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# INTRODUCTION

This document is the user manual for PIQUANT, the software used for quantitative X-ray spectrum analysis of data taken with the Planetary Instrument for X-ray Lithochemistry (PIXL).

## X-Ray Spectroscopy

PIXL is part of the Mars 2020 payload and is a micro-focus X-ray fluorescence (XRF) spectrometer for fine-scale measurements of elemental distribution in rocks and soils. PIXL has an arm-mounted sensor head, body-mounted electronics, and a rover deck-mounted calibration / reference target.

In XRF spectroscopy, X-rays hit a target surface, causing the target to fluoresce. The characteristic energies and number of emitted fluorescent X-rays are determined by the target’s elemental composition. Semiconductor detector electronics count the emitted X-rays and sort the counts by energy into histograms to produce a spectrum. This process occurs through the following steps. Upon striking the detector, an X-ray photon produces a number of electrons proportional to the photon energy. Readout electronics convert this charge into a voltage pulse and measure the height of the pulse. A digital pulse processor counts the number of pulses of a specific pulse height. The result is a histogram of X-ray counts vs. X-ray pulse height. This histogram is calibrated using a material with a few known peaks to convert the histogram to a spectrum of X-ray counts vs. X-ray energy. Detector temperature and the temperature-dependent resistance of the cable between the sensor head and the body-mounted electronics may affect this calibration. To facilitate energy calibration and determining its dependence on temperature (and any other variables) the calibration process can be mostly automated.

The X-ray spectrum yields information about the elemental composition of the spot measured by the primary X-ray beam. Its information is encoded in the energy and intensity of the X-rays. To extract this information the peaks corresponding to the emission lines of each element must be identified and their net intensity extracted. This part of the process is usually called spectrum processing. Once the net intensities for a peak associated with each element are found, they are converted to element abundances by accounting for the atomic effects of each element and the effect of overall composition on the intensity that escapes from the target being analyzed. A predicted intensity is calculated using a physics-based model for X-ray interactions referred to as the fundamental parameters model. The target composition input to this model is adjusted until the predicted intensity matches the intensity from the X-ray spectrum.

## PIQUANT Operation

Each X-ray spectrum will be analyzed to identify the element peaks present in the spectrum and to quantify each of those elements. The net peak area is found by subtracting the background and fitting the known peak shape to each spectral peak. This net area is converted to elemental abundance using a physics-based model (the fundamental parameters method of X-ray fluorescence spectroscopy), aided by a suite of calibration standards and element calibration factors (ECFs). The element calibration factors are determined by measuring a suite of standard reference materials that have well-known composition and can be checked and adjusted on Mars using the PIXL Calibration Target.

The PIXL instrument is designed to collect XRF spectra over a rectangular area by maneuvering the sensor head across the surface of the sample. A hexapod mounting structure with six actuators controlling the lengths of the legs is used to maneuver the sensor head. Each spectrum is integrated for several seconds. Hence one operational science observation can yield many X-ray spectra. PIQUANT will handle this large number of spectra by producing sums, deriving predicted spectra profiles and processing each dataset to yield composition information. The output is a format that is suitable for visualization of the spectra, the resulting fits and diagnostic information, and elemental composition from each spectrum. This information can also be plotted as maps or grids showing the spatial dependence of rock composition as well as data quality.

X-ray spectrum analysis can be automated for spectra that have a large number of X-ray counts and thus a good signal-to-noise ratio from Poisson counting statistics. This will typically be true for the bulk sum spectra and for spectra taken in grid or line scans. However, it may not be true for high-density maps where the integration time per spectrum is limited because of the large number of spectra collected. In this case spectra will have to be categorized in some fashion that reserves as much of the scientific information. Spectra from each category may then be summed to get adequate signal-to-noise for quantitative abundances to be determined. For example, rock components can be identified from a coarse composition of major elements, from visual inspection, or using nonparametric approaches like principal component analysis or t-distributed stochastic neighbor embedding. Separately summing the spectra from a single rock component gives good abundances for that component with little cross-contamination from other components, retaining the element abundance information about each individual component.

PIQUANT predecessors were developed under previous NASA projects and its core components have been tested thoroughly. The automated portions of the analysis are implemented in a C++ command line tool that can be run via an automated pipeline. A graphical user interface, written in Python, facilitates human interaction in cases where human judgment is necessary and for manual processing. The interface calls the same command line tool so that the data analysis is always consistent.

All processing steps generate output that documents what processing was done, when it was completed, and which files were used as inputs and what files were produced. Human-generated inputs from the graphical user interface are written to files before being used for actual processing. These outputs can optionally be appended to a log file to provide saved documentation of the processing performed.

The result of the spectral and image processing will be a large set of data hypercubes, each of which will contain a specific type of information (such as X-ray spectra, net peak intensities, elemental abundances, etc.) with a spatial location for each measurement. Once these data are processed and saved, they are used to produce maps, grids, line scans, or other desired displays for the science team. In addition, diagnostic information for human and/or automated validation of results can be displayed on the same scale as the visual and X-ray measurements for rapid identification of problems. This consistent display is very helpful in assessing the quality of measurements and identifying problems with either the individual spectra or their processing steps. Such problems often occur in only a few spectra and it is important to be able to tell at a glance which spectra are affected.

## Overview of Operation

PIQUANT follows the Model View Controller organization. Each part of this organization method is described in the subsections that follow.

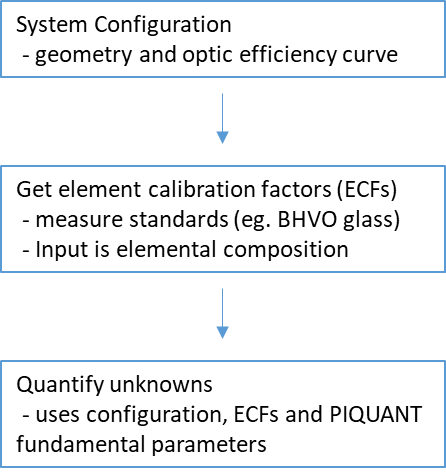
### Model

The model is the mathematical calculations and spectrum processing algorithms that perform the actual spectrum analysis. It is centered around a physics-based model commonly referred to as the fundamental parameters method of X-ray fluorescence spectroscopy. This model predicts the emitted intensity of X-rays at the characteristic energy of each element for a specific composition of the target. Inverting this model by adjusting the composition to match the measured intensity of the corresponding peak in the spectrum gives the measured target composition. The intensity of each peak is found from a fit to the peak using the detailed output of the model. The fundamental parameters model also includes such things as the primary excitation spectrum, the detector quantitative response and peak shape, and X-ray interactions in the target rock material. An important step is removal of the background under the peaks to obtain their actual intensity. The background is found empirically using the SNIP algorithm of van Espen [Van Grieken and Markowicz, *Handbook of X-Ray Spectrometry* 2nd Ed., 2001].

The peaks contributed to the spectrum from each element are calculated separately using the physics model. The expected intensity of each emission line is calculated from the given composition (for a standard) or a guess at the composition (for an unknown). Lines are grouped by principal atomic energy level (K, L, M, or N) and summed to obtain a component of the spectrum arising from that element. The components plus the background are then fit to the spectrum using linear least squares. To obtain a good fit, and thus accurate peak intensities, the energy calibration of the spectrum must match the calculation. Linear least squares cannot adjust the energy calibration because it enters the peak calculations in a nonlinear fashion. The energies of the element emission lines are assumed to be known accurately, and are thus in the right place in the calculation, but the energy calibration of the spectrum may not be accurate enough to obtain a good fit via linear least squares. The energy calibration is adjusted between each iteration of the linear least squares to obtain the best fit but it is not allowed to change by more than the width of the element peaks to avoid misidentification of peaks. The energy-dependent detector energy resolution (peak width) is also adjusted within certain limits to obtain a good fit. This procedure yields accurate intensities for the element peaks, which directly translates into quantitative accuracy for the element abundance.

Quantitative analysis is aided by a suite of calibration standards and element calibration factors (ECFs). The model reads the information on standards from a standards input file. This information is used to fit the spectra from the standards and, by comparing the results to the given composition, a calibration factor for each element in the suite of standards is obtained. These element calibration factors are written to a file and used to quantify unknown targets.

The model is implemented as a command line tool in C++ to provide fast calculations and for easy inclusion in automated workflow pipelines.



**Figure 1. Typical PIQUANT processing steps**

### View

The View module displays the results of the analysis performed by the model. The main role of the view component is to plot the spectrum vs X-ray energy together with the fit and any other energy-dependent information to help evaluate the spectrum and its analysis. This plot shows the peaks in the spectrum and their shape. The plot also displays the model results both in the form of the individual peaks from each element, the overall fit, and the background. Residual and expected statistical variance can also be plotted. The viewer displays these parts of the plot in different colors and allows each to be turned on and off in the display.

### Controller

The controller allows human input and interaction with the model and viewer. It lets the user choose the actions to be performed and the input and output files for the model. It also automatically invokes the viewer to plot the results if a single spectrum is processed. Finally, it allows the user to choose the option of writing the text output to a log file and chooses which file to use for this purpose.

Each type of processing only requires a certain subset of the inputs. All the inputs are visible but for each chosen action only the required inputs are enabled. The inputs that are not used are disabled (which usually appears as grayed-out controls). Once the inputs are specified, the model is invoked via a GO! button at the bottom of the controller. If any required inputs have not been specified a dialog indicating the missing input is displayed.

The inputs are in editable text boxes that allow the user to modify their contents and to specify input either by typing or copying from an outside source. Buttons also allow selection of files using the system file dialogs.

