MigrationCorrection©

A program to correct for element migration.
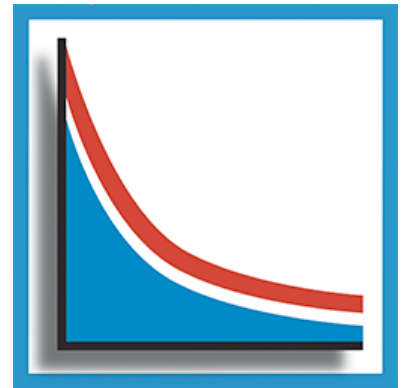
1 - Introduction

Some elements, such as Na and K, will migrate away from the heat of the electron beam during an electron microprobe analyses. This is particularly a problem when the material being analyzed is non-crystalline, like a glass. A crystal structure greatly reduces the ability of an element to migrate in a material, but in a glass the elements are not constrained to particular sites. Therefore on heating, the more mobiles elements will be driven away. This is particularly a problem for sodium, though other elements like potassium also exhibit this particular phenomenon. During the time it takes to make an analysis, the measured counts for Na can drop considerably (Fig. 1).

This obviously causes a serious problem when trying to quantify the amount of Na in a glass. There are a number of strategies that have been used in the past to overcome this problem. These include:

1) Broaden the beam. If the beam diameter is wider, the electron density will be less and therefore less heating will take place.

2) Lower the beam current. This will also reduce the amount of heating in the sample. However it will also reduce the number of X-rays produced. Therefore longer counting times will be required.

Figure 1. Na counts over time in a Na-rich glass.

3) Use a cold stage to reduce heating in the sample (Nielsen and Sigurdsson, 1981).

4) Measure the count rate over time and back-calculate the count rate at time zero. Use this new calculated count rate to then calculate the abundance of Na in the sample.

In many cases, the fourth option is the analyst's only choice, particularly when the materials being analyzed are small volcanic glass shards. In such cases, the beam cannot be broadened
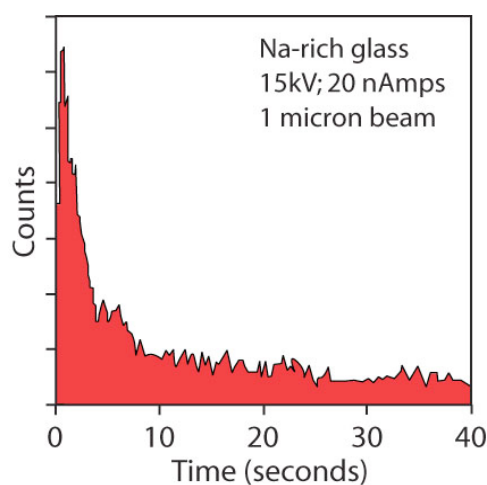
because the shards are too small; cold stages are not typically available, and even lowering the beam current won't stop the loss in counts. This program, *MigrationCorrection*, allows a user to collect a series of element measurements and then back-calculate the count rate to time zero. The user then runs the *JEOL Off-Line Correction* program to convert the new calculated count rate to a weight percentage.

2 – Analysis Setup

In order to measure a series of count rates for a given element over a period of time, the *JEOL Quantitative Analysis* program must be setup properly. Each element that is expected to exhibit migration during the analyses must be analyzed multiple times on the same spectrometer. In the example shown in Figure 2, Na and K are each set to be measured five times in the *Analysis Element Condition* tab. All other elements of interest are then included in a normal manner. The number times that Na and K are analyzed is up to the user. In most circumstances, analyzing each of the migrating element 5 or 6 times should be adequate, though. However, the *MigrationCorrection* software will allow each element to be analyzed up to 50 times.

Figure 2. Elements in the Analysis Element Condition tab selected for analyses. The element conditions shown are for the first time Na is measures.

