

We can break up the process of doing EPMA into 4 broad steps:

- Preparation: preparing the sample, acquiring the proper standards, setting up the electron beam instrument for proper operation;
- Acquisition: acquiring the **raw** x-ray intensities (EDS or better, WDS) = getting K-ratios
- **Correction**: applying an iterative matrix correction, as the raw x-ray intensities measured are **never** in the correct proportions to the elements in the sample = running a **matrix correction on the K-ratios**
- Quality control: verifying that the results are OK.

This week your assignment focuses upon the 3rd step, the matrix correction. In modern instruments, this can be pretty much a “black box” operation. The matrix correction is many times referred to by the 3 letters ZAF (Z=atomic number correction; A=absorption correction; F=fluorescence correction). One more modern version goes by the name of “phi-rho-Z”.

This week I am having you go through an older version of ZAF. You will step through doing many of the equations used in the ZAF. (I will not have you calculate the Fluorescence correction; I give them to you.) William’s book¹ gives a step by step account, and I have distributed that to you. And to make this most clear, I am giving you the steps and just ask that you “fill in the blanks”, showing your work step by step.

The problem: your probe is working fine, but an industrial saboteur has attacked and compromised your blackbox ZAF program, and your boss wants an answer by tomorrow 7 AM ...your company’s fate rests upon whether the alloy is (by weight, not atomic) Cu₆₀Au₄₀ or Cu₇₀Au₃₀ (again, **weight** fractions). Luckily you wrote down the K-ratios before the computer ate the data. So you pull out your probe notes to see how you could do it with your calculator (ok, excel spreadsheet).

Your probe was set to $E_0 = 25 \text{ keV}$, with a **take off angle of 40°**. You have averaged the raw numbers and found the following K ratios: **Cu Ka k = 0.640 and Au La k = 0.337**. (Pure element standards used.)

Warning. Gotchas. Beware. Do not make these common mistakes:

1. Rounding of numbers. Do not round until the very very last step. In all calculations keep at least 4 decimal places until very very last step.
2. When you are asked to provide the critical edge energy, make 100% sure you know which edge you are being asked for. La is the L3 or LIII edge, right?
3. Make sure, in the calculations below, when it asks for a parameter for the “alloy”, you understand that this means you are taking a summation of {property of A times the weight fraction of element A} + {property of B times the weight fraction of element B}. Note that this is laid out in the Williams reprint.
4. If you end up with a negative number, what does that tell you?? That you are doing something wrong... Go back and re-read the Williams step by step procedure. You should not get a negative number in the calculations.

¹ Williams, 1987, Introduction to X-Ray Spectrometry, Allen & Unwin (out of print)

Step 0

You first recall that Castaing's first approximation might give you a good first guess: take the k ratios, sum them up and if not equal to 1.000, normalized each so that they sum to 1.000. Cu _____ and Au _____ (normalized fractions)

Note 1: I am clarifying Williams' terminology, so critical edge is E_{critical} , not E_c

Note 2: Do NOT uncritically use the numbers from Williams' example! His example is at 20 keV, whereas yours is at 25 keV, and there are a couple of typos (noted)! And his example is Cu and Al, not Cu and Au.

Note 3: Write down all the steps (values) in each equation!

Required data --don't make errors here! Understand critical (binding) energy is NOT the same as the characteristic peak energy

Atomic numbers (Z): Cu _____ Au _____
Atomic weights (A): Cu _____ Au _____
Excitation potentials (E_{critical}): Cu K _____ keV Au L _____ keV

Atomic Number (Z) Correction

Step 1: Calculate the mean electron energies $\bar{E} = (E_0 + E_{\text{critical}})/2$

Cu $E_{\text{mean}} =$

Au $E_{\text{mean}} =$

Step 2: Calculate stopping power coefficients S

(a) First calculate the mean ionization energy J using the equation (**note: this is in eV!!**)

$$J = (9.76 * Z) + (58.8 * (Z^{-0.19}))$$

$J(\text{Cu}) =$

$J(\text{Au}) =$

(b) Starting here, it gets complicated, and we have to distinguish now when we refer to an element (e.g. Cu, Au) whether it is as the x-ray or as the target, as now we have 4 combinations (Cu Ka vis a vis Cu, Cu Ka vis a vis Au, Au La vis a vis Cu, Au La vis a vis Au) and then we have to combine the proper combinations to make Cu Ka vis a vis the alloy, Au La vis a vis the alloy.

Calculate the S values using the equation (**note: here use J in keV!!**)

$$S = \left(\frac{Z^{target}}{A^{target}} \right) \ln \left(\frac{1.166 * E_{mean}^{xray}}{J^{target}} \right) \quad \text{and show all your work.}$$

(i) For Cu K generation:

(there is a typo in the Williams first line [S pureCu], a “)” where it should not be...don't do it!

