Epsilon 4 X-ray Fluorescence Spectrometer – Basic Data Collection and Analysis of an Unknown Sample using the Omnian Procedure

The Omnian method is a standardless method that can be used if no suitable standards for your sample are available. Detailed information about your sample is required to obtain reliable analysis data using Omnian. Please carefully evaluate sample preparation and data processing procedures before collecting data.

The method described below is a general and somewhat simplified procedure. It is intended as a starting point only and should be augmented and modified for every sample type based on the nature of the material to be analyzed, and the type of information you are interested in obtaining.

Sample Preparation (choice of cup and foil/film)

The Omnian method is often used in combination with samples that are “as prepared” (i.e. loose powders or solids with a flat surface). If you expect to have many samples of a similar kind, consider investing into developing a dedicated sample preparation method and obtaining suitable standards.

Even for an Omnian data collection, some decisions have to be made prior to prepping the sample. The two most obvious are the choice of sample cup, and the choice of foil/film.

For a pressed/fused pellet or a dust free solid piece of material with a flat surface that fits the sample holder, use no cup or foil.

If your sample is a powder or liquid, or if it is a solid but too small to fit the sample holder (or plain dusty), you need to use a cup and foil. The choice depends on the amount of material available, and the types of elements you want to analyze for.

XRF is a bulk method and requires reasonably large amounts of sample. The X-ray beam on the Epsilon is an oval 10-12 mm in diameter. If you can, use a cup that is larger than this diameter! The amount of sample used should be sufficient to be “infinitely thick”, i.e., none of the X-rays should completely penetrate through the sample. The instrument can partially correct for samples that are too thin (“finite thickness effects” in the sample processing parameters), but if possible at all, use enough material to avoid less accurate data due to finite sample thickness.

If enough sample is available, use a cup wider than the beam and of sufficient size so that it is filled about halfway up (or at least “infinitely thick”).

If less sample is available, use one of the “small mass” sample holders (and use one of the “small mass” processing parameter files).

Sample cups are provided beside the instrument at no charge. These cups are multi-use and need to be cleaned after you have finished your analysis (wiping off with water and methanol). For trace analysis, or
when analyzing liquids use of a new cup for each analysis is recommended (single use cups have to be provided by the instrument user).

When choosing a support film several factors should be considered, including film absorption, film strength, and chemical resistance and film contamination. The most common foils in use are mylar and polypropylene (trade name “Prolene”). Mylar is the most easy to use, but has a number of contaminants (mostly Ca, P and Cl) and is more absorbing than polypropylene. 3.6 µm mylar is most often used when analyzing for heavier elements and when Ca, P and Cl are of little interest. Polypropylene tends to wrinkle more than mylar, but absorbs X-rays less and has fewer contaminants (traces of Si). 4.0 µm polypropylene is often used for light element analysis. Both types of films are provided for sample prep beside the instrument in the form “easy snap” foils with a paper rim for ease of sample cup assembly.

Put the cup on a clean surface (weighing paper), place the film in between the two cups and press the second half of the cup or the snap on ring down fast and hard. Try not to touch the film with bare hands!

Place the cup or small mass sample holder with the foil down on a clean surface and fill it with your powder or liquid, or place a flat side of the solid onto the foil as close to the center of the cup as possible.

**Loading the Sample(s)**

When no other analysis is running, lift the lid of the spectrometer and place your samples in the sample changer (note which sample you placed in which position). Black plastic rings are available to keep smaller sample cups centered in the sample holder.

Open the main valve of the helium tank. Do not adjust the regulator unless the pressure deviates substantially from 1 bar.

On the desktop computer, switch to or open the Epsilon Software (do not open a second copy of the Epsilon software).
Data Measurement

In the Measure dropdown menu, select Measure Omnian.

In the pop-up window, select your program of choice (e.g. Omnian).

The Measure Omnian Sample window will pop up.
In the Unknown Sample tab, enter your sample identification code. Select Omnian Or Omnian Fast for the calibration and GENERAL for quantification (a typical Omnian data collection will take 15 minutes, a Omnian Fast measurement will take around 6 minutes). Select an appropriate option for the Processing Parameters.

