

Optimal interpretation and decomposition of XRF spectra.



Stefan Graham, s144140, 06/2017 Supervisor: John Leif Jørgensen, DTU Space Co-supervisor: Abigail Allwood, JPL Caltech

DTU Space National Space Institute

Ĩ

Abstract

This thesis researches a method of decomposing x-ray fluorescent (XRF) spectral data in situ for elemental analysis and optimal compression. The focus of this report is on the application to the Planetary Instrument for X-ray Lithochemistry (PIXL) to be mounted on the Mars 2020 rover.

For this project, I have used a hand held commercial XRF to measure the spectrum of brass. Using the measured spectrum of brass, I tested decomposition and elemental analysis methods. Comparing the percentages calculated by the commercial XRF instrument with the percentages calculated with the method described in this report resulted in an error of \pm 4-7 %. To further test the decomposition the PIXL team at the Jet Propulsion Laboratory(JPL) has supplied a representative spectrum of the reference glass, BHVO-2G. For BHVO-2G I have calculated and compared the chemical composition of measurements with a one second sample and a 300 second sample. The 300 second sample resulted in element detection down to the 0.1 % level. A 1 second sample time resulted in detection of elements down to 1 % percentage level.

Data transfer from Mars to Earth is limited so to maximize scientific return the highest level of lossless (i.e. no loss in quality) compression possible is desired. Uncompressed the spectral data from PIXL would take approximately 5 days to be sent from Mars to Earth. Using generic lossless compression methods, the level of compression achievable is in the range of 75-90 % depending on the degree of measurement noise [1]. In this report, it is found that by first decomposing the spectral data a compression level of 98.51 % is achievable. A 98.51 % compression would reduce the time to send the PIXL data from Mars to Earth from 5 days to 1 hours and 47 minutes.

Contents

1	Intr	roduction 4		
	1.1	Mars 2020 Mission		
	1.2	Planetary Instrument for X-ray Lithochemistry 4		
	1.3	My Work		
2	The	eory 8		
	2.1	X-ray Fluorescence		
		2.1.1 XRF instrumentation		
		2.1.2 Characteristic X-ray		
		2.1.3 Bremsstrahlung Radiation		
		2.1.4 X-ray Attenuation		
	2.2	Poisson Statistics		
	2.3	Spectrum Processing Methods		
		2.3.1 Median Filter		
		2.3.2 Curve Fitting		
		2.3.3 Chemical Decomposition		
3	B Data Collection and Database			
	3.1	X-MET 800		
		3.1.1 Time. Current and Voltage		
	3.2	Samples		
	3.3	Spectra from PIXL		
	3.4	Database used for Chemical Composition Calculation 19		
		3.4.1 Database of Relative Intensities		
		3.4.2 Attenuation Correction of Database		
4	Spe	ctrum Decomposition 23		
-	4 1	Bremsstrahlung Bemoval 23		
	1.1	4.1.1 Median Filter 23		
		4.1.2 Polynomial Fitting 23		
		4.1.3 Comparison		

4.2 Curve Fitting								
	4.2.1 Peak Finding	25						
	4.2.2 Peak Fitting	26						
Dis	Discussion of Results 27							
5.1	Accuracy of Chemical Decomposition	27						
	5.1.1 Solution to System of Equations	27						
	5.1.2 Comparison with X-MET 800	28						
	5.1.3 Error Inspection	28						
5.2	Impact of sample time on chemical composition	29						
5.3	Analysis of Noise Distribution	30						
	5.3.1 Statistical Distribution	32						
	5.3.2 Auto Correlation	32						
	5.3.3 Impact of sample time on SNR	33						
5.4	Compression Level Discussion	34						
Cor	nclusion	35						
6.1	Summary	35						
6.2	Results of Comparisons.	35						
6.3	Future Work	36						
Арі	pendix	37						
T. 1								
7.1	X-MET 800 settings	37						
$7.1 \\ 7.2$	X-MET 800 settings	37 37						
$7.1 \\ 7.2$	X-MET 800 settings	37 37 37						
7.1 7.2	X-MET 800 settings	37 37 37 38						
7.1 7.2	X-MET 800 settingsMatlab implementations7.2.1XRayAbsorbtionInAir.m7.2.2generateMatrix.m7.2.3decomposition.m	37 37 37 38 38						
	 4.2 Dis 5.1 5.2 5.3 5.4 Con 6.1 6.2 6.3 Apj 	4.2 Curve Fitting 4.2.1 Peak Finding 4.2.2 4.2.2 Peak Fitting 4.2.2 Peak Fitting 4.2.2 Discussion of Results 5 5 5 5.1 Accuracy of Chemical Decomposition 5 5 5.1.1 Solution to System of Equations 5 5 5.1.2 Comparison with X-MET 800 5 5 5.1.3 Error Inspection 5 5 5.2 Impact of sample time on chemical composition 5 5 5.3 Analysis of Noise Distribution 5 5 5.3.1 Statistical Distribution 5 5 5.3.2 Auto Correlation 5 5 5.4 Compression Level Discussion 5 5 6.1 Summary 5 5 5 6.3 Future Work 5 5 5 6.3 Future Work 5 5 5						

Chapter 1

Introduction

1.1 Mars 2020 Mission

Mars is the second closest planet from Earth with a diameter roughly half that of Earth's. The cratered, rocky surface of Mars contains geologic features also seen on Earth such as valleys, desserts and polar ice caps [3]. Due to the thin atmosphere (1% pressure of Earth), little volcanic activity and no subduction, Mars has an abundance of rocks that are billions of years old[2]. Ancient rocks on Mars reveal the geologic history and can indicate if life has ever existed on the planet.

Currently, there is an automated motor vehicle (Mars rover) exploring the planet's surface determining the role of water on Mars. In 2012 NASA announced that it would be launching a second Mars rover scheduled for launch in 2020. The mission objective is to uncover the geologic history of Mars while looking for indications of past life forms though small(0.1 mm) scale geologic features [4].

The Mars rover's payload consist of 7 instruments; this report will focus on the payload named Planetary Instrument for x-ray Lithochemistry (PIXL) to be mounted on the rovers robotic arm.

