

26. Quantitative EDX

EDX Intensity

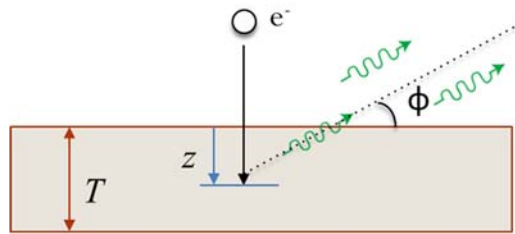
We discussed characteristic X-ray emission as a possible outcome of the ionization of atoms during electron bombardment in TEM. The X-ray emission energies for each element are well documented, but the detected intensity emitted from a thin TEM foil at some energy in a particular experiment will be proportional to a range of parameters that typically combine as linear factors:

$$I(E) = \alpha(E) \cdot D_e \cdot n \cdot T \cdot A(T, E) \cdot \sum_k x_k \cdot g_k(E)$$

Here, $I(E)$ is the intensity at energy E ; $\alpha(E)$ is a geometric factor that encapsulates the solid angle subtended by the detector and the efficiency of the detector; D_e is the electron dose, which is proportional to product of the beam current density and the acquisition time; n is the atomic concentration, which can be measured in atoms/cm³; T is the foil thickness; $A(T, E)$ is a correction to account for the absorption of X rays that are generated in buried regions below the escape surface of the TEM foil. The sum is over elements k present in the specimen, each with atomic fraction x_k . Each element generates X rays at some rate $g_k(E)$, which is essentially the characteristic emission spectrum for the given element convoluted with the broadened response function of the EDX system.

X-ray absorption

Consider X rays generated at a depth z below the top surface of a thin foil, which are detected outside of the foil at some angle ϕ . These X rays must propagate through a distance $\csc\phi \cdot z$ of foil to reach the surface. If the absorption in the foil at the X-ray energy is described by an attenuation coefficient $\mu(E)$, and we assume generation is uniform throughout the foil thickness (i.e., the incident electron beam is unattenuated in the foil), then the differential contribution from depth z to the total intensity varies $dI \propto \exp[-\mu(E) \cdot \csc\phi \cdot z]$.



Integrating over thickness to find the total intensity emitted from the foil

$$I \propto \int_{z=0}^T e^{-\mu(E) \cdot \csc\phi \cdot z} \cdot dz$$

We can now identify the absorption factor to be

$$A(T, E) = \frac{1 - e^{-\mu(E) \cdot \csc\phi \cdot T}}{\mu(E) \cdot \csc\phi}$$

We usually know ϕ from the detector geometry and we can estimate T , but the attenuation coefficient depends on composition, which is the information we are trying to measure.

Absorption correction

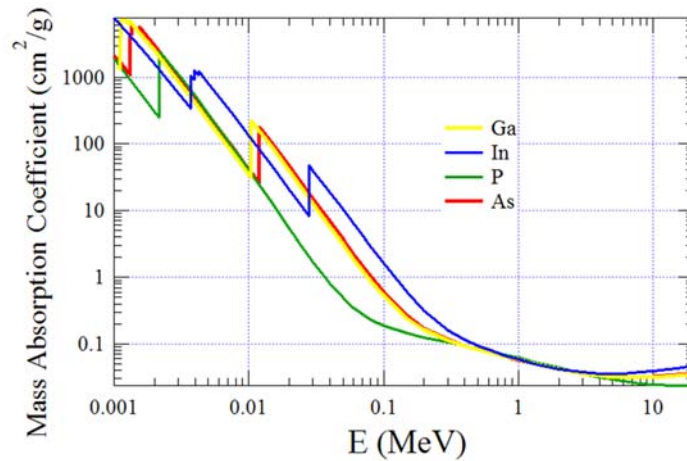
X-ray scattering cross-sections $\sigma_k(E)$ for elements are related to the atomic form factors, which can be determined from detailed calculations of the electronic structures of atoms. If we have only a single element, based on our earlier analysis of scattering, we would use

$$\mu(E) = n \cdot \sigma_k(E) = \frac{N_A \cdot \rho \cdot \sigma_k(E)}{M_k}$$

where N_A is Avogadro's number, ρ is the mass density, and M_k is the molar atomic mass. The ratio

$$\left(\frac{\mu(E)}{\rho} \right)_k = \frac{N_A \cdot \sigma_k(E)}{M_k}$$

is called the mass-attenuation coefficient for element k . These are tabulated for nearly all elements (c.f., <https://www.nist.gov/pml/x-ray-mass-attenuation-coefficients>). They show an overall decrease with energy, along with a sharp increase above the characteristic transitions of each element.