# QUICK START GUIDE

## Essential Inputs

An energy calibration relating the X-ray energy to the channels in the histogram is required before any processing can be performed on the spectrum. This calibration is usually included in the spectrum input file, but for PIXL data downlinked from the rover it will have to be added on the ground. Calculations of spectra from physical principles does not use an input spectrum, so the energy calibration must come from another source. The configuration file that gives the detailed description of the instrument for the physics model also has a place for energy calibration and this is used for calculation-only runs or if the input spectrum does not include a calibration. For test spectra or other uncalibrated spectra PIQUANT can find an energy calibration using two prominent peaks if given the elements that produced the peaks (see Section 3.1.1). For convenience in plotting and subsequent processing of the spectrum, an energy calibration found in this way is saved in the options field of the controller interface and used in any subsequent processing (until deleted or the interface terminates). **This energy calibration overrides any input from a file.** It can be removed by deleting it from the options text field. (See Section 3.3 for option formatting.)\_

For unknown materials, a list of the elements to be quantified must be input using the element fit control list. Automated peak identification is not yet implemented (although it may be in the future but it is a hard problem and often unreliable). For standards, this list is not required because it comes from the given composition. The element fit control list also serves to control the fitting algorithm that fits the peaks in the spectrum. Specific emission lines (designated by atomic energy levels K, L, M, or N) can be identified for use in quantifying each element. Elements can be added that are fit in the spectrum but ignored for quantification (such as the Ar peak from an air path). Peaks from specific elements, such as spurious small peaks that may be present, can be removed from the fit if necessary to obtain a better fit. The syntax for the element fit control list is an element symbol (or an atomic number), optionally followed by an atomic energy level and/or a single-letter qualifier. The element symbol is followed by an underscore to separate the levels and qualifiers. Allowed atomic energy levels are K, L, M, and N. Qualifiers are I for include in the fit but ignore and X for exclude from the fit. A qualifier without an atomic energy level applies to all emission lines in the fit from that element.

Entries in the element fit control list can be separated by commas or blanks, or any combination. Tabs are treated as blanks.

The information in the element fit control list can also be input via the standards input file for automatic inclusion in the processing of each standard during calibration. The same letters are used with the same meanings although the format is different. File formats are given in Section 7.

## PIQUANT Graphical User Interface Step-by-Step

Following these steps allows a user to perform the basic analysis of an XRF spectrum and produce quantitative elemental abundances.

1. Double click on the file PIQUANT\_GUI.exe
2. In a few seconds the main window will appear
3. Choose an action from the buttons at the top
4. The inputs that are needed will become active
5. Choose the input files and fill in the element fit control list if necessary
6. Press the Go! button at the bottom
7. Output text will appear in the text box above the Go! button
8. The plot (if any) will appear in a separate window
9. Output text can be selected and copied

# PIQUANT GRAPHICAL USER INTERFACE DETAILS

The PIQUANT GUI consists of a main window that has all the input information and a plot window for displaying the spectrum information output by the calculations. The plot window is not visible until a plot is produced.

The main window has three sections: the action buttons at the top, input file names and the element fit control list in the center, and the output text box and Go! button at the bottom. Each of these is described in a subsection that follows.

The plot window is mostly self-explanatory. There is a toolbar at the bottom (provided by the matplotlib package that is used to display the data). The toolbar allows zooming, panning, setting the scales and axes (including log axes) and saving the plot as an image. The toolbar functions can be discovered by trying them as the results are visible immediately.

The following figure shows the main window and labels the sections as described above.

Text window

}

File selection inputs

}

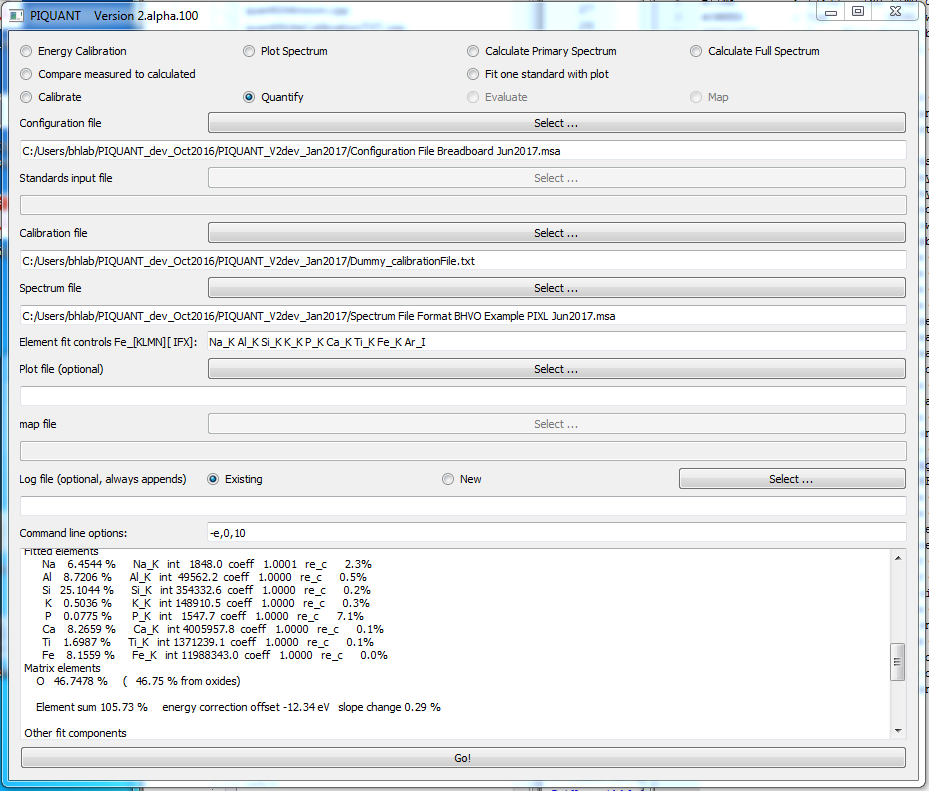
**}**

Action buttons

Go! button

Element fit control list

Command line options

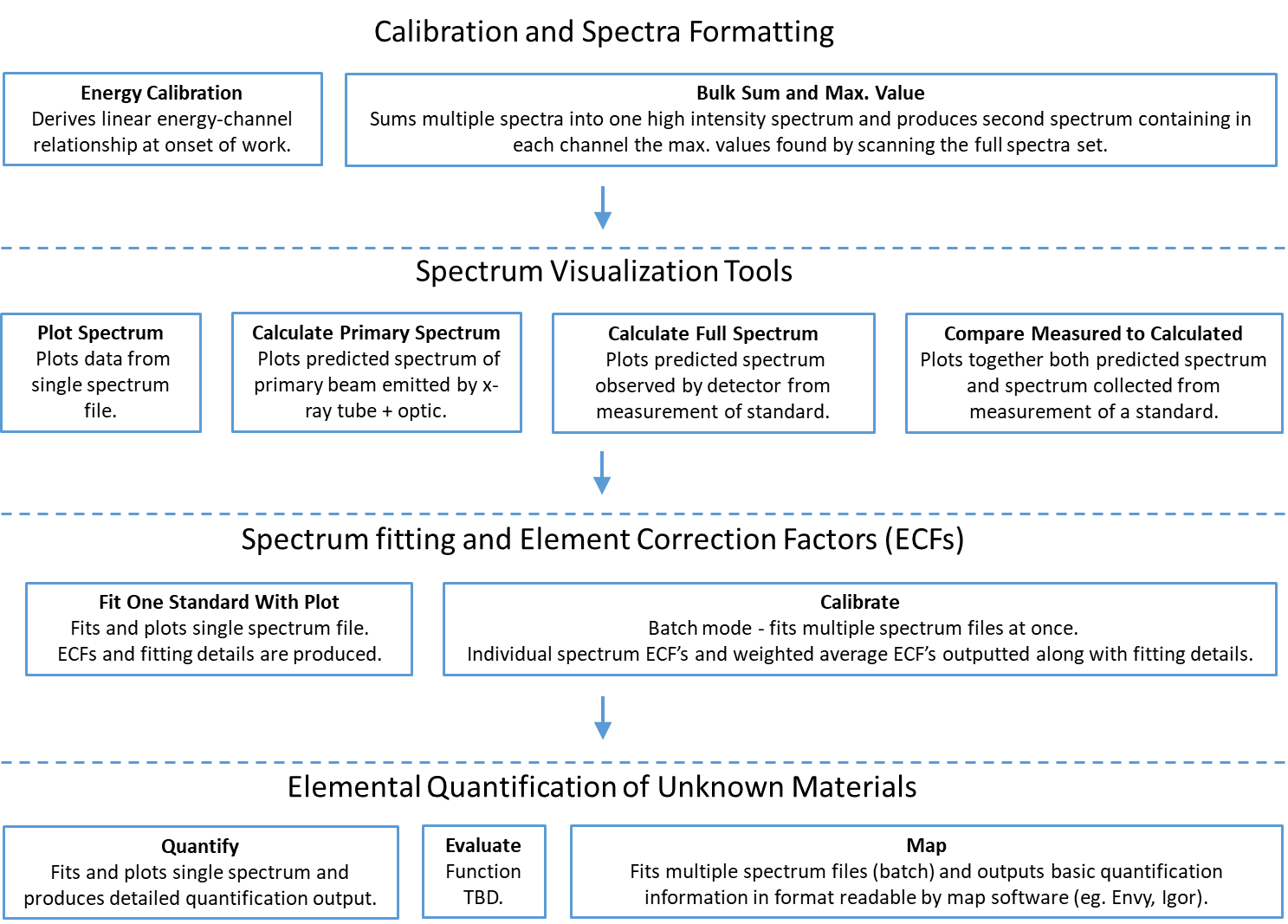


**Figure 2. PIQUANT graphical user interface main window with sections labeled**

## Actions

The action buttons at the top of the interface allow the user to choose which step in the analysis process is to be performed. Each action corresponds to a radio button, where only one button can be selected at a time.

Each action button performs a particular step in the spectrum analysis process. In the following subsections details are given: what the step accomplishes, the inputs needed, and how to choose the inputs. The complete list of inputs is always displayed in the GUI but the ones that are not needed for the chosen action are grayed out and are not active. None are active when the GUI first appears and will remain that way until an action is chosen. Once an action is chosen, the active inputs must be given a value before the Go! button is pressed.



