A Monte Carlo Approach to the Simulation of Characteristic X-Ray Yields for the APXS Instrument

by

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ABSTRACT

A Monte Carlo Approach to the Simulation of Characteristic X-Ray
Yields for the APXS Instrument

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In this thesis a new Monte Carlo simulation (MCYAC) is created and employed, which simulates measurements taken by the Alpha Particle X-ray Spectrometer (APXS) on the Mars Science Laboratory rover. Several consistency checks are conducted to test the validity of MCYAC. The checks verify that the simulation gives consistently reasonable results.

The results of the Monte Carlo simulation are compared to those found experimentally, with experimental X-ray yields per second calculated using the GUAPX least squares fitting program. The largest source of discrepancy between these programs is thought to come from the geometry values of the APXS instrument used in the Monte Carlo simulation, some of which are unknown.
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0.1 Introduction

Planetary exploration has grown in importance as a field of research over the past several decades. Unmanned spacecraft have been sent to many of the planets, moons, and smaller objects within our solar system with the intent of investigating its origins. These spacecraft are equipped to send us information about the celestial bodies on which they land.

In order to study the elemental composition of other planets, ingenuity and resourcefulness are required. For many years the techniques of X-ray fluorescence (XRF) and electron probe micro-analysis (EPMA) have been used in geological analysis. More recently, particle-induced X-ray emission (PIXE) has also found application in this area. These methods have traditionally used setups ranging in size from that of a milk carton, for X-ray fluorescence analyzers, up to room-sized particle accelerators to determine material composition. More recently, a method was introduced by E. J. Franzgrote [1], which was later extensively refined by R. Rieder [2], to use both XRF and PIXE methods which, when combined, examine many geologically significant major elements in one compact, soup can-sized device, suitable for space exploration.

0.1.1 The APXS instrument

The Alpha Particle X-ray Spectrometer (APXS) is a close-proximity instrument that uses X-ray emission spectroscopy to analyze the elemental composition of geological specimens [3]. Successive versions are present on both Mars Exploration Rovers (MER) and on the Mars Science Laboratory (MSL) Rover to determine the in situ chemical composition of geological specimens on the surface of Mars [4].

The APXS employs six curium-244 sources, which are placed in an annulus around a collimated silicon drift detector (SDD) [5, 4]. In the most recent iteration of the APXS instrument, three of the six curium sources are covered in alternating order to
prevent alpha particles from these sources from reaching the sample surface. This was done to increase the relative intensity of characteristic X-rays produced from heavy elements such as zinc, germanium, bromine, and strontium [6].

The APXS is affixed to the robotic arm of the MER and MSL rovers, which allows the instrument to be placed near the sample for measurements [4, 3]. The APXS carries a contact sensor to ensure that the sensor head of the instrument never touches the sample, as this could contaminate the sources and detector window (refer to FIG. 1). Surface contact with this sensor is ideal since the distance between the sample and detector is known and fosters reproducible results, as well as minimizing the sample to detector distance, which maximizes the count rate and achieves the minimum exposure time. However, if the sample is jagged, at an awkward angle, or is comprised of loose, fluffy soils, it is not advisable to put the instrument in contact with the sample surface. In these cases a standoff distance is introduced for the safety of the instrument.

The curium-244 sources are radioactive. In a radioactive decay process, the nucleus undergoes alpha decay, disintegrating into plutonium-240 and an alpha particle. The disintegration energy manifests itself as kinetic energy of the alpha particle and daughter nucleus. Because of the large difference in mass between the alpha particle and plutonium nucleus, conservation of momentum dictates that the alpha particle recoils with much greater velocity than the daughter nucleus. This alpha particle exists within a potential well formed by the nuclear attractive force and the repulsive Coulomb interaction between the positively charged nucleus and alpha particle. Classically the alpha particle has insufficient energy to escape from this potential well. However, quantum mechanics tells us there exists a probability that the alpha particle will tunnel through the potential energy barrier, and in so doing escape the nucleus [7].
Figure 1: Schematic of the Alpha Particle X-ray Spectrometer (Reprinted from Gellert et. al. [2006])
Often, after radioactive decay, the plutonium nucleus is left in an excited state [7]. The nucleus may then undergo a transition to a lower energy state by one of two competing processes: emission of a gamma ray photon or the internal conversion process. In the internal conversion process, the interaction of nuclear electric and magnetic multipole fields with bound orbital electrons causes the ejection of an orbital electron from its shell [8]. The de-excitation of orbital vacancies that are created give rise to a plutonium X-ray series. We therefore have emission of both alpha particles and X-ray photons from the curium sources.

PIXE analysis is the practice of bombarding a specimen with charged particles such as protons or alpha particles in order to excite/liberate inner shell electrons through Coulomb interaction, creating electron vacancies that will be filled by electrons from higher shells, and will often produce an X-ray photon of specific energy in the process [9, 11, 10].

The XRF process involves exposing a sample to a beam of photons, which may generate characteristic X-rays in the sample through electron vacancy creation by the photo-electric effect [12]. There are two dominant photon scattering processes in the range (1-20 keV) in which we are interested [13, 9, 12]: Compton scattering, and Rayleigh or low-energy Thomson scattering. Both of these interaction mechanisms have a much lower probability of interaction with an atom per unit path length (cross-section) than that of the photo-electric effect.

PIXE is almost exclusively responsible for inducing characteristic X-ray emission from the light elements, while the heavier elements are excited by XRF. At element number Z = 21 the PIXE and XRF contributions to the observed characteristic X-rays are approximately equal. The characteristic X-rays of the lightest elements (Z<11) are so highly attenuated by the detector window that they are not detected [5]. The combination of the two excitation mechanisms allow for detection of elements from sodium to bromine for MER [4] and yttrium for MSL.
## 0.1.2 The Homogeneity Assumption

The yield equation, which will be derived in chapter II, relates the observed X-ray yield of a specific element in a sample measurement to the concentration of that element within the sample [14]. The two most important terms in this equation are the matrix terms, which describe the interactions of the PIXE and XRF processes with the sample [14, 15]. These terms can be rigorously determined using an atomic physics database that accounts for the ionization cross-sections of charged particles, photo-ionization cross-sections, ion stopping powers, and photon attenuation coefficients, with the assumption that the atoms are uniformly distributed throughout the sample at the sub-micron level [14, 15]. We call the assumption of uniform distribution the “homogeneity assumption”, and the effect of the atomic arrangement of the sample on the above list of processes “matrix effects”, which are described by the matrix terms in the yield equation [6]. The samples of interest to the APXS are geological in origin, which means they are generally comprised of multiple mineral phases.

Given that α-particles emitted from curium-244 have a maximum kinetic energy of 5806 keV, we expect the PIXE process for the lightest elements (from sodium to silicon) to generate characteristic X-rays from atoms at sample depths less than 10µm. For XRF we expect the Plutonium L X-rays to excite characteristic X-rays from depths in the tens and even hundreds of micrometers [4]. Thus the mineral grains may be larger than the penetration depth of incident radiation, especially for the PIXE process in the lightest elements [4, 14, 15].

Logically, many of the exciting alpha particles that interact with the lightest elements, along with the characteristic X-rays that head toward the detector produced by these interactions, will only interact within a single mineral grain, and thus the actual matrix effects are determined by the matrix of a single mineral and not by a matrix that is an “average” of mineral phases within the sample [14]. Since matrix effects are
accounted for using the homogeneity assumption, the yield equation is affected, and hence also the relationship between the observed yield and elemental concentrations that are derived from this observed yield.

Thus far all analyses of APXS data have used the homogeneity assumption, as does this work. Due to the complexity of the atomic structure of natural geological specimens, we must make some assumptions about the distribution of atoms in our sample when attempting to simulate APXS measurements, as is done in this work. Without some simplifying assumption computation would not be possible. Thus the assumption of homogeneity is likely necessary on some level, and functionally viable in many cases, though it may lead to exceptional results that deviate from reality by a larger margin than the uncertainty derived from the results of the spectral fitting program. A method for a possible improvement to the homogeneity assumption will be presented in chapter VI.

0.1.3 Motivation

In the following chapter, we build up the X-ray yield equation, which allows us to understand the underlying physics of the APXS instrument and its processes clearly and allows us to quantify each process. By examining each term of the yield equation in detail, we can get a firm understanding of the fundamental physics involved in the generation of an APXS spectrum.

The Monte Carlo simulation of the APXS instrument developed for this thesis can be used as a predictive tool for instrument X-ray yields. This is accomplished by closely following the yield equation and modeling its underlying physics. Since the assumptions are relatively few, it can be used to confirm other less time-intensive methods of analysis that make more assumptions. If yield results obtained from the simulation and measured yields from the spectral fitting program do not align, one can isolate the problem area within the yield equation using the simulation and simultaneously
better understand the instrument or the sample under examination.

The current Monte Carlo simulation is built upon principles developed in the simulation of M. Omand [16]. Having the benefits of time and hindsight allows for an expansion of this tool. The current Monte Carlo simulation takes more of the physical parameters of the APXS instrument into account, while simultaneously making fewer assumptions. Beyond this, the new approach allows for easier access and computation of useful information, as will be seen in the coming pages.

A benefit of the full Monte Carlo approach taken in this thesis is the straightforward calculation of the average angles of characteristic X-ray photons that enter the collimated silicon drift detector of the APXS instrument at any distance from the sample surface. Previously finding the “effective angles” required a lengthy minimization process that relied upon comparison of yields given by another program. Now similar information is available as a byproduct of using the Monte Carlo method to fully simulate the instrument. The average angles require only the geometry of the instrument as input, and do not rely on calculated yields, minimizing the room for error. Details of this process will be discussed in chapter IV.

One of the most important aspects of this Monte Carlo simulation is as an X-ray yield prediction tool that will allow the user to find a yield for a given concentration. The method for accomplishing this is described in chapter IV. This will allow the current program or a similar simulation to be part of a larger program that is capable of accounting for the heterogeneous distribution of minerals in samples. Details of this future work are discussed in chapter VI.

Work on the GUAPX spectral fitting program was also done for this thesis and motivation behind the modifications to the GUAPX program is straightforward. The added features allow for much faster analysis of data and for an increased number of physical parameters and processes to be taken into account. The edits to this program provide either more understandable or more correct results when the program
0.2 A Fundamental Parameters Approach

0.2.1 The X-ray Yield Equation

The following chapter will outline the yield equation, which incorporates all of the fundamental physics involved in PIXE and XRF events to determine the elemental X-ray yields expected from a given sample undergoing APXS analysis. This equation forms the backbone for both the GUAPX fitting program and the simulation that is the focus of the current work.

The yield equation is composed of two terms: the XRF term, which represents the intensity of the various characteristic X-rays induced by the XRF process, and the PIXE term, which represents the intensity expected from the PIXE process within the sample \[14, 17\]. We will start examining the yield equation in detail by first focusing on the XRF portion of the equation, then the PIXE portion, and finally combine the two.

0.2.1.1 Interaction Physics

We define the linear attenuation coefficient, labeled \(\mu\) or \(\mu_{\text{lin}}\), which gives the attenuation along a given length of target material and includes all three absorption and scatter processes that remove photons from a beam \[12, 13\]. We also define the more widely used mass attenuation coefficient, \(\frac{\mu}{\rho}\), where \(\rho\) is the mass density. It is usually in units of \(\text{cm}^2/\text{g}\) \[12, 13\].

For an “infinitely thick” sample, photons from an incoming beam will interact with a target element at depth \(x\), which can be broken up into \(n\) slices of thickness \(dx\), where \(dx\) is the slice of the target in which the photon interacts. This implies \(x = ndx\). We assume the beam is entering the sample at some angle \(\theta\) to the sample normal. Thus,
the probability of attenuation through a layer of thickness $dx$ is given by $\mu_{lin} \frac{dx}{\cos \theta}$. Therefore the probability that no interaction takes place in that layer is given by $1 - \mu_{lin} \frac{dx}{\cos \theta}$. Then the probability that no interaction takes place in $n$ layers is:

$$\left(1 - \mu_{lin} \frac{dx}{\cos \theta}\right)^n.$$  \hfill (1)

Taking the limit of infinitesimal layer thickness gives:

$$\lim_{dx \to 0, \, n \to \infty} \left(1 - \mu_{lin} \frac{dx}{\cos \theta}\right)^n.$$ \hfill (2)

But, as we defined above, $x = ndx \Rightarrow dx = \frac{x}{n}$, and so we see:

$$\lim_{n \to \infty} \left(1 - \frac{\mu_{lin} \cdot x}{n \cdot \cos \theta}\right)^n \equiv e^{-\frac{\mu_{lin} \cdot x}{\cos \theta}}.$$ \hfill (3)

However, the probability of a photon reaching a certain depth can also be given by the ratio of the number of photons that arrive at that depth to the number of initial particles, $\frac{N}{N_0}$. Thus we have:

$$N = N_0 e^{-\frac{\mu_{lin} \cdot x}{\cos \theta}},$$ \hfill (4)

for the number of photons arriving at depth $x$.

