Embracing Uncertainty: Modeling Uncertainty in EPMA - Part II

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Abstract

This, the second in a series of articles present a new framework for considering the computation of uncertainty in electron excited X-ray microanalysis measurements, will discuss matrix correction. The framework presented in the first article will be applied to the matrix correction model called "Pouchou and Pichoir's Simplified Model" or simply "XPP". This uncertainty calculation will consider the influence of beam energy, take-off angle, mass-absorption coefficient, surface roughness and other parameters. Since uncertainty calculations and measurement optimization are so intimately related, it also provides a starting point for optimizing accuracy through choice of measurement design.

1 Introduction

1.1 Recap

In part I of this series[Ritchie, 2020], the framework for propagating uncertainties in *multi-variate measurement models* described in the BIPM JCGM 102[ISO/JCGM, 2011] is presented and applied to some common microanalysis calculations like converting between various representations of composition. This model is a generalization of the conventional univariate models which depend on the first order term in a Taylor series expansion. This generalization is expressed in the matrix equation

$$\mathbb{U}(\mathbf{y}) = \mathbb{J}(\mathbf{Y})|_{\mathbf{X}=\mathbf{x}} \cdot \mathbb{U}(\mathbf{x}) \cdot \mathbb{J}(\mathbf{Y})^{\mathsf{T}}\Big|_{\mathbf{X}=\mathbf{x}}$$
(1)

where $\mathbb{U}(\mathbf{x})$ is the covariance or uncertainty matrix and $\mathbb{J}(\mathbf{Y})$ is the Jacobian matrix, a matrix of partial derivatives of the multivariate measurement model with respect to the input variables.

To apply this model, it is necessary is to know the input uncertainties and to be able to compute the partial derivatives. The computation of the partial derivatives can be daunting unless you realize that the standard chain rule of differential calculus applies to Jacobians like it applies to univariate derivatives. If a complex function $\mathbf{f}(\mathbf{X})$ can be broken down into a sequential steps, $\mathbf{f}(\mathbf{X}) = \mathbf{g}(\mathbf{h}(\mathbf{X}))$, then by the chain rule,

$$\mathbb{J}(\mathbf{f}(\mathbf{X})) = \mathbb{J}(\mathbf{g}(\mathbf{Z}))|_{\mathbf{Z}=\mathbf{h}(\mathbf{X})} \mathbb{J}(\mathbf{h}(\mathbf{X})).$$
⁽²⁾

This is the strategy we will apply in Part II to the process of matrix correction. It is beneficial but not necessary to understand the mathematics. Section 3 explains some of the consequences of the math in terms of practical measurement decisions.

1.2 Compositional Analysis

Compositional analysis by electron excited X-ray spectroscopy is an indirect, comparative measurement. The X-ray intensities measured on an unknown material are compared with X-ray intensities measured on standard materials of known composition. The ratio of the X-ray intensities for a specific transition associated with a specific element (called the k-ratio) is, to a crude approximation, equal to the mass fraction of that element. This is often called 'Castaing's First Approximation'[Castaing, 1951]. However, it is necessary to compensate for differences in electron transport and X-ray transmission between the unknown and standard material. This process is an *implicit multivariate measurement model* called "matrix correction." The model is *implicit* because it is not possible to analytically solve the equation for the mass fraction and *multivariate* because it is not possible to solve for one element in an unknown material without simultaneously solving for all the other elements in the material. The equation

$$k_i - \frac{C_{unk,i}}{C_{std,i}} ZAF_i(\mathbf{C}_{unk}, \mathbf{C}_{std_i}; \mathbf{Q}) = 0$$
(3)

where *i* indexes the elements, $C_{unk,i}$ and $C_{std_i,i}$ are the mass-fractions in the unknown and standard, respectively, $ZAF_i(\mathbf{C}_{unk}, \mathbf{C}_{std_i}; \mathbf{Q})$ is the matrix correction factor which is a function of the composition of the standards and unknown and other parameters \mathbf{Q} like beam energy and take-off angle, is inherently coupled. Note that the standard for each element may be distinct as reflected by the index *i* on std_i .

The measurement proceeds by collecting intensity data from the standard and unknown materials to determine k_i . \mathbf{C}_{std} is known as are the other parameters \mathbf{Q} . However, \mathbf{C}_{unk} appears in the mass-fraction ratio and also the expression $ZAF_i(\mathbf{C}_{unk}, \mathbf{C}_{std_i}; \mathbf{Q})$. An initial guess is made for \mathbf{C}_{unk} and the left-hand side (LHS) of Equation 3 is evaluated. The result is compared to $\mathbf{0}$ and the estimates of \mathbf{C}_{unk} are updated to attempt to bring the LHS closer to zero. This process, called "iteration", is repeated until all the LHS are deemed sufficiently close to zero[Reed, 1993; Springer, 1976; Wegstein, 1958].

There are tens-of-different models in the literature for the $ZAF_i(...)$ -term and hundreds of possible permutations of models (e.g. [Armstrong et al., 2013]). Furthermore, there are many different reasonable selections of input parameters for these models. Over time and with experience, the zoo of models has been culled to a handful that remain in common usage. These include Pouchou and Pichoir's two models[Pouchou & Pichoir, 1991], Armstrong's CITZAF model[Armstrong, 1995] and Bastin's PROZA96 model[Bastin et al., 1998]. All of these represent a class of models, called " $\phi(\rho z)$ models", which combine the atomic number and absorption correction terms into a single model based on the an assumed mass-depth (ρz where ρ is the density and z is a depth) distribution of inner shell ionization. While the older style of $Z \cdot A \cdot F$ correction models have largely fallen out of favor (the JEOL microprobe system being a significant exception), the language of Z, atomic number correction, A, absorption correction, and F, fluorescence correction, continues to be used to discuss $\phi(\rho z)$ models. $\phi(\rho z)$ models represent a mechanism to calculate the Z and Aterms. We will not further discuss the fluorescence correction term, F, in this paper.

In general, distinct matrix correction models produce similar but not identical results. For most of the important experimental parameters, the models have similar behavior. For example, all the models predict that the absorption correction increases as the incident beam energy increases. While there are reasons to favor one model over another in specific situations, "XPP" has become quite popular in both commercial products and in academic use. For this reason, we have chosen to work with this model. However, the insights from this model are likely to hold for other matrix correction models.

2 Matrix Correction

2.1 Mass Absorption Coefficients

We choose to use the Chantler elemental mass absorption coefficients (MACs)[Chantler, 1995, 2000; Chantler et al., 2005] as published on the National Institute of Standards and Technology (NIST) web site. This tabulation is computed using a self-consistent Dirac-Hartree-Fock framework across a range of X-ray energies which fully encompasses the range seen in X-ray microanalysis measurements. In addition, the tabulation provides a self-consistent set of edge energies which helps to eliminate inconsistencies between edge energies and characteristic Xray energies. The MAC at intermediate energies can be estimated using log-log interpolation, .

In the simple linear model used in X-ray microanalysis, the MAC for a material M as a function of energy E, $[\mu/\rho]_M(E)$, is computed as linear combination of elemental MACs, $[\mu/\rho]_z(E)$ where z is the atomic number.

$$[\mu/\rho]_{M}(E) = \sum_{z} C(z) [\mu/\rho]_{z}(E)$$
(4)

where C(z) is the mass-fraction of the element z.

Regions of energy	$f_2, [\mu/\rho]_{PE}, \mu_{PE}$
within the tabulated range	Solids, liquid
Below 200 eV (correlations, photons)	100% to $200%$
$200\mathrm{eV}$ to $500\mathrm{eV}$	50% to $100%$
$500\mathrm{eV}$ to $1000\mathrm{eV}$	5% to $20%$
Near edges (within 0.1%	50~%
Near K edges (within 10%)	10% to $20%$
Near K edges $(1.1 < E_0/E_K < 1.2)$	3%
Well above K edges $(E_0/E_K > 1.2)$	1%
Near L_I , M_I - M_{III} edges (within 15%)	15% to $30%$
Near L_I , M_I - M_{III} edges $(1.15 < E_0/E_{edge} < 1.4)$	4%
Well above L_I , M_I - M_{III} edges $(E_0/E_{edge} > 1.4)$	1%
Near $L_{II,III}$, $M_{IV,V}$ edges $(1.15 < E_0/E_{edge} < 1.4)$	4%
Well above $L_{II,III}$, $M_{IV,V}$ edges $(E_0/E_{edge} > 1.4)$	1%
Above $200 \mathrm{keV}$	2% to $3%$

Table 1: Estimates of the uncertainty in the MACs as detailed in Chantler 2000's[Chantler, 2000] Table 2 for elemental solids and liquids.

The elemental MACs have associated uncertainties. At high energies ($\gtrsim 2.0 \text{ keV}$) these uncertainties can be as low as 1.0 % but, at lower energies and near absorption edges, the uncertainties can be much, much larger. Chantler[Chantler, 2000] suggested estimates of uncertainties according to a set of rules which depend upon such properties as X-ray energy and proximity to an absorption edge. The relevant columns of Chantler's Table 2 is replicated in Table 1.

