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

X-ray Crystallography Laboratory

Purdue Department of Chemistry

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.

Before you start

The "**Recal Standard**" should be run once daily, before running any measurements. Do this first, as it takes about 20 minutes (you can prep you samples while waiting for the recal measurement to finish).

When no other analysis is running, lift the lid of the spectrometer and check the position the recal standard sample is in. Close the lid again and open the main valve of the helium tank. Do not adjust the regulator unless the pressure deviates substantially from 1 bar.
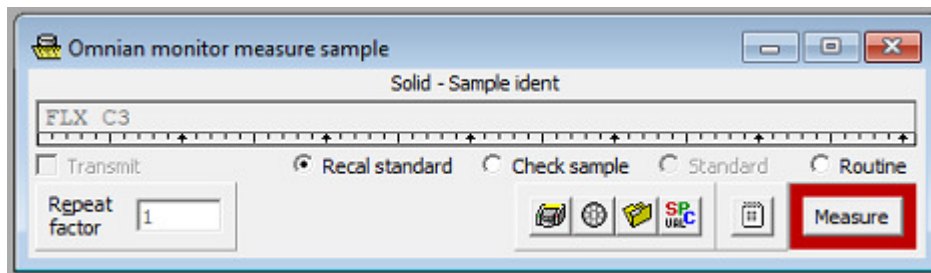
On the desktop computer, switch to or open the Epsilon Software (do not open a second copy of the Epsilon software). From the "Measure" dropdown option, select "Measure application".
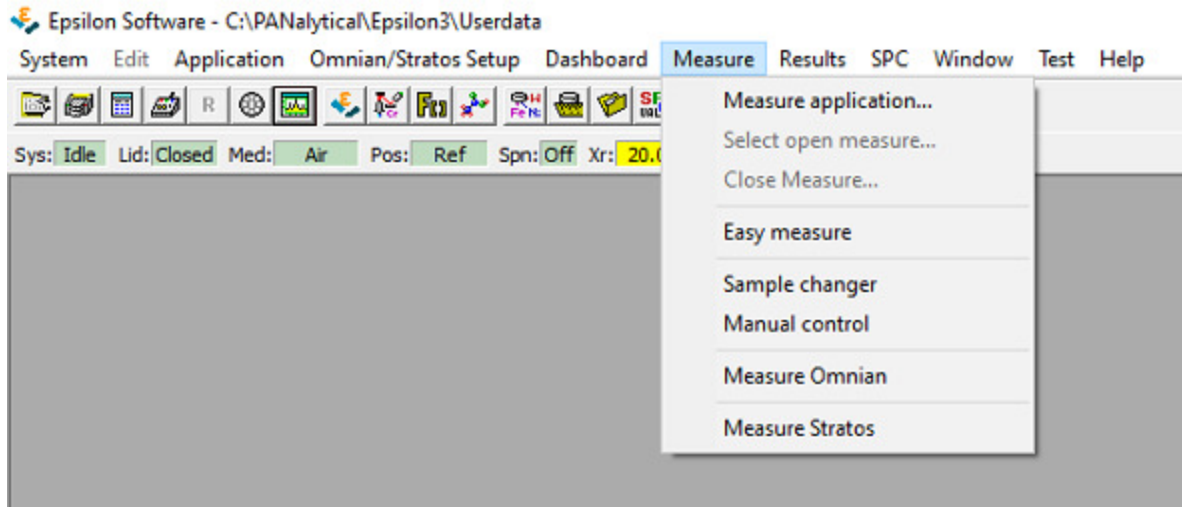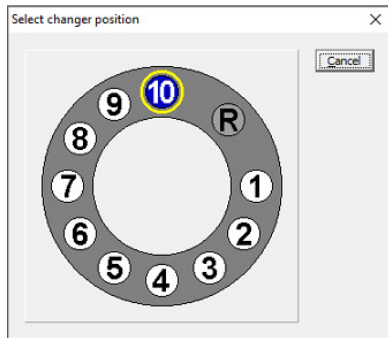
Select "Omnian monitor".
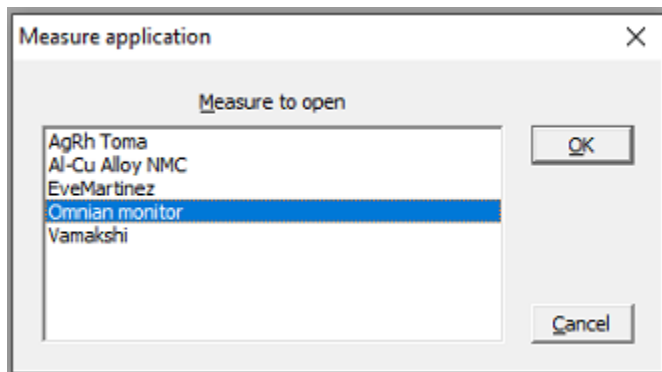
Select "Recal standard", click "Measure".

Select the position of the Recal standard sample, and the measurement will start.

The measurement will take about 20 minutes. The result should state that it was "completed successfully".

	Al	Al1	Ca	Fe	K	Mg	Mn	Na ∧
Unit	cps	cps	cps	cps	cps	cps	cps	cps
K factor	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
RMS	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
Correlation	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
Original D	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.00000
Original E	1.000000	1.000000	1.000000	1.000000	1.000000	1.000000	1.000000	1.00000
Original F	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.00000
D value	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.00000
E value	? 1.049032	? 1.061169	? 1.011549	? 1.001757	? 0.960580	? 1.048691	? 0.997063	? 1.067 ∨

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 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 films are the most easy to use, but have a number of contaminants (mostly Ca, P and Cl) and are more absorbing than polypropylene. The **3.6 µm mylar films are** 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). The **4.0 µm polypropylene** films are 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 <u>down fast and hard</u>. ***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.