S pure Cu =

S pure Au =

S alloy (here you are going to use your first approximation fractions from step 0 above_
S alloy =

(ii) For Au L generation”

S pure Cu =

S pure Au =

S alloy =

Step 3: Calculate the backscatter coefficients (R) using the following equation

$$R = \frac{1}{1 + \langle 0.008 * (1 - W^{xray}) * Z^{target} \rangle} \quad \text{where } W = \frac{E_{critical}}{E_0} \quad (\text{=the overvoltage reciprocal})$$

Show all your work.

(a) Calculate the W factors

For Cu K, W =

For Au L, W =

(b) Calculate the R values, using the above equation:

(i) For Cu K generation:

R pure Cu =

R pure Au =

R alloy =

(ii) For Au L generation:

R pure Cu =

R pure Au =

R alloy

Step 4: Calculate the Z-correction (“atomic number”) factors for each of the xrays using the equation

$Zfactor = \left(\frac{R_{standard}}{R_{unknown}} \right) * \left(\frac{S_{unknown}}{S_{standard}} \right)$ recalling that in the worked out example the “alloy” is the unknown, and that the pure element is used as the standard. Show all your work.

(a) Cu: Z-factor =

(b) Au: Z-factor =

Step 5: Apply the correction factors to the raw (original uncorrected NOT the normalized concentrations) k ratios to obtain the first-cycle corrected compositions:

(a) Cu = $0.640 \times \underline{\hspace{2cm}} = \underline{\hspace{2cm}}$ or $\underline{\hspace{2cm}}$ wt %

(b) $Au = 0.337 \times \underline{\hspace{2cm}} = \underline{\hspace{2cm}}$ or $\underline{\hspace{2cm}}$ wt%

Now the absorption (A) correction:

Use the following Mass Absorption Coefficients (from Goldstein et al):

Absorbers	Emitters (x-rays)	
	Cu (Ka)	Au (La)
Cu	53.7	245.5
Au	208.6	127.5

Starting values: use the fractions you determined in Step 5 of the Z correction above:
 Cu $\underline{\hspace{2cm}}$ Au $\underline{\hspace{2cm}}$ which when normalized are Cu $\underline{\hspace{2cm}}$ Au $\underline{\hspace{2cm}}$

Step 1. Calculate the h values where

$$h = 1.2 * \frac{A}{Z^2}$$

Cu metal: h =

Au metal: h =

Alloy: h =

Step 2: Calculate the chi (χ) values where

$$\chi = \left(\frac{\mu}{\rho} \right) \text{cosec} \psi \text{ where } \mu/\rho \text{ is the mass absorption coefficient, cosec is the inverse sin function}$$

($1 / \sin \psi$) and psi (ψ) is the take off angle

(a) for Cu Ka:

Cu metal: chi =

Au metal: chi =

Alloy: chi =

(b) for Au La:
Cu metal: χ =

Au metal: χ =

Alloy: χ =

Step 3: Calculate the sigma (σ) values where

$$\sigma = \frac{4.5 \times 10^5}{E_0^{1.65} - E_{critical}^{1.65}}$$

(a) for Cu K: σ =

(b) for Au L: σ =

Step 4: Calculate the $f(\chi)$ values, where

$$f(\chi) = \frac{1 + h}{\left(1 + \frac{\chi}{\sigma}\right) * \left[1 + \left(h * \left\{1 + \frac{\chi}{\sigma}\right\}\right)\right]}$$

(a) for Cu Ka:

$f(\chi)$ (Cu) =

$f(\chi)$ (Au) - not required (Cu Ka not measured on Au standard)

$f(\chi)$ (alloy)

(b) for Au La:

$f(\chi)$ (Cu) - not required (Au La not measured on Cu standard)

$f(\chi)$ (Au) =

$f(\chi)$ (alloy) =

Step 5: Calculate the A-factors where $A = \frac{f(\lambda)_{standard}}{f(\lambda)_{unknown}}$

(a) for Cu Ka: A =

(b) for Au La: A=

Step 6: Apply the A-correction to the Z-corrected compositions:

(a) Cu = _____ x _____ = _____ (fraction) or _____ wt% (do not normalize)

(b) Au= _____ x _____ = _____ (fraction) or _____ wt% (do not normalize)

Fluorescence Correction – you are not required to do the calculations. The F correction factors will be close to: Cu – 0.96 and Au 1.00)

Why is there a downward F correction for Cu? _____

When you multiply the above ZxA corrected values by the F factor, what results do you get?

Cu = _____ x _____ = _____ (fraction) or _____ wt% (do not normalize)

Au = _____ x _____ = _____ (fraction) or _____ wt% (do not normalize)

Fill in the table with the values your determined for the Z and A factors, plus the ones I gave you for F:

	Z	A	F
Cu			
Au			

For Cu, which factor made the greatest change? _____ the least change? _____

For Au, which factor made the greatest change? _____ the least change? _____

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