12.119 Problem Set: Electron Microprobe

Question 1: Characteristic X-rays

For the following elements decide which one of the three diffracting crystals would be the best to measure the X-ray intensities of MgKα, CaKα and FeKα. The optimal range of **2θ** for each crystal is between 30° and 130° and the best peak shape is achieved closest to the middle of the **2θ** range of the spectrometer. Recall Bragg's Law, **nλ = 2dsinθ**. We are typically interested in first order diffractions (i.e., **n=1**).

Diffracting Crystal	Lattice spacing (2d) (nm)
TAP	2.5757
PET	0.8742
LiF	0.4027

Element	Kα X-ray wavelength (λ) (nm)
Mg	0.989
Ca	0.33584
Fe	0.193735

Question 2: Quantitative analysis using Bence-Albee corrections

The X-ray intensity generated for an element "**i**" is proportional to the concentration ($\mathbf{C_i}$) of that element in the sample. However, the X-ray intensity emitted ($\mathbf{I_i}$) is different from the generated intensity because of the effects of average atomic number (**Z**), absorption (**A**) and fluorescence (**F**) arising from the presence of other elements in the sample and the standard. This is known as the matrix effect. The emitted intensity ($\mathbf{I_i}$), concentration ($\mathbf{C_i}$) and matrix correction factors (**ZAF**) are related by the following equation:

$$\mathbf{C_i^{unk} / C_i^{std} = (I_i^{unk} / I_i^{std}) * ZAF} \quad (1)$$

where, "**unk**" denotes the unknown compound, "**std**" the standard, and $\mathbf{I_i^{unk} / I_i^{std}}$, the X-ray intensity ratio, is known as the "k-ratio" of element **i** ($\mathbf{k_i}$):

$$\mathbf{k_i = I_i^{unk} / I_i^{std}} \quad (2)$$

ZAF includes the combined effects of the matrices of the unknown and the standard. Since the standard composition is known, the contribution to **ZAF** from the standard is also known. The concentration in the standard divided by its own matrix correction factors is the standard correction factor (**CF**). The contribution to **ZAF** from the unknown is denoted by **β**. Hence, for element **i** in the unknown compound with **n** elements:

$$\mathbf{C_i = \beta_i k_i CF_i} \quad (3)$$

where,

$$\beta_i = (C_1\alpha_{i1} + C_2\alpha_{i2} + \ldots + C_i\alpha_{ii} + \ldots + C_n\alpha_{in})/(C_1 + C_2 + \ldots + C_i + \ldots + C_n) \quad (4)$$

where, α_{ij} is the α-factor, a constant for element **i** in the binary system **i-j**, at a given value of electron beam energy E_0 and take-off angle ψ. The value of α_{ii}, which is the α-factor of element **i** in itself, is unity.

Since both C_i and β_i are unknown in the above equations, an iterative procedure is used to determine C_i. In the first step, an initial "first approximation" concentration of each element is calculated as:

$$C_i^0 = k_i\, CF_i \quad (5)$$

Using these "first approximation" concentrations, the initial values of β are calculated as:

$$\beta_i^0 = (C_1^0\,\alpha_{i1} + C_2^0\,\alpha_{i2} + \ldots + C_i^0\,\alpha_{ii} + \ldots + C_n^0\,\alpha_{in})/(C_1^0 + C_2^0 + \ldots + C_i^0 + \ldots + C_n^0) \quad (6)$$

Then, the next set of concentrations is calculated using the β^0 values and equation (3). In turn, the next set of β values are calculated using equation (6). This procedure is repeated until the differences between successive calculated β values are arbitrarily small. This happens after 3 or 4 iterations. The final calculated concentrations are determined using equation (3) and the final calculated β values.

In the following problem, the measured (emitted) X-ray intensities of Mg, Si and Fe in standards and an olivine sample are given. *Synthetic forsterite* for Mg and Si, and *Marjalotti olivine* for Fe were used as standards. Although we measure the intensities of the elements, the Bence-Albee correction procedure calculates the concentrations as oxides because the standard composition is defined in terms of oxides. The α-factors at E_0=15 keV and ψ=40^o are provided. Calculate the concentrations of MgO, SiO_2 and FeO in the sample using the iterative procedure discussed above (repeat up to 4 iterations).

	MgO	**SiO_2**	**FeO**	**comment**
I_i^{std}	393.46	328.81	22.1	standard intensity
CF	0.5473	0.3364	0.1018	standard correction factor
I_i^{unk}	329.72	325.26	14.51	measured intensity in the sample
α_{Mg-i}	1	1.085	2.101	alpha factors: α_{Mg-Mg}, α_{Mg-Si}, α_{Mg-Fe}
α_{Si-i}	1.414	1	1.3	alpha factors: α_{Si-Mg}, α_{Si-Si}, α_{Si-Fe}
α_{Fe-i}	1.119	1.126	1	alpha factors: α_{Fe-Mg}, α_{Fe-Si}, α_{Fe-Fe}
k_i	...	...	...	k-ratio
C_i^0	...	...	...	"first approximation"concentration
β_i^0	...	...	...	first β
C_i^1	...	...	...	concentration after first iteration
β_i^1	...	...	...	β after first iteration
...	...	...	...	successive iterations
C_i	...	...	...	final concentration

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