Check the helium tank and open the main valve if necessary. Do not adjust the regulator unless the pressure deviates substantially from 1 bar.
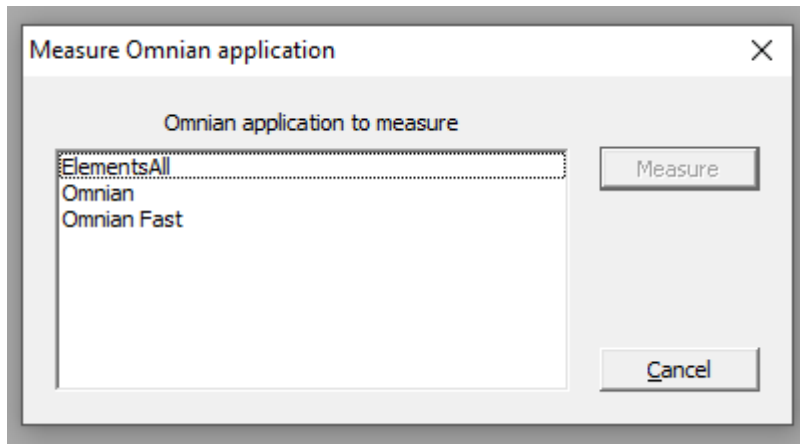
On the desktop computer, switch to or open the Epsilon Software (do not open a second copy of the Epsilon software).
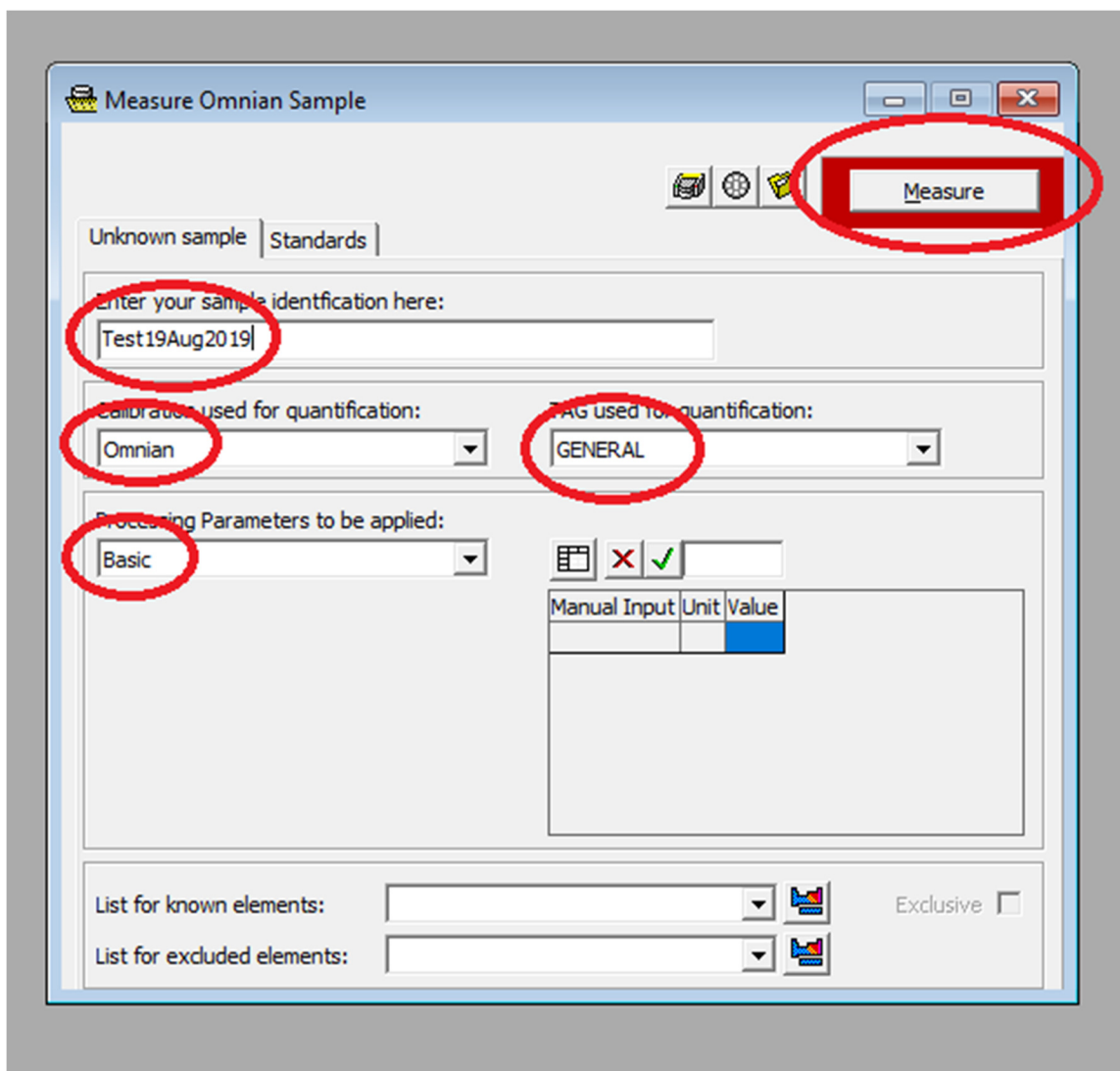
Data Measurement