However, Chantler does not provide any guidance on uncertainties when combining the elemental MACs to produce material MACs. The models that Chantler uses are atomic models and do not include terms to handle the atom's environment. The linear approximation in Equation 4 is observed to work wellenough at moderate to high energies and away from absorption edges. High energy X-rays are absorbed most efficiently by a process involving the ionization of an inner atomic shell. The inner atomic shells are largely unaffected by the bonding environment. However, lower energy X-rays are energetic enough to only excite near valence shells which are influenced by the local bonding environment. This suggests that we would expect at least as large uncertainties as in Table 1 in combining elemental MACs for materials. This was discussed in detail in Part I[Ritchie, 2020].

2.2 Pouchou and Pichoir's XPP Model

While the XPP model is discussed in earlier articles[Pouchou & Pichoir, 1984, 1985, 1986], the presentation in the book Electron Probe Quantitation[Pouchou & Pichoir, 1991] is the most complete and is the primary reference for this work. For XPP, Pouchou and Pichoir chose the ansatz

$$\phi(\rho z) = A \exp(-a\rho z) + (B\rho z + \phi(0) - A) \exp(-b\rho z)$$
(5)

for the $\phi(\rho z)$ -curve. While data is sparse, this shape is seen to crudely match the shape of measured and Monte Carlo-modeled $\phi(\rho z)$ -curves. They then provide models to calculate values for A, a, B, and b from $\phi(0)$, the slope of $\phi(\rho z)$ at $\rho z = 0$,

$$P = \left. \frac{d\phi(\rho z)}{d\rho z} \right|_{\rho z = 0},\tag{6}$$

the integral of $\phi(\rho z)$, representing the number of primary ionizations,

$$F = \int_0^\infty \phi(\rho z) \, d\rho z \tag{7}$$

and the mean depth of ionization,

$$\bar{R} = (1/F) \int_0^\infty \rho z \,\phi(\rho z) \,d(\rho z). \tag{8}$$

2.3 Breaking the Problem into Steps

This article will demonstrate how to break up the XPP calculation into an efficient set of steps which 1) calculate each intermediary quantity once and only once; 2) order and group these calculations in an efficient manner; 3) combine the calculation into a single monolithic calculation for all elements, characteristic X-ray lines, instrumental conditions, standards and unknown; 4) propagate uncertainties in the input parameters through the calculation in a manner that maintains correlations from the inputs through the intermediary quantities to the resultant quantities; and 5) compute the sensitivity of the matrix correction factor relative to each input variable.

2.4 Tracking Input and Intermediary Values

It is critical to keep close track of variables as each input and intermediary variable must be represented by one-and-only-one column in the Jacobian matrix. The calculation proceeds in a series of steps in which intermediary quantities and their Jacobian are calculated. Each step provides intermediary values that are needed by subsequent steps. Careful ordering of the steps ensures that intermediary quantities are available when needed. For efficiency, we also desire that intermediary variables are calculated no sooner than necessary. Each step should be sufficiently simple that the Jacobian elements can be readily calculated. Careful ordering and parallelization of the steps can lead to substantial increases in computational speed.

Matrix correction is particularly challenging to implement because the number and character of the input, intermediary and output parameters vary from measurement-to-measurement. Input data may not be provided in the form required by the calculation and must be transformed before use. For example, a composition expressed as oxide fractions or atomic percent must be converted to mass fraction while maintaining covariance relationships. The number of input parameters can vary by an order-of-magnitude between binary unknowns with simple standards and multi-element unknowns with many complex standards. Thus it is critical to implement a calculation scheme which is flexible enough to keep track of varying input and output values and all the intermediaries generated by the calculation. It is critical to keep track of the contents of each row and column of the Jacobian matrix as it is constructed step-by-step. Sometimes it is necessary to reorder the Jacobian. Sometimes, it is beneficial to discard columns after the values they represent are no longer needed by the calculation.

Often the same calculation is performed on many different inputs. For example, we typically need to calculate the material MAC for multiple different standards and the unknown material. The $\phi(\rho z)$ -curve needs to be calculated for the standards and the unknown. Many aspects of these calculations can be performed in parallel on multi-core CPUs so long as the inputs are tracked carefully so that they can be recombined at a later step in the calculation. Since many of the computations are performed using matrix multiplication, it can be much more efficient to divide a calculation into M products of $N/M \times N/M$ matrices rather than a single $N \times N$. Whenever possible, calculations are performed independently and combined only when necessary.

It is critical when proceeding in parallel that even when the calculations are performed separately, that, when the same quantity is used in different calculations, the bookkeeping reflects that it was identically the same quantity referenced in each calculation. In other words, the same label must be used throughout the entire calculation to refer to a single input, intermediary or output variable. It is not sufficient that the numerical values be the same.

An intuitive way to understand the necessity of maintaining the identity of variables is to consider an uncertainty calculation performed using the Monte Carlo method[ISO/JCGM, 2008]. At each iteration of the Monte Carlo calculation, the algorithm proceeds by assigning a randomized value drawn from the variable appropriate distribution to each value with an associated uncertainty. Over an ensemble of such randomized draws, the distributions of the random variates will approach the desired distribution. For each draw, the entire model is calculated and the resulting values tabulated. Over an ensemble of calculations, the resulting distribution of values will approach the distribution of the output variables. However, if instead of assigning the input randomized values once, we were create new randomized values each time a value appeared in the calculation, we would end up with a very different and incorrect distribution.

Consider, for example, the effective beam energy. The effective beam energy is identically the same for all elements measured in a single spectrum. The beam energy may be 1% high or 1% low but it is the same value for the entire spectrum. It may even vary during the acquisition of the spectrum (due to charging, for example) but the effect of the variation will be identical for all the elements. It is the same random variable for all calculations associated with that one spectrum. However, if we collect a second spectrum from a different material, the sample may have very different conductivity properties which might lead to different levels of charging and result in a different effective beam energy. Thus while the two beam energies are nominally the same value, the characteristics of their uncertainty may be very different.

Unfortunately, it is rarely clear cut how to handle different but related variables like beam energy. It really depends upon the majority source of uncertainty and whether that source is correlated between the measurements. For example, if unknown to you the beam energy on your instrument is consistently off by a constant bias, this will be reflected in all measurements equivalently - this source is correlated. However, if the difference is due to differences in charging on various semi-conductive samples then this contribution will be uncorrelated. To address this problem, you might decide to model the beam energy using a more sophisticated model with multiple input parameters that accounts for the various different sources of uncertainty. However, uncertainty calculations can become arbitrarily complex as we attempt to refine our understanding and our models of the input parameters. In the end, we have to make an educated judgement when to say good enough is good enough.

In the end, for the specific case of effective beam energy, I suspect that a good answer is to take the Duane-Hunt limit as the effective beam energy and add a small uncertainty for conductive samples and larger uncertainty for semi-conductive and coated non-conductive samples. However, representing the Duane-Hunt limit is a single number when it can change during the acquisition process due to charging and discharging ias already a simplification.

It should be noted that for complex energy-dispersive X-ray spectroscopy (EDX) measurements consisting of many characteristic lines for many elements, there may be hundreds of input parameters including mass fractions, mass absorption coefficients, mean ionization potentials, ionization cross-section exponents, weights-of-lines, beam energies, k-ratios and others. The issues associated with using multiple characteristic lines in a matrix correction will be discussed in a future article. While wavelength-dispersive spectrometer (WDS) measurements depend on fewer characteristic X-ray lines, the total number of input parameters can also be large when all the parameters associated with each k-ratio measurement are taken into account.

Because the number and character of the parameters change from measurement to measurement, careful bookkeeping of parameters is critical. This is why we have implemented a mechanism which allows us to perform these calculations using a well-vetted numerical algorithm library (Apache Commons Math 3.6.1) with custom extensions to label the rows and columns of the vectors and matrices. These extensions implement three mechanisms for propagating the uncertainties from input variables to output variables. They are 1) an analytical approach based on Jacobian matrices as described in Evaluation of Measurement Data Supplement 2 to the "Guide to the Expression of Uncertainty in Measurement" Extension to Any Number of Output Quantities[ISO/JCGM, 2011] (JCGM:102); 2) a Monte Carlo approach based as described in ISO Evaluation of Measurement Data Supplement 1 to the "Guide to the Expression of Uncertainty in Measurement" Propagation of Distributions Using a Monte Carlo Method[ISO/JCGM, 2008] (JCGM:101); and 3) a finite difference approach which approximates the Jacobian matrices as described in JCGM:102.

Variable	Reference	Notes
$C_{M,z}$		Mass fraction of element z in material M (standard
		or unknown)
E_0		Incident beam energy
t_C		Conductive or other coating thickness
Δz		Surface roughness parameter
θ		Take off angle (assumes perpendicular sample)
J_z	PAP Eqn. 7	Mean ionization potential of element z
A_z		Atomic weight of element z
E_a		Ionization edge energy (not considered to have un-
		certainty.)
m	PAP p.36	Exponent in the expression for the ionization cross
		section
$\left[^{\mu / ho } ight] _{M,l}$		Mass absorption coefficient (Material M , line l)

Table 2: Input variables. The top five represent experimental parameters and the bottom five represent physical parameters. While all the physical parameter have associated uncertainties, in some, the uncertainties are sufficiently small that they are unlikely to ever make a substantive contribution to the final uncertainties. The PAP column identifies where these parameters are defined within Pouchou and Pichoir, 1991[Pouchou & Pichoir, 1991].