Current suggested options available are:

<table>
<thead>
<tr>
<th></th>
<th>Intended for:</th>
<th>Conditions assumed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basic</td>
<td>solid sample</td>
<td>normalizes to 100%, nothing else specified</td>
</tr>
<tr>
<td>Bead</td>
<td>lithium borate fused pellet</td>
<td></td>
</tr>
<tr>
<td>Solid</td>
<td>solid sample</td>
<td>normalizes to 100%, nothing else specified</td>
</tr>
<tr>
<td>Metal Complexes SMH</td>
<td>metal complexes and organic materials with some heavy elements; loose powder</td>
<td>Mylar 3.6 µm film, ca. 0.2 g sample, 10 mm diameter, 0.9 mm thick, ca 2.8 g/cm³ density; does not normalize (“residue” assumed to be “organic”)</td>
</tr>
</tbody>
</table>
Small mass oxides | Small amounts of metal oxide loose powder | Mylar 3.6 μm film, ca. 0.2 g sample, 6 mm diameter, 0.8 mm thick, ca 8.8 g/cm³ density; does normalize to 100%
---|---|---
Small mass metals | Small amounts of loose metal powders | Mylar 3.6 μm film, ca. 0.2 g sample, 6 mm diameter, 0.8 mm thick, ca 8.8 g/cm³ density; does normalize to 100%
---|---|---
Solid carbon oxides | Solid in carbon matrix | no foil/film, matrix carbon, reported as oxides, not normalized
---|---|---
Solid CAs | Solid calcium/aluminum oxide matrix | Prolene 4 μm foil/film, matrix “C₃H₆”, reported as oxides, normalizes to 100%
---|---|---
Steel | | 20 g, 40 mm diameter, 8.050 g/cm³ density, normalizes to 100%

Use Basic or Solid only if no more suitable option is available (talk to Dr. Zeller for setting up processing parameters for your type of sample).

Click the Measure button.

The sample changer position window will pop up. Select the position of the sample. If the lid is closed clicking the position will start the data collection. (Keep the lid open if you want to add additional samples)

At this point you can also start additional measurements. Samples must have been prepared and loaded prior to starting the running analysis as the lid will be locked during an active measurement. Go back to
the Measure Omnian Sample window (if still open), or start again with the Measure dropdown window. In the Measure Omnian Sample window set up additional data collections as described above, click the Measure button and select the position of your second, third etc sample.

To check the estimated completion of all samples queued, maximize the Progress window.

To monitor the process of your data collection, open the Online Status window. It shows the various steps of the measurement that are queued, including the acceleration voltage and current as well as the filters used for each scan.
To monitor the live spectrum while the measurement is running, open the Online Results Spectrum Window.

In this window you can do a first preliminary inspection of your data while the measurement is running. Select the active scan at the top of the window. Move the mouse atop of a peak of interest in the scan and possible matching XRF lines will be listed in the left top corner of the Online Results Spectrum Window.

To zoom in, drag a box using the left mouse button. To unzoom, click the unzoom icon. (no right mouse click options are available in the Online Results Spectrum Window)

Once a measurement has finished, the results of the automatic analysis can be viewed, and the data can be inspected and reprocessed to exclude elements that were wrongly assigned to be present, etc.

**Processing of Results**

To see the results, click the Results dropdown menu and select Open Results.
In the pop-up window that opens, select Omnian, then click OK.

In the Omnian Results window, find your measurement of interest. If it is not listed in the default view, you can search for results and narrow the results by date and time.

Double-click your measurement of interest to see the default results at the bottom of the Omnian Results window. Note elements that have a very low percentage or that you did not expect to be present in your sample.
To see the spectrum and edit possible elements, click the Omnian Elements icon (blue-red periodic table icon). It will open the Omnian Result Spectra and Omnian Elements windows.
Peaks in the spectra that were assigned to an element and were used in the quantification are labeled. If a scan is selected (middle of top of the Omnian Result Spectra window) scans are also highlighted in the colour of their scan. Only selected regions of each scan are used for quantification. The margins that are used are marked by vertical dashed lines in the colour of their scan.

If a section of the combined overlaid spectra is too busy, you can uncheck selected scans (middle of top of the Omnian Result Spectra window).

Colour codes and conditions for the six Omnian Scans are as follows:

<table>
<thead>
<tr>
<th>Condition Name</th>
<th>Element lines used:</th>
<th>Tension (kV)</th>
<th>Current (µA)</th>
<th>Filter</th>
<th>Helium?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Omnian 5</td>
<td>F–Si</td>
<td>5</td>
<td>60</td>
<td>none</td>
<td>yes</td>
</tr>
<tr>
<td>Omnian 4</td>
<td>P–Cl</td>
<td>9</td>
<td>30</td>
<td>Ti</td>
<td>yes</td>
</tr>
<tr>
<td>Omnian 3</td>
<td>K–V, Te–Ba</td>
<td>12</td>
<td>25</td>
<td>Al, 50 µm</td>
<td>no</td>
</tr>
<tr>
<td>Omnian 2</td>
<td>Cr–Co, Pr–Tm</td>
<td>20</td>
<td>15</td>
<td>Al, 200 µm</td>
<td>no</td>
</tr>
<tr>
<td>Omnian</td>
<td>Ni–Mo, Yb–Am</td>
<td>50</td>
<td>6</td>
<td>Ag</td>
<td>no</td>
</tr>
<tr>
<td>Omnian 1</td>
<td>Tc–Sb</td>
<td>50</td>
<td>6</td>
<td>Cu, 500 µm</td>
<td>no</td>
</tr>
</tbody>
</table>
You can also zoom in by dragging a box using the right mouse button. To unzoom, click the unzoom icon or use the right mouse click options.