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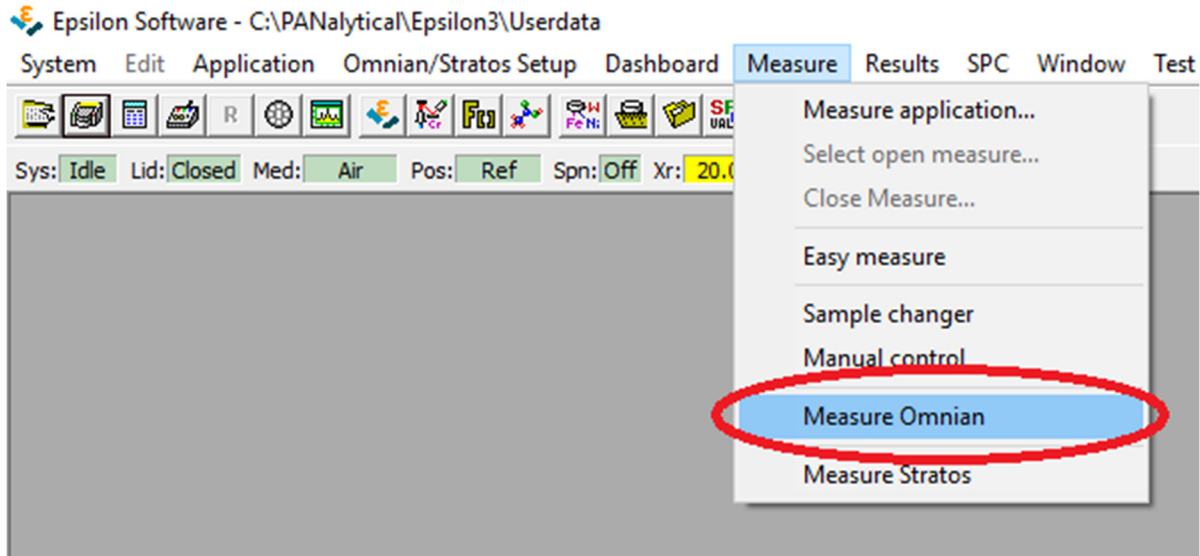
In the pop-up window, select your program of choice (e.g. "Omnian").

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 (check occasionally for new methods added):

	Intended for:	Conditions assumed
Basic	solid sample	normalizes to 100%, nothing else specified
Bead	lithium borate fused pellet	
Solid	solid sample	normalizes to 100%, nothing else specified
Metal Complexes SMH	metal complexes and organic materials with some heavy elements; loose powder	Mylar 3.6 μm film, ca. 0.2 g sample, 10 mm diameter, 0.9 mm thick, ca 2.8 g/cm^3 density; does not normalize ("residue" assumed to be "organic")

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/cm^3 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/cm^3 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 "C_3H_6" , reported as oxides, normalizes to 100%
Steel		20 g, 40 mm diameter, 8.050 g/cm^3 density, normalizes to 100%

Use Basic or Solid only if no more suitable option is available. See **Appendix 1** and 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)
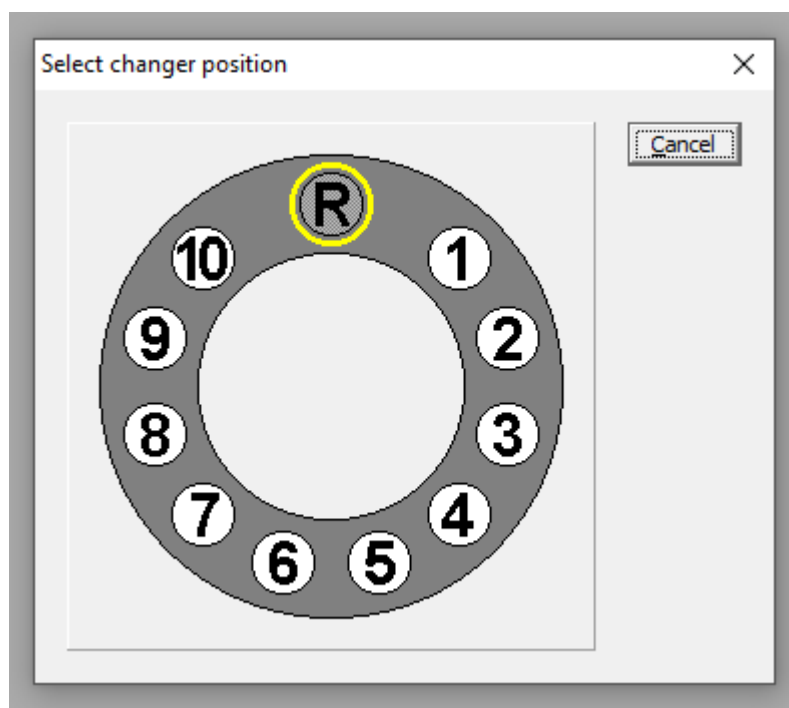
At this point you can also start additional measurements. Samples must have been prepared and loaded prior to starting the running analysis as the lid will be locked during an active measurement. Go back to

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.

