



# Optimized Compton fitting and modeling for light element determination in micro-X-ray fluorescence map datasets

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## ARTICLE INFO

### Keywords:

Micro-XRF map  
Compton  
Rayleigh  
Compton/Rayleigh Ratio  
Mars 2020  
PIXL

## ABSTRACT

The Planetary Instrument for X-ray Lithochemistry (PIXL) is an X-ray fluorescence instrument scheduled to fly to Mars on NASA's 2020 rover (Allwood et al., 2015). It will be capable of quantifying elements with atomic number of at least 11 using X-ray fluorescence (XRF), but the detector window blocks fluorescence from lighter elements. Important elements otherwise invisible include carbon, oxygen, and nitrogen, which can make up anions in minerals of scientific interest. X-rays scattered by all elements can be detected, so the ratio of Compton to Rayleigh scatter may be measured and used to infer the presence of elements for which there is no detectable fluorescence. We have refined a fundamental parameters model to predict the Compton/Rayleigh ratio for any given composition that can be compared to an experimentally measured ratio. We compare with a published Monte Carlo model (Schoonjans et al., 2012) and to experimental values for a set of seven materials. Compton/Rayleigh ratios predicted by the model are in good, though imperfect, agreement with experimental measurements. A procedure for consistently computing the Compton/Rayleigh ratio from a noisy spectrum has also been developed using a variation on a common background removal method and peak fitting.

## 1. Introduction

The Planetary Instrument for X-ray Lithochemistry (PIXL) is intended to fly on NASA's Mars 2020 rover [1,3]. The purpose of PIXL is to quantify elemental abundances in Martian rocks and regolith, and it can do this using X-ray fluorescence for elements heavier than sodium. In places where data is limited, such as Mars, it is desirable to analyze both X-ray fluorescence and X-ray scatter that appear in the same spectrum.

Both Compton (incoherent) and Rayleigh (coherent) scattering occur at some level for all elements, but the relative strength of the scattering varies with composition. The cross section for Rayleigh scattering approximately varies with  $Z^3$ , where  $Z$  is atomic number, while the Compton scattering varies with  $Z$ , so the Compton/Rayleigh ratio decreases roughly as  $Z^{-2}$  [4,5]. Calculated more precisely, this ratio can reveal the presence of otherwise invisible elements. Peaks in the spectrum that arise from the anode in the X-ray source and scatter off the sample provide a signal from which we can measure the Compton and Rayleigh scatter separately. This idea has been used in previous studies to determine the average atomic number, weighted by mass concentration (often indicated as  $Z_{\text{eff}}$ ) [6].

With a micro-XRF mapping instrument such as PIXL, datasets can be large and include hundreds of spectra. Speed is more of an issue and as collection time decreases, signal-to-noise does as well, so an automated procedure that can handle more noise is necessary. Total height rather than peak area (measuring from zero to the top of the peak with no background subtraction), has been used as a way around background subtraction issues [6]. However, the area is a more robust measurement, which is important for noisy datasets, so we use net peak area.

Furthermore, we compare the measured Compton/Rayleigh ratio to a model rather than correlating it to  $Z_{\text{eff}}$  to improve the accuracy, flexibility, and generality of the relation. Commonly, the ratio decreases with atomic number, but there are exceptions. Various definitions of  $Z_{\text{eff}}$  can be used to fine-tune the correlation, but it remains a decreasing function of atomic number and mass, and exceptions persist [6–8]. Silicon, for example, has a higher ratio than calcium carbonate even though its atoms are on average heavier. This type of anomaly is predictable, and modeling specific compositions can account for it. To determine an empirical relationship between Compton/Rayleigh ratio and  $Z$ , a calibration curve must be measured with the correct geometry and sample conditions [8]. Angle, shape of the sample surface, and distance between the X-ray source, sample, and detector all affect the

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<https://doi.org/10.1016/j.nimb.2018.09.023>

Received 13 July 2018; Received in revised form 13 September 2018; Accepted 13 September 2018

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intensity of scattered X-rays. A fundamental parameters model and prediction, once validated, can be easily adjusted for variations in experimental setup, eliminating the need for new calibration measurements. Once the ratio has been determined for a sample and the composition is predicted more precisely, this knowledge can be used to adjust for matrix effects and correct absolute fluorescence intensities, increasing overall accuracy [9].

Using the analysis presented here, one can infer the presence of elements with  $Z < 11$  that are otherwise invisible to an XRF instrument like PIXL. Elements such as carbon and oxygen are below this atomic number limit, and these particular elements may improve understanding of Mars' past climate. Past high levels of carbon dioxide in the atmosphere may have ended up as carbonate minerals through geochemical sequestration, and water may have become trapped in hydrated minerals. Similar analysis has been done for the alpha particle X-ray spectrometers (APXS) carried by previous Mars rovers [10,11]. Scattered peaks were successfully used by Curiosity's APXS to identify pure  $\text{SiO}_2$  rather than other silicon-containing minerals such as silicates [12]. Carbonates, sulfates and perchlorates (and states of hydration of the latter two mineral types) all potentially provide information about Mars' past environment. In turn, the environment sets constraints on past habitability and astrobiology. The blindness to light elements is a common problem that limits the information provided by X-ray fluorescence spectra, and we seek to expand this limit.