**Figure 3. Actions performed to obtain XRF spectra information using PIQUANT**

### Energy Calibration

This performs a calibration of the relation between channels in the pulse-height histogram and the energy of the incident X-rays. The algorithm takes as input the histogram and the elements corresponding to the two largest peaks in the histogram. The highest point in the histogram (the channel with the most counts) is found and taken as the first peak. The peak center is found via a 5-point average around the highest channel. An exclusion zone is then put into place around this peak from 15% above the peak channel to 10% below the peak channel. This is to prevent finding beta or other secondary peaks from the same element associated with this peak. The channel with the highest counts in the remaining part of the histogram is then found and treated similarly to find the center of the second peak. If either peak has fewer than 100 counts, an error message is generated and the calibration fails. The element fit control list is then inspected and the first two entries are used to associate the peaks with energy. The energy of the emission line from the elements in the list are used, and the K lines are used if no energy level is given. The order of the elements is not important, as the lower energy emission line will always be associated with the peak in the lower channel number. The energy of the starting channel and the energy per channel is computed and output to the screen.

For spectra with more than one detector, the energy calibration applies to the sum of the detectors. To obtain an energy calibration for a single detector use the –d option. Using –d,0 selects the first detector and the zero can be replaced by one for the second detector or any integer up to the number of detectors minus one. (See also Section 4.4.3.)

The energy calibration is also entered in the options text box. This will cause the new energy calibration to be used for any subsequent actions until a new energy calibration is run, the text is deleted from the options, or the GUI is restarted. This allows further processing of a histogram that has no energy calibration without having to enter the new energy calibration into the spectrum or configuration files. Note that the new energy calibration will override any energy calibration in the spectrum or configuration files. The new energy calibration remains in the command line options text box so that several spectra with the same energy calibration can be processed, or a calibration spectrum can be used to find the energy calibration and then other spectra taken at the same time can be processed using the new energy calibration.

For histograms with only one major peak, only one element can be entered in the element fit control list. In that case, the starting channel will be assumed to correspond to zero energy and only the energy per channel will be calculated.

Inputs: Spectrum file (see Section 7 on file formats)

Element fit control list (one or two elements), e.g., Ca Fe to designate the dominant calcium and iron Kα peaks found in BHVO2

Outputs: Energy offset and slope to output text box and options text box

### Plot Spectrum

This action produces a plot of the spectrum read in from a spectrum file. The file format is detected automatically (see Section 7 for supported formats in the current version). The counts in each channel are plotted vs. energy or vs. channel number if no energy calibration is available. An energy calibration is sought in the options text box and the spectrum file in that order. (No configuration file is read in this case.)

This command can also be used to display plot files written earlier and any comma-separated-values file that has the title and headers on the first two lines in a form that matches plot files in addition to spectrum files.

Inputs: Spectrum file or CSV plot file (see Section 7 on file formats)

Outputs: A plot file is written and displayed in the plot window

### Calculate Primary Spectrum

The fundamental parameters method is used to calculate the primary spectrum that is expected from the instrument configuration specified in the configuration file. The spectrum consists of the output of the X-ray tube (or other X-ray source) as modified by the filter material and optic (if any) in the primary beam. Because the spectrum consists of characteristic emission lines with very narrow energy width plus a continuum emission, the spectrum is calculated as if the primary beam were incident directly on the detector described in the configuration. (Do not try this in practice unless you have taken precautions to not overload and/or damage the detector, as the primary beam is typically too strong to enter the detector directly and will damage it without reducing its intensity somehow.) This approach yields a spectrum with the characteristic emission lines as peaks on the continuum background, which is easy to visualize in a plot. None of the materials in the emitted fluorescence nor the interactions in the target are included in the calculation, but the detector response is included (with escape peaks).

The resulting spectrum can thus be compared to a measurement of the primary spectrum if the beam is attenuated, or the solid angle reduced, sufficiently to get a measurement with an energy-dispersive detector. The calculation is multiplied by the live time in the configuration file, so set it to unity to get photons per second.

To obtain the actual spectrum that impinges on the target (rather than the spectrum that would be measured with a detector), set the detector active area to some very large number and its Be window thickness to zero. Note that the height of the characteristic emission lines will depend on the detector resolution and the continuum intensity will depend on the channel energy width, although the integral intensities for both will always be correct.

The plot file and its display in the plot window are the only outputs from this action, although the output text window has some useful ancillary information. Note also that an energy calibration must be available in the configuration file to perform this calculation, otherwise an error results and there is no plot output.

Inputs: Configuration file (see Section 7 on file formats)

Outputs: The calculated primary spectrum is written to the plot file and is displayed in the plot window

### Calculate Full Spectrum

The fundamental parameters method is used to calculate the spectrum expected from the instrument configuration specified in the configuration file and for the target composition of the first standard in the standards input file. The contributions from individual elements and energy levels are placed into different columns in the plot file, as are the background from scatter of the continuum and the characteristic peaks from the source via Compton and Rayleigh scatter. The full calculated spectrum obtained by summing these various contributions is also output.

The plot file and its display in the plot window are the only outputs from this action, although the output text window has some useful ancillary information including some information on PIXL L5 requirements for the X-ray Subsystem (XRS). Note that an energy calibration must be available to perform this calculation, otherwise an error results and there is no plot output.

Inputs: Configuration file (see Section 7 on file formats)

Standards input file (reads only the first standard in the file)

Outputs: A plot file is written and displayed in the plot window

### Compare Measured to Calculated

This is identical to the full spectrum calculation except that a measured spectrum is read in and included in the plot. The energy calibration and number of channels are taken from the input spectrum.

Inputs: Configuration file (see Section 7 on file formats)

Standards input file (reads only the first standard in the file)

Spectrum file

Outputs: A plot file is written and displayed in the plot window

### Fit One Standard with Plot

To improve quantitative elemental performance, PIQUANT uses standards with known composition to determine individual element calibration factors for each element. The calibration factors are found by fitting the standard using the same calculation and fitting routines as for unknown measurements but only retaining the fit coefficients and not modifying the composition of the standard. To achieve the best possible fit, there is considerable control over the fitting process.

When performing an actual calibration, many standards are processed at once via an automated sequence with the fit controls included in the standards input file (see Section 3.1.8). In this case the large number of plots are not produced. To make it easier to make the initial determination of the fit controls for a specific standard, this action will fit a single standard (the first one in the standards input file) and display a comprehensive plot of the fit quality. The display includes all of the contributions to the calculation (see Section 3.1.4) as they were adjusted by the fit. The residual and the original measured spectrum are also displayed.

The text output has a list of all the components used in the fit along with their coefficients and an indication of the relative uncertainty of the coefficients assuming Poisson counting statistics for the measured spectrum. Note that this does not write a calibration file, it only produces the text and plot. Also, the measured spectrum file is read from the standards input file, not the spectrum file in the main window.

The element fit control list is used to determine which elements and which components are included in the fit to the measured spectrum. All elements in the standards composition will be included unless overridden by inputs in this list. This format and composition of this list are described in a separate section following (with the file selection boxes).

Inputs: Configuration file (see Section 7 on file formats)

Standards input file (reads only the first standard in the file)

Element fit control list (required)

Outputs: A plot file is written with the measured spectrum, fit, and all fit components

The plot is displayed in the plot window

### Bulk Sum and Max Value

When a large number of short-dwell spectra are taken for a map, or several spectra are taken at different locations on a standard, it is often desirable to sum the spectra to produce a single spectrum with a longer dwell time. In such a sum, elements that appear in only one or a few individual spectra may get lost in the average. A spectrum that contains the maximum value for each channel across all the map spectra will highlight these rarely occurring elements.

The bulk sum and max value action takes a sequence of spectra as input and produces these two outputs – a sum across all the spectra and a spectrum with the maximum value for each channel. The spectra are aligned using the individual energy calibrations before summing. The sum is quantified after it is produced. The max value spectrum is only plotted and/or written to the plot file.

See the quantify action (Section 3.1.9) for more information on the processing of the sum, particularly the fit control list. See the map action (Section 3.1.10) for the sequence of spectrum names.

Inputs: Configuration file (see Section 7 on file formats)

Calibration file

Spectrum file

Element fit control list (required)

Outputs: The output text box has entries with complete quantification and fit information.

A plot file is written with the sum spectrum, maximum value spectrum, the fit, and all fit components from the quantification

The plot is displayed in the plot window

### Calibrate

To produce the calibration file with the element calibration factors based on a wide set of standards, batch processing is used in the calibration action. The configuration file is used for the instrument description and applies to all the spectra processed together. The composition of each standard as well as the measured spectrum file are input via the standards input file.

The standards are processed as their information is read in from the standards input file. Any number of standards can be included and all will be processed once the Go! button is pressed. Any errors will prevent the writing of the calibration file, although processing of the standards will continue to locate any additional errors.

A calibration file will be written with the element calibration factors.

The element fit control list is used to determine which elements and which components are included in the fit to the measured spectrum. Any choices in this list will be applied to all spectra and will override any information in the standards input file. If nothing is specified in the standards input file then all elements in the given composition and all emission lines in the spectrum range will be included in the fit. This is usually not the best choice, so some entry in the element fit control list is required for this action. If the new standards input file format is used, any information in that file will be used but can be overridden using entries in the element fit control list.

Inputs: Configuration file (see Section 7 on file formats)

Standards input file

Calibration file name (a new file will be created or an existing file overwritten)

Element fit control list (optional)

Outputs: A calibration file is written with the element calibration factors

The output text box has an entry for each standard with complete calibration and fit information. (No plot or plot file is produced.)

### Quantify

This is used to determine the element abundances represented by the peaks in the measured spectrum of an unknown target. The instrument configuration used in the fundamental parameters calculation is input via the configuration file. The measured spectrum is input from the spectrum file name in the main window. The element calibration factors read in from the calibration file will be applied during the quantification.

Because the composition is unknown, the list of elements present in the target must be given in the element fit control list. If no energy level is chosen for the emission lines to be used to quantify the element, then the K lines will be used unless they are not in the spectrum range, in which case the L lines will be used. Likewise the M lines will be used if the K and L lines are not in the spectrum range, although this is rare. K, L, M or N lines can be chosen for quantification.