Online status - Measuring sample

System status	Lid	Medium	Sample changer
Ok - Busy	Locked	Air	1

X-ray tube	Tube filter	Spinner
50.000 kV, 300 ÂµA	6: Ag	On

	Pelt A Det °C	Last gain
	0.586 -14.3	3:17:17

Release spectrometer

Measuring - Sample ident

Test19Aug2019

	Application	Sequence	Position		
	<Omnian>	1/1	1	Clear	Abort

Conditions	kV	uA	Filter	Medium	Time (s)	Inp kcps	Out kcps	%Dead
Omnian	50.000	2	Ag	Air	61	888.089	592.173	33.3
Omnian1	50.000	2	Cu-500	Air	124			
Omnian2	20.000	2	Al-200	Air	64			
Omnian3	12.000	2	Al-50	Air	124			
Omnian4	9.000	2	Ti	Helium	184			
Omnian5	5.000	2	<none>	Helium	184			

To monitor the live spectrum while the measurement is running, open the Online Results Spectrum Window (green icon depicting a spectrum).

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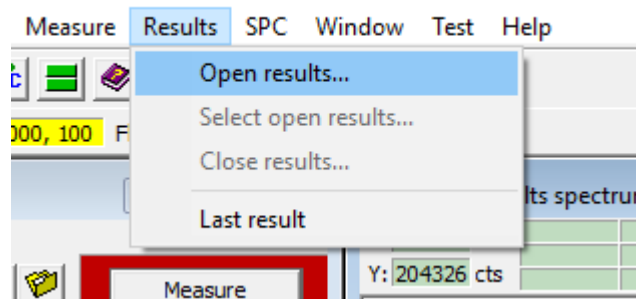
To zoom in, drag a box using the left mouse button. To unzoom, click the unzoom icon (ex-d out magnifying glass). (no right mouse click options are available in the Online Results Spectrum Window)
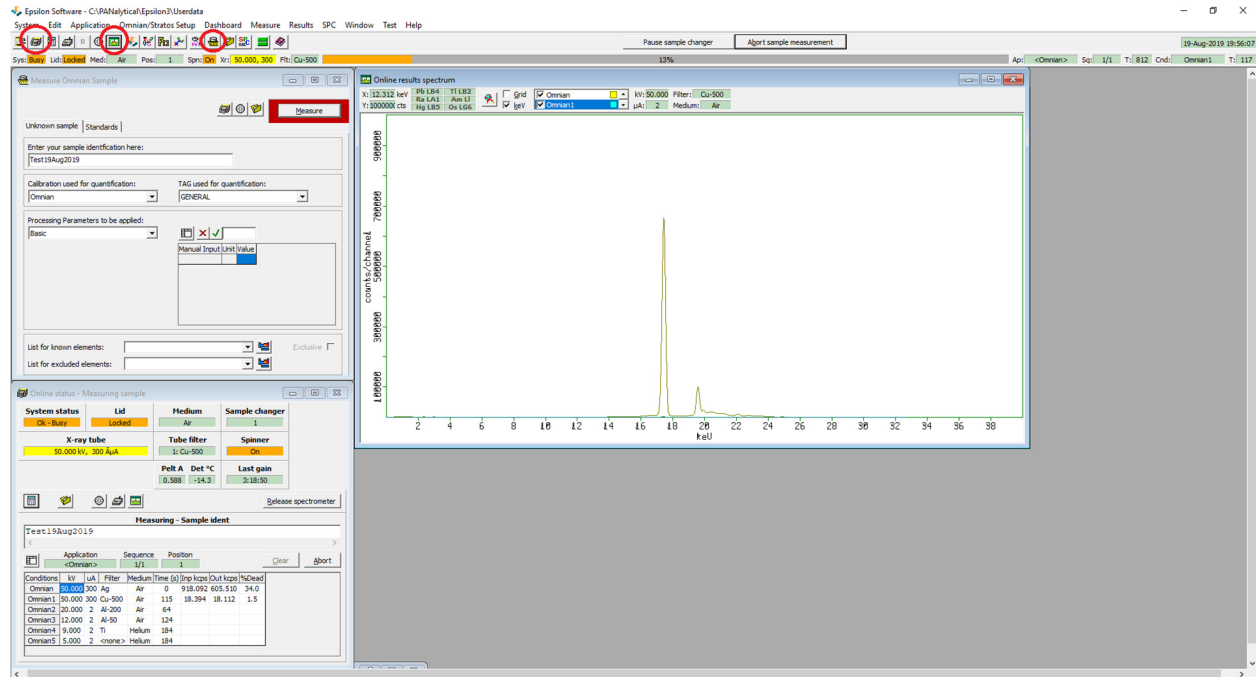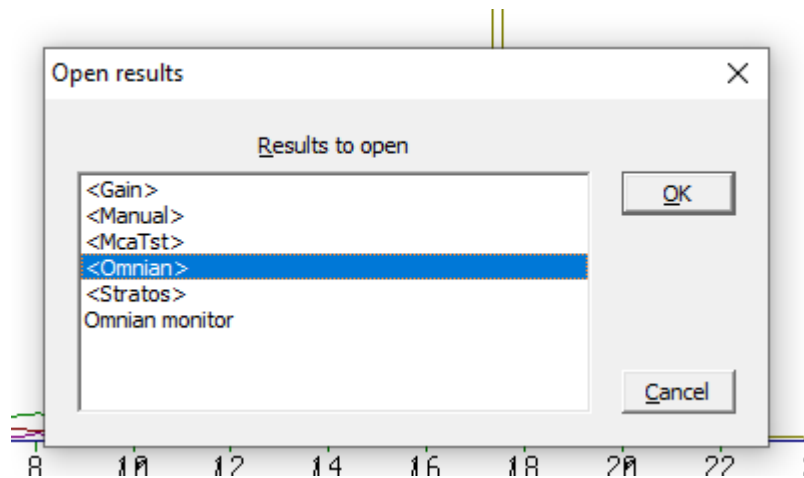

Once a measurement has finished, the results of the automatic analysis can be viewed, and the data can be inspected and reprocessed to exclude elements that were wrongly assigned to be present, elements that were missed by the, and other mistakes by the automated procedure.