1.2 Planetary Instrument for X-ray Lithochemistry

PIXI is included on the mission to measure the small scale chemical variation in rock samples and correlate the chemical composition with visible surface features[5]. The correlation makes it possible to analyze the spatial variation in chemistry in non-homogeneous rocks such as across rock boundaries and in conglomerates.

To measure the elemental composition PIXL uses a micro focus x-ray fluorescence instrument (XRF). XRFs measure elemental chemistry by bombarding a sample with x rays causing ionization(i.e. the displacement of an electron). The ionization results in the emission of a photon which can then be measured using a photon detector. By sorting the photons by energy results in a spectrum that can be used to calculate the chemical composition. PIXL is a micro focus XRF (0.12 mm beam diameter) meaning that the chemical composition of 0.1 mm spots can be measured[5]. Measuring the spots in a grid PIXL can create chemical maps such as figure 1.1 where each pixl has a corresponding spectrum.



Figure 1.1: Chemical composition variation of conglomerate using a 20 mm by 10 mm mapping and 0.15 mm step size [5].

Although, it only takes 4-24 minutes for data to travel from Mars to Earth, the two satellites orbiting Mars require line of site with Earth to send

data. Line of site is only possible for a total of 16 hours per day limiting the amount of data transferred to Mars [6]. Due limited data transfer, each payload on the rover is constrained to send a certain amount of scientific data back to Earth per day. For PIXL the data constraint is 16 Megabits per day. An uncompressed 2 mm by 2 mm spectral map (approximately 10 times smaller than figure 1.1) contains a total spectral data of 66 Megabits. Uncompressed, the spectral map would take approximately 5 days to send to Earth [6]. To increase scientific return, it is therefore essential to compress the spectral data as much as possible before sending it to Earth.

1.3 My Work

For the PIXL mission it is required that the raw data gets losslessly compressed i.e. the original spectral data can be reconstructed from the compressed signal without any losses. General-purpose lossless compression algorithms do exist but by considering physical characteristics of spectral data a higher level of compression can be achieved. This report will focus on using physical insights of x-ray fluorescence to compress the spectral data for the PIXL mission.

The compression method involves decomposing the spectrum into three constituent parts:

- A polynomial describing the continuous background spectrum (Bremsstrahlung)
- A sum of Gaussian functions describing each individual peak
- Measurement noise, found by subtracting the two above functions from the spectrum

The decomposition process is illustrated in figure 1.2. The idea is then that the number of parameters needed for reconstructing the spectrum is reduced to the background polynomial coefficients and Gaussian function parameters. For losslessly reconstructing the spectrum the noise after subtracting the two functions is also needed. If the noise is Gaussian distributed with a small variance it should be highly compressible.

The Gaussian functions contain all the useful information about chemical composition. Therefor, the decomposition can also be used to calculating the elemental composition.

This report first describe the theory needed for the project. The experimental setup is then described along with the database used for calculating the chemical composition. The spectral data comes from two sources. The



Figure 1.2: Block diagram representing decomposition and reconstruction of a simulated spectrum

spectrum of brass I have measured with a commercial XRF. The spectra of the reference glass, BHVO-2G, is a spectrum measured by the PIXL team at the JPL. Using the spectra from the two sources methods of curve fitting are tested and the decomposition is performed. Using the decomposition, the elemental composition is calculated for varying sample times. Lastly, we will look at the resulting noise distribution and discuss the level compression achieved. Throughout this report Matlab is used for data processing.

Chapter 2

Theory

This chapter explains the theory needed for understanding the method of decomposition. The theory includes the principals of x-ray fluorescent instrumentation and the mathematics for linear and non-linear regression.

2.1 X-ray Fluorescence

2.1.1 XRF instrumentation

Fluorescence is the emission of light from a material due to the absorption of electromagnetic radiation. X-ray fluorescence works by shining an x-ray beam (primary radiation) on a sample causing the sample to emit fluorescence. The fluorescence is then detected by the photon detector. Each detected photon is sorted into a bin corresponding to its energy, creating a histogram (spectrum) with the number of photons of a given energy detected in each bin. The sum of all histogram values or the area under the spectrum represents the total fluorescent energy emitted. The process is illustrated in Figure 2.1.

In the x-ray tube the electrons are accelerated by an electric field to generate the primary x-ray radiation. To produce a micro sized x-ray beam PIXL uses a polycapillary optic. The polycapillary optic focuses the x-ray beam down to a 100 μ m spot by reflecting the x-rays though a tapered lens. A common but less effective method of producing a micro x-ray beam is by using a micro sized pinhole to block surrounding x-rays. By using a polycapillary optic PIXL produces a micro x-ray beam that has a 140 higher flux than a pinhole optic[9]. A high x-ray flux causes more excitation in the sample and therefore a higher count rate. The higher count rate means that a shorter sampling time can be used. With a short sample time PIXL can quickly



Figure 2.1: Microfoucs XRF detection

move the x-ray beam to a new spot thereby quickly mapping out an area with high resolution. Three important mechanisms account for the shape of the XRF spectrum; Characteristics x-rays, Bremsstrahlung radiation and xray attenuation.

2.1.2 Characteristic X-ray

Characteristic X-rays produce a discrete line spectrum meaning that the radiation only contains certain energies in a range [8]. Characteristic X-rays are produced when an x-ray beam is fully absorbed by a material causing ionization. An inner shell electron gets emitted leaving a vacancy which subsequently gets filled by an outer shell electron. Replacement of an inner shell electron by an outer shell electron causes the release of energy in the form of a photon (Figure 2.2). The released energy is equal to the energy difference between the inner and outer shell.

All elements have a unique shell energy level, and therefore the photon energy is characteristic of the element and is called characteristic radiation. When an electron from the 3rd shell (L shell) fills the vacancy in the innermost shell, the K shell, it is known as the elements $K\alpha$ radiation.

The $K\alpha$ radiation is usually the highest energy of an element's characteristic radiation. Likewise, each characteristic radiation line has a similar name depending on the electrons final and initial shell (such as L or M shell). In general, the $K\alpha$ characteristic radiation from elements of large atomic number releases more energetic photons. For example, $K\alpha$ emission from iron (Z = 26) is of energy 6.4 keV while the $K\alpha$ of Carbon (Z = 6) is 0.28 keV. The characteristic radiation appears on a spectrum as a line centered on a characteristic energy level. In practice, the line is a broadened bell-shaped



curve superimposed on a continuous radiation (Figure 2.3).