All of the Na measurements need to be done by one spectrometer and if K is also being analyzed, it needs to be done on another spectrometer. The non-migrating elements are typically analyzed on the remaining spectrometers. If the user cannot put the non-migrating elements onto separate spectrometers and have to put them on the same spectrometers as the migrating elements, then they must be run after the migrating elements.

The user must now set the analytical conditions for the multiply measured elements in a particular manner. For this example, the Na and K should be setup as shown in Figures 2 and 3. The first 4 times that Na and K are measured, the peak counting times are set to between 1 and 3 seconds, and the background counting time is set to "0". The last time these elements are analyzed, the peak counting time is set to the same amount of time as previously for Na and K. However, the background counting time is now set to 5 seconds (Fig. 3). This will cause the background measurements to be skipped the first four times Na and K are measured.
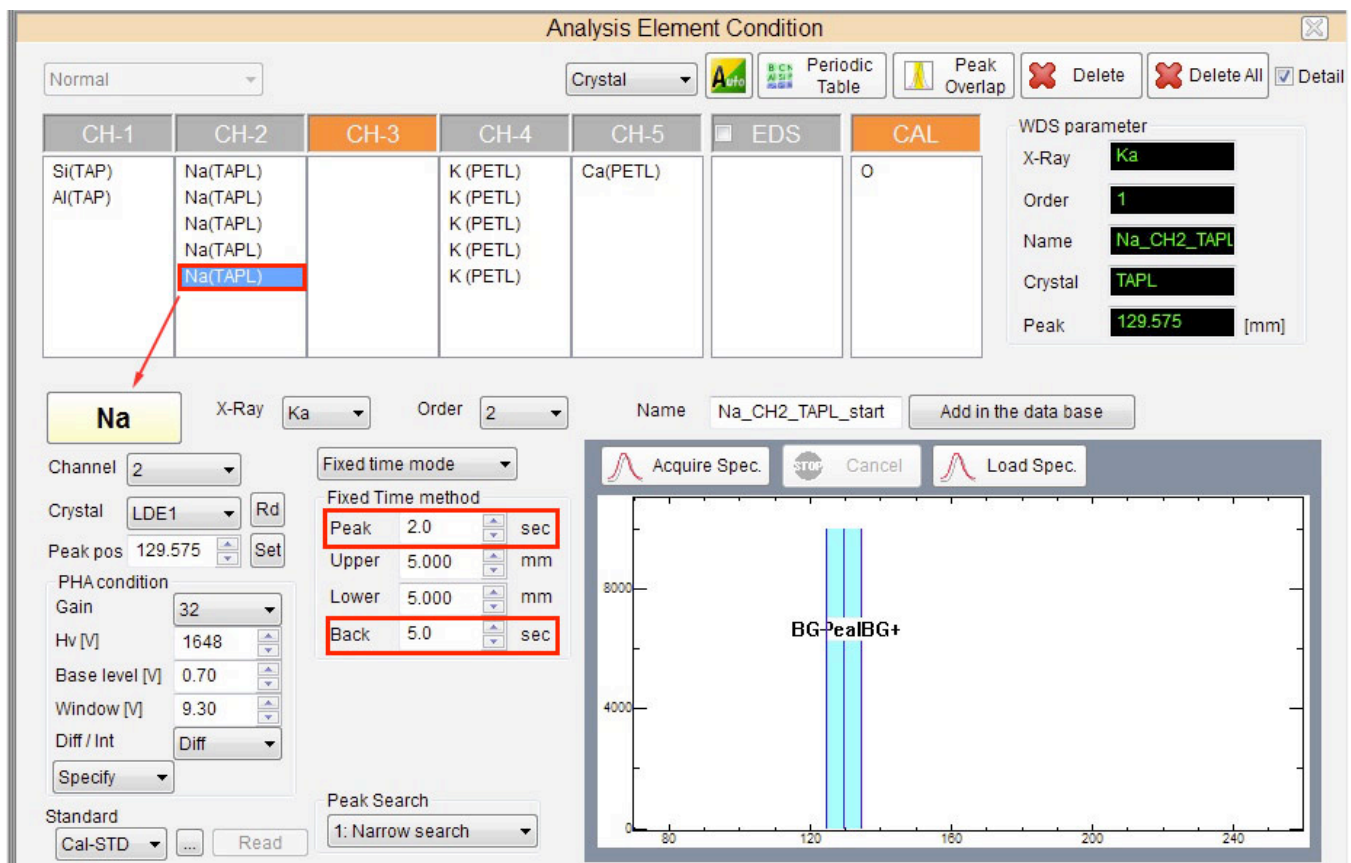