Processing of Results

To see the results, click the Results dropdown menue and select "Open Results".

In the pop-up window that opens, select "Omnian", then click "OK".

Open results   ×

                        Results to open

<Gain>		OK
<Manual>		
<McaTst>		
<Omnian>		
<Stratos>		
Omnian monitor		Cancel

   8   10   12   14   16   18   20   22

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. Look for 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.
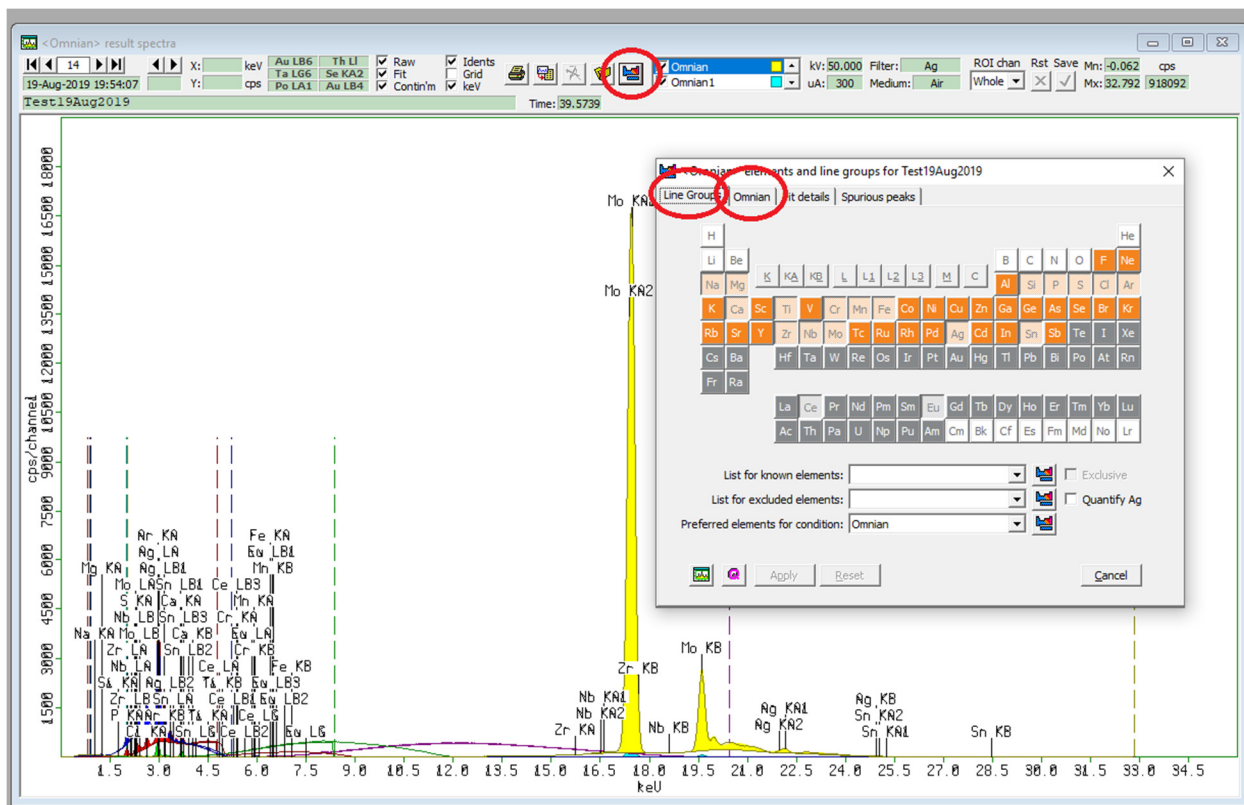
Peaks in the spectra that were assigned to an element and were used in the quantification are labeled. If a scan is selected (middle of top of the Omnian Result Spectra window) scans are also highlighted in the colour of their scan. Only selected regions of each scan are used for quantification. The 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:

Condition Name	Element lines used:		Tension (kV)	Current (µA)	Filter	Helium?
	K lines	L lines				
Omnian 5	F–Si		5	60	none	yes
Omnian 4	P–Cl		9	30	Ti	yes
Omnian 3	K–V	Te–Ba	12	25	Al, 50 µm	no
Omnian 2	Cr–Co	Pr–Tm	20	15	Al, 200 µm	no
Omnian	Ni–Mo	Yb–Am	50	6	Ag	no
Omnian 1	Tc–Sb		50	6	Cu, 500 µm	no

