorption of X-ray photons in the sample volume under consideration by element i . Next we determine the production of $K\alpha$ fluorescent radiation of this element. Finally, we examine the attenuation of this $K\alpha$ radiation on its way back to the detector.

Incident Radiation Absorption Effects

The radiation intensity that reaches the sample volume element (highlighted in Figure 2) is attenuated in traveling a pathlength x . Therefore, the intensity that reaches the sample volume under consideration is as follows:

$$I = I_0 \exp(-\mu_s \rho x) \quad [1]$$

Here μ_s = mass absorption coefficient of the sample as a whole at the excitation energy (E_0), and ρ = the sample density. This was addressed in a previous tutorial (5).

Some of the radiation that reaches this volume element is absorbed. The fraction of radiation intensity (dI) absorbed is just $(\mu_s \rho dx)$. However, only some of this incoming radiation intensity is absorbed by element i . This fraction is the concentration of the element multiplied by the ratio of its mass absorption coefficient to that of the sample ($C_i [\mu_i/\mu_s]$). Therefore, the absorption by element i in the volume element under consideration is given by

$$[C_i (\mu_i/\mu_s)] (\mu_s \rho dx) = C_i \mu_i \rho dx \quad [2]$$

Then the incoming intensity that is absorbed by element i in the volume element under consideration and thus available to

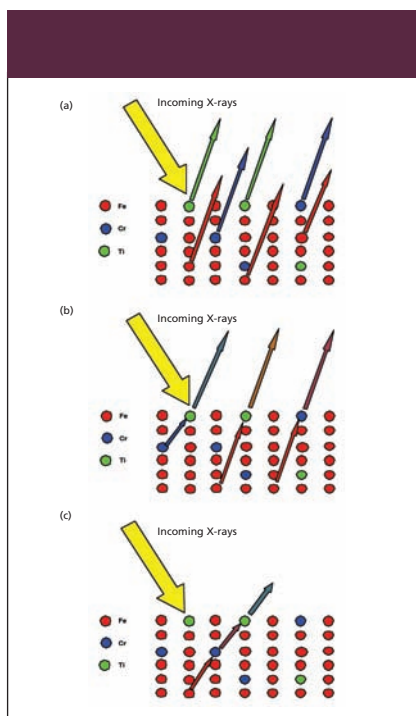


Figure 1: X-ray fluorescence: (a) primary, (b) secondary, and (c) tertiary.

produce $K\alpha$ fluorescence is found by multiplying this fraction [2] by equation 1:

$$dI = I_0 (C_i \mu_i \rho dx) \exp(-\mu_s \rho x) \quad [3]$$

Photoelectric Emission

The $K\alpha$ fluorescence of element i is determined by the number of absorbed photons, given by equation [3], and the probabilities associated with three atomic events:

- The probability that a K-shell electron will be ejected rather than an L- or M-shell electron.
- The probability of $K\alpha$ emission in preference to other K lines.
- The probability of $K\alpha$ radiation rather than an Auger electron.

Absorption Jump Ratio

The first factor, the probability that a K-shell electron will be ejected rather than an L- or M-shell electron, is given by what is called the K-shell "absorption jump ratio" (J_K):

$$J_K = (r_K - 1)/r_K \quad [4]$$

Here, r_K is the K-shell absorption jump defined as the ratio of the mass absorption coefficients at the K absorption edge (Figure 3):

$$r_K = \mu_{\max}/\mu_{\min} \quad [5]$$

These jump ratios have been measured and are shown in Table I.

Transition Probability

The probability that $K\alpha$ radiation will be emitted rather than that of another K line is called $g_{K\alpha}$ and is given by

$$g_{K\alpha} = I(K\alpha)/[I(K\alpha) + I(K\alpha\beta)]$$

or

$$g_{K\alpha} = [I(K\alpha)/I(K\beta)]/\{[I(K\alpha)/I(K\beta)] + 1\} \quad [6]$$

Some values for the $K\alpha/K\beta$ intensity ratio are given in Table II.

Fluorescence Yield

The last factor, the probability of $K\alpha$ radiation rather than the production of an Auger electron, is called the fluorescence yield ω_K . Figure 4 shows the difference in fluorescence yield between the $K\alpha$ and $L\alpha$ spectral lines.