Figure 3. Elements in the Analysis Element Condition tab selected for analyses. The element conditions shown are for the last time Na is measures.

The background will then only be analyzed after the last time the element peak counts are measured. Therefore the spectrometer does not move until all of the peak counts have been measured, ensuring rapid peak measurements, with no time lost between each one.

As previously mentioned, the length of the counting time for each measurement is up to the user. Counting times between 1 and 3 seconds have been found to work well. However it is critical that the same counting times are used for each time the migrating element is measured.

The quantitative analyses can now be run as normal. The JEOL software will average the measurements for each element that has been measured multiple times. Therefore the initial results will not reflect the true concentrations of the migrated elements. However the individual measurements have been stored in the JEOL files, this allows us to extract the data and then interpolate back to what the count rate must have been at time zero.

3 – Migration Correction

The program *MigrationCorrection* has two functions. First it will allow the user to correct for lost counts that are a result of migration away from the electron beam by mobile elements. Secondly, it will allow the user to correct for small drift in the counts that may occur over long periods of time. When the program is first run, it will display the window shown in Figure 4.
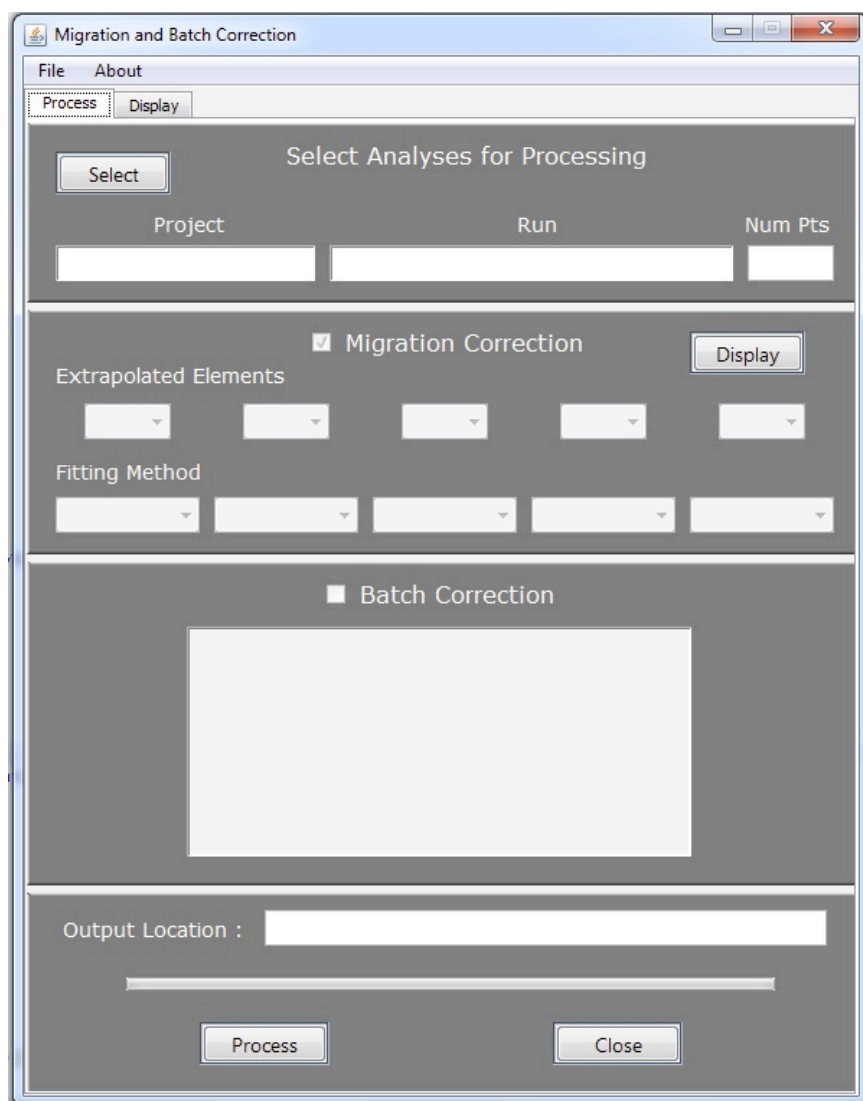