You can also zoom in by dragging a box using the right mouse button. To unzoom, click the 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 can happen for the most

intense peaks of each scan. Escape peaks occur when a photon loses 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 in energy than the actual 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".
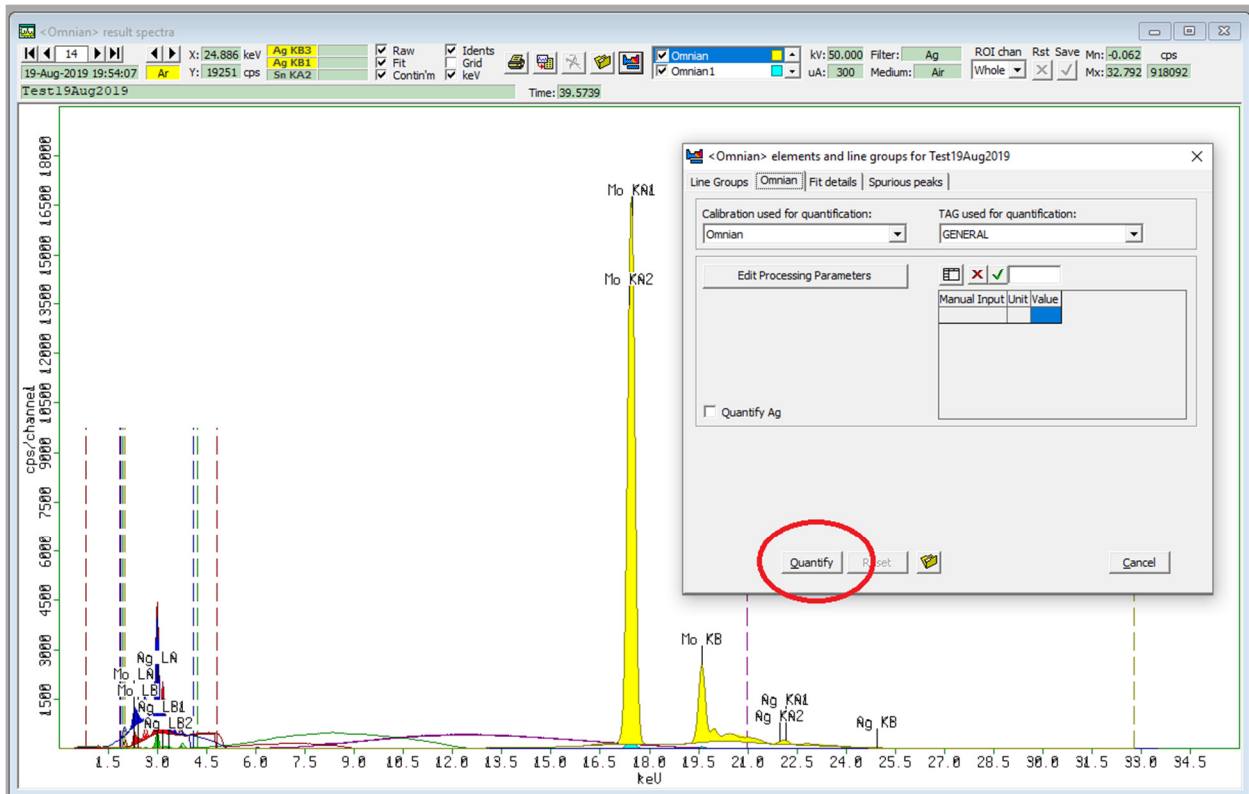
The new results based on the new element list will be listed in the Omnian Results window. If you closed this window, click the folder icon to the right of the Quantify button to reopen it.
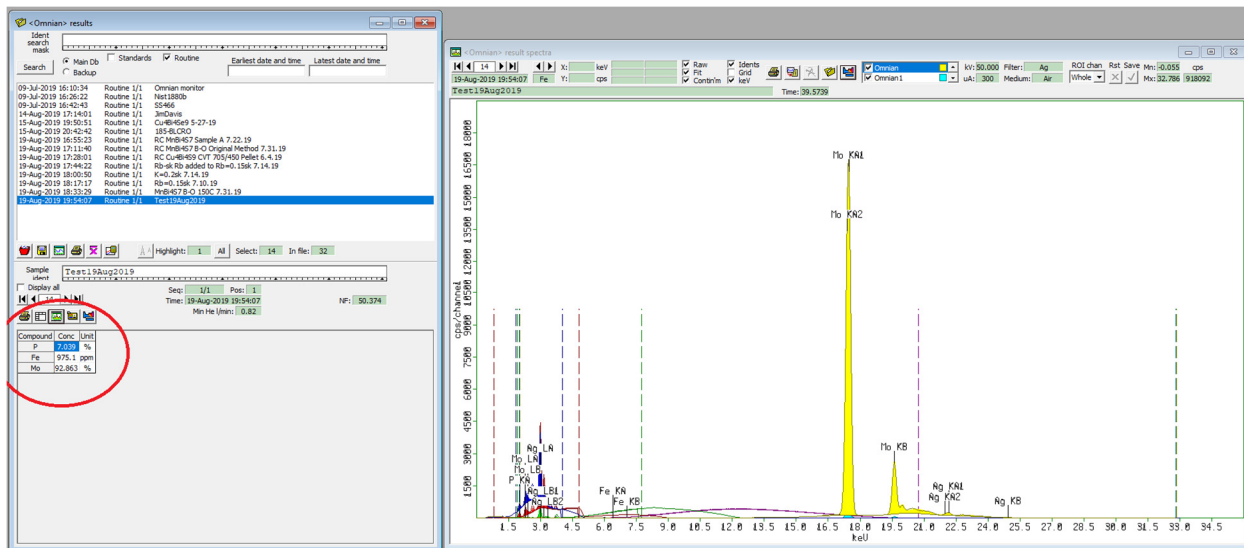
Inspect the results. If necessary, return to the Omnian Result Spectra and Omnian Elements windows and continue with element assignments or removal, editing of processing parameters, etc, until you are satisfied with the results.