Figure 2.2: Mechanism producing characteristic x-rays [7]



Figure 2.3: Simulated spectrum illustrating Bremsstrahlung radiation and broaden characteristic lines

2.1.3 Bremsstrahlung Radiation

In contrast to the discrete characteristic radiation, bremsstrahlung radiation is the continuous radiation observed in the XRF spectra. Continuous radiation means that the spectrum contains all photon energies in a certain energy range [8]. In a spectrum, the bremsstrahlung radiation appears as the smooth continuous curve superimposed with the characteristic radiation (Figure 2.3). Bremsstrahlung is produced when an electron is decelerated/deflected by the positively charged nucleus hence the origin of the name braking radiation. The deceleration decreases the electron's kinetic energy causing the release of energy in the form of photons. The process is illustrated in figure 2.4. As the electron slows down, kinetic energy decrease towards zero.

The bremsstrahlung radiation is the source of the x-ray excitation in XRF. Inside the XRF electrons are accelerated towards a metal target (anode) by an electric field. When the accelerated electrons meet the the metal target, they are slowed down releasing bremsstrahlung radiation.

The cut-off energy level of the bremsstrahlung is equal to the kV in keV of the high voltage power source. For example, a high voltage of 40 kV produces a spectrum with cut-off energy at 40 kev. Past the cut-off energy no characteristic energy levels can be excited so by setting the high voltage the level of excitation can be varied.



Figure 2.4: Mechanism producing Bremsstrahlung radiation [13].

2.1.4 X-ray Attenuation

When an x-ray beam passes through a material it loses intensity due to two processes; absorption and scattering. Absorption occurs when energy is absorbed by the material causing an increase in thermal energy. Scattering on the other hand is the deviation of the x-ray from a straight line and does not cause a transfer of energy. The attenuation coefficient for absorption and scattering describes how easily the x-ray penetrates though a material. The total attenuation coefficient is the sum of the absorption, μ_a and scattering attenuation coefficient, μ_s .

$$\mu = \mu_a + \mu_s \tag{2.1}$$

The attenuation coefficient of a mixture is the linear combination of each element's weight fraction.

$$\mu_{total} = \Sigma_i w_i \mu_i \tag{2.2}$$

Where μ_i and w_i are the attenuation coefficient weight percentage of the ith element [16].

The attenuation of radiation is dependent on the photon energy. High energy photons travel though materials easily while low energy photons quickly get blocked.

The attenuation of an x-ray beam though a depth, l, is given by the Beer-Lambert law:

$$\frac{N}{N_0} = e^{-\mu l} \tag{2.3}$$

where μ is the total Mass attenuation coefficient and N/N_0 is the fraction of photons passing though the material. In this report the Beer-Lambert law is used to correct for the attenuation in the atmosphere.

2.2 Poisson Statistics

Photons are detected in discrete amounts and the arrival of each photon in a given time interval is independent of the arrival of next photon. Photon count data therefore follows a Poisson distribution. The Poisson distribution is characterized by having the mean equal to the variance. The measurement noise of count data similarly follows a Poisson distribution. All the spectral data analyzed in this report are Poisson distributed.

2.3 Spectrum Processing Methods

2.3.1 Median Filter

A 1-dimensional median filter is used to smooth data with large variations. The median filter uses data points on either side of the measurement value to calculate the median thereby removing large peaks and troughs in the data. The order of the median filter specifies how many neighbors to include in the median calculation. An order of 10 means that 5 data point are included on either side when calculating the median. The higher the order

the larger the degree of smoothing. The median filter is tested as a method of bremsstrahlung removal.

2.3.2 Curve Fitting

Polynomial fitting

Polynomial fitting is a method of linear regression where a polynomial is fitted to the measured data values. The polynomial function is of the form:

$$y(x) = p_1 x^n + p_2 x^{n-1} \dots + p_n x + p_{n-1}$$
(2.4)

Where y_j is the data points as a function of energy (x) in the spectrum and p_j is the parameter to be found. Writing the function for each data point we get a system of equation represented in matrix form as:

$$\begin{bmatrix} x_1^n & x_1^{n-1} & \cdots & 1 \\ x_2^n & x_2^{n-1} & \cdots & 1 \\ \vdots & \vdots & \ddots & \vdots \\ x_m^n & x_m^{n-1} & \cdots & 1 \end{bmatrix} \begin{bmatrix} p_1 \\ p_2 \\ \vdots \\ p_j \end{bmatrix} = \begin{bmatrix} y_1 \\ y_2 \\ \vdots \\ y_m \end{bmatrix}$$

In matrix notation, we have:

$$\mathbf{X}\vec{p} = \vec{y} \tag{2.5}$$

The chosen coefficients p will found by minimizing the sum of squares

$$min(S) = min(\sum_{i=1}^{j} (p_j - y_j)^2)$$
 (2.6)

For m > n the solution the that minimizes equation 2.6 is given by:

$$\hat{\vec{p}} = (\mathbf{X}\mathbf{X}^T)^{-1}\mathbf{X}^T\vec{y}$$
(2.7)

Polynomial fitting is used in this report as a method of bremsstrahlung removal.

Non-linear least squares on Gaussian function

Non-linear least squares is used when the function parameters are non-linear such as in the case of a Gaussian function. The Gaussian function is a bellshaped curve with the function:

$$f(x) = a \exp\left(-\frac{(x-b)^2}{2c^2}\right)$$
(2.8)

The parameters a and b represent the height and positioning of the curve, respectively. The parameter c is the standard deviation and defines the width

of the curve. The function can be made linear by approximation with the Taylor series expansion. The Taylor series use the partial derivatives of each parameter at the point $\vec{p_0} = [a_0, b_0, c_0]$ [11]:

$$f(x;\vec{p}) \approx f(x;\vec{p}_0) + \frac{\partial f}{\partial a}|_{\vec{p}_0}(a-a_0) + \frac{\partial f}{\partial b}|_{\vec{p}_0}(b-b_0) + \frac{\partial f}{\partial c}|_{\vec{p}_0}(c-c_0)$$
(2.9)

The equation now consists of linear coefficients as in equation 2.4 and can similarly be written in matrix form. The system can then be solved using the same method as linear regression i.e. equation 2.7.