To find the total number of emitted X-rays, we first need the number of photons absorbed by a layer at depth $x$ with thickness $dx$ that excite atoms in this layer. To obtain this we take the derivative of equation (4), where we replace the linear attenuation coefficient with the photoelectric absorption coefficient, $\tau$, in (4) since it is the photoelectric effect that is responsible for creating electron vacancies in our excited atoms that result in fluorescence [13]. Thus we define:
\[ N_{\text{photo}} = N_0 e^{-\frac{\tau \cdot x \cos \theta}{\cos \theta}}, \]  

which yields the derivative:

\[ dN_{\text{photo}} = N_0 e^{-\frac{\tau \cdot x}{\cos \theta}} \times \left( -\frac{\tau \cdot dx}{\cos \theta} \right) \]

\[ = -N_{\text{photo}} \times \left( \frac{\tau \cdot dx}{\cos \theta} \right). \]

It should also be noted here that in the energy range in which we are interested (1 - 20keV), \( \tau \propto Z^5 \) [9, 18], and is therefore highly dependent on atomic number. For this reason, X-ray fluorescence gives a larger yield for elements of higher atomic number.

The “atomic physics term”, \( F_i \), is a combination of various X-ray physics parameters for element \( i \) [17, 6]. It includes the number of atoms per gram, given by \( \frac{N_A}{A_i} \), where \( N_A \) is Avogadro’s number, and \( A_i \) is the atomic mass of element \( i \). It also includes a factor for the probability of radiative de-excitation (rather than non-radiative transitions, i.e. the Auger effect), which contributes to the detected line energy counts. This atomic fluorescence yield is labeled \( \omega_i \) [13, 9, 17].

Upon de-excitation via characteristic K X-ray emission, a fraction, \( b_i \) (branching ratio), of the total K-shell X-rays produced will be \( K_\alpha \) X-rays. We work with the \( K_{\alpha1} \) line, which is the most intense K-shell line, less intense lines are calculated relative to it using well known intensity ratios [19, 20, 17].

Thus our atomic physics term for element \( i \), as a function of the properties of element \( i \) alone is given by:

\[ F_i = \omega_i b_i \cdot \frac{N_A}{A_i}. \]

(8)
The K-shell is the shell of interest for detected energy line counts. The probability of interaction of the K-shell with a photon that has energy greater than the binding energy of the K-shell is given by the photoelectric cross-section for the K-shell, $\tau_K$. We use these factors to obtain the total number of photons emitted by the sample from layer $dx$ at depth $x$. Our equation for element $i$ for the number of photons emitted by this layer, $dN_{\text{emit}}$ is

$$dN_{\text{emit}} = dN_{\text{photo}} \tau_i \cdot F_i.$$ (9)

This equation gives the amount of radiation of the energy lines of interest generated in the sample layer under examination. Now we need to account for attenuating effects to this radiation as it leaves the sample. Outgoing radiation will undergo the same type of attenuation due to interaction with its surroundings as an incoming beam. However, the angle of the outgoing radiation with respect to the normal will generally be different. We will call this exiting angle $\phi$. Thus our factor for attenuation of outgoing radiation is very similar to that of incoming radiation, but this factor will depend on the characteristic radiation of the element in question, so we include a superscript $i$,

$$\exp \left[ -\frac{\mu_{\text{lin}}^i \cdot x}{\cos \phi} \right].$$ (10)

When a target is irradiated and fluoresces, the excited atoms radiate their characteristic x-rays isotropically. However, due to the limited size and shape of the APXS instrument, only a fraction of the emitted radiation is seen by the detector. The emitted radiation can be assumed to leave the target with no preferential direction, i.e. isotropically. Thus, the fraction of radiation incident on the detector surface is a section of a spherical surface, and can be described using an equation for the two dimensional equivalent of arc-length, $\Omega r^2$, where $\Omega$ is called the solid angle. The fraction of radiation that reaches the detector is given by the fraction of this "solid
angle surface area” over the surface area of the total area covered by the emitted radiation, i.e. a sphere at the same radius. Since the radii are the same, they cancel in the fraction and we get:

$$\frac{\Omega}{4\pi}.$$ \hfill (11)

Though the solid angle clearly depends on the depth of radiation emission and thus energy [11], we will assume that this depth is small compared to the distance between the sample surface and the detector and therefore has a negligible effect on the solid angle. This is a safe assumption for the energy range and geometries in which we are working.

We have taken into consideration the effects produced in getting incident radiation to layer $dx$ and returning the fluorescent radiation of an element to the detector. The results are summarized in the equation: [13],

$$dN_{detector} = dN_{emit} \times \frac{\Omega}{4\pi} \cdot e^{-\mu_{lin}x}. \hfill (12)$$

Now we assume that the elements within the sample are homogeneously distributed and sum up all the contributions by all the layers of thickness $dx$ using an integral from the surface ($x = 0$) to the full thickness, which we have assumed is infinite. We note that $dN_{emit}$ is dependent on its thickness, $dx$.

$$N_{detector} = N_0 \cdot f_L \cdot F_i \cdot \tau_i \cdot \frac{\Omega}{4\pi \cos \theta} \times \left( \frac{\mu_{lin}}{\cos \theta} + \frac{\mu_{lin}^i}{\cos \phi} \right)^{-1}. \hfill (13)$$

We have included the fraction, $f_L$, which is the fraction of alpha decays in curium-244 that result in emission of a Pu L X-ray [6], which allows us to determine the
balance between characteristic X-rays produced by the PIXE process and those produced by the XRF process. This equation gives the theoretical number of fluorescent x-rays that reach the detector due to the XRF process.

Next we examine the PIXE process. As an ion moves through a material it loses kinetic energy. This is because the ion is undergoing inelastic Coulomb interactions with the bound electrons [11, 9]. The interactions with electrons make up the vast majority of interactions that the ions undergo, since the number of collisions with nuclei is small. Because the momentum transfer to the electrons is small compared to the total momentum of the ion at its typical energies, the path of the ion is very close to linear [11].

The ability of material to slow down and stop an incident charged particle is called the “stopping power.” The stopping power gives the differential energy loss over a differential path length traversed by the particle for a given material [12]. In order to eliminate much of the dependence of stopping power on the specific material used, we divide out the material density, to get the standard definition of stopping power [18]:

\[ S_M(E) = -\frac{1}{\rho} \frac{dE}{dx}. \]  

For a compound, the stopping power is a concentration-weighted sum of the various elemental stopping powers.

When comparing different absorber materials, the factor \( nZ \), with \( n \) as the number density of the absorber atoms, gives the electron density of that material. It can therefore be seen that materials with higher atomic number and higher density will have a greater stopping power [12].

The probability that an inner shell is ionized by a charged particle is given by the ionization cross section, \( \sigma_{K,i} \), which is dependent on ion energy (see Ref. [9] for a detailed discussion). This PIXE cross section has the property \( \sigma_{K,i} \propto \frac{1}{Z^4} \) [13], which
is in obvious contrast to the photoelectric absorption cross section, as mentioned above, where $\tau \propto Z^5$ [9]. These processes can thus be seen as complementary since XRF is obviously suited to higher $Z$ elements, while PIXE will have a much higher probability of generating X-rays for low $Z$ elements. We will return to this topic later.

To find the number of X-rays incident on the detector from PIXE processes, first we must look at the number of K-shell vacancies produced along a path of length $dx$.

We include the original number of particles, $N_0$, the X-ray branching ratio $b_i$, the atomic X-ray yield fraction from the K-shell, $\omega_{K,i}$, and the K-shell ionization cross section, $\sigma_{K,i}(E)$, which corresponds to the cross section presented at a depth $x$ and hence energy $E$ [11, 9]. The number of K-shell vacancies is thus:

$$dN_K = N_0 b_i \omega_{K,i} \sigma_{K,i}(E) dx. \quad (15)$$

We can rearrange the equation for $dx$ and substitute equation (14) to get:

$$dN_K = -\frac{N_0 b_i \omega_{K,i} \sigma_{K,i}(E) dE}{S_M(E) \rho}. \quad (16)$$

In order to find the number of X-rays produced, we must consider the fractional contribution of a desired shell (K shell in our case), $b_i$. According to the K-shell cross section, the incident particle may create an electron vacancy in the K-shell. Upon de-excitation, via characteristic K X-ray emission process, a fraction, $b_i$, of the total K X-rays produced will be $K_\alpha$ X-rays, which are dominant over the $K_\beta$ X-rays. We work with the $K_{\alpha 1}$ line, which is the $K - L_3$ transition. This is the most intense K-shell line. The less intense lines can be calculated using well known intensity ratios relative to this K-shell line [19, 20].

In similar fashion to equation (4) we define X-ray production along the path of the ion, using the stopping power to account for the energy loss. Integrating along the infinitesimal pieces of path length, $dx$, using the same angle convention as before, we
have the stopping power at depth \( x \) and we integrate from the final energy, \( E_f \), to the initial energy, \( E_0 \). We are left with:

\[
x = \frac{\cos \phi}{\rho} \int_{E_0}^{E_f} \frac{dE}{S_M(E)},
\]

which, upon substitution into (4), gives the full transmission factor:

\[
T_i(E) = \exp \left[ -\Sigma_M \left( \frac{\mu}{\rho} \right) \frac{\cos \phi}{\cos \theta} \int_{E_0}^{E_f} \frac{dE}{S_M(E)} \right].
\]

The sum is over all the matrix elements [11].

Putting all of the relevant PIXE factors together and accounting for solid angle considerations we have:

\[
dN_{\text{PIXE}1} = -N_0 \omega K,i b_i \Omega T_i(E) \sigma_{K,i}(E) dE.
\]

Rather than use the inverse mass density, \( \frac{1}{\rho} \), which is the volume per gram, we prefer to use the number of atoms per gram, given by \( \frac{N_A}{A_w} \), because this quantity lends itself better to the available information, i.e. counts from a detector, yet conveys the same type of information about the sample. We then have the equation:

\[
dN_{\text{PIXE}} = -N_0 \omega K,i b_i N_A \Omega T_i(E) \sigma_{K,i}(E) dE.
\]

We integrate this expression over all sections of the path [11] to find the total number of X-rays excited by PIXE that reach the detector. However, since we have changed our variable to energy, we change the limits of integration to the final and initial energies, as before, flipping the limits to eliminate the negative sign.

We can now combine our element-specific fundamental parameters for fluorescence
yield and X-ray branching ratio with the factor for number of atoms per gram into one atomic physics factor, $F_i$ (equation (8)), as we did for XRF. This yields,

$$N_{\text{PIXE}} = N_0 \cdot F_i \cdot \frac{\Omega}{4\pi} \times \int_{E_0}^{E_f} \frac{\sigma_{K,i}(E)T_i(E)dE}{S_M(E)}.$$  \hspace{1cm} (21)

0.2.1.2 Detector Considerations

The final two factors in the yield equation are the X-ray transmission fraction, $t_i$, and the intrinsic detector efficiency, $\epsilon_i$, for element $i$. The factor $t_i$ accounts for transmission through intervening media between the sample surface and detector window. There are four layers present for characteristic X-rays to penetrate: the beryllium window, a surface dead layer or layer of incomplete charge collection (ICC), the nitrogen column, and the detector contact [11, 17]. The intrinsic efficiency, $\epsilon_i$, depends on these four layers of material that characteristic X-ray photons must penetrate in order to interact with the sensitive volume of the SDD detector. The intrinsic efficiency also accounts for X-rays that penetrate the silicon wafer [11]. We will examine the detector efficiency in greater depth in chapter IV. With these factors included we get the yield equations for element $i$, which is dependent on the concentration of the element of interest [5, 17]. For both XRF and PIXE respectively this can be written as:

$$Y_{\text{XRF},i} = N_0 \cdot f_L \cdot F_i \cdot C_i \cdot \frac{t_i \Omega}{4\pi \cos \theta} t_i \epsilon_i \times \left( \frac{\mu_{\text{lin}}}{\cos \theta} + \frac{\mu_{\text{lin}}^i}{\cos \phi} \right)^{-1}, \hspace{1cm} (22)$$

$$Y_{\text{PIXE},i} = N_0 \cdot F_i \cdot C_i \cdot \frac{\Omega}{4\pi} t_i \epsilon_i \times \int_{E_0}^{E_f} \frac{\sigma_{K,i}(E)T_i(E)dE}{S_M(E)}. \hspace{1cm} (23)$$

As for an APXS with indeterminate geometry with respect to the instrument and sample placement, such as the one on the MSL, the solid angle, $\Omega$, cannot be known, nor can the number of alpha particles and X-rays striking the sample, since an
accurate number is not available for open and closed source activities of the Cm-244 sources (i.e. \(N_0\)). The source activity is combined with the solid angle to form “a single instrumental factor \(H\)” [5, 17], which is empirically determined using a suite of standard reference materials [5, 17]. We can therefore write our yield terms:

\[
Y_{\text{XRF},i} = H f L C_i [t_i \epsilon_i] M_{\text{XRF},i},
\]

\[(24)\]

\[
Y_{\text{PIXE},i} = H F_i C_i [t_i \epsilon_i] M_{\text{PIXE},i}.
\]

\[(25)\]

Where we have defined matrix terms, \(M_i\), to illustrate that the characteristic X-ray yield of element \(i\) depends on the elements that comprise the sample matrix and the affects of the matrix on exciting alpha particles and X-rays as well as outbound characteristic radiation from the element in question [5]. Explicitly these terms are:

\[
M_{\text{XRF},i} = \frac{\tau_i}{\cos \theta} \times \left( \frac{\mu_{\text{lin}}}{\cos \theta} + \frac{\mu_{\text{lin}}^i}{\cos \phi} \right)^{-1},
\]

\[(26)\]

\[
M_{\text{PIXE},i} = \int_{E_0}^{E_f} \frac{\sigma_{K,i}(E) T_i(E) dE}{S_{M}(E)}.
\]

\[(27)\]

The source irradiates the sample for a duration, \(T\) [6]. We must multiply our yields by the duration of the measurement in order to arrive at a final yield as detected by the APXS for the entire measurement.