The three different methods should produce similar results except in extraordinary situations. This triple redundant approach is how we convinced ourselves that the analytic partial derivatives are implemented correctly. For day-to-day use, the analytical approach is considered to be optimal as it is 1) relatively computationally efficient; 2) facilitates tracking the sensitivity to input uncertainties; and 3) it is deterministic.

2.4.1 Input Variables

Table 2 lists the variable inputs to the model. Additional details are provided in the paragraphs below. *Measurement* and *physics* parameters are values provided to the model by the user or from tabulations. *Output* parameters are computed during a calculation step. *Output* parameters from one step can become *intermediary* parameter inputs to subsequent steps. Each step lists the physics, measurement, intermediary and output parameters required.

Measurement Parameters Measurement parameters are those values which represent characteristics of the samples or parameters associated with instrumental choices. By the time that the uncertainty calculation is performed, the values for the unknown sample's mass fractions have been established through iteration. The uncertainties have been established for the composition of the standards and the other input parameters and we desire to calculate the uncertainty associated with the composition of the unknown.

- $C_{M,z}$ The mass fraction of element z for the material M. The uncertainty in the composition of the standard is propagated through to the final estimate of the standard material. (One for each element in each independent material involved in the measurement unknown, standards and coatings.)
- E_0 The kinetic energy of the incident electron beam. (One per spectrum/independent X-ray measurement.)
- t_C Thickness of a conductive or other coating on the surface of the sample. Assumed to be thin enough to have negligible effect on the trajectory or energy of the incident beam. If the samples are coated simultaneously then it is likely that the magnitudes are similar and uncertainties are highly correlated. (One per sample)
- Δz An estimate of the scale of surface roughness. (One per sample)
- θ The nominal take-off angle. Under the near normal conditions considered in this model, the uncertainty in the take-off angle is due to uncertainty in the position of the detector (fixed) and the uncertainty due to uncontrolled tilt of the sample (variable). The model chooses to emphasize the later as this tends to be more significant overall. (One per measurement)

Physics Parameters

- J_z Mean ionization potential for element z. Used to compute electron energy loss during transport through a material. Influences the range of the electron. (One per element)
- A_z Atomic weight for element z. The atomic weight is handled specially as in most cases the nominal book value is suitable for standards and unknown. However, there are situations in which a sample has been isotopically modified in which a different value might be required for the standard and unknown. (Optionally: one per element per material)
- E_a The ionization edge energy for the edge associated with the *a*-th atomic shell. This value is sufficiently well known relative to its use that no uncertainty is associated with it.
- m The exponent in the expression for the ionization cross-section. By associating an uncertainty with m, it allows us to model how uncertainty in the ionization cross-section influences the cross-section and the matrix correction.
- $[\mu/\rho]_{M,l}$ The MAC for the *l* characteristic X-ray in the material (or element) M. The MAC has long been recognized as one of the major sources of uncertainty in matrix correction. The MAC associated with a coating is labeled $[\mu/\rho]_{C,l}$.

Intermediary Parameters The output from one step often becomes the input to the next step. Various different intermediary parameters and the associated uncertainties are calculated in the model. The values and uncertainties associated with these parameters may be tracked to the end of the calculation or they may be dropped after they are no longer required. Dropping them can result in substantially faster calculations.

2.5 The Calculation

The calculation has been carefully organized as a series of 12 sequential steps (See Table 3). At each step, all the necessary parameters are either an input variable or an intermediary value calculated in a previous step. No parameter is calculated twice. At each step, the parameters being calculated are presented, followed (slightly indented) by the partial derivatives with respect to the physics, measurement and intermediary input parameters. Partials derivatives not presented can be assumed to be equal to zero. Each step represents a Jacobian and the full uncertainty propagation is represented by the matrix product of all 12 Jacobians.

		- P T	$\bullet \bullet \overline{W} Q_1^A(E_0) [y_S] \overline{\eta} J(U_0) q$	• • R	\bullet \bullet \bullet F R	$\bullet \bullet $	 ● ● ● ● ● 	\bullet \bullet \bullet \bullet A B	X	\bullet \bullet \bullet \bullet $F_R(\chi)$	• $F_{R,C}(\chi)$	• 2 A	
	$M J Z_b$	•	•	•	•	•							
$t_z \theta$									•	•	•		
$\left[\theta / \mu \right]$									•	•	•		
E_a			•	•									
$n = E_{(}$			•	•	•	•							
Z	•	ľ											
A	•												
ſ	•		•							(
Inputs	Step 1	Step 2	Step 3	Step 4	Step 5	Step 6	Step 7	Step 8	Step 9	Step 16	Step 11	Step 12	

an additional column is added. When a value is used as an input to a step, a \bullet is placed in the column. Intermediate values may be discarded when there is no \bullet in the column below the current step. The final step involves combining two iterations through the first 11 steps - once for the unknown and once for the standard. Table 3: This table summarizes the twelve steps in the calculation. The first row are physics and experimental values that are input into the calculation. The items \mathbf{J} , \mathbf{A} and \mathbf{Z} should be interpreted as the mean ionization potential, atomic number and mass fraction for all the elements in the material under consideration. When a new intermediate variable is computed in a step,

2.5.1 Step M, J and \overline{Z}_b

The first step involves calculating parameters dependent upon C_z , the elemental mass fraction, and J_z , the mean ionization potential, for all elements z present in the material. The mean ionization potential was allowed to have an uncertainty as J_z is an empirical parameter with numerous parameterizations in the literature and it influences the penetration depth of the incident electrons, a key parameter in the $\phi(\rho z)$ -model.

The three parameters calculated in this step are M (defined in Eqn. 5 of PAP), J (defined in Eqn. 6 of PAP) and \overline{Z}_b (defined on page 59 of PAP).

Physics J_z, A_z

Measurement C_z

Intermediary None

Outputs M, J, \overline{Z}_b

Reduced mass

$$M = \sum_{z} C_{z}(Z_{z}/A_{z})$$

$$\frac{\partial M}{\partial C_{z}} = (Z_{z}/A_{z})$$

$$\frac{\partial M}{\partial A_{z}} = -(C_{z}Z_{z})/A_{z}^{2}$$
(9)

Effective material mean ionization potential (MIP). The MIP is the amount of energy required on average to eject a valence electron.

$$\log(J) = \frac{1}{M} \sum_{z} C_{z}(Z_{z}/A_{z}) \log(J_{z})$$

$$\frac{\partial J}{\partial J_{z}} = \left(\frac{J}{M} \frac{Z_{z}}{A_{z}}\right) \frac{C_{z}}{J_{z}}$$

$$\frac{\partial J}{\partial C_{z}} = \left(\frac{J}{M} \frac{Z_{z}}{A_{z}}\right) (\log(J_{z}) - \log(J))$$

$$\frac{\partial J}{\partial A_{z}} = \left(\frac{J}{M} \frac{Z_{z}}{A_{z}}\right) \frac{C_{z}}{A_{z}} (\log(J) - \log(J_{z}))$$

$$\bar{Z}_{b} = \left(\sum_{z} C_{z} Z_{z}^{1/2}\right)^{2}$$

$$\frac{\partial \bar{Z}_{b}}{\partial C_{z}} = 2\sqrt{Z_{z} \bar{Z}_{b}}$$

$$(10)$$

2.5.2 Step D, P, T

These functions parameterize the model the deceleration of electrons in the sample. With $f(V)=\sum_{k=1}^3 D_k V^{P_k},$

$$\frac{dE}{d\rho s} = \frac{-M}{J} \frac{1}{f(V)}.$$
(12)

Physics m The exponent in ionization cross-section expression (see p. 36 of PAP)

Intermediaries J

Outputs D, P, T

$$\mathbf{D} = \left(6.6 \times 10^{-6}, \ 1.12 \times 10^{-5} (1.35 - 0.45J^2), \ 2.2 \times 10^{-6}/J \right)$$
(13)
$$\frac{\partial \mathbf{D}}{\partial J} = \left(0.0, \ -1.008 \times 10^{-5}J, \ -2.2 \times 10^{-6}/J^2 \right)$$

$$\mathbf{P} = (\ 0.78, \ 0.1, \ 0.25J - 0.5 \) \tag{14}$$
$$\frac{\partial \mathbf{P}}{\partial J} = (\ 0.0, \ 0.0, \ 0.25 \) \tag{15}$$

$$T_{k} = 1 + P_{k} - m$$

$$\frac{\partial \mathbf{T}}{\partial J} = \frac{\partial \mathbf{P}}{\partial J}$$

$$\frac{\partial T_{k}}{\partial m} = -1$$
(15)

2.5.3 Step $Q_l^A(E_0)$, [1/s]

Physics J_z, m, E_a

Measurement E_0

Intermediaries M, J, D, P, T

Outputs $Q_l^A(E_0)$ (ionization cross-section), [1/s] (inverse stopping power), $\bar{\eta}$ (backscatter coefficient), $J(U_0) \overline{W}$ and q.