Element calibration factors are used to adjust the quantification results. Each factor is an average over the standards that contain the respective element. Any elements that are missing in all standards will use the average calibration factor calculated from the available elements. If the calibration file is the new format then the weights for each standard will be used in the average. If the calibration file is in the older text format, the average will be unweighted.

Inputs: Configuration file (see Section 7 on file formats)

Calibration file

Spectrum file

Element fit control list (required)

Outputs: The output text box has entries with complete quantification and fit information.

A plot file is written with the measured spectrum, fit, and all fit components

The plot is displayed in the plot window

### Map

This action quantifies a sequence of spectra and produces a comma-separated-values file with the location of each spectrum (from the spectrum file) and the quantification results from each spectrum. The results for each spectrum appear on a single line in the output map file. This file can be used to create quantitative maps or line scans from the sequence of spectra. No plot is produced by this action, and it can take large amounts of time depending on how many spectra are in the sequence and how many elements are in the fit control list. (For 10,000 spectra it can take up to 10 hours; we are working to improve this.)

The sequence of spectra is specified by entering the file name of the first spectrum in the sequence. All spectra in numerical sequence and that can be found in the same folder or directory will be processed, starting with the given file name. Processing will stop as soon as a file in the sequence cannot be found. This can be modified using the –m option in the command line options to specify the number of files to process (e.g., –m,10 to process only the next 10 files; see Section 3.3 on command line options).

The spectrum files should have sequential numbers in the file names. Two formats for these sequence numbers are accepted. Once has the number at the end preceded by an underscore (e.g., spectrum\_1.msa, spectrum\_2.msa, …). The number must be immediately before the dot at the end of the file name. This is the name sequence produced by the LabView program that runs the breadboard and Stony Brook instruments. The second format is to include the number immediately after the letters Seq (case sensitive, e.g., abcSeq123spectrum.msa, abcSeq124spectrum.msa, …). The Seq and number digits can be anywhere in the file name but the characters Seq must not appear anywhere else and there must not be anything else between the Seq characters and the number. This is a historical format from the Mars Borehole instrument and is not presently used by PIXL. The sequencing code is modular and versatile, so other ways to indicate the sequence number in the file name can be implemented in future versions if necessary.

Inputs: Configuration file (see Section 7 on file formats)

Calibration file

Spectrum file

Element fit control list (required)

Outputs: The output text box has entries with complete quantification and fit information for all the spectra

A map file is written with the location and element percents for all spectra, one spectrum per line, and each element always in the same column

## File Selection Inputs

Most of the inputs are in the form of files prepared in advance and then selected using the main window of the graphical user interface. File formats are described in Section 7. Many of the files are produced automatically, such as the spectrum files that are produced during data collection. Push the select button to bring up a system file dialog to point to the location of the file. The full path to the file will be placed into the text line under the select button. This text can be edited to change the path if desired or a path can be entered manually (or via copy and paste). The dialogs will show only the correct file type for the input being selected.

The text line for the element fit control list is different in that it can only be entered manually (or via copy and paste). It is direct text sent to the PIQUANT calculation engine and is not a file path. The text consists of a list of element symbols or atomic numbers and some single-letter instructions. The actions that use this input vary in how it is interpreted. (See Section 2.1 on essential inputs.)

The plot file selection is optional. If a plot will be produced and a plot file is not specified, the plot information will be written to a temporary file and the plot produced from this file. The temporary file will be deleted when the plot is completed.

The log file is always available. If a log file name is specified, the text output that appears in the output text window above the Go! button will be appended to the log file after a date and time stamp. A new log file can be created or an existing file chosen, depending on the choice beside the select button. In either case the log entries will always be appended, never overwritten. Note that the log file is written after the text is displayed in the window, so nothing new will be written to the log file until the action completes. This may take a while for big maps.

## Command Line Options

Several modifications of the processing during the actions are possible using the command line options. These options take the form of a minus sign followed by a single letter. Some options have numerical values separated by commas after the letter. An example is –d,0 to select just the first detector from dual-detector spectra or –b,60,5,30 to optimize the background for a spectrum of the NIST 610 standard. These options are included for flexibility and are a slightly awkward to use at present. In the future the plan is to provide a graphical interface for using the most popular options that is more intuitive and has the values chosen graphically, from drop-down lists, or some similar method.

At present these options are passed directly to the command line program that does the actual calculations for the graphical user interface. For a complete listing of the options available as of this release and a description of their effects and accepted values, see Section 4.4.

## Text Output Box and Go! Button

Text output is displayed in the text output box at the bottom of the main window. For some actions this is the main information displayed, and for some it is ancillary information and the main output is the plot. The text box is scrollable and editable, although the details of how to edit may vary depending on the operating system.

If a log file is specified, the content of this window is appended to the log file (see Section 3.2).

None of the inputs are checked or used until the Go! button is pressed. The inputs are then checked to see if all required inputs have been specified. If not, a dialog is displayed showing which input is missing. Once all inputs are verified as present (although not interpreted), the model is invoked to read the input files, perform the requested processing, and write the outputs. Once the model is finished the plot (if any) is displayed in a separate window. The calculations may take several minutes depending on how many channels are in the spectra, how many elements are being quantified, and how many spectra (standards in calibrate or unknowns in map) are being processed. The text output always has the execution time at the end, so future execution times can be estimated. The time increases roughly linearly with the number of channels and spectra and as the square of the number of elements (because of secondary fluorescence cross-calculations). Using the element fit control list can help reduce the execution time as well as improve the fit.

The graphical user interface will be unresponsive after the Go! button is depressed until the action completes and the new text appears in the window. The only way to interrupt the action is to terminate the PIQUANT\_CommandLine process using tools provided by the operating system. Note that for large maps the action may take several hours and will give no indication until it completes. Every attempt is made to find errors immediately rather than after a long wait.

# Command Line Tool

## Command Line Usage

The actual calculations as well as reading and writing all the files are handled in a command line tool written in C++. This command line tool can be called directly from a terminal window, included in scripts and batch files, and called as a subprocess from other applications. (This is how the GUI accesses it.) Each action listed above has a corresponding sub-command in the argument list.

The text output that is displayed in the text output window of the main window for the GUI is the same text that is produced by the command line tool. That text is written to standard output and will show up in a terminal window. Including a terminal output file (see Section 4.3) will cause this text to go to the file instead.

## Sub-commands

Each of the actions described in the GUI sections has a corresponding sub-command in the command line tool. The GUI sections have a more complete description of how each sub-command works and what the arguments mean, especially the element fit control list.

Only the first three letters of the sub-command need to be entered except for calculate, which needs four letters. The sub-commands are not case sensitive. The full word can be entered but only the first three or four letters are checked. The sub-command cannot contain any blanks.

Only a brief description, the expected arguments, and any special notes on use of the command line are included here. See the corresponding sections in the GUI actions for more general usage information.

### Energy Calibration

Associates the two largest peaks with elements from the element fit control list and calculates the energy of the first channel and the energy per channel.

Argument list: Spectrum file (read)

Element fit control list (one or two elements)

### Plot

This sub-command converts a spectrum file from the accepted formats to a comma-separated-values file with energy in the first column and the individual detector spectra in subsequent columns. It also adds the background in another column and the standard deviation from counting statistics in another column. If there is more than one detector the sum is also plotted. If there is no valid energy calibration the first column contains the channel number with the first channel being zero. In this case the detectors are not summed and the background may not be very good.

Argument list: Spectrum file (read)

Plot file (overwritten)

### Primary

Calculate the primary spectrum.

Argument list: Configuration file (read)

Plot file (overwritten, optional but the only output of the calculation)

### Calculate

Calculates the full spectrum of the first standard in the standards input file.

Argument list: Configuration file (read)

Standards input file (read)

Plot file (overwritten, optional but only output of the calculation)

### Compare

Compare a measured spectrum with a full spectrum calculation.

Argument list: Configuration file (read)

Standards input file (read)

Spectrum file (read)

Plot file (required, overwritten)

### Fit

Fit one standard and produce a plot file. Note that the element fit control list is required but does not need any entries. It can be an empty quoted string.

Argument list: Configuration file (read)

Standards input file (read)

Element fit control list (required)

Plot file (required, overwritten)

### Sum

Sum a sequence of spectra and produce a sum spectrum and a maximum value spectrum. See the map action (Section 3.1.10) for a description of spectrum file name sequencing. See the bulk sum action (Section 3.1.7) for a description of the sum and max value processing. The sum spectrum is quantified after it is computed.

Argument list: Configuration file (read)

Calibration file (read)

Spectrum file, first in the sequence (read)

Element fit control list (required)

Plot file (required, overwritten)

### Calibrate

Read the standards input file and produce a calibration file of element calibration factors. The calibration file will not be accessed if errors in the input are detected.

Argument list: Configuration file (read)

Standards input file (read)

Calibration file (overwritten if no errors)

Element fit control list (optional but must be present if any options)

### Quantify

Quantify the amount of the given list of elements in an unknown sample from a measured XRF spectrum.

Argument list: Configuration file (read)

Calibration file (read)

Spectrum file (read)

Element fit control list (required)

Plot file (required, overwritten)

### Map

Reads a sequence of spectra and produces a map file. The map file is a comma-separated values file with the location of each spectrum and the percents of each element in columns, with each spectrum on a separate line. No plot file is produced. The final columns may contain some diagnostic information, such as the goodness-of-fit parameter (reduced chi squared), to help distinguish any poorly-quantified spectra.

Argument list: Configuration file (read)

Calibration file (read)

Spectrum file, first in the sequence (read)

Element fit control list (required)

Map file (required, overwritten)

## Command Line Arguments

The sub-command determines the rest of the argument list and how it is interpreted. The preceding sections give the expected argument list for each sub-command. An error results if the argument list does not match what is expected for the sub-command.

All file arguments are full path. The system file open is used so its rules apply for file paths. See Section 7 on file formats for a description of each type of file.