Since both the PIXE and XRF processes contribute to the intensity of a given line, and we know the ratio between their contributions, the total yield can be found by combining their individual yields [5]. The plutonium emits approximately 20 L X-ray lines that excite elements to produce radiation in the samples [5, 17]. However, 15 of them are considered to be intense enough for our use. Thus we must sum over the XRF yields produced by these Pu L X-rays to get the total XRF yield. This gives us:
\[ Y_i = HC_i TF_i [t_i \epsilon_i](\Sigma f_L M_{XRF,i} + M_{PIXE,i}). \] (28)

This is the overall yield equation used by GUAPX, and the program developed for this thesis to find the elemental yields of samples [5, 17].

0.3 A History of the Work Done in this Area

0.3.1 The Previous Monte Carlo Method

M. Omand previously took a simulation approach to imitate the measurements taken by the APXS. A random number generator was employed to create event locations where alpha particles and X-rays would probabilistically strike the sample surface.

The original simulation is based on three back-end programs: the random number generator created by M. Omand and updated by S. Andrushenko, the yield program PIXRF, developed by J. Maxwell, and the Melissa program, which handles the calculation of the effective area of the detector. We define the effective area of the detector as the locus of points on the detector that a given characteristic X-ray generated on the sample surface may possibly strike. This program is again written by M. Omand and updated by S. Andrushenko. The processes of these programs that are employed in the current work are examined here in some detail.

The first step in the Omand Monte Carlo random number generator is to randomly generate an emission point on the curium source. Then, using the constraints of the physical set-up of the APXS instrument, this Monte Carlo approach generates two random angles. \( \theta_1 \), is the angle from the emission point on the source to the sample surface, and \( \theta_2 \), is the angle from the interaction point on the sample surface to the detector [16]. For computational efficiency, these angles are constrained, using the geometry of the APXS instrument, to be less than two respective maximum angles.
The $\theta_1$ and $\theta_2$ angles are found in reverse order of the physical process. The first constraint is that the angle $\theta_2$ must be less than the maximum angle allowed by the limiting collimator of the APXS. This maximum angle is labeled $\theta_{2\text{max}}$ as illustrated in FIG. 2. Using this angle and the vertical distance from the detector to the sample, Omand defines the boundary on the sample surface that correlates with the effective area, i.e., the sample area from which characteristic X-rays may strike the detector. From this boundary, we define an angle, $\theta_{1\text{max}}$, from the vertical, to a line segment that spans the farthest edge of the source to the farthest point on this outer boundary, as seen in FIG. 3. Anything outside the range of maximum $\theta$ values
is of no interest, hence, when picking random numbers for the Monte Carlo angles, they are only generated within these ranges.

Omand used an approximation in these calculations. She assumed that the sample surface to detector distance and the sample surface to source distance are the same, as seen in FIG. 3. Using the diagram from Omand’s paper, the sample surface to source distance for the MER instrument is 26.2 mm, while the distance from the source surface to the detector is an additional 6.0 mm from the sample surface. Therefore the approximation puts the detector and collimators 6 mm closer to the sample. The location of the detector thus deviates from reality by a 19% margin. Using the geometry of the MSL instrument, this same approximation also results in the detector location being 19% closer to the sample surface than it actually is. Therefore this approximation is a significant deviation from reality, however, Omand’s already lengthy effective area calculations would become more cumbersome, if not impossible, without this approximation.

In the Monte Carlo simulation, spherical coordinates are used to simulate the vector of emission from the source. This is because the $\alpha$-particles and plutonium X-rays emanate isotropically from the source. The azimuthal direction from the source is randomly chosen between zero and $2\pi$, since the $\alpha$-particle/plutonium X-ray may leave the source in any azimuthal direction. The zenith angle, $\theta_1$, is chosen between zero and $\theta_{1\text{max}}$ for reasons discussed above. The length of the vector, $r$, is found using the source-to-sample distance divided by the cosine of $\theta_1$. This is a legitimate method for creating $r$ since $\theta_1$ is randomly generated.

These randomly generated spherical coordinates are used to create a location for characteristic X-ray emission on the sample surface. This point is translated into Cartesian coordinates and labeled $(x_2, y_2)$. 

20
Figure 3: Diagram created by M. Omand to describe the determination of the angle, $\theta_{1max}$, (labeled as $\sigma_{1max}$ here).
Figure 4: Diagram created by M. Omand to describe the determination of the angle, \( \theta_2 \), (labeled as \( \sigma_2 \) here).
At this point in the simulation, the horizontal distance between \((x_2, y_2)\) and the centre of the detector, \(h_2\), is found. The inverse tangent of \(h_2\) divided by the sample-to-detector height, \(TotalZ\), is then calculated as a possible \(\theta_2\) angle, as seen in FIG. 4. This step is an approximation that treats the detector as a “point detector” located at the centre of the detector location. If this angle is less than \(\theta_{2max}\), then the two angles and the \((x_2, y_2)\) location are recorded, otherwise the points are discarded. This procedure is repeated iteratively until the specified number of points, usually 10 000, is reached.

The final product is a .csv file that lists (usually) 10 000 of the following coordinates: \(\theta_1\), \(\theta_2\), \(x_2\), \(y_2\). Each \((x_2, y_2)\) coordinate pair represents an emission location on the sample surface. The corresponding \(\theta_2\) value is a zenith angle of a characteristic X-ray path that could enter the detector. To emphasize, there is no azimuthal angle associated with the coordinates. Omand has not defined the direction of this X-ray path. These coordinates do not describe a path that is constrained to enter the detector, they are simply coordinates limited to angles that could enter the (point) detector if a specific (range of) azimuthal direction(s) were specified.

In a separate step, the program PIXRF by J. Maxwell is run. This program creates a theoretical yield surface as a function of incoming and outgoing angles (\(\theta_1\) and \(\theta_2\) respectively). The yield surface is reported as a grid, the increment of which is selected by the user (5 deg was used by Omand). The following equation from Abramowitz and Stegun (pg. 882) is used to interpolate the randomly generated \((\theta_1, \theta_2)\) values from the Monte Carlo simulation onto the surface using the grid to find the X-ray yields:
\[ f(x_0 + ph, y_0 + qk) = q \left( \frac{(q - 1)}{2} \right) f_{0,-1} + p \left( \frac{(p - 1)}{2} \right) f_{-1,0} \]
\[ + (1 + pq - p^2 - q^2) f_{0,0} + p \left( \frac{(p - 2q + 1)}{2} \right) f_{1,0} \]
\[ + q \left( \frac{(q - 2p + 1)}{2} \right) f_{0,1} + pq f_{1,1}. \]

The higher order terms have been omitted \((O^3\) and higher).

The angles are successively interpolated onto the surface, outputting an angle-dependent yield for each location [16]. Separately, an effective solid angle is developed [16]. This effective solid angle gives the area of the detector seen by the locations of emitted characteristic X-rays from the sample surface. A “correction factor” of effective detector area to total detector area is applied to this yield based on the effective area specific to locations of the sample. Here the approximation is again made that the detector and the curium sources lie on the same plane. The yields are summed for each element concentration that was input into the program, giving either total yield or yield per unit concentration, depending on user preference [16]. These yield values may be corrected for detector efficiency effects [16]. The detector efficiency drops when detecting low energy characteristic X-rays due to attenuation by the beryllium window and the nitrogen layer. The detector efficiency also drops when irradiated by high energy characteristic X-rays, since these X-rays may penetrate the silicon wafer of the silicon drift detector of the APXS.

0.3.1.1 Effective Angles

Effective angles were developed by M. Omand in a study of the angle dependence of X-ray yields of the APXS instrument [16]. The idea behind these angles is, in the words of M. Omand, “if all of the simulated radiation were incident at one angle, the total yield would replicate that observed from the Monte Carlo” [16]. In order to accomplish this, the ratio,
\[ R_i = \frac{\Sigma Y_{tot}}{\Sigma Y(\theta_1, \theta_2)} \]  

is computed for each element, \( i \), in a sample and for every angle pair generated by the Monte Carlo simulation [16]. The average value of the ratios, \( AR \) is found and the angle pairs, \( (\theta_1, \theta_2) \), with the corresponding minimum value of \( |1 - AR| \), are chosen [16].

The yield equation, as used in the GUAPX and YAC programs, require a pair of well-defined angles, and the optimized pair of incoming and outgoing angles \( (\theta_1, \theta_2) \) serve this purpose in the yield equation.

### 0.3.2 The Need for a New Approach

M. Omand made the approximation that the alpha particles traverse the titanium foil always at an angle normal to the foil. However, the angle of the alpha particle relative to the titanium foil determines the actual path length of the alpha particle in titanium. This distance, or foil thickness as experienced by the alpha particle, when combined with the stopping power of titanium, can be used to determine the quantity of energy that the alpha particle has lost when it emerges from the titanium foil, as will be seen in chapter IV. If we assume that the titanium foil has a uniform thickness, we can calculate the foil thickness traversed by an alpha particle, and thus determine the impact of the angle of the path through the titanium foil on the energy of each emerging alpha particle. This decrease in energy of the alpha particles will result in a lower characteristic X-ray yield.

Correction of this approximation was assessed by S. Andrushenko, who determined that addressing the problem within the given computer code was not possible. The best option would be to rewrite the code and switch to a full Monte Carlo approach. For each \( \theta_1 \) angle chosen by the Monte Carlo, an alpha particle energy would be called
from a table that gives alpha particle energies as they vary with angle after emerging from the titanium foil. However, running a single simulation using this method would require approximately 35 days of computing time.

Andrushenko worked on a simulation that did not include the new Monte Carlo approach he had suggested. Hence, a rewrite of the Andrushenko code was undertaken by the author. The Andrushenko simulation was predicated on the Omand work. It sought to add flexibility in terms of geometric inputs, allowing geometry of APXS instruments other than the one present on the MER mission. The MER geometry had been coded directly into the program of Omand. The work of Andrushenko also brought unity by combining the Omand code with the yield program, PIXRF, developed by J. Maxwell; and did so with a user-friendly interface.

The Andrushenko program, Sim-APXS, is based on the three back-end programs discussed above, and uses compiled versions of them. They could not be changed, checked or read to be better understood. They are essentially black boxes. Thus, the present rewrite of the code included demystifying these black boxes to clarify some of the underlying science that was going on, as well as make improvements to the code such as modularization and better commenting.

The current work is named MCYAC, for Monte Carlo YAC, YAC being the yield program of J. Maxwell, the evolution of the PIXRF code used earlier by Omand.

### 0.4 The Current Simulation

If we are to rely on the results of the simulation developed for this thesis, we must ensure that every step is developed correctly. For this reason, consistency checks are undertaken at every step and this will need to continue as the current program is developed to completion in the future.

Some of the current work is based on the previous work of Andrushenko and Omand.
Many of the ideas for creating the current user interface come from the Andrushenko code, Sim-APXS. Also, some of the ideas behind how to create the new Monte Carlo simulation come from the work of M. Omand. The current work started with the code for Sim-APXS and evolved from there into its own entity, being rewritten from scratch.

0.4.1 Geometric Considerations

The new program takes a different approach from the idea of effective detector area. Rather than use the Monte Carlo approach just to find the points on the sample surface that could enter the detector, then scaling the yield by a correction factor for the effective area, the Monte Carlo method is carried all the way through the simulation. This entails finding sample surface points that are excited by the source, as Omand did. From here we deviate, by continuing to use the Monte Carlo approach to simulate characteristic X-rays generated at the sample surface that pass through the collimator of the APXS, and strike the detector. This allows us to avoid use of the Ω factor in the yield equation.

Now we describe in detail the deviation of the new Monte Carlo approach from the old. First, we remove the approximation that the surface to detector distance is the same as the surface to source distance. This approximation was originally implemented to make the effective detector area calculation simpler. Since the effective area is not used in the new approach, there is no longer a need for this approximation. The former method gives maximum angles for θ₁ and θ₂ of 43.5° and 25.2° respectively for the MER geometry. These angles are close to the true maxima of 45.4° and 28.8° obtained from [16]. These are reasonably good estimates. However, once the approximation is removed, the new code calculates maximum angles of 46.4° and 29.2°, clearly closer to the true values. The fact that there is still a small discrepancy in these numbers suggests that the dimensioning used for the simulation of the MER
<table>
<thead>
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<th>Variable</th>
<th>Value (mm)</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
<tr>
<td>collimator2radius</td>
<td>1.5</td>
</tr>
<tr>
<td>samptocol2</td>
<td>17.0</td>
</tr>
<tr>
<td>samptocol1</td>
<td>20.4</td>
</tr>
<tr>
<td>totalZ</td>
<td>21.1</td>
</tr>
<tr>
<td>detarea</td>
<td>10.0</td>
</tr>
</tbody>
</table>

Table 1: Instrument dimensions for the MSL APXS instrument

APXS instrument may not be perfect.