Ionization cross section - parameterizes the likelihood of a core-shell ionization.

$$Q_l^A(E_0) = \frac{\log(U_0)}{U_0^m E_a^2} \qquad \text{where } U_0 = E_0/E_a \tag{16}$$

$$\frac{\partial Q_l^A(E_0)}{\partial E_0} = \frac{1 - m \log(U_0)}{U_0^{m+1} E_a^3}$$
$$\frac{\partial Q_l^A(E_0)}{\partial m} = -Q_l^A(E_0) \log(U_0)$$

Inverse of the stopping power - The stopping power is a measure of how quickly an electron will slow in a material.

$$[1/s] = \frac{U_0}{V_0 M} \sum_{k=1}^3 h_k$$

$$= \frac{J}{M E_a} \sum_{k=1}^3 h_k$$
(17)

where

$$h_k = D_k (V_0/U_0)^{P_k} (T_k U_0^{T_k} \log(U_0) - U_0^{T_k} + 1) / T_k^2,$$

and $U_0 = E_0/E_a$, $V_0 = E_0/J$ and $V_0/U_0 = E_a/J$.

$$\frac{\partial [1/s]}{\partial D_k} = \frac{J}{ME_a} \frac{h_k}{D_k}$$

$$\frac{\partial [1/s]}{\partial P_k} = \frac{Jh_k}{ME_a} \log(E_a/J)$$

$$\frac{\partial [1/s]}{\partial T_k} = \frac{J}{ME_a} \frac{1}{T_k} \left(D_k U_0^{T_k} \left(\frac{E_a}{J} \right)^{P_k} \log(U_0)^2 - 2h_k \right)$$

$$\frac{\partial [1/s]}{\partial M} = \frac{-[1/s]}{M}$$

$$\frac{\partial [1/s]}{\partial E_0} = \frac{J \log(U_0)}{E_0 E_a M} \sum_{k=1}^3 D_k \left(\frac{E_a}{J} \right)^{P_k} U_0^{T_k}$$

$$\frac{\partial [1/s]}{\partial J} = \frac{1}{ME_a} \sum_{k=1}^3 (1 - P_k) h_k$$

$$\bar{\eta} = 1.75 \times 10^{-3} \bar{Z}_b + 0.37 \left[1 - \exp(-0.015 \bar{Z}_b^{1.3}) \right]$$

$$\frac{\partial \bar{\eta}}{\partial \bar{Z}_b} = 1.75 \times 10^{-3} + 7.215 \times 10^{-3} \exp(-0.015 \bar{Z}_b^{1.3}) \bar{Z}_b^{0.3}$$
(18)

$$J(U_0) = 1 + U_0(\log(U_0) - 1)$$
(19)

$$\frac{\partial J(U_0)}{\partial E_0} = \log(U_0)/E_a$$

where $J(U_0)$ is a intermediate parameterization in the backscatter factor model of Coulon and Zeller[Coulon & Zeller, 1973] as quote by PAP.

Because \overline{W} , the average backscatter coefficient, and q, a useful intermediary, are univariate functions of only \overline{Z}_b , they are trivially handled using the univariate chain rule and are not worth breaking out into a separate step.

$$\overline{W} = 0.595 + \overline{\eta}/3.7 + \overline{\eta}^{4.55}$$

$$\frac{\partial \overline{W}}{\partial \overline{Z}_b} = (1/3.7 + 4.55\overline{\eta}^{3.55}) \frac{\partial \overline{\eta}}{\partial \overline{Z}_b}$$

$$q = \frac{2\overline{W} - 1}{1 - \overline{W}}$$

$$\frac{\partial q}{\partial \overline{Z}_b} = \frac{1}{(\overline{W} - 1)^2} \frac{\partial \overline{W}}{\partial \overline{Z}_b}$$

$$(21)$$

2.5.4 Step *R* **and** $\phi(0)$

Measurement E_0

Physics E_a

Intermediaries $\bar{Z}_b, q, \bar{\eta}$

Outputs R (backscatter factor), $\phi(0) = \phi(\rho z)|_{z=0}$

$$G(U_{0}) = \frac{U_{0} - 1 - (1 - U_{0}^{-1 - q})/(1 + q)}{(2 + q)J(U_{0})}$$

$$\frac{\partial G(U_{0})}{\partial E_{0}} = \frac{1 - U_{0}^{-2 - q}}{E_{a}J(U_{0})(2 + q)}$$

$$\frac{\partial G(U_{0})}{\partial q} = \frac{\frac{(1 - U_{0}^{-1 - q}) - U_{0}^{-1 - q}\log(U_{0})}{1 + q} - G(U_{0})J(U_{0})}{J(U_{0})(2 + q)}$$

$$\frac{\partial G(U_{0})}{\partial J(U_{0})} = \frac{-G(U_{0})}{J(U_{0})}$$

$$R = 1 - \bar{\eta}\overline{W}[1 - G(U_{0})]$$

$$\frac{\partial R}{\partial \bar{\eta}} = \overline{W}[G(U_{0}) - 1]$$

$$(22)$$

$$\frac{\partial R}{\partial \overline{W}} = \overline{\eta}[G(U_0) - 1]$$

$$\frac{\partial R}{\partial E_0} = \overline{\eta}\overline{W}\frac{\partial G(U_0)}{\partial E_0}$$

$$\frac{\partial R}{\partial q} = \overline{\eta}\overline{W}\frac{\partial G(U_0)}{\partial q}$$

$$\frac{\partial R}{\partial J(U_0)} = \overline{\eta}\overline{W}\frac{\partial G(U_0)}{\partial J(U_0)}$$

$$\phi(0) = 1 + 3.3(1 - 1/U_0^{2-2.3\overline{\eta}})\overline{\eta}^{1.2}$$

$$\frac{\partial \phi(0)}{\partial \overline{\eta}} = 3.96\overline{\eta}^{0.2}(1 - U_0^{2.3\overline{\eta}-2}) - 7.59\overline{\eta}U_0^{2.3\overline{\eta}-2}\log(U_0)$$

$$\frac{\partial \phi(0)}{\partial E_0} = -3.3\overline{\eta}^{1.2}(2.3\overline{\eta} - 2)U_0^{2.3\overline{\eta}-3}/E_a$$
(24)

2.5.5 Step F, \bar{R}

Measurement E_0

 ${\bf Intermediaries} \ \bar{Z}_b, \, [1\!\!/ s], \, Q_l^A(E_0), \, \phi(0), \, R$

Outputs $F = \int_0^\infty \phi(\rho z) \ d\rho z, \ \bar{R}$ (average depth of ionization)

Here the expressions $[{}^{F\!/\!\bar{R}}]$ and F are computed directly and then \bar{R} is computed.

$$X = 1 + 1.3 \log(\bar{Z}_b) \qquad Y = 0.2 + \bar{Z}_b/200$$
(25)
$$\frac{\partial X}{\partial \bar{Z}_b} = 1.3/\bar{Z}_b \qquad \frac{\partial Y}{\partial \bar{Z}_b} = 1/200$$

$$[F/R] = 1 + \frac{X \log(1 + Y(1 - U_0^{-0.42}))}{\log(1 + Y)}$$
(26)

$$\begin{split} \frac{\partial [F/\bar{R}]}{\partial X} &= \frac{\log(1+Y(1-U_0^{-0.42}))}{\log(1+Y)}\\ \frac{\partial [F/\bar{R}]}{\partial Y} &= \frac{X \left[\frac{(U_0^{0.42}-1)\log(1+Y)}{U_0^{0.42}+(U_0^{0.42}-1)Y} - \frac{\log(1+Y-Y/U_0^{0.42})}{1+Y} \right]}{\log(1+Y)^2} \end{split}$$

$$\begin{split} &\frac{\partial ^{[F/\bar{R}]}}{\partial \bar{Z}_b}=\frac{\partial ^{[F/\bar{R}]}}{\partial X}\frac{\partial X}{\partial \bar{Z}_b}+\frac{\partial ^{[F/\bar{R}]}}{\partial Y}\frac{\partial Y}{\partial \bar{Z}_b}\\ &\frac{\partial ^{[F/\bar{R}]}}{\partial U_0}=\frac{0.42XY}{U_0^{1.42}(1+Y(1-U_0^{-0.42}))\log(1+Y)} \end{split}$$

F is the area under the $\phi(\rho z)$ curve.

$$F = R [1/s] / Q_l^A(E_0)$$

$$\frac{\partial F}{\partial R} = \frac{[1/s]}{Q_l^A(E_0)}$$

$$\frac{\partial F}{\partial [1/s]} = \frac{R}{Q_l^A(E_0)}$$

$$\frac{\partial F}{\partial Q_l^A(E_0)} = \frac{-R [1/s]}{Q_l^A(E_0)^2}$$
(27)

Under most measurement conditions, $[{\it F}/{\bar {\it R}}] > = ~\phi(0).$ In which case,

$$\bar{R} = F/\left[F/\bar{R}\right]$$

$$\frac{\partial \bar{R}}{\partial F} = \frac{1}{\left[F/\bar{R}\right]}$$

$$\frac{\partial \bar{R}}{\partial \left[F/\bar{R}\right]} = \frac{-F}{\left[F/\bar{R}\right]^2}.$$
Otherwise, if $\left[F/\bar{R}\right] < \phi(0),$

$$\bar{R} = F/\phi(0)$$

$$\frac{\partial \bar{R}}{\partial F} = \frac{1}{\phi(0)}$$

$$\frac{\partial \bar{R}}{\partial \phi(0)} = \frac{-F}{\phi(0)^2}.$$
(28)

The derivatives with respect to R, [1/s] and $Q_l^A(E_0)$ are computed from $\frac{\partial \bar{R}}{\partial F}$ for the two cases.