Fluorescence yields have been deter-

Table I: Some K shell absorption jump ratios

| Element | Atomic Number | J_K |
|---------|---------------|-------|
| Ti | 22 | 0.888 |
| V | 23 | 0.885 |
| Cr | 24 | 0.882 |
| Mn | 25 | 0.880 |
| Fe | 26 | 0.877 |
| Co | 27 | 0.874 |
| Ni | 28 | 0.872 |
| Cu | 29 | 0.869 |
| Zn | 30 | 0.867 |
| Mo | 42 | 0.842 |

mined both experimentally and theoretically (Table III).

Excitation Factor

The product of these three probabilities gives us the excitation factor Q :

$$Q = J_K g_{K\alpha} \omega_K = [(r_K - 1)/r_K] g_{K\alpha} \omega_K \quad [7]$$

Fluorescence Radiation Absorption

The fluorescent radiation (E_i) from element i in the volume element is attenuated in traveling the path length x to the

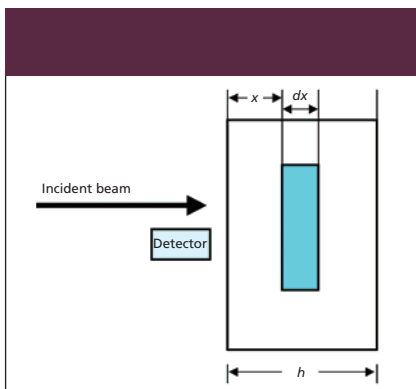


Figure 2: Excitation-sample-detector geometry.

detector. The fraction transmitted is given by

$$\exp(-\mu_{s,Ei} \rho x) \quad [8]$$

Geometric Considerations

The fluorescence radiation is emitted uniformly in every direction. The fraction that enters the detector is given by

$$(\Omega/4\pi) \quad [9]$$

where Ω is the solid angle defined by the detector collimator, and 4π is the total solid angle.

In the geometry as shown in Figure 5, the detector (radius, a) is a distance (d) away from the source of radiation, the fluorescence produced by the element under consideration. Then the solid angle is given by

$$\Omega = 2\pi [1 - d/\sqrt{d^2 + a^2}] \quad [10]$$

If $d \gg a$, this is approximately $\Omega = \pi a^2/d^2$

Putting It All Together

The contribution to the intensity of the primary fluorescence $dI_i(x)$ of element i is given by the product of the above factors in equations 3, 7, 8, and 9. After integration, the result is

$$I_i = \{[(I_0 C_i \mu_i Q) (\Omega/4\pi)]/(\mu_s + \mu_{s,Ei})\} \{1 - \exp[-\rho h (\mu_s + \mu_{s,Ei})]\} \quad [11]$$

The steps to equation 11 are provided in the appendix.

The form of $I_i(h)$ is shown in Figure 6. The primary fluorescence radiation intensity rapidly approaches a maximum

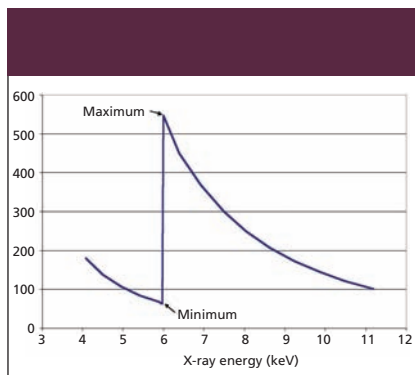


Figure 3: K absorption edge for chromium.

with increasing sample thickness.

Application 1: The Thick Sample

For a thick sample, where h becomes sufficiently large, the exponential term of equation [11] becomes negligible compared to 1. Then we are left with

$$I_i = [(I_0 C_i \mu_i Q) (\Omega/4\pi)]/(\mu_s + \mu_{s,Ei})$$

Substituting from equation 7 for Q and rearranging terms, we get

$$I_i = (I_0 C_i J_K g_{K\alpha} \omega_K) (\Omega/4\pi) [\mu_i/(\mu_s + \mu_{s,Ei})] \quad [12]$$

Example: A Pure Metal

Consider the example of a piece of pure iron excited by 10 mCi ^{109}Cd radioisotope ($E = 22.1$ keV). (Note: The curie [Ci] is the unit of nuclear activity and equals 3.7×10^{10} disintegrations per second.) Then the numbers for equation [12] are

$$I_0 \sim 2.5 \times 10^7 \text{ photons/s per steradian}$$

$$C_i = 1.0 \text{ (100\%)}$$

$$J_K = 0.877$$

$$g_{K\alpha} = 0.882$$

$$\omega_K = 0.347$$

$$\mu_i = \mu_s \text{ (at 22.1 keV)} = 18.55 \text{ cm}^2/\text{g}$$

$$\mu_{s,Ei} \text{ (at 6.4 keV)} = 70.46 \text{ cm}^2/\text{g}$$

The solid angle Ω , as computed in this example, is based upon a detector area of 25 mm^2 ($a \sim 2.8 \text{ mm}$) and sample-detector distance of $d \sim 22 \text{ mm}$. Then, using equation 10, we find $\Omega = 0.05$ steradian. Making the substitutions, we find $I_i = 5570$ counts per second (cps).