The new approach begins with the method used by Omand, right up to the point in her program where the sample surface points, \((x_2, y_2)\), are first generated. Once we have our random point on our sample surface, \((x_2, y_2)\), we want to create a random vector from this point onto the plane coincident with the surface of the detector. We will call the point defined by the intersection of the vector with this plane, \((x_3, y_3)\). Using this method eliminates the approximation of a point detector.

The relevant MSL APXS instrument dimensions used in the simulation to obtain the results discussed in the following chapters are given in Table I. It should also be noted that the dimension from the centre of the source to the centre of the detector is 7.5mm. The use of these dimensions and a visual explanation of the coordinates used to create the remainder of the Monte Carlo simulation are given in FIG. 5.

We create \((x_3, y_3)\) in two steps. First, we account for the fact that the radiation will be emitted isotropically from the interaction point on the sample surface. Thus, we again use spherical coordinates, this time to generate the vector that creates our point on the detector plane. In this step we randomly generate a ray. For ease of
Figure 5: Diagram of the various coordinates used in the derivation of the Monte Carlo simulation.
computation, this ray initially intersects the origin of the coordinate system on the cylindrical axis of symmetry on the plane of the sample surface, which we take as our $x-y$ plane. In a later step we shift the ray. This ray also intersects the plane of the detector at a point that we label $(x_t, y_t)$, which, of course, also becomes shifted. Both the unshifted and shifted points have a $z$-coordinate, which we call $\text{total}Z$, since it lies on the plane of the detector.

To generate the initial ray in spherical coordinates, we want a random angle from the $z$-axis that lies within the possible range of angles. Thus, we choose $0 \leq \theta_2 \leq \theta_{2\text{max}}$. We can have this vector point in any azimuthal direction, so we choose $\phi_2$ such that $0 \leq \phi_2 < 2\pi$. In order to ensure that $(x_t, y_t)$ lies on the plane of the detector, we define $r_2 = \frac{\text{total}Z}{\cos(\theta_2)}$. Thus, in spherical coordinates we get the points:

$$
x_t = r_2 \sin(\theta_2) \cos(\phi_2) \tag{31}
$$

$$
y_t = r_2 \sin(\theta_2) \sin(\phi_2).
$$

Second, we shift this point over by an amount $(x_2, y_2)$ so that our simulated characteristic X-ray emission vector originates at the surface point where the characteristic X-ray would be generated. Thus we have:

$$
x_3 = x_2 + x_t \tag{32}
$$

$$
y_3 = y_2 + y_t.
$$

Now that we have $(x_3, y_3)$, we ensure that it lies on the detector, otherwise we discard this point and start again in Monte Carlo fashion. To do this we use an “if” statement: “If $\sqrt{x_3^2 + y_3^2} < \text{detector radius}$, then continue.”

It is beneficial to work on a single plane. We do this by projecting the points we generate onto the plane of the sample surface. To distinguish these points from the unprojected counterparts, we include the subscript “$_{\text{proj}}$”. We note that $(x_t, y_t)$ defines a direction vector that points in the direction of $(x_2, y_2)$ to $(x_3, y_3)_{\text{proj}}$. Its
magnitude \( |t| = \sqrt{x_t^2 + y_t^2} \), is the distance from \((x_2, y_2)\) to \((x_3, y_3)_{\text{proj}}\).

To find whether or not the ray from \((x_2, y_2)\) to \((x_3, y_3)\) will pass through the collimator, we define the intersection of the simulated characteristic X-ray emission vector with the plane of the collimator opening, which we call “collimator 2”, and the plane of the end of the collimator farthest from the sample, labeled “collimator 1”, in-keeping with the nomenclature of Omand. We label the intersections points \((x_4, y_4)\) and \((x_5, y_5)\) for collimator 2 and collimator 1 respectively, and project them onto the sample plane, giving \((x_4, y_4)_{\text{proj}}\) and \((x_5, y_5)_{\text{proj}}\).

To find the distance traveled from \((x_2, y_2)\) to \((x_4, y_4)_{\text{proj}}\) and \((x_5, y_5)_{\text{proj}}\), we use scale factors. These are chosen such that they create a constant of the geometry, as shown later. However, first we find them in their most basic form. This is done by dividing by \( |t| \) in order to make \((x_t, y_t)\) a unit vector. We can see that \( \text{samptocol2} \cdot \tan(\theta_2) / |t| \) gives the distance from \((x_2, y_2)\) to \((x_4, y_4)_{\text{proj}}\). We have a similar case for \((x_2, y_2)\) to \((x_5, y_5)_{\text{proj}}\).

\[
A = \frac{\text{samptocol2} \cdot \tan(\theta_2)}{|t|} \\
B = \frac{\text{samptocol1} \cdot \tan(\theta_1)}{|t|}
\]  

(33)

Using similar triangles, we can calculate these values in a different way from the distances sampletocollimator1 (samptocol1), samptocol2 and totalZ. Since these values are constants of the geometry, they can be calculated before the iteration, saving substantial computing time. Thus, in the program we use:

\[
A = \frac{\text{samptocol2}}{\text{totalZ}} \\
B = \frac{\text{samptocol1}}{\text{totalZ}}
\]  

(34)

We are now in a position to find the points \((x_4, y_4)_{\text{proj}}\) and \((x_5, y_5)_{\text{proj}}\). To do so, we start at \((x_2, y_2)\), scaling the direction vector \((x_t, y_t)\), by the factors \(A\) and \(B\):
\[(x_4, y_4)_{\text{proj}} = (x_2 + A \cdot x_t, y_2 + A \cdot y_t). \quad (35)\]

Similarly,

\[(x_5, y_5)_{\text{proj}} = (x_2 + B \cdot x_t, y_2 + B \cdot y_t). \quad (36)\]

As a final check for the path of the characteristic X-ray from the sample surface to the detector to pass through the collimator, the logic of the computer code reads: If \(\sqrt{x_2^2 + y_2^2} < \text{collimator2radius}\) and \(\sqrt{x_5^2 + y_5^2} < \text{collimator1radius}\) then save the points.

In the simulation, only one source is simulated and rotational symmetry is assumed. When looking at a plot from where the points that reach the detector come, however, it is more intuitive to look at the effects of all six sources. Therefore the following plots are created by taking the contribution of a single source as calculated by the Monte Carlo random number generator and rotating it around the central axis (centre of the detector) in five multiples of \(\frac{\pi}{3}\) radians. The first plot (FIG. 6) is a three-dimensional histogram of the points \((x_2, y_2)\), from where the characteristic radiation that enters the detector is coming, in standard MSL geometry.

To make this graph yet more intuitive we look at a profile of FIG. 6, given in FIG. 7. FIG. 7 shows the radial dependence of the number of counts coming from the sample surface at a specified distance from the detector centre. A logarithmic plot is included in FIG. 7 to elucidate the steepness of the peak. The Gaussian profile is very steep due to the collimation of the detector.

In order to check the Monte Carlo simulation as thoroughly as possible, various extreme geometries are input and the results examined as a “sanity check.” These geometries include a very narrow collimator, a very long collimator, and, finally, a
Figure 6: 3-Dimensional histogram of the locations of emitted radiation that enter the detector.
Figure 7: Profiles in x of the distribution of emitted radiation that enters the detector.
very short and wide collimator with a very small source and detector area to replicate a point source and point detector. In each case the results are very reasonable. The method is also checked by J. O’meara, C. Tabert, and R. Pardo.

This theoretical approach has not been tested experimentally. In order to test the validity of the results, a physical experiment must be conducted. This experiment will be proposed in the future work section so that the results of the Monte Carlo simulation can be confirmed or refuted. There also exists the possibility that disagreement will be observed despite the simulation being correct, which would imply that one or more of the assumed instrument dimensions used in the simulation are incorrect.

There are a number of benefits from the new Monte Carlo method. First, it enables us to find the alpha particle energy variation through the titanium source cover. Second, we have the actual angles at the detector interface with which to find the attenuation by the detector window.

Third, we no longer need to make the assumption of a point detector anywhere in the simulation. Fourth, the very difficult geometry calculations when finding the effective area, with the inherent assumptions and approximations, are no longer necessary or relevant. There now exists a simple continuity between the alpha particles and X-rays leaving the source, traversing the titanium foil, striking the sample, exciting characteristic X-rays that leave in any direction, and counting only those that enter the collimator and strike the detector.

This is not to say that the current program is without approximations or is even complete. However, there now exist fewer approximations and more aspects of the APXS instrument that are accounted for.

To explain what the current simulation entails, we will start at the curium source and work through to detection of the characteristic X-rays, explaining the methods employed as we follow this path. The first consideration is addressed above: obtain-
ing coordinates and associated angles of the exciting radiation and alpha particles, as well as the angles and locations of characteristic X-rays incident on the detector. Next, we look at the alpha particles leaving the source and traversing the titanium foil, accounting for the energy loss in the foil, followed by the characteristic X-rays and their interaction with the detector and detector window.

0.4.2 Alpha Particle Traverses Titanium Foil

In order to correct the approximation of not including the effect of the angle at which the alpha particles traverse the titanium foil, first we need a method to find the energy lost by the alpha particles to the titanium.

The initial kinetic energy of alpha particles leaving the surface of a curium source is 5806keV. In the current simulation, each alpha particle and Pu L X-ray is taken to be emitted from some random location, \((x_1, y_1)\), on a curium source. It also leaves the source in a random direction. We define the location \((x_2, y_2)\) on the sample as described above. An alpha particle must traverse the titanium foil in order to get from \((x_1, y_1)\) to \((x_2, y_2)\) and the path has an associated angle from the normal, \(\theta_1\). For samples on Mars, there is a carbon dioxide atmosphere; for samples in the lab, however, there is no atmosphere since the APXS is kept in vacuum for testing. The paths through all media are assumed to be straight lines. Thus far, attenuation of alpha particles through the \(\text{CO}_2\) atmosphere has not been accounted for in the MCYAC program. This has not affected the outcomes, however, since the samples in question have been examined in the lab where they are in vacuum.

As discussed in chapter II, we wish to find the energy lost by the alpha particle to the titanium foil. To do this, we use the stopping power formula [12]:

\[
S(E) = \frac{dE}{dx},
\]  

(37)
where $E$ is the energy of the particle and $dx$ the infinitesimal distance traveled. Rearranging and integrating we find:

$$\Delta E = \int_0^t \left( \frac{dE}{dx} \right) dx. \tag{38}$$

A useful form of the stopping power is given by Ziegler [21]:

$$\frac{1}{S} = \frac{1}{S_{\text{low}}} + \frac{1}{S_{\text{high}}}, \tag{39}$$

where we have:

$$S_{\text{low}} = 4.71E^{0.5087}$$

$$S_{\text{high}} = \left( \frac{65280}{E} \right) \ln(1 + \left( \frac{8806}{E} \right) + (0.005948E)). \tag{40}$$

The constants are specific to titanium and $E$ is the energy of the particle.

To evaluate our expression for $\Delta E$, we use numerical integration. This is done by taking the expression for stopping power to get the change in energy that the particle experiences while traversing a thin section of foil. A section thickness is required (i.e. $dx = 0.01\mu m$). We perform calculations using the points $dx = 0\mu m$ and $dx = 0.01\mu m$, and subtract the outcome of the second from the outcome of the first. Since this is a linear approximation of integration, it yields the approximate energy loss after the particle has traversed the prescribed distance of 0.01$\mu m$.

We take the outcome of this calculation, subtract it from the original energy and use this as the energy of the particle as it begins to traverse the next thin section of foil. Using the energy loss to find the approximate energy after traversing the length of the thin section, we successively calculate energies at distances incremented by our chosen $dx$ to twice the thickness of the foil, and build a table of energy values at
respective foil thicknesses from this energy-distance relationship.

We use this table in MCYAC, by dividing the total foil thickness by the cosine of $\theta_1$ for each alpha particle path to get the distance the particle travels within the foil. This distance is then compared to the table of thicknesses until a close match is found (less than 0.005 $\mu$m). The energy associated with this match is taken and placed beside its corresponding angle and coordinate pair from the file “random theta pairs x and y.csv” in a list variable within the MCYAC program.

Since the detector is not fully characterized, it is impossible to know the exact dimensions of the titanium foil that the alpha particles are traversing. Fortunately the energy of the alpha particles striking the sample surface was found by N. Boyd to be approximately 5000 keV [24].

In order to get a best estimate of the foil thickness, MCYAC was used in a different way. An average of alpha particle energies as they vary across the sample surface was found and output. The thickness of titanium foil is an input for the program and can thus be changed run by run. The thickness was adjusted and a trial and error approach was used to find the weighted average energy to match the measured value of 5000 keV. A thickness of 3.45 $\mu$m was found. This value includes compensation for alpha particles generated below the surface of the curium source that undergo energy loss as they traverse the curium.