Inspect all scans for peaks that are not assigned to a found element (no label and not highlighted in colour). Also inspect for all minor elements (ppm and low % range) if these are correctly assigned or should be taken out.

Step 1:
Uncheck very minor elements in the periodic table and click Apply. For elements that you are not sure if they might be present or not, select them one by one, click apply, and check if a peak is present where the line(s) for this element are. Check if the area under the peak matches with the curve fit after clicking Apply (the scan has to be selected for the colour highlight of the curve fit to be shown). For elements with no visible peaks or unreasonable curve-fits leave the element unselected in the periodic table.

Step 2:
In the next step check for missed elements. Look for clearly resolved peaks that have no XRF line assigned to them and that have no colour highlight even though the scan is selected and the peak is within the area used for quantification. Move the mouse cursor atop of the peak and check in the upper right corner of the Omnian Result Spectra window for possible line assignments. Move the mouse a bit to the right and left to make sure you do not miss any possible elements.

Check possible candidate elements in the periodic table and click Apply. Inspect the exact position of the added line and the match of the curve fit. Do this for all possible elements for each unassigned peak (one element at a time), paying attention to lines added for each element in other positions. Of the candidates, pick the element that fits the missing peak AND the remaining spectrum best. If two or more elements fit the peak, check if both might be present. If no element gives a good fit, leave this peak blank and proceed to the next unassigned peak.

Ignore peaks outside the area that is used for quantification in each scan (dotted vertical boundary lines). Ignore peaks from Ag (the anode material is silver) and Ar (Ar in air is detected), but include Ag and Ar in the periodic table selection. Ignore broad features that do not match the typical peak shape (Compton scattering around the silver lines, etc)

Continue until no major lines remain unassigned or no improvement can be achieved any more.

Step 3:
For very large peaks, the tail of the peak might be not fitted adequately. If this is the case, click the “fit details” tab, select the scan where you would like to fit the tails better and check “fit tails”, then apply.

Comment: There might be some properly fitted but unlabeled peaks. These are most likely sum peaks or escape peaks. Sum peaks occur when two photons arrive at the detector at exactly the same time, and the sum of their energies is counted rather than the individual energies. This is most likely to happen for the most intense peaks of each scan. Escape peaks occur when a photon losses the excitation energy of
the Si Kα peak (silicon is the main detector material), 1.74 eV. For the most intense peaks, escape peaks are found at 1.74 eV lower than the main peak. Both sum and escape peaks are properly handled by the software and they can be ignored once identified. They can be easily identified by unselecting the element you suspect them to originate from. The fit for the sum and escape peaks will disappear together with that of the main peak.

Step 4:

Unless all processing parameters have been taken care off during data collection setup, click the button “Edit Processing Parameters” in the Omnian tab. Add as much detail about your sample as possible (e.g. foil/film used, whether to normalize the analysis results (to 100%) or use a matrix as balance (specify the matrix material), etc. The quality of the analysis results depends heavily on accurate and detailed processing parameters being provided.

Step 5:

Click the Omnian tab in the Omnian Elements window. Click Quantify.

The new results based on the new element list will be listed in the Omnian Results window. If you closed this window, click the folder icon to the right of the Quantify button to reopen it.
Inspect the results. If necessary, return to the Omnian Result Spectra and Omnian Elements windows and continue with element assignments or removal, editing of processing parameters, etc, until satisfied with the results.

**Exporting / saving of results**

A right mouse click in the Omnian Result Spectra window allows to copy the image to clipboard (can be copied in MS word file, Paint, etc), to print the spectrum (to pdf), to export the spectrum (as a *.mps file, substantial editing required to import into other software) or to show in staggered view (“Show in 3D”).

A right mouse click in the Omnian Result window allows to copy the numerical results to clipboard, or to print the results (to pdf).

**Wrapping up**

Close the main valve of the He tank if no more samples are going to be run the next hour.

Take samples out of the instrument, collect the bulk of your sample, and clean the sample cups for the next user (in most cases, wiping cups with water and methanol is sufficient). Weighing paper, used foils, and paper towels from cleaning can go into the normal trash ONLY if the analyzed samples are chemically and environmentally harmless. All harmful waste (including weighing paper, used foils, and paper towels) have to be collected by the user and be properly disposed following established Purdue procedures. No waste sample is to be left in the analysis lab.