The full path argument for the plot file is required when it is used because there is no provision for a temporary file and the argument list is order-dependent. It can be omitted from some sub-commands, where it is optional, if there are no arguments following it. Note that there is no display of the plot, only writing the CSV plot file.

The element fit control list must be enclosed in quotes if it contains any blanks or horizontal tabs. Once the argument is passed to the command line tool it is parsed just as if it came from the graphical user interface, so its use is as described above. Note that it is optional for some actions in the GUI but must always be present in the command line arguments if it is listed under a sub-command (although it can sometimes be an empty quoted string).

A full path argument for the terminal output file can always be appended to the argument list. It must follow all other, required arguments and must precede any options (Section 7). The terminal output file can be used as a log file because it includes a header and time stamp. It always appends and most operating systems will create a file opened for append if one does not already exist.

## Command Line Options

A few options can be added to the end of the argument list. They are denoted by a minus sign as the first character. Each option must not contain any blanks, although any number of options can be included and must be separated by one or more blanks (the system argument separator is relied upon for this task so its rules apply). No arguments will be inspected for options until all required arguments are found, so required file names that start with a minus sign are (in principle) possible, but not optional file name arguments. Numbers to be entered with the options must be separated from the option letter by a comma and subsequent numbers must be separated by commas with no blanks or tabs.

As of this writing only the following options are available: –e, –b, –d, –m, and -q.

Options are under active development so check for what options are available on the current version. Options may be added without documentation in the future to aid in debugging, testing, code development, or other special purposes.

### Energy Calibration Option, –e

An energy calibration option is available to override the calibration in the spectrum and/or configuration files, or to enter a calibration if one is not present in either of those files. It consists of a minus sign and the lower case letter e followed by two numbers separated by commas. The energy of the first channel and the energy increment per channel follow the letter e separated by commas. For example: –e,–5.25,10.3 (units are electron Volts and electron Volts per channel, and the energy per channel must be positive). At present there is only one energy calibration allowed, so it applies to all detectors if there is more than one in the spectrum file. In the future this may be handled differently as we gain more experience with multiple detectors.

### Background Control Option, –b

An option is included to override the defaults for background removal. It consists of a minus sign and the lower case letter b, followed by up to 3 numbers separated by commas. The first number is the channel where the background algorithm will start processing, and the values in any channels below this will be ignored. The second number is the width in channels for the smoothing component of the background algorithm. The third number is the number of iterations to be performed by the background algorithm. These numbers can be used empirically by observing their effects on the net spectrum and the background curve displayed in the plots. To understand their action more fully see more on the SNIP background algorithm [Van Grieken and Markowicz, *Handbook of X-Ray Spectrometry* 2nd Ed., 2001]. For example, entering the option –b,25,12,24 would cause the background algorithm to start at channel 25, use a width of 12 channels, and perform 24 iterations. Note that all values are in channels, not energy, and must be integers. Any of the three values can be omitted and the default values will be used, but the commas must still be present if any values follow an omitted value.

### Detector Select Option, –d

For spectrum files that have more than one detector, the detector signals are summed prior to processing the spectrum. If only one detector should be processed, this option can select any of the detectors in the spectrum file and process only that signal. The option consists of a minus sign and the lower case letter d, followed by a comma and a single integer giving the number of the detector to be selected. The first detector is number zero. The numbers correspond to the columns in the spectrum file, starting with zero and going up to the number of columns minus one. An error results if the number is equal to or larger than the number of columns.

### Maximum Sequence Spectra, –m

For maps and bulk sum / max channel actions, the spectrum file gives the first file name in a sequence of spectra. This option allows only a limited number of spectra in the sequence to be processed. Normally all the spectra that can be found with sequentially numbered file names will be processed. If this option is given processing stops after the indicated number of spectra are found. The format of the option is a minus sign and the lower case letter m, followed by a comma and a single integer giving the number of spectra to process. An example is –m,5 to process five spectra starting with the spectrum file given in the file selection box or command line argument. Four additional spectrum files will be processed (if found) with the sequence number in the file name incremented for each one. If any sequential spectrum file is not found processing stops with an error. See the section above on Maps for more information about the spectrum file name sequencing.

### Map File Output Options, –q

For maps an output CSV file is generated with one line of data for each spectrum processed as part of the map. The information on these lines can be controlled via the –q option. The –q is followed by a comma and a set of letters strung together without any spaces or other separators (for example, -q,PIET to include percents, intensities, errors, and total counts). Each letter designates a particular type of information to include given in the list below. Some entries are one per element, and including that letter will include that entry for all of the elements in the element fit control list (in the order they appear in the element fit control list). Other entries are one per spectrum and will appear only once on each line. All of the information included in the map output file will be included on the header line (usually the second line in the file after the title line). Note that the letters are case sensitive. In general, upper case letters are used for values calculated as part of the quantitative analysis and lower case letters are used for auxiliary information from the spectrum file that is not used in PIQUANT but included in the map file for downstream processing. Output headers and values appear in the same order as their corresponding letters are entered in the –q option.

Entries for the –q option to be included in the map output file (note case sensitive):

These entries are one per quantified element in the element fit control list

The elements are in the same order as in the element fit control list

P percents (default if no entries in quant map options)

I intensities

E relative errors

L fit coefficients

K Element Calibration Factors used for quantification

G Given percent (for standards, used with Evaluate)

H Relative error vs given (used with Evaluate)

These entries are one per spectrum processed

T total counts

X reduced chi squared

C energy calibration

R detector resolution

N number of iterations

F spectrum file name

S sequence number in file name

V live time

M Real time

7 Region counts (default region is 1 to 7.25 keV)

These entries are for auxiliary information not used by PIQUANT:

x Location with respect to X axis

y Location with respect to Y axis

z Location with respect to Z axis

i Column location in visible image

j Row location in visible image

s PIXL SCLK (Spacecraft clock ticks)

r Mars 2020 Round Trip Tracking token

d PIXL Data Product Category

p PIXL Motion Counter

e Events from histogram header

t Triggers from histogram header

o Overflows from histogram header

u Underflows from histogram header

b Baseline samples from histogram header

a Preamp resets from histogram header

s Saturates from histogram header

l Live time from histogram header (fast channel live time)

n Universal Sequence Number from PIXL data product header

### Fit Control Options, –f and -g

These two options control the behavior for fitting the calculated spectrum components to the measured spectrum for unknowns and standards. Normally the energy calibration is adjusted to match the measured spectrum to the calculated energies so that the peaks align properly. The peak width (energy resolution) is also adjusted for the calculated spectrum to match the measured peak widths. Both of these adjustments assure that the intensities, taken from the calculated peaks, are as accurate as possible. Failing to match the energy calibration in particular will bias the calculation to smaller peak heights. However, some short integration spectra have enough noise that these adjustments cause unacceptable variations when fitting the spectra. For this reason the adjustments can be disabled using these options. –f disables the adjustment of the energy calibration. -g disables the adjustment of the detector resolution. All peaks are calculated using the resolution in the configuration file. Note that disabling the energy calibration adjustment may cause the resolution adjustment not to be done since the peak positions must match fairly well for the resolution adjustment to work properly. Likewise the peak energy shift can not be evaluated correctly if the energy mismatch is too great. The algorithm has built-in checks that prevent adjustment of either the energy or resolution if any of these checks fail.

-f Disable adjustment of the energy calibration during spectrum fits

-g Disable adjustment of the peak widths (detector resolution) during spectrum fits

### Compton Convolution Option, -s

The Compton scatter components (incoherent scatter from individual emission lines and the continuum background from an X-ray tube) have width from the Doppler broadening. This makes is computationally expensive to further broaden them with the detector response and it usually not necessary to get a good fit to the spectrum. However, when it is necessary the computation expense may be worth it. The –s option enables convolution of these calculated spectrum components with a Gaussian whose width is determined by the detector resolution. The convolution uses a brute-force method which is computationally expensive but accurate. The Gaussian width varies across the spectrum with the energy, as determined by the detector resolution function. Note that only the Gaussian component of the detector response is used, not the tails from incomplete charge collection or other features in the detector response.

# Examples

## GUI

Figure 4 is an example of how to use the PIQUANT GUI to quantify an XRF spectrum. It uses a BHVO spectrum taken on the PIXL Breadboard in 2017. The main window is shown first with the Quantify action button selected and all the necessary inputs specified. The quantification can be seen in the text section near the bottom. This section can be scrolled to show additional information. Note the list of elements and emission lines to be used for quantification in the “element fit controls” near the center of the window. Note also that a dummy calibration file is used, which contains all ones for the element calibration factors. The results are strongly dependent on the configuration file and can be improved by using a better calibration to get good values for the element calibration factors.

## Command Line

The command line arguments to produce Figure 4 follow. Each argument is listed on a separate line for clarity, in reality they would be on the same line and separated by blanks. Note the single quotes for the file names that contain blanks and for the Element Fit Controls, which are needed but can be single or double quotes (depending on the operating system and shell constraints).