0.4.3 Adapting to Computational Constraints

The yield terms in the yield equation are found using the program “ya2a.exe” written by John Maxwell, which is an upgrade of the program PIXRF used by M. Omand. This program uses matrix composition, sample thickness, $\alpha$-particle to L X-ray ratio, $\alpha$-particle energy, and incoming and outgoing angles (with respect to a normal) [22]. This input, along with a database of physical information, is used to find probabilities of inner shell ionizations yielding fluorescent X-rays. The program includes contribu-
tions from secondary fluorescence. The “ya2a” program takes a user specified range of angles at defined periodic intervals and assigns yields to each of these coordinates, just as the PIXRF program did.

Many points (50000) are desired from the Monte Carlo simulation in order to achieve good statistics. Because the time taken to run the ya2a program is about half a minute, it is impractical to run each Monte Carlo generated point through this program due to constraints in processing power. Two methods were conceived for processing the random coordinates. Both methods involve running the program “Standalonerandomnum2”, then setting up bins, or “bags” for various ranges of $\theta_1$ values, exploiting the fact that the alpha particle energy is inversely proportional to its angle through the titanium foil. We use this energy for the alpha particle input energy in the ya2a program, which in turn finds the yield at the specific energy for the specified range of angles.

Thus, the effect of the $\theta_1$ angle on characteristic X-ray yield is two-fold. First, it affects the energy of the alpha particle that strikes the sample, which changes the cross-sections of the atoms in the sample. This effect has not been accounted for in previous APXS instrument simulations. Second, it has an impact on the calculation of the depth profile performed by the ya2a program. This effect was accounted for by Omand in her simulation using the PIXRF program.

Both methods proposed for the examination of the effects of angle on alpha particle energy are limited in accuracy by the averaging of the energy of each bag. However, though the energy of each bag is averaged, each set of randomly generated angles, $(\theta_1, \theta_2)$, in the simulation is treated individually.

In the first method, we take the range of possible $\theta_1$ values and break it up into several smaller predefined ranges (bags). We loop through the file of random coordinates, sorting each random coordinate into its appropriate bag. Once this is done, we match each angle to its corresponding energy after it emerges from the titanium foil, using
the list of alpha particle energies at various angles as described above. For each bag
this energy is averaged. The program ya2a is run for each bag, using the appropriate
average energy and range of angles.

There are two ways in which this method is sub-optimal. First, it is easier to work
with bags of the same size. With the aforementioned method, the bags of small an-
gles are more dense than those of the larger angles, based on smaller probabilities
of large $\theta_1$ alpha particles producing characteristic X-rays in locations likely to reach
the detector. The second derives from the first. With very few angles in the high
angle bags, a single extreme angle can hold great sway over the average energy of that
bag, due to the small number of angles available to average. This leads to increased
statistical uncertainty. If we were to have the same number of angles in each bag,
the outliers would be balanced because extreme angles are averaged in with a much
larger number of “normal” angles.

The second method involves sorting coordinates by increasing $\theta_1$ (decreasing energy)
using the “Shell Sort” algorithm (D. Shell, 1959), and dividing the $\theta_1$ values into
equally sized bags. The energy associated with each coordinate pair is found using
the method described above, and the average energy and maximum and minimum
$\theta_1$ and $\theta_2$ values are found for each bag. Angle intervals, or step values, by which to
increment $\theta_1$ and $\theta_2$, are input by the user into the MCYAC program. The maximum
and minimum $\theta_1$ and $\theta_2$ values of each bag are rounded to the nearest multiple of
the increment value, and these numbers are to be used to create a domain for their
bag. Using this domain, along with the increment value, arrays of $\theta_1$ and $\theta_2$ values
are created for each bag. What we end up with is a matrix of $\theta_1$ and $\theta_2$ pairs for each
bag, henceforth referred to as the coordinate pair matrices.

When creating the coordinate pair matrices, we start at the minimum and continue
each matrix two steps beyond the maximum $\theta_1$ and $\theta_2$ values so that we can reference
matrix points above the maximum. The reason for this is explained below. The ma-
trix of angles for each bag is created by the program “ya2a.exe”, which also assigns yield values to each matrix point. The result is sets of three dimensional matrices with $\theta_1, \theta_2$ coordinate pairs and unique associated yields, dependent on alpha particle energy, as the third dimension. These matrices are found one at a time in sequential order and erased to make room for the next. This is done because of constraints in interfacing between the MCYAC and ya2a programs.

In order to associate the appropriate averaged alpha particle energy with its corresponding bag of sorted random coordinate pairs, the bags are taken one at a time. Each point (coordinate pair) within a bag is successively compared with the points that comprise its associated matrix, which was created in a previous step. The closest matrix point to each random coordinate pair is found using a rounding algorithm. Once the nearest point is found, the six point bivariate interpolation is performed for the random coordinate using five of the nearest matrix entries as described in chapter III.

In the interpolation equation, $f_{0,0}$ is the matrix point in $\theta_1, \theta_2$ nearest to the random coordinate at which we are looking. The point $f_{1,0}$ is the matrix point that is one interval above $f_{0,0}$ in $\theta_1$ etc. Using this convention we find all the coordinates required for the interpolation.

If a random coordinate is rounded to a $\theta$ value that is at the maximum edge of a bag, then we require points above the maximum in order to complete the interpolation. Thus, we produce $\theta$ values on the grid that are two steps beyond the grid point that is created by the maximum $\theta$ value from the bag.

We apply the outcome of the six point interpolation to the yield and thus have an interpolated yield for the random coordinate pairs that we generated in the Monte Carlo simulation. This is a theoretical total yield. It does not include detector efficiency factors and seven percent correction for elements with $Z < 15$ (see Ph.D. thesis of Christopher M. Heirwegh), applied to provide equivalence to the measured yield.
The 7% corrections reflect systematic error in the widely-used XCOM attenuation database for the combination of low photon energies and absorbers having very low Z.

The reasoning behind breaking the data up into bags is to segregate the data into regions of similar energies that are small enough that they can be operated on using a personal computer. The bags allow us to look at the realistic effects of how alpha particle energies vary at the sample surface. Another reason behind breaking the data into bags is computational efficiency. For a typical run of 50000 points, if we process each energy individually, YAC needs to be called 50000 times. The computational power required to call YAC and process the results for many coordinate pairs becomes unreasonable very quickly, especially since additional calculations need to be done on the data. Rather than call YAC 50000 times, we run John Maxwell’s ya2a program ten times (for most investigations). Each time the ya2a program is called with an energy that is the average over the energies of that bag along with the coordinates specific to the bag in question and the ya2a program creates the aforementioned matrices.

Another method we have employed to increase computing speed is to use the maximum and minimum $\theta$ values to define a domain for the surfaces. Using these values we only need to generate the small portion of the coordinate pair matrix necessary to encompass each bag. This decreases the search space for every iteration of the MCYAC program when finding the nearest matrix point to each of the given random coordinate pairs for interpolation. Thus, we have implemented two methods to decrease the required computation time. First, each sub-space associated with its bag is searched far fewer times (a factor of the number of bins). Second, each sub-space that is searched is substantially smaller than the full space given by the full range of points. Once the interpolation of an angle pair is complete, the angle pair, element number, and yield are stored in a “results” file.
In the program created by M. Omand (2005), a yield surface is created for the given alpha particle energy. The random points are interpolated onto this surface using the six point interpolation described above. Hence, only one alpha particle energy is used and the variation of energies that reaches the surface is lost.

In the new method, each time we call the program ya2a with a different energy, we are creating a different surface. This surface is described by the three dimensional matrices discussed above. We thus interpolate each of our results onto the surface that correlates with the unique energy we have given the program. This is, by no coincidence, the surface that correlates to the angle range we are examining. We are then able to interpolate a small subset of points (via angle) onto each unique surface that we have created, thus accounting for the energy variation by angle in small pieces described by the bag size. Since the PIXE yield surfaces and the XRF yield surface are different, we add the interpolated yield points from both to get a total yield.

The method described above is chosen in order to balance computation time with precision. Though this method gives less precise results than processing each point individually, it is computationally feasible and, most importantly, allows us to get a sense of the magnitude of error introduced by assuming the alpha particles traverse the titanium foil at normal angles. However, there is still a matter of how many bags are required to give consistent results and whether or not the results will converge using this method. This potential problem is now investigated.

Since the range of angles is about $0^\circ$ to $45^\circ$ for $\theta_1$ values, and we are now using up to 60 bags, the surfaces that we interpolate onto are very small. Therefore, we decrease the angle step size in order to get more precision out of our interpolations. For this reason, the step size is chosen to be $1^\circ$ for these runs of the simulation.

Since standard statistical error on the counts of the X-ray yields for this exercise would be many times larger than the range of X-ray yields with which we are concerned, it was decided to use four sets of runs of MCYAC, each set with a different random
<table>
<thead>
<tr>
<th>Number of bags</th>
<th>Average X-ray yield</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4576.3</td>
<td>0.7</td>
</tr>
<tr>
<td>5</td>
<td>4570.1</td>
<td>0.4</td>
</tr>
<tr>
<td>10</td>
<td>4569.5</td>
<td>0.3</td>
</tr>
<tr>
<td>20</td>
<td>4569.2</td>
<td>0.5</td>
</tr>
<tr>
<td>60</td>
<td>4567.5</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Table 2: Table of average simulated X-ray yields of the NIST 70a sample and their standard deviations for various numbers of bags.

This allows us to ascertain the significance of the results using the standard deviation. A corrected sample standard deviation is employed and the number of Monte Carlo points used for each set of runs is 50000. Each of the four sets contains five runs of the Monte Carlo simulation. Each set uses 1, 5, 10, 20, and 60 bags. The simulated silicon X-ray yield of these runs is found and graphed in FIG. 8. Though silicon is shown, the trend is checked in the light elements sodium and aluminum and is found to be similar for these elements. We also note that there is no significant change in yield for heavy elements. The sample used for this exercise is NIST 70a and silicon is chosen based on its high statistics in the sample. The average simulated silicon X-ray yield and the standard deviation for each of the averages is given in TABLE II. The magnitude of the standard deviations indicate that the averages are meaningful relative to one another. We can see in FIG. 8 that the results converge nicely.

This result is not unique to the NIST 70a sample, the experiment was also done with the MicaMg sample using up to 100 bags in the largest run. The results are very similar.

The effect of including the angle through the titanium foil for the run of 60 bags versus
Figure 8: Convergence of results is seen as the number of bags is increased. The average X-ray yield counts for four sets of runs versus the number of bags used to attain these X-ray yields.
the run of 1 bag changes the results by a factor of 0.998. Moreover, it appears that
the amount of change in the X-ray yield behaves as an exponential tail, diminishing
with increasing number of bags. Though computational constraints prevent us from
treating each point individually, the trend indicates that energy variation due to path
angles of alpha particles traversing the titanium foil source cover has a very small
effect on the characteristic X-ray yield of light elements.

The number of bags for a standard run of the simulation program is chosen to be 10,
since increasing the number to 20 has a large effect on the computation time, but a
relatively small effect (about 0.01% difference) on the precision of the measurement.

0.4.4 Transmission of an X-Ray Entering the Detector

The process by which the characteristic X-ray yield counts are compiled is as follows:
a list of counts of sample-specific elements is created in the form of (usually) 50000
lines using the Monte Carlo simulation and the ya2a program as described above.
Each line in the list contains the counts of elements in the sample given at specific
angle pairs \((\theta_1, \theta_2)\) that are dictated by the Monte Carlo simulation. The lines from
the list are taken one by one and the thickness of each layer is divided by the cosine of
\(\theta_2\) for each line so that an angle-dependent thickness can be used as the “\(t\)” variable
in the factors that comprise the detector efficiency in the following equation. The
detector efficiency is composed of five transmission factors. Each of the transmission
factors can be set to one if the absorber lengths are changed to zero on the MCYAC
user interface. Detector efficiency is calculated using attenuation factors, gathered
from the XCOM database, for the beryllium window, the aluminum contact, and a
nitrogen layer. Additionally, there is a layer of incomplete charge collection (ICC) in
the silicon drift detector (SDD) and a factor for the X-rays that escape the silicon
wafer.

Each of the materials in the APXS detector window attenuates X-rays of different en-
ergies by different amounts. Since we are interested in characteristic X-rays of many different elements we must use transmission factors that uniquely account for the characteristic X-rays of each element in order to find the intrinsic detector efficiency. Similarly, the factor for the ICC layer is dependent on the specific wavelengths of the characteristic X-rays that interact with that layer. The ICC layer is accounted for empirically using values from J. L. Campbell [23]. In MCYAC, transmission factors are found for each layer of the detector window at all relevant characteristic X-ray photon energies, along with the factors for ICC.

Applying the transmission factors to the characteristic X-ray counts occurs successively by processing the lines of the “results.csv” file one at a time. The results file contains both the characteristic X-ray counts and the angle pair for which this yield occurs. The transmission factors for a specific line of the results file is calculated using the $\theta_2$ value that is unique to that line. When this is done for each element on the first line, and the transmission factors are applied to the number of counts of each of the elements in the first line, processing of the first line is complete.

The number of counts of each element in the first line is added to a zero in an array. The zero acts as a placeholder in the array for the newly calculated counts. When the second line is processed, the calculated detector efficiency is applied to the counts for the second line, and the result is added to the previous counts for that element, and the sum is stored. This process is repeated for every line in the list, giving a sum of counts for each element in all lines, with transmission factors being applied individually to each element of each line as the counts are summed.