2.3.3 Chemical Decomposition

System of equations

To calculate the chemical composition from an XRF spectra we use linear least squares regression. Each number of counts, y, at a energy level E_i represents the sum of the constituent elements in the material. An equation of the number of counts in each energy bin in the spectrum can be written as:

$$y(E_i) = k[p_1x_1(E_i) + p_2x_2(E_i) + \dots + p_jx_j(E_i)]$$
(2.10)

Where x_j is the photon count of the pure substance j at E_i . For example, 1000 photons (x_{Fe}) come from iron at the energy $E_i = 6.4 keV$. The variable p_j represents the percentage of the substance j (e.g. $p_{Fe} = 0.5$) contained in the sample. Lastly, k is a parameter that corrects for the atmospheric attenuation. The atmospheric attenuation, k, depends on the detector sample distance and different on Mars than on Earth. Each energy bin has a corresponding equation which combined creates a system of equations of the form:

$$k\mathbf{A}\vec{p} = \vec{b} \tag{2.11}$$

$$k \begin{bmatrix} x_1(E_1) & x_2(E_1) & \cdots & x_j(E_1) \\ x_1(E_2) & x_2(E_2) & \cdots & x_j(E_2) \\ \vdots & \vdots & \ddots & \vdots \\ x_1(E_i) & x_2(E_i) & \cdots & x_j(E_i) \end{bmatrix} \begin{bmatrix} p_1 \\ p_2 \\ \vdots \\ p_j \end{bmatrix} = \begin{bmatrix} y(E_1) \\ y(E_2) \\ \vdots \\ y(E_i) \end{bmatrix}$$

Solution using Single Value Decomposition

To ensure numerical stability the solution to equation 2.11 is found using the single value decomposition (SVD). The SVD is a matrix factorization method which is used to find the pseudoinverse of \mathbf{A} . The SVD of the matrix \mathbf{A} is given by:

$$\mathbf{A} = \mathbf{U}\Sigma\mathbf{V}^* \tag{2.12}$$

Where Σ is a diagonal matrix of the same size as **A**. U and V are square matrices where the * represents the conjugate transpose. Since **A** is not a square matrix it does not have an inverse but by using the SVD a pseudo inverse can be found as:

$$\mathbf{A}^{+} = \mathbf{V}\Sigma^{+}\mathbf{U}^{*} \tag{2.13}$$

Where Σ^+ consists of the reciprocal of non-zero diagonal elements in Σ then transposed.

The solution to the least square problem is then:

$$\hat{\vec{x}} = k\mathbf{A}^+ \vec{b} \tag{2.14}$$

Uncertainty Estimate

A confidence interval for the least squares solution is found using the variancecovariance matrix:

$$\mathbf{C} = \mathbf{A}^+ \mathbf{C}_{obs} (\mathbf{A}^+)^T \tag{2.15}$$

Where C_{obs} is a diagonal matrix with the variance of each observation in the diagonal. For this report the measurements are Poisson distributed photons counts. The variance is therefore equal to the mean i.e. the photon count. The confidence interval is then the square root of the corresponding diagonal elements of **C** multiplied by the t-distribution:

$$\pm t_{\alpha/2}\sqrt{C_{jj}} \tag{2.16}$$

For a 95% confidence interval t = 1.96.

Chapter 3

Data Collection and Database

Previous sections explained the theory behind X-ray fluorescence. This chapter introduces the X ray fluorescent instrument, explains how samples were taken in practice and describes the samples from the PIXL team at JPL. Lastly, the database used for chemical decomposition is introduced and the preprocessing necessary is applied.

3.1 X-MET 800

The XRF instrument used for this report is the X-MET 800 by Oxford instruments. The hand held X-MET 800 is connected to the bench-top stand (Figure 3.1) as a safety measure and to decrease background radiation.

To measure the spectrum a sample is placed inside the stand directly over the photon detector. Using the accompanying software, the sample time, current and voltage is chosen. The sample time can be changed to any number while the high voltage power source and currents are fixed. Appendix 7.1 list the available combinations of voltages and currents.

To start measuring, the trigger is pressed down. The X-MET measures for the duration of the sample time. Once finished the estimated chemical composition and the spectrum is outputted to the PC.

All sample taken using the X-MET 800 have 2048 channels and a channel width of 0.025012 keV.

3.1.1 Time, Current and Voltage

Changes in sample time, current and voltage impact the measured spectrum.



Figure 3.1: (1)Experimental setup of XRF attached to benchtop stand with data transfer to PC. (2)Iron sample placed over sensor

Sample Time

A longer sample time allows for more photons to be detected meaning a higher count in the spectrum.

Three samples have been taken using the X-MET 800 where a variable sample time has been used. The three samples have been taken at 60, 30 and 15 second to demonstrate that the time is proportional to the photon count(Figure 3.2). For comparison, the 15 second and 60 second spectrum is interpolated to 30 seconds by multiplying by 2 and 0.5 respectively. The residuals of the interpolation are centered around zero the variance is correlated with the peaks so larger counts have a higher variance (Figure 3.3).

Current

Similarly, to the sample time, the current causes a proportional change in the number of counts. Higher total energy is emitted corresponding to larger area under the spectrum. The X-MET 800 changes the anode material for different current settings causing the proportionality not to be observed in



Figure 3.2: Cu spectrum with sampling time of 60, 30 and 15 seconds



Figure 3.3: Residuals after correction 15 and 60 second sample to 30 seconds

practice.

Voltage

Unlike current and time, increasing the voltage causes excitation at higher energy levels resulting in new characteristic lines in the spectrum. The increase in voltage also cause the bremsstrahlung to shift towards higher energy levels.

The cut-off energy level for the bremsstrahlung is determined by the voltage used. If using a voltage of X kV the cut-off for the bremsstrahlung is at X keV. Furthermore, the number of counts is proportional to the voltage. A higher voltage results in a proportionally larger number of counts. Comparing spectra measured at different voltages is only possible below the minimum cut off energy of the two spectra.