$$\begin{split} &\frac{\partial \bar{R}}{\partial R} = \frac{\partial \bar{R}}{\partial F} \frac{\partial F}{\partial R} \\ &\frac{\partial \bar{R}}{\partial [{}^1\!/s]} = \frac{\partial \bar{R}}{\partial F} \frac{\partial F}{\partial [{}^1\!/s]} \\ &\frac{\partial \bar{R}}{\partial Q_l^A(E_0)} = \frac{\partial \bar{R}}{\partial F} \frac{\partial F}{\partial Q_l^A(E_0)} \end{split}$$

2.5.6 Step P, b

Measurement E_0

Intermediaries $\bar{R}, F, \bar{Z}_b, \phi(0)$

Outputs $P = \left. \frac{d\phi(\rho z)}{d\rho z} \right|_{z=0}$ (PAP Eqn. 29), *b* (Parameter in Eqn. 5, PAP Appendix 4)

$$g = 0.22 \log(4 \,\bar{Z}_b) \left(1 - 2 \exp(-\bar{Z}_b(U_0 - 1)/15)\right)$$
(30)
$$\frac{\partial g}{\partial \bar{Z}_b} = \frac{g}{\bar{Z}_b \log(4\bar{Z}_b)} + 0.029\bar{3} \exp(-\bar{Z}_b(U_0 - 1)/15)(U_0 - 1) \log(4\bar{Z}_b)$$
$$\frac{\partial g}{\partial U_0} = 0.029\bar{3} \exp(-\bar{Z}_b(U_0 - 1)/15)\bar{Z}_b \log(4\bar{Z}_b)$$

$$h = 1 - 10(1 - 1/(1 + U_0/10))/\bar{Z}_b^2$$
(31)

$$\frac{\partial h}{\partial \bar{Z}_b} = 20(1 - 1/(1 + U_0/10))/\bar{Z}_b^3$$

$$\frac{\partial h}{\partial U_0} = \frac{-1}{((1 + U_0/10)\bar{Z}_b)^2}$$

$$b = \sqrt{2} \left(1 + \sqrt{1 - \bar{R}} \phi(0)/F \right) / \bar{R}$$
(32)

$$\frac{\partial b}{\partial \bar{R}} = \frac{-b}{\bar{R}} - \frac{\phi(0)}{F\bar{R}\sqrt{2(1 - \phi(0)\bar{R}/F)}}$$

$$\frac{\partial b}{\partial \phi(0)} = \frac{-1}{F\sqrt{2(1 - \phi(0)\bar{R}/F)}}$$

$$\frac{\partial b}{\partial F} = \frac{\phi(0)}{F^2\sqrt{2(1 - \phi(0)\bar{R}/F)}}$$
converte a b⁴ and determine relation it is less than 0.0 h \bar{D}^2(h - 2\phi(0)/F)

Compute $g h^4$ and determine whether it is less than $0.9 b \bar{R}^2(b - 2\phi(0)/F)$. If it is less then proceed to calculate P as

$$P = g h^{4} F/\bar{R}^{2}$$

$$\frac{\partial P}{\partial g} = P/g$$

$$\frac{\partial P}{\partial h} = 4P/h$$
(33)

$$\frac{\partial P}{\partial F} = P/F$$
$$\frac{\partial P}{\partial \bar{R}} = -2P/\bar{R}.$$

Otherwise, redefine $g h^4 = 0.9 b \bar{R}^2 (b - 2\phi(0)/F)$, in which case

$$P = 0.9 b \bar{R}^2 (b - 2\phi(0)/F) F/\bar{R}^2$$

$$= 0.9(b^2 F - 2b\phi(0))$$

$$\frac{\partial P}{\partial \phi(0)} = 1.8 \left[(Fb - \phi(0)) \frac{\partial b}{\partial \phi(0)} - b \right]$$

$$\frac{\partial P}{\partial F} = 0.9b^2.$$
(34)

2.5.7 Step *a*

Physics/Measurement None

Intermediaries $\phi(0), P, \bar{R}, F, b$

Outputs a (Parameter in Eqn. 5), ϵ (relates a and b)

$$a = \frac{P + b(2\phi(0) - bF)}{bF(2 - b\bar{R}) - \phi(0)}$$
(35)
$$\frac{\partial a}{\partial P} = \frac{1}{bF(2 - b\bar{R}) - \phi(0)} \frac{\partial a}{\partial \phi(0)} = \frac{3b^2F + P - 2b^3F\bar{R}}{(bF(2 - b\bar{R}) - \phi(0))^2} \frac{\partial a}{\partial \bar{R}} = \frac{b^2F(P + 2b\phi(0) - b^2F)}{(bF(2 - b\bar{R}) - \phi(0))^2} \frac{\partial a}{\partial F} = b\frac{(P(b\bar{R} - 2) + b\phi(0)(2b\bar{R} - 3))}{(bF(2 - b\bar{R}) - \phi(0))^2} \frac{\partial a}{\partial b} = -2\frac{F(P - b(\phi(0) + P\bar{R}) + b^2(F - \phi(0)\bar{R})) + \phi(0)^2}{(bF(2 - b\bar{R}) - \phi(0))^2}$$

PAP ensure that a and b are sufficiently different by enforcing a minimum on the quantity ϵ defined as

$$\epsilon = \begin{cases} (a-b)/b & \text{if } |(a-b)/b| > 10^{-6} \\ 10^{-6} & \text{otherwise.} \end{cases}$$
(36)

If $\epsilon = 10^{-6}$ then $a = b(1 + \epsilon)$.

$$\frac{\partial \epsilon}{\partial b} = \begin{cases} \left(b\frac{\partial a}{\partial b} - a\right)/b^2 & \text{if } \epsilon \neq 10^{-6} \\ 0 & \text{otherwise} \end{cases}$$
$$\frac{\partial \epsilon}{\partial a} = \begin{cases} \frac{1}{b} & \text{if } \epsilon \neq 10^{-6} \\ 0 & \text{otherwise} \end{cases}$$

The partial derivatives of ϵ with respect to P, $\phi(0)$, \overline{R} and F can be computed using the chain rule.

2.5.8 Step A and B

Physics/Measurement None

Intermediaries ϵ , b, F, P, $\phi(0)$

Outputs A and B (Parameters in Eqn. 5)

$$B = \frac{b^2 F(1+\epsilon) - P - \phi(0)b(2+\epsilon)}{\epsilon}$$

$$\frac{\partial B}{\partial \epsilon} = \frac{P + 2b\phi(0) - b^2 f}{\epsilon^2}$$

$$\frac{\partial B}{\partial b} = \frac{(2b(1+\epsilon)F - (2+\epsilon)\phi(0))}{\epsilon}$$

$$\frac{\partial B}{\partial b} = b^2 \left(\frac{1+\epsilon}{\epsilon}\right)$$

$$\frac{\partial B}{\partial P} = \frac{-1}{\epsilon}$$

$$\frac{\partial B}{\partial \phi(0)} = -b\left(\frac{2+\epsilon}{\epsilon}\right)$$

$$A = \left(\frac{B}{b} + \phi(0) - bF\right) \left(\frac{1+\epsilon}{\epsilon}\right)$$

$$\frac{\partial A}{\partial \epsilon} = \frac{-A}{\epsilon(1+\epsilon)} + \left(\frac{1}{b}\frac{\partial B}{\partial \epsilon}\right) \left(\frac{1+\epsilon}{\epsilon}\right)$$

$$\frac{\partial A}{\partial b} = \left(\frac{1}{b}\frac{\partial B}{\partial b} - \left(\frac{B}{b^2} + F\right)\right) \left(\frac{1+\epsilon}{\epsilon}\right)$$

$$\frac{\partial A}{\partial F} = \left(\frac{\frac{\partial B}{\partial F} - b^2}{b}\right) \left(\frac{1+\epsilon}{\epsilon}\right)$$
(37)

$$\frac{\partial A}{\partial \phi(0)} = \left(\frac{b + \frac{\partial B}{\partial \phi(0)}}{b}\right) \left(\frac{1 + \epsilon}{\epsilon}\right)$$
$$\frac{\partial A}{\partial P} = \frac{1}{b} \frac{\partial B}{\partial P} \left(\frac{1 + \epsilon}{\epsilon}\right)$$

2.5.9 Step χ

Physics $[\mu/\rho]_M$

Measurement θ

Intermediaries None

Outputs χ (The reduced MAC)

$$\chi = [\mu/\rho]_M \csc(\theta)$$

$$\frac{\partial \chi}{\partial [\mu/\rho]_M} = \csc(\theta)$$

$$\frac{\partial \chi}{\partial \theta} = -\chi \cot(\theta)$$
(39)

2.5.10 Step $F_R(\chi)$

Measurement dz

Intermediaries b, A, B, $\phi(0)$, ϵ

Outputs $F_R(\chi)$ (Emitted intensity compensated for surface roughness)

We have extended the base XPP model to include a term to model X-ray absorption variability due surface roughness. The model is quite crude but nonethe-less provides a useful mechanism for estimating how much of an influence surface quality will have on a measurement.

$$F_R(\chi) = \exp(-z\chi)F(\chi) \tag{40}$$

The surface roughness is defined by a parameter $z = 0 \pm \Delta z$ where Δz is a measure of the vertical roughness experienced by the exiting X-rays. Characterizing roughness is extremely difficult. A full characterization at a certain horizontal resolution involves creating a height map of the surface using an atomic force, confocal or similar microscope. There are summary metrics that have been developed to encapsulate properties of the height map - 2D mean roughness, root-mean squared roughness, spectral analysis, fractal analysis and many others. None of these however can be readily converted into a simple number that can be used in uncertainty calculations. Furthermore, it is rare that we actually have a height map on a sample of interest. Instead, rather than un-necessarily complicate the issue a crude, ill-defined but intuitive parameter, Δz , which should be thought of as a vertical length scale of features near the beam entry point, was selected.