As a specific example and check, we now look at the calculation of the transmission factor for the first element, sodium, in the first line in a run of the concentration file “MicaMg.txt”, and compare the result to what was obtained using a hand-held calculator.

First, we take the angle from the sample to the detector, $\theta_2$ ($\theta_2 = 0.379$ radians in
this case). The attenuation coefficients are obtained from the XCOM database [25] for $K_\alpha$ X-rays. For characteristic X-rays of element $i$ traversing the Be window, we use the equation:

$$
\epsilon_i^{Be} = \exp \left( -\frac{\mu_i}{\rho_i} \frac{t_{Be}}{\cos(\theta_2)} \right). \quad (41)
$$

We have similar factors for the CO$_2$, N$_2$, and Al layers. To find a factor that will give us the number of $K_\alpha$ X-rays from element $i$ that deposit their energy within the silicon portion of the detector via the photo-electric effect we use:

$$
1 - \epsilon_i^{Si}. \quad (42)
$$

Thus we have the detector efficiency for element $i$ given by:

$$
\epsilon_i = \epsilon_i^{Be} \cdot \epsilon_i^{CO_2} \cdot \epsilon_i^{N_2} \cdot \epsilon_i^{Al} \cdot (1 - \epsilon_i^{Si}). \quad (43)
$$

Each of these factors have been calculated for sodium in TABLE III.

Though we have used a nominal Be window thickness of $t = 0.0008$ cm, which is an input on the MCYAC user interface, this number has changed to 0.00102 cm as per work by G. Perrett and J. L. Campbell. The following is calculated for $K_\alpha$ X-rays of Na. Multiplying all these together, we get $\epsilon_{Na} = 0.327$, which agrees perfectly with the factor that MCYAC produces.

As a final feature, we also include a term for incomplete charge collection, assuming it has been determined by experiment. This is an option in the MCYAC program, chosen with a check box on the user interface. The final factor will be:

$$
\epsilon_{Na}^{total} = \epsilon_{Na} \cdot \epsilon_{cc}. \quad (44)
$$
<table>
<thead>
<tr>
<th>Attenuator</th>
<th>Atten. Coeff. ( \frac{\mu}{\rho} ) (cm(^2)/g)</th>
<th>Density (g/cm(^3))</th>
<th>Thick. (cm)</th>
<th>Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>538</td>
<td>1.84</td>
<td>0.0008</td>
<td>0.426</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>3538</td>
<td>0.0001977</td>
<td>2.151</td>
<td>0.850</td>
</tr>
<tr>
<td>N(_2)</td>
<td>2970</td>
<td>0.001251</td>
<td>0.018</td>
<td>0.931</td>
</tr>
<tr>
<td>Al</td>
<td>1065</td>
<td>2.702</td>
<td>0.00001</td>
<td>0.970</td>
</tr>
<tr>
<td>Si</td>
<td>1409</td>
<td>2.33</td>
<td>0.045</td>
<td>1.000</td>
</tr>
</tbody>
</table>

Table 3: Table of transmission factors calculated for the APXS detector window for characteristic sodium K\(_{\alpha}\) X-rays.

Applying this factor to the number of counts completes the detected yield for sodium on the first line of the Monte Carlo results.

In MCYAC, the user is allowed to specify the elements for which they would like to see the yield. The final yield and the element number are displayed on the screen. Apart from this, the program outputs all element numbers from the sample with their associated final yield, the ICC values used, the last line of transmission factors, and a comma separated list of the yields for easy copying and pasting along with the average \( \theta_1 \) and \( \theta_2 \) angles in radians.

### 0.5 Outcomes

We better understand the underlying physics of the APXS by observing various outcomes found by manipulating, through simulation, the parameters of the APXS instrument. Not only can we see what happens when we vary our parameters, but we obtain a quantitative measurement of the effect that is produced from the simulation. This will allow us to test simplifying assumptions that are used in analyzing APXS data and to quantify the magnitude of the error introduced by these assumptions. For this reason it is important to include as few approximations and empiricisms in the simulation as possible.
0.5.1 Comparison of Simulation Approaches

To test the validity of the results obtained thus far, they are checked against the output of a similar program, YAC, written by John Maxwell. YAC is similar to ya2a, however, the two programs are used in very different ways. YAC is run once using “effective angles” to obtain characteristic X-ray counts as if all the incoming Pu L X-rays and alpha particles were incident at the incoming effective angle, and the outgoing characteristic X-rays left the sample at the outgoing effective angle. In contrast, ya2a is run many times, and creates yield surfaces in the form of coordinate pair matrices as described above. The results of YAC, though available only at a specified pair of angles, are well-tested and reliable, and thus a correlation with the results of MCYAC implies that the calculations up to this stage are being done properly.

0.5.1.1 Effective Angles and the Monte Carlo Simulation

An initial consistency test simply involves running ya2a and YAC with the same single angle inputs to ensure that the two programs behave the same way. The ya2a program is simply run successively with the same input angles rather than using random Monte Carlo points. The test is done using the “MicaMg” sample file, with sample file name, “MicaMg.txt”. The results from the two programs are essentially identical, with no difference in the yields up to four significant digits.

For testing purposes, it is desirable to introduce one new parameter at a time. This allows us to monitor the effects of each parameter on the results of the simulation, ensuring the results are physically reasonable. For the next tests, the energy loss of the alpha particles traversing the titanium foil has been neglected, and the energy held constant at the same energy as that used in YAC, for the aforementioned reason. A checkbox was created on the user interface of the MCYAC program, which reads “Disable Energy Loss Through Ti Foil”. Checking this box causes the program to simply not call the module that accounts for the energy loss of the alpha particles.
traversing the titanium foil.

ya2a requires an input of $10^6$ Pu L X-rays and the corresponding number of alpha particles from the curium source. A ratio of 5.3 alpha particles for each Pu L X-ray, as found by G. Perrett, is used [26]. The sample used is again, “MicaMg”. The random number generator, “Standalonerandomnum2”, created by this author is run using 50000 random coordinates. The number of random coordinates is divided into 10 bags, for reasons described in Chapter IV, section B, to be run through ya2a, and the yields for every run are added together. However, when the yields are summed, the result is then 50000 times larger than each individual run. Therefore, the final count is divided by the number of random coordinates (50000), which brings the counts down to the same order of magnitude as YAC.

In order to create the following table, a step size of $2^\circ$ in both $\theta_1$ and $\theta_2$ is used to create the coordinate pair matrices. A small step size minimizes the increment on the yield surface used by the six point bivariate interpolation, which in turn reduces error due to round-off of higher order terms in the interpolation equation. A 7% correction factor may be applied to the four lightest elements in the MCYAC program, via checkbox; see [28] and the thesis of C. Heirwegh for the reasoning behind these corrections. However, since the correction was not included in YAC at the time the test was conducted (though this ability has since been added to YAC), the correction was not activated in MCYAC. For comparison reasons, the counts have been normalized to the counts of silicon (in measured APXS spectra of rocks, silicon generally has the best statistics). YAC is run with both the effective and average angles of $(19^\circ, 22^\circ)$ and $(19^\circ, 13^\circ)$ respectively. The results are given in TABLE IV. With the yields all lying within a few percent difference, we can see that the results between the two programs are consistent, verifying that the simulated results of the Monte Carlo make sense thus far.
Table 4: The counts relative to Si produced by YAC and MCYAC with the percent difference. YAC is run using both the effective and average angles for comparison with MCYAC. The very small percent differences between YAC and MCYAC show consistency between the two programs.
As discussed above, in the Monte Carlo simulation of Omand, the angles of the radiation entering the detector are not known, hence the yields are examined as a way to determine the angles that best describe a situation where, “if all of the simulated radiation were incident at one angle, the total yield would replicate that observed from the Monte Carlo” [16]. As we can see, the effective angles, (19°, 22°), of Andrushenko give good results.

However, using the new, full Monte Carlo simulation method, we now have access to the actual angles that enter the detector. Rather than use the method of Omand and Andrushenko, the author simply found the average incoming and outgoing angles from a 50000 point simulation. An average closely fits the quoted description by Omand [16], of what effective angles are meant to accomplish. The clearly smaller percent differences between MCYAC and YAC given by the single input of average angles into YAC over the single input effective angles into YAC, as displayed in TABLE IV, illustrate that average angles better approximate the results of the rigorous Monte Carlo simulation than the effective angles. The sole criterion for choosing effective angles is the coincidence with the results of YAC (PIXRF in Omand’s case) with the Monte Carlo simulation. Since the average angles give results closer to those of YAC than the effective angles, the average angles of (19°, 13°) are an improvement over the effective angles of (19°, 22°).

The only difference between the two runs of YAC is a change in the angles from the effective angles (19°, 22°) to the average angles (19°, 13°). Unfortunately, there is no quantitative argument for the average angles being the best possible angles. However, there appear to be advantages, over and above the better results seen in TABLE IV, to using average angles rather than effective angles.

There is a dependence on the geometry of the APXS instrument as regards effective and average angles. On the Mars mission, the APXS instrument is placed at various distances from the sample it is analyzing. It is a very simple matter to change the
distance to the sample in the "Standalonerandomnum2" Monte Carlo simulation, which yields average angles at any distance from the sample. This could easily be done for every measurement taken by the APXS instrument. The angles could then be used in GUAPX to give results that are specific to the distance at which the measurement is taken. On the other hand, it is a very difficult and time-consuming process to find effective angles for a given geometry. It is impractical to calculate these angles for every measurement taken by the APXS instrument.

0.5.1.2 Trends between the Two Methods

A study is conducted by running MCYAC with its options set such that the angle dependence through the titanium foil and attenuation of characteristic X-rays at the detector interface are not accounted for. The results of these runs are compared to the results of YAC, which is run with average angles. The purpose is twofold. Since convergence of the results of alpha particle angle variation through titanium foil and calculations of attenuation through the detector interface have been tested, it remains to test the effects of the implementation of the Monte Carlo method on yield alone in order to ensure consistency in this part of the program. Additionally, we can quantify the difference created by using single incoming and outgoing angles versus the spectrum of angles given by a full Monte Carlo approach as regards sample yields to examine the difference created by use of the average angle approximation. We will also see features created solely by using single incoming and outgoing angles versus the probabilistic spread of 50000 points created by the Monte Carlo approach of MCYAC.

It would not make sense for the results of the Monte Carlo method to vary greatly from those of YAC. Thus minimal deviation is desired as well as a consistency of results among different samples to confirm the Monte Carlo approach espoused in this thesis. This will ensure that the results found thus far are reasonable and consistent.
All the available mono-mineralic GRM concentration files from the MSL APXS calibration exercise [6] are used in the following tests to check whether the emergent trends are consistent across the elements of these minerals, and not specific to a certain mineral type. The mono-mineralic concentrations are used because this allows us to avoid complications that arise due to mineral phase effects, as discussed in Chapter I.

Since the YAC and MCYAC programs give essentially the same result when the same physical considerations are accounted for (see previous section), any systematic divergence must be due to the use of the Monte Carlo method. When the results are compiled, a continuous trend emerges, seen in FIG. 9. The departure of the YAC results, with average angles, from those of MCYAC suggest that the systematic divergence of the yield obtained with average angles is element dependent and very small, always lying within one percent difference. The fact that the behaviour of this trend is reasonably consistent for each element in every mineral suggests that the divergence is due to the effect that incoming and outgoing angles have on the characteristic X-ray yield of each element, and not the specific sample under examination, which confirms consistency of the MCYAC results.

We want to study the differences between the two methods, therefore we look at the percent difference. The counts in FIG. 9 and Table V are not normalized, since we desire the total divergence between the two methods. The table is simply an example of what the data behind the graph look like. This table is created using the MicaMg sample. This experiment was repeated using effective angles for the MicaMg and FKN samples. The trend was similar with differences all within 3 percent.

This experiment is repeated for nine minerals and the percent difference between YAC and MCYAC is plotted against the element number in the following graph. There is a clear trend in the data. This trend shows the effect of using a Monte Carlo
<table>
<thead>
<tr>
<th>Element #:</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
<th>19</th>
<th>20</th>
<th>22</th>
<th>24</th>
<th>25</th>
<th>26</th>
<th>30</th>
<th>37</th>
<th>38</th>
</tr>
</thead>
<tbody>
<tr>
<td>(YAC) Counts:</td>
<td>16.48</td>
<td>2629</td>
<td>1308</td>
<td>2621</td>
<td>0.424</td>
<td>1.158</td>
<td>6.267</td>
<td>451.8</td>
<td>2.432</td>
<td>38.520</td>
<td>0.635</td>
<td>16.37</td>
<td>778.3</td>
<td>9.655</td>
<td>106.2</td>
<td>2.682</td>
</tr>
<tr>
<td>(MCYAC) Counts:</td>
<td>16.62</td>
<td>2650</td>
<td>1317</td>
<td>2637</td>
<td>0.426</td>
<td>1.164</td>
<td>6.290</td>
<td>452.9</td>
<td>2.439</td>
<td>38.71</td>
<td>0.638</td>
<td>16.48</td>
<td>783.8</td>
<td>9.720</td>
<td>106.8</td>
<td>2.694</td>
</tr>
<tr>
<td>% Difference:</td>
<td>0.9</td>
<td>0.8</td>
<td>0.7</td>
<td>0.6</td>
<td>0.6</td>
<td>0.5</td>
<td>0.4</td>
<td>0.2</td>
<td>0.3</td>
<td>0.5</td>
<td>0.6</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Table 5: Unnormalized differences between the YAC and MCYAC programs for MicaMg
simulation that includes a spectrum of incoming and outgoing angles versus using the average angle approximation.