Exporting / saving of results

A right mouse click in the Omnian Result Spectra window allows to copy the image to the clipboard (can be copied into an MS word file, Paint, etc), to print the spectrum (to pdf), to export the spectrum (as an *.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.
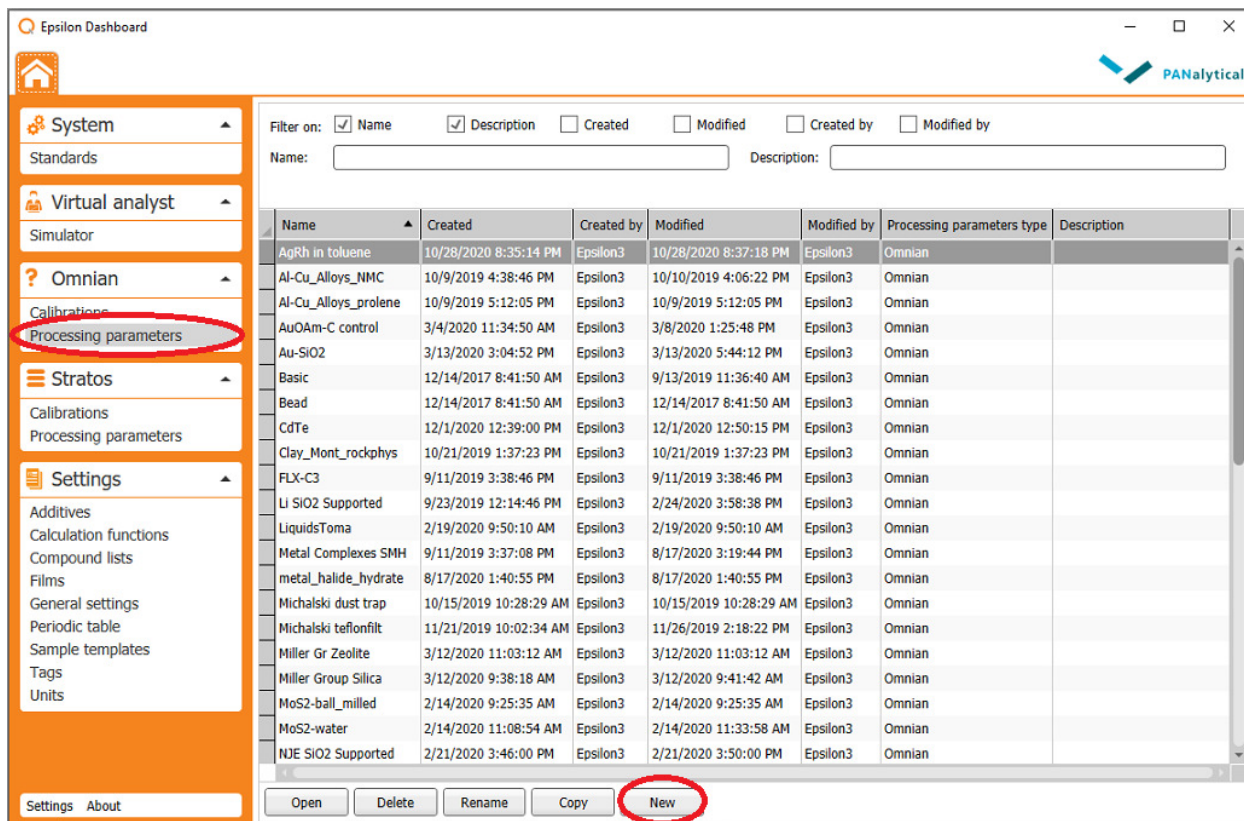
Appendix 1. Creating a method

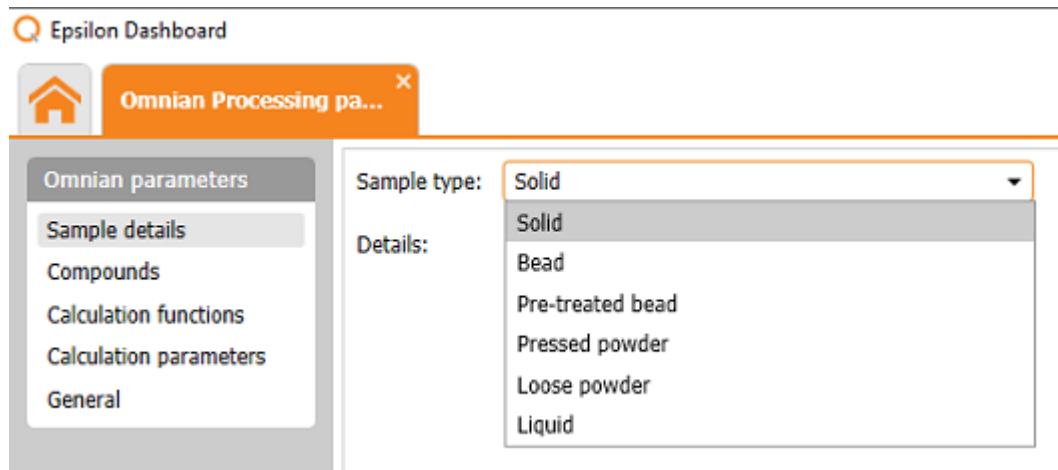Within the Epsilon software, click the Dashboard link.
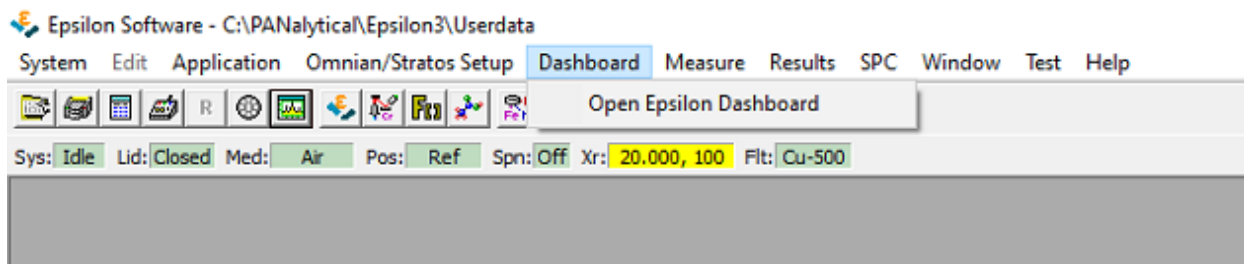
The password is "Epsilon".