Because the model does not account for how roughness effects the electron trajectory, it will fail when the surface roughness is of the order of the electron range. Intuitively, we don't expect surface roughness to have a strong influence on the backscatter coefficient because, over micrometer scale distances, the sample is still on average flat and the electron beam momentum perpendicular to the surface. This is very different from the situation in which the sample is tilted.

$$F_{R}(\chi)|_{z=0} = \frac{\phi(0) + B/(b+\chi) - Ab\epsilon/(b(1+\epsilon) + \chi)}{b+\chi}$$

$$\frac{\partial F_{R}(\chi)}{\partial z}|_{z=0} = -\chi F_{R}(\chi)$$

$$\frac{\partial F_{R}(\chi)}{\partial A}|_{z=0} = \frac{-b\epsilon}{(b+\chi)(b(1+\epsilon) + \chi)}$$

$$\frac{\partial F_{R}(\chi)}{\partial B}|_{z=0} = \frac{1}{(b+\chi)^{2}}$$

$$\frac{\partial F_{R}(\chi)}{\partial b}|_{z=0} = \frac{\left(\frac{-B}{(b+\chi)^{2}} + \frac{-A_{\chi}\epsilon}{(b(1+\epsilon) + \chi)^{2}}\right) - F_{R}(\chi)}{b+\chi}$$

$$\frac{\partial F_{R}(\chi)}{\partial \chi}|_{z=0} = \frac{\left(\frac{Ab\epsilon}{(b(1+\epsilon) + \chi)^{2}} - \frac{B}{(b+\chi)^{2}}\right) - F_{R}(\chi)}{b+\chi}$$

$$\frac{\partial F_{R}(\chi)}{\partial \phi(0)}|_{z=0} = \frac{1}{b+\chi}$$

$$\frac{\partial F_{R}(\chi)}{\partial \epsilon}|_{z=0} = \frac{-Ab}{(b(1+\epsilon) + \chi)^{2}}$$
(41)

2.5.11 Step $F_{R,C}(\chi)$

Physics $[\mu/\rho]_{C,l}$

Measurement t_C , θ

Intermediaries $F_R(\chi)$

Outputs $F_{R,C}(\chi)$ (Emitted intensity compensated for roughness and coatings)

We also implement a crude model of absorption by a surface coating. Typically surface coatings are used to place a conductive layer on the surface of a nonconductive material to dissipate accumulated charge. However, this model can also be used to model thin surface contamination layers like oxide layers on certain metals. The model assumes that the only effect of the layer is to absorb outgoing Xrays. It neglects the influence of the layer on the energy and incident direction of the incoming electron beam.

The additional absorption is modeled

$$F_{R,C}(\chi) = \exp\left(-\left[\frac{\mu}{\rho}\right]_{C,l} t_C \csc(\theta)\right) F_R(\chi) |_{z=0}$$

$$\frac{\partial F_{R,C}(\chi)}{\partial t_C} = -F_{R,C}(\chi) \left[\frac{\mu}{\rho}\right]_{C,l} \csc(\theta)$$

$$\frac{\partial F_{R,C}(\chi)}{\partial \theta} = F_{R,C}(\chi) \left[\frac{\mu}{\rho}\right]_{C,l} t_C \csc(\theta) \cot(\theta)$$

$$\frac{\partial F_{R,C}(\chi)}{\partial \left[\frac{\mu}{\rho}\right]_{C,l}} = -F_{R,C}(\chi) t_C \csc(\theta)$$

$$\frac{\partial F_{R,C}(\chi)}{\partial F_R(\chi)} = F_{R,C}(\chi) / F_R(\chi) |_{z=0}$$

$$(42)$$

Some labs coat their standards and unknown at the same time to ensure that the layer thicknesses are equivalent across the samples. In this case, the thickness may not be known with precision but the uncertainty in the thickness is correlated across the samples. If the samples and unknown are coated at different times, the thickness may not be known with any worse precision but the thicknesses are less correlated. The degree of correlation between the thicknesses reflects the similarity of the procedure used to coat standard and unknown.

2.5.12 Step Z and A

Physics/Measurement None

Intermediaries $F_{R,C}^{Unk}(\chi), F^{Unk}, F_{R,C}^{Std}(\chi), F^{Std}$

Outputs Z (the atomic number correction), A (absorption correction)

All the previous steps must be performed once for the unknown and once for the standard. This step combines the results of the unknown and standard calculations to determine the conventional Z (atomic number correction) and A (absorption) correction factors. The calculation can proceed in parallel (on separate CPUs as distinct calculations, for example) for the unknown and all necessary standards for each characteristic X-ray involved in the measurement.

$$A = \frac{F_{R,C}^{Unk}(\chi)/F^{Unk}}{F_{R,C}^{Std}}$$

$$\frac{\partial A}{\partial F_{R,C}^{Unk}(\chi)} = A/F_{R,C}^{Unk}(\chi)$$
(43)



Figure 1: Examples of simulated K240 spectra at various incident beam energies scaled the same maximum intensity.

$$\begin{split} &\frac{\partial A}{\partial F^{Unk}} = -A/F^{Unk} \\ &\frac{\partial A}{\partial F^{Std}_{R,C}(\chi)} = -A/F^{Std}_{R,C}(\chi) \\ &\frac{\partial A}{\partial F^{Std}} = A/F^{Std} \end{split}$$

$$Z = F^{Unk}/F^{Std}$$

$$\frac{\partial Z}{\partial F^{Unk}} = 1/F^{Std}$$

$$\frac{\partial Z}{\partial F^{Std}} = -Z/F^{Std}$$
(44)

3 Example Calculation

To demonstrate various ways that these uncertainty calculations can provide insight into measurements of composition, we will explore four perspectives on the uncertainty budget for engineered glass K240 (see Table 4).

Beam Energy What beam energy produces the smallest overall uncertainty?

- Mass Absorption Coefficients How does uncertainty in the elemental MACs contribute to the uncertainty in the matrix correction?
- **Standard Selection** How does the choice of standard (pure element, binary vs. similar, matched standard) influence the uncertainty budget?
- **Surface roughness** How smooth does the surface need to be to produce a negligible contribution to the uncertainty budget?



Figure 2: The total absolute uncertainty on the measurement of mass fraction in K240 for beam energies between 12 keV to 30 keV. The standards selected were pure elements (Mg, Si, Ti, Zn, Zr) and binary compounds (BaF₂ for Ba and SiO₂ for O). A) The uncertainty for O is largest over the entire range of beam energies. It increases as the excitation depth and thus also the mean absorption path length increases. Many but not all elements show this pattern. Elements like Zn however show a decrease in uncertainty as the overvoltage increases from barely able to excite (U = 1.2) at the lowest beam energies. B) The same measurement except measured oxygen has been replaced with oxygen computed from stoichiometric assumptions.

		Mass	Atomic	Char.	Mass Abs.	Ionization
Element	Z	Fraction	Fraction	X-ray	Co efficient	Energy (keV)
Oxygen	8	0.3400	0.6290	O K- L_3	5813	0.53
Magnesium	12	0.0302	0.0368	Mg K-L ₃	3281	1.31
Silicon	14	0.1870	0.1971	Si K- L_3	1583	1.84
Titanium	22	0.0600	0.0371	Ti K- L_3	225	4.97
Zinc	30	0.0402	0.0182	$Zn \text{ K-L}_3$	104	9.66
Zirconium	40	0.0740	0.0240	$\operatorname{Zr} L_3$ - M_5	1518	2.22
Barium	56	0.2687	0.0579	Ba L ₃ -M ₅	190	5.25

Table 4: The nominal composition of K240 glass and characteristic line choice. K240 is an engineered glass and the composition is not certified. The 'Char X-ray' column contains the characteristic line used. At 15 keV and 20 keV, the beam is insufficiently energetic to excite the K-shell in Zr and Ba so we measure a L-family transition.

3.1 Beam Energy

Figure 2 shows the calculated uncertainty for the measurement of K240 using BaF_2 as a standard for Ba, SiO_2 as a standard for O and pure elements for the rest. The uncertainty in the k-ratios was selected to model a dose of about 60 nA s. The roughness was assumed to be about 10 nm and the uncertainty in the take-off angle of 40° was assumed to be about 0.5°. The uncertainty in the beam energy was assumed to ± 0.1 keV at all beam energies. The samples were assumed to have no conductive coating. These values were selected to be somewhat typical yet interesting. The characteristic X-rays selected for each line are those listed in Table 4.