For a composite sample, containing multiple elements, the attenuation coefficient becomes

$$\mu(E) = \sum_k n_k \cdot \sigma_k(E)$$

where n_k is the concentration of element k . The concentration of each element can be related to its atomic ratio and the density of the composite by

$$n_k = \frac{N_A \cdot \rho \cdot x_k}{\sum_\ell x_\ell \cdot M_\ell}$$

This gives the combined mass-attenuation coefficient for the composite

$$\frac{\mu(E)}{\rho} = \frac{\sum_k N_A \cdot x_k \cdot \sigma_k(E)}{\sum_\ell x_\ell \cdot M_\ell}$$

Now we substitute the tabulated mass-attenuation coefficients

$$\sigma_k(E) = \frac{M_k}{N_A} \cdot \left(\frac{\mu(E)}{\rho} \right)_k$$

This gives a combined mass-attenuation coefficient of

$$\frac{\mu(E)}{\rho} = \sum_k \left[\frac{x_k \cdot M_k}{\sum_\ell x_\ell \cdot M_\ell} \cdot \left(\frac{\mu(E)}{\rho} \right)_k \right] = \sum_k y_k \cdot \left(\frac{\mu(E)}{\rho} \right)_k$$

using the mass ratios

$$y_k = \frac{x_k \cdot M_k}{\sum_\ell x_\ell \cdot M_\ell}$$

The dependence on composition tells us that we will need to assume a composition to include the absorption correction, then iterate using the computed composition until convergence.

k-factors

Say we know the EDX intensity at two different energies that are associated with different elements.

$$I(E_1) = \alpha(E_1) \cdot D_e \cdot n \cdot T \cdot A(T, E_1) \cdot g_1(E_1) \cdot x_1$$

$$I(E_2) = \alpha(E_2) \cdot D_e \cdot n \cdot T \cdot A(T, E_2) \cdot g_2(E_2) \cdot x_2$$

We can take the intensity ratio to eliminate common factors

$$\frac{I(E_2)}{I(E_1)} = \frac{\alpha(E_2) \cdot \cancel{D_e} \cdot \cancel{n} \cdot \cancel{T} \cdot A(T, E_2) \cdot g_2(E_2) \cdot x_2}{\alpha(E_1) \cdot \cancel{D_e} \cdot \cancel{n} \cdot \cancel{T} \cdot A(T, E_1) \cdot g_1(E_1) \cdot x_1}$$

The remaining ratio is proportional to the composition ratio

$$\frac{I_2}{I_1} = \frac{1}{k_{12}} \cdot \frac{x_2}{x_1}$$

The parameter k_{12} is called the Cliff-Lorimer ratio for these two elements

$$\frac{x_2}{x_1} = k_{12} \cdot \frac{I_2}{I_1}$$

ζ-factors

The expression above can be written as

$$\frac{I_2}{I_1} = \frac{x_2/\zeta_2}{x_1/\zeta_1}$$

We often have a bit more information to work with. We usually have relationships among the compositions of various constituents. For example, if 1 and 2 are the only elements present in the specimen, we know that $x_1 + x_2 = 1$, so $x_2 = 1 - x_1$. Now we can see that

$$\frac{1 - x_1}{x_1} = \frac{\zeta_2 \cdot I_2}{\zeta_1 \cdot I_1}$$

A little algebra gives

$$x_1 = \frac{\zeta_1 \cdot I_1}{\zeta_1 \cdot I_1 + \zeta_2 \cdot I_2}, \quad x_2 = \frac{\zeta_2 \cdot I_2}{\zeta_1 \cdot I_1 + \zeta_2 \cdot I_2}$$

Watanabe and Williams (2006) showed that we can generalize the above form as follows

$$x_i = \frac{\zeta_i \cdot I_i}{\sum_j \zeta_j \cdot I_j}$$

The nice thing here is that each ζ -factor is associated with one element, rather than pairs of elements. This makes them more extensible than k-factors, as we now discuss.

Relating pairs of elements

Say we have two alloys with known compositions, one with formula $A_{1-x}B_x$, and the other with formula $A_{1-y}C_y$. From EDX measurements, we can determine the ratios ζ_B/ζ_A

$$\frac{x}{1-x} = \frac{\zeta_B}{\zeta_A} \cdot \frac{I_B}{I_A} \rightarrow \frac{\zeta_B}{\zeta_A} = \frac{x}{1-x} \cdot \left(\frac{I_B}{I_A}\right)^{-1}$$

and ζ_C/ζ_A

$$\frac{y}{1-y} = \frac{\zeta_C}{\zeta_A} \cdot \frac{I_C}{I_A} \rightarrow \frac{\zeta_C}{\zeta_A} = \frac{y}{1-y} \cdot \left(\frac{I_C}{I_A}\right)^{-1}$$

Now we wish to study a new alloy with formula $B_{1-z}C_z$. We could determine z if we knew ζ_C/ζ_B

$$\frac{z}{1-z} = \frac{\zeta_C}{\zeta_B} \cdot \frac{I_C}{I_B}$$

Fortunately, the ζ -factors are related

$$\frac{\zeta_C}{\zeta_B} = \frac{\zeta_C}{\zeta_A} \cdot \frac{\zeta_A}{\zeta_B}$$