PIQUANT\_CommandLine

Quant

‘Configuration File Breadboard Jun2017.msa’

Dummy\_calibrationFile.txt

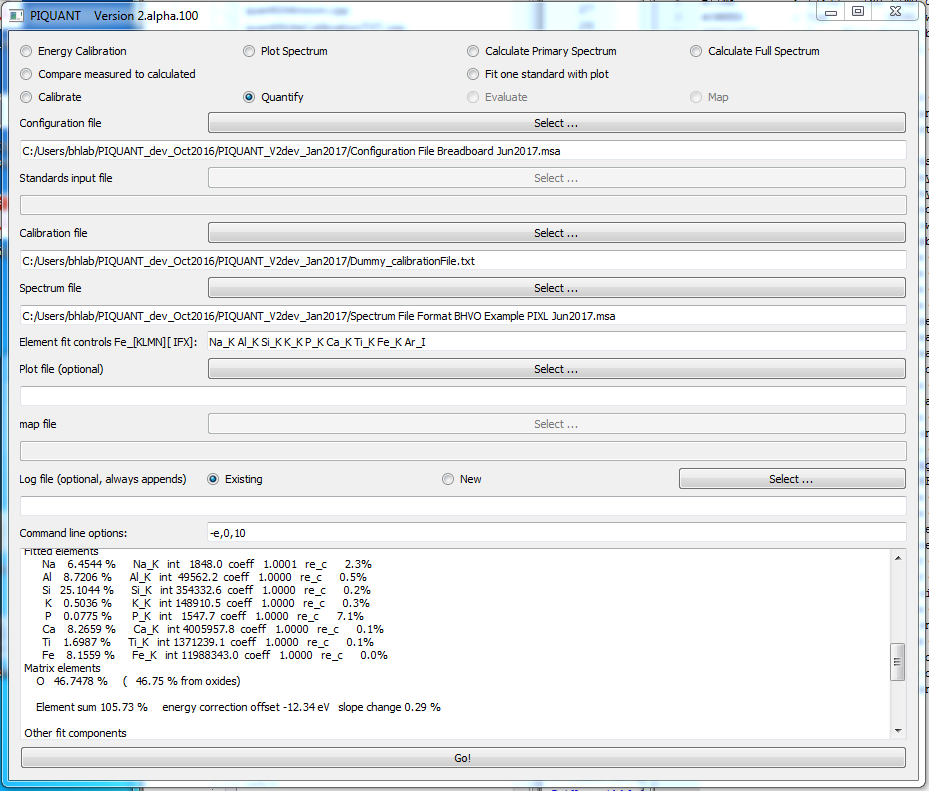
‘Spectrum File Format BHVO Example PIXL Jun2017.msa’

'Na\_K Al\_K K\_K P\_K Ca\_K Ti\_K Fe\_K Ar\_I'

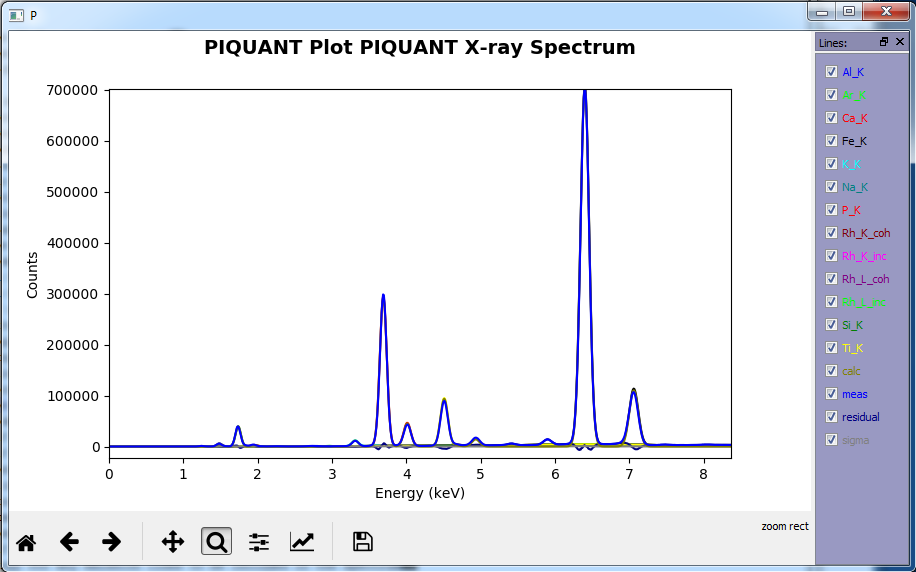
temp\_plot.csv

temp\_log.txt

Note that the plot file name and the terminal output file name are both temporary files. Change these to more useful file names for typical use. The last argument, the terminal output file, can be omitted for the output to go to stdout (usually the terminal window from which the command line tool was run, but it can be piped elsewhere). Option arguments can follow these arguments (with or without the terminal output file).



**Figure 4. PIQUANT graphical user interface**



**Figure 5. Plot resulting from input in Figure 4 after clicking the Go! button**

# Configuration Inputs for Physics Model

## Primary Excitation (X-Ray Source)

**Anode Z** – the atomic number of the X-ray tube anode

**Voltage** – the accelerating voltage applied to the X-ray tube

**Electron incidence angle** – the angle between the surface of the X-ray tube anode and the electron beam. An angle of 90 degrees implies normal incidence. A negative value implies a transmission anode.

**Tube takeoff angle** – the angle between the anode surface and the direction in which the emitted X-rays are accepted for the specimen (or the optic in this case). The emerging X-ray beam covers a range of angles, so this angle is usually measured at the center axis of the exit beam.

**Tube Be window thickness** – the thickness of the beryllium exit window on the X-ray tube.

**Tube current** – the electron current impinging on the anode of the X-ray tube. This is usually taken as the emission current from the filament but can also be measured at the anode.

## Elements in the Primary Beam

**Optic** - the transmission of the optic in the incident X-ray beam as a function of energy.

**Incident path length** – the length of the path between the window of the X-ray tube and the point where the X-rays impinge on the specimen (at the nominal standoff distance). This is for calculating the effects of the atmosphere on the incident beam so it should not include any parts of the beam path that are handled separately, such as enclosed portions of the path or portions under vacuum.

**Incident solid angle** – the solid angle of the X-rays emitted by the X-ray tube anode that reach the specimen. This is usually determined by an aperture on the X-ray tube or by the optic.

## Geometry and Specimen

**Incident angle** – the angle between the incident X-ray beam and the specimen surface. An angle of 90 degrees implies normal incidence. This can vary with tilt of the specimen surface so is usually specified with a flat specimen at the nominal position.

**Atmosphere composition** – the composition of any gas in the beam path.

**Window material** – the composition of any material used as a window on the front of the instrument and in the path of the incident and emitted X-rays. Note that the incident and emitted paths may have different windows but this is a single window that applies to both.

**Window thickness** – the thickness of the window material.

**Emergence angle** – the angle between the specimen surface and the X-ray beam accepted by the detector. Again the X-ray beam accepted by the detector will cover a range of angles so this is specified at the axis between the emission point on the specimen and the center of the detector. An angle of 90 degrees implies normal incidence.

**Emergent path length** – the length of the path from the point from which X-rays emerge from the specimen to the window on the detector (at the nominal standoff distance). The same comments apply to this parameter as to the incident path length.

## Detector Description

**Detector solid angle** – the solid angle of X-rays emitted by the specimen that are accepted by the detector.

**Window** – Composition and thickness of the detector entrance window.

**Active layer** – Composition and thickness of the active layer that absorbs the X-rays and produces the signal.

**Energy resolution** – width of peaks at a reference energy (usually the Mn Ka emission line at 5898 eV, the dominant emission from an 55Fe source).

**Detector incidence angle** – this is the angle between the direction that the X-rays impinge on the detector and the detector surface. It is almost always 90 degrees.

**Minimum energy** – This is the minimum energy for any emission lines to be included in the spectrum. Any emission lines below this energy will not be included in any fits to the spectrum. Also, the background removal will start at the channel corresponding to this energy if the spectrum has a valid energy calibration (unless overridden by the background control option).

# File Formats

The formats of the various files needed or produced by PIQUANT are described in this section. The formats are given as examples files with comments and other documentation included with the data in the file. All these files are useable as shown. All files are ASCII flat text files and can be examined with any text editor.

The configuration and spectrum data files are distinguished by the file extension. Older standards input and calibration files have a .txt extension. Newer standards input and calibration files have a .csv extension. The files are interpreted based on the extension found in the file name unless otherwise indicated.

## Configuration Files

The configuration files describe an individual instrument and contain all the information for the physics-based fundamental parameters model. This information is described in Section 6. Note that the information in this file must be accurate to get reliable calculations or quantification.

Configuration files are generally identical to the spectrum files with the same file extension but with zero number of spectrum data points. Several of the keywords in the ISO standards that these file formats are based on are required in the standard. These keywords are included in the configuration files even though they are not relevant to the configuration but only to the spectrum data. A spectrum can be included in a configuration file but will be ignored.

### Old XSP Configuration Files

These files are an older format that was used for the Mars Borehole XRF instrument. They were used to analyze data for the PIXL breadboard instrument before the PIXL instrument was selected and during the early design process. It was based on an earlier version of the ISO standard in the next section. That older standard did not provide for user-defined keywords so several ad-hoc keywords were created for this format. This format is gradually being replaced by the new MSA configuration file format.

#FORMAT : EMSA/MAS Spectral Data File

#VERSION : 1.0

#TITLE : PIXL best model for current FM configuration (1 hr, side window tube, 32 mm standoff, 2 det)

#DATE : 07/01/2015

#TIME : 0:00:00 AM

#OWNER : Tim

#NPOINTS : 0

#NCOLUMNS : 1

#XUNITS : eV

#YUNITS : COUNTS

#DATATYPE : Y

#XPERCHAN : 10

#OFFSET : 0

#LIVETIME : 3600

#SIGNALTYPE : XRF

anode\_z: 45

BEAMKV: 28.00

tube\_inc\_angle: 30

tube\_takeoff\_angle: 70

tube\_be\_window: 0.150

tube\_current: 0.02

filter\_z: 1

filter\_thick: 0

excit\_angle: 90.00

emerg\_angle: 70.00

solid\_angle: 0.00000912

path\_type: 2

inc\_path\_length: 3.0

emerg\_path\_length: 3.2

window\_type: 2

window\_thick: 0

detector\_type: 2

minimum\_energy: 900

optic\_type: 3

#SPECTRUM

#ENDOFDATA

### New MSA Configuration Files

These files follow the ISO 22029 standard[[1]](#footnote-1)†, which details the EMSA/MAS standard file format for spectral data exchange. The format is a keyword and value format and was developed for X-ray emission spectra taken with electron microscopes. User-defined keywords are provided in the standard and several have been defined for PIXL (and are also applicable to other XRF instruments). The format has also been adapted to accommodate multiple detectors. Multiple columns are allowed in the standard for spectrum data and this was extended to include multiple entries for energy calibration, live time, and similar keywords.

#FORMAT : EMSA/MAS spectral data file

#VERSION : TC202v2.0 PIXL

#COMMENT : The first two lines must appear exactly as shown, other keywords can be in any order.