3.2 Samples

When using the X-MET 800 no sample preparation is necessary although a smooth, clean surface produces the most accurate results. Samples of a variety of metals including iron, titanium, copper and brass along with several rocks and fossils have been measured. This report will focus on the brass sample. Brass is an alloy of copper and zinc. Since, brass is mainly composed of two elements it is used to test the accuracy of the chemical decomposition.

The brass spectrum has been measured using 40 kV high voltage, 8 μA current and a sample time of 20 seconds.

3.3 Spectra from PIXL

For this project, the PIXL team at JPL have supplied spectra taken using the PIXL instrument. One of the spectra used in this report is of a reference glass certified by the U.S. Geological Survey with the label BHVO-2G. BHVO-2G is composed of 17 elements and is one of the 4 calibration targets PIXL will be using during the mission on Mars. The spectra of BHVO-2G has been taken in a variety of conditions including Earth air, simulated Mars air and vacuum. Furthermore, measurement have been made using varying sample times. The spectra of BHVO-2G are:

- BHVO-2G 15kev, 1 μ A, (300/120/30/2/1) seconds (air)
- BHVO-2G 28kev, 20 $\mu \mathrm{A}$, 3600 s (vacuum)
- BHVO-2G 28kev, 20 μ A, 3600 s (6.2 torr CO_2 , Simulated Mars air)

All spectra from PIXL contain 4096 channels and have a channel width of 0.00717. The resolution of the PIXL data is 3.5 times higher than the X-MET 800. The supplied spectra have been used for decomposition since the spectra from the X-MET are preprocessed in an unknown way.

3.4 Database used for Chemical Composition Calculation

For calculating the chemical composition, a database of characteristic radiation is used. This section introduces the database and the preprocessing applied.

3.4.1 Database of Relative Intensities

To create the **A** matrix from Equation 2.11 we use the database from the X-Ray Data Booklet created by the Center for X-ray Optics and Advanced Light Source at Lawrence Berkeley National Laboratory [19]. The database consists of the energy and the relative intensities between each characteristic radiation series of an element. The table is sorted in ascending order based on the energy of the characteristic line. The maximum line intensity in each series ($K\alpha$, $K\beta$ ect.) is given a value of 1. As an example, iron (Fe) has a $K\alpha_2$ line half as intense as the $K\alpha_1$ line. Each elements intensity in the database table is mapped over to the corresponding energy in the matrix **A** (Figure 3.4).



Figure 3.4: Generating the A matrix from the X-ray Data Booklet

3.4.2 Attenuation Correction of Database

Because the database is created for elements in a vacuum, a correction for the atmospheric attenuation is applied to the **A** matrix. When x-rays travels though air between the sample and the detector some of the photons are not detected due to attenuation. The sensor-sample distance and the medium the x-ray travels though are therefore factors in the degree of attenuation. For this project I have compared the degree of attenuation in both a Mars and Earth environment.

The mass attenuation coefficients for Earth's air has been downloaded from the XCOM database maintained by National Institute of Standards and Technology[12]. The mass attenuation coefficients for Mars air is from B. Teliili, International Journal of Physics and Research, 2013[16].

Comparing the two coefficients (Figure 3.5) we see that the Mars attenuation coefficient is similar in shape to that of the Earth's atmosphere. Calculating the attenuation using equation 2.3 with a sample-detector distance of 2 cm we get Figure 3.6. Despite the Mass attenuation similarity, the absorption in the two atmospheres are different due to the large difference in density; Mars has a mean density of 0.02 kg/m^3 while the atmospheric density is approximately 1.2041 kg/m^3 on Earth. The lower density means that the attenuation is lower on Mars than on Earth.

To correct for the attenuation in the database to Earth's atmosphere we multiply each row of \mathbf{A} element wise with the attenuation in Figure 3.6. Although the attenuation correction is multiplied element wise and a function of distance we use the notation $k\mathbf{A}$ where k represents the atmospheric correction on \mathbf{A} .



Figure 3.5: Mass attenuation coefficient for Earth air (from XCOM NIST database) and for Mars atmosphere (from IJPR)



Figure 3.6: Attenuation in on Mars and Earth using a sampledetector distance of 2 cm.

Mars Atmosphere vs Vacuum Example

To illustrate the effect of the atmospheric attenuation on samples I compared a BHVO-2G spectrum measured in vacuum to same sample measured in simulated Mars air. The two spectra in Figure 3.7 demonstrate that there is a difference between the two spectra at low energy levels. At the energy level 1.802 kev there are 12.2 % more counts measured in the vacuum compared to Martian atmosphere.

Dividing element wise the two spectra (e.g. vacuum/Mars air) results in Figure 3.8 where the Mars attenuation has been included. We see that the attenuation follows the general trend of the data and converges towards one for higher energies. To correct the vacuum spectrum to Mars air I multiply the spectrum with the attenuation as with the database. The result of the correction is that the 12.2 % error is decreased to 1%. This example has shown that by correcting for attenuation the method can be adapted to different atmospheric environments and varying detector-sample distances.



Figure 3.7: BHVO-2G measured in vacuum along with measurement taken in simulated Mars atmosphere



Figure 3.8: Calculated attenuation in Mars atmosphere along with vacuum divide by simulated Mars spectrum

Chapter 4

Spectrum Decomposition

Using the spectra previously described we perform the process of decomposing the spectrum into its parts. To decompose the spectrum, we first fit and subtract the bremsstrahlung. From the bremsstrahlung free spectrum, we find all local maxima and fit each peak to a Gaussian function.

4.1 Bremsstrahlung Removal

To remove the bremsstrahlung radiation from the spectrum two options have been considered; median filtering and polynomial fitting.

4.1.1 Median Filter

The median filter described in theory Section 2.3.1 has been implemented using the medfilt1() function in Matlab. An order of 900 has been found to yield the smoothest result.

4.1.2 Polynomial Fitting

The second method of removing the bremsstrahlung is fitting a polynomial to the spectrum as described in theory Section 2.3.2. A low order polynomial will not contain the large variations and peaks in the spectrum instead it will follow a smooth polynomial curve. The polynomial fitting procedure described the theory section has been implemented using the polyfit() function in Matlab. For the polynomial fitting a 3rd order polynomial has been chosen to fit the bremsstrahlung. Using a third order polynomial means that the bremsstrahlung is described by just 4 parameters.