An experimental setup with geometry postulated in this derivation was not available. However, measurements made on a handheld energy-dispersive XRF

Table II: Some measured relative intensities

| Element | Atomic Number | $K\alpha/K\beta$ |
|---------|---------------|------------------|
| Ti | 22 | 7.52 |
| Cr | 24 | 7.52 |
| Fe | 26 | 7.46 |
| Ni | 28 | 7.41 |
| Zn | 30 | 7.41 |
| Zr | 40 | 5.41 |
| Mo | 42 | 5.18 |

spectrometer with quite different geometry, but otherwise identical to the parameters provided earlier, gave $I_i = 1335$ cps. This number is certainly "in the ballpark."

Application 2: The Thin-Film Approximation

For a thin film, h is very small. Now note the mathematical relationship that for $x \ll 1$, $1 - \exp(-x) = x$. Therefore, the term $\{1 - \exp[-\rho h (\mu_s + \mu_{s,Ei})]\}$ of equation 11 reduces to just $[\rho h (\mu_s + \mu_{s,Ei})]$. We can now rewrite this equation as

$$I_i = \{[(I_0 C_i \mu_i Q) (\Omega/4\pi)]/(\mu_s + \mu_{s,Ei})\} [\rho h (\mu_s + \mu_{s,Ei})]$$

Simplifying

$$I_i = (I_0 C_i \mu_i Q) (\Omega/4\pi) (\rho h) \quad [13]$$

for a given experimental geometry and excitation conditions, equation 13 can be rewritten as $I_i = kC_i$. That is, the fluorescent intensity is directly proportional to the concentration of the fluorescing element.

Discussion

Relative Rates

The result of this fundamental parameters computation as expressed in equations 11–13 is seldom used. Thus, the exercise of the pure metal example is not common. Instead, one generally creates an intensity ratio, referencing the analyte intensity to that of the pure element. In this way, many factors cancel out.

Consider equation 12 for analyte element i :

$$I_i = (I_0 C_i J_K g_{K\alpha} \omega_K) (\Omega/4\pi) [\mu_i/(\mu_s + \mu_{s,Ei})]$$

Now we write equation 12 for the same element but with concentration 100%, so that $C_i = 1$:

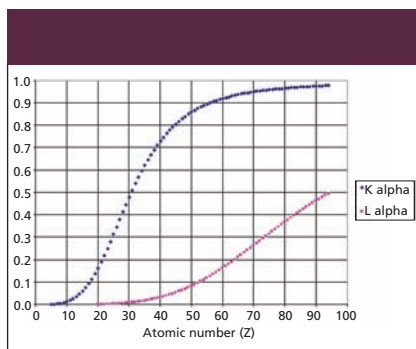


Figure 4: Fluorescence yield vs. atomic number.

$$I_{100} = (I_0 J_K g_{K\alpha} \omega_K) (\Omega/4\pi) [\mu_i / (\mu_s + \mu_{s,Ei})]$$

The relative rate ($R_i = I_i/I_{100}$) then reduces to the simple form $R_i = kC_i$.

Secondary and Tertiary Fluorescence

The previous discussion considers only primary fluorescence. Matrix effect corrections come into play when we consider secondary and tertiary fluorescence. It should be noted “that secondary fluorescence accounts for 50% of the observed emission in extreme cases, while tertiary fluorescence rarely reaches 2–3% and is generally considered negligible” (4).

While the principles remain the same, the mathematics of secondary and tertiary fluorescence corrections becomes increasingly difficult.

Sources of Error

There are several possible sources of error in this fundamental parameters approach to calibration in XRF (6):

- The completeness of the characteristic X-ray model
- The degree of uncertainty in the fundamental parameters themselves, and
- The model of the excitation source.

The first factor refers to whether secondary and tertiary fluorescence effects have been included in the computation. (See comments in the previous section.)