#COMMENT : Updated Feb. 7, 2018 to include ##TRIGGERS and ##EVENTS keywords

#TITLE : This is a descriptive title (NB: this keyword must be present even if no title)

#TITLE : This file is based on the PIXL Breadboard configuration of August 2017

#TITLE : The title keyword can be repeated several times if necessary

#COMMENT : Comments can appear anywhere except in the spectrum data.

#DATE : Date in the format DD-MMM-YYYY, for example 30-SEP-2017

#TIME : 12:22 The time of day at which the spectrum was recorded, in 24-hour format

#OWNER : NewBB (PIXL will use this to indicate which instrument took the data.)

#NPOINTS : 0 This should be zero for configuration only files

#NCOLUMNS : 2 This will be ignored for configuration files

#XUNITS : eV

#YUNITS : COUNTS

#DATATYPE : Y (This would be YY for two detectors.)

#XPERCHAN : 10.0, 10.0 eV per channel, will be used if the spectrum file is not calibrated

#OFFSET : 0.00, 0.0 eV of first channel, will be used if the spectrum file is not calibrated

#SIGNALTYPE : XRF

#COMMENT : The above keywords (except the comments) are always required in the ISO 22029:2012(E) format.

#COMMENT : Generally, the keywords that apply to all spectra will be in the configuration file

#COMMENT : and only the keywords for information unique to each spectrum will appear in the spectrum files.

#COMMENT : However, any keywords can appear in the spectrum files and will override the configuration values.

#COMMENT : The keywords below are instrument configuration information and will normally by in the configuration file.

##ANODE : 45 Atomic number of anode in X-ray tube

#BEAMKV : 28.00 X-ray tube voltage in kilovolts

##TUBEINCANG : 90.00 X-ray tube electron incident angle in degrees

##TUBETAKEOF : -90.0 X-ray tube takeoff angle in degrees (negative for transmission anode)

##TUBEWINDOW : 0.275 X-ray tube Be window thickness in mm

#EMISSION : 20 X-ray tube emission current in microAmps

##FILTERZ : 1 Primary beam filter material - atomic number of metal foil

##FILTERTH : 0 Primary beam filter thickness in microns

##OPTICFILE : 5 File name of optic transmission function (5 for 2017 breadboard, 3 for old PIXL breadboard, 0 for no optic)

##INCSR : 0.0017 Solid angle from source in steradians (can include normalization for optic file)

##INCANGLE : 90.00 Incident angle of primary X-ray beam in degrees (90 is normal incidence)

#ELEVANGLE : 70.00 Elevation angle of detector, in degrees (90 is normal to surface)

#AZIMANGLE : 180.0 Azimuth angle between incident beam plane and detected beam plane

##GEOMETRY : 1.0 Geometric correction factor

#SOLIDANGLE : 1.571 Solid angle collected by the detector in steradians

#COMMENT : This is for one detector, double for two detectors

#EDSDET : SDBEW Type of XRF detector (SDBEW, SIBEW, CDBEW, or GEBEW, for SDD, Si\_PIN, CdTe, or Ge)

#TBEWIND : 0.0017 Thickness of Be window on detector in cm

#TACTLYR : 0.050 Thickness of active layer of detector in cm

##DETRES : 129 Detector energy resolution in eV (at 5.9 keV, Mn Ka emission line, Fe55 source)

##ATMOSPHERE : He Atmosphere in X-ray beam path, can be Vac, He, Mars, Earth, Air

##PATHINCLEN : 2.0 Length of incident beam path in cm

##PATHEMGLEN : 3.2 Length of emerging beam path in cm

##WINDOWTYPE : None Type of window between instrument and specimen (None, B4C, Plastic, Zr, Al, Nylon, or Al2O3)

##WINDOWTH : 0.00 Thickness of above window in microns (0 = No window)

#COMMENT : Live time is given in the configuration file for calculations without reading a measured spectrum

#LIVETIME : 1.0, 1.0 seconds (separate by commas if more than one detector

##MINIMUM\_EN : 900 Minimum energy in eV for any emission lines to be included in the spectrum

#COMMENT : Optional keywords we may want to consider in the future:

#COMMENT : #CHECKSUM (See definition in standard)

#COMMENT : #BEAMDIAM beam diameter on specimen (nanometers)

#COMMENT : #THICKNESS thickness of specimen (nanometers)

## Standards Input Files

### Old Text Standards Input File (.txt)

This was an ad-hoc format that contained only the essential information for processing measured spectra from standard materials and producing element calibration factors. It contained just the spectrum file name and the percents of elements present in the standard. Each standard had a separate complete entry and the format was not very flexible. It is in the process of being replaced by a commas-separated-value format with much more information.

The file contained a single element fit list at the beginning. It was ignored but was required for proper reading of the file.

// Any line that starts with two slashes is a comment

// Calibration spectra and compositions for producing new calibration file

// Composition from "ReducedStandardsComposition.xls"

// The first non-comment line must be the element list for unknown analysis

// The number of elements followed by element symbols

// Blank or tab separated (not commas) and case sensitive

16 Na Mg Al Si P K Ca Ti V Cr Mn Fe Ni Cu Zn Sr

// Data from Standards\_Emily\_Oct2013

// With compositions from standardCompositions.txt of Dec. 2, 2013 3:20pm

BHVO-2G\_100uA\_28kV.mca

// The number of elements followed by element symbols and percents

// Blank or tab separated (not commas) and case sensitive

18 Na 1.6469 Mg 4.3599 Al 7.1449 Si 23.3250 P 0.2146 K 0.4317 Ca 8.1475 Ti 1.6362 V 0.0317 Cr 0.0280 Mn 0.1290 Fe 8.6029 Ni 0.0119 Cu 0.0127 Zn 0.0103 Sr 0.0389 Zr 0.0172 O 44.5883

### New CSV Standards Input File (.csv)

This format was developed to give much more control over individual standards, how they were fit, and how they are used to produce the element calibration factors (ECFs). It uses comma-separated values with few keywords and fixed fields for the elemental information. It is much more flexible and can be extended as necessary.

The new calibration file format is identical to this file. Note the ECF and ECF error fields at the end of each element line. If these fields are present in the standards input file they are ignored.

Comment, The information on each input line is given below

Comment, A more detailed description of the input values is given at the end of this file

Comment, This file is useable as-is

Comment, Each line consists of comma-separated values, either text or numbers

Comment, If a text value contains a comma, it must be enclosed in quotes "like this, for example"

Comment, Each line can start with either a keyword or an element symbol

Comment, Keywords are not case sensitive but element symbols ARE case sensitive

Comment, Each standard description starts with the Standard keyword, which resets all values

Comment, The standard keyword is optionally followed by one or more names for the standard

Standard,BHVO-2,"Basalt Hawaiian Volcanic Observatory"

Comment, The Comment keyword can appear anywhere and the rest of the line is ignored

Comment, except that comments are stored and written to the calibration file

Comment, Orig tot %: 100.2100

Comment, Each line that begins with an element symbol has fields in a fixed order

Comment, The fields are: Element symbol, Emission line [KLMN], Fit qualifier [XIFM], Type (see below), Amount, Uncertainty, Oxide ratio, and Weight

Comment, See the end of this file for a more complete description of these fields

Si , , , , 23.325%, 0.6a, 2, 1

Ti , , , , 1.6366%, 0.04a, 2, 1

Al , , , , 7.14475%, 0.2a, 1.5, 1

Fe , , , , 8.6029%, 0.2a, 1.5, 1

Mn , , , , 0.09990%, 0.004a, 1, 1

Mg , , , , 4.35988%, 0.12a, 1, 1

Ca , , , , 8.14739%, 0.2a, 1, 1

Na , , , , 1.6469%, 0.08a, 0.5, 1

K , , , , 0.43167%, 0.01a, 0.5, 1

P , , , , 0.11783%, 0.02a, 2.5, 1

V , , , , 317.0ppm, 11a, 0, 1

Cr , , , , 280.0ppm, 19a, 0, 1

Co , , , , 45.0ppm, 3a, 0, 1

Ni , , , , 119.0ppm, , 0, 1

Cu , , , , 127.0ppm, 7a, 0, 1

Zn , , , , 103.0ppm, 6a, 0, 1

Rb , , , , 9.8ppm, 1a, 0, 0

Sr , , , , 389.0ppm, 23a, 0, 1

Y , , , , 26.0ppm, 2a, 0, 1

Zr , , , , 172.0ppm, 11a, 0, 1

Comment, The Spectrum keyword gives the name of the measured spectrum file for this standard

Comment, This keyword triggers the fitting of the spectrum and writing the ECFs for this

Comment, standard to the calibration file.

SPECTRUM, USGS\_BHVO2\_He\_28kV\_20uA\_1hr.mca

Comment, At this point, additional element lines can be entered, which will modify the

Comment, information already entered for this standard. Then another Spectrum line

Comment, can be entered to produce more calibration entries with the modified

Comment, information and a different measured spectrum.

Comment, Detailed description of the values on an element line (not case sensitive unless indicated)

Comment, Element symbol Case-sensitive, one or two letters, only the first one capitalized

Comment, Emission line [KLMN] Denotes which emission lines this entry applies to, allowed values are K, L, M, or N

Comment, (if no emission line is specified this applies to all lines for this element)

Comment, Fit qualifier [XIFM] Controls how the emission line will be treated in fitting the spectrum

Comment, Allowed values are X, I, F, and M

Comment, X means to exclude this emission line from the fitting

Comment, (it will not be calculated or used to fit the spectrum)

Comment, I means fit this line but ignore it, do not include it in the standard composition

Comment, F is reserved for future use

Comment, M is for matrix, it is treated the same as X

Comment, Type Spectrum component type, for future use in calibrating scatter peaks

Comment, Allowed values are inc (or Com) for incoherent or Compton scatter,

Comment, coh (or Ray) for coherent or Rayleigh scatter, and bkg for background

Comment, The default type is E for Element and is the only type used for now

Comment, Amount Amount of the element present in the standard composition, in percent

Comment, The amount can be followed by the percent sign (%)

Comment, The amount can also be entered as a fraction

Comment, in this case the number must be followed immediately by the letter f

Comment, The amount can also be entered as parts-per-million

Comment, in this case the number must be followed immediately by the letter p (can be ppm)

Comment, If amounts are entered for the same element on different lines, the last one read will be used.