4.1.3 Comparison



Figure 4.1: BHVO-2G spectrum with bremsstrahlung fitted using a median filter and a 3rd order polynomial

The two methods of removing the bremsstrahlung are tested on the spectrum of BHVO-2G (Figure 4.1). The polynomial fit creates a smooth fit that matches the function well in the middle but diverges at the boundary points. The divergence at the two ends means that the high and low energy photon count is under or over estimated. The median filter on the other hand follows the boundary well but is less smooth in the middle where there is a lot of variation.

For calculating the chemical composition the median filter is the best method since it does not diverge at the boundaries. For compression on the other hand the polynomial fit is preferred since it can be reconstructed from 4 parameters.

4.2 Curve Fitting

Each peak position in an XRF spectrum represents the position of a characteristic line of an element. The area under the broadened curve represents the true photon intensity of the characteristic line. To transform the spectrum into a line spectrum the position of each peak needs to be found and the corresponding area calculated. Throughout this section the measured spectrum of brass has been used as an example to illustrate the procedure. Before curve fitting the bremsstrahlung has been subtracted using a median filter.

4.2.1 Peak Finding

Each peak is found using the built in findpeaks() function in Matlab. Findpeaks() takes the spectrum as an input along with two parameters; minimum distance and the minimum prominence. Minimum distance is a measure of how closely spaced the peaks are, for this project a value of 0.2 keV is used. The minimum prominence is a measure of the peak height relative to the surrounding peaks. For the minimum prominence a value of 4 is used.

Using findpeak method, the local minima points are also found. The section of the spectrum between a peak and two minima is the section that will be used for fitting.



Figure 4.2: Peak finding on brass spectrum where red and blue pointers illustrate the local maximums and minimum points.

Using peakfind most small significant peaks are detected although several significant peaks go undetected (Figure 4.2) The undetected peaks occur at 7.5 keV and 15 keV. Not detecting overlapping peaks is a potential problem

because $K\alpha$ and $K\beta$ characteristic lines of an element are usually closely spaced

4.2.2 Peak Fitting

The section between two local minima is fitted to a Gaussian function using non-linear least squares. The curve fitting is implemented in Matlab using the function fit(x,y,'gauss1'). After finding the function that minimizes the sum of squared errors the area under the function is calculated using trapezoidal numeric integration. The area under each fitted peak is illustrated as red line spectrum in figure 4.3. The position of each area matches with the corresponding peak position indicating a correct calculation.



Figure 4.3: Areas under each peak for brass spectrum.

Throughout this report a Gaussian peak has been chosen to fit the spectrum. The fit could potentially be improved by using another function such as a Lorentzian or Voigt[18]. Lorentzian or Vogit are also bell shaped but differ from the Gaussian function at the two tails.

Chapter 5

Discussion of Results

In this section I use the decomposed spectrum to:

- Calculate the chemical composition of brass and compare the results with the composition calculated by the X-MET 800.
- Compare the effect of sample time on the chemical composition of BHVO-2G
- Inspect the noise distribution after decomposition i.e. after removing the bremsstrahlung and subtracting the Gaussian peaks. And compare signal to noise ratios of spectra measured with different sample times.
- Discuss the level of compression using the decomposition method.

5.1 Accuracy of Chemical Decomposition

5.1.1 Solution to System of Equations

The chemical composition is calculated for the brass spectrum previously decomposed where the calculated areas (Figure 4.3) constitute the vector, \vec{b} . As described in Chapter 3 the database of relative intensities of each characteristic line is used to generate the **A** matrix. Using a sample-sensor distance of 2 cm the Earth atmosphere attenuation correction is applied.

A solution to the system of equations is calculated using the single value decomposition to find the pseudo inverse:

$$\vec{x} = k\mathbf{A}^+ \vec{b} \tag{5.1}$$

To ensure that each value in \vec{x} is less than one and that the sum is equal to one we divide by the vector sum:

$$\hat{\vec{x}}_{\%} = \frac{\hat{\vec{x}}}{sum(\hat{\vec{x}})} \tag{5.2}$$

5.1.2 Comparison with X-MET 800

The results from the chemical decomposition are compared to the values calculated by the X-MET 800 (Table 5.1). The implemented algorithm finds the 3 element Cu, Zn and Pb with the largest volume fraction. The calculated percentages are not within the 95 % confidence intervals. There is an error of +7% on Cu, an error of -4% on Zn and an error of 2.6% on Pb. Lastly, the element 50 Sn (0.28%) is not detected.

Element	Own algorithm $\%$	+/- %	X-MET %	+/- %
29 Cu	64.011	0.126	57.36	0.243
30 Zn	35.042	0.067	38.81	0.177
82 Pb	0.551	0.008	3.2	0.077
50 Sn	0	0	0.28	0.042

Table 5.1: Comparison of own decomposition algorithm vs commercial XRF

5.1.3 Error Inspection

The largest source of error is from fitting the bremsstrahlung. In the brass spectrum between 10 keV and 15 keV there is an undershoot which usually wouldn't be present (Figure 5.1). The undershoot indicates that the X-MET 800 performs a baseline subtraction or filtering before outputting the spectrum.

A second source of error is because the the database does not account for inter element relative intensities. For example, the maximum $K\alpha$ line for copper may be larger than the maximum $K\alpha$ line of zinc where the database treats them as being equal.



Figure 5.1: Brass spectrum with undershoot between 10 and 15 keV that usually wouldn't be present.

5.2 Impact of sample time on chemical composition

In this section we look at the impact of sample time on the chemical composition method. The chemical composition is calculated for BHVO-2G at 15kev, 1 μ A , 300 s and 1 s both in air.

The bremsstrahlung of BHVO-2G has been subtracted using a polynomial fit and each peak is fitted to a Gaussian function. The chemical composition is then calculated as previously. BHVO-2G contains 17 elements. For the 300 second sample the decomposition detects 13 where the elements not detected are Mg, S, P and Ag.

Although the true percentage chemical composition of BHVO-2G is not known the 4 elements not detected would be expected to be present at the 0.1-1 % level. The one second calculation detects 7 of the 17 elements (Figure 5.2). Elements with a percentage less than 1 % are not detected along with the lighter elements (Si, Al and K).

The calculated percentages are listed in in appendix 7.3 in table 7.1.