## 2. Methods

### 2.1. Experimental setup

Experimental spectra were measured with the geometry and apertures shown in Fig. 1. The X-ray source used was a Comet X-ray tube with a silver anode and the spectrum was measured with an Amptek x-123 SDD. Tube voltage and current were 40 kV and 5  $\mu\text{A}$ , respectively. Samples included pure elements as well as water and a polyimide and are summarized in Table 1. To validate the fundamental parameters model, spectra were measured eight times for 2000s each. The Compton/Rayleigh ratio was calculated from each and averaged.

Many additional spectra were taken to examine the effects of low signal strength. For these brief collections, 10 measurements were taken of each sample at each time point.

### 2.2. Model description

Modeling of specific compounds is more precise and versatile than correlating the average atomic number and scattering ratio. In past studies, rather than predicting a ratio for each possible composition, a relationship between average atomic number and scattering ratio has been determined experimentally [6,13]. However, there is not a strict relationship and modeling can eliminate error. Given that scattering measurements are not the primary purpose of XRF (hence F for

**Table 1**

Materials. Powder and liquid samples were placed in a cup behind an ultra-thin (3.6  $\mu\text{m}$ ) Mylar window. Foil and sheet samples were stacked to the total thickness listed without a window except for the Kapton stack, which was wrapped in Mylar to ease handling.

Material	State	Thickness (cm)
Calcium Carbonate	Mallinckrodt calcium carbonate powder, 99.0 + %	1.0
Copper	Alfa Aesar copper foil, 0.127 mm sheet, 99.99 + %	0.0127
Kapton	DuPont 0.003 in. sheets	0.4
Molybdenum	Alfa Aesar molybdenum foil, 0.0125 mm sheets, 99.95%	0.015
Nickel	Nickel foil, 0.2 mm sheets	0.08
Silicon	0.04 cm wafers	0.120
Water	Macron HPLC grade water, 6795-10	1.0

fluorescence), signal strength is expected to be sub-optimal and elimination of this error is advantageous. Modeling can also accommodate unforeseen changes in sample geometry and conditions without the need to recreate a calibration curve. Modeled spectra were created from a new fundamental parameters model as well as an independently developed Monte Carlo model, XMI-MSIM [2]. Models were run to mimic our experimental setup as closely as possible. The same fitting procedure was applied to these modeled spectra as to the measured spectra to generate a modeled ratio for each sample composition.

Sample fluorescence lines calculated by each model are qualitatively indistinguishable, and the main differences are in the scattered peaks. For a complete description of the fundamental parameters model, see the review article by Mantler in Beckhoff [14]. An older text by Tertian and Claisse has more details about coherent and incoherent scattering as well as the actual form of the fundamental parameters equations used here [15]. The tube spectrum is calculated according to Ebel [16], and Compton and Rayleigh scattering is computed based on theory presented by van Sprang and Bekkers [17]. Constants and data are drawn from a database previously published by Elam et al. [18].

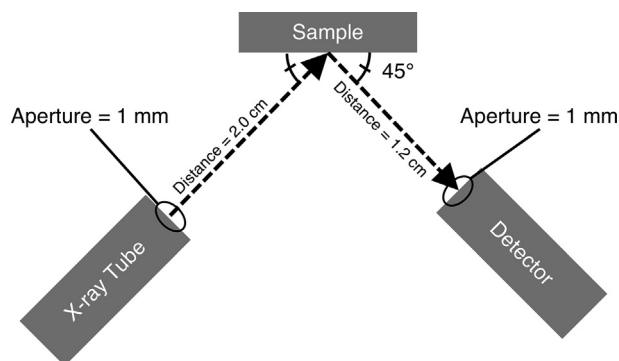
## 3. Spectrum analysis

### 3.1. Background subtraction

The spectrum of radiation emitted by the X-ray tube includes fluorescence lines from the anode in addition to bremsstrahlung radiation, which forms the continuum. While some X-rays are absorbed, others scatter off the sample and are collected in the measured spectrum. Of interest here are the scattered anode fluorescence lines, which appear as distinct peaks; the scattered bremsstrahlung continuum is background to be subtracted. Each anode fluorescence line produces a Rayleigh scattered peak and a Compton scattered peak that can be used to calculate a Compton/Rayleigh ratio. They sit on top of the scattered continuum, so the continuum must be estimated to calculate the area of the Compton and Rayleigh scattered peaks and their ratio.

A more accurate background estimation is required because scattered peaks are typically an order of magnitude weaker than fluorescence from the sample. Background removal methods that work for standard XRF analysis are insufficient because scattered peaks are small compared to the error in baseline estimation. The shape of the background from the scattered continuum is controlled by the spectrum that is emitted by the tube, absorption, Rayleigh and Compton scatter in the sample, and attenuation in the detector. This combination has placed it beyond our ability to model from first principles with sufficient accuracy for peak fitting, though others have attempted [19]. Therefore, we calculate the background continuum empirically from the measured spectrum.

An empirical background calculation removes meaningful peaks from the spectrum to reveal the baseline. This calculated baseline can



**Fig. 1.** Experimental Geometry.

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