To create a new Omnian method, click on "Processing Parameters" under "Omnian".

If a similar method exists, select it and click "Open". To start from scratch, click "New".

Click on "Sample details" in the side panel, select the Sample type (see below for options).

If the weight or size of the sample is available (and about the same for all samples run with this method) check the box for "Enter weight and size" and fill in the details. Weight and size are required for correction for "Finite thickness effects" (under "Calculation parameters").

Click on Compounds in the side panel.

Choose your report options. If you would like all data to be reported in % (rather than some in % , some in ppm) change "Report concentrations in ppm if below" to a small number (e.g. 1 ppm).

If there are fillers, binders, or other compounds not detectable by XRF (e.g. water, an oil, an organic matrix) add it as a "Compound". Click "Add Compound" on the right. Fill in the chemical formula or name, and select from the options.

Click on "Calculation parameters" in the side panel.
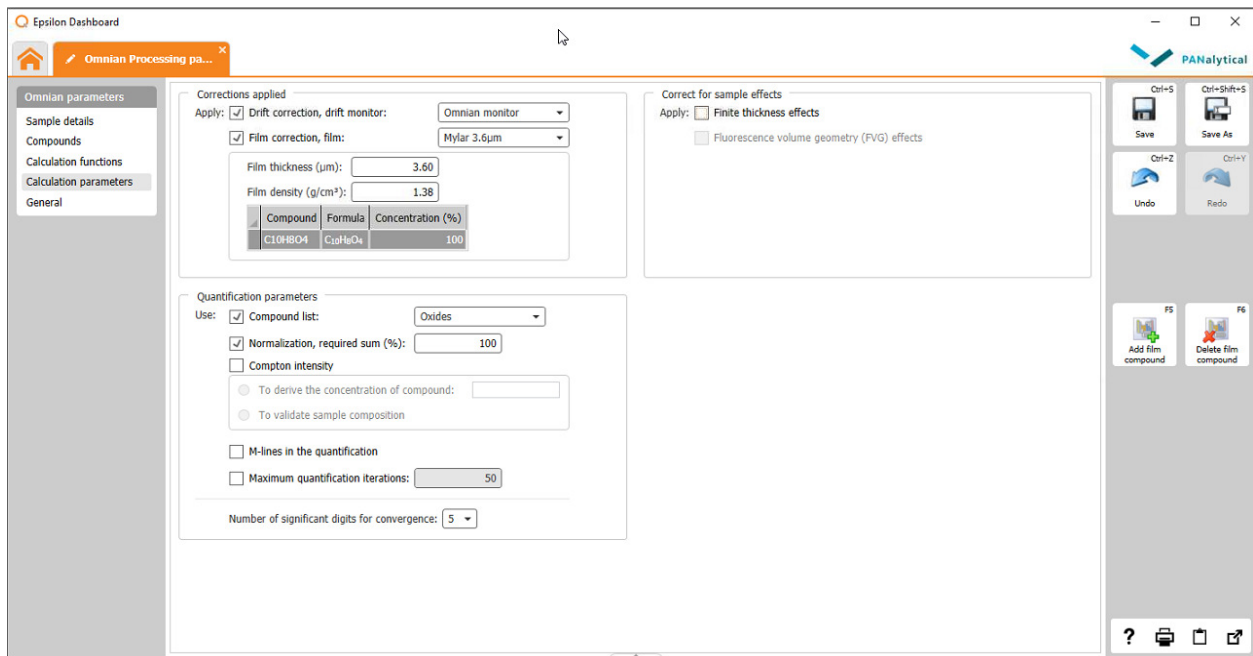
Under "Corrections applied", check the box for "Drift correction, drift monitor", select "Omnian monitor" from the options.

If you use a film to hold your sample in place, check the box for "Film correction, film" and select the type and thickness of film from the options (the Purdue lab stocks Mylar 3.6 µm and Prolene 4 µm). You can add additional film types via the button "Add film component" on the right.

Under "Sample effects", if your sample amount is small and the thickness is less than the penetration depth of the X-rays (depends on the materials X-ray absorption coefficient), check the box for "Finite thickness effects" and for "Fluorescence volume geometry (FVG) effects". These options require weight and size (Finite thickness) and thickness and density (FVG) to be specified (under sample details).

Under "quantification parameters", leave the checkbox for "Compound list" blank if you would like to use element weight percent for quantification. If you want to use oxides or other compounds for quantification, place a checkmark at "Compound list" and select from the options. Additional Compound lists can be created from the Main menue under "Settings".

If there are no compounds that are invisible to XRF (light elements not accounted for in the compound lists), place a checkmark in the box for "Normalization, required sum %: 100".

If you expect large amounts of very heavy elements to be present (lanthanides, actinides), place a checkmark in the box for "M-lines in the quantification".

Save your method using the "Save As" button in the right upper corner of the Dashboard.