The fact that the yields from MCYAC are consistently higher than those of YAC makes sense for the following reason: using the dimensions from TABLE I and simplified two-dimensional geometry in figures 3 and 5 it is trivial to calculate that a path using the average incident angle (19°) fails to reach a location on the sample surface that is directly below the collimator opening. Since the incident angles of points generated by the Monte Carlo simulation that are located under the collimator are all greater than the average angle, the average depth of characteristic X-ray generation is shallower for these events. Additionally, the θ value of the path towards the detector must be less than about 8° in order to pass through the collimator from these locations, defining a shorter path out of the sample than using the average angle of 13°. A combination of these effects causes characteristic X-rays generated in these locations to be less highly attenuated by the sample matrix than those found using the average angles. Since the Monte Carlo simulation points found below the collimator opening comprise the majority of simulated characteristic X-rays detected (see FIG. 6 and 7), there is a greater yield of characteristic X-rays generated in the area where they are most likely to be detected. Thus we expect characteristic X-ray yields from the Monte Carlo simulation to be higher than those calculated using the single angle approximation.

We see that there are two distinct trends in FIG. 9. The first trend runs from sodium to potassium, elements excited almost exclusively by the PIXE process. The second trend runs from around manganese to zirconium, which are elements excited almost exclusively by the XRF process. The feature between these two trends belongs to elements excited by both PIXE and XRF processes. Since we are finding the difference between two programs that use the yield equation on the same samples, two trends makes sense. In the yield equation (equation (28)) we have two terms, one
for PIXE and one for XRF. The first trend comes from the difference between the PIXE contributions as calculated by the PIXE portion of the yield equation in each program while the XRF portion is essentially zero for these elements. For elements where the PIXE portion is essentially zero what we see is the difference between the XRF portions of the yield equation as calculated by each program. Thus, in a manner of speaking, we see one continuous trend, which is broken up due to the fact that we are comparing two programs that are both calculating yield using two terms that are effectively alternately zero and non-zero for different element ranges.

Given that we have already determined that characteristic X-rays less attenuated by the sample matrix are those most likely to be detected, we would therefore expect the difference between the MCYAC and YAC programs to cause this trend to be pronounced for characteristic X-rays that are highly attenuated by their respective sample matrices and diminished for characteristic X-rays that are not highly attenuated by their respective matrices. Thus it appears that a trend across the samples that have been chosen for the simulation is that characteristic X-rays of the lighter elements are more highly attenuated by sample matrices than the characteristic X-rays of heavy elements. This is of course not true in general for individual samples.

0.5.2 The Effect of Angles on Detector Window Transmission

One of the benefits of MCYAC over the other programs is that the angle associated with each incoming characteristic X-ray is known. This allows us to account uniquely for the attenuation of each characteristic X-ray entering the detector, giving us excellent precision in calculating detector window transmission factors, details of which are given in chapter IV, section D. Since the window thickness is related exponentially to the yield in the yield equation, even minor discrepancies in thickness have a significant impact on the final calculated yield.
Figure 9: The trend of the percent differences between YAC and MCYAC X-ray yields versus element number for nine minerals.
A study is conducted to compare the effect that angle has on the attenuation at the detector interface. Since inclusion of angle in calculation of transmission factors increases the effective thickness of the attenuating layers, it is expected that there will be higher counts for the light elements when the angle at the detector interface is assumed to be zero (all angles are measured from the normal as in previous chapters). For the following comparison, the usual 50000 coordinates are used. Since we are only considering attenuation through the detector, and through its effective windows of beryllium and nitrogen, $\alpha$-particle energy is kept constant in MCYAC in order to isolate the effects of attenuation at the detector.

The following table (TABLE VI) is populated with intrinsic detector efficiencies for a wide range of elements. For efficiencies in row A of TABLE VI, the transmission factors for the detector interface are run with zero angle, which is the same as treating the incoming photons as traversing the intervening media at right angles. For efficiencies in row B, the window transmission factors calculated for the detector interface include the array of angles of the characteristic X-ray paths that enter the detector as given by the Monte Carlo simulation.

Efficiencies in row C are created by a specialized program designed solely to find transmission factors at a defined angle. The value of the average angle for outgoing radiation, i.e. $\theta_2 = 12.9^\circ$, is input into the program. This simulates the effect of using the average angle to find transmission factors.

It is seen by the percent difference between A and B that when we do not include the spread of angles in the calculation of thickness for the window transmission factors, our efficiencies are higher for the lighter elements, as expected. This leads to overestimation of the detected X-ray yield, since X-ray yield is directly proportional to detector efficiency in equation (28).
Table 6: Simulation data showing trends for including angular dependence in transmission factors.

<table>
<thead>
<tr>
<th>Element #:</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
<th>19</th>
<th>20</th>
<th>22</th>
<th>24</th>
<th>25</th>
<th>26</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>A:</td>
<td>0.3311</td>
<td>0.5266</td>
<td>0.6829</td>
<td>0.7305</td>
<td>0.8113</td>
<td>0.8693</td>
<td>0.9066</td>
<td>0.9531</td>
<td>0.9658</td>
<td>0.9810</td>
<td>0.9889</td>
<td>0.9913</td>
<td>0.9932</td>
<td>0.9951</td>
</tr>
<tr>
<td>B:</td>
<td>0.3182</td>
<td>0.5145</td>
<td>0.6734</td>
<td>0.7221</td>
<td>0.8050</td>
<td>0.8648</td>
<td>0.9033</td>
<td>0.9514</td>
<td>0.9646</td>
<td>0.9803</td>
<td>0.9885</td>
<td>0.9910</td>
<td>0.9929</td>
<td>0.9969</td>
</tr>
<tr>
<td>C:</td>
<td>0.3218</td>
<td>0.5180</td>
<td>0.6762</td>
<td>0.7246</td>
<td>0.8069</td>
<td>0.8662</td>
<td>0.9043</td>
<td>0.9519</td>
<td>0.9650</td>
<td>0.9805</td>
<td>0.9886</td>
<td>0.9911</td>
<td>0.9930</td>
<td>0.9957</td>
</tr>
<tr>
<td>% Difference AB:</td>
<td>4.0</td>
<td>2.3</td>
<td>1.4</td>
<td>1.2</td>
<td>0.8</td>
<td>0.5</td>
<td>0.4</td>
<td>0.2</td>
<td>0.1</td>
<td>0.1</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>-1.1</td>
</tr>
<tr>
<td>% Difference BC:</td>
<td>-1.1</td>
<td>-0.7</td>
<td>-0.4</td>
<td>-0.3</td>
<td>-0.2</td>
<td>-0.2</td>
<td>-0.1</td>
<td>-0.1</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>
Figure 10: Graph showing the effects that inclusion of angle in the thickness calculation of the attenuating layers has on detector efficiencies. The curve shown is the difference between detector efficiencies that include the angle in the effective thickness (Monte Carlo), and those that assume a path with angle zero.
At higher element numbers, the increased energy of the characteristic X-rays renders attenuation by the detector window essentially non-existent. In the heaviest elements, we see an increase in the detector efficiency when the angle is included (see FIG. 10), which leads to an increase in the number of counts recorded by the detector. For elements such as rubidium and strontium, the only factor of the detector efficiency that is not effectively unity is the factor that accounts for the fraction of characteristic X-rays absorbed by the silicon detector. The reason for this increase in yield is that the characteristic X-rays of these elements are energetic enough to traverse the silicon wafer without depleting their energy within the wafer. This leads to fewer counts of the element in question. When we account for a range of angles of the incoming characteristic X-rays we allow for a range of effective silicon wafer thicknesses within which the X-ray photon may be absorbed, the smallest possible thickness being that of the X-ray with the path normal to the wafer. Thus accounting for the range of effective silicon wafer thicknesses leads to higher counts of the heavy elements.

Once the transmission factors begin to differ from unity, the deviation grows rapidly, as depicted in FIG. 10, because of the exponential dependence of the factors on thickness. We can see in the comparison of our results from efficiencies B to efficiencies C that the conditions of efficiencies C give results that are closer to efficiencies B than the conditions given by efficiencies A. It is evident that use of the average angle in the calculation of the detector efficiency is an improvement over using no angle at all when calculating the thickness, especially for the lightest and heaviest elements, as these are most affected by angle as explained in the preceding paragraph.

0.5.3 Comparison with GUAPX

Thus far we have compared the behaviour of the Monte Carlo simulation, MCYAC, with the YAC program. The results have been consistently reasonable, with clear
patterns emerging between the two programs. However, what we ultimately desire from the simulation are results that align with actual detected yields. To compare the simulation with real data we use results found from the program GUAPX.

GUAPX is a program used to fit spectra obtained by a combination of PIXE and XRF. GUAPX employs the Levenberg-Marquardt non-linear least-squares fitting approach to model the counts per second of incoming characteristic X-rays in terms of Gaussian peaks [5]. The program then converts the peak areas to elemental concentrations taking into consideration matrix effects, detector properties, etc. [5].

Along with concentration, GUAPX outputs peak areas. These peak areas are the counts per second that the APXS has detected, where the X-rays have been attenuated by the detector before being counted, and matrix effects have occurred within the sample before the X-rays reach the detector. This is the scenario that MCYAC is simulating. ya2a accounts for matrix effects within the sample, assuming homogeneous distribution of elements, and MCYAC accounts for X-ray attenuation through the detector interface.

The MCYAC yields are found using $3.45 \mu m$ titanium foil thickness for reasons explained above. The ICC layer is not accounted for, since the exact effects of the ICC are not quantified with a high level of precision and are not used in GUAPX. The CO$_2$ atmosphere is taken to be zero since the measurements are taken in vacuum in the APXS laboratory. Note that an effective beryllium window thickness of $10.2 \mu m$ is used instead of the nominal $8 \mu m$, due to the effects of a dura-coated beryllium detector window [29]. The standard 50000 points with step size of $2^\circ$ in both $\theta_1$ and $\theta_2$ are used in the Monte Carlo simulation. All other dimensioning for the Mars Science Laboratory required for the running of this program comes from engineering drawings gathered by N. Boyd and S. Andrushenko and reviewed by S. Stargardter and the author in consultation with R. Gellert, as presented in the previous chapter.

In this comparison, we start with the sample composition in terms of a normalized
concentration and use the X-ray Yield Equation to find an X-ray yield [5], which is a result comparable with the area under the curve fitted by GUAPX. To reiterate, single-mineral geochemical reference materials are used because of their relative homogeneity in terms of elemental distribution, which allows us to avoid complications due to mineral phase effects. The following graph (FIG. 11) shows the difference between GUAPX results and the simulation results for all the mineral geological reference materials (GRMs) available. Again the results are normalized to silicon. This averts geometry-based error in the GUAPX yields, which are affected by several percent in either direction by slight variation in the sample to detector distance.

A partial re-calibration of the APXS instrument has recently been done, which gives superior energy resolution. This new information leads to an upward change in the Mg concentrations in both the GLO and MicaFe samples by a factor of 1.046. This factor has been included in calculations done for figures 11 and 12.

The trend in this data shows high counts for the simulation in the light element range, reasonable results for the intermediate elements, and low counts for the simulated results of the heavier elements (Z=30, 37). Since there is a trend in the data, we are justified in averaging the differences for each mineral to create a graph of these averaged differences (FIG. 12). This is done in order to examine the general trend in the data. A polynomial curve of best fit has been added using Microsoft Excel's fitting function to show the trend in the data. The result for nickel (Z=28) is removed from this graph because there is only one mineral with an appreciable amount of this element present, so it is not a true average.

Once averaged, we can see a definite trend to the difference between the two counts. The APXS instrument is not fully characterized. The silicon wafer thickness, the nitrogen column pressure, and the beryllium window thickness may be different than the values used in the simulation, and differences between the actual values and the
Figure 11: Graph showing the percent differences between GUAPX and MCYAC for the elements of the mineral GRMs.
Figure 12: Graph showing the average percent differences between GUAPX and MCYAC for the elements of the mineral GRMs with trend curve.

values used in the simulation could cause large discrepancies between the actual and simulated X-ray yields.

In summary, we see a systematic discrepancy between the results of MCYAC and GUAPX. The largest source of discrepancy between these programs may come from the geometry of the APXS instrument, used in the MCYAC simulation, some of which is unknown. Estimates are used for some of the APXS dimensions based on the previous MER geometry. A dimension of significance is the distance between the inner collimator and the detector. Decreasing this distance allows for larger values of the maximum angles of excitation and emission, and hence larger average angles. As
examined above, a larger angle will decrease the number of characteristic X-rays that are detected for light elements. It simultaneously increases the number of counts from heavier elements. This is precisely the trend that is seen in the difference between GUAPX and MCYAC and a correction of this nature would offset it, bringing the light and heavy elements into balance.