Figure 4. The main window of the program MigrationCorrection.

The first step in the program is to select the quantitative analysis data that need to be processed. The window for selecting the data will open by clicking on the *Select* button in the upper-right corner of the main window (Fig. 5), or by going to the menu item, *File >> Open*. Either method opens the *Import JEOL Qnt Data* window shown in Figure 5.
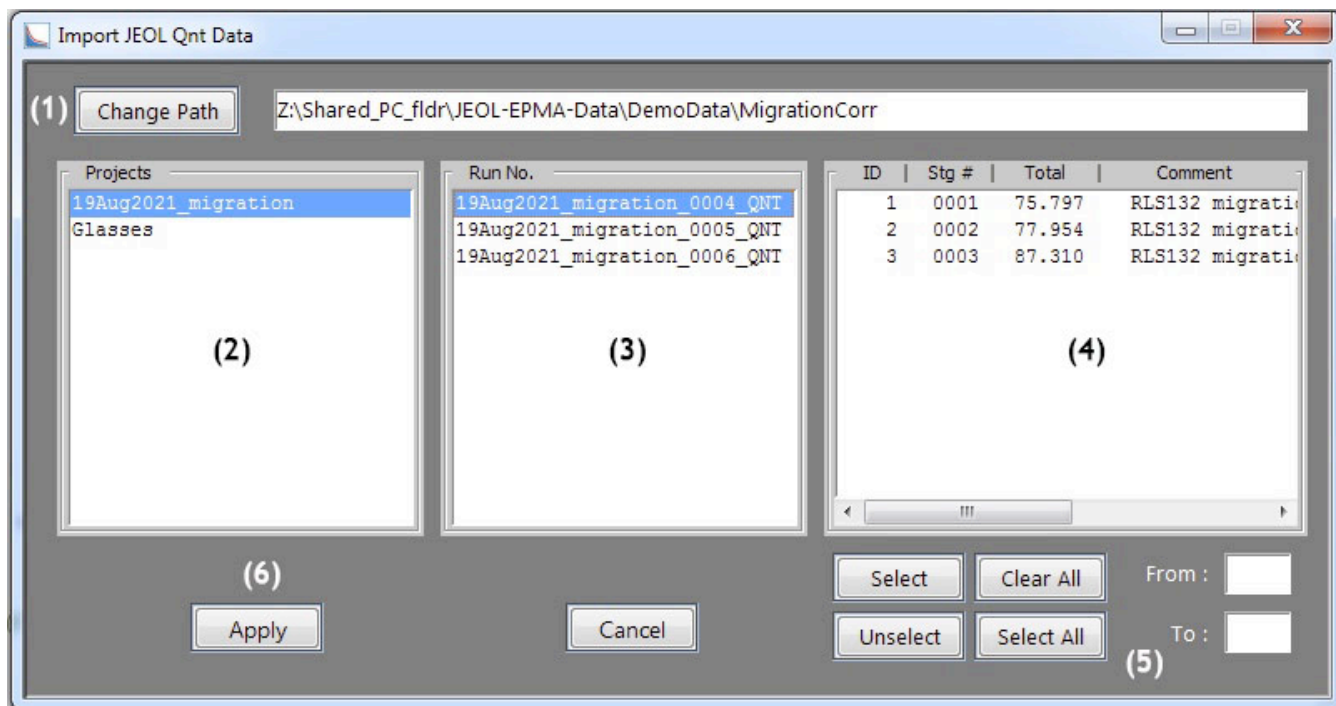

Figure 5. Import JEOL Qnt Data window allows the user to select the JEOL Project, Run No. and then the individual data points to be corrected.