Figure 5.2: Comparison of chemical composition with sample time of 1 second and 300 second. Mg, S, P and Ag are not detected despite being present.

Error inspection

Inspecting the four elements not detected in the 300 s sample we see that they all have characteristic peaks at the lower energy (<4 keV) levels which do not align with the peaks in the spectrum (Figure 5.3.) The misalignment could be due an error in the definition of the energy axis or drift in the detector (hence the calibration targets use). For the 1 second sample elements with a percentage less than one percentage have such a low intensity that they are not detected. Since, not all elements are visible in the spectrum the division by the sum in equation 5.2 causes an over estimation of some of the elements especially V, Mn and Fe are overestimated. The largest element, Fe, is overestimated by 7%.

The overestimation could be corrected for by calibrating the database exactly to the PIXL instrument. Creating a custom database for PIXL would increase accuracy and eliminate the need for the sum in equation 5.2.

5.3 Analysis of Noise Distribution

Subtracting the bremsstrahlung and the fitted Gaussian peaks results in the measurement noise contained in the spectrum. The measurement noise is one of the three components needed for lossless reconstruction of the spec-



Figure 5.3: BHVO-2G spectrum with the characteristic line position of the elements not detected (Mg, P, S, Ag) from 300 second sample.

trum. For optimal compression it is desired that the noise distribution to be uncorrelated and follow a zero mean Gaussian distribution.

In this section the resulting noise after decomposition is inspected for the 300 and one second sample of BHVO-2G. Signal to Noise ratios are calculated for sample times ranging from 1-300 seconds.



Figure 5.4: Noise after bremsstrahlung and Gaussian peak subtraction on 300 and 1 second sample

5.3.1 Statistical Distribution

For both the 300 and 1 second sample we find that the large noise correspond to the largest peaks (Figure 5.4). The observed variance-photon count proportionality is expected since the photon count data is Poisson distributed (variance = mean).

Both the 1 second and 300 second have non zero mean (close to one)sample and follows a slightly right skewed Gaussian distribution (Figure 5.6). Since, the two distributions are not normally distributed with zero mean the level of compression may not be as good as otherwise.



Figure 5.5: Histogram of noise distribution for 300 second and 1 second sample

5.3.2 Auto Correlation

There appears to be some correlation in the noise to test this we calculate the auto correlation function (ACF). The ACF measures the degree of correlation between previous values. Ideally, there would be no correlation between previous values in the noise resulting in a one in lag zero and zero in all other lags. For the 300 second sample, we find that there is high degree of correlation. In lag one the ACF is 0.5 then gradually decreases to zero. The correlation indicates that not all peaks in the spectrum have been fitted to a Gaussian function.

The one second sample on the other hand has uncorrelated noise. After lag 1 the ACF is below the 95% confidence level. The values above the confidence interval are relatively small and some protrusion is accepted. The reason for the one second sample being uncorrelated while the 300 is correlated is likely because the one second sample has fewer peaks and a lower signal to noise ratio (SNR).



Figure 5.6: Auto Correlation function of the noise for 300 second and 1 second sample

5.3.3 Impact of sample time on SNR

The spectrum of BHVO-2G has been decomposed for different sample times and the signal to noise ratio (SNR) is calculated for each.

The SNR is a measure of useful information in a signal. In the case of spectral data, it compares the ratio of bremsstrahlung plus peaks to the level of noise. SNR is measured in decibels and is calculated as the ratio of the power in each signal.

$$SNR_{db} = 10log_{10}(\frac{P_{Signal}}{P_{Noise}})$$
(5.3)

Table 5.2 demonstrates that longer sample time results in a larger signal to noise ratio. There is a substantial drop of 12 dB between 30 second and 2 second sample time measurements whereas the drop between 300 to 30 seconds is 6.5 dB. More sample times are needed to conclude if there is a systematic proportionality with the sample time.

Sample time[s]	SNR_{dB}
300	38.03
120	35.32
30	31.48
2	19.65
1	16.26

Table 5.2: SNR for a variety of sample times.

5.4 Compression Level Discussion

By decomposing a spectrum into bremsstrahlung, Gaussian peaks and measurement noise a large degree of compression can be achieved.

The spectrum of BHVO-2G contains 4096 data points. Fitting each peak to a Gaussian function results in 19 peaks each described by three parameters.

To recreate all the peaks 19 * 3 = 57 parameters are necessary. The bremsstrahlung has been fitted with a third order polynomial. Recreating the bremsstrahlung requires 4 parameters; the three coefficients plus the intercept. After peak and bremsstrahlung subtraction we are left with the noise consisting of 4096 data points.

For lossless reconstruction, the 61 parameters along with the noise of the spectrum are to be sent from Mars to Earth. Not taking into account the noise the number of parameters has been reduced by $\frac{4096-61}{4096} = 98.51\%$. The next step from here is to estimate an accurate total compression ratio. An accurate total compression would take into account the noise distribution and potentially further compression of the 61 parameters by a generic compression method. The compression ratio would then need to be compared to other available compression methods to asses its usefulness for the Mars mission.

Chapter 6

Conclusion

6.1 Summary

This thesis implemented a method of decomposing X-ray fluorescence spectra for the instrument PIXL. The spectra are decomposed into three parts; bremstrahlung, Gaussian peaks and measurement noise. The bremsstrahlung is fitted using polynomial fitting and each peak in a spectrum is fitted to a Gaussian function using non-linear regression. Subtracting the bremsstrahlung and the fitted peaks results in the measurement noise which is needed for reconstruction. Using the decomposition, the chemical composition can be calculated by least squares regression. By correcting for attenuation in the atmosphere the chemical decomposition has been demonstrated to work in both an Earth and Mars atmosphere meanwhile allowing for varying photon detector distances. The decomposition into bremsstrahlung and Gaussian peaks can be used for losslessly compressing the spectral data.

6.2 Results of Comparisons.

In conclusion this report has found that:

- The chemical decomposition correctly finds the largest three elements in a measured brass spectrum, although the chemical percentages have an error of 4-7% compared to the X-MET 800. The large error is likely from the X-MET's preprocessing of the spectral data causing a poor bremsstrahlung fit.
- With a 300 second sample time elements, down to 0.1 % are detected. With a 1 second sample time, elements with a volume fraction less than 1 % are not detected along with the light elements (Z < 14).