0.6 Future Work

MCYAC is essentially a building block. Though a foundation has been laid, nothing has been built on it. A motivation behind the development of this program was to restructure the homogeneity assumption such that it is implemented on the level of minerals rather than used across all elements of a geological specimen. This issue has not yet been addressed. Though all the desired features of MCYAC have not been completed and experimental verification of its predictions are forthcoming, there is clearly consistency between the MCYAC simulation and the GUAPX fitting program, which indicates that it is worth comparing the simulation outcomes with those of experiment.

0.6.1 Limitations of the Current Simulation

0.6.1.1 Where the simulation currently stands

Thus far the MCYAC simulation is able to give results that are reasonably close to the results of other programs with which it has been checked, namely YAC and GUAPX. Additionally, elemental trends have emerged among the mineral samples, showing a consistent discrepancy between the different analytical methodologies, which is indicative of consistent behaviour of the MCYAC program itself. This is an excellent step in the development of the program. However, there is much more that must be done to complete the program, most importantly, an experimental check of its
validity, which will be discussed shortly.
The program ya2a, which accounts for matrix effects within MCYAC, is capable of processing the effects of including an additional layer of material on the surface of a sample. An ability such as this has many applications, including the study of soil or powder layers on the APXS titanium observation tray. This feature could be included in the current simulation; the user interface for this option has already been created. Research could be conducted on the effects of using average angles rather than effective angles in the GUAPX program, with the results of the GUAPX program using the average angles being compared with the results of the MCYAC simulation and the certificate concentrations of the minerals being examined.

Finally, average angles can easily be calculated at various standoff distances of the APXS instrument. A test could be conducted where sample measurements are taken with the APXS at various distances from the sample. The average angles for these distances can be calculated and used in the GUAPX program to discern the level of impact that inclusion of appropriate average angles has on the correctness of the GUAPX concentration calculations.

0.6.1.2 Verification of Simulated Results

In order to ensure that the results of the Monte Carlo simulation are correct, an experiment needs to be conducted to confirm or reject the simulated results. As per R. Gellert, the experiment needs to include a way to control the number of X-ray counts coming from an element placed at a specified distance from a point on the sample plane aligned with the centre of the detector (sample centre). Counts would be taken in a symmetric manner at various radii from the sample centre. These counts can be normalized, and the resulting relative counts compared with a profile of relative counts produced by the Monte Carlo simulation.

Since characteristic X-rays of light elements are generated symmetrically about the
sample centre by the three alpha-particle emitting curium sources of the APXS instrument, it is desirable for the object being tested to contain this same symmetry about the centre. Therefore a series of rings would be very effective. The rings should be as flat as possible in order to eliminate counts from the ring edges, which are not considered by the MCYAC program. Also, it would be convenient for the area of each ring to be the same so that the counts given by each ring are comparable.

To implement this experiment with these constraints, rings of aluminum could be machined, each with different radii, including a disc at the centre. Use of aluminum is advantageous because characteristic X-rays of aluminum are almost exclusively excited by the PIXE process when exposed to the curium-244 sources. Five rings would give a clear shape of the curve of the profile of characteristic X-ray counts. Three rings with radii ranging from one to four millimeters should be used to cover the steepest part of the curve of the predicted profile.

The rings need to be centred and mounted in an aluminum-free substance, so the counts from the mounting do not interfere with the counts from the aluminum rings, and each ring mounted in an individual sample tray. When taking the measurements, the exposure times need to be recorded and the counts divided by this time to ensure that when results are compared, the counts from each ring have no associated time dependence.

The counts per second of each ring can be divided by the counts of the ring with the highest number of counts per second. One may then compare the results of the profile of the successive rings with the profile of counts found using the Monte Carlo simulation, examining the dependence of the rate of change on distance from the centre of the detector. Conclusions can then be drawn as to the validity of the simulation in an experimental scenario in which the correct modelling of incoming and outgoing angles plays an important role in the accuracy of the results.
0.6.2 Using the Simulation to Address Mineral Phase Effects

The MCYAC program may be used as a component within an optimization program designed to account for mineral phase effects. Minerals have a definite chemical composition and therefore a mono-mineralic specimen will contain relatively consistent ratios of the same major elements. However, atomic sites of the lattice structure of minerals do not necessarily contain one specific element, but may be inhabited by various elements. Also, there are frequently many mineral types in any given geological sample. There may exist large quantities of a specific element within a given mineral and only trace amounts of that same element within a different mineral, and both of these minerals may reside within a single sample. Furthermore, some of the elements detected in a sample will exist in one mineral phase virtually exclusively. With no simplifying assumption, the aforementioned complications create virtually insurmountable difficulties in simulating the exact results of an APXS measurement on a geological sample, thus establishing the need for the homogeneity assumption, described in the first chapter.

We previously reasoned that the homogeneity assumption causes discrepancies in yield calculations. However, the assumption is more accurate in the case of individual minerals, since minerals are relatively homogeneous compared to multi-mineral geological samples. Thus, if we perform interaction calculations on minerals within a sample rather than the entire sample, we narrow the scope of the elements that we consider, and are able to predict the proportion of those elements more accurately. By shifting the homogeneity assumption to minerals rather than applying it to an entire sample, the subset of elements used to calculate matrix effects becomes much more representative of the elements with which the actual alpha-particles and photons interact, allowing increased accuracy in the predicted elemental yield of the observed sample.

Currently, a program is being developed by G. Perrett and J. A. Maxwell that will
optimize the elemental distribution in minerals of samples detected by the APXS. To accomplish this, MCYAC, or a similar program, will be run to predict the X-ray yield of each mineral present in the sample, using the homogeneity assumption. Because the penetration depth of the exciting radiation from the APXS is shallow, the portion of the sample that is excited can be approximated as an area [23]. This approximated sample “surface area” is divided up percentage-wise into sub-areas. Each of these sub-areas represent a specific mineral thought to exist in the sample. The goal is to bundle the elements found in geological specimens into the constituent minerals they form in the sample, in the quantities that are present in the sample. This allows us to account for matrix effects more accurately than viewing a geological specimen as a homogeneous soup with all atoms equally likely to interact with the X-rays and particles involved in an APXS measurement.

0.7 Changes to the GUAPX Program

In addition to the simulation program, edits and additions were made to the GUAPX spectral fitting program, the most extensive addition being “Batch B mode”.

0.7.1 The GUAPX Program

When APXS spectra are analyzed by the least squares fitting package GUAPX, written by J. Maxwell, S. Andrushenko and modified by D. Thomson, the input is a spectrum in terms of counts from the APXS silicon drift detector. The first line of the spectrum is the “livetime”, or the duration during which the APXS instrument was run. We take the number of counts and normalize by the livetime. This allows spectra of differing durations, and therefore significantly different counts per peak, to be compared directly. The detected counts are placed in a histogram based on the energy of the photon
that created the count. Peaks form around channels that correspond to the specific energy levels of the characteristic photons of the elements in the sample. These peaks are generally Gaussian in shape [12] and are fit, along with the rest of the spectrum, by the GUAPX program [27]. Background counts that are due to extraneous effects, such as bremsstrahlung photon escape and the Compton continuum, are removed using the digital “top hat” convolution filter [23]. After GUAPX has produced a fit that minimizes the $\chi^2$, the area under the fitted curve is calculated to give the number of counts per second.

0.7.2 Batch B Mode

Batch B mode is a mode of GUAPX that allows the user to fit up to several hundred spectra in succession through a single parameter (Par) file without having to replace each spectrum manually then run the standard GUAPX fitting routine for each spectrum. Using GUAPX in this mode speeds up the spectral fitting process greatly, allowing the user to fit many times more spectra than the original program would allow.

As input, Batch B mode first requires instrument specific experimental setup information. Next, an empirical correction factors (ECF) file, the “H-value”, which is a constant of the APXS instrument discussed in chapter II, and a “Par” file, which contains the parameters of the sample and instrument required to fit the given spectra. Aside from these inputs, the mode requires a list of spectra as input.

The GUAPX interface communicates with its back-end programs using temporary files that are overwritten every time the program is run. To run batch mode, the user specified par file is written into the temporary par file, the above inputs are also written onto this par file, and these parameters act as a template for all spectral fitting that takes place for the batch.

Once the par file information is acquired, the first spectrum, the spectrum file name,
live time, and spectrum header information are automatically input into the temporary par file, and fitted using the back-end apxbg program, written by John Maxwell. The apxbg program outputs a large body of information for each spectrum, called a “Megafile”.

The list of spectral files is processed in order using the par file information given in the initial step. The only information that changes with each successive run of the program is the spectrum and spectrum information. At the end of each iteration, the Megafile produced by the apxbg program is appended to the end of a csv file, called a “Gigafile”. When all spectra have been run the Gigafile is closed and saved in its own folder.

Beyond the standard testing that must be done when programming to ensure consistent and correct results, the program was tested by E. Nield of the APXS science team. She altered every parameter, ran varying numbers of varying spectra in varying order, and checked all of the results against single standard runs of the GUAPX program. In short, Batch B Mode has been thoroughly tested by a third party and found to yield results consistent with those found by running the program in the usual fashion.

0.7.3 Changes to the GUAPX Program

Though the largest addition made to the GUAPX program was Batch B mode, many other changes were also made. Some of the changes are simple, such as including the ECF file name in the parameter file, causing the spectral files to default to .sda instead of .sdf when a spectral file is opened, and removing comments from spectral file headers and writing them in the parameter file.

Other changes have a greater impact on the GUAPX program: it was found that the program retained information from its previous run upon reopening GUAPX and running a new file. Additionally pressure compensation based on Mars temperature
information is added. This is an application of the usual inverse dependence of pressure on temperature that includes a check to ensure that either both temperature and pressure are supplied by the user, or neither is supplied. Along this same vein is the integration of the pressure calculator of S. Taylor that returns the atmospheric pressure on Mars of the MER mission for a given sol.

Other additions are still more substantial. The first of these is the addition of .dcf (distance correction factor) files to the running of GUAPX. The .dcf file is a list of empirical correction factors specific to each element, which compensates for the distance of the APXS instrument sources to the sample surface. This addition requires allowing the user to pick from a list of specified distances (the user would round to the nearest distance offering), then matching the correction factor to whichever element is present in the sample and multiplying it to the H-value and element correction from the .ecf file, along with a possible seven percent correction to the light elements.

The second substantial addition is the inclusion of minerals in GUAPX. The idea is to reduce the usage of the homogeneity assumption by introducing the chemical formulae of specific minerals that are suspected of being present within a given sample. For each element in a sample, the user may pick a mineral that contains that element. This is accomplished using a drop down menu. The minerals in the drop down menu are sorted from a minerals file in the special matrices folder within GUAPX, and selected by the program so that, for a given element, only minerals that include that specific element are given in the drop down menu. Each mineral has an associated chemical formula that is stored in the background. Once a mineral is selected, it is added to the temporary parameter file for use by apxbg. If no mineral is selected for a given element, or “homogeneous” is selected from the drop down menu, then the homogeneity assumption is implied for that element.
0.8 Conclusions

In this work, we have discussed the APXS instrument and the homogeneity assumption, which is a necessary assumption on some level, for the analyzing of spectra from the instrument. We have reviewed the yield equation using a fundamental parameters approach and looked at the various terms that need to be included when simulating the APXS instrument.

We have examined the benefits of the full Monte Carlo approach taken in this work and have researched and compared the previous Monte Carlo method to the new one, discussing the need for the approach taken in this work. Unique to the new Monte Carlo method is the ability to find the average angle entering the detector. The test devised by M. Omand for discerning effective angles was conducted on both the average angles found in this thesis, and the effective angles of S. Andrushenko. It was found that average angles better fit the criteria set out by Omand.

The current simulation was examined in detail, discussing how to account for alpha particle energy variation caused by varying path lengths of alpha particles traversing the titanium foil. The convergence of these results was also examined, along with the difficulties in creating a program that accounts for these effects, yet can still be run on a desktop computer, how those difficulties were overcome, and how the transmission factors are found for every Monte Carlo angle that enters the detector. A comparison was conducted to ensure that the results of the MCYAC program up to this point are valid. The results of MCYAC were compared to the well-tested YAC program and it was found that the results all lie within one percent difference, which helps to confirm the MCYAC program up to this point. Trends between the two programs emerged.

The effect of including angles in the thickness term in transmission factors was addressed. Specifically, the transmission factors for the detector interface are found, using the angles provided by the Monte Carlo simulation. The transmission factors found using the Monte Carlo simulation results are compared to transmission factors
found using the assumption that the radiation entering the detector is always normal to the detector. It was found that there is a significant difference in the results for light and heavy elements when using the angles of the Monte Carlo simulation versus simply assuming normal incidence of the incoming characteristic X-rays. These transmission factors are compared to those found by using the average angle entering the detector, and it is discovered that the results are much closer when the average angle is used to calculate the thickness in the transmission terms.

As a final comparison, the results of the simulation are compared to the counts per second from GUAPX. There is reasonable agreement between the two sets of data. A trend emerges between the differences of the two programs. It is seen that this trend is similar to the trend found when path angle is not included in the calculation of the transmission factor.

We looked at where the simulation is headed, what could be done to improve it and what would be required to test it to ensure that it is producing good results. An experiment was proposed to verify or refute the results of the MCYAC simulation. Also, ideas for how to use the simulation to address mineral phase effects were given. Finally a survey of changes made to the GUAPX program was completed, with sufficient detail to make future modifications to the major areas of change relatively straightforward.
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