Figure 2 A) shows that the the uncertainty in oxygen is the largest and increases with beam energy. This is largely a consequence of two influences. First, the overvoltage is large, even at 12 keV, so there is little benefit from additional overvoltage. Second, the MAC is relatively large for O K-L₃ in K240. Thus as the beam energy increases, the excitation volume increases and the mean emission depth increases leading to a decreasing fraction of the O K-L₃ X-rays escaping the sample and a larger dependence on the uncertainty in the MAC. Zr L₃-M₅, Mg K-L₃ and Si K-L₃ show similar behavior for similar reasons.

As the ionization edge energy increases and the mass absorption coefficient decreases, the dependence on beam energy changes. Zn K-L₃ has the highest ionization edge energy and the smallest MAC. At the lower beam energies, the low overvoltage produces few X-rays and poor count statistics produces a lot of uncertainty. This could be mitigated by measuring with a larger probe dose. Since the MAC is small, even at the highest beam energies, most of the X-rays escape the sample and the absorption correction plays a relatively small role in the uncertainty budget. Ba L_3-M_5 and Ti K-L₃ display similar behaviour to Zn K-L₃.

Any optimization of the total uncertainty is going to be dominated by the uncertainty in the oxygen. If fact, the uncertainty in the oxygen can feed back through the matrix correction into the other element uncertainties and increase them. One strategy to deal with this is to calculate the oxygen using stoichiometric assumptions. In this way, the uncertainty in the oxygen is a simple function (see Part I) of the uncertainties in the other elements and is not dependent on the O K-L₃ MAC in K240 and other less well known parameters. The result is shown in Figure 2 B. In comparison, the net uncertainty (added in quadrature) for A is minimum at 12 keV but the net uncertainty for B) is at a minimum at 17 keV. In A) the oxygen uncertainty dominates and we might benefit from selecting a beam energy even smaller than 12 keV.

Of course, the quadrature metric is only one of many possible metrics that can be used to optimize the measurement process. If your primary interest is a single trace element, then you may choose to optimize on this element and the process would likely be influenced by the generating a sufficient overvoltage to strongly ionize the line of interest.

3.2 Mass Absorption Coefficients

Figure 3 reveals a lot about the relationship between the uncertainty in the input parameters and the resulting uncertainty in the output parameters. The figure represents a subset of the full correlation matrix but focuses on the relationship between input and output variable. The figure is color coded to reveal the Pearson's correlation coefficient that describes the relationship between the two random variables under consideration. The absolute value of the correlation coefficient quantifies how much information knowledge about one variable reveals about the other. The sign determines how multiplying and dividing the variables will influence the resulting uncertainty. Dividing positively correlated variables will have reduced uncertainty relative to uncorrelated variables will emultiplying negatively correlated variables will increase uncertainty relative to uncorrelated variables will increase uncertainty relative to uncorrelated variables while multiplying negatively correlated variables will increase uncertainty relative to uncorrelated variables will multiplying negatively correlated variables will have decreased uncertainty.

Consider the relevant example of a matrix matched standard. The matrix correction factor of two similar material will be positively correlated and close to unity. Taking the ratio will reduce the uncertainty of the resulting value leading to accurate measurements that don't have a strong dependence on the matrix correction factors. Contrary to common perception, it isn't the fact that the magnitude of the matrix correction are similar that is critical. It is the fact that the matrix correction factors are highly correlated that ultimately reduces the resulting uncertainty.

Consider the top set of rows representing the absorption correction terms in Figure 3. In general, each absorption correction output is correlated with the uncertainty in the beam energies and take-off angles at which the standard and unknown were collected but not the beam energies or take-off angles at which other standards were collected. This output is also weakly correlated with the mean ionization potential for all elements as the stopping power depends on other elements. The absorption correction terms are also correlated with



ionization potentials, the take-off angles, the mass absorption coefficients and the ionization cross section. The significance and combined ZAF (matrix correction) outputs. The vertical axis represent the output parameters and the horizontal axis represents a combination of input and calculated parameters. Positively correlated parameters are shown in shades of blue Proceeding from parameters. To the right of the output parameters are blocks of input parameters representing the beam energies, the mean of the contribution from the uncertainty associated with each of the input parameters is determined both by the correlation Figure 3: A color encoded visualization of the covariance matrix elements related to the Z (atomic number), A (absorption) left-to-right on the horizontal axis, the square blocks on the left represents the correlation relationships between the output and negatively correlated parameters are shown in shades of red as shown in the scale in the upper-left. coefficient and the magnitude of the uncertainty associated with the input parameters.



Figure 4: The calculated mass absorption coefficients (MACs) for K240 glass and the mass-fraction weighted elemental MACs. The Mg K-L₃ transition is seen to be predominantly absorbed by barium due to the proximity of the Ba L-edges and despite the proximity of the titanium K-edge, the O K-L₃ is almost equally absorbed by all the elements.

the mass absorption coefficients for the measurement's characteristic X-ray for all the elements present in the material. The terms are more correlated with elements that are stronger absorbers. Like the beam energy and take-off angle, the absorption term is only correlated with the surface roughness associated with the sample and the standard. The ionization cross section is also diagonal. The rows at the bottom of Figure 3 represent the atomic number correction. The atomic number correction is seen to correlate with the beam energy of the standard and unknown. It also correlates with the mean ionization potential. However, there is no relationship between the atomic number correction and the take-off angle, mass absorption coefficients, surface roughness or ionization cross-section. The rows in the middle of Figure 3 represent the total matrix correction, the product of the Z, A and F-terms. As one would expect, the product inherits correlation relationships from both the atomic number and absorption terms.

We can dig further into the relationship between the absorption correction and the mass absorption coefficients (MACs). Consider Figure 4. These plots show the elemental mass absorption coefficients and the computed effective mass absorption coefficient for K240 glass (red). The horizontal axis represents energy and the vertical axis represents the strength of the absorption coefficient in cm^2/g . The magnitude of the elemental MACs are scaled by the elemental mass fraction in K240 glass to represent each element's contribution to the material MAC. The general trends seen in the elemental MACs are those you would expect. As X-ray energy increases, the MACs generally become smaller as the material becomes more transparent. However, this trend is disrupted at absorption edges. These edges are at the energy necessary to ionize a core shell in the element. There is an abrupt increase in the MAC at the absorption edge when it becomes energetically possible for an X-ray to ionize that shell. Thus the relationship between a characteristic X-ray's energy and the ionization edge energies of the other elements in the material often determines the importance

	Simple	:					
	A	dA	dA/A	A	dA	dA/A	$\frac{[dA/A]_s}{[dA/A]_c}$
A[Ba L ₃ -M ₅]	1.015	0.001	0.11%	0.986	0.000	0.03%	4.28
$A[O K-L_3]$	0.761	0.065	8.61%	1.021	0.071	6.93%	1.24
A[Si K-L ₃]	0.611	0.014	2.29%	0.997	0.003	0.33%	6.86
A[Ti K-L ₃]	0.948	0.001	0.09%	0.986	0.000	0.02%	3.60
A[Mg K-L ₃]	0.389	0.040	10.23%	0.389	0.040	10.23%	1.00
$A[Zn \ K-L_3]$	0.977	0.001	0.12%	0.977	0.001	0.12%	1.00
$A[Zr L_3-M_5]$	0.746	0.064	8.58%	0.746	0.064	8.58%	1.00

Table 5: Comparing how the uncertainty in the absorption correction changes when simple standards (pure elements or simply stoichiometric compounds) are replaced with a standard material similar to the unknown, K240. For the columns labeled "Simple", the standards were pure elements except for O and Ba which were SiO₂ and BaF₂ respectively. For the columns labeled, "BaSi(Ti₃O₉)", "BaSi(Ti₃O₉)" was used as a standard for Ba, Si, Ti, and O. The right-most column represents the ratio of the uncertainty for the simple standard relative to the similar standard. The use of a similar standard improved the uncertainty of the absorption correction by a factor of 1.2 to 6.9 for those elements. As expected, the elements for which pure elements were used in both measurements, the uncertainty was unchanged.

of the absorption correction term. The energies of the characteristic X-rays used in this calculation are shown as vertical lines labeled O, Mg, Si, Ba and Ti. Zn K-L₃ and Zr L₃-M₅ are above the range of energies displayed and are not visible.

The least energetic X-ray involved in the measurement process is the O K-L₃. The MAC for O K-L₃ is the largest in K240. The energy of the O K-L₃ X-ray is just below the O K-edge and just above the Ti L-edges. Ba, Ti, Zr and Si all contribute almost equally to the total MAC. The proximity to the Ti L-edges is likely to increase the total uncertainty of the material MAC. When we look at Figure 3, we see that the absorption correction is most significantly negatively correlated with the Ti elemental MAC followed by a significant positive correlation with the Si elemental MAC.

The next least energetic X-ray is the Mg K-L₃. As Figure 4 shows, the Ba elemental MAC is the dominant contribution to the K240 material MAC and Figure 3 shows that the absorption correction is strongly negatively correlated with the Ba elemental MAC.