- The noise after decomposition of BHVO-2G has been found to follow a rightly skewed Gaussian distribution. The noise from the 300 second sample exhibited some correlation indicating information still contained in spectrum whereas the one second sample was found to have uncorrelated noise.
- For reconstruction of the original signal 62 parameter and the noise distribution are needed. Disregarding the 4096 noise values the number of parameters for lossless reconstruction has been reduced by 98.51 % compared to the spectrum length.

6.3 Future Work

The problem which has been solved is how to decompose the spectrum into its constituent parts and the method of calculating the elemental chemistry. Two important parts of the problem remain to be solved.

One is to achieve a higher accuracy on the chemical composition. A higher accuracy achieved by creating a database of relative intensities that takes into account inter element variations in intensity and is calibrated to the PIXL instrument.

The second part to be solved is to estimate an accurate compression ratio. An accurate measure of compression would estimate how much the noise distribution can compressed in practice. The next step is then to compare the level of compression to other lossless compression methods.

Chapter 7

Appendix

7.1 X-MET 800 settings

The following high voltage power sources and currents are available when taking samples on the X-MET 800.

- 8kV- μ A150
- $8kV-\mu A50$
- 13kV- μ A10
- 15kV- μ A10
- 40kV-µA40
- 40kV-µA8
- 45kV-µA30
- 50kV-µA30

7.2 Matlab implementations

7.2.1 XRayAbsorbtionInAir.m

XRayAbsorbtionInAir.m is function that loads the mass attenuation coefficient from the XCOM database and calculates the attenuation in the air. It takes as input the number of channels in the spectrum and the sensor-sample length in cm.

7.2.2 generateMatrix.m

generateMatrix.m function takes as input the number of channels in the spectrum. From the NIST database it creates the **A** matrix needed for calculating the chemical composition.

7.2.3 decomposition.m

Decomposition.m is a script that decomposes the spectrum of BHVO-2G, calculates the chemical composition and the signal to noise ratio.

7.3 Chemical composition of BHVO-2G

Element	% at 300 s	% at 1 s
26 Fe	60.336 ± 0.1433	67.503 ± 2.7734
20 Ca	18.944 ± 0.0919	17.066 ± 1.3567
22 Ti	6.7185 ± 0.0538	5.7172 ± 0.7733
14 Si	4.0618 ± 0.1030	0
18 Ar	3.5902 ± 0.0429	2.865 ± 0.5702
25 Mn	1.5582 ± 0.0286	2.1879 ± 0.5055
13 Al	1.527 ± 0.1314	0
19 K	1.2409 ± 0.0229	0
23 Ag	0	0.98637 ± 0.19629
23 V	0.36954 ± 0.0079	1.4141 ± 0.42398
29 Cu	0.28031 ± 0.0121	0
24 Cr	0.25861 ± 0.0088	0
28 Ni	0.10939 ± 0.0076	0
30 Zn	0.10751 ± 0.0050	0

Table 7.1: Chemical decomposition of BHVO-2G. 12 Mg, 15 S, 16 P are not detected despite being present.

Bibliography

- Lossless Astronomical Image Compression and the Effects of Noise, W. D. Pence, R. Seaman, and R. L. White Published 2009 May 4, Astronomical Society of the Pacific, Volume 121, Number 878
- [2] Universe 9th Edition, by Roger Freedman
- [3] Mars, University of Oregon http://abyss.uoregon.edu/ js/ast121/lectures/lec12.html
- [4] Report of the Mars 2020 Science Definition Team, J.F. Mustard, July 1, 2013.
- [5] NASA Mars 2020 PIXL overview http://mars.nasa.gov/mars2020/mission/instruments/pixl/
- [6] Data Rates/Returns, Mars Science Laboratory, Curiosity: https://mars.nasa.gov/msl/mission/communicationwithearth/data/9
- [7] Physics in Medicine Lectures Week 1 Plain Film Imaging https://koukalaka.wordpress.com/tag/cathode-rays/
- [8] Characteristic Lines in X Ray Spectra, LSCphysics, Leyton Sixth Form College https://www.youtube.com/watch?annotation_ id=annotation_ 1261050427& feature=iv& src_ vid=e7vk7aD1Xb1& v=mm14eKpb1cE
- [9] Texture-specific elemental analysis of rocks and soils with PIXL: The Planetary Instrument for X-ray Lithochemistry on Mars 2020, Abigail Allwood, Jet Propulsion Laboratory
- [10] Applied Multivariate Statistical Analysis 6th edition, Richard Arnold Johnson, Dean W. Wichern, 1982
- [11] Non-linear least squares, Wikipedia https://en.wikipedia.org/wiki/Non-linear_least_squares

- [12] X Ray Mass Attenuation Coefficients, National Institute of Standards and Technology http://physics.nist.gov/PhysRefData/XrayMassCoef/ComTab/air.html
- [13] Bremsstrahlung Wikipedia page https://en.wikipedia.org/wiki/Bremsstrahlung
- [14] Singular value decomposition Wikipedia https://en.wikipedia.org/wiki/Singular_ value_ decomposition
- [15] Polycapillary Focusing Optics X-Ray, XOS https://www.xos.com/xray-optics/focusing-optics/family?productCategoryId=51857795171
- [16] Determination of Total Mass Attenuation Coefficients, Effective Atomic Numbers and Effective Electron Density for the Martian Atmosphere, B. Tellili, International Journal of Physics and Research (IJPR), 2013
- [17] Mars Fact Sheet, NASA Space Science Data Coordinated Archive(NSSDCA) https://nssdc.gsfc.nasa.gov/planetary/factsheet/marsfact.html
- [18] Hollas, M.J. (1996). Modern Spectroscopy (3rd ed.). Wiley. pp. 30–34.
- [19] X-RAY DATA BOOKLET, Center for X-ray Optics and Advanced Light Source, Lawrence Berkeley National Laboratory http://xdb.lbl.gov/xdb.pdf

Acknowledgment

I would like to thank my supervisor John Leif Jørgensen and the rest of the The Planetary Instrument for X-ray Lithochemistry team at the Jet Propulsion Laboratory for supplying representative spectra of BHVO-2G for this thesis.