Comment, Uncertainty Uncertainty in the amount of this element in the standard, default is relative percent

Comment, The uncertainty can be entered as an absolute value in the same units as the

Comment, amount but it must be followed immediately by the letter a (for absolute)

Comment, Oxide ratio Number of oxygen atoms attached to each atom of the element. Default is zero.

Comment, For example, for Al2O3 the oxide ratio would be 1.5

Comment, A value of -1 can be entered and will cause the default oxide ratio for this element to be used

Comment, Weight When computing the ECFs to be used to quantify an unknown, the ECF from this standard for this

Comment, element and emission line will be weighted by this factor. The default is unity.

Comment, Set this value to zero to include the element in the composition but not use the ECFs.

Comment, Zero is also useful for elements with small amounts whose peaks are too small for a good fit.

Comment, (The following two values are added when this information is written to the calibration file.

Comment, If they are included in the standards input file they will be ignored.)

Comment, ECF Element Calibration Factor

Comment, It is the fit coefficient that gives the ratio to actual peak size in the measured spectrum

Comment, relative to the calculated peak size using the fundamental parameters quantitative

Comment, calculation for this standard composition.

Comment, ECF sigma Uncertainty in the ECF as a relative percent based on the spectrum counting statistics

Comment, including any correlations in the fit.

Comment, Intensity Net peak intensity for this element emission line in the spectrum, from the fit.

## Calibration Files

### Old Text Calibration File (.txt)

This file contained only the atomic numbers of elements for which ECFs were calculated from standards and the actual ECF values.

0 Lines that start with zero are skipped.

0 Number of element followed by atomic numbers

0 The immediately followed by a line of corresponding ECF values

0 (no comment allowed after the element list)

8 11 14 15 17 19 20 26 92 299

0.5686 0.5686 8.3526 2.2013 0.5686 0.2160 0.3353 0.4282 0.0000 0.0000

0 There are a few numbers at the end of the element and ECF lists.

0 They are ignored but must be present.

### New CSV Calibration File (.csv)

The new calibration file format is identical to the standards input file. Note the ECF and ECF error fields at the end of each element line. This information is added from the calibration results when the calibration file is written. The calibration file contains all of the information from the standards input file with the ECF fields added. The ECF values for each standard are included separately so that the ECFs used for a particular unknown can be adjusted as desired based on the complete information about each standard. Currently all standards are used and only the weights affect the calculation of ECFs for unknowns. The complete set of information is read in for possible future use in more sophisticated ECF calculations that may be individualized for each unknown.

## Spectrum Files

### MSA Format

This format is identical to the new MSA configuration files described above. The number of data points must be correct for the spectrum data. The spectrum data is read until the specified number of points has been read. If an end of file or the end of data marker are found before all of the points are read an error results. Many of the configuration keywords are usually omitted from the spectrum files but all of the required keywords from the relevant ISO standard must be present.

An example of an MSA spectrum file from the PIXL Breadboard instrument is given here with most of the actual spectrum data removed. This format is produced when maps are collected using the LabView software on the PIXL breadboard or the Stony Brook instrument. A few comments have been added that are not written by the LabView software.

#FORMAT : EMSA/MAS spectral data file

#VERSION : TC202v2.0 PIXL

#COMMENT : Updated Feb. 7, 2018 to include ##TRIGGERS and ##EVENTS keywords

#TITLE : Control Program v6 Test 5

#OWNER : JPL BREADBOARD vx

#DATE : 01-29-2018

#TIME : 09:27:54

#NPOINTS : 4096

#NCOLUMNS : 2

#XUNITS : eV

#YUNITS : COUNTS

#DATATYPE : YY

#XPERCHAN : 10.0, 10.0 eV per channel

#OFFSET : 0.0, 0.0 eV of first channel

#SIGNALTYPE : XRF

#COMMENT : Comments like this can be included anywhere except in the spectrum data.

#COMMENT : Fields above will be written to config file and spectrum files; fields below only config file.

#XPOSITION : 0.000

#YPOSITION : 0.000

#ZPOSITION : 0.000

#LIVETIME : 121.0, 121.0

#REALTIME : 121.1, 121.1

#COMMENT : The livetime from XIA pulse processing is not the usual livetime. It must be adjusted

#COMMENT : by the ratio of output to input counts. These quantities are read from the pulse processor and included

#COMMENT : using the following two keywords. PIQUANT will make the correction if it finds these keywords.

##TRIGGERS : 194764, 195575

##EVENTS : 190020, 190882

#SPECTRUM :

0, 0

0, 0

0, 0

0, 0

#ENDOFDATA :

### MCA Format

These spectrum files are specific to the software that is provided with the Amptek and Ketek X-ray detectors. Both detector formats can be read and are distinguished by reading the first line of the file. The format is not described here and was discovered empirically from files written by the respective detector software. This format is not written by any of the PIXL instruments unless the software from the detector manufacturer is being used to collect spectra.

### XSP Format

This format is identical to the old XSP configuration files. The number of data points must be correct for the spectrum data. The spectrum data is read until the specified number of points has been read. If an end of file or the end of data marker are found before all the points are read an error results. Some of the configuration keywords can be omitted from the spectrum files but all the required keywords from the old ISO standard must be present. This format is not currently written by any PIXL instruments or software.

## Plot File

The plot file is a comma-separated-values file. The first line is the title of the plot. The second line contains the headers for each column. These headers will be used in the legend for the plot. The remaining lines have the energy (or channel number) in the first column and the energy-dependent spectrum information in subsequent columns. The number of columns is determined automatically and the spectrum data runs to the end of the file. This is an example of a plot file with most of the spectrum data removed. In the plot file, each component of the spectrum fit has the background added to it for better visual overlay with the measured spectrum.

PIQUANT X-ray Spectrum

Energy (keV), meas, calc, bkg, sigma, residual, Fe\_K, Ca\_K, Na\_K, Rh\_L\_inc

3.60761, 57576, 55720.1, 1292.67, 239.954, 1855.94, 1292.67, 55720.1, 1292.67, 1292.67

3.61764, 82441, 81193.8, 1300.26, 287.129, 1247.23, 1300.26, 81193.8, 1300.26, 1300.26

3.62767, 113485, 112983, 1307.53, 336.878, 502.055, 1307.53, 112983, 1307.53, 1307.53

3.6377, 150707, 149950, 1314.3, 388.213, 756.938, 1314.3, 149950, 1314.3, 1314.3, 1314.3, 1314.3

3.64773, 190301, 189685, 1320.82, 436.237, 616.016, 1320.82, 189685, 1320.82, 1320.82

3.65776, 229284, 228609, 1326.33, 478.838, 674.734, 1326.33, 228609, 1326.33, 1326.33

3.66779, 262717, 262442, 1331.33, 512.561, 274.719, 1331.33, 262442, 1331.33, 1331.33

3.67782, 285616, 286943, 1336.08, 534.432, -1327.44, 1336.08, 286943, 1336.08, 1336.08

3.68785, 298316, 298778, 1340.64, 546.185, -461.688, 1340.64, 298778, 1340.64, 1340.64

3.69788, 296816, 296263, 1345.11, 544.81, 552.875, 1345.11, 296263, 1345.11, 1345.11

3.70791, 280309, 279760, 1348.69, 529.444, 548.938, 1348.69, 279760, 1348.69, 1348.69

## Map File

The map file is a comma-separated-values file with the location of each spectrum and the percents of each element in columns, with each spectrum on a separate line. The location information is precisely as read from the spectrum data file. The first line is a title from the spectrum file or the first spectrum file name. The second line is a list of the column headings including the element symbols for any element percent columns. The final columns may contain some diagnostic information, such as the goodness-of-fit parameter (reduced chi squared), to help distinguish any poorly-quantified spectra. This is an example of a simple map file produced by PIQUANT.

10-7-16-1 Fresh Surface

X, Y, Z, Ca, Ti, Mn, Fe, Co, chisq

0.0000, 0.0000, -3.3500, 5.3299, 0.0225, 0.0401, 0.3760, 0.0376, 0.22

0.100000, 0.000000, -3.350000, 5.8467, 0.0116, 0.0397, 0.2188, 0.0105, 0.21

0.200000, 0.000000, -3.350000, 6.5944, 0.0006, 0.0484, 0.1590, 0.0024, 0.25

0.300000, 0.000000, -3.350000, 7.8825, 0.0003, 0.0665, 0.1776, 0.0010, 0.28

0.400000, 0.000000, -3.350000, 9.2958, 0.0000, 0.0850, 0.2114, 0.0158, 0.31

0.500000, 0.000000, -3.350000, 9.9761, 0.0027, 0.1363, 0.2460, 0.0157, 0.65

0.600000, 0.000000, -3.350000, 9.7767, 0.0064, 0.1133, 0.2620, 0.0029, 0.58

0.700000, 0.000000, -3.350000, 7.2178, 0.0100, 0.0690, 0.2177, 0.0011, 0.36

0.800000, 0.000000, -3.350000, 4.5039, 0.0268, 0.0352, 0.4258, 0.0000, 0.23

0.900000, 0.000000, -3.350000, 1.5232, 0.0164, 0.0145, 0.1541, 0.0000, 0.15

1.000000, 0.000000, -3.350000, 0.1047, 0.0030, 0.0000, 0.0074, 0.0000, 0.08

## Log File

This is a text file with the same text that appears in the text window in the GUI interface or the output of the command line tool. A header giving the PIQUANT version and compile date is written at the beginning of the file and the current date and time when the PIQUANT calculations started is also written. Information is always appended to this file, any existing information is never overwritten.

1. † ISO 22029:2012. Microbeam analysis — EMSA/MAS standard file format for spectral-data exchange. See International Organization for Standardization, https:// www.iso.org/standard/56211.html [↑](#footnote-ref-1)