Once the *Import JEOL Qnt Data* window has been opened, click on the *Change Path* button (item #1, Fig. 5) to select the correct path for the desired analysis data. This button will open a standard file dialog window (Fig. 6) from which the directory **containing** the projects of interested must be selected. It is imperative to select the correct directory at this point. The JEOL file structure is very specific. If a directory is selected that is higher or lower in the file structure, then the data will not be displayed in the *Import JEOL Qnt Data* window.

If the proper Path directory has been selected, then all of the Projects that contain quantitative analysis data will be displayed in the first column (item #2) of the *Import JEOL Qnt Data* window (Fig. 5). If there are no Projects that contain quantitative analysis data in this directory, then this column will be blank. If one of the listed Projects is selected by the users, then all of the quantitative analysis Runs in that Project will be displayed in the center column (item #3). Likewise, if one of the Runs has been selected, then all of the quantitative analysis points in that Run will be displayed in the last column (item #4).

The analytical points that need to be corrected can be selected from the window in Figure 5 using a number of methods. Continuous blocks of analyses can be selected using a combination of a mouse-click and a <ctrl> mouse-click.
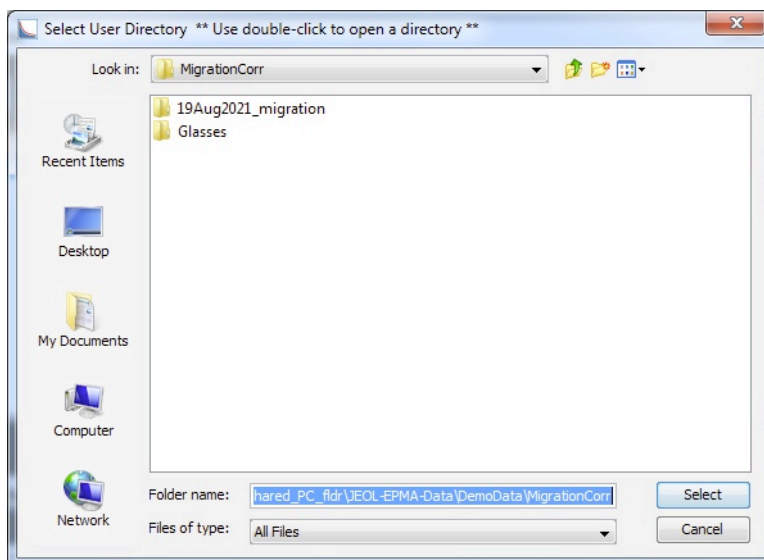

Figure 6. The "Change Path" button opens a standard file dialog window. This allows the user to select the directory above the Project of interest.

Discontinuous selections can be made using the various buttons in the window (Fig. 5, item #5).

Select button	Select all analyses that fall between the *From* and *To* values.
Unselect button	Unselect all analyses that fall between the *From* and *To* values.
Select All button	Select all the analyses in the list.
Clear All button	Unselect all of the analyses in the list.

Once the desired analyses have been selected, the user can click on the *Apply* button (item #6, Fig. 5). This will load all of those data points into the *MigrationCorrection* program. The Project and Run name from where the data came from will be displayed, as well as the number of selected analyses.