A significant contribution is the uncertainty in the basic X-ray physics constants used in the computation, such as the fluorescence yield and transition probabilities.

In this derivation, we have assumed a monochromatic and parallel beam of incident X-rays. The monochromatic part can be approximated by radioisotope sources of X-rays. However, with X-ray tubes, the excitation is decidedly poly-

chromatic. The modeling of this excitation spectrum is empirical and provides an additional source of uncertainty.

The derivation presented here is about as simplified as possible while remaining true to the basics. More advanced fundamental parameter models (as noted in the references) attempt to account for some of these sources of error.

Possibility of Fundamental Parameters in Optical Emission Spectroscopy

Will we ever be able to compute theo-

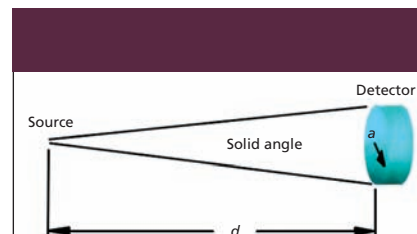


Figure 5: Source-detector geometry.

retical calibrations in optical emission spectroscopy (OES)? Certainly a theoretical framework exists for OES (7). However, the richness of the spectra coupled with the complexity of the excita-

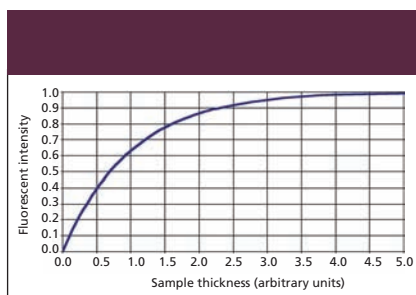


Figure 6: Primary fluorescence intensity as a function of sample thickness.

tion sources has made progress difficult.

Nevertheless, fairly recently, some work has been done using numerical modeling methods (8,9). The referenced work models the glow-discharge source, perhaps the least unwieldy of the optical emission excitation sources. The second reference provides the first explicit calculation of the optical emission spectra of argon and copper atoms. Even more recently, this same Belgian research group has done some work on modeling the laser ablation process (10).

Some progress has been made in this direction. It is a development that the spectrochemist surely will watch with

Table III: Some K fluorescence yields

| Element | Atomic Number | ω_K |
|---------|---------------|------------|
| Ti | 22 | 0.219 |
| V | 23 | 0.250 |
| Cr | 24 | 0.282 |
| Mn | 25 | 0.314 |
| Fe | 26 | 0.347 |
| Co | 27 | 0.381 |
| Ni | 28 | 0.414 |
| Cu | 29 | 0.445 |
| Zn | 30 | 0.479 |
| Mo | 42 | 0.765 |

interest in the coming years.

Appendix: Derivation of Equation 11

Combining equations 3–6, we get

$$\begin{aligned} dI_i &= dI Q (\Omega/4\pi) \exp(-\mu_{s,Ei} \rho x) \\ dI_i &= I_0 (C_i \mu_i \rho dx) \exp(-\mu_s \rho x) Q \\ &(\Omega/4\pi) \exp(-\mu_{s,Ei} \rho x) \end{aligned}$$

Combining the exponential terms gives

$$dI_i = (I_0 C_i \mu_i \rho Q) (\Omega / 4\pi) \exp[-\rho x (\mu_s + \mu_{s,Ei})] dx$$

Integrating from $x = 0$ to $x = h$ gives the primary fluorescence intensity from the incident radiation.

Now, let $A = (I_0 C_i \mu_i \rho Q) (\Omega/4\pi)$ and $B = \rho (\mu_s + \mu_{s,Ei})$.

Then, $dI_i = A \exp(-Bx)dx$, or $I_i = \int A \exp(-Bx)dx$

Because $\int \exp(ax) = \exp(ax)/a$, we have $I_i = (A/B) [1 - \exp(-Bh)]$.

Therefore,

$$\begin{aligned} I_i &= \{[(I_0 C_i \mu_i \rho Q) (\Omega/4\pi)] / [\rho (\mu_s + \mu_{s,Ei})]\} \{1 - \exp[-\rho h (\mu_s + \mu_{s,Ei})]\} \\ I_i &= \{[(I_0 C_i \mu_i Q) (\Omega/4\pi)] / (\mu_s + \mu_{s,Ei})\} \{1 - \exp[-\rho h (\mu_s + \mu_{s,Ei})]\} \quad [11] \end{aligned}$$

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