3.3 Standard Selection

The use of standards with a composition similar to the unknown is a common tactic for improving the accuracy of a compositional measurement. When the standard and unknown are identically compositions, the matrix correction will be unity with zero uncertainty $((x + \epsilon)/(x + \epsilon) = 1 \text{ except for } x \pm \epsilon = 0)$. There



Figure 5: The total uncertainty measuring the elements in K240 glass for two different selections of standards. A) Simple standards BaF_2 for $Ba L_3-M_5$, SiO_2 for O K-L₃ and pure elements for the remainder. B) Similar standards $BaTiSi_3O_9$ for $Ba L_3-M_5$, Ti K-L₃, Si K-L₃ and O K-L₃ and pure elements for the remainder. Using similar standards is seen to improve the uncertainty budget for Si, Ti, O and less so Ba, the elements that the standard and unknown have in common. The improvement increases with beam energy as the absorption correction becomes more significant.

will continue to be uncertainty from other uncontrolled factors like the beam energy and surface roughness. The classic strategy has been to select a material that produces a correction factor close to unity. However, a matrix correction factor near unity is necessary but not sufficient for improved accuracy. It is entirely possible to have matrix correction factors which are coincidentally close to unity even when the uncertainties remain large.

Table 5 compares the absorption correction when measuring K240 glass using simple pure element or binary stoichiometric compounds with measuring it using a similar material Benitoite (BaTi(Si₃O₉). The similar standard lack the elements Mg, Mn and Zr so we continue to use pure elements for these. The magnitude of the absorption correction generally is closer to unity for the similar standard than the simple standards. For example, there is a 24% correction for O using a SiO₂ standard but a 2% correction using Benitoite. Furthermore, when we compare the ratio of the fractional uncertainty for simple vs similar standards we see that the uncertainty is improved by a factor of between 1.2 for oxygen and 6.9 for silicon using a similar standard.

The uncertainty is reduced because of the correlations between the matrix correction factors associated with the unknown and the standard. When the unknown and standard are identical, the correlation coefficient is unity and magnitudes are equal so the uncertainties cancel in a ratio. More often, there is partial cancellation. At a minimum, the numerator and denominator share the MAC associated with the characteristic X-ray in its source element. The more elements that are shared and the closer the mass fractions of these elements are, the more common MACs are shared between the unknown and standard. Similarly, the stopping power and backscatter corrections will share more input parameters when the elements and their mass fractions are similar.

For a specific measurement, you could apply these calculations and applying them to all relevant standard materials available in your lab to determine the optimal standards for each element in the unknown. You will need an estimate of the composition of the unknown but a standardless quantification would probably be adequate for this purpose.

Figure 5 compares the fractional and absolute uncertainty for a measurement of K240 glass at various different beam energies for simple standards and similar standards. In general, we see that the uncertainty in the measurements are seen to increase with beam energy for most elements (O, Mg, Si, Zr) and decrease for a few (Ti, Ba and Zn). This difference largely reflects the difference between strongly absorbed elements for which the absorption correction increases with increasing beam energy and those with low absorption and lower overvoltage. The MACs for these elements in K240 is tabulated in Table 4. For O, Mg, Si and Zr, the MACs are between $5800 \text{ cm}^2 \text{ g}^{-1}$ and $1500 \text{ cm}^2 \text{ g}^{-1}$. For Ti, Ba and Zn, the MACs are between $104 \text{ cm}^2 \text{ g}^{-1}$ and $225 \text{ cm}^2 \text{ g}^{-1}$ so the absorption correction is diminished by an order-of-magnitude or more for these elements. Furthermore, the edge energy for Zn K is 9.7 keV so the overvoltage at 12 keVis minimal and any uncertainty in the beam energy is amplified.



Figure 6: The total uncertainty measuring the elements in K240 glass for two different selections of standards. A) Simple standards BaF_2 for $Ba L_3-M_5$, SiO_2 for O K-L₃ and pure elements for the remainder. B) A standard with identical composition to the unknown. Since the compositions are identical, nominally the matrix corrections are unity and the matrix correction uncertainty is zero. However, the remaining uncertainty is due to uncorrelated uncertainties in beam energy, take-off angle and the measured k-ratios between standard and unknown.



Figure 7: The total uncertainty in the measured mass fraction as a function of surface roughness shown on a log-log plot. The softer X-ray lines show the influence of roughness much before the harder X-ray lines. Oxygen is already showing the influence at 10 nm while zinc is almost uneffected well above 100 nm.

3.4 Surface Roughness

It is well known that careful surface preparation is critical for accurate composition measurements. However, there is very little guidance about what constitutes adequate surface preparation. This is largely because the question is very dependent on the sample and the design of the measurement. While it is possible to model complex sample geometries using some Monte Carlo simulators ([Llovet et al., 2005; Ritchie & Scott, 2006; Ritchie, 2005; Salvat et al., 2006], it is very time consuming to run the number of models to adequately sample a single roughness. Furthermore, roughness is very difficult to quantify as there are so many different ways for a surface to be rough. However, if we give up on developing the perfect model and are willing to accept a crude model of surface roughness like that proposed herein, we can provide general guidance and a rough estimate of the consequences of poor surface preparation. Even a crude model is a large step in the right direction. Since many occasional users of X-ray microanalysis are not familiar with the influence of surface preparation, a simple model will provide them with much more information than they would otherwise have. Based on a simple question about approximate surface roughness scale, these models can provide an estimate of the uncertainty and also an estimate of how much better then uncertainty would be if the sample is better prepared.

While it is possible to model the effect of surface roughness on both the sample and the unknown, we will present an example based on K240 glass which only consider roughness on the unknown. A moderate beam energy of 15.0 keV provides an overvoltage of at least 1.5 for all measured lines. Figure 7 clearly

shows that adequate surface preparation is very element dependent. As you'd expect, the uncertainty in the light elements is largest overall but also the knee at which surface roughness becomes significant occurs at lower roughnesses. For example, the estimated uncertainty in O is more than 1% and the knee occurs around 10 nm. The uncertainty for Ba is also significant but the knee occurs at near 100 nm. For Si and Mg, the knee occurs a little above 10 nm. Soft X-rays generally require a better surface preparation than hard X-rays because of larger mass absorption coefficients. Fortunately, since the uncertainty monotonically decreases with improved surface preparation, selecting the surface preparation for the most challenging element will be adequate for all elements.

4 Conclusions

An uncertainty model can be implemented in a similar manner for any of the many other matrix correction models. While the various different matrix correction models are known to give slightly different results, the overall uncertainty calculation is likely to give substantially the same results as the XPP model. This is because 1) uncertainty calculations are by their nature crude; and 2) while the details may differ, the dependence on the various input parameters and physical processes is likely to show similar dependence model-to-model. This does point out one shortcoming of this approach to developing an uncertainty budget: it doesn't account for the reality that there are better models and worse matrix correction models and that even the best model has uncertainty that goes beyond simply the selection of input parameter values. For one, the shape of the ansatz (Equation 5) does not reflect the true shape of the $\phi(\rho z)$ curve. Monte Carlo modeling and a handful of measurements show that the ansatz is reasonable and among the more realistic. Armstrong proposed an orthogonal approach to matrix model uncertainty [Armstrong et al., 2013]. His approach is to calculate the same matrix correction problem using a variety of different matrix correction models and look at the inter-model variability. This approach assumes that the model is the source of the error and the input parameters are not. The optimal implementation of Armstrong's approach would use a handful of equally credible models. However, in practice, Armstrong's implementation mixes crude $Z \cdot A \cdot F$ -models with more credible $\phi(\rho z)$ -models. It, therefore, probably overestimates the model uncertainty for the more credible matrix correction models. Regardless, this approach is valuable because it acknowledges that the models are not perfect and will contribute to the overall uncertainty budget.

It is common to think of uncertainty calculations as largely an academic exercise and only of interest to the expert. However, this perspective overlooks the way in which uncertainty calculations can be used to assist the analysts to make better measurements.

Imagine microanalysis software that would guide a novice (or, for that matter, an expert) through the measurement process. Through a combination of interviewing the analyst about the sample and the measurement, extracting information from scanning electron microscope (SEM) images and acquiring quick test spectra, the software could draw some preliminary conclusions about the composition and morphology of the sample (e.g. The size and homogeneity of the region to be analyzed). From these, the software could estimate the consequences of non-ideal measurement parameters. Commonly these could include sample inhomogeneity, sample preparation, poor choice of beam energy, probe current and acquisition time and choice of elemental standards. The analyst could be informed of these consequences and provided with a ranked list of suggestions to improve the measurement. The analyst gets to decide how to proceed. If the measurement is intended to be "quick-and-dirty" then they might not change anything and accept the base-level consequences. However, if the application demands more accuracy and precision, the analyst could choose from the list of suggestions those that best achieved the desired goal. While typically there is only one way to make the optimal measurement, there may be a handful of alternatives to make a "good enough" measurement. The software could further query the analyst about which measurement parameters are costly or impractical to change and which aren't. The measurement could then be reoptimized based on the analysts choices. Much of this would be transparent to the analyst who would be asked to answer a handful of straightforward and easy-to-answer questions.

Clearly, this vision remains distant. Hopefully, readers of this paper see how the calculations described herein bring us a little bit closer. All the other components are feasible with currently available technology. We could imagine using computer vision including, potentially, convolutional neural networks to interpret SEM images (particularly backscattered electron images) and extract estimates of morphological and other sample related parameters. This information could inform an intelligent actor that could probe the sample using X-ray measurements to collect additional information. Much of this would replicate, *in silico*, the actions and though-processes of an experienced analyst. The results would be a system that helps the analyst to make informed decisions based on quantitative inputs to produce data, in a cost-effective manner, that is likely to be fit for purpose. Sounds like a bright future for e⁻-beam X-ray microanalysis.

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