If there are any elements that were analyzed multiple times in those analysis, those elements will be displayed in the "Migration Correction" part of the main window (Fig. 7). By default, no fitting method is automatically selected. The user can select between the following choices:

Log	Fit the data using a logarithmic scale for the counts.
Linear	Fit the data using a linear equation.
Poly (2nd)	Fit the data using a 2nd order polynomial curve.
Poly (3rd)	Fit the data using a 3rd order polynomial curve.

If the user now selects the *Display* button, the *Display* tab will be shown, and both the measured values and the fitting curve will be plotted (Fig. 8).
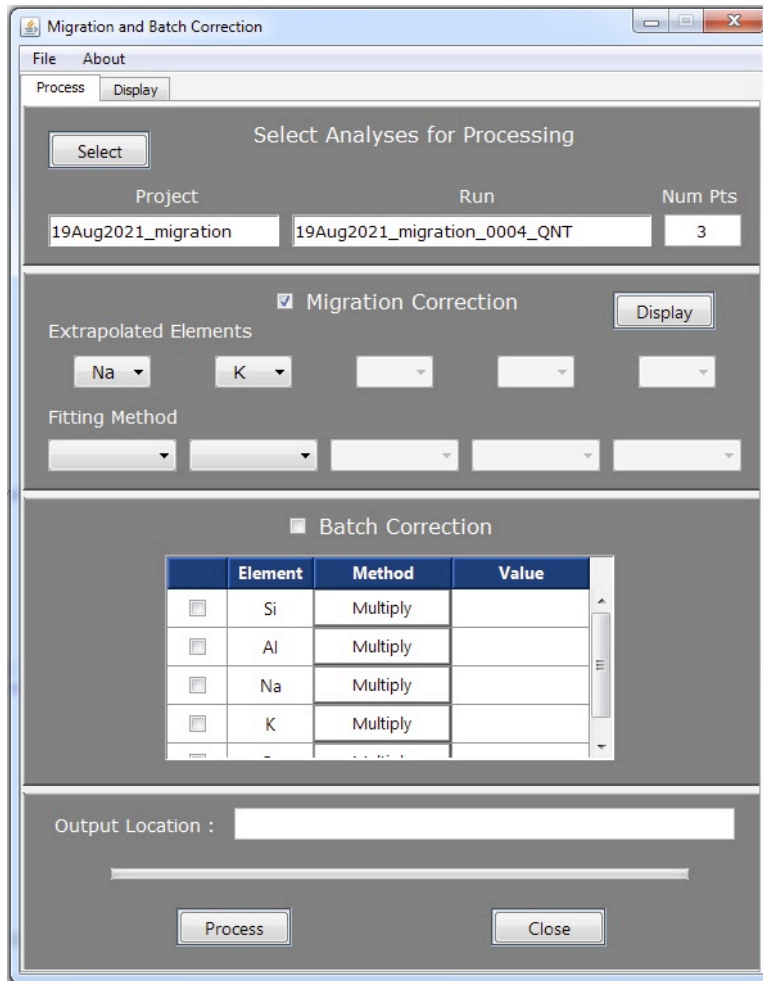
Figure 7. Main window of the MigrationCorrection program after a set of analyses have been imported.

The user can switch back and forth between the *Process* tab and the *Display* tab, which are displayed at the top-right corner of the main window. Different fitting curves can be tried to determine the best fit. Once a new fitting curve has been selected, the results will be displayed only if the *Display* button has been clicked on again.

In the *Display* window (Fig. 8), the user can select between the different elements to be displayed by using the *Display Element* drop-down menu, and can step through the list of analytical points by using the *Next* and *Back* buttons.
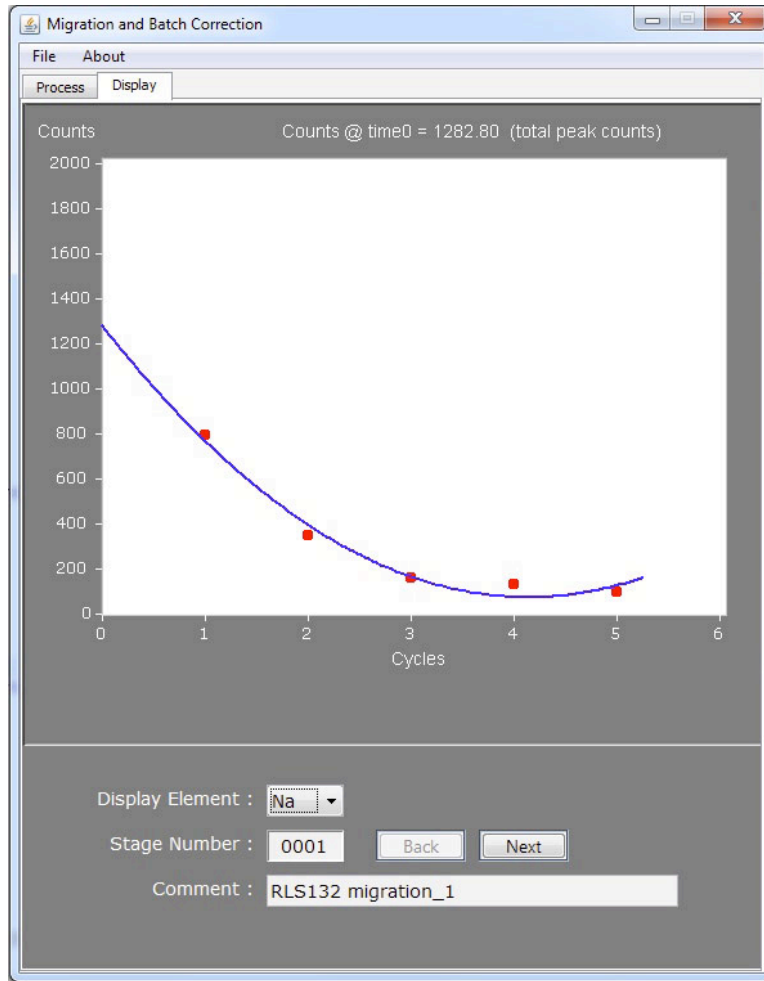
Figure 8. Display window showing the data and fitting curve for one particular analysis.

Once the user is satisfied with the fitting curve that has been selected, the processed data can be output to a file using the Process button. This will write out all of the time-zero data to a new Run created in the same Project. The location of this file will be displayed in the main window, as "Output Location". The user cannot specify this location. It will always be created as the next Run in that particular Project.

4 – Batch Correction

The *MigrationCorrection* program can also be used to adjust the raw counts in order to correct for minor drift over long periods of analyses. When a set of analyses is loaded into the program, the entire list of analyzed elements is displayed in the *Batch Correction* portion of the main window (Fig. 7).

To make a batch correction, first select the Batch Correction checkbox. Then select the checkbox for the element of interest. Next select the correction method. The element can be corrected for by either multiplying a constant to each of the measured values or a constant can be added to the measured value. To divide the measured value by a constant, simply put the constant in as the equivalent fraction. Likewise to subtract a value from the measured value, simply put it in as a negative value.

Once the method of correction and the value has been entered for each element, simply simply clicking on the Process button can then process the data. Again this will write out the new corrected counts to a new Run in the same Project. The name of the Run will be listed as the *Output Location*.

5 – Final Processing

Whether the user is correcting the data for an element migration or is correcting the dataset by a set value, the MigrationCorrection program does not calculate new weight percent values for the analyses. It only writes out the new interpolated raw counts into a new Run that is sequentially next for that Project. The data must now be reprocessed using the *JEOL Off-line Correction* program. This will then create another Run that contains the full ZAF corrected results using the new interpolated raw counts.

References:

Nielsen, C.H., and H. Sigurdsson, 1981, Quantitative methods for electron microprobe analysis of sodium in natural and synthetic glasses. American Mineralogist, vol. 66, p. 547-552.

Notes:

1) The MigrationCorrection program only works with WDS analyses, not with EDS analyses.